METHOXY POLY (ETHYLENE GLYCOL) METHACRYLATE - BASED COPOLYMERS ON THE APPLICATIONS OF CONCRETE ADMIXTURES, MESOPOROUS MATERIALS, AND RHEOLOGY MODIFIERS

A Dissertation
Presented to
The Graduate Faculty of The University of Akron

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

Pattarasai Tangvijitsakul
December, 2015
METHOXY POLY (ETHYLENE GLYCOL) METHACRYLATE - BASED COPOLYMERS ON THE APPLICATIONS OF CONCRETE ADMIXTURES, MESOPOROUS MATERIALS, AND RHEOLOGY MODIFIERS

Pattarasai Tangvijitsakul

Dissertation

Approved: 

Accepted:

Advisor
Dr. Mark D. Soucek

Department Chair
Dr. Sadhan C. Jana

Committee Chair
Dr. Kevin Cavicchi

Dean of the College
Dr. Eric J. Amis

Committee Member
Dr. Avraam I. Isayev

Interim Dean of the Graduate School
Dr. Chand Midha

Committee Member
Dr. Li Jia

Date

Committee Member
Dr. Chrys Wesdemiotis
ABSTRACT

Hydrophilic copolymers were prepared and used in different applications including dispersant additives for cement, thin film batteries, and thickener in water-borne latex coating respectively.

The copolymers were prepared using methoxy [poly (ethylene glycol) methacrylate] or MPEGMA and methacrylic acid (MAA) by different polymerization techniques e.g. reversible addition-fragmentation chain transfer (RAFT) polymerization, conventional radical polymerization, and esterification process. Different ratios of monomers and different side chain lengths of MPEGMA were utilized in order to investigate those effects of the fluidity of fresh cement/concrete. The effect molecular weight, molecular weight distribution, and the copolymer structures on fluidity of fresh cement/concrete were also studied. In addition, it was found that a new RAFT polycarboxylate terpolymer (containing in-situ defoaming groups) not only able to provide a reasonable cement fluidity over a long period of time, but also able to control the amount of generated bubbles at the same time. This may probably lead to a new candidate admixture for an outdoor concrete structural application that requires freeze-thaw resistance without adding separate defoaming agents.
A new series of amphiphilic block copolymers, poly (methoxy poly (ethylene glycol) methacrylate) - \textit{block} - poly (butyl acrylate) [PMPEGMA – \textit{b} – PBA] were successfully synthesized \textit{via} RAFT polymerization and were characterized \textit{via} Nuclear Magnetic Resonance (NMR) and \textit{Gel Permeation Chromatography} (GPC). These block copolymers were then used as micelle templates for mesoporous mixed metal oxide materials between cobalt and/or nickel for thin film battery.

A new fatty acid-based rheology modifier, poly [methoxy poly (ethylene glycol) methacrylate]-\textit{block}–poly (oleic acid) [PMPEGMA–\textit{b}–POA], was also synthesized by RAFT polymerization. The steady-shear properties of a well-characterized conventional latex, thickened with the different concentrations of the resulting fatty acid - based rheology modifier, were measured at constant pH and temperature. Shear thinning behavior in the latex solution with PMPEGMA homopolymer was observed. In addition, hydrophobically modified rheology modifier increased the thickening effect in the latex solution due to the transient intermolecular and intramolecular associations.
ACKNOWLEDGMENTS

I would like to express my sincere gratitude to my research advisor, Dr. Mark D. Soucek, for his invaluable guidance and encouragement throughout my doctoral dissertation. I also would like to extend my gratitude towards my committee members, Dr. Kevin Cavicchi, Dr. Avraam I. Isayev, Dr. Li Jia, and Dr. Chrys Wesdemiotis for their contribution, suggestion, and support.

I would like to thank Dr. Bryan Vogt for giving me a great opportunity for the research cooperation related to the application of mesoporous materials. Sarang Bhaway has put tons of effort in order to make this study happen i.e. fabrication of mixed metal oxide mesopores materials, characterization, and valuable discussion.

I would like to thank Dr. Nicole Zacharia, Dr. Yuanqing (Kane) Gu, and Jon R. Page for their help and guidance with GPC characterization. I would like to thank the University of Akron Magnetic Resonance Center, Dr. Venkat Dudipala, Chun Gao, and Stephanie Bilinovich for their experimental support and valuable discussion. I also would like to thank the University of Akron Mass Spectrometry Center, Dr. Aleer M. Yol, Michelle Kushner, and Selim Gerislioglu for their experimental support and discussion.

This research would not have been possible without the financial assistance from Euclid Chemical Company. In particular, I would like to thank Keith Franey, John
Langham, Brad Nemunaitis, Arthur Greenberg, and Jane Krivos for their experimental help, guidance, and encouragement.

I would like to thank my research group members for their encouragement and help given to me during my research work. I am grateful to Ali Javadi for his helpful discussion related to my doctoral dissertation.

Finally, I would like to dedicate this doctoral dissertation to my family for their love and support in every stage of my life.
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>List Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF FIGURES</td>
<td>xiii</td>
</tr>
<tr>
<td>LIST OF SCHEMES</td>
<td>xix</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>xx</td>
</tr>
<tr>
<td>CHAPTER</td>
<td></td>
</tr>
<tr>
<td>I. INTRODUCTION</td>
<td></td>
</tr>
<tr>
<td>II. BACKGROUND</td>
<td></td>
</tr>
<tr>
<td>2.1 Concrete</td>
<td></td>
</tr>
<tr>
<td>2.1.1 Manufacture of cement</td>
<td></td>
</tr>
<tr>
<td>2.1.2 Basic compositions of cement</td>
<td></td>
</tr>
<tr>
<td>2.1.3 Major oxide compounds of ordinary Portland cement</td>
<td></td>
</tr>
<tr>
<td>2.1.4 Minor oxide compounds of ordinary Portland cement</td>
<td></td>
</tr>
<tr>
<td>2.1.5 Setting and hardening of cement</td>
<td></td>
</tr>
<tr>
<td>2.1.6 Hydration reactions of cement</td>
<td></td>
</tr>
<tr>
<td>2.1.7 Development of cement paste structure</td>
<td></td>
</tr>
<tr>
<td>2.2 Admixtures in concrete</td>
<td></td>
</tr>
<tr>
<td>2.2.1 Air-entraining agents</td>
<td></td>
</tr>
<tr>
<td>2.2.2 Defoaming agents</td>
<td></td>
</tr>
<tr>
<td>2.2.3 Accelerating admixtures</td>
<td></td>
</tr>
<tr>
<td>2.2.4 Retarding admixtures</td>
<td></td>
</tr>
<tr>
<td>2.2.5 Waterproofing admixtures</td>
<td></td>
</tr>
</tbody>
</table>
2.2.6 Corrosion-inhibiting admixtures ................................................................. 19
2.2.7 Dispersing admixtures .................................................................................. 20
2.3 Mechanism of air-entraining agents in concrete ............................................. 21
2.4 Mechanism of defoaming agents in concrete .................................................. 24
2.5 Mechanism of dispersing admixtures in concrete ......................................... 27
2.6 Mesoporous materials ...................................................................................... 29
  2.6.1 Classification of porous materials ................................................................. 29
  2.6.2 Synthesis mechanism for the creation of mesoporous materials .......... 30
  2.6.3 Applications of mesoporous materials ........................................................ 38
2.7 Thickeners for water-based coating systems .................................................. 39
2.8 Radical copolymerization and controlled radical copolymerization .......... 40

III. THE SYNTHESIS AND CHARACTERIZATION OF STARTING MATERIALS:
    METHOXY POLY (ETHYLENE GLYCOL) METHACRYLATE AND WATER
    SOLUBLE RAFT AGENT .................................................................................... 46
  3.1 Overview .......................................................................................................... 46
  3.2 Materials ........................................................................................................... 46
  3.3 Instrumentation .................................................................................................. 47
  3.4 Synthesis ........................................................................................................... 48
    3.4.1 Synthesis of methoxy poly (ethylene glycol) methacrylate (MPEGMA) .... 48
    3.4.2 Synthesis of 2-Methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester. 50
    3.4.3 Synthesis of water soluble RAFT agent: 4-cyanopentanoic acid
dithiobenzoate (CPADB) ...................................................................................... 51
  3.5 Results and discussion ....................................................................................... 54
    3.5.1 Characterization of methoxy poly (ethylene glycol) methacrylate (MPEGMA) .................................................................................................................. 54
    3.5.2 Characterization of 2-Methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl
ester ......................................................................................................................... 61
3.5.3 Characterization of water soluble RAFT agent: CPADB ........................................ 63

3.6 Conclusions .............................................................................................................. 65

IV. THE SYNTHESIS OF POLYCARBOXYLATE ADMIXTURES FOR CONCRETE VIA CONVENTIONAL RADICAL POLYMERIZATION AND ESTERIFICATION PROCESS .................................................................................................................. 66

4.1 Overview .................................................................................................................... 66

4.2 Introduction ................................................................................................................ 67

4.3 Materials .................................................................................................................... 69

4.4 Instrumentation ......................................................................................................... 70

4.5 Synthesis .................................................................................................................... 70

4.5.1 Synthesis of polycarboxylate copolymers via conventional radical polymerization .................................................................................................................. 70

4.5.2 Synthesis of polycarboxylate copolymers via esterification process .......... 73

4.6 Results and discussion ............................................................................................... 76

4.6.1 Characterization of polycarboxylate copolymers via conventional radical polymerization .................................................................................................................. 77

4.6.2 Characterization of polycarboxylate copolymers via esterification process... 78

4.7 Conclusions ................................................................................................................ 82

V. THE SYNTHESIS OF NEW POLYCARBOXYLATE ADMIXTURES FOR CONCRETE VIA RAFT POLYMERIZATION .................................................................................................................. 83

5.1 Overview .................................................................................................................... 83

5.2 Introduction ................................................................................................................ 84

5.3 Materials .................................................................................................................... 86

5.4 Instrumentation ......................................................................................................... 87

5.5 Synthesis .................................................................................................................... 88

5.5.1 Synthesis of PMPEGMA - random – PMAA via RAFT polymerization ...... 88

5.5.2 Synthesis of PMPEGMA - block – PMAA via RAFT polymerization ...... 91
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>The appearance of C₃S (hexagonal shape) and C₂S (round black shape) in Ordinary Portland cement</td>
</tr>
<tr>
<td>2-2</td>
<td>Process of setting and hardening of cement</td>
</tr>
<tr>
<td>2-3</td>
<td>Illustration of hydration of cement paste</td>
</tr>
<tr>
<td>2-4</td>
<td>Bubbles rise to liquid surface follow Stoke’s law</td>
</tr>
<tr>
<td>2-5</td>
<td>(a) Lamella formed by the bubble that rises to the liquid surface and then broken due to lack of surfactant; (b) Surfactants to stabilize the bubble and lamella preventing it from drainage</td>
</tr>
<tr>
<td>2-6</td>
<td>(a) Formula of a typical air-entraining agent derived from pine oil or tall oil processing; (b) mechanism of air entrainment when an anionic surfactant with a nonpolar hydrocarbon chain is added to the cement paste</td>
</tr>
<tr>
<td>2-7</td>
<td>Mechanism of defoaming agents</td>
</tr>
<tr>
<td>2-8</td>
<td>Lamella rupture by a low surface tension particle</td>
</tr>
<tr>
<td>2-9</td>
<td>Defoaming through hydrophobic particles</td>
</tr>
<tr>
<td>2-10</td>
<td>Effect of dispersing admixtures in breaking up cement flocs</td>
</tr>
<tr>
<td>2-11</td>
<td>Steric stabilization dispersion of cement grains by polycarboxylate superplasticizers</td>
</tr>
<tr>
<td>2-12</td>
<td>Hard-templating method leading to mesoporous non-siliceous materials</td>
</tr>
<tr>
<td>2-13</td>
<td>Different self-assembled structures formed by amphiphilic block copolymers in a block-selective solvent</td>
</tr>
<tr>
<td>2-14</td>
<td>Mesostructured thin-film formation by dip-coating using EISA method</td>
</tr>
<tr>
<td>2-15</td>
<td>A typical RAFT agent structure</td>
</tr>
</tbody>
</table>
2-16 Possible polymer chains that can be present in RAFT polymerization................. 45
3-1 Synthesis pathway of a methoxy poly (ethylene glycol) methacrylate for different
chain lengths (m = 12, 24, and 48) .................................................................................................................................................. 49
3-2 Synthesis of 2-methyl-acrylic acid (dibuthoxy-phosphoryloxy)-alkyl ester .......... 50
3-3 Synthesis of diethyl ammonium dithiobenzoate.................................................. 52
3-4 Synthesis of bis (thiobenzoyl) disulfide ............................................................... 53
3-5 Synthesis of water soluble RAFT agent: CPADB ................................................. 53
3-6 FT-IR spectra (a) MPEG 550, 950, and 2000; (b) MPEGMA 550, 950, and 2000 ... 54
3-7 1H-NMR spectrum of MPEGMA 550 (CDCl$_3$ as a solvent) ............................. 56
3-8 Mass Spectra of MPEGMA 550 ............................................................................ 57
3-9 1H-NMR spectra of MPEGMA 950 and MPEGMA 2000 (CDCl$_3$ as a solvent) .... 58
3-10 Mass Spectra of MPEGMA 950 .......................................................................... 59
3-11 FT-IR spectrum of 2-Methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester 61
3-12 1H-NMR of 2-Methyl acrylic acid (dibuthoxy-phosphoryloxy) – ethyl ester ........ 62
3-13 1H-NMR of diethyl ammonium dithiobenzoate .................................................. 63
3-14 1H-NMR of bis (thiobenzoyl) disulfide ............................................................... 64
3-15 1H-NMR of 4-cyanopentanoic acid dithiobenzoate .......................................... 64
4-1 Synthesis of polycarboxylate copolymers via conventional radical polymerization
(initiators can be Na$_2$S$_2$O$_5$/NaHSO$_3$ or AIBN) ................................................................. 73
4-2 Chemical structures of methacrylic acid, AIBN as an initiator, and toluene as a
solvent used for synthesis of polycarboxylate admixtures ............................................. 74
4-3 Esterification process of PMAA with MPEG for the synthesis of polycarboxylate
copolymers .......................................................................................................................... 76
4-4 1H-NMR of polycarboxylate copolymer via conventional radical polymerization... 77
4-5 1H-NMR of poly (methacrylic acid) or PMAA ....................................................... 80
4-6 1H-NMR of polycarboxylate copolymer via esterification process ...................... 81
5-1 Chemical structures of methoxy poly (ethylene glycol) methacrylate (n= 12, MPEGMA550; n = 24, MPEGMA950, and n = 48, MPEGMA 2000), Methacrylic acid (MAA), and CPADB RAFT agent used for synthesis random copolymers of PMPEGMA - random - PMAA................................................................. 91

