Chapter 1

Dynamic Chemistry Toolbox for Sustainable Materials
Chapter 1

1.1 Introduction

Since the invention of plastics in the middle of the 19th century, plastics changed the world, not only becoming the most widely used chemical products, but also bringing increasingly serious problems in energy, environment, and health by immoderate accumulation of undegradable plastic wastes. In 2019, global plastics production reached up to 368 million tonnes according to a recent study by PlasticsEurope.\textsuperscript{1} Half of it (51%) was mainly attributed to production distributed by Asia and 16% from Europe. Aiming at building a sustainable plastic economy, polymer recycling has been identified as a urgent goal by industry and academy in the past decades. Since 2006, recycling has shown a positive development trend. For instance, the recycling for the collected plastic post-consumer waste has increased by 92%. However, 25% of the waste is still ending up in landfills (Fig. 1.1).\textsuperscript{1}

![Figure 1.1 Plastic post-consumer waste treatment in 2018. Adapted with permission from ref. 1. Copyright © 2020, PlasticsEurope.](image)

In 2019, 50.7 million tonnes of plastic were used in European countries.\textsuperscript{1} The biggest end-use market is the packaging industry, 39.6% of the total European plastic requirement. The second and third larger end-use market comes from construction and automotive industry, respectively. The plastic waste resulting from packaging is the key issue by far. On the other hand, with the advent of COVID-19, single-use plastic-based medical waste has increased dramatically. For example, 116 million single-use face masks were produced in China per day in February 2020, which is 12 times the usual quantity.\textsuperscript{2} The continuous increasing global health crisis is causing the global plastics pollution to become worse and is putting extra pressure on waste management.
Today’s chemical sector follows a linear path (Fig. 1.2, left),\(^3\) in which the feedstocks come from unrenewable fossil resources, and most plastics waste is relegated to the landfills, incineration or are leaked into the environment at the end of single-use life. Given the need for Sustainable Development proposed by the United Nations,\(^4\) countries have paid more attention to the problem of plastic pollution and have taken corresponding measurements to promote a circular chemical economy (Fig. 1.2, right). In 2018, about 42% of plastic post-consumer packaging waste was collected in Europe to be recycled by mechanical recycling.\(^1\) However, the complicated sorting process and the existence of contaminants and additives make mechanical recycling inefficient for the circular economy. Not only that, but mechanical recycling often leads to the loss of material properties and product value compared to the original plastics.\(^5\)

**Figure 1.2** Characteristics of today’s and tomorrow’s chemical sectors. Adapted with permission from ref. 3. Copyright © 2020, American Association for the Advancement of Science.
To achieve the goal of a truly sustainable economy, functions, properties, and recyclability should be combined into a single material, enabling the transformation from linear processes to circular processes. A few solutions have been proposed to facilitate the building of circular plastic economy: (i) New plastics with durability, long use-life, and self-repairing ability are needed to extend the service life of plastics and to release the pressure of plastic waste disposal; (ii) Developing new plastics with enhanced properties and repeating processability can improve the mechanical recycling efficiency and enhance the product value and recycling profit; (iii) Chemical recycling (to retain the pure monomers, building blocks) offers an ideal solution to truly sustainable plastics. However, it is also recognized as the most challenging goal.\(^6\)

Commonly used plastics include thermoplastics and thermosets. Thermoplastics are polymers that can be readily melted and reprocessed under mild condition. Thermosets are covalently crosslinked networks with high mechanical robustness and durability to survive under specific conditions (e.g. high temperatures, high-pressure humid environment, and chemical corrosion). The irreversible covalently crosslinked network also makes them unable to be recycled under industrially applicable conditions.\(^7\) Toward recyclable and durable materials, attention should be paid towards the development of new-generation plastics that combines the advantages of thermoplastics and thermosets. Efforts have been made and milestones have been reached by chemists in recent years to introduce dynamic chemistry elements into the realm of polymer chemistry and materials.\(^8-9\) As a result of the rapid development of supramolecular chemistry and dynamic covalent chemistry, several versatile and readily accessible dynamic chemistry tools have been exploited and used for the design “smart” polymeric materials, i.e., so-called “Dynamers”\(^10\) that can repair, adapt, respond, and be recycled.

