

The Application of Atom Transfer Radical Polymerization to Improve The Preparation of Porous Polymer-based Materials

Melissa A. Lamson

Carnegie Mellon University

Department of Chemistry

June 2016

In partial fulfillment of the requirements for the PHD degree in Chemistry

Acknowledgements

I would like to dedicate this thesis to my family. Without my parent's, David and Diana Lamson, love, support, and constant encouragement to go above and beyond my normal expectations, I would not have been able to do half of what I have achieved. My brother, Nicholas Lamson, has not only been a wonderful, kind, and caring sibling since day one, he has also become one my closest friends and without his support and constant wit, that always puts a smile on my face, I know the past five years would have been unthinkably more difficult.

I would like to express my gratitude toward Prof. Krzysztof Matyjaszewski. I want to thank Kris first for accepting me into his group and giving me the opportunity to develop as a scientist and polymer chemist. I also want to thank him for giving me the opportunity to manage his lab. This was an invaluable experience that allowed me to learn people and management skills that many PhD. students do not obtain in graduate school. The overall educational experience in Kris' group has opened many doors for me that I would have not have had access to without Kris and his guidance over the past 5 years.

I would also like to thank Dr. Jim Spanswick for always being supportive and encouraging when I encountered research problems and for always offering helpful suggestions.

I would like to thank my committee members, Prof. Tomek Kowalewski and Prof. Robert Tilton for their invaluable feedback during my PhD and providing fruitful

collaborations. I gratefully thank Prof. Newell Washburn and Prof. Tara Meyer for joining my committee for the final defense.

I am very grateful to all of my collaborators, who are mentioned in the preface section of each chapter. Without their interactions much of this work would be impossible to achieve. I want to specially thank Dr. Michael S. Silverstein, Dr. Jacob Mohin, and Dr. Maciek Kopec, who were my most frequent collaborators and who provided not only research collaboration, but fruitful discussion throughout the past five years.

I would like to thank my mentors, Dr. Wenwen Li and Dr. Mingjiang Zhong, for thoroughly teaching me not only about ATRP, but how to conduct research. Their discussions and willingness to answer my countless questions truly helped me to develop as a scientist in my first two years. I would also like to thank my informal postdoc mentors, Dr. Kristin Schroeder, Dr. Dominik Konkolewicz, and Dr. Andrew J. D. Magenau, for countless invaluable discussions on science and multiple aspects of PhD life. As a member of the Matyjaszewski group over the past five years, I met many incredible people who introduced me to customs and cultures from around the world, as well as discussing their scientific expertise. This has proven to be an incredible experience and I thank everyone who has been in the Matyjaszewski group for being so open and wonderful to work with. I am especially thankful to Tom Ribelli, Andria Fortney, Dr. Antonina Simakova, Dr. Katarzyna Wegner, Dr. Valerie Williams, Matthew Mackenzie, Sangwoo Park, Pawel Kryszewski, and Alex Bertuccio for being great friends and/or lab mates over the years and all of my other friends at Carnegie Mellon for their camaraderie throughout the difficult process of getting a PhD.

I kindly thank Prof. Roberto Gil and Dr. Gayathri Withers for all of their help with the NMR during the past 5 years and for always having a working facility. I would also like to thank Dr. Rea Freeland for her support and advice during my PhD process.

Abstract

This work explores the application of Atom Transfer Radical Polymerization (ATRP) to improve various aspects of synthesizing well-defined porous polymer-based materials. The thesis specifically focuses on two particular classes of materials; mesoporous nitrogen-doped nanostructured carbons (N-doped nanocarbons) and polymerized high internal phase emulsions (polyHIPEs). The introductory chapter discusses, in great detail, reversible deactivation radical polymerization (RDRP) methods, including ATRP, that can be used to synthesize polyacrylonitrile-based precursors for the preparation of N-doped nanocarbons and discusses their potential applications. The introductory chapter also details the requirements for formation of HIPEs and polyHIPEs, with a focus on the various hurdles that must be overcome for polyHIPEs to become commercially viable and widely applicable materials. Chapter 2 focuses on the synthesis of PAN-containing block copolymer (BCP) precursors by initiators for continuous activator regeneration (ICAR) and metal free (MF) ATRP, which allow for a significant reduction in the concentration of Cu-catalyst required for synthesis of well-defined BCPs; to 1 ppm in ICAR ATRP or no metal catalyst in MF ATRP. Chapter 3 discusses the synthesis of a range of PAN-based stars and characterization of carbon materials derived from these precursors. Chapter 4 discusses the synthesis and use of tetrazine cross-linked SiO_2 -*g*-Poly(4-cyanostyrene) as precursor for nitrogen-doped nanocarbons. The application of ATRP to prepare materials for use in HIPE systems and synthesize polyHIPEs was investigated in Chapter 5, where optimized conditions for activators generated by electron transfer (AGET) ATRP were developed to synthesize fully

degradable polyHIPEs from commercially available monomers and cross-linker. Chapter 6 details the synthesis poly(ethylene oxide) and poly(*n*-butyl acrylate) mikto-arm stars that preferentially formed water in oil HIPEs and were able to stabilize water-in-xylene emulsions with star loading (vs. total emulsion) down to 0.005 wt% and water-in-styrene HIPEs down to 0.04 wt%. In a final step towards preparing a surfactant free stable polyHIPEs these mikto-arm stars were functionalized with reactive alkyl halide or vinyl moieties, so they could be incorporated into the polyHIPE network, as well as stabilize the HIPE, which is discussed in Chapter 7.

Table of Contents

Acknowledgements.....	ii
Abstract.....	v
List of Abbreviations.....	xvii
List of Figures.....	xxvi
List of Tables.....	xxxv
List of Schemes.....	xxxvi
Chapter 1: Nitrogen-doped Nanocarbons Templated from Polyacrylonitrile Block Copolymers and (Polymerized) High Internal Phase Emulsions.....	1
1.1 Introduction.....	2
1.1.1 Chemical Vapor Deposition.....	2
1.1.2 Carbon Obtained by the Direct Pyrolysis of Organic Precursors.....	3
1.1.3 Nanostructured Carbon Obtained by Pyrolysis of Organic Precursors..	3
1.1.3.1 Hard Templating.....	4
1.1.3.2 Soft Templating.....	4
1.2 Controlled Synthesis of Polyacrylonitrile and Its Copolymers.....	7
1.2.1 Conventional Radical and Anionic Polymerization.....	8
1.2.2 Reversible Deactivation Radical Polymerization (RDRP).....	10
1.2.3 Homopolymerization of Acrylonitrile (AN).....	12
1.2.3.1 ATRP.....	12
1.2.3.1.1 Normal ATRP.....	12
1.2.3.1.2 ATRP Activator Regeneration Methods for PAN..	14
1.2.3.2 RAFT Polymerization.....	18

1.2.3.3 NMP.....	21
1.2.4 Random Copolymerization of AN.....	22
1.2.5 Block Copolymerization of AN.....	23
1.2.5.1 ATRP.....	25
1.2.5.2 RAFT Polymerization.....	26
1.2.5.3 NMP.....	27
1.2.5.4 Non-RDRP Method to Polymerize the First Block.....	27
1.2.6 Other Architectures Containing PAN.....	28
1.2.6.1 Stars.....	28
1.2.6.2 Bottlebrushes and Particle Brushes.....	29
1.2.6.3 Comb and Graft Copolymers.....	31
1.2.6.4 Branched	32
1.3. Nanostructured Carbons from PAN and Its Copolymers: PAN cyclization and carbonization.....	32
1.3.1 PAN Homopolymers.....	33
1.3.1.1 Hard Templating.....	34
1.3.1.2 Soft Templating: Surfactants/Polymers and Solvents.....	35
1.3.2 PAN-containing Block Copolymers: BCP templating with PAN- <i>b</i> -PBA...35	
1.3.3 Synthesis of Nanocarbons from Other Block Copolymers.....	38
1.3.3.1 PtBA- <i>b</i> -PAN.....	38
1.3.3.2 PAN- <i>b</i> -PAA.....	38
1.3.3.3 PAN- <i>b</i> -PS.....	39
1.3.3.4 PAN- <i>b</i> -PMMA.....	39

1.3.3.5 PCL- <i>b</i> -PAN.....	40
1.3.4 Long-range ordered Nanocarbons: Zone casting.....	40
1.3.5 Nanocarbon from Molecular Bottle Brushes.....	42
1.3.6 Combining Soft and Hard Templating: PAN- <i>b</i> -PS, PVAc- <i>b</i> -PAN, PAN- <i>b</i> -PEO.....	43
1.4. Applications of Nanocarbons Derived from Copolymer Templating.....	44
1.4.1 Supercapacitor.....	44
1.4.2 CO ₂ Capture.....	45
1.4.3 Oxygen Reduction Reaction (ORR).....	45
1.4.4 Dye Sensitized Solar Cells.....	46
1.5. Nitrogen Doped Nanocarbon Templated from PAN Block Copolymers: Conclusions and Thesis Aim.....	46
1.6. High Internal Phase Emulsion (HIPE) and PolyHIPEs.....	48
1.6.1 HIPEs.....	48
1.6.2 PolyHIPEs.....	49
1.6.3 PolyHIPE Applications.....	51
1.6.4 Motivation: How to Make PolyHIPEs Viable Materials.....	52
1.6.4.1 Degradability.....	52
1.6.4.2 Mechanical Strength.....	53
1.6.4.3 Surfactant Amount.....	55
1.6.5 HIPE and PolyHIPE Thesis aim and study.....	57
1.7. Acknowledgements.....	58
1.8 References.....	58

Chapter 2: Synthesis of Block Copolymers Containing Polyacrylonitrile by ICAR

ATRP and Metal Free ATRP.....	70
2.1 Preface.....	70
2.2 Introduction to ICAR and Metal Free ATRP.....	71
2.3 Synthesis of Polyacrylonitrile by ICAR ATRP.....	76
2.3.1 Introduction.....	76
2.3.2 Experimental.....	76
2.3.2.1 Materials.....	76
2.3.2.2 ICAR ATRP of AN.....	77
2.3.2.3 Chain Extension of PAN-Br with BA by ICAR ATRP....	77
2.3.2.4 Characterization.....	78
2.3.3 Results and Discussion.....	79
2.3.3.1 Initiator/Catalyst Study.....	79
2.3.3.2 Influence of AIBN Loading.....	83
2.3.3.3 Influence of Catalyst Loading.....	85
2.3.3.4 Influence of Targeted DP.....	87
2.3.3.5 Chain extension of PAN-Br with BA.....	88
2.4 Synthesis of PAN- <i>b</i> -PS by ICAR ATRP.....	90
2.4.1 Introduction.....	90
2.4.2 Experimental.....	90
2.4.2.1 Materials.....	90
2.4.2.2 Polymerization of Styrene by ICAR ATRP.....	91
2.4.2.3 Polymerization of Acrylonitrile by ICAR ATRP.....	91

2.4.2.4 Chain Extension of PAN-Br with Styrene by ICAR ATRP..	92
2.4.2.5 Characterization.....	92
2.4.3 Results and Discussion.....	93
2.5 Synthesis of Polyacrylonitrile by Metal Free ATRP.....	97
2.5.1 Introduction.....	97
2.5.2 Experimental.....	98
2.5.2.1 Materials.....	97
2.5.2.2 Characterization.....	98
2.5.2.3 Synthesis of Phenothiazine Derivatives.....	99
2.5.2.4 General Procedure for MF ATRP of AN.....	100
2.5.2.5 General Procedure for Chain Extension of PAN-Br with MMA by MF ATRP.....	100
2.5.3 Results and Discussion.....	101
2.6 Conclusions.....	107
2.7 References.....	108
Chapter 3: Polyacrylonitrile-based Stars as Templates for Nitrogen-doped Nanocarbons.....	111
3.1 Preface.....	111
3.2 Introduction.....	112
3.3 Experimental.....	114
3.3.1 Materials.....	114
3.3.2 Synthesis of PAN-Br.....	115
3.3.3 Synthesis of PAN- <i>b</i> -PBA-Br.....	115

3.3.4 Synthesis of PAN-based stars.....	116
3.3.5 Pyrolysis of Star Samples.....	116
3.3.6 Characterization.....	117
3.4 Results and Discussion.....	118
3.4.1 Synthesis of Stars from PAN-Br.....	118
3.4.2 Synthesis of Stars from PAN- <i>b</i> -PBA-Br.....	125
3.4.3 Characterization of Carbons Derived from PAN-based Stars.....	131
3.5 Conclusions.....	133
3.6 Acknowledgements.....	134
3.7 References.....	134
Chapter 4: Polymerization of 4-Cyanostyrene by ATRP and Tetrazine Cross-linking of Poly(4-Cyanostyrene) to Form a Carbon Precursor.....	136
4.1. Preface.....	136
4.2. Introduction.....	137
4.3 Experimental.....	140
4.3.1 Materials.....	140
4.3.2 Polymerization of 4-Cyanostyrene by Normal ATRP.....	141
4.3.3 Grafting 4-Cyanostyrene from Silica Particles.....	141
4.3.4 Cross-linking of SiO ₂ - <i>g</i> -P(4-CNSt) to form Tetrazine x-SiO ₂ - <i>g</i> -P(4-CNSt).....	142
4.3.5 Carbonization.....	142
4.3.6 Characterization.....	143
4.4 Results and Discussion.....	144

4.4.1 Polymerization of 4-Cyanostyrene by Normal ATRP and Rate Comparison to Other Substituted Styrene.....	144
4.4.2 Grafting 4-Cyanostyrene from Silica Particles.....	146
4.4.3 Cross-linking of 4-Cyanostyrene to Form Tetrazine-units and Pyrolysis to from N-doped Nanocarbons.....	148
4.5 Conclusions.....	154
4.6 Acknowledgements.....	155
4.7 References.....	155
Chapter 5: Synthesis of Degradable PolyHIPEs by AGET ATRP.....	158
5.1 Preface.....	158
5.2 Introduction.....	159
5.3 Experimental.....	162
5.3.1 Materials.....	162
5.3.2 Synthesis of PolyHIPEs.....	162
5.3.2.1 Synthesis of CC-BPMDA and SS-BPMDA PolyHIPEs..	162
5.3.2.2 Synthesis of SS-bpy PolyHIPEs (Table 4.3.1).....	163
5.3.3 PolyHIPE Degradation.....	164
5.3.4 SS-BPMDA Swelling Experiments.....	165
5.3.5 Grafting from SS-BPMDA.....	165
5.3.6 Characterization.....	166
5.4 Results and Discussion.....	167
5.5 Conclusions.....	180
5.6 Acknowledgements.....	181
5.7 References.....	181

Chapter 6: PEO-based Stars as Efficient Stabilizers for Normal Emulsions and High

Internal Phase Emulsions.....183

6.1 Preface.....183

6.2 Introduction.....184

6.3 Experimental.....187

6.3.1 Materials.....187

6.3.2 Synthesis of PEO–Poly(DVB) Star Polymers (SD64) via Cross-linking of
Macromonomers.....188

6.3.3 Synthesis of PEO-Based Star Polymers via Cross-Linking of
Macroinitiators.....189

6.3.4 Generation of Emulsions.....189

6.3.5 Generation of HIPE and Polymerization to form PolyHIPE.....190

6.3.6 Characterization.....191

6.4 Results and Discussion.....193

6.4.1 PEO–Poly(DVB) Homo-arm Star Polymers as Stabilizers for O/W
Emulsions.....194

6.4.2 PEO–PBA–Poly(DVB) Mikto-arm Star Polymers as Stabilizers for Water-
in-Xylene Emulsions.....200

6.4.3 Interfacial Tensions.....206

6.4.4 Generation of Water-in-Styrene/DVB HIPEs with PEO-PBA-Poly(DVB)
Miktoarm Star Polymers and Polymerization to Form PolyHIPEs.....208

6.5 Conclusions.....212

6.6 Acknowledgements.....213

6.7 References.....	214
Chapter 7: Reactive Star Surfactants Designed to Stabilize HIPEs and Incorporate into PolyHIPEs.....	216
7.1 Preface.....	216
7.2 Introduction.....	217
7.3 Experimental.....	219
7.3.1 Materials.....	219
7.3.2 Synthesis of P(BA- <i>co</i> -HEA)-Br Macroinitiator.....	220
7.3.3 Synthesis of PEO-P(BA- <i>co</i> -HEA)-Poly(DVB) Miktoarm Stars and Purification.....	221
7.3.4 Functionalization of PEO-P(BA- <i>co</i> -HEA)-Poly(DVB) Miktoarm Stars with alkyl halide (reactive star for ATRP = RS _{ATRP}).....	222
7.3.5 Functionalization of PEO-P(BA- <i>co</i> -HEA)-Poly(DVB) Miktoarm Stars with Methacrylate groups (reactive star for conventional radical polymerization = RS _{RP}).....	222
7.3.6 Generation of HIPEs and PolyHIPEs with RS _{ATRP} and Degradation of PolyHIPEs.....	223
7.3.7 Generation of HIPEs and PolyHIPEs with RS _{RP}	225
7.3.8 Characterization.....	226
7.4 Results and Discussion.....	227
7.4.1 Functionalization of PEO-P(BA- <i>co</i> -HEA)-Poly(DVB) Miktoarm Stars with ATRP Initiating Sites (RS _{ATRP}).....	227
7.4.2 Generation of HIPEs and PolyHIPEs with RS _{ATRP}	229

7.4.2.1 EHMA/EGDMA HIPEs Polymerized by AGET ATRP...	230
7.4.2.2 EHMA/DSDMA HIPEs Polymerized by AGET ATRP...	231
7.4.2.3 Degradation of PEHMA-Poly(DSDMA) PolyHIPEs.....	233
7.4.3 Functionalization of PEO-P(BA- <i>co</i> -HEA)-Poly(DVB) Miktoarm Stars with ATRP Initiating Sites (RS _{RP}).....	234
7.4.4 Generation of HIPEs and PolyHIPEs with RS _{RP}	236
7.4.4.1 Investigation of Conditions for Stable HIPE Polymerization.....	236
7.4.4.2 Investigation of the Amount Cross-linker on PolyHIPE Structure.....	237
7.4.4.3 Investigation of HIPE Polymerization to Improve PolyHIPE Yield.....	239
7.5 Conclusions.....	241
7.6 Acknowledgements.....	242
7.7 References.....	243
Chapter 8: Summary and Outlook.....	244

List of Abbreviations

Polymers

Polystyrene	PS
Poly(4-vinyl pyridine)	P4VP
Resorcinol-formaldehyde resin	RFR
Poly(ethylene oxide)	PEO
Poly(methyl methacrylate)	PMMA
Poly(isoprene)	PI
Poly(acrylic acid)	PAA
Polyacrylonitrile	PAN
Poly(<i>n</i> -butyl acrylate)	PBA
Poly(styrene- <i>co</i> -acrylonitrile)	PSAN
Poly(<i>t</i> -butyl acrylate)	PtBA
Poly(2-methoxyethyl acrylate)	PMEA
Poly(cysteamidacrylate)	PCAA
Poly(ϵ -caprolactone)	PCL
Poly(L-lactic acid)	PLLA
Poly(dimethyl siloxane)	PDMS
Poly(<i>N</i> -isopropylacrylamide)	PNIPAM
Poly(hydroxyethyl methacrylate)	PHEMA
Poly(2-ethylhexyl methacrylate)	PEHMA
Poly(divinyl benzene)	Poly(DVB)
Poly(stearyl acrylate)	PA18

Poly(ethylene glycol dimethacrylate)	PEGDMA
Poly(4-cyanostyrene)	Poly(4-CNSt)

Monomers and Cross-linkers

Acrylonitrile	AN
Itaconic acid	IAn
Trimethylsilyl protected hydroxyethyl acrylate	HEA-TMS
Vinyl benzyl chloride	VBC
Styrene	St
Divinyl benzene	DVB
2-Ethylhexyl acrylate	EHA
2-Ethylhexyl methacrylate	EHMA
<i>n</i> -butyl acrylate	<i>n</i> -BA
Propylene fumarate dimethacrylate	PFDMA
Methyl methacrylate	MMA
Di(ethylene glycol) diacrylate	DEGDA
1,6-Hexanediol diacrylate	HDDA
Ethylene glycol diacrylate	EGDA
Poly(ethylene glycol) methyl ether methacrylate (avg. M_n 300)	OEOMA ₃₀₀
Bis(2-methacryloyloxyethyl) disulfide	DSDMA
Poly(ethylene oxide) methyl ether methacrylate macromonomer	PEO MM
Stearyl acrylate	A18
Polyhedral oligomeric silsesquioxane with 8 methacrylate groups	POSS-8

Ethylene glycol dimethacrylate	EGDMA
4-Cyanostryene	4-CNS _t

ATRP Ligands

2,2'-bipyridine	bpy
Tetramethylguanidino-tris(2-aminoethyl)amine	TMG ₃ -TREN
Triphenyl phosphine	PPh ₃
Iminodiacetic acid	IMA
Isophthalic acid	IA
Tris[(2-pyridyl)methyl]amine	TPMA
1,1,4,7,7-Pentamethyldiethylenetriamine	PMDETA
Tris[2-dimethylamino)-ethyl] amine	Me ₆ TREN
N,N,N',N'-Tetrakis(2-pyridylmethyl)ethylenediamine	TPEN
N,N-Bis(2-pyridylmethyl) octadecylamine	BPMODA
4,4'-Dinonyl-2,2'-dipyridine	dNbpy

ATRP Initiators

2-Bromopropionitrile	BPN
2-Chloropropionitrile	CPN
Ethyl 2-Bromoisobutyrate	EBiB
Ethyl α -bromophenylacetate	EBPA
1,1,1-Tris(4-chlorosulfonylphenyl)-ethane ¹³	3PSC
Ethyl α -chlorophenylacetate	ECPA

1-Bromoethyl benzene	PEBr
----------------------	------

Other Chemicals

Azobisisobutyronitrile	AIBN
------------------------	------

Dimethyl sulfoxide	DMSO
--------------------	------

N,N'-dimethylformamide	DMF
------------------------	-----

N-methyl-2-pyrrolidone	NMP
------------------------	-----

Tetrahydrofuran	THF
-----------------	-----

dichloromethane	DCM
-----------------	-----

Methanol	MeOH
----------	------

Ethylene carbonate	EC
--------------------	----

2-Cyanopyridine	CP
-----------------	----

Methyl isobutyl ketone	MIBK
------------------------	------

1-Bromoethyl benzene	PEBr
----------------------	------

diethyl 2,3-dicyano-2,3-diphenylsuccinate	DCDPS
---	-------

Tin (II) 2-ethylhexanoate	Sn(EH) ₂
---------------------------	---------------------

1-Butyl-3-methylimidazolium tetrafluoroborate	[C ₄ mim][BF ₄]
---	--

10-Phenylphenothiazine	Ph-PTZ
------------------------	--------

2-Cyanoethyl dithiobenzoate	CED
-----------------------------	-----

2-Cyanoprop-2-yl dithiobenzoate	CPDB
---------------------------------	------

Dibenzyl trithiocarbonate	DBTC
---------------------------	------

Bis(thiobenzoyl) disulfide	BTBDS
----------------------------	-------

Bis(thiophenylacetoyl) disulfide	BTPADS
----------------------------------	--------

[(Carbazole-9-carbodithioate)-2-methyl propionic acid] phenyl ester	BCCDP
Cyanoethyl dodecyl trithiocarbonate	CEDT
2-Cyano-2-propyl dodecyl trithiocarbonate	CPDT
2,2,5-Trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane	TPPA
<i>n</i> -Tert-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide	DPEN or SG1
2,2,6,6-Tetramethyl-1-piperidinyloxy	TEMPO
2-Dodecylsulfanylthiocarbonylsulfanyl-2-methyl propionic acid	DMP
Anodic aluminum oxide	AAO
Sorbitan monooleate	Span-80
1,1'-Azobis(cyclohexanecarbonitrile)	ABCN
10-(4-methoxyphenyl)-phenothiazine	4-MeOPh-PTZ
10-(1-naphthalenyl)-phenothiazine	Nap-PTZ
Tributylphosphine	Bu ₃ P
Tetrabutylammonium bromide	TBABr
Benzoyl peroxide	BPO
Potassium persulfate	KPS
(4-Butoxy-2,2,6,6-tetramethyl piperidin-1-yl)oxy	bTEMPO
2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile)	V-70
Triethyl amine	TEA
Methacryloyl chloride	MAC

Polymerization Methods

Free radical polymerization	RP
-----------------------------	----

Reversible deactivation radical polymerization	RDRP
Atom transfer radical polymerization	ATRP
Reversible addition fragmentation chain-transfer	RAFT
Nitroxide-mediated polymerization	NMP
Reverse atom transfer radical polymerization	RATRP
Activators regenerated by electron transfer ATRP	ARGET ATRP
Initiators for continuous activator regeneration ATRP	ICAR ATRP
Supplemental activators and reducing agents ATRP	SARA ATRP
Ring opening metathesis polymerization	ROMP
Activators generated by electron transfer ATRP	AGET ATRP
Surface initiated ATRP	SI-ATRP

Other Abbreviations

Chemical vapor deposition	CVD
Block Copolymer	BCP
Nitrogen-doped nanostructured carbons	N-doped nanocarbons
Gel permeation chromatography	GPC
Gradient polymer elution chromatography	GPEC
Molecular weight	MW
Molecular weight distribution	MWD
High molecular weight	HMW
Molecular weight from GPC	$M_{n,GPC}$
Molecular weight from NMR	$M_{n,NMR}$

Theoretical molecular weight	$M_{n,theory}$
Dispersity	M_w/M_n
Refractive index	RI
Multi-angle light scattering	MALLS
Chain transfer agent	CTA
Acrylonitrile-butadiene rubber	NBR
Shell cross-linked micelles	SCKs
Energy dispersive x-ray spectroscopy	EDAX spectroscopy
Atomic force microscopy	AFM
Small angle x-ray scattering	SAXS
Grazing incidence small-angle X-ray scattering	GISAXS
X-ray photoelectron spectroscopy	XPS
Differential scanning calorimetry	DSC
Thermogravimetric analysis	TGA
Transmission electron microscopy	TEM
Scanning electron microscopy	SEM
Brunauer-Emmet-Teller	BET
Barrett-Joyner-Halenda	BJH
Kruk-Jaroniec-Sayari	KJS
BET surface area	S_{BET}
Microporous surface area	S_{micro}
Mesoporous surface area	S_{meso}
^1H nuclear magnetic resonance spectroscopy	NMR

Dynamic light scattering	DLS
Order-disorder transition temperature	T_{ODT}
Rate of polymerization	R_p
Rate constant of propagation	k_p
Rate constant of termination	k_t
Rate constant of deactivation	k_{deact}
Rate of decomposition	k_{dc}
Initiation efficiency	f
Concentration of radical conventional radical initiator	$[I_2]$
Concentration of alkyl halide	$[P_n\text{-X}]$ or $[R\text{-X}]$
Alkyl halide	$R\text{-X}$
Concentration of deactivator species	$[\text{Cu}^{\text{II}}\text{X}_2/\text{L}]$
Degree of polymerization	DP_n
Monomer conversion	p
Apparent rate of polymerization	k_p^{app}
Monomer concentration	$[M]$
Concentration of growing radicals	$[P_n^\bullet]$
Chain end functionality	CEF
Flory-Huggins interaction parameter	χ
Copolymer templated nanocarbons	CTNCs
Electrical double layer	EDL
Specific capacitance per unit area	C_{sa}
Oxygen reduction reaction	ORR

Dye sensitized solar cells	DSSC
High Internal Phase Emulsion	HIPE
Medium Internal Phase Emulsion	MIPE
Water-in-oil	W/O
Oil-in-water	O/W
Polymerized HIPE	polyHIPE
Room temperature	RT
Hydrodynamic diameter	D_n
Hydrophile–lipophile balance	HLB
Hammett constant	σ
Glass transition temperature	T_g

Sample Abbreviations

PolyHIPE synthesized with non-degradable cross-linker and CuBr ₂ /BPMODA catalyst	CC-BPMODA
PolyHIPE synthesized with a degradable cross-linker and CuBr ₂ /BPMODA catalyst	SS-BPMODA
PolyHIPE synthesized with a degradable cross-linker and CuBr ₂ /bpy	SS-bpy
Mikto-arm star with 30 % PBA	MS _{PBA30}
Mikto-arm star with 50% PBA	MS _{PBA50}
Mikto-arm star with 90% PBA	MS _{PBA90}
Dense PEO star with 64 arms	S _D 64
Loose PEO star with 30 arms	S _L 30

Loose PEO star with 35 arms	S_{L35}
Reactive mikto-arm star with alkyl-halide functionality	RS_{ATRP}
Reactive mikto-arm star with methacrylate functionality	RS_{RP}
P(4-CNSt) grafted from 15 nm silica particles	$SiO_2(15)-g-P(4-CNSt)$
P(4-CNSt) grafted from 120 nm silica particles	$SiO_2(120)-g-P(4-CNSt)$
Tetrazine cross-linked $SiO_2(15)-g-P(4-CNSt)$	$x-SiO_2(15)-g-P(4-CNSt)$
Tetrazine cross-linked $SiO_2(120)-g-P(4-CNSt)$	$x-SiO_2(120)-g-P(4-CNSt)$
Carbonized $x-SiO_2(15)-g-P(4-CNSt)$	$C-x-SiO_2(15)-g-P(4-CNSt)$
Carbonized $x-SiO_2(120)-g-P(4-CNSt)$	$C-x-SiO_2(120)-g-P(4-CNSt)$

List of Figures

Figure 1.1. preparation of well-defined carbon nanostructures. Step 1: film casting of PS-P4VP/resorcinol supramolecular assembly; Step 2: solvent annealing; Step 3: *in situ* polymerization of resorcinol and formaldehyde by exposing the film to formaldehyde gas; Step 4: pyrolysis of the polymeric film in N_2 ; Reproduced from reference 28

Figure 1.2.3.1. Reagents used in ATRP of AN

Figure 1.2.3.2. chain transfer agents used in RAFT polymerization of AN

Figure 1.2.3.3. nitroxides used for NMP of AN

Figure 1.2.6.1: synthesis of PBA-*b*-PAN 3-armed stars; Reproduced from reference 150

Figure 1.2.6.2: PBA-*b*-PAN-*b*-PAA cross-linked brushes for nanostructured carbon; Reproduced from reference 152

Figure 1.2.6.3: Synthesis of PAN-*b*-PNIPAM, PAN-*b*-(PHEMA-*g*-PNIPAM), and PAN-*co*-(PHEMA-*g*-PNIPAM); Reproduced from reference 156

Figure 1.3.1. Types of nitrogen in N-doped carbon

Figure 1.3.2.1. (a) SAXS profiles of PAN₉₉-*b*-PBA₇₀ annealed at 200 ° C (dotted) and its corresponding CTNC pyrolyzed at 700 ° C (solid). (b) XPS high-resolution N1s spectra of mesoporous carbon prepared from PAN₉₉-*b*-PBA₇₀. Reproduced from reference 165

Figure 1.3.3 Fabrication of carbon nanofibers from PAN-*b*-PS BCP templating;

Reproduced from reference 188

Figure 1.3.4. (a) Long-range order in thin films of PBA₂₄₀-*b*-PAN₁₂₄ BCPs prepared by zone-casting and pyrolysis to form nanostructured carbon; (b) AFM phase images (left: copolymer; right: carbon); (c) GISAXS patterns acquired at 90° to casting direction (top: copolymer; bottom: carbon); (d) schematic illustration of lamellar order (left: copolymer; right: carbon); (e) azimuthal profiles of maxima in 2D Fourier transforms of AFM images and maxima in GISAXS patterns corresponding to the lamellar period. Reference reproduced from 192

Figure 1.4. synthesis of binder free CTNC-based electrodes for ORR; Reproduced from reference 163

Figure 1.6.1. W/O HIPE and polyHIPE formation

Figure 1.6.2. SEM image of a typical polyHIPE structure; V= void and W= window;

Scale bar= 20 μm; Reproduced from reference 204

Figure 1.6.4.1. Structures of cross-linkers in degradable polyHIPEs

Figure 1.6.4.2. Synthesis of poly(dicyclopentadiene) based polyHIPEs; Reproduced from reference 221

Figure 1.6.4.3. Representation of HIPE stabilized by salt/temperature responsive core cross-linked star polymers; Reproduced from reference 287

Figure 2.3.2. Correlation between $M_{n,NMR}$ and $M_{n,GPC}$ determined using linear PEO calibration standards for PAN samples with MWs in the range 3,000 – 20,000. DMF containing 10 mM LiBr was used as the eluent at 50 °C and PS-based columns

Figure 2.3.3.1. First-order kinetic plots for (a) $[AN]:[R-X]:[CuBr_2]:[TPMA]:[AIBN]=400:1:0.02:0.06:0.05$ and (b) $[AN]:[R-X]:[CuBr_2]:[TPEN]:[AIBN]=400:1:0.02:0.06:0.05$. (c) MW and M_w/M_n evolution and (d) GPC traces for conditions $[AN]:[BPN]:[CuBr_2]:[TPMA]:[AIBN]=400:1:0.02:0.06:0.05$; AN:DMSO= 1:1.25 (v/v), T = 65 °C.

Figure 2.3.3.2. Effect of AIBN concentration on ICAR ATRP of AN; (a) first-order kinetic plot; (b) MW and M_w/M_n evolution. $[AN]:[BPN]:[CuBr_2]:[TPMA]=200:1:0.01:0.03$; AN:DMSO= 1:1.25 (v/v); T = 65 °C, 10 hours.

Figure 2.3.3.3. Effect of catalyst concentration on ICAR ATRP of AN; (a) first-order kinetic plots, (b) MW and M_w/M_n evolution $[AN]:[BPN]:[AIBN]:[CuBr_2]:[TPMA]=200:1:0.1:n:3n$. AN:DMSO= 1:1.25 (v/v), T = 65 °C, 10 hours; GPC traces of ICAR ATRP of AN with different catalyst concentrations: conditions: $[AN]:[BPN]:[AIBN]:[CuBr_2]:[TPMA]=200:1:0.1:n:3n$; n = 0.0002 (a), 0.002 (b), or 0.005 (c); AN:DMSO= 1:1.25 (v/v), T = 65 °C, 10 hours

Figure 2.3.3.4. Effect of target DP on ICAR ATRP of AN with 10 ppm catalyst; (a) first-order kinetic plots; (b) MW and M_w/M_n evolution; $[AN]:[BPN]:[AIBN]=x:1:0.1$; $[CuBr_2]:[TPMA]=1:3$; AN:DMSO= 1:1.25 (v/v); T = 65 °C, 10 hours; (c) GPC traces for conditions $[AN]:[BPN]=400:1$

Figure 2.3.2.5. 1H NMR spectrum of a PAN-Br macroinitiator ($M_{n,NMR}=4100$, $M_w/M_n=1.23$) synthesized by ICAR ATRP (a); conditions: $[AN]:[BPN]:[AIBN]:[CuBr_2]:[TPMA]$

= 200:1:0.1:0.01:0.06; AN:DMSO= 1:1.25 (v/v), T = 65 °C, 4 hours. Chain extension of PAN macroinitiator with n-butyl acrylate by ICAR ATRP (b); [BA]:[PAN-

Br]:[CuBr₂/TPMA]:[AIBN] = 200:1:0.01:0.1; BA:DMF =1:2 (v/v); T = 60 °C, 5.5 hours

Figure 2.4.3.1. Semi-logarithmic kinetic and conversion plots (a) and MW and MWD (b)

for ICAR ATRP with BPN or EBiB as the initiator; conditions: [St]:[R-

X]:[CuBr₂]:[TPMA]:[ABCN]= 100:1:0.01:0.03:0.1 at 90 °C with St:DMF= 1:2 (v:v)

Figure 2.4.3.2: Semi-logarithmic kinetic and conversion plots (a) and MW and MWD (b)

of styrene polymerization by ICAR ATRP; [St]:[BPN]:[CuBr₂]:[TPMA]:[AIBN]=

100:1:0.01:0.03:0.1 at 60 °C with St:DMF= 1:2 (v:v)

Figure 2.4.3.3. Semi-logarithmic kinetic and conversion plots(a) and MW and MWD (b)

for chain extension of PAN-Br with styrene by ICAR ATRP; [St]:[PAN-Br]:[CuBr₂]:

[TPMA]:[AIBN]= 100:1:0.04:0.12:0.1 at 60 °C with St:DMF= 1:2 (v:v)

Figure 2.4.3.4. Evolution of molecular weight distribution for chain extension of PAN-

Br with styrene by ICAR ATRP; [St]:[PAN-Br]:[CuBr₂]:[TPMA]:[AIBN]=

100:1:0.04:0.12:0.1 at 60 °C with St:DMF= 1:2 (v:v)

Figure 2.5.1. Structures of phenothiazine derivatives used as photocatalysts in MF ATRP

Figure 2.5.3.1. (a) Semi-logarithmic kinetic plots of polymerization of AN by MF ATRP

with conditions: [AN]:[EBPA]:[1] = 100:1:0.1 in DMF or DMSO, irradiation by 2.1 or

4.9 mW/cm² UV light; (b) number-average molecular weight (M_n , filled symbols), and

dispersity (M_w/M_n , open symbols) versus conversion for MF ATRP of AN

Figure 2.5.3.2. Semi-logarithmic kinetic plots of polymerization of AN by MF ATRP

under conditions: [AN]:[EBPA]:[1]= x:1:0.1, where x= 100(black), 200 (red), or 50

(blue)

Figure 2.5.3.3. ^1H NMR spectrum of PAN in DMSO- d_6 , obtained from photo-induced metal-free ATRP under conditions $[\text{AN}]:[\text{EBPA}]:[1] = 100:1:0.1$ in DMF

Figure 2.5.3.4. GPC traces of PAN-Br and PAN-*b*-PMMA (a); ^1H NMR spectrum of PAN-*b*-PMMA in DMSO- d_6 (b); obtained from photo-induced metal-free ATRP under conditions $[\text{PAN-Br}]:[\text{MMA}]:[1] = 1:200:0.2$, MMA:DMF = 1:2 (v/v) at rt and irradiation by 2.1 mW/cm^2 UV light.

Figure 3.4.1.1. MWD of PAN₄₁-Br and PAN₄₁-Poly(DEGDA); Peak fitting of PAN₅₀-Poly(DEGDA) to determine area (b); $[\text{PAN}_{41}\text{-Br}]:[\text{DEGDA}]:[\text{CuBr}]:[\text{TPMA}] = 1:5:0.25:0.3$

Figure 3.4.1.2. MWD of PAN₄₃-Br and evolution of PAN₄₃-Poly(DEGDA); Peak fitting of PAN₄₃-Poly(DEGDA) to determine area (b); $[\text{PAN}_{43}\text{-Br}]:[\text{DEGDA}]:[\text{CuBr}]:[\text{TPMA}] = 1:5:0.25:0.3$

Figure 3.4.1.3. MWD of PAN₄₉-Br and evolution of PAN₄₉-Poly(DEGDA); Peak fitting of PAN₄₉-Poly(DEGDA) to determine area (b); $[\text{PAN}_{49}\text{-Br}]:[\text{DEGDA}]:[\text{CuCl}]:[\text{TPMA}] = 1:5:0.25:0.3$

Figure 3.4.1.4. MWD of PAN₅₆-Br and PAN₅₆-Poly(HDDA); Peak fitting of PAN₅₆-Poly(HDDA) to determine area (b); $[\text{PAN}_{56}\text{-Br}]:[\text{HDDA}]:[\text{CuBr}]:[\text{TPMA}] = 1:5:0.25:0.3$

Figure 3.4.1.5. MWD of PAN₈₇-Br and evolution of PAN₈₇-Poly(HDDA); Peak fitting of PAN₈₇-Poly(HDDA) to determine area (b); $[\text{PAN}_{87}\text{-Br}]:[\text{HDDA}]:[\text{CuBr}]:[\text{TPMA}] = 1:5:0.25:0.3$

Figure 3.4.1.6. MWD of PAN₈₇-Br and PAN₈₇-Poly(EGDA) (a); Peak fitting of PAN₈₇-Poly(EGDA) to determine area (b); $[\text{PAN}_{87}\text{-Br}]:[\text{EGDA}]:[\text{CuBr}]:[\text{TPMA}] = 1:15:0.25:0.3$

Figure 3.4.2.1. MWD of PAN₃₀-*b*-PBA₁₈-Br and evolution of PAN₃₀-*b*-PBA₁₈-Poly(HDDA); Peak fitting of PAN₃₀-*b*-PBA₁₈-Poly(HDDA) to determine area (b); [PAN-*b*-PBA-Br]:[HDDA]:[CuBr]:[TPMA]= 1:10:0.25:0.3

Figure 3.4.2.2. MWD of PAN₃₀-*b*-PBA₁₈-Br and evolution of PAN₃₀-*b*-PBA₁₈-Poly(HDDA); Peak fitting of PAN₃₀-*b*-PBA₁₈-Poly(HDDA) to determine area (b) [PAN-*b*-PBA-Br]:[HDDA]:[CuBr]:[TPMA] = 1:10:0.35:0.6

Figure 3.4.2.3. MWD of PAN₇₉-*b*-PBA₁₀-Br and evolution of PAN₇₉-*b*-PBA₁₀-Poly(HDDA) (a); Peak fitting of PAN₇₉-*b*-PBA₁₀-Poly(HDDA) to determine area (b); [PAN-*b*-PBA-Br]:[HDDA]:[CuBr]:[TPMA]= 1:10:0.35:0.6

Figure 3.4.2.4. MWD of PAN₇₉-*b*-PBA₁₀-Br and PAN₇₉-*b*-PBA₁₀-Poly(HDDA) (a); Peak fitting of PAN₇₉-*b*-PBA₁₀-Poly(HDDA) to determine area (b); [PAN-*b*-PBA-Br]:[HDDA]:[CuBr]:[TPMA]= 1:5:0.35:0.6

Figure 3.4.2.5. MWD of PAN₇₉-*b*-PBA₄₄-Br and evolution of PAN₇₉-*b*-PBA₄₄-Poly(HDDA); Peak fitting of PAN₇₉-*b*-PBA₄₄-Poly(HDDA) to determine area (b); [PAN-*b*-PBA-Br]:[HDDA]:[CuBr]:[TPMA]= 1:5:0.35:0.6

Figure 3.4.2.6. MWD of PAN₅₀-*b*-PBA₁₄-Br and evolution of PAN₅₀-*b*-PBA₁₄-Poly(HDDA) (a); Peak fitting of PAN₅₀-*b*-PBA₁₄-Poly(HDDA) to determine area (b) [PAN-*b*-PBA-Br]:[HDDA]:[CuBr]:[TPMA]= 1:5:0.35:0.6

Figure 3.4.2.7. MWD of PAN₅₀-*b*-PBA₂₃-Br and evolution of PAN₅₀-*b*-PBA₂₃-Poly(HDDA) (a); Peak fitting of PAN₅₀-*b*-PBA₂₃-Poly(HDDA) to determine area (b); [AN-*b*-PBA-Br]:[HDDA]:[CuBr]:[TPMA]= 1:5:0.35:0.6

Figure 3.4.3. N₂ adsorption isotherms for nanocarbon samples derived from PAN-stars

Figure 4.2. Select reagents used in the study of substituted styrene polymerization by ATRP from reference 9

Figure 4.4.1.1. Semi-logarithmic kinetic and conversion plots (a) and MW and MWD plot for the ATRP of 4-CNSt with the using conditions [4-CNSt]:[PEBr]:[CuBr]:[CuBr₂]:[bpy]= 100:1:1:0.05:3, with a [4-CNSt]₀ of 4.37 mM in DMF at 110 °C

Figure 4.4.1.2. Semi-logarithmic kinetic and conversion plots (a) and evolution of MW (b) for the ATRP of 4-CNSt with conditions of [4-CNSt]:[EBiB]:[CuBr]:[CuBr₂]:[bpy]= 100:1:0.9:0.1:2 at 80 °C in DMF.

Figure 4.4.2.1. 15 nm and 120 nm silica particles characterization and ATRP initiator structure

Figure 4.4.2.2. MWD curve for P(4-CNSt) cleaved from 15 nm silica particle

Figure 4.4.2.3. MWD curve for P(4-CNSt) cleaved from 120 nm silica particle

Figure 4.4.3. SEM images of (a) SiO₂(15)-*g*-P(4-CNSt), (b) SiO₂(120)-*g*-P(4-CNSt), (c) x-SiO₂(15)-*g*-P(4-CNSt), (d) x-SiO₂(120)-*g*-P(4-CNSt)

Figure 4.4.4. DLS analysis of (a) SiO₂(15)-*g*-P(4-CNSt) and (b) x- SiO₂(15)-*g*-P(4-CNSt) in DMF at RT

Figure 4.4.5. TGA curves for x-SiO₂(15)-*g*-P(4-CNSt) (black) and SiO₂(120)-*g*-P(4-CNSt) (blue) particles

Figure 4.4.6. Pore size distribution of C-x-SiO₂(15)-*g*-P(4-CNSt) (black) and C-x-SiO₂(120)-*g*-P(4-CNSt) (blue) before (a) and after (b) HF etching of silica particles

Figure 4.4.7. SEM images of (a) C-x-SiO₂(15)-*g*-P(4CNSt) and (b) C-x-SiO₂(120)-*g*-P(4CNSt)

Figure 5.4.1. SEM images of CC-BPMODA (a), SS-BPMODA (b,d), and SS-bpy (c,e) polyHIPEs

Figure 5.4.2. Molecular weight distribution of degraded SS-BPMODA from GPC analysis with THF eluent and linear PS-standards

Figure 5.4.3. Images of SS-BPMODA (a) and SS-bpy (b) reaction mixtures immediately after polymerization

Figure 5.4.4. Stress-strain curves for compression testing of SS-BPMODA and SS-bpy

Figure 5.4.5. SS-BPMODA before (left) and after (right) swelling with anisole for 24 hours

Figure 5.4.6. Molecular weight distribution of degraded SS-BPMODA and degraded SS-BPMODA after 24 and 48 hour chain extension with EHMA; GPC with THF eluent and PS standards

Figure 5.4.7. Molecular weight distribution of degraded SS-BPMODA and degraded material after 24 and 48 hour chain extension with OEOMA₃₀₀; GPC with THF eluent and PS standards

Figure 5.4.8. SEM image of SS-BPMODA after chain extension with OEOMA₃₀₀ for 24.5 hours

Figure 6.4.1.1. Images of oil-in-water emulsions stabilized by different amounts of PEO star polymer, S_D64

Figure 6.4.1.2. Micrographs at 40× magnification of diluted oil-in-water emulsions formed using the PEO star polymer S_D64 as stabilizer: (a–c) xylene in water (star polymer amount: (a) 0.01, (b) 0.1, and (c) 0.5 wt %); (d–f) cyclohexane in water (star polymer amount: (c) 0.01, (d) 0.1, and (e) 0.5 wt %). Scale bar 50 μm

Figure 6.4.2.1. Images of water-in-xylene and water-in-cyclohexane emulsions stabilized by different amount of PEO–PBA–poly(DVB) miktoarm star polymers (MS_{PBA50})

Figure 6.4.2.2. Micrographs at 40× magnification of diluted water in xylene emulsion formed by using PEO–PBA–poly(DVB) miktoarm star polymers (MS_{PBA50}) as stabilizer, star polymer amount: (a) 0.005, (b) 0.01, (c) 0.1, and (d) 0.5 wt %. Scale bar 50 μ m.

Figure 6.4.4.1. PS-PDVB polyHIPE samples 1 (a), 2 (b), and 3 (c) from MS_{PBA50} stabilized W/O HIPEs

Figure 6.4.4.2. PS-PDVB polyHIPE samples 4 (a,b) and 5 (c,d) from MS_{PBA50} stabilized W/O HIPEs

Figure 6.4.4.3. Structure of A18 (a) and POSS-8 (b)

Figure 6.4.4.4. PA18/POSS-8 Shape Memory PolyHIPE

Figure 7.4.1. Molecular weight distribution of PEO-P(BA-co-HEA)-Poly(DVB) stars before (left) and after (right) functionalization with BrIBr (alkyl halide)

Figure 7.4.2. SEM image of PEHMA-PEGDMA polyHIPE synthesized from RS_{ATRP} stabilized HIPE and polymerized by RP at two different magnifications

Figure 7.4.2.1. (a) SEM image of PEHMA-PEGDMA synthesized by AGET ATRP with RS_{ATRP} (0.16 wt%) and, (b) EBiB and SEM image of PEHMA-PEGDMA synthesized by AGET ATRP with RS_{ATRP} (0.04 wt%), (c) Structure of BPMODA,

Figure 7.4.2.2. (a) PEHMA-PDSDMA polyHIPEs with 0.04 wt% RS_{ATRP} , (b) 0.16 RS_{ATRP} , (c) 0.13 wt% RS_{ATRP} and EBiB, and (d) the structure of DSDMA

Figure 7.4.2.3. (a) Degradation of PEHMA-PDSDMA polyHIPEs and (b) molecular weight distribution of degraded PEHMA-PDSDMA synthesized with 0.13 wt% RS_{ATRP} and EBiB

Figure 7.4.3. Molecular weight distribution of PEO-P(BA-co-HEA)-Poly(DVB) stars before (left) and after (right) functionalization with MAC (methacrylate)

Figure 7.4..4.1. (a) SEM images of polyHIPEs from St/DVB HIPES stabilized by 0.1 wt% RS_{RP} and polymerized with BPO at 60 °C and (b) with V-70 at 40 °C

Figure 7.4.4.2. SEM images of polyHIPEs from HIPES stabilized by 0.1 wt% RS_{RP} and polymerized with V-70 at 40 °C using a St:DVB molar ratio of (a) 26:1, (b) 53:1 and (c) 109:1.

Figure 7.4.3.3. SEM images of polyHIPEs from St/DVB HIPES stabilized by 0.1 wt% RS_{RP} and polymerized with (a) V-70 at 30 °C for 24 hours, (b) V-70 and BPO at 30 °C for 24 hours and 70 °C for 24 hours, and (c) V-70 and BPO at 70 °C for 24 hours

Figure 7.3.3.4. SEM image of polyHIPE from EHA/EGDA HIPE stabilized by 0.1 wt% RS_{RP} and polymerized at 35 °C for 24 hours using V-70 as the initiator

List of Tables

Table 1.2.3.1. normal ATRP of AN

Table 1.2.3.2. Conditions for activator regeneration ATRP of AN

Table 1.2.3.3. RAFT polymerization of AN

Table 1.2.3.4. NMP of AN

Table 2.3.3.1. Effect of ligand and initiator on ICAR ATRP of AN

Table 2.3.3.2. Effect of AIBN concentration on ICAR ATRP of AN

Table 2.2.3.3. Effect of catalyst concentration on ICAR ATRP of AN

Table 2.3.3.4. Effect of target DP on ICAR ATPR of AN with 10 ppm catalyst

Table 2.4.3. PAN-*b*-PS samples and MW characterization

Table 2.5.3. Photo-induced MF ATRP of Acrylonitrile

Table 3.4.1. PAN star samples

Table 3.4.2. PAN-*b*-PBA Star Samples

Table 3.4.3. Characterization of N-doped Nanocarbons Templated by PAN-Stars

Table 4.2. Hammett constant for substituted styrenes and apparent rate coefficients in ATRP

Table 4.4.3. SiO₂-*g*-Poly(4-CNSt) and tetrazine cross-linked samples

Table 4.4.4. DSC characterization of P(4-CNSt) samples

Table 4.4.5. Surface area measurements of x-SiO₂-*g*-P(4-CNSt), and C-x-SiO₂-*g*-P(4-CNSt)

Table 5.3.1. Conditions for polyHIPE synthesis

Table 5.4.1. Data from stress-strain curves in Fig. 4.3.4

Table 5.4.2. Swelling of SS-BPMODA with anisole or EHMA

Table 5.4.3. Molecular weight data of degraded SS-BPMODA before and after chain extension with EHMA

Table 5.4.4. Molecular weight data of degraded SS-BPMODA before and after chain extension with OEOMA₃₀₀

Table 6.3.5.1. Styrene/DVB HIPE Recipes

Table 6.3.5.2. A18 with DVB or POSS8 cross-linker HIPE Recipes

Table 6.4.1. PEO Star Polymers as Stabilizers for Xylene-in-Water Emulsion

Table 6.4.2. PEO-PBA-Poly(DVB) Mikto-arm Star Polymers as Stabilizers for Water-in-Xylene Emulsions

Table 6.4.3. Xylene/Water Interfacial Tensions (mN/m) for 0.01 and 0.1 wt % Star Polymer Solutions at RT^a

Table 6.4.4. St/DVB HIPE Descriptions and PolyHIPE Densities

Table 7.3.1. HIPE and PolyHIPE Conditions with RS_{ATRP}

Table 7.3.2. Styrene and DVB HIPE and PolyHIPE Conditions with RS_{RP}

Table 7.3.3. EHA and EGDA HIPE and PolyHIPE Conditions with RS_{RP}

List of Schemes

Scheme 1.2.2.1. RDRP processes

Scheme 1.2.2.2. Macromolecular engineering by RDRP methods; Reproduced from reference 79

Scheme 1.2.3.3. Activator Regeneration ATRP

Scheme 1.2.3.4. RAFT polymerization of AN using CED as the transfer agent

Scheme 1.2.5. The Halogen Exchange Technique in ATRP

Scheme 1.3.1. PAN oxidative stabilization (left) and carbonization (right). Reproduced from reference 165

Scheme 1.3.2. Preparation of copolymer templated nanocarbons (CTNCs). Reproduced from reference 185

Scheme 2.2.1. ICAR ATRP

Scheme 2.2.2. Iodine-mediated Polymerization

Scheme 2.2.3. Metal-free ATRP

Scheme 2.5.3. Chain extension of PAN with MMA by photo-induced metal-free ATRP

Scheme 3.4. Synthesis of PAN-based stars

Scheme 4.4.3. Cross-linking of benzonitrile to form tetrazines via the Pinner method

Scheme 5.4.1. SS-BPMODA Chain Extension

Scheme 6.4. PEO star polymers as stabilizers for O/W or W/O emulsions

Scheme 7.4.1. Synthesis and functionalization of RS_{ATRP}

Scheme 7.4.3. Synthesis and Functionalization of RS_{RP}

Chapter 1

Nitrogen-doped Nanocarbons Templated from Polyacrylonitrile Block Copolymers and (Polymerized) High Internal Phase Emulsions

1.1 Introduction

Carbon-based materials play a large role in applications ranging from everyday products, such as carbon fiber frames for bicycles or filler in tires, to more advanced technological applications, like electrodes. The development of synthetic diamonds and highly oriented pyrolytic graphite in the 1960's sparked interest into engineering carbon.¹ This field has been particularly reenergized by the discovery of fullerenes in 1985² and carbon nanotubes in 1991.³ More recently, mesoporous nanostructured carbons have been heavily researched and found numerous applications, including hydrogen storage, gas sorption and separation, CO₂ capture, supercapacitors, electrodes for lithium ion batteries, and water purification.⁴⁻⁶ To improve and tune mesoporous nanostructured carbons for certain applications, multiple synthetic techniques have been developed. The main

synthetic strategies are chemical vapor deposition techniques, pyrolysis of organic precursors, including small molecules, biomass, and polymeric species, and templating methods to prepare nanostructured carbon from organic polymers. Physical/chemical vapor deposition, while allowing atomic scale precision in nanostructure control, are relatively expensive, have limited yield and require complex equipment. While pyrolysis of organic precursors is applicable to large scale production, they offer very limited control of carbon nanostructure. Templating methods present novel and promising routes toward the preparation of nanostructured carbon with controlled design and relatively low cost.

1.1.1 Chemical Vapor Deposition

As previously mentioned, physical/chemical vapor deposition allows for exceptional control over the nanostructure of the carbon material. Additionally it is time saving and does not require solvents.⁷ Chemical vapor deposition (CVD) is frequently used for the synthesis of carbon nanotubes.^{4,8} Hard templates, including zeolites and mesoporous silica, are commonly used in chemical vapor deposition to template carbons.^{6,9} Typical precursors include methane, propylene gas, acetonitrile, methanol, ethylene, and many others.^{6,7,9} Recent efforts have focused on hetero-atom doping with nitrogen or sulfur^{10,11} and in situ CVD processes, where many parameters can be tuned, allowing for more control over the carbon structure.¹² The major draw-back of CVD is the low carbon yield, making its commercial feasibility limited.

1.1.2 Carbon Obtained by the Direct Pyrolysis of Organic Precursors

Large-scale production of carbon materials utilizes precursors, like pitches (petroleum, coal, coal tar, coal chars, mesophase pitch), polymers (polyacrylonitrile, phenolic and furan resins, polyaniline, polypyrrole) and biomass.¹³ The resulting materials contain graphitic microstructures and disordered amorphous species. Some of the most widely known commodity carbon materials include carbon blacks, activated carbons and carbon fibers. Engineering carbons are also widely used in electrochemistry as electrode materials, due to good thermal and electrical conductivities, low density, good corrosion resistance, low thermal expansion, and relatively low cost.¹⁴ Carbon fibers, the most widely used engineered carbon, owe their excellent mechanical strength to high orientation of graphitic planes along the fiber axis, which is facilitated by high molecular orientation from, the most common precursor, polyacrylonitrile fibers or mesophase pitches.^{15,16} The numerous applications of carbon fibers and carbon fiber composites result from their excellent mechanical strength and current efforts focus on increasing carbon fiber's strength.^{15,16}

1.1.3 Nanostructured Carbon Obtained by Pyrolysis of Organic Precursors

Ordered mesoporous carbons, or nanostructured carbons, can have significant benefits over engineered carbons, as surface area, pore size, and pore size distribution are easily tuned. This makes them viable for a wider variety of applications, including gas capture and storage, electrodes, supercapacitors, and many more. There are two main ways to synthesize nanostructured carbon: hard and soft templating.

1.1.3.1 Hard Templating

Ordered mesoporous carbon were first successfully prepared by the Ryoo¹⁷ and Hyeon¹⁸ groups in 1999. Ryoo et al. synthesized ordered carbon molecular sieves from sucrose using mesoporous silica molecular sieves as a “hard” template.¹⁷ Hyeon et al. synthesized a mesoporous carbon from phenol and formaldehyde with regular three-dimensionally interconnected 2 nm pore arrays by templating carbon from MCM-48.¹⁸

Mesoporous silica is still the most common hard template. Recently, the literature has focused on synthesizing heteroatom doped carbons from mesoporous silica templates.^{19,20} Formation of hierarchical carbons from silica templates has also been explored. One interesting example used high internal phase emulsion templating to synthesize a macroporous silica template that was soaked in phenolic resin, carbonized, and removed to create a micro-meso-macroporous carbon.²¹ Macroporous carbons have also been synthesized by opal or colloidal crystal templates.^{22,23} The same silica spheres can be used to template carbon spheres.²⁴

1.1.3.2 Soft Templating

The majority of soft templated carbons are prepared with Pluronic surfactant. Pluronic F127, with structure of poly(ethylene oxide)₁₀₀-*b*-poly(propylene oxide)₆₅-*b*-poly(ethylene oxide)₁₀₀, is most commonly used.^{25,26} Highly ordered carbons with high surface areas, up to ~1000 m²/g, can be templated with Pluronic F127.²⁵ In aqueous solutions, Pluronic F127 can be used to assemble resorcinol-formaldehyde micelles that when dried and carbonized to form 3D-carbon frameworks with surface areas up to ~650 m²/g.²⁷

One of the first reports of nanostructured and highly ordered mesoporous carbons synthesized using block copolymers came from Dai and coworkers (Figure 1.1).²⁸ They developed a simple method involving the preorganization of resorcinol monomers in a well ordered polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) film. This was followed by the *in situ* polymerization of the resorcinol monomers with formaldehyde vapor to form ordered nanostructured resorcinol–formaldehyde resin (RFR). Upon carbonization, the nanostructured RFR was transformed into a highly ordered nanoporous carbon film when the PS-*b*-P4VP template was decomposed into gaseous species. After this report, this templating method for nanostructured carbons gained significant attention.

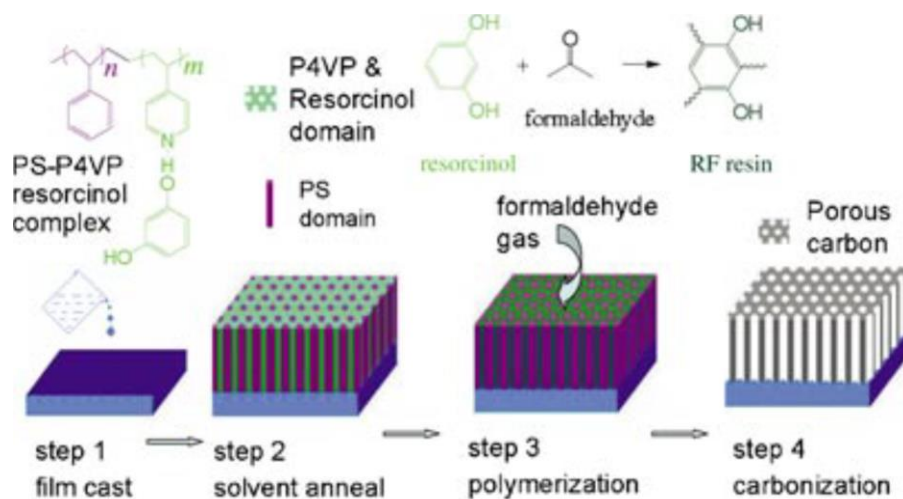


Figure 1.1. Preparation of well-defined carbon nanostructures. Step 1: film casting of PS-P4VP/resorcinol supramolecular assembly; Step 2: solvent annealing; Step 3: *in situ* polymerization of resorcinol and formaldehyde by exposing the film to formaldehyde gas; Step 4: pyrolysis of the polymeric film in N₂; Reproduced from reference 28

Zhang et al. extended this process to synthesize mesoporous carbons using poly(ethylene oxide)-*b*-poly(methyl methacrylate)-*b*-polystyrene (PEO-*b*-PMMA-*b*-PS) triblock copolymers to template RFR resins.²⁹ After carbonization and removal of the PEO-*b*-PMMA-*b*-PS the carbon material had a surface area up to 900 m²/g and tunable wall thickness, depending on the resol to template ratio. Werner, et al. used poly(isoprene)-*b*-polystyrene-*b*-poly(ethylene oxide) (PI-*b*-PS-*b*-PEO) triblock copolymers that phase separate into a gyroidal morphology to template phenol-formaldehyde resins.³⁰ After carbonization and removal of the triblock copolymer template, the carbons also exhibited a gyroidal morphology. Using a special solvent processing technique, gyroidal gradients can be formed from PI-*b*-PS-*b*-PEO and gradient carbons were templated.³¹ More recently, Liu, et al. made mesoporous carbon nanoparticles using PEO-*b*-PS as a template to form nanostructured RFR.³² Based on the size of the PEO-*b*-PS block copolymer, the size of the mesoporous carbon particles can be tuned. After carbonization and removal of PEO-*b*-PS the carbon nanoparticles can achieve surface areas up to 646 m²/g. Lin et al. formed “kippah vesicles” from PS-*b*-PEO and used them to template “bowl-shaped” polydopamine.³³ During pyrolysis the polydopamine was converted to carbon and the PS-*b*-PEO was removed to form “bowl-shaped” hollow carbons that showed superior performance as supercapacitors, due to their unique packing.³³

Research has also focused on directly using block copolymers to template and form carbon materials. Huang, et al. cross-linked the PS phase with UV irradiation in PEO-*b*-PS micelles and carbonized them to form porous carbon nanospheres.³⁴ This process was taken one step further using bottle-brush structured polymers with

polystyrene-*b*-poly(acrylic acid) (PS-*b*-PAA) brush arms.³⁴ The PS phase was cross-linked by UV irradiation and rod-like carbon nano-objects were formed. Cheng, et al. used a similar UV cross-linking strategy with PS-*b*-P4VP to form nanostructured carbon.³⁵

Since 2002, our groups at Carnegie Mellon University have focused on using polyacrylonitrile (PAN) to form nanostructured carbon materials. We have developed methods to use PAN-based block copolymers (BCPs) to template well-organized nanostructured carbon materials, where the PAN block is converted to carbon and the second block, typically poly(*n*-butyl acrylate) (PBA), is removed during carbonization to create pores. Simple carbonization, without any solvent processing, can be used with these BCPs, as they preorganize into well-defined nanostructures upon heating. Using PAN as the carbon precursor has an added benefit, in that it forms nitrogen-doped (N-doped) carbons, which are currently heavily investigated for numerous applications. Synthetic methods for PAN will be summarized, with a focus on reversible deactivation radical polymerization (RDRP) methods, nanostructured carbons (nanocarbons) formed from PAN and a brief overview of some recent applications of PAN-based BCP-templated nanostructured carbon will be discussed.

1.2 Controlled Synthesis of Polyacrylonitrile and Its Copolymers

PAN and its copolymers exhibit properties that allow them to be used in many applications, including acrylic fibers, nitrile rubbers, thermoplastics, carbon composites, etc. One of the most important applications of PAN is the preparation of carbon fibers.^{36,37} Acrylonitrile (AN) is a challenging monomer to polymerize, as it has a high

rate constant of propagation and termination (k_p and k_t). Additionally, PAN is only soluble in polar organic solvents, such as dimethyl sulfoxide (DMSO), N,N'-dimethylformamide (DMF) or N-methyl-2-pyrrolidone (NMP), and 50 wt% NaSCN or 70 wt% $ZnCl_2/ZnBr_2$ aqueous solutions.³⁸⁻⁴¹

1.2.1 Conventional Radical and Anionic Polymerization

Commercial PAN and its copolymers are usually synthesized by free radical polymerization (RP). RP of AN is carried out in solution, suspension or emulsion, in the presence of radical initiators, such as azobisisobutyronitrile (AIBN). RP is the simplest and lowest-cost route to synthesize bulk quantities of high molecular weight PAN.

Many attempts have been made to synthesize isotactic PAN to create acrylic and carbon fibers with higher tenacity. Highly isotactic PAN has been achieved via inclusion polymerization of AN/urea canal complex at extremely low temperatures (77-195 K) with electron beam, γ -ray or UV irradiation to initiate polymerization.⁴²⁻⁴⁶ Recently, completely isotactic PAN was synthesized by initiating the polymerization of AN at 77 K in highly organized urea canals and increasing the temperature to 163-183 K for the propagation step.⁴⁶ This allows for long radical lifetime and prevents bimolecular termination and chain-transfer reactions, resulting in the molecular weight increasing with conversion, narrow molecular weight distribution, 1.5, and completely isotactic PAN (mm >99%).

Additionally, RP has been used to synthesize more complex architectures containing PAN. Limited examples include block copolymers of PEO-*b*-PAN, graft

copolymers, and spherical nanoparticles.⁴⁷⁻⁵² However, RP does not provide control over the molecular weight (MW), molecular weight distribution (MWD) nor functionality.

In order to prepare PAN with controlled molecular structure and to synthesize more complicated architectures, such as block, graft,⁵³ star,⁵⁴ and brush copolymers,⁵⁵ anionic polymerization has been utilized. Living anionic polymerization of AN has been reported using organometallic initiators, including organocopper,^{56,57} di(organoimido) chromium(VI) complexes,⁵⁸ methoxo- β -diketone nickel catalysts,⁵⁹ and cobalt-based catalysts.⁶⁰ The use of dialkylmagnesium initiators in a water-based system has yielded PAN with high molecular weights and increased isotacticity.⁶¹ A generalized synthetic methodology for obtaining functional carbanion metal-free ammonium methanide initiators.⁶²

Jordan and coworkers utilized Cy_3PCuMe and $(\text{Bipy})_2\text{FeEt}_2$ to induce the polymerization of acrylonitrile that had exhibited characteristics of an anionic mechanism.⁶³ More intriguingly, this group synthesized PAN by insertion polymerization using cationic palladium alkyl complexes. This kind of insertion polymerization seems to indicate that AN can be polymerized through a cationic mechanism.⁶⁴ However, compared to free radical PAN, PAN synthesized by ionic polymerization usually possesses lower molecular weight and exhibits significant branching. Branching arises by inter- or intramolecular abstraction of $-\text{CH}_2\text{CH}(\text{CN})-$ methine protons from the polymer backbone by the propagating carbanion.^{63,65}

1.2.2 Reversible Deactivation Radical Polymerization (RDRP)

RDRP methods, also called controlled radical polymerization (CRP), are the most used tools in macromolecular engineering to obtain well-defined polymers in quantities suitable for large-scale production.⁶⁶⁻⁶⁸ All RDRP methods, atom transfer radical polymerization (ATRP),⁶⁹⁻⁷³ reversible addition fragmentation chain-transfer (RAFT) polymerization,⁷⁴⁻⁷⁶ and nitroxide-mediated polymerization (NMP),⁷⁷ involve a fast dynamic equilibrium between dormant species and active radical species to provide control. The polymerization conditions are selected so the equilibrium between dormant and active species is strongly shifted towards the dormant state, in order to establish a low concentration of propagating radicals, and reduce the occurrence of unavoidable termination reactions (Scheme 1.2.2.1). ATRP utilizes transition metal catalysts that reversibly activate and deactivate radicals on growing polymer chains via transfer of halogen atoms. RAFT polymerization utilizes dithioesters, trithiocarbamates or xanthates⁷⁴ and NMP uses nitroxides^{77,78} to reversibly (de)activate radicals on growing polymer chains.

Through the process of reversible (de)activation of radicals and long radical lifetimes, RDRP methods allow for the preparation of well-defined polymers with predetermined MW, narrow MWD, high functionality and complex architectures. As shown in Scheme 1.2.2.2, RDRP allows for the synthesis of various novel materials, including polymers with controlled topologies, like stars, combs, hyperbranched, and controlled networks, and compositions, such as blocks, grafts, and gradient copolymers.^{77,79,80} Macromolecular engineering allows for the precise control over the molecular structure at the nanoscale to achieve uniform polymer chains. These uniform

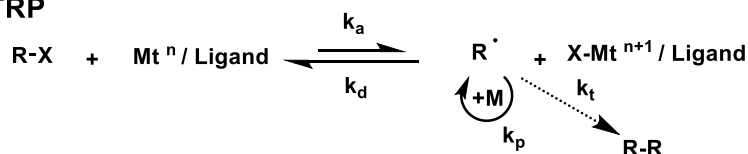
polymers can then be preassembled or can self-assemble into new materials with interesting macroscopic properties.

One major consideration when preparing PAN via RDRP methods is the accuracy of PAN characterization by gel permeation chromatography (GPC) in N,N-dimethylformamide (DMF) equipped with a refractive index (RI) detector.

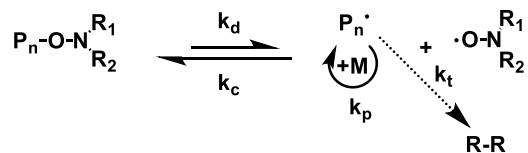
Characterization of PAN's MW by this method was reported to significantly overestimate the MW, as compared to linear polystyrene (PS) standards.^{81,82} Thus, to determine the actual molecular weight of PAN, ¹H NMR or GPC with a multi-angle light scattering (MALLS) detector should be employed.^{83,84} Reports have suggested that when PAN molecular weight determined by GPC with RI detection and linear PS or PMMA standards was compared to its molecular weight determined by GPC with MALLS detection or ¹H NMR, the value was 2.5 to 3 times higher.^{83,84}

Scheme 1.2.2.1. RDRP processes

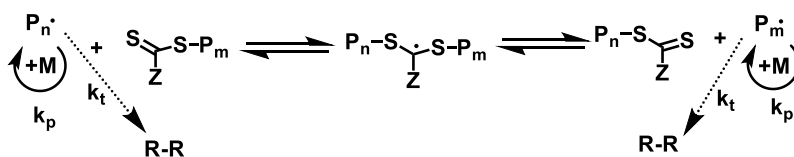
ATRP



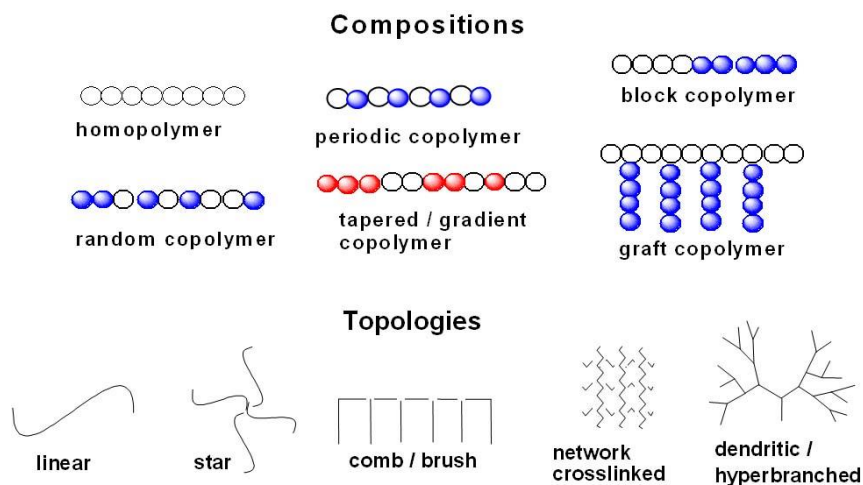
NMP



RAFT



Scheme 1.2.2.2. Macromolecular engineering by RDRP methods; Reproduced from reference 79



1.2.3 Homopolymerization of Acrylonitrile (AN)

Tables 1.2.3.1-1.2.3.4 and Figures 1.2.3.1-1.2.3.3 summarize homopolymerization of AN using all three RDRP methods, ATRP, RAFT polymerization, and NMP.