5-2 A series of GPC chromatogram of RAFT PMPEGMA550 - r - PMAA.................. 96
5-3 A series of GPC chromatogram of RAFT PMPEGMA950 - r - PMAA............... 97
5-4 A series of GPC chromatogram of RAFT PMPEGMA2000 - r - PMAA............. 97
5-5 A series of GPC chromatogram of RAFT PMPEGMA950 - r - PMAA (molar ratio = 1:3) with different ratios of CPADB/AIBN................................................................. 99
5-6 Molecular images of synthesized polycarboxylate copolymers via RAFT polymerization ........................................................................................................... 100
5-7 1H-NMR spectra of (a) sodium methacrylate monomer, (b) MPEGMA950 monomer, and (c) PMPEGMA950 - random - PMAA ............................................................................. 101
5-8 13C-NMR spectra of (a) sodium methacrylate monomer, (b) MPEGMA950 monomer, and (c) PMPEGMA950 - random - PMAA ............................................................................. 104
5-9 1H-NMR of PMPEGMA950 by RAFT polymerization...................................... 106
5-10 1H-NMR of PMPEGMA950 - b - PMAA by RAFT polymerization............. 107
5-11 GPC chromatograms (a) PMPEGMA950 (Mn = 11,000, PDI = 1.26) and its series of PMPEGMA950 - b - PMAA, (b) PMPEGMA950 (Mn = 17,500, PDI =1.32) and its series of PMPEGMA950 - b - PMAA ......................................................................................... 110
5-12 GPC chromatogram of polycarboxylate copolymer and polycarboxylate terpolymer synthesized via RAFT polymerization................................................................. 112
5-13 1H-NMR of polycarboxylate terpolymer by RAFT polymerization ............. 113
5-14 MALDI-TOF mass spectrum of polycarboxylate terpolymer before purification. 115
5-15 MALDI-TOF mass spectrum of polycarboxylate terpolymer before purification + 1 wt. % of 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester monomer...... 116
5-16 MALDI-TOF Mass spectrum of polycarboxylate terpolymer before purification + 5 wt. % of 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester monomer...... 116

6-1 Flocs formation by cement particles (a) without dispersing admixture e.g. superplasticizers and (b) dispersion of flocs after addition of dispersing admixture .... 123
6-2 (a) Instrument for a slump test in lab scale, and (b) an example of cement spread for a slump test measurement ................................................................. 127

6-3 (a-c) Sands, rocks, and cement used in an actual concrete test at Euclid Chemical Company, and (d) a concrete mixer ................................................................. 129

6-4 Actual slump test at Euclid Chemical Company .................................................. 129

6-5 Air content measurement by pressure method ................................................... 131

6-6 Compressive strength for concrete (a) concrete cylinders, (b) preparation of fresh concrete in cylinders, and (c) Forney compression machine ......................................... 132

6-7 Cement slump tests on the effect of polycarboxylate superplasticizers synthesized via RAFT polymerization with different side chain lengths ........................................... 135

6-8 Cement slump tests on the effect of polycarboxylate superplasticizers (PMPEGMA550 - random - PMAA) with different molar ratios of monomers .......... 138

6-9 Cement slump tests on the effect of polycarboxylate superplasticizers (PMPEGMA950 - random - PMAA) with different molar ratios of monomers .......... 139

6-10 Cement slump tests on the effect of polycarboxylate superplasticizers (PMPEGMA2000 - random - PMAA) with different molar ratios of monomers .......... 140

6-11 Conformation model of polycarboxylate copolymer in water and in alkaline and high ion concentration liquid ................................................................. 142

6-12 Slump diameter in various mixing times of fresh cement with different ratios of unreacted monomers mixed with RAFT PMPEGMA - random - PMAA ............... 145

6-13 Molecular images of PMPEGMA950 - random – PMAA with different CAPDB/AIBN molar ratios [(1.1:1 in Run 9), (3.3:1 in Run 10), and (6.6:1 in Run 11) in Table 5-4] ......................................................................................................................... 147

6-14 Cement slump tests on the effect of polycarboxylate superplasticizers (PMPEGMA950 - random - PMAA) with different molecular weights ............... 148

6-15 Bridging effect of large polycarboxylate copolymers on the flocculation of cement particles ........................................................................................................ 150

6-16 Cement slump tests on the effect of molecular weight distribution of polycarboxylate copolymers (PMPEGMA950 - random – PMAA) ................................. 151

6-17 Molecular images of PMPEGMA950 - random - PMAA (Run 10 in Table 5-4) and a series of PMPEGMA950 – block – PMAA (Run 3 – Run 7 in Table 5-3) ............... 154
6-18 Cement slump tests on the effect of polycarboxylate copolymer structures (PMPEGMA950 - random - PMAA and PMPEGMA950 - block - PMAA) ................. 155

6-19 Cement slump tests between polycarboxylate copolymer and polycarboxylate terpolymer ........................................................................................................ 157

6-20 Defoaming characteristic test: (a) Polycarboxylate 1, (b) RAFT polycarboxylate copolymer, (c) RAFT polycarboxylate copolymer with tributyl phosphate, and (d) RAFT polycarboxylate terpolymer ........................................................................................................ 158

7-1 Chemical structures of monomers (a) Methoxy poly (ethylene glycol) methacrylate (n = 11, MPEGMA 475; n = 24, MPEGMA 950), (b) Butyl acrylate (BA), and RAFT agent (c) CPADB ........................................................................................................ 170

7-2 GPC chromatograms of samples withdrawn during RAFT homopolymerization of PEGAMA 475 (run 1 in Table 7-1) ........................................................................................................ 180

7-3 GPC chromatograms of samples withdrawn during RAFT homopolymerization of PEGAMA 950 (run 2 in Table 7-1) ........................................................................................................ 180

7-4 GPC chromatograms of PMPEGMA 475 and series of PMPEGMA 475 - b - PBA 182

7-5 GPC chromatograms of PMPEGMA 950 and series of PMPEGMA 950 - b - PBA 182

7-6 1H-NMR of PMPEGMA 475/950 ........................................................................................................................................................................ 183

7-7 1H-NMR of PMPEGMA 475/950 – b – PBA ........................................................................................................................................ 184

7-8 TGA of (a) PMPEGMA 475 and a series of PMPEGMA 475 - b - PBA, (b) PMPEGMA 950 and a series of PMPEGMA 950 - b - PBA ............................................ 186

7-9 Decomposition temperatures of (a) PMPEGMA 475 and a series of PMPEGMA 475 - b - PBA, (b) PMPEGMA 950 and a series of PMPEGMA 950 - b - PBA ............ 188

7-10 TGA of mixed metal-citric acid complexes for finding the processing temperature of their carbonate and oxide formation ........................................................................ 191

7-11 Summary of onset temperature for carbonate and oxide formation of mixed metal-citric acid complexes for fabrication of mesoporous materials ......................... 192

7-12 FT-IR spectra of PMPEGMA 475 – b - PBA micelle templated metal nitrate-citric acid film containing nickel : cobalt = 50:50 for (a) as solution cast, (b) carbonate formation at 240 °C for 1 h, and (c) oxide formation at 350 °C for 30 min .......... 194
7-13 AFM images of micelle templated (a) Ni(CO$_3$)$_y$, (b) Ni$_{0.25}$Co$_{0.75}$(CO$_3$)$_y$, (c) Ni$_{0.50}$Co$_{0.50}$(CO$_3$)$_y$, (d) Ni$_{0.75}$Co$_{0.25}$(CO$_3$)$_y$, and (e) Co(CO$_3$)$_y$, (Scale bar = 200 nm in all micrographs) .................................................................................................................. 196

7-14 AFM images of PMPEGMA 475 – b - PBA micelle templated mesoporous (a) NiO, (b) Ni$_{0.25}$Co$_{0.75}$O$_2$, (c) Ni$_{0.50}$Co$_{0.50}$O$_2$, (d) Ni$_{0.75}$Co$_{0.25}$O$_2$, and (e) Co$_3$O$_4$. (Scale bar = 200 nm in all micrographs) .................................................................................................................. 197

8-1 Chemical structure of the conventional latex ........................................................................... 204

8-2 FT-IR spectra of (a) the PMPEGMA and (b) the PMPEGMA-b-POA............................... 209

8-3 $^1$H NMR of the PMPEGMA in CDCl$_3$ ............................................................................... 210

8-4 $^1$H NMR of the PMPEGMA-b-POA................................................................................ 211

8-5 GPC chromatograms of the PMPEGMA and PMPEGMA-b-POA ............................. 212

8-6 Steady-shear viscosity for latex solutions thickened with homopolymer (PMPEGMA) in different concentrations .................................................................................................................. 214

8-7 Steady-shear viscosity for latex solutions thickened with 3 wt. % of homopolymer (PMPEGMA) and its block copolymer (PMPEGMA-b-POA) .............................................................. 215

8-8 Steady-shear viscosity for latex solutions thickened with 5 wt. % of homopolymer (PMPEGMA) and its block copolymer (PMPEGMA-b-POA) .............................................................. 216

8-9 Steady-shear viscosity for latex solutions thickened with 10 wt. % of homopolymer (PMPEGMA) and its block copolymer (PMPEGMA-b-POA) .............................................................. 216
## LIST OF SCHEMES

<table>
<thead>
<tr>
<th>Scheme</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1 General mechanism of controlled free radical polymerizations</td>
<td>41</td>
</tr>
<tr>
<td>2-2 Mechanism of a RAFT polymerization</td>
<td>44</td>
</tr>
<tr>
<td>5-1 Chemical structures of methoxy poly (ethylene glycol) methacrylate (n = 24, MPEGMA950), Methacrylic acid (MAA), CPADB RAFT agent, and macro RAFT agents (PMPEGMA950) used for synthesis block copolymers of PMPEGMA950 - b - PMAA</td>
<td>94</td>
</tr>
<tr>
<td>5-2 Chemical structures of MPEGMA950 (n = 24), Methacrylic acid (MAA), 2-methyl acrylic acid (dibutoxy-phosphoryloxy) – alkyl ester, and CPADB RAFT agent, used for synthesis polycarboxylate terpolymer via RAFT polymerization</td>
<td>95</td>
</tr>
<tr>
<td>7-1 Chemical structures of methoxy poly (ethylene glycol) methacrylate (n = 11, MPEGMA 475; n = 24, MPEGMA 950), n-Butyl acrylate (BA), CPADB RAFT agent, and macro RAFT agents (PMPEGMA 475/950) used for synthesis block copolymers of PMPEGMA - b - PBA</td>
<td>175</td>
</tr>
<tr>
<td>8-1 (a) Synthesis of the PMPEGMA using RAFT homopolymerization and (b) synthesis of the PMPEGMA-b-POA using RAFT copolymerization</td>
<td>208</td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1 Oxide constituent compositions of Ordinary Portland Cement</td>
<td>10</td>
</tr>
<tr>
<td>2-2 Oxide compound compositions of Ordinary Portland Cement</td>
<td>10</td>
</tr>
<tr>
<td>2-3 Duration of each major oxide component in cement to reach 80% of hydration reaction</td>
<td>16</td>
</tr>
<tr>
<td>3-1 MPEGs and MPEGMAs group frequencies by FT-IR</td>
<td>55</td>
</tr>
<tr>
<td>3-2 $^1$H-NMR assignment of MPEGMA 550</td>
<td>56</td>
</tr>
<tr>
<td>3-3 Peak assignment in MALDI-TOF mass spectrum of MPEGMA 550</td>
<td>57</td>
</tr>
<tr>
<td>3-4 $^1$H-NMR assignment of MPEGMA 950 and MPEGMA 2000</td>
<td>58</td>
</tr>
<tr>
<td>3-5 Peak assignment in MALDI-TOF mass spectrum of MPEGMA 950</td>
<td>60</td>
</tr>
<tr>
<td>3-6 2-Methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester group frequencies by FT-IR</td>
<td>61</td>
</tr>
<tr>
<td>4-1 Summary of the synthesis of polycarboxylate copolymers synthesized via conventional radical polymerization between MPEGMA 950 and MAA monomer</td>
<td>72</td>
</tr>
<tr>
<td>4-2 Summary of esterification reaction for the synthesis of polycarboxylate copolymers</td>
<td>76</td>
</tr>
<tr>
<td>4-3 Molecular weights and PDI of polycarboxylate copolymers via conventional radical copolymerization</td>
<td>77</td>
</tr>
<tr>
<td>4-4 Molecular weights and PDI of poly (methacrylic acid) or PMAA</td>
<td>79</td>
</tr>
<tr>
<td>4-5 Molecular weights and PDI of polycarboxylate copolymers via esterification reaction between PMAA and MPEG</td>
<td>79</td>
</tr>
<tr>
<td>5-1 Copolymers synthesized via RAFT polymerization between MPEGMA (550, 950, and 2000) and MAA monomer</td>
<td>89</td>
</tr>
<tr>
<td>5-2 Synthesis summary of macro RAFTs PMPEGMA 950</td>
<td>92</td>
</tr>
</tbody>
</table>
5-3 Summary of block copolymerization of PMPEGMA and PMAA via RAFT polymerization ......................................................... 93