We begin this review with summarizing the dynamic chemistry toolbox for the construction of dynamic materials, including dynamic covalent bonds and noncovalent (supramolecular) interactions. Next we discuss the diverse functions and applications of dynamers in this exciting and rapidly emerging field.
1.2 Dynamic chemistry toolbox

With the rapid development of supramolecular chemistry and dynamic covalent chemistry (DCC), a class of reversible and adaptable (supra)molecular linkages have been exploited and used for designing dynamic polymeric materials with “smart” properties. This section will summarize and discuss the recently emerged dynamic chemistry tools exhibiting versatility in material design and functional applications, especially focusing on those serving as candidates for sustainable, recyclable polymers and materials.

1.2.1 Dynamic covalent bonds

Dynamic covalent chemistry enables covalent molecular bonds to dissociate and reform reversibly under thermodynamic control. The ways to achieve external control include physical or chemical stimuli, such as temperature, light, mechanical stress, acid/base and redox processes. The feature of dynamic configuration and adaption of building blocks in the covalent system offers many opportunities for the design of smart materials. Various classes of dynamic covalent bonds have been explored and developed in the past few years,\textsuperscript{11-26} including S-S bond, Se-Se bond, C-N bond, C-O bond, B-O bond, and C-C bond (Table 1.1). Specifically, these dynamic covalent tools have been used for constructing healable or malleable materials based on the corresponding reversible reactions, such as disulfide exchange,\textsuperscript{11} acylhydrazone exchange,\textsuperscript{15} imine transamination,\textsuperscript{20} and vinylogous urethane transamination,\textsuperscript{21} transesterification,\textsuperscript{22} boronic ester hydrolysis,\textsuperscript{24} and cycloaddition reactions.\textsuperscript{25-26} Notable, many of them involve the formation of water or other small entities, which can be useful for gel-type materials, but become a drawback when applied into solvent-free systems. One of the few examples that can undergo homolysis, \textit{i.e.}, dissociation and exchange, is the disulfide bond, making it capable of dynamic exchange in the presence of proper stimuli, such as heat, light, or mechanical force.
Table 1.1 Representative examples of dynamic covalent chemistry.

<table>
<thead>
<tr>
<th>Reaction type</th>
<th>Chemical reactions</th>
<th>Condition</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dynamic exchange reactions</td>
<td>(\sim X \sim \to \sim X \sim \leftrightarrow \sim X \sim)</td>
<td>Disulfide exchange: X = S, Diselenide exchange: X = Se, Siloxane exchange: X-X = Si-O-Si</td>
<td>13-15</td>
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<tr>
<td>Dynamic C-N bond</td>
<td></td>
<td></td>
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<tr>
<td>Schiff-base bond regeneration</td>
<td>(\sim C \sim \leftrightarrow \sim C \sim)</td>
<td>RT</td>
<td></td>
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<tr>
<td>Acylhydrazone formation</td>
<td>(\sim C \sim \leftrightarrow \sim C \sim)</td>
<td>Heating/ Water/pH</td>
<td></td>
</tr>
<tr>
<td>Oxime formation</td>
<td>(\sim C \sim \leftrightarrow \sim C \sim)</td>
<td>Excess alkoxyamine /RT</td>
<td></td>
</tr>
<tr>
<td>Aminal formation</td>
<td></td>
<td>Water</td>
<td>16-23</td>
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<tr>
<td>Amide exchange</td>
<td></td>
<td>Amido catalyst</td>
<td></td>
</tr>
<tr>
<td>Imine transamination</td>
<td>(\sim C \sim \leftrightarrow \sim C \sim)</td>
<td>Heat/Catalyst</td>
<td></td>
</tr>
<tr>
<td>Vinylogous urethane transamination</td>
<td>(\sim C \sim \leftrightarrow \sim C \sim)</td>
<td>Heat/Catalyst</td>
<td></td>
</tr>
<tr>
<td>Dynamic C-O bond</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transesterification</td>
<td>(\sim C \sim \leftrightarrow \sim C \sim)</td>
<td>Heat/Catalyst</td>
<td>24-25</td>
</tr>
<tr>
<td>Transcarbonation</td>
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<td>Catalyst</td>
<td></td>
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<td>Dynamic B-O bond</td>
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<td>Boronic ester hydrolysis</td>
<td>(\sim C \sim \leftrightarrow \sim C \sim)</td>
<td>Water</td>
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<td>Dynamic C-C bond</td>
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<td>Diels-Alder cycloaddition</td>
<td>(\sim C \sim \leftrightarrow \sim C \sim)</td>
<td>Heating</td>
<td>27-28</td>
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<td>[2+2] Cycloaddition reactions</td>
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1.2.2 Dynamic non-covalent (supramolecular) chemistry

