University of Groningen

Conversion of CO₂ into organic carbonates: a venture into catalysis, reaction design and product modification

Kamphuis, Arjen

DOI:

[10.33612/diss.202245750](https://doi.org/10.33612/diss.202245750)

IMPORTANT NOTE: You are advised to consult the publisher's version (publisher's PDF) if you wish to cite from it. Please check the document version below.

Document Version

Publisher's PDF, also known as Version of record

Publication date:

2022

[Link to publication in University of Groningen/UMCG research database](#)

Citation for published version (APA):

Kamphuis, A. (2022). *Conversion of CO₂ into organic carbonates: a venture into catalysis, reaction design and product modification*. [Thesis fully internal (DIV), University of Groningen]. University of Groningen. <https://doi.org/10.33612/diss.202245750>

Copyright

Other than for strictly personal use, it is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), unless the work is under an open content license (like Creative Commons).

The publication may also be distributed here under the terms of Article 25fa of the Dutch Copyright Act, indicated by the "Taverne" license. More information can be found on the University of Groningen website: <https://www.rug.nl/library/open-access/self-archiving-pure/taverne-amendment>.

Take-down policy

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Downloaded from the University of Groningen/UMCG research database (Pure): <http://www.rug.nl/research/portal>. For technical reasons the number of authors shown on this cover page is limited to 10 maximum.

**Conversion of CO₂ into organic
carbonates:
a venture into catalysis, reaction
design and product modification**

A.J. Kamphuis

2022

university of
 groningen

faculty of science
and engineering

The work described in this thesis was carried out at the Department of Chemical Engineering, ENgineering and TEchnology institute Groningen (ENTEG), Faculty of Science and Engineering at the University of Groningen, the Netherlands

Cover design and artwork by: Marika Kamphuis and Arjen Kamphuis

Printed by: Ipskamp Printing B.V.

university of
 groningen

Conversion of CO₂ into organic carbonates: a venture into catalysis, reaction design and product modification

PhD thesis

to obtain the degree of PhD at the
University of Groningen
on the authority of the
Rector Magnificus Prof. C. Wijmenga
and in accordance with
the decision by the College of Deans.

This thesis will be defended in public on

Monday 21 February 2022 at 14.30 hours

by

Aeilke Jan Kamphuis

born on 21 August 1990
in Marum

Supervisors

Prof. P.P. Pescarmona
Prof. F. Picchioni

Assessment Committee

Prof. H.J. Heeres
Prof. C.E. Koning
Prof. A.W. Kleij

Dedicated to Marika, Maura & Bo

Table of Contents

CHAPTER 1: CO₂-FIXATION INTO CYCLIC AND POLYMERIC CARBONATES: PRINCIPLES AND APPLICATIONS 11

1.1.	INTRODUCTION	12
1.2.	CATALYSTS FOR THE FIXATION OF CO ₂ INTO CYCLIC AND POLYMERIC CARBONATES	15
1.2.1.	Homogeneous catalytic systems	18
1.2.2.	Heterogeneous catalytic systems	25
1.2.3.	Effect of CO ₂ source on catalyst performance	30
1.3.	APPLICATIONS OF CO ₂ -BASED CYCLIC AND POLYMERIC CARBONATES	30
1.3.1.	Properties of cyclic carbonates	31
1.3.2.	Properties of polycarbonates prepared from CO ₂ and epoxides	34
1.3.3.	Towards fully renewable CO ₂ -based cyclic and polymeric carbonates.....	38
1.3.4.	Application of cyclic and polymeric carbonates in the preparation of polymer products	41
1.3.5.	Application of cyclic and polymeric carbonates in Li-ion batteries ..	58
1.3.6.	Polycarbonates in biomedical and pharmaceutical applications	68
1.3.7.	Other applications of CO ₂ -based polycarbonates	76
1.4.	CONCLUDING REMARKS AND PERSPECTIVES	77
1.5.	THESIS OUTLINE	80
	REFERENCES	81

CHAPTER 2: TI AND ZR AMINO-TRIS(PHENOLATE) CATALYSTS FOR THE SYNTHESIS OF CYCLIC CARBONATES FROM CO₂ AND EPOXIDES 97

2.1.	INTRODUCTION	98
2.2.	EXPERIMENTAL	100
2.2.1.	Materials.....	100
2.2.2.	Equipment	101
2.2.3.	Synthesis of the amino-tBu-tris(phenolate) ligand (1)	101
2.2.4.	Synthesis of titanium(IV) amino-tBu-tris(phenolate) isopropoxide (2a).....	102
2.2.5.	Synthesis of titanium(IV) amino-tBu-tris(phenolate) chloride (2b)	102
2.2.6.	Synthesis of zirconium(IV) amino-tBu-tris(phenolate) isopropoxide (3a).....	102
2.2.7.	Synthesis of zirconium(IV) amino-tBu-tris(phenolate) chloride (3b).....	103
2.2.8.	Catalytic tests	103
2.3.	RESULTS AND DISCUSSION	104

2.4. CONCLUSIONS.....	112
REFERENCES.....	113
SUPPLEMENTARY INFORMATION	117

CHAPTER 3: HIGHLY SELECTIVE SINGLE-COMPONENT FORMAZANATE FERRATE(II) CATALYSTS FOR THE CONVERSION OF CO₂ INTO CYCLIC CARBONATES 127

3.1. INTRODUCTION	128
3.2. EXPERIMENTAL SECTION	129
3.2.1. General Considerations.....	129
3.2.2. Synthesis of the iron complexes	130
3.2.3. Catalytic tests.....	132
3.3. RESULTS AND DISCUSSION	133
3.4. CONCLUSIONS.....	141
REFERENCES.....	141
SUPPLEMENTARY INFORMATION	144

CHAPTER 4: TAILOR-MADE POLYCARBONATES DERIVED FROM CO₂: TUNING THE PROPERTIES VIA THIOL-ENE CLICK MODIFICATION..169

4.1. INTRODUCTION	170
4.2. EXPERIMENTAL.....	172
4.2.1. Materials	172
4.2.2. Methods.....	173
4.2.3. Catalyst synthesis.....	174
4.2.4. Catalytic experiments	174
4.2.5. Post-polymerisation modification.....	175
4.3. RESULTS AND DISCUSSION	180
4.3.1. Catalytic polymerisation of VCHO and CO ₂	180
4.3.2. Post-polymerisation modification of PVCHC	182
4.3.3. Specific properties and potential applications of the functionalized polycarbonates.....	187
4.2. CONCLUSIONS.....	194
REFERENCES.....	195
SUPPLEMENTARY INFORMATION	200

CHAPTER 5: A PH-RESPONSIVE AND HYDROLYTICALLY DEGRADABLE CO₂-BASED POLYCARBONATE PREPARED BY FUNCTIONALISATION USING THIOL-ENE CHEMISTRY 229

5.1. INTRODUCTION	230
5.2. EXPERIMENTAL.....	232

5.2.1.	Materials.....	232
5.2.2.	Methods	233
5.2.3.	Synthesis of PVCHC.....	233
5.2.4.	Thiol-ene click modification.....	235
5.2.5.	Degradation experiments of PVCHC-COOH.....	235
5.2.6.	Evaluation of cytotoxicity	235
5.3.	RESULTS AND DISCUSSION	238
5.4.	CONCLUSIONS	250
	REFERENCES	251
	SUPPLEMENTARY INFORMATION	254
SUMMARY		262
SAMENVATTING		266
LIST OF PUBLICATIONS		270
ACKNOWLEDGEMENTS		272

Chapter 1: CO₂-fixation into cyclic and polymeric carbonates: principles and applications

The reaction between carbon dioxide and epoxides is an attractive pathway for CO₂-utilisation as it leads to the formation of two different, yet both valuable products: cyclic and polymeric carbonates. In this review, the advancements made within this field are critically discussed with special attention to the potential of these two classes of compounds as green chemical products. First, an overview is provided of the various types of homogeneous and heterogeneous catalytic systems developed for achieving the reaction of carbon dioxide with epoxides with high activity and selectivity towards either the cyclic or the polymeric carbonate products. Then, the chemical and physical properties of the cyclic and polycarbonate products are discussed, focussing on the correlation between such properties and the potential applications of each class of compounds. Finally, the most relevant applications of these materials, both potential and industrially implemented, are critically reviewed covering the fields of polymer products, energy storage devices, and biomedical and pharmaceutical applications.

Part of this chapter has been published: A. J. Kamphuis, F. Picchioni and P. P. Pescarmona, *Green Chem.*, 2019, 21, 406–448; DOI: 10.1039/C8GC03086C.

1.1. Introduction

In current chemical product development, the focus of research lies increasingly on environmental friendliness and overall sustainability. Various ways exist to improve the green character of a chemical product, ranging from the substitution of hazardous components of an existing product with safer and more sustainable alternatives, to the design and development of completely novel green chemical products. Incentives for the development of these chemical products can stem from various origins, such as the ambition to design a safer manufacturing process, to decrease the dependence on depleting fossil resources or to reduce waste generation during the production and disposal stages. Criteria and guidelines for these ambitions are summarised by the 'Twelve Principles of Green Chemistry'.¹ The utilisation of carbon dioxide as a building block for chemical products has the potential of fulfilling many of these principles and, accordingly, is receiving growing attention from the academic community, from the industry and, more in general, from the whole society. CO₂ is a renewable and abundant C₁-feedstock and is inexpensive as it is being generated as a waste gas in enormous quantities globally²⁻⁴ (the total worldwide CO₂ emissions were estimated to be 36.2 billion tonnes in 2015).⁵ Being the most oxidised form of carbon, it is extremely stable and hence non-toxic and non-flammable.³⁻⁵ Although chemically rather inert, CO₂ can act as a greenhouse gas by absorbing a fraction of the radiation emitted by the Earth and then re-emitting it towards the planet.⁶ Therefore, the increasing emissions of carbon dioxide in the atmosphere have been identified as one of the main causes of global warming.⁷⁻⁹ Various strategies have been considered in order to counter the accumulation of anthropogenic CO₂ in the atmosphere, including improving energy efficiency and minimising heat losses, increasing the usage of fuels with low or no carbon content (*e.g.* hydrogen) and of renewable energy sources, applying climate engineering approaches (*e.g.* reforestation and afforestation), carbon capture and storage/sequestration (CCS) and carbon capture and utilisation (CCU).⁹ The latter refers to processes aimed at capturing CO₂ at the location where it is emitted and at reusing it, so that it will not enter the atmosphere. The capture is typically limited to localised industrial emissions with high CO₂ concentration, whereas recovering carbon dioxide from, *e.g.*, residential and transportation sources would be technologically, logistically and economically more demanding.^{9,10} The largest industrial source of CO₂ emissions is represented by power plants based on fossil fuel combustion (Table 1.1). Other major sources for CCU include the cement industry (where CO₂ is generated from the conversion of CaCO₃ into CaO), the iron and steel industry, the oil and gas industry (where non-marketable gas is flared, and

hence is converted into CO₂) and ammonia production.^{7,11} Conceptually, CCU represents a very attractive option in the context of carbon neutrality and of a circular economy.¹² However, a number of hurdles need to be overcome before this approach can be implemented. Although technologies are available to capture high amounts of CO₂ with an efficiency of over 80% from large CO₂ emitters such as power plants and cement factories, full-chain technologies including capture, separation, transport and utilisation are still quite costly.⁹

Table 1.1. Global industrial CO₂ emissions in 2014 from: fuel combustion (including all industrial energy-related CO₂ emissions), fugitive emissions (mostly consisting of flaring of non-marketable gas during oil and gas production) and industrial process emissions (including non-energy generation of CO₂ in *i.a.* the cement industry and ammonia production)⁷

Source of CO ₂ emission	Amount of emitted CO ₂ (Mtonnes/year)
Fuel combustion	32 381
<i>Power and heat production</i>	<i>13 625</i>
<i>Fuel used in the extraction and refining of fossil feedstock</i>	<i>1 683</i>
<i>Manufacturing industries and construction</i>	<i>6 230</i>
<i>Transport and other sources^a</i>	<i>10 843</i>
Fugitive emissions^b	483
Industrial processes^b	2 468

^a Such as commercial/institutional activities, agriculture/forestry, fishing and residential. ^b Data from 2010.

Additionally, the final utilisation step represents a relevant challenge because the conversion of CO₂ is limited by its high thermodynamic and kinetic stability.^{13–15} The thermodynamic stability can be overcome by reacting CO₂ with high-energy substrates such as hydrogen, amines or epoxides,^{3,14,16–19} or by providing an energy input in the form of heat,²⁰ electric current²¹ or radiation;²² whereas the kinetic barrier can be overcome by employing a suitable catalyst for the chosen conversion reaction. The conversion of carbon dioxide into fuels is a very attractive option, in view of the large-scale applicability and because it would allow reconverting CO₂ into the same kind of compounds from which it was generated, leading to a circular carbon economy and thus helping to prevent the accumulation of anthropogenic CO₂ in the atmosphere. The possible products of CO₂ reduction include, in increasing order of reduction degree, CO, formic acid, formaldehyde, methanol and higher alcohols, methane and higher hydrocarbons.^{23,24} All these products are industrially relevant, but only those with higher degree of reduction can be employed as fuels. The reduction of CO₂ can be carried out either through direct reaction with H₂ or through an electrochemical or photochemical route:

- The reaction with H_2 has been widely studied and suitable catalysts for this reaction have been developed.^{25–27} However, this route is not yet sustainable because the H_2 needed for this reaction is currently produced from a fossil resource as CH_4 through the steam reforming and water-gas shift reactions,²⁸ whereas efficient and cost-competitive photochemical and/or electrochemical technologies for the production of H_2 through H_2O splitting are not yet mature.^{29–31}
- The direct routes based on the electrochemical or photochemical reduction of CO_2 with concomitant oxidation of H_2O are very attractive from the point of view of sustainability as they can rely on a renewable form of energy (*e.g.* electric power from wind turbines or solar radiation), but they are still facing important challenges in terms of activity in the conversion of CO_2 and product selectivity,^{32,33} particularly if the target product requires the exchange of several electrons (*e.g.* 6 e^- for the reduction of CO_2 to CH_3OH ; 8 e^- for the reduction to CH_4).

Alternatively to its conversion into fuels, CO_2 can be used as feedstock for the production of polymers and fine chemicals.³⁴ Examples include the reaction of CO_2 with epoxides leading to either cyclic or polymeric carbonates;^{13,23,24,35} the formation of dimethyl carbonate via transesterification of CO_2 -derived ethylene carbonate or propylene carbonate with methanol, or via the direct reaction of carbon dioxide with methanol;^{23,35} the reaction of CO_2 with glycerol to produce glycerol carbonate;^{23,35,36} carboxylation of ethylene, phenol salts and aryl and alkyl halides to produce, respectively, acrylic acid, salicylic acid and a variety of aryl and alkyl carboxylic acids;^{13,23,24,35} and the reaction of CO_2 with ammonia to generate urea.^{23,35} The market for these CO_2 -based chemicals is considerable (see Table 1.2 for the estimated market of selected products). Therefore, the utilisation of carbon dioxide as substitute for conventional petroleum-based building blocks can result in a significant decrease in dependence on non-renewable fossil feedstock needed for product manufacturing. While this is a target of large societal and industrial relevance, it is important to realise that CO_2 fixation into chemical products, such as those reported in Table 1.2, will most likely not have a major impact on mitigating the concentration of CO_2 present in the atmosphere, as the amount of carbon dioxide that would be converted yearly is only a small fraction of the anthropogenic CO_2 that is annually emitted into the atmosphere.^{2,23} Among the above-mentioned routes for CO_2 fixation into valuable chemical products, the 100% atom efficient reaction of CO_2 with epoxides is an attractive CO_2 -valorisation pathway that has gained increasing attention during the past few decades.³

Table 1.2. Polymers and fine chemicals potentially* made from CO₂, with estimates of their market size^{35,38}

Chemical	Examples of applications	Estimated market size
Cyclic carbonates	Battery electrolyte, reactive intermediate, solvent.	100 kt/y (in 2013)
Bisphenol-A-based polycarbonates	Car manufacturing, CDs and DVDs, optical lenses, construction.	5-6 Mt/y (in 2016)
Dimethyl carbonate	Reagent, solvent, battery electrolyte, gasoline additive.	≥200 kt/y (in 2013)
Acrylic acid	Monomer for polymers used as e.g. superabsorbents, detergents, adhesives and coatings.	2.5 Mt/y (in 2014)
Urea	Liquid fertiliser.	240 Mt/y (in 2016)

*Note that the synthesis method employing CO₂ is not necessarily the (only) current route to produce these chemicals

This review focuses on this route, by providing an overview of the progress made in the catalytic synthesis of cyclic and polymeric carbonates and in their applications. The major classes of catalysts that have been developed to enable the reaction of carbon dioxide with epoxides are reviewed in section 1.2. The physicochemical properties of the cyclic and polymeric carbonates directly derived from CO₂ and their correlation with the potential applications of these compounds are discussed in the first part of section 1.3. The rest of this section provides a critical review of the existing and potential applications of these carbonate products, with special focus on polymeric products (e.g. coatings, adhesives and foams), electrolytes in energy storage devices, and biomedical applications.

1.2. Catalysts for the fixation of CO₂ into cyclic and polymeric carbonates

The catalysed reaction of CO₂ with an epoxide producing a polymer containing carbonate linkages was reported for the first time in 1969.³⁷ Since then, growing research efforts have been dedicated to the development of catalytic systems for this reaction, as well as towards the employment of a variety of different epoxide

Fig. 1.1. General scheme of the reaction of an epoxide with CO₂.

substrates. These include petroleum-based epoxides such as ethylene oxide, propylene oxide and cyclohexene oxide as well as (potentially) bio-based epoxides such as limonene oxide and vinylcyclohexene oxide. The reaction of an epoxide with CO₂ can in principle yield two possible products: a five-membered cyclic carbonate and/or a polymeric carbonate (Fig. 1.1). The catalytic systems that are used to promote the conversion of carbon dioxide and epoxides into these organic carbonates generally consist of a Lewis base acting as a nucleophile, often assisted by a Lewis acid species in the form of one or more metal centres. The most commonly proposed reaction mechanism is depicted in Fig. 1.2.^{14,17,19} The first step of the catalytic cycle is the activation of the epoxide ring by the Lewis acid (**1** in Fig. 1.2), which promotes the nucleophilic attack by the Lewis base leading to the opening of the epoxide ring. The formed alkoxide intermediate (**2**) can in turn act as a nucleophile and attack CO₂ to form a carbonate intermediate (**3**). The following step is either a ring closure (**4a**) to produce a cyclic carbonate (**5a**), or the alternating insertion of more epoxide and CO₂ molecules (**4b** and **5b**) to yield a polycarbonate (**6b**).^{14,17,19} The consecutive insertion of two epoxide molecules in the polymer chain may also occur, leading to the presence of ether linkages in the polycarbonate. Besides this, other reaction mechanisms have been proposed, in some cases specific to a type of catalyst (*e.g.* β-diiminate zinc complexes – see Fig. 1.3).^{39,40} A wide variety of homogeneous and heterogeneous catalytic systems has been developed for the reaction of CO₂ with epoxides, with the purpose of increasing the activity but also of maximising the selectivity towards either the cyclic carbonate or the polycarbonate product. Numerous excellent reviews exist on the catalysis of CO₂/epoxide reactions,^{3,13,14,24,41,42} including few focussing only on the synthesis of cyclic carbonates^{16,43–50} or only on polycarbonates.^{2,4,5,15,17,51–55} The reader interested in a detailed overview of the numerous existing catalytic systems and/or in the various proposed reaction mechanisms is kindly referred to the above-mentioned references. Here, we provide a systematic and concise overview of the main classes of catalysts that have been studied for the CO₂/epoxide reaction, by rationalising them on the basis of their nature and of the type of active sites.

Fig. 1.2. Proposed reaction mechanism for the reaction of CO₂ with epoxides yielding either cyclic or polymeric carbonates, in the presence of a Lewis acid (typically a metal centre, M) that activates the epoxide, and a Lewis base (X⁻) acting as nucleophile.

Therefore, the catalysts were categorised into homogeneous and heterogeneous systems, which were further divided with respect to their catalytic species: systems containing Lewis base functionalities, or systems presenting a combination of Lewis acid and base species. For the latter group, a distinction is made between metal-based and metal-free catalysts. For each of these categories, we summarised the main assets and drawbacks (Table 1.3).

1.2.1. Homogeneous catalytic systems

Lewis base homogeneous catalysts that only consist of an ionic nucleophile (Hom1 in Table 1.3) are typically organic halides such as quaternary ammonium salts, phosphonium salts and ionic liquids.^{16,42,44,46,56} Neutral Lewis bases such as strong organic bases are also used as homogeneous catalysts.^{42,44} A selection of commonly employed homogeneous Lewis base compounds is shown in Fig. 1.3: tetrabutylammonium halides (TBAX),^{57–60} imidazolium halides,^{46,61} bis(triphenylphosphine)iminium halides (PPNX)⁶² and 4-dimethylaminopyridine

(DMAP).^{63,64} When these Lewis bases are employed as catalysts in the absence of a Lewis acid (that would coordinate the growing polycarbonate chain, see Fig. 1.2), the ring closure becomes the most favourable step after the formation of the carbonate intermediate, leading to the selective formation of the cyclic carbonate product. The major limitation in the use of Lewis base homogeneous catalysts is that the separation of the produced cyclic carbonates by distillation is quite energy-intensive, due to the fact that cyclic carbonates have high boiling points (see Table 1.7).⁶³ Moreover, tetraalkylammonium halides tend to undergo thermal degradation through a dequaternisation reaction, which would hamper their reuse if the removal of the carbonate is carried out by distillation at high temperature.⁶⁵ Lewis base catalysts typically require relatively high reaction temperatures ($\geq 80\text{ }^{\circ}\text{C}$) to achieve good carbonate yields.^{14,16}

In order to increase the activity and reach high conversions also under milder conditions, the Lewis base catalysts are often combined with Lewis acids. The most widely employed type of Lewis acid sites is provided by metal cations complexed by suitable organic ligands. A wide range of metal complexes have been studied, with zinc, chromium, cobalt, aluminium and iron being the most common metal atoms.^{4,16,24,41,43,45,54,66} The metal-based Lewis acid complexes are usually combined with one of the aforementioned Lewis bases. Such homogeneous binary catalytic systems (Hom2 in Table 1.3) constitute the class of catalysts for the CO_2 /epoxide reaction that has been most actively studied so far. The best representatives of this type of catalytic systems are characterised by very high activity even under mild conditions ($T \leq 60\text{ }^{\circ}\text{C}$, $p(\text{CO}_2) \leq 10\text{ bar}$) and can display high selectivity towards either the cyclic or the polymeric carbonate. Often, the selectivity can be tuned by varying the type of nucleophilic species and the nucleophile-to-metal ratio. A nucleophile that is a better leaving group (as I^-) will tend to favour the ring-closure step (**4a** in Fig. 1.2), thus leading to higher selectivity towards the cyclic carbonate product, whereas a worse leaving group (as Cl^-) will tend to remain bound to the intermediate, thus promoting the growth of the polymer chain (**4b** and **5b**).^{14,17} It was also observed that at a nucleophile-to-metal ratio > 1 , the nucleophile can tend to displace the carbonate intermediate from the metal centre, thus favouring the ring-closure step (Fig. 1.2, **4a**).^{17,19}

The selectivity between cyclic and polymeric carbonate can also be adjusted by changing the reaction temperature. Cyclic carbonates are the thermodynamically favoured products of the reaction, while the formation of the polycarbonates generally has lower activation energy. Therefore, higher reaction temperatures will promote the formation of the cyclic product, whereas lower reaction temperatures

can lead to a kinetic control of the reaction, thus favouring the polymeric product.¹⁷ Additionally, higher CO₂ pressure (up to carbon dioxide in the liquid or supercritical state) can increase the reaction rate by improving the contact between the reaction components, while also favouring the formation of the polycarbonate product by enhancing the rate of the CO₂-insertion step (Fig. 1.2, **5b**).¹⁷ The tuning of the above-mentioned parameters often allows to achieve the selective formation of either the cyclic or polymeric carbonate (Table 1.4, entries 1-7), and even to switch effectively the selectivity between the two products while using the same metal complex (Table 1.4, entries 23-24).^{19,67}

Among the classes of metal complexes employed as homogeneous catalysts for the synthesis of cyclic and polymeric carbonates from CO₂ and epoxides, metal-porphyrins received considerable attention (**1** in Fig. 1.3 and Table 1.4, entries 1-7). Their planar geometry makes them especially suitable for the coordination of terminal epoxides to the Lewis acidic metal centre.⁴³ Though metal(III)-porphyrins can contain a nucleophilic species as axial ligand (**1a**, **1b** and **1c** in Fig. 1.3), the activity of these complexes is significantly enhanced by using them in combination with a Lewis base acting as nucleophile for the ring-opening of the epoxide.²⁴ Used metal centres include aluminium,^{68,69} chromium^{70,71} and cobalt.^{72,73} More recently, a series of highly active bifunctional metalloporphyrin catalysts containing both Lewis acid sites (magnesium or zinc) and Lewis base functionalities has been reported (**1d** and **1e** in Fig. 1.3).^{74,75} Another important class of homogeneous catalysts that has been investigated extensively for the synthesis of both cyclic carbonates as well as polycarbonates consists of metal complexes with salen/salphen-based ligands (Fig. 1.3, **2**). Various metal centres have been examined, including chromium,^{76,77} aluminium⁷⁸ and cobalt^{79,80} incorporated in salen complexes (Fig. 1.3, **2a-c** and Table 1.4, entries 8-13) and zinc in salphen complexes⁸¹ (Fig. 1.3, **2d** and Table 1.4, entry 14). An advantage of salen ligands is that their synthesis is easier and that they are less expensive than *e.g.* porphyrin ligands. Moreover, the synthesis method has the potential to be scaled-up, which is an important asset for a possible industrial use of these catalysts.⁴³ Similarly to the case with porphyrins, salen/salphen-based catalysts with metal(III) centres contain an axial ligand that can act as a nucleophile, and can thus function as bifunctional catalysts in the CO₂/epoxide reaction. However, they often require a Lewis base co-catalyst in order to reach sufficient product yields. In the case of zinc(II)-salphen, no axial ligand is present and including a separate Lewis base becomes strictly necessary to perform the opening of the epoxide ring. Although salen and salphen catalysts show high activity for the conversion of terminal epoxides, they are

Table 1.3. Overview of catalyst categories for the CO₂/epoxide reaction

Catalytic system			Code	Activity	Selectivity	Stability	Reusability	Cost
Homogeneous	Lewis base		Hom1	+/-	Cyclic	+/- (issue: thermal stability under operating conditions)	-	++
	Lewis acid + Lewis base	Metal-based	Hom2	++	Tuneable cyclic/polymeric	+ (Al, Fe, Cr) - (Co porphyrin/salen, Zn β -diiminate)	-	-
		Metal-free	Hom3	+	Cyclic	+	-	++
Heterogeneous	Lewis base		Het1	-	Cyclic	+/- (issue: thermal stability under operating conditions)	+	+
	Lewis acid + Lewis base	Metal-based	Het2	+	Polymeric (Zn glutarate)/cyclic (others)	+ (Zn glutarate) +/- (MOFs)	++ +/- (MOFs)	+ (Zn glutarate) - (MOFs)
		Metal-free	Het3	+	Cyclic	+	++	+

generally significantly less active towards internal epoxides.⁴³ Furthermore, while Cr-based salen complexes were reported to be air-stable,⁷⁷ many highly active Co-salen complexes are air and moisture sensitive.¹⁷ Moreover, Co-based salen and porphyrin catalysts were observed to deactivate during CO₂/propylene oxide copolymerisation through reduction of the cobalt centre.^{2,82} Zinc β -diiminates represent another well-studied class of homogeneous catalysts that has found widespread application in polymerisations of CO₂ with a broad range of epoxides (Fig. 1.3, **3**).^{39,83,84} The catalytic behaviour of this type of complexes proved to be highly tuneable by modifying the substituents present on the N-aryl ring and the diamine backbone (Table 1.4, entries 15-17).^{14,85} The zinc β -diiminate complexes can exist both in dimeric (bimetallic) or monomeric (monometallic) form, with the former being most likely the main responsible for the catalytic activity. These metal-complexes do not need addition of a Lewis base to be able to catalyse effectively the reaction.³⁹ Zinc β -diiminate catalysts are very selective towards the polycarbonate product and are very active with various epoxides, including challenging substrates as functionalised cyclohexene oxides⁸⁶ and limonene oxide.⁸⁷ A limitation of the zinc β -diiminates is their sensitivity to air and moisture, which imposes to prepare and use them under inert conditions.^{39,83,84} Another type of Zn-based catalyst is the bimetallic macrocyclic phenolate zinc complex **4a** (Fig. 1.3), which gained attention by showing high activity towards epoxide/CO₂ polymerisation even at very low CO₂ pressure (1 atm) (Table 1.4, entry 18).^{88,89} Moreover, this zinc complex was observed to be air-stable.⁸⁸ In addition to zinc,

Fig. 1.3. Selected homogeneous catalysts for the CO₂/epoxide reaction.

other metals that have been investigated in this type of complex include iron⁹⁰ and magnesium (Fig. 1.3, **4b** and **4c**).⁹¹ The iron bimetallic macrocyclic phenolate complex was able to catalyse the reaction of CO₂ with cyclohexene oxide, propylene oxide and styrene oxide, although the addition of a Lewis base (PPNCl) was required with the latter two epoxides. Additionally, a shift in selectivity from complete selectivity towards poly(cyclohexene carbonate) formation to full selectivity towards cyclic cyclohexene carbonate formation was realised by increasing the

catalyst loading (by a factor 10), lowering the CO₂ pressure (from 1.0 to 0.1 MPa) and by addition of PPNCI (Table 1.4, entries 19 and 20).⁹⁰

Table 1.4. Performance of selected homogeneous metal-based catalytic systems in the reaction of CO₂ with epoxides

#	Cat.	Cat. loading (mol %) ^a	Epox.	Conv/Yield (%)	Sel _{PC:CC} (%) ^b	TON _{metal} ^c	TON _{LB} ^d	Temp. (°C)	CO ₂ pressure (bar)	Time (h)	M _n (g/mol)	PDI	Ref
1	1a''	1/1 EtPH ₃ PBr	CHO	100 (C)	100:0	100	50	RT	49	14 d	6200	1.06	69
2	1b'	0.014/0.088 DMAP	EB	100 (C)	0:100	7073	984	50	54	100	-	-	70
3	1b''	0.036/0.31 DMAP	CHO	63 (Y)	100:0	1743	291	110	228	8	3450	1.19	71
4	1c	0.039/0.077 2 DMAP	PO	42 (Y)	0:100	1102	367	120	17	1.33	-	-	72
5	1c	0.2/0.15 DMAP	PO	95 (Y)	95:5	475	271	40	51	48	149000	1.18	73
6	1d	0.005/0	EH	80 (Y)	0:100	16000	4000	120	10	3	-	-	74
7	1e	0.005/0	EH	88 (Y)	0:100	17600	4400	120	10	3	-	-	74
8	2a'	0.075/0.075 DMAP	PO	69 (Y)	n.a.	916	458	100	6.9	1	-	-	76
9	2a''	0.040/0	CHO	10 (C)	n.a.	250	250	80	58.5	24	8900	1.2	77
10	2b	0.02/0.02 TBABr	EO	44 (Y)	n.a.	2220	1110	110	150-160	1	-	-	78
11	2b	0.1/0.1 TBABr	EO	96 (C)	0:100	960	480	30	25	72	-	-	78
12	2c'	0.2/0	PO	49 (Y)	>99:<1	243	243	25	55.2	3	15300	1.22	79
13	2c''	0.067/0.133 DMAP	PO	27 (Y)	n.a.	400	133	100	20.7	0.33	-	-	80
14	2d	2.5/2.5 TBAI	EH	80 (C)	0:100	32	32	45	10	18	-	-	81
15	3a	0.1/0	CHO	45 (C)	100:0	449	-	50	6.9	2	19100	1.07	83
16	3b	0.1/0	CHO	48 (C)	100:0	494	-	50	6.9	2	31000	1.11	83
17	3c	0.1/0	CHO	38 (C)	100:0	382	-	50	6.9	0.17	22900	1.09	85
18	4a	0.2/0	CHO	53 (C)	94:6	264	264	100	1	21	7360	1.21	88
19	4b	0.02/0	CHO	25 (C)	99:1	1285	643	80	10	24	17200	1.03	90
20	4b	0.2/0.4 PPNCI	CHO	41 (C)	0:100	205	51	80	1	48	-	-	90
21	4c'	0.02/0	CHO	33 (C)	>99:<1	1650	1650	100	1	20	14600/3500	1.02/1.08	91
22	5a'	0.0005/0.05 PPNBr	EH	36 (C)	<1:>99	72000	720	90	10	2	-	-	92
23	5b'	0.5/5 PPNCI	CHO	85 (C)	0:96	170	17	85	80	3	-	-	19
24	5b'	0.5/0.5 PPNCI	CHO	98 (C)	>99:<1	196	196	85	80	3	n.a.	n.a.	19

^a Catalytic loading in molar percentage of epoxide substrate, based on moles of metal sites/based on moles of nucleophilic species added separately. ^b Selectivity towards polycarbonate:cyclic carbonate. ^c Turnover number expressed as mol of converted epoxide (when the conversion was reported) or mol of produced carbonate (when the yield was reported) per mol of metal sites. ^d Turnover number expressed as mol of converted epoxide or mol of produced carbonate per mol of nucleophilic species. n.a. = not available. CHO: cyclohexene oxide; EB: 1,2-epoxybutane; EH: 1,2-epoxyhexane; EO: ethylene oxide; PO: propylene oxide. PDI: polydispersity index, M_w/M_n.

One of the most promising types of homogeneous catalysts for epoxide/CO₂ conversion consists of an aluminium(III) centre combined with an amino trisphenolate ligand (Fig. 1.3, **5a**).^{18,92,93} The complex needs to be combined with a Lewis base, such as TBAX or PPNX: this binary catalytic system showed to be highly active for the reaction of CO₂ with a wide range of epoxide substrates.⁹² Considerable variations in catalytic activity were observed between Al(III) amino trisphenolate complexes with different substituents on position 2 and 4 of the phenolate rings.¹⁸

Recently, it was shown that the methyl-substituted aluminium amino trisphenolate complex used in combination with PPNCl or PPNBr is able to efficiently catalyse the copolymerisation of CO₂ with the highly challenging limonene oxide.⁹⁴ In addition to aluminium-based complexes, iron-based amino trisphenolate (Fig. 1.3, **5b**; Table 1.4, entries 23-24) and amino bis(phenolate) complexes have also been used in CO₂ conversion reactions, allowing to switch effectively the selectivity between cyclic and polymeric carbonates by tuning the type and relative amount of organic halide used as nucleophile source.^{19,67} When considering the potential for applicability of these catalysts, besides their activity, selectivity and stability, it is important to take into account the cost of the synthesis and the availability of the employed elements. In this context, only six metals are classified as abundant worldwide: aluminium, iron, calcium, sodium, potassium and titanium (in order of decreasing abundance).⁴⁵ Of these metals, which have the additional advantage of displaying relatively low-toxicity,⁹⁵ aluminium and iron were employed in highly active and selective catalysts for the synthesis of CO₂-based carbonates and seem thus an optimum choice from a sustainability point of view.⁴⁵

The metal-based complexes discussed above can reach excellent catalytic performance but their applicability can be hampered by their often costly and complex synthesis procedure. Against this backdrop, the development and investigation of metal-free catalysts for the CO₂/epoxide reaction has gained increasing attention in recent years. Organocatalysts are considered as a non-toxic, low-cost and more sustainable alternative to metal-based catalysts.^{42,48,49} Additionally, organocatalysts generally possess good stability and inertness towards air and moisture and in some cases can be derived from renewable resources.⁴² Moreover, the use of organocatalysis instead of metal complexes has the potential to increase the safety of consumer products by minimising the amount of metal residues that may cause health hazards.⁴² On the other hand, the catalytic activity of organocatalysts is still significantly lower compared to the best metal-based homogeneous catalysts and cyclic carbonates are typically the only products, thus

excluding polycarbonates from the scope of these catalysts.⁴² In addition to the previously discussed homogeneous catalysts that only possess a Lewis base functionality (e.g. TBAX, PPNX and DMAP in Fig. 1.3), the newest generation of metal-free homogeneous organocatalysts includes both Lewis acid and Lewis base functionalities (Hom3 in Table 1.3). These can be present in a bifunctional single-component catalyst or in a binary system consisting of two separate components. The first category typically consists of onium salts or ionic liquids containing hydroxyl, carboxylic acid or amino moieties, such as protic tetraalkylammonium halides (e.g. Table 1.5, entry 1),^{96–99} protic phosphonium halides (e.g. Table 1.5, entry 2),^{100,101} protic imidazolium compounds (e.g. Table 1.5, entry 3)^{102–104} and functionalised DMAP.¹⁰⁵ In these systems, the protic functional groups can activate the epoxide substrate by interacting with its O atom through hydrogen bonding.^{42,48,65,106}

Table 1.5. Performance of selected homogeneous metal-free catalytic systems in the reaction of CO₂ with epoxides

#	Cat.	Cat. loading (mol %) ^a	Epox.	Conv./Yield (%)	Sel _{PC:CC} (%) ^b	TON _{LA} ^c	TON _{LB} ^d	Temp. (°C)	CO ₂ pressure (bar)	Time (h)	M _n (g/mol)	PDI	Ref
1	2-Hydroxyethyl-TBAI	0.1/0	EB	39 (Y)	n.a.	392	392	150	20	1	-	-	96
2	2-Hydroxyethyl-TBPI	2/0	EB	92 (Y)	n.a.	46	46	90	10	2	-	-	100
3	HEMIMBr	1.6/0	PO	99.2 (C)	0:>99	62	62	125	20	1	-	-	102
4	Pyrogallol/TBABr	3 ^e /3	PO	79 (Y)	n.a.	26 ^e	26	60	20	1.67	-	-	107
5	Tannic acid/TBAI	0.05 ^e /2.0	EH	24 (Y)	<1:>99	472 ^e	12	80	10	2	-	-	108
6	Et ₃ B/PPNCl	0.050/0.025	CHO	90 (Y)	95:5	1800	3600	80	10	6	28300	1.9	119

^a Catalytic loading in molar percentage of epoxide substrate, based on moles of Lewis acid sites/based on moles of nucleophilic species added separately. ^b Selectivity towards polycarbonate:cyclic carbonate. ^c Turnover number expressed as mol of converted epoxide (when the conversion was reported) or mol of produced carbonate (when the yield was reported) per mol of Lewis acid sites. ^d Turnover number expressed as mol of converted epoxide or mol of produced carbonate per mol of nucleophilic species. ^e Note that these compounds contain several potential Lewis acid sites, but that in this case the catalyst molar loading and TON_{LA} are calculated based on the whole molecule. n.a. = not available. CHO: cyclohexene oxide; EB: 1,2-epoxybutane; EH: 1,2-epoxyhexane; PO: propylene oxide. PDI: polydispersity index, M_w/M_n.

In the second category, several protic compounds containing hydroxyl or carboxylic acid moieties have been employed as catalysts in combination with Lewis bases, including bio-based compounds such as pyrogallol (Table 1.5, entry 4),^{65,107} gallic acid,¹⁰⁷ tannic acid (Table 1.5, entry 5)¹⁰⁸ and water¹⁰⁹ but also other phenolic compounds,^{110,111} silanediol complexes,¹¹² fluorinated alcohols,^{107,113,114} boronic

acids,¹¹⁵ carboxylic acid-containing amines,¹¹⁶ simple alcohols¹¹⁷ and cavitand-based polyphenols.¹¹⁸ The relative weakness of the hydrogen bonding between the protic groups of these catalysts and the epoxides compared to the typical strong coordination of an epoxide with a metal, explains why cyclic carbonates are the only products when these organocatalysts are employed. On the other hand, there exist a report of the synthesis of polycarbonates from CO₂ and epoxides using metal-free catalysts (Table 1.5, entry 6).¹¹⁹ However, a strongly pyrophoric and water- and air-sensitive compound as triethylborane was employed as a Lewis acid, which limits the applicability of the catalytic system and diminishes the 'green' character typically associated with organocatalysts.

1.2.2. Heterogeneous catalytic systems

The most extensively studied type of catalysts for the fixation of CO₂ through the reaction of CO₂ with epoxides are homogeneous systems, but the importance of an efficient and straightforward separation and reutilisation of the catalyst stimulated the investigation of several heterogeneous systems. Various Lewis base heterogeneous catalysts have been developed (Het1 in Table 1.3, for a selected example see catalyst **1** in Fig. 1.4),¹²⁰ with the active sites being provided by immobilised ionic liquids,^{120–128} onium salts^{129–131} and non-ionic organic bases.^{132–134} Polymers^{121,128,129,131} and silica-based materials,^{120,122–126,130,132–134} including ordered mesoporous silica with high specific surface area such as MCM-41^{126,134} and SBA-15,^{122,125} have been studied as supports to immobilise these active species. The immobilisation is realised through robust, covalent bonding to prevent the leaching of active species into the reaction mixture. These heterogeneous catalysts solve the separation problems associated with homogeneous catalytic systems, but they typically need high temperatures (≥ 100 °C) in order to reach high conversion rates of the epoxides.^{135,136} The performance of a selection of heterogeneous Lewis base catalysts for the CO₂/epoxide reaction is displayed in Table 1.6, entries 1–3. Similarly to the case of homogeneous catalysts, the presence of a Lewis acid that activates the epoxide towards the nucleophilic attack by the Lewis base enhances the activity of the heterogeneous systems (Het2 in Table 1.3, for a selected example see catalyst **2** in Fig. 1.4).¹³⁷

Examples of these systems include supported metal catalysts functionalised with Lewis base moieties, such as Zn/SBA-15 functionalised with ammonium groups,¹³⁸ and the immobilisation of metal complexes that had previously proven to be promising homogeneous catalysts, such as bifunctional Al-salen complexes supported on polystyrene¹³⁹ or silica (Table 1.6, entry 4).¹³⁷ A different class of materials that can present Lewis acid sites and that has been increasingly studied as

Fig. 1.4. Selected heterogeneous catalysts for the $\text{CO}_2/\text{epoxide}$ reaction: (1) Multilayered covalently supported ionic liquid phase (mlic-SILP); (2) Immobilised metal complex; (3) Metal-organic framework (MOF); (4) Porphyrin-based metal-functionalised porous organic polymers (metal-POP).

heterogeneous catalysts for the $\text{CO}_2/\text{epoxide}$ reaction are metal-organic frameworks (MOFs).¹⁴⁰ These highly porous crystalline materials consist of metal nodes interconnected through organic linkers so that a crystalline structure is generated. MOFs can be prepared with different (micro)pore sizes and display very high surface area (typically $S_{\text{BET}} > 1000 \text{ m}^2/\text{g}$). The metal nodes can contain coordinatively unsaturated sites displaying Lewis acid behaviour.¹⁴¹ Many MOF structures show high affinity towards CO_2 adsorption. This feature and the possible presence of Lewis acid sites render them potentially suitable candidates as heterogeneous catalysts for CO_2 fixation.^{49,141} This type of MOF (e.g. MOF-5,¹³⁵ MOF-

505,¹³⁶ Cr-MIL-100,¹⁴² Cr-MIL-101^{142,143}, UMCM-1-NH₂¹⁴⁴, In₂(OH)(btc)(Hbtc)_{0.4}(L)_{0.6}·3H₂O,¹⁴⁵ USTC-253-TFA¹⁴⁶ and gea-MOF-1¹⁴⁷ (Table 1.6, entry 5, and catalyst **3** in Fig. 1.4)) can act as heterogeneous catalysts for the CO₂/epoxide reaction in combination with an organic halide. In this case the catalytic system is partially homogeneous, which is a drawback in terms of catalyst separation and reutilisation. An alternative approach to introduce metallic Lewis acid sites into MOFs is based on the use of organic linkers that, besides connecting the metal nodes, are able to form complexes with single metal sites. This strategy has been employed to develop zirconium-based porphyrin MOFs¹⁴⁸ (Table 1.6, entry 6) and copper-based MOFs incorporating azamacrocyclic ligands.¹³⁶ In addition to MOFs solely containing Lewis acid sites, the organic linkers of specific MOFs possess Lewis basic moieties (e.g. ZIF-8,¹⁴⁹ ZIF-67,¹⁵⁰ ZIF-68,¹⁵¹ ZIF-90¹⁵² (Table 1.6, entry 7) and Co-MOF-74¹⁵³) or can be functionalised with a nucleophile source (e.g. amine moieties,¹⁴⁹ pyridinium iodide,¹⁵⁴ quaternised hydrazine¹⁵⁵ (Table 1.6, entry 8) and quaternised ammonium^{156,157} and phosphonium groups¹⁵⁷) so that both Lewis acid and Lewis base active sites are present in the solid catalyst. Functionalisation of the organic linkers with bulky nucleophilic species can however cause a decrease in pore volume and surface area, with possible limitations for the diffusion of reactants and products.^{154–158} Although promising results have been achieved with MOFs as catalysts for the CO₂/epoxide reaction, many of these materials still suffer from low stability under the employed reaction conditions, which leads to deactivation of the catalyst, thereby limiting reusability.¹⁴² Further limitations that can be encountered with MOF catalysts reported in the literature include the need to use very high loading of homogeneous organic halides,^{136,159,160} high reaction temperature,^{147,150–152} and diffusion limitations of reactants, products and organic halides.¹⁴²

Another class of materials containing metal centres in a porous structure that has gained increasing attention in recent years as heterogeneous catalysts for the CO₂/epoxide reaction is represented by metal-functionalised porous organic polymers (metal-POPs).^{161–166} One of the key features of these porous organic polymers is that they can be synthesised in numerous types of amorphous porous structures incorporating various organic functional groups,^{161,163} thereby introducing a large degree of freedom in tuning properties such as type and amount of active sites, surface area, pore volume and pore size.^{162,164} The ability to tune the pore volume and pore size of POP materials could prevent diffusion limitations of reactants and products,¹⁶⁴ which on the other hand is a common drawback with functionalised MOFs. The Lewis acid metal centres can be incorporated in the material via different strategies, e.g. crosslinking of pre-synthesised metal-organic

Table 1.6. Performance of selected heterogeneous catalytic systems in the reaction of CO₂ with epoxides

#	Cat.	Cat. loading (mol %) ^a	Epox.	Conv/ Yield (%)	Sel _{PC:CC} (%) ^b	TON _{LA} ^c	TON _{LB} ^d	Temp (°C)	CO ₂ pressure (bar)	Time (h)	M _n (g/mol)	PDI	Ref
1	SiO ₂ - <i>p</i> -xylene-I (mlc-SILP)	0/0.42	SO	99 (C)	<1:>99	-	237	150	80	3	-	-	120
2	<i>n</i> -Bu ₄ NBr/SiO ₂	0/1	PO	97 (Y)	n.a.:98	-	97	150	80	10	-	-	130
3	TBD@silica	0/0.27	PO	100 (C)	0:100	-	367	150	50	24	-	-	132
4	[Al(salen)] ₂ -Br/ amorphous silica	5/10	SO	78 (C)	n.a.	16	8	RT	1	20	-	-	137
5	gea-MOF-1/TBABr	0.15/0.15	EB	94 (Y)	n.a.	627	627	120	20	6	-	-	147
6	PCN-224(Co)/TBACl	0.090/0.20	PO	42 (C)	n.a.	461	194	100	20	4	-	-	148
7	ZIF-90	0.59/n.a.	PO	88 (C)	n.a.:92	151	n.a.	120	12	8	-	-	152
8	F-ZIF-90	0.088/n.a.	AGE	75 (Y)	0:100	855	n.a.	120	11.7	6	-	-	155
9	Mg-por/pho@POP	0.005/n.a.	PO	78 (Y)	n.a.:>98	15600	n.a.	140	30	1	-	-	161
10	FDU-HEIMBr	n.a./0.5	PO	99 (Y)	<1:>99	n.a.	198	110	10	3	-	-	177
11	mQC-1.I	0.8/0.4	PO	98 (C)	<1:>99	121	242	120	12	3	-	-	185
12	Zn glutarate	0.33/0	PO	n.a.	96:n.a.	7146 ^e	n.a.	80	40	20	103000	2.8	190
13	Zn ₃ [Co(CN) ₆] ₂ /tBuOH	0.028/0	CHO	95 (C)	43.5:0	3340 (Zn)	n.a.	100	38	2	47250	3.4	191

^a Catalytic loading in molar percentage of epoxide substrate, based on moles of Lewis acid sites/based on moles of nucleophilic species. ^b Selectivity towards polycarbonate:cyclic carbonate. ^c Turnover number expressed as mol of converted epoxide (when the conversion was reported) or mol of produced carbonate (when the yield was reported) per mol of Lewis acid sites. (Note: in the case of metal-containing catalysts, the TON is expressed as mol of converted epoxide per mol of metal sites, though this might lead to an underestimation of the actual TON values because not all metal sites are necessarily acting as Lewis acid active sites).¹⁴² ^d Turnover number expressed as mol of converted epoxide or mol of produced carbonate per mol of nucleophilic species. ^e In grams of polymer per moles of zinc. n.a. = not available. AGE: allyl glycidyl ether; CHO: cyclohexene oxide; EB: 1,2-epoxybutane; PO: propylene oxide; SO: styrene oxide. PDI: polydispersity index, M_w/M_n.

complexes by organic linkers,^{161,162,164,166–168} or synthesis of a microporous organic network, in which metal ions are introduced afterwards.^{163,165,168} Examples of metal-POP catalytic systems that have been evaluated for the CO₂/epoxide reaction include binary systems where the metal-POP was combined with an organic halide^{165–168} as well as fully heterogeneous bifunctional systems where the metal-POP contained both Lewis acid and Lewis base sites.^{161–164} A bifunctional porphyrin-based metal-POP system containing magnesium metal sites and quaternary phosphonium bromide species displayed one of the highest turnover numbers for heterogeneous catalysts for the conversion of CO₂ and epoxides into cyclic carbonates (Table 1.6, entry 9, Fig. 1.4).¹⁶¹ The activation of the epoxide can also be

achieved without metal sites if protic groups are present at the surface of the heterogeneous catalyst (Het3 in Table 1.3). One of the first examples of this type of catalysts are the silica-supported phosphonium salts, for which it was proposed that the surface silanols can activate the epoxide and thus enhance the activity of the immobilised salt in their proximity.¹⁶⁹ Typically, metal-free heterogeneous catalysts with Lewis acid and Lewis base functionalities are prepared by tailored synthesis of the immobilised active groups as in polymer-supported ionic liquids with hydroxyl or carboxylic acid moieties,^{170–174} hydroxyl- or carboxylic-acid-containing ionic liquids grafted on silica,^{125,175,176} hydroxyl- and carboxylic-acid-functionalised ionic liquids immobilised on a mesoporous polymeric substrate¹⁷⁷ (Table 1.6, entry 10) and hydroxyl-functionalised quaternary ammonium moieties grafted on polystyrene or silica.^{178–180} Metal-free covalent organic frameworks (COFs) have also been reported as heterogeneous catalysts for the reaction of CO₂ with epoxides.^{181,182} Being constructed from molecular organic building blocks, the type of functional groups (e.g. Lewis bases¹⁸² or Lewis acids¹⁸¹) as well as the size and shape of the pores of these catalyst can be tailored.

Other examples of materials that possess metal-free Lewis acid moieties include bio-based compounds such as cellulose and chitosan. Cellulose has been investigated as a bio-based heterogeneous catalyst for the CO₂/epoxide reaction both in the presence of a homogeneous Lewis base^{183,184} and as bifunctional single-component system with immobilised quaternary ammonium moieties (Table 1.6, entry 11).¹⁸⁵ Chitosan, which is a polysaccharide derived from naturally occurring chitin extracted from the shells of *e.g.* shrimps and crabs,¹⁸⁶ was functionalised to introduce quaternary ammonium moieties^{187,188} or imidazolium moieties¹⁸⁹ and was subsequently evaluated as a bio-based and metal-free heterogeneous catalyst for the CO₂/epoxide reaction, displaying similar but slightly lower activity compared to the best cellulose-based catalysts. All the heterogeneous catalysts described above yield cyclic carbonate as the main product, because the nucleophile-to-Lewis acid ratio is > 1, or because the activation of the epoxide occurs through mild hydrogen-bonding, or finally because the reaction temperature is relatively high (> 100°C). There exist also metal-based heterogeneous catalytic systems that allow the selective copolymerisation of CO₂ with epoxides, generally with propylene oxide as substrate.^{192–195} The two main types of such heterogeneous catalysts are zinc carboxylates, with zinc glutarate (Table 1.6, entry 12) being the most active representative, and double metal cyanides.⁵³ Zinc glutarate and other zinc carboxylates are industrially relevant, as they are easy to handle, non-toxic, air-stable and economically viable.^{2,5} Double metal cyanide catalysts [Zn₃(M(CN)₆)₂,

where the most commonly employed metals are $M = \text{Co(III)}$ or Fe(III)]^{52,53} show high activity for polymerisation reactions with a variety of epoxides, including propylene oxide^{196–198} and cyclohexene oxide (Table 1.6, entry 13),^{191,196,198} but they exhibit low CO_2 uptake and commonly yield poly(ether carbonates) rather than pure polycarbonates.⁵³ In contrast to homogeneous catalytic systems, heterogeneous catalysts such as zinc carboxylates and double metal cyanides generally need more extreme reaction conditions for epoxide/ CO_2 polymerisations, namely a high CO_2 pressure.⁵³

1.2.3. Effect of CO_2 source on catalyst performance

Although having received relatively little attention so far,^{199–204} the source of CO_2 used for the reaction with epoxides is of importance, especially in the perspective of large scale production. When carbon dioxide is employed that has been captured from industrial sources such as the ones discussed in section 1.1 (Table 1.1), it often contains impurities, including H_2S , CO , SO_x , NO_x and water.²⁰⁵ The effect of these impurities on the catalytic system is of crucial concern, as these compounds could potentially influence the activity of the catalytic system by poisoning the active sites or could even cause catalyst degradation. Few studies investigated the effect of using carbon dioxide with lower degree of purity and containing the contaminants commonly found in flue gases.^{50,199–204} In general, these studies showed that several catalytic systems active in the CO_2 /epoxide reaction (*e.g.* bimetallic aluminium salen/tetrabutylammonium bromide,¹⁹⁹ immobilised bifunctional bimetallic aluminium salen,^{200,201} YCl_3 /tetrabutylammonium bromide,²⁰² magnesium bimetallic macrocyclic phenolate²⁰³ and zirconium on silica/tetrabutylammonium bromide²⁰⁴) are quite insensitive towards common flue gas impurities. This supports the feasibility of this reaction as pathway for the utilisation of waste CO_2 .⁵⁰ In the perspective of the industrial application of a novel catalyst in the reaction of CO_2 with epoxide to produce either cyclic or polymeric carbonates, future research should increasingly include investigations of the influence of the CO_2 purity on the catalyst performance.

1.3. Applications of CO_2 -based cyclic and polymeric carbonates

The two products of the reaction between CO_2 and epoxides, *i.e.* cyclic carbonates and polycarbonates, differ both in structure and in properties, thereby generally finding rather different kinds of applications.

1.3.1. Properties of cyclic carbonates

The two cyclic carbonates that are most widely employed are ethylene carbonate (EC) and propylene carbonate (PC). Both are polar aprotic compounds - see Table 1.7 for their dielectric constant, dipole moment and other selected physicochemical properties.²⁰⁶ Due to their biodegradability, low toxicity, low vapour pressure and high flash point, these two cyclic carbonates are greener alternatives to traditional, more harmful polar aprotic solvents such as dimethylformamide (DMF), hexamethylphosphoramide (HMPA), N-methyl-2-pyrrolidone (NMP), dimethylacetamide and acetonitrile, with propylene carbonate being a more viable solvent as it is a liquid at room temperature whereas ethylene carbonate has a melting point of 36 °C.^{17,208–211} A drawback of propylene and ethylene carbonate is their relatively high boiling point, which implies a more difficult and costly separation and recycling.²¹¹ Their applications as solvents include cleaning,²¹² paint stripping²¹³ and degreasing,²¹⁴ and the use as electrolyte components in batteries (see section 1.3.5). Another relevant application of cyclic carbonates is as reactants for chemical syntheses, providing a greener alternative to toxic and/or volatile compounds as phosgene (see section 1.3.4.1), epoxides and cyanates. In the presence of a catalyst, typically an alkali compound, five-membered cyclic carbonate

Fig. 1.5. Alkylation of protic aromatic compounds with five-membered cyclic carbonates in the presence of an alkali catalyst. X = O, NH, S or COO; B is an alkali.²⁰⁷

of a catalyst, typically an alkali compound, five-membered cyclic carbonates can be used to alkylate protic aromatics such as phenols, thiophenols, aniline and aromatic carboxylic acids (Fig. 1.5).²⁰⁷

Although the reaction can be carried out through a more direct path via reaction of the aromatic compounds with epoxides (*e.g.* ethylene oxide or propylene oxide), employing carbonates rather than epoxides has a few advantages: (i) cyclic carbonates are less toxic than the corresponding epoxides and, therefore, safer to handle; (ii) no need for high-pressure equipment, which would be required when working with volatile epoxides, as the alkylation reaction is typically carried out at relatively high temperatures (100-200 °C); (iii) no additional solvents are needed, as the cyclic carbonate can act as both solvent and reactant.²⁰⁷ Aromatic compounds that are typically used in this reaction include: hydroquinone, which is reacted with two molecules of EC to produce a compound employed as spacer in the synthesis of high-strength polyurethanes;²¹⁵ cardanol (a compound derived from cashew nut oil), which is reacted with EC and PC to produce plasticisers;²¹⁶ resorcinol, which upon reaction with EC and PC also produces compounds used as spacers in polyurethane synthesis;²¹⁷ and cyanuric acid, which is reacted with EC to form a crosslinking agent for polyester resins used to coat underwater electric cables.^{207,218} In addition to the alkylation of aromatic compounds containing hydroxyl, thiol or amino groups, aromatics bearing carboxyl groups can be reacted with five-

Fig. 1.6. Reaction of five-membered cyclic carbonates with aliphatic amines (a) and alcohols (b). R₁, R₂, R₃ and R₄ = hydrogen, alkyl.²⁰⁷

membered cyclic carbonates to introduce alkyl ester moieties.²⁰⁷ Moreover, the hydroxyl group of the product of this reaction (Fig. 1.5, X = COO) can react further with the carboxyl group of a second aromatic, thus forming a diester compound. Following this route, multifunctional carboxylic acids such as terephthalic acid have been reacted with PC or EC to synthesise polyester oligomers, which were subsequently used as prepolymers to produce polyester resins.^{207,219} In addition to the synthesis of building blocks for polymer production, the reaction of aromatic carboxylic acids with cyclic carbonates has also been employed in polymer modification, *e.g.* to lower the amount of free-acid end groups in poly(ethylene terephthalate) [PET] with the purpose of increasing the chemical resistance of the polymer²²⁰ or of increasing the rate of reaction with isocyanates to produce polyurethane foams;²²¹ and to enhance the performance of superabsorbing polymers used in diapers and feminine hygiene products, by crosslinking the acid groups present in the employed polymer (sodium polyacrylate).^{207,222} Compared to the previously mentioned protic aromatic compounds containing hydroxyl or amino groups, the reaction of aliphatic alcohols and amines with five-membered cyclic carbonates proceeds differently (Fig. 1.6.a).

In the case of primary or secondary amines (and of ammonia), a urethane (carbamate) product is formed.²⁰⁷ Although similar compounds can be formed via the reaction of diols with urea, such route requires high temperatures (120-170 °C), while five-membered cyclic carbonates can react with primary amines at room temperature.²⁰⁷ In most cases a catalyst is not required, but strong bases can be used to increase the reaction rate.²⁰⁷ The use of cyclic carbonates and amines to produce urethane linkages provides a greener alternative to the common synthesis of polyurethanes, which is based on the reaction of toxic di- or polyisocyanates with

Table 1.7. Physicochemical properties of ethylene and propylene carbonate (hazard data obtained from REACH)^{223,224}

Cyclic carbonate	Boiling point (°C)	Melting point (°C)	Flash point (°C)	Vapour pressure (kPa)	Dielectric constant	Dipole moment (D)	Density (g/mL)	Hazards
246	36	143	0.003 (25 °C)	89.78 (40 °C)	4.9	1.32 (39 °C)	Harmful if swallowed, causes serious eye irritation, may cause damage to organs (kidney) through prolonged or repeated exposure if swallowed.
242	-49	135	0.004 (25 °C)	66.14 (20 °C)	4.9	1.20 (20 °C)	Causes serious eye irritation.

polyols (see section 1.3.4.3 for further information on this).^{207,225} This type of reaction pathway also finds application in epoxy resins (see section 1.3.4.2). Aliphatic alcohols react with five-membered cyclic carbonates similarly to aliphatic amines, but a successive reaction with a second alcohol compound can also occur, thereby forming a linear carbonate and a diol (Fig. 1.6.b).²⁰⁷ This additional step typically does not occur with aliphatic amines, except at high temperatures ($\geq 150\text{ }^{\circ}\text{C}$).²⁰⁷ A well-known example of this reaction is the transcarbonation of cyclic carbonates (*e.g.* ethylene or propylene carbonate) with methanol to produce dimethyl carbonate (DMC), a non-toxic and biodegradable compound that can be used in methylation and carbonylation reactions as greener substitute for the highly toxic reactants conventionally used (dimethyl sulphate and phosgene, respectively).²²⁶ An important industrialised example of the application of a cyclic carbonate as alternative to the extremely toxic phosgene through transcarbonation reactions is the Asahi Kasei industrial process,²²⁷ which represents a greener route for the synthesis of aromatic bisphenol-A-based polycarbonates (see 1.3.4.1 for more detailed information).

When, instead of simple alcohols, diols are employed in the reaction with five-membered cyclic carbonates, other five-membered cyclic carbonates, six-membered cyclic carbonates and polycarbonates can be formed.²⁰⁷ In this context, the reaction of ethylene carbonate and propylene carbonate with glycerol to form glycerol carbonate is a promising synthesis route as it allows converting a large-scale bio-based by-product from biodiesel manufacturing as glycerol into a valuable organic compound that can find application as low-volatility solvent in varnishes, glues, cosmetics and pharmaceuticals and as organic building block for preparing epichlorohydrin and polymers such as hyperbranched polyethers, polyesters, polycarbonates, polyurethanes and polyamides.^{23,35,36,228–232} This route to synthesise glycerol carbonate is more viable compared to the direct reaction of glycerol with CO_2 , which is thermodynamically unfavourable and thus results in low yields unless the formed water is removed from the reaction mixture.^{228,233} Among the products of the reaction of diols with five-membered cyclic carbonates, six-membered cyclic carbonates have been studied as starting materials for polymerisation reactions, as these compounds display lower thermodynamic stability and are thus more readily polymerised compared to their five-membered counterparts.^{43,207}

1.3.2. Properties of polycarbonates prepared from CO_2 and epoxides

Polycarbonates can be prepared by the polymerisation of carbon dioxide with a wide range of epoxides (Table 1.8), with propylene oxide and cyclohexene oxide

being the most widely studied monomers. These polycarbonates are related to the bisphenol-A-based aromatic polycarbonates mentioned above, as they are all characterised by the carbonate group in their backbone, but differ markedly in terms of physicochemical properties and thus in potential applications due to the absence of aromaticity in the polycarbonate backbone. Bisphenol-A-based polycarbonates (BPA-PC) display excellent physicochemical properties such as relatively high T_g , high heat and impact resistance, transparency and dimensional stability, which make them suitable as engineering plastics for a wide variety of applications including automotive industry, construction, optics and electronics.^{17,227} On the other hand, the first generation of CO₂/epoxide polycarbonates, often based on propylene oxide or cyclohexene oxide, have different thermal and mechanical properties as well as lower thermal stability compared to BPA-PC. As a result, these polycarbonates cannot be employed as engineering plastics.^{4,14,17} More specifically, poly(propylene carbonate)s (PPC) have significantly lower glass transition temperature (T_g) compared to bisphenol-A-based polycarbonate and thus display elastic behaviour (high elongation at break and impact strength) and lower tensile modulus and tensile strength (Table 1.8).¹⁷ Poly(cyclohexene carbonate)s (PCHC) have higher T_g and approach the mechanical properties of bisphenol-A-based polycarbonate in terms of tensile modulus and strength, but they display inferior impact properties and elongation at break and, thus, are brittle at room temperature (Table 1.8).¹⁷

Although the typical characteristics of BPA-PC (*i.e.* relatively high T_g , no crystallinity and outstanding impact behaviour),^{4,234,235} remain unreachable benchmarks for poly(propylene carbonate) and poly(cyclohexene carbonate), attempts have been reported to match the high T_g values (~ 150 °C) by reacting CO₂ with other epoxides. Examples include polycarbonates prepared from CO₂ and indene oxide (with a T_g up to 138 °C vs. ~ 150 °C for BPA-PC),^{236,237} limonene oxide (T_g of 130 °C, improved pencil hardness (B vs 8B) and higher transparency (94% vs 89%) compared to BPA-PC)^{234,238} and limonene dioxide (T_g up to 135 °C for unmodified CO₂/limonene dioxide polycarbonates).²³⁹ Although the T_g of these CO₂-based polycarbonates match that of BPA-PC, their impact behaviour was not studied, thereby not (yet) demonstrating their suitability as replacements for BPA-PC in rigid engineering plastic.

An overview of selected thermal and mechanical properties of several polycarbonates is given in Table 1.8. It can be seen that the glass-transition temperature is strongly dependent on the molecular weight of the polymer (the T_g increases with the molecular weight up to a certain value of M_n , above which it remains approximately constant).¹⁷ The obtained molecular weights for CO₂/epoxide copolymers are typically lower than the maximum theoretical values

that would be calculated assuming a living anionic polymerisation mechanism. This occurs because the polymerisation is sensitive towards traces of protic compounds (*i.e.* water, alcohols or acids), that can cause chain transfer reactions (see Fig. 1.7) resulting in termination of the polymer chain and thus leading to relatively low molecular weight polymers.^{5,53} While the presence of adventitious water typically limits the molecular weight of polycarbonate chains (*i.e.* $M_n < 20$ kg/mol), its role as chain transfer agent can also be exploited to generate low molecular weight polycarbonates with terminal hydroxyl groups,²⁰³ which can serve as polyols for polyurethane synthesis (see section 1.3.4.3).

In addition to the influence of the polymer molecular weight on the glass transition temperature, the rigidity of the structure of the polycarbonate backbone affects the T_g , which decreases in the order of aromatic > alicyclic > linear aliphatic units in the backbone (*i.e.* T_g : BPA-PC > PCHC > PPC). Furthermore, a substantial decrease in T_g is observed upon an increase in the length of the alkyl side chains (T_g : poly(propylene carbonate) > poly(butane carbonate) > poly(pentene carbonate) > poly(hexane carbonate)). This can be ascribed to an increasing free volume of the polymeric chains, which results in less interaction between these chains producing an increase in mobility. Although CO₂-based polycarbonates are typically amorphous polymers, semi-crystalline stereoregular poly(propylene carbonate)s and poly(cyclohexene oxide)s were also synthesised, by employing a chiral catalyst, an enantiopure epoxide monomer, or both.^{17,240,241} These poly(cyclohexene oxide)s possess high melting temperature ($T_m = 215$ - 230 °C), which increases their potential to be used in products that are regularly subjected to high temperatures.²⁴⁰ The thermal properties of poly(propylene carbonate) also improved upon introduction of stereoregularity. More specifically, the initial degradation temperature of stereoblock poly(propylene carbonate) ($T_{d5\%} = 253$ °C) with isotactic (S)- and (R)-blocks is higher than that of atactic poly(propylene carbonate) ($T_{d5\%} = 229$ °C).²⁴¹ Notably, the T_g of isotactic poly(propylene carbonate) was lower than that of atactic poly(propylene carbonate) with similar molecular weight ($T_g = 24$ °C

Fig. 1.7. Chain transfer reaction with a protic compound (*i.e.* water, alcohols or acids) during the polymerisation of CO₂ and epoxides catalysed by a Lewis acid (M) and a nucleophile (X).