5-4 $^1$H resonance assignments of (a) sodium methacrylate monomer, (b) MPEGMA monomer, and (c) PMPEGMA - random - PMAA................................................................. 102

5-5 $^{13}$C resonance assignments of (a) sodium methacrylate monomer, (b) MPEGMA monomer, and (c) PMPEGMA - random - PMAA................................. 105

5-6 Summary of synthesized block copolymers PMPEGMA950 - b - PMAA: molecular weights and their poly dispersity index (PDI) ................................................................. 109

5-7 $^1$H resonance assignments of polycarboxylate terpolymer (PMPEGMA - co - PMAA - co - poly [2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester]) synthesized via RAFT polymerization ......................................................... 114

6-1 Slump diameter in various mixing times of fresh cement with different ratios of unreacted monomers mixed with RAFT PMPEGMA-random-PMAA ............... 144

6-2 Summary of molecular weights and PDI of polycarboxylate copolymers (PMPEGMA950 - random – PMAA) synthesized by different methods .................... 151

6-3 Lab shake test of different type of polycarboxylate admixtures with/without defoaming agent.................................................................................. 158

6-4 Actual concrete tests for polycarboxylate admixtures without air entraining agent 161

6-5 Actual concrete tests for polycarboxylate admixtures with air entraining agent ..... 162

7-1 Synthesis summary of RAFT poly (MPEGMA) .................................................. 172

7-2 Summary of Block Copolymerization of PMPEGMA and PBA via RAFT polymerization ................................................................................. 174

7-3 Precursor compositions and processing conditions for fabrication of cobalt oxide, nickel oxide and their mixed metal oxide (Ni$_x$Co$_{1-x}$O$_3$) composites.............................. 177

7-4 $^1$H resonance assignments of PMPEGMA 475/950 ........................................ 184

7-5 $^1$H resonance assignments of PMPEGMA 475/950 - b - PBA ................... 185

7-6 Calculation of mole fraction of PBA in block copolymer series PMPEGMA 475/950 - b - PBA by using $^1$H-NMR................................................................. 189

7-7 Summary of synthesized amphiphilic block copolymers PMPEGMA 475/950 - b - PBA; molecular weight, decomposition temperature, and mole fraction of PBA........ 190

xxi
8-1 $^1$H NMR resonance assignments of the PMPEGMA and PMPEGMA-$b$-POA ....... 210
CHAPTER I
INTRODUCTION

Methoxy poly (ethylene glycol) methacrylate or MPEGMA is a water soluble monomer that has attracted a great deal of attention over the years. When it is combined with other monomers to create various types of copolymers, these can be used for many industrial applications for example; dispersants, stabilizers, thickeners, emulsifiers \(^1\), and stimuli responsive materials \(^2,3\).

In this research work, a reversible-addition fragmentation chain transfer (RAFT) polymerization was a main method in order to fabricate numerous types of copolymers in different fascinating applications because it was simple compared to other controlled free radical polymerization techniques (such as nitroxide mediated polymerization (NMP) and atom transfer radical polymerization (ATRP)) with controlled molecular weights, controlled block locations, and narrow molecular weight distribution \(^4-9\). The applications by using MPEGMA-based copolymers in this research work include new polycarboxylate admixtures for concrete, new amphiphilic block copolymers for mesoporous materials, and a new fatty acid-based thickener for water-based coating system. The first application by using MPEGMA-based copolymers is about a new admixture in concrete. During a concrete processing, especially concrete in the truck
mixture at the jobsite needs a good flowability that users can get the most advantage form. Superplasticizers have been widely used on that purpose because they provide an outstanding flowability of the fresh concrete. Polycarboxylate superplasticizers (comb-like copolymers, with grafted poly (ethylene oxide) or PEO, pendant groups) have been proven to be effective additive to enhance flowability and additional strength of concrete \(^{10-12}\). The structure of polycarboxylate admixture consists of two different parts: A main chain molecule that includes the surface active portion (carboxylic group) and a side chain (grafted poly (ethylene oxide)). Previously, there were many studies about the influence of the side chain length in polycarboxylate copolymers on dispersion properties. Nawa et al. \(^{13}\) reported that the short side chain graphed to the back bone main chain showed good dispersing ability in concrete. In contrast to Yamada et al. \(^{14}\), they discovered that polycarboxylate copolymers with longer side chains exhibit higher dispersing power. In such cases, the conclusions were based on an assumption that the comb-like copolymers with different side chain lengths had been fully adsorbed.

Currently, polycarboxylate admixtures need several more additives for stabilization in the concrete system. The main problem is air which can be astutely characterized as good and bad air. Good air is proper air entrainment in which air bubbles of a proper size (small) and isolated from each other provide the ability for the cement or concrete to expand and contract without breaking the cement matrix. This provides for freeze-thaw resistance. The bad air is caused by foaming that spirals out of control during the mixing of carboxylate admixture. The resulting bubble formation is large and randomly distributed leading to considerable reduction in strength of concrete. As a consequence of bad air, defoaming agents are added to control or eliminate the
foaming. However, it is a two step-process for adding polycarboxylate admixtures and defoaming agents in the concrete mixture. For these reasons, the challenge is to fabricate a new type of polycarboxylate admixture for concrete that having both ability to increase cement/concrete fluidity and ability to eliminate bad bubbles at the same time. It may require an additional separate step for another admixture, air entraining agent, to promote good air once again into the concrete/cement. Therefore, various types of polycarboxylate using MPEGMA-based copolymers were synthesized by varying charge densities, side chain length of PEO repeating units of MPEGMA, molecular weights, and their molecular weight distributions in order to study the effect of those variables on the fluidity of cement/concrete. In addition, a new functional defoaming agent acting as an *in-situ* defoaming agent was copolymerized into a new polycarboxylate admixture. The defoaming ability, the cement/concrete fluidity, and mechanical properties were performed.

Copolymers synthesized in the second part comprise of hydrophilic block and hydrophobic block. Specifically, these types of copolymers can be called amphiphilic block copolymers. Recently, there were uses of amphiphilic block copolymers as stimuli-responsive materials e.g. chemical stimuli or physical stimuli. Moreover, the amphiphilic block copolymers have also been used as templates in order to generate mesoporous metal oxide materials 15-17. For instance; cobalt oxide can be used as an electrode material for lithium-ion batteries and nickel oxide is broadly used in many applications including electro-chromic display devices, fuel cell electrodes, etc.17 The most common method to receive porous templates is evaporation induced self-assembling (EISA) soft-templating method by using the benefit or micelle arrangement of amphiphilic block copolymers 18.
Due to the advantages of amphiphilic block copolymers, this part of the research work would like to focus on synthesizing a new type of block copolymer by using MPEGMA-based copolymer for mixed metal oxide (nickel and cobalt) mesoporous templates for battery application. MPEGMA was first homopolymerized and acted as hydrophilic part. Butyl acrylate (BA) as a hydrophobic part was then further block copolymerized to form poly [ (methoxy poly (ethylene glycol) methacrylate] - block - poly (butyl acrylate) [PMPEGMA – b – PBA] by RAFT polymerization. This is a new type of block copolymer in the fabrication of mesoporous metal oxide area. The challenge was to achieve the well-distributed arrangement between micelles of these block copolymers and mixed metal materials. In addition, to overcome the stability of mixed metal oxide structures after gradually increasing the temperature to remove block copolymer micelles was another challenge for this part of research work.

Copolymers used in the last part of this work are also amphiphilic block copolymers in the application of thickeners in water-based coating system. Generally, there are three main types of thickener for water-based system including celluloses, acrylic thickeners [Alkali Swellable Emulsions (ASE)/Hydrophobically modified Alkali Swellable Emulsions HASE], and associative thickeners [Hydrophobically modified Ethylene oxide Urethane thickeners (HEUR)]

Celluloses are not so popular because it is easy to biodegrade. ASE and HASE normally contribute strong shear thinning, anti-setting, and anti-sagging properties, but they are pH sensitive. In contrast to acrylic thickeners, HEUR is widely used because of a non-ionic in nature, thus being pH-independent. Due to a great benefit of non-ionic associative thickener, the last part of this work would like to concentrate on fabrication a new type of block copolymer by using
MPEGMA-based copolymer. MPEGMA was first homopolymerized and acted as hydrophilic part. In case of hydrophobic part, a fatty acid might be a good candidate. Fatty acids are bio-renewable resources, which are inexpensive and applicable in many industrial applications. Soucek group has been used various types of free fatty acids and triglycerides from many vegetable oils for the alkyd synthesis \(^{23-25}\). Malti and De \(^{26}\) illustrated the possibility to polymerize various kinds of fatty acid containing monomers from renewable resources. For these reasons, oleic acid (OA) was chosen as a hydrophobic part and was then further block copolymerized to form poly [(methoxy poly (ethylene glycol) methacrylate] - block - poly (oleic acid) [PMPEGMA – b – POA] by RAFT polymerization. The rheological properties were investigated.
CHAPTER II

BACKGROUND

2.1 Concrete

Concrete is the most widely used construction material nowadays. Communities around the world rely on concrete as a safe, strong and simple building material. It is used in all types of construction; from the domestic work to gigantic buildings. Although concrete is not strong and tough as steel, it is still the most widespread used engineering material. This may be because concrete has extraordinary resistance to water. The ability of concrete to tolerate the water without serious degradation, even better than wood and ordinary steel. This makes it for a perfect material for construction. Moreover, the use of concrete is the affluence of structural concrete elements that can be designed into different shapes and sizes. This is for the reason that the fresh concrete is of a plastic consistency, which allows it to flow easily into prefabricated formwork. Furthermore, in case of the economic point of view, concrete is usually the most affordable because it is commonly obtainable in most parts of the world. Concrete is usually made up of different components i.e. aggregate, water, cement, and admixtures. The aim is to mix these materials in order to make concrete to be easy to transport, place, compact, finish, and finally be harden to give a strong and durable product. The amount of each material
(i.e. cement, water, admixtures and aggregates) affects the properties of hardened concrete. When cement powder is mixed with water, it forms a cement paste. This paste acts like glue and holds or bonds the aggregates together. There are two basic types of aggregates: 1) coarse aggregate—crushed rock, gravel or screenings and 2) fine aggregate—fine and coarse sands and crusher fines. Aggregates should be strong and hard. These properties contribute to a stronger final hardened concrete. Also; they should be chemically inactive, durable to stand up to wear, tear and weathering. For the cement, the most commonly used and versatile cement is Portland cement. It was invented in 1824 by Joseph Aspdin. Since then, the Portland cement has receive notably reputation to be the most well-known construction material throughout the World. It has been substituted the old cementitious materials that were originally made up of a mixture between calcined clay and lime. The invention of Portland cement brought the vanguard of construction material. It provided everyone’s satisfaction for a durable and strong binder for constructions \(^{28,29}\). In the following sections, many interesting topics will be explained in detail in order to understand the behavior of cement when it interacts with other components e.g. water and concrete admixtures. Manufacture and component of cement will be mentioned in section 2.1.1 to 2.1.4. Hydration reaction of cement and development of cement paste will be discussed in section 2.1.5 to 2.1.7. Followed by types of concrete admixtures and their mechanisms in section 2.2 to 2.5.
2.1.1 Manufacture of cement

The raw materials used in the manufacture of Portland cement are comprised of:

- **Calcareous materials** – which are calcium-rich materials such as limestone and chalk.
- **Argillaceous materials** – which are silica-alumina-rich materials i.e. silica, alumina, clay, and shale.
- **Iron oxide materials** – for example iron ore and laterite.

Cement can normally be manufactured by two following methods:

**Wet process**:

In this process, the raw materials like chalk, clay, and iron oxide are ground in a wet ball mill containing 29% - 33% water before feeding to the kiln. The water will enable the starting materials to be mixed homogeneously. Nevertheless, this method is no longer used at the present time because it needs much higher fuel consumption for getting off the water during the process.

