University of Groningen

Design and synthesis of new amphiphilic copolymers using controlled radical polymerization methods

Migliore, Nicola

DOI:

[10.33612/diss.180999130](https://doi.org/10.33612/diss.180999130)

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:

2021

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

Citation for published version (APA):

Migliore, N. (2021). *Design and synthesis of new amphiphilic copolymers using controlled radical polymerization methods: study of solution properties as function of polymer composition and architecture*. [Thesis fully internal (DIV), University of Groningen]. University of Groningen.
<https://doi.org/10.33612/diss.180999130>

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.

Design and synthesis of new amphiphilic copolymers using controlled radical polymerization methods

Study of solution properties as function of polymer
composition and architecture

Nicola Migliore

university of
groningen

Design and synthesis of new amphiphilic copolymers using controlled radical polymerization methods

Study of solution properties as function of polymer composition
and architecture

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

Tuesday 26 October 2021 at 9.00 hours

By

Nicola Migliore

born on 19 October 1992
in Modica (Rg), Italy

Supervisor

Prof. dr. F. Picchioni

Co-Supervisor

Dr. P. Raffa

Assessment Committee

Prof. dr. V. Castelvetro

Prof. dr. M. M. G. Kamperman

Prof. dr. P. P. Pescarmona

*Dedicated to my beloved
Picciuotti ri San Giovanni*

Table of Contents

Chapter 1

Introduction	11
1.1. Amphiphilic polymers	13
1.1.1. Classification of Amphiphilic polymers	13
1.2. Synthesis of amphiphilic polymers	15
1.2.1. Reversible addition-fragmentation chain-transfer polymerization ..	16
1.2.2. Atom transfer radical polymerization	22
1.3. Solution properties of amphiphilic polymers.....	28
1.3.1. Self-assembly of amphiphilic polymers	29
1.3.2. Surface activity	32
1.3.3. Rheology.....	34
1.4. Applications of amphiphilic polymers	35
1.4.1. Enhanced Oil Recovery	35
1.4.2. Emulsion stabilization	37
1.4.3. Biomedical applications	38
1.4.4. Conductive organic nanocomposites	40
1.5. Bio-based amphiphilic polymers	41
1.6. Thesis outline	43
List of abbreviation Chapter 1	44

Chapter 2

The effect of macromolecular structure on the rheology and surface properties of amphiphilic random Polystyrene-r-Poly(meth)acrylate copolymers prepared by RDRP	57
2.1. Introduction	59
2.2. Experimental Section	62
2.2.1. Materials	62
2.2.2. Synthesis.....	62
2.2.3. Characterization.....	64
2.3. Results and discussion.....	65

2.3.1.	Synthesis.....	65
2.3.2.	¹ H-NMR and TGA characterization	66
2.3.3.	Hydrolysis and solubility	69
2.3.4.	Rheology.....	71
2.3.5.	Surface activity	74
2.3.6.	Comparison between PS-r-AA 1:1.57 neutralized using NaOH or Et ₃ N	77
2.4.	Conclusions	79
	Supporting Information to Chapter 2.....	81
	List of Abbreviation Chapter 2	88

Chapter 3

Synthesis and solution properties of poly(p, α dimethylstyrene-co-maleic anhydride): the use of a monomer potentially obtained from renewable sources as a substitute of styrene in amphiphilic copolymers.....

3.1.	Introduction	95
3.2.	Experimental Section	97
3.2.1.	Materials	97
3.2.2.	Synthesis.....	98
3.2.3.	Characterization.....	100
3.3.	Results and discussion.....	102
3.3.1.	Polymers synthesis	102
3.3.2.	Polymers solution studies	105
3.4.	Conclusions	110
	Supporting Information to Chapter 3.....	112
	List of abbreviations Chapter 3	127

Chapter 4

Amphiphilic Copolymers Derived from Butanosolv Lignin and Acrylamide: Synthesis, Properties in Water Solution, and Potential Applications.....

4.1.	Introduction	133
-------------	---------------------------	------------

4.2. Experimental Section	135
4.2.1. Materials	135
4.2.2. Synthesis	136
4.2.3. Characterization	138
4.3. Results and discussion.....	140
4.3.1. Synthesis of butoxylated lignin-g-acrylamide (LigBu-g-PAM) and butoxylated lignin-bromide-g-acrylamide (LigBr-g-PAM) polymers.....	140
4.3.2. Water solubility	146
4.3.3. Solution properties.....	147
4.3.4. Application testing of lignin based amphiphilic copolymers	149
4.4. Conclusions	150
Supporting Information to Chapter 4.....	152
List of abbreviations Chapter 4	167

Chapter 5

Synthesis and solution properties of bio-based Lactic Acid-derived polymeric surfactants with structure-dependent thermoresponsive behaviour	171
5.1. Introduction	173
5.2. Experimental section	175
5.2.1. Materials	175
5.2.2. Synthesis	176
5.2.3. Characterization.....	179
5.3. Results and discussion.....	181
5.3.1. Synthesis	181
5.3.2. Self-assembly and thermoresponsive behaviour	187
5.3.3. Surface Tension and preliminary Emulsion studies with different oil	190
5.4. Conclusions	193
Supporting Information to Chapter 5.....	195
List of Abbreviation Chapter 5	204

Chapter 6

Synthesis of poly(1-vinylimidazole)-<i>block</i>-poly(9-vinylcarbazole) copolymers via RAFT and their use in chemically responsive graphitic composites	209
6.1. Introduction	211
6.2. Experimental Section	213
6.2.1. Materials	213
6.2.2. Synthesis	214
6.2.3. Characterization	217
6.3. Results and discussion	218
6.3.1. Synthesis and polymers characterization	218
6.3.2. Spectroscopic characterization	224
6.3.3. Preparation of conductive composites	225
6.3.4. Resistance responsiveness of the MWCNTs-composites with organic chemicals	228
6.4. Conclusions	231
Supporting Information to Chapter 6	233
List of Abbreviations Chapter 6	250

Appendix

Summary	257
Samenvatting	261
Riassunto	265
List of Publications	269
Acknowledgments	271