Table 1.8. Selected thermal and mechanical properties of CO₂-based polycarbonates

Polycarbonate	M _n (kg/mol) [PDI]	T _g (°C)	T _{d,initial} (°C)	T _{d50%} (°C)	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Impact strength (J/cm)	Transmission (%)	Ref
Poly(ethylene carbonate)	-	10	217	-	3-8	-	>600	-	-	242
Poly(propylene carbonate)	7.5 [3.8]	28	235	-	212	9	8	-	-	242
	-	38	-	-	1353	14.7	203.1	7.27	-	243
	69.5 [1.09]	42	-	252	-	-	-	-	-	244
	-	25-45	±240	-	700-1400	7-30	-	-	-	245
Poly(butene carbonate)	180 [1.15]	9	-	241	-	-	-	-	-	246
Poly(pentene carbonate)	7.5 [5.1]	-4	246	-	-	-	-	-	-	242
Poly(hexene carbonate)	9.5 [4.8]	-10	250	-	-	-	-	-	-	242
	-	-15	-	253	-	-	-	-	-	246
Poly(cyclohexene carbonate)	8 [4.2]	105	282	-	2460	11.8	0.5	-	-	242
	63 [1.06]	118	-	310	-	-	-	-	-	244
	-	125	-	-	2707	29.4	1.3	1.31	-	243
Poly(vinyl-cyclohexene carbonate)	-	107	-	-	2110	36.7	1.3	1.02	-	243
Poly(limonene carbonate)	53.4 [1.10]	130	250 ^a	265 ^b	950	55	15	-	94	238
	3.69 [1.34]	72	226 ^c	-	-	-	-	-	-	247
	10.6 [1.43]	112	-	-	-	-	-	-	-	94
Poly(limonene oxide carbonate)	11.4 [1.29]	135	-	-	-	-	-	-	-	239
Poly(indene carbonate)	9.7 [1.12]	138	239	257	-	-	-	-	-	237
Bisphenol-A polycarbonate	-	149	-	458	2000-2800	43-51	15-75	9	89	4,234,235

^a T_{d5%}. ^b T_{d,max}. ^c T_{d10%}. PDI: polydispersity index, Mw/Mn.

vs T_g = 34 °C, respectively).²⁴¹ In general, CO₂-epoxide copolymers are biodegradable.^{248–250} For example, it has been shown that poly(propylene carbonate) is biodegradable in air, water and soil, and that the process does not generate toxic substances.¹⁷

The properties of the polycarbonates prepared by properties of CO₂/epoxide polycarbonates, including (i) terpolymerisation (*i.e.* reaction of CO₂ with an epoxide and a third monomer that can be another epoxide, an anhydride or caprolactone);^{251–253} (ii) block-copolymerisation (*i.e.* sequential growth of a polymer consisting of different blocks of which at least one is based on CO₂/epoxide copolymerisation)^{86,243,254} (iii) post-polymerisation modification of the functional

groups that might be present along the backbone;²⁵² (iv) end-group modification by using functional compounds as chain transfer agents (if the functional compound contains two or more groups that can give chain transfer, polymer extension or branching can be achieved^{17,255}); (v) blending of polycarbonates with other polymers or with inorganic solids.^{17,256,257}

Particularly, the post-polymerisation modification is a highly versatile approach: when epoxide substrates such as limonene oxide (LO), cyclohexadiene oxide (CHDO), vinyl-cyclohexene oxide (VCHO) or 2-vinylloxirane (VO) (Table 1.9) are used in the CO₂/epoxide copolymerisation reaction, polycarbonates are produced that contain unsaturated moieties. These groups provide a synthetic toolbox to introduce a variety of functionalities, thereby making it possible to tune the chemical and mechanical properties of the polymer.^{234,247,247,258–265} The interest towards the industrial application of CO₂-based polycarbonates is testified by the several patents describing these products and the processes for their manufacturing,^{266,267} filed by small, dedicated enterprises or large chemical companies including BASF,^{268,269} Covestro (former Bayer Material Science),^{270–273} Novomer^{274,275} (currently part of Saudi Aramco), Empower Materials,²⁷⁶ Cardia Bioplastics²⁷⁷ and SK Group.^{278,279} Additionally, some patents are owned by universities.^{280,281}

1.3.3. Towards fully renewable CO₂-based cyclic and polymeric carbonates

The two epoxides that are most commonly employed for the large-scale synthesis of CO₂-based cyclic and polymeric carbonates, *i.e.* ethylene oxide and propylene oxide, are synthesised industrially from ethylene and propylene. Although commonly derived from petrochemical feedstock, interest has increased for developing bio-based routes for producing these two compounds. Ethylene can be produced via a bio-based route through the dehydration of ethanol²⁸⁷ or via the cracking of bio-naphtha.²⁸² Several plants where bio-ethanol is converted into ethylene have been or are being established in Brazil, India and China.^{282,287} Additionally, various synthetic routes for the production of propylene from renewable resources have been suggested: (i) from methanol via methanol-to-olefins technology (MTO);^{282,284} (ii) by hydrodeoxygenation of glycerol, which is the main side product of biodiesel manufacturing;²⁸³ (iii) by dehydrogenation of propane obtained as a by-product of biodiesel manufacturing;^{282,284} (iv) by conversion of vegetable oil into propylene via catalytic cracking;^{282,284} (v) by dehydration of ethanol to ethylene, followed by dimerisation to form butene, and a final metathesis reaction step with ethylene;^{282,284} (vi) by dehydration of butanol

Table 1.9. Selected epoxides with their sources and hazards

Epoxide	Structure	Boiling point (°C)	Hazards	Toxicity	Source (stage)
Ethylene oxide (EO)		10.7	Extremely flammable, toxic if inhaled, may cause genetic defects or cancer.	LC ₅₀ : 800 ppm (rat, 4 h, inhalation)	Bio-based (commercial), ²⁸² petroleum-based (commercial)
Propylene oxide (PO)		34	Extremely flammable, toxic if inhaled, may cause genetic defects or cancer.	LD ₅₀ : 380 mg/kg (rat, oral)	Bio-based (proposed), ^{282–284} petroleum-based (commercial)
Epichlorohydrin (ECH)		115–117	Flammable, toxic, corrosive, may cause cancer.	LD ₅₀ : 90 mg/kg (rat, oral)	Bio-based (commercial), ²⁸² petroleum-based (commercial)
2-Vinylloxirane (VO)		66	Highly flammable, suspected of causing genetic defects.	n.a.	Bio-based (partially commercial), ²⁸⁵ petroleum-based (commercial)
Styrene oxide (SO)		194	Harmful, irritant, toxic if inhaled, may cause genetic defects or cancer.	LD ₅₀ : 1500 mg/kg (mouse, oral)	Petroleum-based (commercial)
Cyclohexene oxide (CHO)		129–130	Flammable, toxic, corrosive.	LD ₅₀ : 1058 mg/kg (rat, oral)	Bio-based (proposed), ²⁸⁶ petroleum-based (commercial)
Cyclohexadiene oxide (CHDO)		n.a.	n.a.	n.a.	Bio-based (proof of concept) ^{264,286}
Vinyl-cyclohexene oxide (VCHO)		169	Flammable, harmful, suspected of causing cancer.	LD ₅₀ : 1904 mg/kg (rat, oral)	Bio-based (precursors are commercially available), ²⁸⁵ petroleum-based (commercial)
Limonene oxide (LO)		n.a.	Flammable, may cause eye, skin and respiratory system irritation.	n.a.	Bio-based (commercial)

LC₅₀ = lethal concentration of toxic agent sufficient to cause death of 50% of the subject population. LD₅₀ = lethal dose of toxic agent sufficient to cause death of 50% of the subject population. n.a. = not available.

(derived from the fermentation of carbohydrates or via a bio-based syngas-route) to yield butene, followed by a metathesis step with ethylene.^{282,284}

In addition to the technological challenges in producing ethylene oxide and propylene oxide from bio-based sources, these routes should ideally also be cost-efficient in order to be able to compete with the low cost of their petroleum-based counterparts. Albeit the production of ethylene and propylene carbonate through the conversion of carbon dioxide with respectively ethylene oxide and propylene oxide is a well-established industrial process,^{129,288} the use of ethylene oxide and propylene oxide results in serious safety concerns due to the combination of high toxicity and volatility of both epoxides (especially ethylene oxide, which is a gas at room temperature). Cyclohexene oxide has a higher boiling point and is thus safer to use, but it is more expensive and is still usually derived from petroleum.²³⁸ Small amounts of cyclohexene have been observed during the hydrodeoxygenation of lignin-derivable phenols, although these quantities typically do not exceed more than a few percent.^{289–291}

More recently, increasing attention has been given to the use of bio-based epoxides for the synthesis of cyclic and polymeric carbonates by reaction with CO₂. Among these, limonene oxide and limonene dioxide^{87,234,238,239,247,260,292} can be produced through the well-studied epoxidation of (R)-(+)-limonene, a naturally occurring terpene that is extracted from *e.g.* citrus peels (generated as abundant waste of the juice extraction from orange and other citrus fruits).²⁹³ Unsaturated fatty acids and esters derived from triglycerides (*e.g.* those in vegetable oils) contain one or more double bonds that can be converted into epoxide groups and, subsequently, into cyclic or polymeric carbonates.^{294,295} Other bio-based epoxides can be prepared through multiple synthetic steps, and include 4-vinylcyclohexene oxide,^{258,263,296} which can be synthesised via Diels-Alder dimerisation of bio-butadiene²⁹⁷ followed by epoxidation of the double bond; 1,4-cyclohexadiene oxide,^{264,286} which can be synthesised via selective epoxidation of one of the two double bonds in 1,4-cyclohexadiene, a by-product of the self-metathesis of some polyunsaturated fatty acids derived from plant oils.^{264,286} Epichlorohydrin^{298,299} can be derived from bio-based glycerol in a two-step process, but the use of HCl as chloride source decreases the greenness of this option.³⁰⁰ Epichlorohydrin is also the starting compound used to prepare glycidyl ether-based epoxides, which have been employed as substrates in the CO₂/epoxide polymerisation reaction.^{301–305} For all these bio-based resources, a challenge might be represented by their availability (and cost), which should match the desired market size of the targeted application of the cyclic or polymeric carbonate product.³⁰⁶

Although the utilisation of bio-based epoxides increases the renewable character of CO₂-based cyclic and polymeric carbonates, the hazards originating from the high toxicity of epoxides are still a concern (Table 1.9). A solution would be to directly synthesise the CO₂-based carbonates from the alkene from which the epoxides are generally prepared. This one-pot procedure would be advantageous both from the point of view of sustainability and of industrial applicability, as avoiding the purification and handling of epoxides would result in higher safety and lower process costs.¹⁴ This process requires a multifunctional catalytic system (either a one-component system or two separate non-interfering catalysts) that is able to promote both the oxidation of alkenes to epoxides and the subsequent reaction with CO₂ to form carbonates. So far, only few studies have been conducted concerning this one-pot route, typically employing a combination of known oxidation catalysts with CO₂/epoxide catalysts.^{14,307–312} The main issue encountered is the formation of side products during the epoxidation step, leading to low selectivity of the carbonate end-product. A further challenge is to develop a catalytic process operating at mild conditions, using a green oxidant such as H₂O₂ or O₂ rather than organic peroxides.³¹³

1.3.4. Application of cyclic and polymeric carbonates in the preparation of polymer products

Several strategies have been developed for the application of both cyclic and polymeric carbonates produced from CO₂ in the preparation of polymer products. These strategies range from the use of cyclic carbonates as reactive intermediates in the formation of urethane linkages or as precursors for transcarbonation reactions to synthesise aromatic polycarbonates, to the application of CO₂-based polycarbonates in functional coatings, as polyols for polyurethane production and in polymeric blends and composites. These strategies find a variety of applications, in some cases reaching industrial production, as reviewed in more detail in the following sub-sections (1.3.4.1-5).

1.3.4.1. Bisphenol-A-based polycarbonates prepared using cyclic carbonates as alternative to phosgene

Bisphenol-A-based polycarbonates (BPA-PC) are one of the major classes of polymer products with a yearly worldwide demand of 4.1 million tonnes (in 2017)³¹⁴ and with a broad range of applications as engineering plastics in optics, electronics, for automotive parts and as construction materials. The major industrial process for the production of these polycarbonates involves the use of the highly toxic phosgene as reactant and of methylene chloride (which is a suspected highly carcinogenic

compound) as polymerisation solvent, resulting in Cl-impurities in the polycarbonate product that negatively impact its quality, in corrosion of processing equipment caused by the formed NaCl/HCl side-products and in large amounts of contaminated wastewater that require proper treatment and disposal.

An alternative, much greener route for the synthesis of aromatic bisphenol-A-based polycarbonates was developed by Asahi Kasei by using ethylene carbonate instead of the extremely toxic phosgene to introduce carbonate moieties in the polymer through transcarbonation reactions (Fig. 1.8).²²⁷ This route was industrialised in 2002 and has several assets from the point of view of green chemistry: (i) it converts CO₂, ethylene oxide and bisphenol A into two useful products, *i.e.* polycarbonate and ethylene glycol, with high yield and selectivity (>99%); (ii) it does not involve phosgene or chlorinated compounds; (iii) the process is solvent-free; (iv) the carbon dioxide used in the process is a by-product from the production of ethylene oxide; (v) all intermediate products are completely used or recycled; (vi) no waste products nor wastewater are generated, thereby eliminating expensive and difficult purification and separation steps; (vii) it is less material- and energy-intensive compared to the conventional process.^{14,227}

The first step in the process is the cycloaddition of CO₂ to ethylene oxide to form ethylene carbonate and ethylene glycol, followed by conversion of ethylene carbonate into dimethyl carbonate by reaction with methanol (see Fig. 1.8). Next, a second transcarbonation is carried out by reacting dimethyl carbonate with phenol to obtain diphenyl carbonate, which in turn is reacted with bisphenol A to generate the final polycarbonate product. Ethylene carbonate is first converted into dimethyl carbonate, as direct reaction of ethylene carbonate with phenol would result in ring-opening of the cyclic carbonate, followed by loss of CO₂ and, hence, of the carbonate moiety (see Fig. 1.5).²⁰⁷ The obtained dimethyl carbonate is then converted into diphenyl carbonate because dimethyl carbonate is unsuitable as polymerisation reactant for obtaining high molecular weight polycarbonate since the reaction of the terminal hydroxyl groups of the polycarbonate oligomers with the methyl carbonate group is far less favourable due to the high basicity of the methoxide anion compared to the phenoxide anion.³¹⁵ The methanol and phenol are fully recovered via (reactive) distillation and reused in the process. Finding an alternative to the toxic ethylene oxide reactant would further increase the sustainability of this route. Additionally, it would be desirable to find an alternative to bisphenol A, which is under scrutiny as it is suspected to have adverse effects on human health (*i.e.* endocrine disruption) and has thus been banned from use in infant-food containers

in various countries including several members of the European Union, China, Japan, Australia, Canada and USA.³¹⁶

1.3.4.2. Cyclic carbonates in epoxy resin applications

Natural and synthetic resins are important precursors for countless everyday commodities (the definition of resin in this review is that provided by IUPAC: “*soft solid or highly viscous substance, usually containing prepolymers with reactive groups*”³¹⁷). Amongst the various existing resin types, epoxy resins are a class of thermosetting resins characterised by the presence of reactive epoxide moieties, finding widespread application in *i.a.* coatings, adhesives, foams, laminates, composites and electronic materials.^{318,319} Their extensive utilisation is a result of their excellent properties upon curing (*i.e.* upon crosslinking of the resin into a higher molar mass polymeric network),³²⁰ including high tensile strength and Young’s modulus, high thermal stability, broad solvent resistance, high adhesion strength, heat resistance and high electrical resistance. These properties can be tuned by varying the type of epoxy resin, curing agent and curing process.^{319,321}

The main drawback of traditional epoxy resins is that upon curing they tend to produce brittle materials with low elasticity and impact resistance, as a consequence of their typically high crosslink density.^{322,323} These properties can be improved via various routes, the main strategy being based on the addition of a ductile second phase (*e.g.* rubbers, polyurethanes or acrylates) that precipitates during curing, resulting in a product with a multiphase morphology and increased impact resistance.³²³

Another strategy to increase the toughness of the cured product is to chemically modify the resin by introducing specific functional groups that generate flexible linkages upon curing. In this context, the influence of urethane bonds on the final properties of cured epoxy resins used in lacquers and adhesives was investigated.^{322,324,325} Several paths to introduce urethane linkages were examined via CO₂/epoxide chemistry (Fig. 1.9). A first approach consists in converting part of the terminal epoxide groups of the resin into cyclic carbonates, thereby producing epoxy resins with various amounts (up to 54%) of cyclic carbonate moieties (Fig. 1.9.A).³²⁴ These cyclic carbonate groups can be converted into urethane bonds via curing with amines (Fig. 1.6.a). When this approach was applied to commercial epoxy resins based on bisphenol-A diglycidyl ethers, higher curing rates by reaction with triethylenetetramine were observed for the resins containing cyclic carbonate moieties. This was attributed to a lower activation energy for the reaction between a cyclic carbonate and an amine compared to the reaction between an epoxide and an amine. A further difference between epoxide and carbonate groups in the

Fig. 1.8. General overview of the Asahi Kasei non-phosgene polycarbonate production process.

reaction with primary amines is that the secondary amine formed upon reaction with the epoxide can react further with another epoxide, whereas the urethane linkage formed upon reaction with the carbonate is not prone to further crosslinking. As a consequence, lower crosslink density is generally obtained with resins containing cyclic carbonate groups. While it is often observed that incorporation of additives in epoxy resins can result in a significant decrease in mechanical properties such as tensile strength and tensile modulus,³²³ CO₂-modification was measured to only cause a slight decline in tensile properties of the cured resins (selected properties are shown in Table 1.10, entries 1 and 2).

On the other hand, the compressive properties improved considerably, with exceptional rises in compressive strength and strain, and the adhesive properties were also enhanced, as shown by the higher values of lap shear strength and tensile-peel strength in the CO₂-modified material (Table 1.10, entries 1 and 2). These improvements were ascribed to increased van der Waals interactions within the crosslinked networks due to the presence of polar urethane bonds and residual cyclic carbonate moieties. The CO₂-modification also caused a considerable increase in the viscosity of the resin, thereby limiting its applicability as adhesive or coating.³²² In order to decrease the viscosity of the modified epoxy resins, aliphatic CO₂-based cyclic carbonates (*e.g.* the cyclic carbonate analogue of triethylene glycol diglycidyl ether) were added to the resins as thinners and reactive ingredients (Fig. 1.9.B).³²² The presence of aliphatic cyclic carbonate additives led to a decrease in dynamic viscosity and to lower crosslinking density upon curing with triethylenetetramine, but also enhanced the impact resistance, the tensile strength and elongation at break (Table 1.10, entries 3 and 4), indicating improved flexibility of the cured modified resin in comparison to the original epoxy resin. While this enhanced ductility could partially be ascribed to the decrease in crosslink density, the authors related the enhanced tensile properties to increased van der Waals interactions due to the presence of polar groups, *i.e.* the urethane bonds formed during curing and residual cyclic carbonate groups. Adhesion studies were also conducted, showing that the enhanced flexibility resulted in an increased resin

Fig. 1.9. Possible CO₂-based modifications of the various components of epoxy resin formulations: (A) Conversion of terminal epoxide groups into cyclic carbonates. (B) Reactive cyclic carbonates as additives (note: only the cyclic carbonate analogue of triethylene glycol diglycidyl ether is shown as example). (C) Modification of triethylenetetramine with cyclic carbonates (note: multisubstituted products are not shown), R₁ = *e.g.* -CH₃, -C₆H₆, -CH₂-O-CH₂-CH=CH₂. (D) Modification of the tetrafunctional epoxy resin (4,4'-methylenebis(*N,N*-diglycidyl aniline)).

adhesion to aluminium surfaces and in a higher shear strength (Table 1.10, entries 3 and 4). On the other hand, the cured resins incorporating cyclic carbonates displayed inferior chemical resistance compared to the cured unmodified epoxy resin, which was ascribed to the lower crosslink density. Alternatively to the modification of the epoxy resin via introduction of cyclic carbonate groups, the final properties of the cured resin can also be tuned by modifying the amine crosslinking

agent via reaction with cyclic carbonates.³²⁵ Triethylenetetramine, used as amine curing agent in epoxy resins, was reacted with various cyclic carbonate compounds, *e.g.* propylene carbonate, styrene carbonate and the carbonate from allyl glycidyl ether, to produce modified curing agents (Fig. 1.9.C). This modification of the amine crosslinking agent resulted in a lower crosslink density in the final cured product, a similar trend as observed in the case of the CO₂-modified epoxy resin.³²⁴ This was ascribed to the fact that part of the amine groups are consumed due to reaction with cyclic carbonates, which prevents them from participating in crosslinking reactions with epoxide groups. Although the tensile and compressive properties did not substantially improve (Table 1.10, entries 5 and 6), the adhesive properties were significantly enhanced, which was again ascribed to enhanced interactions between the polar urethane moieties of the cured resin and the test surface, and to increased flexibility as a result of the lower crosslink density.

The epoxy resins discussed above consist of linear bifunctional epoxides. For traditional thermosets based on epoxy resins, the use of a multifunctional curing agent (typically amines) is normally exploited in order to achieve higher crosslinking densities and a variety of corresponding mechanical and thermal properties. However, it is also possible to use a multifunctional epoxide. This higher number of epoxide groups per molecule leads to cured resins with higher crosslink density, better chemical resistance, higher thermal stability and better cohesiveness compared to cured resins originating from linear bifunctional epoxides.³¹⁸ Although this could yield products with similar crosslinking densities as compared to traditional ones obtained through multifunctional amines, the resulting thermal and mechanical behaviour could be different (different chemical structure at and between the crosslinking points). In this respect, these synthetic routes offer a relevant strategic flexibility.

Multifunctional epoxides have also been investigated with respect to CO₂-modification. For example, a tetrafunctional epoxy resin (4,4'-methylenebis(*N,N*-diglycidyl aniline), Fig. 1.9.D) was modified by converting a fraction of the epoxide moieties into cyclic carbonate groups (18 and 48%).³¹⁸ Similarly to the above-mentioned bifunctional epoxy resins,^{322,324,325} higher curing rates with diethylenetriamine were observed for the tetrafunctional CO₂-modified epoxy resins. The thermal properties were also affected by the CO₂-modification (Table 1.10, entries 7 and 8): the observed lower *T_g* of the final crosslinked network and the slight decrease in initial decomposition temperature were ascribed to the decrease in crosslink density.

Table 1.10. Mechanical and adhesive properties of polymer products prepared employing cyclic or polymeric carbonates

#	Composition	T _g (°C)	T _{d,initial} (°C)	Tensile strength (MPa)	Tensile modulus (MPa)	Yield stress (MPa)	Elongation at break (%)	Compressive properties		Lap shear strength (MPa)	Tensile-peel strength (kN/m)	Ref
								Strength (MPa)	Strain (%)			
1	Epoxy/triethylenetetramine	-	208-210	29	-	11	4.0	118	13.5	6.3	0.60	324
2	CO ₂ -modified epoxy / triethylenetetramine	-	208-210	23-29	-	8.5-12	3.2-3.8	196-235	42-50	7.5-8.7	1.47-2.10	324
3	Epoxy/triethylenetetramine	-	-	37	-	12	4.0	260	50	4.1	107	322
4	Epoxy/TGDEC/triethylenetetramine	-	-	47-69	-	13-15	5.4-8.0	235-275	45-55	5.1-5.7	108-127	322
5	Epoxy/triethylenetetramine	-	-	26	2010	7	1	223	63	6.4	0.059	325
6	Epoxy/carbonate-modified triethylenetetramine	-	-	17-72	1710-2110	5-12	1-8	88-261	36-58	7.6-14.4	0.11-0.22	325
7	Tetrafunctional epoxide/diethylenetriamine	186	325	-	-	-	-	-	-	-	-	318
8	CO ₂ -modified tetrafunctional epoxide (48%)/diethylenetriamine	149	309	-	-	-	-	-	-	-	-	318
9	Poly(propylene carbonate-ether) polyurethane	18.7	-	52	579 (100% elongation)	-	410	-	-	-	-	326
10	Poly(butylene adipate glycol) polyurethane	-	-	68	57.8 (100% elongation)	-	781	-	-	-	-	326
11	Poly(propylene oxide glycol) polyurethane	-	-	20	7.96 (100% elongation)	-	930	-	-	-	-	326
12	Polyadipate polyurethane	-	-	-	-	-	-	-	-	-	21	327
13	Poly(propylene carbonate)/polyadipate polyurethane	-	-	-	-	-	-	-	-	-	14-22	327
14	Polyhydroxyurethanes based on carbonated soybean oil/short amines	15-18	227-239 (5 wt%)	-	2.0	-	126-129	-	-	-	-	328
15	Polyhydroxyurethanes based on carbonated soybean oil/oligoamide	-5-1	340-353 (5 wt%)	-	169-224	-	286-406	-	-	-	-	328
16	Limonene dicarbonate/ polyhydroxyurethane networks	55-70	-	-	2400-4100	7-21	1-2	-	-	-	-	329

1.3.4.3. Polyurethanes prepared using cyclic and polymeric carbonates

Polyurethanes constitute an important class of polymer products, which are typified by the presence of urethane (carbamate) linkages. Having an estimated market size of approximately 20 million tonnes/year,³³⁰ the main application of polyurethanes is in the production of rigid and flexible foams, coatings and adhesives. The synthesis of polyurethanes typically involves an addition reaction between a di- or polyisocyanate and a compound with at least two hydroxyl groups. In foams these two components are: a diisocyanate (typically, 4,4'-methylene diphenyl diisocyanate (MDI) for rigid foams and toluene-2,4-diisocyanate (TDI) for flexible foams); and a polyol (*i.e.* a polymer containing at least two hydroxyl groups), with the number of hydroxyl functional groups (f) being higher for rigid foams ($3 < f < 6$) than for flexible foams ($2 < f < 3$). The diisocyanate and the polyol react to produce crosslinked polymer networks that can be employed as thermal insulating and structural foams in diverse fields such as, for rigid foams, construction and automotive industry and, for flexible foams, furniture, automotive seating, sound insulation and footwear.^{331–334}

Rigid polyurethane foams are characterised by a high strength-to-weight ratio, low density, low thermal conductivity and low moisture permeability, while flexible foams possess excellent elasticity and low sound conductivity.^{331–334} In addition to thermosetting foams, thermoplastic polyurethane-based elastomers also exist (typically synthesised from diisocyanates and diols, *i.e.* compounds with $f = 2$) that are employed in applications where properties such as high tear and tensile strength or good wear and abrasion resistances are required, *e.g.* medical implants, paints, coatings and binders.^{332,335} In paints and coatings, aliphatic isocyanates (*e.g.* 1,6-hexamethylene diisocyanate (HDI)) are typically used instead of aromatic isocyanates, as the latter are more prone to UV-degradation.³³⁶

A general drawback of polyurethane formulations for foams is that products prepared with polyesters as polyols exhibit excellent mechanical properties but poor hydrolysis resistance, while polyurethanes prepared using polyethers as polyols possess proper hydrolysis resistance but insufficient oxidation resistance and display poor mechanical properties.^{326,327} Since CO₂-epoxide-based polycarbonates share similarities with both polyesters and polyethers with regard to the chemical structure but have lower tendency to hydrolyse compared to polyesters, polycarbonate polyols have been investigated as an alternative to conventional polyester and polyether polyols. Additionally, employing CO₂-based poly(carbonate-ether) polyols is a greener option, as it allows increasing the

renewable content of the polymer (up to 43 wt.% CO₂ in the case of poly(propylene carbonate)). This approach, commonly referred to as the “Dream Production”, has been pioneered by Bayer Material Science (currently Covestro),^{337,338} using a double metal cyanide (DMC) catalyst to produce poly(carbonate-ether) polyols from CO₂, propylene oxide and an alcohol starter. For this application, poly(carbonate-ether) polyols are employed rather than polyols with only carbonate linkages, as the presence of ether bonds leads to polyols with lower T_g value [-60 °C for poly(propylene carbonate-ether) with a CO₂-content of 7.1 wt.%], which allows processing with the standard industrial equipment used in polyurethane foam production.³³⁷ It was estimated via life-cycle analysis that the production of these CO₂-based poly(carbonate-ether) polyols requires 13-16% less fossil resources than the production of conventional petroleum-based polyols,³³⁹ indicating that substitution of petroleum-based polyols with CO₂-based polyols is very promising, both from a sustainability point of view and with respect to cost reduction. Since 2016, Covestro has been commercially producing polyols with up to 20% CO₂-content for use in flexible polyurethane foams, with an annual production capacity of 5000 tonnes.³⁴⁰ Another example of a commercial polyurethane product made from CO₂-polycarbonate polyols is the foam prepared using poly(propylene carbonate) polyols by Saudi Aramco (Converge polyols, formerly part of Novomer).³⁴¹ The advantages of CO₂-based poly(carbonate-ether)s as polyols for polyurethane synthesis over their polyester and polyether counterparts was further demonstrated by synthesising a series of polyurethanes from poly(propylene carbonate-ether) polyols and comparing them with polyurethanes incorporating polyester (poly(butylene adipate glycol)) or polyether (poly(propylene oxide glycol)) segments.³²⁶ It was observed that the polycarbonate-based polyurethane (with 66% carbonate linkages and 34% ether linkages) exhibited better mechanical properties, although with a lower elongation at break compared to the other two polyurethanes, indicating a more rigid plastic behaviour (Table 1.10, entries 9-11). In addition, the poly(carbonate-ether)-based polyurethane exhibited better resistance against hydrolysis and oxidation compared to the polyester and polyether polyurethanes, which was ascribed to the presence of ether linkages with good hydrolysis resistance and to the relatively hydrophobic and rigid propylene carbonate repeating units, which might limit the permeation of water and, thus, increase the hydrolysis and oxidation resistance.

Numerous other accounts exist in the scientific literature on the usage of CO₂-derived polycarbonates in polyurethane synthesis. An example thereof are the poly(urethane-urea)s where both the soft diol segments and the hard polyurea

segments are derived from CO₂, via the reaction of poly(propylene carbonate-ether) diols with isocyanates and oligoureas made from a diamine reacted with CO₂.³⁴² Another example are the poly(ethylene carbonate-ether)/MDI polyurethane elastomers displaying shape memory behaviour, which was attributed to the low T_g of the soft segments in the polyurethane (-4.5 °C).³⁴³ Other thermoplastic polyurethanes were prepared from various ratios of poly(propylene carbonate) polyols and polyether polyols reacted with an aliphatic diisocyanate and a diol as chain extender.³⁴⁴ Increasing polycarbonate content typically yielded, in addition to improved rigidity, enhanced corrosion resistance of coated metal surfaces compared to thermoplastic polyurethanes with higher polyether content. This was ascribed to the hydrophobic nature of the incorporated polycarbonate polyols, thereby shielding the metal surface from water and oxygen, as supported by the higher water contact angles displayed by the polyurethanes with higher polycarbonate content. In addition to linear poly(carbonate-ether) polyols, star-shaped CO₂-based polyols have also been prepared, via a two-step process starting with the synthesis of a hyper-branched poly(propylene oxide) copolymer with glycerol branching points, which was subsequently used as macro-initiator for the reaction with propylene oxide and CO₂, generating a polyether core with poly(propylene carbonate) arms.³⁴⁵ These star-shaped structures possess low T_g values between -8 and 10 °C, due to the flexible polyether core. Other star-shaped CO₂-based polyols were prepared via the reaction of CO₂ and propylene oxide in the presence of trimesic acid as an initiation-transfer agent, resulting in oligo(carbonate-ether)s with three arms.³⁴⁶ These three-armed polyols were subsequently studied for their potential in shape-memory polyurethanes in biomedical applications (see section 1.3.6).³⁴⁷

A variety of compounds containing two or more -OH groups can be used as chain transfer agents (see section 1.3.2) from which polycarbonate branches can be grown. By employing organo-phosphorous compounds as chain transfer agents in CO₂/epoxide polymerisation, flame-retarding poly(propylene carbonate) polyols can be prepared.^{255,348} Both the polycarbonate polyols, as well as the resulting thermoplastic polyurethane products were proved to be non-flammable. The flame-retarding properties of these thermoplastic polyurethanes might be exploited for applications in interior materials such as artificial leather, decorating sheets and hot-melt adhesives.^{255,348} The favourable properties of CO₂-based carbonates as polyols in polyurethane formulations also promoted research focussed on specific applications, *e.g.* on polyurethane foams for automotive seating formulations.³⁴⁹ Polyurethane formulations were prepared using different ratios of CO₂-based

aliphatic polycarbonates, either linear or branched, mixed together with a fully petroleum-based polyether polyol, a blend of isocyanates and a mixture of additives. Wet compression set tests indicated that the fully petroleum-based foams retained their original shape better after deformation, while the higher compression modulus showed that the CO₂-based foams are stiffer and deform less under load. This was explained by the smaller average pore size in polyurethane foams with increasing polycarbonate polyol content, caused by the higher viscosity of the CO₂-based polyols compared to the polyether polyol, resulting in less pore expansion by gravity during the initial foaming stage.

Another field of application where polyurethanes are widely employed is the footwear industry. Substitution of traditional polyester and polyether polyols was investigated by employing mixtures of poly(propylene carbonate) and poly(1,4-butylene adipate) polyols to produce polyurethane adhesive networks upon reaction with a diisocyanate (MDI).³²⁷ The thermal (*i.e.* melting viscosity and softening temperature) and adhesive properties (*i.e.* tensile-peel strength, Table 1.10 entries 12 and 13), of these polyurethanes were in suitable ranges for footwear applications. In practical applications where the degradation of the polyurethane network is not a drawback but rather a requirement, the biodegradable nature of CO₂-based polycarbonates such as poly(propylene carbonate) can represent an asset. This is the case in marine anti-biofouling coatings, which aim at preventing the growth of marine organisms on ships by slow degradation accompanied by controlled release of anti-biofouling agents. In this context, polyurethane coatings with different molecular weights and incorporating an anti-biofouling agent were prepared from poly(propylene carbonate), hexamethylene diisocyanate and 1,4-butanediol.³⁵⁰ The polyurethane coating with the lowest molecular weight showed the best anti-biofouling performance, probably due to the highest degradation rate and, hence, the highest release rate of anti-biofouling agent. Based on the degradation data, the lifetime of the coating was estimated to be at least 6 months. These features are promising for marine anti-biofouling applications, although the mechanical properties of these coatings still have to be thoroughly investigated. Although several CO₂/epoxide polycarbonates have been shown to be suitable as precursors for polyurethanes, most epoxide building blocks are petroleum-based. In an effort to decrease the dependence from depleting fossil feedstocks, polycarbonates synthesised from bio-based epoxides such as limonene oxide have been investigated as greener polyols for polyurethane synthesis.³⁵¹ For this purpose, poly(limonene carbonate) was synthesised and subjected to reaction with different compounds containing one or more hydroxyl groups (*i.e.* 1,3-propanediol (1,3-PD),

Fig. 1.10. Limonene-based carbonates for polyurethane applications: (A) Poly(limonene carbonate) polyols (R_1 = OH or functional group obtained by reaction with 1,3-PD, 1,10-DCD, isosorbide, TMP or PE). (B) Thiol-modified poly(limonene carbonate) polyols, incorporating primary hydroxyl groups as side groups (R_2 = $-(CH_2)_2-$ or $-(CH_2)_6-$). (C) Limonene dicarbonate as polyhydroxyurethane precursor.

1,10-decanediol (1,10-DCD), isosorbide, trimethanolethane (TMP) and pentaerythritol (PE)) to produce hydroxyl end-capped, lower molecular weight polycarbonates suitable for polyurethane curing (Fig. 1.10.A), with glass transition temperatures between 71 and 99 °C.³⁵¹ Curing of the modified poly(limonene carbonate) polyols using a solvent-casting method with a curing agent with three isocyanate groups yielded crosslinked polyurethane coatings that displayed poor solvent resistance. This was ascribed to incomplete curing of the coating, which was related to the low reactivity of the secondary or tertiary hydroxyl moieties in the end-groups of the unfunctionalised poly(limonene carbonate)s (*i.e.* those with R_1 = OH in Fig. 1.10). To overcome this limitation, poly(limonene carbonate) was functionalised with primary hydroxyl groups by reacting the pendant vinyl groups present in the polycarbonate backbone with a mercaptoalcohol (2-mercaptoethanol or 6-mercaptohexanol) through a thiol-ene reaction (Fig. 1.10.B).²⁵⁹

Curing of the modified poly(limonene carbonate)s with polyisocyanate produced polyurethane coatings that were evaluated with respect to their chemical resistance, thermomechanical properties and mechanical performance (Table 1.11, entry 1). Acetone rubbing tests showed sufficient to good solvent resistance, whereas the measured König hardness of 167-182 s indicated that these polyurethane coatings can be classified as hard. On the other hand, the cured coatings lacked a good reverse impact resistance, which was ascribed to a low elongation at break caused by the brittle nature of the material. These results show that through multiple modification steps it is possible to functionalise fully renewable poly(limonene carbonate) in such a way that it can be used as a polyol in polyurethane coatings. However, the brittle character of poly(limonene carbonate) limits the applicability in polyurethane coatings that require high impact resistance.

Table 1.11. Properties of CO₂-based polymeric coatings

#	Coating	T _g (°C)	Acetone resistance ^a	Pencil hardness	König hardness (s) ^b	Reverse impact resistance	Ref
1	Mercaptoalcohol-modified poly(limonene carbonate) polyurethane	-	Sufficient to good	2H	167-182	Unsatisfactory ^c	259
2	Poly(cyclohexene carbonate-co-4- vinylcyclohexene carbonate)/trithiol (solvent coated)	-	Good	-	-	Good ^d	251
3	Poly(cyclohexene carbonate-co-4- vinylcyclohexene carbonate)/trithiol (powder coated)	85 - 104	Good	6-8H	-	Unsatisfactory ^d	251
4	Poly(limonene carbonate)/trithiol	-	Sufficient to good	H-2H	103-114	Unsatisfactory ^e	358
5	Poly(cyclohexadiene carbonate)/trithiol	-	Sufficient to good	H-2H	123-159	Unsatisfactory ^e	358
6	Poly(limonene-8,9-oxide carbonate)/trithiol	150	Good	2H	-	-	239

^a 75 double rubs with a tissue soaked in acetone. ^b Standardised König pendulum hardness test, with the damping time reported in seconds. ^c Measured in accordance to ASTM D2794, 1 kg ball from 0.1 m height. ^d Measured in accordance to ASTM D2794, 1 kg ball from 0.5 m height. ^e Testing method not described.

Although this system shows the potential of polyurethanes prepared from bio-based polyols derived from limonene oxide and CO₂, it requires the use of di- or polyisocyanates, which is not preferred due to the health issues associated with these compounds.³⁵² Furthermore, isocyanates are commercially produced using the toxic phosgene as a precursor, which is another reason to search for greener alternatives. In order to produce cyanate-free polyurethanes, different synthesis routes can be followed based on the reaction between carbonate moieties and amino groups (see section 1.3.1, Fig. 1.6.a).

A first route involves the reaction of two molecules of a cyclic carbonate with a diamine to produce a bis-hydroxyalkylcarbamate that can be subsequently polymerised through self-condensation to generate linear polyurethanes (Fig. 1.11.A).³⁵³ A second pathway uses dialkyl carbonates (typically dimethyl carbonate) instead of cyclic carbonates, which can be reacted with a diamine to generate a bis-alkylcarbamate that can be polymerised to produce a polyurethane via reaction with a diol (Fig. 1.11.B).³⁵³ The disadvantage of this route is that, in addition to the required second component (diol) for the polymerisation, an extra reaction step is necessary to synthesise the dialkyl carbonate from a CO₂-based cyclic carbonate

Fig. 1.11. Non-isocyanate polyurethanes based on the reaction of an organic carbonate with a diamine: (A) Reaction between two cyclic carbonates and a diamine producing a bis-hydroxyalkylcarbamate (R_1 = alkyl). (B) Reaction between two alkyl carbonates and a diamine producing a bis-alkylcarbamate (R_1, R_2, R_3 = alkyl). (C) Reaction between bicyclic carbonates and diamines producing polyhydroxyurethanes (R_1 = alkyl, R_2 = monomeric or polymeric unit).

(typically ethylene carbonate or propylene carbonate) and two alcohols (see section 1.3.1, Fig. 1.6.b). In a third approach, a bicyclic carbonate is reacted with a diamine, yielding polyhydroxyurethanes that slightly differ from typical cyclic carbonate/amine-based polyurethanes due to the presence of pendant hydroxyl groups in the polyurethane backbone (Fig. 1.11.C).³⁵⁴ Polyhydroxyurethanes typically possess high degradation temperatures (up to 388 °C), improved chemical resistance and are hydrophilic due to the high density of hydroxyl groups and the resulting strong hydrogen bonds between these groups and the urethane moieties, rendering these polymers especially suitable for coating applications.³⁵⁴ The bicyclic carbonate can be a monomer (*e.g.* prepared from glycerol carbonate and a diacid/diacyl chloride such as terephthalic acid)³³⁵ or a polymer (*e.g.* poly(dimethylsiloxane)) bearing terminal cyclic carbonate groups.³⁵⁵

In order to increase the renewable nature of these isocyanate-free urethanes, a bio-based building block was developed by epoxidising the unsaturated bonds in

soybean oil, followed by reaction with CO₂ to introduce cyclic carbonate moieties.³⁵⁶ Subsequent reaction with di- and triamines resulted in crosslinked polyhydroxyurethane networks. A trend of increasing T_g and decreasing elongation at break was observed by decreasing the length of the diamines or by using triamines as curing agents. In another study on the synthesis of polyhydroxyurethanes from carbonated soybean oil, large diamines prepared via amidification of fatty acid dimers were used.³²⁸ Whereas the polyhydroxyurethanes produced from carbonated soybean oil reacted with short diamines (*i.e.* 1,4-butanediamine and 1,5-pentanediamine) were brittle, those prepared using the large diamines showed thermoplastic behaviour (Table 1.10, entries 14 and 15 respectively). This was ascribed to a higher intake of carbonated soybean oil in the former case, resulting in a higher crosslink density of the final polyhydroxyurethane network. In another study of bio-based carbonated precursors for polyurethanes, carbonated fatty acid diesters derived from sunflower oil were used as building blocks.³⁵⁷ Both fatty acid diesters with two internal epoxide moieties and with two terminal epoxide moieties were successfully converted into their cyclic carbonate analogues. Subsequent reaction of these bicyclic carbonates with diamines yielded linear polyurethanes with molecular weights up to 13500 g mol⁻¹ and glass transition temperatures around -15 °C.

Another type of bio-based bicyclic carbonate (Fig. 1.10.C) can be obtained by the epoxidation of both double bonds of limonene (see section 1.3.3) followed by CO₂-cycloaddition.³²⁹ This building block was used to synthesise both linear polyhydroxyurethanes and crosslinked thermoset polyhydroxyurethane networks by reaction with diamines or triamines, respectively. The mechanical properties of the obtained polyhydroxyurethane thermosets are shown in Table 1.10, entry 16. The relatively high Young's modulus and low elongation at break are an indication of strong and rigid structures, which might originate from the presence of hydroxyl groups and the resulting hydrogen bonding with the urethane moieties,³⁵⁴ but might also be related to the intrinsic rigidity of the limonene units.

It should be noted that, although non-isocyanate polyurethanes prepared via the reaction between cyclic carbonates and amines are promising from an environmental and safety point of view, this reaction is quite slow compared to the reaction between isocyanates and alcohols,³³⁵ rendering these non-isocyanate polyurethanes unsuitable for application as rigid foams, which requires very rapid formation of the urethane network upon mixing of the precursor components.

1.3.4.4. *CO₂-based polycarbonates as components of polymeric coatings*

In addition their use as components in polyurethane coatings (see 1.3.4.3), CO₂-derived polycarbonates have also been investigated for other types of polymeric coatings. Most of the current commercial powder coating formulations consist of petroleum-based semi-aromatic polyesters combined with curing agents, pigments, flow improvers and other additives, which are typically coated onto metal substrates by electrostatic coating followed by curing between 160 and 200 °C.²⁵¹ The glass transition temperature of the initial polyester is optimally between 45 and 100 °C, which is high enough to prevent stickiness of small powder particles but low enough to exhibit appropriate flow properties at common curing temperatures.²⁵¹ Aiming at a greener alternative to these conventional coatings, various CO₂-based polycarbonates were synthesised and used to prepare coatings via a solvent-casting method.²⁵¹ For example, terpolymers produced from cyclohexene oxide, 4-vinylcyclohexene oxide and CO₂, blended with a trithiol crosslinking agent and either a UV or thermal initiator were cast from solution to create a polymer film, which was subsequently cured by respectively UV or thermally induced radical curing. The obtained transparent coatings showed good impact and chemical resistance (Table 1.11, entry 2).

In addition to solvent-based coating, powder coating was also employed to prepare coatings from the cyclohexene/4-vinylcyclohexene polycarbonate. The powder-coated polycarbonate showed unsatisfactory impact resistance when subjected to the reverse falling dart impact test (Table 1.11, entry 3). This was ascribed to the rather high T_g of the cured resin (85-104 °C) and to a higher film thickness compared to the polycarbonate coating prepared via solvent-casting. The powder-coated polymer displayed similar proper acetone resistance as the solvent-casted coating, with no visual damage observed after 75 acetone double rubs. The pencil hardness of the polycarbonate powder was rather high (Table 1.11, entry 3), indicating a high scratch resistance. Based on these features, the cyclohexene/4-vinylcyclohexene polycarbonate shows potential in powder coating applications, although incorporation of *e.g.* propylene carbonate moieties in the polycarbonate backbone might be needed to decrease the glass transition temperature and improve the impact resistance.

The fully bio-based polycarbonates synthesised from CO₂ and limonene oxide already discussed in section 1.3.4.3 as components of polyurethane coatings can also be functionalised in a different way to enable the preparation of alternative polymeric coatings. Reaction of the pending vinyl groups of poly(limonene

carbonate) (Fig. 1.10.A) with a trithiol compound in the presence of a radical initiator and under UV irradiation produced transparent coatings (Table 1.11, entry 4).³⁵⁸ Using the same curing method, transparent coatings prepared from a different bio-based polycarbonate derived from cyclohexadiene oxide and CO₂ were also tested with regard to their mechanical and adhesive properties (Table 1.11, entry 5).³⁵⁸ The coatings exhibited a hard and brittle character, typically observed for other CO₂-polycarbonate based coatings (Table 1.11). The coatings prepared from poly(cyclohexadiene carbonate) typically possessed a higher König hardness than the poly(limonene carbonate)-based coatings, which was related to the higher intrinsic stiffness of the former polycarbonate due the absence of bulky isopropenyl groups present in poly(limonene carbonate), that possibly lead to enhanced free volume between the poly(limonene carbonate) chains. In addition to employing the vinyl groups of poly(limonene carbonate) for crosslinking purposes, these groups can also be converted into other functional groups via *e.g.* thiol-ene chemistry to produce functional coatings. For example, incorporation of quaternised ammonium moieties produced a coating with anti-bacterial properties.²³⁴ Another strategy consists in epoxidising both double bonds of limonene to prepare limonene dioxide and to polymerise this compound with CO₂. The obtained polycarbonate displayed pendant epoxide groups, which were subsequently reacted with a trithiol compound to produce a thermoset coating with a very high T_g, and promising properties such as good acetone resistance and scratch resistance (Table 1.11, entry 6).²³⁹

1.3.4.5. CO₂-based polycarbonates as components of polymer blends and composites

The use of CO₂-based polycarbonates as drop-in chemicals in conventional polymer blends is of potential commercial interest and has been investigated by various companies. This is exemplified by Siemens and BASF, which produced a polymer blend consisting of CO₂-derived poly(propylene carbonate) and poly(hydroxybutyrate) as a substitution for conventional petroleum-based acrylonitrile-butadiene-styrene (ABS) plastic.^{17,359} Typically, poly(propylene carbonate) is suitable as an additive in polymer blends to increase the elasticity of other polymers, owing to its high elongation at break and impact strength (Table 1.8).³⁶⁰ By combining poly(propylene carbonate) with other biodegradable materials (*e.g.* starch), biodegradable composites can be produced (see section 1.3.6 for their biomedical applications).^{245,361} For the production of composites consisting of CO₂-based polycarbonates and inorganic materials (*e.g.* glass or fibres) a proper interaction between the polycarbonate and the inorganic surface is typically

required. Incorporation of functionalities, such as silicon-, boron- or phosphorous-containing moieties or sulfonic or carboxylic acid groups, along the polymer chains or as terminal groups can be used to improve the ability of polycarbonates to adhere to or wet a selected inorganic surface.^{17,362}

In addition to the application of CO₂-based polycarbonates in blends and composites for consumer polymer products, combination of these polycarbonates with other polymers has also been investigated for utilisation in energy storage devices (section 1.3.5) and biomedical or pharmaceutical applications (section 1.3.6).

1.3.5. Application of cyclic and polymeric carbonates in Li-ion batteries

Since half a century ago, batteries have become a crucial commodity in everyday life. Although the first electrochemical cell dates back to the end of the eighteenth century,^{363,364} it was during the late 1960s that innovation in the field of energy storage devices received an enormous boost due to widespread applications as those in consumer electronics, but also for more specific ones as medical implant devices.³⁶⁴ An important breakthrough that allowed an increase in energy density, and thus a decrease in the weight of batteries, was the development of rechargeable lithium-based batteries, which operate through transportation of Li⁺ cations between the two electrodes during charge and discharge (Fig. 1.12). Lithium has the highest electrochemical equivalent and is the lightest of all metals, which results in an exceptionally high energy density in Li-ion batteries.^{364–366} Nowadays, lithium-ion batteries are employed in a wide variety of applications, ranging from high-end (consumer) electronics and power tools to hybrid electric vehicles.^{367,368}

1.3.5.1. Cyclic carbonates in liquid electrolyte formulations

Batteries consist of two electrodes that are connected via an ion-conductive electrolyte, which can be liquid or solid. In the case of lithium-ion batteries, non-aqueous electrolytes have to be used due to the incompatibility of lithium with water. The most common liquid electrolytes employed in Li-ion batteries consist of a lithium salt (e.g. LiPF₆) dissolved in a suitable organic solvent.³⁶⁸ The solvent should have sufficiently high polarity to grant the efficient dissolution of the lithium salt and should be inert under the operating conditions.³⁶⁹ Since oxidation and reduction reactions occur at the two electrodes, the use of protic solvents is impractical, as they tend to undergo redox reactions under battery operating conditions.³⁶⁹ Taking these requirements into account, cyclic carbonates such as ethylene carbonate and propylene carbonate were identified as appropriate polar aprotic solvents for electrolyte formulations.^{364,368,370} The optimal liquid electrolyte formulation for

Fig. 1.12. General scheme of a lithium-ion battery (left, reprinted from J. Power Sources, 2010, 195, 2419-2430, with permission from Elsevier) and the most common organic carbonates used in liquid electrolytes (right).

lithium-ion batteries is characterised by: (1) High Li⁺-conductivity: typical ionic conductivities for state-of-the-art organic liquid electrolyte solvents are in the range of $10^{-3} - 10^{-2} \text{ S cm}^{-1}$,^{365,371} (2) a lithium transference number (*i.e.* the fraction of the total current carried by the lithium-ions) approaching unity in order to limit concentration polarisation within the cell,^{371,372} (3) a high dielectric constant component (*e.g.* ethylene carbonate, propylene carbonate), needed to dissolve the lithium salts in a sufficiently high concentration; (4) thermal and chemical stability of the electrolyte combined with inertness towards the other battery components (especially the electrodes), to maximise the cycle life of the battery; (5) a low melting point and a high boiling point, which enable keeping the mixture in the liquid state in a wide temperature range; (6) a low viscosity component (*e.g.* 1,2-dimethoxyethane), in order to promote ion transport; (7) overall safety (*e.g.* a high flash point, no or low toxicity); (8) cost competitiveness.^{369,373}

For the first generation of commercial lithium-ion batteries, Sony used an electrolyte consisting of propylene carbonate, 1,2-dimethoxyethane and LiClO₄ as the lithium salt.³⁷⁴ Nowadays, the majority of lithium-ion batteries use an electrolyte formulation consisting of LiPF₆, ethylene carbonate, and one or more linear alkyl carbonates (*e.g.* dimethyl carbonate, diethyl carbonate and methyl ethyl carbonate, Fig. 1.12).^{369,375} Efforts are continuously being devoted to improve the properties of lithium-ion batteries with respect to capacity, safety and stability/lifetime. Propylene carbonate was eventually replaced by ethylene carbonate due to reaction of the former with the anode of the battery, which causes degradation of the anode and eventually leads to a decrease in battery lifetime and may result in health hazards due to the possibility of internal short circuits.³⁶⁹ The use of ethylene carbonate as electrolyte solvent enhanced the stability of the battery, because ethylene carbonate has the ability to form a passive layer between the electrolyte

and the anode, the so-called solid electrolyte interface (SEI), which suppresses electrolyte intercalation on the graphite anode surface.^{376,377} Ethylene carbonate is typically mixed with one or more solvents (*e.g.* dimethyl carbonate, methyl ethyl carbonate and diethyl carbonate) to compensate for its high melting point ($\sim 36\text{ }^{\circ}\text{C}$), thus allowing the batteries to be used in a wider temperature range.^{366,369} However, even the common electrolyte composition consisting of LiPF_6 , ethylene carbonate and one or more linear carbonates still has a temperature limit of $-20\text{ }^{\circ}\text{C}$, thereby hindering the use of these batteries at very low temperatures.³⁶⁹

In addition to ethylene carbonate, propylene carbonate and the above-mentioned alkyl carbonates, various other potential electrolyte solvents have been investigated in order to further improve lithium-based batteries. In this context, halogenated cyclic carbonates such as chloroethylene carbonate, fluoroethylene carbonate and trifluoropropylene carbonate (Fig. 1.12) were investigated as electrolyte solvents with the purpose of improving the cycle life of batteries, as these carbonates were expected to possess an enhanced ability to form a SEI layer on the surface of the anode.^{369,378,379} Additionally, lowering the melting point of the electrolyte by adding halogenated carbonates would improve low-temperature performance.^{369,379} Particularly, several studies have been conducted towards the use of chloroethylene carbonate in electrolyte applications.^{378,380–382} It was observed that the combination of chloroethylene carbonate and propylene carbonate as electrolyte solvent significantly reduced the electrolyte degradation typically associated with propylene carbonate-based electrolytes. This effect was ascribed to the proposed formation of a protective SEI film by decomposition of chloroethylene carbonate.³⁸⁰ Several properties (*i.e.* capacity loss and irreversible and reversible capacity) of an electrochemical cell employing the chloroethylene carbonate/propylene carbonate electrolyte solvent were found to be comparable to a cell with the benchmark ethylene carbonate/dimethyl carbonate solvent.³⁸¹ However, the charge capacity was observed to be significantly lower in the case of chloroethylene carbonate/propylene carbonate ($\sim 90\%$ versus $> 99\%$ for an electrochemical cell with an ethylene carbonate/dimethyl carbonate electrolyte solvent), which was hypothesised to be caused by an unwanted side reaction between chloroethylene carbonate and the graphite anode.³⁸¹ Fluoroethylene carbonate was investigated in an effort to overcome the complications encountered with chloroethylene carbonate.³⁸³ Although a charge efficiency of over 99% was achieved and similar low electrolyte degradation was observed, a dramatic decrease in cycle life was seen compared to chloroethylene carbonate (37% decrease in discharge capacity over 200 cycles versus a 20% decrease over 800 cycles).^{381,383}

In the context of green chemistry, it should be noted that chloroethylene carbonate can be produced from bio-based resources via the conversion of glycerol-derived epichlorohydrin³⁸⁴ and CO₂. However, compounds containing halogens are in general not desirable as components in consumer products due to their possible toxic effects and poor biodegradability.

Although liquid electrolytes have been employed in lithium-ion batteries for several decades and extensive research has been carried out to optimise these electrolytes with respect to performance and safety, obstacles still exist that are inherent to the use of conventional liquid electrolytes. One of the safety issues that arises from the use of conventional liquid electrolytes is the high flammability of the commonly used alkyl carbonates.^{368–370} Since various fluorinated organic compounds serve as flame-retardants, trifluoropropylene carbonate (flash point of 134 °C) was studied as a safer alternative to conventional alkyl carbonates, but its high viscosity limited the ionic conductivity of the electrolyte.^{369,385,386} Another safety issue is related to the typically employed LiPF₆ salt, which becomes reactive towards the electrolyte components at temperatures above 55 °C, possibly leading to permanent damage and explosion hazards.^{369,370} As the seriousness of fire and explosion hazards becomes more pronounced with larger scale, these safety issues are particularly crucial for large-format batteries, and thereby limit the applicability of liquid electrolyte lithium-ion batteries in *e.g.* electrical vehicles and industrial operations.^{369,370}

1.3.5.2. Polycarbonates in polymer-based electrolytes

Polymeric electrolytes have gained considerable attention as possible replacements for conventional liquid electrolytes, due to a number of potential advantages. First of all, safety issues connected to flammability of volatile organic solvents and electrolyte instability could be minimised or even completely avoided by using non-flammable polymers.^{365,369,370} Secondly, the higher dimensional stability and mechanical strength of polymeric electrolytes as compared to liquid electrolytes would allow the production of lithium-ion batteries with a wide range of possible shapes.^{365,369} Also, the dimensional stability that polymers typically offer could eliminate the need of battery components such as a separator, further simplifying the manufacturing process and production costs.^{369,373} Various types of electrolytes incorporating CO₂-based polycarbonates have been explored, both as SPE (solid polymer electrolyte) and GPE (gel polymer electrolyte). SPEs consist of a blend of one or more polymers wherein a lithium salt is dispersed (Fig. 1.13.A), while GPEs consist of a polymeric matrix swollen by a solvent containing a lithium salt (Fig. 1.13.C). A noteworthy sub- class of SPEs is that of Single Lithium-Ion Conducting

Solid Polymer Electrolytes (SLIC-SPEs), where the anions, instead of being mobile, are anchored to the polymer chains (Fig. 1.13.B).³⁷⁰

1.3.5.2.1. Polycarbonate-based Solid Polymer Electrolytes

Poly(ethylene oxide) was the first polymer to be investigated for potential application in solid polymer electrolytes for lithium-based batteries.^{365,387} The first attempts to incorporate SPEs in lithium batteries were limited to large, stationary batteries, as these systems required relatively high operating temperatures (between 60 and 80 °C) and poly(ethylene oxide) tends to crystallise below 60 °C, which is accompanied by a significant drop in ionic conductivity of the electrolyte (between 10^{-6} and 10^{-5} S cm⁻¹ at room temperature).^{366,388} This low ionic conductivity compared to the state-of-the-art organic liquid electrolyte solvents severely limits the application in lithium-ion batteries used at room temperature.^{365,369,371,389}

To date, one of the few commercialised SPE-containing lithium-ion batteries is used as a power source for an electric car developed by Bolloré, wherein poly(ethylene oxide) is employed as SPE component.³⁷⁰ In recent years, the application of aliphatic polycarbonates, and specifically poly(ethylene carbonate), as solid polymeric electrolytes has gained increasing attention. Aliphatic polycarbonates generally display low glass transition temperature (see section 1.3.2, Table 1.8), accompanied by high chain mobility and ion transport required for proper battery operation.³⁹⁰ These features render aliphatic polycarbonates particularly attractive for electrolyte applications.³⁹¹ Additionally, the polar nature of the carbonate group offers a high solvation power towards numerous salts.³⁸⁹

One of the first reports on CO₂-derived polycarbonates as electrolytes was based on the use of various polycarbonates synthesised via the coupling of CO₂ with a range of glycidyl ethers (Fig. 1.14.A) using a zinc glutarate catalyst.^{304,392} Electrochemical analysis showed that these polycarbonate-based electrolytes (with ionic conductivities reaching 10^{-6} S cm⁻¹ at 30 °C) did not represent an improvement compared to the benchmark poly(ethylene oxide) electrolytes. Increasing the amount of lithium salt in the electrolyte formulation and raising the operating temperature, drastically improved the ionic conductivity. Poly(*n*-butyl-glycidyl ether carbonate) with 65 wt.% LiTFSI (lithium bis(trifluoromethane sulphonyl) imide) showed enhanced ionic conductivities in the order of 10^{-5} S cm⁻¹ at 25 °C and 10^{-3} S cm⁻¹ at 120 °C,³⁰⁵ the latter being close to the typical ionic conductivities for liquid electrolyte lithium-ion batteries at room temperature ($\geq 10^{-3}$ S cm⁻¹). For comparison, an electrolyte consisting of poly(ethylene oxide) with 65 wt.% LiTFSI displayed ionic conductivity in the order of 10^{-5} S cm⁻¹ at 20 °C and in the order of 10^{-3} S cm⁻¹ at 80 °C.³⁹³ The presence of pendant ether groups is not a strict

Fig. 1.13. Schematic drawing of different types of polymer electrolytes: (A) Solid Polymer Electrolyte. (B) Single Lithium-Ion Conducting Solid Polymer Electrolyte. (C) Gel Polymer Electrolyte.

requirement, as proven by a poly(ethylene carbonate) electrolyte with 80 wt.% loading of LiTFSI salt that displayed an ionic conductivity in the order of $10^{-5} \text{ S cm}^{-1}$ at 30 °C. In general, the increase in the amount of lithium salt in poly(ethylene carbonate)-based electrolytes leads to an increase in ionic conductivity.³⁹⁴ However, the lithium salt concentration was also observed to impact the thermomechanical properties of the polymeric electrolyte, as the glass transition temperature and storage modulus initially increased for LiTFSI concentrations up to a molar ratio of 0.2 (approximately 39 wt.% LiTFSI), while for higher lithium salt concentrations a decrease in these quantities was observed.³⁹⁴ The inclusion of several types of additives in the formulation of polymeric electrolytes based on polycarbonates has been studied. Ionic liquids have very low vapour pressures, are non-flammable and possess high ionic conductivities (in the order of $10^{-3} \text{ S cm}^{-1}$ at room temperature),³⁹⁵ making them potentially valuable additives in (polymeric) electrolyte formulations.³⁶⁷ This was investigated by preparing a polycarbonate-based electrolyte consisting of poly(ethylene carbonate), a LiTFSI salt and a pyrrolidinium-based ionic liquid (Pyr₁₄TFSI) as a plasticiser and an ionic conductivity enhancer.³⁹⁶ However, ionic conductivities ranging from $10^{-7} \text{ S cm}^{-1}$ at 50 °C to $10^{-5} \text{ S cm}^{-1}$ at 90 °C were obtained, which are too low for battery applications and are inferior compared to the benchmark poly(ethylene carbonate)/LiTFSI electrolytes.³⁸⁹ This drawback is partially counterbalanced by a rather high lithium transference number (0.66 at 80 °C).³⁹⁶ Inorganic fillers have been reported to increase the ionic conductivity of poly(ethylene oxide)-based electrolytes at ambient temperatures by preventing crystallisation at $T < 60 \text{ °C}$, and to enhance their mechanical properties.³⁸⁸

In analogy to this approach, inorganic fillers have been included in polycarbonate-based electrolytes. For example, a submicron-sized silica fibre was added to the aforementioned poly(ethylene carbonate)/LiTFSI/Pyr₁₄TFSI electrolyte formulation,³⁹⁷ leading to a slight enhancement of the mechanical properties (the

Fig. 1.14. Glycidyl ether-based polycarbonates for application in polyelectrolytes: (A) Solid Polymer Electrolyte. (B) Single Lithium-Ion Conducting Solid Polymer Electrolyte.

Young's modulus increased from 0.35 to 0.39 MPa) and an increase in ionic conductivity ($10^{-7} \text{ S cm}^{-1}$ at 30 °C and $10^{-5} \text{ S cm}^{-1}$ at 80 °C), which is nevertheless still far from the requirements for battery applications. The addition of TiO_2 as inorganic filler to a poly(ethylene carbonate) electrolyte with LiFSI salt (with 0.53:1 polymer-to-salt molar ratio) proved more effective,²⁵⁷ leading to an increase of the lithium transference number from 0.54 to 0.81 at 60 °C upon addition of 1 wt.% TiO_2 , while also resulting in an increase in ionic conductivity, reaching values in the order of $10^{-5} \text{ S cm}^{-1}$ at 30 °C and $10^{-3} \text{ S cm}^{-1}$ at 80 °C.

Another approach to improve the ionic conductivity of SPEs is to alter the chemical structure of the polymer chains, in order to decrease the glass transition temperature and, thus, to increase the chain mobility at lower temperatures. In the context of polycarbonate-based electrolytes, this pathway was explored by tuning the CO_2 /epoxide polymerisation reaction so that both carbonate and ether linkages are present in the polymer backbone.³⁹⁸ This allowed combining the high lithium transference number commonly associated with aliphatic polycarbonates with lower glass transition temperature bestowed by ether linkages, resulting in a poly(ethylene carbonate/ethylene oxide)/LiFSI electrolyte with an ionic conductivity in the order of $10^{-4} \text{ S cm}^{-1}$ at 60 °C and a lithium transference number of 0.66 (under optimised salt concentrations).³⁹⁸ On the other hand, a low T_g can be a drawback because the practical application of polyelectrolytes also requires mechanical and dimensional stability. In the case of electrolytes based on poly(ethylene carbonate), glass transition temperatures as low as -47 °C have been reported,²⁵⁷ which limits the practical applicability of these polyelectrolytes as a self-standing membrane in battery applications.³⁹⁹ To overcome this obstacle, efforts have been made to combine a poly(ethylene carbonate)/LiFSI electrolyte with a three-dimensionally ordered macroporous polyimide matrix.³⁹⁹ Ionic conductivity in the order of 10^{-5} S

cm⁻¹ was reached at 30 °C, which was only slightly lower than the conductivity without the polyimide matrix. DSC measurements did not show any significant change in the glass transition temperature after combination of the electrolyte with the polyimide matrix, indicating that the matrix does not influence the ionic conductivity by altering the T_g . Although the authors did not perform any mechanical analysis, they were able to fabricate an all-solid-state lithium battery incorporating the poly(ethylene carbonate)/LiFSI/polyimide electrolyte, which showed a higher battery capacity than the same battery with a conventional ethylene oxide/propylene oxide copolymer electrolyte and did not suffer short circuit failures nor mechanical instability during 30 charge/discharge cycles.³⁹⁹

Next to the extensive research towards poly(ethylene carbonate)-based electrolytes, poly(propylene carbonate) has also been investigated as potential solid polymer electrolyte in energy storage devices.⁴⁰⁰ Various blends with different ratios of poly(propylene carbonate), poly(ethylene oxide) and a LiClO₄ salt produced polymeric electrolytes that showed enhanced ionic conductivity compared to conventional pure poly(ethylene oxide).⁴⁰¹ The highest measured ionic conductivity was in the order of 10⁻⁵ S cm⁻¹ at room temperature for an electrolyte incorporating a 1:1 mass ratio of poly(propylene carbonate):poly(ethylene oxide) mixed with 10 wt.% LiClO₄. Polyelectrolytes consisting solely of poly(propylene carbonate) and LiClO₄ possess an ionic conductivity in the order of 10⁻⁵ S cm⁻¹ at room temperature and 10⁻³ S cm⁻¹ at 80 °C for an electrolyte with a poly(propylene carbonate)-to-LiClO₄ molar ratio of 10:1.⁴⁰² It is worth noting that the ionic conductivity of poly(propylene carbonate)-based electrolytes is typically higher than that of poly(ethylene carbonate)-based electrolytes. This has been attributed to the presence of the pendant methyl groups on the poly(propylene carbonate) chains, imparting a lower degree of crystallinity, which was observed to positively influence the ionic conductivity.⁴⁰²

The addition of the 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM⁺BF₄⁻) ionic liquid to a poly(propylene carbonate) electrolyte containing LiClO₄ led to an increase in ionic conductivity from 10⁻⁶ S cm⁻¹ to 10⁻³ S cm⁻¹ at 20 °C.⁴⁰³ This increase in conductivity is the opposite of what was observed for the addition of an ionic liquid to the above-mentioned poly(ethylene carbonate)-based electrolyte,³⁹⁶ where incorporation of a ionic liquid resulted in a decrease in conductivity (though it should be noted that the type of ionic liquid, the lithium salt and the relative amounts of these components differed in the two cases). The increase in conductivity of the poly(propylene carbonate)-based electrolyte observed in this work was explained by FTIR measurements, which showed that the presence of the

ionic liquid cations caused a weakening of the complexation between poly(propylene carbonate) and Li-ions, resulting in a higher lithium-ion mobility. Thermal analysis indicated that addition of 3 mass eq. of BMIM⁺BF₄⁻ compared to poly(propylene carbonate) also caused a significant decrease in the T_g from 3 to -70 °C, while the thermal stability improved (T_{d5%} increased from 166 to 231 °C). A drawback of this system is that at ionic liquid-to-polycarbonate weight ratios ≥ 1, the polyelectrolyte is not anymore a self-standing solid film, but rather a soft, sticky and non-fluidic gel. On the other hand, ionic conductivities at weight ratios < 1 are in the range of 10⁻⁴ S cm⁻¹ or less (20 °C), which is less attractive with respect to application in lithium batteries.