**Dry process**:

In this process, the raw materials e.g. lime stone, shale, and iron oxide are mixed and ground in a dry environment without water involved before feeding to the kiln. This is the modern method to produce Portland cement nowadays. This is because it is a less complicated process and needs less fuel consumption comparing to the wet process.
Once these raw materials are mixed (either from wet or dry process), they will be fed into the kiln. The kiln, which is normally used, is a rotary kiln. The processing temperature is around 1,400 – 1,500 °C. In this temperature, all materials will be entirely mixed and transform to “clinker” (lumpy burned residue). After cooling down the clinker, it will be mixed and ground again with gypsum. Gypsum is added around 3% - 6% to retard the cement solidification, leading to the convenient usage in the future. Finally, it is the step of storage of different types of cement in silos 32.

2.1.2 Basic compositions of cement

There are several reaction steps once all starting raw materials of cement are fed into the kiln. The water will evaporate out of the ingredients. Then, CO₂ will emit from limestone and chalk (calcareous materials) and leave CaO as a residual compound. From this point, there are some chemical reactions between CaO from calcareous materials and argillaceous materials with iron oxide materials, in which these reactions will lead to basic components of cement 32.

Portland cement obtained from previous steps is comprised of two types of oxide groups;

*The major oxide constituents* – CaO, SiO₂, Al₂O₃, and Fe₂O₃ (90 wt. % of cement).

*The minor oxide constituents* – MgO, K₂O, Na₂O, TiO₂, P₂O₅, and gypsum.
Table 2-1 Oxide constituent compositions of Ordinary Portland Cement

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Approximate Content (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Major oxide constituents</strong></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>60 – 67</td>
</tr>
<tr>
<td>SiO₂</td>
<td>19 - 25</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>3 - 8</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>4 - 6</td>
</tr>
<tr>
<td><strong>Minor oxide constituents</strong></td>
<td></td>
</tr>
<tr>
<td>MgO</td>
<td>0.1 – 5.5</td>
</tr>
<tr>
<td>K₂O + Na₂O</td>
<td>0.3 – 0.5</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0.1 – 0.4</td>
</tr>
<tr>
<td>P₂O₅</td>
<td>0.1 – 0.2</td>
</tr>
<tr>
<td>SO₃</td>
<td>1.0 – 3.0</td>
</tr>
</tbody>
</table>

The major oxide constituents as shown in Table 2-1 will react with each other to form four important oxide compounds during clinker formation as mentioned previously.

2.1.3 Major oxide compounds of ordinary Portland cement

Table 2-2 Oxide compound compositions of Ordinary Portland Cement

<table>
<thead>
<tr>
<th>Chemical Compound</th>
<th>Chemical Formula</th>
<th>Abbreviated Formula</th>
<th>Approximate Content (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tricalcium Silicate</td>
<td>3 CaO · SiO₂</td>
<td>C₃S</td>
<td>40 – 55</td>
</tr>
<tr>
<td>Dicalcium Silicate</td>
<td>2 CaO · SiO₂</td>
<td>C₂S</td>
<td>15 – 25</td>
</tr>
<tr>
<td>Tricalcium Aluminate</td>
<td>3 CaO · Al₂O₃</td>
<td>C₃A</td>
<td>5 – 11</td>
</tr>
<tr>
<td>Tetracalcium Aluminoferrite</td>
<td>4 CaO · Al₂O₃ · Fe₂O₃</td>
<td>C₄AF</td>
<td>14 - 20</td>
</tr>
</tbody>
</table>
Table 2-2 shows four main oxide compounds of Portland cement. Detail of each compound will be described in following section.

*Tricalcium silicate (C₃S):*

C₃S has a hexagonal shape and its color is grey (shown below in Figure 2-1). C₃S hydrates and hardens rapidly within 2-3 h. Therefore, it is mainly responsible for the early strength development.

*Dicalcium silicate (C₂S):*

C₂S has a round shape and its color is black (shown below in Figure 2-1). C₂S hydrates and hardens slowly and contributes to late strength development. However, in the long term, the strength by C₂S will be close enough to that of C₃S.

![Figure 2-1 The appearance of C₃S (hexagonal shape) and C₂S (round black shape) in Ordinary Portland cement](image)

*Tricalcium Aluminate (C₃A):*

C₃A hydrates faster than silicate compounds (C₃S and C₂S) and may cause the flash set, leading to a lot of heat generated around 850 J/g. The addition of gypsum can
prevent a flash set by regulating setting and hardening behavior of C₃A as well as C₃S. However, C₃A contributes relatively low to the strength development.

*Tetracalcium Aluminoferrite* (*C₄AF)*:

C₄AF hydrates quickly but gives very little to the strength development.

2.1.4 Minor oxide compounds of ordinary Portland cement

*Gypsum* (*CaSO₄·2H₂O)*:

Gypsum is added to control the cement setting and hardening behavior during the grinding of clinker. In addition, gypsum is also known as a “set retarder”, which retards the flash setting effect of C₃A and C₃S. Amount of gypsum added should be a proper quantity that in order to get a little cement shrinkage and achieve maximum cement strength.

*Magnesium oxide* (*MgO)*:

The raw materials of Portland cement is mostly comprised of MgCO₃. When it is combusted, it will give MgO and CO₂. CO₂ will emit and some parts of MgO will be mixed to be clinker. The residual of MgO can react with water, hydration reaction, leading to the expansion of cement volume and can expand cracks in the concrete.

*Alkali oxides* (*Na₂O, K₂O)*:

They might give a disadvantage in case of using with some types of aggregate. Some types of aggregate mixed with cement can react with alkali oxides, cause the expansion of the concrete and can possibly make the crack to the concrete.
2.1.5 Setting and hardening of cement

Figure 2-2 shows the process of setting and hardening of cement. Cement sets and provides the strength of the concrete within a reasonable time. When cement is mixed with water, it will be in a state of liquid paste, which can be called “Dormant Period”. After that, this cement paste becomes a little hard and cannot flow easily. This point it can be called “Initial Set”. So, it can be defined that the “Initial Setting time” is the time once the cement is mixed with the water to the time which the cement paste remains in plastic condition and can be molded into any shape until it reaches the initial set. The setting of cement will continue and become harder until it reaches the “Final Set”. So, it
can also define the “Final Setting time” is the time during which the cement paste loses its plasticity and becomes rigid. From this point, the cement paste still hardens and stiffens, also could resist more weight when the time goes by. This process is called “Hardening”. By and large, setting refers to a change from a fluid to a solid state and hardening refers to the gain in strength of a set cement paste.

2.1.6 Hydration reactions of cement

When cement particles have an interaction with water, there is a surface charge development owning to a polar characteristic of water. Ionization happens, leading to ions transfer in the system such as $\text{Ca}^{2+}$, $\text{H}^-\text{O}^-$, $\text{K}^+$, $\text{Na}^+$, $\text{Mg}^{2+}$, $\text{SO}_4^{2-}$, etc. Besides interparticle forces, cement paste becomes stiffen and harden because of chemical reactions known as cement hydration. Cement hydration reactions are very complicated, thus it is good to mention the hydration reaction of calcium silicate phases (C$_3$S and C$_2$S) and the aluminate phases (C$_3$A and C$_4$AF) separately $^{35}$.

*Hydration of Calcium Silicates (C$_3$S and C$_2$S)*

\[
2(3\text{CaO} \cdot \text{SiO}_2) + 6\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + 3\text{Ca(OH)}_2 \quad (2-1)
\]

or $2\text{C}_3\text{S} + 6\text{H}_2\text{O} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + 3\text{Ca(OH)}_2$

\[
2(2\text{CaO} \cdot \text{SiO}_2) + 4\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + \text{Ca(OH)}_2 \quad (2-2)
\]

or $2\text{C}_2\text{S} + 4\text{H}_2\text{O} \rightarrow \text{C}_3\text{S}_2\text{H}_3 + \text{Ca(OH)}_2$

From those reactions, it can be noticed that there are two important products; Calcium Silicate Hydrate (CSH), which is the main glue that binds sand and aggregate
particles together in concrete and Ca(OH)$_2$, which gives the basic property to the cement paste (pH ≈ 12.5) to prevent the iron rusting.

*Hydration of Tricalcium Aluminate (C$_3$A):*

C$_3$A hydration will happen immediately when cement interacts with water, leading to the sudden of cement hardening.

$$3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 6\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O} \quad (2-3)$$

or $C_3A + 6H_2O \rightarrow C_3AH_6$

For retarding this reaction, “gypsum” (CaSO$_4 \cdot 2H_2O$) is usually added in the cement grinding process. It reacts with C$_3$A, turning into a protective layer on the surface of C$_3$A called “Ettringite”.

$$C_3A + 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + 30\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O} \quad (2-4)$$

“Ettringite” layer will also retard the C$_3$A hydration. So, at the initial phase, cement paste hardening will vastly depend on hydration of C$_3$S and C$_2$S. When there are ettringite layers, the solid volume will increase, causes lots of pressure and then leading to break those ettringite layers. In this moment, hydration of C$_3$A can happen. In the meantime, new ettringite layers can be created and also retard the hydration of C$_3$A again. This process will stop until there are not sufficient sulphate ions to produce ettringite. Therefore, once the available sulphate has been consumed, the ettringite reacts with C$_3$A to create the new content compound known as “monosulphate”.


Hydration of Tetracalcium Aluminoferrite (C₄AF):

Hydration of C₄AF will happen at the beginning once water reacts with cement. C₄AF reacts with gypsum and Ca(OH)₂, producing sulfoaluminate and sulfoferrite.

\[ 4\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3 + \text{CaSO}_4 \cdot 2\text{H}_2\text{O} + \text{Ca(OH)}_2 \rightarrow 3\text{CaO(Al}_2\text{O}_3 \cdot \text{Fe}_2\text{O}_3)\cdot 3\text{CaSO}_4 \]  

(2-5)

Table 2-3 Duration of each major oxide component in cement to reach 80% of hydration reaction

<table>
<thead>
<tr>
<th>Major Oxide Compounds</th>
<th>Time (Day)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S</td>
<td>10</td>
</tr>
<tr>
<td>C₂S</td>
<td>100</td>
</tr>
<tr>
<td>C₃A</td>
<td>6</td>
</tr>
<tr>
<td>C₄AF</td>
<td>50</td>
</tr>
</tbody>
</table>

2.1.7 Development of cement paste structure

![Figure 2-3 Illustration of hydration of cement paste](image)

Figure 2-3 Illustration of hydration of cement paste
According to the hydration of individual major oxide compositions mentioned in previous part, it can be seen that the main products are CSH gel and ettringite, which cover the surface of cement particles. This corresponds to the “Dormant Period” in setting and hardening of cement process. In this state, it will be in a state of liquid paste and loss of workability is comparatively low. When the dormant period finishes, the “Initial set” starts. It is the stage that CSH gel covered on the cement particles begin to break. Thus, the hydration continues and the amount of products from this hydration reaction is much greater than before. This leads to fulfill the space between cement particles, then contacting to each other, causing the setting of the cement paste. When the time goes by, there will be a very high concentration of the products from hydration reactions, which will impede the movement of cement particles and end up with the “Final set”, in which the cement paste becomes rigid. Setting is largely due to the hydration of C₃S and it represents the development of hydrate structure, which eventually results in compressive strength. This can be illustrated in Figure 2-3.

2.2 Admixtures in concrete

Admixtures have been well reviewed in many publications 34, 35. Chemical admixtures are compositions either liquid or solid that are added to concrete, mortars or cementitious grouts whilst in the unset and plastic state in order to change the properties of these materials in that state and/or when they have changed to a hard solid. Admixtures are not the same as additives, which are chemicals pre-blended with the cementitious mix. These materials for instance are added to the cement during its manufacture to assist in grinding, give pigmentation and control the setting characteristics e.g. gypsum 31.
There are two main groups of admixtures; mineral and chemical admixtures. Mineral admixtures reduce cost, reduce permeability, increase strength and change other concrete properties e.g. fly ash, silica fume, and ground granulated blast furnace slag. Chemical admixtures reduce the cost of construction, modify the properties of concrete and improve the quality of concrete during mixing, transportation, placing and curing. There are various types of chemical admixtures.

2.2.1 Air-entraining agents

They introduce tiny air bubbles in concrete during the mixing process. It helps protect against damage caused by repeated freezing and thawing cycles. It also imparts better workability, improved homogeneity, decreased segregation and decreased bleeding. More than 80% of Portland-cement concrete pavements in the United States contain air-entrained admixtures. Entrapped air, are large air voids while entrained air, are tiny voids between 10 to 1000 micrometers. The admixture may be a liquid added during batching or a powder blended with the cement.

2.2.2 Defoaming agents

These materials are used when the volume of entrained air is more than the desired amount. Normally, they will be used with air-entraining agents to control freeze-thaw stability.
2.2.3 Accelerating admixtures

These materials speed up the cement hydration process so resulting in shortened setting times, and higher earlier strengths, they are of practical significance for both site concreting and pre-casting.

2.2.4 Retarding admixtures

These materials reduce the rate of hydration of cement, delay the stiffening of concrete and mortars, reduce the incidence of “Cold Joints” when one layer of concrete is placed upon another, and maintain workability for longer at higher ambient temperatures.

2.2.5 Waterproofing admixtures

They reduce the capillary absorption of water into the hardened concrete. They reduce surface absorption and water permeability of the concrete by acting on the capillary structure of the cement paste. They will not significantly reduce water penetrating through cracks or through poorly compacted concrete.