Non-covalent interactions widely exist in nature and are particularly important for biopolymers. For example, multiple non-covalent interactions are responsible for the folding of polypeptide chains. Inspired by the non-covalent interactions from nature, scientists tried to take the advantages of non-covalent chemistry to synthesize molecules with precise architectures and self-assembly ability. The concept of supramolecular polymer chemistry was pioneered by Lehn in 1987 based on noncovalent intermolecular interactions where the dynamics are in the domain beyond molecules. Supramolecular chemistry consisting of non-covalent bonds includes hydrogen bonding, metal-ligand coordination, host-guest chemistry, π-π stacking, ionic interactions, van der Waals interactions, and electrostatic interactions (Table 1.2). Compared to covalent bonds, non-covalent bonds are relatively weak but enhance the material with multiple reversible interactions. The dynamic feature endows supramolecular polymers, i.e., polymers formed by noncovalent linkages, with reversibility to rearrange their network topology under mild conditions.

Among the noncovalent tool box, hydrogen bonds are the most known and widely used ones because of their directionality and versatility. Usually, the strength of the non-covalent interaction formed by a single hydrogen bond is not high. To increase the degree of polymerization or improve the material properties, multiple hydrogen bonds must be considered. This could be achieved by tuning the number, the orientation, or the order of hydrogen bonds, resulting in increased strength of hydrogen bond interaction and more stable complexes. In recent years, the design of new synthetic systems ranging from gels to polymers in supramolecular chemistry has attracted tremendous attention. Especially in the development of solvent-free polymeric materials, the advantage of multiple hydrogen bonds could be fully explored comparing to the solvent-containing polymeric materials.
Table 1.2 Representative examples of noncovalent (supramolecular) chemistry.

<table>
<thead>
<tr>
<th>Interaction type</th>
<th>Molecular structure</th>
<th>Condition</th>
<th>Ref.</th>
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</thead>
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<td>H-bonding</td>
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<td>32-35</td>
</tr>
<tr>
<td>Metal-ligand coordination</td>
<td><img src="image2" alt="Metal-ligand structure" /></td>
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<td>36-37</td>
</tr>
<tr>
<td>Host-guest chemistry</td>
<td><img src="image3" alt="Host-guest structure" /></td>
<td></td>
<td>38</td>
</tr>
<tr>
<td>π-π stacking</td>
<td><img src="image4" alt="π-π stacking structure" /></td>
<td>RT</td>
<td>39</td>
</tr>
<tr>
<td>Ionic interactions</td>
<td><img src="image5" alt="Ionic interactions structure" /></td>
<td>Pressure/RT</td>
<td>40-41</td>
</tr>
<tr>
<td>Electrostatic interactions</td>
<td><img src="image6" alt="Electrostatic interactions structure" /></td>
<td>RT</td>
<td>43</td>
</tr>
</tbody>
</table>
1.3 Dynamic functions of polymer materials

The intrinsic dynamic features on the supramolecular level have attracted increasing attention and have been introduced into dynamic materials, particularly in the dynamic polymers field based on dynamic covalent and non-covalent chemistries. The dynamic materials could mimic the self-healing function in biological systems by reversible exchange and reorganization of components in response to multiple physical and/or chemical agents. Moreover, the dynamic properties also enable the supramolecular materials or polymeric materials to be stimulus-responsive, processable, or chemically recyclable. The following part will focus on recent developments of dynamic polymeric materials illustrating key properties, i.e., self-healing ability, processability, and chemical recyclability.