One of the disadvantages of using SPEs composed of a polymer matrix and a lithium salt is the generally low lithium transference number, caused by the fact that only a small amount of the ionic current is related to the motion of lithium-ions, while the rest of the ionic current is related to the motion of the mobile anions (*e.g.* TFSI⁻, FSI⁻, ClO₄⁻).^{370,391} This leads to polarisation within the cell, giving rise to undesired effects such as voltage drop, limited power supply and, finally, leading to cell failure.^{370,391} A possible approach to overcome this limitation is the substitution of conventional polymer electrolyte systems with single lithium-ion conducting solid polymer electrolytes (SLIC-SPEs, Fig. 1.13.B), which can be prepared by immobilising the anions in the polymeric backbone in the form of functional pendant groups.^{370,391} For this purpose, a single-ion polycarbonate was synthesised by reacting allyl glycidyl ether and propylene oxide with CO₂, employing a zinc glutarate catalyst.³⁹¹ The pendant vinyl groups on the polycarbonate backbone were functionalised with 3-mercaptopropionic acid and subsequently lithiated with lithium hydroxide to produce a single-ion-conducting polymer (Fig. 1.14.B). This single-ion polycarbonate electrolyte displayed an ionic conductivity in the range of 10⁻⁴ S cm⁻¹ at 80 °C and a lithium transference number of 0.86, which is considerably higher than most lithium transference numbers determined for analogous polycarbonate-based SPEs containing lithium salts.

1.3.5.2.2. Polycarbonate-based Gel Polymer Electrolytes

Although solid polymer electrolytes generally impart better mechanical properties, flexible battery manufacturing and safer operation than liquid ones, they still suffer from moderate conductivities at operating conditions (*vide supra*). Gel polymer electrolyte (GPE)s contain both a polymeric matrix and a liquid in which a lithium salt is dissolved (Fig. 1.13.C) and, in this sense, they can be considered hybrid systems between SPE and liquid electrolytes. Therefore, GPE systems may optimally combine the best of both worlds, although the risk is to combine the worst of both

worlds as well. For example, GPEs typically display higher ionic conductivities than SPEs but the safety issues associated with liquid electrolytes (*i.e.* flammable components and electrochemical instability) are not completely avoided.^{368,370} GPEs are currently used in lithium-ion polymer batteries (LiPBs) employed in electrical vehicles and consumer goods such as mobile phones and notebooks, typically incorporating polymers such as poly(ethylene oxide), poly(acrylonitrile), poly(methyl methacrylate) and poly(vinylidene fluoride).^{368,369,373} CO₂-based polycarbonates have also been studied as components of GPEs. Terpolymerisation of CO₂, propylene oxide and maleic anhydride, followed by radical crosslinking with dicumyl peroxide as radical initiator, produced a polymer matrix that was used as a GPE in combination with a liquid LiClO₄/ethylene carbonate/dimethyl carbonate electrolyte.⁴⁰⁴ This system showed rather high ionic conductivities (in the range of 10⁻³ S cm⁻¹ at room temperature and 10⁻² S cm⁻¹ at 50 °C) and a lithium transference number of 0.42. A lithium cell incorporating this gel polyelectrolyte exhibited an initial battery capacity only slightly lower than that of commercial fully liquid electrolyte batteries.^{404,405}

Blending of aliphatic polycarbonates with other polymers can also produce matrices with potential utilisation in GPE applications. A blended polybutadiene/poly(propylene carbonate) crosslinked matrix (70:30 mass ratio) in which a liquid LiPF₆/ethylene carbonate/dimethyl carbonate electrolyte was absorbed, displayed ionic conductivities in the range of 10⁻³ S cm⁻¹ between room temperature and 80 °C.⁴⁰⁶ Thermal and mechanical analysis indicated that the polymeric electrolyte had proper thermal and mechanical stability due to a slightly higher initial degradation temperature than pure poly(propylene carbonate) (272 °C vs. 260 °C) and an achievable preparation of a robust, self-standing and flexible film with the absence of liquid flow. A lithium-ion battery cell containing this electrolyte maintained 84% of the original capacity value after 70 charge/discharge cycles. Similarly high ionic conductivities were measured for a different GPE system consisting of an electrospun poly(vinylidene fluoride)/ poly(propylene carbonate) matrix swollen by a LiPF₆/ethylene carbonate/dimethyl carbonate liquid electrolyte.⁴⁰⁷ Moreover, excellent cycling stability was observed with no apparent capacity decrease even after 100 charge/discharge cycles, whereas a commercial polymeric matrix based on polyethylene preserved 90% of the original capacity under the same conditions.

1.3.6. Polycarbonates in biomedical and pharmaceutical applications

Both natural as well as man-made polymers find a wide variety of uses in the field of medicine, where they are being employed in wound dressings, drug delivery applications, surgical implants and medical devices.⁴⁰⁸ For the specific utilisation of polymers inside the human body, the most important features are biodegradability and biocompatibility. Biodegradability should be carefully tuned because an unwanted degradation profile, *e.g.* slow degradation of short-term implants or fast degradation of long-term tissue scaffolds, and harmful degradation products can severely limit the range of applicability.⁴⁰⁹ Biocompatibility is also crucial because biomedical polymers that have to perform a task inside the human body (*e.g.* drug delivery systems and implants such as tissue scaffolds) should accomplish the desired function without causing any unwanted local or systemic effects in the patient.⁴¹⁰ For the specific application of biomaterials as implants in the human body, the mechanical and chemical stability are also important, as the pH in different tissues ranges from 1 to 9 and daily activities exert stresses of approximately 4 MPa on bones and stresses in the range of 40-80 MPa on tendons and ligaments.⁴¹¹ Polyesters such as poly(lactic acid), poly(glycolic acid), poly(lactic-glycolic acid), polycaprolactone and polyhydroxyalkanoates are the most intensely studied polymers in the field of biomedical applications due to their biodegradability, low toxicity and the related good biocompatibility.^{408,409,412} However, one of the disadvantages of employing polyesters is that *in vivo* biodegradation of the majority of the used polyesters generates acidic products, thereby decreasing the local pH and triggering necrosis of host cells and inflammatory responses.^{409,413,414} Consequently, for implantation sites that exhibit low metabolic activity and, therefore, cannot sufficiently process degradation products, polyester-based materials are not an optimal choice.⁴⁰⁹ CO₂-based aliphatic polycarbonates have been studied as a possible alternative to polyesters as materials for biomedical and pharmaceutical applications,^{248–250} owing to their biodegradability (see section 1.3.2) and good biocompatibility.

Although typically not derived from CO₂, a related aliphatic polycarbonate, poly(trimethylene carbonate), has already been approved for application in biological fields by the United States Food and Drug Administration (FDA).^{415,416} Poly(propylene carbonate) is the most widely studied CO₂-based polymer for biomedical applications. Studies on both base-catalysed hydrolysis as well as thermal decomposition showed that propylene carbonate and 1,2-propanediol are the major initial degradation products of poly(propylene carbonate)

decomposition.^{417,418} Apart from causing serious eye and slight skin irritation at high concentrations, propylene carbonate was reported not to display any significant toxicity during *in vivo* tests via oral insertion and inhalation (although the effects on the human body have not yet been thoroughly investigated),^{223,419} while 1,2-propanediol is commonly used in a variety of food applications and in the medical and pharmaceutical industry, it displays no toxicity and can be metabolised by the human body.⁴²⁰ Additionally, it has been suggested that poly(propylene carbonate) will eventually degrade into CO₂ and water,^{413,414,421,422} which would trigger less inflammatory responses compared to the degradation products of polyesters, although no scientific study has been presented in which this degradation pathway is observed.

Poly(propylene carbonate) typically displays an elastic behaviour and possesses an amorphous structure accompanied by a glass transition temperature in the range of body temperature (35-40 °C), which, in combination with its biodegradability, renders it potentially interesting for biomedical applications in soft tissue scaffolds or drug delivery. On the other hand, the low glass transition temperature and moderate mechanical strength (Table 1.12, entries 1a-d) make it unsuitable for application in rigid tissue scaffolds such as bone substitutes.^{413,423} With the target of tuning the properties of poly(propylene carbonate) towards biomedical applications, this CO₂-based polymer has been combined with other polymers (*e.g.* polyesters), either through terpolymerisation reactions or as blends. The thermal and mechanical properties of several researched poly(propylene carbonate)-based formulations for biomedical applications are summarised in Table 1.12. On a critical note, it can be seen that the characterisation of these properties is often incomplete. A more thorough analysis of the thermal and mechanical properties of these formulations would be advisable to be able to fully appraise the potential of these materials in biomedical applications such as tissue engineering. Polymer films of poly(carbonate-co-ester)s that were prepared by terpolymerisation of CO₂, propylene oxide and caprolactone were compared with pure poly(propylene carbonate) and polycaprolactone with respect to the degradation behaviour employing various enzymes at either 37 or 60 °C.^{412,424} The degradation rates of poly(propylene carbonate- ϵ -caprolactone) were comparable to those of conventional polycaprolactone homopolymers. The study did not include an investigation of the structure and effects of the degradation products. This would have been desirable, since the products of polycaprolactone degradation have been reported to cause necrosis of host cells and inflammation.^{409,413,414} Another approach consisted in blending poly-3-hydroxybutyrate, which is characterised by a

relatively stiff, rigid and brittle structure,⁴²⁵ with poly(propylene carbonate), which exhibits a more elastic behaviour with relatively low tensile strength.⁴¹³ *In vivo* radiolabelling studies showed that pure poly(propylene carbonate) degraded much faster than the poly(propylene carbonate)/poly-3-hydroxybutyrate blend. Both the pure polycarbonate and the blend exhibit good biocompatibility, as they did not show any toxicity *in vivo* and displayed proper biocompatibility with *in vitro* red blood cells. Although the mechanical properties of the poly(propylene carbonate)/poly-3-hydroxybutyrate blend still have to be investigated, the material shows potential to be used in biomedical applications that require longer degradation times than pure poly(propylene carbonate).

Polymers incorporating glycerol building blocks (*e.g.* polyglycerol ethers, polyglycerol carbonates, polyether esters or polycarbonate esters containing glycerol units) have also received extensive attention in the field of biomedicine due to: (i) their biodegradability yielding non-toxic products such as glycerol and CO₂; (ii) the presence of pendant hydroxyl groups that can be functionalised with chemotherapeutic agents, antibacterial compounds, anti-inflammatory agents, fluorescent tags or material-property modifiers; (iii) their suitability to be used in manufacturing techniques such as electrospinning.⁴²⁶ Within this group, CO₂-based glycerol polycarbonates have been synthesised via polymerisation of benzyl glycidyl ether and carbon dioxide, followed by deprotection of the polymer to produce atactic and isotactic poly(1,2-glycerol carbonate)s.⁴²⁶ The degradation behaviour of these CO₂-based poly(1,2-glycerol carbonate)s (Fig. 1.15.A) was monitored (at 37 °C) and compared to the degradation of poly(1,3-glycerol carbonate) (Fig. 1.15.B), a polymer that is synthesised via ring-opening polymerisation of six-membered cyclic carbonates and that has been investigated for use in biomedical applications such as drug-loaded buttressing films for the prevention of tumour recurrence after surgical resection,⁴²⁷ and particles for drug delivery.⁴²⁸ It was seen that the CO₂-based poly(1,2-glycerol carbonate)s exhibited rather high degradation rates with a half-life time of 2-3 days, while poly(1,3-glycerol carbonate) did not show any degradation over a course of 4 days under the same conditions. This difference in degradation behaviour was attributed to a higher tendency of the primary hydroxyl group in the poly(1,2-glycerol carbonate) repeating unit to initiate an intramolecular attack compared to the secondary hydroxyl present in the poly(1,3-glycerol carbonate) repeating unit. This behaviour can prove advantageous for biomedical applications that require fast degradation rates. In a related study, poly(glyceric acid carbonate) (Fig. 1.15.C) was synthesised as a CO₂-based and biodegradable analogue of poly(acrylic acid) for application in *e.g.* drug delivery.⁴²⁹ Crosslinked

Table 1.12. Thermal and mechanical properties of poly(propylene carbonate)-based formulations for biomedical applications

Polymer formulation	#	T _g (°C)	T _m (°C)	T _d (°C)	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)	Compressive modulus (MPa)	Compressive yield strength (MPa)	Storage modulus (MPa)	Ref
Poly(propylene carbonate) [PPC]	1a	-	-	-	-	-	-	0.38	-	-	432
	1b	25-45	-	±240 (initial)	700-1400	7-30	-	-	-	-	245
	1c	29	-	-	-	-	-	-	0.13	30	423
	1d	-	-	245 (DSC)	-	-	-	0.2	-	-	414
Electrospun PPC fibres	2a	38	103	210 (5 wt%)	10190	22.11	10.71	-	-	-	433
	2b	-	-	-	429.63	7.37	154.93	-	-	-	434
Electrospun PPC/ 15 wt.% gelatine/ acetic acid	3	-	-	-	295.72	7.72	95.26	-	-	-	434
PPC/ 1 wt.% graphite oxide	4	39.5	-	-	-	-	-	-	1	1600	423
PPC/ 50 wt.% starch	5	-	-	270 (DSC)	-	-	-	33.9	-	-	414
PPC/ starch/ plasticiser/ bioglass	6	-	-	-	-	-	-	80.0	-	-	421

hydrogels derived from poly(glyceric acid carbonate) readily degraded in basic water (pH = 8.4), while analogues crosslinked hydrogels based on poly(acrylic acid) did not. This was ascribed to the presence of biodegradable carbonate linkages in the poly(glyceric acid carbonate) chains. For the application of polymers in tissue scaffolds, the biocompatibility is also related to the attachment of living cells to the biomaterial and the subsequent spreading over the implant. In this context, the hydrophobicity of aliphatic polycarbonates such as poly(propylene carbonate) and poly(cyclohexene carbonate) is a limitation as it leads to poor cell adhesion and slow biodegradation.^{422,430} One way to overcome this issue is by incorporating hydrophilic moieties in the polycarbonate chains, *e.g.* via terpolymerisation of CO₂, propylene oxide and a hydrophilic monomer such as ME₃MO (2-((2-(2-(2-methoxyethoxy)ethoxy)ethoxy)methyl) oxirane (Fig. 1.15.D).⁴³⁰ Polycarbonates containing at least 26 mol % of ME₃MO showed reversible thermo-responsive solubility in water with lower critical solution temperatures between 7.0 and 35.2 °C. Another study investigating the hydrophilicity of CO₂-based polycarbonates

Fig. 1.15. Examples of aliphatic polycarbonates that have been evaluated for their potential in biomedical applications: (A) Poly(1,2-glycerol carbonate). (B) Poly(1,3-glycerol carbonate). (C) Poly(glyceric acid carbonate). (D) Terpolymer synthesised from CO₂, propylene oxide and ME₃MO.

focussed on a series of poly(carbonate-ether)s made from CO₂ and ethylene oxide, in which the carbonate content ranged from 1 to 43 mol%.⁴³¹ It was observed that by varying the molecular weight of the polymer and the amount of carbonate units, water-soluble polycarbonates can be prepared with lower critical solution temperature between 21.5 and 84.1 °C. Specifically, poly(ethylene carbonate-ether) with 26 mol% carbonate content displayed a lower critical solution temperature of 36.1 °C (i.e. close to human body temperature). The possibility to tune poly(ethylene carbonate-ether) and the aforementioned polycarbonate derived from CO₂/propylene oxide/Me₃MO to possess lower critical solution temperature is promising with respect to application in biomedical materials, as thermo-responsive water solubility has potential in controlled drug delivery systems,⁴³⁵ construction of tissue engineering scaffolds,⁴³⁶ molecular gates and gene carriers.⁴³⁷

In addition to terpolymerisation, surface modification of polycarbonates has also been explored to enhance the biocompatibility of aliphatic polycarbonates. A potential advantage of surface modifications is that only the polymeric surface is altered, while the bulk mechanical strength is maintained. Surface modification by aminolysis with polyethylenimine was used to introduce amino groups on the surface of a poly(propylene carbonate) membrane.⁴²² These amino functionalities served as an initial layer for consecutive layer-by-layer assembly, in which multiple

molecular layers of polyethylenimine/gelatine were deposited on the amino-functionalised poly(propylene carbonate) surface, based on the ionic interaction of the positively charged polyethyleneimine and negatively charged gelatine at pH = 7.4. A decrease in water contact angle after surface modification indicated the increased hydrophilicity of the modified poly(propylene carbonate). With respect to biocompatibility, the composite consisting of poly(propylene carbonate) with three bilayers of polyethylenimine/gelatine possessed enhanced compatibility with cells compared to both unmodified poly(propylene carbonate) as well as to a polycaprolactone benchmark, probably due to the presence of the outer gelatine layer that can suppress the cytotoxicity generally displayed by polyethyleneimine.⁴²² The improved biocompatibility of poly(propylene carbonate)/polyethylenimine/gelatine with living cells indicates that the material could be a potential alternative to conventional polycaprolactone for tissue engineering applications. To investigate this further, foaming of poly(propylene carbonate) with supercritical CO₂ and subsequent modification by aminolysis and layer-by-layer assembly techniques were employed to produce three-dimensional poly(propylene carbonate)/polyethylenimine/gelatine foam structures.⁴³² A maximum compressive modulus of 0.38 MPa was obtained for unmodified poly(propylene carbonate) (Table 1.12, entry 1a), while an average decrease in modulus of 13% was seen after modification with polyethyleneimine and gelatine. Despite this decrease, the values are still in the range required for meniscal tissue (0.22 MPa) and articular cartilage (0.51-15.3 MPa) repairs.⁴³² However, for utilisation of the polymer in temporary tissue scaffolds that are meant to degrade in the human body, studies investigating the biodegradability of the polymer and the biocompatibility of the degradation products should still be conducted, especially since polyethyleneimine is known to exhibit cytotoxicity.

In the context of applied tissue engineering, the three-dimensional structure of biomedical scaffolds, though often not thoroughly investigated,⁴³⁸ can significantly influence the biodegradability and mechanical properties of the material. Ideally, the scaffold should display: (i) porosity that enables cell migration and the transport of nutrients and waste, (ii) a surface that promotes cell adhesion, growth, migration and differentiation, and (iii) a degradation profile that closely matches the regeneration profile of the desired natural tissue.⁴³⁴ Three-dimensional poly(propylene carbonate) architectures were prepared via electrospinning, which readily allows the production of interconnected flexible nanofibrous structures.⁴³³ These electrospun poly(propylene carbonate) structures displayed slightly lower thermal stability and slightly enhanced mechanical properties compared to

conventional poly(propylene carbonate) (Table 1.12, compare entry 2a to 1b). Additionally, cell adhesion experiments indicated proper biocompatibility of the three-dimensional poly(propylene carbonate) structures, as the cells were seen to grow, migrate and differentiate. Electrospinning was also applied to blends of CO₂-based polycarbonates with a hydrophilic polymer such as gelatine.⁴³⁴ Although cell culture experiments showed that these blends possessed enhanced biocompatibility compared to pure poly(propylene carbonate), high content of gelatine also resulted in a decline in mechanical strength compared to pure poly(propylene carbonate) fibres (Table 1.12, entry 2b), as a consequence of the poor mechanical properties of gelatine. This negative effect was partially countered by addition of a small amount of acetic acid (Table 1.12, entry 3), probably due to the increased miscibility of poly(propylene carbonate) and gelatine, which was related to the pH-dependent behaviour of gelatine.

Whereas addition of gelatine led to a decrease in mechanical strength, the mechanical properties of poly(propylene carbonate) can be enhanced by means of other additives, which can be as diverse as graphite oxide⁴²³ or starch.⁴¹⁴ Addition of as little as 1 wt.% graphite oxide to poly(propylene carbonate) significantly increased the glass transition temperature, storage modulus and compressive yield strength of the obtained composite compared to the pure polymer (Table 1.12, compare entry 4 to 1c), without affecting negatively the biocompatibility.⁴²³ Also blending of poly(propylene carbonate) with starch remarkably affected the mechanical and thermal properties, as shown by the significant increase in the compressive modulus and decomposition temperature upon blending with 50 wt.% starch (Table 1.12, compare entry 5 to 1d).⁴¹⁴ *In vitro* and *in vivo* biocompatibility studies combined with degradation measurements showed that the poly(propylene carbonate)/starch blends possessed excellent cytocompatibility, as shown by the formation of only a scar tissue as a mild inflammatory response after *in vivo* implantation of the composite. The long-term (2 months) *in vivo* degradation of the poly(propylene carbonate)/starch composite was compared with that of poly(lactic acid) and showed that, in contrast to poly(lactic acid), the polycarbonate/starch blend was properly tolerated, without the occurrence of inflammation and immune cell responses. *In vitro* biodegradation studies indicated that the degradation rate of the poly(propylene carbonate)/starch blend after 8 weeks (13 wt.%) is comparable to that of poly(lactic acid) (8 wt.%). Although the biocompatibility and biodegradation of the polycarbonate/starch blend seem promising, the relatively hydrophobic surface of the composite might limit its practical application as it can restrict or delay cell growth and ultimately hamper tissue regeneration.⁴²¹ To

enhance the interaction of the polycarbonate/starch composite with living cells, water and glycerol were added as plasticisers together with 10 wt.% bioglass.⁴²¹ The addition of plasticisers improved the compressive modulus considerably (Table 1.12, entries 5 and 6), while the addition of bioglass enhanced the cell growth on the polycarbonate/starch composite. The material was used to produce biomedical screws that were well tolerated in *in vivo* tests and exhibited higher degradation rates than the poly(lactic acid) analogues, accompanied by an enhanced bone regeneration profile. These features show that poly(propylene carbonate)/starch composites incorporating plasticisers and bioglass possess great potential for applications in musculoskeletal tissue repair.

In addition to rigid and strong mechanical structures useful as tissue scaffolds, flexible polymers also find use in biomedical applications, especially in cases in which it is difficult to insert biomedical implants in the human body due to obstruction by organs, bones and veins or in sensitive areas such as the eyes or arteries. In these cases, flexible shape-memory materials can offer advantages over rigid structures, as they can be folded, deformed and subsequently introduced, *e.g.* through small catheters, where they can recover their original shape once placed in the desired location and orientation.⁴³⁹ Within this group of materials, polyurethanes exhibiting shape-memory have been investigated for utilisation in endovascular intervention procedures.⁴³⁹ Shape-memory polyurethanes based on polycarbonate polyols (see also section 1.3.4.3) have also been reported.³⁴⁷ Star-type oligo(carbonate-ether)s with three arms were synthesised via the reaction of CO₂ and propylene oxide in the presence of trimesic acid as an initiation-transfer agent.³⁴⁶ Consecutive reaction of these triol compounds with polyethylene glycol and 1,6-hexamethylene diisocyanate afforded crosslinked CO₂-based polyurethane networks.³⁴⁷ Shape-memory tests showed that by tuning the molecular composition it was possible to obtain polyurethane networks that after deformation almost immediately recovered their original structure upon immersion in water at 70 °C. Furthermore, initial cytotoxicity tests indicated that the shape-memory polymer possesses good biocompatibility.

In addition to the utilisation of CO₂-based polycarbonates in tissue engineering, research has also been devoted to the exploration of these polymers in pharmaceutical applications such as drug delivery^{440,441} and tumour imaging.⁴¹⁵ A poly(carbonate-ester) synthesised via terpolymerisation of CO₂, 1,2-butylene oxide and ϵ -caprolactone was examined as carrier for the antibiotic drug pazufloxacin mesilate.⁴⁴⁰ The drug release rate could be tuned by varying the carbonate/ester ratio: both faster hydrolytic degradation as well as higher drug release rates were

observed for poly(carbonate-ester)s with higher ϵ -caprolactone content. Similar trends in drug release behaviour were observed for poly(carbonate-ester)s synthesised from CO₂, propylene oxide and ϵ -caprolactone carrying the insecticide imidacloprid.⁴⁴¹ This can be ascribed to the higher hydrolytic degradation rate of the ester blocks compared to the carbonate blocks. In recent work, an amphiphilic polycarbonate based on the triblock copolymer poly(allyl glycidyl ether carbonate)-poly(propylene carbonate)-poly(allyl glycidyl ether carbonate) was functionalised and labelled with gadolinium as MRI contrast agent.⁴¹⁵ The resulting polymer micelles were evaluated for utilisation in tumour imaging. While *in vitro* investigations indicated that the polycarbonate/gadolinium micelles degraded into non-toxic products, *in vivo* experiments showed that the polymer micelles were cleared from the body within 72 h without any evidence of toxicity. Furthermore, the polycarbonate-based contrast agent showed superior MRI imaging capability compared to a commercial gadolinium contrast agent.

For the sake of completeness, it should be noted that not all polycarbonates that can be potentially employed in biomedical applications are synthesised via polymerisation of CO₂ and epoxides, as aliphatic polymeric carbonates can also be produced via ring-opening polymerisation of six-membered cyclic carbonates.^{442–445} Via this method several functional groups that are useful in biomedical applications can be incorporated in the polycarbonates,^{442–446} with potential applications including drug and gene delivery^{447–449} and antibacterial/antifouling coatings for medical devices.⁴⁵⁰ These six-membered cyclic carbonates can still be derived from CO₂ via two pathways: (1) synthesis of a five-membered cyclic carbonate through the reaction between CO₂ and an epoxide, followed by transcarbonation with a 1,3-diol (see section 1.3.1). However, this route requires multiple reaction steps and will be hampered by the possible presence of other protic functionalities in the diol compound (*i.e.* hydroxyl or amino groups); (2) direct reaction of CO₂ with an oxetane to form a six-membered cyclic carbonate, which is typically more difficult due to the lower accessibility and reactivity of oxetanes compared to epoxides.⁴²

1.3.7. Other applications of CO₂-based polycarbonates

In addition to the application of CO₂-based polymeric carbonates in the major fields discussed in sections 1.3.4–1.3.6 (*i.e.* polymer products, battery applications and biomedical applications), these polycarbonates also find use in other applications. While some of these are yet of mere academic interest, others have already reached commercial status. Examples of the latter include the use of poly(propylene carbonate) and poly(cyclohexene carbonate) as sacrificial binder material in the production of ceramics and adhesives,^{15,242,451} owing to the clean and controllable

thermal decomposition of these polycarbonates at temperatures below 300 °C. In recent years, Novomer investigated the end-chain modification of poly(propylene carbonate) and poly(ethylene carbonate) to incorporate functional groups and the use of these polycarbonates in block-copolymers with hydrophilic polymers.^{274,362,452} The obtained polymers were studied as drop-in alternatives to conventional polymers such as polypropylene and polystyrene.¹⁷ Another application for which poly(propylene carbonate) is considered of commercial interest is as packaging material, especially when the poly(propylene carbonate) chains have low ether linkage content and high head-to-tail ratio, which results in improved processability.⁴⁵³ Packaging material for food and medical devices is of particular interest, as it was observed that the mechanical properties (*i.e.* tensile modulus, ultimate strength and tear resistance) of poly(propylene carbonate) are comparable yet slightly better than those of low-density polyethylene, whereas the permeability to oxygen and water is remarkably lower.^{267,454} The excellent barrier properties for oxygen and water also creates potential for poly(propylene carbonate)s to be used as barrier adhesive in oxygen- and water-resistant materials.^{255,455} In contrast, poly(limonene carbonate) possesses very high gas permeability, which, combined with its relatively good mechanical properties, transparency and thermal insulation properties, renders it potentially suitable for application as “breathing glass” in energy-efficient buildings or in greenhouses, providing passive ventilation through these windows and thereby eliminating the need for additional ventilation systems.⁴⁵⁶

1.4. Concluding remarks and perspectives

The synthesis of cyclic and polymeric carbonates via the reaction of CO₂ with epoxides is a thriving pathway for the fixation of CO₂ into valuable products, both from an academic as well as an industrial point of view. In the last decades, numerous homogeneous and heterogeneous catalytic systems (or combinations of the two) have been developed for this reaction, thus enabling the reaction of carbon dioxide with a wide array of epoxides, with high yields and selectivities towards either the cyclic carbonate or the polycarbonate products. Future advancements within CO₂/epoxide catalysis will probably bring forth novel systems in the relatively new field of metal-free organocatalysis, as well as catalytic systems that are able to convert typically challenging substrates such as bio-based epoxides and functional epoxides. Both these advancements would further increase the green character of this reaction. In the perspective of commercial application, another challenge will be to develop robust and reusable catalysts that are able to perform under the often

less-than-ideal conditions of industrial process (*e.g.* impurities in the CO₂ feed), while still maintaining high activity and selectivity. Another challenge related to catalyst design will lie in developing multifunctional catalytic systems that are able to promote both the reaction between CO₂ and epoxides and the prior epoxidation of the corresponding alkene with high activity and selectivity, in order to allow the one-pot synthesis of cyclic and polymeric carbonates from alkenes. This combined pathway would be advantageous from a green chemistry point of view since it would allow to avoid handling of toxic epoxides and would result in improved process efficiency.

The products of the reaction between CO₂ and epoxides, *i.e.* cyclic carbonates and polycarbonates, have been extensively studied with regard to their potential applications. One of the earliest and possibly largest applications of cyclic carbonates (mainly ethylene carbonate and propylene carbonate) is as electrolyte components in lithium-ion batteries, which was already commercialised almost three decades ago. On the other hand, the use of CO₂-based polycarbonates in solid polymer electrolytes is still limited by unsatisfactory ionic conductivities and insufficient lithium transference numbers at ambient temperatures. The incorporation of additives such as inorganic fillers or ionic liquids may enhance these properties, though the influence of such additives still needs to be rationalised and controlled. Gel polymer electrolytes incorporating polycarbonates already possess electrochemical and mechanical properties that are suitable for practical application in lithium-ion batteries, but safety concerns related to the presence of flammable solvents still need to be tackled.

Another example of industrial application of cyclic carbonates is the Asahi Kasei process to produce bisphenol-A-based polycarbonates from ethylene carbonate as starting material,²²⁷ which received numerous rewards due to its several assets from the point of view of green chemistry. The industrial application of this process has been expanding in recent years, being estimated to soon reach an annual worldwide production capacity of 1 million tonnes of non-phosgene bisphenol-A-based polycarbonate. Also CO₂-based polycarbonates have found industrial application in the field of polymer products, namely with their use as polyols in polyurethane production, which has been commercialised by Covestro with an annual capacity of 5000 tonnes of CO₂-based polycarbonate polyols.³⁴⁰ The tuneable thermal, chemical, mechanical and biodegradable properties of CO₂-based polycarbonates offer many opportunities for developing sustainable functional materials with potential in biomedical and pharmaceutical applications. However, on the road to commercialisation there is a need for more comprehensive, systematic studies in

which both the functional properties of the employed polycarbonate systems (*e.g.* mechanical strength) and their biocompatibility and biodegradability are fully assessed.

When considering the current commercialised applications of CO₂-based cyclic and polymeric carbonates, it can be seen that the epoxide starting materials employed in most cases (*i.e.* ethylene oxide and propylene oxide) are currently produced from fossil feedstock. A crucial future challenge will lie in replacing these petroleum-based epoxides with bio-based substitutes, while still maintaining the characteristics of the carbonate products that makes them suitable for their specific applications, *e.g.*, high ionic conductivity in the case of cyclic or polymeric carbonates as components of battery electrolytes, appropriate thermal and mechanical properties in the case of polycarbonates in polymer products such as polyurethane foams, and proper biocompatibility in the case of polycarbonates as tissue scaffolds in biomedical applications. In order to attain these properties, various strategies discussed in this review can be followed, including reaction during or after formation of the carbonate products with other compounds (*e.g.* transcarbonation reactions of cyclic carbonates or block-copolymerisation of polycarbonates with other polymers), blending of the carbonate products with other materials and modification to introduce functional groups. The extent to which petroleum-based epoxides can be substituted by bio-based alternatives will also depend on the availability of the latter and, hence, the costs associated with the production of these compounds. In addition, although CO₂-based polycarbonates are typically biodegradable, recycling of these materials is preferred from a circular economy point of view. In general, a life-cycle analysis using a cradle-to-grave approach (or even better a cradle-to-cradle approach) that takes into account the nature of the raw materials, how these are produced, how they are converted and whether the final products can be recycled will be essential to evaluate the potential commercialisation of new products based on CO₂-based cyclic and polymeric carbonates. Although the path towards the substitution of fossil-based chemical products with renewable alternatives is still difficult and uncertain, this review highlighted the potential of CO₂-based cyclic and polymeric carbonates to contribute to this crucial target for our planet.

1.5. Thesis outline

This thesis offers an insight in the field of organic carbonate synthesis through the reaction of CO₂ with epoxides. *Chapter 1* has supplied an extensive review of recent literature on this pathway for CO₂-utilisation. First, various types of homogenous and heterogeneous catalytic systems for the reaction of CO₂ with epoxides are discussed. Hereafter, the chemical and physical properties of the two classes of carbonate products, cyclic and polymeric, are elaborated on. The last part of the chapter focusses on the most relevant applications of the cyclic and polymeric carbonate products in the fields of polymer products, energy storage devices, and biomedical and pharmaceutical applications.

In *Chapter 2* the application of four amino-tris(phenolate)-based metal complexes containing Ti(IV) or Zr(IV) centres as homogeneous catalysts for the conversion of CO₂ and epoxides into cyclic carbonates is discussed. These group (IV) metal complexes are combined with a tetrabutylammonium halide to generate a binary catalytic system active in the CO₂/epoxide conversion reaction. Both the optimisation of catalyst type and amount and the exploration of a broad substrate scope are elaborated on.

The utilisation of anionic mono(formazanate) iron(II) complexes bearing labile halide ligands as single-component catalysts for the reaction of CO₂ with epoxides is reported in *Chapter 3*. The influence of the halide ligand and of the electronic properties of the formazanate ligand backbone on the catalytic activity is discussed. Furthermore, several terminal and internal epoxide are researched as substrates for the reaction with carbon dioxide to form cyclic carbonate products.

In *Chapter 4* the synthesis of a bio-based polycarbonate, poly(vinylcyclohexene carbonate) (PVCHC), prepared through the copolymerisation reaction of CO₂ with 4-vinylcyclohexene oxide is described. Furthermore, this CO₂-based polycarbonate is further modified by converting the polymeric pendant vinyl moieties through atom-efficient thiol-ene click chemistry. Various modifications are elaborated on, including the introduction of pendant alkyl, hydroxyl, carboxyl, amino or aromatic groups into the polycarbonate backbone.

Chapter 5 evaluates the potential of a CO₂-based polycarbonate containing carboxylic acid pendant group, PVCHC-COOH, for biomedical and pharmaceutical applications. The pH-responsive water solubility of PVCHC-COOH and the degradation rates and products of the hydrolytic degradation of PVCHC-COOH are

discussed. Furthermore, the *in vitro* cytotoxicity of both PVCHC-COOH and of its degradation products is investigated.

References

- 1 P. Anastas and N. Eghbali, *Chemical Society Reviews*, 2010, **39**, 301–312.
- 2 D. J. Darensbourg, *Chemical Reviews*, 2007, **107**, 2388–2410.
- 3 Q. Liu, L. Wu, R. Jackstell and M. Beller, *Nature Communications*, 2015, **6**, 5933.
- 4 M. R. Kember, A. Buchard and C. K. Williams, *Chemical Communications*, 2011, **47**, 141–163.
- 5 S. Klaus, M. W. Lehenmeier, C. E. Anderson and B. Rieger, *Coordination Chemistry Reviews*, 2011, **255**, 1460–1479.
- 6 S. Solomon, Ed., *Climate change 2007: the physical science basis: contribution of Working Group I to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, 2007.
- 7 IEA, *CO₂ emissions from fuel combustion 2016*, OECD Publishing, Paris, 2016.
- 8 B. Diczfalusy and M. Wråke, *Energy Technology Perspectives 2012: Pathways to a Clean Energy System*, Organisation for Economic Cooperation and Development (OECD), International Energy Agency (IEA), Paris, 2012.
- 9 D. Y. C. Leung, G. Caramanna and M. M. Maroto-Valer, *Renewable and Sustainable Energy Reviews*, 2014, **39**, 426–443.
- 10 S. Anderson and R. Newell, *Annual Review of Environment and Resources*, 2004, **29**, 109–142.
- 11 J. G. J. Olivier, G. Janssens-Maenhout, M. Muntean and J. A. H. W. Peters, *Trends in global CO₂ emissions: 2016 report*, The Hague: PBL Netherlands Environmental Assessment Agency, Ispra: European Commission, Joint Research Centre, 2016.
- 12 M. Peters, B. Köhler, W. Kuckshinrichs, W. Leitner, P. Markewitz and T. E. Müller, *ChemSusChem*, 2011, **4**, 1216–1240.
- 13 R. Martín and A. W. Kleij, *ChemSusChem*, 2011, **4**, 1259–1263.
- 14 P. P. Pescarmona and M. Taherimehr, *Catalysis Science & Technology*, 2012, **2**, 2169.
- 15 G. W. Coates and D. R. Moore, *Angewandte Chemie International Edition*, 2004, **43**, 6618–6639.
- 16 M. North, R. Pasquale and C. Young, *Green Chemistry*, 2010, **12**, 1514.
- 17 M. Taherimehr and P. P. Pescarmona, *Journal of Applied Polymer Science*, 2014, **131**, 41141.
- 18 C. J. Whiteoak, N. Kielland, V. Laserna, F. Castro-Gómez, E. Martin, E. C. Escudero-Adán, C. Bo and A. W. Kleij, *Chemistry A European Journal*, 2014, **20**, 2264–2275.
- 19 M. Taherimehr, S. M. Al-Amsyar, C. J. Whiteoak, A. W. Kleij and P. P. Pescarmona, *Green Chemistry*, 2013, **15**, 3083.
- 20 W. C. Chueh, C. Falter, M. Abbott, D. Scipio, P. Furler, S. M. Haile and A. Steinfeld, *Science*, 2010, **330**, 1797–1801.
- 21 D. T. Whipple and P. J. A. Kenis, *The Journal of Physical Chemistry Letters*, 2010, **1**, 3451–3458.
- 22 B. Kumar, M. Llorente, J. Froehlich, T. Dang, A. Sathrum and C. P. Kubiak, *Annual review of physical chemistry*, 2012, **63**, 541–569.
- 23 K. M. K. Yu, I. Curcic, J. Gabriel and S. C. E. Tsang, *ChemSusChem*, 2008, **1**, 893–899.
- 24 C. Maeda, Y. Miyazaki and T. Ema, *Catalysis Science & Technology*, 2014, **4**, 1482.
- 25 C. Schild, A. Wokaun, R. A. Koepfel and A. Baiker, *The Journal of Physical Chemistry*, 1991, **95**, 6341–6346.

- 26 G. Garbarino, P. Riani, L. Magistri and G. Busca, *International Journal of Hydrogen Energy*, 2014, **39**, 11557–11565.
- 27 W. Wang, S. Wang, X. Ma and J. Gong, *Chemical Society Reviews*, 2011, **40**, 3703–3727.
- 28 W.-H. Chen, M.-R. Lin, J.-J. Lu, Y. Chao and T.-S. Leu, *International Journal of Hydrogen Energy*, 2010, **35**, 11787–11797.
- 29 T. L. LeValley, A. R. Richard and M. Fan, *International Journal of Hydrogen Energy*, 2014, **39**, 16983–17000.
- 30 M. Ni, M. K. H. Leung, D. Y. C. Leung and K. Sumathy, *Renewable and Sustainable Energy Reviews*, 2007, **11**, 401–425.
- 31 J. D. Holladay, J. Hu, D. L. King and Y. Wang, *Catalysis Today*, 2009, **139**, 244–260.
- 32 S. Nahar, M. Zain, A. Kadhum, H. Hasan and Md. Hasan, *Materials*, 2017, **10**, 629.
- 33 J. Qiao, Y. Liu, F. Hong and J. Zhang, *Chemical Society Reviews*, 2014, **43**, 631–675.
- 34 T. Sakakura, J.-C. Choi and H. Yasuda, *Chem. Rev.*, 2007, **107**, 2365–2387.
- 35 M. Aresta, A. Dibenedetto and A. Angelini, *Chemical Reviews*, 2014, **114**, 1709–1742.
- 36 J. R. Ochoa-Gómez, O. Gómez-Jiménez-Aberasturi, B. Maestro-Madurga, A. Pesquera-Rodríguez, C. Ramírez-López, L. Lorenzo-Ibarreta, J. Torrecilla-Soria and M. C. Villarán-Velasco, *Applied Catalysis A: General*, 2009, **366**, 315–324.
- 37 S. Inoue, H. Koinuma and T. Tsuruta, *Journal of Polymer Science Part C: Polymer Letters*, 1969, **7**, 287–292.
- 38 R. van Eldik and M. Aresta, *CO₂ Chemistry*, Elsevier Science, Waltham, 2014.
- 39 D. R. Moore, M. Cheng, E. B. Lobkovsky and G. W. Coates, *Journal of the American Chemical Society*, 2003, **125**, 11911–11924.
- 40 M. North and R. Pasquale, *Angewandte Chemie*, 2009, **121**, 2990–2992.
- 41 D. J. Darensbourg and M. W. Holtcamp, *Coordination Chemistry Reviews*, 1996, **153**, 155–174.
- 42 G. Fiorani, W. Guo and A. W. Kleij, *Green Chemistry*, 2015, **17**, 1375–1389.
- 43 C. Martín, G. Fiorani and A. W. Kleij, *ACS Catalysis*, 2015, **5**, 1353–1370.
- 44 D.-H. Lan, N. Fan, Y. Wang, X. Gao, P. Zhang, L. Chen, C.-T. Au and S.-F. Yin, *Chinese Journal of Catalysis*, 2016, **37**, 826–845.
- 45 J. W. Comerford, I. D. V. Ingram, M. North and X. Wu, *Green Chemistry*, 2015, **17**, 1966–1987.
- 46 Q. He, J. W. O'Brien, K. A. Kitselman, L. E. Tompkins, G. C. T. Curtis and F. M. Kerton, *Catalysis Science & Technology*, 2014, **4**, 1513–1528.
- 47 A. Decortes, A. M. Castilla and A. W. Kleij, *Angewandte Chemie International Edition*, 2010, **49**, 9822–9837.
- 48 M. Cokoja, M. E. Wilhelm, M. H. Anthofer, W. A. Herrmann and F. E. Kühn, *ChemSusChem*, 2015, **8**, 2436–2454.
- 49 V. B. Saptal and B. M. Bhanage, *Current Opinion in Green and Sustainable Chemistry*, 2017, **3**, 1–10.
- 50 R. R. Shaikh, S. Pornpraprom and V. D'Elia, *ACS Catalysis*, 2018, **8**, 419–450.
- 51 S. Paul, Y. Zhu, C. Romain, R. Brooks, P. K. Saini and C. K. Williams, *Chemical Communications*, 2015, **51**, 6459–6479.
- 52 C. Romain, A. Thevenon, P. K. Saini and C. K. Williams, in *Carbon Dioxide and Organometallics*, ed. X.-B. Lu, Springer International Publishing, Cham, 2015, vol. 53, pp. 101–141.
- 53 G. Trott, P. K. Saini and C. K. Williams, *Philosophical Transactions of the Royal Society A: Mathematical, Physical and Engineering Sciences*, 2016, **374**, 20150085.
- 54 H. Sugimoto and S. Inoue, *Journal of Polymer Science Part A: Polymer Chemistry*, 2004, **42**, 5561–5573.
- 55 S. J. Poland and D. J. Darensbourg, *Green Chemistry*, 2017, **19**, 4990–5011.

- 56 B.-H. Xu, J.-Q. Wang, J. Sun, Y. Huang, J.-P. Zhang, X.-P. Zhang and S.-J. Zhang, *Green Chemistry*, 2015, **17**, 108–122.
- 57 H.-Y. Ju, M.-D. Manju, K.-H. Kim, S.-W. Park and D.-W. Park, *Journal of Industrial and Engineering Chemistry*, 2008, **14**, 157–160.
- 58 V. Caló, A. Nacci, A. Monopoli and A. Fanizzi, *Organic Letters*, 2002, **4**, 2561–2563.
- 59 C. A. Montoya, A. B. Paninho, P. M. Felix, M. E. Zakrzewska, J. Vital, V. Najdanovic-Visak and A. V. M. Nunes, *The Journal of Supercritical Fluids*, 2015, **100**, 155–159.
- 60 P. Mazo and L. Rios, *Journal of the American Oil Chemists' Society*, 2013, **90**, 725–730.
- 61 L. A. Bivona, O. Fichera, L. Fusaro, F. Giacalone, M. Buaki-Sogo, M. Gruttadauria and C. Aprile, *Catalysis Science*, 2015, **5**, 5000–5007.
- 62 W. N. Sit, S. M. Ng, K. Y. Kwong and C. P. Lau, *The Journal of Organic Chemistry*, 2005, **70**, 8583–8586.
- 63 R. A. Shiels and C. W. Jones, *Journal of Molecular Catalysis A: Chemical*, 2007, **261**, 160–166.
- 64 K. R. Roshan, R. A. Palissery, A. C. Kathalikkattil, R. Babu, G. Mathai, H.-S. Lee and D.-W. Park, *Catalysis Science & Technology*, 2016, **6**, 3997–4004.
- 65 C. J. Whiteoak, A. Nova, F. Maseras and A. W. Kleij, *ChemSusChem*, 2012, **5**, 2032–2038.
- 66 A. Buonerba, A. De Nisi, A. Grassi, S. Milione, C. Capacchione, S. Vagin and B. Rieger, *Catalysis Science & Technology*, 2015, **5**, 118–123.
- 67 C. J. Whiteoak, E. Martin, M. M. Belmonte, J. Benet-Buchholz and A. W. Kleij, *Advanced Synthesis & Catalysis*, 2012, **354**, 469–476.
- 68 T. Aida and S. Inoue, *Journal of the American Chemical Society*, 1983, **105**, 1304–1309.
- 69 T. Aida, M. Ishikawa and S. Inoue, *Macromolecules*, 1986, **19**, 8–13.
- 70 W. J. Kruper and D. D. Dellar, *The Journal of Organic Chemistry*, 1995, **60**, 725–727.
- 71 S. Mang, A. I. Cooper, M. E. Colclough, N. Chauhan and A. B. Holmes, *Macromolecules*, 2000, **33**, 303–308.
- 72 R. L. Paddock, Y. Hiyama, J. M. McKay and S. T. Nguyen, *Tetrahedron Letters*, 2004, **45**, 2023–2026.
- 73 H. Sugimoto and K. Kuroda, *Macromolecules*, 2008, **41**, 312–317.
- 74 T. Ema, Y. Miyazaki, S. Koyama, Y. Yano and T. Sakai, *Chemical Communications*, 2012, **48**, 4489.
- 75 T. Ema, Y. Miyazaki, J. Shimonishi, C. Maeda and J. Hasegawa, *Journal of the American Chemical Society*, 2014, **136**, 15270–15279.
- 76 R. L. Paddock and S. T. Nguyen, *Journal of the American Chemical Society*, 2001, **123**, 11498–11499.
- 77 D. J. Darensbourg and J. C. Yarbrough, *Journal of the American Chemical Society*, 2002, **124**, 6335–6342.
- 78 X.-B. Lu, R. He and C.-X. Bai, *Journal of Molecular Catalysis A: Chemical*, 2002, **186**, 1–11.
- 79 Z. Qin, C. M. Thomas, S. Lee and G. W. Coates, *Angewandte Chemie International Edition*, 2003, **42**, 5484–5487.
- 80 R. L. Paddock and S. T. Nguyen, *Chemical Communications*, 2004, 1622.
- 81 A. Decortes, M. Martínez Belmonte, J. Benet-Buchholz and A. W. Kleij, *Chemical Communications*, 2010, **46**, 4580.
- 82 W. Xia, K. A. Salmeia, S. I. Vagin and B. Rieger, *Chemistry European Journal*, 2015, **21**, 4384–4390.
- 83 M. Cheng, E. B. Lobkovsky and G. W. Coates, *Journal of the American Chemical Society*, 1998, **120**, 11018–11019.
- 84 M. Cheng, D. R. Moore, J. J. Reczek, B. M. Chamberlain, E. B. Lobkovsky and G. W. Coates, *Journal of the American Chemical Society*, 2001, **123**, 8738–8749.

- 85 D. R. Moore, M. Cheng, E. B. Lobkovsky and G. W. Coates, *Angewandte Chemie International Edition*, 2002, **41**, 2599–2602.
- 86 J. G. Kim, C. D. Cowman, A. M. LaPointe, U. Wiesner and G. W. Coates, *Macromolecules*, 2011, **44**, 1110–1113.
- 87 C. M. Byrne, S. D. Allen, E. B. Lobkovsky and G. W. Coates, *Journal of the American Chemical Society*, 2004, **126**, 11404–11405.
- 88 M. R. Kember, P. D. Knight, P. T. R. Reung and C. K. Williams, *Angewandte Chemie International Edition*, 2009, **48**, 931–933.
- 89 F. Jutz, A. Buchard, M. R. Kember, S. B. Fredriksen and C. K. Williams, *Journal of the American Chemical Society*, 2011, **133**, 17395–17405.
- 90 A. Buchard, M. R. Kember, K. G. Sandeman and C. K. Williams, *Chemical Communications*, 2011, **47**, 212–214.
- 91 M. R. Kember and C. K. Williams, *Journal of the American Chemical Society*, 2012, **134**, 15676–15679.
- 92 C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin and A. W. Kleij, *Journal of the American Chemical Society*, 2013, **135**, 1228–1231.
- 93 J. González-Fabra, F. Castro-Gómez, A. W. Kleij and C. Bo, *ChemSusChem*, 2017, **10**, 1233–1240.
- 94 L. Peña Carrodeguas, J. González-Fabra, F. Castro-Gómez, C. Bo and A. W. Kleij, *Chemistry A European Journal*, 2015, **21**, 6115–6122.
- 95 K. S. Smith and H. L. Huyck, *The environmental geochemistry of mineral deposits*, 1999, **6**, 29–70.
- 96 H. Büttner, K. Lau, A. Spannenberg and T. Werner, *ChemCatChem*, 2015, **7**, 459–467.
- 97 C. Carvalho Rocha, T. Onfroy, J. Pilmé, A. Denicourt-Nowicki, A. Roucoux and F. Launay, *Journal of Catalysis*, 2016, **333**, 29–39.
- 98 A. J. R. Amaral, J. F. J. Coelho and A. C. Serra, *Tetrahedron Letters*, 2013, **54**, 5518–5522.
- 99 K. R. Roshan, T. Jose, D. Kim, K. A. Cherian and D. W. Park, *Catalysis Science & Technology*, 2014, **4**, 963–970.
- 100 H. Büttner, J. Steinbauer and T. Werner, *ChemSusChem*, 2015, **8**, 2655–2669.
- 101 T. Werner and H. Büttner, *ChemSusChem*, 2014, **7**, 3268–3271.
- 102 J. Sun, S. Zhang, W. Cheng and J. Ren, *Tetrahedron Letters*, 2008, **49**, 3588–3591.
- 103 M. H. Anthofer, M. E. Wilhelm, M. Cokoja, M. Drees, W. A. Herrmann and F. E. Kühn, *ChemCatChem*, 2015, **7**, 94–98.
- 104 M. Liu, L. Liang, X. Li, X. Gao and J. Sun, *Green Chemistry*, 2016, **18**, 2851–2863.
- 105 Z. Zhang, F. Fan, H. Xing, Q. Yang, Z. Bao and Q. Ren, *ACS Sustainable Chemistry & Engineering*, 2017, **5**, 2841–2846.
- 106 J. Ma, J. Liu, Z. Zhang and B. Han, *Green Chemistry*, 2012, **14**, 2410–2420.
- 107 M. Alves, B. Grignard, S. Gennen, R. Méreau, C. Detrembleur, C. Jerome and T. Tassaing, *Catalysis Science & Technology*, 2015, **5**, 4636–4643.
- 108 S. Sopeña, G. Fiorani, C. Martín and A. W. Kleij, *ChemSusChem*, 2015, **8**, 3248–3254.
- 109 J. Sun, J. Ren, S. Zhang and W. Cheng, *Tetrahedron Letters*, 2009, **50**, 423–426.
- 110 Y.-M. Shen, W.-L. Duan and M. Shi, *Advanced Synthesis & Catalysis*, 2003, **345**, 337–340.
- 111 J.-Q. Wang, J. Sun, W.-G. Cheng, K. Dong, X.-P. Zhang and S.-J. Zhang, *Physical Chemistry Chemical Physics*, 2012, **14**, 11021.
- 112 A. M. Hardman-Baldwin and A. E. Mattson, *ChemSusChem*, 2014, **7**, 3275–3278.
- 113 S. Gennen, M. Alves, R. Méreau, T. Tassaing, B. Gilbert, C. Detrembleur, C. Jerome and B. Grignard, *ChemSusChem*, 2015, **8**, 1845–1849.
- 114 M. Alves, R. Méreau, B. Grignard, C. Detrembleur, C. Jerome and T. Tassaing, *RSC Advances*, 2016, **6**, 36327–36335.
- 115 J. Wang and Y. Zhang, *ACS Catalysis*, 2016, **6**, 4871–4876.

- 116 X.-F. Liu, Q.-W. Song, S. Zhang and L.-N. He, *Catalysis Today*, 2016, **263**, 69–74.
- 117 N. Aoyagi, Y. Furusho and T. Endo, *Tetrahedron Letters*, 2013, **54**, 7031–7034.
- 118 L. Martínez-Rodríguez, J. Otalora Garmilla and A. W. Kleij, *ChemSusChem*, 2016, **9**, 749–755.
- 119 D. Zhang, S. K. Boopathi, N. Hadjichristidis, Y. Gnanou and X. Feng, *J. Am. Chem. Soc.*, 2016, **138**, 11117–11120.
- 120 P. Agrigento, S. M. Al-Amsyar, B. Sorée, M. Taherimehr, M. Gruttadauria, C. Aprile and P. P. Pescarmona, *Catalysis Science & Technology*, 2014, **4**, 1598–1607.
- 121 Y. Xie, Z. Zhang, T. Jiang, J. He, B. Han, T. Wu and K. Ding, *Angewandte Chemie*, 2007, **119**, 7393–7396.
- 122 C. Aprile, F. Giacalone, P. Agrigento, L. F. Liotta, J. A. Martens, P. P. Pescarmona and M. Gruttadauria, *ChemSusChem*, 2011, **4**, 1830–1837.
- 123 J.-Q. Wang, X.-D. Yue, F. Cai and L.-N. He, *Catalysis Communications*, 2007, **8**, 167–172.
- 124 L. Han, S.-W. Park and D.-W. Park, *Energy & Environmental Science*, 2009, **2**, 1286.
- 125 W. Cheng, X. Chen, J. Sun, J. Wang and S. Zhang, *Catalysis Today*, 2013, **200**, 117–124.
- 126 S. Udayakumar, M. Lee, H. Shim, S. Park and D. Park, *Catalysis Communications*, 2009, **10**, 659–664.
- 127 C. Calabrese, L. F. Liotta, E. Carbonell, F. Giacalone, M. Gruttadauria and C. Aprile, *ChemSusChem*, 2017, **10**, 1202–1209.
- 128 S. Ghazali-Esfahani, H. Song, E. Păunescu, F. D. Bobbink, H. Liu, Z. Fei, G. Laurenczy, M. Bagherzadeh, N. Yan and P. J. Dyson, *Green Chemistry*, 2013, **15**, 1584.
- 129 Y. Du, F. Cai, D.-L. Kong and L.-N. He, *Green Chemistry*, 2005, **7**, 518.
- 130 J.-Q. Wang, D.-L. Kong, J.-Y. Chen, F. Cai and L.-N. He, *Journal of Molecular Catalysis A: Chemical*, 2006, **249**, 143–148.
- 131 Q. Zhang, S. Zhang and S. Li, *Macromolecules*, 2012, **45**, 2981–2988.
- 132 K. M. K. Yu, I. Curcic, J. Gabriel, H. Morganstewart and S. C. Tsang, *The Journal of Physical Chemistry A*, 2010, **114**, 3863–3872.
- 133 S. R. Jagtap, V. P. Raje, S. D. Samant and B. M. Bhanage, *Journal of Molecular Catalysis A: Chemical*, 2007, **266**, 69–74.
- 134 A. Barbarini, R. Maggi, A. Mazzacani, G. Mori, G. Sartori and R. Sartorio, *Tetrahedron Letters*, 2003, **44**, 2931–2934.
- 135 J. Song, Z. Zhang, S. Hu, T. Wu, T. Jiang and B. Han, *Green Chemistry*, 2009, **11**, 1031.
- 136 W.-Y. Gao, Y. Chen, Y. Niu, K. Williams, L. Cash, P. J. Perez, L. Wojtas, J. Cai, Y.-S. Chen and S. Ma, *Angewandte Chemie International Edition*, 2014, **53**, 2615–2619.
- 137 M. North, P. Villuendas and C. Young, *Chemistry A European Journal*, 2009, **15**, 11454–11457.
- 138 M. Liu, B. Liu, L. Liang, F. Wang, L. Shi and J. Sun, *Journal of Molecular Catalysis A: Chemical*, 2016, **418–419**, 78–85.
- 139 J. Meléndez, M. North and P. Villuendas, *Chemical Communications*, 2009, 2577.
- 140 H. He, J. A. Perman, G. Zhu and S. Ma, *Small*, 2016, **12**, 6309–6324.
- 141 M. H. Beyzavi, C. J. Stephenson, Y. Liu, O. Karagiari, J. T. Hupp and O. K. Farha, *Frontiers in Energy Research*, 2015, **2**, 63.
- 142 M. Taherimehr, B. Van de Voorde, L. H. Wee, J. A. Martens, D. E. De Vos and P. P. Pescarmona, *ChemSusChem*, 2017, **10**, 1283–1291.
- 143 O. V. Zalomaeva, A. M. Chibiryayev, K. A. Kovalenko, O. A. Kholdeeva, B. S. Balzhinimaev and V. P. Fedin, *Journal of Catalysis*, 2013, **298**, 179–185.
- 144 R. Babu, A. C. Kathalikkattil, R. Roshan, J. Tharun, D.-W. Kim and D.-W. Park, *Green Chemistry*, 2016, **18**, 232–242.
- 145 L. Liu, S.-M. Wang, Z.-B. Han, M. Ding, D.-Q. Yuan and H.-L. Jiang, *Inorganic chemistry*, 2016, **55**, 3558–3565.

- 146 Z.-R. Jiang, H. Wang, Y. Hu, J. Lu and H.-L. Jiang, *ChemSusChem*, 2015, **8**, 878–885.
- 147 V. Guillerme, Ł. J. Weseliński, Y. Belmabkhout, A. J. Cairns, V. D'Elia, Ł. Wojtas, K. Adil and M. Eddaoudi, *Nature Chemistry*, 2014, **6**, 673–680.
- 148 D. Feng, W.-C. Chung, Z. Wei, Z.-Y. Gu, H.-L. Jiang, Y.-P. Chen, D. J. Darensbourg and H.-C. Zhou, *Journal of the American Chemical Society*, 2013, **135**, 17105–17110.
- 149 C. M. Miralda, E. E. Macias, M. Zhu, P. Ratnasamy and M. A. Carreon, *ACS Catalysis*, 2012, **2**, 180–183.
- 150 B. Mousavi, S. Chaemchuen, B. Moosavi, Z. Luo, N. Gholampour and F. Verpoort, *New Journal of Chemistry*, 2016, **40**, 5170–5176.
- 151 L. Yang, L. Yu, G. Diao, M. Sun, G. Cheng and S. Chen, *Journal of Molecular Catalysis A: Chemical*, 2014, **392**, 278–283.
- 152 J. Tharun, G. Mathai, A. C. Kathalikkattil, R. Roshan, Y.-S. Won, S. J. Cho, J.-S. Chang and D.-W. Park, *ChemPlusChem*, 2015, **80**, 715–721.
- 153 H.-Y. Cho, D.-A. Yang, J. Kim, S.-Y. Jeong and W.-S. Ahn, *Catalysis Today*, 2012, **185**, 35–40.
- 154 J. Tharun, K.-M. Bhin, R. Roshan, D. W. Kim, A. C. Kathalikkattil, R. Babu, H. Y. Ahn, Y. S. Won and D.-W. Park, *Green Chemistry*, 2016, **18**, 2479–2487.
- 155 T. Jose, Y. Hwang, D.-W. Kim, M.-I. Kim and D.-W. Park, *Catalysis Today*, 2015, **245**, 61–67.
- 156 X. Zhou, Y. Zhang, X. Yang, L. Zhao and G. Wang, *Journal of Molecular Catalysis A: Chemical*, 2012, **361–362**, 12–16.
- 157 D. Ma, B. Li, K. Liu, X. Zhang, W. Zou, Y. Yang, G. Li, Z. Shi and S. Feng, *Journal of Materials Chemistry A*, 2015, **3**, 23136–23142.
- 158 A. C. Kathalikkattil, R. Babu, J. Tharun, R. Roshan and D.-W. Park, *Catalysis Surveys from Asia*, 2015, **19**, 223–235.
- 159 W.-Y. Gao, C.-Y. Tsai, L. Wojtas, T. Thiounn, C.-C. Lin and S. Ma, *Inorganic Chemistry*, 2016, **55**, 7291–7294.
- 160 P.-Z. Li, X.-J. Wang, J. Liu, J. S. Lim, R. Zou and Y. Zhao, *Journal of the American Chemical Society*, 2016, **138**, 2142–2145.
- 161 W. Wang, Y. Wang, C. Li, L. Yan, M. Jiang and Y. Ding, *ACS Sustainable Chemistry & Engineering*, 2017, **5**, 4523–4528.
- 162 Y. Chen, R. Luo, Q. Xu, J. Jiang, X. Zhou and H. Ji, *ChemSusChem*, 2017, **10**, 2534–2541.
- 163 C. Li, W. Wang, L. Yan, Y. Wang, M. Jiang and Y. Ding, *Journal of Materials Chemistry A*, 2016, **4**, 16017–16027.
- 164 H. Li, C. Li, J. Chen, L. Liu and Q. Yang, *Chemistry An Asian Journal*, 2017, **12**, 1095–1103.
- 165 Z. Dai, Q. Sun, X. Liu, C. Bian, Q. Wu, S. Pan, L. Wang, X. Meng, F. Deng and F.-S. Xiao, *Journal of Catalysis*, 2016, **338**, 202–209.
- 166 J. Chun, S. Kang, N. Kang, S. M. Lee, H. J. Kim and S. U. Son, *Journal of Materials Chemistry A*, 2013, **1**, 5517.
- 167 Y. Chen, R. Luo, Q. Xu, W. Zhang, X. Zhou and H. Ji, *ChemCatChem*, 2017, **9**, 767–773.
- 168 Y. Xie, T.-T. Wang, X.-H. Liu, K. Zou and W.-Q. Deng, *Nature Communications*, , DOI:10.1038/ncomms2960.
- 169 T. Takahashi, T. Watahiki, S. Kitazume, H. Yasuda and T. Sakakura, *Chemical Communications*, 2006, 1664.
- 170 J. Sun, W. Cheng, W. Fan, Y. Wang, Z. Meng and S. Zhang, *Catalysis Today*, 2009, **148**, 361–367.
- 171 R. A. Watile, K. M. Deshmukh, K. P. Dhake and B. M. Bhanage, *Catalysis Science & Technology*, 2012, **2**, 1051.
- 172 W.-L. Dai, L. Chen, S.-F. Yin, W.-H. Li, Y.-Y. Zhang, S.-L. Luo and C.-T. Au, *Catalysis Letters*, 2010, **137**, 74–80.

- 173 T.-Y. Shi, J.-Q. Wang, J. Sun, M.-H. Wang, W.-G. Cheng and S.-J. Zhang, *RSC Advances*, 2013, **3**, 3726.
- 174 C. J. Whiteoak, A. H. Henseler, C. Ayats, A. W. Kleij and M. A. Pericàs, *Green chemistry*, 2014, **16**, 1552–1559.
- 175 L. Han, H.-J. Choi, S.-J. Choi, B. Liu and D.-W. Park, *Green Chemistry*, 2011, **13**, 1023.
- 176 A. Sainz Martinez, C. Hauzenberger, A. R. Sahoo, Z. Csendes, H. Hoffmann and K. Bica, *ACS Sustainable Chem. Eng.*, 2018, **6**, 13131–13139.
- 177 W. Zhang, Q. Wang, H. Wu, P. Wu and M. He, *Green Chemistry*, 2014, **16**, 4767–4774.
- 178 C. Kohrt and T. Werner, *ChemSusChem*, 2015, **8**, 2031–2034.
- 179 X. Chen, J. Sun, J. Wang and W. Cheng, *Tetrahedron Letters*, 2012, **53**, 2684–2688.
- 180 T. Jose, S. Cañellas, M. A. Pericàs and A. W. Kleij, *Green Chemistry*, 2017, **19**, 5488–5493.
- 181 Y. Zhi, P. Shao, X. Feng, H. Xia, Y. Zhang, Z. Shi, Y. Mu and X. Liu, *J. Mater. Chem. A*, 2018, **6**, 374–382.
- 182 O. Buyukcakir, S. H. Je, S. N. Talapaneni, D. Kim and A. Coskun, *ACS Appl. Mater. Interfaces*, 2017, **9**, 7209–7216.
- 183 S. Liang, H. Liu, T. Jiang, J. Song, G. Yang and B. Han, *Chemical Communications*, 2011, **47**, 2131–2133.
- 184 J. Sun, W. Cheng, Z. Yang, J. Wang, T. Xu, J. Xin and S. Zhang, *Green Chemistry*, 2014, **16**, 3071.
- 185 K. R. Roshan, T. Jose, A. C. Kathalikkattil, D. W. Kim, B. Kim and D. W. Park, *Applied Catalysis A: General*, 2013, **467**, 17–25.
- 186 M. Rinaudo, *Prog. Polym. Sci.*, 2006, **31**, 603–632.
- 187 Y. Zhao, J.-S. Tian, X.-H. Qi, Z.-N. Han, Y.-Y. Zhuang and L.-N. He, *Journal of Molecular Catalysis A: Chemical*, 2007, **271**, 284–289.
- 188 J. Tharun, Y. Hwang, R. Roshan, S. Ahn, A. C. Kathalikkattil and D.-W. Park, *Catalysis Science & Technology*, 2012, **2**, 1674.
- 189 J. Sun, J. Wang, W. Cheng, J. Zhang, X. Li, S. Zhang and Y. She, *Green Chemistry*, 2012, **14**, 654.
- 190 S. Klaus, M. W. Lehenmeier, E. Herdtweck, P. Deglmann, A. K. Ott and B. Rieger, *Journal of the American Chemical Society*, 2011, **133**, 13151–13161.
- 191 S. Chen, G.-R. Qi, Z.-J. Hua and H.-Q. Yan, *Journal of Polymer Science Part A: Polymer Chemistry*, 2004, **42**, 5284–5291.
- 192 M. Ree, J. Y. Bae, J. H. Jung and T. J. Shin, *Journal of Polymer Science Part A: Polymer Chemistry*, 1999, **37**, 1863–1876.
- 193 Y. Z. Meng, L. C. Du, S. C. Tiong, Q. Zhu and A. S. Hay, *Journal of Polymer Science Part A: Polymer Chemistry*, 2002, **40**, 3579–3591.
- 194 M. Ree, J. Y. Bae, J. H. Jung, T. J. Shin, Y.-T. Hwang and T. Chang, *Polymer Engineering & Science*, 2000, **40**, 1542–1552.
- 195 R. Eberhardt, M. Allmendinger, M. Zintl, C. Troll, G. A. Luinstra and B. Rieger, *Macromolecular Chemistry and Physics*, 2004, **205**, 42–47.
- 196 I. Kim, M. J. Yi, K. J. Lee, D.-W. Park, B. U. Kim and C.-S. Ha, *Catalysis Today*, 2006, **111**, 292–296.
- 197 S. Chen, Z. Hua, Z. Fang and G. Qi, *Polymer*, 2004, **45**, 6519–6524.
- 198 I. Kim, M. J. Yi, S. H. Byun, D. W. Park, B. U. Kim and C. S. Ha, *Macromolecular Symposia*, 2005, **224**, 181–192.
- 199 I. S. Metcalfe, M. North, R. Pasquale and A. Thursfield, *Energy Environ. Sci.*, 2010, **3**, 212–215.
- 200 M. North, B. Wang and C. Young, *Energy & Environmental Science*, 2011, **4**, 4163.
- 201 J. Meléndez, M. North, P. Villuendas and C. Young, *Dalton Transactions*, 2011, **40**, 3885–3902.