2.2.6 Corrosion-inhibiting admixtures

They can significantly reduce maintenance costs of reinforced concrete structures throughout a typical service life of 40-60 years. Structures especially at risk are those exposed to a maritime environment or other situations where chloride penetration of the concrete is likely. Such structures include jetties, wharves, mooring dolphins, and sea walls.
2.2.7 Dispersing admixtures

Dispersing admixtures are one of the most important concrete admixtures nowadays. They are good in terms of concrete processing. This is may be because they improve concrete flowability. These chemical molecules will adsorb onto the surface of cement particles in a way that causes them to distribute uniformly in the aqueous phase, leading to predominant improvement of fresh cement fluidity. This interaction may have an effect on the plastic viscosity or cohesion of the cement mix. They are normally used to increase the fluidity of the cement mix at a given water content due to plasticizing action. Additionally, they are able to reduce the water content of the cement mix at a given fluidity, leading to an improvement of concrete strength and durability. Superplasticizers (also called high range water-reducing admixtures) are the most famous these days among other dispersing admixtures. They can decrease three to four times of the mixing water at a given concrete mixture compared to normal water-reducing admixtures. There are currently three main chemical types: the sulphonated polymers of naphthalene, melamine formaldehyde condensates and the polycarboxylate ethers. These dispersing admixtures can either be used alone or blended with other concrete admixtures in order to obtain the desired properties of concrete during the mixing process or after the concrete becomes harden for instance wide range of rheological properties, increase in retardation, workability retention, air entrainment and other properties.

Three mechanisms of concrete admixtures that are related to this research will be described in the following sections including the mechanism of air-entrainment, defoaming agents, and dispersing admixtures in concrete.
2.3 Mechanism of air-entraining agents in concrete

As mentioned in a previous section; to prevent damage from the repeated freeze-thaw cycles in concrete, some good air, which provides air bubbles of a proper size (small) and isolated from each other should be introduced in the system. In a concrete world, an admixture that gives this kind of property is called “air entraining agent. However, it is not easy to control the amount and size of air because there are various factors that can affect the air system e.g. concrete paste components (aggregates), temperature in a concrete mixing, type of mixer, time of mixing, speed of mixing, and other admixtures (such as superplasticizer) \(^3\). All of these variables will make the role of air entraining agent in concrete system much more complicated. To understand how this air entraining agent really work, its mechanism should be really comprehended.

![Stoke’s Law](image)

Stoke’s Law: \( V \sim \frac{R^2}{\eta} \)

Where \( V \) = Velocity of rise

\( R \) = Radius of a bubble

\( \eta \) = Viscosity of a liquid

Figure 2-4 Bubbles rise to liquid surface follow Stoke’s law \(^3\)

Air bubble or foam is a dispersion of a gas in a liquid, characterized by very large interfacial area. Typically, the gas is encapsulated within the liquid and these bubbles formed in the liquid follow “Stoke’s Law” (as seen in Figure 2-4). The bigger the bubble, the greater that velocity toward the surface. The lower the viscosity of the system, the faster of these bubbles go to the surface. So, viscosity and bubble size are related. In
Figure 2-5 (a), it can be seen that the bubble that rises to the surface will form a “lamella”. However, there is nothing to stabilize this air bubble (i.e. pure liquid do not form stable foam) \(^{40}\). When that lamella get into 10 nm and also thin, the liquid that is in the lamella drains. It collapses and air gets into the bubble, then the bubble will disappear. On the contrary, concrete having freeze-thaw ability is not pure material, it contains not only a cement, water, aggregates, or chemical admixtures, but also a surfactant-type molecules (specifically an air entraining agent).

![Diagram of lamella and surfactant](image)

Figure 2-5 (a) Lamella formed by the bubble that rises to the liquid surface and then broken due to lack of surfactant; (b) Surfactants to stabilize the bubble and lamella preventing it from drainage \(^{39}\)

In Figure 2-5 (b), these surfactants are hydrophilic on one end, and hydrophobic on the other end. Polar on one end, and non-polar on the other end. These are aligned at the air-liquid interphase. The hydrophilic is in the water. The hydrophobic end does not want to be in a water, but aligns itself at the air interphase. This is the most favorable place for it to relocate. They relocate both internal and external surface of that lamella and they prevent that liquid in the lamella from drain. They do that because of hydrophilic end of that molecule carrying the surface charges. These charge surfaces are not closed together, they set up the “electrostatic repulsion force”, which keep those bubbles isolated from each other and prevents bubble coalescence. Therefore, there are
two steps for generating stable air bubbles in concrete. First, by the concrete mixing process, then followed by the air stabilization, which is attributed to the added air entraining agent.

Figure 2-6 (a) Formula of a typical air-entraining agent derived from pine oil or tall oil processing; (b) mechanism of air entrainment when an anionic surfactant with a nonpolar hydrocarbon chain is added to the cement paste

When the air-entraining agent molecules are added to the fresh cement system, there are three places for them to be

*Adsorbed or absorbed on the cement particles* – Cement particle surfaces have charges and high free surface energy. Surfactant molecules are able to adsorb or absorb on the cement surfaces in order to decrease the free surface energy, which is thermodynamically preferable. The amount of surfactant adsorbed or absorbed on solid surfaces contributes little to the air bubble formation and stability.

*Adsorbed at the water-air interfaces* – The adsorbed molecules have preferred orientations as described in the previous section. Again, the hydrophobic tail aligns itself at the air interphase. The hydrophilic head of that molecule carrying the surface charge, which will create the “electrostatic repulsion force” keeping those bubbles isolated from each other and prevents bubble coalescence.
Soluble or slightly soluble in a water – This will reduce the surface tension of the water. Unlike other possible places to be, the orientation of these surfactant molecules is quite random. The amount of water soluble surfactant molecules is important. This is probably because they can set up the dynamic equilibrium between the surfactant molecules that are at the water-air interface and that are adsorbed or absorbed on cement particle.

2.4 Mechanism of defoaming agents in concrete

Defoaming agents or defoamers have an ability to get rid of air bubbles in a concrete system in one of two ways. First, they might displace the surfactants from the air bubble walls. Or second way, they just locally burst those bubbles 40.

It has to be insoluble in a continuous phase. It has to be incompatible with a continuous phase. It has to have positive entering coefficient, meaning that it has to favorably enter the lamella. It has to have a positive spreading coefficient because there is a very large interfacial between air and liquid. So, it has to go into the lamella and spread very rapidly.
Defoamers are carefully formulated materials because they are insoluble and incompatible. They have a positive spreading and entering coefficient. They drift into that lamella. There are two points of view that responsible for the mechanism, physical site and chemistry. In a physical aspect, the ingredients are driven into the lamella. When those particles are the right size, they actually push those surfactant molecules at their nearly interphase out of the way. Behind them is the region of pure liquid. Because those surfactants push down the air bubbles, that lamella is able to drain and thin; air into the bubbles and the bubbles will collapse. In addition, when the mixing occurs through shear, the presence of surfactants will reduce the physical particle size of those defoamer particles. So when these particles are reduced small enough from physical size, they are still into the lamella, but they are not big enough to push anything out of the way. So that is why defoamers are needed in later step of the manufacturing process. Therefore, when the cement is subjected to shear by mixing process, additional defoamers are needed because that first set of defoamers put in have been consumed. They reduced in physical size through shear.
In a chemistry part of these defoamers; because they lower surface tension, they lower surface energy particles. As known that “liquid movement is away from area of low surface tension to the area of higher surface tension”; so when defoamers are going to lamella, these low surface tension particles move in, the liquid in this lamella is trying to get away from it. When it does that, the lamella gets thinner. Ultimately, that liquid will detach itself from those low surface tension particles. Air will enter the bubble and the bubble will collapse. Therefore, defoamers enter into the lamella and then these low surface energy will either spread or detach the lamella to form bridging, which will separate lamella. The air is then created and moves into that bubble and the bubble will collapse (as seen in Figure 2-8).
Another defoaming mechanism is through hydrophobic particles. A defoaming agent is driven into the lamella. Because of the chemistry, typically will use tributyl phosphate, ethoxylated/propoxylated alcohol, or certain amines. It absorbs the hydrophobic end and it will create the region of shown liquid. So this region of the lamella, which is shown liquid, will start to drain and allow air bubbles to come in (as seen in Figure 2-9).

2.5 Mechanism of dispersing admixtures in concrete

When water is added to cement, hydration reactions of cement occur as mentioned in previous section. Cement particles tend to form into small flocs. These small flocs trap water inside them causing the cement mix to be less fluid. By adding dispersing admixtures in concrete formulation, they will adsorb onto the cement surfaces and disintegrate those flocs into individual cement grains. These grains pass each other easily, resulting in more fluidity of cement mix (as shown in Figure 2-10).
Polycarboxylate ether (PCE) with the copolymer between carboxylic group (it is normally neutralized as the sodium salt and takes on a negative charge in aqueous solution) and polyethylene glycol based monomer is the most recent development of dispersing admixture. The PCE molecules adsorb onto the cement surface through the negative charges on the PCE molecules onto the positively charged calcium ions on the cement surface. The dispersion is then caused by the oxygen atoms of polyethylene glycol side chains and the water molecules in the aqueous phase forming hydrogen bonds that spread the side chains out into the water. The steric effect theory (as shown in Figure 2-11) presumes that dispersibility increases as the side chain branches lengthen.\textsuperscript{14, 31, 41, 42}

![Figure 2-10 Effect of dispersing admixtures in breaking up cement flocs.](image)

![Figure 2-11 Steric stabilization dispersion of cement grains by polycarboxylate superplasticizers.](image)
2.6 Mesoporous materials

Porous material is a continuous and solid network material filled through voids. In case of nanoporous materials, the pore or voids should have diameter around 1-100 nm. If internal voids of any material can be filled with gas, that material will be known as porous material. Occasionally, the pores can possibly be filled with a liquid or even a solid. Porosity offers materials having higher surface area with low density compared to dense materials \(^43\).

2.6.1 Classification of porous materials

Nanoporous materials can be categorized into two types \(^43\):

1) Depending on pore size – This is also be divided into three categories:

*Microporous materials* – have pore diameter < 2 nm i.e. zeolites, metal organic framework, etc.

*Mesoporous materials* – have pore diameter between 2 and 50 nm, for example, silica and metal oxides, etc.

*Macroporous materials* – have pore diameter > 50 nm e.g. cotton, sponge, and some metal oxides, etc.

2) Depending on building framework – the framework can be made up of by different ways; purely inorganic (such as pure silica, metal oxide, mixed metal oxide, etc.), purely organic (porous polymer, porous carbon, etc.), and organic-inorganic hybrid.
2.6.2 Synthesis mechanism for the creation of mesoporous materials

Mesoporous materials (pores with diameters, 2-50 nm) can be used in many applications e.g. absorption, separation\textsuperscript{44}, catalysis, biomedical field, and energy storage\textsuperscript{45, 46} based on their notable physicochemical properties i.e. high surface area (~ 400 - 1000 m\textsuperscript{2}/g), large pore volume, and high stability ~ 500 – 600 °C. There are two major mechanistic pathways to synthesize these mesoporous materials including hard-templating method (nanocasting) and soft-templating method. For fabrication of mesoporous materials, this template will act like a structure directing agent, helping to create or design porosity in the matrix\textsuperscript{19}.

**Hard-templating method (nanocasting):**

There are four main steps to produce mesoporous materials via this method including 1) preparation of the template; 2) infiltrating a guest precursor into the pore system of the prepared template; 3) transformation of the guest precursor into a target product; and 4) template removal. This hard-templating method can be demonstrated as shown in Figure 2-12.

![Figure 2-12](image)

Figure 2-12 Hard-templating method leading to mesoporous non-siliceous materials\textsuperscript{17}

Choosing a proper template for this hard-templating pathway is very crucial. From previous literatures; there are two mesoporous templates that have been extensively
used, mesoporous carbon and mesoporous silica. Between these two templates, mesoporous silica is the most favorable template for fabrication of other mesoporous materials. This is for the reasons that it has comparatively uniform pore size distribution and has extremely ordered nanoscale structures. Depending on which pore system of mesostructured templates has been used, various shapes of mesostructured target materials after nanocasting can be possibly achieved. For example, if the pore system has a unidimensional cylindrical shape (as seen in Figure 2-12), nanowire or tube arrays will be obtained; when the pore system is bicontinuous, then bicontinuous or lower symmetry replica will be achieved; and if the pore system is spherical, this will give nanosphere arrays of the target product 47, 48.

In case of the guest precursor selection, it should be very inert to the template used. This means there will be no any reaction in the process of the precursor infiltration. For instance; if the wet impregnation method is applied, this guest precursor should be in a liquid form. It can probably be dissolved in a solvent, or even be in a melt state. This is because in this liquid form, this guest precursor can simply be infiltrated into the porous systems of the template by capillary force. Speaking of infiltrating method of the guest precursor into the pores of the template, an appropriate pathway is required. There are plenty pathways that have been used e.g. a two solvent method, a surface function method, a melt method, or an organic solvent reflux method 49-51. However, among other methods, evaporation induced capillary condensation is the most favorable pathway that has been widely used. For the period of the evaporation process, the surrounding solvent molecules of the template are able to evaporate quickly. Consequently, the remaining liquid will be introduced into the pores of the template by capillary force 17, 52.
In the step of transformation of the precursor into the target material, this can be done by calcination in an air ambient if mesoporous silica is used as a template. However, for an oxygen sensitive material such as carbon template, an inert environment is strongly desirable in the period of thermal treatment process.