1.3.1 Self-healing polymers

Self-healing is an autonomous repairing process after physical damage. The reversible interactions needed for repairing could be non-covalent interactions or dynamic covalent bonds. Physical damage involves cleavage and slippage of the polymer chains. Segmental rearrangements and conformational changes or diffusion should then bring reactive chain ends into contact allowing them to repair themselves. Numerous efforts have been made to explore self-healing polymeric materials in the last decade. Moreover, healable materials are usually soft resulting in a limited application scope. However, a major challenge still remains on how to design autonomously self-healable materials with enhanced mechanical performances. The trade-off between stiffness and self-healing ability makes the development of polymeric materials with intrinsic self-healing ability and high mechanical properties highly challenging. Thus, combining the features of mechanical robustness and self-healing ability should be a crucial topic when designing new polymeric networks to extend the practicality of these materials.

Urban and coworkers designed new self-healing copolymers that depend on noncovalent van der Waals interactions. Two readily available and commercially relevant monomers, methyl methacrylate (M) and butylacrylate (B), formed alternating sequence copolymers that could efficiently self-repair after mechanical damage without intervention (Fig. 1.3A). Interestingly, only copolymers with near-equal incorporation of M and B showed efficient and autonomous healing. This
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phenomenon was attributed to the key-and-lock interactions of interdigitating alkyl pendant groups between polymer chains. Modeling analysis further suggested that the existence of helix-like chain conformations and the interchain van der Waals forces triggered the self-healing of poly(methyl methacrylate-co-butyl acrylate) materials. Although dipolar forces are relatively weak compare to other noncovalent interactions, the ubiquitous intermolecular and/or intramolecular interactions running through the whole polymer network play a crucial role in achieving the mechanical integrity of polymeric materials. The same group took advantage of the noncovalent dipolar interactions and developed self-healable thermoplastic copolymers (Fig. 1.3B). In their study, the dipolar forces are present through all macromolecules and fluorine-containing copolymers. The self-healing ability of the copolymers could be attributed to the combination of dipolar interactions between C-F and C=O bonds facilitating the self-repair process. These pioneering studies highlighted fundamental features of macromolecules, like the chain conformation and cooperative weak interactions, which can be utilized for the design of structurally simple and functionally dynamic materials.

Figure 1.3 (A) Van der Waals interactions-driven self-healing copolymer, poly(methyl methacrylate-co-butyl acrylate). Adapted with permission from ref. 42. Copyright © 2018, Springer Nature Limited. (B) Chemical structure of 2,2,2-trifluoroethyl methacrylate and n-butyl acrylate. Alternating/random p(TFEMA/nBA).
methacrylate (TFEMA) and n-butyl acrylate (nBA) as well as the scheme of dipolar forces-driven self-healing poly(TFEMA/nBA) copolymers. Reformed with permission from ref. 51. Copyright© 2021, Wiley-VCH GmbH.

Most autonomous self-healing rubbers are based on moisture-sensitive hydrogen bonding and/or van der Waals interactions, and therefore lack stability against moisture. To integrate high strength, high stretchability, and room-temperature self-healing into one polymer, Bao and coworkers introduced a unique metal-ligand interaction (Fig. 1.4),53 combining strong metal-ligand bonding and weak metal-ligand bonding in a single ligand to get highly dynamic metal-ligand interactions. The weaker metal complexes can readily break and re-form, while the stronger metal-ligand interactions can confine the metal ions allowing a rapid bond re-formation. The cooperative effect of multiple metal-ligand interactions enables the polymers to be highly stretchable and self-healable with good mechanical and dielectric strength.