1.2.3.1 ATRP

1.2.3.1.1 Normal ATRP

We reported the synthesis of well-defined PAN by ATRP with predefined molecular weights and low dispersities (1.01).^{85,86} This was achieved by using CuX/2,2'-bipyridine (bpy; X = Br or Cl) as the catalyst, 2-bromopropionitrile (BPN) or 2-chloropropionitrile (CPN) as initiators, and ethylene carbonate as the solvent. Controlled polymerization of AN based on CuBr/bpy, CuCl/bpy, Cu₂O/bpy, and CuO/bpy, in the presence of alkyl, alkylsulfonyl, and arenesulfonyl halides was reported.⁸⁷ CuBr/tetramethylguanidino-tris(2-aminoethyl)amine (TMG₃-TREN) was used for a

catalyst in ethylene carbonate to successfully control the ATRP of AN.⁸⁸ The final PAN had PDI 1.25 and MW of 8000.⁸⁸ In addition to a “traditional” solvent ethylene carbonate, 2-cyanopyridine was used to synthesize well-defined PAN by ATRP.⁸⁹ The unique feature of this solvent is that it does not contain easily extractable hydrogens, but at the same time has a high polarity to dissolve PAN.⁸⁹

Several reverse ATRP (RATRP) routes for controlled radical polymerization of AN have been described.⁹⁰⁻⁹² A hexa-substituted ethane thermal iniferter, diethyl 2,3-dicyano-2,3-diphenylsuccinate (DCDPS), was used as the initiator when CuCl_2/bpy , $\text{FeCl}_3/\text{triphenyl phosphine (PPh}_3\text{)}$, or $\text{FeCl}_3/\text{iminodiacetic (IMA) acid}$ was the catalyst.^{90,92,93} FeCl_3/IMA or $\text{FeCl}_3/\text{isophthalic acid (IA)}$ were used with azobisisobutyronitrile (AIBN) as the radical initiator in RATRP.⁹¹ All of the well-defined PAN samples were then used as a macroinitiator for chain-extension with AN, proving that high chain-end functionality was retained. These reports claimed that the molecular weight obtained from GPC ($M_{n,\text{GPC}}$) was close to those from NMR ($M_{n,\text{NMR}}$), which is in doubt, since all other reports indicated that GPC analysis resulted in significantly higher molecular weight than the actual molecular weight characterized by NMR, due to the poor solubility of calibration standard, PS, in DMF.^{81,82}

Table 1.2.3.1. normal ATRP of AN

Source	Catalyst	Ligand	Initiator	Solvent	Temp. (°C)	Conv	M _n	PDI
Matyjaszewski et al. ^{85,86} Tang et al. ⁹⁴	CuBr	bpy	BPN	EC	44-65	~90 %	<15,000 (NMR)	<1.1 (MALDI)
Barboiu et al. ⁸⁷	CuCl	bpy	CPN	EC	100	60%	5000 (GPC)	1.15
	CuCl	bpy	TMSC	EC	100	68%	5400 (GPC)	1.28
	Cu ₂ O	bpy	BPN	EC	100	73%	8400	1.15
	Cu ₂ O	bpy	MBSC	EC	100	71%	6700	1.37
	CuO	bpy	MSC	EC	100	45%	6900	1.17
Brar et al. ⁸⁸	CuBr	TMG ₃ -TREN	BPN	EC	45	70%	8000 (NMR)	1.25
Lazzari et al. ⁸⁹	CuBr	bpy	BPN	CP	55	50%	3000 (NMR)	<1.1
Hou et al. ⁹⁰⁻⁹³	CuCl ₂	bpy	DCDPS	Bulk	70	43%	4800 (GPC)	1.17
	FeCl ₃	IPA	AIBN	DMF	60	54%	6200 (GPC)	1.18
	FeCl ₃	IMA	DCDPS	DMF	70	38-74%	5500-12300 (GPC)	≤1.25
	FeCl ₃	PPh ₃	DCDPS	Bulk	70	50%	7000	1.16
	FeCl ₃	IMA	AIBN	DMF	60	38%	5200	1.16

MALDI= Matrix assisted desorption/ionization time of flight mass spectroscopy, BPN = 2-

bromopropionitrile, CPN = 2-chloropropionitrile, TMSC = trichloromethanesulfonyl chloride, MBSC = 4-

methoxybenzenesulfonyl chloride, MSC = methanesulfonyl chloride, TMG₃-TREN =

tetramethylguanidino-tris(2-aminoethyl)amine, IPA = isophthalic acid, IMA = iminodiacetic acid, PPh₃ =

triphenylphosphine, bpy = bipyridine, AIBN = azobisisobutyronitrile, DCDPS = diethyl 2,3-dicyano-2,3-

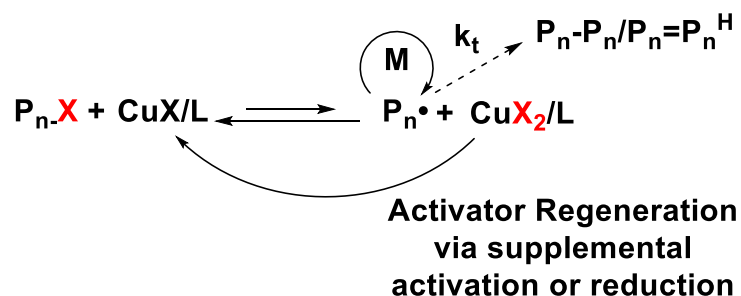
diphenylsuccinate, EC = ethylene carbonate, DMF = dimethylformamide, CP = 2-cyanopyridine

1.2.3.1.2 ATRP Activator Regeneration Methods for PAN

With the advent of activator regeneration methods for ATRP, several researchers have investigated these methods for PAN synthesis. These methods reduce Cu(II) to Cu(I), after termination events, using reducing agents, like tin (II) 2-ethylhexanoate (Sn(EH)₂ or ascorbic acid, in activators regenerated by electron transfer (ARGET) ATRP,

conventional radical initiators, like AIBN, in initiators for continuous activator regeneration (ICAR) ATRP, and zero-valent metals in supplemental activators and reducing agents (SARA) ATRP (Scheme 1.2.3.3).⁷² Activator regeneration ATRP methods greatly decrease the amount of post-polymerization purification needed to obtain metal-free PAN, which is necessary for many applications.

Scheme 1.2.3.3. Activator Regeneration ATRP



We first reported the synthesis of well-defined PAN by ARGET ATRP.⁸³ PAN with molecular weights as high as 161,000 ($M_{n,GPC}$) were obtained with reasonably low M_w/M_n values (1.18-1.47). This was achieved using BPN as an initiator, EC or DMSO as a solvent, tin(II) 2-ethylhexanoate ($Sn(EH)_2$) or glucose as a reducing agent, and 25-75 ppm of $CuCl_2$ /tris[(2-pyridyl)methyl]amine (TPMA) catalyst. Chen et al. conducted ARGET ATRP in ionic liquids and used 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA) as a ligand, with $CuBr_2$ to form the ATRP catalyst, and a reducing agent.⁹⁵ In 1-butyl-3-methylimidazolium tetrafluoroborate ($[C_4mim][BF_4]$) higher conversion could be reached, $M_{n,GPC}$ up to 43,700, and narrow molecular weight distributions (MWDs; $M_w/M_n=1.25$) could be achieved than when DMF was used for the solvent. Despite good results, it must be noted that the authors use a higher ATRP catalyst concentration (>1000

ppm) than is typically employed (≤ 100 ppm) in ARGET ATRP. Along the same lines, Yu et al. used tris[2-dimethylamino)-ethyl] amine (Me_6TREN) as a ligand to form the ATRP catalyst, with CuBr_2 , and as a reducing agent.⁹⁶ DMSO was shown to be the best solvent, with a reaction temperature of 25 °C, as $M_{n,\text{GPC}}$ ranging from 4,300-10,500 and M_w/M_n values ranging from 1.13-1.32.

AN was polymerized by ICAR ATRP using CuBr_2/bpy as a catalyst, ethyl 2-bromoisobutyrate (EBiB) as an initiator, AIBN as the free radical initiator source, and DMSO as the solvent.⁹⁷ At 70 °C the $M_{n,\text{GPC}}$ reached 4100 with a narrow MWD ($M_w/M_n=1.07$) with 400 ppm of catalyst in the system. At high radical initiator concentrations with 100 ppm of CuBr_2/bpy catalyst, 80% conversion was reached in 3 hours, but with a large discrepancy between theoretical and experimental MWs, due to the initiation of new polymer chains by AIBN.⁹⁸

SARA ATRP, sometimes called single electron transfer living radical polymerization (SET-LRP), has also been explored for PAN synthesis under low ppm catalyst conditions. $\text{Zn}(0)$ powder was used as a supplemental activator and reducing agent, EBiB as an initiator, 5 to 50 ppm CuBr_2/bpy as a catalyst, ethylene carbonate (EC) as a solvent, and conducted the reaction at 25 °C. Conversion reached above 70%, when 50 ppm Cu-catalyst was used. The $M_{n,\text{GPC}}$ reached as high as 28,200 with dispersiteis remaining low <1.2 .⁹⁹ SARA ATRP was conducted by adding $\text{Cu}(0)$ powder to a solution of AN, DMSO, ligand bpy^{100} or $\text{Me}_6\text{TREN}^{101}$ (ligand), and EBiB¹⁰⁰ or BPN¹⁰¹ (initiator). The reaction in both cases, unsurprisingly, proceeds slowly (12 hours to reach $>90\%$ conversion¹⁰⁰ or 40 hours to reach 70% conversion¹⁰¹), as activation of alkyl halides by $\text{Cu}(0)$ is much slower than by $\text{Cu}(\text{I})$ -catalyst complexes.¹⁰²

As previously discussed, the use of ATRP activator regeneration methods allow for the use of low Cu-catalyst loadings (<100 ppm) and simplify the purification of PAN. Recently, we have focused on gaining a better understanding of AN polymerization by ICAR ATRP and focused on determining the best initiator, catalyst, amount of AIBN, and catalyst loading to obtain well-defined PAN. Polymerization of AN by metal free ATRP using a photocatalyst, 10-phenylphenothiazine (PTZ, Figure 1.2.3.1),¹⁰³ was also explored, so removal of the Cu-catalyst could be avoided. In both cases well-defined PAN was synthesized and could be chain-extended to form a block copolymer. These results will be discussed in Chapter 2.

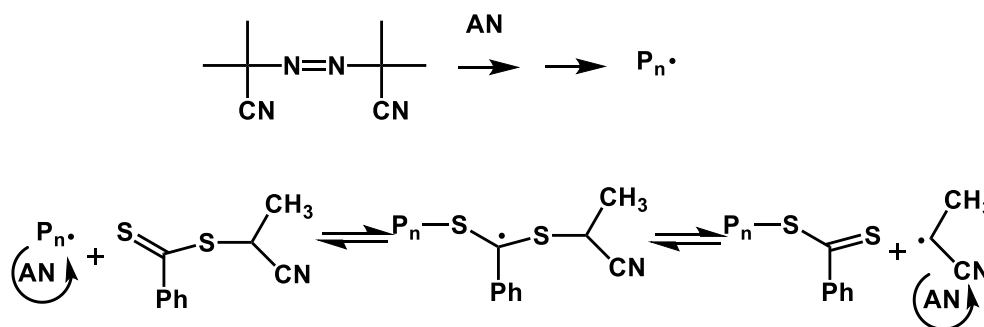
Table 1.2.3.2. Conditions for activator regeneration ATRP of AN

Source	Method	Catalyst (Amount)	Reducing Agent	R-X	Solvent	T (°C)	Conv (%)	M _n	PDI
Dong et al. ⁸³	ARGET	CuCl ₂ /TPMA (50 ppm)	glucose	BPN	DMSO	40	69	161,300 (GPC)	1.18
Chen et al. ⁹⁵	ARGET	CuBr ₂ /PMDETA (1250 ppm)	PMDETA	EBiB	[C ₄ mim] [BF ₄]	65	64	43,650 (GPC)	1.25
Yu et al. ⁹⁶	ARGET	CuBr ₂ /Me ₆ TREN (250 ppm)	Me ₆ TREN	EBiB	DMSO	25	22- 79	4,300- 10,500 (GPC)	1.13- 1.32
Liu et al. ^{97,98}	ICAR	CuBr ₂ /bpy (50 or 400 ppm)	AIBN	EBiB	DMSO	60- 70	40- 86	4,100 - 11,700 (GPC)	1.07- 1.38
Yu et al. ⁹⁹	SARA	CuBr ₂ /bpy (50 ppm)	Zn (0)	EBPA	DMSO	RT	72	4,100 (GPC)	1.53
Liu et al. ¹⁰¹	SARA	CuBr ₂ /Me ₆ TREN (200 ppm)	Cu (0)	BPN	DMSO	25	43	44,100	1.25

R-X = alkyl halide initiator, ARGET = activators regenerated by electron transfer, ICAR = initiators for continuous activator regeneration, SARA= supplemental activators and reducing agents, TPMA = tris[(2-pyridyl)methyl]amine, PMDETA = 1,1,4,7,7-pentamethyldiethylenetriamine, Me₆TREN = tris[2-dimethylamino)-ethyl] amine, bpy = 2,2'-bipyridine, PTZ = 10-phenylphenothiazine, AIBN= azobisisobutyronitrile, BPN= 2-bromopropionitrile, EBiB = 2-bromoisobutyrate, EBPA = ethyl α-bromophenylacetate, DMSO = dimethyl sulfoxide, [C₄mim][BF₄] = 1-butyl-3-methylimidazolium tetrafluoroborate, EC = ethylene carbonate

When using CED for RAFT polymerization, the expelled $\text{CH}_3\text{-CH}(\text{CN})\bullet$ radicals turned out to effectively initiate the polymerization of AN, as they resemble propagating radicals (Scheme 1.2.3.4). The RAFT agent 2-cyanoprop-2-yl dithiobenzoate (CPDB) was demonstrated to be an efficient chain transfer agent (CTA) for the preparation of PAN with controlled molecular weight (below 6000) and narrow MWD ($\text{PDI} \leq 1.10$).¹⁰⁵ It was found that the polymerization rate was directly proportional to the concentration of AIBN and exhibited negative exponential dependence on the concentration of CPDB. AN was polymerized using dibenzyl trithiocarbonate (DBTC) as the chain-transfer agent.¹⁰⁶ They were able to obtain PAN with $M_{n,\text{NMR}}$ up to 8400 and low dispersity (<1.2). The key to their success was ascribed to the improvement of the interchange frequency between dormant and active species through the reduction of the activation energy for the fragmentation of the intermediate. CPDB was used as a RAFT agent for AN polymerization and showed that EC was the best solvent, giving high molecular weight PAN ($M_n > 20,000$) and dispersity as low as 1.05.¹⁰⁷

Scheme 1.2.3.4. RAFT polymerization of AN using CED as the transfer agent



New RAFT agents, outside of the typical, have been explored for the controlled polymerization of AN. Disulfide compounds were explored as RAFT agents for AN

polymerization.¹⁰⁸ Bis(thiobenzoyl) disulfide (BTBDS) and bis(thiophenylacetoyl) disulfide (BTPADS) were both used to synthesize PAN with $M_{n, GPC}$ up to 230,000, but with relatively high dispersities (≥ 1.5). Despite broad MWD, this proved a good method to copolymerize AN with itaconic acid (IAN) and obtain high molecular weight (HMW) polymer.

Recently, HMW PAN was synthesized by RAFT polymerization. 1,4-[2-(carbazole-9-carbodithioate)-2-methyl propionic acid] phenyl ester (BCCDP) was used as a CTA for AN polymerization.¹⁰⁹ Using DMSO as a solvent, the authors were able to synthesize PAN with viscosity molecular weight (M_{η}) up to 405,100 and dispersities ranging from 1.14 to 1.32. In a separate study, four other CTAs were investigated and it was determined that cyanoethyl dodecyl trithiocarbonate (CEDT) or 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT) worked well to target HMW PAN.¹¹⁰ Additionally, they determined that lowering the amount of radical initiator, relative to the CTA, and decreasing the temperature to 30 °C allowed them to reach higher conversions and molecular weight PAN.

Table 1.2.3.3. RAFT polymerization of AN

Source	CTA	Initiator	Solvent	T (°C)	Conv (%)	M_n	PDI
Tang et al. ¹⁰⁴	CED	AIBN	EC	60	40	4000 (NMR)	1.05
An et al. ¹⁰⁵	CPDB	AIBN	DMF	65	50	5600 (NMR)	1.06
Liu et al. ¹⁰⁷	CPDB	AIBN	EC	90	50	26,000 (viscosity)	1.05
Liu et al. ¹⁰⁶	DBTC	AIBN	DMF	60	58	5700 (NMR)	1.18
Liu et al. ¹⁰⁸	BTBDS	AIBN	EC	80	50	39,800 (GPC)	1.50
	BTPADS	AIBN	EC	80	67	38,000 (GPC)	1.53

Niu et al. ¹⁰⁹	BCCDP	AIBN	DMSO	75	60	405,100 (viscosity)	1.32
Moskowitz et al.	CEDT	V-70	EC	30	62	70,300	1.09
	CPDT	V-70	EC	30	63	84,800	1.24

CED = 2-cyanoethyl dithiobenzoate, CPDB = 2-cyanoprop-2-yl dithiobenzoate, DBTC = dibenzyl

trithiocarbonate, BTBDS = bis(thiobenzoyl) disulfide, BTPADS = bis(thiophenylacetoyl) disulfide, BCCDP = 1,4-[2-(carbazole-9-carbodithioate)-2-methyl propionic acid] phenyl ester, CEDT= cyanoethyl dodecyl trithiocarbonate, CPDT= 2-cyano-2-propyl dodecyl trithiocarbonate, V-70= 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile)

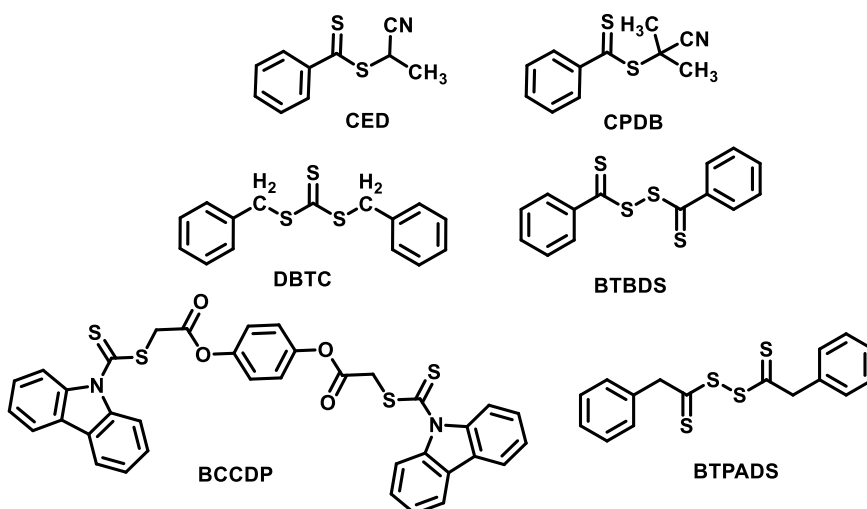


Figure 1.2.3.2. chain transfer agents used in RAFT polymerization of AN

1.2.3.3 NMP

Hawker and coworkers reported controlled NMP of AN with 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane (TPPA).⁷⁸ The molecular weight could be controlled from 4000 to 50000 with dispersity below 1.2. Our group used n-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide (DEPN or SG1) to form PAN with controlled molecular weight and polydispersity.⁹⁴ Since 2003, there have been no other

reports on the synthesis of PAN by NMP. Meanwhile, there has been however some theoretical studies of the geometries and energetics of transition states for radical deactivation reactions. This includes competitive combination and disproportionation reactions, where quantum mechanical calculations were used to model 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO)-mediated free-radical polymerization of AN.¹¹¹

Table 1.2.3.4. NMP of AN

Group	Nitroxide	Initiator	Solvent	Temp., °C	Conv.	M _n	PDI
Benoit et al. 78	TPPA	TPPA	DMF	120	/	55000 (GPC)	1.13
Tang et al. 94	DEPN or SG1	AIBN	EC	120	90%	26,000 (GPC)	1.20

TPPA= 2,2,5-trimethyl-3-(1-phenylethoxy)-4-phenyl-3-azahexane, DEPN/SG-1= n-tert-butyl-1-diethylphosphono-2,2-dimethylpropyl nitroxide

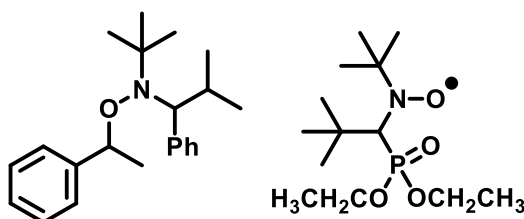


Figure 1.2.3.3. nitroxides used for NMP of AN

1.2.4 Random Copolymerization of AN

With regard to RDRP random copolymerization of acrylonitrile, there are numerous reports describing the use of ATRP, NMP, and RAFT polymerization that focused on the copolymerization of acrylonitrile with styrene to produce commercially important PSAN.^{74,112-118} Copolymerization of acrylonitrile with other monomers, such as methyl methacrylate,³⁷ ethyl methacrylate,¹¹⁹ maleic anhydride,¹²⁰ itaconic acid,¹²¹

methyl acrylate, *n*-butyl acrylate, *t*-butyl acrylate,¹²² acrylamide,¹²³ and N-isopropylacrylamide is a well-studied topic. This is due to an emphasis on improving PAN-derived carbon fibers by controlling their MW, MWD, and comonomer distribution. Interestingly, RAFT polymerization has recently been used to synthesize acrylonitrile-butadiene rubber (NBR) to obtain polymers with controlled molecular weight and low polydispersities (≥ 1.2).¹²⁴⁻¹²⁶

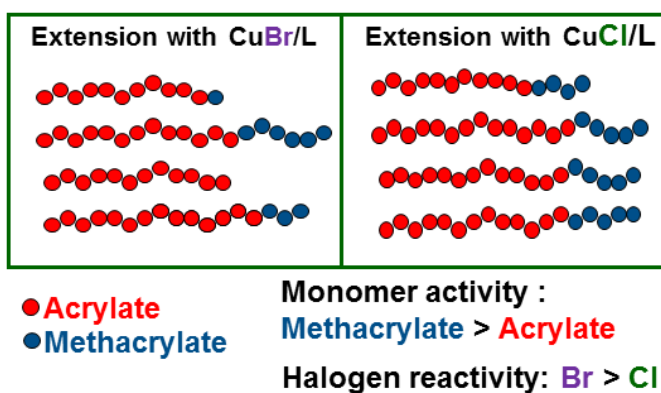
1.2.5 Block Copolymerization of AN

RDRP methods are compatible with a wide range of monomers including acrylates, methacrylates, acrylamides, and styrene and allows for simple synthesis of block copolymers (BCPs).^{79,127,128} ATRP, RAFT polymerization and NMP have been employed to prepare various types of BCPs, some of which have been composed of the same class of monomers such as two different methacrylates, or by using different classes of monomers, such as an acrylate and a methacrylate. Synthesis of well-defined BCPs by RDRP requires high blocking efficiency, which depends on the block sequence. Chain extension from a specific “A” block to the desired “B” block can be possible while the extension from “B” block to the same “A” block is not possible.¹²⁹ For example, in ATRP a methacrylate macroinitiator can be chain-extended with acrylate monomers with good control over the synthesis of the second block. However, in the reverse sequence of block formation, an acrylate based macroinitiator chain extended with methacrylate monomer usually exhibits poor control.¹³⁰ In order to attain high blocking efficiency, the rate of cross-propagation should be comparable to the rate of the subsequent propagation reaction.¹³¹ In other words, the rate of the methacrylate addition to the acrylate must be

the same as the addition of the methacrylate to itself. This is defined by a product of rate constant of radical addition and a relevant ATRP equilibrium constant.

In ATRP, this can be achieved by introducing a halogen exchange technique (Scheme 1.2.5).¹³¹⁻¹³³ Starting from Br-terminated polymer chains and switching to Cl-terminated chains in the presence of CuCl/ligand via atom transfer alters the equilibrium constants, which are much higher for Br than for Cl derivatives. The equilibrium constants follow the strength of C-X bonds. The rate of cross-propagation for a bromine-terminated acrylate is comparable to the propagation rate for chlorine-terminated methacrylate, because the C-Br bond has lower bond dissociation energy than the C-Cl bond.¹³² Violation of these rules leads to lower chain-extension efficiency. In the NMP and RAFT processes it is difficult to alter these equilibrium constants because similar techniques cannot be introduced.^{127,128}

Scheme 1.2.5. The halogen exchange technique in ATRP



When synthesizing well-defined BCPs with PAN it is crucial to note additional issues besides blocking sequence. PAN has low solubility in many solvents and is generally only well solubilized in DMSO, DMF, or other highly polar solvents.³⁹ Due to

PAN's limited solubility well-defined BCP may not be synthesized due to precipitation of the PAN or the second block if it is not soluble in a highly polar solvent.

All three RDRP methods were employed to prepare PAN-based BCPs by carefully selecting blocking order and solvent that solubilizes both blocks, typically DMF. The synthesis of PAN containing polymers was further extended to different topologies such as triblock, three-armed stars, molecular brushes, shell cross-linked micelles and organic/inorganic hybrids, as discussed in Section 1.2.6. These PAN-based BCPs and polymer architectures can be used as precursors to prepare nanostructured carbon with a variety of morphologies, as described in the Section 1.3.

1.2.5.1 ATRP

The earliest report on the synthesis of PAN BCPs by ATRP dates back to 2001.¹³⁴ The authors of the study claimed successful chain extension of a poly(methyl methacrylate) (PMMA) macroinitiator with PAN, but neither kinetic plots nor molecular weight evolution and molecular weight distribution were presented in this report. The only evidence of PAN formation came from an FTIR spectrum, which cannot confirm if a BCP was synthesized.

Our studies indicated that PAN with high chain-end functionality can be easily prepared and chain-extended with *n*-BA in homogeneous solutions of DMF to form a BCP.⁹⁴ In the preparation of block copolymers starting from a PBA macroinitiator, the use of the halogen exchange technique gave better control over the polymerization of AN than without halogen exchange.⁹⁴ It should be noted that although the chain-extension from PAN to *n*-BA has higher efficiency than the opposite direction, the chain-extension

from PBA to AN is more practical, because the low solubility of PAN necessitates a large excess of solvent (i.e. DMF or DMSO), so PAN does not precipitate during the chain extension. Poly(*t*-butyl acrylate)-*b*-poly(acrylonitrile) (PtBA-*b*-PAN) was synthesized in a similar way, except a CuI/bpy catalyst was used for extension of PtBA-Br with AN, instead of CuCl/bpy.¹³⁵

Other block copolymers containing PAN have been synthesized by ATRP. PAN-*b*-PS BCPs with relatively narrow MWD (PDI=1.32) were synthesized.⁸⁹ Poly(2-methoxyethyl acrylate)-*b*-polyacrylonitrile (PMEA-*b*-PAN) was synthesized using CuBr/PMDETA as the catalyst to polymerize MEA in bulk at 60 °C and extending it with AN using halogen exchange ATRP (CuCl/bpy catalyst) in ethylene carbonate at 70 °C. Well-defined PMEA-*b*-PAN with $M_{n,NMR}$ up to 29,500 and M_w/M_n values ranging from 1.19 to 1.29 was synthesized.¹³⁶ Well-defined PAN-*b*-PMMA block copolymers have been synthesized by multiple groups by normal ATRP with low polydispersities.¹³⁷⁻¹³⁹

1.2.5.2 RAFT Polymerization

We used CED to efficiently prepare PAN that can be chain extended with *n*-BA to form well-defined PAN-*b*-PBA BCPs with low dispersity (1.17).¹⁰⁴ It was demonstrated that dibenzyl trithiocarbonate as the chain transfer agent can also yield well-defined PAN-*b*-PBA with low dispersity (PDI=1.16).¹⁰⁶ Polyacrylonitrile-*b*-poly(acrylic acid) (PAN-*b*-PAA) BCPs with different ratios of the two blocks were synthesized using 2-dodecylsulfanylthiocarbonylsulfanyl-2-methyl propionic acid (DMP) as the RAFT agent.¹⁴⁰ Recently RAFT polymerization was used to synthesize poly(acrylonitrile-*b*-cysteamidacrylate) (PAN-*b*-PCAA) using DMP as a chain transfer agent.¹⁴¹

1.2.5.3 NMP

In NMP, the presence of excess SG1 played an important role in controlling the blocking efficiency for PAN-*b*-PBA BCP.⁹⁴ The excess SG1 increased the initial rate of deactivation and finally resulted in a decrease in the polydispersities (1.18) of the BCP. The cross-propagation from PAN to *n*-BA was less efficient than that from PBA to AN.⁹⁴ No other PAN containing BCPs have been synthesized by NMP.

1.2.5.4 Non-RDRP Method to Polymerize the First Block

ATRP and RAFT polymerization allow for easy synthesis of BCPs where the first block was synthesized by other means, such as anionic or condensation polymerization, via functionalization of the first block with an ATRP initiator or a RAFT agent. Low molecular weight diblock copolymers of PS-*b*-PAN were prepared using sequential living and RDRP approaches. The PS block was anionically synthesized, terminated with an ATRP initiator, and chain extended with AN using a CuBr/PMDETA catalyst system and 2-cyanopyridine as the solvent. The PS-*b*-PAN had low polydispersity, <1.35.

PEO-*b*-PAN,¹⁴² poly(ϵ -caprolactone)-*b*-polyacrylonitrile (PCL-*b*-PAN),^{143,144} poly(L-lactic acid)-*b*-polyacrylonitrile (PLLA-*b*-PAN),¹⁴⁴ and pentablock copolymers PAN-*b*-PEO-*b*-PPO-*b*-PEO-*b*-PAN¹⁴⁵ were all prepared by functionalization of the first, anionically synthesized block(s) with an ATRP initiator and subsequent chain extension with AN. A macro-RAFT agent was utilized to make PEO-*b*-PAN nanoparticles via dispersion RAFT polymerization.¹⁴⁶ Additionally, poly(dimethyl siloxane) (PDMS) functionalized on both ends to form a macro-RAFT agent was extended with AN to make PAN-*b*-PDMS-*b*-PAN.¹⁴⁷

Poly(aryl ether)-*b*-polyacrylonitrile was synthesized via condensation of 5-cyano-4-fluoro-2-propylphenolate with initiation from (4-fluorophenyl)(4-(1-hydroxyethyl)phenyl)methanone. The poly(aryl ether) was functionalized with an alkyl-bromide, and chain extended with AN via ATRP.¹⁴⁸ The authors discovered that the PAN-macroinitiators degraded when extended to aromatic poly(aryl ethers), due to the high temperatures required for the polycondensation reactions.

1.2.6 Other Architectures Containing PAN

RDRP methods have allowed for the synthesis of complex polymer architectures. Stars, bottle and particle brushes, comb, graft, and branched PAN have all been synthesized.

1.2.6.1 Stars

Many star architectures containing PAN were reported in the literature. Three arm stars were synthesized using 1,1,1-tris(4-chlorosulfonylphenyl)-ethane¹³ (3PSC) as a 3-arm initiator and polymerizing AN by ATRP, in the presence of Cu₂O/bpy catalyst.⁸⁷ However, the length of each arm was very short with an average of five monomer units per arm.

Well-defined PAN star polymers with 3, 4 and 6 arms have been successfully synthesized, along with star-branched polymers with a hyperbranched poly(ester amide) as a core.¹⁴⁹ The catalyst system and solvent were CuBr/bpy and ethylene carbonate, respectively, and solution viscometry was used to determine the molecular weight of the stars.

Three-arm BCP stars of PBA-*b*-PAN were synthesized. This was accomplished using a tri-functional ATRP initiator to polymerize *n*-BA by normal ATRP and then using halogen exchange with normal ATRP to chain extend with AN (Figure 1.2.6.1).¹⁵⁰ The stars had a narrow MWD ($M_w/M_n=1.25$) and the PAN content ranged from 8 to 31 wt%. These stars were utilized as thermoplastic elastomers.

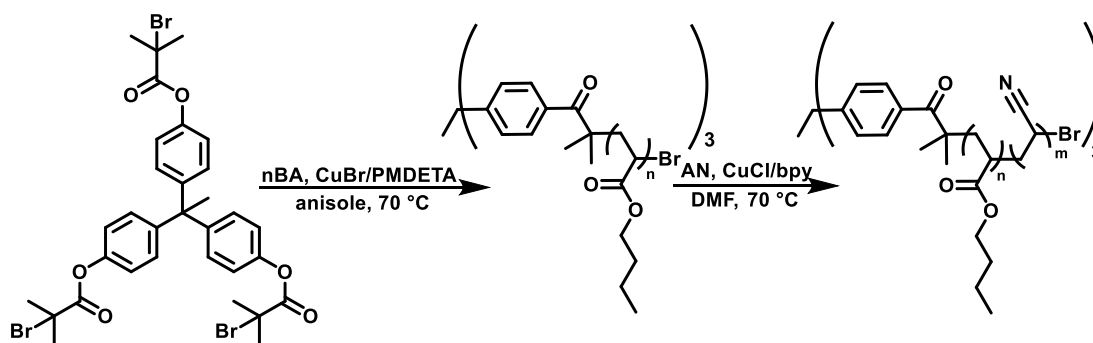


Figure 1.2.6.1: synthesis of PBA-*b*-PAN 3-armed stars; Reproduced from reference 150

ATRP of AN from a POSS core that contained eight ATRP initiating sights was reported.¹⁵¹ Each star arm had a low degree of polymerization (<10) and low dispersity (<1.07-1.38). The POSS-*g*-PAN stars were introduced into Nafion® and used as methanol fuel cell membranes.

1.2.6.2 Bottlebrushes and Particle Brushes

PAN based bottlebrushes were described in the literature.¹⁵² Trimethylsilyl protected hydroxyethyl acrylate (HEMA-TMS) was polymerized by ATRP and functionalized with ATRP initiators to make a backbone. *n*-BA was then polymerized by ATRP to create a PBA brush. The PBA brush was chain extended with AN by halogen

exchange normal ATRP and further chain extended with *t*BA and the PtBA was hydrolyzed into PAA. The brushes has low dispersities (<1.3) and were pyrolyzed to create nanostructured carbons.

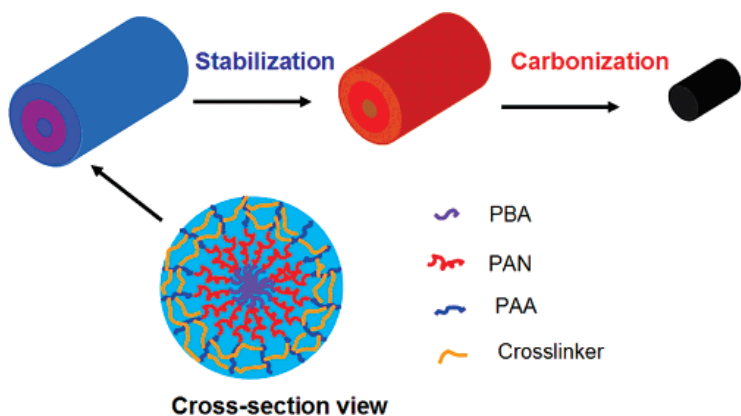


Figure 1.2.6.2: PBA-*b*-PAN-*b*-PAA cross-linked brushes for nanostructured carbon;

Reproduced from reference 152

Silica nanoparticles (20 ± 4 nm) were functionalized with 2-bromoisobutyrate (BiB) groups and AN was grafted from the silica particles (Si-*g*-PAN).¹⁵³ The silica particles were etched with HF and the PAN chains had DP of 280 and M_w/M_n of 1.06 or DP of 220 and M_w/M_n of 1.31.¹⁵³ The Si-*g*-PAN was used to make nanostructured carbon films.

Particle brushes were also synthesized by grafting PAN from Fe_3O_4 particles by surface-initiated RAFT polymerization.¹⁵⁴ The Fe_3O_4 -*g*-PAN particles showed improved solubility. Magnetic carbon fibers were prepared by coaxially spinning the magnetic nanoparticle brushes with PAN homopolymer and then carbonizing the fibers.

Cross-linked PMMA (x-PMMA), synthesized by microemulsion ATRP, was used to form particle brushes.¹⁵⁵ After microemulsion polymerization by ATRP the x-PMMA

has active Br-chain ends accessible on the surface that were chain extended with AN. Dynamic light scattering analysis confirmed successful PAN grafting through a size increase from 24 nm to 50 nm. The x-PMMA-*g*-PAN particles brushes were pyrolyzed to form nanostructured carbon.

1.2.6.3 Comb and Graft Copolymers

In addition to brushes and stars, comb, graft, or branched polymers containing PAN have been reported. RAFT polymerization and ATRP were combined to synthesize three types of copolymers with PAN and poly(*N*-isopropylacrylamide) (PNIPAM): PAN-*b*-PNIPAM, PAN-*b*-(PHEMA-*g*-PNIPAM), and PAN-*co*-(PHEMA-*g*-PNIPAM) (Figure 1.2.6.3).¹⁵⁶ The thermoresponsive nature and the surface wettability of the PAN/PNIPAM copolymers were investigated in thin film. PAN was grafted from many supports, usually containing vinyl benzyl chloride (VBC) and by ATRP.¹⁵⁷⁻¹⁶⁰

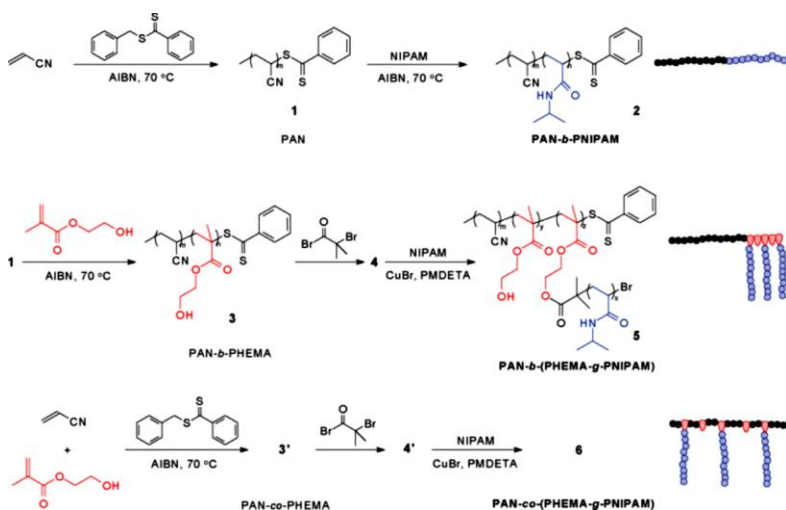


Figure 1.2.6.3: Synthesis of PAN-*b*-PNIPAM, PAN-*b*-(PHEMA-*g*-PNIPAM), and PAN-*co*-(PHEMA-*g*-PNIPAM); Reproduced from reference 1

1.2.6.4 Branched

PAN branched copolymers can easily be synthesized in a controlled manner by RAFT polymerization, using an asymmetric divinyl cross-linker, like allyl methacrylate.¹⁶¹ The degree of branching, molecular weight, and dispersity indices were investigated by changing the temperature, cross-linker to monomer molar ratio, and chain transfer agent to initiator molar ratio. A branched architecture was confirmed by ¹H NMR and GPC analyses and the intrinsic viscosities were found to be much lower than that of linear polymers.

1.3. Nanostructured Carbons from PAN and Its Copolymers: PAN cyclization and carbonization

PAN has been used for many years as a carbon precursor, especially for carbon fibers.^{15,36,162} However, it recently has gained attention as a carbon precursor for N-doped nanostructured carbons (nanocarbons).¹⁶³ PAN is a unique polymer precursor for carbon materials, as it can undergo cyclization of its nitrile groups during oxidative stabilization at 200-300 °C (Scheme 1.3.1).^{164,165} It can then be further carbonized, without losing its entire nitrogen content, at 400 to 800 °C under an inert atmosphere (Scheme 1.3.1).¹⁶⁵ The PAN cyclization allows for a high degree of molecular orientation and low pyrolysis temperature (≤ 800 °C) allows for good retention of N-species, especially pyridinic and pyridonic (Figure 1.3.1).¹⁶⁵ It is also possible to incorporate oxygen into the carbon structure (Figure 1.3.1), so pyrolysis (> 400 °C) should be conducted in an inert atmosphere.

Scheme 1.3.1. PAN oxidative stabilization (left) and carbonization (right). Reproduced from reference 165

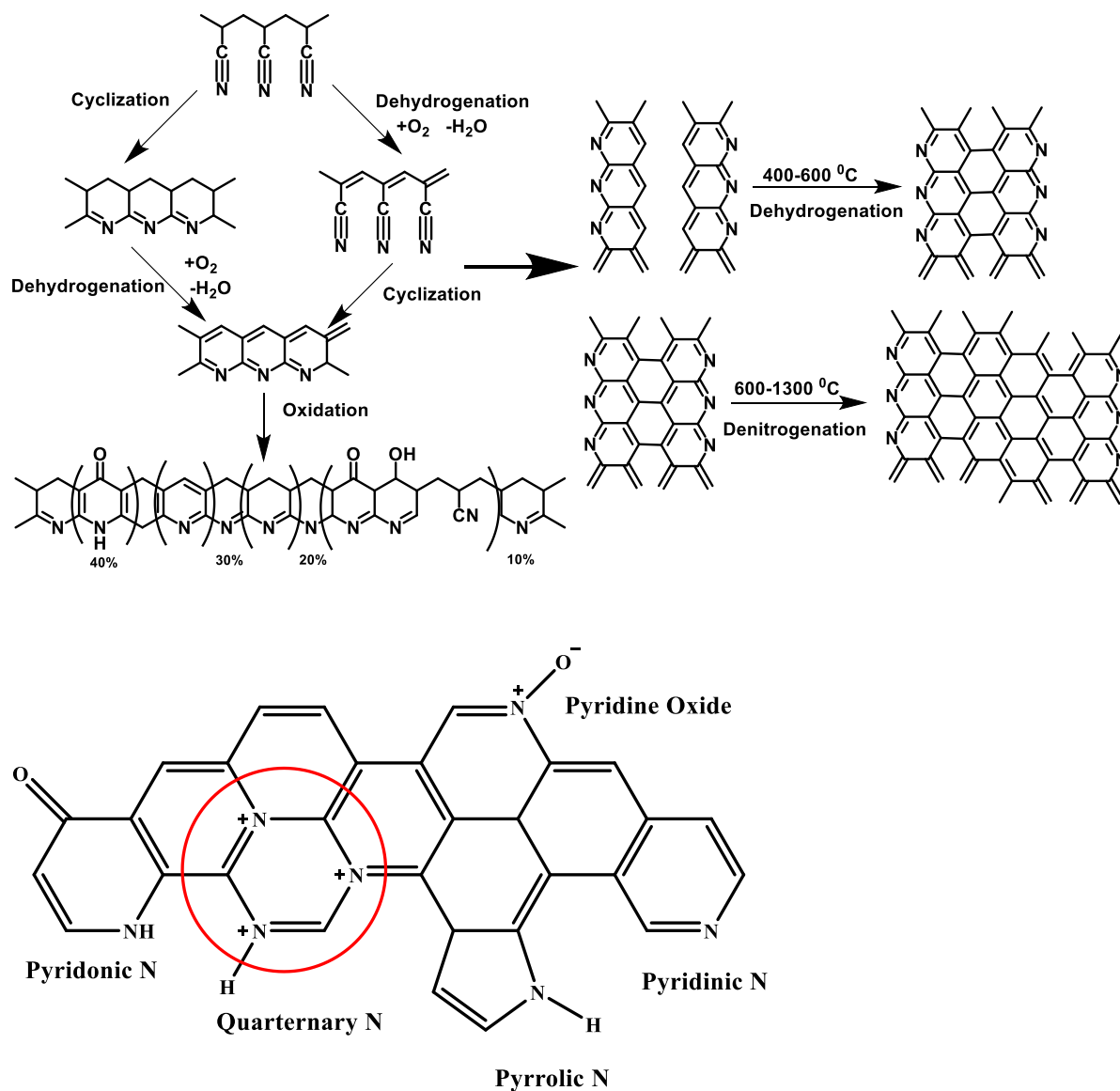


Figure 1.3.1. Types of nitrogen in N-doped carbon

1.3.1 PAN Homopolymers

Research groups have utilized both hard and soft templating with homopolymer PAN precursor to form nanocarbons. Hard templating generally results in more ordered

carbon materials, but has a distinct disadvantage, because the hard template is generally removed with either NaOH or HF. Soft templates are typically removed during the carbonization process, upon vaporization, but this method often gives less control over the carbon structure, including pore size distribution and surface area.

1.3.1.1 Hard Templating

Early reports on the fabrication of nanocarbons used vapor deposition and polymerization of AN to form PAN-coated silica particles.¹⁶⁶ The nanocarbon had highly uniform and tunable mesopores. Mesoporous silica has also been used to template nanocarbons by either polymerizing AN within or from the silica template.¹⁶⁷⁻¹⁷⁴ This allows for the formation of mesoporous carbon with surface areas (S_{BET}) over 1000 m²/g and highly tunable pore size.¹⁷³ As discussed in the previous synthetic section, SiO₂-*g*-PAN particle brushes were synthesized that yielded nanoporous carbon films with 14 nm pores, resulting from the silica, and surface areas up to 450 m²/g.¹⁵³

Salt-assisted sphere-to-cylinder micelle conversion in microemulsion was used to form PAN nanofibers. Iron(III) chloride was used as a structure-directing agent and was coordinated by PAN nanoparticles, which were then converted into carbon nanofibers.¹⁷⁵ Carbon nanofibers were also successfully prepared by a route consisting of the graphitization of PAN previously formed inside the nanosized pores of sepiolite or anodic aluminum oxide.^{176,177}

Despite excellent control over the pore size and surface area, hard templating of nanostructured carbons has a major disadvantage in removal of the template. In the case

of silica-based hard templates they can only be removed by concentrated NaOH solutions or HF. Hard template removal adds additional complication to nanocarbon scale up.

1.3.1.2 Soft Templating: Surfactants/Polymers and Solvents

Nanocarbons have been synthesized using PAN as a carbon precursor and soft templating techniques. Electrospinning PAN with silicone surfactants,¹⁷⁸ poly(ethylene glycol),¹⁷⁹ Nafion ®,¹⁸⁰ or PMMA¹⁸¹ and carbonization have proven to be good techniques to synthesize nanostructured carbons with surface area ranging from 500 m²/g up to 1600 m²/g.

Solvent templating can be utilized to form interesting hierarchically porous nanocarbons. PAN and DMSO solutions were frozen, freeze-dried to remove the DMSO, and pyrolyzed to create nanostructured carbons with 3, 10, and 100 nm pores.¹⁸² Cotton-like porous carbons were prepared by electrospinning PAN into water, lyophilizing to remove water, and carbonization.¹⁸³ Phosphorous and nitrogen doped (P/N-doped) carbons were synthesized by mixing PAN, DMF, H₂O, and H₃PO₄ and allowing the H₂O and DMF to slowly evaporate before pyrolysis.¹⁸⁴ The P/N-doped carbon, when pyrolyzed at 900 °C, had micro- and macropores.

1.3.2 PAN-containing Block Copolymers: BCP templating with PAN-*b*-PBA

BCP templating has been shown to easily control the nanocarbon structure, through the nanoscale phase separated morphology of the BCP precursors to form nanocarbons with accessible N atoms along the pore walls (Scheme 1.3.2). Our group employed the strategy of BCP templating to form nanocarbons using PAN₄₅-*b*-PBA₅₃₀-*b*-

PAN₄₅ triblock copolymers. Small angle x-ray scattering (SAXS) analysis showed that domain spacing was preserved at carbonization temperatures of 600 and 1000 °C. (178) The phase separated morphology of PBA-*b*-PAN BCPs was studied by varying the wt% of PAN.¹⁶⁴ Spherical domains of PAN were formed when PAN content was ~6 wt%. Increasing the PAN content to 15 wt% yielded a cylindrical morphology, whereas slight increase to 18 wt% formed lamellae-like morphology. PAN contents of 38 to 55 wt% yielded a bicontinuous morphology.

When converted to carbon, only the bicontinuous morphology was able to fully fuse the PAN phase together and form carbons with good retention of the phase separated morphology.^{164,165} atomic force microscopy (AFM) and small angle x-ray scattering (SAXS) analysis have confirmed that the PAN-*b*-PBA bicontinuous morphology was retained after carbonization (Figure 1.3.2.1a). X-ray photoelectron spectroscopy (XPS) analysis shows that N-functionality was also preserved when the BCPs were pyrolyzed at 700 °C (Figure 1.3.2.1b). However, SAXS analysis does show broadening in the d-spacing from BCP to carbon, which could result from the PAN-*b*-PBA reaching its order-disorder transition temperature (T_{ODT}) at a temperature similar to PAN thermal cyclization (Figure 1.3.2.1). CTNCs also have N-functionality aligned along the pore walls, due to the high crystallinity of PAN driving orientation during phase separation and good retention of this orientation through cyclization of PAN during thermal oxidative stabilization.^{165,185}

Scheme 1.3.2. Preparation of copolymer templated nanocarbons (CTNCs). Reproduced from reference 185

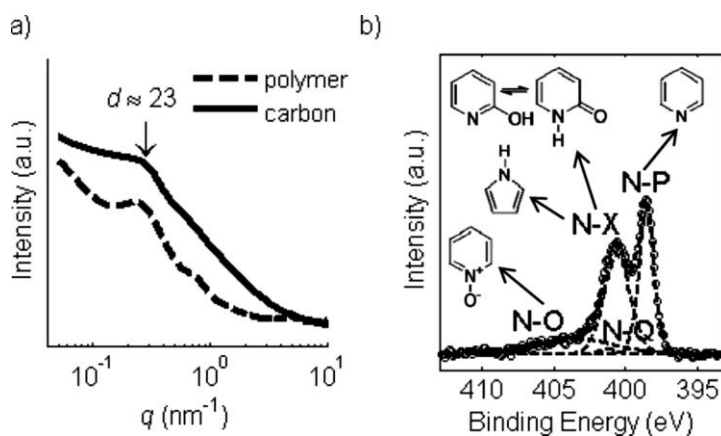
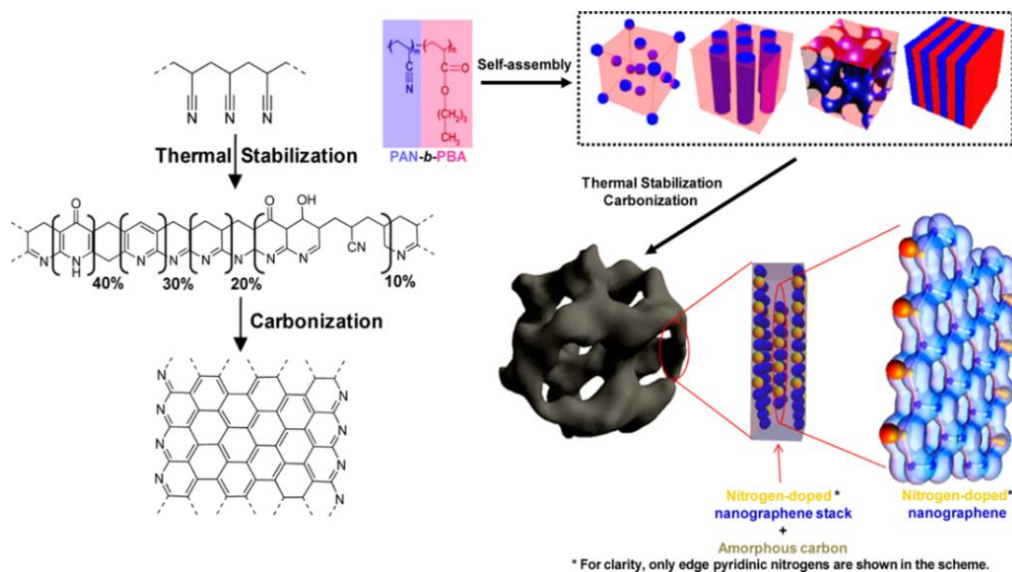


Figure 1.3.2.1. (a) SAXS profiles of PAN₉₉-*b*-PBA₇₀ annealed at 200 °C (dotted) and its corresponding CTNC pyrolyzed at 700 °C (solid). (b) XPS high-resolution N1s spectra of mesoporous carbon prepared from PAN₉₉-*b*-PBA₇₀. Reproduced from reference 165

1.3.3 Synthesis of Nanocarbons from Other Block Copolymers

1.3.3.1 PtBA-*b*-PAN

PtBA-*b*-PAN was used to form carbon/Fe₃O₄ composites.¹³⁵ The phenol-functionalized Fe₃O₄ nanoparticles form H-bonds with PAN, preferentially dispersing it in the carbon forming phase. As characterized by SAXS, the block copolymers exhibited a disordered morphology until the addition of 10 or 20 wt% of Fe₃O₄ particles, which promoted a cylindrical morphology. The surface area of the carbon/Fe₃O₄ composites was increased from 414 m²/g to 540 and 757 m²/g with the addition of 10 and 20 wt% of Fe₃O₄ particles, respectively.

1.3.3.2 PAN-*b*-PAA

PAN-*b*-PAA were used as water soluble carbon precursors to form shell cross-linked micelles (SCKs) that can be carbonized to form carbon nanoparticles. In one example, micelles were formed from PAN-*b*-PAA and the PAA phase was cross-linked, resulting in SCKs with uniform distribution of heights (average height of 9 ± 0.5 nm), as seen from AFM.¹⁸⁶ After carbonization, the carbon nanospheres were observed by AFM with a decrease in height from the SCKs, which can be related to the volatilization of the cross-linked PAA shell and carbonization of PAN block.

Another report uses a similar procedure to form micelles of PAN-*b*-PAA in water, but instead cross-linked the PAN-phase by introducing HAuCl₄ and formed gold nanoparticles.¹⁴⁰ AFM and transmission electron microscopy (TEM) analysis revealed that the carbon nanospheres have similar size to the gold cross-linked SCKs. After pyrolysis the gold nanoparticles are no longer detectable by energy dispersive x-ray

(EDAX) spectroscopy, which could mean the nanoparticles were buried within the carbon.

1.3.3.3 PAN-*b*-PS

Studies on the phase separation of PS-*b*-PAN are most often reported, after PAN-*b*-PBA, to template nanocarbons.^{89,187-189} SAXS analysis of PS-*b*-PAN showed small d-spacing of 12-14 nm, but a disordered morphology.¹⁸⁷ Upon carbonization, good preservation of the PS-*b*-PAN phase separated morphology was obtained with or without a substrate. Using the strong phase separation of PS-*b*-PAN, Lazzari, et al. micellized the BCP to form worm-like aggregates (Figure 3.2.1.4).¹⁸⁸ Upon carbonization, carbon nanofibers were formed.

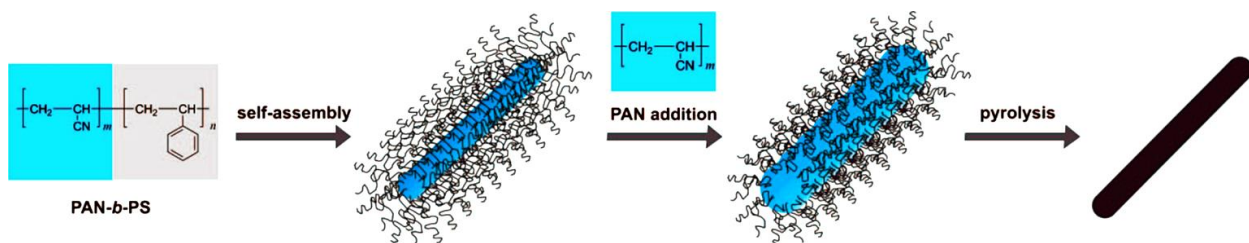


Figure 1.3.3 Fabrication of carbon nanofibers from PAN-*b*-PS BCP templating;

Reproduced from reference 188

1.3.3.4 PAN-*b*-PMMA

Several literature reports have synthesized nanostructured carbon from PAN-*b*-PMMA.¹³⁷⁻¹³⁹ Typically a high DP of PAN (>400) and low DP of PMMA (< 100) were targeted, so the BCP phase separated into a cylindrical morphology. The nanostructured carbons had surface areas up to 428 m²/g and pore size ~ 10 nm. However, the ceiling

temperature of PMMA (200-325 °C)¹⁹⁰ is similar to the cyclization temperature of PAN (200-300 °C),¹⁹¹ which may cause collapse of the nanocarbon and result in lower surface areas. Thus, PAN may not fully cross-link before PMMA begins to depolymerize and the BCP morphology would not be well retained.

1.3.3.5 PCL-*b*-PAN

The phase separation and carbonization of PCL-*b*-PAN was studied.¹⁴³ PCL-*b*-PAN with $f_{\text{PAN}}^V = 0.6$ showed lamellar phase separation, whereas a hexagonal cylindrical structure was observed for $f_{\text{PAN}}^V = 0.33$, as confirmed by TEM and SAXS analysis. The nanostructured carbons derived from PCL-*b*-PAN show good retention of morphology, by SAXS analysis, with slight broadening of the d-spacing. This is attributed to the cross-linking of the PAN phase during thermal stabilization before the degradation of PCL at ~400 °C.

1.3.4 Long-range ordered Nanocarbons: Zone casting

The zone-casting method was used to fabricate PBA-*b*-PAN or PAN-*b*-PBA-*b*-PAN films with a long-range lamellar order.¹⁹² The more commonly used drop-casting technique afforded PBA-*b*-PAN films with short-range order.¹⁹² Zone-casting deposits a polymer solution, PAN-*b*-PBA in DMF, onto a moving substrate (Figure 1.3.4 a). The syringe temperature, deposition rate, and rate of substrate movement were all controlled, which allows for control over film thickness (tens of nanometers to several micrometers) and film size (several square cm). A PBA₂₄₀-*b*-PAN₁₂₄ precursor was zone-cast from a DMF solution. The resulting film exhibited an edge-on lamellae structure with a d-

spacing of ~ 36 nm, as determined using grazing incidence small-angle X-ray scattering (GISAXS) (Figure 1.3.4c) and AFM (Figure 1.3.4b). The lamellae were oriented perpendicular to the casting direction, indicating that the solvent evaporation front induced the domain formation.

The lamellar $\text{PBA}_{240}\text{-}b\text{-PAN}_{124}$ film was heated under air at 280°C to stabilize the PAN domains and subsequently heated under nitrogen at 800°C to convert PAN into carbon and to volatilize the PBA domains. This way, a lamellar carbon film was obtained that exhibited the same spacing (37 nm) as the copolymer film and orientation was preserved. However, if removed from the substrate, the d-spacing decreases and carbon orientation was lost, most likely due to collapse of the carbon structure.

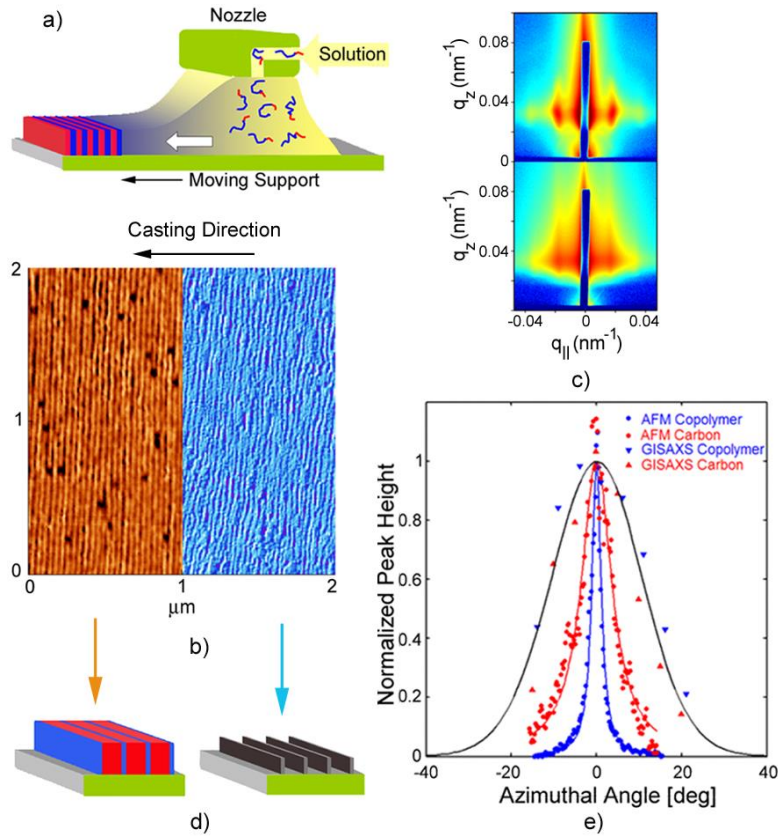


Figure 1.3.4. (a) Long-range order in thin films of PBA₂₄₀-*b*-PAN₁₂₄ BCPs prepared by zone-casting and pyrolysis to form nanostructured carbon; (b) AFM phase images (left: copolymer; right: carbon); (c) GISAXS patterns acquired at 90° to casting direction (top: copolymer; bottom: carbon); (d) schematic illustration of lamellar order (left: copolymer; right: carbon); (e) azimuthal profiles of maxima in 2D Fourier transforms of AFM images and maxima in GISAXS patterns corresponding to the lamellar period. Reference reproduced from 192

1.3.5 Nanocarbon from Molecular Bottle Brushes

Well-defined molecular brushes containing PAN-based segments in the side chains were prepared by ATRP using a “grafting from” technique.¹⁵² The chosen side chains were PBA-*b*-PAN BCPs or PBA-*b*-PAN-*b*-PtBA triblock copolymers. Due to solubility of the side chains in polar DMF solvent, these brushes displayed collapsed, worm-like structures after deposition on surfaces, as observed by AFM. Interestingly, brushes with ABC tri-block copolymer side chains (PBA-*b*-PAN-*b*-PtBA) had a necklace-like structure, which may be due to the strong interaction between the terminal PtBA block and inner PBA block. The PtBA block was hydrolyzed to PAA and cross-linked. The shell cross-linked brushes showed high morphological stability when transferring from solution to substrates, which was demonstrated by the increased height of the brushes compared to brushes without shell crosslinking.

The brush copolymers were used as template molecules for nanostructured carbons.¹⁵² Single shell crosslinked brushes exhibited a high stability during pyrolysis to form single carbon nanoobjects. Therefore, the shell crosslinked brushes with rigid

structures were subjected to thermal treatment: stabilization of the PAN segments at 250 °C and subsequent pyrolysis at 600 °C. The height of the structures after thermal stabilization was determined to be 11.6 nm. The carbon nanostructures preserved the shape of the original shell crosslinked brushes, although slight shrinking was observed, due to the thermal treatment. The height was relatively low, 5.4 nm, and the more round shape, compared to typical rod-like structures of bottle brushes, was due to the low aspect ratio of backbone length to the side chain length after shell crosslinking of the brushes.

1.3.6 Combining Soft and Hard Templating: PAN-*b*-PS, PVAc-*b*-PAN, PAN-*b*-PEO

The combination of hard and soft templating can give rise to unique templated carbon structures. Kruk, et al. utilized PEO-*b*-PAN BCPs as a soft template for mesoporous silica.¹⁴² If the BCP was left in the mesoporous silica template, it could be converted to carbon. After silica removal, mesoporous carbon was formed with surface areas up to 900 m²/g.

Mesoporous carbon fibers were synthesized from PVAc-*b*-PAN BCPs by compressing them into an anodic aluminum oxide (AAO) membrane, carbonizing, and removing the AAO membrane.¹⁹³ The carbon nanotube's morphology was tuned by changing the block ratios or the pyrolysis heating rate. Similarly, AAO membranes were used with PAN-*b*-PS BCP precursors to fabricate carbon nanotubes.¹⁹⁴ The nanotube's wall thickness was controlled by either changing the concentration of the BCP precursor solution or by using a multiple casting and pyrolysis steps.

1.4. Applications of Nanocarbons Derived from Copolymer Templating

Our group has explored the use of copolymer templated nanocarbons (CTNCs) for multiple applications. Their excellent activity in many applications resulted from the highly accessible nitrogen species located along the pore walls. Incorporation of N into the carbon framework add basic or catalytic sites, that improve electrochemical activity.¹⁶⁵ Additionally, pyridinic nitrogen should have the highest activity in many applications (Figure 1.3.1). Thus, CTNCs are unique materials that can be used for many electrochemical applications, as well as for a wide variety of other applications, because the carbon structure has highly accessible pyridinic nitrogen. Non-electrochemical applications for CTNCs include CO₂ capture or gas separation sorbents and heavy metal or liquid sorbents.^{195,196}

1.4.1 Supercapacitor

Due to their high power density at energy densities above those of conventional capacitors, supercapacitors have become a heavily researched area.¹⁶⁵ The electrical double layer (EDL), the interface between the electrode and electrolyte, stores the supercapacitor's electrical charge.¹⁶⁵ Thus, supercapacitor materials should balance a high surface area and porosity to allow for an optimal EDL. Most carbon based materials have achieved a specific capacitance per unit area (C_{sa}) between 5 and 25 $\mu\text{F}/\text{cm}^2$.¹⁶⁵

CTNC supercapacitor materials were fabricated using PAN₉₉-*b*-PBA₇₀ and had a surface area $\sim 500 \text{ m}^2/\text{g}$ and 18% nitrogen content.¹⁸⁵ The C_{sa} was 33 $\mu\text{F}/\text{cm}^2$ and showed 85% retention of capacity after 2000 cycles. When surface area was increased by KOH or CO₂ activation, pseudocapacitance dramatically decreased, which was attributed to the

decrease in nitrogen content. Reports of CTNCs templated by PAN-*b*-PMMA^{138,139} and PAN-*b*-PtBA¹³⁵ have also been used to fabricate supercapacitor materials.

1.4.2 CO₂ Capture

CTNCs were successfully employed as CO₂ sorbents. PAN₉₉-*b*-PBA₇₀ was used to template CTNCs with a surface area $\sim 350 \text{ m}^2/\text{g}$.¹⁹⁶ The adsorption capacity at 1 atm was $\sim 2 \text{ mmol/g}$, which is comparable with other carbon-based sorbents that have a much higher surface area. Depending on the pyrolysis and activation conditions the selectivity for CO₂ over N₂ was 7 to 10 times higher than commercially available activated carbon.

1.4.3 Oxygen Reduction Reaction (ORR)

Replacement of the Pt-based catalyst for the oxygen reduction reaction (ORR) in fuel cells is crucial for its viability, based on availability and cost of Pt.¹⁹⁷ Thus, metal-free carbon-based catalysts have been heavily researched as a catalyst for ORR. Recently, it was verified that the carbon atoms adjacent to the pyridinic N sites have the highest activity in N-doped carbon for ORR.^{197,198}

CTNCs can be used as binder free films for ORR, as the PAN₉₉-*b*-PBA₇₀ precursor can be drop-cast onto a glassy carbon electrode and pyrolyzed at 800 °C to directly attach the CTNC to the electrode (Figure 1.4).¹⁶³ This method significantly simplified the preparation of carbon-based ORR electrodes. Moreover, the CTNCs show electrocatalytic activity matching that of Pt, high kinetic current density, and close to 4 e⁻ transfer, which is critical for ORR.

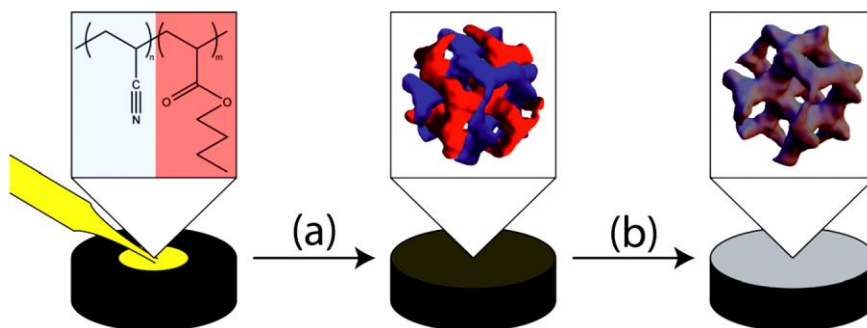


Figure 1.4. synthesis of binder free CTNC-based electrodes for ORR; Reproduced from reference 163

1.4.4 Dye Sensitized Solar Cells

Much like ORR electrodes, Pt based counter electrodes are used in dye sensitized solar cells (DSSC). CTNCs, with surface areas ~ 460 to $570 \text{ m}^2/\text{g}$, were applied as a CE in DSSC with a $\text{Co}(\text{bpy})_3^{2+/3+}$ electrolyte and JK-306 dye.^{199,200} The CTNCs efficiently reduced the $\text{Co}(\text{bpy})_3^{3+}$, as shown by the low charge transfer resistance. When the CTNC CE was used, the efficiency and fill factor of the JK-306/ $\text{Co}(\text{bpy})_3^{2+/3+}$ redox couple increased by 10.32% and 73.5%, respectively, under one sun illumination.

1.5. Nitrogen Doped Nanocarbon Templated from PAN Block Copolymers:

Conclusions and Thesis Aim

CTNCs are useful for a variety of applications, including CO_2 capture, ORR reaction catalysts, supercapacitors, and DSSC electrodes. PAN precursors have been reported for the use in Li-ion¹⁸² or Li-S batteries.^{173,201} Due to CTNCs high accessible N-sites and simple templating approach, they may be good candidates for battery applications, especially for Li-S batteries, where simple ball-milling can be used to mix the PAN-based precursor and sulfur.²⁰¹ Using CTNCs as liquid or metal sorbents is

another area where they could exhibit superior performance. CTNCs may be uniquely suited to capture uranium or other heavy metals, as the accessible pyridinic N-sites can easily coordinate metals.

The fabrication of CTNCs was not possible without the development of RDRP techniques, especially ATRP, over the past 20 years. However, many of the CTNC BCP precursors were fabricated using normal ATRP, which requires extensive purification to remove the Cu-based catalyst, especially if CTNCs are to be used in catalysis/energy storage. Thus, Chapter 2 focuses on the development of ICAR ATRP with low ppm Cu-catalyst loadings to synthesize PAN-based BCPs. Chapter 2 will also discuss the use of metal-free ATRP to synthesize PAN.

CTNC fabrication via BCP templating has one draw-back that results from the properties of BCPs. As previously discussed, it is possible that the BCP can reach its ODT temperature before cyclization of PAN, leading to a loss of morphology, large pores, and lower surface area. Thus, Chapter 3 will discuss the use of PAN-based star templates to avoid the ODT of BCPs by “attaching” them to a cross-linked core.

Chapter 4 will discuss a new precursor for N-doped nanocarbons. 4-cyanostyrene (4-CNSt) was grafted from silica particles and cross-linked, via the Pinner method, to form tetrazine units. The cross-linked material was carbonized and the materials were studied to determine the highest achievable surface area and structure of the N-doped nanocarbon.