- 202 A. Barthel, Y. Saih, M. Gimenez, J. D. A. Pelletier, F. E. Kühn, V. D'Elia and J.-M. Basset, *Green Chemistry*, 2016, **18**, 3116–3123.
- 203 A. M. Chapman, C. Keyworth, M. R. Kember, A. J. J. Lennox and C. K. Williams, *ACS Catalysis*, 2015, **5**, 1581–1588.
- 204 M. J. Kelly, A. Barthel, C. Maheu, O. Sodpiban, F.-B. Dega, S. V. C. Vummaleti, E. Abou-Hamad, J. D. A. Pelletier, L. Cavallo, V. D'Elia and J.-M. Basset, *Journal of CO₂ Utilisation*, 2017, **20**, 243–252.
- 205 B. Wetenhall, J. M. Race and M. J. Downie, *International Journal of Greenhouse Gas Control*, 2014, **30**, 197–211.
- 206 J. Rumble, *CRC Handbook of Chemistry and Physics, 98th Edition*, CRC Press, Boca Raton, 2017.
- 207 J. H. Clements, *Industrial & Engineering Chemistry Research*, 2003, **42**, 663–674.
- 208 C. Beattie, M. North and P. Villuendas, *Molecules*, 2011, **16**, 3420–3432.
- 209 H. L. Parker, J. Sherwood, A. J. Hunt and J. H. Clark, *ACS Sustainable Chemistry & Engineering*, 2014, **2**, 1739–1742.
- 210 T. Sakakura and K. Kohno, *Chemical Communications*, 2009, **11**, 1312.
- 211 D. Prat, A. Wells, J. Hayler, H. Sneddon, C. R. McElroy, S. Abou-Shehade and P. J. Dunn, *Green Chem.*, 2016, **18**, 288–296.
- 212 J. R. Machac and E. T. Marquis, WO Pat. 2000050524 A1, 2001.
- 213 E. T. Marquis, R. E. Baldwin, J. R. Machac, K. Darragas and S. A. Woodrum, WO Pat. 2001042376 A1, 2001.
- 214 J. A. Lucas and Z. E. Halar, US Pat. 5449474 A, 1995.
- 215 M. Kawasaki, Y. Ohbuchi, Y. Maeda and S. Sato, US Pat. 5021534, 1991.
- 216 Z. Dai and M. J. Chen, US Pat. 6229054, 2001.
- 217 R. B. Durairaj, US Pat. 6303732, 2001.
- 218 F. A. Lavalley, F. A. Lavalley, US Pat. 6046326, 2000.
- 219 H. Nava, US Pat. 5714568, 1998.
- 220 S. D. Lazarus, K. Chakravarti, H. H. Rowan and J. G. Neal, US Pat. 4171422, 1982.
- 221 J. M. Trowell and S. F. Lange, US Pat. 4897429, 1990.
- 222 K. Dahmen and R. Mertens, US Pat. 5409771, 1995.
- 223 European Chemicals Agency (ECHA), Propylene carbonate substance information, <https://echa.europa.eu/substance-information/-/substanceinfo/100.003.248>, (accessed on December 11, 2018).
- 224 European Chemicals Agency (ECHA), Ethylene carbonate substance information, <https://echa.europa.eu/en/substance-information/-/substanceinfo/100.002.283>, (accessed on December 11, 2018).
- 225 H. Blattmann, M. Fleischer, M. Bähr and R. Mülhaupt, *Macromolecular Rapid Communications*, 2014, **35**, 1238–1254.
- 226 P. Tundo and M. Selva, *Accounts of Chemical Research*, 2002, **35**, 706–716.
- 227 S. Fukuoka, M. Kawamura, K. Komiya, M. Tojo, H. Hachiya, K. Hasegawa, M. Aminaka, H. Okamoto, I. Fukawa and S. Konno, *Green Chemistry*, 2003, **5**, 497–507.
- 228 M. O. Sonnati, S. Amigoni, E. P. Taffin de Givenchy, T. Darmanin, O. Choulet and F. Guittard, *Green Chemistry*, 2013, **15**, 283–306.
- 229 A. Behr, J. Ilting, K. Irawadi, J. Leschinski and F. Lindner, *Green Chemistry*, 2008, **10**, 13–30.
- 230 G. Rokicki, P. Rakoczy, P. Parzuchowski and M. Sobiecki, *Green Chemistry*, 2005, **7**, 529.
- 231 J. Ma, J. Song, H. Liu, J. Liu, Z. Zhang, T. Jiang, H. Fan and B. Han, *Green Chem.*, 2012, **14**, 1743–1748.
- 232 S. Kondawar and C. Rode, *Energy Fuels*, 2017, **31**, 4361–4371.

- 233 J. George, Y. Patel, S. M. Pillai and P. Munshi, *Journal of Molecular Catalysis A: Chemical*, 2009, **304**, 1–7.
- 234 O. Hauenstein, S. Agarwal and A. Greiner, *Nature Communications*, 2016, **7**, 11862.
- 235 H. A. Stretz, P. E. Cassidy and D. R. Paul, *Journal of Applied Polymer Science*, 1999, **74**, 1508–1515.
- 236 D. J. Darensbourg and S. J. Wilson, *J. Am. Chem. Soc.*, 2011, **133**, 18610–18613.
- 237 D. J. Darensbourg and S. J. Wilson, *Macromolecules*, 2013, **46**, 5929–5934.
- 238 O. Hauenstein, M. Reiter, S. Agarwal, B. Rieger and A. Greiner, *Green Chemistry*, 2016, **18**, 760–770.
- 239 C. Li, R. J. Sablong and C. E. Koning, *Angewandte Chemie International Edition*, 2016, **55**, 11572–11576.
- 240 G. Wu, S. Jiang, X. Lu, W. Ren and S. Yan, *Chinese Journal of Polymer Science*, 2012, **30**, 487–492.
- 241 K. Nakano, S. Hashimoto, M. Nakamura, T. Kamada and K. Nozaki, *Angewandte Chemie International Edition*, 2011, **50**, 4868–4871.
- 242 S. D. Thorat, P. J. Phillips, V. Semenov and A. Gakh, *Journal of applied polymer science*, 2003, **89**, 1163–1176.
- 243 T.-J. Hsu and C.-S. Tan, *Polymer*, 2002, **43**, 4535–4543.
- 244 W.-M. Ren, X. Zhang, Y. Liu, J.-F. Li, H. Wang and X.-B. Lu, *Macromolecules*, 2010, **43**, 1396–1402.
- 245 G. Luinstra, *Polymer Reviews*, 2008, **48**, 192–219.
- 246 J. E. Seong, S. J. Na, A. Cyriac, B.-W. Kim and B. Y. Lee, *Macromolecules*, 2010, **43**, 903–908.
- 247 C. Martín and A. W. Kleij, *Macromolecules*, 2016, **49**, 6285–6295.
- 248 J. H. Jung, M. Ree and H. Kim, *Catalysis Today*, 2006, **115**, 283–287.
- 249 L. C. Du, Y. Z. Meng, S. J. Wang and S. C. Tjong, *Journal of Applied Polymer Science*, 2004, **92**, 1840–1846.
- 250 G. Kim, M. Ree, H. Kim, I. J. Kim, J. R. Kim and J. I. Lee, *Macromolecular research*, 2008, **16**, 473–480.
- 251 C. E. Koning, R. J. Sablong, E. H. Nejad, R. Duchateau and P. Buijsen, *Progress in Organic Coatings*, 2013, **76**, 1704–1711.
- 252 M. Scharfenberg, J. Hilf and H. Frey, *Advanced Functional Materials*, 2018, **28**, 1704302.
- 253 Y. Xu, L. Lin, M. Xiao, S. Wang, A. T. Smith, L. Sun and Y. Meng, *Progress in Polymer Science*, 2018, **80**, 163–182.
- 254 Y. Li, J. Hong, R. Wei, Y. Zhang, Z. Tong, X. Zhang, B. Du, J. Xu and Z. Fan, *Chemical Science*, 2015, **6**, 1530–1536.
- 255 A. Cyriac, S. H. Lee, J. K. Varghese, J. H. Park, J. Y. Jeon, S. J. Kim and B. Y. Lee, *Green Chemistry*, 2011, **13**, 3469.
- 256 Z. Zhang, Z. Mo, H. Zhang, X. Wang and X. Zhao, *Macromolecular Chemistry and Physics*, 2003, **204**, 1557–1566.
- 257 Y. Tominaga and K. Yamazaki, *Chemical Communications*, 2014, **50**, 4448.
- 258 M. Taherimehr, J. P. C. C. Sertã, A. W. Kleij, C. J. Whiteoak and P. P. Pescarmona, *ChemSusChem*, 2015, **8**, 1034–1042.
- 259 C. Li, S. van Berkel, R. J. Sablong and C. E. Koning, *European Polymer Journal*, 2016, **85**, 466–477.
- 260 N. Kindermann, À. Cristòfol and A. W. Kleij, *ACS Catalysis*, 2017, **7**, 3860–3863.
- 261 D. J. Darensbourg and F.-T. Tsai, *Macromolecules*, 2014, **47**, 3806–3813.
- 262 J. Geschwind, F. Wurm and H. Frey, *Macromolecular Chemistry and Physics*, 2013, **214**, 892–901.

- 263 J.-F. Zhang, W.-M. Ren, X.-K. Sun, Y. Meng, B.-Y. Du and X.-H. Zhang, *Macromolecules*, 2011, **44**, 9882–9886.
- 264 D. J. Darensbourg, W.-C. Chung, C. J. Arp, F.-T. Tsai and S. J. Kyran, *Macromolecules*, 2014, **47**, 7347–7353.
- 265 D. J. Darensbourg and Y. Wang, *Polymer Chemistry*, 2015, **6**, 1768–1776.
- 266 G. Bleys, *Technology Watch: Carbon Dioxide Conversion*, Essenscia, 2016.
- 267 B. Bahramian, A. Fathi and F. Dehghani, *Polymer Degradation and Stability*, 2016, **133**, 174–181.
- 268 A. K. Brym, P. Deglmann, J. Dengler, S. Klaus, M. Lehenmeier, P. Lutz-Kahler, B. Rieger and V. Warzelhan, WO Pat. 2012139994 A1, 2012.
- 269 P. Deglmann, A. K. Brym, B. Rieger, M. Lehenmeier and S. Klaus, WO Pat. 2013030317 A1, 2013.
- 270 T. E. Müller, C. Gürtler, M. A. Subhani and W. Leitner, WO Pat. 2015128277 A1, 2015.
- 271 J. Hofmann, S. Braun, K. Laemmer, A. Wolf and M. Traving, WO Pat. 2016001206 A1, 2016.
- 272 T. E. Müller, C. Gürtler, M. Wohak, J. Hofmann and T. Carlson, WO Pat. 2016079065 A1, 2016.
- 273 C. Wamprecht, W. Kaufhold and C. Gürtler, WO Pat. 2014060300 A3, 2014.
- 274 S. D. Allen, A. E. Cherian, C. A. Simoneau and J. J. Farmer, WO Pat. 2011163133 A1, 2011.
- 275 J. J. Farmer, WO Pat. 2012037282 A3, 2012.
- 276 J. G. Sant'Angelo, X. Chen and V. D. McGinnis, US Pat. 6248860 B1, 2001.
- 277 C. Chen and J. Scheirs, WO Pat. 2011026171 A1, 2012.
- 278 J. Jeong, S. J. Na, S. Sudevan, M. Ok, Y. Han, K. J. Chung, B. Y. Lee, A. Cyriac and S. Lee, WO Pat. 2012108696 A3, 2016.
- 279 K. J. Chung, Y. G. Han, J. S. Jeong, V. J. Kodiyan, B. Y. Lee, S. J. Na, M. A. Ok and S. Sudevan, WO Pat. 2011105846 A3, 2012.
- 280 G. W. Coates, S. Lee, Z. Qin and N. J. Robertson, WO Pat. 2008024363 A3, 2008.
- 281 K. Nozaki, K. Nakano, WO Pat. 2008150033 A1, 2008.
- 282 E. de Jong, A. Higson, P. Walsh and M. Wellisch, *Bio-based Chemicals: Value Added Products From Biorefineries*, IEA Bioenergy, 2012.
- 283 V. Zacharopoulou, E. S. Vasiladou and A. A. Lemonidou, *Green Chemistry*, 2015, **17**, 903–912.
- 284 J. S. Plotkin, *Green Propylene*, Nexant, 2009.
- 285 Genomatica, <https://www.genomatica.com/>, (accessed on March 16, 2018).
- 286 M. Winkler, C. Romain, M. A. R. Meier and C. K. Williams, *Green Chemistry*, 2015, **17**, 300–306.
- 287 A. Mohsenzadeh, A. Zamani and M. J. Taherzadeh, *ChemBioEng Reviews*, 2017, **4**, 75–91.
- 288 B. Elvers, *Ullman's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2003.
- 289 M. M. Ahmad, M. F. R. Nordin and M. T. Azizan, *American journal of applied sciences*, 2010, **7**, 746–755.
- 290 F. E. Massoth, P. Politzer, M. C. Concha, J. S. Murray, J. Jakowski and J. Simons, *The Journal of Physical Chemistry B*, 2006, **110**, 14283–14291.
- 291 P. M. Mortensen, J.-D. Grunwaldt, P. A. Jensen and A. D. Jensen, *ACS Catalysis*, 2013, **3**, 1774–1785.
- 292 F. Auriemma, C. De Rosa, M. R. Di Caprio, R. Di Girolamo, W. C. Ellis and G. W. Coates, *Angewandte Chemie*, 2015, **127**, 1231–1234.
- 293 V. Negro, G. Mancini, B. Ruggeri and D. Fino, *Bioresource technology*, 2016, **214**, 806–815.

- 294 N. Tenhumberg, H. Büttner, B. Schöffner, D. Kruse, M. Blumenstein and T. Werner, *Green Chemistry*, 2016, **18**, 3775–3788.
- 295 F.-T. Tsai, Y. Wang and D. J. Darensbourg, *Journal of the American Chemical Society*, 2016, **138**, 4626–4633.
- 296 G. Si, L. Zhang, B. Han, H. Zhang, X. Li and B. Liu, *RSC Advances*, 2016, **6**, 22821–22826.
- 297 E. V. Makshina, M. Dusselier, W. Janssens, J. Degrevé, P. A. Jacobs and B. F. Sels, *Chemical Society Reviews*, 2014, **43**, 7917–7953.
- 298 G.-P. Wu, S.-H. Wei, W.-M. Ren, X.-B. Lu, T.-Q. Xu and D. J. Darensbourg, *Journal of the American Chemical Society*, 2011, **133**, 15191–15199.
- 299 G.-P. Wu, P.-X. Xu, X.-B. Lu, Y.-P. Zu, S.-H. Wei, W.-M. Ren and D. J. Darensbourg, *Macromolecules*, 2013, **46**, 2128–2133.
- 300 B. M. Bell, J. R. Briggs, R. M. Campbell, S. M. Chambers, P. D. Gaarenstroom, J. G. Hippler, B. D. Hook, K. Kearns, J. M. Kenney, W. J. Kruper, D. J. Schreck, C. N. Theriault and C. P. Wolfe, *CLEAN - Soil, Air, Water*, 2008, **36**, 657–661.
- 301 Y. Hu, L. Qiao, Y. Qin, X. Zhao, X. Chen, X. Wang and F. Wang, *Macromolecules*, 2009, **42**, 9251–9254.
- 302 J. Hilf, M. Scharfenberg, J. Poon, C. Moers and H. Frey, *Macromolecular Rapid Communications*, 2015, **36**, 174–179.
- 303 J. Geschwind and H. Frey, *Macromolecules*, 2013, **46**, 3280–3287.
- 304 Y. Tominaga, T. Shimomura and M. Nakamura, *Polymer*, 2010, **51**, 4295–4298.
- 305 M. D. Konieczynska, X. Lin, H. Zhang and M. W. Grinstaff, *ACS Macro Letters*, 2015, **4**, 533–537.
- 306 F. Parrino, A. Fidalgo, L. Palmisano, L. M. Ilharco, M. Pagliaro and R. Ciriminna, *ACS Omega*, 2018, **3**, 4884–4890.
- 307 J. Sun, L. Liang, J. Sun, Y. Jiang, K. Lin, X. Xu and R. Wang, *Catalysis Surveys from Asia*, 2011, **15**, 49–54.
- 308 N. V. Maksimchuk, I. D. Ivanchikova, A. B. Ayupov and O. A. Kholdeeva, *Applied Catalysis B: Environmental*, 2016, **181**, 363–370.
- 309 F. D. Bobbink and P. J. Dyson, *Journal of Catalysis*, 2016, **343**, 52–61.
- 310 F. Chen, T. Dong, T. Xu, X. Li and C. Hu, *Green Chem.*, 2011, **13**, 2518–2524.
- 311 J. Wu, J. A. Kozak, F. Simeon, T. A. Hatton and T. F. Jamison, *Chemical Science*, 2014, **5**, 1227–1231.
- 312 X. Yang, J. Wu, X. Mao, T. F. Jamison and T. A. Hatton, *Chemical Communications*, 2014, **50**, 3245–3248.
- 313 D. Zhang, E. A. del Rio-Chanona, J. L. Wagner and N. Shah, *Sustainable Production and Consumption*, 2018, **14**, 152–160.
- 314 IHS Markit: Polycarbonate Market Overview, May 2018, http://www.media-tech.net/2018/wp-content/uploads/2018/06/Mediatech-2018-Polycarbonate-Market_Wiesweg.pdf, (accessed on August 15, 2018).
- 315 O. Haba, I. Itakura, M. Ueda and S. Kuze, *Journal of Polymer Science Part A: Polymer Chemistry*, 1999, **37**, 2087–2093.
- 316 R. Huang, Z. Liu, H. Yin, Z. Dang, P. Wu, N. Zhu and Z. Lin, *Science of the Total Environment*, 2018, **626**, 971–981.
- 317 Horie K., Barón Máximo, Fox R. B., He J., Hess M., Kahovec J., Kitayama T., Kubisa P., Maréchal E., Mormann W., Stepto R. F. T., Tabak D., Vohlídal J., Wilks E. S., and Work W. J., *pac*, 2004, **76**, 889.
- 318 M. Khoshkish, H. Bouhendi and M. Vafayan, *Journal of Materials Science*, 2014, **49**, 6813–6819.
- 319 F.-L. Jin, X. Li and S.-J. Park, *Journal of Industrial and Engineering Chemistry*, 2015, **29**, 1–11.

- 320 Alemán J. V., Chadwick A. V., He J., Hess M., Horie K., Jones R. G., Kratochvíl P., Meisel I., Mita I., Moad G., Penczek S., and Stepto R. F. T., *pac*, 2007, **79**, 1801.
- 321 H. Gu, C. Ma, J. Gu, J. Guo, X. Yan, J. Huang, Q. Zhang and Z. Guo, *Journal of Material Chemistry C*, 2016, **4**, 5890–5906.
- 322 G. Rokicki and C. Wojciechowski, *Journal of applied polymer science*, 1990, **41**, 647–659.
- 323 J. H. Hodgkin, G. P. Simon and R. J. Varley, *Polymers for Advanced Technologies*, 1998, **9**, 3–10.
- 324 G. Rokicki and M. Lewandowski, *Macromolecular Materials and Engineering*, 1987, **148**, 53–66.
- 325 G. Rokicki and R. Laziński, *Macromolecular Materials and Engineering*, 1989, **170**, 211–225.
- 326 J. Wang, H. Zhang, Y. Miao, L. Qiao, X. Wang and F. Wang, *Green Chemistry*, 2016, **18**, 524–530.
- 327 E. Orgilés-Calpena, F. Arán-Aís, A. M. Torró-Palau and C. Orgilés-Barceló, *International Journal of Adhesion and Adhesives*, 2016, **70**, 218–224.
- 328 L. Poussard, J. Mariage, B. Grignard, C. Detrembleur, C. Jérôme, C. Calberg, B. Heinrichs, J. De Winter, P. Gerbaux, J.-M. Raquez, L. Bonnaud and Ph. Dubois, *Macromolecules*, 2016, **49**, 2162–2171.
- 329 M. Bähr, A. Bitto and R. Mülhaupt, *Green Chemistry*, 2012, **14**, 1447.
- 330 Statista, Market size forecast of polyurethane worldwide from 2016 to 2021, <https://www.statista.com/statistics/720341/global-polyurethane-market-size-forecast/>, (accessed on 27 August 2018).
- 331 N. Mahmood, Z. Yuan, J. Schmidt and C. Xu, *Renewable and Sustainable Energy Reviews*, 2016, **60**, 317–329.
- 332 J.-M. Raquez, M. Deléglise, M.-F. Lacrampe and P. Krawczak, *Progress in Polymer Science*, 2010, **35**, 487–509.
- 333 A. Kuta, Z. Hrdlička, A. Strachota and M. Špírková, *Materials and Manufacturing Processes*, 2009, **24**, 1214–1216.
- 334 P. Cinelli, I. Anguillesi and A. Lazzeri, *European Polymer Journal*, 2013, **49**, 1174–1184.
- 335 E. Delebecq, J.-P. Pascault, B. Boutevin and F. Ganachaud, *Chemical Reviews*, 2013, **113**, 80–118.
- 336 B.-H. Lee and H.-J. Kim, *Polymer Degradation and Stability*, 2006, **91**, 1025–1035.
- 337 J. Langanke, A. Wolf, J. Hofmann, K. Böhm, M. A. Subhani, T. E. Müller, W. Leitner and C. Gürtler, *Green Chemistry*, 2014, **16**, 1865–1870.
- 338 J. Langanke and A. Wolf, *Organic Process Research & Development*, 2015, **19**, 735–739.
- 339 N. von der Assen and A. Bardow, *Green Chemistry*, 2014, **16**, 3272–3280.
- 340 Covestro, CO₂ Dreams, <https://www.co2-dreams.covestro.com>, (accessed on August 16, 2018).
- 341 Converge polyols, <http://www.saudiaramco.com/en/home/our-business/downstream/converge.html>, (accessed on August 10, 2018).
- 342 Z. Ying, C. Wu, S. Jiang, R. Shi, B. Zhang, C. Zhang and F. Zhao, *Green Chemistry*, 2016, **18**, 3614–3619.
- 343 S. Xu and M. Zhang, *Journal of Applied Polymer Science*, 2007, **104**, 3818–3826.
- 344 P. Alagi, R. Ghorpade, Y. J. Choi, U. Patil, I. Kim, J. H. Baik and S. C. Hong, *ACS Sustainable Chemistry & Engineering*, 2017, **5**, 3871–3881.
- 345 J. Hilf, P. Schulze, J. Seiwert and H. Frey, *Macromolecular Rapid Communications*, 2014, **35**, 198–203.
- 346 S. Liu, Y. Qin, X. Chen, X. Wang and F. Wang, *Polymer Chemistry*, 2014, **5**, 6171–6179.
- 347 S. Liu, Y. Qin, X. Wang and F. Wang, *Journal of Renewable Materials*, 2015, **3**, 101–112.
- 348 S. H. Lee, A. Cyriac, J. Y. Jeon and B. Y. Lee, *Polymer Chemistry*, 2012, **3**, 1215.

- 349 M. DeBolt, A. Kiziltas, D. Mielewski, S. Waddington and M. J. Nagridge, *Journal of Applied Polymer Science*.
- 350 Y. Chen, Z. Liu, S. Han, J. Han and D. Jiang, *Journal of Applied Polymer Science*, , DOI:10.1002/app.43667.
- 351 C. Li, R. J. Sablong and C. E. Koning, *European Polymer Journal*, 2015, **67**, 449–458.
- 352 D. Bello, C. A. Herrick, T. J. Smith, S. R. Woskie, R. P. Streicher, M. R. Cullen, Y. Liu and C. A. Redlich, *Environmental Health Perspectives*, 2006, **115**, 328–335.
- 353 L. Maisonneuve, O. Lamarzelle, E. Rix, E. Grau and H. Cramail, *Chemical Reviews*, 2015, **115**, 12407–12439.
- 354 B. Nohra, L. Candy, J.-F. Blanco, C. Guerin, Y. Raoul and Z. Mouloungui, *Macromolecules*, 2013, **46**, 3771–3792.
- 355 K. R. Aguiar, V. G. Santos, M. N. Eberlin, K. Rischka, M. Noeske, G. Tremiliosi-Filho and U. P. Rodrigues-Filho, *RSC Advances*, 2014, **4**, 24334–24343.
- 356 B. Tamami, S. Sohn and G. L. Wilkes, *Journal of Applied Polymer Science*, 2004, **92**, 883–891.
- 357 A. Boyer, E. Cloutet, T. Tassaing, B. Gadenne, C. Alfos and H. Cramail, *Green Chemistry*, 2010, **12**, 2205.
- 358 T. Stößer, C. Li, J. Unruangsri, P. K. Saini, R. J. Sablong, M. A. R. Meier, C. K. Williams and C. Koning, *Polymer Chemistry*, 2017, **8**, 6099–6105.
- 359 J. Y. Jeon, J. J. Lee, J. K. Varghese, S. J. Na, S. Sujith, M. J. Go, J. Lee, M.-A. Ok and B. Y. Lee, *Dalton Transactions*, 2013, **42**, 9245–9254.
- 360 G. A. Luinstra and E. Borchardt, in *Synthetic biodegradable polymers*, Springer, Berlin, 2012, pp. 29–48.
- 361 X. L. Lu, F. G. Du, X. C. Ge, M. Xiao and Y. Z. Meng, *Journal of Biomedical Materials Research Part A*, 2006, **77A**, 653–658.
- 362 S. D. Allen, J. J. Farmer and C. A. Simoneau, WO Pat. 2012154849 A1, 2012.
- 363 V. S. Bagotsky, *Journal of Solid State Electrochemistry*, 2011, **15**, 1559–1562.
- 364 B. Scrosati, *Journal of Solid State Electrochemistry*, 2011, **15**, 1623–1630.
- 365 C. Sun, J. Liu, Y. Gong, D. P. Wilkinson and J. Zhang, *Nano Energy*, 2017, **33**, 363–386.
- 366 J.-M. Tarascon and M. Armand, *Nature*, 2001, **414**, 359–367.
- 367 M. Armand and J.-M. Tarascon, *Nature*, 2008, **451**, 652–657.
- 368 B. Scrosati and J. Garche, *Journal of Power Sources*, 2010, **195**, 2419–2430.
- 369 K. Xu, *Chemical Reviews*, 2004, **104**, 4303–4418.
- 370 H. Zhang, C. Li, M. Piszcz, E. Coya, T. Rojo, L. M. Rodriguez-Martinez, M. Armand and Z. Zhou, *Chemical Society Reviews*, 2017, **46**, 797–815.
- 371 T. B. Reddy and S. Hossain, in *Handbook of batteries*, McGraw-Hill, New York, 2002, vol. 3, pp. 1–62.
- 372 D. Fauteux, A. Massucco, M. McLin, M. Van Buren and J. Shi, *Electrochimica Acta*, 1995, **40**, 2185–2190.
- 373 C. A. Vincent, *Solid State Ionics*, 2000, **134**, 159–167.
- 374 Y. Nishi, H. Azuma and A. Omaru, US Pat. 4959281, 1990.
- 375 K. Ozawa, Ed., *Lithium Ion Rechargeable Batteries*, Wiley-VCH Verlag GmbH & Co. KGaA, Tokyo, 2009.
- 376 S.-K. Jeong, M. Inaba, R. Mogi, Y. Iriyama, T. Abe and Z. Ogumi, *Langmuir*, 2001, **17**, 8281–8286.
- 377 J.-T. Lee, Y.-W. Lin and Y.-S. Jan, *Journal of Power Sources*, 2004, **132**, 244–248.
- 378 M. Winter, R. Imhof, F. Joho and P. Novák, *Journal of Power Sources*, 1999, **81–82**, 818–823.
- 379 M. C. Smart, B. V. Ratnakumar, V. S. Ryan-Mowrey, S. Surampudi, G. K. S. Prakash, J. Hu and I. Cheung, *Journal of Power Sources*, 2003, **119–121**, 359–367.

- 380 Z. X. Shu, R. S. McMillan, J. J. Murray and I. J. Davidson, *Journal of the Electrochemical Society*, 1995, **142**, L161–L162.
- 381 Z. X. Shu, R. S. McMillan, J. J. Murray and I. J. Davidson, *J. Electrochem. Soc.*, 1996, **143**, 2230–2235.
- 382 M. Winter and P. Novák, *Journal of The Electrochemical Society*, 1998, **145**, L27–L30.
- 383 R. McMillan, H. Sleg, Z. X. Shu and W. Wang, *Journal of Power Sources*, 1999, **81**, 20–26.
- 384 R. A. Sheldon, *Green Chemistry*, 2014, **16**, 950–963.
- 385 M. Inaba, Y. Kawatate, A. Funabiki, S.-K. Jeong, T. Abe and Z. Ogumi, *Electrochimica acta*, 1999, **45**, 99–105.
- 386 J. Arai, H. Katayama and H. Akahoshi, *Journal of The Electrochemical Society*, 2002, **149**, A217.
- 387 G. S. MacGlashan, Y. G. Andreev and P. G. Bruce, *Nature*, 1999, **398**, 792–794.
- 388 F. Croce, G. B. Appetecchi, L. Persi and B. Scrosati, *Nature*, 1998, **394**, 3.
- 389 Y. Tominaga, V. Nanthana and D. Tohyama, *Polymer journal*, 2012, **44**, 1155.
- 390 M. A. Ratner and D. F. Shriver, *Chemical Reviews*, 1988, **88**, 109–124.
- 391 K. Deng, S. Wang, S. Ren, D. Han, M. Xiao and Y. Meng, *ACS Applied Materials & Interfaces*, 2016, **8**, 33642–33648.
- 392 M. Nakamura and Y. Tominaga, *Electrochimica Acta*, 2011, **57**, 36–39.
- 393 M. Marzantowicz, J. R. Dygas, F. Krok, J. L. Nowiński, A. Tomaszewska, Z. Florjańczyk and E. Zygadło-Monikowska, *Journal of Power Sources*, 2006, **159**, 420–430.
- 394 T. Okumura and S. Nishimura, *Solid State Ionics*, 2014, **267**, 68–73.
- 395 M. Galiński, A. Lewandowski and I. Stępnia, *Electrochimica Acta*, 2006, **51**, 5567–5580.
- 396 K. Kimura, J. Hassoun, S. Panero, B. Scrosati and Y. Tominaga, *Ionics*, 2015, **21**, 895–900.
- 397 K. Kimura, H. Matsumoto, J. Hassoun, S. Panero, B. Scrosati and Y. Tominaga, *Electrochimica Acta*, 2015, **175**, 134–140.
- 398 T. Morioka, K. Nakano and Y. Tominaga, *Macromolecular Rapid Communications*, 2017, **38**, 1600652.
- 399 K. Kimura, M. Yajima and Y. Tominaga, *Electrochemistry Communications*, 2016, **66**, 46–48.
- 400 H. Yue, J. Li, Q. Wang, C. Li, J. Zhang, Q. Li, X. Li, H. Zhang and S. Yang, *ACS Sustainable Chemistry & Engineering*, 2018, **6**, 268–274.
- 401 X.-Y. Yu, M. Xiao, S.-J. Wang, Q.-Q. Zhao and Y.-Z. Meng, *Journal of Applied Polymer Science*, 2010, **115**, 2718–2722.
- 402 G. P. Dukhanin, A. N. Gaidadin and I. A. Novakov, *Russian Journal of Applied Chemistry*, 2014, **87**, 1868–1871.
- 403 D. Zhou, R. Zhou, C. Chen, W.-A. Yee, J. Kong, G. Ding and X. Lu, *The Journal of Physical Chemistry B*, 2013, **117**, 7783–7789.
- 404 X. Yu, M. Xiao, S. Wang, D. Han and Y. Meng, *Journal of Applied Polymer Science*, 2010, **118**, 2078–2083.
- 405 N. Nitta, F. Wu, J. T. Lee and G. Yushin, *Materials Today*, 2015, **18**, 252–264.
- 406 X. Huang, J. Huang, J. Wu, X. Yu, Q. Gao, Y. Luo and H. Hu, *RSC Advances*, 2015, **5**, 52978–52984.
- 407 X. Huang, S. Zeng, J. Liu, T. He, L. Sun, D. Xu, X. Yu, Y. Luo, W. Zhou and J. Wu, *The Journal of Physical Chemistry C*, 2015, **119**, 27882–27891.
- 408 W. Amass, A. Amass and B. Tighe, *Polymer International*, 1998, **47**, 89–144.
- 409 R. P. Brannigan and A. P. Dove, *Biomater. Sci.*, 2017, **5**, 9–21.
- 410 D. F. Williams, *Biomaterials*, 2008, **29**, 2941–2953.
- 411 S. Ramakrishna, J. Mayer, E. Wintermantel and K. W. Leong, *Composites science and technology*, 2001, **61**, 1189–1224.

- 412 Y. Hwang, H. Kim and M. Ree, *Macromolecular Symposia*, 2005, **224**, 227–238.
- 413 J. Ma, Z. Liu, F. Wang, Q. Zhou, C. Feng and F. Li, *Journal of Bionic Engineering*, 2013, **10**, 514–521.
- 414 I. Manavitehrani, A. Fathi, Y. Wang, P. K. Maitz and F. Dehghani, *ACS Applied Materials & Interfaces*, 2015, **7**, 22421–22430.
- 415 Y. Li, S. Liu, X. Zhao, Y. Wang, J. Liu, X. Wang and L. Lu, *Theranostics*, 2017, **7**, 4689–4698.
- 416 X. Jiang, H. Xin, J. Gu, X. Xu, W. Xia, S. Chen, Y. Xie, L. Chen, Y. Chen, X. Sha and X. Fang, *Biomaterials*, 2013, **34**, 1739–1746.
- 417 M. Qingwei, Q. Yusheng, Z. Xiaojiang, W. Xianhong and W. Fosong, *Acta Polymerica Sinica*, 2010, 217–221.
- 418 X. H. Li, Y. Z. Meng, Q. Zhu and S. C. Tjong, *Polymer Degradation and Stability*, 2003, **81**, 157–165.
- 419 K. R. Stone, *Environmental Profile for Propylene Carbonate*, United States Environmental Protection Agency, Washington DC, 1998.
- 420 J. A. Ruddick, *Toxicology and applied pharmacology*, 1972, **21**, 102–111.
- 421 I. Manavitehrani, A. Fathi, Y. Wang, P. K. Maitz, F. Mirmohseni, T. L. Cheng, L. Peacock, D. G. Little, A. Schindeler and F. Dehghani, *Biomacromolecules*, 2017, **18**, 1736–1746.
- 422 X. Zhong, Z. Lu, P. Valtchev, H. Wei, H. Zreiqat and F. Dehghani, *Colloids and Surfaces B: Biointerfaces*, 2012, **93**, 75–84.
- 423 G. Yang, J. Su, J. Gao, X. Hu, C. Geng and Q. Fu, *The Journal of Supercritical Fluids*, 2013, **73**, 1–9.
- 424 Y. Hwang, M. Ree and H. Kim, *Catalysis Today*, 2006, **115**, 288–294.
- 425 S. P. Valappil, S. K. Misra, A. R. Boccaccini and I. Roy, *Expert Review of Medical Devices*, 2006, **3**, 853–868.
- 426 H. Zhang and M. W. Grinstaff, *Journal of the American Chemical Society*, 2013, **135**, 6806–6809.
- 427 R. Liu, J. B. Wolinsky, J. Walpole, E. Southard, L. R. Chirieac, M. W. Grinstaff and Y. L. Colson, *Annals of Surgical Oncology*, 2010, **17**, 1203–1213.
- 428 P. Kallinteri, S. Higgins, G. A. Hutcheon, C. B. St. Pourçain and M. C. Garnett, *Biomacromolecules*, 2005, **6**, 1885–1894.
- 429 H. Zhang, X. Lin, S. Chin and M. W. Grinstaff, *Journal of the American Chemical Society*, 2015, **137**, 12660–12666.
- 430 L. Gu, Y. Qin, Y. Gao, X. Wang and F. Wang, *Journal of Polymer Science Part A: Polymer Chemistry*, 2013, **51**, 2834–2840.
- 431 L. Gu, Y. Gao, Y. Qin, X. Chen, X. Wang and F. Wang, *Journal of Polymer Science Part A: Polymer Chemistry*, 2013, **51**, 282–289.
- 432 X. Zhong and F. Dehghani, *Green Chemistry*, 2012, **14**, 2523.
- 433 N. Nagiah, U. T. Sivagnanam, R. Mohan, N. T. Srinivasan and P. K. Sehgal, *Advanced Engineering Materials*, 2012, **14**, B138–B148.
- 434 X. Jing, M. R. Salick, T. Cordie, H.-Y. Mi, X.-F. Peng and L.-S. Turng, *Industrial & Engineering Chemistry Research*, 2014, **53**, 9391–9400.
- 435 J. Kost and R. Langer, *Advanced Drug Delivery Reviews*, 2012, **64**, 327–341.
- 436 N. M. Alves, I. Pashkuleva, R. L. Reis and J. F. Mano, *Small*, 2010, **6**, 2208–2220.
- 437 I. Roy and M. N. Gupta, *Chemistry & biology*, 2003, **10**, 1161–1171.
- 438 A. Welle, M. Kröger, M. Döring, K. Niederer, E. Pindel and I. S. Chronakis, *Biomaterials*, 2007, **28**, 2211–2219.
- 439 A. Metcalfe, A.-C. Desfaits, I. Salazkin, L. Yahia, W. M. Sokolowski and J. Raymond, *Biomaterials*, 2003, **24**, 491–497.
- 440 Y. Liu, K. Huang, D. Peng, S. Liu and H. Wu, *Journal of Polymer Science Part A: Polymer Chemistry*, 2007, **45**, 2152–2160.

- 441 H. Li and Y. Niu, *International Journal of Polymeric Materials and Polymeric Biomaterials*, 2018, **67**, 192–198.
- 442 N. H. Park, M. Fevre, Z. X. Voo, R. J. Ono, Y. Y. Yang and J. L. Hedrick, *ACS Macro Letters*, 2016, **5**, 1247–1252.
- 443 S. Tempelaar, L. Mespouille, O. Coulembier, P. Dubois and A. P. Dove, *Chemical Society Reviews*, 2013, **42**, 1312–1336.
- 444 J. Feng, R.-X. Zhuo and X.-Z. Zhang, *Progress in Polymer Science*, 2012, **37**, 211–236.
- 445 F.-Y. Qiu, M. Zhang, F.-S. Du and Z.-C. Li, *Macromolecules*, 2017, **50**, 23–34.
- 446 K. Fukushima, *Biomaterials Science*, 2016, **4**, 9–24.
- 447 W. Chen, F. Meng, R. Cheng, C. Deng, J. Feijen and Z. Zhong, *Journal of Controlled Release*, 2014, **190**, 398–414.
- 448 Z. Y. Ong, K. Fukushima, D. J. Coady, Y.-Y. Yang, P. L. R. Ee and J. L. Hedrick, *Journal of Controlled Release*, 2011, **152**, 120–126.
- 449 X. Zhang, Z. Zhang, X. Su, M. Cai, R. Zhuo and Z. Zhong, *Biomaterials*, 2013, **34**, 10296–10304.
- 450 C. Yang, X. Ding, R. J. Ono, H. Lee, L. Y. Hsu, Y. W. Tong, J. Hedrick and Y. Y. Yang, *Advanced Materials*, 2014, **26**, 7346–7351.
- 451 Empower Materials, www.empowermaterials.com, (accessed on August 1, 2017).
- 452 S. D. Allen, C. A. Simoneau, J. M. Salladay, D. M. Hatfield and J. W. Stevens, WO Pat. 2010062703 A1, 2011.
- 453 S. D. Allen, EP Pat. 2451860 A2, 2012.
- 454 F. Gao, Q. Zhou, Y. Dong, Y. Qin, X. Wang, Z. Xiaojiang and W. Fosong, *Journal of Polymer Research*, , DOI:10.1007/s10965-012-9877-6.
- 455 D. D. Dixon and M. E. Ford, US Pat. 4142021 A, 1979.
- 456 O. Hauenstein, Md. M. Rahman, M. Elsayed, R. Krause-Rehberg, S. Agarwal, V. Abetz and A. Greiner, *Advanced Materials Technologies*, 2017, **2**, 1700026.

Chapter 2: Ti and Zr amino-tris(phenolate) catalysts for the synthesis of cyclic carbonates from CO₂ and epoxides

Herein, we report the application of four amino-tris(phenolate)-based metal complexes incorporating Ti(IV) or Zr(IV) centres (**2a-3b**) as homogeneous catalysts for the conversion of CO₂ and epoxides into cyclic carbonates. The four complexes were synthesised, characterised and then evaluated in combination with tetrabutylammonium iodide, bromide or chloride as binary catalytic systems for the reaction of CO₂ with 1,2-epoxyhexane as epoxide substrate at 90 °C and 12 bar CO₂ pressure for 2 h. The catalytic systems comprising the two Ti(IV) complexes (**2a** and **2b**) showed similar performance. One notable exception was the catalytic system consisting of titanium complex **2b**, bearing an axial Cl-ligand, and tetrabutylammonium chloride, which displayed higher catalytic activity compared to other titanium-based systems. Even higher activity was achieved with Zr(IV) complex **3a**, bearing an axial isopropoxide ligand, which reached turnover numbers up to 1920 for the reaction of CO₂ with 1,2-epoxyhexane at 90 °C and 12 bar CO₂ pressure for 2 h. This performance is comparable with that of state-of-the-art catalysts for this reaction. The catalytic system consisting of complex **3a** and tetrabutylammonium bromide was investigated further by checking its applicability with a broad substrate scope, achieving quantitative conversion of several epoxides with CO₂ into cyclic carbonate products at 90 °C and 12 bar CO₂ pressure for 18 h. The selectivity towards the cyclic carbonate products was ≥ 98% for all studied terminal epoxides and ≥ 80% for all examined cyclohexene-type epoxides.

Part of this chapter has been published: A. J. Kamphuis, M. Tran, F. Picchioni, P.P. Pescarmona, *Green Chemical Engineering*, 2022, DOI: 10.1016/j.gce.2021.12.009.

2.1. Introduction

In the context of the sustainable synthesis of chemical products, the use of CO₂ as feedstock is an attractive option as it allows the valorisation of a waste, greenhouse gas generated worldwide in enormous amounts. The challenges within CO₂-conversion are related to the high thermodynamic and kinetic stability of this molecule.^{1,2} Reaction with high free-energy substrates such as epoxides and hydrogen can be employed to overcome the thermodynamic stability of CO₂, while catalysts are required to enhance the reaction kinetics in order to reach high reaction rates. Among the different routes for CO₂-utilisation,^{3–12} the reaction with epoxides to form cyclic or polymeric carbonates (Fig. 2.1) has received considerable attention.^{2,13–34} Already since the first half of the 20th century, two widely-used carbonate compounds, ethylene carbonate and propylene carbonate, have been produced via the reaction of CO₂ with ethylene oxide and propylene oxide, respectively.^{35,36} These two cyclic carbonates are employed in a variety of commercial applications, including in electrolytes for lithium-based batteries,³⁷ as green polar aprotic solvents³⁸ and as intermediates for the synthesis of other chemicals, including polymers such as bisphenol-A-based polycarbonates³⁹ and polyurethanes.⁴⁰ The other possible product of the reaction between epoxides and CO₂, *i.e.* the polycarbonates, are commercially applied as polyols for polyurethane synthesis,⁴¹ as sacrificial binders for the production of ceramics and adhesives,⁴² and are being investigated for application as packaging material,⁴³ performance coatings⁴⁴ and for utilisation in biomedical applications.^{45,46}

Numerous homogeneous catalytic systems have been developed for promoting the reaction of CO₂ with epoxides. The most studied among these catalysts consist of binary systems comprising a Lewis acid compound that coordinates and activates the epoxide, typically a metal-organic complex, and a Lewis base, which acts as a nucleophile in the ring-opening of the epoxide.^{14,47} In the proposed reaction mechanism (Fig. 2.2), the titanium and zirconium complexes presented in this work act as Lewis acid compounds. In line with previous reports and based on our results (*vide infra*), we propose that during the catalytic cycle these complexes adopt a

Fig. 2.1. General scheme of the reaction of CO₂ with epoxides, yielding cyclic and/or polymeric carbonates.

Fig. 2.2. Proposed mechanism of the formation of cyclic carbonates from the reaction of CO₂ with epoxides catalysed by the binary systems presented in this work, consisting of a metal complex (R-M-L, where M = Ti or Zr, R is the amino-tris(phenolate) ligand and L is the axial ligand, *i.e.* OiPr or Cl; see Fig. 2.3 for the actual structure of the complex) with Lewis acid character for activating the epoxide towards the nucleophilic attack by a Lewis base (X⁻ = Cl⁻, Br⁻ or I⁻, originating from TBAX).

conformation in which the axial ligand remains coordinated to the metal centre.⁴⁸ A wide range of metal complexes in which the metal centre acts as Lewis acid active site have been studied, with the most common metals being zinc, chromium, cobalt, magnesium, aluminium and iron.^{49–63} Together with the metal species, the nature of the organic ligand plays a key role in determining the activity of the complex and the selectivity towards either the cyclic or the polymeric carbonate. Well-known complexes researched for this reaction include metallocporphyrins,^{64,65} metal-salen/salphen complexes,^{66–71} bimetallic macrocyclic phenolates^{72–74} and amino-bis/tris(phenolate)s.^{75–81,81} Particularly, iron and aluminium amino-tris(phenolate) metal complexes have been found to display high activity towards the reaction of CO₂ with epoxides, with extremely high turnover frequency reached with the binary system consisting of aluminium amino-tris(phenolate) and bis(triphenylphosphine)iminium bromide (PPNBr).⁷⁵ The remarkably high activity of iron and aluminium complexes prepared with amino-tris(phenolate) ligands inspired us to study this type of ligand in combination with titanium and zirconium

Fig. 2.3. Synthesis of complexes 2a-3b.

as Lewis acid catalysts for the reaction of CO_2 with epoxides. So far, group (IV) metals such as titanium^{82–95} and zirconium^{82,91,95–97} have received limited attention concerning their application as homogeneous catalysts for this reaction. In this work, we report the synthesis of four amino-tris(phenolate)-type complexes with Ti (IV) or Zr (IV) metal centres (Fig. 2.3, complexes **2a–3b**) and demonstrate their promising catalytic activity in the conversion of CO_2 to cyclic carbonates employing a broad scope of epoxides. To the best of our knowledge, this is the first time that the synthesis of a zirconium amino-tris(phenolate) complex bearing an axial Cl-ligand is reported and also the first time that Zr-amino-tris(phenolate) complexes are reported for application as catalysts for the reaction of CO_2 with epoxides. Among the Ti- amino-tris(phenolate) complexes, **2a** has been recently reported in combination with PPNCl as catalytic system for the copolymerisation of CO_2 with cyclohexene oxide,⁴⁸ whereas the activity of complex **2b** in this reaction was so far unexplored.

2.2. Experimental

2.2.1. Materials

2,4-di-*tert*-butylphenol (99%, Sigma-Aldrich), hexamethylenetetramine ($\geq 99.8\%$, Sigma-Aldrich), aqueous formaldehyde (37 wt%, Sigma-Aldrich), titanium(IV) isopropoxide (97%, Sigma-Aldrich), benzene ($\geq 99.0\%$, Sigma-Aldrich), chloroform-*d* (99.8% , Sigma-Aldrich), hydrochloric acid (37–38 wt%, Boom), magnesium sulphate (Boom), chloroform ($\geq 99.8\%$, Macron), diethyl ether ($\geq 99.0\%$, Macron), toluene ($\geq 99.5\%$, Macron), hexane ($\geq 95\%$, Macron), 1,2-epoxyhexane (97%, Sigma-Aldrich), cyclohexene oxide (97%, Sigma-Aldrich), tetrabutylammonium iodide ($\geq 99\%$, Sigma-Aldrich), tetrabutylammonium bromide ($\geq 99\%$, Sigma-Aldrich), tetrabutylammonium chloride ($\geq 97\%$, Sigma-Aldrich), mesitylene (98%, Sigma-Aldrich), epichlorohydrin ($\geq 99\%$, Sigma-Aldrich), allyl glycidyl ether ($\geq 99\%$, Sigma-Aldrich), styrene oxide (97%, Sigma-Aldrich), (+)-limonene oxide (mixture of *cis* and

trans, 97%, Sigma-Aldrich), compressed nitrogen gas (N₂, ≥ 99.999%, Linde Gas) and compressed carbon dioxide (≥ 99.7%, Linde Gas) were used as received. Zirconium (IV) isopropoxide - isopropanol complex (99.9%, Alfa Aesar) and zirconium (IV) chloride (>99.5%, Alfa Aesar) were stored and used under nitrogen atmosphere. Dry toluene, diethyl ether, hexane and tetrahydrofuran were obtained by passing these solvents through a series of drying columns before storing them under nitrogen atmosphere. Tetrahydrofuran-d₈ (Euriso-top) and benzene-d₆ (>99.8%, Sigma-Aldrich) were dried over a Na/K alloy, vacuum transferred to a Schlenk flask and stored under nitrogen. All air- and moisture-sensitive compounds were handled and stored under nitrogen atmosphere using standard Schlenk and glovebox techniques.

2.2.2. Equipment

¹H NMR spectra were recorded on a Varian Oxford 300 MHz apparatus or on a Bruker 600 MHz apparatus with 64 scans and a relaxation time of 10 s, using chloroform-d, benzene-d₆ or tetrahydrofuran-d₈ as solvents. ¹³C NMR spectra were recorded on a Bruker 600 MHz apparatus with 2048 scans and a relaxation time of 1 s or on a 300 MHz Varian Mercury PlusNMR apparatus with 8192 scans and a relaxation time of 1 s, using chloroform-d, benzene-d₆ or tetrahydrofuran-d₈ as solvents. ¹H NMR and ¹³C NMR spectra were referenced using residual solvent resonances and ppm values are reported relative to tetramethylsilane (TMS). FTIR spectra were recorded using a Shimadzu IRtracer-100 equipped with an ATR sample unit with a wavenumber range of 4000-600 cm⁻¹, a resolution of 4 cm⁻¹ and 64 scans.

2.2.3. Synthesis of the amino-*t*Bu-tris(phenolate) ligand (1)

The synthesis of the ligand was performed according to a literature procedure.⁵⁹ Briefly, 2,4-di-*tert*-butylphenol (8.25 g, 40 mmol), hexamethylenetetramine (0.47 g, 3.3 mmol) and 37% aqueous formaldehyde (1.21 g, 14.2 mmol) were added to a 250 mL round-bottom flask equipped with a reflux condenser. The mixture was stirred at 125 °C for 48 h, after which the reaction was quenched with CHCl₃ (100 mL). The organic layer was washed with demineralised water (3 x 100 mL) and subsequently dried over MgSO₄. The organic phase was concentrated using rotary evaporation and the desired product was obtained as a white solid (6.46 g, 72%) after recrystallisation from diethyl ether. ¹H NMR (400 MHz, CDCl₃): δ 7.25 (d, 3H, ArH), 6.99 (d, 3H, ArH), 6.56 (s, 3H, ArOH), 3.65 (s, 6H, CH), 1.40 (s, 27H, *t*Bu), 1.27 (s, 27H, *t*Bu). ¹³C NMR (300 MHz, CDCl₃): δ 151.5, 142.2, 136.5, 125.7, 124.1, 121.9, 56.7, 35.0, 34.3, 31.7, 29.8. The full spectra can be found in the Supplementary Information (Fig. S2.1 and S2.2).

2.2.4. Synthesis of titanium(IV) amino-*t*Bu-tris(phenolate) isopropoxide (**2a**)

Titanium(IV) amino-*t*Bu-tris(phenolate) isopropoxide (**2a**) was synthesised according to a method from the literature.⁵⁹ A mixture of the amino-*t*Bu-tris(phenolate) ligand **1** (1.18 g, 1.75 mmol) and dry diethyl ether (50 mL) were added to a 100 mL three-necked flask under nitrogen atmosphere. Whilst stirring, titanium (IV) isopropoxide (0.52 mL, 1.75 mmol) was slowly added to the solution. The mixture was stirred at room temperature for 3 h and subsequently concentrated under reduced pressure, after which the obtained crude yellow product was slowly dissolved in hot hexane. The purified product was obtained after recrystallisation at -18 °C for 48 h, yielding yellow crystals (1.13 g, 83%). ¹H NMR (400 MHz, C₆D₆): δ 7.45 (d, 3H, ArH), 6.82 (d, 3H, ArH), 5.48 (h, 1H, CH in CH(CH₃)₂) 3.97 (d, 3H, CH), 2.88 (d, 3H, CH), 1.49 (d, 6H, CH₃ in CH(CH₃)₂), 1.44 (s, 27H, *t*Bu), 1.27 (s, 27H, *t*Bu). ¹³C NMR (300 MHz, C₆D₆): δ 161.2, 142.6, 135.6, 124.9, 124.5, 123.2, 79.8, 59.3, 35.4, 34.6, 32.0, 30.0, 27.0, 27.0, 23.1, 14.4. The full spectra can be found in the Supplementary Information (Fig. S2.3 and S2.4).

2.2.5. Synthesis of titanium(IV) amino-*t*Bu-tris(phenolate) chloride (**2b**)

Titanium (IV) amino-*t*Bu-tris(phenolate) chloride (**2b**) was synthesised from **2a** following an ion-exchange procedure reported in the literature.⁶⁰ Complex **2a** (0.25 g, 0.32 mmol) was dissolved in benzene (20 mL) and placed in a 100 mL separation funnel, after which 25 mL 1M aqueous HCl was added. The mixture was shaken for 10 min, followed by removal of the aqueous layer and drying of the organic layer over MgSO₄. The desired product was obtained as an orange solid (0.18 g, 75%) by concentrating the organic solution under reduced pressure. ¹H NMR (400 MHz, C₆D₆): δ 7.43 (d, 3H, ArH), 6.75 (d, 3H, ArH), 3.95 (d, 3H, CH), 2.53 (d, 3H, CH), 1.66 (s, 27H, *t*Bu), 1.32 (s, 27H, *t*Bu). ¹³C NMR (300 MHz, C₆D₆): δ 161.6, 144.3, 136.5, 124.3, 124.0, 123.8, 59.0, 35.4, 34.7, 31.9, 29.9. The full spectra can be found in the Supplementary Information (Fig. S2.5 and S2.6).

2.2.6. Synthesis of zirconium(IV) amino-*t*Bu-tris(phenolate) isopropoxide (**3a**)

Zirconium (IV) amino-*t*Bu-tris(phenolate) isopropoxide (**3a**) was synthesised according to a procedure from the literature.⁶¹ A Schlenk flask was loaded with the zirconium (IV) isopropoxide isopropanol complex (0.47 g, 1.23 mmol) in a nitrogen-filled glovebox. Subsequently, the complex was dissolved in dry toluene (20 ml). The ligand **1** (0.84 g, 1.23 mmol) was dissolved in toluene (40 ml) under nitrogen atmosphere in a second Schlenk flask equipped with a pressure-equalising dropping

funnel. The mixture containing the zirconium complex was added dropwise to the ligand solution at 0 °C while stirring. The resulting mixture was stirred for 2 h while it was allowed to slowly return to room temperature. Subsequently, the mixture was concentrated under reduced pressure, and the obtained white crude solid was dissolved in hot dry toluene. After recrystallisation for 48 h at -18 °C, white crystals were obtained. The crystals were washed with dry hexane and dried under reduced pressure at 50 °C, which yielded the desired product (0.48 g, 48%). The product was stored and handled under strictly inert and moisture-free atmosphere. ¹H NMR (600 MHz, C₆D₆): δ 7.49 (d, 3H, ArH), 6.89 (d, 3H, ArH), 4.87 (h, 1H, CH in CH(CH₃)₂), 4.54 (d, 3H, CH), 3.01 (d, 3H, CH), 1.66 (s, 27H, tBu), 1.55 (d, 6H, CH₃ in CH(CH₃)₂), 1.35 (s, 27H, tBu). ¹³C NMR (600 MHz, C₆D₆): δ 158.0, 141.1, 136.6, 125.3, 124.8, 123.8, 72.9, 60.5, 35.4, 34.4, 32.1, 31.1, 30.1, 27.8. The full spectra can be found in the Supplementary Information (Fig. S2.7 and S2.8).

2.2.7. Synthesis of zirconium(IV) amino-tBu-tris(phenolate) chloride (3b)

Zirconium (IV) amino-tBu-tris(phenolate) chloride (**3b**) was synthesised using a similar procedure to that employed for preparing **3a**. Zirconium (IV) chloride (0.500 g, 2.15 mmol) was dissolved in dry tetrahydrofuran (50 ml) and was slowly added to a solution of ligand **1** (1.44 g, 2.15 mmol) in dry tetrahydrofuran (50 ml) under nitrogen atmosphere at 0 °C, after which the resulting mixture was stirred for 2 h and allowed to slowly return to room temperature. After concentrating the mixture under reduced pressure, the obtained white crude solid was dissolved in a minimum amount of hot dry tetrahydrofuran, after which dry toluene was added as non-solvent to produce a saturated solution. Recrystallisation for 48 h at -18 °C yielded needle-like white crystals, which were subsequently washed with dry toluene and dried at 50 °C under reduced pressure to obtain the final product (0.33 g, 19%). The product was stored and handled under strictly inert and moisture-free atmosphere. ¹H NMR (600 MHz, THF-d₈): δ 7.55 (s, 3H, ArH), 7.40 (s, 3H, ArH), 4.26 (s, 3H, CH₂), 3.58 (m, 4H, THF), 1.73 (m, 4H, THF), 1.40 (s, 27H, tBu), 1.32 (s, 27H, tBu). ¹³C NMR (600 MHz, THF-d₈): δ 153.2, 143.8, 139.6, 126.5, 67.2, 50.6, 35.7, 34.9, 31.8, 30.3, 25.1. The full spectra can be found in the Supplementary Information (Fig. S2.9 and S2.10).

2.2.8. Catalytic tests

The catalytic reactions between CO₂ and epoxides were carried out in a high-throughput CO₂ reactor unit manufactured by ILS-Integrated Lab Solutions GmbH. This CO₂ reactor unit consists of: (i) a reactors block in which 10 reactions can be

performed simultaneously in individually-stirred, separate batch reactors (84 mL volume each, 30 mm internal diameter), which was used in this work; and (ii) a single batch reactor with the same dimensions as the other batch reactors but equipped with a borosilicate glass window that allows visualising the phases present in the reaction mixture. The CO₂ reactor unit can be operated in a pressure range of 1-200 bar and a temperature range of 20-200 °C. For each test, the chosen amounts of group (IV) metal complex and of tetrabutylammonium halide, 30.0 mmol epoxide and 3.0 mmol internal standard (mesitylene) were weighed into a glass vial (30 mm external diameter, 46 mL volume) equipped with a magnetic stirring bar and closed with a screw cap containing a silicone/PTFE septum. Next, the closed glass vials were transferred into the 10-reactors block. To allow gas flow into and from the vials, each septum was pierced with two needles. Then, the reactors block was closed and the reactors were purged 3 times with N₂ (5 bar) and then were pressurised with CO₂ (10 bar). Next, 10 min were waited (to prevent deterioration of the rubber O-rings), after which the reactors were depressurised to atmospheric pressure. After waiting an additional 10 min, the batch reactors were pressurised with 10 bar CO₂. Upon reaching 10 bar, the reactors were heated to 90 °C, which resulted in a final pressure of around 12 bar in each batch reactor. The described procedure of purging, pressurising and heating the 10-reactors block required approximately 1 h. After reaching the desired reaction temperature and pressure, the start of the catalytic test was defined as the moment at which the magnetic stirring was turned on. The reactions were performed for either 2 or 18 h at 900 rpm stirring speed. At the end of the catalytic test, the magnetic stirring was stopped, the reactor heating was turned off and the water-cooling system was switched on to cool down the reactors. Once room temperature was reached, the reactors were depressurised. The process of cooling and depressurising the 10-reactors block lasted approximately 45 min. Upon reaching atmospheric pressure, the reactors block was opened and the test vials were removed. An aliquot of each sample was analysed by ¹H NMR and FTIR.

2.3. Results and discussion

Four amino-tris(phenolate) complexes with Ti (IV) or Zr (IV) as metal centres (Fig. 2.3, complexes **2a-3b**) were synthesised and investigated in combination with a tetrabutylammonium halide as binary catalytic systems for the conversion of CO₂ and epoxides into cyclic carbonates. These group (IV) metals were chosen as catalytic sites because their ionic radius is larger than that of the more commonly employed Al (III) and their higher oxidation state implies that the complex contains

an anionic axial ligand (Y = Cl or OiPr, see Fig. 2.3). These features are expected to influence the catalytic behaviour of the complex, with the larger ionic radius possibly providing enhanced accessibility to the metal centres. The amino-tris(phenolate) ligand bearing *t*Bu-groups on the phenolate rings (**1**) as well as complexes **2a** and **3a** were synthesised according to literature procedures.^{98,100} Straightforward ion-exchange of **2a** with aqueous HCl resulted in the formation of complex **2b**.⁹⁹ Complex **3b** was synthesised here for the first time, by reacting ZrCl₄ with the amino-tris(phenolate) ligand **1** and following a procedure adapted from the one used for preparing **3a**. The successful synthesis of ligand **1** and of the four metal complexes was demonstrated by ¹H NMR and ¹³C NMR analysis (see Figures S2.1-S2.10 in the Supporting Information).

We started the evaluation of the catalytic performance of the titanium (IV) amino-tris(phenolate) complexes **2a** and **2b** in the reaction of CO₂ with epoxides by testing them in combination with a tetrabutylammonium halide (TBAX, X = Cl, Br, I) in a benchmark reaction employing 1,2-epoxyhexane as epoxide substrate (12 bar CO₂, 90 °C, 2 h). The catalytic loading and the type of tetrabutylammonium halide acting as nucleophile were varied to study the influence of these parameters on the conversion and selectivity of the reaction (Table 2.1). No epoxide conversion was achieved without using a separate nucleophile source, (Table 2.1, entries 1 and 11) indicating that complexes **2a** and **2b** cannot act as single-component catalysts. The tetrabutylammonium halides without the presence of complexes **2a** and **2b** display only low activity under the employed reaction conditions (Table 2.1, entries 21-23). A remarkable increase in 1,2-hexene carbonate yield was achieved when the metal complexes **2a** and **2b** were combined with the tetrabutylammonium halides in a binary catalytic system (Table 2.1, entries 2-10 and 12-20). Employing complex **2a**, the highest cyclic carbonate yields were achieved using TBABr as nucleophile (Table 2.1, compare entries 5-7 to 2-4 and 8-10), obtaining turnover numbers (relative to the metal complex) up to 1000. The nucleophilicity of the halide anions increases in the order I⁻ < Br⁻ < Cl⁻ and their leaving group ability increases in the order Cl⁻ < Br⁻ < I⁻, rendering I⁻ the worse nucleophile and Cl⁻ the worse leaving group. Taking this into account and considering the generally proposed reaction mechanism (Fig. 2.2),^{14,47} it can be reasoned that the Br⁻ anion provides the optimal balance between nucleophilicity (step 2) and leaving group ability (step 5a) and, thus, results in the highest reaction rate when combined with this metal complex. Ion-exchange of the axial OiPr-group of **2a** with a Cl-group, thereby forming complex **2b**, did not have a significant impact on the activity of the complex in combination with TBAI or TBABr as nucleophile (Table 2.1, compare entries 12-17 with entries 2-7). On the other

Table 2.1. Reaction of CO₂ with 1,2-epoxyhexane catalysed by complexes **2a-2b** in combination with TBAX.

#	Ti-complex	Ti-complex loading (mol%) ^a	Nucleophile source	Cyclic carbonate yield (%) ^b	TON _{metal} ^c
1	2a	0.05	-	0	-
2	2a	0.025	TBAI	10	400
3	2a	0.05	TBAI	18	360
4	2a	0.25	TBAI	38	152
5	2a	0.025	TBABr	25	1000
6	2a	0.05	TBABr	35	700
7	2a	0.25	TBABr	75	300
8	2a	0.025	TBACl	13	520
9	2a	0.05	TBACl	24	480
10	2a	0.25	TBACl	38	152
11	2b	0.05	-	0	-
12	2b	0.025	TBAI	14	560
13	2b	0.05	TBAI	18	360
14	2b	0.25	TBAI	42	168
15	2b	0.025	TBABr	25	1000
16	2b	0.05	TBABr	41	820
17	2b	0.25	TBABr	76	304
18	2b	0.025	TBACl	27	1080
19	2b	0.05	TBACl	43	860
20	2b	0.25	TBACl	83	332
21	-	-	TBAI	5	-
22	-	-	TBABr	4	-
23	-	-	TBACl	3	-

Reaction conditions: 30 mmol epoxide, 3 mmol mesitylene as NMR internal standard, 0.25 mol% nucleophile source (TBAX, with X = Cl, Br or I) relative to the epoxide (if applicable), 90 °C, 12 bar CO₂ pressure, 2 h. The selectivity towards the cyclic carbonate product was > 99% in all cases, as indicated by ¹H NMR spectroscopy (see Fig. S2.11 for a representative spectrum). ^a Relative to the epoxide. ^b The yield of the cyclic carbonate (1,2-hexene carbonate) was determined based on the ¹H NMR signals of the carbonate product and epoxide substrate. ^c TON = turnover number, expressed as mol of converted epoxide per mol of metal complex.

hand, the combination of **2b** with TBACl as nucleophile displayed remarkably higher activity compared to the counterpart catalytic system based on complex **2a**, reaching the highest epoxide conversions and cyclic carbonate yields among the investigated titanium amino-tris(phenolate) complexes, with turnover numbers up to 1080 (Table 2.1, entries 18-20). This unusual trend in catalytic activity could originate from differences in steric effects around the metal centre. Assuming that the axial ligands of **2a** and **2b** are not very labile, since it was shown that the isopropoxide and chloride groups do not act as nucleophiles in the benchmark reaction (Table 2.1, entries 1 and 11), we might conclude that the axial ligands

remain coordinated to the metal centre during the catalytic cycle. This means that an anionic intermediate complex would form after steps 2 and 3 of the mechanism in Fig. 2.2, in line with what has been proposed in the literature for similar catalysts.⁴⁸ The rate of step 4a is not only determined by the leaving ability of the halide that is involved in the nucleophilic attack (*vide supra*), but can also be promoted by the displacement of the carbonate intermediate by another halide.⁷⁷ This displacement may occur more readily when the axial ligand is the less sterically hindered Cl (compared to OiPr) and when the halide promoting the displacement is smaller (and thus with Cl⁻ rather than with Br⁻ or I⁻). This would explain the observed high activity of the binary catalytic system consisting of complex **2b** and TBACl.

For each binary catalytic system defined by the combination of a metal complex (**2a** or **2b**) and of a TBAX (X = Cl, Br, I), three molar ratios between metal and organic halide were tested, *i.e.* 1:1, 1:5 and 1:10. In line with logical expectations, increasing the loading of metal complex (while keeping the TBAX loading constant) led to higher cyclic carbonate yields (with a maximum of 83% for the 2b/TBACl system, Table 2.1 entry 20), though at the price of lower turnover numbers on a metal content base. The amount and type of halide can also have a strong influence on the selectivity between cyclic and polymeric carbonate.^{77,80} In general, higher relative amounts of organic halide promote the displacement of the carbonate intermediate, thus favouring the ring closure (steps 4a and 5a in Fig. 2.2), leading to the formation of the cyclic carbonate product.⁷⁷ As a consequence, higher selectivity towards the cyclic carbonate products are generally observed when the organic halide is used in excess relatively to the metal complexes, whereas the formation of the polycarbonate is more favourable when the metal to halide ratio is equal to 1 or lower.⁷⁷ With metal complex **2a** or **2b**, full selectivity (> 99%) towards the cyclic hexene carbonate was observed with all the tetrabutylammonium halides types and ratios. This is attributed to the nature of the epoxide and to the reaction being performed at relatively high temperature (90 °C), which promotes the formation of the thermodynamically-favoured cyclic carbonate product.¹

Stimulated by the promising results obtained with the titanium amino-tris(phenolate) complexes, we continued our study of group (IV) metals as Lewis acid centre catalysts for the reaction of CO₂ with epoxides with the corresponding zirconium-based complexes **3a** and **3b**. Zirconium (IV) has a relatively larger radius than titanium (IV) and, hence, is anticipated to be better accessible to the epoxide substrate. The zirconium-based amino-tris(phenolate) complexes **3a** and **3b** were tested as Lewis acid catalysts in combination with TBAX using the same reaction

conditions employed for the titanium-based complexes (1,2-epoxyhexane as epoxide substrate, 90 °C, 12 bar CO₂, 2 h, see Table 2.2). Similarly to complexes **2a** and **2b**, **3a** and **3b** did not display any activity without the presence of an additional nucleophile (Table 2.2, entries 1 and 11). Employing complex **3a** in combination with TBABr as nucleophile source, resulted in the highest observed activity in this work in terms of turnover numbers (Table 2.2, entries 5-7), reaching a remarkably high $\text{TON}_{\text{metal}} = 1920$. Notably, no considerable differences in cyclic carbonate yields were observed upon employing either 0.05 mol% or 0.25 mol% of **3a** relative to the epoxide substrate. More specifically, in the case of TBACl (entries 9 and 10) only a slightly higher conversion was achieved using 0.25 mol% **3a**, while for TBAI (entries 3 and 4) and TBABr (entries 6 and 7) even slightly lower conversions were obtained. This trend is significantly different from what we observed with the Ti-complexes **2a** and **2b** (*vide supra*). These results indicate that complex **3a** is highly active already at relatively low metal-to-nucleophile ratios. The fact that increasing the metal loading above a certain metal-to-nucleophile ratio (*i.e.* approximately 1:5) does not lead to higher product yield suggests that above this ratio the reaction kinetics is no longer influenced significantly by the amount of Lewis acid sites, but is controlled rather by the amount of nucleophile. However, a decrease in solubility of complex **3a** caused by the increased polarity of the reaction medium induced by the conversion of the epoxide into the cyclic carbonate might not be excluded as explanation of the observed behaviour.