![Figure 1.4](image_url)  
**Figure 1.4** (A) Structure of the [Fe(Hpdca)2]⁺ moiety undergoing reversible rupture and reconstruction during tensile stretching. (B) Condition of the sample after 72 h of healing at room temperature. The location of the former mechanical damage is marked with a circle. (C) Photo of the dielectric elastomer actuator after the application of a high voltage. The high electric field induced an area expansion of 3.6%, but it did not cause a dielectric breakdown at the location of the self-healing event. Reformed with permission from ref. 53. Copyright© 2016, Springer Nature Limited.
Polymers relying on noncovalent interactions are relatively softer. Although some healable and robust polymer materials cross-linked by dynamic covalent bonds have been investigated, high temperatures (normally higher than 120°C) are needed for the reorganization of cross-linked polymer networks. Aida and coworkers reported amorphous poly(ether-thioureas) noncovalently cross-linked by dense H-bonds (Fig. 1.5). Owing to the geometrically nonlinear zigzag arrays of H-bonds between thiourea units, the poly(ether-thioureas) do not induce unfavorable crystallization, which will make the polymer brittle. Although the diffusion dynamics of the resulting polymer chains is slow, the segmental motion such as the exchange of H-bonded thiourea pairs leads to inter-penetration of polymer chains while slip motion is favoured by the polyether units, which is responsible for the rapid healing ability upon
1.3.2 Processable thermosets (Vitrimers)

Thermosets are widely used in daily life due to their outstanding features of mechanical robustness and thermal/chemical stability. However, the permanently crosslinked polymer network makes them very difficult to be reprocessed or recycled to enable the sustainability of the materials. Arguably a goal in polymer industry is to develop polymeric materials that can be repeatedly moldable and reprocessable like thermoplastics yet maintaining the mechanical robustness of thermosets. Supramolecular materials exhibiting dynamic functions mostly bear low stiffness and poor thermal and chemical stability due to the intrinsic weakness and lability of noncovalent bonds. Thus, replacing the irreversible covalent crosslinking network in thermosets with dynamic covalent linkages offers an approach for constructing adaptable crosslinked network simultaneously combining the robustness of covalent bonds with the reversibility of noncovalent bonds.

The concept of “vitrimer” was coined by Leibler in 2011, referring to malleable thermosets crosslinked by dissociable covalent linkages with adaptable crosslinking topologies by thermally activated bond-exchange reactions. Taking advantage of reversible transesterification reaction and inexpensive chemical feedstocks, a vitrimer network was prepared, exhibiting silica-like stiffness at room temperature, while becoming flowing and malleable at above 140°C (Fig. 1.6A). The topology structure can be rearranged by the reversible exchange reactions without depolymerization and can maintain the total number of crosslinks. The resulting polymers exhibit excellent malleability, reparability, recyclability, and yet have solvent resistant ability making these new polymers a potential replacement for the composites of elastomers and thermosets in industries.

Arguably the key bottleneck for vitrimers is how to use low-cost feedstocks to form high-performance polymers with applicability. Leibler group further introduced the metathesis reaction of dioxaborolanes into commercial polymers with carbon-carbon backbones, such as poly(methyl methacrylate) (PMMA), polystyrene (PS), and polyethylene (HDPE) by incorporating functional monomers during polymerization (Fig. 1.6B). Benefiting from the low-cost commercial feedstocks, dioxaborolane-based vitrimers bring possibilities for large-scale production of recyclable yet robust
polymers. In recent years, a number of other dynamic covalent tools have also been applied into the design of vitrimer materials.

**Figure 1.6** (A) Topological rearrangements via transesterification reactions preserve the network integrity in the hydroxy-ester network. Reprinted with permission from ref. 56. Copyright © 2011, The American Association for the Advancement of Science. (B) Cross-linking of functional polymers containing pendant dioxaborolane units by means of metathesis with a bis-dioxaborolane. Reprinted with permission from ref. 57. Copyright © 2017, The American Association for the Advancement of Science.