1.6. High Internal Phase Emulsion (HIPE) and PolyHIPEs

1.6.1 HIPEs

High internal phase emulsions (HIPEs) are generally highly viscous emulsions with an internal phase ranging from 74 up to 99 vol %.²⁰²⁻²⁰⁴ They are historically water in oil (W/O) emulsions, but there are also reports of oil in water (O/W) HIPEs were reported in the literature.²⁰²⁻²⁰⁴ Recently, medium internal phase emulsions (MIPEs), containing 30 to 74 vol % internal phase, have been reported.²⁰⁴⁻²⁰⁶ W/O HIPEs are prepared by slowly adding the internal aqueous phase to the external organic phase while applying vigorous stirring, usually with a mechanical stirrer, or other agitation (Figure 1.6.1).²⁰²

Due to their high internal phase ratio, HIPEs typically form polyhedral, instead of spherical droplets, or a polydisperse droplet size distribution.^{206,207} HIPEs require a large amount of surfactant (up to 30% of the external phase) to form a fully stable HIPE.^{203,204,208} However there are only a few surfactants that stabilize HIPEs. The non-ionic surfactant sorbitan monooleate (SMO or Span-80) is the most common surfactant utilized for w/o HIPE stabilization.^{205,206,208} Surfactants that form a stable HIPE must be completely insoluble in the dispersed phase, to prevent phase inversion and generation of “normal” emulsions and should rapidly absorb at the interface to reduce the interfacial tension between the oil and water phases.²⁰⁸ Once absorbed at the interface, the surfactants that stabilize the HIPE should have the ability to pack at the droplet surface in a way that promotes formation and stabilization of the convex interface and a rigid film at the interface.²⁰⁸ This phenomenon can be enhanced by increasing the interfacial tension between the oil and aqueous phases either by selecting a more hydrophobic oil phase or

adding a salt, like NaCl, to the aqueous phase, which decreases water-surfactant and increases surfactant-surfactant interactions.²⁰⁸

HIPEs were originally reported in the 1960's and have been utilized in the cosmetic and food industries.^{203,205} In the mid-1990's HIPE research experienced a revival, especially as a simple method to template macroporous polymers.^{202,205,209}

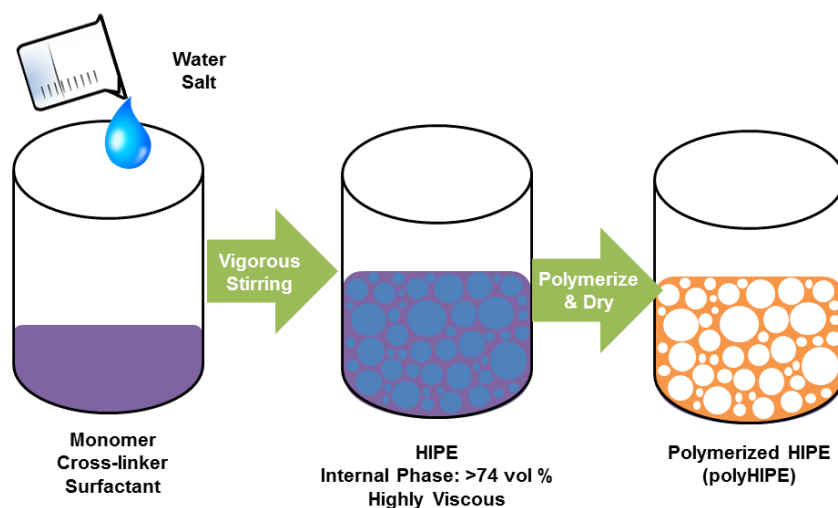


Figure 1.6.1. W/O HIPE and polyHIPE formation

1.6.2 PolyHIPEs

If the HIPE's external phase contains a polymerizable molecule, polymerized HIPEs (polyHIPEs) can be formed after polymerization and the removal of the internal phase (Figure 1.6.2).²⁰² PolyHIPEs have macropores (voids), of 1 to 100 μm that are fully interconnected by smaller windows and pores (Figure 1.6.2).^{203,204} Pores and windows are formed during polymerization, due to shrinkage in the polymer gel phase relative to the liquid continuous phase, caused by density changes, that lead to the polymer film rupturing at its thinnest point.²⁰⁴ The resulting fully interconnected porous structures

display high porosities, up to 99 %, and low densities, typically 0.10 to 0.15 g/cm³.^{202,209} Large amounts of cross-linking monomer (≥ 10 vol % continuous phase) is necessary to avoid collapse of the polyHIPE structure.²⁰⁸ Historically, polyHIPEs are polystyrene (PS) based and use divinylbenzene (DVB) as a cross-linker.²⁰² Styrene (St) based HIPEs have good stability and PS based polyHIPEs exhibit good mechanical properties.²⁰²

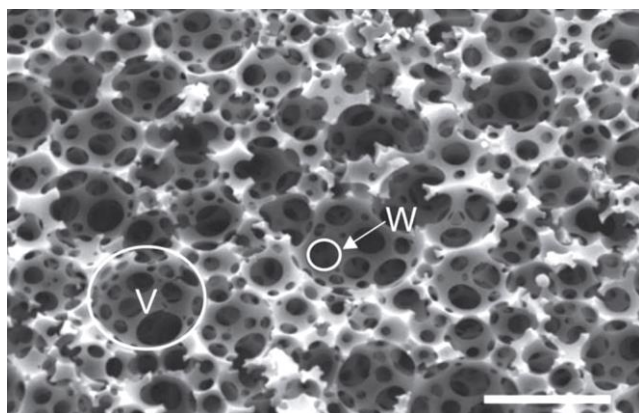


Figure 1.6.2. SEM image of a typical polyHIPE structure; V= void and W= window;
Scale bar= 20 μm ; Reproduced from reference 204

The void size can be tuned to some extent by increasing the internal phase volume fraction from 74 up to 99 vol%.²⁰² The void size, and more importantly, the interconnecting windows and pores, can be tuned by decreasing or increasing the amount of surfactant.²⁰² A surfactant content below 4 wt%, vs. external phase, results in a closed-cell morphology.^{202,204,208} More interconnected structures are formed upon increasing the surfactant content. However, once the surfactant content reaches ~ 50 wt% (vs. external phase) the polyHIPE material becomes weak and collapses.^{202,208} Addition of a costabilizer to the internal phase, such as NaCl for an aqueous internal phase, can also

reduce the void size, up to an order of magnitude in some cases, by increasing HIPE stability.^{202,208}

PolyHIPEs have been synthesized by many methods. A thermally initiated free radical polymerization (RP) is the most commonly reported method.²⁰⁶ Ultraviolet photoinitiation and ⁶⁰Co γ -ray initiation have also been reported.^{206,210} However, several recent papers have utilized reversible deactivation radical polymerization (RDRP) methods, like atom transfer radical polymerization (ATRP)²¹¹ and reversible addition-fragmentation chain-transfer (RAFT) polymerization.²¹²⁻²¹⁵ Biodegradable polyHIPEs were synthesized using thiol-ene or thiol-yne chemistry.²¹⁶⁻²¹⁹ PolyHIPEs synthesized by ring opening metathesis polymerization (ROMP)²²⁰⁻²²³ and polycondensation reactions,²²⁴ with an emphasis on formation of polyurethane foams,²²⁵⁻²²⁷ have also been reported.

1.6.3 PolyHIPE Applications

Due to their ease of synthesis, high porosity, interconnectivity, and low density, polyHIPEs have been used in a variety of fields and many industrial patents have been filed. Industrial applications include liquid absorbents and carriers,²²⁸⁻²³¹ polyelectrolyte containing foams,²³² heat and sound insulation,²³³ carbon materials,^{234,235} electrodes,²³⁶ and gas storage.^{237,238} In the literature polyHIPEs have found many additional applications, including fire retardants,²³⁹ column materials,²⁴⁰ waste water treatment,²⁴¹ CO₂ capture,²⁴² and catalyst supports,^{243,244}

The most frequently targeted market for polyHIPEs has been the biomedical field. Proposed applications for polyHIPEs include shape-memory drug delivery implants²⁴⁵ and materials for prevention of antibacterial infection.²⁴⁶ Many researchers have shown

that polyHIPEs make excellent scaffolds for cell and tissue growth.^{216,217,247,248} One of the most interesting biomedical applications used injectable HIPEs that cure at body temperature to act as biodegradable bone scaffolds.²⁴⁹⁻²⁵³

1.6.4 Motivation: How to Make PolyHIPEs Viable Materials

1.6.4.1 Degradability

PolyHIPE research has focused on synthesis of degradable polyHIPEs to make them viable for biomedical applications. As previously mentioned, thiol-ene and thiol-yne chemistry can be used to synthesize fully degradable structures (Figure 1.6.4.1 a).²¹⁶⁻²¹⁸ Early research focused on using a degradable divinyl-polycaprolactone (divinyl-PCL; Figure 1.6.4.1 b) cross-linker copolymerized with styrene or 2-ethylhexyl acrylate (EHA) to form a polyHIPE. The majority of the polyHIPE structure can be removed via degradation of the PCL chains, but the C-C backbone remains and limits their utility.²⁵⁴⁻²⁵⁶ PCL-polyols can form fully degradable poly(ester urethane urea)-based polyHIPEs when combined with diisocyanates.^{225,251} Lastly, monomers with degradable ester bonds, like propylene fumarate dimethacrylate (PFDMA; Figure 1.6.4.1 b), can be used to synthesize fully degradable polyHIPEs when homopolymerized or copolymerized with styrene.^{249,252,253}

Few of the reports discuss the degradation timescale, method, or product's toxicity. One report, where a trivinyl-PCL compound was polymerized with a trithiol compound by thiol-ene polymerization, investigated the degradation products of the polyHIPE and showed good cell viability results.²¹⁷ However, any variation from this system may exhibit high cytotoxicity and decrease the utility of the polyHIPE.

Additionally, most cases utilized precursors, like propylene fumarate dimethacrylate, that are not commercially available and add additional synthetic steps and cost to polyHIPE formation.^{249,252,253} Synthesis of degradable polyHIPEs without complicated monomer synthesis and by a radical polymerization process, so a wide variety of commercially available monomers can be used to tune the polyHIPE properties, would greatly improve the utility of degradable polyHIPEs for biomedical applications.

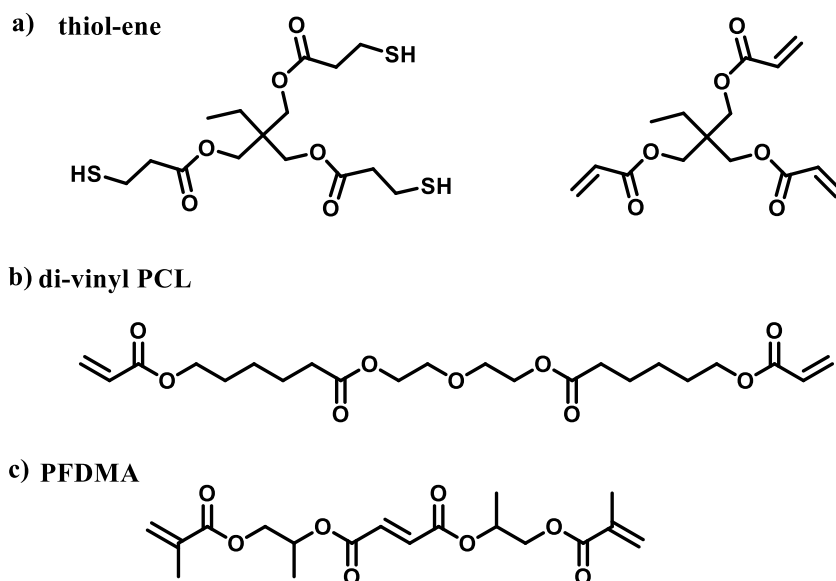


Figure 1.6.4.1. Structures of cross-linkers in degradable polyHIPEs

1.6.4.2 Mechanical Strength

Improvements in the mechanical properties of polyHIPE's, including modulus and toughness, are needed for many applications. PS based polyHIPEs exhibit high modulus and toughness, and these properties are easily tuned by increasing cross-linking or surfactant content or by copolymerizing with a stiffer monomer.²⁰⁸ The porosity of styrene-based polyHIPEs can also be tuned to increase the mechanical properties,²⁵⁷

especially when hierarchal macropores are targeted.²⁵⁸ Styrene based polyMIPEs, where the MIPE internal phase was 40 to 60% of the emulsion, exhibited better mechanical properties than polyHIPEs while still possessing high porosities.²¹³ A few non-styrene based polyHIPEs, including tetrazole-based^{259,260} or PMMA,²¹⁰ which presents HIPE stabilization challenges, exhibited improved mechanical properties.

Many researchers have created polyHIPE composites, with silica,^{257,261,262} magnetic nanoparticles,²⁶³ clay,²⁶⁴ titania nanoparticles and rods,²⁶⁵ or carbon nanotubes,²⁶⁵ to increase the mechanical strength. The simplest method for preparation of a polyHIPE composite is through generation of a nanoparticle-stabilized Pickering HIPE since upon polymerization the silica particles become trapped within the polyHIPE wall.²¹¹ In some cases a vinyl-functionalized inorganic molecule, such as silsesquioxane, was incorporated into the polyHIPE wall to impart better mechanical properties.^{261,266,267}

Alternative polymerization methods have shown promising results for improved mechanical performance in polyHIPEs. Poly(dicyclopentadiene) based polyHIPEs and polyMIPEs, synthesized via ROMP, were shown to have excellent mechanical properties (Figure 1.6.4.2).²²⁰⁻²²² Currently, the simplest method to improve the mechanical properties of polyHIPEs have utilized RAFT polymerization.²¹⁴ The authors simply added a RAFT agent to a RP of St and DVB in HIPE and obtained a three-fold increase in the polyHIPEs mechanical properties, which was attributed to the formation of a uniform cross-linked network.²¹⁴ Further research should be conducted to determine if other RDRP methods also improve the mechanical properties of polyHIPEs.

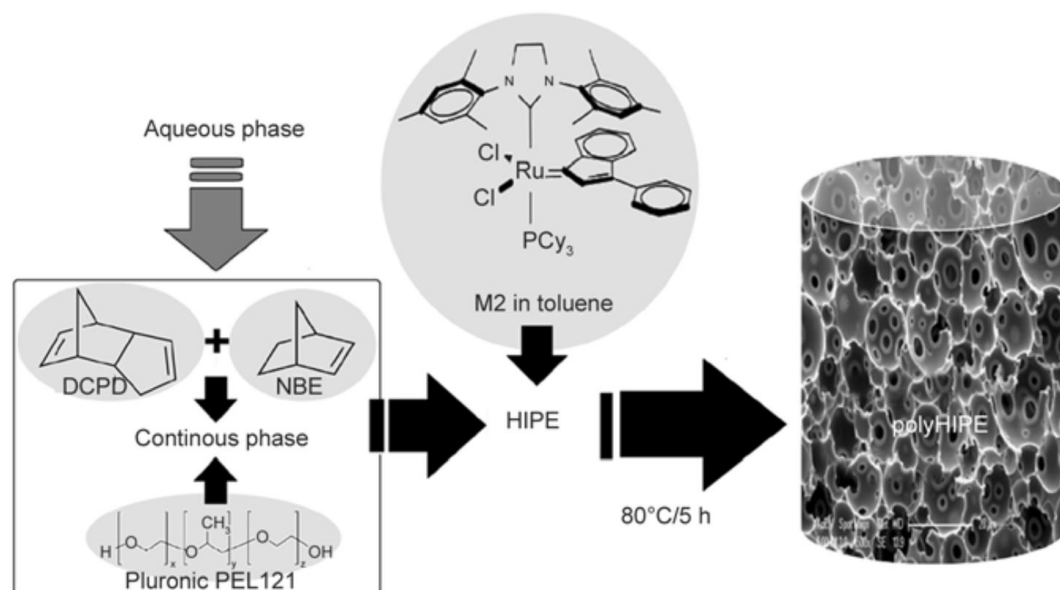


Figure 1.6.4.2. Synthesis of poly(dicyclopentadiene) based polyHIPEs; Reproduced from reference 221

1.6.4.3 Surfactant Amount

As discussed in the introduction, only a few specific surfactants, used in high quantities, can stabilize HIPEs. The large amount of surfactant must be removed for most applications, limiting the ability to scale up the preparation of polyHIPE materials. Thus, there has been a great deal of research expended on alternative stabilizers. Random and block copolymers have been shown to be efficient stabilizers for HIPEs, including poly(styrene-*co*-methyl methacrylate-*co*-acrylic acid),^{268,269} polystyrene-*b*-poly(ethylene oxide),^{270,271} polystyrene-*b*-poly(acrylic acid),²⁷⁰ poly(1,4-butadiene)-*b*-poly(ethylene oxide),²⁷⁰ poly(1,4-butadiene)-*b*-poly(acrylic acid),²⁷⁰, poly(*n*-butyl acrylate)-*b*-poly(acrylic acid),²¹⁵ and poly(butylene oxide)-*b*-poly(ethylene oxide).²⁰⁸ Generally, large amounts of block copolymer surfactants are required to form a fully stable HIPE.

Inorganic nanoparticles were shown to be efficient stabilizers for Pickering HIPEs at amounts as low as 1 wt% (vs the external phase). Silica nanoparticles,^{211,246,272-274} carbon nanotubes,²⁷⁵ (reduced) graphene oxide,²⁷⁶⁻²⁷⁹ and magnetic nanoparticles²⁸⁰ have all been shown to be efficient stabilizers. However, as previously discussed, inorganic particles can be trapped within the polyHIPE walls, which is undesirable for certain applications.

For this reason, polymeric nanoparticles have been investigated as HIPE stabilizers. Poly(urethane urea) cross-linked nanoparticles were used to stabilize O/W HIPEs to synthesize hydrophilic polyHIPEs.²⁸¹ Researches have explored a variety of polymer architectures, including hyperbranched and dendritic structures, which were successful at HIPE stabilization.^{243,244,282} Two of the most efficient polymer architectures for HIPE stabilization are Janus particles or core cross-linked star polymers. Janus particles, formed by crosslinking the P4VP block of a poly(4-vinyl pyridine)-*b*-poly(methyl methacrylate) (P4VP-*b*-PMMA) to create a “tadpole” structure, were able to stabilize HIPEs at concentrations as low as 0.05 wt% (vs. total emulsion).^{283,284} Core cross-linked star polymers have also been explored for HIPE stabilization and are ideal candidates for further study, because their hydrophobicity is easily tuned by changing the composition of the arms. Responsive stars have been shown to efficiently emulsify, down to 1 wt% (vs. total emulsion), and demulsify via a response to thermal, salt, or pH triggers (Figure 1.6.4.3).²⁸⁵⁻²⁸⁷ However, core cross-linked star polymers have not been explored to the fullest extent and tuning hydrophobicity may result in more efficient stabilizers.

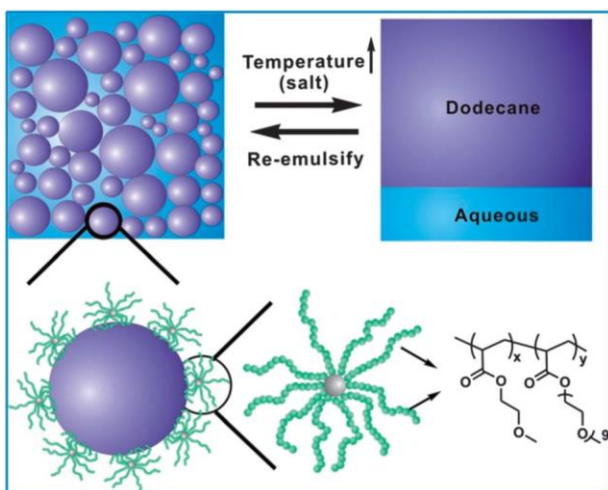


Figure 1.6.4.3. Representation of HIPE stabilized by salt/temperature responsive core cross-linked star polymers; Reproduced from reference 287

1.6.5 HIPE and PolyHIPE Thesis aim and study

HIPEs are unique and interesting emulsion systems that can easily be employed to template macroporous polymers, polyHIPEs. Many advances have been made in understanding how HIPE and polyHIPE systems behave, which has led to a wide variety of applications for polyHIPEs. However, if polyHIPE materials are to find industrial acceptance, in addition to a wider variety of applications, improvements must be made. One of the objectives of this thesis was to target specific areas where HIPE systems and polyHIPEs can be improved, including degradability, mechanical properties, and reduction of the amount of surfactant required for HIPE stabilization. In all cases, atom transfer radical polymerization (ATRP) was utilized to either polymerize monomers in a stable HIPE or synthesize surfactants to use for HIPE stabilization. In Chapter 4, activators generated by electron transfer (AGET) ATRP was used to synthesize degradable polyHIPEs. These polyHIPEs also exhibited improved mechanical properties.

Chapters 5 and 6 discuss research directed at synthesis and use of mikto-arm star surfactants to stabilize HIPEs and study how they can be incorporated into the polyHIPE structure, so removal of surfactant is no longer necessary.

1.7. Acknowledgements

I would like to thank Michal Kruk and Chaunbing Tang for their initial work done gathering references, outlining and writing about the synthesis of PAN and its use to form carbon materials as a review.

1.8. References

- (1) Dresselhaus, M. S. *Annual Reviews in Materials Science* **1997**, 27, 1.
- (2) Kroto, H. W.; Heath, J. R.; O'Brien, S. C.; Curl, R. F.; Smalley, R. E. *Nature* **1985**, 318, 162.
- (3) Iijima, S. *Nature* **1991**, 354, 56.
- (4) Nishihara, H.; Kyotani, T. *Advanced materials* **2012**, 24, 4473.
- (5) Shen, W.; Fan, W. *J. Mater. Chem. A* **2013**, 1, 999.
- (6) Liang, C.; Li, Z.; Dai, S. *Angewandte Chemie* **2008**, 47, 3696.
- (7) Wu, Z.; Li, W.; Xia, Y.; Webley, P.; Zhao, D. *Journal of Materials Chemistry* **2012**, 22, 8835.
- (8) Shah, K. A.; Tali, B. A. *Materials Science in Semiconductor Processing* **2016**, 41, 67.
- (9) Xia, Y.; Yang, Z.; Mokaya, R. *Nanoscale* **2010**, 2, 639.
- (10) Castro-Muniz, A.; Hoshikawa, Y.; Kasukabe, T.; Komiyama, H.; Kyotani, T. *Langmuir : the ACS journal of surfaces and colloids* **2016**, 32, 2127.
- (11) Hassani, F.; Tavakol, H.; Keshavarzipour, F.; Javaheri, A. *RSC Advances* **2016**, 6, 27158.
- (12) He, C.; Zhao, N.; Shi, C.; Liu, E.; Li, J. *Advanced materials* **2015**, 27, 5422.
- (13) *Carbon Materials*; Pergamon: Oxford, 1999.
- (14) Kinoshita, K. *Carbon: electrochemical and physicochemical properties*; Wiley: Hoboken, N.J., 1988.
- (15) Chand, S. *Journal of Materials Science* **2000**, 35, 1303.
- (16) Morris, E. A.; Weisenberger, M. C.; Abdallah, M. G.; Vautard, F.; Grappe, H.; Ozcan, S.; Paulauskas, F. L.; Eberle, C.; Jackson, D.; Mecham, S. J.; Naskar, A. K. *Carbon* **2016**, 101, 245.
- (17) Ryoo, R.; Joo, S. H.; Jun, S. *Journal of Physical Chemistry B* **1999**, 103, 7743.

- (18) Lee, J.; Yoon, S.; Hyeon, T.; Oha, S. M.; Kimb, K. B. *Chemical Communications* **1999**, 2177.
- (19) Shi, Q.; Zhang, R.; Lv, Y.; Deng, Y.; Elzatahrya, A. A.; Zhao, D. *Carbon* **2015**, 84, 335.
- (20) Jiang, T.; Wang, Y.; Wang, K.; Liang, Y.; Wu, D.; Tsiakaras, P.; Song, S. *Applied Catalysis B: Environmental* **2016**, 189, 1.
- (21) Ungureanu, S.; Birot, M.; Deleuze, H.; Schmitt, V.; Mano, N.; Backov, R. *Carbon* **2015**, 91, 311.
- (22) Kajii, H.; Take, H.; Yoshino, K. *Synthetic Materials* **2001**, 121, 1315.
- (23) Moriguchi, I.; Nakahara, F.; Furukawa, H.; Yamada, H.; Kudo, T. *Electrochemical and Solid-State Letters* **2004**, 7, A221.
- (24) Wang, D.; Fu, A.; Li, H.; Wang, Y.; Guo, P.; Liu, J.; Zhao, X. S. *Journal of Power Sources* **2015**, 285, 469.
- (25) Braghiroli, F. L.; Fierro, V.; Parmentier, J.; Pasc, A.; Celzard, A. *Green Chem.* **2016**.
- (26) Goscianska, J.; Olejnik, A.; Nowak, I.; Marciniak, M.; Pietrzak, R. *Chemical Engineering Journal* **2016**, 290, 209.
- (27) Mitome, T.; Hirota, Y.; Uchida, Y.; Nishiyama, N. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2016**, 494, 180.
- (28) Liang, C.; Hong, K.; Guiochon, G. A.; Mays, J. W.; Dai, S. *Angewandte Chemie* **2004**, 43, 5785.
- (29) Zhang, J.; Deng, Y.; Wei, J.; Sun, Z.; Gu, D.; Bongard, H.; Liu, C.; Wu, H.; Tu, B.; Schüth, F.; Zhao, D. *Chemistry of Materials* **2009**, 21, 3996.
- (30) Werner, J. G.; Hoheisel, T. N.; Wiesner, U. *ACS Nano* **2014**, 8, 731.
- (31) Hesse, S. A.; Werner, J. G.; Wiesner, U. *ACS Macro Letters* **2015**, 4, 477.
- (32) Liu, C.; Yu, M.; Li, Y.; Li, J.; Wang, J.; Yu, C.; Wang, L. *Nanoscale* **2015**, 7, 11580.
- (33) Lin, Z.; Tian, H.; Xu, F.; Yang, X.; Mai, Y.; Feng, X. *Polym. Chem.* **2016**, 7, 2092.
- (34) Huang, J.; Tang, C.; Lee, H.; Kowalewski, T.; Matyjaszewski, K. *Macromolecular Chemistry and Physics* **2007**, 208, 2312.
- (35) Sun, Y.; Huang, W.; Liou, J.; Lu, Y.; Shih, K.; Lin, C.; Cheng, S. *RSC Advances* **2015**, 5, 105774.
- (36) Minus, M. L.; Kumar, S. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Wiley: Hoboken, N. J., 2007, p 729.
- (37) Spörl, J. M.; Ota, A.; Beyer, R.; Lehr, T.; Müller, A.; Hermanutz, F.; Buchmeiser, M. R. *Journal of Polymer Science Part A: Polymer Chemistry* **2014**, 52, 1322.
- (38) Iovleva, M.; Smirnova, V.; Budnitskii, G. *Fibre Chemistry* **2001**, 33, 262.
- (39) Eom, Y.; Kim, B. C. *Polymer* **2014**, 55, 2570.
- (40) Goldfein, M.; Kozhevnikov, N.; Rafikov, E.; Stepukhovich, A.; Kosyreva, R. *Polymer Science USSR* **1975**, 17, 2630.
- (41) Huang, X. *Materials* **2009**, 2, 2369.
- (42) Yamazaki, H.; Miyazaki, Y.; Kamide, K. *Polymer Journal* **1991**, 23, 765.
- (43) Minagwa, M.; Yamada, H.; Yamaguchi, K.; Yoshi, F. *Macromolecules* **1992**, 25, 503.

- (44) Minagwa, M.; Nouchi, K.; Tozuka, M.; Chujo, R.; Yoshi, F. *Journal of Polymer Science Part A: Polymer Chemistry* **1995**, 33, 665.
- (45) Minagwa, M.; Okada, Y.; Nouchi, K.; Sato, Y.; Yoshi, F. *Colloid and Polymer Science* **2000**, 278, 757.
- (46) Zou, J.-T.; Wang, Y.-S.; Pang, W.-M.; Shi, L.; Lu, F. *Macromolecules* **2013**, 46, 1765.
- (47) Sui, K.; Gu, L. *Journal of Applied Polymer Science* **2003**, 89, 1753.
- (48) Boguslavsky, L.; Baruch, S.; Margel, S. *Journal of colloid and interface science* **2005**, 289, 71.
- (49) Cho, D. W.; Oh, K. S.; Bae, W.; Kim, H.; Lee, Y.-W. *Colloid and Polymer Science* **2008**, 287, 179.
- (50) Sui, K.; Liang, H.; Zhao, X.; Ma, Y.; Zhang, Y.; Xia, Y. *Macromolecular Chemistry and Physics* **2012**, 213, 1717.
- (51) Das, S.; Oyola, Y.; Mayes, R. T.; Janke, C. J.; Kuo, L. J.; Gill, G.; Wood, J. R.; Dai, S. *Industrial & Engineering Chemistry Research* **2015**.
- (52) Kuo, L.-J.; Janke, C. J.; Wood, J. R.; Strivens, J. E.; Das, S.; Oyola, Y.; Mayes, R. T.; Gill, G. A. *Industrial & Engineering Chemistry Research* **2015**.
- (53) Khisti, R. S.; Sivaram, S.; Dhal, P. K. *Macromolecules* **1994**, 27, 2883.
- (54) Jiang, Y.; Zhang, H.; Du, L.; Zhang, K.; Wang, J. *Journal of Applied Polymer Science* **2007**, 106, 28.
- (55) Cao, C. a.; Zhuang, X.; Su, Y.; Zhang, Y.; Zhang, F.; Wu, D.; Fengb, X. *Polym. Chem.* **2014**, 5, 2057.
- (56) Shirai, H.; Nagatomo, Y.; Inaki, Y.; Takemoto, K. *Journal of Macromolecular Science: Part A - Chemistry* **1974**, 8, 935.
- (57) Saegusa, T.; Horiguchi, S.; Tsuda, T. *Macromolecules* **1975**, 8, 112.
- (58) Siemeling, U.; Kölling, L.; Stammmler, A.; Stammmler, H.-G.; Kaminski, E.; Fink, G. *Chemical Communications* **2000**, 1177.
- (59) Shono, T.; Mori, M.; Shinra, K. *Journal of Polymer Science Part A-1* **1970**, 8, 1981.
- (60) Tsuchihara, K.; Suzuki, Y.; Asai, M.; Soga, K. *Chemistry Letters* **1999**, 891.
- (61) Nakano, Y.; Hisatani, K. *Polymer International* **1994**, 35, 249.
- (62) Sivaram, S.; Dhal, P. K.; Kashikar, S. P.; Khisti, R. S.; Shinde, B. M.; Baskaran, D. *Macromolecules* **1991**, 24, 1697.
- (63) Schapen, F.; Foley, S. R.; Jordan, R. F. *Journal of the American Chemical Society* **2004**, 126, 2114.
- (64) Terán, N.; Estrada, M. R.; Ogawa, T. *Journal of Macromolecular Science, Part A* **2005**, 42, 1679.
- (65) Ono, H.; Hisatani, K.; Kamide, K. *Polymer Journal* **1993**, 25, 245.
- (66) *Controlled radical polymerization*, ACS Symp. Ser.; Matyjaszewski, K., Ed.; American Chemistry Society: Washington, D.C., 1998; Vol. 685.
- (67) Matyjaszewski, K.; Davis, T. P. *Handbook of radical polymerization*; John Wiley & Sons: Hoboken, 2003.
- (68) *Progress in Controlled Radical Polymerization: Mechanisms and Techniques* *Controlled Radical Polymerization: State-of-the-Art in 2011*; Matyjaszewski, K., Ed.; American Chemistry Society: Washington, D.C., 2012; Vol. 1100.

- (69) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.
- (70) Wang, J.; Matyjaszewski, K. *Journal of the American Chemical Society* **1995**, *117*, 5614.
- (71) Ouchi, M.; Terashima, T.; Sawamoto, M. *Chemical Reviews* **2009**, *109*, 4963.
- (72) Matyjaszewski, K. *Macromolecules* **2012**, *45*, 4015.
- (73) Golas, P. L.; Mueller, L. A.; Coote, M. L.; Matyjaszewski, K. In *Encyclopedia of Polymer Science and Technology*; 4 ed.; Mark, H. F., Ed.; John Wiley and Sons, Inc.: 2014; Vol. 1, p 720.
- (74) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffery, J.; Le, T. P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559.
- (75) Chiefari, J.; Mayadunne, R. T. A.; Moad, C. L.; Moad, G.; Rizzardo, E.; Postma, A.; Skidmore, M. A.; Thang, S. H. *Macromolecules* **2003**, *36*, 2273.
- (76) Chong, Y. K.; Krstina, J.; Le, T. P. T.; Moad, G.; Postma, A.; Rizzardo, E.; Thang, S. H. *Macromolecules* **2003**, *36*, 2256.
- (77) Hawker, C. J. *Accounts of Chemical Research* **1997**, *30*, 373.
- (78) Benoit, D.; Chaplinski, V.; Braslau, R.; Hawker, C. J. *Journal of the American Chemical Society* **1999**, *121*, 3904.
- (79) Patten, T. E.; Matyjaszewski, K. *Advance Materials* **1998**, *10*, 900.
- (80) Coessens, V.; Pintauer, T.; Matyjaszewski, K. *Progress in Polymer Science* **2001**, *26*, 337.
- (81) Kranz, D.; Baumann, H.; Pohl, H. U. *Angew. Makromol. Chem.* **1972**, *26*, 67.
- (82) Mori, S. *Analytical Chemistry* **1983**, *55*, 2414.
- (83) Dong, H.; Tang, W.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 2974.
- (84) Pan, X.; Lamson, M.; Yan, J.; Matyjaszewski, K. *ACS Macro Letters* **2015**, *4*, 192.
- (85) Matyjaszewski, K.; Jo, S. M.; Paik, H.; Gaynor, S. G. *Macromolecules* **1997**, *30*, 6398.
- (86) Matyjaszewski, K.; Jo, S. M.; Paik, H.; Shipp, D. A. *Macromolecules* **1999**, *32*, 6431.
- (87) Barbiou, B.; Percec, V. *Macromolecules* **2001**, *34*, 8626.
- (88) Brar, A. S.; Kaur, S. *Journal of Polymer Science Part A: Polymer Chemistry* **2005**, *43*, 5906.
- (89) Lazzari, M.; Chiantore, O.; Mendichi, R.; López-Quintela, M. A. *Macromolecular Chemistry and Physics* **2005**, *206*, 1382.
- (90) Hou, C.; Ji, C.; Wang, C.; Qu, R. *Journal of Polymer Science Part A: Polymer Chemistry* **2006**, *44*, 226.
- (91) Hou, C.; Liu, J.; Wang, C. *Polymer International* **2006**, *55*, 171.
- (92) Hou, C.; Qu, R.; Liu, J.; Guo, Z.; Wang, C.; Ji, C.; Sun, C.; Wang, C. *Polymer* **2006**, *47*, 1505.
- (93) Hou, C.; Qu, R.; Ji, C.; Wang, C.; Wang, C. *Polymer International* **2006**, *55*, 326.
- (94) Tang, C.; Kowalewski, T.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 1465.
- (95) Chen, H.; Liu, D.; Song, Y.; Qu, R.; Wang, C. *Polymers for Advanced Technologies* **2011**, *22*, 1513.

- (96) Yu, Y.-H.; Liu, X.-H.; Jia, D.; Cheng, B.-W.; Ren, Y.-L.; Zhang, F.-J.; Li, H.-N.; Chen, P.; Xie, S. *Journal of Polymer Science Part A: Polymer Chemistry* **2013**, *51*, 1690.
- (97) Liu, X.-h.; Wang, J.; Zhang, F.-j.; An, S.-l.; Ren, Y.-l.; Yu, Y.-h.; Chen, P.; Xie, S. *Journal of Polymer Science Part A: Polymer Chemistry* **2012**, *50*, 4358.
- (98) Liu, X.-h.; Wang, J.; Yang, J.-s.; An, S.-l.; Ren, Y.-l.; Yu, Y.-h.; Chen, P. *Journal of Polymer Science Part A: Polymer Chemistry* **2012**, *50*, 1933.
- (99) Yu, Y.-H.; Liu, X.-H.; Jia, D.; Cheng, B.-W.; Zhang, F.-J.; Li, H.-N.; Chen, P.; Xie, S. *Journal of Polymer Science Part A: Polymer Chemistry* **2013**, *51*, 1468.
- (100) Chen, Q.; Zhang, Z.; Zhou, N.; Cheng, C.; Tu, Y.; Zhu, Y. *Journal of Polymer Science Part A: Polymer Chemistry* **2011**, *49*, 1183.
- (101) Liu, X.-H.; Zhang, G.-B.; Li, B.-X.; Bai, Y.-G.; Li, Y.-S. *Journal of Polymer Science Part A: Polymer Chemistry* **2010**, *48*, 5439.
- (102) Konkolewicz, D.; Wang, Y.; Krys, P.; Zhong, M.; Isse, A. A.; Gennaro, A.; Matyjaszewski, K. *Polymer Chemistry* **2014**, *5*, 4409.
- (103) Treat, N. J.; Sprafke, H.; Kramer, J. W.; Clark, P. G.; Barton, B. E.; Read de Alaniz, J.; Fors, B. P.; Hawker, C. J. *Journal of the American Chemical Society* **2014**, *136*, 16096.
- (104) Tang, C.; Kowalewski, T.; Matyjaszewski, K. *Macromolecules* **2003**, *36*, 8587.
- (105) An, Q.; Qian, J.; Yu, L.; Luo, Y.; Liu, X. *Journal of Polymer Science Part A: Polymer Chemistry* **2005**, *43*, 1973.
- (106) Liu, X.-H.; Zhang, G.-B.; Lu, X.-F.; Liu, J.-Y.; Pan, D.; Li, Y.-S. *Journal of Polymer Science Part A: Polymer Chemistry* **2006**, *44*, 490.
- (107) Liu, X.-H.; Li, Y.-G.; Lin, Y.; Li, Y.-S. *Journal of Polymer Science Part A: Polymer Chemistry* **2007**, *45*, 1272.
- (108) Liu, X.-h.; Zhang, G.-b.; Li, B.-x.; Bai, Y.-g.; Pan, D.; Li, Y.-s. *European Polymer Journal* **2008**, *44*, 1200.
- (109) Niu, S.; Zhang, L.; Zhu, J.; Zhang, W.; Cheng, Z.; Zhu, X. *Journal of Polymer Science Part A: Polymer Chemistry* **2013**, *51*, 1197.
- (110) Moskowitz, J. D.; Abel, B. A.; McCormick, C. L.; Wiggins, J. S. *Journal of Polymer Science Part A: Polymer Chemistry* **2016**, *54*, 553.
- (111) Kaim, A.; Megiel, E. *Journal of Polymer Science Part A: Polymer Chemistry* **2006**, *44*, 914.
- (112) Acar, M. H.; Matyjaszewski, K. *Macromolecular Chemistry and Physics* **1999**, *200*, 1094.
- (113) Chong, B. Y. K.; Ercole, F.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1999**, *32*, 6895.
- (114) Baumann, M.; Schmidt-Naake, G. *Macromolecular Chemistry and Physics* **2001**, *202*, 2727.
- (115) Taube, C.; Schmidt-Naake, G. *Chem. Eng. Technol.* **2001**, *10*, 1013.
- (116) Tsarevsky, N. V.; Sarbu, T.; Gobelt, B.; Matyjaszewski, K. *Macromolecules* **2002**, *35*, 6142.
- (117) Consolante, V.; Maric, M.; Penlidis, A. *Journal of Applied Polymer Science* **2012**, *125*, 3963.
- (118) Wang, G.-X.; Lu, M.; Hou, Z.-H.; Wu, H. *Journal of Polymer Research* **2013**, *20*.
- (119) Brar, A. S.; Saini, T. *Journal of Polymer Science Part A: Polymer Chemistry* **2006**, *44*, 1975.

- (120) Niu, S.; Ding, M.; Chen, M.; Feng, T.; Zhang, L.; Wei, L.; Cheng, Z.; Zhu, X. *Journal of Polymer Science Part A: Polymer Chemistry* **2013**, *51*, 5263.
- (121) Nguyen-Thai, N. U.; Hong, S. C. *Carbon* **2014**, *69*, 571.
- (122) Chernikova, E. V.; Poteryaeva, Z. A.; Plutalova, A. V. *Polymer Science Series B* **2014**, *56*, 109.
- (123) Chernikova, E. V.; Kishilov, S. M.; Plutalova, A. V.; Kostina, Y. V.; Bondarenko, G. N.; Baskakov, A. A.; Il'in, S. O.; Nikolaev, A. Y. *Polymer Science Series B* **2014**, *56*, 553.
- (124) Kaiser, A.; Brandau, S.; Klimpel, M.; Barner-Kowollik, C. *Macromolecular rapid communications* **2010**, *31*, 1616.
- (125) Dürr, C. J.; Emmerling, S. G. J.; Kaiser, A.; Brandau, S.; Habicht, A. K. T.; Klimpel, M.; Barner-Kowollik, C. *Journal of Polymer Science Part A: Polymer Chemistry* **2012**, *50*, 174.
- (126) Dürr, C. J.; Hlalele, L.; Kaiser, A.; Brandau, S.; Barner-Kowollik, C. *Macromolecules* **2013**, *46*, 49.
- (127) Nicolas, J.; Guillaneuf, Y.; Lefay, C.; Bertin, D.; Gigmes, D.; Charleux, B. *Progress in Polymer Science* **2013**, *38*, 63.
- (128) Keddie, D. J. *Chemical Society reviews* **2014**, *43*, 496.
- (129) Matyjaszewski, K.; Xia, J. *Chemical Reviews* **2001**, *101*, 2921.
- (130) Matyjaszewski, K.; Shipp, D. A.; McMurtry, G. P.; Gaynor, S. G.; Pakula, T. *Journal of Polymer Science Part A: Polymer Chemistry* **2000**, *38*, 2023.
- (131) Matyjaszewski, K.; Shipp, D. A.; Wang, J.; Grimaud, T.; Patten, T. E. *Macromolecules* **1998**, *31*, 6836.
- (132) Shipp, D. A.; Wang, J.; Matyjaszewski, K. *Macromolecules* **1998**, *31*, 8005.
- (133) Peng, C.-H.; Kong, J.; Seeliger, F.; Matyjaszewski, K. *Macromolecules* **2011**, *44*, 7546.
- (134) Alipour, M.; Massoumi, B.; Safa, K. D.; Entezami, A. *Iranian Polymer Journal* **2001**, *10*, 99.
- (135) Lin, Y.; Wang, X.; Qian, G.; Watkins, J. J. *Chemistry of Materials* **2014**, *26*, 2128.
- (136) Brar, A. S.; Saini, T. *European Polymer Journal* **2007**, *43*, 1046.
- (137) Nguyen, C. T.; Kim, D.-P. *Journal of Materials Chemistry* **2011**, *21*, 14226.
- (138) Yan, K.; Kong, L.-B.; Dai, Y.-H.; Shi, M.; Shen, K.-W.; Hu, B.; Luob, Y.-C.; Kangb, L. *Journal of Materials Chemistry A* **2015**, *3*, 22781.
- (139) Yan, K.; Kong, L.-B.; Shen, K.-W.; Dai, Y.-H.; Shi, M.; Hu, B.; Luo, Y.-C.; Kang, L. *Applied Surface Science* **2016**, *364*, 850.
- (140) Aqil, A.; Detrembleur, C.; Gilbert, B.; Jerome, R.; Jerome, C. *Chemistry of Materials* **2007**, *19*, 2150.
- (141) Oschmann, B.; Tahir, M. N.; Mueller, F.; Bresser, D.; Lieberwirth, I.; Tremel, W.; Passerini, S.; Zentel, R. *Macromolecular rapid communications* **2015**, *36*, 1075.
- (142) Kruk, M.; Dufour, B.; Celer, E. B.; Kowalewski, T.; Jaroniec, M.; Matyjaszewski, K. *Chemistry of Materials* **2006**, *18*, 1417.
- (143) Ho, R.; Wang, T.; Lin, C.; Yu, T. *Macromolecules* **2007**, *40*, 2814.
- (144) Yu, T.-L.; Huang, B.-H.; Hung, W.-C.; Lin, C.-C.; Wang, T.-C.; Ho, R.-M. *Polymer* **2007**, *48*, 4401.

- (145) Stefik, M.; Sai, H.; Sauer, K.; Gruner, S. M.; DiSalvo, F. J.; Wiesner, U. *Macromolecules* **2009**, *42*, 6682.
- (146) Kim, J. S.; Jeon, H. J.; Lee, K. M.; Im, J. N.; Youk, J. H. *Fibers and Polymers* **2010**, *11*, 153.
- (147) Yue, Z.; Wang, D. X.; Liu, J. Q.; Zhang, J.; Feng, S. Y. *Chinese Chemical Letters* **2012**, *23*, 989.
- (148) Ajioka, N.; Yokoyama, A.; Yokozawa, T. *Macromolecular rapid communications* **2008**, *29*, 665.
- (149) Pitto, V.; Voit, B. I.; Loontjens, T. J. A.; van Benthem, R. A. T. M. *Macromolecular Chemistry and Physics* **2004**, *205*, 2346.
- (150) Dufour, B.; Tang, C.; Koynov, K.; Zhang, Y.; Pakula, T.; Matyjaszewski, K. *Macromolecules* **2008**, *41*, 2451.
- (151) Zhang, X.; Tay, S. W.; Liu, Z.; Hong, L. *Journal of Membrane Science* **2009**, *329*, 228.
- (152) Tang, C.; Dufour, B.; Kowalewski, T.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 6199.
- (153) Tang, C.; Bombalski, L.; Kruk, M.; Jaroniec, M.; Matyjaszewski, K.; Kowalewski, T. *Advanced materials* **2008**, *20*, 1516.
- (154) Niu, S.; Zhang, L.; Wang, N.; Zhu, J.; Zhang, W.; Cheng, Z.; Zhu, X. *Reactive and Functional Polymers* **2013**, *73*, 1447.
- (155) Wu, D.; Li, Z.; Zhong, M.; Kowalewski, T.; Matyjaszewski, K. *Angewandte Chemie* **2014**, *53*, 3957.
- (156) Wan, L.; Lei, H.; Ding, Y.; Fu, L.; Li, J.; Xu, Z. *Journal of Polymer Science Part A: Polymer Chemistry* **2008**, *46*, 92.
- (157) Chen, Y.; He, M.; Wang, C.; Wei, Y. *Journal of Materials Chemistry A* **2014**, *2*, 10444.
- (158) Yue, Y.; Zhang, C.; Tang, Q.; Mayes, R. T.; Liao, W.-P.; Liao, C.; Tsouris, C.; Stankovich, J. J.; Chen, J.; Hensley, D. K.; Abney, C. W.; Jiang, D.-e.; Brown, S.; Dai, S. *Industrial & Engineering Chemistry Research* **2015**.
- (159) Yue, Y.; Mayes, R. T.; Kim, J.; Fulvio, P. F.; Sun, X. G.; Tsouris, C.; Chen, J.; Brown, S.; Dai, S. *Angewandte Chemie* **2013**, *52*, 13458.
- (160) Brown, S.; Yue, Y.; Kuo, L.-J.; Mehio, N.; Li, M.; Gill, G.; Tsouris, C.; Mayes, R. T.; Saito, T.; Dai, S. *Industrial & Engineering Chemistry Research* **2016**.
- (161) Liu, X.-H.; Zhang, G.-B.; Li, B.-X.; Bai, Y.-G. *Journal of Applied Polymer Science* **2009**, *114*, 663.
- (162) Frank, E.; Steudle, L. M.; Ingildeev, D.; Spörl, J. M.; Buchmeiser, M. R. *Angewandte Chemie* **2014**, *53*, 5262.
- (163) Zhong, M.; Jiang, S.; Tang, Y.; Gottlieb, E.; Kim, E. K.; Star, A.; Matyjaszewski, K.; Kowalewski, T. *Chemical Science* **2014**, *5*, 3315.
- (164) Kruk, M.; Tang, C.; Dufour, B.; Matyjaszewski, K.; Kowalewski, T. *Nanostructured Carbons from Block Copolymers*; Wiley: Weinheim, Germany, 2006.
- (165) McGann, J. P.; Zhong, M.; Kim, E. K.; Natesakhawat, S.; Jaroniec, M.; Whitacre, J. F.; Matyjaszewski, K.; Kowalewski, T. *Macromolecular Chemistry and Physics* **2012**, *213*, 1078.
- (166) Jang, J.; Lim, B.; Choi, M. *Chem Commun (Camb)* **2005**, 4214.
- (167) Lu, A.; Kiefer, A.; Schmidt, W.; Schuth, F. *Chemistry of Materials* **2004**, *16*, 100.

- (168) Kruk, M.; Dufour, B.; Celer, E. B.; Kowalewski, T.; Jaroniec, M.; Matyjaszewski, K. *Journal of Physical Chemistry C* **2005**, *109*, 9216.
- (169) Kruk, M.; Kohlhaas, K. M.; Dufour, B.; Celer, E. B.; Jaroniec, M.; Matyjaszewski, K.; Ruoff, R. S.; Kowalewski, T. *Microporous and Mesoporous Materials* **2007**, *102*, 178.
- (170) Kruk, M.; Dufour, B.; Celer, E. B.; Kowalewski, T.; Jaroniec, M.; Matyjaszewski, K. *Macromolecules* **2008**, *41*, 8584.
- (171) Cao, L.; Kruk, M. *Polymer* **2015**, *72*, 356.
- (172) Chang, Y.; Hong, F.; Liu, J.; Xie, M.; Zhang, Q.; He, C.; Niu, H.; Liu, J. *Carbon* **2015**, *87*, 424.
- (173) Liu, Y.; Zhao, X.; Chauhan, G. S.; Ahn, J.-H. *Applied Surface Science* **2016**.
- (174) Yang, X.; Wu, D.; Chen, X.; Fu, R. *Journal of Physical Chemistry C* **2010**, *114*, 8581.
- (175) Jang, J.; Bae, J. *Angewandte Chemie* **2004**, *43*, 3803.
- (176) Fernández-Saavedra, R.; Aranda, P.; Ruiz-Hitzky, E. *Advanced Functional Materials* **2004**, *14*, 77.
- (177) Huang, S.; Shimizu, T.; Sakaue, H.; Shingubara, S.; Takahagi, T. *Japanese Journal of Applied Physics* **2005**, *44*, 5289.
- (178) Huang, K.; Yao, Y.; Yang, X.; Chen, Z.; Li, M. *Materials Chemistry and Physics* **2016**, *169*, 1.
- (179) Huang, K.; Li, M.; Chen, Z.; Yao, Y.; Yang, X. *Electrochimica Acta* **2015**, *158*, 306.
- (180) Tran, C.; Kalra, V. *Journal of Power Sources* **2013**, *235*, 289.
- (181) Kim, B.-H.; Yang, K. S.; Ferraris, J. P. *Electrochimica Acta* **2012**, *75*, 325.
- (182) Roberts, A. D.; Wang, S.; Zhang, X. *Journal of Materials Chemistry A* **2014**, *2*, 17787.
- (183) Ryu, S.; Lee, C.; Park, J.; Lee, J. S.; Kang, S.; Seo, Y. D.; Jang, J.; Kim, B. S. *Angewandte Chemie* **2014**, *53*, 9213.
- (184) Yan, X.; Yu, Y.; Ryu, S.-K.; Lan, J.; Jia, X.; Yang, X. *Electrochimica Acta* **2014**, *136*, 466.
- (185) Zhong, M.; Kim, E. K.; McGann, J. P.; Chun, S. E.; Whitacre, J. F.; Jaroniec, M.; Matyjaszewski, K.; Kowalewski, T. *Journal of the American Chemical Society* **2012**, *134*, 14846.
- (186) Tang, C.; Qi, K.; Wooley, K. L.; Matyjaszewski, K.; Kowalewski, T. *Angewandte Chemie* **2004**, *43*, 2783.
- (187) Belanger, J. M.; Penelle, J.; Russel, T. P. *Macromolecules* **2006**, *39*, 1766.
- (188) Lazzari, M.; Scalarone, D.; Hoppe, C. E.; Vazquez-Vazquez, C.; Lopez-Quintela, M. A. *Chemistry of Materials* **2007**, *19*, 5818.
- (189) Lazzari, M.; Scalarone, D.; Vazquez-Vazquez, C.; López-Quintela, M. A. *Macromolecular rapid communications* **2008**, *29*, 352.
- (190) Kashiwagi, T.; Hirata, T.; Brown, J. E. *Macromolecules* **1985**, *18*, 131.
- (191) Rahaman, M. S. A.; Ismail, A. F.; Mustafa, A. *Polymer Degradation and Stability* **2007**, *92*, 1421.
- (192) Tang, C.; Tracz, A.; Kruk, M.; Zhang, R.; Smilgies, D.; Matyjaszewski, K.; Kowalewski, T. *Journal of the American Chemical Society* **2005**, *127*, 6918.

- (193) Thomassin, J.-M.; Debuigne, A.; Jérôme, C.; Detrembleur, C. *Polymer* **2010**, *51*, 2965.
- (194) Chen, J. T.; Shin, K.; Leiston-Belanger, J. M.; Zhang, M.; Russell, T. P. *Advanced Functional Materials* **2006**, *16*, 1476.
- (195) Yang, Y.; Wang, J.; Wu, F.; Ye, G.; Yi, R.; Lu, Y.; Chen, J. *Polym. Chem.* **2016**, *7*, 2427.
- (196) Zhong, M.; Natesakhawat, S.; Baltrus, J. P.; Luebke, D.; Nulwala, H.; Matyjaszewski, K.; Kowalewski, T. *Chemical communications* **2012**, *48*, 11516.
- (197) Wu, Z.; Iqbal, Z.; Wang, X. *Frontiers of Chemical Science and Engineering* **2015**, *9*, 280.
- (198) Guo, D.; Shibuy, R.; Akiba, C.; Saji, S.; Kondo, T.; Nakamura, J. *Science* **2016**, *351*, 361.
- (199) Lim, K.; Ju, M. J.; Song, J.; Choi, I. T.; Do, K.; Choi, H.; Song, K.; Kim, H. K.; Ko, J. *ChemSusChem* **2013**, *6*, 1425.
- (200) Ju, M. J.; Choi, I. T.; Zhong, M.; Lim, K.; Ko, J.; Mohin, J.; Lamson, M.; Kowalewski, T.; Matyjaszewski, K.; Kim, H. K. *Journal of Materials Chemistry A* **2015**, *3*, 4413.
- (201) Wei, S.; Ma, L.; Hendrickson, K. E.; Tu, Z.; Archer, L. A. *Journal of the American Chemical Society* **2015**, *137*, 12143.
- (202) Cameron, N. R. *Polymer* **2005**, *46*, 1439.
- (203) Kimmins, S. D.; Cameron, N. R. *Advanced Functional Materials* **2011**, *21*, 211.
- (204) Pulko, I.; Krajnc, P. *Macromolecular rapid communications* **2012**, *33*, 1731.
- (205) Silverstein, M. S. *Polymer* **2014**, *55*, 304.
- (206) Silverstein, M. S. *Progress in Polymer Science* **2014**, *39*, 199.
- (207) Lissant, K. J. *Journal of Colloidal and Interfacial Science* **1966**, *22*, 462.
- (208) Silverstein, M. S.; Cameron, N. R. In *Encyclopedia of Science and Technology*; 4 ed.; Wiley: Hoboken, N.J., 2010.
- (209) Cameron, N. R.; Krajnc, P.; Silverstein, M. S. *Colloidal Templating*; Wiley: Hoboken, N.J., 2011; Vol. 4.
- (210) Huš, S.; Krajnc, P. *Polymer* **2014**, *55*, 4420.
- (211) Gurevitch, I.; Silverstein, M. S. *Macromolecules* **2011**, *44*, 3398.
- (212) Anderson, K. L.; Nazarov, W.; Musgrave, C. S. A.; Bazin, N.; Faith, D. *Journal of Radioanalytical and Nuclear Chemistry* **2013**, *299*, 969.
- (213) Luo, Y.; Wang, A.-N.; Gao, X. *Soft Matter* **2012**, *8*, 7547.
- (214) Luo, Y.; Wang, A.-N.; Gao, X. *Soft Matter* **2012**, *8*, 1824.
- (215) Khodabandeh, A.; Arrua, R. D.; Desire, C. T.; Rodemann, T.; Bon, S. A. F.; Thickett, S. C.; Hilder, E. F. *Polymer Chemistry* **2016**, *7*, 1803.
- (216) Caldwell, S.; Johnson, D. W.; Didsbury, M. P.; Murray, B. A.; Wu, J. J.; Przyborski, S. A.; Cameron, N. R. *Soft Matter* **2012**, *8*, 10344.
- (217) Johnson, D. W.; Langford, C. R.; Didsbury, M. P.; Lipp, B.; Przyborski, S. A.; Cameron, N. R. *Polym. Chem.* **2015**, *6*, 7256.
- (218) Lovelady, E.; Kimmins, S. D.; Wu, J.; Cameron, N. R. *Polym. Chem.* **2011**, *2*, 559.
- (219) Sergent, B.; Birot, M.; Deleuze, H. *Reactive and Functional Polymers* **2012**, *72*, 962.
- (220) Kovačič, S.; Jeřábek, K.; Krajnc, P.; Slugovc, C. *Polym. Chem.* **2012**, *3*, 325.

- (221) Kovačič, S.; Matsko, N. B.; Jerabek, K.; Krajnc, P.; Slugovc, C. *J. Mater. Chem. A* **2013**, *1*, 487.
- (222) Mert, E. H. *Express Polymer Letters* **2015**, *9*, 344.
- (223) Kovačič, S.; Preishuber-Pflugl, F.; Pahovnik, D.; Zagar, E.; Slugovc, C. *Chem Commun (Camb)* **2015**, *51*, 7725.
- (224) Audouin, F.; Birot, M.; Pasquinet, E.; Deleuze, H.; Besnard, O.; Poullain, D. *Journal of Applied Polymer Science* **2008**, *108*, 2808.
- (225) David, D.; Silverstein, M. S. *Journal of Polymer Science Part A: Polymer Chemistry* **2009**, *47*, 5806.
- (226) Gu, R.; Konar, S.; Sain, M. *Journal of the American Oil Chemists' Society* **2012**, *89*, 2103.
- (227) Singhal, P.; Rodriguez, J. N.; Small, W.; Eagleston, S.; Van de Water, J.; Maitland, D. J.; Wilson, T. S. *Journal of polymer science. Part B, Polymer physics* **2012**, *50*, 724.
- (228) Sherrington, D. C.; Kirkintilloch, S.; Small, P. W.; Unilever Patent Holdings BV: 1990; Vol. US 4965289.
- (229) Lindsay, J. D.; Ko, Y. C.; Kimberly-Clark Worldwide, Inc: 2006; Vol. US 7053131.
- (230) Malone, B. A.; Mork, S. W.; The DowChemical Company: 2001; Vol. US 6299808.
- (231) Lepizzera, S.; Pith, T.; Arkema: 2006; Vol. FR 04 2876290
- (232) Soo, P. P.; Clear, S. C.; Sura, R. K.; Parthasarathy, R. V.; Innovative Properties Company: 2004; Vol. US 204510.
- (233) LaVon, G. D.; Young, G. A.; Taylor, G. W.; The Procter & GambleCompany: 1992; Vol. US 5147345.
- (234) Cohen, N.; Silverstein, M. S. *Polymer* **2011**, *52*, 282.
- (235) Israel, S.; Gurevitch, I.; Silverstein, M. S. *Polymer* **2015**, *72*, 453.
- (236) Ma, Y.; Asfaw, H. D.; Edström, K. *Chemistry of Materials* **2015**, *27*, 3957.
- (237) Cooper, A. I.; Bray, C. L.; Su, F.; Carter, B. O.; Wang, W.; Adams, D. J.; Ulive Enterprises Limited, UK,: 2009; Vol. WO 2009 068912.
- (238) Jonschker, G.; Koch, M.; Pahnke, J.; Schwab, M.; Merck Patent GmbH,Germany: 2009; Vol. WO 2009 095153.
- (239) Gurevitch, I.; Silverstein, M. S. *Macromolecules* **2012**, *45*, 6450.
- (240) Tebboth, M.; Kogelbauer, A.; Bismarck, A. *Industrial & Engineering Chemistry Research* **2015**, *54*, 7284.
- (241) Schofield, W. C. E.; Bain, C. D.; Badyal, J. P. S. *Chemistry of Materials* **2012**, *24*, 1645.
- (242) He, H.; Li, W.; Lamson, M.; Zhong, M.; Konkolewicz, D.; Hui, C. M.; Yaccato, K.; Rappold, T.; Sugar, G.; David, N. E.; Damodaran, K.; Natesakhawat, S.; Nulwala, H.; Matyjaszewski, K. *Polymer* **2014**, *55*, 385.
- (243) Liu, H.; Wan, D.; Du, J.; Jin, M. *ACS applied materials & interfaces* **2015**, *7*, 20885.
- (244) Ye, Y.; Jin, M.; Wan, D. *Journal of Materials Chemistry Part A* **2015**, *3*, 13519.
- (245) Gurevitch, I.; Silverstein, M. S. *Soft Matter* **2012**, *8*, 10378.
- (246) Zou, S.; Wei, Z.; Hu, Y.; Deng, Y.; Tong, Z.; Wang, C. *Polymer Chemistry* **2014**, *5*, 4227.

- (247) Hayward, A. S.; Eissa, A. M.; Maltman, D. J.; Sano, N.; Przyborski, S. A.; Cameron, N. R. *Biomacromolecules* **2013**, *14*, 4271.
- (248) Viswanathan, P.; Ondeck, M. G.; Chirasatitsin, S.; Ngamkham, K.; Reilly, G. C.; Engler, A. J.; Battaglia, G. *Biomaterials* **2015**, *52*, 140.
- (249) Moglia, R. S.; Holm, J. L.; Sears, N. A.; Wilson, C. J.; Harrison, D. M.; Cosgriff-Hernandez, E. *Biomacromolecules* **2011**, *12*, 3621.
- (250) Moglia, R.; Whitely, M.; Brooks, M.; Robinson, J.; Pishko, M.; Cosgriff-Hernandez, E. *Macromolecular rapid communications* **2014**, *35*, 1301.
- (251) Moglia, R. S.; Robinson, J. L.; Muschenborn, A. D.; Touchet, T. J.; Maitland, D. J.; Cosgriff-Hernandez, E. *Polymer (Guildf)* **2014**, *56*, 426.
- (252) Moglia, R. S.; Whitely, M.; Dhavalikar, P.; Robinson, J.; Pearce, H.; Megan Brooks; Stuebben, M.; Cordner, N.; Cosgriff-Hernandez, E. *Biomacromolecules* **2014**, *15*, 2870.
- (253) Robinson, J. L.; Moglia, R. S.; Stuebben, M. C.; McEnery, M. A. P.; Cosgriff-Hernandez, E. *Tissue engineering. Part A* **2014**, *20*, 1103.
- (254) Lumelsky, Y.; Zoladan, J.; Levenberg, S.; Silverstein, M. S. *Macromolecules* **2008**, *41*, 1469.
- (255) Lumelsky, Y.; Lalush-Michael, I.; Levenberg, S.; Silverstein, M. S. *Journal of Polymer Science Part A: Polymer Chemistry* **2009**, *47*, 7043.
- (256) Lumelsky, Y.; Silverstein, M. S. *Macromolecules* **2009**, *42*, 1627.
- (257) Ikem, V. O.; Menner, A.; Horozov, T. S.; Bismarck, A. *Advanced materials* **2010**, *22*, 3588.
- (258) Wong, L. L. C.; Villafranca, P. M. B.; Menner, A.; Bismarck, A. *Langmuir : the ACS journal of surfaces and colloids* **2013**, *29*, 5952.
- (259) Youssef, C.; Backov, R.; Treguer, M.; Birot, M.; Deleuze, H. *Journal of Polymer Science Part A: Polymer Chemistry* **2010**, *48*, 2942.
- (260) Audouin, F.; Birot, M.; Pasquinet, E. r.; Besnard, O.; Palmas, P.; Poullain, D.; Deleuze, H. *Macromolecules* **2011**, *44*, 4879.
- (261) Wu, R.; Menner, A.; Bismarck, A. *Journal of Polymer Science Part A: Polymer Chemistry* **2010**, *48*, 1979.
- (262) Audouin, F.; Heise, A. *Polymer* **2014**, *55*, 403.
- (263) Li, T.; Liu, H.; Zeng, L.; Yang, S.; Li, Z.; Zhang, J.; Zhou, X. *Journal of Materials Chemistry* **2011**, *21*, 12865.
- (264) Ciria, F.; Berber, E.; Sen, S.; Mert, E. H. *Journal of Applied Polymer Science* **2015**, *132*, 41333.
- (265) Menner, A.; Salgueiro, M.; Shaffer, M. S. P.; Bismarck, A. *Journal of Polymer Science Part A: Polymer Chemistry* **2008**, *46*, 5708.
- (266) Normatov, J.; Silverstein, M. S. *Macromolecules* **2007**, *40*, 8329.
- (267) Normatov, J.; Silverstein, M. S. *Journal of Polymer Science Part A: Polymer Chemistry* **2008**, *46*, 2357.
- (268) Zhang, S.; Chen, J. *Chemical communications* **2009**, 2217.
- (269) Zhang, S.; Zhu, Y.; Hua, Y.; Jegat, C.; Chen, J.; Taha, M. *Polymer* **2011**, *52*, 4881.
- (270) Viswanathan, P.; Johnson, D. W.; Hurley, C.; Cameron, N. R.; Battaglia, G. *Macromolecules* **2014**, *47*, 7091.
- (271) Mathieu, K.; Jérôme, C.; Debuigne, A. *Macromolecules* **2015**, *48*, 6489.

- (272) Gurevitch, I.; Silverstein, M. S. *Journal of Polymer Science Part A: Polymer Chemistry* **2010**, 48, 1516.
- (273) Zheng, X.; Zhang, Y.; Wang, H.; Du, Q. *Macromolecules* **2014**, 47, 6847.
- (274) Xu, H.; Zheng, X.; Huang, Y.; Wang, H.; Du, Q. *Langmuir : the ACS journal of surfaces and colloids* **2016**, 32, 38.
- (275) Menner, A.; Verdejo, R.; Shaffer, M.; Bismarck, A. *Langmuir : the ACS journal of surfaces and colloids* **2007**, 23, 2398.
- (276) Zheng, Z.; Zheng, X.; Wang, H.; Du, Q. *ACS applied materials & interfaces* **2013**, 5, 7974.
- (277) Wong, L. L. C.; Barg, S.; Menner, A.; do Vale Pereira, P.; Eda, G.; Chowalla, M.; Saiz, E.; Bismarck, A. *Polymer* **2014**, 55, 395.
- (278) Hu, Y.; Huang, J.; Zhang, Q.; Yang, Y.; Ma, S.; Wang, C. *RSC Advances* **2015**, 5, 103394.
- (279) Yi, W.; Wu, H.; Wang, H.; Du, Q. *Langmuir : the ACS journal of surfaces and colloids* **2016**, 32, 982.
- (280) Vilchez, A.; Rodriguez-Abreu, C.; Esquena, J.; Menner, A.; Bismarck, A. *Langmuir : the ACS journal of surfaces and colloids* **2011**, 27, 13342.
- (281) Zhu, Y.; Zhang, S.; Hua, Y.; Chen, J.; Hu, C. P. *Polymer* **2010**, 51, 3612.
- (282) Ye, Y.; Wan, D.; Du, J.; Jin, M.; Pu, H. *Journal of Materials Chemistry A* **2015**, 3, 6297.
- (283) Xu, F.; Fang, Z.; Yang, D.; Gao, Y.; Li, H.; Chen, D. *ACS Appl Mater Interfaces* **2014**, 6, 6717.
- (284) Yi, F.; Xu, F.; Gao, Y.; Li, H.; Chen, D. *RSC Advances* **2015**, 5, 40227.
- (285) Chen, Q.; Cao, X.; Liu, H.; Zhou, W.; Qin, L.; An, Z. *Polymer Chemistry* **2013**, 4, 4092.
- (286) Chen, Q.; Deng, X.; An, Z. *Macromolecular rapid communications* **2014**, 35, 1148.
- (287) Chen, Q.; Xu, Y.; Cao, X.; Qin, L.; An, Z. *Polym. Chem.* **2014**, 5, 175.

Chapter 2

Synthesis of Block Copolymers Containing Polyacrylonitrile by ICAR ATRP and Metal Free ATRP

2.1 Preface

This chapter describes the development of conditions to polymerize acrylonitrile (AN) by ICAR ATRP and by metal free ATRP. Cu-catalyst loading, alkyl-halide initiator, amount of radical initiator, and solvent conditions were studied for ICAR ATRP of AN. Photocatalyst structure, initiator structure, light source intensity, and solvent conditions were studied for metal free ATRP. Well-defined polyacrylonitrile (PAN) was obtained by both methods and chain extended with *n*-butyl acrylate, styrene, or methyl methacrylate to confirm high chain-end functionality and good control of the polymerization. PAN and its block copolymers were characterized by GPC and ¹H NMR.

Work in this chapter was partially published in Lamson, M.; Epshtein-Assor, Y.; Silverstein, M. S.; Matyjaszewski, K. Synthesis of Degradable PolyHIPEs by AGET ATRP *Polymer* 2013, 54, 4480. Copyright © 2013 Elsevier

For this project I worked closely with Maciek Kopec, Hangjun Ding, and Dr. Mingjiang Zhong to develop the ICAR ATRP conditions for the polymerization of AN and to characterize these samples by GPC and ^1H NMR. Dr. Xiangcheng Pan and I worked to develop the conditions for metal free ATRP of AN and to characterize the resulting PAN by GPC and ^1H NMR. All investigations into the synthesis and characterization of PAN-*b*-PS were conducted on my own.

2.2 Introduction: ICAR and Metal-free ATRP

Polyacrylonitrile (PAN) exhibits excellent properties, resulting in utility in several important applications, including carbon fibers^{1,2} and mesoporous carbons.³ Commercial PAN is usually synthesized by conventional (free) radical polymerization (RP), in the presence of radical initiators, such as azobisisobutyronitrile (AIBN). PAN synthesized by RP typically has a high molecular weight ($\text{MW} > 150,000$), but there is little control over the MW and the molecular weight distribution (MWD). With the introduction of reversible-deactivation radical polymerization (RDRP) techniques, such as atom transfer radical polymerization (ATRP) and reversible-addition fragmentation transfer (RAFT) polymerization, PAN with predefined MW, narrow MWD, and complex architectures can be synthesized.⁴⁻⁸

ATRP was used to synthesize block copolymers (BCPs) containing PAN-segments, such as poly(*n*-butyl acrylate)-*block*-polyacrylonitrile (PBA-*b*-PAN)^{6,9} poly(*tert*-butyl acrylate)-*block*-polyacrylonitrile (PtBA-*b*-PAN),¹⁰ poly(ethylene oxide)-*block*-polyacrylonitrile (PEO-*b*-PAN),¹¹ poly(acrylic acid)-*block*-polyacrylonitrile (PAA-*b*-PAN),¹² and polyacrylonitrile-*block*-polystyrene (PAN-*b*-PS)¹³ diblock copolymers.

Also, more complex PAN architectures such as BCP stars,¹⁴ molecular brushes,¹⁵ inorganic hybrids,¹⁶ and core-shell structures with poly(methyl methacrylate) (PMMA) cross-linked cores and PAN shells¹⁷ were prepared. PBA-*b*-PAN BCPs, synthesized by ATRP, were utilized as precursors to create carbon arrays where the carbon structure reflected the morphology of the precursor BCP.⁹ Recently, this strategy was extended to the synthesis of electrochemically-active, nitrogen-enriched porous nanocarbons by pyrolysis of self-assembled PBA-*b*-PAN BCPs.^{18,19} These materials exhibit superior performance as electrode materials for supercapacitors,¹⁹ CO₂ sorbents,²⁰ electrocatalysts for the oxygen reduction reaction (ORR),²¹ and counter electrodes in dye-sensitized solar cells.²²

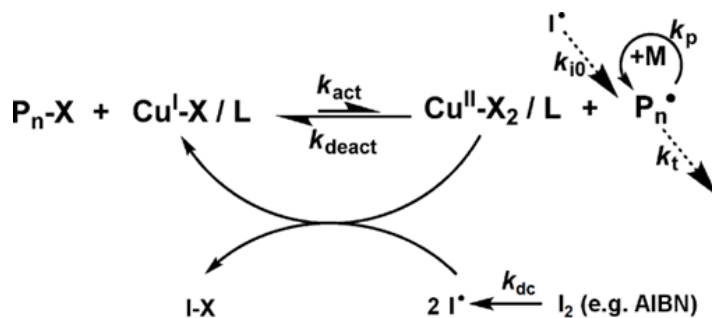
However all prior PBA-*b*-PAN BCPs were synthesized via normal ATRP, with high catalyst loadings (i.e., > 1,000 ppm). Consequently, a multistep purification process was required in order to reduce the residual copper catalysts in a BCP below 1 ppm.²¹ The possible influence of various residual metals (mostly Fe and Co) on N-doped carbons electrocatalytic activity has become a serious concern.^{23,24} Thus, there is a strong need for the development of synthetic methods that utilize small amounts of metal catalyst.

Procedures employing lower catalyst concentrations that were used for PAN synthesis, include activators regenerated by electron transfer (ARGET),²⁵⁻²⁷ initiators for continuous activator regeneration (ICAR),^{28,29} and supplemental activators and reducing agents (SARA) ATRP.³⁰⁻³² For example, the synthesis of PAN by ARGET ATRP resulted in high MW PAN ($M_n = 161,300$) with a narrow MWD ($M_w/M_n = 1.18$).²⁵ This was achieved with tin(II) 2-ethylhexanoate (Sn(EH)₂) or glucose as a reducing agent and with CuCl₂/tris[(2-pyridyl)methyl]amine (TPMA) catalyst loadings as low as 25 or 75

(ppm vs. monomer). However, when using BCP precursors for nitrogen-doped carbons in catalytic applications, it is not recommended to use ARGET ATRP with $\text{Sn}(\text{EH})_2$, as Cu and Sn could be introduced into the final carbon.

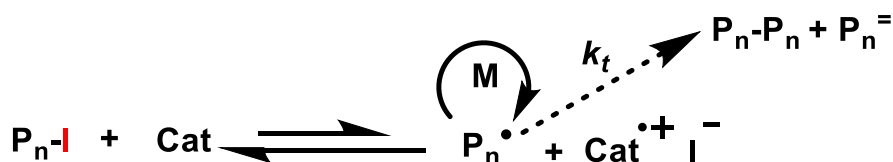
ICAR ATRP (Scheme 2.2.1), which utilizes conventional radical initiators, such as AIBN, to regenerate the Cu (I) activator species from the Cu(II) deactivator species to compensate for the loss of the activator species due to termination events, could provide a more suitable route.³³ Any remaining AIBN or by-products from its reduction of the CuBr_2 /ligand complex should not remain in the final carbon material after pyrolysis, making this technique a viable procedure to synthesize carbon precursors with lower concentrations of residual metals. ICAR ATRP of acrylonitrile (AN) with $\text{CuBr}_2/2$, 2'-bipyridine (bpy) as the catalyst, ethyl 2-bromoisobutyrate (EBiB) as the initiator and AIBN as the free radical initiator source, in DMSO at 70 °C was reported.²⁹ Well-defined, low MW PAN was obtained ($M_n = 4100$, $M_w/M_n = 1.07$), when 400 ppm of CuBr_2/bpy catalyst was used. At high radical initiator concentrations with 100 ppm of CuBr_2/bpy catalyst, 80% conversion was reached in 3 hours, but with a large discrepancy between theoretical and experimental MWs, due to the initiation of new polymer chains by AIBN.²⁸ Therefore, ICAR ATRP system was studied for the polymerization of PAN to determine the lowest catalyst loadings to synthesize well-define PAN.