In contrast to the results obtained with the titanium-based complexes, significantly lower cyclic carbonate yields were achieved for the zirconium complex bearing an axial chloride ligand (**3b**) compared to the complex bearing an axial isopropoxide ligand (**3a**). We hypothesise that residual THF solvent molecules could coordinate to the zirconium metal centre, similarly to what has been observed for aluminium-based amino-tris(phenolate) complexes.⁷⁶ This would hinder the coordination of the epoxide substrate and thus lead to lower catalytic activity in the reaction between 1,2-epoxyhexane and CO₂. Additionally, the axial chloride ligand is expected to lead to an increased Lewis acidity of the zirconium metal compared to the axial isopropoxide ligand. This increased Lewis acidity would hinder the release of the carbonate intermediate and thus the subsequent ring closure that yields the cyclic carbonate product (step 5a in Fig. 2.2), thereby hampering the overall reaction rate. Analogously to what observed with complexes **2a** and **2b**, complete selectivity towards the cyclic hexene carbonate product was obtained with complexes **3a** and **3b**, irrespectively of the type and relative amount of tetrabutylammonium halide that was employed. In order to compare the activity of the most active metal

Table 2.2. Reaction of CO₂ with 1,2-epoxyhexane catalysed by complexes **3a-3b**.

#	Zr-complex	Zr-complex loading (mol%) ^a	Nucleophile source	Cyclic carbonate yield (%) ^b	TON _{metal} ^c
1	3a	0.05	-	0	-
2	3a	0.025	TBAI	30	1200
3	3a	0.05	TBAI	44	880
4	3a	0.25	TBAI	39	156
5	3a	0.025	TBABr	48	1920
6	3a	0.05	TBABr	63	1260
7	3a	0.25	TBABr	57	228
8	3a	0.025	TBACl	35	1400
9	3a	0.05	TBACl	42	840
10	3a	0.25	TBACl	47	188
11	3b	0.05	-	0	-
12	3b	0.025	TBAI	8	320
13	3b	0.05	TBAI	9	180
14	3b	0.25	TBAI	27	108
15	3b	0.025	TBABr	8	320
16	3b	0.05	TBABr	10	200
17	3b	0.25	TBABr	21	84
18	3b	0.025	TBACl	6	240
19	3b	0.05	TBACl	7	140
20	3b	0.25	TBACl	12	48
21	Al amino-<i>t</i>Bu-tris(phenolate)	0.05	TBAI	45	900

Reaction conditions: 30 mmol epoxide, 3 mmol mesitylene as NMR internal standard, 0.25 mol% nucleophile source (TBAX, with X = Cl, Br or I) relative to the epoxide (if applicable), 90 °C, 12 bar CO₂ pressure, 2 h. The selectivity towards the cyclic carbonate product was > 99% in all cases as confirmed by ¹H NMR spectroscopy (see Fig. S2.11 for a representative spectrum). ^a Relative to the epoxide. ^b The yield of the cyclic carbonate (1,2-hexene carbonate) was determined based on the ¹H NMR signals of the carbonate product and epoxide substrate. ^c TON = turnover number, expressed as mol of converted epoxide per mol of metal complex.

complex identified in this work (**3a**) with the state-of-the-art aluminium amino-tris(phenolate) complex, we prepared the Al-complex with the same amino-*t*Bu-tris(phenolate) ligand following a literature procedure (see the Supporting Information for more details).⁷⁶ The obtained Al-complex was tested under the same reaction conditions employed with complexes **2a-3b** and using TBAI as nucleophile, to recreate the conditions reported in literature for this Al-complex as catalyst for the CO₂/epoxide reaction.⁷⁶ A 1,2-hexene carbonate yield of 45% with a turnover number of 900 was achieved (Table 2.2, entry 21), which indicates that our complex **3a** (Table 2.2, entry 3) has a virtually identical activity to this reference binary catalytic system. However, complex **3a** achieved significantly better

performance with TBABr than with TBAI (Table 2.2), indicating that superior activity can be achieved by careful selection of the type and amount of metal amino-tris(phenolate) complex and tetrabutylammonium halide.

Based on the catalytic tests with 1,2-epoxyhexane as substrate, complex **3a** was selected as the most promising Lewis acid catalyst. To study the versatility of complex **3a** (in combination with TBABr) with regards to the reaction of CO₂ with epoxides, a substrate scope evaluation was performed using various terminal and internal epoxides (Table 2.3). Under the employed reaction conditions (90 °C, 12 bar CO₂, 18 h), all terminal epoxides (*i.e.* 1,2-epoxyhexane, propylene oxide, epichlorohydrin, allyl glycidyl ether and styrene oxide; Table 2.3, entries 1-5) were converted into the corresponding cyclic carbonates in near quantitative yields, with turnover numbers up to 2000. This result confirms not only the notable activity of the binary system consisting of complex **3a** and TBABr, but also the complete selectivity towards the cyclic carbonate product regardless of the steric and electronic effects of the different functional groups of the terminal epoxides. The activity of complex **3a** was drastically lower when internal epoxides were used as substrates (Table 2.3, entries 6-8). For cyclohexene oxide and vinylcyclohexene oxide, only a moderate conversion was achieved (Table 2.3, entries 6 and 7 respectively), whereas in the case of limonene oxide no carbonate product was observed under the employed reaction conditions (Table 2.3, entry 8). The lower activity with these internal epoxides is in line with trends typically observed in the literature,^{75,80} and has been attributed to the higher steric hindrance around the epoxide group, which hampers the initial nucleophilic attack (step 2 in Fig. 2.2), and to the geometric strain that characterises the two adjacent rings of the obtained carbonates.¹⁰¹

The inactivity in the conversion of limonene oxide is most probably related to the additional bulkiness of the methyl group adjacent to the epoxide moiety combined with the intrinsic conformation around the zirconium metal centre of **3a**. It was also observed that when cyclohexene oxide and vinylcyclohexene oxide were used as substrate, the selectivity towards the cyclic carbonate product was not complete (Table 2.3, entries 6 and 7) and a significant fraction of polycarbonate product was also observed (see Fig. S2.12 and S2.13 for the FTIR spectra). This is a known phenomenon which presumably originates from the geometric ring strain of the two interconnected rings in the cyclic carbonate product, rendering it less thermodynamically favourable.⁶⁷ Although the selectivity towards the cyclic carbonate product was not complete, it was significantly higher compared to that

observed in other reports of the reaction of CO₂ with cyclohexene oxide using related amino-tris(phenolate)-based metal complexes as catalysts, which instead were selective towards the polycarbonate.⁴⁸ Such difference in selectivity can be explained with the fact that in this work we used (i) a higher nucleophile-to-metal ratio and (ii) bromide (from TBABr) instead of chloride (from PPNCl) as nucleophile, which both promote the selectivity towards the cyclic carbonate product.⁷⁷

Table 2.3. Substrate scope of the reaction of CO₂ with various terminal and internal epoxides, catalysed by the binary catalytic system consisting of complex **3a** and TBABr.

#	Epoxide	Conv. (%) ^a	Sel. ^{cyclic} carbonate (%) ^b	TON _{metal} ^c
1		>99	>99	2000
2		>99	>99	2000
3		99	98	1980
4		98	>99	1960
5		>99	>99	2000
6		19	80	380
7		17	92	340
8		<1	-	-

Reaction conditions: 30 mmol epoxide, 3 mmol mesitylene as NMR internal standard, 0.05 mol% of complex **3a** relative to the epoxide, 0.25 mol% TBABr relative to the epoxide, 90 °C, 12 bar CO₂ pressure, 18 h. ^a Conversion determined based on the ¹H NMR signals of the carbonate product and epoxide substrate. ^b Selectivity towards the cyclic carbonate determined by FTIR analysis on the basis of the relative intensity of the C=O stretch signal of the cyclic carbonate and polycarbonate. ^c TON = turnover number, expressed as mol of converted epoxide per mol of metal.

The activity of our optimum catalytic system, consisting of complex **3a** in combination with TBABr, was shown to be comparable to that of an Al amino-*t*Bu-tris(phenolate) complex in combination with TBAI under identical reaction conditions (Table 2.2).

In order to expand the comparison, we compiled a selection of state-of-the-art binary catalytic systems for the synthesis of cyclic carbonates from CO₂ and epoxides (Table S2.1). For this purpose, we selected metal complexes that are either based on amino-tris(phenolate) ligands but with different metals (Al, Fe), or are based on Ti or Zr centres but with different ligands. It is important to note that these catalytic systems were tested under different conditions from each other and from our work. This means that a quantitative comparison of the catalytic performances is not possible, as this would require the tests to be carried out with the same epoxide substrate and under the same conditions in terms of temperature, CO₂ pressure, catalyst loading and reactor configuration. Still, if the TON and TOF values based on the moles of metal and those based on the moles of halide are considered while taking into account the different reaction conditions (Table S2.1), it can be concluded that the catalytic system based on complex **3a** is competitive with the most active counterparts reported in the literature.^{48,82,83,86,97,102,103}

2.4. Conclusions

In this work, we showed that amino-tris(phenolate)-based complexes incorporating group (IV) metal centres (*i.e.* titanium and zirconium) in combination with tetrabutylammonium halides (*i.e.* iodide, bromide and chloride) are highly active and fully selective binary catalysts for the atom-efficient reaction of CO₂ with terminal epoxides yielding the corresponding cyclic carbonate products. Titanium amino-tris(phenolate) complex **2b**, incorporating an axial chloride ligand, showed the highest catalytic activity among the titanium-based complexes, whereas zirconium amino-tris(phenolate) complex **3a**, bearing an axial isopropoxide ligand, provided the highest overall catalytic activity. The catalytic performance of complex **3a** in combination with TBAI is comparable with that of a state-of-the-art homogeneous catalytic system from the literature (consisting of an Al-amino-tris(phenolate) complex in combination with TBAI), and could be further optimised by using TBABr as nucleophile source. This binary catalytic system (complex **3a**, 0.05 mol% relative to the epoxide, in combination with 0.25 mol% TBABr), achieved remarkably high turnover numbers (up to 2000) when tested at 90 °C, 12 bar CO₂ pressure, 18 h. This catalytic system was highly versatile in the reaction of terminal epoxides with CO₂, achieving quantitative conversion of a variety of terminal

epoxides with different functionalities with full selectivity towards the corresponding cyclic carbonates. The presented results demonstrate the potential of group (IV) metal complexes based on amino-tris(phenolate) ligands as highly active catalysts for the conversion of CO₂ with epoxides into cyclic carbonates.

References

- 1 M. Taherimehr and P. P. Pescarmona, *J. Appl. Polym. Sci.*, 2014, **131**, 41141.
- 2 Q. Liu, L. Wu, R. Jackstell and M. Beller, *Nat. Commun.*, 2015, **6**, 5933.
- 3 S. Dabral, U. Licht, P. Rudolf, G. Bollmann, A. S. K. Hashmi and T. Schaub, *Green Chem.*, 2020, **22**, 1553–1558.
- 4 S. Dabral, B. Bayarmagnai, M. Hermesen, J. Schießl, V. Mormul, A. S. K. Hashmi and T. Schaub, *Org. Lett.*, 2019, **21**, 1422–1425.
- 5 A. Cervantes-Reyes, K. Farshadfar, M. Rudolph, F. Rominger, T. Schaub, A. Ariaferd and A. S. K. Hashmi, *Green Chem.*, 2021, **23**, 889–897.
- 6 C. Johnson, S. Dabral, P. Rudolf, U. Licht, A. S. K. Hashmi and T. Schaub, *ChemCatChem*, 2021, **13**, 353–361.
- 7 N. A. Tappe, R. M. Reich, V. D’Elia and F. E. Kühn, *Dalton Trans.*, 2018, **47**, 13281–13313.
- 8 D. J. Faria, L. M. dos Santos, F. L. Bernard, I. S. Pinto, I. P. Romero, V. V. Chaban and S. Einloft, *J. CO₂ Util.*, 2021, **53**, 101721.
- 9 M. R. Reithofer, Y. N. Sum and Y. Zhang, *Green Chem.*, 2013, **15**, 2086–2090.
- 10 P. K. Sahoo, Y. Zhang and S. Das, *ACS Catal.*, 2021, **11**, 3414–3442.
- 11 S. Das, F. D. Bobbink, G. Laurenczy and P. J. Dyson, *Angew. Chem. Int. Ed.*, 2014, **53**, 12876–12879.
- 12 S. Yoshida, K. Fukui, S. Sikuchi and T. Yamada, *J. Am. Chem. Soc.*, 2010, **132**, 4072–4073.
- 13 P. P. Pescarmona and M. Taherimehr, *Catal. Sci. Technol.*, 2012, **2**, 2169.
- 14 A. J. Kamphuis, F. Picchioni and P. P. Pescarmona, *Green Chem.*, 2019, **21**, 406–448.
- 15 P. P. Pescarmona, *Curr. Opin. Green Sustain. Chem.*, 2021, **29**, 100457.
- 16 K. A. Andrea and F. M. Kerton, *Polym. J.*, 2021, **53**, 29–46.
- 17 C. Claver, M. B. Yeamin, M. Reguero and A. M. Masdeu-Bultó, *Green Chem.*, 2020, **22**, 7665–7706.
- 18 D. Prasad, K. N. Patil, N. K. Chaudhari, H. Kim, B. M. Nagaraja and A. H. Jadhav, *Catal. Rev.*, 2020, 1–88.
- 19 Z. Guo, Q. Jiang, Y. Shi, J. Li, X. Yang, W. Hou, Y. Zhou and J. Wang, *ACS Catal.*, 2017, **7**, 6770–6780.
- 20 J. Li, D. Jia, Z. Guo, Y. Liu, Y. Lyu, Y. Zhou and J. Wang, *Green Chem.*, 2017, **19**, 2675–2686.
- 21 J. Martínez, J. Fernández-Baeza, L. F. Sánchez-Barba, J. A. Castro-Osma, A. Lara-Sánchez and A. Otero, *ChemSusChem*, 2017, **10**, 2886–2890.
- 22 M. Cokoja, M. E. Wilhelm, M. H. Anthofer, W. A. Herrmann and F. E. Kühn, *ChemSusChem*, 2015, **8**, 2436–2454.
- 23 M. O. Vieira, W. F. Monteiro, B. S. Neto, R. Ligabue, V. V. Chaban and S. Einloft, *Catal. Lett.*, 2018, **148**, 108–118.

- 24 S. Klaus, M. W. Lehenmeier, C. E. Anderson and B. Rieger, *Coord. Chem. Rev.*, 2011, **255**, 1460–1479.
- 25 G. W. Coates and D. R. Moore, *Angew. Chem. Int. Ed.*, 2004, **43**, 6618–6639.
- 26 R. R. Shaikh, S. Pornpraprom and V. D’Elia, *ACS Catal.*, 2018, **8**, 419–450.
- 27 V. Caló, A. Nacci, A. Monopoli and A. Fanizzi, *Org. Lett.*, 2002, **4**, 2561–2563.
- 28 M. O. Vieira, W. F. Monteiro, B. S. Neto, V. V. Chaban, R. Ligabue and S. Einloft, *React. Kinet. Mech. Catal.*, 2019, **126**, 987–1001.
- 29 L.-F. Xiao, F.-W. Li, J.-J. Peng and C.-G. Xia, *J. Mol. Catal. Chem.*, 2006, **253**, 265–269.
- 30 K. Okuno, R. Nishiyori, M. Hiraki and S. Shirakawa, *Heterocycles*, 2021, **103**, 94–109.
- 31 L.-X. Wu, H.-P. Yang, Y.-B. Guan, M.-P. Yang, H. Wang and J.-X. Lu, *Int. J. Electrochem. Sci.*, 2017, **12**, 8963–8972.
- 32 K. R. Roshan, T. Jose, A. C. Kathalikkattil, D. W. Kim, B. Kim and D. W. Park, *Appl. Catal. Gen.*, 2013, **467**, 17–25.
- 33 F. D. Bobbink, Z. Fei, R. Scopelliti, S. Das and P. J. Dyson, *Helv. Chim. Acta*, 2016, **99**, 821–829.
- 34 J.-Q. Wang, X.-D. Yue, F. Cai and L.-N. He, *Catal. Commun.*, 2007, **8**, 167–172.
- 35 K. Vierling, DE Pat. 740366 C, 1943.
- 36 M. Lichtenwalter, J. F. Cooper, US Pat. 2773070, 1956.
- 37 K. Xu, *Chem. Rev.*, 2004, **104**, 4303–4418.
- 38 J. R. Machac and E. T. Marquis, WO Pat. 2000050524 A1, 2001.
- 39 S. Fukuoka, M. Kawamura, K. Komiya, M. Tojo, H. Hachiya, K. Hasegawa, M. Aminaka, H. Okamoto, I. Fukawa and S. Konno, *Green Chem.*, 2003, **5**, 497–507.
- 40 L. Maisonneuve, O. Lamarzelle, E. Rix, E. Grau and H. Cramail, *Chem. Rev.*, 2015, **115**, 12407–12439.
- 41 J. Langanke, A. Wolf, J. Hofmann, K. Böhm, M. A. Subhani, T. E. Müller, W. Leitner and C. Gürtler, *Green Chem.*, 2014, **16**, 1865–1870.
- 42 Empower Materials, www.empowermaterials.com, (accessed on August 1, 2017).
- 43 S. D. Allen, EP Pat. 2451860 A2, 2012.
- 44 T. Stößer, C. Li, J. Unruangsri, P. K. Saini, R. J. Sablong, M. A. R. Meier, C. K. Williams and C. Koning, *Polym. Chem.*, 2017, **8**, 6099–6105.
- 45 I. Manavitehrani, A. Fathi, Y. Wang, P. K. Maitz, F. Mirmohseni, T. L. Cheng, L. Peacock, D. G. Little, A. Schindeler and F. Dehghani, *Biomacromolecules*, 2017, **18**, 1736–1746.
- 46 Y. Li, S. Liu, X. Zhao, Y. Wang, J. Liu, X. Wang and L. Lu, *Theranostics*, 2017, **7**, 4689–4698.
- 47 F. Castro-Gómez, G. Salassa, A. W. Kleij and C. Bo, *Chem. - Eur. J.*, 2013, **19**, 6289–6298.
- 48 S. K. Raman, A. C. Deacy, L. Pena Carrodegua, N. V. Reis, R. W. Kerr, A. Phanopoulos, S. Morton, M. G. Davidson and C. K. Williams, *Organometallics*, 2020, **39**, 1619–1627.
- 49 M. R. Kember, A. Buchard and C. K. Williams, *Chem. Commun.*, 2011, **47**, 141–163.
- 50 M. North, R. Pasquale and C. Young, *Green Chem.*, 2010, **12**, 1514.
- 51 C. Martín, G. Fiorani and A. W. Kleij, *ACS Catal.*, 2015, **5**, 1353–1370.
- 52 A. J. Kamphuis, F. Milocco, L. Koiter, P. P. Pescarmona and E. Otten, *ChemSusChem*, 2019, **12**, 3635–3641.
- 53 J. A. Castro-Osma, M. North and X. Wu, *Chem. Eur. J.*, 2014, **20**, 15005–15008.

- 54 Q. Zhang, P. Yu, B. Lei, H.-J. Yang, J. Hu, L. Wang, T. Zhou, Q. Jiang, J. Zhu and B. Han, *Catal. Lett.*, 2020, **150**, 2537–2548.
- 55 D. Tian, B. Liu, Q. Gan, H. Li and D. J. Darensbourg, *ACS Catal.*, 2012, **2**, 2029–2035.
- 56 D. R. Moore, M. Cheng, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2003, **125**, 11911–11924.
- 57 S. Klaus, M. W. Lehenmeier, E. Herdtweck, P. Deglmann, A. K. Ott and B. Rieger, *J. Am. Chem. Soc.*, 2011, **133**, 13151–13161.
- 58 F. Della Monica, A. Buonerba and C. Capacchione, *Adv. Synth. Catal.*, 2019, **361**, 265–282.
- 59 F. Della Monica, S. V. C. Vummaleti, A. Buonerba, A. D. Nisi, M. Monari, S. Milione, A. Grassi, L. Cavallo and C. Capacchione, *Adv. Synth. Catal.*, 2016, **358**, 3231–3243.
- 60 A. Buonerba, A. De Nisi, A. Grassi, S. Milione, C. Capacchione, S. Vagin and B. Rieger, *Catal. Sci. Technol.*, 2015, **5**, 118–123.
- 61 X. Wu, J. A. Castro-Osma and M. North, *Symmetry*, 2016, **8**, 4.
- 62 R. Ma, L.-N. He and Y.-B. Zhou, *Green Chem.*, 2016, **18**, 226–231.
- 63 H. Tanaka, Y. Kitaichi, M. Sato, T. Ikeno and T. Yamada, *Chem. Lett.*, 2004, **33**, 676–677.
- 64 H. Sugimoto and K. Kuroda, *Macromolecules*, 2008, **41**, 312–317.
- 65 T. Ema, Y. Miyazaki, J. Shimonishi, C. Maeda and J. Hasegawa, *J. Am. Chem. Soc.*, 2014, **136**, 15270–15279.
- 66 R. L. Paddock and S. T. Nguyen, *J. Am. Chem. Soc.*, 2001, **123**, 11498–11499.
- 67 D. J. Darensbourg and J. C. Yarbrough, *J. Am. Chem. Soc.*, 2002, **124**, 6335–6342.
- 68 Z. Qin, C. M. Thomas, S. Lee and G. W. Coates, *Angew. Chem. Int. Ed.*, 2003, **42**, 5484–5487.
- 69 A. Decortes, M. Martínez Belmonte, J. Benet-Buchholz and A. W. Kleij, *Chem. Commun.*, 2010, **46**, 4580.
- 70 G. A. Luinstra, G. R. Haas, F. Molnar, V. Bernhart, R. Eberhardt and B. Rieger, *Chem. Eur. J.*, 2005, **11**, 6298–6314.
- 71 C.-X. Miao, J.-Q. Wang, Y. Wu, Y. Du and L.-N. He, *ChemSusChem*, 2008, **1**, 236–241.
- 72 M. R. Kember, P. D. Knight, P. T. R. Reung and C. K. Williams, *Angew. Chem. Int. Ed.*, 2009, **48**, 931–933.
- 73 A. Buchard, M. R. Kember, K. G. Sandeman and C. K. Williams, *Chem. Commun.*, 2011, **47**, 212–214.
- 74 M. R. Kember and C. K. Williams, *J. Am. Chem. Soc.*, 2012, **134**, 15676–15679.
- 75 C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin and A. W. Kleij, *J. Am. Chem. Soc.*, 2013, **135**, 1228–1231.
- 76 C. J. Whiteoak, N. Kielland, V. Laserna, F. Castro-Gómez, E. Martin, E. C. Escudero-Adán, C. Bo and A. W. Kleij, *Chem. Eur. J.*, 2014, **20**, 2264–2275.
- 77 M. Taherimehr, S. M. Al-Amsyar, C. J. Whiteoak, A. W. Kleij and P. P. Pescarmona, *Green Chem.*, 2013, **15**, 3083.
- 78 C. Miceli, J. Rintjema, E. Martin, E. C. Escudero-Adán, C. Zonta, G. Licini and A. W. Kleij, *ACS Catal.*, 2017, **7**, 2367–2373.
- 79 K. A. Andrea, E. D. Butler, T. R. Brown, T. S. Anderson, D. Jagota, C. Rose, E. M. Lee, S. D. Goulding, J. N. Murphy and F. M. Kerton, *Inorg. Chem.*, 2019, **58**, 11231–11240.

- 80 M. Taherimehr, J. P. C. C. Sertã, A. W. Kleij, C. J. Whiteoak and P. P. Pescarmona, *ChemSusChem*, 2015, **8**, 1034–1042.
- 81 H. Plommer, L. Stein, J. N. Murphy, N. Ikpo, N. Mora-Diez and F. M. Kerton, *Dalton Trans.*, 2020, **49**, 6884–6895.
- 82 K. Nakano, K. Kobayashi and K. Nozaki, *J. Am. Chem. Soc.*, 2011, **133**, 10720–10723.
- 83 F. Al-Qaisi, E. Streng, A. Tsarev, M. Nieger and T. Repo, *Eur. J. Inorg. Chem.*, 2015, **2015**, 5363–5367.
- 84 Y. Wang, Y. Qin, X. Wang and F. Wang, *ACS Catal.*, 2015, **5**, 393–396.
- 85 J. Hessequik, R. Lalrempuia, H. Nsiri, K. W. Törnroos, V. R. Jensen and E. Le Roux, *Dalton Trans.*, 2016, **45**, 14734–14744.
- 86 H. Kim, S. H. Choi, D. Ahn, Y. Kim, J. Y. Ryu, J. Lee and Y. Kim, *RSC Adv.*, 2016, **6**, 97800–97807.
- 87 D. Bai, H. Jing, Q. Liu, Q. Zhu and X. Zhao, *Catal. Commun.*, 2009, **11**, 155–157.
- 88 Y. M. Byun, J. M. Lee, J. Y. Ryu, M. J. Go, K. S. Na, Y. Kim and J. Lee, *Polyhedron*, 2018, **141**, 191–197.
- 89 M. J. Go, K. M. Lee, C. H. Oh, Y. Y. Kang, S. H. Kim, H. R. Park, Y. Kim and J. Lee, *Organometallics*, 2013, **32**, 4452–4455.
- 90 S. Kim, D. Sarkar, Y. Kim, M. H. Park, M. Yoon, Y. Kim and M. Kim, *J. Ind. Eng. Chem.*, 2017, **53**, 171–176.
- 91 M. Mandal and D. Chakraborty, *J. Polym. Sci. Part Polym. Chem.*, 2016, **54**, 809–824.
- 92 C. C. Quadri and E. Le Roux, *Dalton Trans.*, 2014, **43**, 4242–4246.
- 93 Y. Wang, Y. Qin, X. Wang and F. Wang, *Catal. Sci. Technol.*, 2014, **4**, 3964–3972.
- 94 J. A. Garden, A. J. P. White and C. K. Williams, *Dalton Trans.*, 2017, **46**, 2532–2541.
- 95 M. Mandal, *J. Organomet. Chem.*, 2020, **907**, 121067.
- 96 H.-J. Chuang and B.-T. Ko, *Dalton Trans.*, 2015, **44**, 598–607.
- 97 R. Lalrempuia, F. Breivik, K. W. Törnroos and E. Le Roux, *Dalton Trans.*, 2017, **46**, 8065–8076.
- 98 M. Kol, M. Shamis, I. Goldberg, Z. Goldschmidt, S. Alfi and E. Hayut-Salant, *Inorg. Chem. Commun.*, 2001, **4**, 177–179.
- 99 D. Lionetti, A. J. Medvecz, V. Ugrinova, M. Quiroz-Guzman, B. C. Noll and S. N. Brown, *Inorg. Chem.*, 2010, **49**, 4687–4697.
- 100 M. G. Davidson, C. L. Doherty, A. L. Johnson and M. F. Mahon, *Chem. Commun.*, 2003, 1832–1833.
- 101 Donald. J. Darensbourg, J. C. Yarbrough, C. Ortiz and C. C. Fang, *J. Am. Chem. Soc.*, 2003, **125**, 7586–7591.
- 102 M. Mandal, U. Monkowius and D. Chakraborty, *New J. Chem.*, 2016, **40**, 9824–9839.
- 103 J. Fernández-Baeza, L. F. Sánchez-Barba, A. Lara-Sánchez, S. Sobrino, J. Martínez-Ferrer, A. Garcés, M. Navarro and A. M. Rodríguez, *Inorg. Chem.*, 2020, **59**, 12422–12430.

Supplementary Information

Appendix A: ¹H NMR and ¹³C NMR spectra of amino-tBu-tris(phenolate) (1)

Fig. S2.1. ¹H NMR spectrum of amino-tBu-tris(phenolate) (1).

Fig. S2.2. ¹³C NMR spectrum of amino-tBu-tris(phenolate) (1).

Appendix B: ^1H NMR and ^{13}C NMR spectra of titanium (IV) amino-*t*Bu-tris(phenolate) isopropoxide (2a)

Appendix C: ¹H NMR and ¹³C NMR spectra of titanium (IV) amino-*t*Bu-tris(phenolate) chloride (2b)

Fig. S2.5. ¹H NMR spectrum of titanium (IV) amino-*t*Bu-tris(phenolate) chloride (2b).

Fig. S2.6. ¹³C NMR spectrum of titanium (IV) amino-*t*Bu-tris(phenolate) chloride (2b).

Appendix D: ^1H NMR and ^{13}C NMR spectra of zirconium (IV) amino-*t*Bu-tris(phenolate) isopropoxide (**3a**)

Fig. S2.7. ^1H NMR spectrum of zirconium (IV) amino-*t*Bu-tris(phenolate) isopropoxide (**3a**).

Fig. S2.8. ^{13}C NMR spectrum of zirconium (IV) amino-*t*Bu-tris(phenolate) isopropoxide (**3a**).

Appendix E: ¹H NMR and ¹³C NMR spectra of zirconium (IV) amino-*t*Bu-tris(phenolate) chloride (3b)

Fig. S2.9. ¹H NMR spectrum of zirconium(IV) amino-*t*Bu-tris(phenolate) chloride (3b).

Fig. S2.10. ¹³C NMR spectrum of zirconium(IV) amino-*t*Bu-tris(phenolate) chloride (3b).

Appendix F: Representative ^1H NMR spectrum of the reaction mixture after a catalytic test **Fig. S2.11.** ^1H NMR spectrum of the reaction of CO_2 with 1,2-epoxyhexane catalysed by **3a**/TBACl.

Appendix H: FTIR spectra of the reaction mixture after selected catalytic tests

Fig. S2.12. FTIR spectrum of the reaction of CO₂ with cyclohexene oxide catalysed by **3a**/TBABr.

Fig. S2.13. FTIR spectrum of the reaction of CO₂ with vinylcyclohexene oxide catalysed by **3a**/TBABr.

Appendix G: Synthesis of aluminum (III) amino-tBu-tris(phenolate) catalyst

Nitrogen gas ($\geq 99.999\%$, Linde Gas) was used as received. Dry tetrahydrofuran was obtained by percolating tetrahydrofuran (anhydrous, 99.8%, Sigma-Aldrich) over Al_2O_3 columns (Fluka). The dry tetrahydrofuran was subsequently stored under nitrogen. Trimethylaluminium (2.0 M in heptane, Sigma-Aldrich) and hexane ($\geq 95.0\%$, Macron) were used as received.

Fig. S2.14. Synthesis of aluminium (III) amino-tBu-tris(phenolate) catalyst.

The synthesis of the aluminium complex was performed analogues to literature (Fig. S2.14).¹ The amino-tBu-tris(phenolate) ligand precursor was brought under N_2 -atmosphere in a three-neck round-bottom flask and dissolved in 20 mL dry THF. Trimethylaluminium (2.0 M in heptane, 0.75 mL, 1.49 mmol) was added dropwise using a syringe, the resulting solution was stirred for 2 h at RT. Subsequently, the mixture was concentrated and the product was purified by recrystallisation in THF. The resulting crystals were filtered and washed with hexane. The product was then dried under vacuum at 50 °C for 48 h to yield a white powder.

^1H NMR (400 MHz, CDCl_3): δ 7.21 (d, 3H, ArH), 6.85 (d, 3H, ArH), 4.27 (d, 3H, ArCH_2N), 3.89 (br, 4H, THF), 2.92 (d, 3H, ArCH_2N), 1.91 (br, 4H, THF), 1.40 (s, 27H, tBu), 1.26 (s, 27H, tBu). ^{13}C NMR (300 MHz, CDCl_3): δ 154.9, 139.3, 137.1, 123.9, 123.7, 121.5, 68.4, 59.2, 35.0, 34.2, 31.9, 29.7, 25.7.

Appendix I: Table S2.1 (Catalytic performance of selected metal complexes)

Table S2.1. Overview of state-of-the-art binary catalytic systems (metal complex and organic halide) for the reaction of CO₂ with epoxides to form cyclic carbonates.

#	Metal complex (mol% loading) ^a	Epoxide ^b	Nucleophile source (mol% loading) ^a	Cyclic carbonate yield (%)	TON _{metal} ^c	TOF _{metal} (h ⁻¹) ^d	TON _{halide} ^e	TOF _{halide} (h ⁻¹) ^f	Temp. (°C)	Pressure (bar CO ₂)	Ref.
1	Ti(Cl) amino-tris(phenolate) (0.025)	EH	TBACl (0.25)	27	1080	540	108	54	90	12	This work
2	[Ti(L4)(O ⁱ Pr) ₂] (1)	EH	TBABr (1)	68	68	14	68	14	100	15	2
3	Ti 2-tridentate aminopyridine (0.2)	PO	TBAI (0.2)	95	470	20	470	20	75	10	3
4	Zr(O ⁱ Pr) amino-tris(phenolate) (0.025)	EH	TBABr (0.25)	48	1920	960	192	96	90	12	This work
5	(BOXDIPY)ZrCl (0.05)	PO	PPNCl (0.05)	21	420	35	420	35	60	20	4
6	Zr(NMe ₂) ₃ (K ³ -NNC) (0.25)	SO	TBABr (0.25)	72	288	96	288	96	80	10	5
7	Al amino-tris(phenolate) (0.0005)	EH	PPNBr (0.05)	36	72000	36000	720	360	90	10	6
8	Al amino-tris(phenolate) (0.05)	EH	TBAI (0.25)	96	1920	960	384	192	90	10	6
9	Fe amino-tris(phenolate) (0.25)	EB	TBABr (4.0)	72	288	16	18	1	80	10	7
10	Fe amino-tris(phenolate) (0.5)	EH	TBAI (5.0)	96	192	11	19	1	25	2	8

^a Loading relative to the epoxide. ^b EH = 1,2-epoxyhexane, PO = propylene oxide, SO = styrene oxide, EB = 1,2-epoxybutane. ^c TON_{metal} = turnover number, expressed as mol of converted epoxide per mol of metal. ^d TOF_{metal} = turnover frequency, expressed as mol of converted epoxide per mol of metal per hour. ^e TON_{halide} = turnover number, expressed as mol of converted epoxide per mol of halide. ^f TOF_{halide} = turnover frequency, expressed as mol of converted epoxide per mol of halide per hour. All the catalytic systems reported in this table displayed complete selectivity towards the cyclic carbonate product.

1. C. J. Whiteoak, N. Kielland, V. Laserna, F. Castro-Gómez, E. Martín, E. C. Escudero-Adán, C. Bo, A. W. Kleij, Highly Active Aluminium Catalysts for the Formation of Organic Carbonates from CO₂ and Oxiranes, *Chem. Eur. J.* 20 (2014) 2264–2275.

2. F. Al-Qaisi, E. Streng, A. Tsarev, M. Nieger, T. Repo, Titanium Alkoxide Complexes as Catalysts for the Synthesis of Cyclic Carbonates from Carbon Dioxide and Epoxides, *Eur. J. Inorg. Chem.* (2015) 5363–5367.
3. H. Kim, S. H. Choi, D. Ahn, Y. Kim, J. Y. Ryu, J. Lee, Y. Kim, Facile synthesis of a dimeric titanium(IV) complex with terminal Ti=O moieties and its application as a catalyst for the cycloaddition reaction of CO₂ to epoxides, *RSC Adv.* 6 (2016) 97800–97807.
4. K. Nakano, K. Kobayashi, K. Nozaki, Tetravalent Metal Complexes as a New Family of Catalysts for Copolymerisation of Epoxides with Carbon Dioxide, *J. Am. Chem. Soc.* 133 (2011) 10720–10723.
5. J. Fernández-Baeza, L. F. Sánchez-Barba, A. Lara-Sánchez, S. Sobrino, J. Martínez-Ferrer, A. Garcés, M. Navarro, A. M. Rodríguez, NNC-Scorpionate Zirconium-Based Bicomponent Systems for the Efficient CO₂ Fixation into a Variety of Cyclic Carbonates, *Inorg. Chem.* 59 (2020) 12422–12430.
6. C. J. Whiteoak, N. Kielland, V. Laserna, E. C. Escudero-Adán, E. Martin, A. W. Kleij, A Powerful Aluminum Catalyst for the Synthesis of Highly Functional Organic Carbonates, *J. Am. Chem. Soc.* 135 (2013) 1228–1231.
7. C. J. Whiteoak, E. Martin, E. Escudero-Adán, A. W. Kleij, Stereochemical Divergence in the Formation of Organic Carbonates Derived from Internal Epoxides, *Adv. Synth. Catal.* 355 (2013) 2233–2239.
8. C. J. Whiteoak, E. Martin, M. M. Belmonte, J. Benet-Buchholz, A. W. Kleij, An Efficient Iron Catalyst for the Synthesis of Five- and Six-Membered Organic Carbonates under Mild Conditions, *Adv. Synth. Catal.* 354 (2012) 469–476.

Chapter 3: Highly selective single-component formazanate ferrate(II) catalysts for the conversion of CO₂ into cyclic carbonates

The development of new families of active and selective single-component catalysts based on earth-abundant metal is of interest from a sustainable chemistry perspective. In this context, we report anionic mono(formazanate) iron(II) complexes bearing labile halide ligands, which possess both Lewis acidic and nucleophilic functionalities, as novel single-component homogeneous catalysts for the reaction of CO₂ with epoxides to produce cyclic carbonates. The influence of the halide ligand and the electronic properties of the formazanate ligand backbone on the catalytic activity were investigated by employing complexes **1-3** with and without an additional nucleophile. Very high selectivity was achieved towards the formation of the cyclic carbonate product for various terminal and internal epoxides without the need of a co-catalyst.

This chapter has been published:

A. J. Kamphuis, F. Milocco, L. Koiter, P.P. Pescarmona and E. Otten, *ChemSusChem*, 2019, 12, 3635, DOI: 10.1002/cssc.201900740.

F. Milocco, **2021**, *A journey into the coordination chemistry, reactivity and catalysis of iron and palladium formazanate complexes*, University of Groningen, DOI: 10.33612/diss.160960083.

All authors contributed to this work equally.

3.1. Introduction

The use of carbon dioxide as a C₁-feedstock to produce useful chemicals is highly desirable due to its low cost and its non-toxic and non-flammable nature.¹ One of the biggest challenges associated with the use of CO₂ as a chemical building block is to overcome its high thermodynamic stability. This can be achieved by reacting CO₂ with compounds that are sufficiently high in free energy to result in exergonic reactions. Examples thereof include the hydrogenation of CO₂ to formic acid or methanol,^{1c,2} and the 100% atom-efficient reaction of CO₂ with epoxides to produce cyclic carbonates (CCs) and/or polycarbonates (PCs, Fig. 3.1).³

Both products are relevant for a number of applications.⁴ In particular, CCs are used as green solvents, in electrolytes for Li-ion batteries, and as greener alternatives to toxic reagents such as phosgene.⁵ Another crucial challenge in the fixation of carbon dioxide into CCs and PCs is the development of suitable catalysts, with the purpose of reaching high conversion rates of epoxides and to control the reaction selectivity so that only one of the two products is obtained,³ thus minimising separation costs. Among the many classes of homogeneous and heterogeneous catalysts that have been studied for the reaction of CO₂ with epoxides,^{3,4,6} the binary catalyst systems involving a Lewis acid (e.g. a metal centre) and a nucleophile (e.g. a halide) generally achieve the highest activity and selectivity.⁷ Several metal complexes have been developed, especially based on Al,⁸ Zn,⁹ Co,¹⁰ Cr.¹¹ Recently, growing attention has been dedicated to Fe catalysts.^{12, 13} The use of the latter metal is very attractive due to its abundance, low cost and relatively low toxicity.¹⁴ The Lewis acid centre and the nucleophilic species can be provided by two distinct components (e.g. a metal complex and an organic halide) or be incorporated in a single compound (i.e. a bifunctional catalyst). Examples of bifunctional iron-based catalysts include complexes based on Fe(II)^{13e,15} or Fe(III)^{13a-c,13f,16} with multidentate ligands containing N and/or O donor atoms. A limitation of these systems is that, particularly in the case of conversion of internal epoxides, an additional nucleophilic co-catalyst is typically required to achieve high activity and/or selectivity towards the cyclic carbonate product.

Here, we report for the first time the use of Fe(II) formazanate complexes as active and selective single-component homogeneous catalysts for the selective conversion of CO₂ and epoxides into the corresponding cyclic carbonates. In contrast to β -diketiminates, which have been widely used as ligands in metal complexes with application as homogeneous catalysts,¹⁷ the structurally related formazanates ligands (based on a NNCNN backbone) are much less explored.¹⁸ Recently, some of

Fig. 3.1. Catalysed reaction of CO₂ with epoxides.

us¹⁹ and Holland et al.²⁰ reported formazanate iron complexes, including a stoichiometric reaction with CO₂ to give isocyanate,²¹ but the application of formazanate iron complexes in catalysis has, to the best of our knowledge, not been described so far.

3.2. Experimental Section

3.2.1. General Considerations

The synthesis of the complexes was carried out under nitrogen using standard glovebox, Schlenk, and vacuum-line techniques. THF (Aldrich, anhydrous, 99.8%) was dried by percolation over columns of Al₂O₃ (Fluka); toluene and hexane (Aldrich, anhydrous, 99.8%) were passed over columns of Al₂O₃ (Fluka), BASF R3-11-supported Cu oxygen scavenger, and molecular sieves (Aldrich, 4 Å). THF-*d*₈ (Euriso-top) was vacuum transferred from Na/K alloy and stored under nitrogen. The compounds **1H**,²⁸ **3H**,²⁹ PhNNC(C₆F₅)H³⁰ and FeBr₂(THF)₂³¹ were synthesised according to literature procedures. Ligand **2H** was prepared according to a slightly-adapted version of a literature method³² (see SI for the detailed description). Aniline (Sigma-Aldrich, 99%), hydrochloric acid (Boom B.V., 37-38%), glacial acetic acid (Imsure, 100%), sodium hydroxide (pellets, Acros), sodium nitrite (Sigma-Aldrich), acetone (Boom B.V., technical grade), methanol (Boom B.V., technical grade), hexane (Boom B.V., technical grade), CDCl₃ (Euriso-top), tetrabutylammonium bromide (Sigma-Aldrich, 99%), tetrabutylammonium chloride (Sigma-Aldrich, 99%), tetrabutylammonium iodide (Sigma-Aldrich, 98%), FeI₂ (Alfa Aesar, anhydrous, 97%), potassium bis(trimethylsilyl)amide (Sigma-Aldrich, 95%) were used as received. KH (Sigma-Aldrich, 30 wt% dispersion in mineral oil) was washed several times with hexane to free them from the mineral oil and subsequently dried in vacuo to obtain a fine powder.

NMR spectra were recorded on a Varian Oxford 300 MHz, Varian Mercury 400 MHz, Inova 500 MHz, or Bruker 600 MHz spectrometer. The ¹H and ¹³C NMR spectra were referenced internally using the residual solvent resonances and reported in ppm relative to TMS (0 ppm). FTIR spectra were recorded using a Shimadzu IR tracer-100 equipped with an ATR sample unit with a frequency range of 4000-600 cm⁻¹, a

resolution of 4 cm^{-1} and 64 scans. Cyclic Voltammetry was performed using a three-electrode setup with a silver wire pseudo-reference electrode and a platinum disk working electrode (CHI102, CH Instruments; diameter = 2 mm). The platinum working electrode was polished before the experiment using an alumina slurry ($0.05\text{ }\mu\text{m}$), rinsed with distilled water, and subjected to brief ultrasonication to remove any adhered alumina microparticles. The electrodes were then dried in an oven at $+75\text{ }^{\circ}\text{C}$ overnight to remove any residual traces of water. The CV data were calibrated by adding decamethylferrocene as a THF solution at the end of the experiments. There is no indication that the addition of decamethylferrocene influences the electrochemical behaviour of the products. All electrochemical measurements were performed at ambient temperatures under an inert N_2 atmosphere in THF containing $0.1\text{ M Bu}_4\text{NPF}_6$ as the supporting electrolyte. Data were recorded with *Autolab NOVA* software (version 2.1-2). UV-vis spectra were recorded in a THF solution ($\sim 10^{-5}\text{ M}$) using an Agilent Cary 8454 UV-Visible spectrophotometer.

3.2.2. Synthesis of the iron complexes

3.2.2.1. $\text{Bu}_4\text{N}(\text{PhNNC}(p\text{-tol})\text{NNPh})\text{FeCl}_2\text{ (1Cl)}$

To a solution of **1H** (276.3 mg, 1.0 eq, 0.88 mmol) in 20 mL of THF, tetrabutylammonium chloride (244.3 mg, 1.0 eq, 0.88 mmol), potassium bis(trimethylsilyl)amide (203.0 mg, 1.1 eq, 0.97 mmol) and FeCl_2 (111.4 mg, 1.0 eq, 0.88 mmol) were added as a solid. The dark purple mixture was stirred for 3 days after which the volatiles were removed *in vacuo*. The product was extracted in THF ($2 \times 6\text{ mL}$) and slow diffusion of hexane into the THF solution afforded dark purple crystals which were filtered and washed with toluene and hexane giving **1Br** as product (473.8 mg, 0.69 mmol, 79% yield). The ^1H NMR spectrum was in agreement with the literature.^{19b}

3.2.2.2. $\text{Bu}_4\text{N}(\text{PhNNC}(p\text{-tol})\text{NNPh})\text{FeBr}_2\text{ (1Br)}$

To a solution of **1H** (572.2 mg, 1.0 eq, 1.82 mmol) in 25 mL of THF, tetrabutylammonium bromide (586.7 mg, 1.0 eq, 1.82 mmol), potassium hydride (89.0 mg, 1.2 eq, 2.20 mmol) and $\text{FeBr}_2 \cdot (\text{THF})_2$ (655.0 mg, 1.0 eq, 1.82 mmol) were added as a solid. The dark purple mixture was stirred for 3 days after which the volatiles were removed *in vacuo*. The product was extracted in THF ($2 \times 25\text{ mL}$) and slow diffusion of hexane into the THF solution afforded dark purple crystals which were filtered and washed with toluene and hexane giving **1Br** as product (1024.2 mg, 1.33 mmol, 73% yield). The ^1H NMR spectrum was in agreement with the literature.^{19b}

3.2.2.3. *Bu₄N(PhNNC(*p*-tol)NNPh)FeI₂ (1I)*³³

To a solution of **1H** (565.9 mg, 1.0 eq, 1.80 mmol) in 25 mL of THF, tetrabutylammonium iodide (664.7 mg, 1.0 eq, 1.80 mmol), potassium hydride (87.4 mg, 1.2 eq, 2.20 mmol) and FeI₂ (556.1 mg, 1.0 eq, 1.80 mmol) were added as a solid. After stirring at r.t. for 1 day the volatiles were removed *in vacuo*. The product was extracted in THF (2 x 20 mL) and slow diffusion of hexane into the THF solution afforded a dark purple powder which was filtered and washed with toluene and hexane giving **1I** as product (826.6 mg, 1.14 mmol, 63% yield). ¹H NMR (400 MHz, THF-*d*₈, 25°C): δ = 36.34 (3H, *p*-tol CH₃), 30.07 (4H, Ph *m*-CH), 25.15 (2H, *p*-tol *m*-CH), 2.73 (8H, NBu₄⁺, CH₂), 2.47 (8H, NBu₄⁺, CH₂), 1.37 (8H, NBu₄⁺, CH₂), 0.83 (12H, NBu₄⁺, CH₃), -8.79 (2H, Ph *p*-CH), -9.42 (2H, *p*-tol *o*-CH), -24.49 (4H, Ph *o*-CH) ppm. Anal. Calcd. for C₃₅H₄₆N₅I₂Fe: C 49.96, H 6.17, N 8.09; found: C 50.58, H 6.81, N 7.13.

3.2.2.4. *Bu₄N(PhNNC(C₆F₅)NNPh)FeBr₂ (2Br)*

To a solution of **2H** (858.7 mg, 1.0 eq, 2.20 mmol) in 30 mL of THF, tetrabutylammonium bromide (695.0 mg, 0.98 eq, 2.16 mmol), potassium bis(trimethylsilyl)amide (478.8 mg, 1.1 eq, 2.40 mmol) and FeBr₂·(THF)₂ (791.7 mg, 1.0 eq, 2.20 mmol) were added as a solid. The reaction mixture was stirred for 3 days after which the volatiles were removed *in vacuo*. The product was washed with toluene (20 mL) and subsequently extracted in THF (2 x 15 mL) and slow diffusion of hexane into the orange-brown THF solution at r.t. afforded dark brown solid which was filtered and washed with toluene and hexane giving **2Br** as product (1266.0 mg, 1.49 mmol, 69% yield). ¹H NMR (400 MHz, THF-*d*₈, 25°C): δ = 23.76 (4H, Ph *m*-CH), 4.44 (8H, NBu₄⁺, CH₂), 2.95 (8H, NBu₄⁺, CH₂), 2.19 (8H, NBu₄⁺, CH₂), 1.31 (12H, NBu₄⁺, CH₃), -5.54 (2H, Ph *p*-CH), -16.70 (br, 4H, Ph *o*-CH) ppm. ¹⁹F-NMR (376 MHz, THF-*d*₈, 25°C): δ = -125.12 (1F, C₆F₅ *p*-CF), -130.24 (2F, C₆F₅ CF), -157.72 (2F, C₆F₅ CF) ppm. Anal. Calcd. for C₃₅H₄₆N₅Br₂Fe: C 49.61, H 5.47, N 8.26; found: C 49.36, H 5.53, N 7.86.

3.2.2.5. *Bu₄N(PhNNC(C₆F₅)NNPh)FeI₂ (2I)*

To a solution of **2H** (267.4 mg, 1.0 eq, 0.69 mmol) in 15 mL of THF, tetrabutylammonium iodide (253.0 mg, 1.0 eq, 0.69 mmol), potassium bis(trimethylsilyl)amide (158.2 mg, 1.1 eq, 0.75 mmol) and FeI₂ (218.7 mg, 1.0 eq, 0.69 mmol) were added as a solid. After stirring the reaction mixture for 3 days, the volatiles were removed *in vacuo*. The product was washed with hexane and toluene and subsequently extracted in THF. Slow diffusion of hexane into the orange-brown THF solution at r.t. afforded dark brown solid which was filtered and washed with toluene and hexane giving **2I** as product (393.4 mg, 0.42 mmol, 61% yield). ¹H NMR

(400 MHz, THF-*d*₈, 25 °C): δ = 27.98 (4H, Ph *m*-CH), 2.26 (8H, NBu₄⁺, CH₂), 1.94 (8H, NBu₄⁺, CH₂), 1.72 (8H, NBu₄⁺, CH₂), 1.22 (12H, NBu₄⁺, CH₃), -5.02 (2H, Ph *p*-CH) ppm.*
¹⁹F-NMR (376 MHz, THF-*d*₈, 25 °C): δ = -123.58 (1F, C₆F₅ *p*-CF), -128.89 (2F, C₆F₅ CF), -158.55 (2F, C₆F₅ CF) ppm. Anal. Calcd. for C₃₅H₄₆N₅l₂Fe: C 44.65, H 4.93, N 7.44; found: C 44.42, H 4.88, N 7.39. *The peak of Ph *o*-CH is not visible due to paramagnetic line broadening.

3.2.2.6. Bu₄N(PhNNC(C₆H₄(*p*-OMe))NNPh)FeBr₂ (3Br)

To a solution of **3H** (660.8 mg, 1.0 eq, 2.00 mmol) in 30 mL of THF, tetrabutylammonium bromide (644.7 mg, 1.0 eq, 2.00 mmol), potassium bis(trimethylsilyl)amide (462.0 mg, 1.1 eq, 2.20 mmol) and FeBr₂·(THF)₂ (719.7 mg, 1.0 eq, 2.00 mmol) were added as a solid. The reaction mixture was stirred for 3 days after which the volatiles were removed *in vacuo*. The product was extracted in THF (2 x 20 mL) and slow diffusion of hexane into the fuchsia THF solution at r.t. afforded dark purple solid which was filtered and washed with toluene and hexane giving **3Br** as product (1342.9 mg, 1.71 mmol, 85% yield). ¹H NMR (400 MHz, THF-*d*₈, 25 °C): δ 26.24 (4H, Ph *m*-CH), 24.11 (2H, C₆H₄OCH₃ *m*-CH), 9.38 (3H, C₆H₄OCH₃ *p*-OCH₃), 2.82 (8H, NBu₄⁺ CH₂), 1.30-2.00 (16H, NBu₄⁺ CH₂), 0.91 (12H, NBu₄⁺ CH₃), -7.27 (2H, C₆H₄OCH₃ *o*-CH), -8.93 (2H, Ph *p*-CH), -19.76 (br, 4H, Ph *o*-CH) ppm. Anal. Calcd for C₃₆H₅₃N₅OBr₂Fe: C 54.91, H 6.79, N 8.89; found: C 54.79, H 6.43, N 8.61.

3.2.3. Catalytic tests

The catalytic experiments were conducted in a high-throughput CO₂ reactor unit, constructed by ILS-Integrated Lab Solutions GmbH. This CO₂ reactor unit consists of: (a) a 10-reactors block that allows performing 10 reactions simultaneously in individually-stirred batch reactors in separate batch reactors (84 mL volume each, 30 mm internal diameter); and (b) a single batch reactor with the same dimensions and equipped with a borosilicate glass window to allow visualisation of the phase behaviour within the reactor. The unit can operate in a temperature range of 20-200 °C and a pressure range of 1-200 bar. For each test, 30.0 mmol epoxide, 3.0 mmol mesitylene as internal standard and the appropriate amounts of catalyst and co-catalyst (when used) were weighed into a glass vial (46 mL volume, 30 mm external diameter) equipped with a magnetic stirring bar and a screw cap containing a silicone/PTFE septum. The glass vials were then transferred into the 10-reactors block and each septum was pierced with two thin syringe needles to allow gas to flow in and out of the vials. The reactors block was subsequently closed. The parallel batch reactors were first purged 3 times with 5 bar N₂, after which they were

pressurised to 10 bar CO₂. 10 min were waited before depressurising the reactors to atmospheric pressure in order to prevent damage to the Viton O-rings. After reaching atmospheric pressure, another 10 min were waited. Next, the reactors were pressurised with 10 bar CO₂. After reaching this pressure, the reactors block was heated to 90 °C, which resulted in a final pressure of approximately 12 bar in each batch reactor. The process of purging, pressurising and heating the reactors block took approximately 1 h. The start of the reaction was defined as the moment at which the magnetic stirring was switched on, after reaching the desired reaction temperature and pressure. The reactions were carried out at 900 rpm stirring speed for either 2 or 18 h. At the end of the reaction, the magnetic stirring and the reactor heating were switched off and the water cooling system was turned on to cool down the reactors block. Upon reaching room temperature, the reactors were depressurised. The process of cooling down and depressurising the reactors block took approximately 45 min. After reaching atmospheric pressure, the reactors block was opened and the vials were removed. Small aliquots of each sample were used for ¹H NMR and FTIR analyses.

The recycling tests were conducted in the visualisation reactor of the high-throughput CO₂ reactor unit at 90 °C, 12 bar CO₂ pressure, 2 h, following the same catalytic testing procedure reported above. 1,2-Epoxyhexane and mesitylene were previously dried on molecular sieves and degassed under N₂. For the first run, 30.0 mmol epoxide, 3.0 mmol mesitylene as internal standard and 1.0 mol% of **1Br** relative to the epoxide were employed. After the reaction, cold Et₂O and hexane (in ratio 4:1) were added under N₂. The fuchsia-coloured mixture was stirred until a precipitate formed. Then, the stirring was stopped and the supernatant was decanted. The obtained solid was washed with cold Et₂O and dried obtaining a dark-purple solid, which was directly used in the second catalytic run without any further purification. For the second run, 30.0 mmol epoxide and 3.0 mmol mesitylene were added to the recovered catalyst and the recycling test was carried out under the same conditions as in the first run.

The description of the synthesis of ligand **2H**, the characterisation of the complexes and the ¹H NMR and FTIR spectra used to quantify the conversions and yields of the catalytic tests are provided in the Supporting Information (SI).

3.3. Results and Discussion

The mono(formazanate) ferrate(II) dihalide catalysts, (PhNNC(Ar)NNPh)FeX₂ (Ar = C₆H₄(*p*-Me) (**1**), C₆F₅ (**2**), C₆H₄(*p*-OMe) (**3**); X = Cl, Br, I) were synthesised via a modified procedure of a route previously reported by some of us.^{19b} This new

Fig. 3.2. Synthesis of compounds **1-3**.

procedure uses a one-pot approach that circumvents the isolation of formazanate alkali metal salts, thus allowing to use ligand substitution patterns that would otherwise lead to decomposition (for example, C_6F_5 -substituents engage in nucleophilic aromatic substitution).²² Thus, simply mixing the formazans **1H-3H** with a tetrabutylammonium halide, a base ($\text{KN}(\text{SiMe}_3)_2$) and FeX_2 in THF under inert atmosphere allowed isolation of compounds **1-3** in good yield (60-85%) (Fig. 3.2). Single-crystal X-ray diffraction of the new compounds **2Br/I** and **3Br** (Fig. S3.1) showed geometries close to tetrahedral (τ^4 in the range of 0.91-0.93), similar to those of the previously reported **1Cl/Br** (τ^4 ²³ = 0.89-0.90).^{19b} The Fe-N bond lengths of **2Br/I** and **3Br** (see Table S3.2) are comparable with those of **1Cl/Br**, in agreement with a Fe(II) high-spin ($S = 2$). Compounds **1-3** were characterised in THF- d_8 solution via ^1H and ^{19}F NMR spectra (see SI), which show broad paramagnetically shifted peaks, the number of which is consistent with C_{2v} symmetry. The electrochemical behaviour of compounds **2Br** and **3Br** was studied by cyclic voltammetry in THF solution (0.1 M Bu_4NPF_6 electrolyte, see SI). An anodic scan of **3Br** shows an irreversible oxidation at a peak potential of +0.04 V vs $\text{Fc}^{0/+}$, which is attributed to the $\text{Fe}^{\text{II/III}}$ redox couple in analogy to what has been observed previously for **1Br** ($E_{\text{p,a}} = +0.05$ V vs $\text{Fc}^{0/+}$).^{19b} A second oxidation is observed at +0.42 V vs $\text{Fc}^{0/+}$, which is likely due to bromide oxidation.²⁴ The cyclic voltammogram of the C_6F_5 -substituted complex **2Br** shows an $\text{Fe}^{\text{II/III}}$ couple that is shifted to higher potential by more than 100 mV ($E_{\text{p,a}} = +0.16$ V vs $\text{Fc}^{0/+}$). The iron oxidation potential can be used as an indication of the Lewis acidity of the complex, suggesting that the Fe-centre in **2Br** is a stronger Lewis acid compared to the corresponding sites in **1Br** and **3Br**, as expected when an electron withdrawing group is introduced in the ligand backbone.

The halides in **1Br** were shown to be labile and can be replaced by 4 eq. of 4-methoxyphenyl isocyanide to give the octahedral cationic complex $\text{LFe}(\text{CNC}_6\text{H}_4(p\text{-OMe}))_4\text{Br}$.^{19b} This feature is promising for the application of this class of complexes

as catalysts for the reaction of CO₂ with epoxides. In this context, the ability of these iron formazanates to activate epoxides was investigated by performing an in situ NMR study. Treatment of a THF-*d*₈ solution of **1Br** with successive amounts of 1,2-epoxyhexane (1 to 25 eq.) led to a slight shift in the ¹H NMR spectrum of the signals of the formazanate moiety (Fig. S3.8), while the resonances of the epoxide were hardly affected (Fig. S3.9). Although the changes are relatively minor, we interpret them as indication of an equilibrium involving the exchange of bromide with epoxide, albeit shifted towards the starting materials. A similar experiment with pyridine, which is a stronger Lewis base than epoxyhexane, indeed resulted in extensive broadening of the pyridine resonances when 1 eq. was used, while the peaks sharpen when 25 eq. were added (Fig. S3.10-3.11). These data are consistent with the notion that bromide exchange in **1Br** is facile, but the extent of bromide displacement depends on the nature of the added base. Addition of CO₂ (1 bar) to the NMR tube containing **1Br** and epoxyhexane (25 eq.) produced a small amount of cyclic carbonate after standing at room temperature for 2 h. Warming up to 60 °C overnight led to complete conversion of CO₂ (based on ¹³C NMR), together with an increase of the amount of cyclic carbonate (Fig. 3.3).

Fig. 3.3. ¹H NMR spectrum of **1Br** + 1,2-epoxyhexane (25 eq) + CO₂ (1 bar) (THF-*d*₈, 400 MHz, 25 °C), selected peaks.

Encouraged by these initial studies, complexes **1Cl/Br/I** were evaluated as catalysts for the reaction of CO₂ with 1,2-epoxyhexane in solvent-free conditions at 90 °C, 12 bar CO₂. The experiments were run using 0.25 mol% of Fe complex, both with and without the corresponding tetrabutylammonium halide as co-catalyst (Table 3.1, entries 1-6). Notably, all three formazanate complexes (**1Cl/Br/I**) are active without requiring the addition of a co-catalyst (Table 3.1, entries 1, 3 and 5). This demonstrates that a halide ligand in these ferrate(II) complexes is sufficiently labile to act as nucleophile causing ring-opening of the epoxide, resulting in a bifunctional

Table 3.1. Reaction of 1,2-epoxyhexane with CO₂ catalysed by Fe(II) formazanate complexes (**1-3**).

#	Catalyst	Co-catalyst	Conv. (%) ^a	TON ^b
1	1Cl	-	12	48
2	1Cl	Bu ₄ NCl	19	76
3	1Br	-	36	144
4	1Br	Bu ₄ NBr	50	200
5	1I	-	21	84
6	1I	Bu ₄ NI	28	112
7	2Br	-	24	96
8	2Br	Bu ₄ NBr	41	164
9	2I	-	24	96
10	3Br	-	28	112
11	3Br	Bu ₄ NBr	39	156
12 ^c	1Br	-	47	188
13 ^c	1Br	Bu ₄ NBr	61	244
14 ^{c,d}	1Br	-	>99	100
15 ^{c,e}	1Br^e	-	69	-
16	-	Bu ₄ NCl	3	-
17	-	Bu ₄ NBr	4	-
18	-	Bu ₄ NI	5	-

Reaction conditions: 30 mmol epoxide, 3 mmol mesitylene as internal standard, 0.25 mol% Fe complex relative to the epoxide; 0.25 mol% co-catalyst relative to the epoxide (if applicable), 90 °C, 12 bar CO₂ pressure, 2 h. The Fe complexes (and co-catalysts, if used) are fully soluble at room temperature in the reaction mixture. Selectivity towards the cyclic carbonate was >99% in all cases as confirmed by ¹H NMR spectroscopy (see SI). a Conversion calculated based on the ¹H NMR signals of the carbonate product and epoxide substrate (see SI); all runs were conducted in (at least) duplicate, the reported conversion being an average. b Turnover number expressed as mol of converted epoxide per mol of catalyst complex. c Using anhydrous 1,2-epoxyhexane. d 1.00 mol% of complex **1Br** relative to the epoxide. e Recycled catalyst from entry 14.

catalytic behaviour. A similar mechanism based on a labile metal-halide bond was proposed for (anionic) Fe(III) catalysts.^{16f} Virtually complete selectivity (>99%) towards the cyclic carbonate was observed in all cases. When the corresponding tetrabutylammonium halide was used as co-catalyst in combination with complexes **1Cl/Br/I**, the epoxide conversion could be further improved (Table 3.1, entries 2, 4 and 6). Comparing these results with the activity of the tetrabutylammonium halides under the same conditions but in the absence of iron formazanates (entries 16-18), showed that the presence of the iron complexes leads to substantially increased conversion, thus confirming their catalytic activity.

Among the three formazanate complexes (**1Cl/Br/I**), the activity increased in the order of $X = Cl^- < I^- < Br^-$, both in the presence or absence of a co-catalyst. This trend can be understood considering that the overall catalytic activity depends on the nucleophilicity of the halide, its leaving group ability (see Fig. 3.4 for proposed reaction mechanism) and its interaction with the Lewis acid (i.e. the halide lability from the iron centre).^{3c,8c,25} In the aprotic medium in which the reaction was carried out, the nucleophilicity increases in the order of $I^- < Br^- < Cl^-$, whereas the leaving group ability decreases in the same order. It can be concluded that in this system bromide provides the best balance between nucleophilicity, leaving group ability and lability from the iron centre, thereby leading to the highest catalytic activity. In addition to studying the effect of the anionic nucleophilic species on the catalytic activity, the influence of the cationic counterpart was also investigated. Performing the benchmark reaction (equal conditions to Table 3.1, entry 3) with an analogue of complex **1Br** with PPN (bis(triphenylphosphine)iminium) as counteranion showed no significant difference in catalytic activity (34% conversion).

To further investigate the potential of iron formazanate catalysts in this reaction, the influence of the substituents in the ligand backbone was studied by preparing and testing compounds **2Br**, **2I** and **3Br**. The electron-withdrawing C₆F₅ substituent present in compounds **2Br/I** is expected to lead to a more Lewis acidic Fe centre in comparison to that in complexes **1**, whereas the electron-donating *p*-methoxy group of **3Br** will generate the opposite effect. When comparing the catalytic activity of complex **1Br** (entries 3 and 4) with **2Br** (entries 7 and 8) and **3Br** (entries 10 and 11), it is clear that all iron complexes are active catalysts, both with and without added co-catalyst, and that both electron-withdrawing and -donating groups have a detrimental effect on activity. The lack of a clear correlation between a single parameter (i.e. the Lewis acidity of the metal centre) and catalytic activity is not surprising given the complex balance between the parameters that determine the

Fig. 3.4. Proposed mechanism for the reaction of CO₂ and epoxide catalysed by Fe(II) formazanate complexes (**1-3**).

activity of the system (such as halide dissociation from the metal centre, substrate binding, product release). Complexes **1Br** and **2Br** were also tested using lower loading relative to the epoxide. Under these conditions, a decrease in conversion was observed but a higher TON could be reached (see Table S3.5).

Many homogeneous metal-based catalysts employed in the reaction of CO₂ with epoxide are air- and moisture-sensitive,^{9a} requiring drying of the reagents in order to prevent their deactivation. In the case of the iron formazanate complexes, we investigated the effect of using pre-dried, N₂-saturated 1,2-epoxyhexane on the activity of catalyst **1Br** (Table 3.1, entries 12 and 13). An increase in conversion of around 11% was observed in comparison with the test with untreated 1,2-epoxyhexane (entries 3 and 4, respectively). These results indicate that, though working with anhydrous reagents is beneficial, the formazanate catalyst is not affected in a major way by adventitious water. This is an important asset, as for practical applications the addition of a drying step would lead to significant undesirable costs.

Of all the formazanate complexes examined, **1Br** showed the highest catalytic activity towards the benchmark reaction of CO₂ with 1,2-epoxyhexane, both with and without additional nucleophile. Hence, we chose this complex as single-component catalyst to expand the scope of the reaction by testing various terminal and internal epoxides (Table 3.2; for the substrate scope with complex **2Br** see Table S3.4).

For 1,2-epoxyhexane, the conversion after 18 h (89%) is considerably higher than after 2 h (36%, entry 3 in Table 3.1), showing that formazanate complex **1Br** remains active for an extended period of time. Indeed, addition of Et₂O after the reaction afforded a precipitate that contained intact **1Br** as shown by ¹H NMR spectroscopy (Fig. S3.7). This allowed investigating the recyclability of the catalyst. First, a catalytic test with 1.0 mol% catalyst loading was carried out, which gave quantitative conversion of 1,2-epoxyhexane after 2 h (Table 3.1, entry 14). Subsequently, **1Br** was precipitated by addition of cold Et₂O/hexane (4:1) under N₂ atmosphere. After removal of the supernatant, the solid was washed with cold Et₂O, dried and used without further purification in a second run. Under identical conditions, the recycled catalyst afforded 69% conversion (Table 3.1, entry 15). It should be noted that full catalyst recovery was hampered by its solubility in the carbonate product, and further optimisation is required. Nevertheless, these results show that the recovered catalyst retains substantial activity.