The design concept of tuning silyl ether exchange dynamics for vitrimer was developed by Guan and co-workers (Fig. 1.7A). The resulting silyl-ether-exchange-based polystyrene materials can be remolded by hot-pressing at 160°C for 6 h. It verified the transition from the Williams-Landel-Ferry (WLF) model to the Arrhenius model, because the topology-freezing temperature ($T_v$) (47°C) is lower than the glass transition temperature ($T_g$) (125°C).
Although catalysts can activate and accelerate the exchange of dynamic covalent crosslinks to control viscoelastic properties, the exogenous catalysts may degrade or leach from the polymer network over time. Hence, vitrimers without catalysts are preferred for practical applications. Sumerlin and co-workers developed catalyst-free vitrimers from fully commercially available feedstocks, like methyl methacrylate (MMA), (2-acetoacetoxy)ethyl methacrylate (AAEMA), and tris(2-aminoethyl)amine (TREN). The resulting catalyst-free vinylogous urethane vitrimers maintain the high performance of vinylogous polymers meanwhile exhibiting healing properties allowing mechanical recycling. The vitrimers can also be decrosslinked by adding excess monofunctional amine to achieve chemical upcycling (Fig. 1.7B). These efforts clearly demonstrated the versatility of the dynamic covalent toolbox for
configurating the network architectures and material properties in a reversible manner.

1.3.3 Chemical recycling for polymers

To solve the problem of plastic pollution and achieve a closed-loop sustainable circular economy, mechanical recycling by self-healing and reprocessing cannot offer permanently sustainable materials because it does not enable upcycling, i.e., increasing the profits of the recycled materials. Meanwhile, sorting out commodity post-consumer waste [e.g. polyethylene (PE) and polypropylene (PP)] is still a major challenge for mechanical recycling. For numerous common plastic materials, external additives, such as plasticizers, heat stabilizers, metal deactivators, and flame retardants, not only inhibit the effective mechanical recycling of the end-reycled products but also result in loss of mechanical performances during mechanical recycling.60

Therefore, chemical recycling can provide a solution for achieving monomer recovery from the depolymerization of plastic waste. Although the concept of depolymerizable synthetic polymers has been demonstrated by the supramolecular polymer community, the key bottleneck towards the next-generation alternative polymers rest on the question how to achieve chemically recyclable synthetic polymers with mechanical performances that are comparable with common commercial plastics.61

Chen and co-workers reported a synthetic polymer system based on a γ-butyrolactone (Fig. 1.8A).62 Owing to the trans-ring fusion, hard-to-polymerize γ-butyrolactone could be solvent-free polymerized at room temperature. The resulting polymers show high mechanical performance with a breaking tensile stress at (σb) = 55 MPa, high molecular weight (Mn = 145 kg mol⁻¹), and enhanced thermostability [decomposition temperature (Td) = 340°C], yet could also be chemically recycled to monomers by thermolysis at ≥ 300°C for 1 h or by chemolysis with catalyst (ZnCl₂) at 120°C. This pioneering work explored chemical recycling of synthetic polymers by engineering the thermodynamic equilibrium of ring-opening polymerization via elaborating the ring strain of monomers.
Although high temperature and catalysis could accelerate the depolymerization process, the high energy cost compromises the environment friendly nature and the existence of catalysis, to some extent, may poison the recycled monomers or polymers. Dynamic covalent polymers and networks have emerged as a promising solution to balancing the trade-off between recycling efficiency and mechanical performances. Helms and co-workers developed the closed-loop chemical recycling of crosslinked networks by dynamic covalent diketoenamine bonds (Fig. 1.8B). The resulting poly(diketonenamine) materials could be hydrolyzed in strong aqueous acids, such as H₂SO₄ or HCl, at room temperature.