Scheme 2.2.1. ICAR ATRP

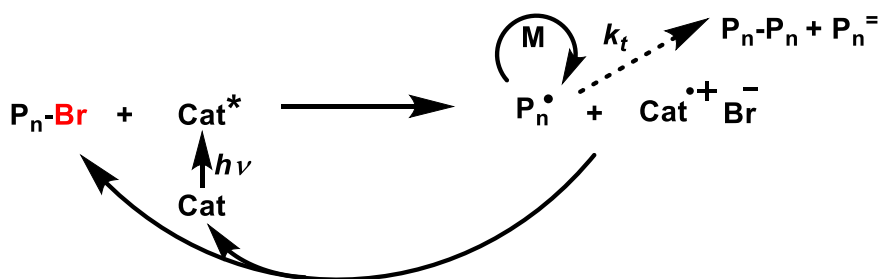


In all of these systems, the concentration of Cu catalyst can be reduced below 100 ppm, but the catalyst must be removed by dialysis, precipitation or filtration if the PAN is to be used for electrocatalytic applications.³⁴ While catalysts can be immobilized or reclaimed using various techniques,^{35,36} it would be desirable to develop an ATRP method that does not use transition metals catalysts for PAN synthesis. Systems based on alkyl iodides and various organic catalysts were previously described (Scheme 2.2.2).³⁷⁻⁴⁰ However, these systems rely on the much weaker C-I bond and the ability of iodine to form various hypervalent species. It remains a challenge to extend such metal-free catalytic systems to alkyl bromides, commonly used in ATRP. Recently, Hawker reported a photo-induced metal-free (MF) ATRP of methyl methacrylate using 10-phenylphenothiazine (Ph-PTZ) as an organic photocatalyst.⁴¹ In MF ATRP, a three component photoredox cycle is conducted. The photoexcited PTZ* activates an alkyl halide and generates radicals, while the PTZ⁺Br⁻ species deactivates the radical and regenerates the ground state PTZ (Scheme 2.2.3). Perylene was also used as a successful photocatalyst for metal-free ATRP.⁴² The metal-free ATRP process was applied to the polymerization of AN to determine if well-defined PAN could be synthesized.

Scheme 2.2.2. Iodine-mediated Polymerization



Scheme 2.2.3. Metal-free ATRP



To confirm that ICAR and MF ATRP of AN were well-controlled, the synthesized PAN was chain extended with *n*-butyl acrylate (*n*-BA), methyl methacrylate (MMA) or styrene (St) by ICAR or MF ATRP. A clean chain extension would confirm that chain-end functionality (CEF) was retained throughout the polymerization when either method was utilized. This is a key requirement, as the primary application for PAN synthesized by ATRP, is intended for block copolymer (BCP) templating of N-doped carbon materials.

2.3 Synthesis of Polyacrylonitrile by ICAR ATRP

2.3.1 Introduction

The main goal of this study was to determine the lowest catalyst loading that could maintain control over the polymerization of AN while providing well defined PAN. The effect of two Cu-based catalysts, alkyl halide initiators, and the amount of AIBN on the kinetics and control of ICAR ATRP of AN were systematically evaluated. Additionally, efficient chain extension of PAN-Br macroinitiator with *n*-butyl acrylate (BA) by ICAR ATRP, yielding a well-defined block copolymer, demonstrated retention of high chain end functionality in the macroinitiator.

2.3.2 Experimental

2.3.2.1 Materials

Acrylonitrile (AN, Sigma-Aldrich, >99%) and *n*-butyl acrylate (BA, Sigma-Aldrich, >99%) were purified by passing over a column of basic alumina to remove the inhibitor. 2-bromopropionitrile (BPN, Sigma-Aldrich, 97%), ethyl 2-bromoisobutyrate (EBiB, Sigma-Aldrich, 98%), ethyl α -bromophenylacetate (EBPA, Sigma-Aldrich, 97%), ethyl α -chlorophenylacetate (ECPA, Sigma-Aldrich, 97%), copper (II) bromide (CuBr₂, Acros Organics, >99%), 2,2'-azoisobutyronitrile (AIBN, Sigma-Aldrich, 98%), dimethylformamide (DMF, Fisher, 99.9%), dimethyl sulfoxide (DMSO, Fisher, 99.9%), methanol (Fisher, 99.9%), and diethyl ether (Fischer, 99%) were used as received. Tris(2-pyridylmethyl)amine (TPMA)⁴³ and N,N,N',N'-tetrakis(2-pyridylmethyl)ethylenediamine (TPEN)⁴⁴ were synthesized according to published procedures.

2.3.2.2 ICAR ATRP of AN

In a typical procedure, 5 mg of AIBN (0.031 mmol, 0.1 equiv.), 5 mL of DMSO and 0.5 mL of DMF were charged into a Schlenk flask and degassed for 30 min. A stock solution of CuBr₂ and TPMA in DMF was prepared and degassed for 10 min, then 0.7 mg (0.003 mmol, 0.01 equiv.) of CuBr₂, and 2.67 mg (0.009 mmol, 0.03 equiv.) of TPMA were added to the Schlenk flask. 3.26 g (61 mmol, 200 equiv.) of degassed AN was added to the above flask, and finally 41 mg (0.3 mmol, 1 equiv.) of BPN was added and the polymerization was started by immersing the flask in an oil bath at 65 °C and conducted for 10 h. The final polymer was isolated by precipitation into methanol/water (4:1, v/v) and dried under vacuum at room temperature overnight.

2.3.2.3 Chain Extension of PAN-Br with BA by ICAR ATRP

2.69 g (0.010 mmol, 1 equiv.) of PAN-Br macroinitiator ($M_{n,NMR}$ 6700, M_w/M_n 1.24) was dissolved in 6 mL of DMF and the solution was added to a 10 mL Schlenk flask containing 0.23 mg (0.001 mmol, 0.01 equiv.) CuBr₂, 0.91 mg (0.003 mmol, 0.03 equiv.) TPMA, and 0.40 mL of DMSO. The contents were bubbled with nitrogen for 30 min. A solution of 3 mL (21 mmol, 200 equiv.) of deoxygenated BA and 1.73 mg (0.01 mmol, 0.1 equiv.) of AIBN was then added dropwise to the flask with vigorous stirring to prevent PAN precipitation. The reaction was conducted at 60 °C for 5.5 h. The resulting block copolymer was precipitated by addition to a methanol/water mixture (1:1, v/v), filtered and dried under vacuum.

2.3.2.4 Characterization

^1H nuclear magnetic resonance (NMR) spectroscopy measurements were performed on a Bruker Avance 300 MHz spectrometer and used to determine the conversion of monomer in DMSO-d_6 and the resulting molecular weights ($M_{n,\text{NMR}}$) of the PAN homopolymer in DMSO-d_6 , and the PAN-*b*-PBA BCP in DMF-d_7 . The apparent molecular weights ($M_{n,\text{GPC}}$) and molecular weight distributions (M_w/M_n) were determined by gel permeation chromatography (GPC). The GPC system used a Waters 515 HPLC pump and a Waters 2414 refractive index detector using PSS columns (Styrogel 10^2 , 10^3 , 10^5 Å) with DMF containing 10 mM LiBr as the eluent at a flow rate of 1 mL/min at 50 °C using linear PEO standards for PAN and PMMA standards for PAN-*b*-PBA block copolymers. It should be noted that commonly used calibration standards (e.g. PMMA) often significantly overestimate $M_{n,\text{GPC}}$ of PAN. However, it was found that when linear PEO standards are used as the calibration standards with DMF as the eluent and PS-based columns, much more accurate results can be obtained. MW determined by ^1H NMR and GPC with PEO calibration showed a high correlation for several PAN samples (Figure 2.3.2).

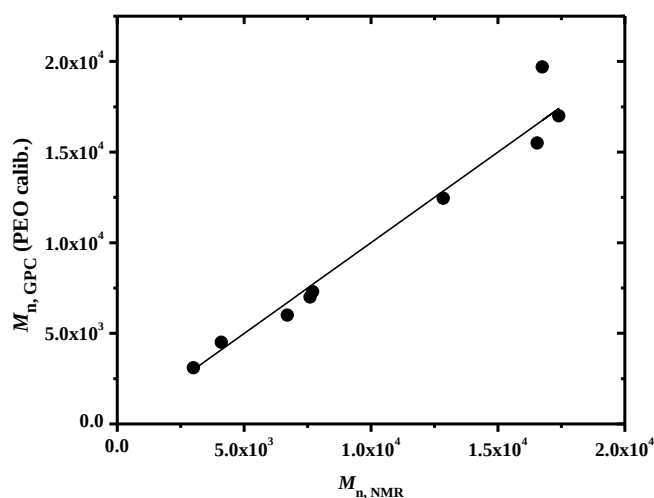


Figure 2.3.2. Correlation between $M_{n, \text{NMR}}$ and $M_{n, \text{GPC}}$ determined using linear PEO calibration standards for PAN samples with MWs in the range 3,000 – 20,000. DMF containing 10 mM LiBr was used as the eluent at 50 °C and PS-based columns

2.3.3 Results and Discussion

2.3.3.1 Initiator/Catalyst Study

The rate of polymerization (R_p) and MWD are described by eq. 1 and 2, respectively, where k_p , k_t and k_{deact} are rate constants of propagation, termination and deactivation, respectively. $[M]$ is the monomer concentration and $[P_n^\bullet]$ is the concentration of growing radicals. k_{dc} , f and $[I_2]$ are the decomposition rate constant, initiation efficiency, and concentration of the conventional radical initiator, respectively. $[P_n\text{-X}]$ is the concentration of alkyl halide, $[Cu^{II}X_2/L]$ is the concentration of the deactivator species, DP_n is the degree of polymerization and p is the monomer conversion. According to eq. 1, the selection of catalyst and amount of catalyst vs. monomer should not affect the R_p in ICAR ATRP, and it should depend exclusively on

the concentration and decomposition rate of the radical initiator used for activator regeneration. However, MW and MWD should be determined by the rate of activation and deactivation (relative to propagation) for each catalyst with deactivation occurring faster than activation, as under all ATRP conditions.³³

$$R_p = k_p[M][P_n \cdot] = k_p[M] \times \sqrt{\frac{k_{dcf}[I_2]}{k_t}} \quad (\text{eq. 1})$$

$$\frac{M_w}{M_n} = 1 + \frac{1}{DP_n} + \left(\frac{k_p[P_n X]}{k_{deact}[Cu^{II}X_2/L]} \right) \left(\frac{2}{p} - 1 \right) \quad (\text{eq. 2})$$

The effect of rate of activation on the ATRP of AN by ICAR ATRP was investigated using four model initiators (R-X) with moderate to high activation rate constants (k_{act}).⁴⁵ EBPA has an intrinsically high k_{act} and ECPA has a k_{act} one order of magnitude lower, due to the stronger C-Cl bond. BPN is structurally similar to PAN's dormant chain-end and was previously shown to be an efficient initiator for AN.^{4,5} EBiB has a moderate k_{act} and serves as a comparison to the other three high activity initiators. Two active Cu-based catalyst complexes, CuBr₂/TPMA and CuBr₂/TPEN, were selected to compare their control over the polymerization. These catalysts exhibit high k_{deact} under ATRP conditions, which is important for achieving control over MW and MWD (eq. 2). Also, the stability constants of both complexes are high, preventing their dissociation by competitive complexation with the CN groups from monomer/polymer or from solvent. A ratio of [AN]:[Initiator]:[AIBN] = 400:1:0.05 was selected in order to form a relatively high MW polymer. The AIBN concentration was low in order to limit the amount of additional PAN chains generated. The ratio of AN:DMSO equal to 1:1.25 (v/v) was chosen to ensure PAN solubility,²⁵ 50 ppm catalyst loading, vs. monomer, was selected

with a 1:6 CuBr₂:ligand ratio, since previous results indicated that these conditions prevented dissociation of Cu-catalyst complexes under the dilute conditions used for AN polymerization.³³

In all cases when CuBr₂/TPMA was employed as the catalyst complex, the polymerization rates were similar (Figure 2.3.3.1a; Table 2.3.3.1, Entries 1-4) with k_p^{app} between 0.0566-0.0738 h⁻¹ and linear first-order kinetics. A larger variability in rates was observed when CuBr₂/TPEN was utilized (Figure 2.3.3.1b). Initiation with BPN, ECPA, and EBiB resulted in linear first-order kinetics with k_p^{app} in the range of 0.0569-0.0783 h⁻¹ (Table 2.3.3.1, Entries 5, 6, and 8), which was similar to the results with CuBr₂/TPMA with these initiators. However, initiation with ECPA showed a decrease in rate after seven hours (Figure 2.3.3.1b). While an induction period was observed for initiation with EBPA, the rate was significantly faster with a k_p^{app} of 0.0923 h⁻¹ (Table 2.3.3.1, Entry 7). The rate also increased after 7 hours, which was attributed to an increase in viscosity.

MW data revealed that CuBr₂/TPMA provided better control over the polymerization, as MWDs, with all initiators, were narrower (M_w/M_n = 1.10-1.25; Table 2.3.3.1, Entry 1-4) than when CuBr₂/TPEN (M_w/M_n = 1.16-1.44; Table 2.3.3.1, Entry 5-8) was utilized. This can be attributed to loss of deactivator species with the TPEN ligand when the halide (Br⁻) coordinates with a free nitrogen species, causing the CuBr₂/TPEN catalyst to exert less control over the polymerization of AN.⁴⁶ A combination of CuBr₂/TPMA catalyst and BPN initiator resulted in the closest experimental to theoretical MW (Figure 2.3.3.1c) and narrowest MWD (1.11; Figure 2.3.3.1d). This combination seems to generate the most efficient system for ICAR ATRP of AN, and it

was used to further investigate the effect of AIBN to initiator ratio and lower catalyst loadings.

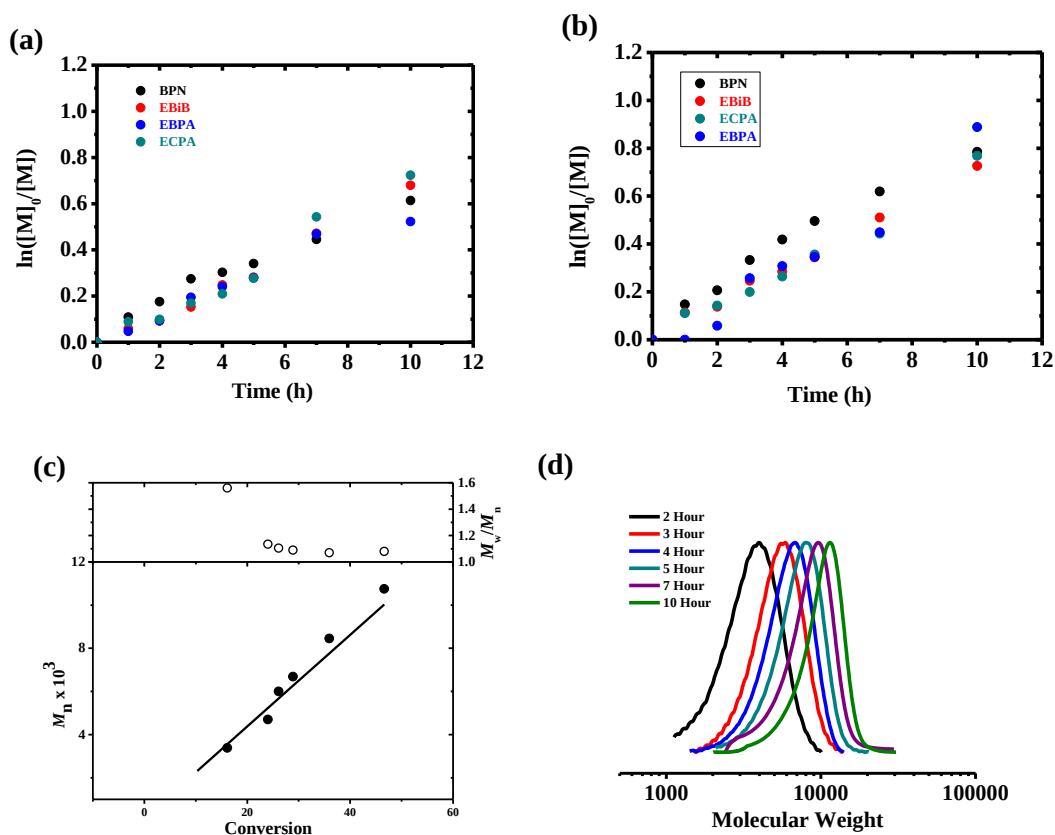


Figure 2.3.3.1. First-order kinetic plots for (a) $[AN]:[R-X]:[CuBr_2]:[TPMA]:[AIBN]=400:1:0.02:0.06:0.05$ and (b) $[AN]:[R-X]:[CuBr_2]:[TPEN]:[AIBN]=400:1:0.02:0.06:0.05$. (c) MW and M_w/M_n evolution and (d) GPC traces for conditions $[AN]:[BPN]:[CuBr_2]:[TPMA]:[AIBN]=400:1:0.02:0.06:0.05$; AN:DMSO= 1:1.25 (v/v), $T = 65\text{ }^\circ\text{C}$

Table 2.3.3.1. Effect of ligand and initiator on ICAR ATRP of AN

Entry	Initiator (R-X) Ligand (L)	Conv (%)	k_p^{app} (h ⁻¹)	$M_{n,theory}$	$M_{n,GPC}$	M_w/M_n
1	R-X: BPN L: TPMA	46	0.0632	9800	9500	1.11
2	R-X: EBiB L: TPMA	49	0.0692	10600	12900	1.14
3	R-X: EBPA L: TPMA	44	0.0566	9400	14500	1.11
4	R-X: ECPA L: TPMA	56	0.0738	12000	15000	1.27
5	R-X: BPN L: TPEN	54	0.0783	11700	15900	1.17
6	R-X: EBiB L:TPEN	52	0.0569	10500	23700	1.20
7	R-X: EBPA L: TPEN	59	0.0474 ^a	12700	15800	1.28
8	R-X: ECPA L:TPEN	54	0.0720	11500	18100	1.33

All polymerizations were conducted with a ratio of [AN]:[R-X]:[CuBr₂]:[L]:[AIBN] =

400:1:0.02:0.12:0.05 at T = 65 °C, AN:DMSO = 1:1.25 (v/v), 10 hours. A k_p^{app} calculated using t from 3 to 7 h, the linear fit from 3 to 10 h gave 0.088 h⁻¹.

2.3.3.2 Influence of AIBN Loading

Different AIBN to BPN ratios were examined to determine the optimal rate of AN polymerization, while still producing a well-defined PAN. The [AN]:[BPN] ratio was maintained at 200:1 in order to achieve higher conversions in shorter time with 50 ppm of CuBr₂/TPMA catalyst. As predicted by eq. 1, R_p scales proportionally to the square root of the AIBN concentration (Figure 2.3.3.2a; Table 2.3.3.2). All conditions showed linear kinetics, with only slight deviations for 0.2 and 0.5 ratios at high conversions, and formed PAN with narrow MWDs, ~1.20.

The lowest AIBN:BPN ratios of 0.05:1 and 0.1:1 showed the closest experimental to theoretical MW values (Table 2.3.3.2b). This indicated that the excellent control can

be achieved while retaining reasonable polymerization rates at these two AIBN concentrations. It should be noted that increasing the amount of AIBN is not recommended. Significant loss of control will occur and, most importantly, chain end functionality (CEF) drastically decreases at higher AIBN loadings. Loss of CEF is due to an increased rate of termination, as previously shown by computer simulations.⁴⁷

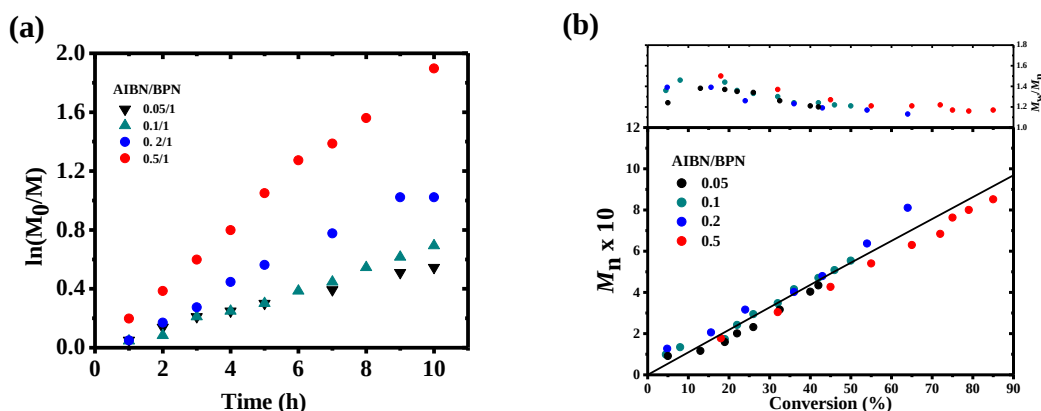


Figure 2.3.3.2. Effect of AIBN concentration on ICAR ATRP of AN; (a) first-order kinetic plot; (b) MW and M_w/M_n evolution. [AN]:[BPN]:[CuBr₂]:[TPMA] = 200:1:0.01:0.03; AN:DMSO= 1:1.25 (v/v); T = 65 °C, 10 hours.

Table 2.3.3.2. Effect of AIBN concentration on ICAR ATRP of AN

Entry	[AIBN]/[BPN]	Conv. (%)	$M_{n, \text{theory}}$	$M_{n, \text{GPC}}$	$k_p^{\text{app}} (\text{h}^{-1})$	M_w/M_n
1	0.05	42	4500	4400	0.0529	1.20
2	0.1	50	5300	5600	0.0721	1.21
3	0.2	64	6800	7600	0.1136	1.14
4	0.5	85	9000	8500	0.1924	1.17

[AN]:[BPN]:[CuBr₂]:[TPMA] = 200:1:0.01:0.03 ; AN:DMSO= 1:1.25 (vol); T= 65 °C, 10 hours.

2.3.3.3 Influence of Catalyst Loading

Since a 0.1:1 AIBN:BPN ratio provided both a reasonable polymerization rate and good control over the reaction, lower catalyst loadings were studied (Figures 2.3.3.3). CuBr₂/TPMA loadings of 10, 25, and 50 ppm resulted in similar polymerization rates with k_p^{app} of 0.0704-0.0888 h⁻¹ (Figure 2.3.3.3a; Table 2.3.3.3, Entries 2-4). This is expected for ICAR ATRP, as the R_p should depend solely on the amount and decomposition rate of AIBN (eq. 1).³³ Experimental MWs closely matched theoretical values (Table 2.3.3.3, Entries 2-4) and dispersity only increased slightly with 10 ppm catalyst loading, to 1.31 (Table 2.3.3.3, Entry 2)

However, at 1 ppm catalyst loading the R_p increased after 5 hours (Figure 2.3.3.3a and k_p^{app} Table 2.3.3.3) and the experimental molecular weights were higher than theoretical values, due to a diminished rate of deactivation resulting from low concentration of Cu(II). The high MW PAN at the beginning of polymerization resulted in a noticeable increase in viscosity of the reaction medium, which could reduce the rate of diffusion controlled radical termination, increase radical concentration and accelerating the overall rate of polymerization. Surprisingly, the increase in viscosity and reduced termination rate, resulted in a controlled reaction. M_w/M_n values decreased to 1.41 at 65% conversion after 10 hours (Figure 2.3.3.3b; Table 3, Entry 1) and MW increased linearly. The CuBr₂/TPMA catalyst exhibited exceptional activity (K_{ATRP}) and stability under the dilute ICAR ATRP conditions, most likely due to the enhanced stabilization of the Cu(I) activator species. Importantly, low catalyst loadings could be used to tune PAN's dispersity, while maintaining control over its MW and the composition of the BCP precursors to N-doped nanocarbons.

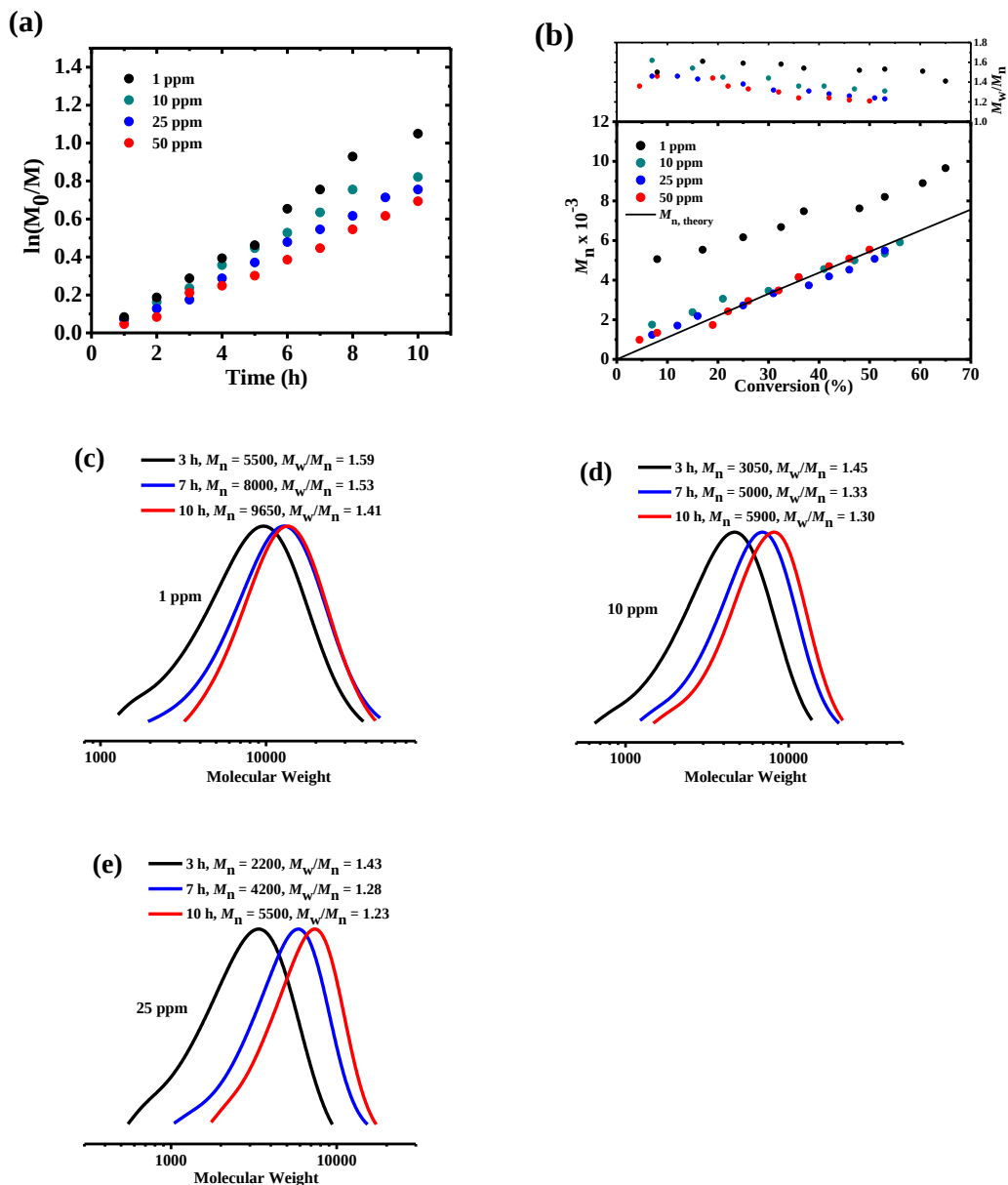


Figure 2.3.3.3. Effect of catalyst concentration on ICAR ATRP of AN; (a) first-order kinetic plots, (b) MW and M_w/M_n evolution [AN]:[BPN]:[AIBN]: [CuBr₂]:[TPMA] = 200:1:0.1:n:3n. AN:DMSO= 1:1.25 (v/v), T = 65 °C, 10 hours; GPC traces of ICAR ATRP of AN with different catalyst concentrations: conditions: [AN]:[BPN]:[AIBN]:[CuBr₂]:[TPMA] = 200:1:0.1:n:3n; n = 0.0002 (a), 0.002 (b), or 0.005 (c); AN:DMSO= 1:1.25 (v/v), T = 65 °C, 10 hours

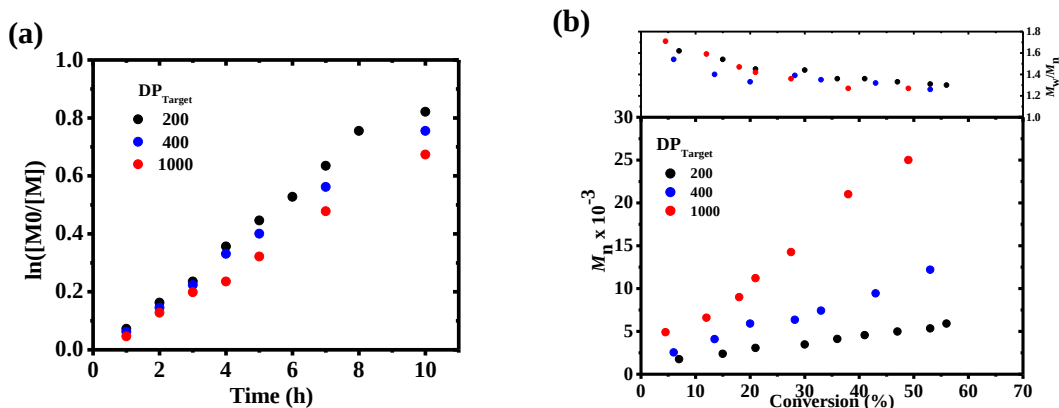
Table 2.2.3.3. Effect of catalyst concentration on ICAR ATRP of AN

Entry	Cu (ppm)	Conversion (%)	$M_{n,theory}$	$M_{n,GPC}$	$k_p^{app} (h^{-1})$	M_w/M_n
1	1	65	6900	9600	0.1140	1.41
2	10	56	6000	5800	0.0888	1.31
3	25	53	5600	5500	0.0794	1.23
4	50	50	5300	5600	0.0704	1.21

[AN]:[BPN]:[AIBN]:[CuBr₂]:[TPMA] = 200:1:0.1:n:3n; vol AN:DMSO= 1:1.25 (v/v); T= 65 °C, 10 hours

2.3.3.4 Influence of Targeted DP

Since PAN synthesized with 10 ppm of CuBr₂/TPMA had a predefined MW and relatively narrow MWD, while providing a significant reduction of catalyst loading. Therefore the targeted degree of polymerization (DP_n) were varied while a catalyst loading of 10 ppm and AIBN:BPN ratio of 0.1:1 was employed. ~50% conversion was achieved within 10 hours for all three targeted DP_n and first-order linear kinetics were observed (Figure 2.3.3.4a). MW increased linearly with conversion (Figure 2.3.3.4b), experimental MWs closely matched the theoretical MW and MWDs were narrow ($M_w/M_n < 1.30$) for higher target DP_n (Figure 2.3.3.4c; Table 4). These results indicated that the optimized conditions can be used to synthesize well-defined PAN over a range of MWs with only 10 ppm of catalyst.



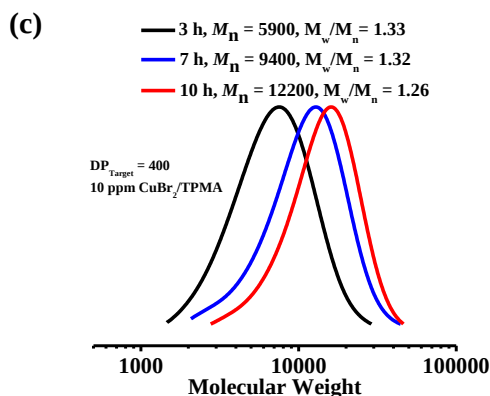


Figure 2.3.3.4. Effect of target DP on ICAR ATRP of AN with 10 ppm catalyst; (a) first-order kinetic plots; (b) MW and M_w/M_n evolution; $[\text{AN}]:[\text{BPN}]:[\text{AIBN}] = x:1:0.1$; $[\text{CuBr}_2]:[\text{TPMA}] = 1:3$; $\text{AN:DMSO} = 1:1.25$ (v/v); $T = 65^\circ\text{C}$, 10 hours; (c) GPC traces for conditions $[\text{AN}]:[\text{BPN}] = 400:1$

Table 2.3.3.4. Effect of target DP on ICAR ATRP of AN with 10 ppm catalyst

Entry	Target DP	Conversion (%)	$M_{n,\text{theory}}$	$M_{n,\text{GPC}}$	$k_p^{\text{app}} (\text{h}^{-1})$	M_w/M_n
1	200	56	6000	5800	0.0888	1.31
2	400	53	11300	12200	0.0780	1.26
3	1000	49	26200	25000	0.0685	1.27

$[\text{AN}]:[\text{BPN}]:[\text{AIBN}] = x:1:0.1$; $[\text{CuBr}_2]:[\text{TPMA}] = 1:3$; vol AN:DMSO = 1:1.25 (v/v); $T = 65^\circ\text{C}$, 10 hours

2.3.3.5 Chain extension of PAN-Br with BA

^1H NMR analysis showed high chain end functionality in the synthesized PANs (CEF > 90%; Fig. 2.3.3.5a), however the accuracy of NMR for measuring the CEF for high MW samples is generally less reliable. Therefore, to confirm high CEF of the PAN-Br macroinitiator ($M_{n,\text{NMR}} = 6700$, $DP = 124$, $M_w/M_n = 1.24$) it was chain extended with BA using ICAR ATRP. A ratio of $[\text{BA}]:[\text{PAN-Br}]:[\text{CuBr}_2/\text{TPMA}]:[\text{AIBN}]$ of 200:1:0.01:0.1 was used and the polymerization was conducted at 60°C in a solution of

DMF (BA:DMF = 1:2 v/v) to ensure solubility of the PAN-Br macroinitiator. The reaction was stopped at a conversion corresponding to a BCP composition of ~40 wt% PAN, as this is the desired composition for a BCP precursor for preparation of N-doped nanocarbons.¹⁹ A clean shift to higher MW was observed during chain extension (Figure 2.3.3.5b) and the experimental MW corresponded closely to the theoretical MW, ($M_{n,theory}$ = 17,000 at 40% conversion). In addition, M_w/M_n remained low, at 1.22, and no tailing was observed, confirming the high chain-end functionality of the PAN macroinitiator and efficient chain extension. The resulting BCP was precipitated by addition of the reaction solution to methanol/water (1:1 v/v) and the MW, determined by NMR, was 16,600. The $M_{n,NMR}$ was in excellent agreement with the theoretical value and corresponded to a composition of PAN₁₂₄-*b*-PBA₇₇ with 40 wt% PAN.

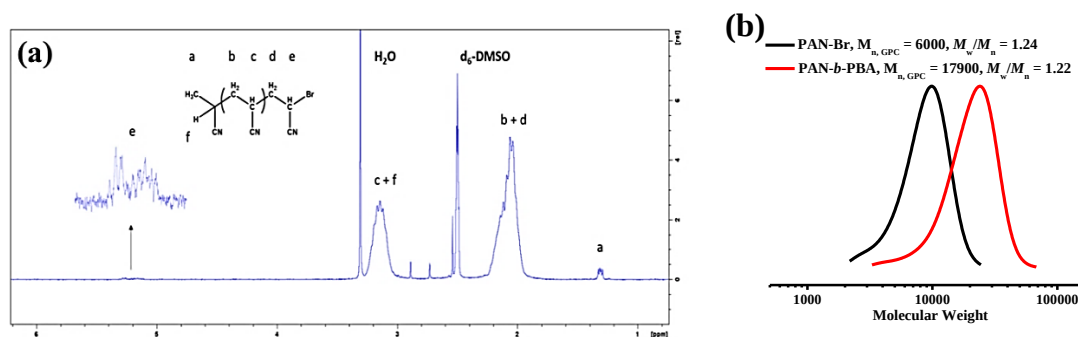


Figure 2.3.2.5. ¹H NMR spectrum of a PAN-Br macroinitiator ($M_{n,NMR}$ = 4100, M_w/M_n = 1.23) synthesized by ICAR ATRP (a); conditions: [AN]:[BPN]:[AIBN]:[CuBr₂]:[TPMA] = 200:1:0.1:0.01:0.06; AN:DMSO= 1:1.25 (v/v), T = 65 °C, 4 hours. Chain extension of PAN macroinitiator with n-butyl acrylate by ICAR ATRP (b); [BA]:[PAN-Br]:[CuBr₂/TPMA]:[AIBN] = 200:1:0.01:0.1; BA:DMF =1:2 (v/v); T = 60 °C, 5.5 hours

2.4 Synthesis of PAN-*b*-PS by ICAR ATRP

2.4.1 Introduction

PAN-*b*-PBA BCPs are good precursors for the preparation of N-doped nanocarbons with surface areas up to 500 m²/g and small pore size distributions.^{19,21} However, nanocarbons with larger surface areas, which are desirable in some applications, could not be achieved by further decreasing block size. One possible reason is that PAN-*b*-PBA reaches its order-disorder transition temperature (T_{ODT}) close to the temperature of PAN cyclization (280 °C) and the PAN and PBA phases becomes miscible in one another.⁴⁸⁻⁵⁰ Thus, we wanted to explore the use of PAN-*b*-PS as a carbon precursor. Based on the Hildebrand solubility parameters, the Flory-Huggins interaction parameter (χ) should be higher for PAN-*b*-PS, which would allow for phase separation at lower DP_n of each block, thereby generating higher surface areas in the resulting carbon material.⁵¹ Additionally, PS should be a good sacrificial block as it depolymerizes at ~400 °C, similar to PBA, and will be removed from the carbon structure.⁵²

PAN-*b*-PS BPCs have been previously synthesized,^{13,53} however, either anionic polymerization or normal ATRP was used to achieve well-defined BCPs. Therefore, a method was developed to synthesize PAN-*b*-PS by ICAR ATRP with low (ppm) loadings of Cu-based catalyst.

2.4.2 Experimental

2.4.2.1 Materials

Acrylonitrile (AN, Sigma, > 99%) and styrene (St, Aldrich, >99%) were purified by passing over a column of basic alumina to remove the inhibitor. 2-bromopropionitrile

(BPN, Aldrich, 97 %), 2-bromoisobutyrate (EBiB, Aldrich, 98%), (CuBr₂, Acros Organics, >99%), 2,2'-azoisobutyronitrile (AIBN, Aldrich, 98%), 1,1'-Azobis (cyclohexanecarbonitrile) (ABCN, Aldrich, 98%), dimethylformamide (DMF, Fisher, 99.9%), and methanol (Fisher, 99.9%) were used as received. Tris(2-pyridylmethyl)amine (TPMA)⁴³ was synthesized via a previously published procedure.

2.4.2.2 Polymerization of Styrene by ICAR ATRP

In a typical procedure, 7.5 mg (30.5 mmol, 0.1 equiv.) of ABCN and 7 mL of DMSO were charged into a Schlenk flask. A stock solution of CuBr₂ and TPMA in DMF was prepared, so that 0.68 mg (0.00305 mmol, 0.01 equiv.) of CuBr₂ and 7.5 mg (0.0305 mmol, 0.03 equiv.) could be added to the Schlenk flask. The mixture was degassed for 20 minutes. 3.2 g (30.5 mmol, 100 equiv.) of degassed St was added to the flask, followed by 41 mg (0.305 mmol, 1 equiv.) of BPN and the polymerization was started by immersing the flask in an oil bath at 90 °C and continued for 10 h.

2.4.2.3 Polymerization of Acrylonitrile by ICAR ATRP

5 mg of AIBN (0.031 mmol, 0.1 equiv.), 5 mL of DMSO and 0.5 mL of DMF were charged into a Schlenk flask and degassed for 30 min. A stock solution of CuBr₂ and TPMA in DMF was prepared and degassed for 10 min, then 0.7 mg (0.003 mmol, 0.01 equiv.) of CuBr₂, and 2.67 mg (0.009 mmol, 0.03 equiv.) of TPMA were added to the Schlenk flask. 3.26 g (61 mmol, 200 equiv.) of degassed AN was added to the above flask, and finally 41 mg (0.3 mmol, 1 equiv.) of BPN was added and the polymerization was started by immersing the flask in an oil bath at 65 °C and conducted for 10 h. The

final polymer was isolated by precipitation into methanol/water (4:1, v/v) and dried under vacuum at room temperature overnight.

2.4.2.4 Chain Extension of PAN-Br with Styrene by ICAR ATRP

In a typical procedure, 0.98 g (0.305 mmol, 1 equiv.) of PAN-Br macroinitiator ($M_{n,NMR}$ 3200, M_w/M_n 1.25) was dissolved in 7 mL of DMF then added to a Schlenk flask followed by 2.7 mg (0.012 mmol, 0.04 equiv.) $CuBr_2$, 11 mg (0.037 mmol, 0.12 equiv.) TPMA, 5 mg (0.0305 mmol, .1 equiv.), then the mixture was bubbled with nitrogen for 30 min. 3.5 mL (30.5 mmol, 100 equiv.) of deoxygenated St was then added dropwise with vigorous stirring to prevent PAN precipitation. The reaction was conducted at 60 °C and after two 10 hr $\frac{1}{2}$ lives of AIBN, a second equivalent was injected so that the reaction could be continued to the desired conversion. The resulting block copolymer was precipitated by addition into methanol/water mixture (1:1, v/v), filtered and dried under vacuum.

2.4.2.5 Characterization

1H NMR spectroscopy measurements were performed on a Bruker Avance 300 MHz spectrometer and used to determine the conversion of monomer in DMSO- d_6 and the resulting MW ($M_{n,NMR}$) of the PAN homopolymer in DMSO- d_6 and the PAN-*b*-PS BCP in DMF- d_7 . The apparent MW ($M_{n,GPC}$) and MWD (M_w/M_n) were determined by gel permeation chromatography (GPC). The GPC system used a Waters 515 HPLC pump and a Waters 2414 refractive index detector using PSS columns (Styrogel 10^2 , 10^3 , 10^4) with DMF containing 10 mM LiBr as the eluent at a flow rate of 1 mL/min at 50 °C using

linear PEO standards for PAN-Br and linear PS standards for PAN and PS standards for PAN-*b*-PS.

2.4.3 Results and Discussion

An ICAR ATRP with CuBr₂/TPMA as the catalyst and a radical initiator with a 10 hr ½ life temperature of 90 °C, ABCN, was used to polymerize styrene. Additionally, to ensure that the conditions developed for St polymerization would translate to good conditions for PAN-Br chain extension, a high DMF dilution was used (St:DMF = 1:2 vol). Two different initiators were evaluated: BPN, due to its similarity to an AN derived radical and EBiB, a standard initiator for St.⁴⁵ The reaction showed linear first-order kinetics and reasonable conversion after 25 hours (Figure 2.4.3.1a). However, M_w/M_n values were high for both initiators (Figure 2.4.3.1b). Initiation with BPN resulted in significantly higher M_n than $M_{n,theory}$ throughout polymerization, which could be caused by termination of the BPN radical at the beginning of polymerization.

A radical initiator with a lower 10 hr ½ life temperature was selected (AIBN; 60 °C) to guarantee no polymer from St thermal self-initiation was produced. Since the conditions being developed were to be used for chain extension of PAN-Br with styrene the BPN initiator was exclusively used. The polymerization conditions were as follows: [St]:[BPN]:[CuBr₂]:[TPMA]:[AIBN] = 100:1:0.01:0.03:0.1. Linear first-order kinetics were observed until two 10 hr ½ lives of AIBN were completed and the polymerization stopped (Figure 2.4.3.2a). The reaction stops because there was not a sufficient amount of AIBN to form radicals and establish a proper Cu^I:Cu^{II} ratio for activation of the alkyl halide and polymerization to continue. The polymerization was restarted by injecting a

second equivalent of AIBN to the reaction mixture. M_n was consistently lower than $M_{n,theory}$, which could be caused by evaporation of styrene during reaction set up or while sampling or initiation of new chains by AIBN (Figure 2.4.3.2b). Nevertheless, M_w/M_n was significantly lower, so these conditions were used for chain extension of PAN-Br with styrene (Figure 2.4.3.2b).

First-order linear kinetics were observed for chain extension of PAN-Br with St under the follow ICAR ATRP conditions: [PAN-Br]:[St]:[CuBr₂]:[TPMA]:[AIBN]= 1:100:0.04:0.12:0.1 at 60 °C with DMF:St= 2:1 (v:v). The amount of Cu-catalyst was higher than previously, 200 to 400 ppm, to achieve control over MW and MWD and to target higher conversions. First-order linear kinetics was observed and ~30% conversion was achieved in ~30 hours, which is reasonable for St at this low temperature (Figure 2.4.3.3a). M_n increases linearly with conversion, but deviated from theory, due to differences between PAN-*b*-PS and PS GPC calibration standards hydrodynamic volume (Figure 2.4.3.3b). M_w/M_n values remain below 1.3 for all samples taken during the polymerization. To target higher conversion and higher PS MWs, either a second equivalent of AIBN was injected or a higher DP was targeted.

Table 2.4.3 summarizes the PAN-*b*-PS samples synthesized in this project by ICAR ATRP. The final samples were investigated as precursor for N-doped nanocarbons.⁵⁴ Despite good phase separation, carbons with low surface areas were obtained and further investigations are needed to draw conclusions on why PAN-*b*-PS was not a good nanocarbon precursor.

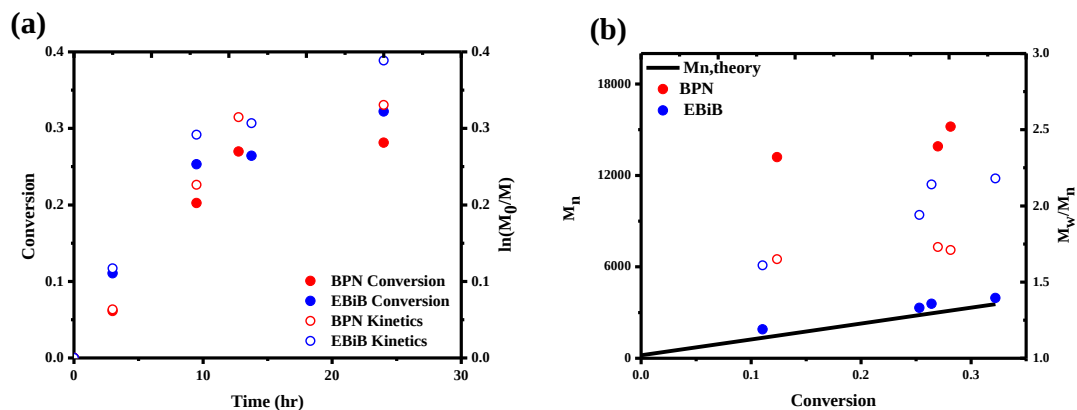


Figure 2.4.3.1. Semi-logarithmic kinetic and conversion plots (a) and MW and MWD (b) for ICAR ATRP with BPN or EBiB as the initiator; conditions: $[St]:[R-X]:[CuBr_2]:[TPMA]:[ABCN] = 100:1:0.01:0.03:0.1$ at 90 °C with $St:DMF = 1:2$ (v:v)

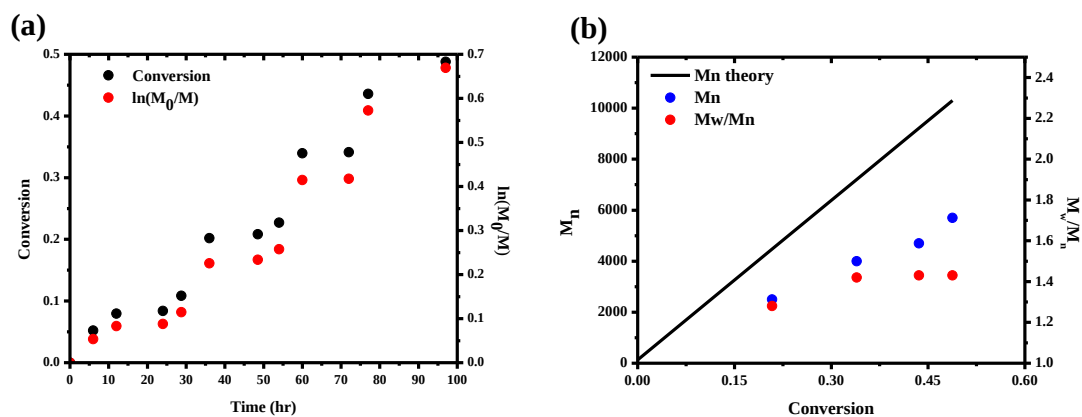


Figure 2.4.3.2: Semi-logarithmic kinetic and conversion plots (a) and MW and MWD (b) of styrene polymerization by ICAR ATRP; $[St]:[BPN]:[CuBr_2]:[TPMA]:[AIBN] = 100:1:0.01:0.03:0.1$ at 60 °C with $St:DMF = 1:2$ (v:v)

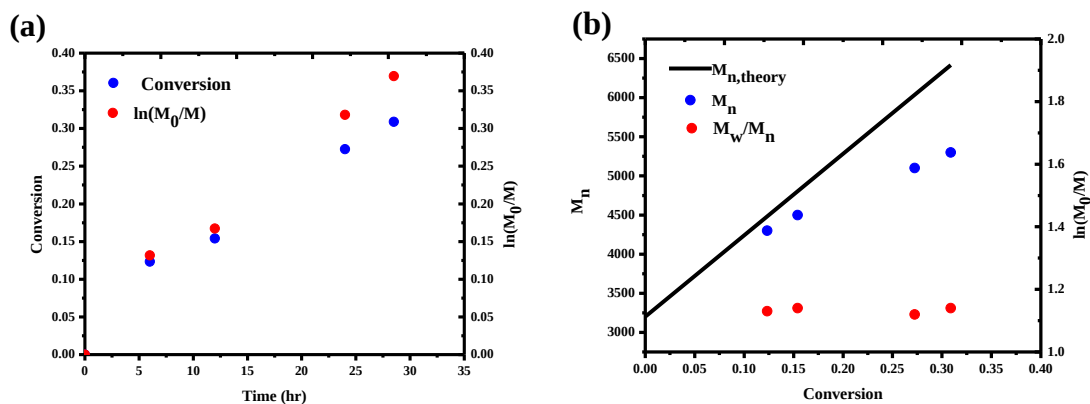


Figure 2.4.3.3. Semi-logarithmic kinetic and conversion plots(a) and MW and MWD (b) for chain extension of PAN-Br with styrene by ICAR ATRP; [St]:[PAN-Br]:[CuBr₂]:[TPMA]:[AIBN]= 100:1:0.04:0.12:0.1 at 60 °C with St:DMF= 1:2 (v:v)

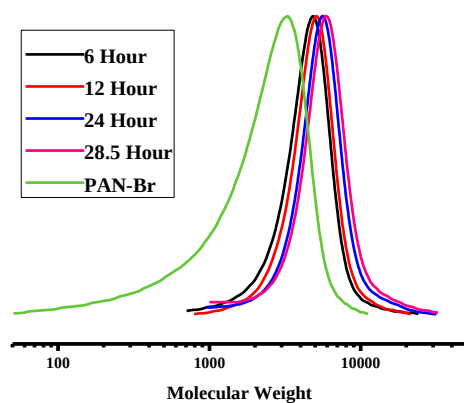


Figure 2.4.3.4. Evolution of molecular weight distribution for chain extension of PAN-Br with styrene by ICAR ATRP; [St]:[PAN-Br]:[CuBr₂]:[TPMA]:[AIBN]= 100:1:0.04:0.12:0.1 at 60 °C with St:DMF= 1:2 (v:v)

Table 2.4.3. PAN-*b*-PS samples and MW characterization

Precursor	$M_{n,NMR}$	M_w/M_n	PAN DP	PSt DP	wt% PSt	Φ_{PSt}
ML-2-59 ^a	3500	1.20	55	5	16	0.18
ML-2-71 ^a	4300	1.14	55	14	33	0.35
ML-2-73 ^a	5100	1.23	55	21	43	0.46
ML-2-74 ^a	5600	1.20	55	26	48	0.51
ML-2-82 ^b	6300	1.12	55	32	54	0.57
ML-2-77 ^b	7000	1.12	55	37	59	0.61
ML-4-80 ^b	8000	n/a	79	27	40	0.40
ML-4-81 ^b	7000	n/a	79	48	53	0.53
ML-4-77 ^c	12900	1.32	145	50	40	0.40
ML-4-78 ^b	11000	1.33	145	32	29	0.30

[AN]:[BPN]:[CuBr₂]:[AIBN]:[TPMA]=100:1:0.01:0.05:0.03; DMSO at 65° C; ^a[St]: [PAN-Br]:[CuBr₂]:

[AIBN]:[TPMA]= 100:1:0.04:0.1:0.12; DMF:St=2:1; T= 60° C; ^b[St]:[PAN-Br]:[CuBr₂]:[AIBN]:[TPMA]=

200:1:0.04 :0.1:0.12; DMF:St = 2.25:1; T= 60° C; ^c[St]:[PAN-Br]:[CuBr₂]:[AIBN]:[TPMA]=400:1:0.08:

0.1:0.24; DMF:St =2.25:1; T= 60° C

2.5 Synthesis of Polyacrylonitrile by Metal Free ATRP

2.5.1 Introduction

Since residual amounts of Cu could potentially impact the properties of the nanostructured carbons, it would be especially interesting to prepare BCP precursors for nanostructured carbons in the absence of any transition metal catalysts.^{23,24} Ph-PTZ and other phenothiazine derivatives, such as 10-(4-methoxyphenyl)-phenothiazine (4-MeOPh-PTZ) and 10-(1-naphthalenyl)-phenothiazine (Nap-PTZ), can be used as organic photocatalysts for ATRP (Figure 2.5.1). All three catalysts were investigated for the MF ATRP of AN. The effect of catalyst concentration, targeted degree of polymerization (DP), solvent, and the intensity of the light source were investigated.

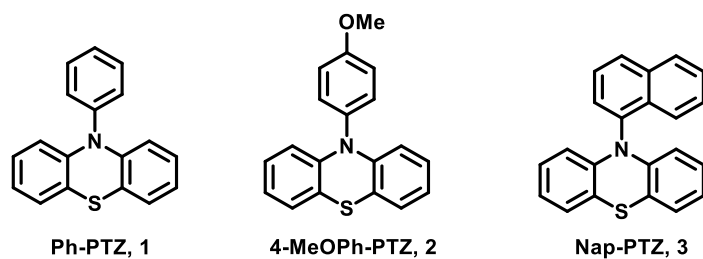


Figure 2.5.1. Structures of phenothiazine derivatives used as photocatalysts in MF ATRP

2.5.2 Experimental

2.5.2.1 Materials

Phenothiazine, chlorobenzene (anhydrous), RuPhos (2-dicyclohexylphosphino-2',6'-diisopropoxybiphenyl), RuPhos Pd G2 (chloro(2-dicyclohexylphosphino-2',6'-diisopropoxy-1,1'-biphenyl)[2-(2'-amino-1,1'-biphenyl)]palladium(II)), 4-bromoanisole, 1-chloronaphthalene, ethyl α -bromophenylacetate, 2-bromopropionitrile, dioxane, DMF and DMSO were purchased from Aldrich. Acrylonitrile (AN) was purchased from Aldrich and purified by passing over a column of basic alumina to remove the inhibitor. All solvents and chemicals were used as received, unless described in detail below.

2.5.2.2 Characterization

^1H nuclear magnetic resonance (NMR) measurements were performed on a Bruker Avance 300 MHz spectrometer. Molecular weight and molecular weight distribution (M_w/M_n) values were determined by gel permeation chromatography (GPC). The GPC system used a Waters 515 HPLC pump and a Waters 2414 refractive index detector using PSS columns (Styrogel 10^2 , 10^3 , 10^5 Å) with 10 mM LiBr-containing DMF as the eluent at a flow rate of 1 mL/min at 50 °C using linear PMMA standards.

The sample was diluted with DMF, and then filtered through 0.2 μm polytetrafluoroethylene (PTFE) membrane filter before injecting into the GPC columns (inject volume: 40 μL) with toluene as the flow marker. All the photo-induced metal-free ATRP reactions were conducted with either a 2.1 mW/cm^2 SHANY® UV or a 4.9 mW/cm^2 MelodySusie® UV photoreactor.

2.5.2.3 Synthesis of phenothiazine derivatives

The synthesis followed a published literature procedure⁴¹: NaOtBu (134 mg, 1.4 mmol), phenothiazine (199 mg, 1 mmol), RuPhos Precat (14 mg, 0.02 mmol, 2 mol %), and RuPhos (8 mg, 0.02 mmol, 2 mol %) were added to a vial with a magnetic stir bar. The vial was evacuated and refilled with nitrogen three times before adding dry dioxane (1 mL) followed by anhydrous chlorobenzene (143 μL , 1.4 mmol) or 4-bromoanisole (175 μL , 1.4 mmol) or 1-chloronaphthalene (90% purity, 190 μL , 1.4 mmol). The vial was placed in an oil bath at 110 $^{\circ}\text{C}$ with stirring for 6 h. The vial was then cooled to room temperature, diluted with CH_2Cl_2 , and the solution washed with water, brine, dried over Mg_2SO_4 , and purified using column chromatography. The solvent was removed under reduced pressure to yield 10-phenylphenothiazine as a white solid, or 4-methoxyphenyl-10-phenothiazine as a white solid or naphthalene-10-phenothiazine (90% purity) as a yellowish solid.

10-Phenylphenothiazine (Ph-PTZ, 1): ^1H NMR (300 MHz, CDCl_3) δ : 7.62 (t, J = 8 Hz, 2H), 7.52 (t, J = 8 Hz, 1H), 7.40 (d, J = 8.5 Hz, 2H), 7.02 (dd, J = 7 Hz, 2 Hz, 2H), 6.86 – 6.79 (m, 4 H), 6.20 (dd, J = 7.2, 1.8 Hz, 2 H) ppm.

4-Methoxyphenyl-10-phenothiazine (MeOPh-PTZ, 2): ^1H NMR (300 MHz, CDCl_3) δ : 7.32 (d, J = 9 Hz, 2 H), 7.12 (d, J = 9 Hz, 2 H), 6.99 (dd, J = 7.4, 1.7 Hz, 2 H), 6.87 – 6.75 (m, 4H), 6.19 (dd, J = 8, 3.4 Hz, 2 H), 3.90 (s, 3H) ppm.

1-Naphthalene-10-phenothiazine (Nap-PTZ, 3): ^1H NMR (300 MHz, CDCl_3) δ : 8.11 (d, J = 8.2 Hz, 1H), 8.0 (t, J = 7.9 Hz, 2H), 7.72 – 7.38 (m, 4H), 7.03 (dd, J = 7.5, 1.8 Hz, 2 H), 6.81 – 6.69 (m, 4H), 6.03 (dd, J = 7.9 Hz, 1.4 Hz, 2H) ppm.

2.5.2.4 General Procedure for MF ATRP of AN

1.3 mL AN (1.05 g, 20 mmol, 100 equiv.), 0.035 mL of ethyl α -bromophenylacetate (EBPA, 48.6 mg, 0.2 mmol, 1 equiv.), 55 mg of Ph-PTZ (1, 0.02 mmol, 0.1 equiv.), and 2.6 mL of DMF were added to a 10 mL Schlenk flask. The flask was tightly sealed and oxygen was removed by three freeze-pump-thaw cycles. The reaction mixture was irradiated by UV light. Samples were removed from the reaction mixture periodically by syringe to obtain the conversion of AN by ^1H NMR in DMSO-d_6 , and number-average molecular weight M_n , and dispersity (M_w/M_n) by GPC in DMF as eluent using linear PMMA standards. The polymer sample was precipitated by addition of methanol to the solution providing PAN as a white powder. A sample of the precipitated and dried PAN was used for M_n determination by ^1H NMR in DMSO-d_6 .

2.5.2.5 General procedure for chain extension of PAN-Br with MMA by MF ATRP

The PAN-Br macroinitiator (102 mg, DP = 34, 0.05 mmol, 1 equiv.), 1.05 mL of MMA (10 mmol, 200 equiv.) and 2.8 mg of Ph-PTZ (1, 0.01 mmol, 0.2 equiv.), and 2.1 mL of DMF were added to a 10 mL Schlenk flask. The flask was tightly sealed and

oxygen was removed by three freeze-pump-thaw cycles. The reaction mixture was irradiated by UV light. After 15 h, a sample was removed from the reaction mixture to obtain the conversion of MMA (52 %) by ^1H NMR, and number-average molecular weight M_n , and dispersity (M_w/M_n) by GPC in DMF as eluent using linear PMMA standards. The solution was added to methanol to obtain PAN-*b*-PMMA precipitate as a white powder. The precipitated PAN-*b*-PMMA was analyzed by ^1H NMR in DMSO- d_6 .

2.5.3 Results and Discussion

Table 2.5.3 summarizes the reaction conditions, conversions, M_n , and M_w/M_n data for MF ATRP of acrylonitrile. Using EBPA as ATRP initiator the polymerizations of AN with photocatalyst 1 (Figure 2.5.1) in DMF provided well-defined PAN (Figure 2.5.3.1; Table 2.5.3; entry 1). Since the MWs obtained from DMF GPC analysis using linear PMMA or polystyrene standards usually overestimated the MW of PAN,⁵⁵ ^1H NMR of the precipitated PAN was used to calculate the absolute number average molecular weights ($M_{n,\text{NMR}}$). Values were similar to the theoretical molecular weights and $M_{n,\text{GPC}}$ based on PMMA standards were ~ 3 times larger than $M_{n,\text{NMR}}$. Therefore, in the following discussion, $M_{n,\text{GPC}}/3$ values were used, as plotted in Figure 2.5.3.1b.

Figure 2.5.3.1a illustrates the first-order semi-logarithmic kinetic plots ($\ln [M]_0/[M]$ versus time), and Figure 2.5.3.1b displays the evolution of M_n and M_w/M_n with conversion. The linear semi-logarithmic plots suggest that the concentration of the propagating radicals was constant throughout the polymerization. With a stronger UV source (Table 2.5.4; entry 10) the rate was initially faster, but decreased with conversion. Molecular weights seem to follow theoretical values after ~ 50 % conversion suggesting

the complete initiation does not occur until this point. Values of $M_w/M_n \sim 1.5$ indicated relatively slow deactivation caused by either low deactivator concentration or low values of deactivation rate constants.

Entries 2 and 3 in Table 2.5.3 show the results from the photo-induced metal-free ATRP of AN targeting two different DP_n (200 and 50). For $DP_n = 200$, the $M_{n,NMR}$ was close to the $M_{n,th}$ values predicted by the 1H NMR conversion (i.e., $M_{n,th} = M_{EBPA} + DP_n \times conv. \times M_{AN} = 243 + DP_n \times conv \times 53$), but the M_w/M_n value was high, 1.85, probably due to the low concentration of catalyst. For targeted $DP_n = 50$, the molecular weight was slightly higher than the theoretical value, indicating low initiation efficiency. The polymerization with target $DP_n = 50$ was slightly faster (Figure 2.5.3.2), because the concentrations of initiator and catalyst were both doubled compared to the amounts employed in entry 1 (Table 2.5.3; i.e., for $DP = 50$, $[EBPA]_0 = 0.1$ M, $[Cat]_0 = 0.01$ M; for $DP = 100$, $[EBPA]_0 = 0.05$ M, $[Cat]_0 = 0.005$ M).

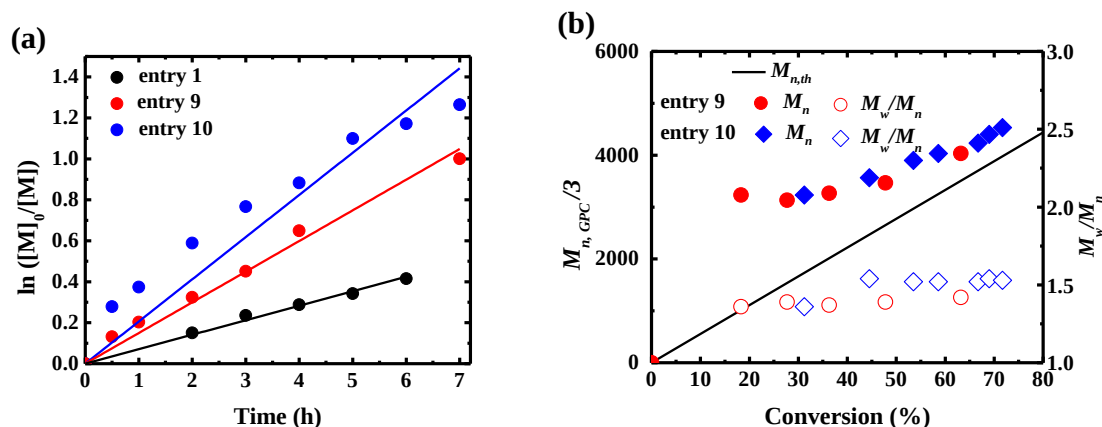


Figure 2.5.3.1. (a) Semi-logarithmic kinetic plots of polymerization of AN by MF ATRP with conditions: $[AN]:[EBPA]:[1] = 100:1:0.1$ in DMF or DMSO, irradiation by 2.1 or 4.9 mW/cm² UV light; (b) number-average molecular weight (M_n , filled symbols), and dispersity (M_w/M_n , open symbols) versus conversion for MF ATRP of AN

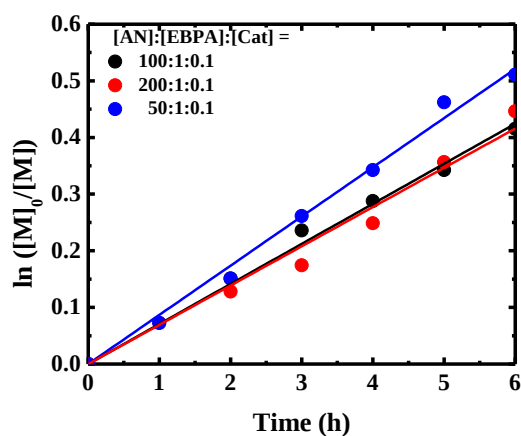


Figure 2.5.3.2. Semi-logarithmic kinetic plots of polymerization of AN by MF ATRP under conditions: $[AN]:[EBPA]:[1] = x:1:0.1$, where $x = 100$ (black), 200 (red), or 50 (blue)

Table 2.5.3. Photo-induced MF ATRP of Acrylonitrile

Entry	catalyst	$[AN]_0:[EBPA]_0:[Cat]_0$	time	Conv. ^a	$M_{n,th}$ _b	$M_{n,NMR}$ _c	$M_{n,GPC}$ _d	M_w/M_n _d
1	1	100:1:0.1	6 h	34%	2040	1990	6200	1.60
2	1	100:0.5:0.05	6 h	36%	4060	4160	13400	1.85
3	1	100:2:0.2	6 h	40%	1300	1890	5670	1.63
4	1	100:1:0.05	6 h	23%	1460	1730	5450	1.88
5	1	100:1:0.2	6 h	31%	1890	1670	5440	1.57
6	2	100:1:0.1	6 h	33%	1990	2470	7490	1.69
7	3	100:1:0.1	15 h	42%	2470	2630	8140	1.62
8	1	100:1 ^g :0.1	14 h	56%	3210	4240	13800	1.52
9 ^e	1	100:1:0.1	7 h	63%	3580	4400	12100	1.42
10 ^{e,f}	1	100:1:0.1	7 h	72%	4060	4060	13600	1.53

^adetermined by ¹H NMR; ^bcalculated based on conversion obtained by ¹H NMR (i.e. $M_{n,th} = M_{EBPA} +$

$[AN]_0/[EBPA]_0 \times \text{conversion} \times M_{AN}$); ^cdetermined by ¹H NMR of precipitated PAN; ^ddetermined by GPC in

DMF, based on linear PMMA as calibration standards; ^eirradiation by 4.9 mW/cm² UV light; ^fin DMSO;

^gBPN instead of EBPA.

The polymerizations of AN with different concentrations of photocatalyst was also investigated with conditions $[AN]:[EBPA]:[1] = 100:1:0.05$ where $[1]_0 = 0.0025$ M. The obtained PAN had slightly higher M_w/M_n than previously obtained (Table 2.5.3 entry 4 vs 1), most likely due to termination reactions that occurred with this low of a catalyst loading. The MF ATRP of AN with $[1]_0 = 0.01$ M provided PAN with better control ($M_w/M_n = 1.57$, Table 2.5.3 entry 5 vs 1).

It is interesting to note that while phenothiazines are powerful inhibitors used for storage of acrylic acid,^{56,57} they can also act as photocatalysts, due to their strongly negative redox potential in the excited state.⁴¹ Hence, two additional phenothiazines derivatives, 2 and 3, were investigated and both successfully provided well-defined PAN in MF ATRP reactions (Table 2.5.3 entries 6 and 7). An induction period (around 1 h) was observed for Nap-PTH catalyzed polymerization of AN.

2-Bromopropionitrile (BPN), is a widely used initiator for ATRP of AN,^{4-6,25} and was tested instead of EBPA for the MF ATRP of AN (Table 2.5.3 entry 8). The molecular weights increased with conversion at the beginning of polymerization, but they were higher than the theoretical values, suggesting that all the initiator was not consumed and that the more active EBPA was a more efficient initiator for MF ATRP.

A stronger UV light source (4.9 mW/cm^2) was also used in MF ATRP of AN under similar polymerization conditions $[AN]:[EBPA]:[1] = 100:1:0.1$ in DMF and provided PAN with better control ($M_w/M_n = 1.42$, Table 2.5.3 entry 9). The kinetic plot showed that the polymerization under a stronger light source (4.9 vs 2.1 mW/cm^2) was faster (entries Table 2.5.3 9 vs 1). Since DMSO is also a suitable solvent for PAN, the polymerization of AN was investigated in DMSO (Table 2.5.3 entry 10). The

polymerization in DMSO was faster than in DMF, and provided PAN with predicted M_n and a dispersity of 1.53. For both entries, 9 and 10, the M_n increased with conversion, but M_n was higher than $M_{n,theory}$ at the beginning of the polymerization (Figure 2.5.3.1b), which indicates slow initiation.

Figure 2.5.3.3 shows the ^1H NMR spectrum of PAN in DMSO-d_6 , obtained from the MF ATRP under the conditions where $[\text{AN}]:[\text{EBPA}]:[1] = 100:1:1$ in DMF (Table 2.5.3 entry 1). Both the ethyl phenylacetate and bromine end groups are observed. The aromatic protons H_a (7.35 ppm), ethyl groups H_b (1.14 ppm), H_c (4.09 ppm) and H_d (3.83 ppm) were from the initiator, and the proton at 5.1 – 5.3 ppm is from the growing end group $\text{CHBr}(\text{CN})$. The backbone of PAN consists of two types of protons: CH_2CHCN (H_e , 2.05 ppm) and CH_2CHCN (H_f , 3.16 ppm). The molecular weight $M_{n,NMR}$ was calculated by comparison of the area of the peaks of H_g from the end group with H_e and H_f from the polymer backbone (i.e., $\text{DP} = [\text{Area}(H_e) + \text{Area}(H_f)] \div 3 \div \text{Area}(H_g)$; $M_{n,NMR} = M_{\text{EBPA}} + \text{DP} \times M_{\text{AN}}$).