When comparing the activity with different substrates, it was observed that **1Br** is especially active in the conversion of terminal epoxides, leading to high conversions (≥84%) for reactions of CO₂ with 1,2-epoxyhexane (Table 3.2, entry 1), epichlorohydrin (entry 3) and allyl glycidyl ether (entry 4). In the case of propylene oxide (entry 2), quantitative conversion was achieved after 18 h with a catalyst loading of 0.25 mol%, accompanied by a propylene carbonate yield of 97% (see Table 3.2, note f). Lowering the catalyst loading to 0.05 mol% resulted in a propylene carbonate yield of 43% (entry 2), with a high TON of 860. The conversion of styrene oxide (entry 5) is slightly lower than that of the other terminal epoxides, which can be related to the steric hindrance of the aromatic group. Internal epoxides are typically more difficult to convert due to steric effects, hence, lower conversions were achieved for the reactions of CO₂ with cyclohexene oxide (entry 6) and vinylcyclohexene oxide (entry 7), while only trace amounts of carbonate product were observed with limonene oxide. Since it has been reported that for highly substituted epoxide smaller nucleophiles are preferred,²⁶ **1Cl** was also tested in the

Table 3.2. Substrate scope of the reaction of various terminal and internal epoxides with CO₂ to produce cyclic carbonates, catalysed by Fe(II) formazanate complex **1Br**.

#	Epoxide	Conv. (%) ^a	Sel. (%) ^b	TON ^c
1		89	>99	356
2 ^f		>99 (97 ^d) 55 ^e (43 ^{d,e})	>99	400 (388 ^d) 1100 ^e (860 ^{d,e})
3		89	98	356
4		84	>99	336
5		70	>99	280
6		32	98	128
7		18	98	72
8		2 ^g	>99 ^g	8 ^g

Reaction conditions: 30 mmol epoxide, 3 mmol mesitylene as internal standard, 0.25 mol% of complex **1Br** relative to the epoxide, 90 °C, 12 bar CO₂ pressure, 18 h. a Conversion calculated based on the ¹H NMR signals of the carbonate product and epoxide substrate (see SI). b Selectivity towards the cyclic carbonate product determined with FTIR analysis by comparing the C=O stretch signal of the cyclic carbonate and polycarbonate, respectively (see SI). c Turnover number expressed as mol of converted epoxide per mol of catalyst complex. d The reported value is based on yield of propylene carbonate. e Catalyst loading of 0.05 mol% of complex **1Br** relative to the epoxide. f The small discrepancy between the conversion of propylene oxide and the yield of propylene carbonate is a consequence of the high volatility of propylene oxide, which leads to evaporation of small amounts of epoxide during purging and depressurisation of the reactor (see experimental section). g Reaction conditions: 30 mmol epoxide, 3 mmol mesitylene as internal standard, 1.00 mol% of complex **1Cl** relative to the epoxide, 90 °C, 12 bar CO₂ pressure, 18 h.

reaction of CO₂ with limonene oxide. With a catalyst loading of 1.00 mol%, **1Cl** gave ca. 2% conversion to the corresponding carbonate (entry 8). Although the reaction is very slow, this result demonstrates that formazanate complexes promote the conversion of this challenging substrate even in the absence of a co-catalyst.

Interestingly, very high selectivity towards the cyclic carbonate product was achieved also with the cyclohexene-type epoxides, which are known to be prone to polymerisation.²⁷ Typically, in the case of other single-component bifunctional catalysts, the polycarbonate is the major product obtained from the reaction between CO₂ and cyclohexene oxide, and the addition of a separate nucleophile is required to form the cyclic product selectively (see Table S3.6 for a detailed comparison with other bifunctional iron-based catalysts in the literature).^{13a,13c,15c,16a,16b}

3.4. Conclusions

We presented the first example of formazanate Fe complexes as homogeneous catalysts for the fixation of CO₂ into cyclic carbonates via reaction with epoxides. The main assets of these complexes are: (i) their ability to act as single-component catalysts, thus obviating the need for an additional nucleophile; and (ii) their remarkable selectivity towards the cyclic carbonate product even in the conversion of internal epoxides such as (substituted) cyclohexene oxides, which generally tend to yield polycarbonates. More generally, this work indicates that anionic metal complexes with loosely bound halide ligands may provide a new entry into single-component transition metal catalysts for CO₂-fixation into organic carbonates.

References

- 1 (a) Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat. Commun.* **2015**, *6*, 5933; (b) J. Artz, T. E. Müller, K. Thenert, J. Kleinekorte, R. Meys, A. Sternberg, A. Bardow, W. Leitner, *Chem. Rev.* **2018**, *118*, 434-504.
- 2 M. Aresta, A. Dibenedetto, A. Angelini, *Chem. Rev.* **2014**, *114*, 1709-1742.
- 3 (a) S. Inoue, H. Koinuma, T. Tsuruta, *J. Polym. Sci. C Polym. Lett.* **1969**, *7*, 287-292; (b) M. North, R. Pasquale, C. Young, *Green Chemistry* **2010**, *12*, 1514-1539; (c) P. P. Pescarmona, M. Taherimehr, *Catal. Sci. Technol.* **2012**, *2*, 2169-2187.
- 4 A. J. Kamphuis, F. Picchioni, P. P. Pescarmona, *Green Chemistry* **2019**, *21*, 406-448.
- 5 (a) J. H. Clements, *Ind. Eng. Chem. Res.* **2003**, *42*, 663-674; (b) T. Sakakura, K. Kohno, *Chem. Commun.* **2009**, 1312-1330.
- 6 S. Klaus, M. W. Lehenmeier, C. E. Anderson, B. Rieger, *Coord. Chem. Rev.* **2011**, *255*, 1460-1479.

- 7 C. Martín, G. Fiorani, A. W. Kleij, *ACS Catal.* **2015**, *5*, 1353-1370.
- 8 (a) T. Aida, S. Inoue, *J. Am. Chem. Soc.* **1983**, *105*, 1304-1309; (b) X. B. Lu, R. He, C. X. Bai, *J. Mol. Catal. A: Chem.* **2002**, *186*, 1-11; (c) C. J. Whiteoak, N. Kielland, V. Laserna, F. Castro-Gómez, E. Martin, E. C. Escudero-Adán, C. Bo, A. W. Kleij, *Chem. Eur. J.* **2014**, *20*, 2264-2275; (d) D. O. Meléndez, A. Lara-Sánchez, J. Martínez, X. Wu, A. Otero, J. A. Castro-Osma, M. North, R. S. Rojas, *ChemCatChem* **2018**, *10*, 2271-2277.
- 9 (a) D. R. Moore, M. Cheng, E. B. Lobkovsky, G. W. Coates, *J. Am. Chem. Soc.* **2003**, *125*, 11911-11924; (b) T. Ema, Y. Miyazaki, S. Koyama, Y. Yano, T. Sakai, *Chem. Commun.* **2012**, *48*, 4489-4491.
- 10 R. L. Paddock, Y. Hiyama, J. M. McKay, S. T. Nguyen, *Tetrahedron Lett.* **2004**, *45*, 2023-2026.
- 11 S. Mang, A. I. Cooper, M. E. Colclough, N. Chauhan, A. B. Holmes, *Macromolecules* **2000**, *33*, 303-308.
- 12 For a recent review, see: F. Della Monica, A. Buonerba, C. Capacchione, *Adv. Synth. Catal.* **2019**, *361*, 265-282
- 13 (a) A. Buchard, M. R. Kember, K. G. Sandeman, C. K. Williams, *Chem. Commun.* **2011**, *47*, 212-214; (b) C. J. Whiteoak, E. Martin, M. M. Belmonte, J. Benet-Buchholz, A. W. Kleij, *Adv. Synth. Catal.* **2012**, *354*, 469-476; (c) M. Taherimehr, J. P. C. C. Sertã, A. W. Kleij, C. J. Whiteoak, P. P. Pescarmona, *ChemSusChem* **2015**, *8*, 1034-1042; (d) D. Alhashmialameer, J. Collins, K. Hattenhauer, F. M. Kerton, *Catal. Sci. Technol.* **2016**, *6*, 5364-5373; (e) F. Chen, N. Liu, B. Dai, *ACS Sustain. Chem. Eng.* **2017**, *5*, 9065-9075; (f) M. Cozzolino, V. Leo, C. Tedesco, M. Mazzeo, M. Lamberti, *Dalton Trans.* **2018**, *47*, 13229-13238.
- 14 (a) I. Bauer, H.-J. Knölker, *Chem. Rev.* **2015**, *115*, 150309133704007; (b) A. Fürstner, *ACS Cent. Sci.* **2016**, *2*, 778-789.
- 15 (a) J. E. Dengler, M. W. Lehenmeier, S. Klaus, C. E. Anderson, E. Herdtweck, B. Rieger, *Eur. J. Inorg. Chem.* **2011**, 336-343; (b) X. Sheng, L. Qiao, Y. Qin, X. Wang, F. Wang, *Polyhedron* **2014**, *74*, 129-133; (c) E. Y. Seong, J. H. Kim, N. H. Kim, K.-H. Ahn, E. J. Kang, *ChemSusChem* **2019**, *12*, 409-415.
- 16 (a) M. A. Fuchs, T. A. Zevaco, E. Ember, O. Walter, I. Held, E. Dinjus, M. Döring, *Dalton Trans.* **2013**, *42*, 5322-5329; (b) M. Adolph, T. A. Zevaco, C. Altesleben, O. Walter, E. Dinjus, *Dalton Trans.* **2014**, *43*, 3285-3296; (c) F. M. Al-Qaisi, M. Nieger, M. L. Kemell, T. J. Repo, *ChemistrySelect* **2016**, *1*, 545-548; (d) E. Fazekas, G. S. Nichol, M. P. Shaver, J. A. Garden, *Dalton Trans.* **2018**, *47*, 13106-13112; (e) F. Della Monica, B. Maity, T. Pehl, A. Buonerba, A. De Nisi, M. Monari, A. Grassi, B. Rieger, L. Cavallo, C. Capacchione, *ACS Catalysis* **2018**, *8*, 6882-6893; (f) F. Della Monica, A. Buonerba, V. Paradiso, S. Milione, A. Grassi, C. Capacchione, *Adv. Synth. Catal.* **2019**, *361*, 283-288.
- 17 (a) L. Bourget-Merle, M. F. Lappert, J. R. Severn, *Chem. Rev.* **2002**, *102*, 3031-3065; (b) R. L. Webster, *Dalton Trans.* **2017**, 4483-4498.

- 18 (a) G. I. Sigeikin, G. N. Lipunova, I. G. Pervova, *Russ. Chem. Rev.* **2006**, *75*, 885-900;
(b) J. B. Gilroy, M. J. Ferguson, R. McDonald, B. O. Patrick, R. G. Hicks, *Chem. Commun.* **2007**, 412, 126-128; (c) M. C. Chang, T. Dann, D. P. Day, M. Lutz, G. G. Wildgoose, E. Otten, *Angew. Chem. Int. Ed.* **2014**, *53*, 4118-4122.
- 19 (a) R. Travieso-Puente, J. O. P. Broekman, M.-C. Chang, S. Demeshko, F. Meyer, E. Otten, *J. Am. Chem. Soc.* **2016**, *138*, 5503-5506; (b) F. Milocco, S. Demeshko, F. Meyer, E. Otten, *Dalton Trans.* **2018**, 47, 8817-8823.
- 20 (a) D. L. J. Broere, B. Q. Mercado, E. Bill, K. M. Lancaster, S. Sproules, P. L. Holland, *Inorg. Chem.* **2018**, *57*, 9580-9591; (b) D. Broere, B. Mercado, J. Lukens, A. Vilbert, G. Banerjee, H. Lant, S. H. Lee, E. Bill, K. Lancaster, S. Sproules, P. Holland, *Chem. Eur. J.* **2018**, *24*, 9417-9425.
- 21 D. Broere, B. Q. Mercado, P. L. Holland, *Angew. Chem.* **2018**, *57*, 6507-6511.
- 22 R. Travieso-Puente, S. Budzak, J. Chen, P. Stacko, J. T. B. H. Jastrzebski, D. Jacquemin, E. Otten, *J. Am. Chem. Soc.* **2017**, *139*, 3328-3331.
- 23 L. Yang, D. R. Powell, R. P. Houser, *Dalton Trans.* **2007**, 955-964.
- 24 (a) J. E. Anderson, C. L. Yao, K. M. Kadish, *J. Am. Chem. Soc.* **1987**, *109*, 1106-1111;
(b) L. Yu, X. Jin, G. Z. Chen, *J. Electroanal. Chem.* **2013**, *688*, 371-378.
- 25 F. Castro-Gómez, G. Salassa, A. W. Kleij, C. Bo, *Chem. Eur. J.* **2013**, *19*, 6289-6298.
- 26 A. Rehman, A. M. López Fernández, M. F. M. Gunam Resul, A. Harvey, *Journal of CO₂ Utilisation* **2019**, *29*, 126-133.
- 27 D. J. Darensbourg, J. C. Yarbrough, C. Ortiz, C. C. Fang, *J. Am. Chem. Soc.* **2003**, *125*, 7586-7591.
- 28 J. B. Gilroy, M. J. Ferguson, R. McDonald, B. O. Patrick, R. G. Hicks, *Chem. Commun.* **2007**, 126-128.
- 29 (a) H. Tezcan, Ş. Can, R. Tezcan, *Dyes and Pigments* **2002**, *52*, 121-127; (b) J. B. Gilroy, S. D. J. McKinnon, B. D. Koivisto, R. G. Hicks, *Org. Lett.* **2007**, *9*, 4837-4840.
- 30 M. C. Chang, E. Otten, *Chem. Commun.* **2014**, 50, 7431-7433.
- 31 S. D. Ittel, A. D. English, C. A. Tolman, J. P. Jesson, *Inorg. Chim. Acta* **1979**, *33*, 101-106.
- 32 I. G. Ryabokon, O. M. Polumbrik, L. N. Markovskii, *Zh. Org. Khim.* **1983**, *19*, 230-232.
- 33 D. L. J. Broere, B. Q. Mercado, J. T. Lukens, A. C. Vilbert, G. Banerjee, H. M. C. Lant, S. H. Lee, E. Bill, S. Sproules, K. M. Lancaster, P. L. Holland, *Chem. Eur. J.* **2018**, *24*, 9417-9425.

Supplementary Information

Appendix A: Experimental Section

Ligand synthesis.

Compound **2H** has been reported previously.^[1,2] Our slightly modified procedure and the associated analytical data are reported below.

PhNNC(C₆F₅)NNHPh (2H). PhNNC(C₆F₅)H (3.24 g, 1.0 eq, 11.3 mmol), sodium hydroxide (3.76 g, 8.3 eq, 94.1 mmol), water (130 mL) and acetone (240 mL) were mixed at 0 °C. A separate flask was charged with aniline (1.05 g, 1.0 eq, 11.3 mmol), water (20 mL) and hydrochloric acid (4 mL) at 0 °C. To the latter mixture a solution of sodium nitrate (0.86 g, 1.1 eq, 12.4 mmol) in water (10 mL) at 0 °C was slowly added and the resulting pale yellow solution was stirred for 30 min at 0 °C. The solution with the *in situ* formed diazonium salt was added dropwise into the first solution at 0 °C, which turned red immediately. The reaction mixture was slowly warmed up to room temperature and after stirring for an additional 30 min acetic acid was added until pH = 7. After stirring for 2 h a dark orange-red reaction mixture was obtained and the product was extracted with CH₂Cl₂ and washed with water. The solution was concentrated and slow diffusion of methanol into the CH₂Cl₂ solution at -30 °C for 2 days afforded a dark orange solid which was washed with cold hexane obtaining 1.78 g of **2H** (4.6 mmol, 40%). ¹H NMR (400 MHz, CDCl₃, 25 °C) δ 12.31 (s, 1H, NH), 7.58 (d, 4H, J = 7.81, Ph *o*-CH), 7.44 (t, J = 7.54, 4H Ph *m*-CH), 7.29 (t, 2H, J = 7.23, Ph *p*-CH) ppm. ¹⁹F NMR (376 MHz, CDCl₃, 25 °C) δ -139.3 (m, 2F, = C₆F₅ *m*-CF), -154.2 (t, 1F, J = 20.9, C₆F₅ *p*-CF), -162.6 (td, 2F, J = 22.3, 7.0, C₆F₅ *o*-CF). ¹³C NMR (151 MHz, CDCl₃, 25 °C) 147.5 (Ph *ipso*-C), 145.4 (dm, J = 244.7, C₆F₅), 141.5 (dm, J = 250.1, C₆F₅), 137.8 (dm, J = 250.9, C₆F₅), 135.5 (NNC₂N), 129.6 (Ph *m*-CH), 128.0 (Ph *p*-CH), 119.11 (Ph *o*-CH). Anal. Calcd. for C₁₉H₁₁F₅N₄: C, 58.47; H, 2.84; N, 14.35. Found: C, 58.74; H 2.98; N, 13.92.

Appendix B: X-ray crystallography

Table S3.1. Crystallographic data for compounds **2Br**, **3Br** and **2I**.

	2Br	3Br	2I
chem formula	C ₃₅ H ₄₆ Br ₂ F ₅ FeN ₅	C ₃₆ H ₅₃ Br ₂ FeN ₅ O	C ₃₅ H ₄₆ I ₂ F ₅ FeN ₅
M_r	847.43	787.50	941.42
cryst syst	monoclinic	trigonal	orthorhombic
color, habit	dark orange, plate	dark purple, block	dark orange, block
size (mm)	0.28 x 0.23 x 0.04	0.24 x 0.17 x 0.07	0.37 x 0.21 x 0.18
space group	P2 ₁	R3c	P2 ₁ 2 ₁ 2 ₁
a (Å)	16.3045(5)	27.0524(8)	10.4595(4)
b (Å)	10.4184(3)	27.0524(8)	16.4118(6)
c (Å)	21.8975(7)	28.0849(9)	22.1383(8)
α (°)	90	90	90
β (°)	90.1190(10)	90	90
γ (°)	90	120	90
V (Å³)	3719.6(2)	17799.8(12)	3800.2(2)
Z	4	18	4
ρ_{calc}, g.cm⁻³	1513	1.322	1.645
Radiation [Å]	Mo K _α 0.71073	Cu K _α 1.54178	Mo K _α 0.71073
μ(Mo K_α), mm⁻¹	2.611	5.667	2.077
F(000)	1728	7344	1872
Temp (K)	293(2)	100(2)	100(2)
θ range (°)	2.97 – 27.15	3.27 – 70.26	2.95 – 27.90
data collected (h,k,l)	-20:20; -12:13; - 28:28	-32:31; -32:30; - 34:34	-13:13; -21:18; - 28:29
no. of rflns collected	50622	118999	67587
no. of indpndt collected	15804	7540	9073
Observed rflns F_o ≥ 2.0 σ (F_o)	15405	7300	8766
R(F) (%)	1.94	2.31	1.91
wR(F²) (%)	4.38	5.09	4.24
Goof	0.906	1.055	1.123
weighting a,b	0, 0	0.0264, 17.6255	0.0122, 2.8804
params refined	874	412	437
min, max resid dens	-0.370, 0.234	-0.260, 0.423	-0.639, 0.703

Single crystals of compounds **2Br**, **3Br** and **2I** were mounted on top of a cryoloop and transferred into the cold nitrogen stream (100 K) of a Bruker-AXS D8 Venture diffractometer. Data collection and reduction was done using the Bruker software

suite APEX3.^[3] The final unit cell was obtained from the xyz centroids of 9810 (**2Br**), 9269 (**3Br**) or 9415 (**2I**) reflections after integration. A multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (*SADABS*). The structures were solved by direct methods using *SHELXT*^[4] and refinement of the structures was performed using *SHELXL*.^[5] The hydrogen atoms were generated by geometrical considerations, constrained to idealised geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. For **2Br**, refinement was poor with several atoms showing unrealistic displacement parameters when allowed to refine freely. *PLATON*^[6] was used to check for possible twinning, which identified a second domain that accounted for ca. 33% of the crystal. With the twin law suggested from *PLATON*, the refinement proceeded smoothly. For **3Br**, initial refinement identified several residual peaks the Fourier difference map with densities of 0.7 - 1.3 e/Å³, which were likely due to disordered solvent. The *PLATON/SQUEEZE* routine was applied to remove its contribution. The structure was ultimately refined as an inversion twin for which *BASF* refined to 0.49.

Table S3.2. Pertinent interatomic distances and bond angles in compounds **1-3Br** and **2I**.

	1Br ^[7]	2Br		3Br	2I
		residue 1	residue 2		
Fe(1) – N(1)	1.9785(17)	1.982(3)	1.980(3)	1.967(3)	1.982(2)
Fe(1) – N(4)	1.9765(17)	1.985(3)	1.980(3)	1.970(3)	1.983(2)
Fe(1) – X(1)	2.4176(4)	2.4145(7)	2.4075(6)	2.4222(6)	2.6124(5)
Fe(1) – X(2)	2.4182(3)	2.4122 (6)	2.4128(7)	2.4173(6)	2.6148(5)
N(1) – N(2)	1.317(2)	1.322(4)	1.313(4)	1.313(4)	1.320(3)
N(3) – N(4)	1.313(2)	1.346(5)	1.320(4)	1.322(4)	1.310(3)
N(2) – C(7)	1.346(2)	1.329(5)	1.343(5)	1.345(4)	1.340(4)
N(3) – C(7)	1.346(3)	1.346(5)	1.344(5)	1.341(4)	1.347(4)
N(1) – Fe(1) – N (4)	91.38(7)	91.87(13)	91.96(13)	91.15(10)	92.29(9)
X(1) – Fe(1) – X(2)	108.304(13)	112.67(3)	113.00(3)	111.80(2)	114.570(16)
(N – Fe – N)/(X – Fe – X)	86.72	88.10	87.63	85.59	86.91

Fig. S3.1. Molecular structures of compound **2Br** (left; only one of the independent molecules shown), **3Br** (middle) and **2I** (right) showing 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

Appendix C: NMR spectral data

Fig. S3.2. ^1H NMR spectrum of **2Br** ($\text{THF-}d_8$, 400 MHz, 25 °C).

Fig. S3.3. ^{19}F NMR spectrum of **2Br** ($\text{THF-}d_8$, 376 MHz, 25 °C).

Fig. S3.4. ¹H NMR spectrum of **2I** (THF-*d*₈, 400 MHz, 25 °C).

Fig. S3.5. ¹⁹F NMR spectrum of **2I** (THF-*d*₈, 376 MHz, 25 °C).

Fig. S3.6. ^1H NMR spectrum of **3Br** ($\text{THF-}d_8$, 400 MHz, 25 $^\circ\text{C}$).

Fig. S3.7. ^1H NMR spectrum of the residual precipitate with 20 mL of Et_2O after the reaction between 1,2-epoxyhexane and CO_2 , cat = **1Br** ($\text{THF-}d_8$, 400 MHz, 25 $^\circ\text{C}$).

Appendix D: *In situ* NMR reactivity studies

In situ NMR reactivity of **1Br** with 1,2-epoxyhexane (EH) in THF-*d*₈.

Fig. S3.8. ¹H NMR spectra of: a) **1Br**, b) **1Br** + 1 eq of EH, c) **1Br** + 5 eq of EH, d) **1Br** + 25 eq of EH (THF-*d*₈, 400 MHz, 25 °C), selected peaks of **1Br**.

Fig. S3.9. ^1H NMR spectra of: a) EH, b) **1Br**, c) **1Br** + 1 eq of EH, d) **1Br** + 5 eq of EH, e) **1Br** + 25 eq of EH (THF- d_8 , 400 MHz, 25 $^\circ\text{C}$), aliphatic region.

In situ NMR reactivity of **1b** with pyridine (py) in THF-*d*₈.

Fig. S3.10. ¹H NMR spectra of: a) **1b**, b) **1b** + 1 eq of py, c) **1b** + 25 eq of py (THF-*d*₈, 400 MHz, 25 °C), selected peaks of **1b**.

Fig. S3.11. ¹H NMR spectra of: a) **1b**, b) **1b** + 1 eq of py, c) **1b** + 25 eq of py (THF-*d*₈, 400 MHz, 25 °C), aromatic and aliphatic region.

Appendix E: Cyclic voltammetry

Table S3.3. Electrochemical parameters for compounds **1-3Br**.

	E^0 vs $Fc^{0/+}$ [V]		
	$nBr^{0/+}$	$nBr^{0/1-}$	$nBr^{1-/2-}$
1Br ^[7]	+ 0.05 ($E_{p,a}$)	- 1.58	- 2.58 ($E_{p,c}$)
2Br	+ 0.16 ($E_{p,a}$)	- 1.53	- 2.47 ($E_{p,c}$)
3Br	+ 0.04 ($E_{p,a}$)	- 1.58	- 2.69 ($E_{p,c}$)

1.5 mM of iron complex in THF, 0.1 M $[Bu_4N][PF_6]$ electrolyte, scan rate = 100 $mV \cdot s^{-1}$.

Fig. S3.12. Cyclic voltammogram of compound **2Br** (ca. 1.50 mM solution of complex in THF; 0.1 M $[Bu_4N][PF_6]$ electrolyte; scan rate = 100 $mV \cdot s^{-1}$).

Highly selective single-component formazanate ferrate(II) catalysts for the conversion of CO₂ into cyclic carbonates

3

Fig. S3.13. Cyclic voltammograms of compound **2Br** (ca. 1.50 mM solution of complex in THF; 0.1 M [Bu₄N][PF₆] electrolyte; scan rate: a) 500 mV·s⁻¹, b) 100 mV·s⁻¹, c) 50 mV·s⁻¹).

Fig. S3.14. Cyclic voltammograms of compound **3Br** (ca. 1.50 mM solution of complex in THF; 0.1 M [Bu₄N][PF₆] electrolyte; scan rate = 0.1 V·s⁻¹).

Appendix F: UV-Vis absorption spectroscopy

Fig. S3.15. UV-Vis absorption spectra of compounds **1-3** in THF.

Appendix G: ¹H NMR spectra of product mixtures after catalysis

Fig. S3.16. ¹H NMR spectrum of the reaction of CO₂ with 1,2-epoxyhexane.

Fig. S3.17. ¹H NMR spectrum of the reaction of CO₂ with styrene oxide.

Fig. S3.18. ^1H NMR spectrum of the reaction of CO_2 with propylene oxide.

Fig. S3.19. ^1H NMR spectrum of the reaction of CO_2 with epichlorohydrin.

Fig. S3.20. ¹H NMR spectrum of the reaction of CO₂ with allyl glycidyl ether.

Fig. S3.21. ¹H NMR spectrum of the reaction of CO₂ with cyclohexene oxide.

Fig. S3.22. ^1H NMR spectrum of the reaction of CO_2 with 4-vinylcyclohexene oxide.

Fig. S3.23. ^1H NMR spectrum of the reaction of CO_2 with limonene oxide.

Appendix H: FTIR spectra of product mixtures after catalysis

Fig. S3.24. FTIR spectrum of the reaction of CO₂ with 1,2-epoxyhexane.

Fig. S3.25. FTIR spectrum of the reaction of CO₂ with propylene oxide.

Fig. S3.26. FTIR spectrum of the reaction of CO₂ with epichlorohydrin.

Fig. S3.27. FTIR spectrum of the reaction of CO₂ with allyl glycidyl ether.

Fig. S3.28. FTIR spectrum of the reaction of CO₂ with styrene oxide.

Fig. S3.29. FTIR spectrum of the reaction of CO₂ with cyclohexene oxide.

Fig. S3.30. FTIR spectrum of the reaction of CO₂ with vinylcyclohexene oxide.

Fig. S3.31. FTIR spectrum of the reaction of CO₂ with limonene oxide.

Appendix I: Catalytic tests

Table S3.4. Substrate scope of the reaction of various terminal and internal epoxides with CO₂ to produce cyclic carbonates, catalysed by Fe(II) formazanate complex **2Br**.

#	Epoxide	Conv. (%) ^[a]	Sel. (%) ^[b]	TON ^[c]
1		66	>99	264
2		>99	>99	400
3		99	>99	396
4		83	>99	332
5		63	>99	252
6		22	99	88
7		15	98	60
8		<1	-	-

Reaction conditions: 30 mmol epoxide, 3 mmol mesitylene as internal standard, 0.25 mol% of complex **2Br** relative to epoxide, 90 °C, initial pressure of 12 bar CO₂ pressure, 18 h. ^[a] Conversion calculated based on the ¹H NMR signals of the carbonate product and epoxide substrate. ^[b] Selectivity towards the cyclic carbonate product determined with FTIR analysis by comparing the C=O stretch signal of the cyclic carbonate and polycarbonate respectively. ^[c] Turnover number expressed as mol of converted epoxide per mol of catalyst complex.

Table S3.5. Reaction of 1,2-epoxyhexane with CO₂ catalysed by Fe(II) formazanate complexes (**1/2Br**).

#	Cat.	Cat. loading (mol%) ^a	Nuc.	Nuc. loading (mol%) ^[a]	Conv. (%) ^[b]	TON _{metal} ^[c]	TON _{nuc} ^[d]
1	1Br	0.25	Bu ₄ NBr	0.25	50	200	100
2	1Br	0.05	Bu ₄ NBr	0.25	12	240	40
3	1Br	0.025	Bu ₄ NBr	0.25	8	320	29
4	2Br	0.25	Bu ₄ NBr	0.25	41	164	82
5	2Br	0.05	Bu ₄ NBr	0.25	12	240	40
6	2Br	0.025	Bu ₄ NBr	0.25	9	360	33

Reaction conditions: 30 mmol epoxide, 3 mmol mesitylene as internal standard, 90 °C, 12 bar CO₂ pressure, 2 h. Selectivity towards the cyclic carbonate was >99% in all cases as confirmed by ¹H NMR spectroscopy. ^[a] Relative to epoxide. ^[b] Conversion calculated based on the ¹H NMR signals of the carbonate product and epoxide substrate; all runs were conducted in (at least) duplicate, the reported conversion being an average. ^[c] Turnover number expressed as mol of converted epoxide per mol of metal sites. ^[d] Turnover number expressed as mol of converted epoxide per mol of active halide (assuming that only one halide per iron complex is active, see proposed mechanism).

Appendix J: Literature comparison

Table S3.6. Reaction of CO₂ with cyclohexene oxide catalysed by iron-based single-component systems.

#	Cat.	Cat. loading (mol%) ^[a]	Nuc.	Nuc. loading (mol%) ^[a]	Temp. (°C)	CO ₂ press. (bar)	Time (h)	Solvent	Conv _{CHO} (%)	Sel _{CC} (%)	Sel _{PC} (%)	TON _{metal} ^[b]	TOF (h ⁻¹) ^[c]	Ref.
1	1Br	0.25	-	-	90	12	18	-	32	98	2	128	7.1	This work
2	A	0.1	-	-	80	10	24	-	70	1	99	347	14.5	[8]
3	A	0.1	PPNCl	0.1	80	1	48	-	41	>99	-	205	4.5	[8]
4	B	0.2	-	-	80	50	20	DCM	0	-	-	-	-	[9]
5	C	0.5	-	-	80	50	20	-	33	-	>99	66	3.3	[10]
6	D	0.5	-	-	60	80	18	-	11	15	85	22	1.2	[11]
7	D	0.5	Bu ₄ NBr	5	60	80	18	-	95	>99	-	200	11.1	[11]
8	E	0.1	-	-	100	10	20	DCM	9	n.a.	n.a.	27	1.4	[12]
9	E	0.036	Bu ₄ NBr	0.3	100	10	20	-	20	n.a.	n.a.	166	8.3	[12]
10	F	1.0	-	-	100	10	20	DMF	34	>99	-	34	1.7	[13]
11	G	2.5	-	-	100	10	20	DMF	28	>99	-	11	0.55	[13]

^[a] Relative to epoxide. ^[b] Turnover number expressed as mol of converted epoxide per mol of metal sites. ^[c] Turnover frequency expressed as mol of converted epoxide per mol of metal sites per hour. CHO: cyclohexene oxide, CC: cyclic carbonate and PC: polycarbonate.

Fig. S3.32. Iron-based single-component catalysts reported in Table S3.6.^[8–12]

References

- 1 O. M. Polumbrik, I. G. Ryabokon, L. N. Markovskii, *Khim. Geterotsikl. Soedin.* **1978**, 266–269.
- 2 I. G. Ryabokon, O. M. Polumbrik, L. N. Markovskii, *Zh. Org. Khim.* **1983**, 19, 230–232.
- 3 Bruker, (2016). APEX3 (V2016.1-0), SAINT (Version 8.37A) and SADABS (Version 2014/5). Bruker AXS Inc., Madison, Wisconsin, USA., n.d.
- 4 G. M. Sheldrick, *Acta Cryst.* **2015**, A71, 3–8.
- 5 G. M. Sheldrick, *Acta Cryst.* **2008**, A64, 112–122.
- 6 A. L. Spek, *Acta Cryst.* **2015**, C71, 9–18.
- 7 F. Milocco, S. Demeshko, F. Meyer, E. Otten, *Dalton Trans.* **2018**, 47, 8817–8823.
- 8 A. Buchard, M. R. Kember, K. G. Sandeman, C. K. Williams, *Chem. Commun.* **2011**, 47, 212–214.
- 9 M. A. Fuchs, T. A. Zevaco, E. Ember, O. Walter, I. Held, E. Dinjus, M. Döring, *Dalton Trans.* **2013**, 42, 5322–5329.
- 10 M. Adolph, T. A. Zevaco, C. Altesleben, O. Walter, E. Dinjus, *Dalton Trans.* **2014**, 43, 3285–3296.
- 11 M. Taherimehr, J. P. C. C. Sertã, A. W. Kleij, C. J. Whiteoak, P. P. Pescarmona, *ChemSusChem* **2015**, 8, 1034–1042.
- 12 F. M. Al-Qaisi, M. Nieger, M. L. Kemell, T. J. Repo, *ChemistrySelect* **2016**, 1, 545–548.
- 13 E. Y. Seong, J. H. Kim, N. H. Kim, K. H. Ahn, E. J. Kang, *ChemSusChem* **2019**, 12, 409–415.

Chapter 4: Tailor-made polycarbonates derived from CO₂: tuning the properties via thiol-ene click modification

This work describes the synthesis of a sustainable, bio-based polycarbonate prepared through the copolymerisation of CO₂ with 4-vinylcyclohexene oxide (poly(vinylcyclohexene carbonate, PVCHC)), for which quantitative yields were achieved using an aluminium amino-tris(phenolate)/tetrabutylammonium halide catalytic system. The resulting polymer was functionalized by converting the pendant vinyl groups into a range of functional groups using atom-efficient thiol-ene click chemistry. This versatile modification tool allowed the preparation of a series of novel polycarbonates containing pendant alkyl, hydroxyl, carboxyl, amino or aromatic groups, whose physicochemical properties were characterized with a combination of techniques (¹H NMR, ¹³C NMR, FTIR, TGA, DSC and GPC). Depending on the functional group attached to the polycarbonate backbone, the polymeric properties were tuned to generate features ranging from pH-dependent water solubility to a remarkably low glass transition temperature. The adaptability of this CO₂-based polycarbonate makes it a specialty chemical with a variety of potential applications, including coating formulations, biomedical applications and consumer goods.

4.1. Introduction

In recent years, the research efforts aiming at developing sustainable chemical processes and products have increased remarkably, both at an academic as well as an industrial level.¹ Within the field of polymer products, two of the major incentives for this paradigm shift are the predicted decrease in availability of non-renewable fossil resources used to prepare plastic products, thereby generating the need to divert to renewable bio-based feedstock, and the enormous amounts of non-recyclable waste generated after these plastic products have fulfilled their duty and are discarded, which can be avoided by using a design for degradation or, even better, a design for recycling rather than a design for persisting.² In the context of sustainable product development, the use of carbon dioxide as building block for the synthesis of chemical materials has many assets. Being globally produced on a large scale as waste gas in both combustion-related processes such as the generation of electricity via burning of fossil feedstock (e.g. coal and gas) and non-combustion processes within the cement, ammonia, iron and steel industry,³ carbon dioxide can be considered as an abundant, cheap and renewable feedstock. Additionally, CO₂ is non-toxic and non-flammable, making it a safe C₁-source that can replace more hazardous chemical substrates. This is exemplified by the commercial Asahi-Kasei process where the use of CO₂ eliminates the need for highly-toxic phosgene in the production of bisphenol-A-based polycarbonates.⁴ Among the reactions that employ CO₂ as feedstock, the direct copolymerisation with epoxides to synthesize polycarbonates (Fig. 4.1) has been receiving increasing attention.^{5–12} In addition to the production of polycarbonates, five-membered cyclic carbonates can also be formed as side products of this reaction.

Although in an initial phase the majority of the research on this reaction was dedicated to the polymerisation of carbon dioxide with petroleum-based epoxides such as propylene oxide^{14–16} and cyclohexene oxide,^{17–21} in recent years the focus has shifted towards the utilisation of epoxides obtainable from renewable sources (e.g. limonene (di)oxide,^{22–26} 1,4-cyclohexadiene^{27,28} glycidyl ether-based compounds^{29–33} and 4-vinylcyclohexene oxide^{34–37}). A variety of applications have been envisioned for these CO₂-based polycarbonates and, in some cases, have

Fig. 4.1. General scheme of the reaction of an epoxide with CO₂.¹³

already been realized, including as polymer electrolytes in battery systems,^{32,33,38} tissue scaffold in biomedical applications^{39–41} and as components in formulations for adhesives, coatings and foams that are applicable in e.g. construction, automotive and footwear industries.^{42–45} Some of these applications have already reached the commercial stage, such as the use of CO₂-based polycarbonates as polyols in polyurethane formulations^{46,47} and as binder material in ceramics and adhesives.⁴⁸ In contrast to conventional rigid aromatic polycarbonates based on bisphenol A, polycarbonates obtained from the copolymerisation of CO₂ with epoxides generally contain aliphatic repeating units originating from epoxides such as propylene oxide and cyclohexene oxide. In the case of cyclohexene-type polycarbonates, this typically translates into similar thermal properties but poorer impact strength and lower elongation at break compared to bisphenol-A-polycarbonate, thus limiting applicability as engineering plastics.^{5,7,13}

Furthermore, CO₂-based polycarbonates are typically hydrophobic due to the lack of polar moieties, leading to poor adhesion of living cells and slow biodegradation,⁴⁹ thereby limiting the range of utilisation in biomedical devices. Several pathways have been explored to modify and optimize the physicochemical properties of CO₂-based polycarbonates, with the purpose of expanding the scope of their applications. These approaches include terpolymerisation of CO₂ with two or more epoxides,^{43,49} block-copolymerisation resulting in polycarbonates with different types of polycarbonate blocks or containing polyester blocks,^{50–52} blending of polycarbonates with other polymers⁵³ or with inorganic solids;⁵⁴ and post-polymerisation modification to introduce functional groups.^{31,37,55–57} Within the context of post-polymerisation modifications, the use of thiol-ene click chemistry has been recognized as an accessible and atom-efficient route to introduce a wide variety of possible functionalities in polymers that possess unsaturated moieties along the polymer backbone.^{55,58–61} This versatile approach has been exploited to introduce crosslinking,^{26,34,62–64} water-solubility,^{28,56,65–67} self-healing ability,⁶⁸ enhanced electrical conductivity³⁸ and starting points for subsequent grafting.^{36,69} However, systematic studies encompassing many different thiols (with different functional groups) and the corresponding comparison between different end products are still very limited in the open literature.⁵⁵

Herein, we report the synthesis of a polycarbonate prepared by copolymerisation of CO₂ with 4-vinylcyclohexene oxide (Fig. 4.2), followed by a systematic investigation of post-polymerisation modifications to introduce selected functional groups along the backbone of the obtained poly(vinyl cyclohexene carbonate) (PVCHC) by employing thiol-ene click chemistry. The physicochemical properties of

Fig. 4.2. Copolymerisation of CO_2 and VCHO, followed by functionalisation of the obtained polycarbonate by thiol-ene click reactions. A simplified graphical representation of the Al (III) amino-tris(phenolate) complex is shown here, for a detailed representation see Fig. S4.2. TBAX = tetrabutylammonium halide (X = Cl or Br).

the resulting modified polycarbonates were investigated and optimized in order to introduce and tailor properties such as hydrophilicity, low glass transition temperature ($T_g < \text{room temperature}$), pH-dependent water solubility and homogeneous biodegradability, thereby creating potential for CO_2 -based polycarbonates to be used in applications ranging from coatings to medicine. To maximize the sustainable character of the produced polycarbonate, 4-vinylcyclohexene oxide (VCHO) was selected as epoxide precursor, as this compound can be produced from biomass via a three-step route starting with the synthesis of bio-based butadiene,⁷⁰ followed by the industrially practiced dimerisation into 4-vinylcyclohexene,⁷¹ and subsequent selective epoxidation to yield the corresponding epoxide substrate. For the polymerisation reaction, an aluminum(III) amino-*t*Bu-tris(phenolate) complex combined with a tetrabutylammonium halide (TBAX, with X = Cl or Br) was chosen as catalytic system due to the previously reported high activity of this system in the reaction of CO_2 with other epoxides, *e.g.*, for the polymerisation of CO_2 and limonene oxide.⁷² Additional assets of this catalytic system are the relatively straightforward synthesis of the aluminum(III) amino-tris(phenolate) complex and the high natural abundance of aluminum.⁷³ For specific information on the mechanism of this reaction, the reader is kindly referred to the literature.^{5–11}

4.2. Experimental

4.2.1. Materials

Compressed nitrogen ($\geq 99.999\%$, Linde Gas) and carbon dioxide ($\geq 99.7\%$, Linde Gas) were used as received. Dry tetrahydrofuran was obtained by percolating tetrahydrofuran (anhydrous, 99.8%, Sigma-Aldrich) over Al_2O_3 columns (Fluka). The dry tetrahydrofuran was subsequently stored under nitrogen. Chloroform-*d* (99.8%,

Sigma-Aldrich) and dimethyl sulfoxide-d₆ (99.5% Sigma-Aldrich) were stored over molecular sieves (0.4 nm). 4-Vinyl-1-cyclohexene-1,2-epoxide (mixture of isomers, 98%, Sigma-Aldrich), mesitylene (98%, Sigma-Aldrich), tetrabutylammonium bromide (≥99.0% Sigma-Aldrich), tetrabutylammonium chloride (≥97.0%, Sigma-Aldrich), dichloromethane (≥99.9%, Macron), methanol (≥99.8%, Macron), hydrochloric acid (37-38 wt%, Boom), deuterium oxide (99.9%, Sigma-Aldrich), 2,2'-azobis(2-methylpropionitrile) (AIBN, ≥98.0%, Sigma-Aldrich), chloroform (≥99.8%, Macron), tetrahydrofuran (Not dry, BHT stabilized, Boom), diethyl ether (≥99.0%, Macron), 2-mercaptoethanol (≥99.0% Sigma-Aldrich), 1-thioglycerol (≥97.0%, Sigma-Aldrich), thioglycolic acid (≥99.0%, Sigma-Aldrich), 2-aminoethanethiol (95%, Sigma-Aldrich), 2-aminoethanethiol hydrochloride (98%, Acros), N-alpha-t-butyloxycarbonyl-L-cysteine (99%, Abcr), thiophenol (99%, Acros), 4-mercaptobenzoic acid (90%, Acros), 4-aminothiophenol (97%, Acros), 1-dodecanethiol (≥98%, Sigma-Aldrich) and sodium hydroxide (≥99 Merck) were used as received.

4.2.2. Methods

¹H Nuclear Magnetic Resonance (¹H NMR) spectra were recorded on a Varian Oxford 300 MHz apparatus (64 scans and a relaxation time of 10 s), using chloroform-d, dimethyl sulfoxide-d₆ or deuterium oxide as solvents. ¹³C NMR spectra were recorded on a Varian Mercury PlusNMR 400 MHz apparatus (8192 scans and a relaxation time of 1 s). The ¹H NMR and ¹³C NMR spectra were referenced using residual solvent resonances. The ppm values are reported relative to tetramethylsilane (TMS). Fourier-Transform Infrared (FTIR) spectra were recorded using a Shimadzu IR Tracer-100 equipped with an attenuated total reflectance (ATR) sample unit with a frequency range of 4000-600 cm⁻¹ and a resolution of 4 cm⁻¹, employing 64 scans. Thermogravimetric Analysis (TGA) was performed on a PerkinElmer Thermogravimetric Analyzer 4000 under a N₂-flow of 20 mL/min in the temperature range from 20 to 900 °C with a temperature ramp of 10 °C/min. Differential Scanning Calorimetry (DSC) measurements were performed on a PerkinElmer Pyris Diamond Differential Scanning Calorimeter under a N₂-flow of 20 mL/min using a temperature ramp of 10 °C/min. Two heating and cooling cycles were measured: the first cycle was disregarded to avoid taking into account the thermal history of the sample. Glass transition temperatures (T_g) were determined by calculating the local maximum of the first derivative of the second heating cycle. Gel permeation chromatography (GPC) analysis of the water-insoluble polymers was carried out on a HP 1100 GPC/SEC System equipped with three Agilent PLgel 3

μm MIXED-E columns in series, using a GBC LC1240 RI detector. The chromatograms were recorded at 40 °C with an eluent flow speed of 1 mL/min, using tetrahydrofuran as eluent. The chromatograms were referenced against polystyrene standards. GPC chromatograms of the water-soluble polymers were recorded on an Agilent 1200 Series GPC/SEC System equipped with three PSS 10 μm Suprema columns in series, with porosities of 100, 1000 and 3000 Å. This system is equipped with an Agilent 1200 Series RI detector. The chromatograms were recorded at 40 °C with an eluent flow speed of 1 mL/min, using water with 0.05 M NaNO_3 as eluent. The chromatograms were referenced against polyacrylamide standards. All molecular weight calculations were done using the PSS WinGPC UniChrom GPC/SEC software. Samples for water contact angle measurements were prepared by solvent coating the polycarbonates from THF on test surfaces (PVCHC on aluminum, PVCHC-OH and PVCHC-Glyc on glass). The coatings were dried overnight at room temperature followed by vacuum drying at 50 °C for 48 h.

4.2.3. Catalyst synthesis

The aluminum(III) amino-*t*Bu-tris(phenolate) catalyst was prepared based on a previously reported method (detailed information can be found in the Supplementary Information, appendix A and B, Fig. S4.1 and S2).⁷⁴

4.2.4. Catalytic experiments

The catalytic experiments were carried out in a high-throughput CO_2 reactor unit constructed by ILS-Integrated Lab Solutions GmbH. This CO_2 reactor consists of: (a) a 10-reactors block that allows performing 10 reactions simultaneously in individually-stirred batch reactors; and (b) a single batch reactor equipped with a borosilicate glass window to allow visualisation of the phase behaviour within the reactor. Each of these batch reactors has volume of 84 mL and an internal diameter of 30 mm. The unit can operate in a temperature range of 20-200 °C and a pressure range of 1-200 bar. For each individual test, 30.0 mmol epoxide, 3.0 mmol mesitylene as internal standard and the chosen amounts of catalytic system were weighed into a glass vial (with a volume of 46 mL and an external diameter of 30 mm) equipped with a magnetic stirring bar and a screw cap with a silicone/PTFE septum. The glass vials were subsequently placed into the 10-reactors block and each septum was pierced with two thin syringe needles to allow gas to flow in and out of the vials. Next, the reactor block was closed and the batch reactors were purged 3 times with 5 bar N_2 , after which they were pressurized to 10 bar CO_2 . After waiting 10 min (to prevent damage to the Viton O-rings), the reactors were depressurized to atmospheric pressure. After waiting another 10 min, the reactors

were pressurized to 50 bar CO₂. Once this pressure was reached, the reactors were heated to the desired reaction temperature. Upon reaching this temperature, the reactors were further pressurized to 80 bar of CO₂. The process of purging, pressurizing and heating the reactors took approximately 1.5 h. The initiation of the reaction was defined as the moment at which the magnetic stirring was turned on, after reaching the desired reaction temperature and pressure. The reactions were carried out at 900 rpm stirring speed for 18 h. All polymerisations were performed in a temperature range of 60 to 100 °C, using different ratios of catalyst and nucleophile compared to VCHO. At the end of the reaction, the magnetic stirring and the reactor heating were turned off and the water cooling system was switched on to cool down the reactors block. After reaching room temperature, the reactors were depressurized. The process of cooling down and depressurizing the reactors block took approximately 1.5 h. Once atmospheric pressure was reached, the reactors block was opened and the vials were removed. Small aliquots of each sample were used for ¹H NMR, FTIR and GPC analyses. After each experiment, the batch reactors were cleaned by washing them with ethanol and by subsequently drying them at 110 °C for 4 h. The reactor lines were cleaned by washing them with ethanol and drying them by purging the lines with 1 bar N₂ for 15 min.

To purify and isolate the produced PVCHC, a standard procedure was utilized. After the reaction of VCHO with CO₂, the obtained reaction mixture was dissolved in a minimum amount of dichloromethane. The polymer was subsequently slowly precipitated in acidified methanol (1 M HCl, 100 mL). These steps were repeated 5 times in order to purify the polycarbonate. Then the product was dried under vacuum at 70 °C for 48 h. The obtained white solid was analyzed by ¹H NMR, ¹³C NMR, FTIR spectroscopy, GPC, TGA and DSC.

¹H NMR (CDCl₃, 300 MHz, Fig. S4.3): δ 5.77 (1H), 5.16-4.96 (2H), 4.96-4.71 (2H), 2.43 (1H), 1.85 (4H), 1.59 (2H). ¹³C NMR (CDCl₃, 400 MHz, Fig. S4.4): δ 156.0, 144.2, 116.6, 76.9-75.3, 37.5, 34.2, 28.7, 28.0. FTIR (cm⁻¹, Fig. S4.22): 1738 (C=O stretch, carbonate), 1639 (C=C stretch, vinyl group). Note that no ether linkages were observed in any of the PVCHC samples.

4.2.5. Post-polymerisation modification

The general modification of PVCHC was performed using thiol-ene click reactions.⁵⁶ In a general procedure, PVCHC (polycarbonate repeating unit taken as 1 mol), the corresponding thiol and AIBN as radical initiator were added in a 1:X:0.33 molar ratio (with X = 5-40) into a three-neck round-bottom flask and brought under N₂

atmosphere. After addition of a dry solvent, the solution was stirred at the chosen reaction temperature for the desired reaction time. Subsequently, the modified polycarbonates were purified by repeated dissolution/precipitation using a suitable solvent/non-solvent system or by dialysis against demineralized water. The final products were dried under vacuum for 48 h and then analyzed by ^1H NMR, ^{13}C NMR, FTIR spectroscopy, GPC, TGA and DSC (see Fig. S4.5-S4.52).

4.2.5.1. *Modification with 2-mercaptoethanol*

PVCHC (0.5000 g, 2.973 mmol of vinyl groups) was reacted with 2-mercaptoethanol (9.291 g, 8.340 mL, 118.9 mmol) using AIBN (0.1611 g, 0.9811 mmol) as a radical initiator. The reaction was performed in 25 mL dry THF for 24 h at 70 °C. The polymer was purified by dissolution of the mixture in a minimum amount of THF followed by slow precipitation in diethyl ether. This step was repeated 5 times to purify the product. PVCHC-OH was obtained as a white solid after vacuum drying at 70 °C for 48 h. Yield: >99% of the vinyl groups was converted.

^1H NMR ($(\text{CD}_3)_2\text{SO}$, 300 MHz, Fig. S4.5): δ 4.74 (3H), 3.51 (2H), 2.59-2.45 (4H), 1.74 (4H), 1.50 (4H), 1.26 (1H). ^{13}C NMR ($(\text{CD}_3)_2\text{SO}$, 400 MHz, Fig. S4.6): δ 152.7, 73.9, 73.2, 60.9, 34.2, 33.8, 31.9, 30.2, 29.0, 25.5, 24.9. FTIR (cm^{-1} , Fig. S4.23): 3393 (O-H stretch, hydroxyl group), 1738 (C=O stretch, carbonate).

4.2.5.2. *Modification with 1-thioglycerol*

PVCHC (0.2500 g, 1.486 mmol of vinyl groups) was reacted with 1-thioglycerol (6.429 g, 5.156 mL, 59.44 mmol) using AIBN (0.08053 g, 0.4904 mmol) as a radical initiator in 12.5 mL dry THF. The purification was carried out as described above for the modification of PVCHC with 2-mercaptoethanol. PVCHC-Glyc was obtained as an off-white solid. Yield: >99% of the vinyl groups was converted.

^1H NMR ($(\text{CD}_3)_2\text{SO}$, 300 MHz, Fig. S4.7): δ 4.75 (1H), 4.70 (2H), 4.52 (1H), 3.55 (1H), 3.35 (2H), 2.66-2.37 (4H), 1.74 (4H), 1.51 (4H), 1.24 (1H). ^{13}C NMR ($(\text{CD}_3)_2\text{SO}$, 400 MHz, Fig. S4.8): δ 152.7, 74.1, 73.2, 71.4, 64.6, 35.2, 34.0, 32.0, 30.3, 29.6, 25.5, 24.9. FTIR (cm^{-1} , Fig. S4.24): 3367 (O-H stretch, hydroxyl groups), 1738 (C=O stretch, carbonate).

4.2.5.3. *Modification with thioglycolic acid*

PVCHC (0.5000 g, 2.973 mmol of vinyl groups) was reacted with thioglycolic acid (10.95 g, 8.262 mL, 118.9 mmol) using AIBN (0.1611 g, 0.9811 mmol) as a radical initiator in 25 mL dry THF for 24 h at 70 °C. The purification was carried out as described above for the modification of PVCHC with 2-mercaptoethanol. PVCHC-COOH was obtained as a white solid. Yield: > 99% of the vinyl groups was converted.

It should be noted that thioglycolic acid is susceptible to self-esterification,⁷⁵ which leads to its partial and reversible conversion into 2-((2-mercaptoacetyl)thio)acetic acid. Since this compound also possesses a thiol moiety, it can also react with the PVCHC vinyl groups through a thiol-ene reaction.

¹H NMR ((CD₃)₂SO, 300 MHz, Fig. S4.9): δ 4.73 (2H), 3.66 (2H), 3.61 (2H), 3.20 (2H), 2.58 (2H), 1.74 (4H), 1.52 (4H), 1.24 (1H). ¹³C NMR ((CD₃)₂SO, 400 MHz, Fig. S4.10): δ 196.2, δ 171.6, 169.6, 152.7, 74.0, 73.2, 41.1, 33.2, 31.8, 30.2, 29.4, 25.4, 24.9. FTIR (cm⁻¹, Fig. S4.25): 1738 (C=O stretch, carbonate), 1699 (C=O stretch, carboxylic acid).

4.2.5.4. Modification with Boc-L-cysteine

PVCHC (0.5000 g, 2.973 mmol of vinyl groups) was reacted with Boc-L-cysteine (N-alpha-t-butyloxycarbonyl-L-cysteine) (3.289 g, 14.87 mmol) and AIBN (0.1611 g, 0.9811 mmol). The reaction was performed in 25 mL dry THF for 24 h at 70 °C. The polymer was purified by repeated dissolution of the mixture in a minimum amount of THF followed by slow precipitation in diethyl ether. PVCHC-Boc-L-cysteine was obtained as an off-white solid after vacuum drying at 70 °C for 48 h. Yield: > 99% of the vinyl groups was converted. ¹H NMR ((CD₃)₂SO, 300 MHz, Fig. S4.11): δ 7.03-6.40 (1H), 4.71 (2H), 4.03 (1H), 2.84 (1H), 2.71 (1H), 2.50 (2H), 1.75 (4H), 1.48 (4H), 1.37 (10H). ¹³C NMR ((CD₃)₂SO, 400 MHz, Fig. S4.12): δ 172.7, 155.2, 152.7, 78.0, 73.1, 67.0, 54.0, 33.1, 31.9, 30.2, 29.1, 28.2, 28.0, 25.1. FTIR (cm⁻¹, Fig. S4.26): 1738 (C=O stretch, carbonate), 1709 (C=O stretch, carboxylic acid/Boc-protecting group).

In order to deprotect the L-cysteine moieties, PVCHC-Boc-L-cysteine was dissolved in THF, followed by slow addition of concentrated aqueous HCl (37%), which resulted in precipitation of an off-white solid (see the Results and Discussion section for the characterisation of this product).

4.2.5.5. Modification with 4-mercaptobenzoic acid

PVCHC (0.2500 g, 1.486 mmol of vinyl groups) was reacted with 4-mercaptobenzoic acid (4.583 g, 29.72 mmol) using AIBN (0.08053 g, 0.4904 mmol) as a radical initiator in 15 mL dry THF for 24 h at 70 °C. The polymer was purified by dissolution of the mixture in a minimum amount of THF followed by slow precipitation in acidified methanol (1 M HCl). This step was repeated multiple times to purify the product. PVCHC-Ar-COOH was obtained as a white solid after vacuum drying at 70 °C for 48 h. Yield: 9% of the vinyl groups was converted.

¹H NMR (CDCl₃, 300 MHz, Fig. S4.13): δ 7.96 (2H), 7.28 (2H), 5.76 (1H), 5.16-4.96 (2H), 4.96-4.71 (2H), 3.33 (1H), 2.99 (1H), 2.42 (1H), 1.84 (5H), 1.59 (4H). ¹³C NMR (CDCl₃, 400 MHz, Fig. S4.14): δ 153.3, 141.6, 130.6, 130.1, 126.5, 114.1, 73.5, 35.0,

31.7, 26.2, 25.5. FTIR (cm^{-1} , Fig. S4.27): 1738 (C=O stretch, carbonate), 1595 (C=C stretch, aromatic).

4.2.5.6. *Modification with 2-aminoethanethiol hydrochloride*

PVCHC (0.5000 g, 2.973 mmol of vinyl groups) was reacted with 2-aminoethanethiol hydrochloride (1.689 g, 14.86 mmol) and AIBN (0.1611 g, 0.9811 mmol). The reaction was performed in 50 mL chloroform for 4 h under reflux conditions. After the reaction, the solvent was evaporated and the resulting solid was dissolved in water. After filtration, the aqueous solution containing the polymer was purified by dialysis against demineralized water (molecular weight cutoff at 3.5 kDa). PVCHC-NH₂·HCl was obtained as a transparent yellowish solid after vacuum drying at 70 °C for 48 h. Yield: >55% of the vinyl groups was converted.

¹H NMR ((CD₃)₂SO, 300 MHz, Fig. S4.15): δ 7.19 (1H), 5.80 (1H), 5.22-4.89 (2H) 4.72 (2H), 2.89 (2H), 2.72 (2H), 2.38 (2H), 2.27 (2H), 1.76 (4H), 1.54 (4H), 1.28 (1H). ¹³C NMR ((CD₃)₂SO, 600 MHz, Fig. S4.16): δ 152.7, 141.3, 114.0, 73.2, 34.5, 33.8, 31.6, 30.1, 29.0, 28.3, 25.6, 25.0. FTIR (cm^{-1} , Fig. S4.28): 1738 (C=O stretch, carbonate), 1599 (N-H bend, ammonium group).

4.2.5.7. *Modification with 4-aminothiophenol*

PVCHC (0.2500 g, 1.486 mmol of vinyl groups) was reacted with 4-aminothiophenol (3.721 g, 29.72 mmol) using AIBN (0.08053 g, 0.4904 mmol) as a radical initiator in 15 mL dry THF for 24 h at 70 °C. The polymer was purified by dissolution of the mixture in a minimum amount of THF followed by slow precipitation in acidified methanol (1 M HCl). This step was repeated multiple times to purify the product. The product was obtained as a white solid after vacuum drying at 70 °C for 48 h. Yield: No change compared to the parent polymer (PVCHC) was observed by ¹H NMR, indicating that < 1% of the vinyl groups was converted.

4.2.5.8. *Modification with thiophenol*

PVCHC (0.2500 g, 1.486 mmol of vinyl groups) was reacted with thiophenol (6.549 g, 6.075 mL, 59.44 mmol) using AIBN (0.08053 g, 0.4904 mmol) as a radical initiator. The reaction was performed in 12.5 mL dry THF for 24 h or 48 h at 70 °C. The polymer was purified by dissolution of the mixture in a minimum amount of THF followed by slow precipitation in acidified methanol (1 M HCl). This step was repeated multiple times to purify the product. PVCHC-Ar was obtained as a white solid after vacuum drying at 70 °C for 48 h. Yield: 27% (24 h reaction time) or 22% (48 h reaction time) of the vinyl groups was converted.

¹H NMR (CDCl₃, 300 MHz, Fig. S4.17): δ 7.36-7.22 (4H), 7.21-7.12 (1H), 5.77 (1H), 5.16-4.96 (2H), 4.96-4.71 (2H), 2.92 (2H), 2.42 (1H), 1.84 (4H), 1.59 (4H), 1.31 (1H). ¹³C NMR (CDCl₃, 400 MHz, Fig. S4.18): δ 153.3, 141.7, 136.6, 129.2, 129.0, 126.0, 114.1, 73.4, 35.0, 32.2, 31.7, 31.2, 30.6, 26.1, 25.4. FTIR (cm⁻¹, Fig. S4.29): 1738 (C=O stretch, carbonate), 1584 (C=C stretch, aromatic), 1481 (C=C stretch, aromatic), 785 (C-H bend, aromatic), 737 (C-H bend, aromatic).

4.2.5.9. Modification with 1-dodecanethiol

PVCHC (0.5000 g, 2.973 mmol of vinyl groups) was reacted with 1-dodecanethiol (12.03 g, 14.24 mL, 59.46 mmol) using AIBN (0.1611 g, 0.9811 mmol) as a radical initiator. The reaction was performed in 25 mL dry THF for 60 min at 70 °C. After the reaction, the solvent was removed via distillation under reduced pressure at room temperature. The polymer was purified by dissolution of the mixture in a minimum amount of THF followed by slow precipitation in methanol. This step was repeated 5 times to purify the product. PVCHC-DDT was obtained as a brown, viscous liquid after drying under reduced pressure at room temperature for 48 h. The polymer was stored under N₂ atmosphere. Yield: 89% of the vinyl groups was converted.

¹H NMR (CDCl₃, 300 MHz, Fig. S4.19): δ 5.77 (1H), 5.16-4.96 (2H), 4.81 (2H), 2.49 (4H), 1.84 (4H), 1.56 (6H), 1.25 (20H), 0.87 (3H). ¹³C NMR (CDCl₃, 400 MHz, Fig. S4.20): δ 153.4, 73.3, 35.7, 32.4, 32.1, 30.6, 30.1-29.0, 26.0, 25.4, 22.8, 14.3. FTIR (cm⁻¹, Fig. S4.30): 2919 (C-H stretch, alkyl), 2851 (C-H stretch, alkyl).

4.2.5.10. Crosslinking with AIBN

PVCHC (0.1000 g, 0.5957 mmol of vinyl groups) was crosslinked using AIBN (0.03222 g, 0.1962 mmol) as a radical initiator. The reaction was performed in 10 mL dry THF for 24 h at 70 °C. The resulting gel was dried at 70 °C under vacuum for 48 h. Yield: 11% of the vinyl groups was converted (determined with FTIR by comparing the decrease of the C=C stretch peak at 1639 cm⁻¹, normalized to the carbonate C=O stretch peak at 1738 cm⁻¹, no baseline correction used, see also Fig. S4.31).

4.2.5.11. Degradation experiments of PVCHC-COOH

PVCHC-COOH (2 mg/mL) was dissolved in an aqueous HCl/NaOH solution at pH 8. The solution was maintained in a closed vial at the chosen temperature (room temperature or 50 °C) for the duration of the experiment, without stirring. The degradation of the polymer was monitored over time by GPC. The pH was checked weekly and adjusted to pH 8 if needed.

4.2.5.12. Solvent coating and curing of PVCHC-DDT

5 mg PVCHC-DDT dissolved in 5 mL dichloromethane was cast on a Teflon dish, dried under vacuum at 20 °C for 24 h and subsequently heated at 100 °C for 5 h in air.

4.3. Results and discussion

4.3.1. Catalytic polymerisation of VCHO and CO₂

A series of poly(vinyl cyclohexene carbonate)s was prepared by the copolymerisation of CO₂ with 4-vinylcyclohexene oxide in the presence of a catalytic system consisting of aluminum(III) amino-*t*Bu-tris(phenolate) and a tetrabutylammonium halide (Fig. 4.2), at different temperatures and loading of the catalytic system (Table 4.1). All reactions were performed with CO₂ at temperature and pressure above its supercritical point and without the use of any solvents, which contributes to the sustainable character of the reaction. The target of these experiments was to achieve high level of epoxide conversion and high selectivity towards the polycarbonate product, in order to minimize the separation and purification steps required for the successive functionalisation of the obtained polymer. Additionally, the aim was to investigate the influence of reaction temperature and the ratio of catalyst to epoxide on the molecular weight average and distribution of the produced polycarbonates. Due to the fact that the reaction proceeds via an anionic polymerisation mechanism,⁹ a lower amount of Lewis base acting as nucleophilic species (*i.e.* TBAX, with X = Cl or Br) translates into fewer starting points for the growing polymeric chains, theoretically resulting in longer chains and higher molecular weight. The molar ratio between Lewis acid species (*i.e.* the Al-complex) and the nucleophile was kept at 1:1 as a higher relative amount of nucleophilic species typically promotes the formation of the cyclic carbonate product (Fig. 4.1), thus influencing negatively the selectivity towards the desired polycarbonate product.^{34,76}

Through this careful tailoring of the reaction conditions, the desired high selectivity towards PVCH was obtained in all catalytic tests, with nearly full selectivity in all cases in which the conversion was > 30% (Table 4.1). This high selectivity towards the polycarbonate product, also at relatively higher reaction temperature (100 °C), is not only related to the employed catalyst and reaction conditions, but is also attributed to the unfavourable formation of the antagonist vinylcyclohexene carbonate product due to the geometric ring strain of its two connected rings.⁷⁷ Nearly full conversion ($\geq 97\%$) was achieved at 80 °C with a 0.5 mol% loading of catalyst (entries 5 and 7) and at 100 °C with a 0.25 mol% (or higher) loading of

catalyst (entries 9, 11 and 12). These results prove that the employed catalytic system based on the Al (III) amino-tris(phenolate) complex displays high activity and selectivity in the copolymerisation of CO₂ and VCHO. The molecular weight of the obtained polycarbonates is primarily influenced by the degree of conversion, as higher levels of conversion resulted in higher molecular weights (*e.g.* compare entry 1 with 5 and 9 and entry 3 with 7). For the tests at low catalyst loading (0.1 mol%) and temperature (≤ 80 °C), low levels of conversion (entries 2, 4, 6 and 8) were achieved and no molecular weight (average and distribution) could be measured with GPC analysis of the crude reaction mixtures, presumably due to the low quantity of polycarbonate product present. No significant differences in molecular weight were observed between polymers prepared at 80 °C and those synthesised at 100 °C (compare *e.g.* entry 5 and 9). Along the same line, no substantial changes

Table 4.1. Catalytic copolymerisation of CO₂ with VCHO.

Entry	Temp (°C)	Catalyst (mol%) ^a	Nucleophile source	Nucleophile (mol%) ^a	Conversion (%) ^b	Selectivity (% PC) ^c	M _n (Da) ^d	M _w (Da) ^d	PDI ^d
1	60	0.5	TBABr	0.5	32	96	1250	1650	1.32
2	60	0.1	TBABr	0.1	3	85	N.o.	N.o.	N.o.
3	60	0.5	TBACl	0.5	33	97	1300	1700	1.31
4	60	0.1	TBACl	0.1	3	84	N.o.	N.o.	N.o.
5	80	0.5	TBABr	0.5	98	98	4600	5750	1.25
6	80	0.1	TBABr	0.1	11	92	N.o.	N.o.	N.o.
7	80	0.5	TBACl	0.5	97	>99	5550	6250	1.13
8	80	0.1	TBACl	0.1	12	93	N.o.	N.o.	N.o.
9	100	0.5	TBABr	0.5	99	>99	6300	7450	1.18
10	100	0.1	TBABr	0.1	90	>99	7850	9100	1.16
11	100	0.5	TBACl	0.5	>99	>99	2800 ^e	3450 ^e	1.23 ^e
12	100	0.25	TBACl	0.25	99	>99	7700	9000	1.17
13	100	0.1	TBACl	0.1	92	>99	6250	7900	1.26

Reaction conditions: 30.0 mmol VCHO, aluminum (III) amino-*t*Bu-tris(phenolate) catalyst, 3 mmol mesitylene as internal standard, 80 bar CO₂, 18 h reaction time. ^a Relative to the epoxide substrate. ^b Determined using ¹H NMR with mesitylene as internal standard. ^c Determined via FTIR by comparing the ratio between the areas of the peaks of the carbonate C=O stretching mode for the polycarbonate (1738 cm⁻¹) and the cyclic carbonate (1801 cm⁻¹). ^d The GPC analysis was conducted using an aliquot of the reaction mixture. Only the polymeric signals were taken into account for molecular weight calculations, in case of catalytic duplo reactions, the GPC data of the polymer with the lowest dispersity (PDI = M_w/M_n) is displayed. ^e Sample contaminated with adventitious ethanol. N.o. = not obtainable.

in molecular weight were observed upon varying the amount of catalyst between 0.1 and 0.5 mol% (compare entries 9 and 10 and entries 12 and 13). Additionally, no significant differences in conversion, selectivity or molecular weight were observed upon employing a different Lewis base nucleophile (TBABr or TBACl). The fact that all synthesised polycarbonates consist of relatively low-molecular weight chains ($M_n \leq 10\,000$ Da) is attributed to the inherent sensitivity of the CO₂/epoxide anionic polymerisation towards chain transfer by protic compounds such as water and alcohols.^{8,9} Although the reactor was purged before each reaction to remove air and moisture, the presence of adventitious water or ethanol in the reactor lines or in the reagents cannot be excluded. Working under strictly water-free conditions is known to promote the formation of higher molecular weight polycarbonates.^{15,78} However, these conditions typically require thorough pre-drying of reagents and working under strictly inert atmosphere, which would eventually limit establishing a robust industrial-scale polymerisation process.