**Figure 1.8** (A) Structures of the cyclic and linear polymers with various catalysts. Reformed with permission from ref. 62. Copyright© 2018, The American Association for the Advancement of Science. (B) Reversible, dynamic covalent diketoenamine bonds and photographs of orthogonal depolymerization of poly(diketonenamine) in strong acid aqueous solution from the plastic waste mixture. Reformed with permission from ref. 63. Copyright© 2019, Springer Nature Limited. (C) Preparation of polyethylene-like polymers and depolymerization process chemically recycled by solvolysis in MeOH solvent. Reformed with permission from ref. 64. Copyright© 2021, Springer Nature Limited.
Polyethylene (PE) products are widely used in daily life, such as plastic bags, films, tubes, etc. Given that, the waste of post-consumer PE products is threatening the sustainable development of the earth. To develop comparable yet more environmentally friendly polyethylene-like polymeric materials, Mecking and co-workers recently demonstrated the closed-loop chemical recycling of polyethylene-like materials by introducing low densities of breakpoints in the polyethylene chain, and using plant oils as the bio-based starting materials (Fig. 1.8C). The key innovation is to introduce dynamic ester bonds between long alkyl chains, which not only preserves the van der Waals interactions and polyethylene-like crystallization of the long alkyl chain, but also enables base-catalyzed depolymerization due to hydrolysis. The high crystallinity endows the materials with comparable mechanical properties to high-density polyethylene materials. Depolymerized monomers can be easily separated from methanol due to the good crystallization ability. External additives can be easily separated from the monomers taking advantage of the difference in solubility.

Polyacetals are another potential candidate for chemical recycling to monomer, but their molecular weight is difficult to be controlled by traditional cationic ring-opening polymerization (ROP) method of 1,3-dioxolane. Coates and co-workers proposed a reversible-deactivation ROP method, where the initiator (chloromethyl methyl ether), catalysts (Lewis acid InBr₃) and proton trap (2,6-di-tert-butyl pyridine) were added into the system to control the molecular weight. The resulting poly(1,3-dioxolane) exhibited comparable mechanical properties to some commodity polyolefins. The depolymerization of poly(1,3-dioxolane) could be achieved by adding strong acid, such as camphorsulfonic acid or diphenylphosphoric acid and even in a commodity plastic waste mixture the isolated yield could up to 96% (Fig. 1.9).
Figure 1.9 (A) Polymerization and depolymerization process of poly(1,3-dioxolane) (PDXL). (B) The change of thermal stability of poly(1,3-dioxolane) after adding 5 mol% camphorsulfonic acid or diphenylphosphoric acid. (C) High isolated yield by chemical recycling method from the mixture of poly(1,3-dioxolane) and some commodity plastics feedstocks. Reprinted with permission from ref. 66. Copyright © 2021, The American Association for the Advancement of Science.

1.4 Summary and outlook

Self-healing polymers summary. Dynamic polymer materials have been widely investigated to satisfy the requirements of a new-generation plastic products with self-healing ability to extend the product life cycle. Dynamic non-covalent bonds have been employed as tools to construct thermoplastic materials with intriguing dynamic features at room temperature. Self-healing capability is highly attractive for the development of a new-generation of plastic products. However, the polymers crosslinked by non-covalent bonds are soft and thermolabile, which limit the practical
application of these types of polymers. A new strategy should be further investigated to address this major issue.

*Processable thermosets summary.* Covalently crosslinked polymers, also known as thermosets, are broadly used in daily life owing to their high performance and durability yet without the self-healing function. However, only a few of them could be collected for mechanical recycling and a high processing temperature is usually necessary. Meanwhile, the thermosets will lose their competing high performance after repeating mechanical recycling. How to achieve a subtle balance between mechanical robustness and material dynamicity is the main challenge for the design of processable thermosets. Vitrimers are emerging by engineering different dynamic covalent crosslinks, exhibiting the features of malleability, repairability without the loss of high mechanical properties. The last but not the least aspect is how to translate the vitrimers to industrially relevant materials. There still is a long way to go for scientific researchers and industrial companies to find effective methodologies to achieve industrial productions.

*Chemically recyclable polymers summary.* Plastic products play an indispensable role in daily life and manufacturing. However, most of the commodity plastic products are disposed of at the end of their lifetime. The carbon-carbon backbone of commercial plastics is too stable and cannot be decomposed naturally even after hundred years. To solve the problem of the mountainous pile of single-use plastics, chemical recycling should be the most promising method for sustainability. On the one hand, plastic waste handling by proper chemical recycling methods could maintain the high quality of monomers, making the repolymerized polymers exhibit comparable mechanical properties compared to the original one. On the other hand, chemical recycling to monomers is the ideal method to reduce the usage of fossil feedstocks and the emission of $\text{CO}_2$ to implement a real close-loop sustainable economy. Although some milestones and efforts have been made in proving the concept, this topic still remains very challenging with regards to the materials performance, recycling cost, economic profits, solvent/catalyst usage, and monomer separation. The solution to our plastic problems, maybe one of the most important research topics in this century, requires researchers from all fields to contribute to the fabrication of a future circular and sustainable plastic economy.
1.5 Outline of this thesis

The research collected in this dissertation is devoted to develop dynamic materials by taking the advantages of dynamic non-covalent bonds or/and dynamic covalent bonds to realize complex dynamic functions.