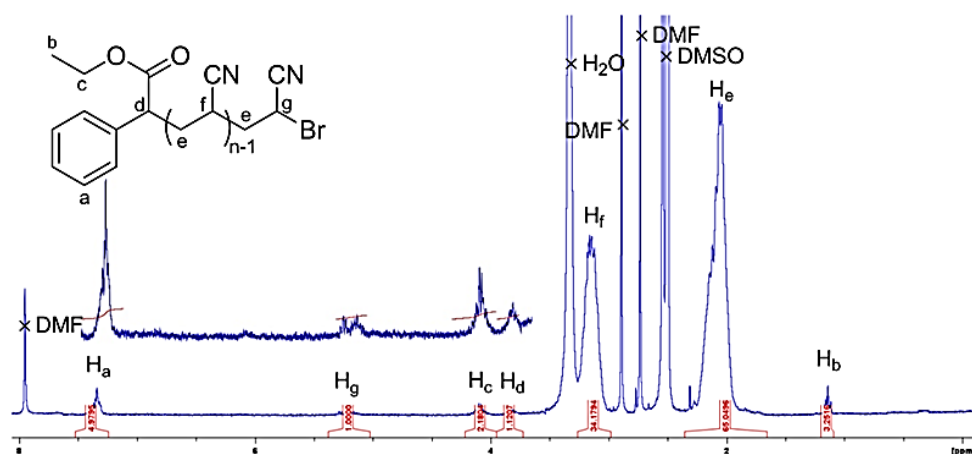
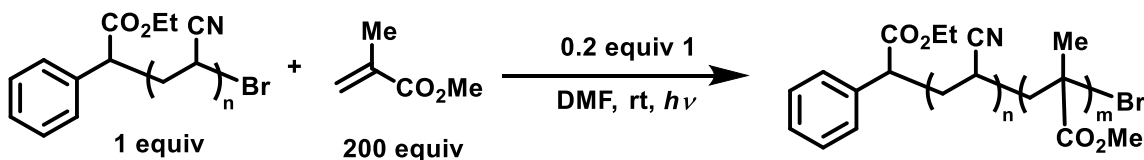


Figure 2.5.3.3. ^1H NMR spectrum of PAN in DMSO-d_6 , obtained from photo-induced metal-free ATRP under conditions $[\text{AN}]:[\text{EBPA}]:[1] = 100:1:0.1$ in DMF

Chain extension of the homopolymer PAN-Br ($M_{n, GPC} = 6200$, $M_w/M_n = 1.60$) was investigated to confirm the utility of this photo-induced metal-free ATRP method (Scheme 2.5.3). Chain extension with MMA was conducted with 0.2 equivalents of macroinitiator PAN-Br (Table 2.5.3 entry 1) at room temperature with UV irradiation for 15 h, providing a well-defined PAN-*b*-PMMA block copolymer ($M_{n, GPC} = 13,600$, $M_w/M_n = 1.79$, Figure 2.5.3.4a). The GPC trace clearly shifted to a higher molecular, which suggests that the synthesized PAN had excellent bromine chain-end functionality and high efficiency for cross propagation. To further confirm this result, the PAN-*b*-PMMA copolymer was isolated via precipitation in methanol, and the ^1H NMR of the BCP in DMSO- d_6 was recorded (Figure 2.5.3.4b). Two types of methyl protons H_h , and H_i at 3.57 ppm, 0.58 – 1.09 ppm as well as the CH_2 protons (H_g , 1.30 – 1.96 ppm) from MMA backbone were observed. The ethyl phenylacetate group from the initiator and the protons from PAN were also clearly preserved. A comparison of the area of the protons from PAN with the protons from PMMA, was used to calculate the DP of PMMA as 103, which is in agreement with 52% conversion of MMA by ^1H NMR in the chain extension reaction.

Scheme 2.5.3. Chain extension of PAN with MMA by photo-induced metal-free ATRP



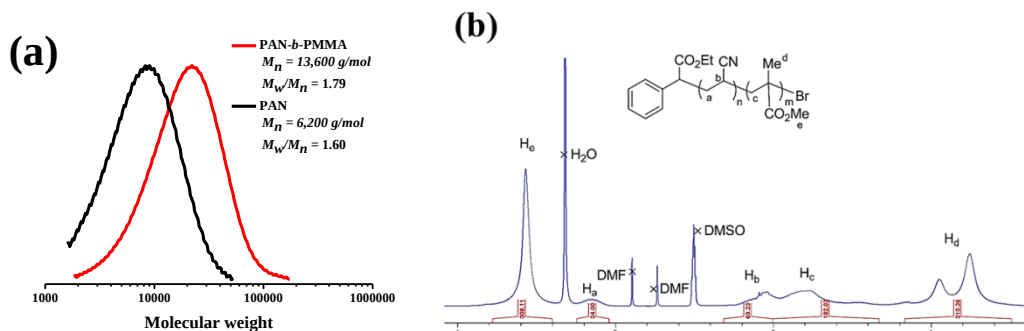


Figure 2.5.3.4. GPC traces of PAN-Br and PAN-*b*-PMMA (a); ^1H NMR spectrum of PAN-*b*-PMMA in DMSO- d_6 (b); obtained from photo-induced metal-free ATRP under conditions $[\text{PAN-Br}]:[\text{MMA}]:[1] = 1:200:0.2$, MMA:DMF = 1:2 (v/v) at rt and irradiation by 2.1 mW/cm^2 UV light.

2.6 Conclusions

The most efficient conditions for ICAR ATRP of AN utilized a $\text{CuBr}_2/\text{TPMA}$ catalyst, while employing BPN as the initiator, and a 0.1:1 ratio of AIBN:BPN in DMSO at 65°C . These conditions were used to synthesize PAN with excellent control over MW and MWD ($M_w/M_n = 1.1 - 1.3$) with catalyst loading ranging from 10 to 50 ppm. Additionally, it was determined that even at a catalyst loading as low as 1 ppm, the $\text{CuBr}_2/\text{TPMA}$ catalyst complex maintained control over the polymerization. The synthesized PAN-Br macroinitiators had high chain-end functionality and were cleanly chain extended with BA using ICAR ATRP with 50 ppm of $\text{CuBr}_2/\text{TPMA}$ catalyst. Conditions were also developed to chain extend the PAN-Br macroinitiators with St by ICAR ATRP at low temperature (60°C) to avoid self-initiation of St. Three PAN-Br macroinitiators of different DPs were chain extended with varying amounts of St and in all cases well-defined BCPs were synthesized.

Three phenothiazine derivatives were evaluated as catalysts for MF ATRP of AN. Both NMR and chain-extension with MMA by MF ATRP, confirm that the synthesized PAN had highly preserved bromine chain-end functionality, which supports the ATRP mechanism. The MF ATRP method will be useful for the synthesis of precursors of electronic materials as they are prepared without residual transitional metals. However, when compared to traditional Cu-based ATRP, this MF method still has room for further improvement; such as improving initiator efficiency, generating polymers with higher molecular weight, and lower dispersity.

2.7 References

- (1) Minus, M. L.; Kumar, S. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Minus, M. L., Kumar, S., Eds.; Wiley: Hoboken, N.J., 2007; Vol. 26.
- (2) Frank, E.; Steudle, L. M.; Ingildeev, D.; Spörl, J. M.; Buchmeiser, M. R. *Angewandte Chemie* **2014**, 53, 5262.
- (3) Xin, W.; Song, Y. *RSC Advances* **2015**, 5, 83239.
- (4) Matyjaszewski, K.; Jo, S. M.; Paik, H.; Gaynor, S. G. *Macromolecules* **1997**, 30, 6398.
- (5) Matyjaszewski, K.; Jo, S. M.; Paik, H.; Shipp, D. A. *Macromolecules* **1999**, 32, 6431.
- (6) Tang, C.; Kowalewski, T.; Matyjaszewski, K. *Macromolecules* **2003**, 36, 1465.
- (7) Tang, C.; Kowalewski, T.; Matyjaszewski, K. *Macromolecules* **2003**, 36, 8587.
- (8) Moskowicz, J. D.; Abel, B. A.; McCormick, C. L.; Wiggins, J. S. *Journal of Polymer Science Part A: Polymer Chemistry* **2016**, 54, 553.
- (9) Kowalewski, T.; Tsarevsky, N. V.; Matyjaszewski, K. *Journal of the American Chemical Society* **2002**, 124, 10632.
- (10) Lin, Y.; Wang, X.; Qian, G.; Watkins, J. J. *Chemistry of Materials* **2014**, 26, 2128.
- (11) Kruk, M.; Dufour, B.; Celer, E. B.; Kowalewski, T.; Jaroniec, M.; Matyjaszewski, K. *Chemistry of Materials* **2006**, 18, 1417.
- (12) Tang, C.; Qi, K.; Wooley, K. L.; Matyjaszewski, K.; Kowalewski, T. *Angewandte Chemie* **2004**, 43, 2783.
- (13) Lazzari, M.; Chiantore, O.; Mendichi, R.; López-Quintela, M. A. *Macromolecular Chemistry and Physics* **2005**, 206, 1382.
- (14) Dufour, B.; Tang, C.; Koynov, K.; Zhang, Y.; Pakula, T.; Matyjaszewski, K. *Macromolecules* **2008**, 41, 2451.

- (15) Tang, C.; Dufour, B.; Kowalewski, T.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 6199.
- (16) Kruk, M.; Dufour, B.; Celer, E. B.; Kowalewski, T.; Jaroniec, M.; Matyjaszewski, K. *J. Phys. Chem. B* **2005**, *109*, 9216.
- (17) Wu, D.; Li, Z.; Zhong, M.; Kowalewski, T.; Matyjaszewski, K. *Angewandte Chemie* **2014**, *53*, 3957.
- (18) McGann, J. P.; Zhong, M.; Kim, E. K.; Natesakhawat, S.; Jaroniec, M.; Whitacre, J. F.; Matyjaszewski, K.; Kowalewski, T. *Macromolecular Chemistry and Physics* **2012**, *213*, 1078.
- (19) Zhong, M.; Kim, E. K.; McGann, J. P.; Chun, S.-E.; Whitacre, J. F.; Jaroniec, M.; Matyjaszewski, K.; Kowalewski, T. *Journal of the American Chemical Society* **2012**, *134*, 14846.
- (20) Zhong, M.; Natesakhawat, S.; Baltrus, J. P.; Luebke, D.; Nulwala, H.; Kowalewski, K. M. a. a. T. *Chemical communications* **2012**, *48*, 11516.
- (21) Zhong, M.; Jiang, S.; Tang, Y.; Gottlieb, E.; Kim, E. K.; Star, A.; Matyjaszewski, K.; Kowalewski, T. *Chemical Science* **2014**, *5*, 3315.
- (22) Ju, M. J.; Choi, I. T.; Zhong, M.; Lim, K.; Ko, J.; Mohin, J.; Lamson, M.; Kowalewski, T.; Matyjaszewski, K.; Kim, H. K. *Journal of Materials Chemistry A* **2015**, *3*, 4413.
- (23) Dai, L.; Xue, Y.; Qu, L.; Choi, H. J.; Baek, J. B. *Chemical reviews* **2015**, *115*, 4823.
- (24) Masa, J.; Xia, W.; Muhler, M.; Schuhmann, W. *Angewandte Chemie International Edition* **2015**, *54*, 10102.
- (25) Dong, H.; Tang, W.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 2974.
- (26) Chen, H.; Liu, D.; Song, Y.; Qu, R.; Wang, C. *Polymers for Advanced Technologies* **2011**, *22*, 1513.
- (27) Yu, Y.-H.; Liu, X.-H.; Jia, D.; Cheng, B.-W.; Ren, Y.-L.; Zhang, F.-J.; Li, H.-N.; Chen, P.; Xie, S. *Journal of Polymer Science Part A: Polymer Chemistry* **2013**, *51*, 1690.
- (28) Liu, X.-h.; Wang, J.; Yang, J.-s.; An, S.-l.; Ren, Y.-l.; Yu, Y.-h.; Chen, P. *Journal of Polymer Science Part A: Polymer Chemistry* **2012**, *50*, 1933.
- (29) Liu, X.-h.; Wang, J.; Zhang, F.-j.; An, S.-l.; Ren, Y.-l.; Yu, Y.-h.; Chen, P.; Xie, S. *Journal of Polymer Science Part A: Polymer Chemistry* **2012**, *50*, 4358.
- (30) Liu, X.; Zhang, G.; Li, B.; Bai, Y.; Li, Y. *Journal of Polymer Science Part A: Polymer Chemistry* **2010**, *48*, 5439.
- (31) Chen, Q.; Zhang, Z.; Zhou, N.; Cheng, Z.; Tu, Y.; Zhu, X. *Journal of Polymer Science Part A: Polymer Chemistry* **2011**, *49*, 1183.
- (32) Yu, Y.-H.; Liu, X.-H.; Jia, D.; Cheng, B.-W.; Zhang, F.-J.; Li, H.-N.; Chen, P.; Xie, S. *Journal of Polymer Science Part A: Polymer Chemistry* **2013**, *51*, 1468.
- (33) Matyjaszewski, K.; Jakubowski, W.; Min, K.; Tang, W.; Huang, J.; Braunecker, W. A.; Tsarevsky, N. V. *Proceedings of the National Academy of Sciences of the United States of America* **2006**, *103*, 15309.
- (34) Honigfort, M. E.; Brittain, W. J. *Macromolecules* **2002**, *35*, 4849.
- (35) Kickelbick, G.; Paik, H.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 2941.
- (36) Shen, Y.; Tang, H.; Ding, S. *Progress in Polymer Science* **2004**, *29*, 1053.
- (37) Goto, A.; Hirai, N.; Nagasawa, K.; Tsujii, Y.; Fukuda, T.; Kaji, H. *Macromolecules* **2010**, *43*, 7971.

- (38) Goto, A.; Suzuki, T.; Ohfuji, H.; Tanishima, M.; Fukuda, T.; Tsujii, Y.; Kaji, H. *Macromolecules* **2011**, *44*, 8709.
- (39) Goto, A.; Ohtsuki, A.; Ohfuji, H.; Tanishima, M.; Kaji, H. *Journal of the American Chemical Society* **2013**, *135*, 11131.
- (40) Ohtsuki, A.; Goto, A.; Kaji, H. *Macromolecules* **2013**, *46*, 96.
- (41) Treat, N. J.; Sprafke, H.; Kramer, J. W.; Clark, P. G.; Barton, B. E.; Alaniz, J. R. d.; Fors, B. P.; Hawker, C. J. *Journal of the American Chemical Society* **2014**, *136*, 16096.
- (42) Miyake, G. M.; Theriot, J. C. *Macromolecules* **2014**, *47*, 8255.
- (43) Britovsek, G. J. P.; England, J.; White, A. J. P. *Inorganic Chemistry* **2005**, *44*, 8125.
- (44) Gagne, R. R.; Kreh, R. P.; Dodge, R. A.; Marsh, R. E.; McCool, M. *Inorganic Chemistry* **1982**, *21*, 254.
- (45) Tang, W.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 1858.
- (46) Kaur, A.; Gorse, E. E.; Ribelli, T. G.; Jerman, C. C.; Pintauer, T. *Polymer* **2015**, *72*, 246.
- (47) Zhong, M.; Matyjaszewski, K. *Macromolecules* **2011**, *44*, 2668.
- (48) Bashir, Z. *Carbon* **1991**, *29*, 1081.
- (49) Bates, F. S. *Science* **1991**, *251*, 898.
- (50) Dalton, S.; Heatley, F.; Budd, P. M. *Polymer* **1999**, *40*, 5531.
- (51) Barton, A. F. *CRC handbook of solubility parameters and other cohesion parameters*; CRC press, 1991.
- (52) Yamaguchi, T.; Watanabe, S.; Shimada, Y. *Chemosphere* **1973**, *2*, 7.
- (53) Belanger, J. M.; Penelle, J.; Russel, T. P. *Macromolecules* **2006**, *39*, 1766.
- (54) Mohin, J. W., Carnegie Mellon University, 2015.
- (55) Mosnáček, J.; Nicolaÿ, R.; Kar, K. K.; Fruchey, S. O.; Cloeter, M. D.; Harner, R. S.; Matyjaszewski, K. *Industrial & Engineering Chemistry Research* **2012**, *51*, 3910.
- (56) Denizligil, S.; Resul, R.; Yagci, Y. *Macromolecular Chemistry and Physics* **1996**, *197*, 1233
- (57) Dossow, D.; Zhu, Q. Q.; Hizal, G.; Yagci, Y.; Schnabel, W. *Polymer* **1996**, *37*, 2821.

Chapter 3

Polyacrylonitrile-based Stars as Templates for Nitrogen-doped Nanocarbons

3.1 Preface

This chapter describes the development of conditions for the preparation of polyacrylonitrile-based stars with either polyacrylonitrile (PAN) homo-arms or polyacrylonitrile-*b*-poly(butyl acrylate) (PAN-*b*-PBA) block copolymer (BCP) arms. The optimized conditions to synthesize well-defined PAN and PAN BCPs with high chain end functionality by ICAR ATRP were developed (Chapter 2) which made it possible to prepare PAN-based stars, via the arm first method. Conditions for the preparation of PAN-based stars via the arm first method, including the type and amount of cross-linker, the concentration of macroinitiator, and polymerization time were studied. The degree of polymerization (DP_n) of the PAN and PBA segments were varied to prepare a library of stars. The stars were used as precursors for nitrogen-doped carbons and the surface area of the resulting carbon material was measured.

I synthesized the majority of the macroinitiators and all PAN-based stars for this project and optimized conditions for the star synthesis. Dr. Maciek Kopec and Rui Yuan

synthesized some of the PAN macroinitiators and Dr. Maciek Kopec pyrolyzed the star samples and analyzed their surface area using N₂ adsorption with BET analysis.

3.2 Introduction

Nitrogen-doped nanostructured carbons (N-doped nanocarbons) templated from PAN-*b*-PBA block copolymers (BCPs) have surface areas up to 500 m²/g and small pore size distributions.¹⁻³ Because of their highly accessible pyridinic nitrogens, they exhibit superior performance as supercapacitors,² CO₂ sorbents,⁴ catalyst for oxygen reduction reaction (ORR),¹ and cathodes in dye sensitized solar cells.⁵ However, limits on the thermal stability of the nanoscale morphology of BCP precursors establish limits on maximizing the surface area. Thus, nanocarbons with higher surface areas could not be achieved by further decreasing block size.³ This limitation could be due to low molecular weight PAN-*b*-PBA BCPs reaching their order-disorder transition temperature (T_{ODT}) close to the temperature of PAN cyclization (280 °C).⁶⁻⁹ Reaching T_{ODT} causes the PAN and PBA phases to become miscible in each other and after the removal of PBA, the carbons collapses.⁶⁻⁹ In addition, a lower BCP DP leads to a weaker phase separation.^{6,10,11} Temperature has a larger effect on BCPs with a low degree of polymerization (DP), as phase separation is dependent on the DP of the BCP and the Flory-Huggins interaction parameter (χ).^{6,10,11} This is a major limitation of using BCPs as precursors for templating N-doped nanocarbons.

One way to avoid the T_{ODT} in BCPs is to “anchor” them to a support, such as a silica wafer or particle. However, this would require the removal of silica with HF or concentrated NaOH, which is undesirable, especially during scale-up. Additionally, the

precursor should allow for easy fabrication of devices, as was exemplified by the fabrication of N-doped nanocarbon electrodes for ORR, by casting PAN-*b*-PBA BCPs from a DMF solution onto a glassy carbon electrode followed by direct *in situ* pyrolysis.¹

It was previously shown that nanocarbon could be formed from bottlebrush copolymers with PBA-*b*-PAN-*b*-PtBA side chains attached to a methacrylate-based backbone.¹² The nanocarbon had good retention of the brush morphology, as observed by AFM, after oxidative stabilization and carbonization. This would not be possible if the T_{ODT} was not circumvented by controlled polymer architecture.

Based on the successful use of bottlebrushes for nanocarbon formation, we proposed to synthesize PAN based star polymers as precursors for nanocarbons. PAN-based stars have been reported in the literature. Three arm PAN stars were synthesized using 1,1,1-tris(4-chlorosulfonylphenyl)-ethane¹³ (3PSC) as a 3-arm initiator and 3, 4 and 6 arm PAN stars were successfully synthesized with a poly(ester amide) as a core.^{13,14} Three-arm BCP stars of PBA-*b*-PAN were synthesized using a tri-functional ATRP initiator to yield a star with a narrow molecular weight distribution (MWD) ($M_w/M_n = 1.25$) and a PAN content ranged from 8 to 31 wt%.¹⁵ These stars were utilized as thermoplastic elastomers. It would be interesting to study these stars as N-doped nanocarbon precursors. Thus, we investigated the synthesis of star polymers, via the arm-first method,¹⁶⁻¹⁹ and examined their use as precursors for N-doped nanocarbons with “anchored” PAN BCP morphology, so the T_{ODT} can be avoided. The arm first method was chosen, as it allows incorporation of a higher amount of arms into the star polymer than the core first method.¹⁷⁻²¹ By attaching the BCP arms to a polymer core the T_{ODT} of the BCP should be avoided during stabilization and carbonization and new pore

architectures could be achieved by star templating, as the core (1-2 nm) should form additional porosity in micropore range, <2 nm.²⁰

This chapter describes the synthesis of PAN-based stars and their use as precursors to N-doped nanocarbons. Conditions for the synthesis of PAN homo-arm stars were developed by investigating different cross-linkers, cross-linker amounts, macroinitiator concentration, and polymerization time. These conditions were used to synthesize PAN-*b*-PBA BCP stars with three different degrees of polymerization (DP_n) of PAN ($DP_{PAN} = 30, 50, \text{ and } 79$) and three different DP_n of PBA segments ($DP_{PBA} \sim 10, 20, 45$). The stars were stabilized at 280 °C and carbonized at 800 °C. The nanocarbon samples were analyzed by N₂ sorption and their total surface areas, as well as mesoporous and microporous surface areas, were determined.

3.3 Experimental

3.3.1 Materials

Acrylonitrile (AN, Sigma-Aldrich, 99%), *n*-butyl acrylate (BA, Sigma-Aldrich, >99%), di(ethylene glycol) diacrylate (DEGDA, Sigma-Aldrich, 95%), 1,6-hexanediol diacrylate (HDDA, Sigma-Aldrich, 80%), ethylene glycol diacrylate (EGDA, Polysciences Inc., 90%) were purified by passing over a column of basic alumina to remove the inhibitor. 2-Bromopropionitrile (BPN, Sigma-Aldrich, 97%), copper (I) bromide (CuBr, Sigma-Aldrich, 99%), copper (I) chloride (CuCl, Sigma-Aldrich, 99%), copper (II) bromide (CuBr₂, Sigma-Aldrich, 99%), α, α' -azoisobutyronitrile (AIBN, Sigma-Aldrich, 98%), dimethylformamide (DMF, Fisher, 99.9%), dimethyl sulfoxide

(DMSO, Fisher, 99.9%), and methanol (Fisher, 99.9%) were used as received. TPMA was synthesized according to a previously published procedure.²²

3.3.2 Synthesis of PAN-Br

PAN-Br was synthesized according to a previously published procedure,²³ also detailed in Chapter 2. In a typical procedure, 5 mg of AIBN (0.031 mmol, 0.1 equiv.), 5 mL of DMSO and 0.5 mL of DMF were added to a Schlenk flask and degassed for 30 min. A stock solution of CuBr₂ and TPMA in DMF was prepared and degassed for 10 min, then 0.7 mg (0.003 mmol, 0.01 equiv.) of CuBr₂, and 2.67 mg (0.009 mmol, 0.03 equiv.) of TPMA were added to the Schlenk flask. 3.26 g (61 mmol, 200 equiv.) of degassed AN was then added to the flask, and finally 41 mg (0.3 mmol, 1 equiv.) of BPN was added and the polymerization was started by immersing the flask in an oil bath at 65 °C and conducted for 10 h. The final polymer was isolated by precipitation into methanol/water (4:1, v/v) and dried under vacuum at room temperature overnight.

3.3.3 Synthesis of PAN-*b*-PBA-Br

PAN-Br was synthesized according to a previously published procedure,²³ also found in Chapter 2. In a typical procedure, 2.69 g (0.010 mmol, 1 equiv.) of PAN-Br macroinitiator ($M_{n,NMR}$ = 6700, M_w/M_n = 1.24) was dissolved in 6 mL of DMF and the solution was added to a 10 mL Schlenk flask containing 0.23 mg CuBr₂, (0.001 mmol, 0.01 equiv.) 0.91 mg TPMA (0.003 mmol, 0.03 equiv.), and 0.40 mL of DMSO. The contents were bubbled with nitrogen for 30 min. A solution of 3 mL (21 mmol, 200 equiv.) of deoxygenated BA and 1.73 mg (0.01 mmol, 0.1 equiv.) of AIBN was then

added dropwise to the flask with vigorous stirring to prevent PAN precipitation. The reaction was conducted at 60 °C for 5.5 h. The resulting block copolymer was precipitated by addition to a methanol/water mixture (1:1, v/v), filtered, and dried under vacuum.

3.3.4 Synthesis of PAN-based stars

In a typical procedure for star synthesis, the PAN-Br macroinitiator was dissolved in DMF by stirring overnight at room temperature to provide a 0.02 to 0.075 mM concentration of the macroinitiator. The solution was added to a Schlenk flask along with DEGDA cross-linker (0.79 mL; 2.36 mmol), and TPMA (41.2 mg; 0.142 mmol). The reaction mixture was purged with N₂ for 20 minutes. CuBr (17.0 mg; 0.118 mmol) was added, under N₂ flow. The flask was sealed and immersed in an oil bath at 60 °C. Samples were removed periodically to monitor the progress of star formation and the reaction was stopped when further increase in the MW of the star, as determined by GPC analysis, ceased. The stars were purified by precipitation into a solution of MeOH:H₂O (80:20), filtered, and dried under vacuum for 24 hours.

For the synthesis of stars with PAN-*b*-PBA-Br macroinitiators, the concentration of macroinitiator in the initial DMF solution was 0.008 to 0.02 mM. All other aspects of the procedures were kept constant.

3.3.5 Pyrolysis of Star Samples

The as-prepared star copolymers were precipitated and the powder was directly carbonized. The powders were stabilized at 280 °C for 1 h under air flow (150 mL/min)

with a heating rate of 1 °C/min from room temperature. The sample was cooled down to room temperature, and then pyrolyzed at 800 °C for 0.5 h under nitrogen gas flow (150 mL/min) after increasing the temperature at a heating rate of 10 °C/min.

3.3.6 Characterization

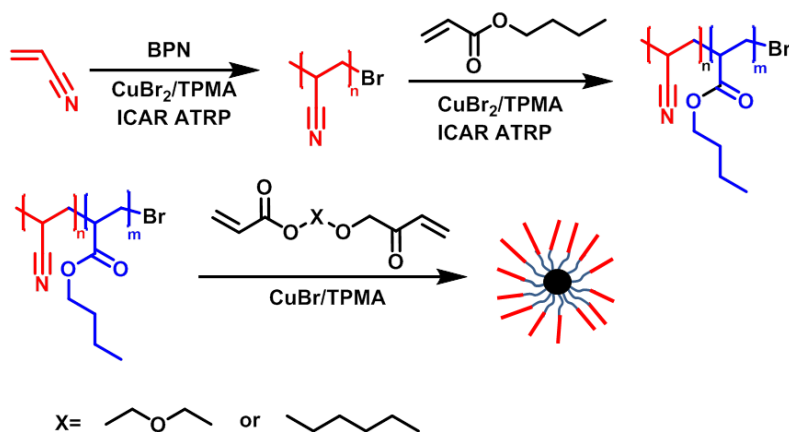
^1H nuclear magnetic resonance (^1H NMR) spectroscopy measurements were performed on a Bruker Avance 300 MHz spectrometer and used to determine the conversion of monomer in DMSO- d_6 , M_n of resulting PAN homopolymer in DMSO- d_6 , and in DMF- d_7 for the resulting PAN-*b*-PBA block-copolymers. The apparent molecular weights and molecular weight distributions (M_w/M_n) were determined by gel permeation chromatography (GPC). The GPC system used a Waters 515 HPLC pump and a Waters 2414 refractive index detector using PSS columns (Styrogel 10^2 , 10^3 , 10^5 Å) with 10 mM LiBr-containing DMF as the eluent at a flow rate of 1 mL/min at 50 °C using linear PEO standards for linear PAN stars and PMMA standards for PAN-*b*-PBA block copolymers. Area fractions of both star and linear polymers were determined by multipeak splitting of the GPC curve using the Gaussian function in OriginPro 8.0 software.

Brunauer-Emmet-Teller (BET) specific surface area measurements were performed using a Micromeritics Gemini VII 2390 Surface Area Analyzer with VacPrep 061 degasser. Carbon samples were degassed at 300 °C and 20 mTorr vacuum for at least 8 hours prior to the measurement. The adsorption isotherms were fitted to the Barrett-Joyner-Halenda (BJH) model with the Kruk-Jaroniec-Sayari (KJS) correction to yield pore-size distributions. The amount of micropores was estimated using the t-plot method with the KJS thickness correction.

3.4 Results and Discussion

PAN-Br and PAN-*b*-PBA-Br macroinitiators were synthesized by ICAR ATRP and cross-linked with an acrylate based cross-linker to form the PAN-based stars, Scheme 3.4. An acrylate based cross-linker was chosen, because carbon templated from PAN-*b*-PBA block copolymers (BCPs) had higher surface areas than carbon derived from PAN-*b*-PS BCPs.^{3,24} A high star yield (>80%) was targeted, because the PAN-Br macroinitiator arms could not easily be removed by dialysis, which is the typical procedure employed to purify star polymers.

Scheme 3.4. Synthesis of PAN-based stars



3.4.1 Synthesis of Stars from PAN-Br

Initially three different ATRP procedures were tested; normal, activators generated by electron transfer (AGET), and activators regenerated by electron transfer (ARGET) ATRP conditions, with a PAN₄₀-Br macroinitiator, to determine which would provide the highest star yield. The only condition that resulted in star formation was normal ATRP with a ratio of reagents: [PAN₄₁-Br]:[DEGDA]:[CuBr]:[TPMA] =

1:5:0.25:0.3. The concentration of PAN-Br in DMF was 0.075 mM, and the polymerization was conducted at 60 °C (Table 3.4.1; Entry 1) over 24 hours. GPC analysis showed a clear shift to higher molecular weight (MW) from the macroinitiator and the star yield was 88% (Figure 3.4.1.1). The star yield was calculated by determining the area fraction of the star and remaining macroinitiator from the molecular weight distribution (MWD) curve.

Table 3.4.1. PAN star samples

Entry	Sample	DP _{PAN}	X-linker ^b	[PAN-Br] (mM)	Star Yield
1	PAN ₄₁ -Poly(DEGDA)	41	DEGDA	0.075	88%
2	PAN ₄₃ -Poly(DEGDA)	43	DEGDA	0.075	80%
3	PAN ₄₉ -Poly(DEGDA) ^a	49	DEGDA	0.038	88%
4	PAN ₅₆ -Poly(HDDA)	56	HDDA	0.033	82%
5	PAN ₈₇ -Poly(HDDA)	87	HDDA	0.020	64%
6	PAN ₈₇ -Poly(EGDA)	87	EGDA ^c	0.025	70%

^aCuCl/TPMA catalyst, ^b[PAN-Br]:[X-linker]= 1:5; [PAN-Br]:[EGDA]= 1:15

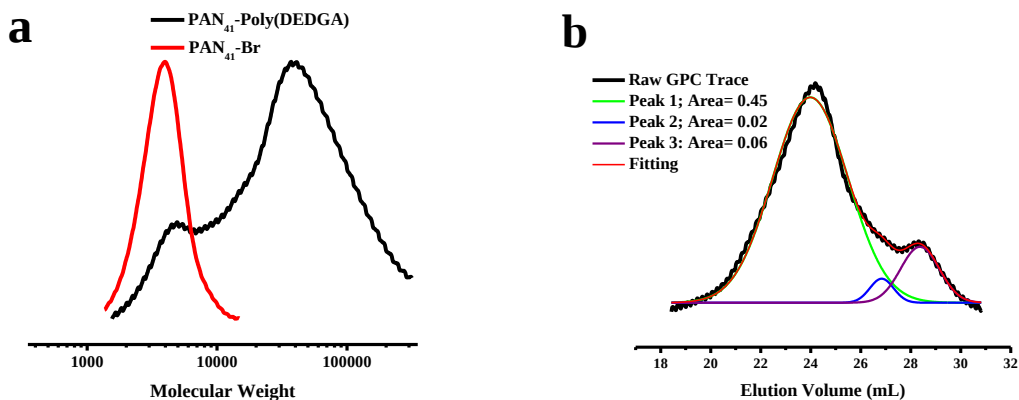


Figure 3.4.1.1. MWD of PAN₄₁-Br and PAN₄₁-Poly(DEGDA); Peak fitting of PAN₅₀-Poly(DEGDA) to determine area (b); [PAN₄₁-Br]:[DEGDA]: [CuBr]:[TPMA]= 1:5:0.25:0.3

Since the star yield was 88% and the shift of the star to higher MW was not clean, it was speculated that chain end functionality of the PAN₄₁-Br macroinitiator was low. Thus, a new macroinitiator, PAN₄₃-Br with high chain end functionality, as confirmed by ¹H NMR, was synthesized and this new sample of PAN₄₃-Br was cross-linked with DEGDA under the same conditions. After a reaction time of only 2 hours, a star polymer was formed in relatively high yield (Figure 3.4.1.2a). After this point little of the remaining macroinitiator was incorporated into the star during the remaining 22 hours of the polymerization. However, the star species MWD broadened and the final star yield was around 80% (Figure 3.4.1.2b), which was similar to the previous reaction, within experimental error, based on GPC and star yield analysis. The broadening of MWD was attributed to star-star coupling.

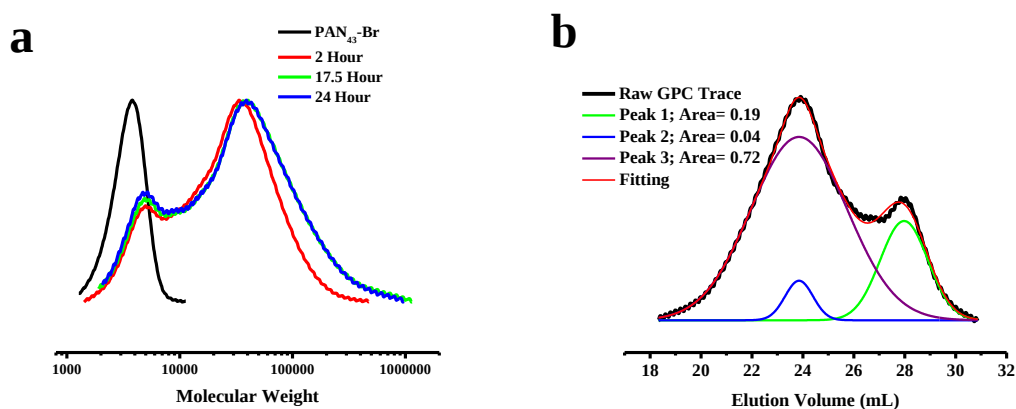


Figure 3.4.1.2. MWD of PAN₄₃-Br and evolution of PAN₄₃-Poly(DEGDA); Peak fitting of PAN₄₃-Poly(DEGDA) to determine area (b); [PAN₄₃-Br]:[DEGDA]:[CuBr]:[TPMA]=1:5:0.25:0.3

As star formation occurs rapidly, CuCl/TPMA was tested as a catalyst and the concentration of the macroinitiator was decreased to slow down the rate of reaction, while keeping all other conditions the same. The increased strength of the C-Cl bond should slow the rate of activation, thus slowing the entire reaction and allow for more uniform star formation. The star yield was 88% (Figure 3.4.1.3b). However, the reaction was rapid and the star species was fully formed in 3 hours. The MWD of the star species broadened with increasing polymerization time indicating star-star coupling and ill-defined stars were formed (Figure 3.4.1.3a).

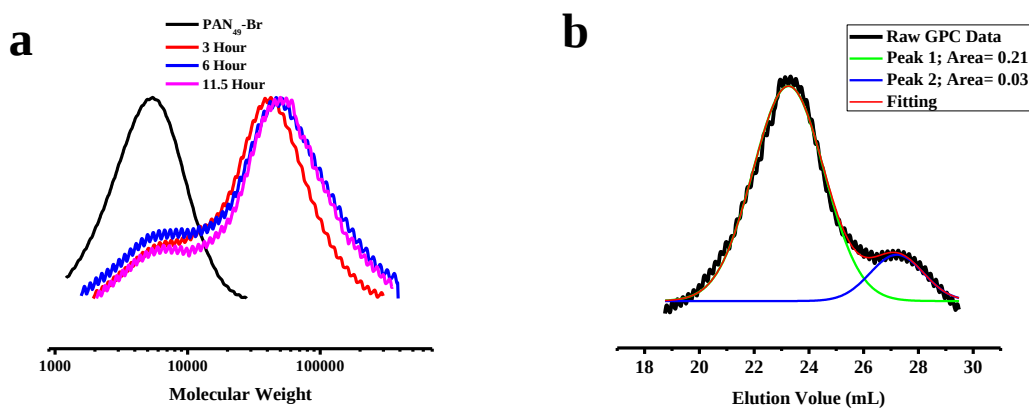


Figure 3.4.1.3. MWD of PAN₄₉-Br and evolution of PAN₄₉-Poly(DEGDA); Peak fitting of PAN₄₉-Poly(DEGDA) to determine area (b); [PAN₄₉-Br]:[DEGDA]:[CuCl]:[TPMA]= 1:5:0.25:0.3

Previous work has shown that higher star yields can be obtained through a self-assembly process.^{25,26} Specifically, mikto-arm stars were synthesized in a water/ethanol mixture using two macroinitiators, poly(N,N'-dimethylacrylamide) and poly(2-methoxyethyl acrylate), and cross-linking them with a hydrophobic cross-linker, 1,6-

hexanediol diacrylate (HDDA).²⁶ The authors postulate that higher star yields are obtained, because the addition of the hydrophobic HDDA cross-linker to the hydrophilic macroinitiators caused micellization. The unreacted HDDA was contained in the core with the hydrophilic macroinitiators on the outside. The micelle structure can lead to higher star yields, as well as the formation of well-defined stars.²⁵

HDDA was used as a hydrophobic cross-linker for PAN₅₆-Br. The ratio of reagents was [PAN₅₆-Br]:[HDDA]:[CuBr]:[TPMA]=1:5:0.25:0.3, the concentration of PAN₅₆-Br in DMF was 0.033 mM, and the reaction was conducted at 60 °C for 48 hours. There was a cleaner shift of the GPC curves from the macroinitiator to the star. The star has $M_n = 27,100$ and $M_w/M_n = 1.37$, which was calculated because of the clean shift of the star species to higher MW, Figure 3.4.1.4a. Well defined stars were obtained when the hydrophobic HDDA cross-linker was used, but the star yield (82%; Figure 3.4.1.4b) did not increase.

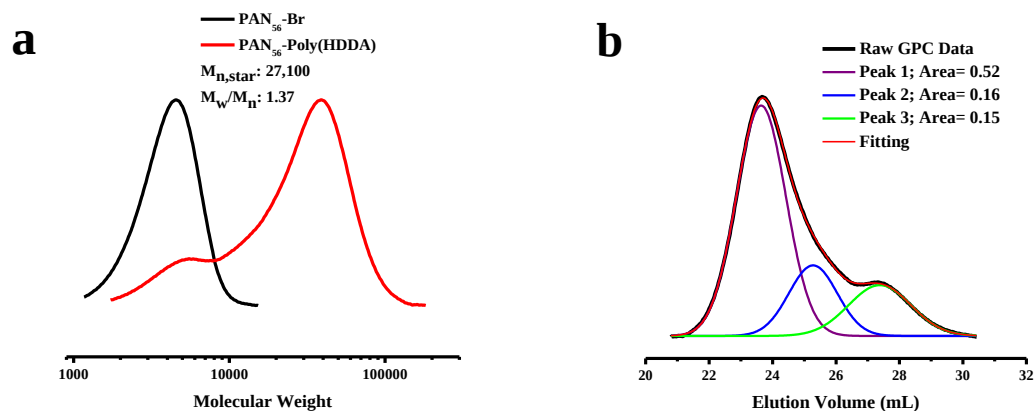


Figure 3.4.1.4. MWD of PAN₅₆-Br and PAN₅₆-Poly(HDDA); Peak fitting of PAN₅₆-Poly(HDDA) to determine area (b); [PAN₅₆-Br]:[HDDA]:[CuBr]:[TPMA]= 1:5:0.25:0.3

Stars were synthesized with a higher MW PAN macroinitiator, PAN₈₇-Br, using the HDDA cross-linker. The ratio reagents was [PAN₈₇-Br]:[HDDA]:[CuBr]: [TPMA] = 1:5:0.25:0.3, and the concentration PAN₈₇-Br in DMF was 0.02 mM. The polymerization was conducted at 60 °C. Due to the increased length and decreased concentration of the macroinitiator, the polymerization proceeded slower and star formation was not observed until the polymerization had been conducted for 24 hours, Figure 3.4.1.5a. After this point the star yield was only 64% (Figure 3.4.1.5b) and did not increase. Two star species were observed in the final product.

Generally, a shorter cross-linker should give a higher star yield, as it can form a more compact cross-linked core. Thus, EGDA was tested as a cross-linker for the longer macroinitiator, PAN₈₇-Br. The amount of cross-linker was also increased, so the ratio of reagents was [PAN₈₇-Br]:[EGDA]:[CuBr]:[TPMA]=1:15:0.25:0.3, with the concentration of PAN₈₇-Br in DMF = 0.025 mM, and the polymerization was conducted 60 °C. Initially, after the reaction was conducted for 24 hours, a gel was formed. The reaction was repeated and it was stopped after 5.5 hours then the star species was analyzed. The star yield (70%; Figure 3.4.1.6b) was slightly higher when using a higher amount of the smaller EGDA cross-linker. However, star-star coupling was observed by formation of a high molecular weight shoulder, Figure 3.4.1.6a, yielding poorly defined stars with a broad MWD.

Thus, it was concluded that the star yield of PAN homo-arm stars is limited to between 80-90% for short macroinitiators and 60-70% for long macroinitiators, no matter which cross-linker, the amount of cross-linker, or DP_{PAN} employed. This could be due to the semi-crystalline nature and rigidity of the PAN macroinitiators forming an

impenetrable shell around the cross-linked core, so no additional arms can be added once the star is initially formed.

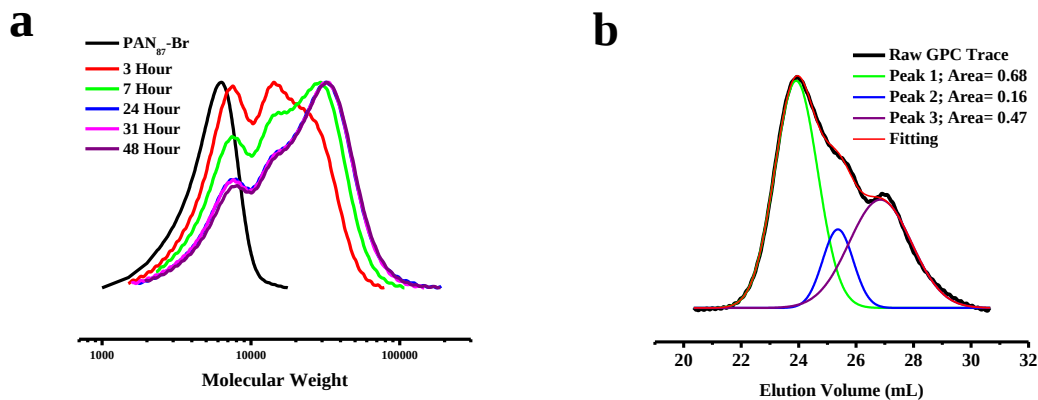


Figure 3.4.1.5. MWD of PAN₈₇-Br and evolution of PAN₈₇-Poly(HDDA); Peak fitting of PAN₈₇-Poly(HDDA) to determine area (b); [PAN₈₇-Br]:[HDDA]:[CuBr]:[TPMA]= 1:5:0.25:0.3

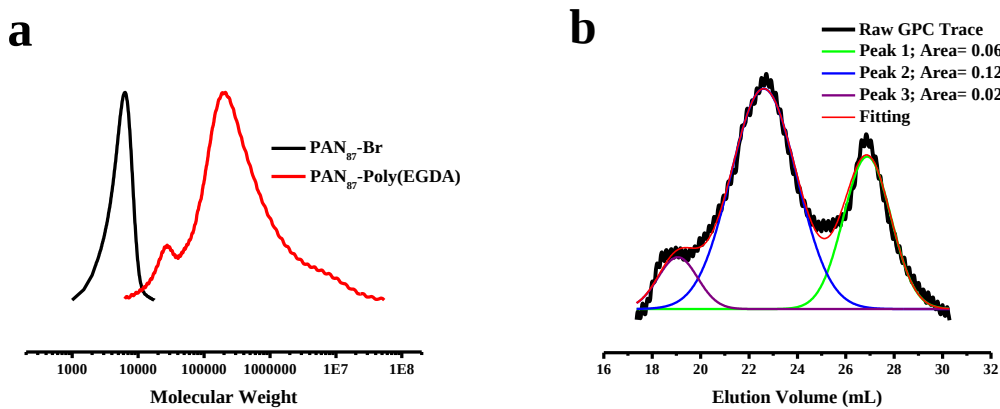


Figure 3.4.1.6. MWD of PAN₈₇-Br and PAN₈₇-Poly(EGDA) (a); Peak fitting of PAN₈₇-Poly(EGDA) to determine area (b); [PAN₈₇-Br]:[EGDA]: [CuBr]:[TPMA]= 1:15:0.25:0.3

3.4.2 Synthesis of Stars from PAN-*b*-PBA-Br

Once conditions were developed for the synthesis of PAN homo-arm stars, they were tailored for the synthesis of PAN-*b*-PBA BCP stars. Three PAN macroinitiators ($DP_{\text{PAN}} = 30, 50, \text{ or } 79$) were synthesized and chain extended with BA while targeting a $DP_{\text{PBA}} = 10, 20, \text{ or } 40$, Table 3.4.2. The stars were cross-linked with the hydrophobic HDDA cross-linker, so the BCP star arms could undergo self-assembly, presumably to a greater extent due to the hydrophobic nature of the PBA block, and form stars.²⁵

Table 3.4.2. PAN-*b*-PBA Star Samples

Entry	Sample	DP_{PAN}	DP_{PBA}	[PAN- <i>b</i> -PBA-Br] (mM)	Star Yield
1	PAN ₃₀ - <i>b</i> -PBA ₁₈ -Poly(HDDA) ^a	30	18	0.008	74%
2	PAN ₃₀ - <i>b</i> -PBA ₁₈ -Poly(HDDA) ^a	30	18	0.020	92%
3	PAN ₇₉ - <i>b</i> -PBA ₁₀ -Poly(HDDA) ^a	79	10	0.02	89%
4	PAN ₇₉ - <i>b</i> -PBA ₁₀ -Poly(HDDA) ^b	79	10	0.020	81%
5	PAN ₇₉ - <i>b</i> -PBA ₄₄ -Poly(HDDA) ^b	79	44	0.01	62%
6	PAN ₅₀ - <i>b</i> -PBA ₁₄ -Poly(HDDA) ^b	50	14	0.02	83%
7	PAN ₅₀ - <i>b</i> -PBA ₂₃ -Poly(HDDA) ^b	50	23	0.02	82%

^a[PAN-*b*-PBA-Br]:[HDDA]= 1:10, ^b[PAN-*b*-PBA-Br]:[HDDA]= 1:5

The BCP, with shorter arms, with a composition of PAN₃₀-*b*-PBA₁₈, were tested for star formation with the reagents in a ratio of [PAN-*b*-PBA-Br]:[HDDA]:[CuBr]:[TPMA]= 1:10:0.25:0.3, and the concentration PAN-*b*-PBA macroinitiator in DMF = 0.08 mM. The polymerization was conducted at 60 °C for 48 hours. Star formation was observed after 3 hours, but additional macroinitiator was no longer being incorporated

into the stars after 8 hours and two star species were observed, Figure 3.4.2.1a. The star yield, including both star species, was only 74% (Figure 3.4.2.1b).

The formation of two star species could be caused by the dilute conditions, so the reaction was repeated with a higher concentration of PAN-*b*-PBA, 0.02 mM, in the initial reaction mixture. After 4.5 hours complete star formation was observed and no additional macroinitiator was incorporated after this time. The star yield was significantly improved, up to 92% (Figure 3.4.2.2b), and the star species was clearly shifted to higher MW from the macroinitiator, Figure 3.4.2.2a.

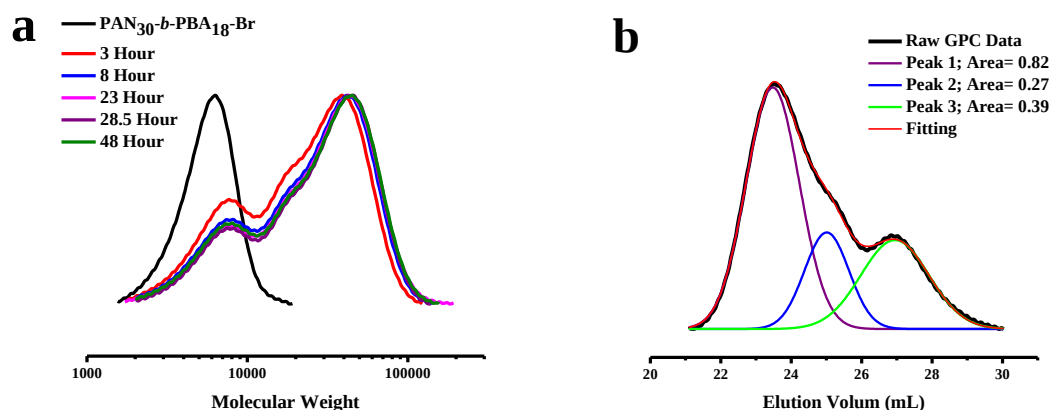


Figure 3.4.2.1. MWD of PAN₃₀-*b*-PBA₁₈-Br and evolution of PAN₃₀-*b*-PBA₁₈-Poly(HDDA); Peak fitting of PAN₃₀-*b*-PBA₁₈-Poly(HDDA) to determine area (b); [PAN-*b*-PBA-Br]:[HDDA]:[CuBr]:[TPMA]= 1:10:0.25:0.3

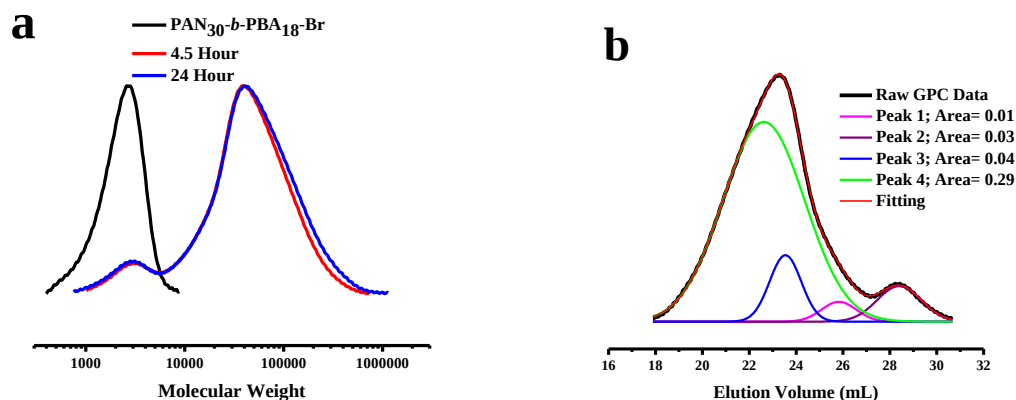


Figure 3.4.2.2. MWD of PAN₃₀-*b*-PBA₁₈-Br and evolution of PAN₃₀-*b*-PBA₁₈-Poly(HDDA); Peak fitting of PAN₃₀-*b*-PBA₁₈-Poly(HDDA) to determine area (b) [PAN-*b*-PBA-Br]:[HDDA]:[CuBr]:[TPMA] = 1:10:0.35:0.6

A higher MW BCP macroinitiator, with $DP_{PAN} = 79$, was used to synthesize stars. The initial ratio of reagents was [PAN-*b*-PBA-Br]:[HDDA]:[CuBr]:[TPMA]= 1:10:0.35:0.6, with the PAN₇₉-*b*-PBA₁₀-Br macroinitiator concentration = 0.02 mM, and the polymerization conducted at 60 °C. These conditions showed star formation in 1.25 hours, but also showed a large amount of star-star coupling generating high MW stars, Figure 3.4.2.3a, which was due to the presence of a high amount of cross-linker. The star yield was 89%, including the star-star coupling species (Figure 3.4.2.3b).

The amount of cross-linker was decreased to a ratio of reagent [PAN-*b*-PBA-Br]:[HDDA]:[CuBr]:[TPMA]= 1:5:0.35:0.6, with a PAN₇₉-*b*-PBA₁₀-Br macroinitiator concentration of 0.02 mM. The polymerization was conducted at 60 °C. Stars were formed in high yield, 81% (Figure 3.4.2.4b), after 9 hours and no star-star coupling was observed when the amount of cross-linker was decreased, Figure 3.4.2.4a.

A BCP with a longer PBA block, PAN₇₉-*b*-PBA₄₄-Br was also used for the synthesis of stars. After testing several conditions, the best conditions employed a reagent ratio of [PAN-*b*-PBA-Br]:[HDDA]:[CuBr]:[TPMA]= 1:5:0.35:0.6, with a macroinitiator concentration of 0.01 mM, and conducting the polymerization at 60 °C for 48 hours. The final product showed the presence of two star species and the star yield was 62%, Figure 3.4.2.5. The low star yield and formation of two star species was attributed to the overall length of the BCP macroinitiator, which has a total DP of 123 which makes star formation difficult as the accessibility of the macroinitiator to the core was significantly hindered by the longer arms that had already been incorporated.

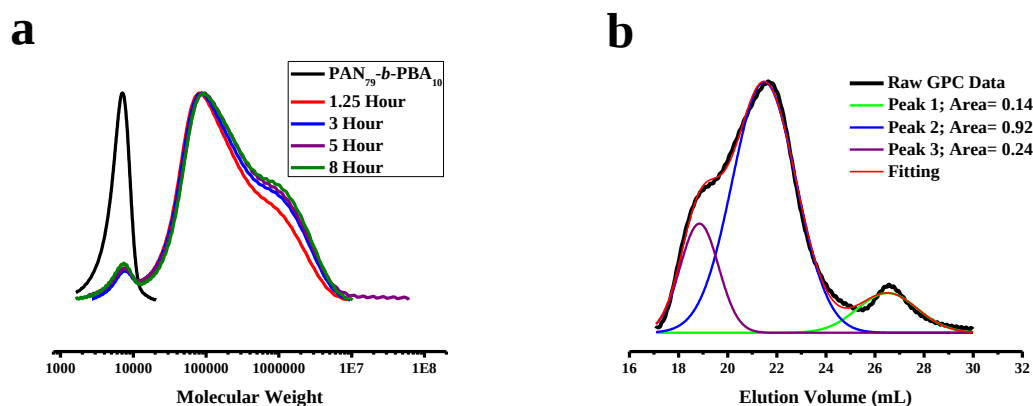


Figure 3.4.2.3. MWD of PAN₇₉-*b*-PBA₁₀-Br and evolution of PAN₇₉-*b*-PBA₁₀-Poly(HDDA) (a); Peak fitting of PAN₇₉-*b*-PBA₁₀-Poly(HDDA) to determine area (b); [PAN-*b*-PBA-Br]:[HDDA]:[CuBr]:[TPMA]= 1:10:0.35:0.6

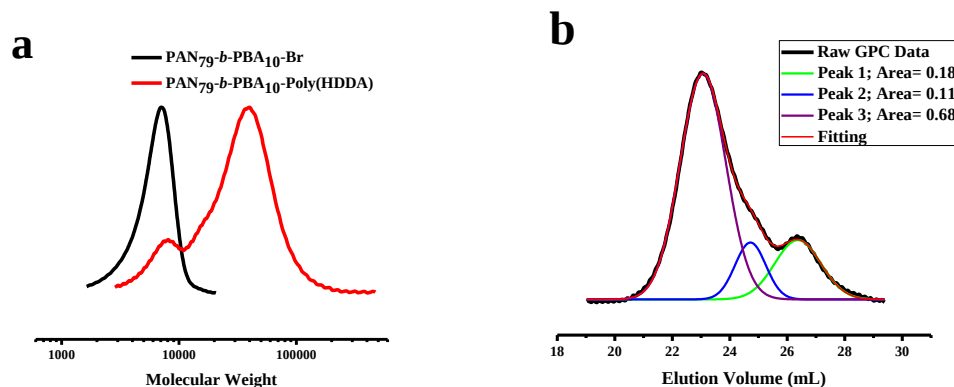


Figure 3.4.2.4. MWD of PAN₇₉-*b*-PBA₁₀-Br and PAN₇₉-*b*-PBA₁₀-Poly(HDDA) (a); Peak fitting of PAN₇₉-*b*-PBA₁₀-Poly(HDDA) to determine area (b); [PAN-*b*-PBA-Br]: [HDDA]:[CuBr]:[TPMA]= 1:5:0.35:0.6

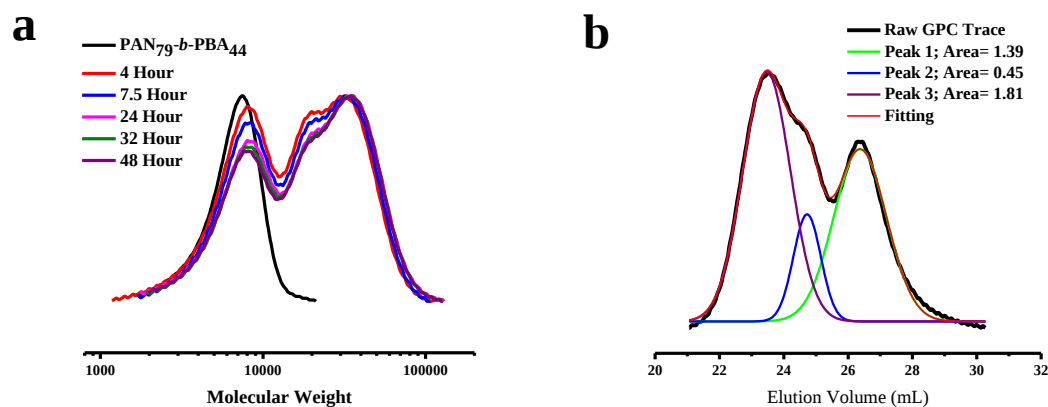


Figure 3.4.2.5. MWD of PAN₇₉-*b*-PBA₄₄-Br and evolution of PAN₇₉-*b*-PBA₄₄-Poly(HDDA); Peak fitting of PAN₇₉-*b*-PBA₄₄-Poly(HDDA) to determine area (b); [PAN-*b*-PBA-Br]:[HDDA]:[CuBr]:[TPMA]= 1:5:0.35:0.6

Star polymers with a medium length BCP, DP_{PAN} of 50, were synthesized. A star, with arm composition of PAN₅₀-*b*-PBA₁₀, was synthesized using a reagent ratio of [PAN-

b-PBA-Br]: [HDDA]:[CuBr]:[TPMA]= 1:5:0.35:0.6, with PAN₅₀-*b*-PBA₁₀ concentration of 0.02 mM in DMF, and polymerization conducted at 60 °C. Star formation was observed during the first two hours and the number of arms increased slightly after 8 hours reaction time, Figure 3.4.2.6a. While the stars were obtained in 83% yield (Figure 3.4.2.6b), they were poorly defined and show low MW tailing, which was not significantly improved by extending the reaction time.

Similar conditions were used to synthesize a star with PAN₅₀-*b*-PBA₂₃ BCP arm composition. The stars were obtained in 82% yield. The polymerization was carried out over 20 hours to ensure full star formation. Less low MW tailing was observed for this star species, but, as in the previous case, did not fully disappear. This indicated that the lower MW star species were not able to incorporate more arms, which was caused by a decreased accessibility to the core, as arms are added.

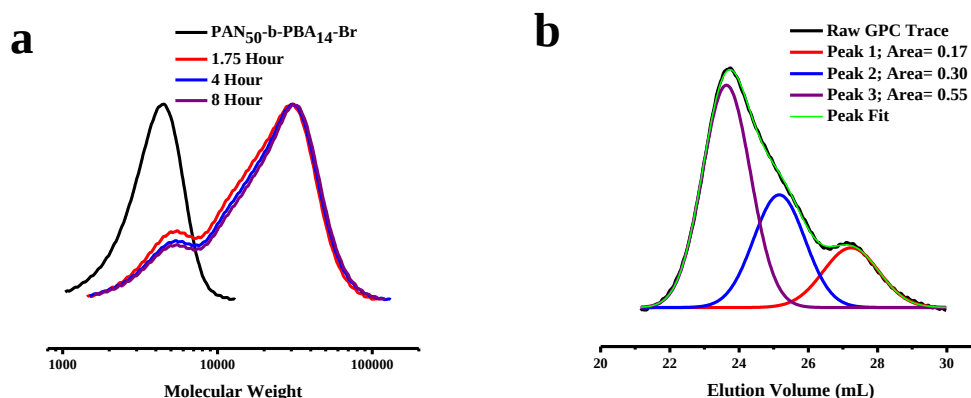


Figure 3.4.2.6. MWD of PAN₅₀-*b*-PBA₁₄-Br and evolution of PAN₅₀-*b*-PBA₁₄-Poly(HDDA) (a); Peak fitting of PAN₅₀-*b*-PBA₁₄-Poly(HDDA) to determine area (b)
[PAN-*b*-PBA-Br]:[HDDA]:[CuBr]:[TPMA]= 1:5:0.35:0.6

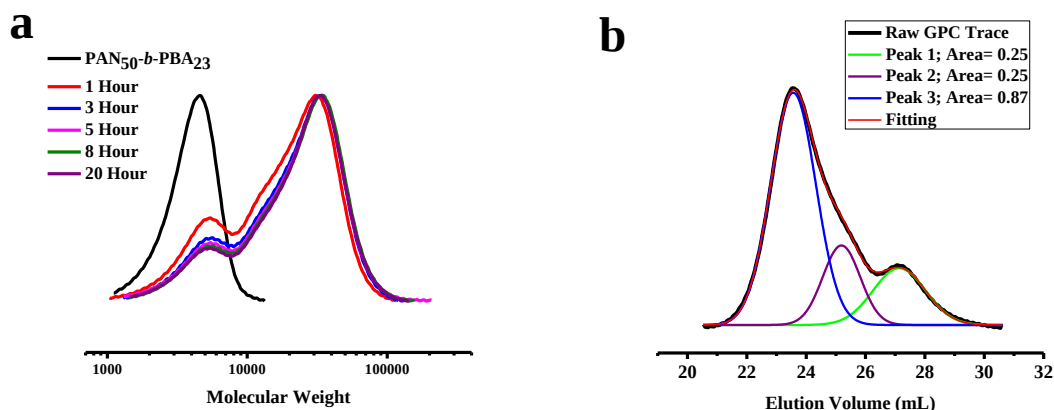


Figure 3.4.2.7. MWD of PAN₅₀-*b*-PBA₂₃-Br and evolution of PAN₅₀-*b*-PBA₂₃-Poly(HDDA) (a); Peak fitting of PAN₅₀-*b*-PBA₂₃-Poly(HDDA) to determine area (b); [AN-*b*-PBA-Br]:[HDDA]:[CuBr]:[TPMA]= 1:5:0.35:0.6

3.4.3 Characterization of Carbons Derived from PAN-based Stars

The PAN-based stars were oxidatively stabilized at 280 °C and carbonized at 800 °C. Pyrolysis yields are consistent with the amount of PAN in the star, Table 3.4.3. The surface area of the carbons was analyzed by N₂ adsorption isotherm with BET analysis, Figure 3.4.3. The microporous (S_{micro}) and mesoporous (S_{meso}) surface areas were also determined.

The highest surface areas were obtained for the samples with the lowest DP_{PAN}. The PAN₄₁-Poly(DEDGA) star formed a carbon with a surface area of 260 m²/g and PAN₃₀-*b*-PBA₁₈-Poly(HDDA) provided a surface area of 390 m²/g, Table 3.4.3. These surface areas were similar to those for PAN-*b*-PBA BCPs with a similar DP_{PAN}.³ However, the S_{micro} for the samples prepared from stars is significantly higher than for carbons formed from BPCs, which are mostly mesoporous. This could indicate that the

“restriction” generated from the cross-linked core helps the PAN-segments form micropores during stabilization and removal of the core formed micropores.

As the MW of the DP_{PAN} segment increased, the surface area decreased significantly and was <100 m²/g for the remaining samples. Lower DP_{PAN} was shown to melt before oxidative cyclization.²⁴ Therefore, if the PAN segments in the star melts before thermal cyclization at 280 °C, the arms are more likely to interdigitate and increase cross-linking between the stars. Interdigitation would result in a carbon with a more interconnected structure, one that does not collapse after removal of the poly(acrylate) species. This would also result in a higher surface area and explain why star precursors with a low DP_{PAN} form higher surface area carbons.

Table 3.4.3. Characterization of N-doped Nanocarbons Templated by PAN-Stars

Sample	wt% PAN	Pyrolysis Yield	S_{BET} (m²/g)	S_{micro} (m²/g)	S_{meso} (m²/g)
PAN ₄₁ -Poly(DEDGA)	48	---	260	245	15
PAN ₃₀ - <i>b</i> -PBA ₁₈ -Poly(HDDA)	19	25 %	390	296	67
PAN ₅₀ - <i>b</i> -PBA ₂₃ -Poly(HDDA)	34	28 %	85	25	10
PAN ₇₉ - <i>b</i> -PBA ₁₀ -Poly(HDDA)	56	42 %	28	---	---
PAN ₇₉ - <i>b</i> -PBA ₄₄ -Poly(HDDA)	32	35 %	5	0	0

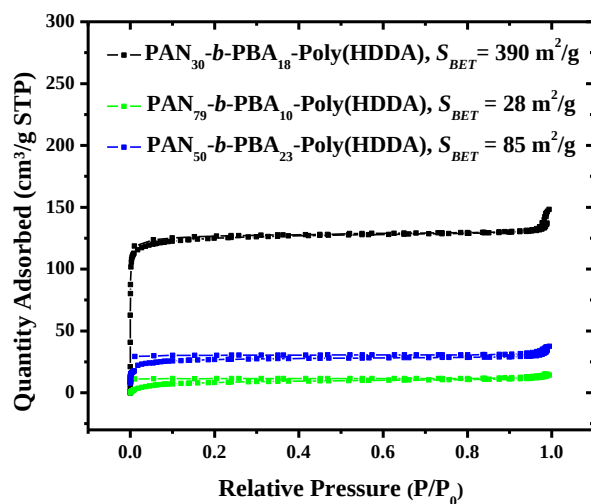


Figure 3.4.3. N₂ adsorption isotherms for nanocarbon samples derived from PAN-stars

3.5 Conclusions

PAN-based stars with acrylate cores were successfully synthesized. PAN homo-arm stars with short DP_{PAN} could be synthesized in yields above 80%. When DP_{PAN} was increased the star yield was significantly decreased. The star yield could not be improved, to reach the initial goal of >95% arm incorporation, regardless of the choice or amount cross-linker used to form the stars or the initial concentration of macroinitiator. Using a smaller cross-linker had little effect while increasing the amount of cross-linker led to star-star coupling. However, switching from a more hydrophilic cross-linker (DEDGA) to a more hydrophobic cross-linker (HDDA) did result in the formation of better defined stars that had a more selective shift towards higher molecular weight from increased incorporation of the macroinitiator. Well-defined PAN-*b*-PBA BCP stars were synthesized using the HDDA hydrophobic cross-linker. As expected, higher star yields were obtained with lower molecular weight BPCs.

The samples were stabilized under air and carbonized to form N-doped nanocarbons. The star precursors with low DP_{PAN} yielded carbons with the highest surface areas, up to 390 m²/g. This was attributed to melting of lower molecular weight PAN before oxidative thermal cyclization. The melting of PAN facilitated interdigitation of the star arms, allowing them to cross-link together, and form a more interconnected carbon that did not collapse upon removal of the poly(acrylate) sacrificial block and cross-linked core.

3.6 Acknowledgements

Dr. Maciek Kopec is acknowledged for pyrolyzing all samples and analyzing the resulting carbons surface areas. Dr. Maciek Kopec and Rui Yuan are thanked for synthesizing some of the PAN-Br macroinitiators.

3.7 References

- (1) Zhong, M.; Jiang, S.; Tang, Y.; Gottlieb, E.; Kim, E. K.; Star, A.; Matyjaszewski, K.; Kowalewski, T. *Chemical Science* **2014**, 5, 3315.
- (2) Zhong, M.; Kim, E. K.; McGann, J. P.; Chun, S. E.; Whitacre, J. F.; Jaroniec, M.; Matyjaszewski, K.; Kowalewski, T. *Journal of the American Chemical Society* **2012**, 134, 14846.
- (3) Zhong, M.; Tang, C.; Kim, E. K.; Kruk, M.; Celer, E. B.; Jaroniec, M.; Matyjaszewski, K.; Kowalewski, T. *Mater. Horiz.* **2014**, 1, 121.
- (4) Zhong, M.; Natesakhawat, S.; Baltrus, J. P.; Luebke, D.; Nulwala, H.; Matyjaszewski, K.; Kowalewski, T. *Chemical communications* **2012**, 48, 11516.
- (5) Ju, M. J.; Choi, I. T.; Zhong, M.; Lim, K.; Ko, J.; Mohin, J.; Lamson, M.; Kowalewski, T.; Matyjaszewski, K.; Kim, H. K. *Journal of Materials Chemistry A* **2015**, 3, 4413.
- (6) Bates, F. S.; Fredrickson, G. H. *Annual Review of Physical Chemistry* **1990**, 41, 525.
- (7) Bashir, Z. *Carbon* **1991**, 29, 1081.
- (8) Bates, F. S. *Science* **1991**, 251, 898.
- (9) Dalton, S.; Heatley, F.; Budd, P. M. *Polymer* **1999**, 40, 5531.
- (10) Leibler, L. *Macromolecules* **1980**, 13, 1602.

- (11) Matsen, M.; Bates, F. S. *Macromolecules* **1996**, 29, 1091.
- (12) Tang, C.; Dufour, B.; Kowalewski, T.; Matyjaszewski, K. *Macromolecules* **2007**, 40, 6199.
- (13) Barbiou, B.; Percec, V. *Macromolecules* **2001**, 34, 8626.
- (14) Pitto, V.; Voit, B. I.; Loontjens, T. J. A.; van Benthem, R. A. T. M. *Macromolecular Chemistry and Physics* **2004**, 205, 2346.
- (15) Dufour, B.; Tang, C.; Koynov, K.; Zhang, Y.; Pakula, T.; Matyjaszewski, K. *Macromolecules* **2008**, 41, 2451.
- (16) Xia, J.; Zhang, X.; Matyjaszewski, K. *Macromolecules* **1999**, 32, 4482.
- (17) Gao, H.; Ohno, S.; Matyjaszewski, K. *Journal of the American Chemical Society* **2006**, 128, 15111.
- (18) Gao, H.; Matyjaszewski, K. *Macromolecules* **2006**, 39, 3154.
- (19) Gao, H.; Matyjaszewski, K. *Macromolecules* **2007**, 40, 399.
- (20) Blencowe, A.; Tan, J. F.; Goh, T. K.; Qiao, G. G. *Polymer* **2009**, 50, 5.
- (21) Gao, H.; Matyjaszewski, K. *Progress in Polymer Science* **2009**, 34, 317.
- (22) Britovsek, G. J. P.; England, J.; White, A. J. P. *Inorganic Chemistry* **2005**, 44, 8125.
- (23) Lamson, M.; Kopeć, M.; Ding, H.; Zhong, M.; Matyjaszewski, K. *Journal of Polymer Science Part A: Polymer Chemistry* **2016**, n/a.
- (24) Mohin, J. W., Carnegie Mellon University, 2015.
- (25) Li, W.; Matyjaszewski, K. *Journal of the American Chemical Society* **2009**, 131, 10378.
- (26) Shi, X.; Zhou, W.; Qiu, Q.; An, Z. *Chemical communications* **2012**, 48, 7389.

Chapter 4

Polymerization of 4-Cyanostyrene by ATRP and Tetrazine Cross-linking of Poly(4-Cyanostyrene) to Form a Carbon Precursor

4.1. Preface

This chapter describes conditions to polymerize 4-cyanostyrene (4-CNSt) by normal ATRP. Conditions to graft 4-CNSt from silica particles were also investigated using surface initiated ATRP (SI-ATRP). Conditions to cross-link the poly(4-CNSt) grafted from silica spheres, via tetrazine formation, were developed and cross-linked nanoparticles were formed. The cross-linked nanoparticles were carbonized and the carbons were analyzed.

I learned how to conduct SI-ATRP from silica particles by working on this project. Specifically, I learned how to tailor conditions to obtain well-defined polymer grafted from particles, calculate the grafting density of polymer on the particle, and how to then perform cross-linking chemistry on polymers grafted from particles.

Dr. Mingjiang Zhong helped to develop the initial conditions for the polymerization of 4-CNSt by normal ATRP. I developed all other conditions for 4-CNSt polymerization by normal ATRP and SI-ATRP, characterized all polymers by GPC and ^1H NMR, and investigated cross-linking conditions. Dr. Benjamin Hui functionalized the silica particles and etched them after growing P(4-CNSt) from them, using HF, so the poly(4-CNSt) could be analyzed by GPC. Dr. Jacob W. Mohin analyzed the samples by DLS. Dr. Dincai Wu and Luyi Chen carbonized the samples and analyzed them by TGA, SEM, and N_2 adsorption isotherm.