Etching is a necessary process in order to remove the whole template and eventually receive a target mesoporous material as desired. In case of a carbon template, it can simply be eliminated by calcination through air ambient. In case of a silica template, the framework can be removed either by NaOH solution or with HF solution. This solution selection is mainly based on the stability of the target material inside the template during the leaching condition.

Here are some examples by using nanocasting method to create metal mesoporous materials. Li et al. used carbon aerogel as a hard template to fabricate a glassy, amorphous disorder mesoporous aluminum oxide (Al₂O₃). The resulting mesoporous had a large pore volume (1.55 cm³ g⁻¹) with a high surface area of 365 m² g⁻¹. Liu and Baker used SBA-15 (silica nanoparticles with hexagonal array of pores) as a hard template to create ordered mesoporous ZrO₂. They also used ZrOCl₂·8H₂O as a precursor for this synthesis. The resultant mesoporous ZrO₂ had a specific surface area around 220 m² g⁻¹ and a pore size of 2.9 nm. Jiao et al. used KIT-6 (large mesoporous silica with bicontinuous body-centered (Ia3d) cubic symmetry) as a hard template to create ordered mesoporous iron oxides.

The advantages of the hard-templating process to fabrication metal mesoporous materials include: (1) the mesoporous replica generally have three-dimensional connected
frameworks. For example, nanowire or tube arrays (as seen in Figure 2-12) have plenty of small pillars, in which they are connected to each nanowire array. This makes them to have 3-D mesoporous frameworks. Those small pillars are created from the mesochannels inside the template; (2) the mesostructures can be varied by selecting different templates i.e. unidimensional cylindrical shape, bicontinuous porous systems, or spherical porous template; (3) nanostructured materials with crystalline can be achieved with a high temperature treatment even though still protected by the template 17.

Soft-templating method:

One of the most effective pathways to synthesize these materials is “soft-templating” like self-assembly of an amphiphilic block copolymers. Amphiphilic block copolymers have received noticeably greatly of attention in terms of their ability to form various types of nanoparticles and mesoporous materials 61. The interesting thing is these polymers obtained by the polymerization of more than one type of monomer, which chemical properties are not compatible with each other i.e. (hydrophilic/hydrophobic, attractive/repulsive) 62.

The hydrophobic part will aggregate in aqueous solution. However, the hydrophilic portion will prevent the aggregates from precipitation 63, 64. Thus far, various types of amphiphilic block copolymers have been synthesized, not only with combinations of block, but also the numerous lengths of each block both hydrophilic and hydrophobic. When the molecular weight of the hydrophobic block is greater than that of hydrophilic block, the copolymer tends to be less water soluble. On the other hand, if the molecular weight of the hydrophilic block is greater than that of the hydrophobic block,
the copolymer is simply dispersed in water and will self-assemble into small, relatively monodisperse \(^{61}\).

The self-assemble structures formed by amphiphilic block copolymers lead to different morphologies depending on many variables. The most important one that dictates the morphology is called “packing parameter” or \(p\). This dimensionless packing parameter, \(p\), will express the inherent molecular curvature and how it will affect on packing of the block copolymer chains. The Equation (1) shown below is the definition of a packing parameter.

\[
p = \frac{V}{a_0 l_c}
\]  

(2-6)

Where \(V\) is the volume of the hydrophobic chains, \(a_0\) is the optimal area of the head group, and \(l_c\) is the length of the hydrophobic tail \(^{65}\). As a general rule; if \(p \leq 1/3\), spherical micelles are favored. When \(1/3 \leq p \leq 1/2\), cylindrical micelles will be obtained. Finally, enclosed membrane structures (vesicles, also known as polymersomes) will be favored when \(1/2 \leq p \leq 1\) \(^{66}\).
The most common and well-known soft-templating routine is evaporation induced self-assembling (EISA) \(^{18}\). The amphiphilic block copolymers that are mentioned above are used as the pore templates. For the EISA pathway, a solution containing inorganic precursors, the block copolymer template, and a solvent is placed onto a substrate. An evaporation of the solvent during this period leads to an arrangement of block copolymer template into micelles above a critical micelle concentration (CMC). Subsequently, micelles and the partially condensed inorganic precursor will assemble into an ordered mesophase. Followed by calcination, mesophase will be converted into a mesoporous oxide film.

For EISA process, a comparatively strong interaction between block copolymer templates and inorganic precursors should be taken into a consideration. This is because that interaction is needed to form ordered mesostructures and avoid macroscale phase
separation. This tendency will be relatively strong if the inorganic precursors are able to establish a stable crystalline structure with high lattice energy. If the interaction is not strong enough, the possibility of phase separation will occur. An inorganic species will precipitate and the micelles block copolymer will remain in a solution. The self-assembly process is customarily govern through a chemical bond between block copolymer templates and inorganic species like hydrogen bond or electrostatic bond. In addition, this cooperative self-assembly is typically involved with the hydrolysis-condensation process of inorganic precursors. This inorganic species needs to be able to condense to extended frameworks under the EISA process. Otherwise, the structures will collapse after micelle template removal. After the completely decomposition of ordered micelles block copolymer template mesoporous metal oxides will be achieved. To remove the block copolymer template, the most common way to do is via calcination.

However, by using an aqueous as a solvent in EISA system, the rate of hydrolysis-condensation process of metal inorganic precursors will be too fast. Dense inorganic network will be obtained and subsequently causes poorly ordered mesoporous structured. Therefore, by using non-aqueous solvent like an alcohol, will delay the rate of hydrolysis-condensation of inorganic metal species, which is greatly favorable for the fabrication of ordered mesoporous materials. This EISA method can be illustrated as shown in Figure 2-14.
Here are some examples by using soft-template to create metal mesoporous materials. Sinha et al. 68 used and pluronic F127 (a triblock copolymer of \((\text{PEG})_{100}-b-(\text{PPO})_{65}-b-(\text{PEG})_{100}\) corresponding to a molecular weight of \(1.15 \times 10^4\) g mol\(^{-1}\) 69 as a surfactant to fabricate mesoporous chromium oxide (Cr\(_2\)O\(_3\)). Metal nitrate was used as an inorganic precursor and a mixture of propanol and ethylene glycol was chosen as a solvent. This mesoporous Cr\(_2\)O\(_3\) material exhibited an outstanding high oxidation ability for volatile organic compounds such as toluene and acetaldehyde. Dahal et al. 70 used pluronic P-123, which is a triblock copolymer of \((\text{PEG})_{20}-b-(\text{PPO})_{70}-b-(\text{PEG})_{20}\) corresponds to a molecular weight of around 5,800 g mol\(^{-1}\) 71, as a surfactant or soft template for creating mesoporous of cobalt oxide (CO\(_3\)O\(_4\)). Banerjee et al. 72 used sodium

Figure 2-14 Mesostructured thin-film formation by dip-coating using EISA method 67
dodecyl sulfate (SDS) as a non-ionic surfactant to obtain ordered mesoporous nickel oxide (NiO). Mesopores did not collapse at a very high calcination temperature around 500 °C. However, a broadening of the pore size distribution was observed.

The benefits of the EISA process to fabrication metal mesoporous materials include: (1) Synthesis procedure is reproducible and relatively simple. (2) It is applicable to a broad range of metal oxides 73. (3) The pore size and pore shape, and even pore thickness can possibly be fine-tuned by varying the amphiphilic block copolymer structures as well as a concentration between block copolymer templates and inorganic precursors respectively 74.

2.6.3 Applications of mesoporous materials

As mentioned previously, mesoporous materials are very useful in various applications e.g. catalyst, energy storage, biomedical field, absorption, and separation. Following are devoted to the applications of some mesoporous metal oxides. Aluminum oxide (Al₂O₃) is widely used as a catalyst and a support in industry, as a result of its high hydrolytic stability 75. Titanium dioxide (TiO₂) has been largely used in various areas i.e. lithium-ion batteries, dye-sensitized solar cells (DSSCs), photo catalysis, and sensing. These are contributed to its exceptional properties both electronic and optical 17, 76-78. Zirconium dioxide (ZrO₂) has been extensively used for both support and catalysts, especially for redox and photo catalyst. This is because it offers high thermal stability and high corrosion resistance 79. Niobium oxide (Nb₂O₅) has received considerable attention as a result of its broad applications. It is applicable in many industrial fields such as gas sensors, electrochromic devices, and optical filters 80. Tantalum oxide (Ta₂O₅) plays an
important role in many areas because of its high dielectric constant. In metal oxide semiconductor devices, it is used as an insulator. It can also be employed in storage capacitors and in large-scale integrated memory cells \(^{81}\). Chromium oxide (Cr\(_2\)O\(_3\)) is useful in magnetic recording, catalysis, and pigments \(^{82}\). Nickel oxide (NiO) is a material for various applications such as electro-chromic display devices, active optical fibers, smart windows, fuel cell electrodes, gas sensors, etc. This is because it has advantageous properties e.g. transparency, conduction, electrochromic and antiferromagnetic properties \(^{17}\). Cobalt oxide (Co\(_3\)O\(_4\)) with high surface area and with small crystal size will offer improved electrochemical activity. Thus, it is a very revolutionary technology, especially in lithium-ion batteries \(^{83,84}\). This is because it provides superior charging rate \(^{85}\).

2.7 Thickeners for water-based coating systems

For every coating system, the flow behavior is crucial for the final appearance. In water-based coating systems, associative thickeners are very popular these days due to their fascinating characteristics. Adding the associative thickeners in the water-based coating system can increase the overall viscosity through physical interaction from hydrophobic groups between thickener molecules and between other components in the water-based system for example: pigments, surfactants, micelles, and the latex particles. These interactions not only increase the overall solution viscosity, but also result in a reversible dynamic network. It is a characteristic that the network is dynamic and the linkage points are constantly restructuring \(^{86}\).

Thickeners for water-based systems include cellulosics, acrylic thickeners [Alkali Swellable Emulsions (ASE)/Hydrophobically modified Alkali Swellable Emulsions HASE)], and associative thickeners [Hydrophobically modified Ethylene oxide Urethane
thickeners (HEUR)]. Celluloses, the world’s most abundant polymer, are usually good for wide range of applications, but easy biodegradable 87. ASE and HASE normally contribute strong shear thinning, anti-setting, and anti-sagging properties, but they are pH sensitive 21, 22. In contrast to acrylic thickeners, HEUR is pH-independent. Thus, HEUR can be categorized into a non-ionic associative rheology modifier. HEUR associative rheology modifier is generally composed of repeating poly (ethylene glycol) units at the center and hydrophobic groups on both or either end. Isocyanate on either side of the poly (ethylene oxide) acts as a linkage in order to attach the polymer backbone to hydrophobic end groups 88. Many research groups have been studied the behavior of HEUR 87, 89-91. To fabricate a new class of non-ionic associative rheology modifier in water-based systems is very fascinating. Rheology modifier-based fatty acid may be a good candidate for this type of application due to various advantages.

2.8 Radical copolymerization and controlled radical copolymerization

Radical copolymers are generally synthesized via free radical polymerization process. They can have different structures; including random copolymers, alternating copolymers, block copolymers, or even graft copolymers 92. A parameter that dictates the copolymer structures is called the reactivity ratio of each monomer. This reactivity ratio has a great impact on the amount of monomers and their distribution in the polymer chains. The monomer having higher reactivity may participate at higher amount in the polymer chain. Therefore, the composition of the comonomers may be different from the composition of comonomer mixture used 93. Controlled/“living” free radical polymerization (CFRP) techniques have received exceptionally interest because of their versatility in engineering complex materials with controlled molecular weights,
controlled block locations, and narrow molecular weight distribution\textsuperscript{4-9}. There are three CFRP techniques most regularly exploited to polymerize vinyl monomers including; nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible-addition fragmentation chain transfer (RAFT) polymerization\textsuperscript{3, 94-96}.

\[
\begin{align*}
M_n-T & \overset{\text{NMP}}{\rightleftharpoons} M_n + T^- & (2-7) \\
M_n-X + Mt(n) & \overset{\text{ATRP}}{\rightleftharpoons} M_n + Mt(n+1)X & (2-8) \\
M_n + M_m-T & \overset{\text{RAFT}}{\rightleftharpoons} M_n-T + M_m & (2-9)
\end{align*}
\]

Scheme 2-1 General mechanism of controlled free radical polymerizations

Based on the general mechanism of both NMP and ATRP polymerization methods, low concentration of radical species is necessary in dynamic equilibrium with dormant species. This is in order to get the living polymerization characteristic. This can be done by decreasing the termination relative to propagation. Thus, the decrease radical concentration is required, leading to the slowdown of propagation. On the other hand, RAFT polymerization shows an advantage over those two methods by having a high concentration of radicals and then having a faster rate of polymerization. This is due to the same concentration of radical species in the equilibrium. Among these three living radical processes, RAFT polymerization has been reported to be the most diverse in monomer choices\textsuperscript{97}.