4.3.2. Post-polymerisation modification of PVCHC

The polycarbonates produced by the copolymerisation of VCHO with CO₂ (PVCHC) are characterized by pendant vinyl moieties suitable for thiol-ene chemistry (Fig. 4.2). Inspired by, amongst others, the elegant work of Greiner *et al.* on the thiol-modification of poly(limonene carbonate),⁵⁵ we explored the versatile thiol-ene reaction by applying it to these (potentially) fully bio-based polycarbonates, in order to introduce a wide array of functional groups, ranging from alkyl to aryl groups and from acidic to basic functions. In this way, we aimed at expanding the range of potential applications of the prepared CO₂-based polycarbonates. Two purified and isolated (see experimental section for the procedure) PVCHC samples extracted from the products of the catalytic experiments (*i.e.* sample **A**, corresponding to Table 4.1, entry 12 and sample **B**, corresponding to Table 4.1, entry 9) were used in this study. The molecular weight average of the isolated PVCHC samples is slightly different compared to the molecular weight average measured from the unpurified reaction aliquot, as can be seen in Table 4.2. This can be explained by the loss of lower molecular weight oligomers during the purification procedure.

The thiol compounds that were selected for this post-polymerisation modification of PVCHC (Fig. 4.3) can be divided into three sub-classes, each corresponding to a different functionalisation approach. The first approach that we investigated was the functionalisation of the polycarbonate with pending groups that are able to form hydrogen bonds, such as hydroxyl (**1**, 2-mercaptoethanol; **2**, 1-thioglycerol), carboxyl (**3**, thioglycolic acid; **4**, Boc-protected L-cysteine; **5**, 4-mercaptobenzoic

Tailor-made polycarbonates derived from CO₂: tuning the properties via thiol-ene click modification

Fig. 4.3. Selected thiol compounds employed in the post-polymerisation modification of PVCHC (Boc = t-butyloxycarbonyl).

acid) and amino (**4**, Boc-protected L-cysteine; **6**, 2-aminoethanethiol hydrochloride; **7**, 4-aminothiophenol) functional groups. These groups will enhance the interaction with polar compounds and thus the hydrophilicity of the polycarbonates. The second approach consisted in functionalisation by means of aromatic compounds (**5**, 4-mercaptobenzoic acid; **7**, 4-aminothiophenol; **8**, thiophenol). This strategy was selected as it was envisioned that increasing the aromatic content would lead to improved rigidity of the polymer chains. Finally, we explored the effect of decorating the polymer backbone with pending long alkyl chains through reaction with an aliphatic thiol (**9**, 1-dodecanethiol), which was anticipated to endow the final product with enhanced elasticity. The functionalisation by thiol-ene chemistry was carried out in the presence of AIBN as radical initiator and employing an excess of thiol in the range of 5 to 40 molar equivalent compared to the vinyl groups, to prevent radical crosslinking between the double bonds of the pendant vinyl groups. Indeed, if the radical reaction was performed in the absence of a thiol compound (Table 4.2, entry 10), a solid product formed as a consequence of intermolecular polymer crosslinking. The product was insoluble in diethyl ether, (hot) THF and (hot) DMSO. The crosslinking between the pendant vinyl groups was confirmed by FTIR analysis (Fig. S4.31 in the Supplementary Information), which showed an 11% decrease in the intensity of the signal corresponding to the C=C stretch vibration of the PVCHC vinyl groups (the signal corresponding to the C=O stretch of the carbonate group was used as an internal reference, assuming that the carbonate

groups remained unaltered). This crosslinking approach provides an alternative to the previously reported use of 1,3-propanedithiol as crosslinker,³⁴ though the increase in the glass transition temperature (T_g) observed here (from 106 to 118 °C) is less marked compared to that obtained with the dithiol (from 75 °C to 130 °C).

The differences in steric hindrance and/or electron donating or withdrawing effects between the various thiol compounds employed in the thiol-ene click-reaction with PVCHC manifest themselves in different reactivity and thus different degree of conversion of the PVCHC vinyl groups (Table 4.2), which was quantified using ^1H NMR (see Supplementary Information for the spectra). Comparing the chemical structure of the thiol and the degree of conversion, it can be concluded that the use of aliphatic thiols led to full conversion of the pendant vinyl groups within 24 h (Table 4.2, entries 1 – 4). In the case of 2-aminoethanethiol hydrochloride (**6**) (entry 6), a reaction time of 4 h and a relatively low thiol-to-vinyl group ratio (5:1) were employed to avoid possible side reactions, which could result in degradation of the polymer backbone, but this limited the functionalisation degree to 55% of the vinyl groups. For the reaction with 1-dodecanethiol (**9**) (entry 9), a reaction time of only 60 min was used to preserve part of the vinyl groups for potential further functionalisation or crosslinking, resulting in a conversion of 89%.

Compared to the aliphatic thiols, the aromatic analogues appeared much less reactive under the examined reaction conditions (Table 4.2, entries 5, 7 and 8). Employing thiophenol (**8**), a vinyl group conversion of only 27% was obtained after 24 h (Table 4.2, entry 8). Doubling the duration of the reaction to 48 h was not beneficial, as it led to a degree of conversion in the same range (data not shown). Based on electronic effects, thiol-ene reactions with aromatic thiols would be expected to be faster than with alkyl thiols, owing to the labile S-H bond of the former originating from the stabilisation of the thiol radical by electron delocalisation over the aromatic ring.⁷⁹ The relatively higher lability of the S-H bond of aromatic thiol compounds typically results in improved kinetics due to the cleavage of the S-H bond being the rate determining step of the thiol-ene reaction.⁷⁹ The fact that the degree of functionalisation of the vinyl groups is lower with aromatic thiols than with the aliphatic ones indicates that, rather than electronic effects, the steric hindrance around the thiol group caused by the aromatic ring dominates the reaction. Under the employed reaction conditions, 4-aminothiophenol (**7**) was completely unreactive (Table 4.2, entry 7). The hydroxyl analogue of **7**, 4-aminophenol, is a known radical scavenger.⁸⁰ Since **7** has a similar molecular structure (*i.e.*, an aromatic ring incorporating a weakly acidic moiety and an electron donating $-\text{NH}_2$ group in the *para* position), it might also exhibit similar

behaviour, which would inhibit the radical thiol-ene reaction, thus explaining the observed lack of functionalisation.

The degradation temperatures of the functionalized PVCHC materials were measured by TGA (see $T_{\text{deg,initial}}$ and $T_{\text{deg,5\%wl}}$ in Table 4.2 and the complete TGA curves in the Supplementary Information). This analysis showed that the incorporation of pendant alkyl and aryl groups did not influence significantly the thermal stability of the functionalized polymers (Table 4.2, entries 8 and 9) compared to the parent polycarbonate. On the other hand, the introduction of protic functional moieties such as hydroxyl, carboxyl and amino groups resulted in decreased thermal stability (both in terms of $T_{\text{deg,initial}}$ and $T_{\text{deg,5\%wl}}$, Table 4.2, entries 1 - 6). Besides the typically intrinsic low thermal stability of moieties containing relatively weak bonds,⁸¹ such as carboxyl, hydroxyl and amino groups, these protic functionalities may promote the hydrolysis of the carbonate bonds in the polymer backbone, thereby releasing CO₂ and causing the observed weight loss. For most functionalized polycarbonates, the thermal degradation started at temperatures above 200 °C, which still offers a relatively large processing window considering their relatively low glass transition temperatures (≤ 120 °C). The only product with lower thermal stability was PVCHC-Boc-L-cysteine (Table 4.2, entry 4), which displayed mass loss starting at 109 °C. This is attributed to thermal removal of the protecting Boc (t-butyloxycarbonyl) group (theoretical weight loss upon deprotection: 26%; first stage weight loss determined with TGA: 30%).⁸²

DSC measurements showed that for most of the tested materials, the introduction of the pendant functional groups along the PVCHC backbone resulted in a drop in T_g compared to the parent polymer (Table 4.2). This can be explained considering that an increase in length of the side groups increases the free volume of the polymer chains, thereby resulting in less chain interaction and thus higher mobility. This is especially noticeable for the polycarbonate functionalized with 1-dodecanethiol (PVCHC-DDT, Table 4.2, entry 9), in which the presence of the long alkyl chains led to a decrease of the T_g to below 0 °C. CO₂-based polycarbonates prepared from linear epoxides bearing long alkyl chains possess similarly low T_g values (e.g. -16 °C for (poly(octene carbonate))).⁸³ However, this is the lowest T_g so far reported for CO₂-based polycarbonates prepared from cyclic epoxides.⁵⁵ It is worth noting that for the polycarbonates that were functionalized with protic groups, our results indicate that the decrease in T_g induced by the presence of side groups outweighs the hydrogen bonding interactions between the protic moieties, which would be expected to lead to an increase in T_g (Table 4.2, entries 1 - 3). For the polycarbonate prepared by partial functionalisation of the vinyl groups with quaternary ammonium

moieties, two transitions were observed by DSC (Table 4.2, entry 6). In addition to the transition at 102 °C corresponding to the T_g of the polycarbonate, a second transition was observed at 120 °C, which is tentatively ascribed to interchain ionic interactions between the pendant quaternary ammonium groups.^{84,85} Modification of PVCHC with **5** (4-mercaptobenzoic acid), **8** (thiophenol) and **9** (1-dodecanethiol)

Table 4.2. Overview of thiol-ene modifications of PVCHC and thermal properties of the produced functionalized polycarbonates.

Entry	Polymer	Conversion of the pendant vinyl groups (%) ^c	M_n (Da) ^d	$T_{deg,initial}$ (°C) ^e	$T_{deg,5\%wt}$ (°C) ^f	T_g^g (°C)
	PVCHC	-	9900 (A)	-	-	106 (A)
			7350 (B)	276 (B)	304 (B)	94 (B)
1	PVCHC-OH ^a	>99	n.a.	235	285	71
2	PVCHC-Glyc ^a	>99	n.a.	232	271	75
3	PVCHC-COOH ^a	>99	n.a.	208	259	75
4	PVCHC-Boc-L-cysteine ^b	>99	n.a.	109	152	119
5	PVCHC-Ar-COOH ^a	8	11300	263	292	106
6	PVCHC-NH ₂ ·HCl ^a	55	n.a.	210	260	102, 120
7	PVCHC-Ar-NH ₂ ^a	<1	-	-	-	-
8	PVCHC-Ar ^a	27	10750	271	302	90
9	PVCHC-DDT ^b	89	13700	279	306	-4
10	PVCHC-AIBN ^a	11 ^h	n.a.	274	297	118

(a) Prepared from PVCHC sample A. (b) Prepared from PVCHC sample B. (c) Conversion of pendant vinyl groups determined by ¹H NMR. (d) Number average molar mass, determined by GPC. (e) Initial degradation temperature (*i.e.* the temperature at which the first loss in weight is observed), determined by TGA. (f) Temperature leading to a 5% weight loss, determined by TGA. (g) Glass transition temperature, determined by DSC (defined as the maximum of the first derivative of the second heating cycle). (h) Determined by FTIR spectroscopy. n.a. = not available.

resulted in an increase in molecular weight (Table 4.2, entries 5, 8 and 9 respectively), as measured by GPC. All observed molecular weights are comparable to the theoretical values based on the measured degree of functionalisation (PVCHC-Ar-COOH, $M_{n,theoretical} = 10689$ Da; PVCHC-Ar, $M_{n,theoretical} = 11669$ Da; PVCHC-DDT, $M_{n,theoretical} = 14788$ Da). Besides the experimental error related to GPC, the small deviations between the observed and theoretical M_n values can be explained by the change in hydrodynamic volume of the modified polycarbonates compared to the unmodified PVCHC, which (along with the increase in molecular weight) influences the retention time in the GPC column and, hence, the observed molecular weight.

For the PVCHC polymers modified with protic thiol compounds, no signals were detected by GPC, thus preventing the determination of their molecular weight. This is attributed to the presence of a high amount of polar groups, which significantly increases the intermolecular interactions between the polymer chains and the eluent, thereby considerably weakening the interactions of the polymer with the relatively apolar GPC column and resulting in elution of the polycarbonates within the exclusion volume of the column (molecular weight cut-off above 54 kDa). A similar phenomenon has been observed before for carboxylic acid-functionalized poly(limonene carbonate).⁵⁵

After the general characterisation of the various functionalized polycarbonates discussed above, we focused on the specific properties of each of these polymeric materials. Each of the realized functionalisations of the PVCHC polycarbonate was chosen to introduce tailored features in the polymeric material, and thus targeting different applications.

4.3.3. Specific properties and potential applications of the functionalized polycarbonates

4.3.3.1. PVCHC-OH and PVCHC-Glyc

The functionalisation of PVCHC with compounds containing one or two hydroxyl groups, as 2-mercaptoethanol and 1-thioglycerol respectively, was aimed at increasing the hydrophilicity of the polymer. CO₂-based polycarbonates such as poly(propylene carbonate) and poly(cyclohexene carbonate) are biodegradable, but their hydrophobicity typically limits their use in biomedical *in vivo* applications.⁴⁹ For example, for utilisation in temporary tissue scaffolds, biodegradation of the polymeric scaffold and simultaneous tissue regeneration (*i.e.* cell adhesion, cell growth and migration) are vital factors that are negatively affected by a hydrophobic scaffold surface.^{41,49} The thiol-ene click approach^{28,55,56,64,65} can provide an

alternative to other strategies that have been employed to enhance the hydrophilicity of CO₂-based polycarbonates, such as terpolymerisation with a hydrophilic monomer,⁴⁹ blending of polycarbonates with hydrophilic compounds such as glycerol and water⁴¹ or using an epoxide precursor containing pendant groups that contain (or are convertible into) hydrophilic moieties.³¹

To evaluate the effect of the functionalisation with hydroxyl groups on the hydrophilicity of the polymer, the wettability of the two modified polymers was compared to that of the parent PVCHC by coating the polymers on a microscope slide glass substrate and measuring the water contact angle (Fig. 4.4). PVCHC-OH and PVCHC-Glyc displayed a water contact angle of $38.6 \pm 1.5^\circ$ and $43.2 \pm 1.4^\circ$, respectively, whereas the parent PVCHC gave a water contact angle of $70.8 \pm 2.6^\circ$. This result confirms the expected increase in the hydrophilicity of PVCHC upon incorporation of hydroxyl groups. However, it should be noted that the polymer with the pendant groups with two hydroxyl moieties gave a slightly lower wettability compared to the polymer functionalized with a group with a single hydroxyl group. This indicates that other parameters contribute to defining the wettability of these two polymers, such as surface roughness⁸⁶ but also, and perhaps crucial here, the ability of these groups to pack at the surface.⁸⁷

Fig. 4.4. Water contact angle measurements. Left: PVCHC. Middle: PVCHC-Glyc. Right: PVCHC-OH.

Besides the aforementioned potential application in biomedical implants, the hydroxyl groups of PVCHC-OH and PVCHC-Glyc could serve as starting points for further reactions, *e.g.* the synthesis of brush copolymers by grafting polyester side chains via ring-opening polymerisation of ϵ -caprolactone.³⁶ In the case of PVCHC-Glyc, the vicinal diol moieties have the potential to be used for other subsequent

functionalisation, *e.g.* through reaction with ketones or aldehydes to yield a polymer with pendant ketal or acetal groups. Since the formation of ketal and acetal groups is acid-catalyzed and is reversible, the obtained polymers could find application in pH-responsive drug delivery.⁸⁸ The hydrophilic nature of PVCHC-OH and PVCHC-Glyc also potentially makes them suitable as hydrogels. If such application were the target, the functionalisation protocol would need to be adjusted to avoid the complete conversion of the pendant vinyl groups achieved in the synthesis of PVCHC-Glyc and PVCHC-OH, in order to preserve a fraction of the double bonds to generate chemically crosslinked hydrogels, which would be applicable as wound dressings,⁸⁹ in tissue engineering⁹⁰ and drug delivery.⁹¹

4.3.3.2. PVCHC-COOH

The functionalisation with a carboxyl group (PVCHC-COOH) was aimed at further enhancement of the hydrophilicity compared to that achieved in PVCHC-OH and PVCHC-Glyc. In previous studies with CO₂-based polycarbonates derived from other epoxides, it was reported that pendant carboxylic acid moieties give rise to pH-dependent water solubility.^{28,55,56,64} Similarly, the functionalisation of PVCHC with carboxylic acid groups generated a polymer that was soluble in water at pH > 7, up to concentrations of 40 mg/mL at room temperature. This property is attractive because water-soluble polymers can find a wide range of applications in consumer goods as scale inhibitors and super adsorbents in cleaning products, and as flocculants, thickeners, emulsifiers and paper-sizing agents in toothpastes, shampoos, skin lotions, disposable diapers, textiles and food-related applications.^{92,93} Most of the water-soluble polymers employed industrially are prepared from acrylic acid, maleic anhydride, methacrylic acid and combinations of these monomers.^{92,94} Except for the short-chain oligomers, the resulting polymers are non-biodegradable,^{92,94} and as a result tend to accumulate in open waters such as lakes and oceans. Since these polymeric contaminants are not visible to the naked eye, their impact is less noticeable and hence potentially more dangerous.⁹²

On the other hand, aliphatic polycarbonates are known to be biodegradable and susceptible to hydrolytic degradation.⁹⁵ The combination of biodegradability and water-solubility would prevent accumulation of polymer contaminants in open waters and increase the sustainability of many consumer products. In this context, we monitored the homogeneous degradation of PVCHC-COOH in an aqueous HCl/NaOH solution (pH 8) by means of GPC analysis (Fig. 4.5). These conditions were chosen because seawater typically has a pH in the 7.5-8.4 range and a salt composition primarily consisting of sodium and chloride ions.⁹⁶ After one month at room temperature, the *M_w* decreased to 89% of the original value (19.2 kDa to 17.1

Fig. 4.5. GPC analysis (with water as eluent) of PVCHC-COOH and of its degradation products after 1 and 2 months at 50 °C.

kDa). After one month at 50 °C, the M_w decreased to 40% of the original value (19.9 kDa to 7.75 kDa). Barely any traces of the original polymer were observed after two months at 50 °C (Fig. 4.5). The fact that PVCHC-COOH is water-soluble already under slightly basic conditions and that it is susceptible to hydrolytic degradation offers attractive prospects for applications in consumer goods as well as in the medical and pharmaceutical industry.^{93,97,98} When solubilized in water, PVCHC-COOH reprecipitates when the solution is acidified to pH values below 7. This pH-dependent water-solubility of PVCHC-COOH makes it a potential candidate for smart drug delivery systems, where stimuli-responsive behaviour is one of the key elements. For example, pH-responsivity can be employed for targeted drug delivery, as variations in pH between different organs, tissues and cellular compartments can be used to trigger drug release.⁹⁹

4.3.3.3. PVCHC-NH₂·HCl

The functionalisation of PVCHC with an amino group was studied because amino-functionalized polymers can be used to bind proteins or drugs and can serve as precursors for the synthesis of charged ammonium-functionalized polymers suitable for *e.g.* anti-bacterial coatings.^{55,100} In our initial approach to prepare an

amino-functionalized polycarbonate we used 2-aminoethanethiol (cysteamine) as reactant. However, the modification reaction of PVCHC with 2-aminoethanethiol was hampered by the occurrence of side-reactions resulting in the degradation of the polycarbonate chains. Most probably, the amine moiety of 2-aminoethanethiol breaks down the carbonate bonds, as indicated by the high relative intensity of the ¹H NMR signals corresponding to the PVCHC end-groups compared to the signals corresponding to the protons adjacent to the carbonate bonds (Supplementary Information, Fig. S4.53). Furthermore, GPC analysis showed a significant decrease in molecular weight compared to the original polymer (Supplementary Information, Fig. S4.54). This issue was circumvented by carrying out the thiol-ene reaction using a quaternized analogue of 2-aminoethanethiol, *i.e.* compound **6** (2-aminoethanethiol hydrochloride), with which no polymer degradation was observed by ¹H NMR (Supplementary Information, Fig. S4.15). The obtained product was a transparent, water-soluble polymer. To the best of our knowledge, this is the first report of the one-step functionalisation of a CO₂-based polycarbonate to introduce quaternary ammonium groups.

To explore the effect of the expected intermolecular ionic interaction between the PVCHC functionalized with ammonium groups and its counterpart functionalized with carboxyl groups, we mixed an aqueous solution of PVCHC-NH₂·HCl with an aqueous solution of PVCHC-COOH neutralized with NaOH (pH = 7). This resulted in the immediate formation of a precipitate. The obtained solid was insoluble in water over a pH range from 3 to 11, as well as in various organic solvents such as THF, chloroform, diethyl ether, methanol and DMSO, demonstrating the anticipated strong interaction between the pendant -COO⁻ groups of the neutralized PVCHC-COOH and the -NH₃⁺ moieties of PVCHC-NH₂·HCl. DSC analysis of the solid did not evidence any thermal transition between room temperature and 200 °C, whereas the polymeric mixture showed signs of thermal degradation above 200 °C. This suggests that strong intermolecular interactions are present in the form of ionic crosslinking, thereby preventing motion of the polymer chains.

4.3.3.4. PVCHC-Boc-L-cysteine

By modifying PVCHC with naturally occurring thiols, fully bio-based functionalized polycarbonates can be obtained. Specifically, L-cysteine, a natural amino acid that is industrially obtained from waste material from animal husbandry (*i.e.* hair and feathers),¹⁰¹ is of interest for biomedical applications due to the presence of both carboxyl and amino moieties, which have the potential to be used as anchoring points for contrasting agents to be used in medical analyses by Magnetic Resonance

Imaging (MRI).¹⁰² To prevent any polymer chain degradation induced by the amino moiety (*vide supra*), we used Boc-protected L-cysteine (**4**) as reactant in the thiol-ene step. Removal of the Boc-group was achieved by treatment with a strong acid, which led to the formation of a precipitate that was insoluble in a range of protic and aprotic organic solvents (THF, ethanol, methanol, DMSO) as well as in acidified (pH 3), neutral (pH 7) and basified (pH 11) water. The presence of both amino and carboxylic acid pendant groups in the deprotected polymer is expected to lead to strong intermolecular ionic crosslinking interactions, which would explain the observed low solubility of the product in the tested solvents. The effectiveness of the deprotection was proven by FTIR analysis of the polymer before and after deprotection (Fig. 4.6), which showed a decrease in intensity of the signals at 1705 cm⁻¹ and 1155 cm⁻¹, corresponding to the C=O stretch vibration and the C-O stretch vibration of the amino ester group of the Boc protecting moiety, respectively. However, the presence of a residual signal at 1155 cm⁻¹ indicates that the Boc protecting groups could not be removed completely.

The fact that addition of an acid to PVCHC-Boc-L-cysteine results in a chemically resistant, most likely crosslinked polymer suggests that this system could potentially be used as a two-component coating or adhesive, similar to epoxy resins and polyurethane formulations. To evaluate the feasibility of this potential application, future studies should focus on the investigation of the mechanical properties of the deprotected PVCHC-L-cysteine.

4.1.1.1. PVCHC-DDT

Functionalisation with a thiol bearing a long alkyl chain was investigated with the aim of reducing the brittle nature of cyclohexene-type polycarbonates^{5,7,13} and to impart a rubber-like behaviour upon subsequent crosslinking.⁵⁵ As shown in Table 4.2 entry 3, functionalisation of 89% of the vinyl groups with **6** (dodecanethiol) affected the thermal behaviour of PVCHC significantly, as evidenced by a decrease of the T_g from 94 to -4 °C. Previous reports showed that the introduction of alkyl ester groups along the backbone of poly(limonene carbonate) by means of thiol-ene chemistry brought about a decrease in the T_g from 130 to 5 °C.⁵⁵ Subsequent solvent coating of such modified poly(limonene carbonate) followed by curing of the remaining double bonds (1-2%) at 100 °C for 5h was reported to yield a crosslinked polymer with improved elasticity (228-342% elongation at break vs. 15% of the original poly(limonene carbonate)). Following a similar curing procedure (see experimental section), PVCHC-DDT did not display any signs of crosslinking, as indicated by the retained solubility in organic solvents. This was confirmed by ¹H

Fig. 4.6. FTIR analysis of the deprotection of PVCHC-Boc-L-cysteine.

NMR (see Fig. S4.21), which showed no decrease in the signals of the double bond of the vinyl groups. No crosslinking was detected even after prolonged curing time (48 h), addition of a radical initiator (AIBN) or by performing the reaction in solution. It was concluded that the pendant vinyl groups of PVCHC are less prone to radical reaction than the pendant double bonds of poly(limonene carbonate), most probably because the methyl group next to the double bond in poly(limonene carbonate) can stabilize the radical intermediate by electron donation. On one hand, this behaviour implies a wider processing temperature window and an expected increase of the shelf life of pre-cured PVCHC-DDT compared to pre-cured poly(limonene carbonate). On the other hand, crosslinking agents (*e.g.* dithiols) would have to be used in order to crosslink PVCHC-DDT and to achieve a rubber-like behaviour.

4.1.1.2. PVCHC-Ar, PVCHC-Ar-COOH and PVCHC-Ar-NH₂

Thiol-ene modifications of CO₂-based polycarbonates are typically reported employing aliphatic thiols. In this work we showed that it is also possible to introduce thiophenolic compounds by the reaction of PVCHC with **5** (4-mercaptobenzoic acid), **7** (4-aminothiophenol) and **8** (thiophenol). Functionalisation

of polycarbonates with aromatic groups is worth being investigated as the presence of these groups along the polymer backbone can improve thermal properties such as the glass transition temperature due to increased interchain interactions (*i.e.* π - π stacking). However, the introduction of pendant aromatic groups did not significantly influence the thermal properties of PVCHC (Table 4.2). This can be ascribed mainly to the low degree of functionalisation that was achieved using the employed aromatic thiols (Table 4.2, entries 5, 7 and 8), most likely due to the steric hindrance of the aromatic moiety, hampering the click reaction. To mitigate these steric effects, compounds such as benzyl mercaptan could be used in future studies to reach higher degrees of conversion.

4.2. Conclusions

In this work, the functionalisation of the CO₂-based poly(vinylcyclohexene carbonate) (PVCHC) by means of thiol-ene click chemistry was systematically investigated employing a varied library of thiols with different functional groups.

PVCHC was readily modified with full conversion of the pendant vinyl groups using linear thiol compounds bearing polar functional groups such as one or two hydroxyls or a carboxyl group. Such functionalisation imparted enhanced hydrophilicity to the polymer and, in the case of PVCHC-COOH, even led to pH-dependent water solubility. Additionally, the degradability of this polymer in a slightly basic aqueous solution (pH 8) was demonstrated. These features are promising for applications in the biomedical field or in consumer goods. Future feasibility studies in this sense should entail an investigation of the surface properties and of the toxicity of these polycarbonates modified with polar terminal groups.

The functionalisation of PVCHC by introducing quaternary ammonium salt groups led to a polymer (PVCHC-NH₂·HCl) that readily formed a precipitate when combined with PVCHC-COOH, strongly suggesting intermolecular ionic crosslinking between the two polymers. The functionalisation of PVCHC with the amino acid L-cysteine as pendant group (PVCHC-Boc-L-cysteine) was achieved through a protected thiol precursor. Once the carboxyl group was deprotected, immediate formation of a precipitate with low solubility in protic and aprotic organic solvents as well as in acidified, neutral and basified water was achieved. This is again attributed to strong intermolecular ionic crosslinking interactions. The rapid formation of insoluble products observed with PVCHC-NH₂·HCl and PVCHC-L-cysteine is promising for potential application as adhesives or coatings. Future feasibility studies for these

target applications should focus on investigating the mechanical properties of the obtained insoluble products.

The modification of PVCHC with thiol groups containing aromatic rings proved more challenging and only a limited degree of functionalisation was achieved due to steric effects. This limitation could probably be overcome employing thiol precursors with an alkyl chain between the -SH group and the aromatic ring, although this would also increase the length of the pendant group and, hence, cause a decrease in the glass transition temperature of the final polymer. Finally, partial functionalisation of PVCHC by reaction with a thiol with a long alkyl chain group (dodecanethiol) led to the expected decrease of the glass transition temperature of PVCHC, generating a polymer that is a viscous liquid at room temperature ($T_g = -4\text{ }^\circ\text{C}$). This modified PVCHC has the potential to be used to produce a rubber if crosslinking of the remaining vinyl groups along the polymer chain will be achieved, e.g. with a dithiol. In summary, our study demonstrated the viability of the thiol-ene reaction to functionalize a CO₂-based polycarbonate with a variety of groups and highlighted the influence of the nature of the introduced functional groups on the physicochemical behaviour of the obtained polymeric materials and, therefore, on their potential applications as specialty chemicals.

References

- 1 P. Anastas and N. Eghbali, *Chem. Soc. Rev.*, 2010, **39**, 301–312.
- 2 R. C. Thompson, C. J. Moore, F. S. vom Saal and S. H. Swan, *Philos. Trans. R. Soc. B Biol. Sci.*, 2009, **364**, 2153–2166.
- 3 IEA, *CO₂ emissions from fuel combustion 2016*, OECD Publishing, Paris, 2016.
- 4 S. Fukuoka, M. Kawamura, K. Komiya, M. Tojo, H. Hachiya, K. Hasegawa, M. Aminaka, H. Okamoto, I. Fukawa and S. Konno, *Green Chem.*, 2003, **5**, 497–507.
- 5 M. Taherimehr and P. P. Pescarmona, *J. Appl. Polym. Sci.*, 2014, **131**, 41141.
- 6 D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388–2410.
- 7 M. R. Kember, A. Buchard and C. K. Williams, *Chem. Commun.*, 2011, **47**, 141–163.
- 8 S. Klaus, M. W. Lehenmeier, C. E. Anderson and B. Rieger, *Coord. Chem. Rev.*, 2011, **255**, 1460–1479.
- 9 G. Trott, P. K. Saini and C. K. Williams, *Philos. Trans. R. Soc. Math. Phys. Eng. Sci.*, 2016, **374**, 20150085.
- 10 H. Sugimoto and S. Inoue, *J. Polym. Sci. Part Polym. Chem.*, 2004, **42**, 5561–5573.
- 11 D. J. Darensbourg and S. J. Wilson, *Green Chem.*, 2012, **14**, 2665.
- 12 A. J. Kamphuis, F. Picchioni and P. P. Pescarmona, *Green Chem.*, 2019, **21**, 406–448.
- 13 P. P. Pescarmona and M. Taherimehr, *Catal. Sci. Technol.*, 2012, **2**, 2169.
- 14 Z. Qin, C. M. Thomas, S. Lee and G. W. Coates, *Angew. Chem. Int. Ed.*, 2003, **42**, 5484–5487.

- 15 C. T. Cohen, T. Chu and G. W. Coates, *J. Am. Chem. Soc.*, 2005, **127**, 10869–10878.
- 16 H. Sugimoto and K. Kuroda, *Macromolecules*, 2008, **41**, 312–317.
- 17 D. R. Moore, M. Cheng, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2003, **125**, 11911–11924.
- 18 S. Mang, A. I. Cooper, M. E. Colclough, N. Chauhan and A. B. Holmes, *Macromolecules*, 2000, **33**, 303–308.
- 19 D. J. Darensbourg and J. C. Yarbrough, *J. Am. Chem. Soc.*, 2002, **124**, 6335–6342.
- 20 M. Cheng, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 1998, **120**, 11018–11019.
- 21 M. R. Kember and C. K. Williams, *J. Am. Chem. Soc.*, 2012, **134**, 15676–15679.
- 22 O. Hauenstein, M. Reiter, S. Agarwal, B. Rieger and A. Greiner, *Green Chem.*, 2016, **18**, 760–770.
- 23 C. M. Byrne, S. D. Allen, E. B. Lobkovsky and G. W. Coates, *J. Am. Chem. Soc.*, 2004, **126**, 11404–11405.
- 24 C. Li, R. J. Sablong and C. E. Koning, *Angew. Chem. Int. Ed.*, 2016, **55**, 11572–11576.
- 25 N. Kindermann, À. Cristòfol and A. W. Kleij, *ACS Catal.*, 2017, **7**, 3860–3863.
- 26 C. Martín and A. W. Kleij, *Macromolecules*, 2016, **49**, 6285–6295.
- 27 M. Winkler, C. Romain, M. A. R. Meier and C. K. Williams, *Green Chem.*, 2015, **17**, 300–306.
- 28 D. J. Darensbourg, W.-C. Chung, C. J. Arp, F.-T. Tsai and S. J. Kyran, *Macromolecules*, 2014, **47**, 7347–7353.
- 29 Y. Hu, L. Qiao, Y. Qin, X. Zhao, X. Chen, X. Wang and F. Wang, *Macromolecules*, 2009, **42**, 9251–9254.
- 30 J. Hilf, M. Scharfenberg, J. Poon, C. Moers and H. Frey, *Macromol. Rapid Commun.*, 2015, **36**, 174–179.
- 31 J. Geschwind and H. Frey, *Macromolecules*, 2013, **46**, 3280–3287.
- 32 Y. Tominaga, T. Shimomura and M. Nakamura, *Polymer*, 2010, **51**, 4295–4298.
- 33 M. D. Konieczynska, X. Lin, H. Zhang and M. W. Grinstaff, *ACS Macro Lett.*, 2015, **4**, 533–537.
- 34 M. Taherimehr, J. P. C. C. Sertã, A. W. Kleij, C. J. Whiteoak and P. P. Pescarmona, *ChemSusChem*, 2015, **8**, 1034–1042.
- 35 G. Si, L. Zhang, B. Han, H. Zhang, X. Li and B. Liu, *RSC Adv.*, 2016, **6**, 22821–22826.
- 36 J.-F. Zhang, W.-M. Ren, X.-K. Sun, Y. Meng, B.-Y. Du and X.-H. Zhang, *Macromolecules*, 2011, **44**, 9882–9886.
- 37 H. Zhang, B. Liu, H. Ding, J. Chen and Z. Duan, *Polymer*, 2017, **129**, 5–11.
- 38 K. Deng, S. Wang, S. Ren, D. Han, M. Xiao and Y. Meng, *ACS Appl. Mater. Interfaces*, 2016, **8**, 33642–33648.
- 39 H. Zhang and M. W. Grinstaff, *J. Am. Chem. Soc.*, 2013, **135**, 6806–6809.
- 40 L. Gu, Y. Gao, Y. Qin, X. Chen, X. Wang and F. Wang, *J. Polym. Sci. Part Polym. Chem.*, 2013, **51**, 282–289.
- 41 I. Manavitehrani, A. Fathi, Y. Wang, P. K. Maitz, F. Mirmohseni, T. L. Cheng, L. Peacock, D. G. Little, A. Schindeler and F. Dehghani, *Biomacromolecules*, 2017, **18**, 1736–1746.

- 42 M. DeBolt, A. Kiziltas, D. Mielewski, S. Waddington and M. J. Nagridge, *J. Appl. Polym. Sci.*
- 43 C. E. Koning, R. J. Sablong, E. H. Nejad, R. Duchateau and P. Buijsen, *Prog. Org. Coat.*, 2013, **76**, 1704–1711.
- 44 E. Orgilés-Calpena, F. Arán-Aís, A. M. Torró-Palau and C. Orgilés-Barceló, *Int. J. Adhes. Adhes.*, 2016, **70**, 218–224.
- 45 C. Li, M. Johansson, P. Buijsen, G. Dijkstra, R. J. Sablong and C. E. Koning, *Prog. Org. Coat.*, 2021, **151**, 106073.
- 46 J. Langanke, A. Wolf, J. Hofmann, K. Böhm, M. A. Subhani, T. E. Müller, W. Leitner and C. Gürtler, *Green Chem.*, 2014, **16**, 1865–1870.
- 47 J. Langanke and A. Wolf, *Org. Process Res. Dev.*, 2015, **19**, 735–739.
- 48 Empower Materials, www.empowermaterials.com, (accessed on August 1, 2017).
- 49 L. Gu, Y. Qin, Y. Gao, X. Wang and F. Wang, *J. Polym. Sci. Part Polym. Chem.*, 2013, **51**, 2834–2840.
- 50 J. G. Kim, C. D. Cowman, A. M. LaPointe, U. Wiesner and G. W. Coates, *Macromolecules*, 2011, **44**, 1110–1113.
- 51 Y. Li, J. Hong, R. Wei, Y. Zhang, Z. Tong, X. Zhang, B. Du, J. Xu and Z. Fan, *Chem. Sci.*, 2015, **6**, 1530–1536.
- 52 M. Jia, D. Zhang, G. W. de Kort, C. H. Wilsens, S. Rastogi, N. Hadjichristidis, Y. Gnanou and X. Feng, *Macromolecules*, 2020, **53**, 5297–5307.
- 53 Z. Zhang, Z. Mo, H. Zhang, X. Wang and X. Zhao, *Macromol. Chem. Phys.*, 2003, **204**, 1557–1566.
- 54 Y. Tominaga and K. Yamazaki, *Chem. Commun.*, 2014, **50**, 4448.
- 55 O. Hauenstein, S. Agarwal and A. Greiner, *Nat. Commun.*, 2016, **7**, 11862.
- 56 D. J. Darensbourg and F.-T. Tsai, *Macromolecules*, 2014, **47**, 3806–3813.
- 57 P. Alagi, G. Zapsas, N. Hadjichristidis, S. C. Hong, Y. Gnanou and X. Feng, *Macromolecules*, 2021, **54**, 6144–6152.
- 58 J. Geschwind, F. Wurm and H. Frey, *Macromol. Chem. Phys.*, 2013, **214**, 892–901.
- 59 S. Tempelaar, L. Mespouille, P. Dubois and A. P. Dove, *Macromolecules*, 2011, **44**, 2084–2091.
- 60 A. B. Lowe, *Polym. Chem.*, 2010, **1**, 17–36.
- 61 G.-L. Liu, H.-W. Wu, Z.-I. Lin, M.-G. Liao, Y.-C. Su, C.-K. Chen and B.-T. Ko, *Polym. Chem.*, 2021, **12**, 1244–1259.
- 62 C. Li, S. van Berkel, R. J. Sablong and C. E. Koning, *Eur. Polym. J.*, 2016, **85**, 466–477.
- 63 T. Stöber, C. Li, J. Unruangsri, P. K. Saini, R. J. Sablong, M. A. R. Meier, C. K. Williams and C. Koning, *Polym. Chem.*, 2017, **8**, 6099–6105.
- 64 D. J. Darensbourg and Y. Wang, *Polym. Chem.*, 2015, **6**, 1768–1776.
- 65 Y. Wang, J. Fan and D. J. Darensbourg, *Angew. Chem. Int. Ed.*, 2015, **54**, 10206–10210.
- 66 G. A. Bhat, A. Z. Rashad, T. M. Folsom and D. J. Darensbourg, *Organometallics*, 2020, **39**, 1612–1618.
- 67 G. A. Bhat, A. Z. Rashad and D. J. Darensbourg, *Polym. Chem.*, 2020, **11**, 4699–4705.
- 68 G.-W. Yang and G.-P. Wu, *ACS Sustain. Chem. Eng.*, 2019, **7**, 1372–1380.

- 69 J.-K. Zhao, G.-W. Yang, X.-F. Zhu and G.-P. Wu, *Polym. Chem.*, 2019, **10**, 5265–5270.
- 70 E. V. Makshina, M. Dusselier, W. Janssens, J. Degreè, P. A. Jacobs and B. F. Sels, *Chem. Soc. Rev.*, 2014, **43**, 7917–7953.
- 71 H. A. Wittcoff, B. G. Reuben and J. S. Plotkin, *Industrial Organic Chemicals*, John Wiley & Sons, Hoboken, 2012, vol. 3rd Edition.
- 72 L. Peña Carrodegua, J. González-Fabra, F. Castro-Gómez, C. Bo and A. W. Kleij, *Chem. Eur. J.*, 2015, **21**, 6115–6122.
- 73 J. W. Comerford, I. D. V. Ingram, M. North and X. Wu, *Green Chem.*, 2015, **17**, 1966–1987.
- 74 C. J. Whiteoak, N. Kielland, V. Laserna, F. Castro-Gómez, E. Martin, E. C. Escudero-Adán, C. Bo and A. W. Kleij, *Chem. Eur. J.*, 2014, **20**, 2264–2275.
- 75 Y. Labat, *Kirk-Othmer Encycl. Chem. Technol.*, 2000.
- 76 M. Taherimehr, S. M. Al-Amsyar, C. J. Whiteoak, A. W. Kleij and P. P. Pescarmona, *Green Chem.*, 2013, **15**, 3083.
- 77 Donald. J. Darensbourg, J. C. Yarbrough, C. Ortiz and C. C. Fang, *J. Am. Chem. Soc.*, 2003, **125**, 7586–7591.
- 78 N. Yi, J. Unruangsri, J. Shaw and C. K. Williams, *Faraday Discuss.*, 2015, **183**, 67–82.
- 79 K. Griesbaum, *Angew. Chem. Int. Ed. Engl.*, 1970, **9**, 273–287.
- 80 E. Bendary, R. R. Francis, H. M. G. Ali, M. I. Sarwat and S. El Hady, *Ann. Agric. Sci.*, 2013, **58**, 173–181.
- 81 K. Król-Morkisz and K. Pielichowska, in *Polymer Composites with Functionalized Nanoparticles*, Elsevier, 2019, pp. 405–435.
- 82 K.-D. Ahn, Y.-H. Lee and D.-I. Koo, *Polymer*, 1992, **33**, 4851–4856.
- 83 S. D. Thorat, P. J. Phillips, V. Semenov and A. Gakh, *J. Appl. Polym. Sci.*, 2003, **89**, 1163–1176.
- 84 R. A. Weiss, R. D. Lundberg and S. R. Turner, *J. Polym. Sci. Polym. Chem. Ed.*, 1985, **23**, 549–568.
- 85 R. A. Weiss, J. J. Fitzgerald and D. Kim, *Macromolecules*, 1991, **24**, 1071–1076.
- 86 K. J. Kubiak, M. C. T. Wilson, T. G. Mathia and Ph. Carval, *Wear*, 2011, **271**, 523–528.
- 87 W. Lin and Y.-L. Hsieh, *J. Polym. Sci. Part B Polym. Phys.*, 1997, **35**, 1145–1159.
- 88 W. Chen, F. Meng, F. Li, S.-J. Ji and Z. Zhong, *Biomacromolecules*, 2009, **10**, 1727–1735.
- 89 E. Caló and V. V. Khutoryanskiy, *Eur. Polym. J.*, 2015, **65**, 252–267.
- 90 A. S. Hoffman, *Adv. Drug Deliv. Rev.*, 2012, **64**, 18–23.
- 91 T. R. Hoare and D. S. Kohane, *Polymer*, 2008, **49**, 1993–2007.
- 92 R. A. Gross and B. Kalra, *Science*, 2002, **297**, 803–807.
- 93 V. G. Kadajji and G. V. Betageri, *Polymers*, 2011, **3**, 1972–2009.
- 94 R. J. Larson, E. A. Bookland, R. T. Williams, K. M. Yocom, D. A. Saucy, M. B. Freeman and G. Swift, *J. Environ. Polym. Degrad.*, 1997, **5**, 41–48.
- 95 R. P. Brannigan and A. P. Dove, *Biomater Sci*, 2017, **5**, 9–21.
- 96 D. Li and S. Liu, in *Water Quality Monitoring and Management*, eds. D. Li and S. Liu, Academic Press, 2019, pp. 233–249.
- 97 C. He, X. Zhuang, Z. Tang, H. Tian and X. Chen, *Adv. Healthc. Mater.*, 2012, **1**, 48–78.

- 98 N. Larson and H. Ghandehari, *Chem. Mater.*, 2012, **24**, 840–853.
- 99 D. Schmaljohann, *Adv. Drug Deliv. Rev.*, 2006, **58**, 1655–1670.
- 100 M. Scharfenberg, J. Hilf and H. Frey, *Adv. Funct. Mater.*, 2018, **28**, 1704302.
- 101 M. Breuer, K. Ditrich, T. Habicher, B. Hauer, M. Keßeler, R. Stürmer and T. Zelinski, *Angew. Chem. Int. Ed.*, 2004, **43**, 788–824.
- 102 Y. Li, S. Liu, X. Zhao, Y. Wang, J. Liu, X. Wang and L. Lu, *Theranostics*, 2017, **7**, 4689–4698.

Supplementary Information

Appendix A: Synthesis of the amino-tBu-tris(phenolate) ligand

2,4-di-*tert*-butylphenol (99%, Sigma-Aldrich), hexamethylenetetramine ($\geq 99.8\%$, Sigma-Aldrich), aqueous formaldehyde (37 wt%, Sigma-Aldrich), chloroform ($\geq 99.8\%$, Macron), magnesium sulphate (Boom), diethyl ether ($\geq 99.0\%$, Macron) and chloroform-d (99.8% , Sigma-Aldrich) were used as received.

Fig. S4.1. Synthesis of the amino-tBu-tris(phenolate) ligand

The synthesis of the ligand was performed as reported in literature (Fig. S4.1).¹ 2,4-di-*tert*-butylphenol (8.25 g, 40 mmol), hexamethylenetetramine (0.47 g, 3.3 mmol) and 37% aq. formaldehyde (1.21 g, 14.2 mmol) were added to a 250 mL round-bottom flask equipped with a reflux condenser. The mixture was stirred at $125\text{ }^\circ\text{C}$ for 48 h, after which the reaction was quenched with CHCl_3 (100 mL). The organic layer was washed with demineralized water (3 x 100 mL) and subsequently dried over MgSO_4 . The organic phase was concentrated using rotary evaporation and the desired product was obtained after recrystallisation from diethyl ether as a white solid (6.46 g, 69%). ^1H NMR (400 MHz, CDCl_3): δ 7.25 (d, 3H, ArH), 6.99 (d, 3H, ArH), 6.56 (s, 3H, ArOH), 3.65 (s, 6H, CH), 1.40 (s, 27H, tBu), 1.27 (s, 27H, tBu). ^{13}C NMR (300 MHz, CDCl_3): δ 151.5, 142.2, 136.5, 125.7, 124.1, 121.9, 56.7, 35.0, 34.3, 31.7, 29.8.

1. Kol, M.; Shamis, M.; Goldberg, I.; Goldschmidt, Z.; Alfi, S.; Hayut-Salant, E. Titanium (IV) complexes of trianionic amine triphenolate ligands, *Inorg. Chem. Commun.* **2001**, 4, 177.

Appendix B: Synthesis of aluminum (III) amino-tBu-tris(phenolate) catalyst

Nitrogen gas ($\geq 99.999\%$, Linde Gas) was used as received. Dry tetrahydrofuran was obtained by percolating tetrahydrofuran (anhydrous, 99.8%, Sigma-Aldrich) over Al₂O₃ columns (Fluka). The dry tetrahydrofuran was subsequently stored under nitrogen. Trimethylaluminum (2.0 M in heptane, Sigma-Aldrich) and hexane ($\geq 95.0\%$, Macron) were used as received.

Fig. S4.2. Synthesis of aluminum (III) amino-tBu-tris(phenolate) catalyst

The synthesis of the aluminum complex was performed similarly to a method previously reported in the literature (Fig. S4.2).² The amino-tBu-tris(phenolate) ligand precursor was brought under N₂-atmosphere in a three-neck round-bottom flask and dissolved in 20 mL dry THF. Trimethylaluminum (2.0 M in heptane, 0.75 mL, 1.49 mmol) was added dropwise using a syringe and the resulting solution was stirred for 2 h at room temperature. Subsequently, the mixture was concentrated and the product was purified by recrystallisation in THF. The resulting crystals were filtered and washed with hexane. The product was then dried under vacuum at 50 °C for 48 h to yield a white powder.

¹H NMR (400 MHz, CDCl₃): δ 7.21 (d, 3H, ArH), 6.85 (d, 3H, ArH), 4.27 (d, 3H, ArCH₂N), 3.89 (br, 4H, THF), 2.92 (d, 3H, ArCH₂N), 1.91 (br, 4H, THF), 1.40 (s, 27H, tBu), 1.26 (s, 27H, tBu). ¹³C NMR (300 MHz, CDCl₃): δ 154.9, 139.3, 137.1, 123.9, 123.7, 121.5, 68.4, 59.2, 35.0, 34.2, 31.9, 29.7, 25.7.

1. Whiteoak, C. J.; Kielland, N.; Laserna, V.; Castro-Gómez, F.; Martin, E.; Escudero-Adán, E. C.; Bo C.; Kleij, A. W. Highly Active Aluminium Catalysts for the Formation of Organic Carbonates from CO₂ and Oxiranes, *Chem. Eur. J.* **2014**, *20*, 2264–2275.

Appendix C: ^1H NMR and ^{13}C NMR spectra of the synthesised polycarbonates

Fig. S4.3. ^1H NMR of PVCHC (Sample B)

Fig. S4.4. ^{13}C NMR of PVCHC (sample B)

Fig. S4.7. ^1H NMR of PVCHC-Glyc Fig. S4.8. ^{13}C NMR of PVCHC-Glyc

Fig. S4.9. ¹H NMR of PVCHC-COOH. Besides the repeating unit of PVCHC-COOH, the spectrum shows the presence of a small fraction ($o = 0.2 n$) of a repeating unit incorporating the product of the (reversible) self-esterification of thioglycolic acid as pendant group.

Fig. S4.10. ¹³C NMR of PVCHC-COOH. Besides the repeating unit of PVCHC-COOH, the spectrum shows the presence of a small fraction of a repeating unit incorporating the product of the (reversible) self-esterification of thioglycolic acid as pendant group.

Fig. S4.15. ¹H NMR of PVCHC-NH₂·HCl Fig. S4.16. ¹³C NMR of PVCHC-NH₂·HCl

Fig. S4.19. ¹H NMR of PVCHC-DDT Fig. S4.20. ¹³C NMR of PVCHC-DDT

Fig. S4.21. ¹H NMR of PVCHC-DDT after curing at 100 °C for 5h

Appendix D: FTIR spectra of the synthesised polycarbonates

Fig. S4.22. FTIR spectrum of PVCHC (Sample B)

Fig. S4.23. FTIR spectrum of PVCHC-OH

Fig. S4.24. FTIR spectrum of PVCHC-Glyc

Fig. S4.25. FTIR spectrum of PVCHC-COOH

Fig. S4.26. FTIR spectrum of PVCHC-Boc-Cys

Fig. S4.27. FTIR spectrum of PVCHC-Ar-COOH

Fig. S4.28. FTIR spectrum of PVCHC-NH₂·HCl

Fig. S4.29. FTIR spectrum of PVCHC-Ar

Fig. S4.30. FTIR spectrum of PVCHC-DDT

Fig. S4.31. FTIR spectrum of PVCHC-AIBN

Appendix E: TGA analysis of the synthesised polycarbonates

Fig. S4.32. TGA of PVCHC

Fig. S4.33. TGA of PVCHC-OH

Fig. S4.34. TGA of PVCHC-Glyc

Fig. S4.35. TGA of PVCHC-COOH

Fig. S4.36. TGA of PVCHC-Boc-L-Cys

Fig. S4.37. TGA of PVCHC-Ar-COOH

Fig. S4.38. TGA of PVCHC-NH₂·HCl

Fig. S4.39. TGA of PVCHC-Ar

Fig. S4.40. TGA of PVCHC-DDT

Fig. S4.41. TGA of PVCHC-AIBN

Appendix F: DSC analysis of the synthesised polycarbonates

Fig. S4.42. DSC of PVCHC (Sample A)

Fig. S4.43. DSC of PVCHC (Sample B)

Fig. S4.44. DSC of PVCHC-OH

Fig. S4.45. DSC of PVCHC-Glyc

Fig. S4.46. DSC of PVCHC-COOH

Fig. S4.47. DSC of PVCHC-Boc-L-Cys

Fig. S4.48. DSC of PVCHC-Ar-COOH

Fig. S4.49. DSC of PVCHC-NH₂HCl

Fig. S4.50. DSC of PVCHC-Ar

Fig. S4.51. DSC of PVCHC-DDT

Fig. S4.52. DSC of PVCHC-AIBN

Appendix G: Analysis of the reaction between PVCHC and 2-aminoethanethiol

Fig. S4.53. ^1H NMR spectrum of the reaction product of PVCHC with 2-aminoethanethiol

Fig. S4.54. GPC chromatogram of the reaction product of PVCHC with 2-aminoethanethiol (original polymer in grey)

Chapter 5: A pH-responsive and hydrolytically degradable CO₂-based polycarbonate prepared by functionalisation using thiol-ene chemistry

CO₂-based polycarbonates have potential as sustainable alternative to conventional petroleum-derived and non-biodegradable polymers. However, often the physiochemical properties of these aliphatic polycarbonates have to be optimised to make them suitable for specific applications. In this context, thiol-ene click chemistry was employed to modify CO₂-based poly(vinyl-cyclohexene carbonate) (PVCHC), by introduction of pendant carboxyl groups along the polymer backbone. The resulting polycarbonate, PVCHC-COOH, was evaluated for potential for biomedical and pharmaceutical applications. In this context, PVCHC-COOH demonstrated a relevant feature as pH-responsivity by becoming water soluble at pH > 7. The hydrolytic degradation of PVCHC-COOH was studied in aqueous solution (pH = 8) at different temperatures (RT, 50 °C and 70 °C). The rate of the hydrolytic degradation reaction as well as the resulting degradation products were characterised using gel permeation chromatography (GPC), nuclear magnetic resonance (¹H and ¹³C NMR), and electrospray ionisation mass spectrometry (ESI-MS). The results showed that PVCHC-COOH fully degrades after 2 weeks at 70 °C, thereby predominantly forming the cyclohexane-1,2-diol analogue of the PVCHC-COOH repeating unit.

The cytotoxicity of PVCHC-COOH and of its degradation products was investigated by means of extraction and direct contact testing using murine fibroblast (L929) cells. The interaction of PVCHC-COOH or its degradation products with the fibroblasts was monitored with fluorescent microscopy, using cytoskeleton (Phalloidin) and nucleus (DAPI) staining, and with a cell proliferation assay (XTT). PVCHC-COOH demonstrated acceptable biocompatibility displaying mild toxicity towards the fibroblasts at higher concentrations (5 and 10 vol%), while the degradation products of PVCHC-COOH showed no signs of cytotoxicity at all within the tested range of concentrations (1.25–10 vol%). The observed pH-responsivity, hydrolytic degradability and proper biocompatibility of PVCHC-COOH render it an attractive candidate for biomedical and pharmaceutical applications.

5.1. Introduction

Aliphatic polycarbonates derived from CO₂ and epoxides are attractive materials owing to the (partial or full) renewable character of the reactants used to prepare them, their biodegradability and the tuneability of their thermal and mechanical properties, the latter being dependent on the epoxide that is employed.^{1–3} However, the actual utilisation of these polycarbonates in practical applications is still limited. For example, the widely studied poly(propylene carbonate) and poly(cyclohexene carbonate) are relatively hydrophobic, which leads to poor cell adhesion and slow biodegradation, thereby limiting their suitability for biomedical applications.^{4,5} Furthermore, while conventional polycarbonates based on bisphenol-A find use in the automotive industry, construction, optics and electronics as engineering plastics,^{1,6} poly(propylene carbonate) and poly(cyclohexene carbonate) have inferior mechanical properties and lower thermal stability and, as a result, are not suitable for application as engineering plastics.^{1,7,8} Various strategies have been employed to tailor the properties of CO₂-based polycarbonates, including terpolymerisation of CO₂ with multiple epoxides,^{5,9} block-copolymerisation to synthesise polymers with different types of polycarbonate blocks or containing polyester blocks,^{10,11} blending of polycarbonates with other polymers¹² or with inorganic solids,¹³ and post-polymerisation modification to introduce functional moieties.^{14–17} Among these methods, post-polymerisation modification has been shown to be a highly versatile approach. More specifically, polycarbonates prepared by employing epoxides such as limonene oxide,^{15,18–20} cyclohexadiene oxide,²¹ vinyl-cyclohexene oxide^{22,23} or 2-vinylloxirane,^{16,24} contain unsaturated moieties that provide a synthetic toolbox to introduce functionalities with which the physicochemical properties of the polymers can be customised. Within this context, thiol-ene click chemistry has been studied as a 100% atom-efficient method to include functional groups along the polycarbonate backbone, thereby introducing crosslinking,^{18,19,22,24–26} water-solubility,^{16,21,27} enhanced electro-conductivity²⁸ or starting points for subsequent grafting.²³

Herein we report a novel polycarbonate containing pendant carboxylic acid groups along the backbone (PVCHC-COOH), which was prepared by the post-polymerisation modification of poly(vinyl-cyclohexene carbonate) (PVCHC) by means of a thiol-ene reaction between the pendant vinyl groups and thioglycolic acid (Fig. 5.1). The introduction of these pendant carboxylic acid groups is anticipated to give rise to pH-dependent water solubility.^{15,16,21,24} This feature is of interest since it is expected to enhance the biodegradability of aliphatic polycarbonates through hydrolytic

Fig. 5.1: Thiol-ene modification of PVCHC with thioglycolic acid.

degradation,²⁹ which is otherwise slow and typically occurs at the surface of the material due to the hydrophobic nature of these polymers.^{30–32} Studies on the degradation of CO₂-based polycarbonates in aqueous solution are rare, so far limited to linear aliphatic polymers only.^{33–35}

To the best of our knowledge, this is the first report of the homogeneous degradation of an alicyclic CO₂-based polycarbonate in aqueous media. The pH-responsivity leading to solubilisation of the thiol-functionalised polycarbonate into a slightly basic aqueous medium is expected to promote rapid degradation.¹⁵ Indeed, the investigation of the hydrolytic degradation of PVCHC-COOH at different temperatures (RT, 50 and 70 °C) demonstrated that our polymer readily degrades in a slightly basic aqueous solution (pH = 8). Furthermore, by analysis of the degradation products, insight was generated into the hydrolytic degradation mechanism. The two main features of PVCHC-COOH, pH-responsive water solubility and biodegradability, are of interest for biomedical and pharmaceutical applications, such as smart drug delivery systems, where pH-responsivity can be employed as a valuable tool for targeted drug delivery, as variations in pH between different organs, tissues and cellular compartments can be used to trigger drug release.³⁶ For *in vivo* utilisation of polymers, biodegradability and biocompatibility are crucial features. The former should be carefully tuned because an unwanted degradation profile, *e.g.* slow degradation of pharmaceuticals or fast degradation of long-term tissue scaffolds, and harmful degradation products can severely limit the range of applicability.^{2,29} The latter is also essential because biomedical polymers that are employed inside the human body should achieve their desired function without causing any unwanted local or systemic effects in the patient.^{2,37}

The most widely studied polymers for biomedical applications include polyesters such as poly(lactic acid), poly(glycolic acid), poly(lactic-glycolic acid), polycaprolactone and polyhydroxyalkanoates, due to their biodegradability, low

toxicity and the related good biocompatibility.^{29,38,39} However, one of the disadvantages of these polyesters is that *in vivo* biodegradation typically generates acidic compounds, thereby decreasing local pH and triggering necrosis of host cells and inflammatory responses.^{29,40,41} CO₂-based aliphatic polycarbonates have been studied as a possible alternative to polyesters for utilisation in biomedical and pharmaceutical applications.^{30,31,42–46} To examine the potential *in vivo* application of PVCHC-COOH, the cytotoxicity of both PVCHC-COOH and its degradation products towards fibroblast (L929) cells was evaluated. The effect of PVCHC-COOH and the degradation products on the cell growth was analysed using fluorescent microscopy, which allowed monitoring the cell morphology and viability. For this purpose, all test samples were subjected to cytoskeleton (Phalloidin) and nucleus (DAPI) staining. Additionally, the response of the cells to the presence of PVCHC-COOH and of its degradation products was also studied with a cell proliferation assay (XTT), with which the metabolic activity of the cells can be quantified.

5.2. Experimental

5.2.1. Materials

Nitrogen gas ($\geq 99.999\%$, Linde Gas) was used as received. Dry tetrahydrofuran (THF) was obtained by percolating tetrahydrofuran (anhydrous, 99.8%, Sigma-Aldrich) over Al₂O₃ columns (Fluka). The dry tetrahydrofuran was subsequently stored under N₂ atmosphere. Demineralised water (Milli-Q), obtained by purifying tap water over a series of filtration and deionisation columns, was used in this work. Chloroform-d (99.8%, Sigma-Aldrich) and dimethyl sulfoxide-d₆ (99.5% Sigma-Aldrich) were stored over molecular sieves (0.4 nm). 4-Vinyl-1-cyclohexene-1,2-epoxide (mixture of isomers, 98%, Sigma-Aldrich), mesitylene (98%, Sigma-Aldrich), tetrabutylammonium bromide ($\geq 99.0\%$ Sigma-Aldrich), tetrabutylammonium chloride ($\geq 97.0\%$, Sigma-Aldrich), dichloromethane ($\geq 99.9\%$, Macron), methanol ($\geq 99.8\%$, Macron), hydrochloric acid (37–38 wt%, Boom), deuterium oxide (99.9%, Sigma-Aldrich), 2,2'-azobis(2-methylpropionitrile) (AIBN, $\geq 98.0\%$, Sigma-Aldrich), thioglycolic acid ($\geq 99.0\%$, Sigma-Aldrich), diethyl ether ($\geq 99.0\%$, Macron), sodium hydroxide (≥ 99 , Merck) and ethanol ($\geq 99.8\%$, Macron) were used as received.

L929 murine fibroblasts were used as cell line (ATCC; ATCC CCL-1). Fluorescein isothiocyanate (FITC)-labelled Phalloidin dissolved in phosphate-buffered saline (PBS, 2 $\mu\text{g}/\text{mL}$) containing 1% (w/v) bovine serum albumin (BSA) was used for cytoskeleton staining. 4',6-Diamidino-2-phenylindole (DAPI) dissolved in phosphate-buffered saline (PBS, 4 $\mu\text{g}/\text{mL}$) containing 1% (w/v) bovine serum albumin (BSA) was

used for nucleus staining. 0.5% (v/v) Triton X-100 solution in PBS and 3.7% (w/v) paraformaldehyde solution in PBS were used to aid the cell staining (all compounds were obtained from Sigma-Aldrich).

5.2.2. Methods

¹H NMR spectra were recorded on a Varian Oxford 300 MHz apparatus (64 scans and a relaxation time of 10 s), using dimethyl sulfoxide-d₆ or deuterium oxide as solvents. ¹³C NMR spectra were recorded on a Varian Mercury PlusNMR 400 MHz apparatus (8192 scans and a relaxation time of 1 s). ¹H NMR and ¹³C NMR spectra were referenced using the resonances of residual solvent. The ppm values are reported relative to tetramethylsilane (TMS). FTIR spectra were recorded using a Shimadzu IRTracer-100 equipped with an ATR sample unit with a frequency range of 4000-600 cm⁻¹ and a resolution of 4 cm⁻¹, employing 64 scans. Thermogravimetric analysis (TGA) was performed on a PerkinElmer Thermogravimetric Analyser 4000 under a N₂ flow of 20 mL/min in the temperature range from 20 to 900 °C with a temperature ramp of 10 °C/min. Differential scanning calorimetry (DSC) measurements were performed on a PerkinElmer Pyris Diamond Differential Scanning Calorimeter under a N₂ flow of 20 mL/min using a temperature ramp of 10 °C/min. Two heating and cooling cycles were measured, the first cycle was disregarded to avoid taking into account the thermal history of the sample. Glass transition temperatures (T_g) were determined by calculating the local maximum of the first derivative of the second heating cycle. Gel permeation chromatography (GPC) analysis was carried out on an Agilent 1200 Series GPC/SEC System equipped with three PSS 10 µm Suprema columns in series, with porosities of 100, 1000 and 3000 Å. This system was equipped with an Agilent 1200 Series RI detector. The chromatograms were recorded at 40 °C with an eluent flow speed of 1 mL/min, using 0.05 M NaNO₃ in water as eluent. The chromatograms were referenced against polyacrylamide standards. All molecular weight calculations were done using the PSS WinGPC UniChrom GPC/SEC software. Electrospray Ionisation-Mass Spectrometry (ESI-MS) measurements were performed on a Thermo Fisher Scientific Orbitrap XL mass spectrometer with an ESI ionisation source in positive or negative mode, in m/z range of 50.00-500.00 or 50.00-600.00, respectively.

5.2.3. Synthesis of PVCHC

The synthesis of PVCHC was conducted in a high-throughput CO₂ reactor unit, constructed by ILS-Integrated Lab Solutions GmbH. This CO₂ reactor unit consists of: (i) a 10-reactors block that allows performing 10 reactions simultaneously in

individually-stirred batch reactors (84 mL volume each, 30 mm internal diameter); and (ii) a single batch reactor with the same dimensions and equipped with a borosilicate glass window. The unit can be operated in a temperature range of 20–200 °C and a pressure range of 1–200 bar. For the synthesis of PVCHC, 30.0 mmol epoxide, 3.0 mmol mesitylene as internal standard and 0.25 mol% (relative to the epoxide) of the catalytic system as described in chapter 4 were weighed into a glass vial (46 mL volume, 30 mm external diameter) equipped with a magnetic stirring bar and a screw cap with a silicone/PTFE septum. The reaction was carried out in duplicate. The glass vials were placed into the reactors block and their septa were pierced with two thin syringe needles to allow gas to flow in and out of the vials. Then, the reactors block was closed, after which it was first purged 3 times with 5 bar N₂, and then pressurised to 10 bar CO₂. After a waiting time of 10 min (to prevent damage to the Viton O-rings), the reactors block was depressurised to atmospheric pressure and, after waiting another 10 min, it was pressurised to 50 bar CO₂. After reaching this pressure, the reactors block was heated up to 100 °C and then further pressurised to 80 bar of CO₂. The process of purging, pressurising and heating the reactors block took approximately 1.5 h. The start of the reaction was defined as the moment at which the magnetic stirring was switched on, after reaching the desired reaction temperature and pressure. The reaction was carried out with a stirring speed of 900 rpm for 18 h. At the end of the reaction, the magnetic stirring and the reactor heating were switched off and the water-cooling system was turned on to cool down the reactors block. Upon reaching room temperature, the reactors block was depressurised. The process of cooling down and depressurising the reactors block took approximately 1.5 h. After reaching atmospheric pressure, the reactor block was opened and the vials were removed. After the experiment, the each batch reactor was cleaned by washing it with ethanol and drying it at 110 °C for 4 h. The reactor lines were cleaned by washing them with ethanol and drying them by purging the lines with 1 bar N₂ for 15 min.

To purify and isolate the produced PVCHC, a standard procedure was employed. After the reaction of VCHO with CO₂, the obtained reaction mixture was dissolved in a minimum amount of dichloromethane. The polymer was subsequently slowly precipitated in acidified methanol (1 M HCl, 100 mL). These steps were repeated 5 times in order to purify the polycarbonate. Then the product was dried under vacuum at 70 °C for 48 h. The obtained white solid was analysed by ¹H NMR, ¹³C NMR, FT-IR spectroscopy, GPC, TGA and DSC.

¹H NMR (CDCl₃, 300 MHz): δ 5.77 (1H), 5.16–4.96 (2H), 4.96–4.71 (2H), 2.43 (1H), 1.85 (4H), 1.59 (2H). ¹³C NMR (CDCl₃, 400 MHz): δ 156.0, 144.2, 116.6, 76.9–75.3, 37.5,

34.2, 28.7, 28.0. FT-IR (cm⁻¹): 1738 (C=O stretch, carbonate), 1639 (C=C stretch, vinyl group).

5.2.4. Thiol-ene click modification

PVCHC (0.5000 g, 2.973 mmol of vinyl groups) was reacted with thioglycolic acid (2.738 g, 2.066 mL, 14.87 mmol) using AIBN (0.1611 g, 0.9811 mmol) as radical initiator. The reaction was performed in 25 mL dry THF for 24 h at 70 °C under N₂ atmosphere. The obtained polymer (PVCHC-COOH) was purified by dissolution of the mixture in a minimum amount of THF followed by slow precipitation in diethyl ether. This step was repeated 5 times to purify the product. PVCHC-COOH was obtained as a white solid after vacuum drying at 70 °C for 48 h. > 99% of the vinyl groups was converted. Thioglycolic acid is susceptible to self-esterification,⁴⁷ hereby partially and reversibly converting into 2-((2-mercaptoacetyl)thio)acetic acid. Since this compound also possesses a thiol moiety, it can likewise react with the PVCHC vinyl groups through a thiol-ene reaction.