4.2. Introduction

The relationship between the polymerization rate and the substituents on the vinyl monomer has been well studied. The substituent alters the electron density of the double bond through inductive and resonance effects and its ability to stabilize the radical.¹⁻⁷ Polar effects can have a strong influence on polymerization rate, although they are not as important in radical polymerization as in ionic reactions.¹⁻⁷ A Hammett relationship can be established for p-substituted styrenes of $\log(k_{\text{px}}^\bullet/k_{\text{pH}}^\bullet) = \sigma\rho$ ($\rho=0.6$), where $k_{\text{px}}^\bullet$ and $k_{\text{pH}}^\bullet$ represent the absolute propagation rate constant of substituted styrene and unsubstituted styrene respectively, σ is the Hammett constant, and ρ is the reaction constant.^{2,8}

The polymerization of substituted styrenes by ATRP was investigated.⁹ The authors polymerized the substituted styrenes using the reagent ratios of $[\text{R-St}]:[\text{PEBr}]:[\text{CuBr}]:[\text{CuBr}_2]:[\text{dNbpy}] = 100:1:1:0.05:3$ in diphenyl ether at 110 °C (Figure 4.2 for reagent structures). It was determined that styrene with electron withdrawing groups

(EWG) had higher polymerization rates and the polymer had narrower molecular weight distributions, as compared to styrene with electron donating groups. The apparent rate of polymerization (k_p^{app}) correlated with the Hammett constant (i.e. higher Hammett constant correlated to higher k_p^{app} ; Table 4.2). Based on the Hammett constant for 4-cyanostyrene (4-CNSt), it was expected that it should have a faster apparent rate of polymerization than all other substituted styrenes, but was not tested, as this monomer was not commercially available until recently.¹⁰

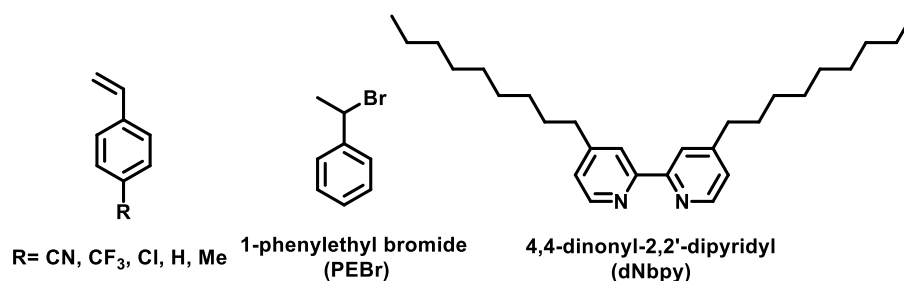


Figure 4.2. Select reagents used in the study of substituted styrene polymerization by ATRP from reference 9

Table 4.2. Hammett constant for substituted styrenes and apparent rate coefficients in ATRP

Substituent	σ^a	$k_p^{app} (\text{s}^{-1}) \times 10^{-5b}$
4-CN	0.66	---
4-CF ₃	0.54	5.47
4-Cl	0.23	2.56
4-H	0.00	1.50
4-Me	-0.17	0.36

^a σ from Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, 91, 165, ^b $[M]:[PEBr]:[CuBr]:[dNbpy]:[CuBr_2]=100:1:1:3:0.05$, at 110 °C in diphenyl ether, $[M]_0 = 4.37 \text{ M}$.

P(4-CNSt) may also be an interesting polymer to investigate, due to its high content of nitrile groups, which are reactive towards many chemistries. Tetrazines are typically synthesized using the Pinner reaction, which involves the reaction of hydrazine with a nitrile group, typically aromatic, with the assistance of sulfur.^{11,12} This forms dihydrotetrazine and upon reduction, a tetrazine is formed. Tetrazines are interesting compounds that can be used for many applications, including propellants, pyrotechnic materials, flame retardants, materials with tunable fluorescence, and electronic materials.¹¹

Based on the wide spread interest of the formation of N-doped carbons and their application in various fields,¹³⁻¹⁸ it is interesting to investigate tetrazine-based materials as N-doped nanocarbon precursors. The synthesis of nitrogen rich compound 3,6-di(azido)-1,2,4,5-tetrazine was reported and used to form nitrogen-rich carbon nitride nanospheres with a size of 5 to 50 nm, but no applications were presented.¹⁹ These nitrogen-rich carbons could be used for a variety of applications, including photocatalytic degradation of pollutants, photocatalytic hydrogen generation, solar fuels production, and capacitors.¹⁶ The use of tetrazine-based precursors could additionally provide higher nitrogen content or different nitrogen species than block copolymer templating derived nanocarbons.^{20,21} Different ratios of nitrogen species or higher nitrogen content could lead to tetrazine-precursor derived carbons utility in not only the previously mentioned applications, but also for other applications of N-doped nanocarbons, like catalysts for the oxygen reduction reaction or dye sensitized solar cells.²²⁻²⁴ Additionally, the use of a sacrificial core, such as spherical silica particles or cross-linked PMMA, has been shown to yield additional porosity in the carbon material after etching or during pyrolysis,

respectively.²⁵⁻²⁷ Thus, anchoring P(4-CNSt) to a silica core could provide added porosity to the carbon materials in addition to the formation of tetrazine cross-linking units.

In this chapter, the synthesis of poly(4-cyanostyrene) by ATRP is reported. Grafting of 4-CNSt from silica particles by SI-ATRP was explored. The SiO₂-*g*-P(4-CNSt) was cross-linked using the Pinner reaction followed by reduction to form tetrazines. The cross-linked samples, x-SiO₂-*g*-P(4-CNSt) were analyzed by DLS, SEM, DSC, and TGA, which revealed that intra- and inter-particle cross-linking occurred. The samples were carbonized and carbons with a 3D nanostructured network and highest surface area of 752 m²/g were obtained after etching the silica particles.

4.3 Experimental

4.3.1 Materials

4-Cyanostyrene (4-CNSt, Alfa Aesar, 99.9%) was passed through a basic aluminum column to remove inhibitor before it was used. Silica nanoparticles, 30% solution in methyl isobutyl ketone (MIBK-ST), effective diameter ~15 and 120 nm, were kindly donated by Nissan Chemical Corp. and used as received. The ATRP initiators 1-(chlorodimethylsilyl) propyl-2-bromoisobutyrate and 1-(chlorodiethylsilyl) propyl-2-bromoisobutyrate were synthesized and attached to the silica particles using a previously reported procedure.²⁸ Copper (I) bromide (CuBr, Aldrich, >99%), copper (II) bromide (CuBr₂, Acros Organics, >99%), NaNO₂, ethyl 2-bromoisobutyrate (EBiB, Aldrich, 98%), 1-bromoethyl benzene (PEBr, Aldrich, 99%), 2,2'-bipyridine (bpy, Aldrich, 99%), sulfur (S₈, Aldrich, 99%), hydrazine hydrate (50-60% solution, Aldrich), glacial acetic

acid (Aldrich, 99%), hydrofluoric acid (HF, 40-45%), dimethylformamide (DMF, Fischer, 99%), and methanol (MeOH, Fisher, 99%) were purchased and used as received.

4.3.2 Polymerization of 4-Cyanostyrene by Normal ATRP

In a typical procedure a stock solution of catalyst containing CuBr, CuBr₂, and bpy in DMF was made under inert conditions, so 9.3 mg (0.06 mmol), 1.6 mg (0.01 mmol) of CuBr₂, and 22.4 mg (0.14 mmol) of bpy were easily added to the reaction via an air tight syringe. 0.93 g of 4-CNSt, 14.0 mg of EBiB, and 1 mL of DMF were added to a Schlenk flask and purged for 20 minutes before the addition of the catalyst. The flask was submerged in an oil bath set at 80 °C for the desired polymerization time. The reaction was stopped by exposure to oxygen and dilution with DMF. P(4-CNSt) was precipitated into MeOH to remove the catalyst and dried under vacuum for 24 hours.

4.3.3 Grafting 4-Cyanostyrene from Silica Particles

In a typical procedure, 0.11 g of silica particles (15 nm with 0.29 mmol/g initiating sites or 120 nm with 0.09 mmol/g initiating sites) were added to a Schlenk flask dispersed in 0.98 mL of DMF using a sonication bath for 20 minutes. 0.40 g of 4-CNSt was added to a Schlenk flask and purged for 20 minutes before the addition of the catalyst. A stock solution of catalyst containing CuBr, CuBr₂, and bpy in DMF was made under inert conditions, so 4.0 mg (0.03 mmol), 0.69 mg (0.003 mmol) of CuBr₂, and 9.7 mg (0.06 mmol) of bpy were easily added to the reaction via an air tight syringe. The flask was submerged in an oil bath set at 80 °C for the desired polymerization time. The reaction was stopped by exposure to oxygen and dilution with DMF. SiO₂-g-P(4-CNSt)

was precipitated into MeOH to remove the catalyst and dried under vacuum for 24 hours. Silica particles were etched with HF to characterize the molecular weight of P(4-CNSt).

4.3.4 Cross-linking of SiO₂-*g*-P(4-CNSt) to form tetrazine x-SiO₂-*g*-P(4-CNSt)

In a typical procedure, 21 mg of SiO₂-*g*-P(4-CNSt) was dissolved in DMF overnight and 10 mg of sulfur was added and stirred until it was well-dispersed in the solution. Hydrazine hydrate (0.25 mL) was added to the solution at 5 μ L/min (total feed time 50 minutes) while heating at 114 °C and stirring. The product was precipitated into MeOH and a yellow dispersion was obtained. The yellow dispersion was centrifuged at 4,000 rpm for 30 minutes and the MeOH was removed. The product was washed twice with hot toluene (70 °C) to remove the sulfur using the same centrifuging process.

The recovered and dried product [x-SiO₂-*g*-P(4-CNSt)] was then dispersed in 3 mL of a NaNO₂ solution (0.1 g/mL). Glacial acetic acid was slowly added (1 mL over 10 minutes) and the solution was stirred overnight. The pink product was washed with water, using the same centrifuge process in the previous step, until neutral pH was reached. The product was dried under vacuum overnight.

4.3.5 Carbonization

The x-SiO₂-*g*-P(4-CNSt) were carbonized at 800 °C for 3 hours. A temperature ramp of 5 °C/min was used under N₂ flow to pyrolyze the samples. The silica particles were etched and the surface area of the carbons were compared before and after etching to the surface area of x-SiO₂-*g*-P(4-CNSt).

4.3.6 Characterization

^1H nuclear magnetic resonance (NMR) spectroscopy measurements were performed on a Bruker Avance 300 MHz spectrometer and used to determine the conversion of monomer in DMSO- d_6 . The apparent molecular weights ($M_{n,\text{GPC}}$) and molecular weight distributions (M_w/M_n) were determined by gel permeation chromatography (GPC). The GPC system used a Waters 515 HPLC pump and a Waters 2414 refractive index detector using PSS columns (Styrogel 10^2 , 10^3 , 10^5 Å) with DMF containing 10 mM LiBr as the eluent at a flow rate of 1 mL/min at 50 °C using linear PS standards. The average hydrodynamic diameter was measured by dynamic light scattering (DLS) on a high performance zeta-sizer from Malvern Instruments, Ltd. Differential scanning calorimetry (DSC) was performed on a TA Instruments Q20 and a Q2000, as well as on a Seiko DSC2100. Gas flows was 60 mL/min, in nitrogen. Sample sizes were between 1 and 5 mg and the heating rate was 10 °C/min. Thermal gravimetric analysis (TGA) was performed on TGA Q50 thermogravimetric analyzer (TA Instruments) with a heating rate of 20 °C/min in O_2 flow. SEM analysis was performed a FEI Tecnai F20 scanning electron microscope. Nitrogen adsorption measurements were carried out using a Micromeritics ASAP 2020 analyzer at 77K. The BET surface area was analyzed by Brunauer-Emmett-Teller (BET) theory. The pore size distribution was analyzed by original density functional theory (DFT) combined with non-negative regularization and medium smoothing. The total pore volume (V_t) was calculated according to the amount adsorbed at a relative pressure P/P_0 of ~ 0.99 .

4.4 Results and Discussion

4.4.1 Polymerization of 4-Cyanostyrene by Normal ATRP and Rate Comparison to Other Substituted Styrene

4-Cyanostyrene (4-CNSt) was polymerized under normal ATRP conditions similar to the conditions used by Qui.⁹ The reagent ratio was [4-CNSt]:[PEBr]:[CuBr]:[CuBr₂]:[bpy]= 100:1:1:0.05:3, with a [4-CNSt]₀ of 4.37 mM in DMF, and the polymerization was conducted at 110 °C. The conditions were slightly altered from Qui's work where diphenyl ether was used as the solvent.⁹ P(4-CNSt) is only soluble in DMF, thus bpy was used instead of dNbpy, due to catalyst solubility issues in DMF when dNbpy was used. The reaction proceeded with semi-logarithmic linear first-order kinetics and had a k_p^{app} of $3.0 \times 10^{-4} \text{ s}^{-1}$ (Figure 4.4.1.1a). The k_p^{app} was higher than all other substituted styrenes (Table 4.2). Based on a ρ -value of 1.5,⁹ the calculated k_p^{app} , using the Hammett equation, for 4-CNSt polymerization with ATRP conditions and 0.5 mol% copper-catalyst loading was calculated to be $1.47 \times 10^{-4} \text{ s}^{-1}$. Thus the experimental value was similar to the calculated theoretical value, but slightly higher, due to the use of DMF, a more polar solvent, instead of diphenyl ether, which is known to enhance the rate of ATRP.²⁹

Molecular weight (MW) increases linearly with conversion and molecular weight distributions (MWD) are low (Figure 4.4.1.1b). M_n deviates from theory as conversion increases, because PMMA standards were used for calibration. However, the reaction stops after it reaches ~80% conversion and was complete in ~2 hours, which is generally too fast for grafting from silica particles, as particle-particle coupling can occur, due to

termination when the radical concentration is too high, and a gel can form. Thus, new conditions were explored.

4-CNSt was polymerized under normal ATRP conditions with reagent ratio of [4-CNSt]:[EBiB]:[CuBr]:[CuBr₂]:[bpy]= 100:1:0.9:0.1:2 at 80 °C in DMF. These conditions were selected to determine if EBiB was an efficient initiator for 4-CNSt. The Cu(I):Cu(II) ratio and temperature were reduced to slow the reaction and obtain better control. Semi-logarithmic linear first-order kinetics was observed and conversion reached ~90% in 17 hours (Figure 4.4.1.2a). From the kinetic plot the k_p^{app} was calculated to be 0.1471 h⁻¹ or 4.0 x10⁻⁵ s⁻¹ (Figure 4.4.1.2a). This value is lower than the value predicted by Jian Qui,⁹ but the reaction was conducted at a much lower temperature (80 °C), than previously (110 °C). 4-CNSt polymerization was conducted at a lower temperature, due to better reproducibility and control over MW and MWD. When the reaction was repeated, the same conversion, 89%, was reached in 17 hours. The M_n of the final polymer was 16,500, which was higher than $M_{n,theory}$ (11,700), due to calibration with PS standards. The M_w/M_n value was 1.4, which was higher than when 4-CNSt was polymerized at a higher temperature, due to low MW (Figure 4.4.1.2). Thus, these conditions were selected to graft P(4-CNSt) from silica particles.

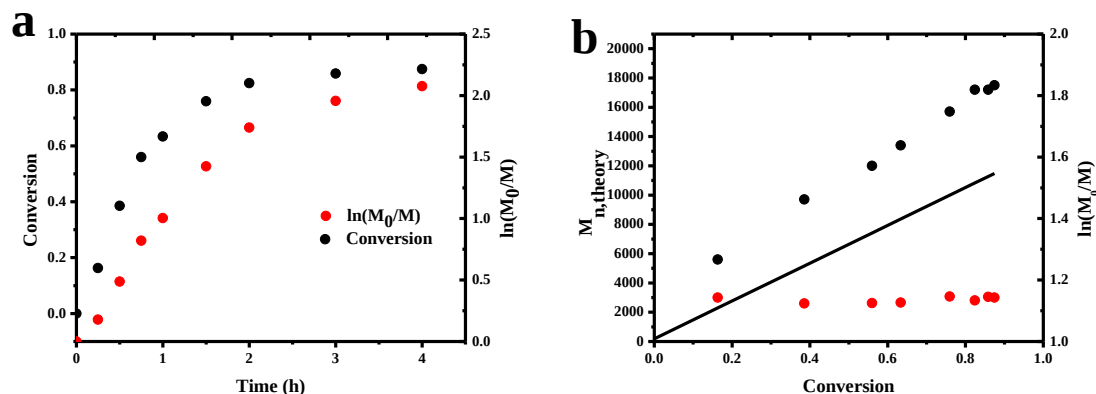


Figure 4.4.1.1. Semi-logarithmic kinetic and conversion plots (a) and MW and MWD plot for the ATRP of 4-CNSt with the using conditions [4-CNSt]:[PEBr]:[CuBr]:[CuBr₂]:[bpy]= 100:1:1:0.05:3, with a [4-CNSt]₀ of 4.37 mM in DMF at 110 °C

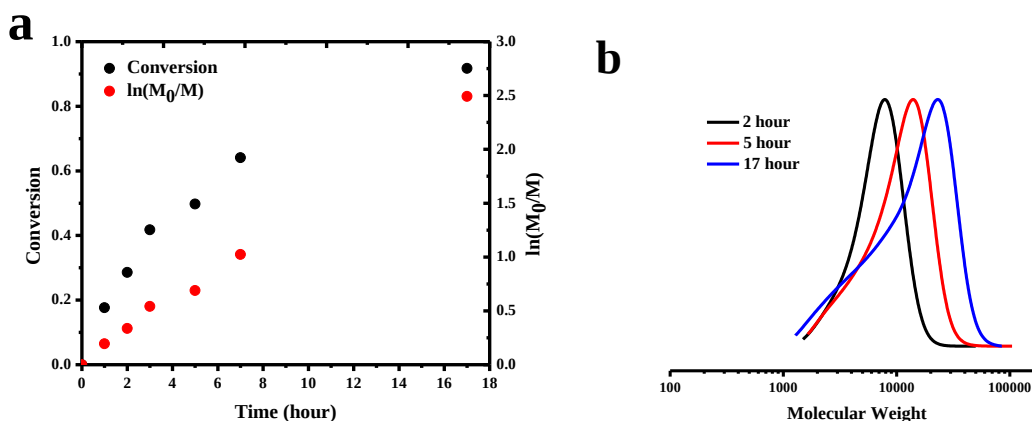


Figure 4.4.1.2. Semi-logarithmic kinetic and conversion plots (a) and evolution of MW (b) for the ATRP of 4-CNSt with conditions of [4-CNSt]:[EBiB]:[CuBr]:[CuBr₂]:[bpy]= 100:1:0.9:0.1:2 at 80 °C in DMF.

4.4.2 Grafting 4-Cyanostyrene from Silica Particles

Silica particles with two different sizes (Figure 4.4.2.1), 15 nm and 120 nm, were used to graft 4-CNSt from to determine if the particle size had an effect on the final

carbon material. The conditions were optimized, so the reagents were in a ratio of [4-CNSt]:[Si-Br]:[CuBr]:[CuBr₂]:[bpy]= 500:1:0.8:0.2:2 in DMF and the polymerization was conducted at 80 °C for 18 hours. The silica particles were etched and the M_n of P(4-CNSt) was 1.53x10⁵ and the M_w/M_n was 1.20. A clean GPC trace could not be obtained, because the amount of polymer recovered after etching the silica particles was too small to make a highly concentrated solution to analyze by DMF GPC.

The reaction conditions were scaled up, so there was enough material for GPC analysis and cross-linking. In 16 hours SiO₂(15)-*g*-P(4-CNSt), with an M_n of 1.13x10⁵ and M_w/M_n value of 1.42 (Figure 4.4.2.2 for characterization), was obtained. The MWD increased due to stirring issues when the reaction was scaled up. The same conditions were used to graft 4-CNSt from 120 nm silica particles, SiO₂(120)-*g*-P(4CNSt), and the polymerization was conducted for 25 hours. After the silica was etched, the obtained polymer had a M_n of 1.12x10⁵ and M_w/M_n value of 1.43 (Figure 4.4.2.3).

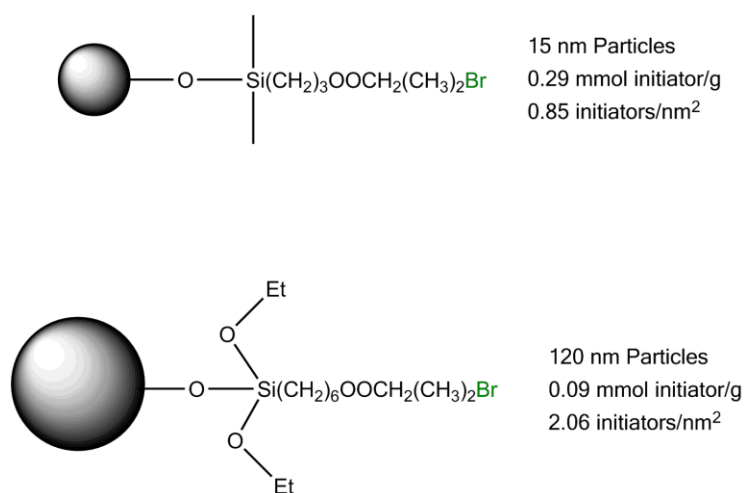


Figure 4.4.2.1. 15 nm and 120 nm silica particles characterization and ATRP initiator structure

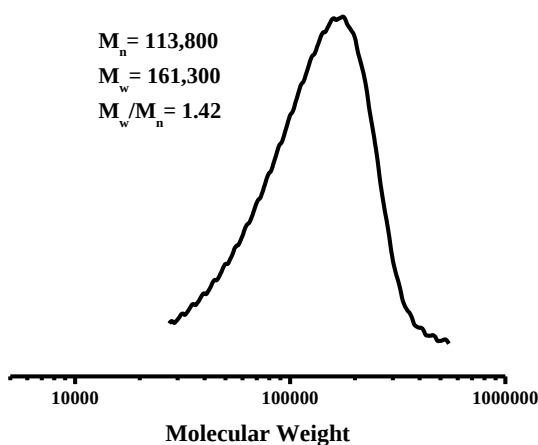


Figure 4.4.2.2. MWD curve for P(4-CNSt) cleaved from 15 nm silica particle

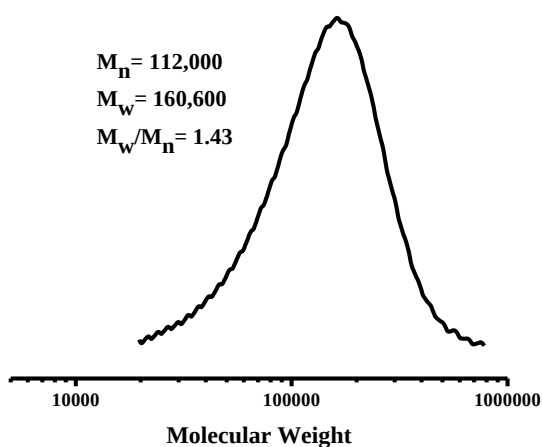


Figure 4.4.2.3. MWD curve for P(4-CNSt) cleaved from 120 nm silica particle

4.4.3 Cross-linking of 4-Cyanostyrene to Form Tetrazine-units and Pyrolysis to from N-doped Nanocarbons

Once $\text{SiO}_2(15)\text{-}g\text{-P}(4\text{-CNSt})$ and $\text{SiO}_2(120)\text{-}g\text{-P}(4\text{-CNSt})$ were synthesized, they were cross-linked, using the Pinner method,^{11,12,19} to form tetrazine cross-links ($x\text{-SiO}_2(15)\text{-}g\text{-P}(4\text{CNSt})$ and $x\text{-SiO}_2(120)\text{-}g\text{-P}(4\text{-CNSt})$; Scheme 4.4.3). In this reaction

dihydropyridazine is formed when the nitrile reacts with hydrazine hydrate, with the assistance of sulfur. The dihydropyridazine can be reduced to pyridazine using diethyl azodicarboxylate or NaNO_2 and acid, like HCl or glacial acetic acid. For cross-linking P(4-CNSt), the use of NaNO_2 and glacial acetic acid was chosen, as the conditions were not as harsh and less hazardous as using HCl or diethyl azodicarboxylate. After the materials was fully cross-linked, a pink product was formed that was completely insoluble in any solvent tested, but could be briefly dispersed in DMF.

SEM imaging and DLS were used to analyze the size of the SiO_2 -*g*-poly(4-CNSt) and pyridazine cross-linked x- SiO_2 -*g*-P(4-CNSt). SEM imaging reveals that the particles become more spherical after cross-linking (Figure 4.4.3). The SiO_2 -*g*-poly(4-CNSt) was ~60 nm and increased to ~1.4 μm (Figure 4.4.4), based on DLS analysis. This would indicate that the poly(4-CNSt) was successfully cross-linked with intra- and inter-particle cross-linking. The SiO_2 -*g*-poly(4-CNSt) with 120 nm particles also undergo intra- and inter-particle cross-linking, indicated by the size increase from 1.3 μm to 2.8 μm (Table 4.4.4).

DSC analysis was conducted to measure the glass transition temperature (T_g) of P(4-CNSt), $\text{SiO}_2(15)$ -*g*-P(4-CNSt), and x- $\text{SiO}_2(15)$ -*g*-P(4-CNSt) (Table 4.4.4). The P(4-CNSt) had a T_g ~177 °C, as expected with the low polydispersity obtained under the ATRP conditions employed.³⁰ When P(4-CNSt) was grafted from silica particles its T_g , unsurprisingly, increased to ~184.5 °C. No T_g was observed for x- $\text{SiO}_2(15)$ -*g*-P(4-CNSt), which indicated that the formation of pyridazine units to cross-link the particles was successful. TGA analysis reveals that after cross-linking the $\text{SiO}_2(15)$ -*g*-P(4-CNSt) had a silica content of 16.1 % and $\text{SiO}_2(120)$ -*g*-P(4-CNSt) had a silica content of 19.5 %

(Figure 4.4.5). The silica amount, coupled with the two stage mass loss profile, indicated that there will be further graphitization of the cross-linked polymer during carbonization.

Scheme 4.4.3. Cross-linking of benzonitrile to form tetrazines via the Pinner method

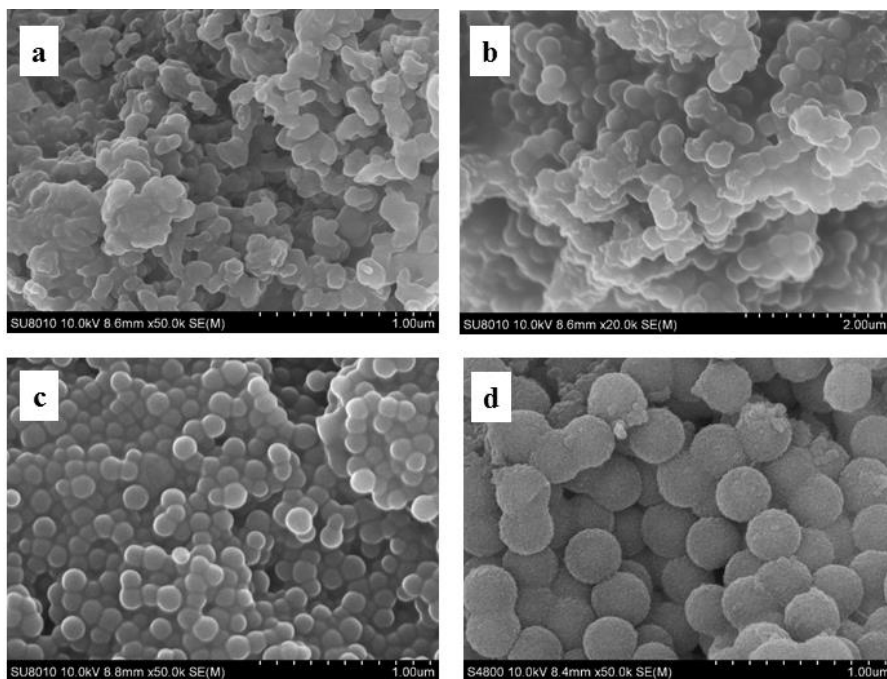
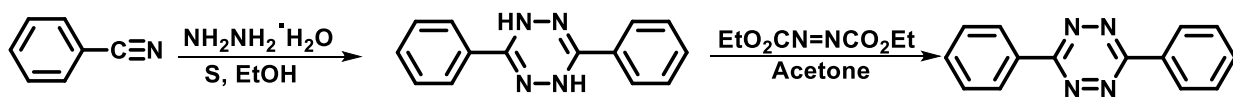


Figure 4.4.3. SEM images of (a) $\text{SiO}_2(15)\text{-g-P}(4\text{-CNSt})$, (b) $\text{SiO}_2(120)\text{-g-P}(4\text{-CNSt})$, (c) $x\text{-SiO}_2(15)\text{-g-P}(4\text{-CNSt})$, (d) $x\text{-SiO}_2(120)\text{-g-P}(4\text{-CNSt})$

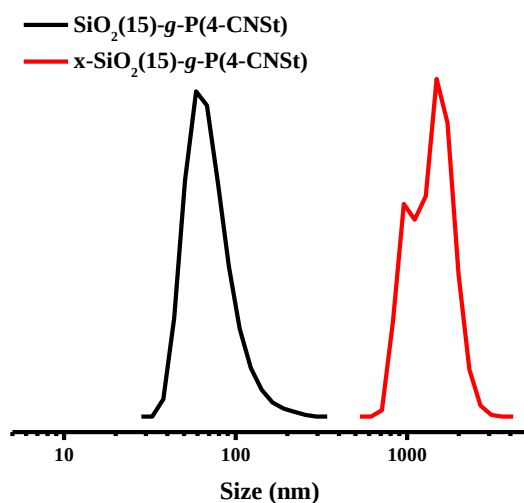


Figure 4.4.4. DLS analysis of (a) $\text{SiO}_2(15)\text{-}g\text{-P}(4\text{-CNSt})$ and (b) $x\text{-SiO}_2(15)\text{-}g\text{-P}(4\text{-CNSt})$ in DMF at RT

Table 4.4.3. $\text{SiO}_2\text{-}g\text{-Poly}(4\text{-CNSt})$ and tetrazine cross-linked samples

Description	DLS Size
$\text{SiO}_2(15)\text{-}g\text{-P}(4\text{-CNSt})$	112 nm
$x\text{-SiO}_2(15)\text{-}g\text{-P}(4\text{-CNSt})$	2.4 μm
$\text{SiO}_2(120)\text{-}g\text{-P}(4\text{-CNSt})$	1.3 μm
$x\text{-SiO}_2(120)\text{-}g\text{-P}(4\text{-CNSt})$	2.8 μm

Table 4.4.4. DSC characterization of $\text{P}(4\text{-CNSt})$ samples

Polymer	T_g ($^\circ\text{C}$)
$\text{P}(4\text{-CNSt})\text{-Br}$	177.5
$\text{P}(4\text{-CNSt})\text{-Br}$	176.5
$\text{SiO}_2(15)\text{-}g\text{-poly}(4\text{CNSt})$	184.5
$x\text{-SiO}_2(15)\text{-}g\text{-P}(4\text{-CNSt})$	Not observed

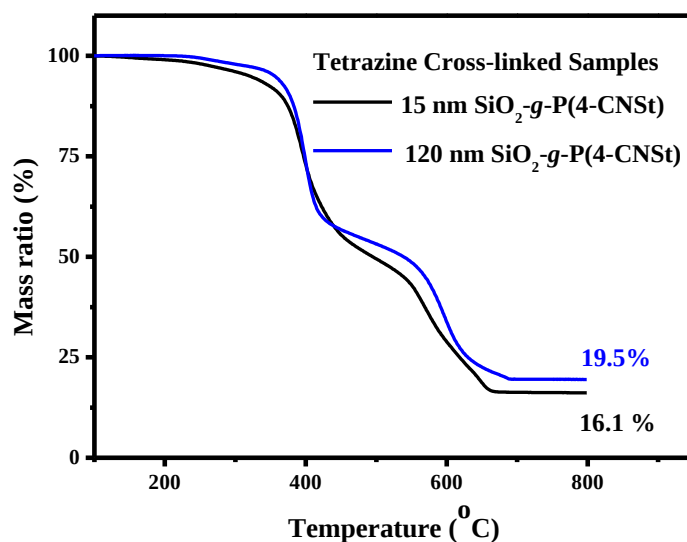


Figure 4.4.5. TGA curves for x-SiO₂(15)-g-P(4-CNSt) (black) and SiO₂(120)-g-P(4-CNSt) (blue) particles

After the cross-linking was confirmed, x-SiO₂(15)-g-P(4-CNSt) and x-SiO₂(120)-g-P(4-CNSt) were carbonized [C-x-SiO₂(15)-g-P(4-CNSt) and C-x-SiO₂(120)-g-P(4-CNSt)] at 800 °C for 3 hours under an inert atmosphere. The initial x-SiO₂-g-P(4-CNSt) samples showed low surface areas ($S_{BET} \sim 20 \text{ m}^2/\text{g}$; Table 4.4.5). After carbonization the surface area dramatically increased ($S_{BET} \sim 350\text{-}375 \text{ m}^2/\text{g}$) and was further increased to $539 \text{ m}^2/\text{g}$ for C-x-SiO₂(15)-g-P(4-CNSt) and $752 \text{ m}^2/\text{g}$ for C-x-SiO₂(120)-g-P(4-CNSt) by etching the silica particles with HF (Table 4.4.5).

Pore size distribution analysis showed that C-x-SiO₂(15)-g-P(4-CNSt), before and after etching, had small micro- and meso-pores (Figure 4.4.6). C-x-SiO₂(15)-g-P(4-CNSt) also exhibited a broad pore size $\sim 10 \text{ nm}$ that further broadens after silica etching. C-x-SiO₂(120)-g-P(4-CNSt) exhibited only micropores before silica etching, which are retained through the HF treatment (Figure 4.4.6). After etching, the pore size distribution

analysis indicated that C-x-SiO₂(120)-*g*-P(4-CNSt) had a small amount of pores ~100 nm in size.

SEM imaging of the carbon materials showed that C-x-SiO₂(15)-*g*-P(4-CNSt) did not retain the spherical morphology from the silica particles, but C-x-SiO₂(120)-*g*-P(4-CNSt) did retain the spherical morphology to an extent (Figure 4.4.7). The better retention of spherical morphology in C-x-SiO₂(120)-*g*-P(4-CNSt) could be due to the use of significantly larger silica particles that form larger pores and a more stable carbon structure and also better inter-particle cross-linking, due to the lower grafting density of SiO₂(120)-*g*-P(4-CNSt), as compared to SiO₂(15)-*g*-P(4-CNSt). Regardless, the use of x-SiO₂(15)-*g*-P(4-CNSt) or x-SiO₂(120)-*g*-P(4-CNSt) resulted in a 3D nanostructured carbon network after pyrolysis and removal of the silica particles via HF etching, which had a relatively high surface area. Due to their high surface area and good interconnectivity, these N-doped nanocarbons could be interesting materials to investigate for their use in many electrochemical applications.

Table 4.4.5. Surface area measurements of x-SiO₂-*g*-P(4-CNSt), and C-x-SiO₂-*g*-P(4-CNSt)

Sample	S_{BET} (m ² /g) before etching	S_{BET} (m ² /g) after etching	S_{micro} (m ² /g) before etching	S_{micro} (m ² /g) after etching
x-SiO ₂ (15)- <i>g</i> -P(4-CNSt)	18	23	n/a	n/a
x-SiO ₂ (120)- <i>g</i> -P(4-CNSt)	22	23	n/a	n/a
C-x-SiO ₂ (15)- <i>g</i> -P(4-CNSt)	348	539	215	229
C-x-SiO ₂ (15)- <i>g</i> -P(4-CNSt)	375	752	327	624

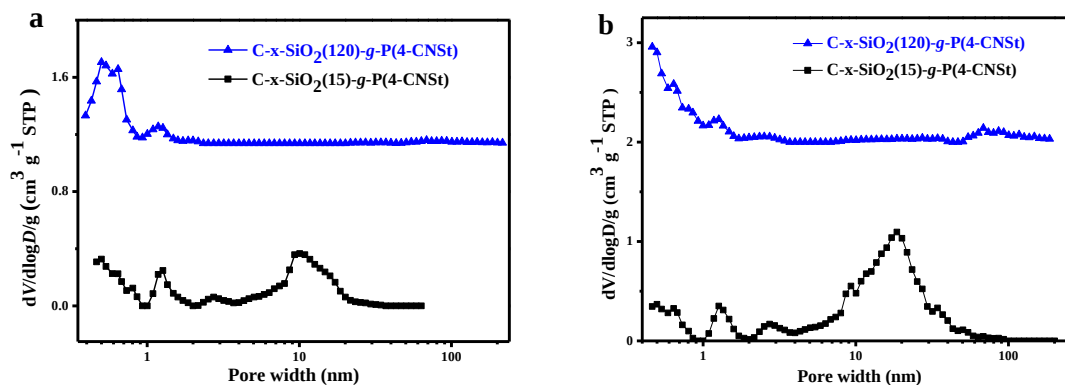


Figure 4.4.6. Pore size distribution of C-x-SiO₂(15)-g-P(4-CNSt) (black) and C-x-SiO₂(120)-g-P(4-CNSt) (blue) before (a) and after (b) HF etching of silica particles

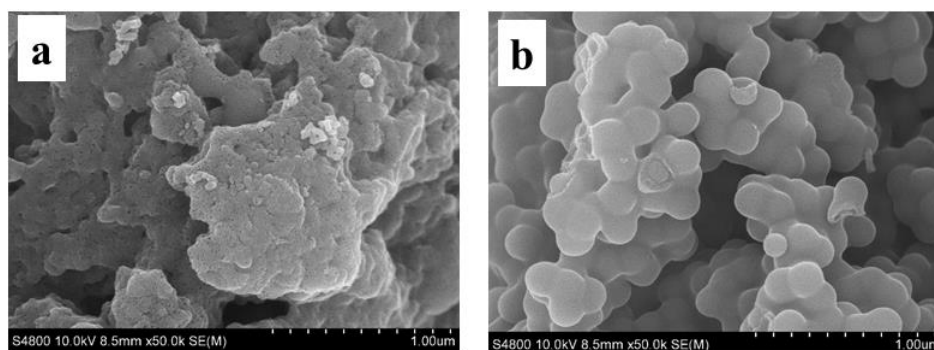


Figure 4.4.7. SEM images of (a) C-x-SiO₂(15)-g-P(4-CNSt) and (b) C-x-SiO₂(120)-g-P(4-CNSt)

4.5 Conclusions

P(4-CNSt) was successfully polymerized via normal ATRP using a reagent ratio of [4-CNSt]:[PEBr]:[CuBr]:[CuBr₂]:[bpy]= 100:1:1:0.05:3 at 110 °C in DMF 1) or [4-CNSt]:[EBiB]:[CuBr]:[CuBr₂]:[bpy]= 100:1:0.9:0.1:2 at 80 °C in DMF. Better control was obtained at 110 °C, but the reaction had too fast a rate to use it for grafting 4-CNSt from silica particles, as increased termination and a gel would result. Poly(4-CNSt) with

M_n of 16,500 and M_w/M_n value of 1.4 was obtained using the conditions with a higher Cu(II) content at 80 °C. 4-CNSt was grafted from silica particles using a reagent ratio of [4-CNSt]:[SiO₂-Br]:[CuBr]:[CuBr₂]:[bpy]= 500:1:0.8:0.2:2 in DMF and the polymerization was conducted at 80 °C for 18 hours. Well-defined P(4-CNSt) was grown from 15 and 120 nm silica particles and the SiO₂-*g*-poly(4-CNSt) was cross-linked to form tetrazine units, x-SiO₂-*g*-P(4-CNSt), using the Pinner reaction followed by reduction with glacial acetic acid/NaNO₂. The successful cross-linking was confirmed via DLS, TGA, SEM and DSC analysis. The x-SiO₂-*g*-P(4-CNSt) were carbonized to form N-doped nanocarbons with a fully interconnected 3D nanostructure and with surface areas up to 752 m²/g.

4.6 Acknowledgements

Dr. Mingjiang Zhong is thanked for his helpful discussion about the polymerization conditions for 4-cyanostyrne by normal ATRP. Dr. Benjamin Hui is thanked for etching the silica particles. Dr. Jacob W. Mohin is thanked for characterizing the thermal properties of P(4-CNSt) samples by DSC. Dr. Dingcai Wu and Liyu Chen are thanked for analyzing, by TGA, SEM, and N₂ isotherms, and carbonizing the SiO₂-*g*-P(4-CNSt) samples.

4.7 References

- (1) Koton, M. M.; Mitin, Y. V.; Florinsky, F. S. *Journal of General Chemistry of the USSR* **1955**, 25, 1415.
- (2) Imoto, M.; Kinoshita, M.; Nishigaki, M. *Die Makromolekulare Chemie* **1965**, 86, 217.
- (3) Matyjaszewski, K. *Journal of Macromolecular Science-Reviews in Macromolecular Chemistry and Physics* **1986**, 26, 1.

- (4) Sim, B.; Milne, P.; Griller, D.; Wayner, D. *Journal of the American Chemical Society* **1990**, *112*, 6635.
- (5) Tang, W.; Kwak, Y.; Braunecker, W.; Tsarevsky, N. V.; Coote, M. L.; Matyjaszewski, K. *Journal of the American Chemical Society* **2008**, *130*, 10702.
- (6) Hodgson, J. L.; Yeh Lin, C.; Coote, M. L.; Marque, S. R.; Matyjaszewski, K. *Macromolecules* **2010**, *43*, 3728.
- (7) Lin, C. Y.; Marque, S. R.; Matyjaszewski, K.; Coote, M. L. *Macromolecules* **2011**, *44*, 7568.
- (8) Coote, M. L.; Davis, T. P. *Macromolecules* **1999**, *32*, 4290.
- (9) Qiu, J.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 5643.
- (10) Driva, P.; Pickel, D. L.; Mays, J. W.; Baskaran, D. *Macromolecules* **2010**, *43*, 6915.
- (11) Clavier, G.; Audebert, P. *Chemical reviews* **2010**, *110*, 3299.
- (12) Kurach, E.; Djurado, D.; Rimarcik, J.; Kornet, A.; Wlostowski, M.; Lukes, V.; Pecaut, J.; Zagorska, M.; Pron, A. *Physical chemistry chemical physics : PCCP* **2011**, *13*, 2690.
- (13) Shen, W.; Fan, W. *J. Mater. Chem. A* **2013**, *1*, 999.
- (14) Wood, K. N.; O'Hayre, R.; Pylypenko, S. *Energy & Environmental Science* **2014**, *7*, 1212.
- (15) Wei, Q.; Tong, X.; Zhang, G.; Qiao, J.; Gong, Q.; Sun, S. *Catalysts* **2015**, *5*, 1574.
- (16) Zhao, Z.; Sun, Y.; Dong, F. *Nanoscale* **2015**, *7*, 15.
- (17) Zhou, M.; Wang, H. L.; Guo, S. *Chemical Society reviews* **2015**.
- (18) Deng, Y.; Xie, Y.; Zou, K.; Ji, X. *Journal of Materials Chemistry A* **2016**, *4*, 1144.
- (19) Huynh, M. H. V.; Hiskey, M. A.; Archuleta, J. G.; Roemer, E. L.; Gilardi, R. *Angewandte Chemie International Edition* **2004**, *43*, 5658.
- (20) McGann, J. P.; Zhong, M.; Kim, E. K.; Natesakhawat, S.; Jaroniec, M.; Whitacre, J. F.; Matyjaszewski, K.; Kowalewski, T. *Macromolecular Chemistry and Physics* **2012**, *213*, 1078.
- (21) Zhong, M.; Tang, C.; Kim, E. K.; Kruk, M.; Celer, E. B.; Jaroniec, M.; Matyjaszewski, K.; Kowalewski, T. *Mater. Horiz.* **2014**, *1*, 121.
- (22) Zhong, M.; Kim, E. K.; McGann, J. P.; Chun, S. E.; Whitacre, J. F.; Jaroniec, M.; Matyjaszewski, K.; Kowalewski, T. *Journal of the American Chemical Society* **2012**, *134*, 14846.
- (23) Zhong, M.; Jiang, S.; Tang, Y.; Gottlieb, E.; Kim, E. K.; Star, A.; Matyjaszewski, K.; Kowalewski, T. *Chemical Science* **2014**, *5*, 3315.
- (24) Ju, M. J.; Choi, I. T.; Zhong, M.; Lim, K.; Ko, J.; Mohin, J.; Lamson, M.; Kowalewski, T.; Matyjaszewski, K.; Kim, H. K. *Journal of Materials Chemistry A* **2015**, *3*, 4413.
- (25) Tang, C.; Bombalski, L.; Kruk, M.; Jaroniec, M.; Matyjaszewski, K.; Kowalewski, T. *Advanced Materials* **2008**, *20*, 1516.
- (26) Wu, D.; Dong, H.; Pietrasik, J.; Kim, E. K.; Hui, C. M.; Zhong, M.; Jaroniec, M.; Kowalewski, T.; Matyjaszewski, K. *Chemistry of Materials* **2011**, *23*, 2024.
- (27) Wu, D.; Li, Z.; Zhong, M.; Kowalewski, T.; Matyjaszewski, K. *Angewandte Chemie* **2014**, *53*, 3957.

- (28) Matyjaszewski, K.; Miller, P. J.; Shukla, N.; Immaraporn, B.; Gelman, A.; Luokala, B. B.; Siclovan, T. M.; Kickelbick, G.; Vallant, T.; Hoffmann, H. *Macromolecules* **1999**, 32, 8716.
- (29) Braunecker, W. A.; Tsarevsky, N. V.; Gennaro, A.; Matyjaszewski, K. *Macromolecules* **2009**, 42, 6348.
- (30) Ishizone, T.; Sugiyama, K.; Hirao, A.; Nakahama, S. *Macromolecules* **1993**, 26, 3009.

Chapter 5

Synthesis of Degradable PolyHIPEs by AGET ATRP

5.1 Preface

The research described in this chapter details the development of conditions to polymerize high internal phase emulsions (HIPEs) by AGET ATRP and create degradable polyHIPEs from commercially available monomers. The catalyst selection was determined to be crucial to achieve fully degradable polyHIPEs, as it must remain in the polymerization phase throughout the polymerization. This was my first emulsion/HIPE project and I learned a lot about the stabilization of and ATRP conditions to polymerize emulsion systems.

In this work I studied the AGET ATRP conditions used to polymerize the HIPEs, conducted degradation of and grafting from studies on the degradable polyHIPEs. I also characterized the polyHIPEs' porous structure by SEM analysis and the polyHIPE's degradation products by GPC. Dr. Mingjiang Zhong performed N₂ adsorption experiments to determine surface area of the polyHIPEs. The polyHIPE samples were

Work in this chapter was partially published in Lamson, M.; Epshtein-Assor, Y.; Silverstein, M. S.; Matyjaszewski, K. Synthesis of Degradable PolyHIPEs by AGET ATRP *Polymer* 2013, 54, 4480. Copyright © 2013 Elsevier

sent to collaborators, Dr. Michael S. Silverstein and Yelena Epshitein-Assor, at Technion-Israel Institute of Technology for analysis of their mechanical properties via compression testing.

5.2 Introduction

As discussed in Chapter 1, polyHIPE materials have found many applications. However they suffer from many draw backs, including low mechanical strength and lack or display poor degradation properties. These drawbacks stem from the dominant procedure used for the synthesis of polyHIPEs, namely, conventional radical polymerization (RP) of a monomer and cross-linker in the external phase of a HIPE, which limits the scope of polyHIPEs in commercial applications.

In RP, cross-linking occurs at low monomer conversion, even if polymer chains are highly diluted,^{1,2} and a large amount of intramolecular cross-linking leads to formation of densely cross-linked domains, or microgels, early in the reaction.^{2,3} At higher conversion these microgels are incorporated into the expanded network structure, producing a heterogeneous network. Networks synthesized by RP have limited swelling properties and are poorly degradable due to the presence of densely cross-linked domains in a non-uniform network.^{1,4,5}

With the introduction of reversible deactivation radical polymerization (RDRP) methods,⁶ such as atom transfer radical polymerization (ATRP),⁷⁻¹² more uniform cross-linked networks were synthesized.^{1,2,4,5} A high concentration of polymer chains are formed early in a RDRP reaction, due to fast initiation of all chains and the number of pendant cross-linkable units per chain is low. Therefore, microgel formation at low

conversion is avoided and a more uniform network is formed under RDRP conditions. Networks synthesized by RDRP methods have shown superior swelling properties and a higher elastic modulus than polymer networks synthesized by RP.^{1,4} Nanogels with a uniform cross-linked network were synthesized, using ATRP in inverse miniemulsion. These nanogels contained a disulfide cross-linker and were fully degradable after addition of tributylphosphine, Bu₃P, unlike similar nanogels synthesized by RP.⁴

The mechanical strength of polyHIPE materials were reported to increase when prepared by a RDRP method, due to the creation of a uniform network. For example when RAFT polymerization was used to copolymerize styrene and divinylbenzene simply by adding a RAFT agent to typical RP under HIPE conditions, the mechanical properties of the resulting polyHIPE were significantly improved.¹³ Both the Young's modulus and crush strength increased three-fold in comparison with the polyHIPE produced by RP, while the characteristic polyHIPE morphology was retained.¹³

ATRP is a powerful and robust RDRP method^{7,8} that has been successfully conducted in different dispersed media, including emulsion, miniemulsion, microemulsion, dispersion, and suspension polymerizations.¹⁴ Currently, the AGET (activators generated by electron transfer) ATRP technique is often applied to polymerizations conducted in dispersed media. This procedure allows the copper catalyst to be introduced in the oxidatively stable Cu^{II}/ligand form and then be reduced to the active Cu^I/ligand form by addition of a reducing agent.^{7,14,15} Not only can polymers with controlled molecular weights and low dispersities be synthesized by ATRP in different dispersed media, but polymers with complex architectures, such as block copolymers, star polymers, or brush polymers, can also be prepared.^{16,17}

AGET ATRP was previously used to synthesize polyHIPE materials.¹⁸ 2-Ethylhexyl acrylate and divinylbenzene were copolymerized by AGET ATRP in a HIPE using CuBr₂ with 2,2'-bipyridine (bpy) ligand as the ATRP catalyst and ascorbic acid as the reducing agent. The primary focus of that report was to determine the type and locus of initiation under different initiating conditions, rather than development of a well-controlled AGET ATRP in a HIPE system. Despite this, it was possible to form a stable HIPE and polymerize it by AGET ATRP. The resulting polyHIPE was obtained in high yield (>90%) with void sizes between 6 and 15 μm indicating that AGET ATRP could be successfully used to polymerize comonomers present in HIPEs.

This chapter reports the development of AGET ATRP conditions suitable for polymerization of W/O (water in oil) HIPEs. The selection of an appropriate hydrophobic ATRP catalyst, in this case a CuBr₂/BPMODA complex, was crucial in order to obtain a well-controlled reaction and a high yield of a polyHIPE (SS-BPMODA) with a fully degradable structure. When a less hydrophobic catalyst (CuBr₂/bpy) was used, the resulting polyHIPE could not be fully degraded. Compression testing demonstrated that the material prepared using the CuBr₂/bpy catalyst had a lower stiffness and yield strength than the fully degradable material synthesized using the CuBr₂/BPMODA catalyst. Additionally, the retention of chain-end functionality in the initial SS-BPMODA polyHIPE was confirmed by chain extension with EHMA and OEOMA₃₀₀ to show that the reaction was well controlled when the CuBr₂/BPMODA catalyst was used for the polymerization.

5.3 Experimental

5.3.1 Materials

2-Ethylhexyl methacrylate (EHMA), poly(ethylene glycol) methyl ether methacrylate, average M_n 300 (OEOMA₃₀₀) and ethylene glycol dimethacrylate (EGDMA) were purchased from Aldrich. Both monomers and cross-linker were passed through a basic alumina column to remove inhibitor before use. EGDMA is a non-degradable cross-linker and will be termed “CC” to reflect the carbon-carbon bonds it contributes to the polymer backbone. Bis(2-methacryloyloxyethyl) disulfide (DSDMA)¹⁹ and N,N-bis(2-pyridylmethyl) octadecylamine (BPMODA)²⁰ were synthesized by previously reported procedures. DSDMA is a degradable cross-linker and will be termed “SS” to reflect the sulfur-sulfur bond that it contributes to the polymer network. All other reagents: ethyl 2-bromoisobutyrate (EBiB, 99 %), Span-80 (99 %), CuBr (99 %), CuBr₂ (99 %), 2,2'-bipyridine (bpy, 99 %), 4,4'-dinonyl-2,2'-dipyridine (dNbpy, 99 %), ascorbic acid (AA, 99 %), tin(II) ethylhexanoate (SnEH₂, 99 %), tetrabutylammonium bromide (TBABr, 99 %), tributylphosphine (Bu₃P, 99 %) and solvents, were purchased from Aldrich and used as received.

5.3.2 Synthesis of PolyHIPEs

5.3.2.1 Synthesis of CC-BPMODA and SS-BPMODA PolyHIPEs (Table 5.3.1)

A non-degradable cross-linker (CC) and the BPMODA ligand were used in the preparation of CC-BPMODA. A degradable disulfide cross-linker (SS) and the BPMODA ligand were used in the preparation of SS-BPMODA. CuBr₂ was complexed with BPMODA and dissolved in the monomer at 60 °C over 1.5 h. The mixture was

cooled to room temperature and surfactant (Span-80), cross-linker, and initiator (EBiB) were added. An aqueous solution of ascorbic acid and TBABr was prepared. The aqueous phase was added dropwise to the organic phase with overhead stirring (200 to 300 rpm), while being chilled by an ice bath to minimize polymerization during HIPE formation. After the HIPE was formed, the same amount of a second ascorbic acid solution, identical in concentration to the solution used to form the HIPE, but not containing TBABr, was added on top of the HIPE to minimize contact of the HIPE with air. The HIPE was placed in an oven for 48 h at 60 °C. The polyHIPE was removed from the oven and Soxhlet extraction was performed for 24 h using deionized water followed by methanol for an additional 24 h. The polyHIPE was dried in a fume hood until constant weight was observed.

5.3.2.2 Synthesis of SS-bpy PolyHIPEs (Table 5.3.1)

A degradable disulfide cross-linker (SS) and the bpy ligand were used to prepare SS-bpy polyHIPEs. This procedure for polyHIPE synthesis was similar to a previously reported method.¹⁸ Briefly, the CuBr₂/bpy catalyst was formed and dissolved in a small amount of water. It was added to the organic phase with monomer, cross-linker, Span-80, and EBiB, to minimize its contact with ascorbic acid in the aqueous phase. Two identical ascorbic acid solutions were made. One solution was added to the organic phase dropwise while overhead stirring (200 to 300 rpm) was applied to form a HIPE. The HIPE was kept in an ice bath throughout formation to minimize polymerization. After the HIPE was formed, the same amount of a second ascorbic acid solution, identical in concentration to the solution used to form the HIPE, was added on top of the HIPE, to

reduce its contact with air. The polymerization was carried out over 48 h at 60 °C in an oven. Soxhlet extraction was performed for 24 h with deionized water and 24 h with methanol. The polyHIPE was dried in a fume hood until a constant weight was observed.

Table 5.3.1. Conditions for polyHIPE synthesis

Reagents	CC-BPMODA (wt %)	SS-BPMODA (wt %)	SS-bpy (wt %)
Organic Phase			
EHMA	11.43	11.40	10.99
Cross-linker	^a 3.42	^b 3.71	^c 3.56
Ligand	^a 0.18	^b 0.18	^c 0.04
CuBr ₂	0.06	0.06	0.06
EBiB	0.20	0.20	0.19
Span-80	4.00	4.00	3.87
Water	0	0	^d 3.87
Aqueous Phase			
Water	80.49	80.23	77.36
Ascorbic Acid	0.06	0.06	0.06
TBABr	0.16	0.16	0

^aEGDMA cross-linker and BPMODA ligand; ^bDSDMA cross-linker and BPMODA ligand; ^cDSDMA

cross-linker and bpy ligand; ^dThe catalyst was dissolved in a small amount of water and then added to the organic phase.

5.3.3 PolyHIPE Degradation

100 mg of the dried polyHIPE was swollen in 10 mL THF and purged with nitrogen for 15 min. Bu₃P was added at a ratio of 20:1 (Bu₃P:DSDMA) for SS-BPMODA and 40:1 for SS-bpy. Bu₃P is a highly effective reducing agent for the degradation of disulfide bonds to thiol groups, in alkyl disulfides and polymeric networks with disulfide cross-linkers.^{21,22} The material was allowed to degrade over 3 to 4 days while stirring was applied and then the solution was passed through a 0.2 µm PFFT filter. The dissolved

polymer that was produced by the degradation of the network structure was analyzed by GPC, when possible.

5.3.4 SS-BPMODA Swelling Experiments

The degradable polyHIPE (SS-BPMODA) was cut into regular shapes and swollen in two solvents, anisole and EHMA. Two samples were measured in each case to determine if results were consistent, as cross-linking may not be homogeneous throughout the polyHIPE. Due to the samples brittle nature, the shapes were not regular in all cases and the dimensions highest dimensions were used. The swelling ratio was calculated by the formula: $[(W_a - W_b)/W_b] \times 100$, where W_a is the weight after swelling and W_b is the weight before swelling.

5.3.5 Grafting from SS-BPMODA

100 mg of SS-BPMODA was swollen in EHMA or anisole for 24 hours before the chain extension reaction was conducted. Grafting from SS-BPMODA with EHMA was carried out under normal ATRP conditions with EHMA (9 mL, 40 mmol), CuBr (2.75 mg; 0.019 mmol), dNbpy (15.7 mg; .038 mmol) and 20 vol% anisole (vs. monomer) at 60 °C.

Chain extension with OEOMA₃₀₀ was carried out under activator generated by electron transfer (AGET) ATRP conditions with OEOMA₃₀₀ (0.68 mL; 2.38 mmol), CuBr₂ (2.65 mg; 0.012 mmol), dNbpy (9.69 mg; 0.024 mmol), Sn(EH)₂ (3.84 mg; 0.009 mmol) with 6 mL of anisole at 60 °C. The chain extended SS-BPMODA polyHIPE sample was swollen in THF and degraded by Bu₃P (20:1 Bu₃P:DSDMA) as previously

reported. The material was allowed to degrade over 3 to 4 days while stirring was applied and then the sample was passed through a 0.2 μm PFFT filter. The dissolved polymer that was produced by the degradation of the chain extended network structure was analyzed by GPC.

5.3.6 Characterization

Apparent molecular weight and dispersity were measured by gel permeation chromatography (GPC) with Polymer Standards Services (PSS) columns (guard 10^5 , 10^3 , 10^2 Å) and THF eluent at 35 °C, flow rate 1.00 mL/min, and a differential refractive index (RI) detector (Waters, 2410). Toluene was used as the internal standard to correct for any fluctuation of the THF flow rate. The apparent molecular weights and dispersity were determined with a calibration based on linear polystyrene standards using WinGPC 6.0 software from PSS.

Scanning electron microscopy (SEM) analysis was conducted using a Hitachi 2460N scanning electron microscope. Small pieces of the dried polyHIPE material were dispersed in MeOH, cast on a glass slide, and placed in a fume hood overnight to evaporate the MeOH. The glass slide was attached to a SEM stub using double stick tape, and coated with gold using a Pelco SC-6 sputter coater. Digital images were obtained using Quartz PCI Image management system software and used to determine the size and range of the voids.

The pore structures of some samples were assessed from the N_2 isotherm curve measured by a gas adsorption analyzer (NOVA2000 series, Quantachrome Instruments). Prior to the nitrogen sorption experiments, all samples were degassed at 70 °C for 48 h to

eliminate any surface contaminants (water or oils). The standard analysis of nitrogen sorption isotherms recorded for all samples studied provided the Brunauer-Emmett-Teller (BET) surface area, S_{BET} , evaluated in the range of relative pressure between 0.04 and 0.2.

PolyHIPEs were cut into cubic samples of approximately 1 cm per side and compression tested at 5 %/min until a deformation of 70 % was reached (Instron 3345). At least three samples were tested for each material. The compressive modulus was calculated from the linear slope of the stress-strain curve at low strains. The yield point was taken as the intersection of the two linear regions that were found in the stress-strain curve at low strains.

5.4 Results and Discussion

As discussed in the introduction, conventional radical polymerization leads to formation of non-uniform and non-degradable polyHIPEs with poor mechanical properties that may limit the utility of the material in some applications. Therefore, inspired by previous work,¹⁸ the use of a RDRP method, AGET ATRP, was explored to determine if degradable materials could be synthesized. First, polymerization conditions were optimized for the preparation of non-degradable polyHIPEs by AGET ATRP. These conditions were then adapted for the synthesis of degradable materials.

CC-BPMODA (Table 5.3.1) was successfully synthesized by polymerizing a W/O HIPE, with EHMA monomer and non-degradable cross-linker, EGDMA, in the external phase, via AGET ATRP. These conditions employed a typical ATRP initiator (EBiB) and a CuBr_2 /BPMODA ATRP catalyst in the external phase. BPMODA ligand was selected

as the ligand due to its highly hydrophobic structure and prior use, with good control, in an ATRP in dispersed media.¹⁴ The CuBr₂/ BPMODA catalyst was reduced to the activator state by ascorbic acid, present in the internal aqueous phase, during interfacial reactions. The addition of a second ascorbic acid solution on top of the HIPE, not only reduced the catalyst contact with air, but ensured the presence of CuBr/BPMODA, the ATRP activator species, throughout the polymerization. TBABr was added to the aqueous phase to assist in prevention of Ostwald ripening and to shift the equilibrium of the Cu^{II} complexes toward the Br-Cu^{II}/L state.^{23,24} These conditions led to formation of the CC-BPMODA in a high yield, 94%.

The macroporous structure of CC-BPMODA was confirmed by SEM imaging. The structure was not typical of a polyHIPE (Fig. 5.4.1a). Large open cell voids were not observed in CC-BPMODA, although highly interconnected macropores with a size of 1 to 5 μm were present.

With the successful development of AGET ATRP under HIPE conditions, the synthesis of polyHIPEs with a degradable structure was targeted. SS-BPMODA (Table 5.3.1) was successfully synthesized after replacing the non-degradable cross-linker, present in the CC-BPMODA conditions, with a disulfide containing degradable cross-linker (DSDMA). SS-BPMODA was obtained in 94% yield. The resulting polyHIPE had a specific surface area, S_{BET} , of 6.4 m²/g, according to N₂ sorption isotherms with BET analysis. SEM imaging verified that SS-BPMODA had a macroporous structure characteristic of a typical polyHIPE (Fig. 5.4.1b, d). The voids were in the range of 3 to 15 μm and had interconnecting 1 μm sized pores that created a highly porous material.

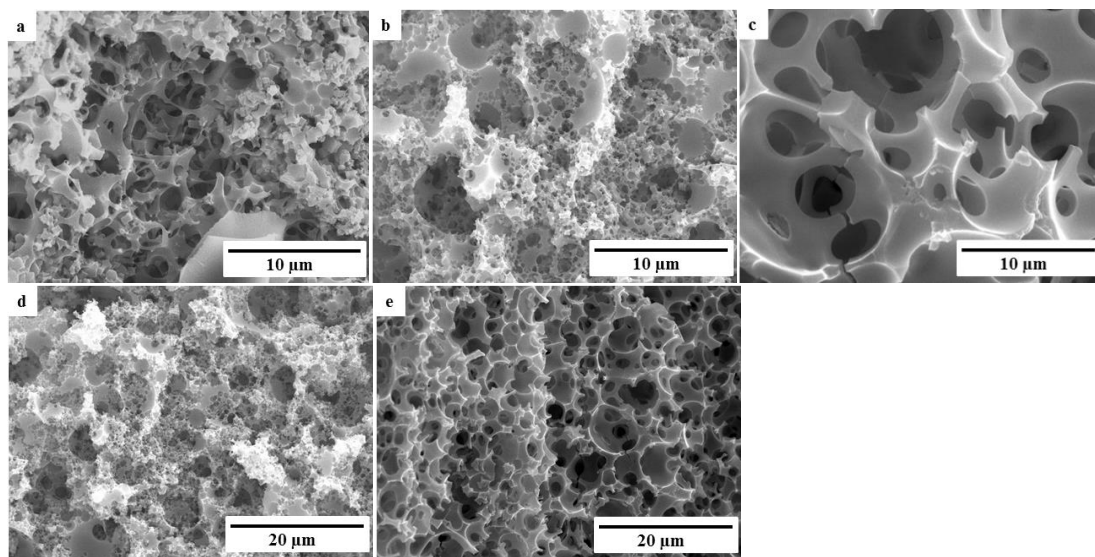


Figure 5.4.1. SEM images of CC-BPMODA (a), SS-BPMODA (b,d), and SS-bpy (c,e) polyHIPEs

SS-BPMODA, when swollen in THF, was fully degradable through reduction of the disulfide bond in the DSDMA cross-linker in the presence of Bu_3P . This degradation was indicated by the THF solution's change from turbid to clear after three days exposure to Bu_3P . Also, the solution could be passed through a $0.2\ \mu\text{m}$ PFFT filter once it became clear. After degradation, GPC analysis revealed that the degraded polyHIPE material had a molecular weight of $M_n = 30,500$ and a dispersity, M_w/M_n , of 1.6 (Fig. 5.4.2). The complete degradation of SS-BPMODA, the relatively narrow molecular weight distribution, and the high molecular weight of the primary chains confirm that a uniform network was formed during the synthesis and this reaction was well controlled by the $\text{CuBr}_2/\text{BPMODA}$ catalyst. The degree of control is noteworthy considering that there was no removal of O_2 during the preparation of the HIPE. This is an important observation since it is difficult to remove O_2 during HIPE preparation due to the mixing conditions

used and the fact that the high viscosity of the HIPE impedes the removal of O₂ after formation. It is typically necessary, when AGET ATRP is carried out in other dispersed media systems, to removed O₂ from the system to obtain well controlled reactions and well defined polymeric materials. Therefore, this successful synthesis without the need for oxygen removal was an important achievement.

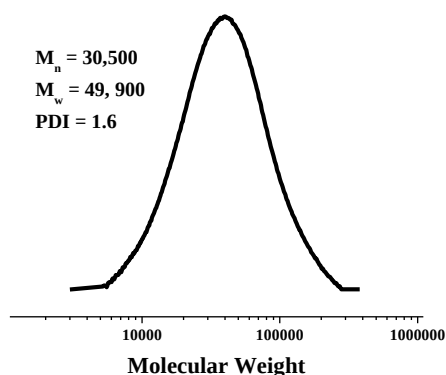


Figure 5.4.2. Molecular weight distribution of degraded SS-BPMODA from GPC analysis with THF eluent and linear PS-standards

To further prove that the proper conditions and catalyst, CuBr₂/BPMODA in this case, must be selected when synthesizing materials by AGET ATRP in dispersed media, conditions similar to a previously reported AGET ATRP of a HIPE were employed.¹⁸ Thus SS-bpy was synthesized (Table 5.3.1) using a CuBr₂/bpy catalyst and a degradable cross-linker for a HIPE polymerization conducted at 60 °C for 48 h. Due to its insolubility in the hydrophobic EHMA monomer the CuBr₂/bpy catalyst was dissolved in water, then it was added to the organic phase to minimize its interaction with and consequent reduction by the ascorbic acid contained in the aqueous phase during HIPE formation. A second solution of ascorbic acid in water was added on top of the polyHIPE

to minimize its contact with air and to ensure the presence of the ATRP activator, CuBr/bpy, during the entire polymerization.

According to SEM imaging the SS-bpy product displayed typical polyHIPE morphology with voids in the range of 5 to 15 μm , (Fig. 5.4.1c, e). Compared to the SS-BPMODA polyHIPE, this material had larger and less interconnecting pores. N_2 sorption isotherms with BET analysis verified that this polyHIPE had a specific surface area of 1.9 m^2/g , which was somewhat lower than that of sample SS-BPMODA. Despite the formation of a typical polyHIPE, this reaction resulted in only a 77 % yield. Attempts were made to degrade SS-bpy, but it was not fully degraded after four days with twice the concentration of Bu_3P used to degrade SS-BPMODA. This was indicated by the continued presence of a cloudy solution that could not be passed through a 0.2 μm PFFT filter or analyzed by GPC.

A comparison of the properties of the SS-BPMODA with SS-bpy samples highlights the superiority of the hydrophobic $\text{CuBr}_2/\text{BPMODA}$ catalyst over the CuBr_2/bpy catalyst when HIPEs are polymerized by AGET ATRP. The $\text{CuBr}_2/\text{BPMODA}$ catalyst provides good control throughout the reaction, resulting in formation of a uniformly cross-linked network and a fully degradable material. On the other hand, the CuBr_2/bpy catalyst does not produce a degradable polyHIPE. The difference in control can be explained by the location of each ATRP catalyst within the HIPE. Fig. 5.4.3a shows an image of SS-BPMODA polyHIPE immediately after polymerization. No green color could be observed in the aqueous ascorbic acid aqueous added as a top layer. $\text{CuBr}_2/\text{BPMODA}$, the ATRP deactivator, was preferentially located in the organic phase, due to BPMODA's hydrophobic structure. However, the top ascorbic acid aqueous

solution was distinctly green in the case of SS-bpy (Fig. 5.4.3b). CuBr₂/bpy, the ATRP deactivator, was preferentially located in the aqueous phase, due to the hydrophilicity of the CuBr₂/bpy complex.

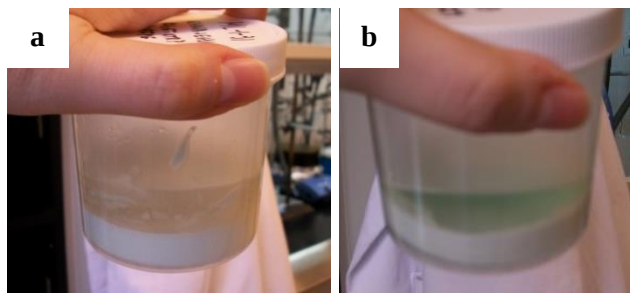


Figure 5.4.3. Images of SS-BPMODA (a) and SS-bpy (b) reaction mixtures immediately after polymerization

The location of the ATRP deactivator is important when considering control in ATRP reactions, because it deactivates the propagating chains into a dormant state. This expands the lifetime of a polymer chain from seconds to hours, minimizes termination reactions, and provides a concurrent growth of all chains.⁷ The polymer chains have uniform length and, at low conversion, have similarly low number of pendant double bonds. It is not until the polymerization reaches high conversion that enough pendant double bonds are incorporated and the polymer chains can crosslink. In contrast, uncontrolled processes lead to high molecular weight chains with many dangling double bonds at low conversions, resulting in premature crosslinking and formation of dense microgels. This is observed in the case of the CuBr₂/bpy catalyst, since a fraction of the deactivator was located in the aqueous phase, resulting in poor control over the polymerization. The chains were not deactivated as often and the polymerization

proceeded with poor control. The deactivator must be located in the polymerization phase. Intramolecular reactions occurred more readily and consequently dense microgel regions were formed in the network, making the network non-degradable in the case of SS-bpy. On the other hand, a hydrophobic catalyst complex, such as $\text{CuBr}_2/\text{BPMODA}$, which is located in the organic phase, was able to exert control throughout the entire polymerization via deactivation of the growing polymer chains. Through the combination of reversible deactivation, diffusion, and relaxation of polymer chains, a fully degradable and uniform cross-linked network can be obtained, as shown for SS-BPMODA.

Attempts were made to synthesize a polyHIPE of EHMA and DSDMA by conventional radical polymerization (RP). All attempts to do so were unsuccessful and most HIPE formulations resulted in phase separation after a few hours in the oven at 60 °C. It was expected that polyHIPEs of EHMA and DSDMA synthesized by RP would not be fully degradable and would have a less uniform network than SS-bpy, due to the lack of control over the polymerization and resulting polymer network in materials prepared by RP.⁴

The mechanical properties of SS-BPMODA and SS-bpy polyHIPEs were studied by compression testing. The stress-strain curves (Fig. 5.4.4) are fairly typical of polyHIPEs, exhibiting a linear region at low strains, a stress plateau region at moderate strains, and a densification region with a rapid increase in stress at the highest strains. The average Young's modulus, yield stress and yield strain determined from the stress-strain curves are presented in Table 5.4.1. The linear portions of the stress-strain curve that were used to determine Young's modulus and the yield point are shown in the insert within Fig. 5.4.4. SS-bpy has a lower Young's modulus and a lower yield stress than SS-

BPMODA. This can again be explained by the fact that the $\text{CuBr}_2/\text{BPMODA}$ catalyst complex exerts better control over the polymerization, due to its preferential location in the external organic phase. The more uniform and, thus, more rigid network in SS-BPMODA formed a polyHIPE with a higher Young's modulus and a higher yield stress. CuBr_2/bpy was located in the aqueous phase and it has limited control over the polymerization, yielding areas of densely cross-linked microgels and a non-uniform network. A non-uniform network should have areas of little or no cross-linking that are more flexible than the highly cross-linked microgel region. It is expected that a polyHIPE made with EHMA and DSDMA and synthesized by RP would exhibit an even lower Young's modulus than SS-bpy and be less stiff, due to its less uniform network.