Chapter 1 presents the global problem of plastic pollution caused by plastic waste and the resulting demand for a new-generation of plastics that can be self-healing, reprocessable, and chemically recycled. This chapter summarizes recent progresses on how the dynamic chemistry toolbox can be used to realize the circular and sustainable plastic economy, including dynamic covalent bonds and dynamic non-covalent bonds (supramolecular chemistry). Representative related polymer materials are introduced and discussed.

Chapter 2 describes a toughening strategy for a dynamic dry supramolecular network by introducing ionic cluster-enhanced iron-carboxylate complexes. The resulting dry supramolecular network simultaneously exhibits tough mechanical strength, high stretchability, self-healing ability, and processability at room temperature. The high performance of these distinct supramolecular polymers is attributed to the hierarchical existence of four types of dynamic combinations in the high-density dry network, including dynamic covalent disulfide bonds, noncovalent H-bonds, iron-carboxylate complexes and ionic clustering interactions. The extremely facile preparation method of this self-healing polymer offers prospects for high-performance low-cost materials among others for protective coatings, biomedical materials, and wearable devices.

Chapter 3 describes the discovery of a simple and robust supramolecular crosslinking strategy based on acylhydrazine units, which can hierarchically crosslink the solvent-free network of poly(disulfides) by forming unique reticular hydrogen bonds, enabling the conversion of a soft into a stiff dynamic material. The resulting supramolecular materials exhibit increase in stiffness of more than two to three orders of magnitude compared to those based on the hydrogen-bonding network of analogous carboxylic acids, simultaneously preserving the repairability, malleability, and recyclability of the materials. The materials also show high adhesion strength on various surfaces while allowing multiple surface attachment cycles.
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without fatigue, illustrating a viable approach how robustness and dynamics can be merged in future material design.

Chapter 4 uses a simple acylhydrazine-based 1,2-dithiolane as the starting material, the disulfide-mediated reversible polymerization and acylhydrazone-based dynamic covalent crosslinking can be combined in an one-pot solvent-free reaction, resulting in mechanically robust, tough, and processable crosslinked materials. The dynamic covalent backbones and crosslinkers endow the network with depolymerization capability under mild conditions and, importantly, virgin-quality monomers can be recovered and separated. This proof-of-concept study shows the opportunities to design chemically recyclable materials using the dynamic chemistry toolbox.

Chapter 5 reports an intrinsically recyclable and reconfigurable poly(disulfide) polymer using a natural small molecule, thioctic acid (TA), as the feedstock. Taking advantage of its dynamic covalent ring-opening polymerization, this material enables a closed-loop chemical recycling network among TA monomers and self-healing elastomers. Mild and complete depolymerization into monomers in diluted alkaline aqueous solution is achieved with yields of recovered monomers up to 86%. The polymer materials can be repeatedly recycled and reused with reconfigurable polymer composition and tunable mechanical properties offering prospects for sustainable functional plastics.

Chapter 6 describes hydrogen-bonded supramolecular microfibers which can perform light-driven spiral deformation by switching an intrinsic azobenzene unit without monomer dissociation. The key design feature rests on rationally spaced multiple hydrogen bonds, which inhibits the disassembly pathway upon irradiation, allowing partial photomechanical actuation of the azobenzene cores in the confined environment of the assemblies. The light-triggered deformation process of the supramolecular microfibers can be controlled in a fully reversible manner. This combination of confinement-inhibited disassembly and photoswitching to induce assembly deformation and actuation along length scales supports a distinctive strategy to design supramolecular materials with photomechanical motion.

1.6 References

Chapter 1