If any reaction can be done by conventional radical polymerization, it should also be performed through RAFT polymerization too. This is because the only difference between those reactions is added RAFT agent. Almost any free radical polymerization
can be adapted to a RAFT polymerization. Meaning all the monomers (e.g. acrylates, methacrylates, styrenes, etc.) that are able to be polymerized by conventional radical polymerization, researchers should be able to establish the condition for controlled RAFT polymerization. It works under all those different conditions that have been done by conventional radical polymerization e.g. bulk, solution, suspension, emulsion. In addition, the range of temperatures used is from 60 °C - 150 °C, which is the same temperature range that typically used in that conventional radical initiator. Most common initiator used in free radical polymerization, such as azobisisobutyronitrile (AIBN) and 4,4'-azobis(4-cyanovarlic acid) (ACVA), are also widely used in RAFT polymerization. In addition to an initiator, a RAFT polymerization system is mainly comprised of monomers, a solvent, and a RAFT agent.

![RAFT agent structure](image)

Figure 2-15 A typical RAFT agent structure

A typical RAFT agent is shown above in Figure 2-15. R: is homolytic leaving group; R·: is used to reinitiate polymerization; and Z: is a group that modifies reactivity of C=S, which has the effect on the radical addition and fragmentation rate. The more stabilizing the Z group is, the longer the lifetime of the intermediate radical adduct; more time for side reactions. The majority of these RAFT agents can be classified as
dithioesters ($Z = \text{alkyl, aryl}$), trithiocarbonates ($Z = \text{SR}$), xanthates ($Z = \text{-OR}$), and dithiocarbamates ($Z = \text{-NR}_2$) \cite{ref1, ref2, ref3, ref4}.

A RAFT polymerization mechanism consists of several steps including: initiation, addition, reinitiation, equilibration, and termination as shown in Scheme 2-2 \cite{ref5}. In initiation step, an initiator dissociate into radical initiators (I·). These radical initiators can either react with a RAFT agent or with a monomer to generate the primary growing chain ($P_1$·). $P_1$· will turn into $P_m$· when more monomers are reacted. In addition-fragmentation step, the radical species ($P_m$), which were formed in the previous step, are added to the RAFT agent (1). Then the R group in a RAFT agent will leave and thus forming a leaving group radical (R·). This R· must be effective in reinitiating polymerization. This step is reversible and thus the intermediate species (2) can lose either the radical active species ($P_m$·) or the leaving group (R·). Next step is called reinitiation step. In this step, the leaving group radical (R·) can react with a monomer to form the primary growing chain ($P_1$·) and the radical active species ($P_m$·) can react with monomers to create a new active radical species ($P_n$·). This new active radical species ($P_n$·) will be able to react further in either the addition-fragmentation step or the equilibration step. The following step is called equilibrium step. When a propagation is established, there will be a dynamic equilibrium between two growing radicals, $P_m$· and $P_n$·. This is the nice thing about RAFT polymerization that it can have a high concentration of radical species than in other controlled polymerization methods. This leads to the faster rate of polymerization. $P_m$· and $P_n$· are in an equilibrium between a dormant state and an active state. When the active polymer chains are in the dormant state, they are bounded to the thiocarbonyl compound. On the other hand, when they are in the active state, polymerization will
continue. Most active radical species are confined into the thiocarbonyl compound in this step and this limits the occurrence of chain termination. Since in the equilibrium step is a chain transfer reaction instead of a termination, the control of the life time of radical is quite limited too. Therefore, limit the amount of time that the radical species can add monomer, then termination will take place.

\[
\begin{align*}
(1) & \quad \text{Initiation} \quad \rightarrow \quad I^* \\
I^* & \xrightarrow{k_1} P^*_1 \\
(2) & \quad P_m^+ + \text{S-S-R} \quad \xrightarrow{Z} \quad P_m^+ + \text{S-R} + \text{S} \quad \xrightarrow{Z} \quad P_m^+ + \text{S-S} \quad \xrightarrow{R^*} \quad P_m^* \\
(3) & \quad \frac{P_n}{k_p} \quad \xrightarrow{P_{n+1}^*} \quad \frac{R^*}{k_{p,1}} \quad \xrightarrow{P_{n+1}^*} \\
(4) & \quad P_n^* + \frac{S-S-P_m}{k_p,1} \quad \xrightarrow{k_\beta} \quad P_n^* + \frac{S-S-P_n}{k_p,1} \quad \xrightarrow{k_\beta} \quad P_n^* + \frac{S-S-P_m}{k_p,1} \\
(5) & \quad P_n^* + \frac{P_m^*}{k_p} \quad \xrightarrow{<k>} \quad P_{n+m} \\
\end{align*}
\]

Scheme 2-2 Mechanism of a RAFT polymerization

Generally, the molar ratios of RAFT agent to initiator are between 5:1 and 10:1. This, in turn, produces polymers with predetermined controlled molecular weights and narrow polydispersity index. In addition, these RAFT agents can be used to control block locations. When conducting RAFT polymerizations, the most important factor for successful reactions is the selection of the proper RAFT agent/monomer combination.
Figure 2-16 Possible polymer chains that can be present in RAFT polymerization

The Figure 2-16 shows everything that can be exist within a RAFT polymerization: 1) some chains that are initiated by this conventional radical initiator; 2) the primary group that the chains are grown from the RAFT agent; 3) some chains that are under termination; and 4) some chains that that have “R” RAFT end and active chain end. It can also be noticed that those polymer chains are not necessary have the same chain length.
3.1 Overview

In this part, methoxy poly (ethylene glycol) methacrylate (MPEGMA) with three different molecular weights, 2-methyl-acrylic acid (dibuthoxy-phosphoryloxy)-alkyl ester or phosphate ester based defoamer, and water-soluble RAFT agent were synthesized. These two monomers MPEGMA and phosphate ester-based defoamer incorporated with methacrylic acid were used to synthesize the polycarboxylate admixtures for the concrete by using conventional radical polymerization and via RAFT polymerization with this water soluble RAFT agent.

3.2 Materials

Methoxy poly (ethylene glycol) (MPEG, 550, 950 and 2,000 g mol\(^{-1}\), Aldrich), sulfur powder (Aldrich, powder 99.98%), sodium methoxide solution (Sigma-Aldrich, 25 wt. % in methanol), benzyl bromide (Aldrich, 98%), diethyl ether (EMD
Millipore, anhydrous), methanesulfonic acid (Sigma-Aldrich, > 99.5%), hydroquinone (Sigma-Aldrich, > 99%), hydrochloric acid (Fisher, ACS Plus), magnesium sulfate (EMD Millipore, anhydrous), diethyl amine (Sigma-Aldrich, >99.5%), ethanol (Decon Labs Inc., 100%), iodine (Sigma-Aldrich, >99.8%), 4,4’-azobis(4-cyanovaleric acid) (Aldrich, >98%), ethyl acetate (Fisher), hexane (Fisher), dithranol matrix (Alfa Aesar, >97%), sodium trifluoroacetate (Aldrich, >98%), and poly (methyl methacrylate) standard (Fluka) were used without further purifications. Azobis (isobutyronitrile) (AIBN) (Aldrich, 98%) was purified by recrystallization from methanol.

3.3 Instrumentation

*FTIR Analysis.* The FT-IR spectra of methoxy poly (ethylene glycol) methacrylate with different molecular weights and 2-Methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester were measured on a Nicolet 380 FTIR spectrophotometer. The results were analyzed using OMNIC software.

*1H-NMR Analysis.* 1H-NMR Analysis of all starting materials was recorded on Varian NMRS-500 nuclear magnetic resonance instrument (500 MHz) using deuterated chloroform (CDCl₃) as a solvent.

*Mass Spectrometry.* Mass spectral experiments were performed to assist in determining the chemical structure of starting materials, using a Bruker ULTRAFLEX-III time-of-flight matrix-assisted laser desorption ionization mass spectrometer (Bruker Daltonics, Billerica, MA) equipped with a Nd:YAG laser, a two-stage gridless reflector, and a single stage pulsed ion extraction source. Separate THF solutions of dithranol matrix (20 mg mL⁻¹), sodium trifluoroacetate (10 mg mL⁻¹), and polymer (10 mg mL⁻¹) were mixed in a ratio of matrix: cationizing salt: polymer (10:1:2), and 0.5 μL of the
resulting mixture was introduced onto the MALDI target plate. The spectra were obtained in the reflection mode. The attenuation of the laser was adjusted to minimize unwanted polymer fragmentation and to maximize the sensitivity. The calibration of mass scale was carried out externally using poly (methyl methacrylate) standard (Fluka) with a similar molecular weight as the sample.

3.4 Synthesis

In this section, MPEGMA with three different molecular weights, phosphate ester based defoamer, and water-soluble RAFT agent were synthesized.

3.4.1 Synthesis of methoxy poly (ethylene glycol) methacrylate (MPEGMA)

Methoxy poly (ethylene glycol) (MPEG) in three different molecular weights (550, 950, and 2,000 g mol\(^{-1}\)), toluene as a solvent, methane sulfonic acid (MSA) as a catalyst, and hydroquinone as a radical polymerization inhibitor were introduced into a 500 mL four-neck round bottom flask, equipped with a condenser together with a dean-stark trap (contained toluene) for collecting the condensed product, a mechanical stirrer, nitrogen gas inlet and outlet adapter, and a dropping funnel. The mixture was gently stirred by the mechanical stirrer under a nitrogen purge in the oil bath at 80 °C. After 30 min, the polymerization was initiated by slowly dropping methacrylic acid (MAA) from a dropping funnel into the reaction flask within 1 h. Then, polymerization continued for 23 h at a temperature of 90 °C. Polymerization was terminated by quenching with an ice bath. After cooling, the product was collected by precipitation in n-hexane three times and dried in a vacuum oven at room temperature. For the purification, tin layer chromatography (TLC) and column chromatography techniques were applied by using
silica gel as a stationary phase and acetonitrile as a mobile phase. MPEGMA fraction was precipitated with n-hexane and dried in vacuum oven at room temperature. Finally, a series of MPEGMA macromonomer was obtained.

To synthesize a series of MPEGMA in different molecular weights, the molar ratio between MPEG and methacrylic acid was 1:2. Methane sulfonic acid was added 1.4 wt. % of total amount of monomers. Hydroquinone was added 0.15 wt. % of total amount of monomers. Toluene was added 22 wt. % of total amount of monomers. The following is the recipe to synthesize MPEGs:

MPEGMA 550 was prepared by using MPEG 550 g mol⁻¹ (165.00 g, 0.30 mol), methacrylic acid (51.65 g, 0.40 mol), methane sulfonic acid (3.00 g, 3.12 x 10⁻² mol), hydroquinone (3.25 x 10⁻¹ g, 2.95 x 10⁻³ mol), and toluene (50.00 g) in a reaction flask.

MPEGMA 950 was prepared by using MPEG 950 g mol⁻¹ (150.00 g, 0.20 mol), methacrylic acid (34.45 g, 1.75 x 10⁻³ mol), methane sulfonic acid (2.6 g, 0.027 mol), hydroquinone (2.75 x 10⁻¹ g, 2.50 x 10⁻³ mol), and toluene (40.00 g) in a reaction flask.

MPEGMA 2000 was prepared by using MPEG 2000 g mol⁻¹ (200.00 g, 0.10 mol), methacrylic acid (17.22 g, 0.20 mol), methane sulfonic acid (2.90 g, 0.03 mol), hydroquinone (0.30 g, 2.72 x 10⁻³ mol), and toluene (45.00 g) in a reaction flask.

![Synthesis pathway of a methoxy poly (ethylene glycol) methacrylate for different chain lengths (m = 12, 24, and 48)](image-url)
3.4.2 Synthesis of 2-Methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester

Our aim was to have a similar chemical structure like tributyl phosphate, a commercial defoaming agent, but have a reactive site (double bond) that can be copolymerized with other monomers. Hydroxy ethyl methacrylate (HEMA) (3.91 g, 0.03 mol) and triethylamine (2.10 g, 0.021 mol) solubilized in dichloromethane (51.0 g, 0.6 mol) were introduced into a 100 mL three-neck round bottom flask equipped with a condenser together with a rubber septum, nitrogen gas inlet and outlet adapter. The mixture was gently stirred by a magnetic bar under a nitrogen purge and subsequently cooled at 0 °C in an ice bath. Then, dibutyl chlorophosphate (5.00 g, 0.022 mol) in the presence of dichloromethane (7.30 g, 0.086 mol) was added dropwise by syringe pump through rubber septum. After that, pyridine (0.95 g, 0.012 mol) was added into the reaction mixture. The solution mixture was continuously stirred under the nitrogen atmosphere for three days at room temperature. In a purification, white precipitate was filtered out, and the solvent was also evaporated. Then, the crude mixture was dissolved in diethyl ether. The organic phase was washed several times with saturated sodium chloride solution in a separatory funnel. The water phase was discarded and the organic phase was distilled under the vacuum. Finally, the modified defoaming agent, 2-methylacrylic acid (dibuthoxy-phosphoryloxy)-alkyl ester was obtained.

![Figure 3-2 Synthesis of 2-methyl-acrylic acid (dibuthoxy-phosphoryloxy)-alkyl ester](image)
3.4.3 Synthesis of water soluble RAFT agent: 4-cyanopentanoic acid dithiobenzoate (CPADB) \(^{86,101-103}\)

This RAFT agent was synthesized in three step-process including synthesis of diethyl ammonium dithiobenzoate, synthesis of bis (thiobenzoyl) disulfide, and finally synthesis of water soluble RAFT agent by using two products synthesized in previous steps. This section explains the synthesis route and experimental part.