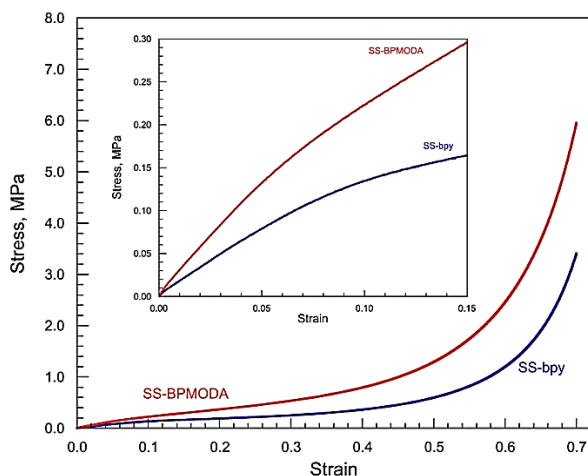


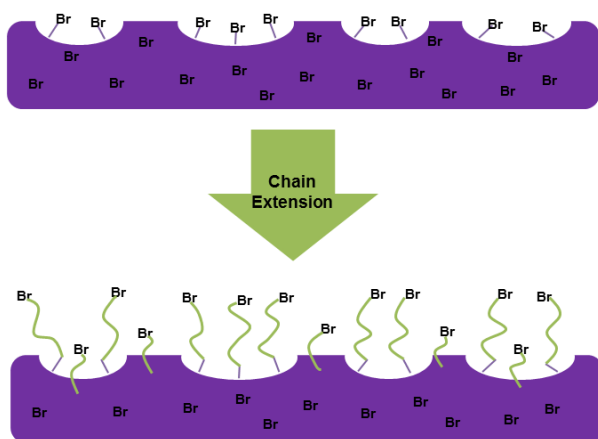
Figure 5.4.4. Stress-strain curves for compression testing of SS-BPMODA and SS-bpy

Table 5.4.1. Data from stress-strain curves in Fig. 5.3.4

Sample	Average Modulus (MPa)	Yield Stress (MPa)	Yield Strain
SS-BPMODA	2.43 ± 0.37	0.228 ± 0.070	0.109 ± 0.05
SS-bpy	1.35 ± 0.50	0.131 ± 0.04	0.121 ± 0.06

Chain extension experiments were conducted to determine if the polyHIPEs, synthesized using the $\text{CuBr}_2/\text{BPMODA}$ catalyst, had high preservation of Br-chain-end functionality. If the reaction was well controlled by the $\text{CuBr}_2/\text{BPMODA}$ catalyst, because it was retained in the polymerization phase throughout the HIPE polymerization, chain extension should be possible. According to Silverstein et al., polymer begins to form at the interface, during interfacial initiation in HIPE, and monomer diffuses to the interface.¹⁸ Therefore, the majority of Br-chain-ends should be located at the polyHIPE surface. The polymer chain end and surfactant are forced into the forming polyHIPE wall and hollow polyHIPE walls can also form.¹⁸ However, due to this migration it is possible for Br-chain-ends to be located within the polyHIPE wall. Thus, chain extension of SS-BPMODA should occur from the easily accessible Br-chain-ends at the surface of the polyHIPE with a lesser amount occurring from chain-ends contained within the polyHIPE wall (Scheme 5.4.1). After degradation the resulting polymer should have a bimodal distribution, as some chains were extended and others were not.

Scheme 5.4.1. SS-BPMODA Chain Extension



PolyHIPEs are able to absorb large amounts of liquid through capillary action and displacement of air within the polyHIPE walls and voids.²⁵ Swelling experiments were performed to ensure monomer would be able to penetrate the densely cross-linked polyHIPE for successful chain extension. SS-BPMODA was swollen in EHMA or anisole and the dimensions were measured and volumes before and after swelling were calculated, as well as the volume increase and swelling ratios (Table 5.4.2). It was determined that all four samples tested, regardless of the swelling solvent, showed similar increases in volume (73.9 % to 81.4 %). The swelling ratios showed more variability. In EHMA the swelling ratios were similar, around 700 %. However, in anisole one sample had a swelling ratio of 587 % and the other was 803 %, because anisole is not an ideal solvent for PEHMA, whereas PEHMA has better solubility, and therefore higher swelling ratio, in its own monomer. However, SS-BPMODA can be swollen in anisole (Figure 4.4.5), as indicated by the high swelling ratio.

Table 5.4.2. Swelling of SS-BPMODA with anisole or EHMA

Solvent	Dimensions before (mm)	Dimensions after (mm)	V _{before} (mm ³)	V _{after} (mm ³)	Volume Increase (%)	Weight before (mg)	Weight after (mg)	Swelling Ratio (%)
Anisole	5x5x2	7x7x4	50	196	75.5	17.6	120.9	587
Anisole	8.5x5.5x2.5	14x9x5	117	630	81.4	42.5	383.6	803
EHMA	7x4.5x2	11x7x4	63	308	79.5	21.7	178.1	720.7
EHMA	6.5x6.5x2.5	11x10.5x3.5	106	404	73.9	36.6	296.4	709.8



Figure 5.4.5. SS-BPMODA before (left) and after (right) swelling with anisole for 24 hours

A new sample of SS-BPMODA was prepared and swollen in EHMA for 24 hours. The chain extension was carried out using normal ATRP with $[\text{EHMA}]:[\text{SS-BPMODA-Br}]:[\text{CuBr}]:[\text{dNbpy}] = 2000:1:1:2$ with 20 vol% anisole at 60 °C. After the reaction, the chain extended SS-BPMODA was degraded with Bu_3P and the resulting polymer was analyzed via GPC. After chain extension for 24 hours little change in molecular weight was observed (Table 5.4.3; Figure 5.4.6). However, after chain extension for 48 hours, the polymer exhibited a bimodal molecular weight distribution (Figure 5.4.6), indicating that the Br-chain-ends at the surface of the polyHIPE were easily extended, and the Br-chain-ends with in the polyHIPE wall were not extended, as predicted.

Table 5.4.3. Molecular weight data of degraded SS-BPMODA before and after chain extension with EHMA

Sample	M_n	M_w	M_w/M_n
SS-BPMODA	10,400	15,800	1.55
24 Hour Extension	12,200	18,500	1.51
48 Hour HMW	391,000	480,000	1.23
48 Hour LWM	13,200	19,100	1.45

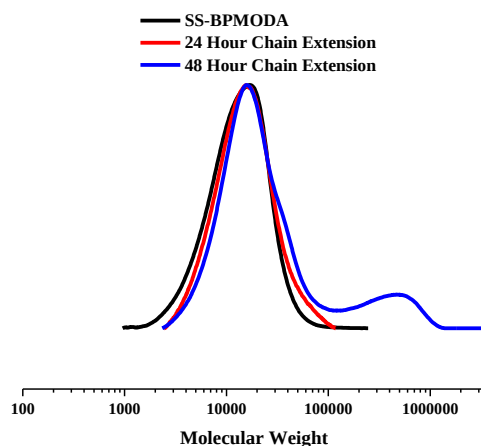


Figure 5.4.6. Molecular weight distribution of degraded SS-BPMODA and degraded SS-BPMODA after 24 and 48 hour grafting EHMA from the polyHIPE; GPC with THF eluent and PS standards

SS-BPMODA was swollen in anisole for 24 hours followed by chain extension with EHMA. AGET ATRP conditions were used with [EHMA]:[SS-BPMODA-Br]:[CuBr]:[dNbpy]: [Sn(EH)₂] = 200:1:1:2:0.8 with 1:8.8 OEOMA₃₀₀: anisole (v/v) at 60 °C. Degradation of SS-BPMODA samples were performed with Bu₃P and the resulting polymers were analyzed. For all reaction times the MWD broadened along with an increase in the M_n (Table 5.4.4; Figure 5.4.7). After 24.5 hours a small hint of a bimodal distribution was observed (Figure 5.4.7), but it is unlikely to grow larger, as the target DP of OEOMA₃₀₀ was low (200:1 OEOMA₃₀₀:SS-BPMODA-Br). SEM analysis of SS-BPMODA that was chain extended with OEOMA₃₀₀ for 24.5 hours showed that it retained its porous structure (Figure 5.4.8). Both successful chain extensions, with EHMA and OEOMA₃₀₀, indicated that the SS-BPMODA had high chain-end

functionality, due to the well-controlled HIPE polymerization when the deactivator species, $\text{CuBr}_2/\text{BPMODA}$, was located in the polymerization phase.

Table 5.4.4. Molecular weight data of degraded SS-BPMODA before and after chain extension with OEOMA_{300}

Sample	M_n	M_w	M_w/M_n
SS-BPMODA	10,400	15,800	1.55
3 hours	12,500	33,700	2.69
5 hours	12,500	37,900	3.00
24.5 hours	14,300	46,700	2.98

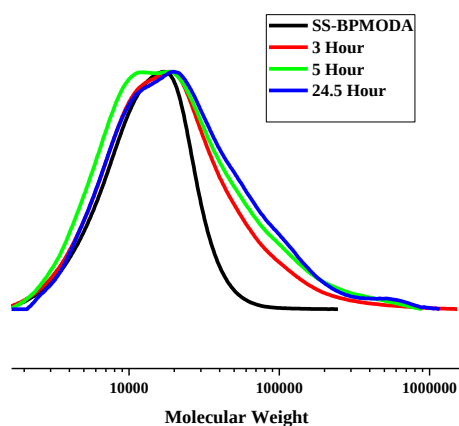


Figure 5.4.7. Molecular weight distribution of degraded SS-BPMODA and degraded material after 24 and 48 hour grafting OEOMA_{300} from the polyHIPE; GPC with THF eluent and PS standards

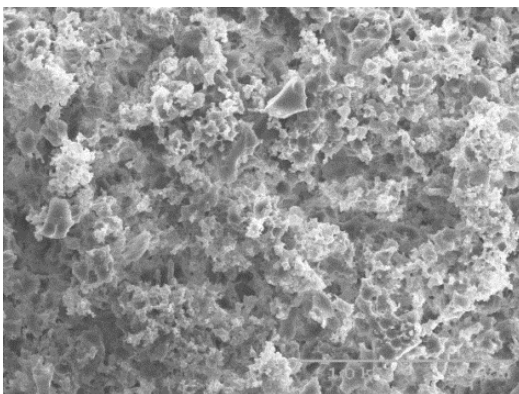


Figure 5.4.8. SEM image of SS-BPMODA after chain extension with OEOMA₃₀₀ for 24.5 hours

5.5 Conclusions

The conditions selected to synthesize the SS-BPMODA polyHIPE resulted in formation of a fully degradable material with a stiffer structure than the SS-bpy polyHIPE. A degradable network is only achieved in a biphasic AGET ATRP when the deactivator is retained in the polymerization phase (CuBr₂/BPMODA) and provides good control over the reaction via frequent deactivation of propagating chains. On the other hand, CuBr₂/bpy deactivators could not produce a degradable network via AGET ATRP in a W/O HIPE, because they were preferentially located in the aqueous phase, and could not deactivate propagating chains often enough to exert control over the reaction. Due to the formation of a uniform network in SS-BPMODA, it exhibited a stiffer structure and higher Young's Modulus than SS-bpy, which has a non-uniform network. SS-BPMODA has a high swelling ratio in EHMA and anisole, which allows for successful chain extension reactions. The successful chain extension of SS-BPMODA further confirmed that polyHIPEs synthesized by AGET ATRP with a catalyst that remains in the polymerization phase (CuBr₂/BPMODA) is a well-controlled reaction, because the

resulting polyHIPEs exhibited good chain end functionality. As predicted, if adequate amount of monomer (2000:1 monomer:SS-BPMODA-Br) was used the degraded polymer exhibited a clear bimodal molecular weight distribution where only chain-ends at the surface were extended. Furthermore, the conditions developed to synthesize SS-BPMODA do not require the removal of O₂ from the system, as is necessary for most ATRP reactions, making it appealing for industrial scale-up. Proper conditions should be selected when using AGET ATRP in dispersed media, with emphasis on catalyst selection, if one seeks to synthesize degradable materials with a relatively high modulus, yield strength, and high chain-end functionality.

5.6 Acknowledgements

Dr. Wenwen Li for helpful discussion, Joseph P. Suhan for his help with the SEM imaging and Dr. Mingjiang Zhong for N₂ sorption measurements are sincerely thanked. Support from the National Science Foundation (DMR 09-69301) and BSF grant (2008152) is acknowledged.

5.7 References

- (1) Ide, N.; Fukuda, T. *Macromolecules* **1999**, *32*, 95.
- (2) Yu, Q.; Xu, S.; Zhang, H.; Ding, Y.; Zhu, S. *Polymer* **2009**, *50*, 3488.
- (3) Gao, H.; Matyjaszewski, K. *Progress in Polymer Science* **2009**, *34*, 317.
- (4) Oh, J. K.; Tang, C.; Gao, H.; Tsarevsky, N. V.; Matyjaszewski, K. *Journal of the American Chemical Society* **2006**, *128*, 5578.
- (5) Yoon, J.; Oh, J. K.; Li, W.; Kowalewski, T.; Matyjaszewski, K. *Hydrogel micro and nanoparticles* **2012**, 169.
- (6) Braunecker, W. A.; Matyjaszewski, K. *Progress in Polymer Science* **2007**, *32*, 93.
- (7) Matyjaszewski, K. *Macromolecules* **2012**, *45*, 4015.
- (8) Xia, J.; Matyjaszewski, K. *Chemical Reviews* **2001**, *101*, 2921.
- (9) Matyjaszewski, K.; Tsarevsky, N. V. *Nature chemistry* **2009**, *1*, 276.
- (10) Tsarevsky, N. V.; Matyjaszewski, K. *Chemical Reviews* **2007**, 107.

- (11) Wang, J.; Matyjaszewski, K. *Journal of the American Chemical Society* **1995**, *117*, 5614.
- (12) Wang, J.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901.
- (13) Luo, Y.; Wang, A.-N.; Gao, X. *Soft Matter* **2012**, *8*, 1824.
- (14) Min, K.; Matyjaszewski, K. *Central European Journal of Chemistry* **2009**, *7*, 657.
- (15) Jakubowski, W.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 4139.
- (16) Min, K.; Gao, H.; Matyjaszewski, K. *Journal of the American Chemical Society* **2005**, *127*, 3825.
- (17) Min, K.; Yu, S.; Lee, H.; Mueller, L.; Sheiko, S. S.; Matyjaszewski, K. *Macromolecules* **2007**, *40*, 6557.
- (18) Gurevitch, I.; Silverstein, M. S. *Macromolecules* **2011**, *44*, 3398.
- (19) Gao, H.; Tsarevsky, N. V.; Matyjaszewski, K. *Macromolecules* **2008**, *38*, 5995.
- (20) Xia, J.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 2434.
- (21) Humphrey, R. E.; Potter, J. L. *Anal. Chem.* **1965**, *37*, 164.
- (22) Tsarevsky, N. V.; Matyjaszewski, K. *Macromolecules* **2005**, *38*, 3087.
- (23) Konkolewicz, D.; Magenau, A. J. D.; Averick, S. E.; Simakova, A.; He, H.; Matyjaszewski, K. *Macromolecules* **2012**, *45*, 4461.
- (24) Simakova, A.; Averick, S. E.; Konkolewicz, D.; Matyjaszewski, K. *Macromolecules* **2012**, *45*, 6371.
- (25) Silverstein, M. S.; Cameron, N. R. In *Encyclopedia of Science and Technology*; 4 ed.; Wiley: Hoboken, N.J., 2010.

Chapter 6

PEO-based Stars as Efficient Stabilizers for Normal Emulsions and High Internal Phase Emulsions

6.1 Preface

The research described in this chapter discusses the use of poly(ethylene oxide) (PEO) based star polymers for stabilization of xylene/water emulsions and high internal phase emulsions (HIPEs). The objective was to determine the lowest star content required for the formation of stable emulsions and significantly decrease the interfacial tension between the xylene and water interface which was studied and correlated to the star structure. PEO-poly(divinylbenzene) stars stabilized oil-in-water (O/W) emulsions and poly(ethylene oxide)-poly(*n*-butyl acrylate)-poly(divinyl benzene) [PEO-PBA-poly(DVB)] miktoarm stars stabilized water-in-oil emulsions (W/O). The PEO-PBA-poly(DVB) stars were also investigated for W/O HIPE stabilization, with a focus on identifying the lowest star polymer loadings required to form a stable HIPE and the formation of polymerized HIPEs (polyHIPEs) with an open cell structure.

Work in this chapter was partially published in Li, W.; Yu, Y.; Lamson, M.; Silverstein, M. S.; Tilton, R. D.; Matyjaszewski, K. *Macromolecules*, **2012**, 45, 9419-9426 Copyright © 2012 American Chemical Society

This project allowed me to explore, and fully understand, how star polymers were synthesized by ATRP. More significantly, I learned crucial purification techniques for star-polymers and how to prevent them from physical aggregation during purification. I also learned how star structure correlates to emulsification behavior and lowering interfacial tension, as well as how to prepare stable HIPEs using star polymers as surfactants.

I synthesized the PEO-PBA-poly(DVB) mikto-arm stars with 50% PEO and densely cross-linked PEO-poly(DVB) stars. The star macromolecules were characterized by GPC with refractive index (RI) and multi-angle light scattering (MALLS), to determine their actual molecular weight and the number of arms in the stars. I also monitored the long term stability of the xylene/water emulsions (during the year long period) and performed all interfacial tension measurements. Synthesis of all other star polymers, xylene/water emulsion stabilization and characterization and imaging of the emulsion droplets was carried out in collaboration with Dr. Wenwen Li and Yao Yu. HIPE stabilization and polymerization experiments, as well as SEM imaging of polyHIPEs and shape-memory performance of polyHIPEs were conducted by Dr. Michael S. Silverstein and Lital Rabinovitch at Technion-Israel Institute of Technology.

6.2 Introduction

The use of amphiphilic block copolymers (BCPs), consisting of a water-soluble hydrophilic block and water-insoluble hydrophobic block, as surfactants for the generation of a stable emulsion has been well documented in the literature.¹ Because of the specific solubility characteristics of each copolymer segment, BCPs are driven to

adsorb at the interface and stabilize the dispersed droplets. Amphiphilic block copolymers can also serve as surfactants for biphasic polymerizations, allowing for the preparation of stable polymer particles with tunable size. Polymeric surfactants have several unique beneficial features when compared to low molar mass surfactants, such as lower surfactant loading for the generation of a stable emulsion, a lower critical micelle concentration (cmc), and low molecular mobility. Low molecular mobility is an important feature of polymeric surfactants when used to stabilize latexes, as they reduce desorption of surfactants from particle surfaces and help to improve the latex stability, making them useful in many applications. In addition, one can easily adjust the emulsification properties of BCPs for a given application by tuning the block ratios. The emulsification properties can also be tuned via introduction of a (non)ionic anchoring block, functional sites, or a stimuli-responsive block, which can tailor the interaction between the polymeric surfactants and the dispersed phase.¹

The development of controlled radical polymerization²⁻⁵ techniques during the past two decades, such as atom transfer radical polymerization,^{2,6-9} enables control over the molecular weight and composition of BCPs with relatively easy experimental set up. The procedures also provide accessibility to a series of copolymers with complex topologies, including brush, branched, and star polymers, and uniform cross-linked polymer networks.¹⁰⁻¹² Star polymers, which contain multiple arms radiating from a central branching point, or core, represent one of the simplest branched topologies.¹³⁻¹⁵ The core-shell microstructure of star polymers generates several unique properties, including tunable solubility, by control of the composition of the arm and core, or introduction of multiple functionalities on the periphery of the star to tune its affinity

towards different substrates or solvents.¹⁶⁻²⁵ The ability to control these properties provide an opportunity to use star-shaped polymers as surfactants for emulsion applications or other biphasic polymerizations.²⁶ However, there are a limited number of reports on star polymer-based emulsifier systems, compared to reports on amphiphilic BCP emulsifiers.²⁷⁻³⁵ Nevertheless, these limited studies do provide some promising results: (1) Star polymers are efficient stabilizers, and generally a lower surfactant loading was needed to reduce the interfacial tension, compared to their linear counterparts. (2) The composition of star copolymers significantly affects their interfacial behavior: more hydrophilic star polymers are good stabilizers for oil-in water (O/W) emulsions, and more hydrophobic star polymers lead to the formation of water-in-oil (W/O) emulsions.

As discussed in Chapter 1, high internal phase emulsions (HIPEs) generally require a large amount of surfactant (up to 30% of the external phase), such as sorbitan monooleate (Span-80) to form a fully stable HIPE.³⁶⁻⁴⁰ Surfactants that form a stable HIPE must be completely insoluble in the dispersed phase, to prevent phase inversion and generation of “normal” emulsions and should rapidly absorb at the interface to reduce the interfacial tension between the oil and water phases.⁴⁰ Research has focused on decreasing the amount of surfactant needed to stabilize HIPEs, but few reports have shown a significant decrease in surfactant loadings. The most promising class of new surfactants are Janus particles or core cross-linked star polymers, which can form stable HIPEs with loadings as low as 1 wt% (vs total emulsion).⁴¹⁻⁴⁵ These papers indicate that investigating star polymers for HIPE stabilization could lead to the development of new

surfactants that are highly efficient stabilizers, at low surfactant loadings, for O/W or W/O HIPEs, especially since the composition of star polymers is tunable.

This chapter will discuss the design and use of a series of PEO-based star polymers as stabilizers/surfactants for the generation of stable oil-in-water or water-in-oil emulsions. The effect of several parameters on the emulsification behavior of the star polymers were studied, including arm composition/hydrophobicity, star size, and compactness. Optimization of the star polymer composition generated xylene-in-water and water-in-xylene emulsions with long-term stability (≥ 1 year) with a concentration of star emulsifiers as low as ~ 0.005 wt %. PEO-PBA-poly(DVB) mikto-arm star polymers were also investigated for W/O HIPE stabilization and subsequent polymerization to form stable polymerized HIPEs (polyHIPEs). The mikto-arm star polymers formed stable HIPEs at loading as low as 0.04 wt% (vs. total emulsion).

6.3 Experimental

6.3.1 Materials

Styrene (St), *n*-butyl acrylate (BA), and divinylbenzene (DVB) were purchased from Aldrich. They were purified by passing through a basic alumina column to remove the inhibitor. Poly(ethylene oxide) methyl ether methacrylate macromonomer (PEO MM) with $M_n = 2080$ and $M_w/M_n = 1.05$, was obtained as a 50 wt % solution in water (Aldrich). The PEO MM was extracted from water with methylene chloride, followed by rotary evaporation of methylene chloride. Poly(ethylene oxide)-based macroinitiators (PEO MI, $M_n = 2200$ or 5200 , Aldrich) and poly(*n*-butyl acrylate)-based macroinitiators (PBA MI, $M_n = 7800$ and $M_w/M_n = 1.10$) were prepared according to the previously

published procedure.²¹ CuBr (98%, Acros) was purified by stirring in acetic acid, it was then filtered, washed with 2-propanol, and then dried under vacuum. Tris[(2-pyridyl)methyl]amine (TPMA) was prepared according to a previously published procedure.⁴⁶ All other reagents CuBr₂, N,N,N',N'',N''-pentamethyldiethylenetriamine (PMDETA), ethyl 2-bromoisobutyrate (EBiB), benzoyl peroxide (BPO), potassium persulfate (KPS), K₂SO₄, stearyl acrylate (A18), polyhedral oligomeric silsesquioxane with 8 methacrylate groups (POSS-8), tetrahydrofuran (THF), dichloromethane (DCM), xylene, cyclohexane and methanol (MeOH) were purchased from Aldrich and used as received.

6.3.2 Synthesis of PEO–Poly(DVB) Star Polymers (S_D64) via Cross-linking of Macromonomers

The ratio of reagents were [PEO MM]₀/[EBiB]₀/[DVB]₀/[CuBr]₀/ [TPMA]₀ = 5/1/15/1/1 and [PEO MM]₀ = 0.167 mM in anisole. PEO MM (5.11 g, 2.5 mmol), DVB (1.3 mL, 7.4 mmol), TPMA (143 mg, 0.49 mmol), and anisole (15 mL) were added to a clean dry Schlenk flask. The flask was degassed by purging with N₂ for 20 minutes. CuBr (0.070 g, 0.49 mmol) was quickly added under positive N₂ pressure and the flask was sealed with a glass stopper and purged for an additional 5 minutes. The flask was emerged in an oil bath at 80 °C. Finally, the N₂-purged initiator EBiB (0.072 mL, 0.49 mmol) was injected into the reaction system, via a syringe, through the side arm of the Schlenk flask. The reaction was stopped after 116 h via exposure to air and dilution with THF.

6.3.3 Synthesis of PEO-Based Star Polymers via Cross-Linking of Macroinitiators

A typical procedure for the synthesis of PEO–PBA–poly(DVB) miktoarm star polymers with 50% PEO arms (MS_{PBA50}) is listed below. The ratio of reagents were $[PEO\ MI]_0/[PBA\ MI]_0/[DVB]_0/[CuBr]_0/[PMDTA]_0 = 0.5/0.5/12/0.8/0.8$ and $[PEO]_0 = 0.015$ mM in anisole. A clean and dry Schlenk flask was charged with PEO MI (1 g, 0.19 mmol initiating sites), PBA MI (1.48 g, 0.19 mmol initiating sites), DVB (0.82 mL, 4.6 mmol), PMDTA (0.080 mL, 0.38 mmol), and anisole (12 mL). The flask was degassed by purging with N_2 for 20 minutes. CuBr (0.200 g, 1.4 mmol) was quickly added under positive N_2 pressure. The flask was sealed with a glass stopper and then purged with N_2 for 5 minutes before it was immersed in an oil bath at 110 °C. The reaction was stopped after 22 h via exposure to air and dilution with THF.

Two other PEO–PBA–poly(DVB) miktoarm star polymers, with 70% PEO arms, MS_{PBA30} , $[PEO\ MI]_0/[PBA\ MI]_0/[DVB]_0 = 0.7/0.3/12$, with 90% PEO arms, MS_{PBA10} , $[PEO\ MI]_0/[PBA\ MI]_0/[DVB]_0 = 0.9/0.1/12$, and two additional PEO–poly(DVB) homoarm star polymers, S_{L35} with $[PEO\ MI]_0/[DVB]_0 = 1/5$, and sample S_{L30} with $[PEO\ MI]_0/[DVB]_0 = 1/3$, were prepared using similar procedures, by simply changing the molar ratio between arm precursors and cross-linker.

6.3.4 Generation of Emulsions

The water/oil ratio was set at 1:1 by weight, and emulsions were formed using a vortex mixer (Fisher Scientific Analogue Vortex Mixer, 120 V at 3000 rpm) for 30 s. Unless otherwise indicated, the star copolymers were dispersed in water before homogenization. After emulsification, the height of each phase, emulsion, neat water,

and/or neat oil, was measured to calculate the volume percentages of oil and water in the emulsion phase. A drop test was conducted to determine the emulsion type by placing one drop of the emulsion phase into neat water or into neat oil. An O/W emulsion droplet disperses readily in water but not in oil and vice versa. All emulsions were stored in closed vials at room temperature, and the emulsion phase fraction was checked regularly to characterize emulsion stability.

6.3.5 Generation of HIPE and Polymerization to form PolyHIPE

The HIPEs were generated according to the recipes in Table 6.3.5.1 and 6.3.5.2. All reagents that were in the organic phase were mixed together and the aqueous phase, containing all desired reagents, were slowly added, dropwise, to the organic phase with vigorous stirring. Once the HIPE was formed it was polymerized by placing it in an oven at 70 °C for 24 hours. The polyHIPEs were purified by Soxhlet extraction with MeOH and dried under vacuum at RT.

Table 6.3.5.1. Styrene/DVB HIPE Recipes

Sample	1	2	3	4	5
External Organic Phase (wt%)					
Styrene	17.99	15.90	8.99	5.30	7.95
DVB	2.00	1.83	1.00	0.59	0.95
BPO	0.00	0.00	0.00	0.24	0.35
Stars in THF ^a	0.00	2.43	1.34	3.52	0.59
Total	19.99	20.16	11.33	9.65	9.84
Internal Aqueous Phase (wt%)					
Water	71.93	77.90	87.58	89.85	89.41
KPS	0.54	0.44	0.25	0.00	0.00
K ₂ SO ₄	1.74	1.50	0.84	0.50	0.75
Stars in water ^a	5.80	0.00	0.00	0.00	0.00
Total	80.01	79.84	88.67	90.35	90.16

^aStars are PEO-PBA-poly(DVB) dispersed in water ($M_{n,PBA} = 7800$, $M_{n,PEO} = 5200$, $M_{w,RI} = 89,000$) or THF ($M_{n,PBA} = 6500$, $M_{n,PEO} = 5200$, $M_{w,RI} = 83,000$)

Table 6.3.5.2. A18 with DVB or POSS8 cross-linker HIPE Recipes

Sample	DVB, wt %		POSS-8, wt %	
	Total	Phase	Total	Phase
External organic phase				
A18	12.20	71.21	11.52	66.47
Stars in THF ^a	4.70	27.44	4.69	27.07
BPO	0.23	1.34	0.49	2.84
POSS-8	0.00	0.00	0.63	3.62
Total	17.14	100.00	17.33	100.00
Internal aqueous phase				
Water	78.67	99.44	82.21	99.44
K ₂ SO ₄	0.44	0.56	0.46	0.56
Total	82.86	100.00	82.67	100.00

^aStars are PEO-PBA-poly(DVB) dispersed in THF ($M_{n,PBA} = 6500$, $M_{n,PEO} = 5200$, $M_{w,RI} = 83,000$)

6.3.6 Characterization

Apparent molecular weight and dispersity were measured by GPC (Polymer Standards Services (PSS) columns (guard, 10^5 , 10^3 , and 10^2 Å), with THF eluent at 35 °C, flow rate 1.00 mL/min, and differential refractive index (RI) detector (Waters, 2410)). Toluene was used as the internal standard to correct for any fluctuation of the THF flow rate. The apparent molecular weights and dispersity were determined with a calibration based on linear polystyrene standards using WinGPC 6.0 software from PSS. The detectors employed to measure the absolute molecular weights were a triple-detector system containing a RI detector (Wyatt Technology, Optilab REX), a viscometer detector (Wyatt Technology, ViscoStar), and a multi-angle laser light scattering (MALLS) detector (Wyatt Technology, DAWN EOS) with the light wavelength at 690 nm. Absolute molecular weights were determined using ASTRA software from Wyatt Technology. The average hydrodynamic diameter of star polymers (D_n) was measured by dynamic light scattering (DLS) on a high performance zeta-sizer from Malvern

Instruments, Ltd. Diluted emulsion droplets were imaged with an inverted bright-field microscope (Leica DMI 6000) at 40 $\times$ magnification. Interfacial tensions of star polymers at the xylene/water interface were measured by the DuNouy ring method.

The density of the polyHIPE was determined using gravimetric analysis. The polymerization yield was based on the polyHIPE mass following drying. The porous structure was characterized using low-vacuum scanning electron microscopy (SEM) of uncoated cryogenic fracture surfaces (FEI Quanta 200, 20 kV). The average polyHIPE void sizes were calculated from the SEM micrographs using a correction for the statistical nature of the cross-section. The shape memory behavior⁴⁷ was evaluated using four cycles of the thermo-mechanical deformation and recovery program with polyHIPE cubes of 1 cm x 1 cm x 1 cm. The cubes were heated to 70 °C in a small oven that encompassed the compression fixture of a tensile testing machine (Instron 3345), left for 1 h, and compressed to 70% deformation. The cubes were cooled to RT in the compression fixture and remained there for 1 h. The unstressed height at RT was measured. The shape fixity ratio was calculated using eq. 1 where F_R is the shape fixity ratio for each cycle, z_i is the initial cube height, z_d is the desired sample height applied via deformation at an elevated temperature, and z_u is the sample height after cooling to RT and the removal of the applied stress. The compressed cubes were heated at 1 °C/min to 80 °C (DMTA IV, Rheometric Scientific). The cube height was measured as a function of temperature, T , using a minimal imposed compressive stress of 50 kPa to maintain contact of the fixture with the sample. The shape recovery ratio was calculated using eq 2. where $R_R(T)$ is the recovery ratio as a function of temperature during each cycle's recovery stage, $z(T)$ is the variation of cube height with temperature, $\epsilon(T)$ is the variation

of strain with temperature, and ε_0 is the initial strain (before recovery) at the imposed sample height z_d .

$$F_R = \frac{z_i - z_u}{z_i - z_d} \quad \text{eq. 1.}$$

$$R_r(T) = \frac{z(T) - z_d}{z_i - z_d} = \frac{\varepsilon_0 - \varepsilon(T)}{\varepsilon_0} \quad \text{eq. 2}$$

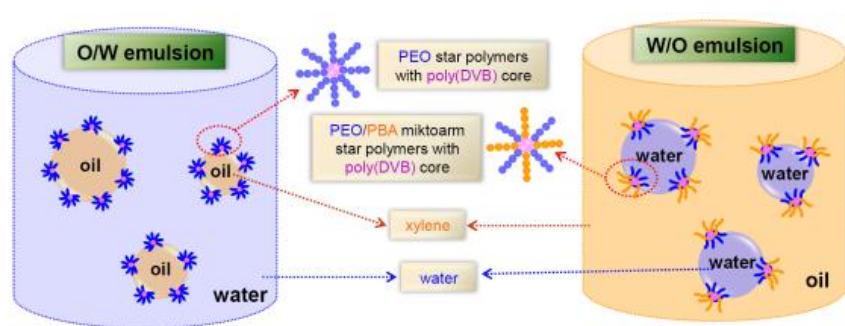
6.4 Results and Discussion

As discussed in the introduction, when star-shaped polymers are used as emulsifiers, one can control the type of emulsion formed by tuning the composition of the star polymer. More hydrophilic star polymers favor the formation of (O/W) emulsions, while star polymers containing a larger fraction of hydrophobic units would lead to the formation of a W/O emulsion.³⁴ Nevertheless, the long-term stability of the generated emulsion was not evaluated in the prior work that established these principles, and a relatively high concentration of star surfactant, 1 wt%, was used.³⁴

The effect of star polymer composition and size/compactness of the star on the preferred emulsion type and the emulsifying efficiency, including star loading and long-term stability, were explored. Two classes of star polymers were prepared and used as emulsifiers: PEO–poly(DVB) homo-arm star polymers and PEO–PBA–poly(DVB) miktoarm star polymers (Scheme 6.4). The use of PEO–poly(DVB) homo-arm star polymers led to the formation of an O/W emulsion, because the hydrophilic PEO arms resulted in better affinity of the star polymers to the aqueous phase. In contrast, the introduction of a certain percentage of hydrophobic PBA arms to the star structure

significantly reduced the affinity of the star polymers to water. These star polymers formed stable W/O emulsions, because the star's increased hydrophobicity increased its affinity to xylene. It was previously reported that a stable emulsion could be formed with the concentration of a star surfactant as low as 0.02 wt % vs aqueous phase.³⁵ The lowest level of star polymer-based surfactants that would generate either an O/W or W/O emulsion with long-term stability was investigated.

Scheme 6.4. PEO star polymers as stabilizers for O/W or W/O emulsions



6.4.1 PEO–Poly(DVB) Homo-arm Star Polymers as Stabilizers for O/W Emulsions

A series of star polymers with PEO arms and a cross-linked hydrophobic poly(DVB) core were synthesized through the cross-linking of either PEO MM or PEO MI arm precursors via the “arm-first” method by ATRP. Polymerization conditions and results are summarized in Table 6.4.1. The star polymers, samples S_D64, S_L35, and S_L30, have an average number of arms per star molecule ranging from 30 to 64 and different degrees of compactness. The ratio of absolute molecular weight determined by MALLS ($M_{w,MALLS}$) to apparent molecular weight determined by GPC ($M_{w,RI}$; using linear PS standards) correlates with the compactness of the star polymer structure. Higher ratios indicate a more compact star structure.²³ The PEO homo-arm star polymers have similar

hydrophile–lipophile balance (HLB) values and are expected to form an O/W emulsion when used as a surfactant.⁴⁸ These star polymers were then evaluated as stabilizers for generation of emulsions with a weight ratio of xylene and water set at 1/1. In all cases O/W emulsions, which were stable for ≥ 1 year, were obtained, although the amount of star polymers required for the generation of a stable emulsion and the formed emulsion phase fraction varied slightly for the different star polymer surfactants.

Table 6.4.1. PEO Star Polymers as Stabilizers for Xylene-in-Water Emulsion

Star ^a	Arm	DVB core wt%	$M_{w,RI}$ ^b	$M_{w,MALLS}$ ^c	N_{arm} ^d	HLB Value	Surfactant amount ^e	$V_{emulsion}$ ^f	$V_{dispersed}$ ^g
S _D 64	PEO 2000	21%	49,300	176,000	64	16	0.5, 0.25, 0.1 or 0.05 wt%	64%	84%
							0.01 wt%	46%	80%
							0.005 wt%	Not stable	n/a
S _L 35	PEO 2000	28%	39,700	99,800	35	14	0.5 wt%	75%	72%
							0.25, 0.1 or 0.05 wt%	71%	76%
							0.01 or 0.005 wt%	Not stable	n/a
S _L 30	PEO 2000	22%	35,900	82,900	30	16	0.5 wt%	75%	72%
							0.25 or 0.1 wt%	71%	76%
							0.05, 0.01 or 0.005 wt%	Not stable	n/a

^aSL or DX; D represents dense star, L represents loose star, and X is the average arm number per star. PEO arms have an average molecular weight around 2000. ^bWeight-average molecular weight of star polymers determined by THF GPC with RI detector, calibration with linear PS as standard. ^cWeight-average molecular weight of star polymers determined by THF GPC with MALLS detector. ^dAverage arm number per star polymer calculated according to the equations shown in a previous paper.²¹ ^eSurfactant amount was calculated based on the total weight of water and xylene used for the emulsion formation. ^fVolume fraction of emulsion phase as compared to total volume of emulsion plus neat water phase. ^gVolume fraction of the dispersed phase in the emulsion phase itself.

Using PEO–poly(DVB) star polymers with a higher number of arms 64 (S_{D64}), and a more compact structure, $M_{w,MALLS}/M_{w,RI} = 3.57$,¹⁸ as stabilizer, a stable xylene-in-water emulsion was formed when the concentration of the star polymer was set at 0.01 wt % (vs. total water and xylene amount). This corresponds to an overall concentration of $\sim 5.26 \times 10^{-4}$ mM star polymer in the system. The formed emulsion phase occupied 46 vol % of the total mixture (Table 6.4.1 and Figure 6.4.1.1) with a neat water layer present at the bottom of the vial and a neat oil layer on top. The volume fraction of xylene droplets dispersed in the emulsion phase was 80 vol %, indicating that S_{D64} preferentially forms a HIPE. When the star concentration was increased to 0.05 wt %, the emulsion phase fraction increased to 64 vol %, and the emulsion phase contained a dispersed xylene volume fraction of 84 vol %. However, only a thin layer of emulsion phase was formed at the oil/water interface when the concentration of the star stabilizer was reduced to 0.005 wt %. A similar trend was observed when the other PEO star polymers with different numbers of PEO arms, S_{L35} and S_{L30} , were used as surfactants. A slight increase of the emulsion phase fraction was observed with an increase in the concentration of star stabilizer.



Figure 6.4.1.1. Images of O/W emulsions stabilized by different amounts of PEO star polymer, S_{D64} ; xylene in water (left) and cyclohexane in water (right)

The HLB value of a surfactant can indicate the capability of forming a certain preferred emulsion type, but it does not capture differences in the emulsifying efficiency of a surfactant. Despite having similar HLB values as S_D64 (HLB 16), when the S_L35 (HLB 14) and S_L30 (HLB 16) PEO homo-arm star polymers were used as stabilizers, the star polymer concentration required for the formation of a stable O/W emulsion was higher than that required for sample S_D64. For instance, 0.05 wt % of S_L35 PEO star polymers stabilizer was required to form a stable emulsion, compared to 0.01 wt% for S_D64 (Table 6.4.1). The different emulsification behavior reflects differences in the star polymer structure, namely star size and compactness, which are not captured by the HLB measurement. The S_L35 star polymer has a smaller size/hydrodynamic volume than S_D64, as indicated by the relatively lower apparent molecular weight. This may lead to less efficiently covering the emulsion droplets by S_L35, resulting in the need for a larger amount of star polymers for the generation of a stable emulsion. On the other hand, once a stable emulsion was generated, for the same amount of star polymer, such as 0.05 or 0.1 wt %, a higher volume fraction of emulsion phase was obtained when using the smaller, but less compact, S_L35 PEO star polymer, $M_{w,star,MALLS}/M_{w,star,RI} = 2.51$. A less compact structure has less densely packed PEO arms in the star, which may affect how the PEO star polymer adsorbs at the interface. Stars with a lower number of arms and less compact structure could result in exposure of the hydrophobic poly(DVB) core to the oil/water interface, which may improve the stabilization effectiveness of the adsorbed layers produced at higher star polymer concentrations. There is precedence for the emulsifying behavior, as similar behavior was exhibited by polymer-grafted silica nanoparticles that were prepared with varying polymer grafting densities.⁴⁹ This explanation was also

supported by the results obtained using the S_L30 star polymer with an even lower number of arms, 30, and a less compact structure, $M_{w,star,MALLS}/M_{w,star,RI} = 2.31$, as a stabilizer. In this case, an even higher concentration of the star surfactant, 0.1 wt %, was required for the formation of a stable emulsion, but a larger fraction of emulsion phase was still obtained compared to the S_D64-stabilized emulsion.

An optical microscope was utilized to image the emulsion droplets, after dilution, to check the droplet size in emulsions stabilized by S_D64. As shown in Figure 6.4.1.2, emulsion droplets with a broad distribution of size were formed. However, a clear decrease in average droplet diameter from ~50 to ~15 μm , was observed when the concentration of the star surfactant was increased from 0.01 to 0.1 wt %. The star polymer concentration at 0.01 wt% was not sufficient to stabilize the larger surface area of the smaller droplets. The droplet size did not change significantly when the star polymer concentration was further increased. This indicated that the emulsion generation method, the vortex mixer, did not provide sufficient power to break the stabilized dispersed droplets to an even smaller size.

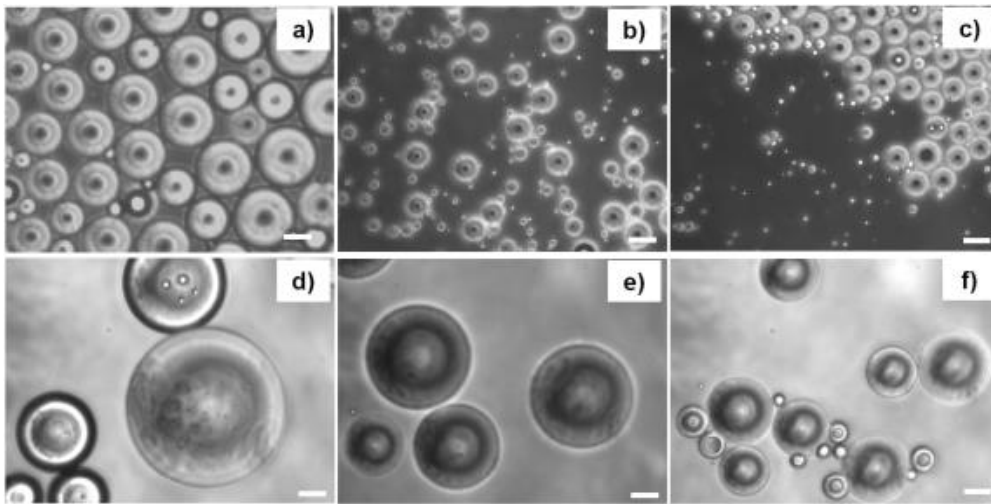


Figure 6.4.1.2. Micrographs at 40× magnification of diluted oil-in-water emulsions formed using the PEO star polymer S_D64 as stabilizer: (a–c) xylene in water (star polymer amount: (a) 0.01, (b) 0.1, and (c) 0.5 wt %); (d–f) cyclohexane in water (star polymer amount: (c) 0.01, (d) 0.1, and (e) 0.5 wt %). Scale bar 50 μm

Stable cyclohexane-in-water emulsions were also prepared using PEO–poly(DVB) S_D64 star polymers as stabilizers (Figure 6.4.1.1). The weight ratio of cyclohexane and water was also set at 1/1. Similar to the xylene-in-water emulsion, low concentrations of the PEO star polymers, 0.01 wt %, were used to generate a stable emulsion. However, emulsion droplets with much larger size were formed when cyclohexane was used as the dispersed phase with the same amount of star polymer stabilizers (Figure 6.4.1.2) compared to the xylene case. Even when the star concentration was set at 0.5 wt %, the majority of the emulsion droplets have a diameter ~100 μm. This was attributed to the different solubility of the PEO star polymers in xylene and cyclohexane. The PEO star polymers are soluble in both xylene and water. Thus, they were efficiently anchored at the xylene/water interface, resulting in the formation of small emulsion droplets. The PEO star polymers may adopt conformations at the cyclohexane/water interface that are less favorable for stabilizing emulsion droplets against coalescence and were thereby unable to stabilize smaller droplets with a higher surface area. With required HLB values for dispersing xylene and cyclohexane of 14 and 15, respectively, both are nearly indistinguishable in the measured HLB values.⁵⁰ The differences in emulsion performance for the same star polymer with two oils highlight the importance of polymer solubility in the oil phase for polymeric emulsifiers.

6.4.2 PEO–PBA–Poly(DVB) Mikto-arm Star Polymers as Stabilizers for Water-in-Xylene Emulsions

PEO homo-arm star polymers are amphiphilic, due to their hydrophilic PEO arms and cross-linked hydrophobic poly(DVB) core. However, the hydrophobic DVB core is buried within the shell of the star polymers and may not be easily accessible to the environment. Therefore, any changes in star compositions or DVB core fraction of the PEO homo-arm stars (Table 6.4.1), had relatively modest effects on the emulsifying performance of these polymers.

In order to more efficiently change the amphiphilicity of the star polymers, or their affinity for different phases of an emulsion system, a series of PEO–PBA–poly(DVB) mikto-arm star polymers were prepared. The “arm-first” method was used to prepare these stars using a mixture of PEO MI and a certain percentage of hydrophobic PBA MI as arm precursors.²¹ ¹H NMR and gradient polymer elution chromatography (GPEC) analysis previously demonstrated that the composition of the mikto-arm stars prepared by ATRP using the “arm-first” method with PBA and PEO macroinitiators corresponds to the initial molar ratios of macroinitiators.²¹ The compositions and molecular weight/arm number of three PEO–PBA–poly(DVB) star polymers are summarized in Table 6.4.2. They have HLB values ranging from 6 to 12, depending on the fraction of PEO arms. An HLB of 6 falls near the upper limit where conventional surfactants are expected to stabilize W/O.⁴⁸ HLB values of 8–16 are the range normally associated with the capability to emulsify O/W, rather than W/O, emulsions.⁴⁸ A turbid and milky solution was obtained when these star polymers were dispersed in water. As expected, the solubility of the mikto-arm star polymers in water was progressively

improved by increasing the ratio of PEO to PBA arms in the star polymer. The introduction of accessible hydrophobic components (PBA arms) to the “surface” of the star polymer, reduces their solubility in water and alters their adsorption behaviors and performance for emulsification.

When PEO–PBA–poly(DVB) mikto-arm star polymers were used as stabilizers for a water/xylene emulsion, a W/O emulsion was expected to form when a sufficient degree of PBA was incorporated into the star polymer. This expectation was based on the affinity of the PBA arms for the oil phase increasing and its affinity for the aqueous phase decreasing with the incorporation of PBA into the star polymer.

Table 6.4.2. PEO–PBA–Poly(DVB) Mikto-arm Star Polymers as Stabilizers for Water-in-Xylene Emulsions

Star ^a	[PEO] ₀ /[PBA] ₀ ^b	DVB core wt%	$M_{w,RI}$ ^c	$M_{w,MALLS}$ ^d	N_{arm} ^e	HLB Value	Surfactant amount ^f	$V_{emulsion}$ ^g	$V_{dispersed}$ ^h
MS _{PBA50}	5/5	22%	8.87×10^4	3.2×10^5	39	6	0.5 or 0.25 wt%	67%	69%
							0.1, 0.05, 0.01 or 0.005 wt%	58%	80%
							0.5 wt%	60%	77%
MS _{PBA30}	7/3	26%	9.35×10^4	3.9×10^5	49	9	0.25, 0.1, 0.05, or 0.01 wt%	55%	84%
							0.005 wt%	51%	91%
							0.5, 0.25, 0.1 or 0.05 wt%	58%	80%
MS _{PBA10}	9/1	30%	9.01×10^4	4.2×10^5	54	12	0.01 or 0.005 wt%	52%	89%

^aMS_{PBAX}; X represents the initial molar fraction of PBA MI in arm precursors. ^bThe initial molar ratio of PEO and PBA arm precursors for star polymer preparation, PEO MI, M_n = 5200, PBA MI, M_n = 7800, and M_w/M_n = 1.10. ^cWeight-average molecular weight of star polymers determined by THF GPC with RI detector, calibration with linear PS as standard. ^dWeight-average molecular weight of star polymers determined by THF GPC with MALLS detector. ^eAverage arm number per star polymer calculated according to the equations shown in a previous paper.²¹ ^fSurfactant amount was calculated based on the total weight of water and xylene used for the emulsion formation. ^gVolume fraction of emulsion phase as compared to total volume of emulsion plus neat xylene phase. ^hVolume fraction of the dispersed phase in the emulsion phase itself.

Water-in-xylene emulsions, with the initial weight ratio of xylene and water set at 1/1, were successfully prepared using all three of the PEO–PBA–poly(DVB) mikto-arm star polymers with concentrations as low as 0.005 wt % (vs total weight of water and xylene; Table 6.4.2). This corresponded to a concentration of $\sim 1.4 \times 10^{-4}$ mM star polymer in the system. A neat xylene layer could be observed on top of the emulsion (Figure 6.4.2.1). The formed emulsions were stable for ≥ 1 year. Adjusting the ratio between the PEO and PBA arms did not influence the generated emulsion type or the stability, but the volume fraction of emulsion phase varied slightly with different star polymers. When PEO–PBA–poly(DVB) mikto-arm star polymers containing 50% PEO arms were employed as the stabilizer (MS_{PBA50} in Table 6.4.2), $\sim 58\%$ emulsion phase was formed with 0.005 wt% star polymer surfactant. Increasing the amount of the star polymer surfactant to 0.25 wt% increased the emulsion phase fraction to $\sim 67\%$. While in the case of using star polymers containing 70% PEO arms (MS_{PBA30} in Table 6.4.2), 55 vol% emulsion phase was found when using 0.005–0.25 wt% star polymer stabilizer. This result may be caused by the improved solubility of the star polymers in water. The

different packing/adsorption of mikto-arm star polymers at the interface would affect the formation of the emulsion. Further increase of PEO percentage to 90%, sample MS_{PBA10}, did not significantly affect the emulsification performance. Only a slightly lower fraction of emulsion phase was obtained with the same amount of MS_{PBA10}, as compared to the emulsions formed by using MS_{PBA50} or MS_{PBA30} as stabilizers. This observation was attributed to the migration of a portion of MS_{PBA10} to the aqueous phase, resulting in a less efficient stabilization. Moreover, the fraction of xylene and water in the formed emulsion phase, using 0.005 wt% of MS_{PBA50} star polymer as surfactant, was calculated to be ~20 vol% of xylene and ~80 vol% of water, respectively. Thus, MS_{PBA50} tends to favor HIPE formation, which is similar to S_D64. Stable water-in-oil emulsions were obtained from all three of the mikto-arm star polymers, even though only one of them had an HLB value close to the range normally associated with formation of W/O emulsions. This is a further indication that the conventional HLB scale, originally developed for less complex surfactant structures, is insufficient for predicting the effects of varying the structure and composition of star polymer emulsifiers.

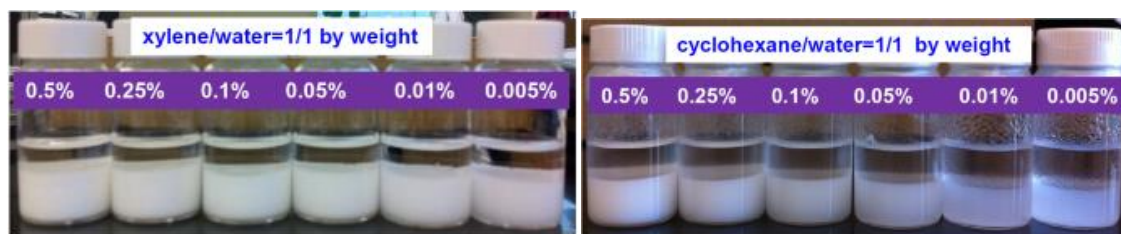


Figure 6.4.2.1. Images of water-in-xylene (left) and water-in-cyclohexane (right) emulsions stabilized by different amount of PEO–PBA–poly(DVB) miktoarm star polymers (MS_{PBA50})

When the star polymers were dispersed in the xylene phase before emulsion generation, water-in-oil emulsions with a similar fraction of emulsion phase were obtained, as when star polymers were dispersed in the aqueous phase before emulsion generation. The PEO-PBA-poly(DVB) mikto-arm star polymers were sufficiently mobile, as they could easily migrate to the xylene/water interfaces to stabilize the dispersed water droplets. This occurred even when they were originally dispersed in the phase (aqueous) that would become the discontinuous phase of the emulsion.

The droplet sizes in the diluted water-in-xylene emulsions were determined using an optical microscope. Similar to the xylene-in-water emulsions formed with PEO homo-arm star polymers, a decrease in the size of the water droplets, from ~ 100 to ~ 10 μm , was clearly observed when the concentration of MS_{PBA50} was increased from 0.005 to 0.1 wt % (Figure 6.4.2.2). Increasing the amount of available star polymers typically allows for the stabilization of droplets with larger surface areas, associated with the formation of smaller droplets. However, the droplet size did not change significantly when MS_{PBA50} concentration was further increased from 0.1 to 0.5 wt %. A sample was carefully taken from the neat xylene layer on top of the emulsion formed by using 0.5 wt % MS_{PBA50} and analyzed by DLS. Star polymers with diameter ~ 10 nm were found in the xylene solution. The pure mikto-arm star polymer MS_{PBA50} showed an average diameter of ~ 12 nm in xylene. Particles of this size were rarely detected in the top xylene layer on emulsions formed using 0.005 wt % of MS_{PBA50} . It is possible that the water/oil interface was saturated by MS_{PBA50} when larger amounts were used for the emulsion generation using a vortex mixer and a fraction of the stars were not utilized for emulsion stabilization allowing some free star polymers to be detected in the continuous oil phase.

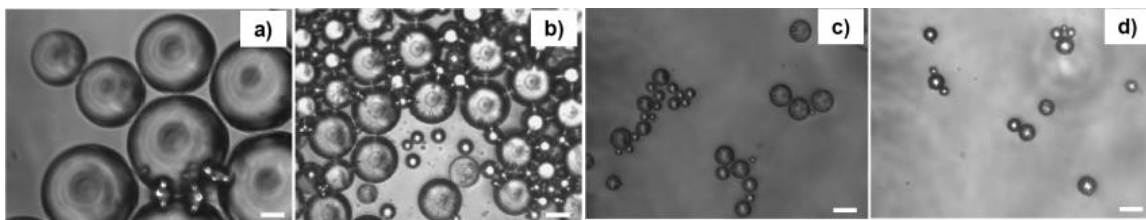


Figure 6.4.2.2. Micrographs at 40 $\times$ magnification of diluted water in xylene emulsion formed by using PEO–PBA–poly(DVB) miktoarm star polymers (MS_{PBA50}) as stabilizer, star polymer amount: (a) 0.005, (b) 0.01, (c) 0.1, and (d) 0.5 wt %. Scale bar 50 μ m.

It is well known that the emulsion droplet size can be tuned, not only by changing surfactant concentration, but also by changing the emulsion generation technique. Thus, these free star polymers could be used for stabilization of even smaller emulsion droplets formed in a higher shear environment. In a separate experiment, ultrasonication was used for the generation of emulsions containing smaller droplets. A Misonix sonicator S-4000 amplitude set at 70%, sonication for 30 s in ice/water bath was used to generate the emulsion. Similar to generation of emulsions with vortex mixing, phase separation occurred with a neat xylene layer appearing on top of emulsions within a couple of hours after sonication. However, smaller emulsion droplets were obtained from ultrasonication. With 0.5 wt % of MS_{PBA50} , the formed emulsion droplets showed an average diameter of ~ 1.6 μ m, as determined by DLS analysis. This value increased to ~ 5.2 μ m, when 0.1 wt % of MS_{PBA50} was used. These emulsions were stable for over 2 weeks. Meanwhile, when the star concentration was further decreased to 0.01 wt %, larger droplets were formed. They had a size ~ 20 μ m after sonication, but the formed emulsion was not stable and, as expected, much larger droplets started to form after 1 day, due to the limited

amount of star polymer available to fully cover and stabilize the smaller droplets' larger surface area.

Cyclohexane was also used as continuous phase for the generation of W/O emulsions with PEO-PBA-poly-(DVB) mikto-arm star polymers as stabilizers. However, in this case, a much higher concentration of star polymer, 0.05 wt %, was used for the generation of a stable emulsion (Figure 6.4.2.1). As was the case with PEO homo-arm stars, the insolubility of PEO and PBA in cyclohexane affected the star adsorption at the oil/water interface and forced them into a configuration that was less favorable for emulsion stabilization. The emulsion droplets observed in the optical microscope further supported this conclusion. Although stable emulsions were formed when a higher concentration of the MS_{PBA50} , >0.05 wt %, was used, the generated emulsion droplets were up to 1 mm in size, even when 0.5 wt % of MS_{PBA50} was added. This was attributed to the relatively less effective stabilization of the interface by star surfactants with a collapsed morphology.

6.4.3 Interfacial Tensions

Star polymers of both the PEO homo-arm type (S_{D64} , S_{L35} , S_{L30}) and the PEO/PBA miktoarm type (MS_{PBA50} , MS_{PBA30} , MS_{PBA10}) demonstrated excellent interfacial tension lowering behavior at the xylene/water interface (Table 6.4.3). This was consistent with the interfacial tension lowering behavior of other nanoparticle brush systems.⁴⁹ The most effective interfacial tension lowering PEO homo-arm star polymer was S_{L30} , which decreased the xylene/water interfacial tension from the clean interface value of 36.6 mN/m to just 2.1 mN/m at a concentration of 0.1 wt %. This was a

substantially greater decrease in the interfacial tension than the values achieved by the other two PEO homo-arm star polymers. Despite the fact that all three PEO homo-arm stars had similar HLB values, S_L30 stands out as being the least compact of the PEO homo-arm star polymers. A greater exposure of the hydrophobic poly(DVB) core in this structure was probably responsible for the superior interfacial tension lowering performance. Nevertheless, S_D64 was the most efficient emulsifier of the three PEO homo-arm stars indicating that lowering interfacial tension alone cannot predict emulsifying efficiency.

All three PEO–PBA mikto-arm star polymers decreased the xylene/water interfacial tension to low values, 2.1–3.4 mN/m, at a 0.1 wt % concentration. The main distinction between the three star samples was the ability of MS_{PBA50} to produce this level of interfacial tension lowering at a lower bulk concentration of 0.01 wt %. This was the least compact, or had the lowest number of arms, of the three PEO–PBA mikto-arm star polymers. The correlation of more effective lowering of interfacial tension with decreasing compactness mirrors the PEO homo-arm results.

Table 6.4.3. Xylene/Water Interfacial Tensions (mN/m) for 0.01 and 0.1 wt % Star Polymer Solutions at RT^a

Star/amount	S _D 64	S _L 35	S _L 30	MS _{PBA50}	MS _{PBA30}	MS _{PBA10}
0.01 wt%	15.5	10.8	4.0	3.8	26.7	16.1
0.1wt%	12.8	10.1	2.1	2.1	4.4	3.4

^aUncertainty is ±0.1 mN/m. The pure xylene/water interfacial tension is 36.6 mN/m.

6.4.4 Generation of Water-in-Styrene/DVB HIPEs with PEO-PBA-Poly(DVB)

Miktoarm Star Polymers and Polymerization to Form PolyHIPEs

PEO-PBA-Poly(DVB) miktoarm star polymers with 50% PEO arms, MS_{PBA50} , showed excellent, and long term, stabilization properties for water-in-xylene emulsions at loadings as low as 0.005 wt%. In addition, MS_{PBA50} preferentially formed high internal phase emulsions (HIPEs) with $\sim 80\%$ water dispersed in $\sim 20\%$ xylene (by volume). Therefore, MS_{PBA50} was studied as a HIPE stabilizer to determine if the surfactant content could be dramatically reduced while still forming HIPEs that are stable throughout a polymerization to form coherent polyHIPEs.

Two batches of MS_{PBA50} were synthesized and one was dispersed in water and the other in THF, which is a better solvent for the PBA arms and the poly(DVB) core than water. Water dispersed MS_{PBA50} was added to the aqueous phase and THF dispersed MS_{PBA50} was added to the organic phase (Table 6.4.4). Initially star loadings between 0.1 and 0.3 wt% (vs total emulsion) were tested, to ensure a stable HIPE was formed (Samples 1-4; Table 6.4.4). Regardless of the phase in which the stars were initially dispersed in (aqueous phase Sample 1 vs organic phase Sample 2; Table 6.4.4), stable HIPEs were formed. Interfacial initiation, with KPS in the aqueous phase, was used to polymerize Samples 1 and 2. They exhibited a closed cell morphology (Figure 6.4.4.1 a and b), which indicates that MS_{PBA50} acts in a manner similar to silica particles, and forms a Pickering HIPE, rather than resembling block copolymer surfactants.⁵¹ Additional evidence that MS_{PBA50} formed a Pickering emulsion was confirmed from the polyHIPE void size, which is typically a direct replica of the droplet size.⁴⁰ The polyHIPE void sizes, and thus the HIPE droplet sizes, for all samples were in the range of

50 to 500 μm , which is typical for Pickering emulsions. Particle based surfactants cover smaller surface areas, leading to larger droplet sizes.³⁹ The internal aqueous phase was increased from 80 to 90 wt%, while keeping the MS_{PBA50} loading constant, in hopes of obtaining an open cell morphology (Sample 3; Table 6.4.4). However polyHIPE Sample 3 still exhibited a closed cell morphology, despite the increased internal phase content that should have forced closer packing of the droplets. Studies with silica particles have shown that the locus of initiation is crucial in Pickering HIPEs. External phase initiation should provide an open cell morphology with some openings in polyHIPEs derived from Pickering HIPEs.^{51,52} Therefore, MS_{PBA50} stabilized St/DVB polyHIPEs were initiated using BPO in the organic phase (Sample 3, Table 6.4.4) and the resulting polyHIPEs did exhibit an open cell morphology (Figure 6.4.4.2 a,b).

To determine the lowest amount of MS_{PBA50} needed to form a stable HIPE, the amount of star surfactant was decreased by a factor of 10 from 0.48 wt% (Sample 4, Table 6.4.4) to 0.04 wt% (vs. total emulsion; Sample 5; Table 6.4.4). A stable HIPE was formed and successfully polymerized to form a polyHIPE with an open cell morphology, due to organic phase initiation. The polyHIPE had a larger average void size ($\sim 200 \mu\text{m}$; Figure 6.4.4.2 c,d) than Sample 4, because the lower amount of stars cannot cover a larger surface area required to form smaller droplets. However, stable HIPE formation with only 0.04 wt% (vs. total emulsion) indicated that MS_{PBA50} was an extremely efficient surfactant for W/O HIPE, as it decreased the surfactant loading to $1/100^{\text{th}}$ of that used with conventional non-ionic surfactants, like Span-80.

Table 6.4.4. St/DVB HIPE Descriptions and PolyHIPE Densities

Sample	1	2	3	4	5
Internal Phase, %	~80	~80	~90	~90	~90
Initiator	KPS	KPS	KPS	BPO	BPO
Dispersion Medium	Water	THF	THF	THF	THF
Stars/Monomers, %	0.50	1.08	1.09	4.80	0.48
Stars/HIPE, %	0.10	0.19	0.11	0.28	0.04
Density, g/cc	0.096	0.077	0.059	0.055	0.060

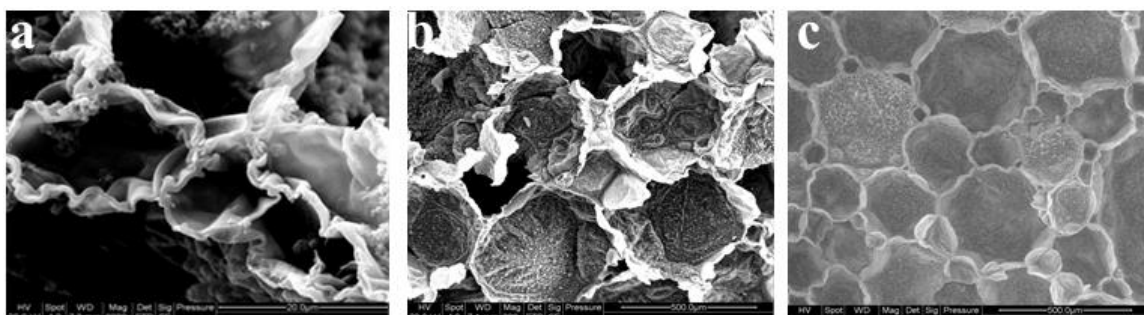


Figure 6.4.4.1. PS-PDVB polyHIPE samples 1 (a), 2 (b), and 3 (c) from MS_{PBA50} stabilized W/O HIPEs

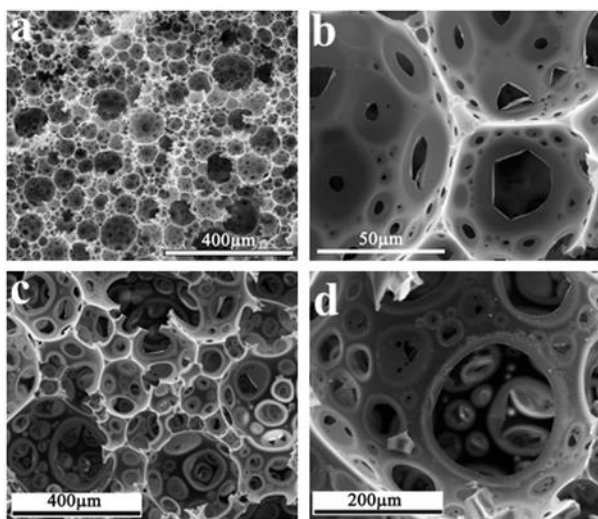


Figure 6.4.4.2. PS-PDVB polyHIPE samples 4 (a,b) and 5 (c,d) from MS_{PBA50} stabilized W/O HIPEs

To confirm that MS_{PBA50} could stabilize other W/O HIPE systems, they were used to stabilize HIPEs with an A18/DVB or A18/POSS-8 organic phase (Figure 6.4.4.3). A18 is an interesting monomer, because the octadecyl units can crystallize below their melting temperature and form shape-memory materials.⁴⁷ MS_{PBA50} efficiently stabilized A18/DVB HIPEs at 0.072 wt % (0.41 wt % of the organic phase) loading, as the HIPE was polymerized to form a polyHIPE. However PA18/PDVB polyHIPEs did not exhibit any shape memory properties. Thus, DVB was replaced by a POSS-8 cross-linker at a much lower loading of 0.63 wt % (vs. total emulsion), which corresponded to a A18:POSS-8 molar ratio of 80:1 (vinyl group ratio 10:1).⁴⁰ Typically monomer:DVB molar ratios are usually between 9:1 and 4:1 (vinyl group ratios between 4.5:1 and 2:1). MS_{PBA50}, at 0.072 wt% (vs. total emulsion), formed a stable A18. POSS-8 HIPE and polymerization with BPO yielded a polyHIPE with an open cell morphology with voids of 20 to 100 μm in size (Figure 6.4.4.4). The polyHIPE was deformed at 70 °C to 70% of its original size using a compressible fixture of a tensile machine and exhibited a shape fixity of 100% after cooling to room temperature. The original shape was recovered by slowly heating to 80 °C. The polyHIPE had 100% shape recovery, indicating that it is an excellent shape memory material.

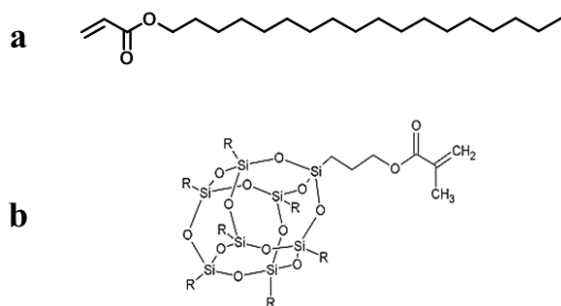


Figure 6.4.4.3. Structure of A18 (a) and POSS-8 (b)

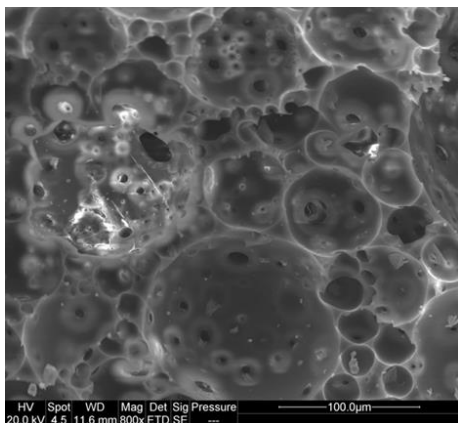


Figure 6.4.4.4. PA18/POSS-8 Shape Memory PolyHIPE

6.5 Conclusions

PEO-based star polymers, either PEO–poly(DVB) or PEO–PBA–poly(DVB) miktoarm star polymers, were prepared and utilized as stabilizers for generating emulsions with long-term stability (≥ 1 year) at extremely low concentrations, <0.01 wt %, corresponding to sub- μM concentrations. The more hydrophilic PEO–poly(DVB) star copolymer favored the formation of xylene-in-water emulsions, while the use of more hydrophobic PEO–PBA–poly(DVB) mikto-arm star polymers as stabilizers resulted in the formation of water-in-xylene emulsions. The high surface activity of the star polymers was confirmed by their ability to produce extremely low interfacial tensions in dilute solutions. In addition, both cyclohexane-in-water (using PEO homo-arm stars) and water-in-cyclohexane (using PEO–PVB mikto-arm stars) emulsions were successfully prepared using the PEO-based star polymer stabilizers. Emulsions with larger droplet size were formed in these cases where neither PEO nor PBA was soluble in the oil, unlike the situation with xylene where both PEO and PBA were soluble in the oil. Structural variations in the star polymers, especially the compactness of the structure, proved to

correlate better with reduction of interfacial tension and emulsifying efficiency than the conventional HLB system.

MS_{PBA50} formed stable W/O Pickering HIPEs at loadings as low as 0.04 wt% with a St/DVB organic phase. The use of star stabilizers for HIPEs can decrease the surfactant loading to 1/100th of the typical loading of common non-ionic surfactants, like Span-80. PolyHIPEs with a closed cell morphology were obtained from polymerization with interfacial initiation however polyHIPEs with an open cell morphology were obtained from polymerization with organic phase initiation. The dependence of polyHIPE morphology, along with large void sizes in the range of 50 to 500 μm , indicated that MS_{PBA50} stabilizes HIPEs in a similar way to silica particles, forming Pickering emulsions. MS_{PBA50} was able to stabilize A18/DVB or, more interestingly A18/POSS-8, and form polyHIPEs indicated that MS_{PBA50} was a useful surfactant for other W/O HIPE systems and could be used to synthesize other interesting polyHIPE materials. The PA18/POSS-8 polyHIPEs showed excellent shape memory behavior.

6.6 Acknowledgements

Financial support from NSF grant (DMR 09-69301 and CBET-0729967), the CRP Consortium at Carnegie Mellon University, and the United States–Israel Binational Science Foundation is appreciated. Dr. Michael S. Silverstein and Lital Rabinovitch are thanked for their extensive help with the studies on star stabilization of HIPEs and polyHIPEs.