¹H NMR ((CD₃)₂SO, 300 MHz, Fig. S5.1): δ 4.73 (2H), 3.66 (2H), 3.61 (2H), 3.20 (2H), 2.58 (2H), 1.74 (4H), 1.52 (4H), 1.24 (1H, m). ¹³C NMRC NMR ((CD₃)₂SO, 400 MHz, Fig. S5.2): δ 196.2, 171.6, 169.6, 152.7, 74.0, 73.2, 41.1, 33.2, 31.8, 30.2, 29.4, 25.4, 24.9. FTIR (cm⁻¹, Fig. S5.6): 1699 (C=O stretch, carboxylic acid).

5.2.5. Degradation experiments of PVCHC-COOH

PVCHC-COOH (2 mg/mL) was dissolved in an aqueous solution of HCl and NaOH with pH 8. The solution was maintained in a closed vial inside an oven at the chosen temperature (room temperature (20 °C), 50 °C or 70 °C) for the duration of the experiment, without stirring. The degradation of the polymer was monitored over time by GPC. The pH was checked weekly, for the degradation experiments at room temperature (20 °C) and 50 °C, or daily, for the degradation experiments at 70 °C, and adjusted to pH 8.

5.2.6. Evaluation of cytotoxicity

In vitro cytotoxicity was examined via an extraction testing procedure and a direct contact testing procedure. The extraction test was employed to investigate the effect of extractable solubles from the biomaterials on the L929 murine fibroblasts, while the direct contact test was used to analyse the interaction between a solid biomaterial film and the fibroblast cells.

5.2.6.1. *Extraction testing procedure*

In conventional extraction tests of biomaterials used for implants, the materials are placed in an extraction solution (*i.e.* typically regular cell culture medium). The materials are then incubated for 24, 48 or 72 h. The resulting extract solution is then brought in contact with the cells to investigate the influence of any compounds that leached out of the biomaterial on the cell proliferation. In this study, we prepared fully-characterised “extract”-like solutions of both the original polymer and of its degradation products in known concentrations. For the extraction testing of PVCHC-COOH, an aqueous solution of NaOH and PVCHC-COOH (40 mg/mL) with pH 7 was prepared. For testing the degradation products of PVCHC-COOH, an aqueous solution containing the degradation products (40 mg/mL) was prepared by maintaining an aqueous solution of NaOH and PVCHC-COOH at 70 °C and pH 8 for 16 days. The degradation of the polymer chains was monitored by GPC analysis. Subsequently, the aqueous solutions of PVCHC-COOH and of the degradation products of PVCHC-COOH were used as simulated extracts in the extraction testing procedure.

We chose the highest extraction test concentration to be 4 mg/mL, which corresponds to 10 vol% PVCHC-COOH solution (or the solution containing its degradation products) and 90 vol% cell culture medium. Samples with lower concentrations were prepared by two-fold serial dilutions (*i.e.* 5 vol%, 2.5 vol% and 1.25 vol%). Cell culture medium consisted of RPMI-1640 supplemented with 10 vol% fetal bovine serum, 2 mM Glutamax, 100 units/mL penicillin and 100 µg/mL streptomycin (obtained from Gibco).

L929 murine fibroblasts were seeded in 24-well culture plates at a concentration of 100,000 cells per well with a volume of 1 mL. After incubation for 24 h in a CO₂ incubator (37 °C, 5% CO₂-enriched air and > 97% humidity), the cells adhered to the bottom of the wells and the cell culture medium was replaced by the prepared extracts. 1 mL of the extract solutions was added per well, and for each of the prepared extracts (*i.e.* PVCHC-COOH: 10%, 5%, 2.5% and 1.25%; degradation products of PVCHC-COOH: 10%, 5%, 2.5%, 1.25%) an extraction test was performed in triplicate. Cells exposed to the extract solutions were incubated for 48 h in a CO₂ incubator.

5.2.6.2. *Direct contact testing procedure*

To examine the effect of direct contact between PVCHC-COOH and fibroblast cells on the cell growth, PVCHC-COOH samples for direct contact cytotoxicity testing were prepared by coating the polycarbonate from solution (1 mL, 20 mg/mL in

ethanol) onto well culture plates with 15 mm diameter wells. Two well culture plates were prepared, each plate having 8 wells coated with PVCHC-COOH. The coatings were obtained by letting the ethanolic solution of PVCHC-COOH dry at room temperature overnight, followed by further drying under vacuum at 80 °C for 3 days. One of the well plates was subjected to a pre-treatment procedure that consisted of contacting the PVCHC-COOH films with 2 mL of cell culture medium (RPMI-1640 supplemented with 10 vol% fetal bovine serum, 2 mM Glutamax, 100 units/mL penicillin and 100 µg/mL streptomycin, obtained from Gibco) per well, in a CO₂ incubator (37 °C, 5% CO₂-atmosphere and > 97% humidity) for 24 h. The medium was removed after 24 h and replaced by 2 mL of fresh medium, after which the well plate was incubated for another 24 h.

The other well plate containing untreated PVCHC-COOH films was not treated with cell culture medium prior to the direct testing procedure. For the direct testing method, a cell culture medium containing fibroblast (2 mL cell culture medium with a concentration of 100,000 cells/mL) was added to both untreated and pre-treated PVCHC-COOH samples. After incubating the samples in a CO₂ incubator for 24 h, half of the samples were fixated with 3.7% PFA. Addition of PFA causes covalent crosslinking between the cells, which acts as a means to preserve chemical and physical characteristics of the cells and to deter cell degradation.⁴⁸ For the other half of the samples, the fibroblast cell culture medium was removed and new cell culture medium (2 mL) was added. These samples were incubated in a CO₂ incubator for another 48 h, after which these samples were too fixated with 3.7% PFA. Effectively, the latter samples were incubated for a total of 72 h. Both sample groups were subsequently stained with Phalloidin and DAPI for fluorescent microscopy measurements.

5.2.6.3. Cytotoxicity analysis

Fluorescent microscopy was used to investigate cell proliferation and growth. For this purpose, the microscopy samples were subjected to cytoskeleton and nucleus staining. In this procedure, the contents of each sample well from the extraction and direct testing procedures were removed until approximately 200 µL well content remained. Subsequently, 500 µL of paraformaldehyde solution (3.7% (w/v) in PBS) was added to the wells for fixation, followed by incubation of the well plates at room temperature for 20 min. After removing the paraformaldehyde solution, 500 µL of Triton X-100 solution (0.5 % (v/v) in PBS) was added and retained in the wells for 3 min. After removal of Triton X-100, the wells were stained with 400 µL of a solution containing FITC-labelled Phalloidin and DAPI. The well plates were incubated at room temperature for 45 min in the dark. Hereafter, the wells were washed three

times with PBS and stored under PBS at 4 °C in the dark until microscope observation. The number of cells visible in the microscopy field of view was determined by counting the cells using ImageJ Image Processing and Analysis Software.

XTT cell proliferation analysis was performed with a Cell Proliferation Kit XTT (PanReac AppliChem, product code A8088,1000). For activation of the XTT, 0.1 mL of activator (phenazine methosulfate, PMS) was added to 5 mL of XTT. Subsequently, 0.25 mL of activated XTT was added to each tested well, followed by incubation of the well plates for 2.5 h at 37 °C under 5% CO₂-enriched air and >97% humidity. The light absorbance of the highly pigmented formazan derivative obtained from the reduction of XTT was measured with a plate spectrophotometer (FluoSTAR Optima, BMG Labtech, wavelengths 460 nm and 690 nm).

5.3. Results and discussion

The purpose of this work was to prepare a hydrophilic CO₂-based polycarbonate, which can display pH-responsive solubility and degradation behaviour in water. If combined with proper biocompatibility, these features would be attractive for biomedical and pharmaceutical applications. To achieve this target, first we prepared poly(vinylcyclohexene carbonate) (PVCHC) by reaction of 4-vinylcyclohexene oxide (a potentially biobased epoxide)² with carbon dioxide, according to a catalytic procedure previously reported (see chapter 4). This CO₂-based polycarbonate had an average molecular weight of 9920 g/mol, a polydispersity index of 1.2 and a glass transition temperature of 106 °C. To impart the desired hydrophilicity, the pendant vinyl groups of the obtained PVCHC were functionalised with carboxyl groups using atom-efficient thiol-ene click chemistry (PVCHC-COOH, Fig. 5.1). This was achieved following a previously reported procedure (see chapter 4), in which PVCHC is reacted with thioglycolic acid in the presence of AIBN as a radical initiator, resulting in full conversion of the pendant vinyl groups (see Fig. S5.1, S5.2 and S5.6 for ¹H NMR, ¹³C NMR and FTIR spectra).

The functionalisation of the polymer with the pendant carboxylic acid groups led to a decrease in the initial degradation temperature (208 °C vs. 276 °C for the parent PVCHC, see Fig. S5.7) and resulted in a lower glass transition temperature (T_g = 75 °C vs. 106 °C for the parent PVCHC, see Fig. S5.8). However, the T_g of PVCHC-COOH is still significantly higher than that reported for other CO₂-derived polycarbonate formulations studied for application in biomedicine (25-45 °C), which are typically based on poly(propylene carbonate).² A higher T_g provides a larger temperature window in which the polycarbonate maintains its structure and mechanical

properties, rendering the polymer suitable for applications that involve higher temperatures. The functionalisation of PVCHC with carboxylic acid groups imparted pH-responsive behaviour: PVCHC-COOH became water-soluble at pH > 7, while at pH < 7 it precipitates from solution. The solubility of PVCHC-COOH in aqueous solutions at pH > 7 is expected to promote the hydrolytic degradation of this polycarbonate due to the enhancement of polymer-water interactions and of the diffusion rates of reactants and degradation products.⁴⁹ This process is referred to as homogeneous degradation, in contrast with the more common and sluggish heterogeneous degradation of aliphatic polycarbonates, in which the polymer is not dissolved in the aqueous phase.

The susceptibility of PVCHC-COOH towards homogeneous hydrolytic degradation was studied by dissolving the polymer in an aqueous NaOH/HCl solution at pH 8 and by monitoring the progress of the degradation at 50 °C using GPC analysis (Fig. 5.2, also see chapter 4). The gradual decrease in intensity of the peak in the polymer region (~18650 g/mol) as a function of time indicates the degradation of the polycarbonate chains into smaller species, in agreement with the concomitant gradual appearance of signals in the oligomeric (1000-5000 g/mol) and monomeric (200-400 g/mol) regions. Major degradation of the polymer chains was observed already after 1 month at 50 °C, as demonstrated by the decrease in weight average molecular weight to 40% of the original value (M_w = 7850 g/mol vs. 19450 g/mol). Barely any traces of the original polymer were observed after 2 months, indicating

Fig. 5.2. 3D-profile of the degradation of PVCHC-COOH at 50 °C monitored with GPC. The red signals correspond to the original polymer while the blue signals correspond to the monomeric and oligomeric degradation products.

almost complete conversion of the polymer chains into oligomeric and monomeric compounds. Next, we investigated the homogeneous degradation of PVCHC-COOH at pH 8 at different temperatures (Fig. 5.3). A substantial difference in the degradation rate, expressed in terms of molecular weight decrease, was observed when the tests were performed at room temperature, 50 and 70 °C (Fig. 5.3A, B and C). The M_w of PVCHC-COOH decreased only 11% compared to the original value (19.25 kg/mol to 17.10 kg/mol) after 1 month at room temperature, while nearly complete degradation of the polymer chains was achieved already after 2 weeks at 70 °C. These results are of practical relevance, as they show that the rate of the hydrolytic degradation of PVCHC-COOH can be controlled by tuning the temperature of the system.

Notably, in all three cases an initial increase in polydispersity index (PDI) was observed, whereas for the experiments performed at 50 and 70 °C the PDI eventually decreased upon approaching complete polymer degradation. It has been proposed that hydrolytic degradation of polymer chains occurs via random chain scission as a consequence of a similar reactivity towards hydrolysis of the hydrolysable repeating units (*i.e.* the carbonate unit in this case), regardless of their position within the polymer chain (*i.e.* no difference in reactivity between bonds at chain ends or in mid segments).⁴⁹ On the other hand, previous studies on the depolymerisation of CO₂-based polycarbonates have shown that, in the presence of a strong base, alicyclic polycarbonates such as poly(cyclohexene carbonate) and poly(cyclohexadiene carbonate) can depolymerise to yield the corresponding *trans*-cyclic carbonate.^{21,50} It has been proposed that this degradation pathway occurs via deprotonation of the polycarbonate chain end, followed by a backbiting reaction.^{21,50} The two potential degradation pathways are displayed in Fig. 5.4.

Although the results displayed in Fig. 5.3 do not offer sufficient information to clearly distinguish between the two degradation mechanisms, the 3D-profile of the degradation of PVCHC-COOH (Fig. 5.2) generates more insight. It can be seen that the degradation of PVCHC-COOH leads to the concurrent formation of two distinctly different types of products: monomeric degradation species (with molecular weights in the range of 200-400 g/mol) and oligomeric species (with molecular weights in the range of 1000-5000 g/mol). This suggests that multiple degradation mechanisms might play a role.

To further investigate the homogeneous degradation of PVCHC-COOH in aqueous medium, the degradation mixture obtained after 16 days at 70 °C, in which no traces

Fig. 5.3. Degradation of PVCHC-COOH over time at pH 8, monitored with GPC. (A) At room temperature. (B) At 50 °C. (C) At 70 °C. Number average molecular weight: $M_n = \frac{\sum N_i M_i}{\sum N_i}$; Weight average molecular weight: $M_w = \frac{\sum N_i M_i^2}{\sum N_i M_i}$; Polydispersity index: $PDI = M_w/M_n$; M_i = molecular weight of a polymer chain, N_i = Number of polymer chains with that molecular weight.

Fig. 5.4. Proposed degradation pathways: (A) hydrolytic random chain scission ($m < n$). (B) Base-catalysed backbiting reaction.

of the original polymer were detected with GPC, was dried under vacuum at 40 °C for 48 h and subsequently analysed by ^1H NMR and ^{13}C NMR using DMSO-d_6 and D_2O as solvents (see Fig. S5.3-S5.5 for the full spectra). The spectra were measured in two different solvents to overcome the issues due to interference of overlapping residual solvent peaks (DMSO at 2.50 ppm and H_2O at 3.33 ppm in DMSO-d_6 ; H_2O at 4.79 ppm in D_2O). This allowed monitoring the characteristic peaks of PVCHC-COOH and of its degradation products (Fig. 5.5). The signal corresponding to the polymeric carbonate bonds (Fig. 5.5, left, a and b) decreased in intensity during the degradation test, confirming a decline in the amount of polycarbonate repeating units. The overlapping signals forming the broad band that appeared slightly upfield ($\delta = 4.6$ ppm) are ascribed to oligomeric species (Fig. 5.5, left, a''' and b''') and/or the cyclic carbonate analogue (Fig. 5.5, left, a'' and b''). Furthermore, new signals emerged between $\delta = 3.50$ -3.85 ppm (Fig. 5.5, right, a' and b'), which is the region where typically protons adjacent to hydroxyl groups appear.⁵¹ ^{13}C NMR analysis confirmed the disappearance of the polycarbonate bonds (Fig. S5.5).

Fig. 5.5. ^1H NMR of PVCHC-COOH (red) and degradation products (blue) in DMSO-d_6 (left) and D_2O (right). Notes: $m < n$; the assignment of the hydroxyl protons of the polymer and oligomer chain ends is omitted for clarity.

The formation of the diol product upon hydrolysis of the carbonate bonds during the degradation test was confirmed by ESI-MS (ESI pos: m/z 257.082 $\{C_{10}H_{18}O_4SNa\}^+$ (calc. m/z 257.082), ESI neg: m/z 233.086 $\{C_{10}H_{17}O_4S\}^-$ (calc. m/z 233.084), Fig. S5.9 and S5.10 respectively). Moreover, no traces of the cyclic carbonate were detected, indicating that the diol is the major product of the homogeneous aqueous degradation of PVCHC-COOH. However, it cannot be excluded that the cyclic carbonate was formed as an intermediate product, as cyclic carbonates are also prone to hydrolysis under basic conditions,^{52,53} which would eventually also lead to formation of the diol as final product of the degradation process.

After having demonstrated the hydrolytic degradability of PVCHC-COOH, the evaluation of the potential of this polymer for biomedical and pharmaceutical applications was continued by studying the cytotoxicity of PVCHC-COOH and of its degradation products by means of extraction testing and direct contact testing, using murine fibroblast (L929) cells, a commonly used reference cell line for cytotoxicity testing of biomedical polymers.^{54,55}

The extraction method is used to study the cytotoxicity of any soluble substances that can be extracted from the testing material, while the direct contact method is employed to examine the effect of contact between the cells and the polycarbonate material on the cell growth. The solutions used in the extraction tests are referred to as extracts, and consisted of a well-characterised aqueous solution of PVCHC-COOH and a well-characterised aqueous solution of the degradation products of PVCHC-COOH. In the extraction testing, after allowing the fibroblast cells to grow in the presence of the extract fluid containing PVCHC-COOH, fluorescent microscopy of the samples showed the presence of cells with homogeneous, normal morphology and normal nuclei (Fig. 5.6), which indicates that the cells were not under major stress.⁵⁶

The amount of cells visible in the microscope field of view is clearly dependent on the polymer concentration, with a decreasing cell count being observed at higher polymer concentration (Fig. 5.7). Compared to the lowest polymer concentration (1.25 vol%), the number of fibroblast cells at the two highest concentrations of PVCHC-COOH (5 and 10 vol%) decreased by 32% (773 vs. 526 cells, respectively) and 33% (773 vs. 520 cells, respectively). The relative differences in cell count, as determined with fluorescent microscopy, was employed as an indirect indication of the relative differences in cell viability (*i.e.* the proportion of live, healthy cells within a population) between the examined samples. According to the ISO 10993-5 standard for the biological evaluation of medical devices,⁵⁵ a quantitatively measured decrease in cell viability of more than 30% is considered a cytotoxic

Fig. 5.6. Fluorescent microscopy of L929 murine fibroblast cells in the presence of PVCHC-COOH (extraction testing). Top: nucleus staining. Bottom: cytoskeleton staining. From left to right: solution containing 10, 5, 2.5 and 1.25 vol% of PVCHC-COOH.

effect. This indicates that PVCHC-COOH displays slight toxicity towards the fibroblast cells when present at higher concentrations. In contrast to the original polymer, the degradation products of PVCHC-COOH affected much less negatively the cell proliferation of the fibroblasts, as indicated by the significantly larger number of cells that was observed in the microscope field of view for each concentration of the solution (Fig. 5.7 and 5.8). No changes in morphological appearance of the cells were observed by qualitative analysis of the microscopy images (Fig. 5.8), suggesting that the degradation products of PVCHC-COOH do not display any signs of cytotoxicity.⁵⁵

Fig. 5.7. Number of cells observed in the fluorescent microscope field of view (extraction testing).

Fig. 5.8. Fluorescent microscopy of L929 murine fibroblast cells in the presence of the degradation products of PVCHC-COOH (extraction testing). Top: nucleus staining. Bottom: cytoskeleton staining. From left to right: solutions containing 10, 5, 2.5 and 1.25 vol% of PVCHC-COOH degradation products.

With the highest concentration of degradation products (10 vol%), a 16% decrease in cell count was observed compared to the lowest concentration (1.25 vol%) of degradation products (739 vs. 882 cells respectively). The relative difference in number of observed cells between the highest and lowest concentration is considerably smaller than for the original PVCHC-COOH polymer. Additionally, the reduction in cell count is in all cases far below the 30% limit stated by the ISO 10933-5 standard, suggesting that within the tested range of concentrations the degradation products of PVCHC-COOH do not exhibit cytotoxicity towards the fibroblast cells.⁵⁵

Further insight in the cytotoxicity of PVCHC-COOH and of its degradation products was obtained in a cell proliferation assay employing XTT. This is a substrate that is converted by metabolically active cells, and is often used as a reference to study cell viability⁵⁷ and, indirectly, also cell growth. When XTT is converted by metabolically active cells, a highly coloured formazan derivative of XTT is formed. The degree of conversion of XTT by the cells in the presence of PVCHC-COOH or of its degradation products was monitored on the basis of the absorbance of light by the sample, with a higher level of absorbance corresponding to a higher amount of the formazan derivative of XTT, which signifies a higher number of metabolically active cells and/or higher metabolic activity of individual cells. The XTT assay showed that the absorbance level for the PVCHC-COOH samples tends to increase with decreasing PVCHC-COOH concentration (Fig. 5.9). The absorbance levels for the samples containing 1.25% PVCHC-COOH are significantly higher than those for the samples with 5% and 10% PVCHC-COOH. Taking the absorbance levels of the 1.25 vol%

Fig. 5.9. Light absorbance levels of the L929 fibroblast XTT samples containing PVCHC-COOH or its degradation products. The reported absorbance level is the average of at least two samples, standard deviations are indicated (for detailed data see Table 5.S1).

samples as reference, cell viability for the 5 and 10 vol% samples decreased by roughly 60% indicating significant cytotoxic potential of PVCHC-COOH, since the decrease in cell viability is far above the 30% limit as stated by the ISO 10993-5 standard.⁵⁵ The trend of a decreasing number of active cells with a higher amount of PVCHC-COOH corresponds well with the results from the fluorescent imaging measurements, confirming that PVCHC-COOH exhibits cytotoxicity towards the fibroblast cells at higher concentrations (though the extent of this cytotoxicity was estimated to be lower by fluorescence).

Comparable results were obtained for a CO₂-based polycarbonate also bearing carboxyl pendant groups, poly(glyceric acid carbonate), which exerted significant toxicity towards NIH fibroblasts 3T3 cells (decrease in cell viability > 30%) at a polymer concentration of 3 mg/mL (10 vol% PVCHC-COOH corresponds to 4 mg/mL).³³ The negative effect of toxic functional groups on L929 fibroblast cells has also been reported for a nitrated polycarbonate, where cell viability decreased with 34% compared to the control sample.⁵⁸ Additionally, several water-soluble cationic polymers (e.g. poly(ethylenimine) and poly(diallyl-dimethyl-ammonium chloride) that were studied as potential drug delivery systems,⁵⁹ displayed severe cytotoxicity at a concentration of 1 mg/mL (which corresponds to the PVCHC-COOH sample with

a concentration of 2.5 vol%) towards L929 fibroblast cells, resulting in complete cell viability inhibition (viability < 10% compared to control group) after 24 h.

In contrast with the original polymer, the degradation products of PVCHC-COOH did not have any adverse effect on the cell viability (Fig. 5.9): the absorbance levels of the samples containing the degradation products seem to remain nearly constant with increasing concentration of the degradation products (the apparent increase observed with 10% degradation products might have been caused by an experimental error as suggested by the relatively large deviations between the measured samples). These results confirm the trends observed in the imaging experiments, indicating that within the tested range of concentrations the degradation products do not exhibit any significant toxic effects towards the fibroblast cells. Although a more in-depth investigation on the apparent difference in cytotoxicity between PVCHC-COOH and its degradation products would need to be conducted in order to draw firm conclusions, it is known that the high molecular weight of polymers can significantly increase the degree of cytotoxicity.⁵⁹

Further investigation of the effects of PVCHC-COOH on the proliferation of the fibroblast cells was conducted with a direct testing method of the polymeric material, with which the interaction between solid PVCHC-COOH films and the liquid cell medium was studied. This test was performed with untreated and pre-treated PVCHC-COOH films coated onto the wells of a well culture plate. The pre-treatment consisted in exposing the PVCHC-COOH films to a cell culture medium (for 48 h), which was subsequently removed prior to the direct contact test and had the purpose of extracting any compounds that easily leach out of the PVCHC-COOH films (*e.g.* solvents used during the synthesis of the PVCHC-COOH films and adventitious monomeric components). The direct contact test was conducted by exposing the PVCHC-COOH films to cell culture medium using two different incubation times, 24 and 72 h (which results in a total exposure time of 72 and 120 h for the pre-treated samples). These incubations were performed in a CO₂ incubator using a cell culture medium with a pH of 7.4. Under these conditions, some degree of polymer degradation cannot be excluded. The fluorescent microscopy images of the untreated samples (Fig. 5.10), showed that the cell concentration was relatively low compared to that in the extraction testing method (*vide supra*). Furthermore, there was significant spacing in between the cells, even showing the presence of large voids in case of an incubation time of 24 h. These void domains indicate that the fibroblasts poorly adhered and proliferated within certain areas on the polycarbonate film. After longer proliferation (72 h), the cells were slightly more

homogeneously distributed across the sample, but cell concentration was still relatively low. In addition to the void areas with low cell concentration, other areas appeared to possess aggregates of fibroblast cells. This phenomenon has also been observed during *in vitro* testing of L929 fibroblasts on poly(ϵ -caprolactone) films and it has been reported to be influenced by film material, material surface, cell type and culture time.⁵⁴ The fluorescent microscopy images of both untreated samples displayed significant alterations in the shape of the cells (Fig. 5.10), which is especially visible on the microscopy images with cytoskeleton staining. The loss of the cell shape could be an indication of cell lysis, eventually leading to cell death. This change in cell morphology means that the untreated PVCHC-COOH films exhibit at least mild to moderate cytotoxicity towards the fibroblast cells (based on ISO 10933-5 qualitative grading).⁵⁵

Fig. 5.10. Fluorescent microscopy of L929 murine fibroblast cells in the presence of untreated PVCHC-COOH (direct testing). Top: nucleus staining. Bottom: cytoskeleton staining. Left: 24 h incubation. Right: 72 h incubation.

Notably, the pre-treated PVCHC-COOH samples showed considerably different results compared to the untreated polymers (see the fluorescent microscopy images in Fig. 5.11). The cell concentration was substantially higher and the cells were more homogeneously distributed throughout the sample compared to the tests with the untreated PVCHC-COOH, showing an increase in biocompatibility of PVCHC-COOH films. Only a minor fraction of cells displaying alterations in the cytoskeleton morphology was observed for the sample with an incubation time of 24 h (Fig. 5.11), which is an indication of slight cytotoxicity. On the other hand, if the cell culture medium was refreshed after 24 h and the incubation time was

prolonged to a total of 72 h, the fibroblast cells were densely packed with little to no spacing between the cells and the original cell morphology was restored. This result indicates that after refreshing the cell medium the cytotoxicity dropped, which allowed the cells to proliferate and grow, thus reestablishing the cell population.⁵⁵

Fig. 5.11. Fluorescent microscopy of L929 murine fibroblast cells in the presence of pre-treated PVCHC-COOH (direct testing). Top: nucleus staining. Bottom: cytoskeleton staining. Left: 24 h incubation. Right: 72 h incubation.

Overall, the pre-treated samples demonstrated significantly better cell proliferation than the untreated samples, as indicated by the higher number of cells observed at the end of the direct testing (Fig. 5.12). Pre-treatment of the PVCHC-COOH films resulted in 1.6 times higher cell count for the samples with 24 h incubation time (348 vs. 540 cells for the untreated and pre-treated samples, respectively) and 2.9 times higher for the samples with 72 h incubation time (331 vs. 955 cells for the untreated and pre-treated samples respectively). This shows that without pre-treatment of the PVCHC-COOH films a significant cytotoxic effect is observed, since cell viability decreased by more than 30%.⁵⁵ These results suggest that multiple additions and extractions of cell culture medium have a positive effect on the growth of the fibroblast cells.

Our hypothesis is that toxic components present in the PVCHC-COOH films are extracted when removing the medium, resulting in the observed decrease in potential cytotoxicity with the fresh medium. These toxic components could consist of residual substrates, solvents or other reaction components from the

Fig. 5.12. Number of cells observed in the fluorescent microscope field of view (direct testing).

polymerisation or thiol-ene modification reactions (*e.g.* thioglycolic acid, AIBN, THF or diethyl ether), which can remain trapped in the polymer chains. Similar observations were made during *in vitro* cytotoxicity evaluation of di-methylamino-ethylmethacrylate/methylmethacrylate copolymers, where washing of the copolymer sample disks with aqueous medium significantly decreased the cytotoxicity of the polymers towards fibroblast cells.⁵⁷ This was also ascribed to removal of toxic leachable species. Another possibility is that the PVCHC-COOH samples degrade over time when exposed to the cell culture medium, resulting in degradation products that exhibit lower toxicity towards the fibroblast cells. However, comparing the observed relatively low rate of the degradation of PVCHC-COOH at room temperature and 50 °C (Fig. 5.3) with the incubating temperature (37 °C), the latter explanation seems less likely.

5.4. Conclusions

In this work, we investigated for the first time the properties of an alicyclic CO₂-based polycarbonate, PVCHC-COOH, for potential biomedical and pharmaceutical applications. This CO₂-based polycarbonate with pendant carboxyl groups was prepared by alternating copolymerisation of CO₂ with the potentially biobased 4-vinylcyclohexene oxide, followed by functionalisation of the polymer with pendant

carboxyl groups by means of thiol-ene click chemistry. The obtained PVCHC-COOH is pH-responsive and becomes water soluble at pH > 7. This favours its hydrolytic degradation in aqueous solution (at pH 8). The rate of degradation can be controlled by tuning the temperature of the treatment, thus enabling to achieve nearly full degradation of the polymer chains after 2 weeks at 70 °C or 2 months at 50 °C. This implies that PVCHC-COOH would persist for several months at lower temperatures (e.g. human body temperature, 37 °C), while it is readily degradable at higher temperatures (i.e. 70 °C and above). An investigation of the degradation pathway indicated that the cyclohexane-1,2-diol analogue of the PVCHC-COOH repeating unit is the major final product of the hydrolytic degradation.

Our study also demonstrated that PVCHC-COOH displays acceptable biocompatibility. However, the extraction of residual contaminants potentially still present in the PVCHC-COOH material is advised to minimise any toxic effects. The degradation products of PVCHC-COOH showed no sign of toxicity towards fibroblasts in the tested range of concentrations (1.25–10 vol%), indicating that PVCHC-COOH degrades into compounds that are harmless for the cells. The pH-responsive water solubility of PVCHC-COOH combined with a proper biocompatibility of PVCHC-COOH at low concentrations creates potential for the utilisation of PVCHC-COOH in smart drug delivery systems. In this context, subsequent research should be devoted to a more detailed study on the tuneability of the PVCHC-COOH pH-responsivity and on the interaction of the polycarbonate with commonly used pharmaceutical drugs.

References

- 1 M. Taherimehr and P. P. Pescarmona, *J. Appl. Polym. Sci.*, 2014, **131**, 41141.
- 2 A. J. Kamphuis, F. Picchioni and P. P. Pescarmona, *Green Chem.*, 2019, **21**, 406–448.
- 3 D. J. Darensbourg, *Chem. Rev.*, 2007, **107**, 2388–2410.
- 4 X. Zhong, Z. Lu, P. Valtchev, H. Wei, H. Zreiqat and F. Dehghani, *Colloids Surf. B Biointerfaces*, 2012, **93**, 75–84.
- 5 L. Gu, Y. Qin, Y. Gao, X. Wang and F. Wang, *J. Polym. Sci. Part Polym. Chem.*, 2013, **51**, 2834–2840.
- 6 S. Fukuoka, M. Kawamura, K. Komiya, M. Tojo, H. Hachiya, K. Hasegawa, M. Aminaka, H. Okamoto, I. Fukawa and S. Konno, *Green Chem.*, 2003, **5**, 497–507.
- 7 M. R. Kember, A. Buchard and C. K. Williams, *Chem. Commun.*, 2011, **47**, 141–163.
- 8 P. P. Pescarmona and M. Taherimehr, *Catal. Sci. Technol.*, 2012, **2**, 2169.
- 9 C. E. Koning, R. J. Sablong, E. H. Nejad, R. Duchateau and P. Buijsen, *Prog. Org. Coat.*, 2013, **76**, 1704–1711.

- 10 J. G. Kim, C. D. Cowman, A. M. LaPointe, U. Wiesner and G. W. Coates, *Macromolecules*, 2011, **44**, 1110–1113.
- 11 Y. Li, J. Hong, R. Wei, Y. Zhang, Z. Tong, X. Zhang, B. Du, J. Xu and Z. Fan, *Chem. Sci.*, 2015, **6**, 1530–1536.
- 12 Z. Zhang, Z. Mo, H. Zhang, X. Wang and X. Zhao, *Macromol. Chem. Phys.*, 2003, **204**, 1557–1566.
- 13 Y. Tominaga and K. Yamazaki, *Chem. Commun.*, 2014, **50**, 4448.
- 14 J. Geschwind and H. Frey, *Macromolecules*, 2013, **46**, 3280–3287.
- 15 O. Hauenstein, S. Agarwal and A. Greiner, *Nat. Commun.*, 2016, **7**, 11862.
- 16 D. J. Darensbourg and F.-T. Tsai, *Macromolecules*, 2014, **47**, 3806–3813.
- 17 Y. Wang and D. J. Darensbourg, *Coord. Chem. Rev.*, 2018, **372**, 85–100.
- 18 C. Martín and A. W. Kleij, *Macromolecules*, 2016, **49**, 6285–6295.
- 19 C. Li, S. van Berkel, R. J. Sablong and C. E. Koning, *Eur. Polym. J.*, 2016, **85**, 466–477.
- 20 N. Kindermann, À. Cristòfol and A. W. Kleij, *ACS Catal.*, 2017, **7**, 3860–3863.
- 21 D. J. Darensbourg, W.-C. Chung, C. J. Arp, F.-T. Tsai and S. J. Kyrán, *Macromolecules*, 2014, **47**, 7347–7353.
- 22 M. Taherimehr, J. P. C. C. Sertã, A. W. Kleij, C. J. Whiteoak and P. P. Pescarmona, *ChemSusChem*, 2015, **8**, 1034–1042.
- 23 J.-F. Zhang, W.-M. Ren, X.-K. Sun, Y. Meng, B.-Y. Du and X.-H. Zhang, *Macromolecules*, 2011, **44**, 9882–9886.
- 24 D. J. Darensbourg and Y. Wang, *Polym. Chem.*, 2015, **6**, 1768–1776.
- 25 T. Stößer, C. Li, J. Unruangsri, P. K. Saini, R. J. Sablong, M. A. R. Meier, C. K. Williams and C. Koning, *Polym. Chem.*, 2017, **8**, 6099–6105.
- 26 C. Li, M. Johansson, P. Buijsen, G. Dijkstra, R. J. Sablong and C. E. Koning, *Prog. Org. Coat.*, 2021, **151**, 106073.
- 27 Y. Wang, J. Fan and D. J. Darensbourg, *Angew. Chem. Int. Ed.*, 2015, **54**, 10206–10210.
- 28 K. Deng, S. Wang, S. Ren, D. Han, M. Xiao and Y. Meng, *ACS Appl. Mater. Interfaces*, 2016, **8**, 33642–33648.
- 29 R. P. Brannigan and A. P. Dove, *Biomater Sci*, 2017, **5**, 9–21.
- 30 L. C. Du, Y. Z. Meng, S. J. Wang and S. C. Tjong, *J. Appl. Polym. Sci.*, 2004, **92**, 1840–1846.
- 31 G. Kim, M. Ree, H. Kim, I. J. Kim, J. R. Kim and J. I. Lee, *Macromol. Res.*, 2008, **16**, 473–480.
- 32 Y. Hwang, M. Ree and H. Kim, *Catal. Today*, 2006, **115**, 288–294.
- 33 H. Zhang, X. Lin, S. Chin and M. W. Grinstaff, *J. Am. Chem. Soc.*, 2015, **137**, 12660–12666.
- 34 M. Scharfenberg, S. Wald, F. R. Wurm and H. Frey, *Polymers*, 2017, **9**, 422.
- 35 F.-T. Tsai, Y. Wang and D. J. Darensbourg, *J. Am. Chem. Soc.*, 2016, **138**, 4626–4633.
- 36 D. Schmaljohann, *Adv. Drug Deliv. Rev.*, 2006, **58**, 1655–1670.
- 37 D. F. Williams, *Biomaterials*, 2008, **29**, 2941–2953.
- 38 W. Amass, A. Amass and B. Tighe, *Polym. Int.*, 1998, **47**, 89–144.
- 39 Y. Hwang, H. Kim and M. Ree, *Macromol. Symp.*, 2005, **224**, 227–238.
- 40 J. Ma, Z. Liu, F. Wang, Q. Zhou, C. Feng and F. Li, *J. Bionic Eng.*, 2013, **10**, 514–521.
- 41 I. Manavitehrani, A. Fathi, Y. Wang, P. K. Maitz and F. Dehghani, *ACS Appl. Mater. Interfaces*, 2015, **7**, 22421–22430.

- 42 J. H. Jung, M. Ree and H. Kim, *Catal. Today*, 2006, **115**, 283–287.
- 43 J. Xu, E. Feng and J. Song, *J. Appl. Polym. Sci.*, 2014, **131**, 39822.
- 44 A. Welle, M. Kröger, M. Döring, K. Niederer, E. Pindel and I. S. Chronakis, *Biomaterials*, 2007, **28**, 2211–2219.
- 45 X. Liang, F. Tan and Y. Zhu, *Front. Chem.*, 2021, **9**, 150.
- 46 X. Zhang, Z.-I. Lin, J. Yang, G.-L. Liu, Z. Hu, H. Huang, X. Li, Q. Liu, M. Ma and Z. Xu, *Nanomaterials*, 2021, **11**, 2312.
- 47 Y. Labat, *Kirk-Othmer Encycl. Chem. Technol.*, 2000.
- 48 S.-O. Kim, J. Kim, T. Okajima and N.-J. Cho, *Nano Conver.*, 2017, **4**, 1–8.
- 49 S. Lyu and D. Untereker, *Int. J. Mol. Sci.*, 2009, **10**, 4033–4065.
- 50 D. J. Darensbourg and S.-H. Wei, *Macromolecules*, 2012, **45**, 5916–5922.
- 51 P. Atkins and J. De Paula, *Atkins' Physical Chemistry (8th Edition)*, Oxford University Press, Oxford, New York, 2006.
- 52 J. H. Clements, *Ind. Eng. Chem. Res.*, 2003, **42**, 663–674.
- 53 B. Ochiai, Y. Satoh and T. Endo, *Green Chem.*, 2005, **7**, 765–767.
- 54 M. C. Serrano, R. Pagani, M. Vallet-Regí, J. Pena, A. Ramila, I. Izquierdo and M. T. Portolés, *Biomaterials*, 2004, **25**, 5603–5611.
- 55 International Organisation for Standardisation - Biological evaluation of medical devices - Part 5: Tests for in vitro cytotoxicity (Standard No. 10993-5), 2009.
- 56 P. T. Kühn, T. L. Meijer, I. Schiavon, M. van Poll, J. van Aken, S. Groen, R. Kuijter, T. G. van Kooten and P. van Rijn, *Macromol. Biosci.*, 2016, **16**, 1693–1702.
- 57 M. L. Knetsch, N. Olthof and L. H. Koole, *J. Biomed. Mater. Res. A*, 2007, **82**, 947–957.
- 58 K. Vani, S. Thomas, V. Prabhawathi, T. Boobalan, S. N. Sawant and M. Doble, *Colloids Surf. B Biointerfaces*, 2013, **108**, 191–198.
- 59 D. Fischer, Y. Li, B. Ahlemeyer, J. Krieglstein and T. Kissel, *Biomaterials*, 2003, **24**, 1121–1131.

Supplementary information

Appendix A: ^1H NMR and ^{13}C NMR spectra of PVCHC-COOH

Fig. S5.1. ^1H NMR spectrum of PVCHC-COOH in DMSO-d_6 . Besides the expected repeating unit of PVCHC-COOH, the spectrum shows the presence of a small fraction ($o = 0.2 n$) of a repeating unit incorporating the product of the (reversible) self-esterification of thioglycolic acid as pendant group.

Fig. S5.2. ¹³C NMR spectrum of PVCHC-COOH in DMSO-d₆. Besides the expected repeating unit of PVCHC-COOH, the spectrum shows the presence of a small fraction of a repeating unit incorporating the product of the (reversible) self-esterification of thioglycolic acid as pendant group.

Fig. S5.3. ¹H NMR spectra of PVCHC-COOH (top) and degradation products (bottom) in DMSO-d₆. The assignment of the hydroxyl protons of the polymer and oligomer chain ends is omitted for clarity.

Fig. S5.4. ^1H NMR spectra of PVCHC-COOH (top) and degradation products (bottom) in D_2O . The signals corresponding to protons a' and b' in the D_2O spectrum (bottom) overlap with signals potentially related to H_2O molecules. The signals corresponding to the cyclic carbonate protons a'' and b'' and oligomeric carbonate protons a* and b* are possibly not visible due to overlap with the residual H_2O signal at $\delta = 4.79$ ppm. The assignment of the hydroxyl protons of the polymer and oligomer chain ends is omitted for clarity.

Fig. S5.5. ^{13}C NMR spectra of PVCHC-COOH (top) and degradation products (bottom) in DMSO-d_6 .

Appendix B: FTIR spectrum of PVCHC-COOH

Fig. S5.6. FTIR spectrum of PVCHC-COOH.

Appendix C: TGA results for PVCHC-COOH

Fig. S5.7. TGA of PVCHC-COOH.

Appendix D: DSC analysis of PVCHC-COOH

Fig. S5.8. DSC of PVCHC-COOH.

Appendix E: ESI-MS experiments

Fig. S5.9. Positive mode ESI measurements of PVCHC-COOH degradation products.

Fig. S5.10. Negative mode ESI measurements of PVCHC-COOH degradation products.

Appendix F: Cell proliferation assay results (XTT)

Table S5.1. Light absorbance levels of the L929 fibroblast XTT samples containing PVCHC-COOH or its degradation products.

Solution concentration (volume)	Absorbance level ^a in the presence of:	
	<i>PVCHC-COOH</i>	<i>Degradation products of PVCHC-COOH</i>
10%	0.274 (SD 0.107)	0.600 (SD 0.112)
5%	0.257 (SD 0.0368)	0.422 (SD 0.0249)
2.5%	0.451 (SD 0.0700)	0.421 (SD 0.0311)
1.25%	0.667 (SD 0.0592)	0.394 (SD 0.0670)

a. The reported absorbance level value is the average of at least two samples, SD = Standard Deviation.

Summary

A growing focus on sustainability is witnessed in today's chemical product development. Although sustainability is a very broad concept, within the field of chemical products this primarily translates into the utilisation of renewable feedstock, safer alternatives for currently used hazardous chemicals, and biodegradable or recyclable end-products. Within the context of sustainable chemical product development, the application of carbon dioxide (CO₂) as feedstock for chemical products is an interesting option as this compound has the potential to be used as low-toxic, non-flammable and inexpensive building block for the production of bulk chemicals, minerals and even polymers. Among the various opportunities for CO₂-utilisation, the reaction between carbon dioxide and epoxides offers an attractive pathway as it leads to the formation of two different, yet both valuable products: cyclic and polymeric carbonates. However, this route also has its challenges, as active and selective catalysts are necessary in order to selectively obtain the desired carbonate products with high yields.

This thesis reports a research effort towards the conversion of CO₂ into organic carbonates, taking the reader on a venture into the catalysis and reaction design of carbon dioxide and epoxide chemistry and post-polymerisation modification of the polycarbonate products.

In *Chapter 1*, the advances made within this field are critically reviewed with special attention to the potential of these two classes of compounds as green chemical products. First, an overview is provided of the various types of homogeneous and heterogeneous catalytic systems developed for achieving the reaction of carbon dioxide with epoxides with high activity and selectivity towards either the cyclic or the polymeric carbonate products. Then, the chemical and physical properties of the cyclic and polycarbonate products are discussed, focussing on the correlation between such properties and the potential applications of each class of compounds. Finally, the most relevant applications of these materials, both potential and industrially implemented, are critically reviewed covering the fields of polymer products, energy storage devices, and biomedical and pharmaceutical applications.

Chapter 2, presents the application of a series of amino-tris(phenolate)-based metal complexes as homogeneous catalysts for the conversion of CO₂ and epoxides into cyclic carbonates. This series of catalysts consists of two metal complexes incorporating titanium(IV) centres and two complexes incorporating zirconium(IV) centres. The four complexes were synthesised, characterised and then evaluated in

combination with tetrabutylammonium iodide, bromide or chloride as binary catalytic systems for the reaction of CO₂ with 1,2-epoxyhexane as epoxide benchmark substrate.

The catalytic systems comprising the two Ti(IV) complexes showed similar performance. One notable exception was the catalytic system consisting of the titanium complex bearing an axial chloride ligand and tetrabutylammonium chloride as nucleophile source, which displayed higher catalytic activity compared to other titanium-based systems. Even higher activity was achieved with the Zr(IV) complex bearing an axial isopropoxide ligand, which reached turnover numbers up to 1920 for the reaction of CO₂ with 1,2-epoxyhexane. This performance is comparable with that of state-of-the-art catalysts for this reaction. The catalytic system consisting of this zirconium complex combined with tetrabutylammonium bromide was explored further by investigating its applicability with a broad epoxide substrate scope, consisting of several terminal and internal epoxides. Quantitative conversion of several epoxides with CO₂ into cyclic carbonate products was achieved under relatively mild reaction conditions.

In contrast to *Chapter 2*, where in addition to a metal complex also a separate nucleophile source was necessary in order to catalyse the reaction of CO₂ with epoxides, in *Chapter 3* a novel type of single-component catalysts based on the earth-abundant metal iron is presented. The homogeneous catalysts consist of anionic mono(formazanate) iron(II) complexes bearing labile halide ligands. The influence of the halide ligand and the electronic properties of the formazanate ligand backbone on the catalytic activity were investigated by employing the developed iron(II) formazanate complexes with and without an additional nucleophile.

The main assets of these complexes are: (i) their ability to act as active single-component catalysts (turnover numbers up to 1100 were achieved), thus obviating the need for an additional nucleophile; and (ii) their remarkable selectivity towards the cyclic carbonate product even in the conversion of internal epoxides such as (substituted) cyclohexene oxides, which generally tend to yield polycarbonates. More generally, this work indicates that anionic metal complexes with loosely bound halide ligands may provide a new entry into single-component transition metal catalysts for CO₂-fixation into organic carbonates.

While the focus of the previous two experimental chapters was on the synthesis and evaluation of homogeneous catalysts for the reaction of CO₂ with epoxides, in *Chapter 4* the development of a broad range of polycarbonate products with

Summary

different functionalities is presented. The synthesis of a sustainable, bio-based polycarbonate was achieved through the copolymerisation of CO₂ with 4-vinylcyclohexene oxide (poly(vinylcyclohexene carbonate), PVCHC). The resulting polymer was functionalised by converting the pendant vinyl groups into a range of functional groups using 100% atom-efficient thiol-ene click chemistry. This versatile modification tool allowed the preparation of a series of novel polycarbonates containing pendant alkyl, hydroxyl, carboxyl, amino or aromatic groups, whose physicochemical properties were characterised with a combination of techniques (¹H NMR, ¹³C NMR, FTIR, TGA, DSC and GPC). Depending on the functional group attached to the polycarbonate backbone, the polymeric properties were tuned to generate features ranging from pH-dependent water solubility (at pH > 7) to a remarkably low glass transition temperature of -4 °C. This chapter demonstrates the viability of the thiol-ene reaction to functionalise a CO₂-based polycarbonate with a variety of groups and highlights the influence of the nature of the introduced functional groups on the physicochemical behaviour of the obtained polymeric materials and, therefore, on their potential applications as specialty chemicals. The adaptable functionality of this CO₂-based polycarbonate makes it a specialty chemical with a variety of potential applications, including coating formulations, biomedical applications and consumer goods.

In *Chapter 5*, one of the modified polycarbonates presented in the previous chapter was further explored. Thiol-ene click chemistry was employed to modify CO₂-based poly(vinylcyclohexene carbonate) (PVCHC), by introduction of pendant carboxyl groups along the polymer backbone. The resulting polycarbonate, PVCHC-COOH, was evaluated for its potential in biomedical and pharmaceutical applications. In this context, PVCHC-COOH demonstrated a relevant feature as pH-responsivity by becoming water soluble at pH > 7. The hydrolytic degradation of PVCHC-COOH was studied in aqueous solution (pH = 8) at different temperatures (room temperature, 50 °C and 70 °C). The rate of the hydrolytic degradation reaction as well as the resulting degradation products were characterised using GPC, ¹H and ¹³C NMR, and ESI-MS. The results showed that the hydrolytic degradation rate of PVCHC-COOH is highly tuneable by varying the temperature. The cytotoxicity of PVCHC-COOH and of its degradation products was investigated by means of extraction and direct contact testing using murine fibroblast (L929) cells. The interaction of PVCHC-COOH or its degradation products with the fibroblasts was monitored with fluorescent microscopy, using cytoskeleton and nucleus staining, and with a cell proliferation assay (XTT). PVCHC-COOH demonstrated acceptable biocompatibility displaying mild toxicity towards the fibroblasts at higher concentrations (5 and 10 vol%), while

the degradation products of PVCHC-COOH showed no signs of cytotoxicity at all within the tested range of concentrations (1.25–10 vol%). The observed pH-responsivity, hydrolytic degradability and proper biocompatibility of PVCHC-COOH at lower concentrations render it an attractive candidate for biomedical and pharmaceutical applications and, more specifically, for smart drug delivery systems.

Samenvatting

Binnen de huidige chemische productontwikkeling wordt een groeiende focus op duurzaamheid gezien. Hoewel duurzaamheid een erg breed concept is, vertaalt zich dit in het gebied van chemische producten voornamelijk in het gebruik van hernieuwbare grondstoffen, veiligere alternatieven voor schadelijke chemicaliën en biodegradeerbare of recyclebare eindproducten. In de context van duurzame chemische productontwikkeling is de toepassing van koolstofdioxide (CO_2) als grondstof voor chemische producten een interessante optie, aangezien deze stof de potentie heeft om gebruikt te worden als laag giftige, niet-brandbare en goedkope bouwsteen voor de productie van bulkchemicaliën, mineralen en zelfs polymeren. Van de verscheidene mogelijkheden voor CO_2 -utilisatie is de reactie tussen koolstofdioxide en epoxides een aantrekkelijke route, aangezien deze leidt tot de formatie van twee verschillende, maar beide waardevolle producten: cyclische en polymere carbonaten. Deze route heeft echter ook een aantal uitdagingen, aangezien actieve en selectieve katalysatoren nodig zijn om de gewenste carbonaatproducten selectief te verkrijgen met een hoge opbrengst.

Dit proefschrift rapporteert een onderzoek naar de omzetting van CO_2 in organische carbonaten, waarin de lezer wordt meegenomen op een reis langs de katalyse en het reactieontwerp van koolstofdioxide en epoxide chemie, en langs de post-polymerisatie modificatie van de polycarbonaatproducten.

In *Hoofdstuk 1* wordt de progressie binnen dit veld kritisch besproken, met een specifieke focus op de potentie van deze twee stofklassen als groene chemische producten. Allereerst wordt een overzicht gegeven van de verscheidene typen van homogene en heterogene katalytische systemen die zijn ontwikkeld voor de reactie van koolstof dioxide met epoxides om hoge activiteit en selectiviteit naar de cyclische of polymere carbonaatproducten te behalen. Vervolgens worden de chemische en fysische eigenschappen van de cyclische- en polycarbonaatproducten bediscussieerd, waarbij wordt gefocust op de correlatie tussen dergelijke eigenschappen en de potentiële applicaties van elk van deze stofklassen. Als laatste worden de meest relevante toepassingen van deze materialen, zowel in potentie als op industriële schaal reeds toegepast, kritisch onderzocht waarbij de gebieden van polymere producten, apparaten voor energieopslag en biomedische en farmaceutische toepassingen worden behandeld.

Hoofdstuk 2 presenteert de toepassing van een serie van amino-tris(phenolaat)-gebaseerde metaalcomplexen als homogene katalysatoren voor de omzetting van

CO₂ en epoxides in cyclische carbonaten. Deze serie van katalysatoren bestaat uit twee metaalcomplexen met titanium(IV) centra en twee metaalcomplexen met zirkonium(IV) centra. De vier complexen werden gesynthetiseerd, gekarakteriseerd en vervolgens geëvalueerd in combinatie met tetrabutylammonium jodide, bromide of chloride als binaire katalytische systemen voor de reactie van CO₂ met 1,2-epoxyhexaan als epoxide referentiesubstraat.

De katalytische systemen bestaande uit de twee Ti(IV) complexen gaven een vergelijkbaar resultaat. Een noemenswaardige uitzondering was het katalytische systeem bestaande uit het titanium complex met een axiaal chloride ligand en tetrabutylammonium chloride als nucleofiele bron, die een hogere katalytische activiteit toonde dan elk van de andere titanium-gebaseerde systemen. Nog hogere activiteit werd behaald met het Zr(IV) complex met een axiaal isopropoxide ligand, waarmee omzettinggetallen tot 1920 werden behaald voor de reactie van CO₂ met 1,2-epoxyhexaan. Deze prestatie is vergelijkbaar met die van moderne katalysatoren voor deze reactie. Het katalytische systeem bestaande uit dit zirkonium complex gecombineerd met tetrabutylammonium bromide werd verder onderzocht door de toepasbaarheid op een brede epoxide substraatscope te bekijken, bestaande uit verscheidene terminale en interne epoxides. Kwantitatieve conversie van verschillende epoxides met CO₂ in cyclische carbonaten werd behaald onder relatieve milde reactiecondities.

In contrast met *Hoofdstuk 2*, waar naast de aanwezigheid van een metaalcomplex ook een separate nucleofiele bron nodig was om de reactie van CO₂ met epoxides te katalyseren, wordt in *Hoofdstuk 3* een nieuw type enkele-component katalysator gepresenteerd, gebaseerd op het op aarde overvloedig voorkomende metaal ijzer. De homogene katalysatoren bestaan uit anionische mono(formazanaat) ijzer(II) complexen met labiele halide liganden. De invloed van het halide ligand en van de elektronische eigenschappen van de formazanaat-ruggengraat op de katalytische activiteit werden onderzocht door de ontwikkelde ijzer(II) formazanaatcomplexen toe te passen met en zonder additionele nucleofiel.

De belangrijkste voordelen van deze complexen zijn: (i) de mogelijkheid om ze als actieve enkele-component katalysatoren te gebruiken (omzettinggetallen tot 1100 werden behaald), waarbij additionele nucleofielen dus niet nodig zijn; en (ii) de uitzonderlijke selectiviteit naar de cyclische carbonaatproducten, zelfs bij de conversie van interne epoxides zoals (gesubstitueerde) cyclohexeenoxides, die normaal gesproken de neiging hebben om polycarbonaten te vormen. In algemenere zin impliceert dit werk dat anionische metaalcomplexen met losgebonden halide liganden mogelijk een nieuwe toevoeging zijn aan de enkele-

component transitie-metaalkatalysatoren voor de fixatie van CO₂ in organische carbonaten.

Terwijl de focus van de vorige twee experimentele hoofdstukken op de synthese en evaluatie van homogene katalysatoren voor de reactie van CO₂ met epoxides was, wordt in *Hoofdstuk 4* de ontwikkeling van een breed scala aan polycarbonaatproducten met verschillende functionaliteiten gepresenteerd. De synthese van een duurzaam, bio-based polycarbonaat werd behaald door middel van copolymerisatie van CO₂ met 4-vinylcyclohexeenoxyde (poly(vinylcyclohexeencarbonaat), PVCHC). Het resulterende polymeer werd gefunctionaliseerd door de vinyl-zijgroepen om te zetten in een serie functionele groepen met behulp van 100% atoom-efficiënte thiol-een klikchemie. Met dit veelzijdige modificatiegereedschap was het mogelijk om een serie nieuwe polycarbonaten te maken met alkyl, hydroxyl, carbonzuur, amino of aromatische groepen, waarbij zijn de fysisch-chemische eigenschappen gekarakteriseerd met een combinatie van technieken (¹H NMR, ¹³C NMR, FTIR, TGA, DSC en GPC). Afhankelijk van de functionele groep vastgemaakt aan de ruggengraat van de polycarbonaat werden de polymeereigenschappen afgesteld en werden kenmerken geïntroduceerd van pH-afhankelijke wateroplosbaarheid (vanaf pH > 7) tot aan een uitzonderlijk lage glasovergangstemperatuur van -4 °C. Dit hoofdstuk demonstreert de geschiktheid van de thiol-een reactie om CO₂-gebaseerde polycarbonaten te functionaliseren met een grote variëteit aan groepen en laat de invloed van de aard van de geïntroduceerde functionele groepen op het fysisch-chemische gedrag van het verkregen polymere materiaal zien en, daarbij, hun potentiële toepassing als speciale chemicaliën. De aanpasbare functionaliteit van dit CO₂-gebaseerde polycarbonaat maakt het een speciale chemicalie met een verscheidenheid aan potentiële toepassingen, zoals coating formulaties, biomedische toepassingen en consumentengoederen.

In *Hoofdstuk 5* wordt een van de gemodificeerde polycarbonaten gepresenteerd in het vorige hoofdstuk verder onderzocht. Thiol-een klikchemie werd gebruikt om CO₂-gebaseerde poly(vinylcyclohexeencarbonaat) (PVCHC) te modificeren, waarmee carbonzuur-zijgroepen aan de ruggengraat van het polymeer werden gezet. Het resulterende polycarbonaat, PVCHC-COOH, werd geëvalueerd met betrekking tot de potentie in biomedische en farmaceutische applicaties. In deze context, PVCHC-COOH demonstreerde pH-responsiviteit door wateroplosbaar te worden bij pH > 7. De hydrolytische degradatie van PVCHC-COOH werd bestudeerd in een aquatische oplossing (pH = 8) bij verschillende temperaturen (kamertemperatuur, 50 °C en 70

°C). De snelheid van de hydrolytische degradatie evenals de resulterende degradatieproducten werden gekarakteriseerd met GPC, ^1H en ^{13}C NMR en ESI-MS. De resultaten lieten zien dat de snelheid van hydrolytische degradatie van PVCHC-COOH zeer goed gestuurd kan worden door de temperatuur te variëren. De cytotoxiciteit van PVCHC-COOH en van de degradatieproducten werden onderzocht door middel van extractie- en directe contacttesten waarbij fibroblasten van muizen werden gebruikt (L929). De interactie van PVCHC-COOH en de degradatieproducten met de fibroblasten werden gemonitord met fluorescentiemicroscopie, waarbij cytoskelet- en nucleuskleuring werd gebruikt, en met een celproliferatietest (XXT). PVCHC-COOH liet een acceptabele biocompatibiliteit zien en demonstreerde een milde toxiciteit naar de fibroblasten bij hogere concentraties (5 en 10 vol%), terwijl de degradatieproducten van PVCHC-COOH geen enkel teken van cytotoxiciteit toonden binnen het geteste concentratiebereik (1,25-10 vol%). De geobserveerde pH-responsiviteit, de hydrolytische degradeerbaarheid en de behoorlijke biocompatibiliteit van PVCHC-COOH bij lagere concentraties maken dit een aantrekkelijke kandidaat voor biomedische en farmaceutische toepassingen en, specifiek, voor systemen voor slimme medicijnafgifte.

List of publications

Peer-reviewed journals

- A.J. Kamphuis, M. Tran, F. Picchioni, P.P. Pescarmona, *Green Chemical Engineering*, Ti and Zr amino-tris(phenolate) catalysts for the synthesis of cyclic carbonates from CO₂ and epoxides, 2022, DOI: 10.1016/j.gce.2021.12.009
- A.J. Kamphuis, F. Milocco, L. Koiter, P.P. Pescarmona and E. Otten, *ChemSusChem*, Highly Selective Single-Component Formazanate Ferrate(II) Catalysts for the Conversion of CO₂ into Cyclic Carbonates, 2019, 12, 3635; DOI: 10.1002/cssc.201900740
- A.J. Kamphuis, F. Picchioni and P. P. Pescarmona, *Green Chem.*, CO₂-fixation into cyclic and polymeric carbonates: principles and applications, 2019, 21, 406–448; DOI: 10.1039/C8GC03086C

Conference proceedings

- A.J. Kamphuis, F. Picchioni, P.P. Pescarmona and M. van Duin, Tailor-made polycarbonates derived from CO₂: Tuning the properties via post-polymerisation modification, Green and Sustainable Chemistry Conference (GREN), 15th of May 2018
- A.J. Kamphuis, M. Tran, F. Picchioni and P.P. Pescarmona, Converting CO₂ into valuable organic carbonates using group (IV) metal catalysts, Netherlands' Catalysis and Chemistry Conference (NCCC), 7th of March 2018
- A.J. Kamphuis, F. Picchioni, P.P. Pescarmona and M. van Duin, Tailor-made polycarbonates derived from CO₂: Tuning the properties via post-polymerisation modification, NWO Chemistry As Innovative Science (CHAINS) Conference, 7th of December 2017
- A.J. Kamphuis, F. Picchioni, P.P. Pescarmona and M. van Duin, Tailor-made polycarbonates derived from CO₂: Tuning the properties via post-polymerisation modification, ENTEG Autumn Meeting, 19th of October 2017
- A.J. Kamphuis, E. Araya-Hermosilla, F. Picchioni and P.P. Pescarmona, Combining the best of two worlds: a polyketone-based hybrid catalytic system for carbon dioxide fixation, Poster presentation ENTEG Autumn Meeting, 6th of October 2016

- A.J. Kamphuis, F. Picchioni and P.P. Pescarmona, Catalytic conversion of CO₂ to organic carbonates using a novel gallium-based homogeneous catalyst, Poster presentation Netherlands' Catalysis and Chemistry Conference (NCCC), 2016
- A.J. Kamphuis, F. Picchioni and P.P. Pescarmona, Catalytic conversion of CO₂ to organic carbonates, Poster presentation ENTEG Autumn Meeting, 8th of October 2015

Acknowledgements

The journey is finally over, my PhD thesis is finished. Although I knew that the day would come that I would write these words, I never expected that it would be seven years after starting this adventure. And what an adventure this has been, not only did I grow as an academic researcher, I also grew as a person. Besides the infinite amount of failed lab experiments (and a few that actually worked), the countless hours spent digging through literature and the numerous scientific discussions, since the start of my PhD I bought a house in Groningen, got married, became a father (of not just one, but recently two beautiful daughters), got a new job and moved to Leeuwarden. It is safe to say that the past seven years did not only teach me valuable lessons in academic research, but also in life itself.

In addition to having learned a lot the past years, I have also met many fantastic people from all over the world. These people contributed a lot to the lessons that I've learned, both in academia and in life, and without them this thesis would most probably not have existed. The famous phrase "Standing on the shoulders of giants" does in my opinion not only relate to science, but also to life in general. That is why I want to take the time to say: thank you.

First and foremost I would like to thank my first promotor, Prof. P.P. Pescarmona. Dear Paolo, thank you for granting me the opportunity to develop myself as an independent researcher. Ever since we started our collaboration together on the conversion of CO₂ into organic carbonates you stimulated me to critically look at everything I read but also, especially, everything I write (the first article drafts that I handed in came back with double the amount of words, but then in red). I remember the many scientific meetings we had, these always lasted significantly longer than we scheduled beforehand because you took the time to really go into the details of our science. This really helped me to grow as a researcher by developing my analytical skills and by learning how to review literature and how to properly put everything in perspective. This not only benefits me in the academic world, but is also something that I will take with me for the rest of my future career. In addition, I want to thank you for all of our talks about culture, travelling, food and life, grazie mille!

I would also like to show my sincere gratitude to my second promotor, Prof. F. Picchioni. Dear Francesco, it is safe to say that without you I would not have started this PhD journey. Working with you during my Master studies inspired me to pursue a PhD in order to better understand how the world around us can be seen as molecules (from self-healing coatings for a Ferrari to tiramisu) and, even better, how

to build molecules that will help to make the world around us a better place. I would also like to thank you for your ever positive constructive feedback, whenever Paolo and I were fighting about a complex polymer-related topic, your insights really helped us to properly guide our scientific discussion in the right direction.

I would also like to express my gratitude to the assessment committee: Prof. C.E. Koning, Prof. A.W. Kleij and Prof. H.J. Heeres. Dear Cor, Arjan and Erik, thank you a lot for making time in your busy schedules to read my work. Your constructive feedback really helped me to improve the quality of this thesis.

A special thanks goes out to my two paranymphs: Pablo and Marika. Thank you guys a lot for helping with the preparations for finalising this journey and for standing by me during my defence.

Furthermore, I would like to thank all the department staff: Leon, Jan-Henk, Gert-Jan, Marcel, Erwin, Anne, Kim and Geraldine. Without your support my research would have already stranded after a couple of weeks due to broken equipment, unexplainable analytical results and administrative chaos. Thank you for being the silent force behind the department (and of course for organising the annual labuitje and Christmas lunch)! I would also like to thank Pieter for all his help with the NMR measurements and Jacob for his support with the XRD analyses.

I would also like to thank all the (assistant) professors from the Chemical Engineering department that I've worked with during my PhD. Ranjita, Patrizio, Jun and Peter, thank you for all the collaborations and conversations we've had throughout the years. Not only did our conversations help me improve the quality of my own research, but also showed me many interesting research topics outside of my own field.

Additionally, I would like to thank all the (former) members of Paolo's research group that I've closely worked with during my research. Dear Bhawan (Mr. Genius), Yasser (habibi), Zahra (dorood!), Zhenchen (蜡笔小新), Yehan, Dina, Nihat, Shun, Jing and Cui, thank you for all the time we spend together during our research. Although we all come from very different places and backgrounds, this did not divide us, but rather helped us learn from each other and made us grow as a team. It was a real pleasure working together with you! A thanks also goes out to Masoumeh, it was always a pleasure to have you with us in Groningen during your research collaboration projects.

A special thanks goes out to my former office mates of 5118.0213: Pablo, Nicola, Frank, Alex and Ciaran. Thank you very much for all the good times we spend in and outside the office, talking about research, future plans, music and life. Our office was always a warm place where everyone was welcome for a chat, coffee, beer and

Acknowledgements

poor taste in music. This office and its people really helped me through the ups and downs of my PhD and offered me friendships for life!

I would like to thank all the PhD and Postdoc colleagues that I have met and worked with during my PhD years. Thank you for all the collaborations, get-togethers, countless coffees, equal amounts of beers and general gezelligheid!: Arne, Tim, Idoia, Ionella, Henk, Jessi, Douwe Sjirk, Homer, Songbo, Laurens, Monique, Esteban, Rodrigo, Zheng, Arjan, Martijn, Francesco, Angela, Susanti, Ria, Yifei, Balaji, Qingqing, Inouk, Henky, Frita, Prima, Afshin, Savitha, Zhenlei, Wenzel, Khaled, Dian, Li and Xiaoying. It is a long list and I am sure I overlooked some people (this does not mean I want to thank you any less!), thank you all for making the Chemical Engineering department such a nice place to work. I really enjoyed the time spent together during my PhD years!

The inorganic chemistry department also became a special place during my PhD journey. Thank you Francesca, Edwin, Raquel, Ranajit and Marco for our collaborations. It was always a pleasure to work together and to also meet each other during the various conferences and get-togethers we attended. We even managed to find a common ground in our work, which eventually ended up as a very nice article and chapter in this thesis (Chapter 3)!

I would also like to express my sincere gratitude to Dr. Theo van Kooten from the Department of Biomedical Engineering for collaborating with me on researching the potential of CO₂-based polycarbonates in biomedical applications, which resulted in a chapter of this thesis (Chapter 5). A thanks also goes out to Gerard Vehof for his contribution to the cytotoxicity experiments.

A thanks also goes out to my former Master students, Henk, Johnny, Jesper and Sabine and Bachelor students, Evangelos, Keisia and Jennifer. You all in your own way helped me grow as a researcher and supervisor.

I also would like to express my sincere gratitude to G.T.D. Bernoulli and its boards, committees and active members during my PhD years. The lounge always felt like a second home, where I could start Monday morning with a warm coffee (and Zaanse huisjes) and end the week on Friday with a cold beer. Not to mention all the crazy and fantastic events and borrels that were organised, including Bernoulli Goes Downhill, Woktober, the top 30 borrel, the constitutional borrels and the annual Christmas dinner. Also a big thanks to all students that I've met during my PhD years, you really contributed to a great atmosphere within the department! (The list is too long to write down here, while the risk that I forget someone is too high).

I also received a lot of support from outside the university over the past seven years. I would like to thank all my friends, including Van Veen, Elmar, Dr. Bart-Jan,

Alexander, Tim, Janneke, Annienke, Aline and Arne for their interest in my PhD and for their friendships.

Furthermore, I would like to thank my family. Papa, mama, Aniek, Lucia, Alexander, Wardy en Door, thank you a lot for having supported me throughout this journey and for always being interested in my research.

Finally, I would like to thank Marika, Maura and Bo. Thank you so much for having supported me throughout this PhD adventure. From spending long days in the lab, to working on finalising my thesis many early mornings, evenings and weekends, you always understood and motivated me to keep going. Thank you for your eternal support, love and for showing me what is truly important in life.

We have now come at the end of this thesis, and thereby, the end of my PhD journey. The last thanks goes out to you as a reader, I hope you enjoyed reading this work.

Leeuwarden, January 2022

A handwritten signature in blue ink, appearing to be 'agkg' followed by a flourish.

A