6.7 References

- (1) Garnier, S.; Laschewsky, A.; Storsberg, J. *Tenside Surfactants Detergents* **2006**, 43, 88.
- (2) Matyjaszewski, K.; Xia, J. *Chemical Reviews* **2001**, 101, 2921–2990.
- (3) Braunecker, W. A.; Matyjaszewski, K. *Progress in Polymer Science* **2007**, 32, 93.
- (4) Tsarevsky, N. V.; Matyjaszewski, K. *Chemical Reviews* **2007**, 107, 2270–2299.
- (5) di Lena, F.; Matyjaszewski, K. *Progress in Polymer Science* **2010**, 35, 959.
- (6) Wang, J.-S.; Matyjaszewski, K. *Journal of the American Chemical Society* **1995**, 117, 5614.
- (7) Matyjaszewski, K.; Tsarevsky, N. V. *Nature chemistry* **2009**, 1, 276.
- (8) Matyjaszewski, K. *Israel Journal of Chemistry* **2012**, 52, 206.
- (9) Matyjaszewski, K. *Macromolecules* **2012**, 45, 4015.
- (10) Oh, J. K.; Drumright, R.; Siegwart, D. J.; Matyjaszewski, K. *Progress in Polymer Science* **2008**, 33, 448.
- (11) Sheiko, S. S.; Sumerlin, B. S.; Matyjaszewski, K. *Progress in Polymer Science* **2008**, 33, 759.
- (12) Lee, H.-i.; Pietrasik, J.; Sheiko, S. S.; Matyjaszewski, K. *Progress in Polymer Science* **2010**, 35, 24.
- (13) Hadjichristidis, N. *Journal of Polymer Science Part A: Polymer Chemistry* **1999**, 37, 857.
- (14) Hadjichristidis, N.; Pitsikalis, M.; Pispas, S.; Iatrou, H. *Chemical Reviews* **2001**, 101, 3747–3792.
- (15) Blencowe, A.; Tan, J. F.; Goh, T. K.; Qiao, G. G. *Polymer* **2009**, 50, 5.
- (16) Ooya, T. *Journal of Controlled Release* **2003**, 93, 121.
- (17) Wang, F.; Bronich, T. K.; Kabanov, A. V.; Rauh, R. D.; Roovers, J. *Bioconjugate Chemistry* **2005**, 16, 397–405.
- (18) Gao, H.; Matyjaszewski, K. *Macromolecules* **2006**, 39, 3154.
- (19) Gao, H.; Matyjaszewski, K. *Macromolecules* **2006**, 39, 7216.
- (20) Whittaker, M. R.; Urbani, C. N.; Monteiro, M. J. *Journal of the American Chemical Society* **2006**, 128, 11360.
- (21) Gao, H.; Matyjaszewski, K. *Journal of the American Chemical Society* **2007**, 129, 11828.
- (22) Gao, H.; Matyjaszewski, K. *Macromolecules* **2007**, 40, 399.
- (23) Gao, H.; Matyjaszewski, K. *Progress in Polymer Science* **2009**, 34, 317.
- (24) Zhu, W.; Nese, A.; Matyjaszewski, K. *Journal of Polymer Science Part A: Polymer Chemistry* **2011**, 49, 1942.
- (25) Zhu, W.; Zhong, M.; Li, W.; Dong, H.; Matyjaszewski, K. *Macromolecules* **2011**, 44, 1920.
- (26) Min, K.; Matyjaszewski, K. *Open Chemistry* **2009**, 7.
- (27) Jérôme, R.; Teyssié, P. *Colloid & Polymer Science* **1979**, 257, 1294.
- (28) Jérôme, R.; Teyssié, P. *Journal of Polymer Science: Polymer Physics Edition* **1980**, 18, 2391.
- (29) Jérôme, R.; Teyssié, P. *Journal of Polymer Science: Polymer Chemistry Edition* **1980**, 18, 3483.
- (30) Jérôme, R.; Teyssié, P. *Journal of Applied Polymer Science* **1981**, 26, 343.

- (31) Burguiere, C.; Pascual, S.; Bui, C.; Vairon, J.-P.; Charleux, B. *Macromolecules* **2001**, *34*, 4439.
- (32) Kukula, H.; Schlaad, H.; Tauer, K. *Macromolecules* **2002**, *35*, 2538.
- (33) Jin, R.-H. *Journal of Materials Chemistry* **2004**, *14*, 320.
- (34) Hadjiyannakou, S. C.; Triftaridou, A. I.; Patrickios, C. S. *Polymer* **2005**, *46*, 2433.
- (35) Qiu, Q.; Liu, G.; An, Z. *Chemical communications* **2011**, *47*, 12685.
- (36) Kimmins, S. D.; Cameron, N. R. *Advanced Functional Materials* **2011**, *21*, 211.
- (37) Pulko, I.; Krajnc, P. *Macromolecular Rapid Communications* **2012**, *33*, 1731.
- (38) Silverstein, M. S. *Polymer* **2014**, *55*, 304.
- (39) Silverstein, M. S. *Progress in Polymer Science* **2014**, *39*, 199.
- (40) Silverstein, M. S.; Cameron, N. R. In *Encyclopedia of Polymer Science and Technology*; Wiley: Hoboken, NJ, 2010.
- (41) Xu, F.; Fang, Z.; Yang, D.; Gao, Y.; Li, H.; Chen, D. *ACS Applied Materials & Interfaces* **2014**, *6*, 6717.
- (42) Yi, F.; Xu, F.; Gao, Y.; Li, H.; Chen, D. *RSC Advances* **2015**, *5*, 40227.
- (43) Chen, Q.; Cao, X.; Liu, H.; Zhou, W.; Qin, L.; An, Z. *Polymer Chemistry* **2013**, *4*, 4092.
- (44) Chen, Q.; Deng, X.; An, Z. *Macromolecular Rapid Communications* **2014**, *35*, 1148.
- (45) Chen, Q.; Xu, Y.; Cao, X.; Qin, L.; An, Z. *Polym. Chem.* **2014**, *5*, 175.
- (46) Xia, J.; Matyjaszewski, K. *Macromolecules* **1999**, *32*, 2434.
- (47) Gurevitch, I.; Silverstein, M. S. *Soft Matter* **2012**, *8*, 10378.
- (48) Griffin, W. C. *Journal of the Society of Cosmetic Chemists* **1949**, *1*, 311.
- (49) Saigal, T.; Dong, H.; Matyjaszewski, K.; Tilton, R. D. *Langmuir : the ACS journal of surfaces and colloids* **2010**, *26*, 15200.
- (50) Marshall, L.; Marcel Dekker: New York, 1987.
- (51) Gurevitch, I.; Silverstein, M. S. *Macromolecules* **2011**, *44*, 3398.
- (52) Gurevitch, I.; Silverstein, M. S. *Journal of Polymer Science Part A: Polymer Chemistry* **2010**, *48*, 1516.

Chapter 7

Reactive Star Surfactants Designed to Stabilize HIPEs and Incorporate into PolyHIPEs

7.1 Preface

This chapter describes the synthesis of reactive mikto-arm star surfactants and their use as stabilizers for high internal phase emulsion (HIPE). PEO-P(BA-*co*-HEA)-poly(DVB) stars were functionalized with alkyl halide ATRP initiators or with methacrylate moieties. The functional stars were incorporated into the final polymer network during polymerization of the reactive star stabilized HIPE.

I developed conditions to synthesize both the reactive mikto-arm stars from PEO-P(BA-*co*-HEA)-poly(DVB) stars that I had also synthesized and characterized via GPC and DLS. I also formulated stable HIPEs with both types of stars and developed polymerization conditions to form polyHIPEs that incorporated both types of stars into the formed copolymers. The polyHIPE yield and the density of the polyHIPEs were determined, and degradation experiments were carried out on degradable polyHIPEs

synthesized by ATRP. Dr. Joseph Suhan helped me obtain the SEM images of the polyHIPEs.

7.2 Introduction

As discussed in Chapters 1 and 5, high internal phase emulsions (HIPEs) generally require a large amount of surfactant (up to 30% of the external phase), such as sorbitan monooleate (Span-80) to form a stable HIPE.¹⁻⁴ In Chapter 6 PEO-PBA-Poly(DVB) mikto-arm stars, with 50% PEO arms (MS_{PBA50}), were shown to be efficient stabilizers for HIPEs. The core-shell microstructure of a star polymer allows for proactive tuning of the composition of the arm and core, or introduction of multiple functionalities on the periphery of the star to tune its ability to stabilize water-in-oil (W/O) or oil-in-water (O/W) HIPEs or impart other utility.⁵⁻⁸ For instance, core cross-linked stars made with pH, temperature, or salt responsive arms have been used to stabilize HIPEs that can be easily demulsified upon application of the response trigger.⁹⁻¹¹

HIPE stabilizers are generally entrapped within the polyHIPE wall and, if they are not removed, can impart additional functionality to the polyHIPE. One interesting use for HIPE stabilizers is as a catalyst, either alone or complexed with a metal. In one example, polyethylenimine@polystyrene (PEI@PS) dendrites were used to stabilize water-in-styrene/divinylbenzene (St/DVB) HIPEs.¹² After polymerization, the PEI@PS was entrapped within the polyHIPE wall and the polyHIPE could be used to efficiently remove organic pollutants from water. In a similar example, PEI@PS dendrites were used to complex gold nanoparticles and stabilize water-in-St/DVB HIPEs.¹³ The gold nanoparticle/PEI@PS complex remained in the polyHIPE wall and was able to

effectively reduce 4-nitrophenol to 4-aminophenol over 7 catalytic cycles.

Comparatively, polyethyleneimine@poly(styrene-co-2-ethylhexyl acrylate) (PEI@P(St-EHA)) was used to complex Pt nanoparticles, incorporate them into the wall of a PS/poly(DVB) polyHIPE, and effectively reduce 4-nitrophenol to 4-aminophenol during 20 cycles.¹⁴ Pt nanoparticles were also imbedded into PS/poly(DVB) polyHIPE support via interaction with the poly(4-vinyl pyridine) (P4VP) head group of the single chain nanoparticle HIPE stabilizers.¹⁵ Suzuki–Miyaura carbon–carbon coupling was performed with the Pt-imbedded polyHIPE catalyst to form biphenyl in high yields with decent recyclability. However, the imbedded stabilizers and their associated nanoparticles could leach from the polyHIPE, depending on the polyHIPEs swellability in the solvent used for these reactions, causing a decreased efficiency and contamination of the reaction products. Therefore, it would be a significant improvement over the existing state of the art, to fully incorporate the stabilizer into the polyHIPE framework. Therefore, it cannot leach from the polyHIPE, especially if the intended use is as a reusable supported catalyst complex.

In addition to providing a catalyst incorporated within the polyHIPE, HIPE stabilizers can also act as a cross-linker to reduce the amount of cross-linker needed to form a stabile polyHIPE. In one example, silica nanoparticles functionalized with alkyl halides, that can act as initiators for atom transfer radical polymerization (ATRP), were used to stabilize a HIPE, initiate the polymerization and cross-link the polyHIPE.¹⁶ When used as the sole cross-linker, the polyHIPEs showed good retention of the HIPE morphology and a closed shell structure, which allowed for their use as flame retardant liquid droplet elastomers. The use of a functional stabilizer as surfactant and cross-linker

could greatly reduce the cost of polyHIPEs, as the amount of cross-linking agent currently needed to form a stable polyHIPE is 20-30% of the organic phase in the HIPE.^{2,17}

This chapter describes the development of PEO-P(BA-*co*-HEA)-poly(DVB) star polymers that were functionalized with either alkyl halides or methacrylate groups. These functional stars are not only efficient HIPE stabilizers, but are designed to be incorporated into the formed polyHIPE network. The alkyl halide reactive stars (RS_{ATRP}) stabilized HIPEs were polymerized via activators for electron transfer (AGET) atom transfer radical polymerization (ATRP).^{18,19} A degradable cross-linker was used to study the effect of the amount of initiating sites (the alkyl halide) had on the polyHIPE network. The methacrylate reactive stars (RS_{RP}) stabilized HIPEs were initially polymerized via conventional (free) radical polymerization (RP) at low temperatures (30-40 °C) to avoid destabilization of the emulsion, but low yields were obtained. Improving the polyHIPE yield and the extent to which the amount cross-linker can be decreased was also investigated.

7.3 Experimental

7.3.1 Materials

Styrene (St, 99 %), *n*-butyl acrylate (BA, 99 %), 2-hydroxyethyl acrylate (HEA, 96 %), 2-ethylhexyl acrylate (EHA, 99 %), 2-ethylhexyl methacrylate (EHMA, 99 %), bis(2-methacryloyloxyethyl) disulfide (DSDMA, 99 %), ethylene glycol dimethacrylate (EGDMA, 99%), ethylene glycol diacrylate (EGDA, 80 %), and divinylbenzene (DVB, 80 %) were purchased from Sigma Aldrich. They were purified by passage through a

basic alumina column to remove the inhibitor. Poly(ethylene oxide)-based macroinitiators (PEO MI, $M_n = 5200$, Aldrich) were prepared according to the previously published procedure from PEO macromonomers purchased from Aldrich.²⁰ CuBr (98%, Acros) was purified by stirring in acetic acid, it was then filtered, washed with 2-propanol, and then dried under vacuum. Tris[(2-pyridyl)methyl]amine (TPMA) and N,N-bis(2-pyridylmethyl) octadecylamine (BPMODA) were prepared according to a previously published procedures.^{21,22} Nufarm kindly donated (4-butoxy-2,2,6,6-tetramethyl piperidin-1-yl)oxy (bTEMPO, 98.6%). 2,2'-Azobis(4-methoxy-2,4-dimethylvaleronitrile) (V-70, 99%) was purchased from Wako Chemicals and used as received. All other reagents Copper (I) bromide (CuBr, 99%), copper (II) bromide (CuBr₂, 99%), N,N,N',N'',N''-pentamethyl diethylenetriamine (PMDETA, 99%), ethyl 2-bromoisobutyrate (EBiB, 99%), benzoyl peroxide (BPO, 99 %), K₂SO₄, CaCl₂, tetrabutylammonium bromide (TBABr, 99%), ascorbic acid (AA, 99 %), tributyl phosphine (Bu₃P, 99 %), triethyl amine (TEA, 99 %), 2-bromoisobutyl bromide (BriBBBr), methacryloyl chloride (MAC), tetrahydrofuran (THF), dichloromethane (DCM), and methanol (MeOH) were purchased from Aldrich and used as received.

7.3.2 Synthesis of P(BA-co-HEA)-Br Macroinitiator

Initiators for continuous activator regeneration (ICAR) ATRP was used to synthesize P(BA-co-HEA)-Br. *n*-BA (14.4 g, 112 mmol) and HEA (0.88 g, 7.5 mmol) were charged to a Schlenk flask along with EBiB (0.36 g, 1.9 mmol), AIBN (30.7 mg, 0.187 mmol) and anisole (3.2 mL). A stock solution of CuBr₂ and TPMA in DMF was prepared, so 4.2 mg CuBr₂ (0.0187 mmol) and 22.6 mg TPMA could be added to the

same Schlenk flask. The solution on the flask was purged with N₂ for 20 minutes, followed by submerging the flask in an oil bath set at 60 °C. Samples were removed periodically to measure conversion and molecular weight of the polymer. The polymerization was stopped after 5 hours by exposing the contents to air and adding THF to dilute the reaction mixture. P(BA-*co*-HEA)-Br was precipitated by adding the reaction solution to aqueous MeOH (MeOH:H₂O = 80:20), the precipitate was filtered off from the liquid and the polymer was dried by blowing air on it for 24 hours.

7.3.3 Synthesis of PEO-P(BA-*co*-HEA)-Poly(DVB) Miktoarm Stars and Purification

A typical procedure for the synthesis of PEO-P(BA-*co*-HEA)-poly(DVB) miktoarm star polymers with 50% PEO arms is detailed below. The ratio of reagents were [PEO MI]₀/[P(BA-*co*-HEA) MI]₀/[DVB]₀/[CuBr]₀/[PMDTA]₀ = 0.5/0.5/12/0.8/0.8 and [PEO]₀ = 0.015 mM in anisole. A clean and dry Schlenk flask was charged with PEO MI (1.27 g, 0.2 mmol initiating sites), P(BA-*co*-HEA) MI (1.01 g, 0.2 mmol initiating sites), DVB (0.69 mL, 4.8 mmol), PMDTA (0.080 mL, 0.4 mmol), and anisole (3.4 mL). The flask was degassed by purging with N₂ for 20 minutes. CuBr (0.058 g, 0.4 mmol) was quickly added under positive N₂ pressure. The flask was sealed with a glass stopper and then purged with N₂ for 5 minutes before it was immersed in an oil bath set at 110 °C. The reaction was stopped after 22 h via exposure to air and dilution with THF. The stars were purified by passing the solution through neutral alumina to remove the Cu-catalyst and dialyzed against MeOH for 48 hours and THF for 1 week to remove the remaining Cu-catalyst and the macroinitiator arms, respectively.

7.3.4 Functionalization of PEO-P(BA-*co*-HEA)-Poly(DVB) Miktoarm Stars with alkyl halide (reactive star for ATRP = RS_{ATRP})

In a typical procedure, the PEO-P(BA-*co*-HEA)-Poly(DVB) stars (2.32 g, 1.0 mmol) were dispersed in 20 mL THF and the solution was dried using MgSO_4 . TEA (0.30 g, 3.0 mmol) was added to the solution and the solution was purged with N_2 for 20 minutes and cooled to 0 °C in an ice bath. BriBBBr (0.69 g, 3.0 mmol) was added dropwise to the reaction mixture. The reaction was stirred for 24 hours at room temperature and the stars were purified by dialysis for 24 hours against H_2O , 24 hours against MeOH, and 48 hours against THF.

7.3.5 Functionalization of PEO-P(BA-*co*-HEA)-Poly(DVB) Miktoarm Stars with Methacrylate groups (reactive star for conventional radical polymerization = RS_{RP})

In a typical procedure, the PEO-P(BA-*co*-HEA)-Poly(DVB) stars (1.43 g, 0.5 mmol) were dispersed in a solution of bTEMPO (0.6 g, 2.7 mmol) in dry THF. Then TEA (0.16 g, 0.15 mmol) was added to the solution and it was purged for 20 minutes and cooled to 0 °C in an ice bath. MAC (0.15 g, 0.15 mmol) was added dropwise to the reaction mixture. The reaction was stirred for 24 hours at room temperature and the stars were purified by dialysis for 24 hours against H_2O , 24 hours against MeOH, and 48 hours against THF.

7.3.6 Generation of HIPEs and PolyHIPEs with RS_{ATRP} and Degradation of PolyHIPEs (Table 7.3.1)

$CuBr_2$ was complexed with BPMODA and dissolved in the EHMA monomer at 60 °C with stirring for 1.5 h. The mixture was cooled to room temperature and surfactant (Span-80), cross-linker, and initiator (EBiB) were added. An aqueous solution of ascorbic acid and TBABr was prepared. The aqueous phase was added dropwise to the organic phase with overhead stirring (200 to 300 rpm), while being chilled by an ice bath to minimize polymerization during HIPE formation. The formed HIPE was then placed in an oven for 48 h at 60 °C. The polyHIPE was removed from the oven and Soxhlet extraction was performed for 24 h using MeOH. The polyHIPE was dried in a fume hood until constant weight was attained.

PolyHIPEs synthesized with the degradable cross-linker, DSDMA, were swollen in THF overnight. Bu_3P was added (DSDMA: Bu_3P = 10:1) and the reaction was stirred at room temperature for 3 days. The degraded product was analyzed by DLS and GPC, when it was able to pass through a 0.2 μm filter.

Table 7.3.1. HIPE and PolyHIPE Conditions with RS_{ATRP}

Entry	1	2	3	4	5	6
Organic Phase (wt%)						
EHMA	9.0	9.0	13.5	13.5	12.0	12.0
X-linker	1.5 ^a	1.0 ^a	2.5 ^a	2.5 ^b	2.0 ^b	2.0 ^b
CuBr ₂	---	0.05	0.05	0.05	0.05	0.05
BPMODA	---	0.15	0.15	0.15	0.15	0.15
RS _{ATRP} (in THF) ^c	3.0	3.0	0.75	0.75	3.0	2.4
BPO	0.5	---	---	---	---	---
EBiB	---	0.1	---	---	---	0.1
Aqueous Phase (wt%)						
Water	85.0	85.55	82.0	82.0	81.65	82.25
Salt	1.0 ^d	1.0 ^d	1.0 ^d	1.0 ^e	1.0 ^e	1.0 ^e
AA	---	0.05	0.05	0.05	0.05	0.05
Stars/HIPE (wt%)	0.16	0.16	0.04	0.04	0.16	0.13
Time (h)	24	48	48	48	48	48
Density (g/cm ³)	0.16	0.12	---	---	0.14	0.21
polyHIPE Yield	99%	93%	79%	49%	76%	99%
Target DP ^f		90	8200	8200	2000	120

All HIPEs were polymerized at 60 °C, ^a X-linker = EGDMA, ^b X-linker = DSDMA, ^c 5.4 wt% solution of RS_{ATRP} in THF, ^d Salt = K₂SO₄, ^e Salt = TBABr, ^f target DP is the molar ratio of monomer versus the Br-initiating sites from the star and EBiB (See calculation below)

Calculation of Target DP (assuming 100 g of total emulsion with 0.04 wt% stars):

Grams of RS_{ATRP}: 0.04 g M_{n,MALLS}: 1.2x10⁵ moles RS_{ATRP}: 3.33x10⁻⁷

moles of Br/RS_{ATRP}: (3.33x10⁻⁷ moles)*25= 8.33x10⁻⁶

[assume 25 P(BA-co-HEA) arms each with 1 alkyl halide initiating site]

moles EHMA= 0.068

[EHMA]:[Br-Star]= 8200

Calculation of Target DP (assuming 100g total emulsion with 0.16 wt% stars)

Grams of RS_{ATRP}: 0.16 g $M_{n,MALLS}$: 1.2×10^5 moles RS_{ATRP}: 1.33×10^{-6}

moles of Br/RS_{ATRP}: $(1.33 \times 10^{-6} \text{ moles}) \times 25 = 3.33 \times 10^{-5}$

[assume 25 P(BA-co-HEA) arms each with 1 alkyl halide initiating site]

moles EHMA = 0.068

[EHMA]:[Br-Star] = 2000

7.3.7 Generation of HIPEs and PolyHIPEs with RS_{RP} (Table 7.3.2 and 7.3.3)

All organic phase reagents were mixed together and the aqueous phase, containing all desired reagents, was slowly added, dropwise, to the organic phase with vigorous stirring. Once the HIPE was formed it was polymerized by placing it in an oven at the desired temperature for 24 hours. The polyHIPEs were purified by washing with MeOH and dried in a fume hood at room temperature until constant weight was observed.

Table 7.3.2. Styrene and DVB HIPE and PolyHIPE Conditions with RS_{RP}

Entry	1	2	3	4	5	6	7	8
Organic Phase (wt%)								
St	14.5	14.5	14.5	15.23	15.59	15.78	15.23	15.23
DVB	1.45	1.45	1.45	0.73	0.36	0.18	0.73	0.73
Radical Initiator	0.35 ^a	0.35 ^a	0.45 ^b	0.45 ^b	0.45 ^b	0.45 ^b	0.45 ^c	0.8 ^d
RS _{RP} (in THF) ^e	1.55	0.63	0.63	0.63	0.63	0.63	0.63	0.63
Aqueous Phase (wt%)								
Water	81.4	81.32	82.22	82.21	82.22	82.21	82.22	81.87
K ₂ SO ₄	0.75	0.75	0.75	0.75	0.75	0.75	0.75	0.75

All HIPEs were stabilized by 0.1 wt% RS_{RP} (vs total HIPE); ^aRadical initiator = BPO and polymerization temperature = 70 °C for 24 hours; ^bRadical initiator = V-70 and polymerization temperature = 40 °C for 24 hours; ^cRadical initiator = V-70 and polymerization was conducted at 30 °C; ^dRadical initiator = V-70 and BPO and polymerization was conducted at either 30 °C for 24 hours and temperature was then increased to 70 °C for 24 hours or at 70 °C for 24 hours; ^e15.8 wt% solution of RS_{RP} in THF

Table 7.3.3. EHA and EGDA HIPE and PolyHIPE Conditions with RS_{RP}

Organic Phase (wt%)	
EHA	15.23
EGDA	0.73
V-70	0.45
Stars (THF) ^a	0.63
Aqueous Phase (wt%)	
Water	82.21
K ₂ SO ₄	0.75

HIPE was stabilized by 0.1 wt% RS_{RP} (vs total HIPE) and polymerized using V-70 as the radical initiation source at 35 °C for 24 hours; ^a15.8 wt% solution of RS_{RP} in THF

7.3.8 Characterization

¹H nuclear magnetic resonance (¹H NMR) spectroscopy measurements were performed on a Bruker Avance 300 MHz spectrometer and used to determine the conversion of *n*-BA and HEA in CDCl₃. Apparent molecular weight and dispersity were measured by GPC (Polymer Standards Services (PSS) columns (guard, 10⁵, 10³, and 10² Å), with THF eluent at 35 °C, flow rate 1.00 mL/min, and differential refractive index (RI) detector (Waters, 2410)). Toluene was used as the internal standard to correct for any fluctuation of the THF flow rate. The apparent molecular weights and dispersity were determined with a calibration based on linear polystyrene standards using WinGPC 6.0 software from PSS. The detectors employed to measure the absolute molecular weights were a triple-detector system containing a RI detector (Wyatt Technology, Optilab REX), a viscometer detector (Wyatt Technology, ViscoStar), and a multi-angle laser light scattering (MALLS) detector (Wyatt Technology, DAWN EOS) with the light wavelength at 690 nm. Absolute molecular weights were determined using ASTRA software from Wyatt Technology. The average hydrodynamic diameter of star polymers (D_n) was measured by dynamic light scattering (DLS) on a high performance zeta-sizer from Malvern Instruments, Ltd.

The density of the polyHIPE was determined using gravimetric analysis. The polymerization yield was based on the polyHIPE mass following drying. The porous structure was characterized using Hitachi 2460N scanning electron microscope (SEM). The dried polyHIPE samples were attached to a glass slide using rubber cement (Elmer's), the rubber cement was dried under vacuum for 10 minutes. The glass slide was attached to a SEM stub using double stick tape, and coated with gold using a Pelco SC-6 sputter coater. Digital images were obtained using Quartz PCI Image management system software and used to determine the size and range of the voids.

7.4 Results and Discussion

7.4.1 Functionalization of PEO-P(BA-co-HEA)-Poly(DVB) Miktoarm Stars with ATRP Initiating Sites (RS_{ATRP})

The ratio of reagents used to synthesize the P(BA-co-HEA)-Br macroinitiator was $[BA]:[HEA]:[EBiB]:[AIBN]:[CuBr_2]:[TPMA] = 60:4:1:0.1:0.01:0.03$ and the reaction was conducted at 60 °C. The M_n of the formed macroinitiator was 6,400 and contained an average of 4 HEA units, as confirmed by 1H NMR. The mixture of P(BA-co-HEA)-Br and PEO-Br macroinitiators was cross-linked with DVB to form mikto-arm stars under the conditions $[PEO]_0/[PBA-co-HEA]_0/[DVB]_0/[CuBr]_0/[PMDTA]_0 = 0.5/0.5/12/1/1$ in anisole at 110 °C, the $[PEO+PBA]_0 = 0.03$ M. Reactive stars with incorporated alkyl halides (RS_{ATRP}) were synthesized via functionalization with $BrIBr$ (Scheme 7.4.1). DLS and GPC analysis showed that the stars maintained the same size, ~15-20 nm, and the M_n remained the same, respectively (Figure 7.4.1).

Scheme 7.4.1. Synthesis and functionalization of RS_{ATRP}

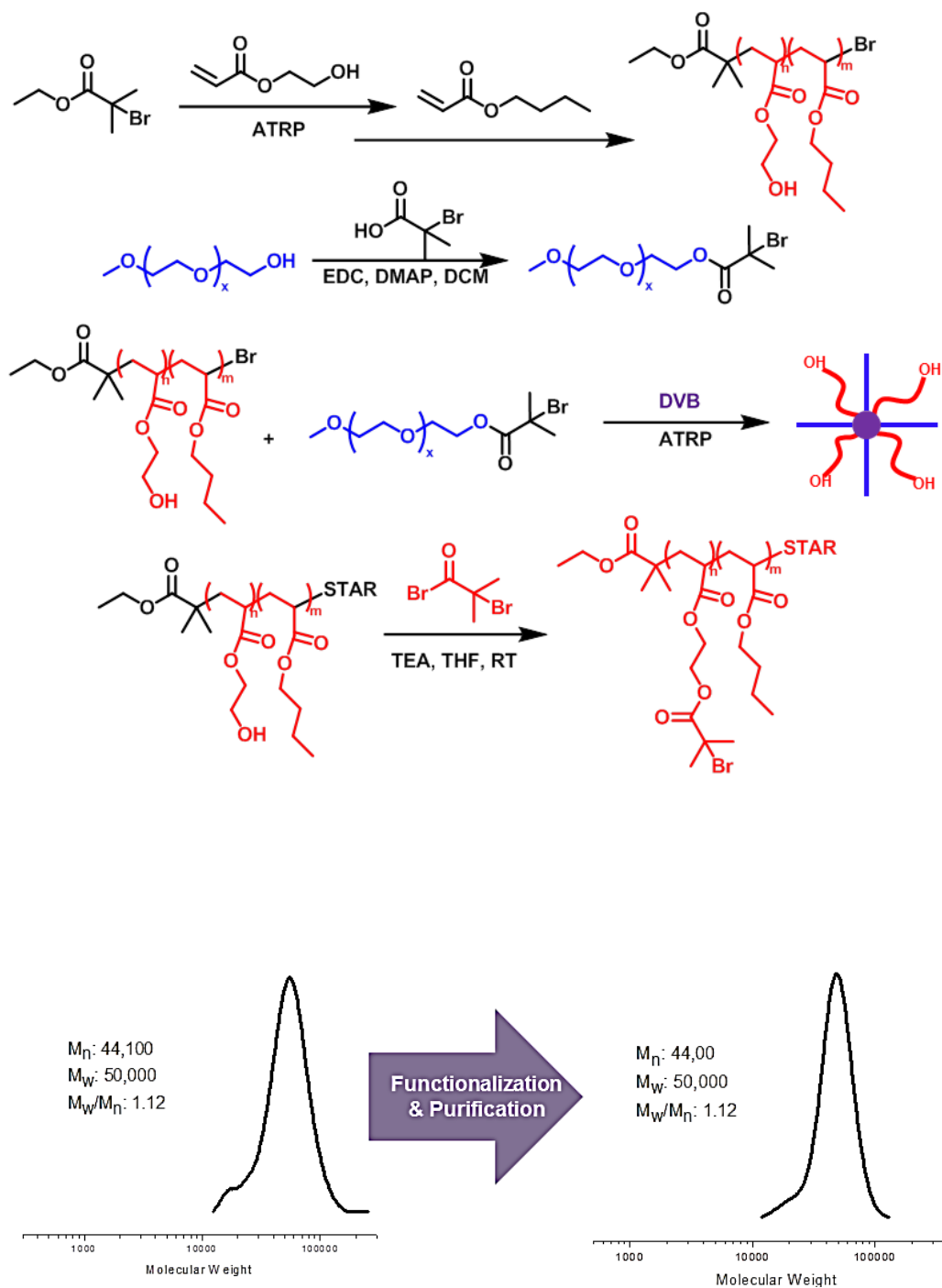


Figure 7.4.1. Molecular weight distribution of PEO-P(BA-*co*-HEA)-Poly(DVB) stars before (left) and after (right) functionalization with Br_iBBr (alkyl halide)

7.4.2 Generation of HIPEs and PolyHIPEs with RS_{ATRP}

The stars were tested for HIPE stabilization using a continuous organic phase consisting of EHMA and EGDMA and the formed HIPE was polymerized using conventional radical polymerization (RP; Table 7.3.1 Entry 1). EHMA and EGDMA were chosen as monomer and cross-linker, so the HIPEs could ultimately be formulated with a degradable methacrylate cross-linker so that degradable polyHIPEs could be synthesized. The concentration of RS_{ATRP} was 0.16 wt% (vs total emulsion), which was higher than the amount of MS_{PBA50} used in Chapter 6, to ensure stability of the HIPE throughout the polymerization. The yield was ~99% after polymerization at 60 °C for 24 hours. The polyHIPE also showed good interconnectivity, but it was observed that there were still some windows within the polyHIPE that were not fully developed (Figure 7.4.2). This is not surprising, as it was previously shown that Pickering HIPEs typically yield close celled structures.^{23,24}

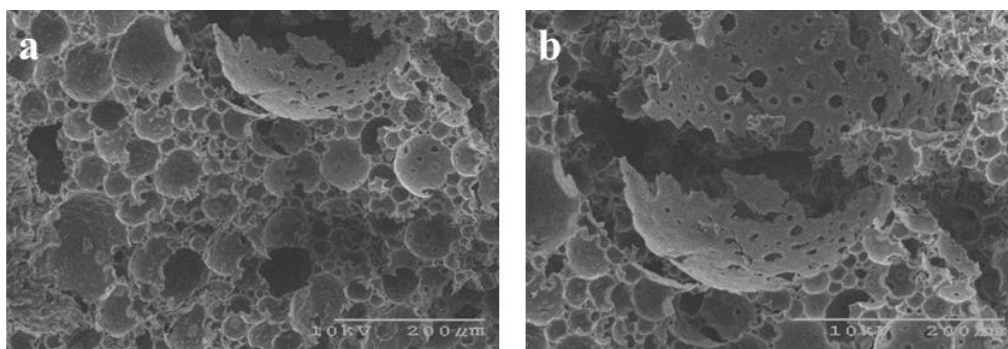


Figure 7.4.2. SEM image of PEHMA-PEGDMA polyHIPE synthesized from RS_{ATRP} stabilized HIPE and polymerized by RP at two different magnifications

7.4.2.1 EHMA/EGDMA HIPEs Polymerized by AGET ATRP

Because there was good stability during the formation of the EHMA/EGDMA RS_{ATRP} polyHIPE, AGET ATRP was used to polymerize the HIPE stabilized by 0.16 wt% RS_{ATRP} vs total emulsion (Table 7.3.1 Entry 2). AGET ATRP conditions initiate polymerization from RS_{ATRP} and therefore ensure its incorporation into the polyHIPE network. To ensure that the HIPE would not be destabilized by the $\text{CuBr}_2/\text{BPMODA}$ catalyst, (Figure 7.4.2.1c for BPMODA structure), a small molecule ATRP initiator, EBiB, was also used to ensure that polymerization would occur. The monomer:initiator ratio is given for all AGET ATRP polymerized samples, which could be considered the target degree of polymerization (DP_n) for the reaction. In this case, a typical target DP_n for ATRP (~ 100) was used, by adding EBiB, which also rules out destabilization of the HIPE as a consequence of targeting too high a target DP_n . Interfacial initiation was used, via reduction of $\text{CuBr}_2/\text{BPMODA}$ in the organic phase with AA in the aqueous phase. The polyHIPE was obtained in 93% yield. Surprisingly, the polyHIPE exhibits a fully interconnected structure (Figure 7.4.2.1a), despite previous findings that Pickering HIPEs polymerized with interfacial initiation formed a closed cell structure.^{23,24} However, the polyHIPE does not show the typical void and window structure, which was previously observed with polyHIPEs synthesized by AGET ATRP (Chapter 5).

Removing the small molecule ATRP initiator significantly increases the target DP_n for this reaction to $\sim 8,200$ (see calculation in section 7.3.4). When no EBiB was added to the polymerization of the HIPEs stabilized by RS_{ATRP} the star content was decreased from 0.16 wt% to 0.04 wt% (Table 7.3.1 Entry 3). The polyHIPE was obtained in 80% yield, which proves that the HIPE polymerization can be initiated from RS_{ATRP}

under AGET ATRP conditions. The polyHIPE structure was similar to that formed under the previous reaction conditions (Figure 7.4.2.1 b). The void and window structure was not observed, but a porous material was obtained.

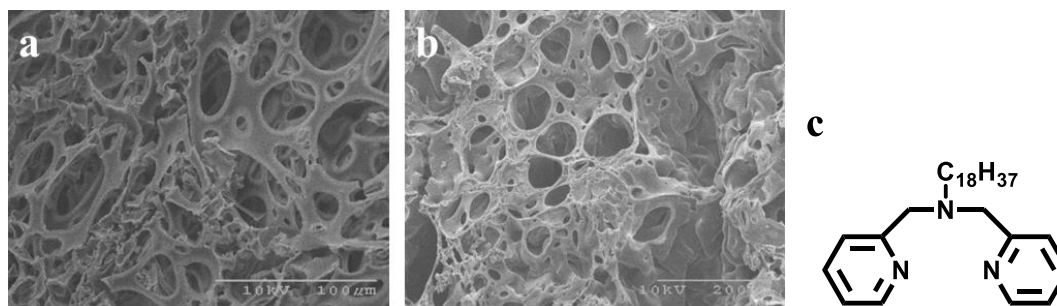


Figure 7.4.2.1. (a) SEM image of PEHMA-PEGDMA synthesized by AGET ATRP with RS_{ATRP} (0.16 wt%) and, (b) EBiB and SEM image of PEHMA-PEGDMA synthesized by AGET ATRP with RS_{ATRP} (0.04 wt%), (c) Structure of BPMODA,

7.4.2.2 EHMA/DSDMA HIPEs Polymerized by AGET ATRP

Since RS_{ATRP} can initiate polymerization under AGET ATRP conditions, degradable polyHIPE were synthesized using the same conditions, by replacement of EGDMA with DSDMA, structure in Figure 7.4.2.2d, (Table 7.3.1 Entry 4). The yield for polyHIPE synthesis with DSDMA was much lower (49 %), than with EGDMA. It is possible that some disulfide bonds were homolytically cleaved to form radicals, which would lead to an increase in termination reactions. It is not likely that the high target DP_n ($\sim 8,200:1$) caused the low yield, as the previous polyHIPE was obtained in much higher yield from a similar HIPE. However, the polyHIPE structure shows the typical void/window structure (Figure 7.4.2.2a). The windows appear as “doughnut” shapes, which is an artifact from the SEM imaging process.

Two more degradable polyHIPEs were synthesized in order to compare initiation from RS_{ATRP} . The first had a 4x higher star content than the previous case, 0.16 wt% stars in the HIPE (Table 7.3.1 Entry 5). Thus, the target DP_n was $\sim 2,000$. The yield was $\sim 80\%$. The SEM images show that the material was not entirely porous and that there may have been destabilization of the HIPE during polymerization or, more likely, collapse of the polyHIPE during purification (Figure 7.4.2.2b).

The last degradable polyHIPE sample was synthesized with 0.13 wt% of reactive stars and the small molecule ATRP initiator, EBiB. The target DP_n in this case is again ~ 100 , which is typical for ATRP conditions (Table 7.3.1 Entry 6) and the polyHIPE yield increased to 99 %. Also, a typical polyHIPE structure was observed, as can be seen in Figure 7.4.2.2c. Large voids were formed that are mostly closed and exhibited few connecting windows.

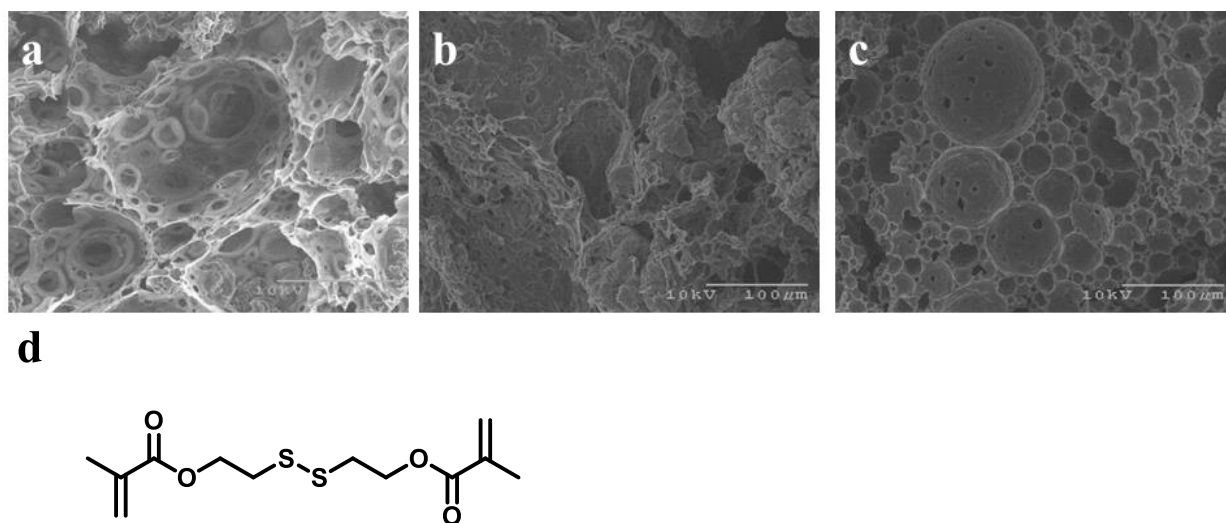


Figure 7.4.2.2. (a) PEHMA-PDSDMA polyHIPEs with 0.04 wt% RS_{ATRP} , (b) 0.16 RS_{ATRP} , (c) 0.13 wt% RS_{ATRP} and EBiB, and (d) the structure of DSDMA

7.4.2.3 Degradation of PEHMA-Poly(DSDMA) PolyHIPEs

The polyHIPEs with degradable cross-linkers were then degraded (Figure 7.4.2.3a) by first swelling them in THF followed by addition of tributyl phosphine (Bu_3P). The solution was then stirred at room temperature for 3 days. Only the polyHIPEs with 100 % star initiation were degraded to the point where they dispersed, but were not fully dissolved, in THF. DLS analysis shows that the 0.04 wt% RS_{ATRP} stabilized polyHIPE (target $\text{DP}_n \sim 8,200$) had particle size $>10 \mu\text{m}$, which is the limit for our DLS model available. The polyHIPE stabilized by 0.16 wt% of RS_{ATRP} ($\sim 2,000$ target DP_n) showed a particle size of $5.5 \mu\text{m}$. It is unsurprising that when target DP_n was decreased the particle size also decreased. In other words, adding ~ 4000 monomer units, in the case of the 8,200:1 and 0.04 wt% RS_{ATRP} , to each star arm, when each star has ~ 25 reactive arms, resulted in a polymer network that can only be degraded to a size $>10 \mu\text{m}$. 4,000 monomer units corresponds to the target DP_n multiplied by the yield and assumes that the yield was similar to conversion.

The final degradable sample that was synthesized under typical ATRP conditions with target $\text{DP}_n \sim 100$ showed full degradation after 3 days, as shown by the formation of clear solution (Figure 7.4.2.3a). The particle sizes were $1.3 \mu\text{m}$ and 30 nm , thus it was possible to analyze the degradation product by GPC. GPC revealed that the degraded product had a $M_n = 10,500$, but a broad molecular weight distribution ($M_w/M_n = 2.98$), which was most likely resulted from the “dual” initiation from stars and from EBiB (Figure 7.4.2.3b).

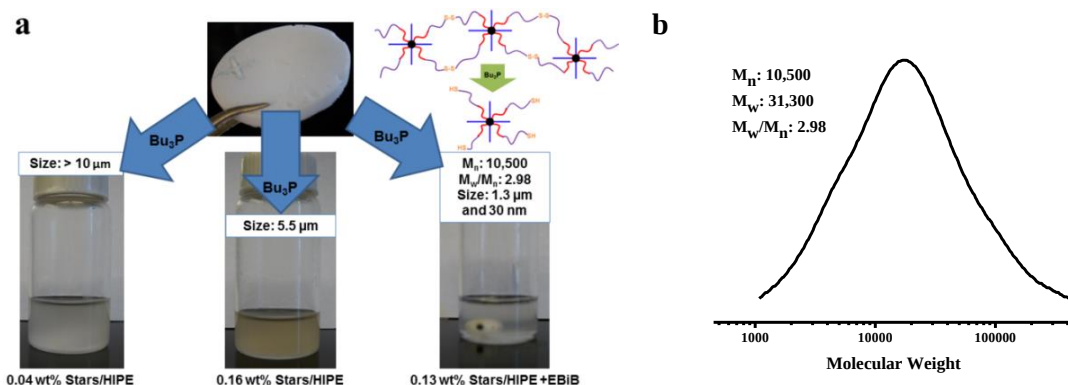


Figure 7.4.2.3. (a) Degradation of PEHMA-PDSDMA polyHIPEs and (b) molecular weight distribution of degraded PEHMA-PDSDMA synthesized with 0.13 wt% RS_{ATRP} and EBiB

7.4.3 Functionalization of PEO-P(BA-co-HEA)-Poly(DVB) Miktoarm Stars with Methacrylate Groups (RS_{RP})

Reactive stars with methacrylate moieties (RS_{RP}) were synthesized via functionalization with MAC (Scheme 7.4.3). DLS analysis showed that the stars maintained the same size, ~15 nm, and GPC analysis showed that the M_n did not drastically increase (Figure 7.4.3). When bTEMPO, a radical trapping agent,^{25,26} was not added to the reaction the stars cross-linked during the functionalization step and a gel was obtained. Therefore after purification of the stars a known concentration of bTEMPO was added to the reaction mixture, to ensure that the stars would not cross-link before use.

Scheme 7.4.3. Synthesis and Functionalization of RS_{RP}

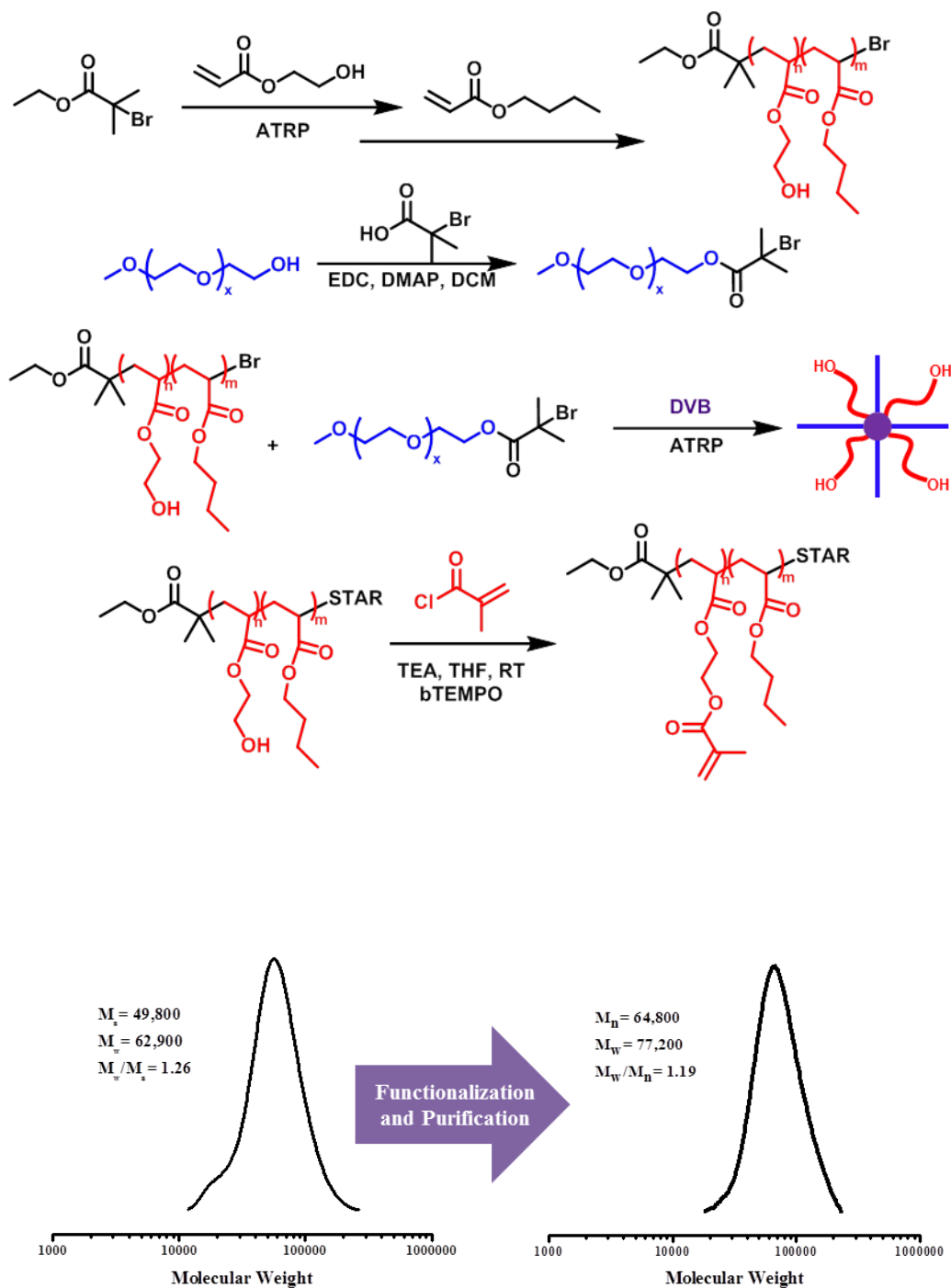


Figure 7.4.3. Molecular weight distribution of PEO-P(BA-co-HEA)-Poly(DVB) stars before (left) and after (right) functionalization with MAC (methacrylate) moieties

7.4.4 Generation of HIPEs and PolyHIPEs with RS_{RP}

Typical HIPE conditions were selected with St/DVB as the continuous oil phase to test the efficiency of RS_{RP} as a stabilizer and determine if it can be incorporated into the polyHIPE network. Organic phase initiation was chosen for this reaction because previous work showed that mikto-arm star stabilized HIPEs only formed open celled polyHIPEs with continuous phase initiation (see Chapter 6). Initially, a HIPE with ~90% internal phase was tested, but the HIPE quickly destabilized after mixing. Thus, ~82% internal phase was used with K₂SO₄ as an additional costabilizer.

7.4.4.1 Investigation of Conditions for Stable HIPE Polymerization

Initial attempts to polymerize RS_{RP} stabilized HIPEs at 70 °C using BPO as the radical initiator (Table 7.3.2, Entry 1) were unsuccessful, as the emulsion destabilized after 1-2 hours heating. The HIPEs were generated via magnetic stirring and it had been determined that when HIPEs were formed using a mechanical stirrer the initial emulsion was stable when using a higher concentration of RS_{RP} in THF solution (15.8 wt% vs 6.3 wt%). However, even under these conditions when the HIPE was heated to 70 °C some destabilization was observed (Table 7.3.2, Entry 2). The synthesized polyHIPE was obtained in 30% yield and had a density of 0.078 g/cm³, and possessed polydisperse voids that ranged in size from 50 to 400 μm (Figure 7.4.4.1a).

The destabilization of the polyHIPEs possibly resulted from the addition of bTEMPO, which prevents the stars from cross-linking and it will retard the polymerization, until it is completely consumed.²⁵ Therefore, since the HIPE structure cannot be “locked-in” within the first hour of polymerization at elevated temperatures (70

°C) the HIPE was destabilized. It is essential that the polyHIPE structure is “locked-in” or polymer is formed early on, with continuous phase initiation, because the emulsion is more likely to destabilize upon heating.²³ To overcome this limitation a radical initiator with a 10 hour $\frac{1}{2}$ life temperature of 30 °C, V-70, was selected. The HIPE was polymerized at 40 °C to generate radicals at a faster rate, so bTEMPO would be removed quickly from the oil phase and the polymerization was started within 1 hour of heating to 40 °C (Table 7.3.2, Entry 3). No destabilization of the HIPE was observed during the polymerization. A polyHIPE was obtained in 43% yield, with a density of 0.077 g/cm³, and a polydisperse void size with small (~50-100 μ m) spherical voids and larger (up to 500 μ m) polyhedral shaped voids (Figure 7.4.4.1b)

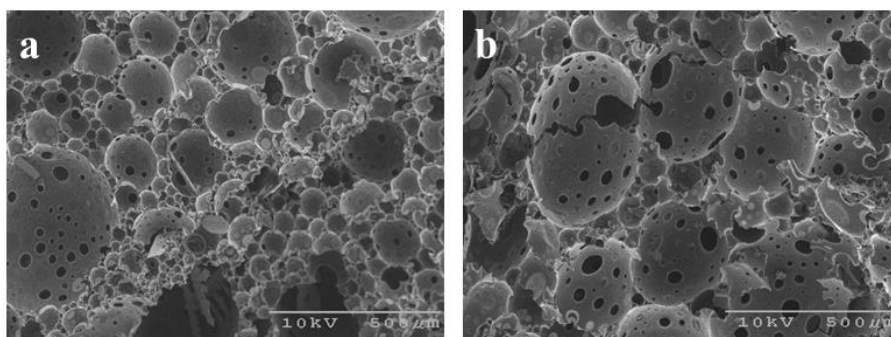


Figure 7.4.4.1. (a) SEM images of polyHIPEs from St/DVB HIPES stabilized by 0.1 wt% RS_{RP} and polymerized with BPO at 60 °C and (b) with V-70 at 40 °C

7.4.4.2 Investigation of the Amount Cross-linker on PolyHIPE Structure

RS_{RP} will not only be incorporated into the polyHIPE network, but it can also act as a cross-linker in the generated polyHIPE network. Therefore, the effects of reducing the amount of cross-linker on the structure of the polyHIPE were investigated. The initial

molar ratio of St:DVB was set at 12.5:1 (or 6:1 for vinyl bonds). This was reduced by half (Table 7.3.2, Entry 4), so the St:DVB molar ratio was 26:1 or (12.5:1 for vinyl bonds). The polyHIPE was obtained in 33% yield, had a density of 0.085 g/cm³, and again had polydisperse void size with spherical droplets ranging from 50 to 500 μ m (Figure 7.4.4.2a). Upon further reduction of the concentration of the cross-linker to generate St:DVB molar ratios of 53:1 or 109:1 (26:1 or 53:1 for vinyl bonds) the yields were slightly decreased to 27 or 31 %, respectively and the polyHIPE structure collapsed (Figure 7.4.4.2 b and c). Thus, it was determined that RS_{RP} does not provide sufficient cross-linking support to allow a decrease in the amount of cross-linker below a molar ratio of 26:1 (St:DVB).

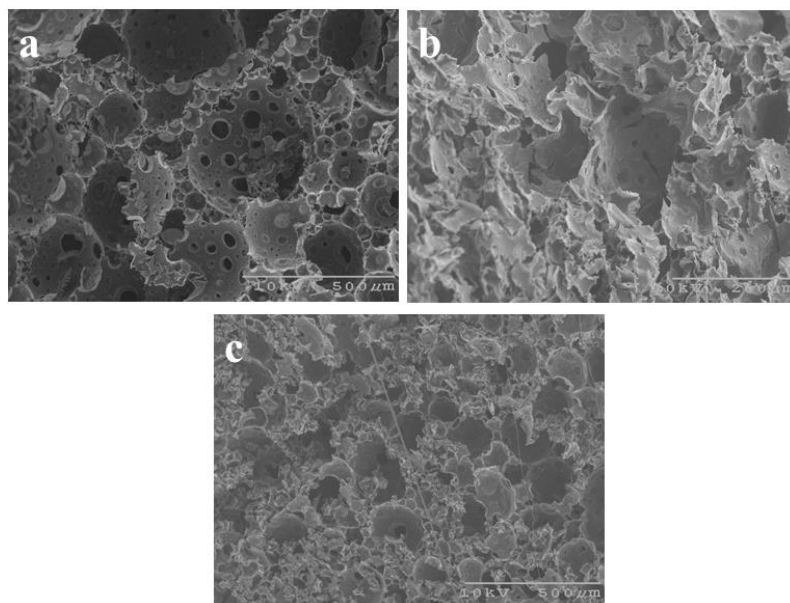


Figure 7.4.4.2. SEM images of polyHIPEs from HIPES stabilized by 0.1 wt% RS_{RP} and polymerized with V-70 at 40 °C using a St:DVB molar ratio of (a) 26:1, (b) 53:1 and (c) 109:1.

7.4.4.3 Investigation of HIPE Polymerization to Improve PolyHIPE Yield

Different combinations of radical initiators and polymerization temperatures were investigated to determine if the yield of the polyHIPE could be improved. However it was possible that using V-70, with a 10 h $\frac{1}{2}$ life at 30 °C, at polymerization temperature of 40 °C, would generate a sufficiently high concentration of radicals resulting in radical-radical termination and inefficient initiation of the polymerization. Therefore, a HIPE, with V-70 radical initiator and 26:1 St:DVB molar ratio, was polymerized at 30 °C (Table 7.3.2, Entry 7). The polyHIPE yield was slightly higher at 48%. The polyHIPE structure displayed a similar porous structure, with mostly closed voids that were ~ 100 μm in size (Figure 7.4.4.3a).

A dual initiation system, with V-70 and BPO, was also investigated to determine if this would increase the yield. A HIPE with 25:1 St:DVB molar ratio was polymerized with a stepwise increase in temperature, 30 °C for 24 hours and 70 °C for 24 hours (Table 7.3.2, Entry 8). Even this procedure did not improve the yield, as the polyHIPE was obtained in 33% yield and again the polyHIPE structure had mostly closed voids ~ 200 μm (Figure 7.4.4.3b). A HIPE was polymerized at 70 °C for 24 hours and resulted in a polyHIPE yield of 47%, which was not a significant improvement, but exhibited a typical polyHIPE structure (Figure 7.4.4.3c). The low yield of PS/PolyDVB most likely resulted from the formation of high molecular weight polymer early in the polymerization, which hinders diffusion of monomer and the radical initiator throughout the oil phase. This will cause a higher amount of radical-radical termination and inefficient initiation of styrene.

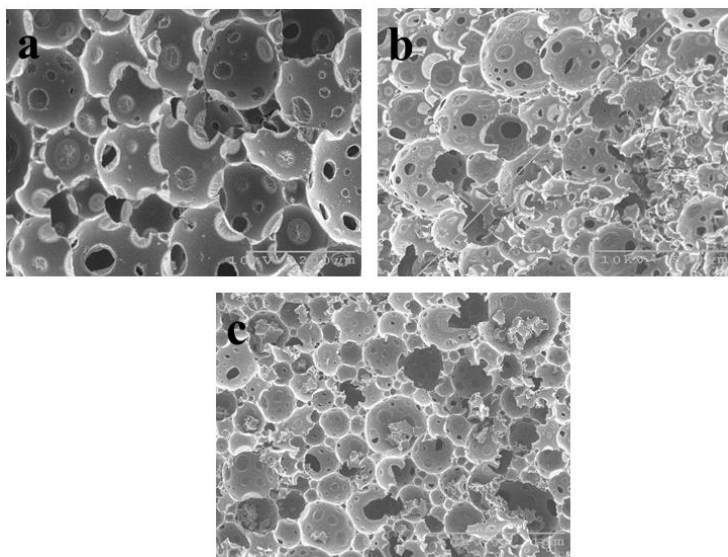


Figure 7.4.3.3. SEM images of polyHIPEs from St/DVB HIPES stabilized by 0.1 wt% RS_{RP} and polymerized with (a) V-70 at 30 °C for 24 hours, (b) V-70 and BPO at 30 °C for 24 hours and 70 °C for 24 hours, and (c) V-70 and BPO at 70 °C for 24 hours

To confirm that the low yields resulted from using styrene/DVB, HIPE's with EHA and EGDA as the reactive monomer and cross-linker in the organic continuous phase were tested (Table 7.3.3). An acrylate based monomer and cross-linker were chosen, due to their higher rate of propagation and the polymer's lower T_g , which should help increase the diffusion of monomer and radical initiator. Both factors combined should result in higher polyHIPE yields. The HIPE was polymerized at 30 °C for 24 hours. The resulting polyHIPE was obtained in a yield of 90% and the density was 0.23 g/cm³. The polyHIPE exhibited a typical structure for a polyHIPE derived from a Pickering HIPE, with mostly closed cells (Figure 7.4.3.4). This indicates that the polymerization conditions were not the cause of the low yields with P(S/DVB). The results can be attributed to the low rate of propagation of styrene, which when coupled

with a dense polymer layer preventing diffusion of monomer and radicals, leads to low yield for the polyHIPE.

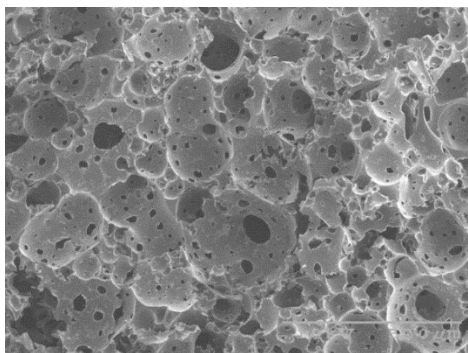


Figure 7.3.3.4. SEM image of polyHIPE from EHA/EGDA HIPE stabilized by 0.1 wt% RS_{RP} and polymerized at 35 °C for 24 hours using V-70 as the initiator

7.5 Conclusions

PEO-PBA-Poly(DVB) mikto-arm stars were successfully functionalized with either alkyl halides (RS_{ATRP}) or methacrylate groups (RS_{RP}). The functionalized stars were able to stabilize HIPEs at amounts down to 0.04 wt%, as previously shown with the non-reactive MS_{PBA50} stars (Chapter 6). The resulting polyHIPEs displayed a mostly closed shell structure, which is common for polyHIPEs synthesized via Pickering HIPE polymerization. A few polyHIPE polymerized by AGET ATRP showed an irregular, interconnected structure with no distinguishable voids.

The RS_{ATRP} stars were shown to successfully initiate polymerization in a HIPE and the resulting polyHIPEs were obtained in reasonable yields and showed a mostly opened shell structure. Varying amounts of RS_{ATRP} and small molecule ATRP initiator,

EBiB, were used to synthesize degradable polyHIPEs. This resulted in different network sizes in the polyHIPE, as shown after degradation by DLS analysis.

The synthesis of RS_{RP} mikto-arm stars required the presence of bTEMPO during the reaction and after purification to prevent irreversible aggregation through chemical cross-linking between the stars. Consequently, the initial conditions employed to polymerize St/DVB HIPEs stabilized by RS_{RP} at 40 °C, with V-70 as the initiation source, resulted in polyHIPE yields of 33-43%. It was determined that the lowest amount of cross-linker that created a stable polyHIPE was $\sim 1/2$ of the typical amount used or 26:1 St:DVB molar ratio. The yields could be slightly improved, to $\sim 50\%$, by conducting the polymerization at 30 °C with V-70 initiator or at 70 °C with a dual initiator system, V-70 and BPO. However, it was determined that it was not the presence of bTEMPO or the polymerization conditions that were causing low yields, but the use of St/DVB as the monomer/crosslinker. This was shown by the successful polymerization of an EHA and EGDA HIPE at 35 °C with V-70 radical initiator, resulting in a 90% yield of the polyHIPE. Thus, it was concluded that the initial formation of a rigid PS layer on the surface of the oil phase did not allow for diffusion of styrene monomer or radicals within the polyHIPE, which, coupled with the low rate of propagation of styrene, resulted in the low yields of P(S/DVB) polyHIPEs.

7.6 Acknowledgements

Joseph P. Suhan for his help with the SEM imaging is sincerely thanked. Support from the BSF grant (2008152) is acknowledged.

7.7 References

- (1) Kimmins, S. D.; Cameron, N. R. *Advanced Functional Materials* **2011**, 21, 211.
- (2) Pulko, I.; Krajnc, P. *Macromolecular rapid communications* **2012**, 33, 1731.
- (3) Silverstein, M. S. *Polymer* **2014**, 55, 304.
- (4) Silverstein, M. S.; Cameron, N. R. In *Encyclopedia of Science and Technology*; 4 ed.; Wiley: Hoboken, N.J., 2010.
- (5) Gao, H.; Matyjaszewski, K. *Macromolecules* **2006**, 39, 3154.
- (6) Gao, H.; Matyjaszewski, K. *Macromolecules* **2006**, 39, 7216.
- (7) Gao, H.; Matyjaszewski, K. *Macromolecules* **2007**, 40, 399.
- (8) Gao, H.; Matyjaszewski, K. *Progress in Polymer Science* **2009**, 34, 317.
- (9) Chen, Q.; Cao, X.; Liu, H.; Zhou, W.; Qin, L.; An, Z. *Polymer Chemistry* **2013**, 4, 4092.
- (10) Chen, Q.; Deng, X.; An, Z. *Macromolecular rapid communications* **2014**, 35, 1148.
- (11) Chen, Q.; Xu, Y.; Cao, X.; Qin, L.; An, Z. *Polym. Chem.* **2014**, 5, 175.
- (12) Ye, Y.; Wan, D.; Du, J.; Jin, M.; Pu, H. *Journal of Materials Chemistry A* **2015**, 3, 6297.
- (13) Ye, Y.; Jin, M.; Wan, D. *Journal of Materials Chemistry A* **2015**, 3, 13519.
- (14) Liu, H.; Wan, D.; Du, J.; Jin, M. *ACS applied materials & interfaces* **2015**, 7, 20885.
- (15) Yi, F.; Xu, F.; Gao, Y.; Li, H.; Chen, D. *RSC Advances* **2015**, 5, 40227.
- (16) Gurevitch, I.; Silverstein, M. S. *Macromolecules* **2012**, 45, 6450.
- (17) Silverstein, M. S. *Progress in Polymer Science* **2014**, 39, 199.
- (18) Min, K.; Gao, H.; Matyjaszewski, K. *Journal of the American Chemical Society* **2005**, 127, 3825.
- (19) Min, K.; Jakubowski, W.; Matyjaszewski, K. *Macromolecular rapid communications* **2006**, 27, 594.
- (20) Gao, H.; Matyjaszewski, K. *Journal of the American Chemical Society* **2007**, 129, 11828.
- (21) Britovsek, G. J. P.; England, J.; White, A. J. P. *Inorganic Chemistry* **2005**, 44, 8125.
- (22) Xia, J.; Matyjaszewski, K. *Macromolecules* **1999**, 32, 2434.
- (23) Gurevitch, I.; Silverstein, M. S. *Journal of Polymer Science Part A: Polymer Chemistry* **2010**, 48, 1516.
- (24) Gurevitch, I.; Silverstein, M. S. *Macromolecules* **2011**, 44, 3398.
- (25) Mardare, D.; Matyjaszewski, K. *Thermal polymerization of styrene in the presence of stable radicals and inhibitors*, DTIC Document, 1994.
- (26) Bencherif, S. A.; Washburn, N. R.; Matyjaszewski, K. *Biomacromolecules* **2009**, 10, 2499.

Chapter 8

Summary and Outlook

The goal of this thesis was to investigate the use of various atom transfer radical polymerization (ATRP) procedures to improve the synthesis of two different classes of porous materials, nitrogen-doped nanostructured carbons (N-doped nanocarbons) and polymerized high internal phase emulsions (polyHIPEs). The polyacrylonitrile-based (PAN-based) block copolymer (BCP) precursors, previously used to template N-doped nanocarbons, were synthesized via normal ATRP which requires high catalyst loadings, 3,000 to 3,500 ppm (vs. monomer). PAN-based BCPs can also reach their order-disorder transition temperature (T_{ODT}) before cyclization, which leads to the polymers becoming miscible within each other, resulting in the loss of phase separated morphology and the collapse of the carbon after carbonization.

Chapter 2 discusses the polymerization of acrylonitrile with reduced catalyst loadings by initiators for continuous activator regeneration (ICAR) ATRP and with a recently developed metal-free (MF) ATRP to synthesize well-defined PAN. PAN synthesized by both methods had high chain end functionality and the PAN

macroinitiators were chain extended to form BCPs. Thermal characterization of BCPs are being conducted to confirm that the N-doped carbons synthesized by these methods have the same properties, since the block order was reversed and the halogen chain end is now Br (previously PBA-*b*-PAN-Cl) for these BCPs. Essentially, it needs to be determined if there is a chain end effect during the stabilization and pyrolysis of the PAN/PBA BCPs. Another aspect of the PAN/PBA BCPs prepared by ICAR ATRP with 1 ppm of catalyst and MF ATRP methods is the possibility to synthesize high chain end functionality PAN with a broader MWD. It has been previously shown that increasing the MWD in one segment of a BPC can result in new and interesting “metastable” morphologies, such as hexagonally perforated lamellae. Synthesis of BCPs with broad MWD in either the PAN or PBA sacrificial block could give access to these interesting morphologies. In addition, higher MWD PAN-*b*-PBA BCPs could give rise to N-doped nanocarbons with new pore structure, or higher surface areas, after pyrolysis of the BCP.

Chapter 3 discusses the synthesis of PAN-based star polymers and their use as precursors for N-doped nanocarbons. The macroinitiator concentration, amount of cross-linker, and cross-linker hydrophobicity were varied to obtain high star yields. PAN homo-polymer armed stars were synthesized in up to 87% yield when a hydrophobic cross-linker was used. PAN-*b*-PBA BCP armed stars were also synthesized in yields up to 82%. The carbon materials templated from the PAN-based stars had surface areas as high as 390 m²/g, when the DP of PAN was less than 40. These carbons were mostly microporous, which was derived from the acrylate-based core and from PAN itself. “Anchoring” the PAN and PAN BCPs to the acrylate core yielded smaller pores than PAN based BCPs, because the T_{ODT} was not reached. The carbons derived from PAN-

based stars will be compared to carbons derived from PAN-based bottle brushes that have long backbones and star-like bottle brushes with short backbones. Additionally, PAN grafted from 7 nm silica particles should be investigated as carbon precursors to determine the effect of a slightly larger core on the pore structure of the carbon to the smaller acrylate cross-linked core in the PAN-based stars.

Chapter 4 investigates an alternative nitrogen-rich carbon precursor, a tetrazine cross-linked material, that was derived from SiO_2 -*g*-poly(4-cyanotstyrene). Cross-linking causes intra, as well as, inter-particle cross-linking, which helps to form 3D interconnected nanocarbons. The carbons formed from these have surface areas up to 752 m^2/g and exhibit a broad pore size distribution. It would be interesting to determine the content and types of nitrogen present in these nanocarbons and examine their use for different applications, such as ORR catalysts or DSSC electrodes.

Prior research into HIPEs and polyHIPEs had revealed some limitations in the existing procedures including high surfactant loadings needed to stabilize HIPEs, preparation of polyHIPEs that are not typically degradable, and the low mechanical strength of polyHIPEs. Chapter 5 discusses the polymerization of HIPEs by activators generated by electron transfer (AGET) ATRP to yield degradable polyHIPEs, and the use of commercially available monomers to prepare polyHIPEs with improved the mechanical properties by synthesizing a more uniform cross-linked network. PolyHIPE materials synthesized by AGET ATRP, with biocompatible monomers and a biodegradable cross-linker, could find potential applications in the biomedical field, as porous materials for tissue engineering scaffolds, especially as the high chain-end functionality allows for post-fabrication fine tuning of the properties by functionalization

of the surface of the pores with small molecules or chain extension with different monomers.

Chapters 6 and 7 discuss the stabilization of HIPEs using star polymers to reduce surfactant loadings. In Chapter 6, PEO-poly(DVB) stars were able to stabilize xylene-in-water emulsions at concentrations as low as 0.01 wt%. The poly(ethylene oxide)-poly(butyl acrylate)-poly(divinyl benzene) mikto-arm stars (MS_{PBA50}) were able to stabilize water-in-xylene emulsions at 0.005 wt% (vs. total emulsion) loading and inherently formed a HIPE. Water-in-oil HIPEs, where the oil phase was comprised of styrene and divinyl benzene, were stabilized throughout the polymerization, by MS_{PBA50} loadings as low as 0.04 wt%. PolyHIPEs were synthesized with large voids (50-500 μm) typical of polyHIPEs derived from the polymerization of Pickering HIPEs. Given the excellent stabilization of HIPEs by MS_{PBA50} , PEO_{2000} -Poly(DVB) stars, S_{D64} , should be tested as a HIPE stabilizer. S_{D64} formed highly stable O/W emulsions with 80 wt% xylene dispersed in 20 wt% water, indicating that it preferentially forms HIPEs. O/W HIPEs are studied to a lesser degree, as there are fewer stabilizers that form stable O/W HIPEs. Additionally, polyHIPEs made from water soluble monomers, like poly(ethylene oxide) methyl ether (meth)acrylate, could inherently provide better cell-scaffold supports and eliminate the need to functionalize the surfaces of PS/PDVB based polyHIPEs, which are currently used as commercially available cell scaffolds. It would also be interesting to undertake an in depth study to determine why star shaped polymers preferentially form HIPEs, as there are few surfactants that have this tendency. A deeper understanding of the relationship between structure and emulsifier behavior could lead to improved design of surfactants for HIPE stabilization or emulsion stabilization in general.

In Chapter 7, an extension of the work in Chapter 6 was done where PEO-PBA-Poly(DVB) stars were functionalized with alkyl halides (RS_{ATRP}), so they could be incorporated into the polyHIPE under ATRP conditions, and with methacrylate groups (RS_{RP}), so they could be incorporated into the polyHIPE by standard free radical polymerization. PolyHIPEs were successfully synthesized with both functional star emulsifiers thereby forming polyHIPEs with no “free” surfactant. The incorporation of RS_{ATRP} into the polyHIPE network was confirmed, when it was employed as the only initiation source and via the degradation of the polyHIPE network formed with degradable cross-linkers. Confirming the incorporation of RS_{RP} is more difficult and will need to be done in the future using cryo-TEM imaging. Simple incorporation of star stabilizers into the polyHIPE network decreases the amount of purification needed, but also could also be employed to incorporate added utility to the polyHIPE, e.g. serve as a ligand for a metal catalyst or as an organic catalyst, making the overall polyHIPE material a recyclable catalyst. Additionally, a responsive (pH or temperature) star could be incorporated into the polyHIPE and, upon response trigger a specific change in the pore morphology, e.g. the pore surface could be tuned to design new membrane materials for separation applications.

In summary this work aimed to improve synthetic methods for N-doped nanocarbon precursors and polyHIPEs. N-doped carbons were synthesized from PAN-based BCPs using low Cu-catalyst loadings or no metal catalysts. PAN-based stars were also shown to be good templates for N-doped nanocarbons. Poly(4-cyanostyrene) grafted from silica particles was used as a precursor to n-doped nanocarbons when cross-linked to form tetrazine units. AGET ATRP conditions to synthesize degradable polyHIPEs

were developed and mikto-arm stars were investigated as either unreactive or reactive surfactants for HIPE stabilization and polyHIPE synthesis. This work advances the understanding on how to better prepare meso- and macroporous polymer-based materials.