*Synthesis of diethyl ammonium dithiobenzoate*

Used 1000 mL three-neck round-bottom flask with a stirring bar inside, connected with condenser equipped with gas outlet adapter. Sulfur powder (75.60 g, 2.35 mol) was mixed with NaOCH\(_3\) solution (497 mL (483 g), 2.18 mol of 25 wt. % in methanol). The flask was then attached to the rubber septum on one side and gas inlet adaptor for another side. Benzoyl bromide (C\(_6\)H\(_5\)-CH\(_2\)-Br) (126 mL (181.19 g), 1.06 mol) was subsequently added to the sulfur/NaOCH\(_3\) mixture drop-wise for over an hour via syringe pump through the rubber septum to form a deep red mixture, with vigorous stirring under ambient N\(_2\) (g). The dark red mixture was refluxed at T = 65 °C for 18 h and then cooled down to room temperature. After that, filtered it by vacuum to remove NaBr salt (a solid was discarded, but kept the red solution). The solvent evaporated by using rotary evaporator to give a remaining red viscous mixture. This mixture was dissolved in deionized water, and then by diethyl ether (≈ 5:8 V/V) in order to extract the wanted material into the organic layer. HCl solution was then added to the water/ether layers until the water layer became colorless. It was transferred to the separatory funnel. The organic layer was kept and the aqueous layer was discarded. Then, washed it again with
water three times (3 x 500 mL), and dried with anhydrous magnesium sulphate (MgSO₄). The MgSO₄ was filtered out and resulting diethyl ether red solution was then precipitated with diethyl amine. This precipitate red solid, diethyl ammonium dithiobenzoate, was kept cold (-5 °C) overnight. Next, this red solid was filtered and dried under vacuum at room temperature.

**Figure 3-3 Synthesis of diethyl ammonium dithiobenzoate**

*Synthesis of bis (thiobenzoyl) disulfide*

Diethyl ammonium dithiobenzoate from previous step (37.2 g, 164 mmol) was dissolved in 200 mL ethanol in 1000 mL three-neck round bottom flask, with a stirrer bar fitted with a condenser and also equipped with gas outlet adapter. A solution of iodine (42 g, 164 mmol, in 500 mL of ethanol) was then added drop-wise at -5 °C over 1.5 h via dropping funnel with robust stirring. After 10 min of iodine addition, a pink precipitate of bis (thiobenzoyl) disulfide was appeared in the flask. When addition of iodine solution was completed, the bis (thiobenzoyl) disulfide was received by filtration. It was the washed with ethanol several times and dried under vacuum at room temperature.
Synthesis of water soluble RAFT agent: CPADB

Bis (thiobenzoyl) disulfide (40 g, 132 mmol) was mixed with 4,4’-azobis(4-cyanovaleric acid) (56 g, 0.2 mol) in 800 mL ethyl acetate in a 1000 mL round-bottom flask. A condenser was attached to the round-bottom flask. The reaction was refluxed at 77 °C for 18 h with magnetic stirring. The red mixture was obtained and cooled at room temperature. The solvent was removed by rotary evaporation. The red oily residue was purified by column chromatography using a silica gel (40-140 mesh). The mobile phase was ethyl acetate: hexane (2:3) by volume. The red fraction was combined and the solvent was removed under vacuum. The thick red oil was placed into a 2-propanol/dry-ice bath, causing red crystals to be appeared after 10 min. The crystals are collected and the product recrystallized from benzene.
3.5 Results and discussion

FT-IR, \textsuperscript{1}H-NMR, and Mass spectrometry (MALDI-TOF) were qualitatively used to analyze the functional groups, atom connectivity, and mass per charge ratio of a series of MPEG, MPEGMA, 2-Methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester, and water soluble RAFT agent, CPADB.

3.5.1 Characterization of methoxy poly (ethylene glycol) methacrylate (MPEGMA)

MPEGMA with three different molecular weights were characterized by different techniques including FT-IR, \textsuperscript{1}H-NMR, and Mass spectrometry (MALDI-TOF).

Figure 3-6 FT-IR spectra (a) MPEG 550, 950, and 2000; (b) MPEGMA 550, 950, and 2000
FT-IR results show very successful synthesis of MPEGMA 550, 950, and 2000. The significant change was the O-H stretching peak of MPEGs at wavenumber 3,200 - 3,400 cm\(^{-1}\) disappeared compared to that of MPEGMAs. In addition, the peak of MPEGMAs at wave number 1,700 - 1,720 cm\(^{-1}\) represents the occurrence of C=O stretching of ester bond. From these two vital changes refer to the complete reaction between MPEGs and methacrylic acid through an esterification reaction, leading to the creation of MPEGMAs.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Wavenumbers (cm(^{-1}))</th>
<th>Functional group</th>
<th>Compounds</th>
<th>Wavenumbers (cm(^{-1}))</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,800 – 2,950</td>
<td>C-H stretching</td>
<td>1,700 – 1,720</td>
<td>C=O stretching of ester bond</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,445 – 1,485</td>
<td>C-H bending of CH(_2) and CH(_3)</td>
<td>1,445 – 1,485</td>
<td>C-H bending of CH(_2) and CH(_3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,370 – 1,380</td>
<td>C-H bending of CH(_3)</td>
<td>1,370 – 1,380</td>
<td>C-H bending of CH(_3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,050 – 1,100</td>
<td>C-O stretching of ether bond</td>
<td>1,210 - 1,320</td>
<td>C-O stretching of ester bond</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,050 – 1,100</td>
<td>C-O stretching of ether bond</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 3-7 \( ^1\)H-NMR spectrum of MPEGMA 550 (CDCl\(_3\) as a solvent)

Table 3-2 \( ^1\)H-NMR assignment of MPEGMA 550

<table>
<thead>
<tr>
<th>Structural Group</th>
<th>( ^1)H NMR (ppm)</th>
<th>Integration area</th>
<th>Splitting pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CH}_2=\text{CR}-\text{CH}_3 )</td>
<td>1.5-1.8</td>
<td>0.05</td>
<td>Singlet</td>
</tr>
<tr>
<td>( \text{R-O-CH}_3 )</td>
<td>3.1-3.3</td>
<td>0.05</td>
<td>Singlet</td>
</tr>
<tr>
<td>( \text{CH}_3\text{-O-CH}_2\text{-CH}_2\text{-O} ) (repeating units)</td>
<td>3.3-3.6</td>
<td>0.82</td>
<td>Triplet</td>
</tr>
<tr>
<td>( \text{-CO}_2\text{CH}_2\text{-CH}_2\text{-O} )</td>
<td>3.5-4.8</td>
<td>0.03</td>
<td>Triplet</td>
</tr>
<tr>
<td>( \text{CH}_3=\text{CR}^- )</td>
<td>5.5-6.5</td>
<td>0.03</td>
<td>Complicated</td>
</tr>
</tbody>
</table>

\( ^1\)H-NMR confirmed the successful synthesis of MPEGMA 550 (as seen in Figure 3-1 and Table 3-2). In the spectrum, at \( \delta \) 5.5-6.5 ppm shows proton resonances attached to double bond of MPEGMA 550. Integration area was used to calculate the repeating units of poly ethylene oxide (PEO) inside MPEGMA 550, which are around 11-12 units.
Table 3-3 Peak assignment in MALDI-TOF mass spectrum of MPEGMA 550

<table>
<thead>
<tr>
<th>m/z observed</th>
<th>a</th>
<th>m/z calculation a,b</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>607.302 11</td>
<td>607.330</td>
</tr>
<tr>
<td></td>
<td>651.326 12</td>
<td>651.357</td>
</tr>
<tr>
<td></td>
<td>695.355 13</td>
<td>695.383</td>
</tr>
</tbody>
</table>

a) Monoisotopic mass of each element was used for the calculation of ion mass. Peaks correspond to sodium complexes ([A+Na]+)

Ion Mass (Peak A) =22.9898+44.0262a+100.0524

b) 1.007825:1H, 12:13C, 15.9949:16O, 100.0524:C5H8O2, and 32.0262:CH3O
Mass spectra of MPEGMA 550 (as seen in Figure 3-8) characterized by Mass spectrometry (MALDI-TOF) shows very narrow distribution of mass per charge ratio. In addition, it shows very clean spectrum without any impurity. The mass per charge ratio between peaks A is around 44 Da, representing the PEO unit. Table 3-3 demonstrates m/z between observation and calculation, which is nearly to each other. Moreover, repeating units of PEO in MPEGMA 550 can be calculated from the detail provided in Table 3-3.

![Figure 3-9 1H-NMR spectra of MPEGMA 950 and MPEGMA 2000 (CDCl3 as a solvent)](image)

**Table 3-4 1H-NMR assignment of MPEGMA 950 and MPEGMA 2000**

<table>
<thead>
<tr>
<th>Structural Group</th>
<th>1H NMR (ppm)</th>
<th>Integration area</th>
<th>Splitting pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_2$=CR-CH$_3$</td>
<td>1.5-1.8</td>
<td>0.04</td>
<td>Singlet</td>
</tr>
<tr>
<td>R-O-CH$_3$</td>
<td>3.1-3.3</td>
<td>0.03</td>
<td>Singlet</td>
</tr>
<tr>
<td>CH$_3$O–CH$_2$–CH$_2$–O- (repeating units)</td>
<td>3.3-3.6</td>
<td>0.91</td>
<td>Triplet</td>
</tr>
<tr>
<td>-CO$_2$CH$_2$CH$_2$O-</td>
<td>3.5-4.8</td>
<td>0.02</td>
<td>Triplet</td>
</tr>
<tr>
<td>CH$_2$=CR-</td>
<td>5.5-6.5</td>
<td>0.03</td>
<td>Complicated</td>
</tr>
</tbody>
</table>
Figure 3-9 shows $^1$H-NMR spectra of MPEGMA 950 and MPEGMA 2000. Both samples were dissolved in CDCl$_3$ for characterization. They both have the same resonances as MPEGMA 550. The only difference is the integration area, particular at $\delta$ 3.3-3.6 (PEO repeating units). The PEO repeating units of MPEGMA 950 were calculated to be around 23-24, while MPEGMA 2000 has PEO repeating units around 48.

![Mass Spectra of MPEGMA 950](image-url)
Table 3-5 Peak assignment in MALDI-TOF mass spectrum of MPEGMA 950

<table>
<thead>
<tr>
<th>m/z observed</th>
<th>m/z calculation&lt;sup&gt;a,b&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A</strong></td>
<td></td>
</tr>
<tr>
<td>739.429</td>
<td>14</td>
</tr>
<tr>
<td>783.454</td>
<td>15</td>
</tr>
<tr>
<td>827.477</td>
<td>16</td>
</tr>
<tr>
<td><strong>B</strong></td>
<td></td>
</tr>
<tr>
<td>759.453</td>
<td>16</td>
</tr>
<tr>
<td>803.481</td>
<td>17</td>
</tr>
</tbody>
</table>

<sup>a</sup> Monoisotopic mass of each element was used for the calculation of ion mass. Peaks correspond to sodium complexes ([A+Na]<sup>+</sup> and [B+Na]<sup>+</sup>)

Ion Mass (Peak A) = 22.9898 + 44.0262a + 100.0524

Ion Mass (Peak B) = 22.9898 + 44.0262b + 32.0262

<sup>b</sup> 1.007825:<sup>1</sup>H, 12:<sup>12</sup>C, 15.9949:<sup>16</sup>O, 100.0524:C<sub>5</sub>H<sub>8</sub>O<sub>2</sub>, and 32.0262:CH<sub>3</sub>O
3.5.2 Characterization of 2-Methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester

2-methyl-acrylic acid (dibuthoxy-phosphoryloxy)-alkyl ester or phosphate ester based defoamer was fully characterized by FT-IR and $^1$H-NMR.

Figure 3-11 FT-IR spectrum of 2-Methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester

Table 3-6 2-Methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester group frequencies by FT-IR

<table>
<thead>
<tr>
<th>Wavenumbers (cm$^{-1}$)</th>
<th>Functional group</th>
</tr>
</thead>
<tbody>
<tr>
<td>2,800 – 2,950</td>
<td>C-H stretching</td>
</tr>
<tr>
<td>1,700 – 1,720</td>
<td>C=O stretching of ester bond</td>
</tr>
<tr>
<td>1,620 – 1,680</td>
<td>C=C stretching</td>
</tr>
<tr>
<td>1,445 – 1,485</td>
<td>C-H bending of CH$_2$ and CH$_3$</td>
</tr>
<tr>
<td>1,370 – 1,380</td>
<td>C-H bending of CH$_3$</td>
</tr>
<tr>
<td>1,260 – 1,340</td>
<td>Asymmetric P=O stretching</td>
</tr>
<tr>
<td>1,140 – 1,210</td>
<td>Symmetric P=O stretching</td>
</tr>
<tr>
<td>920 – 1,088</td>
<td>Out-of-phase P-O-C stretching</td>
</tr>
<tr>
<td>725 – 845</td>
<td>In-phase P-O-C stretching</td>
</tr>
</tbody>
</table>
Figure 3-12 $^1$H-NMR of 2-Methyl acrylic acid (dibuthoxy-phosphoryloxy) – ethyl ester

$^1$H-NMR (CDCl$_3$): $\delta$ = 0.90 (t, H$^6$), $\delta$ = 1.37 (m, H$^4$), $\delta$ = 1.63 (m, H$^4$), $\delta$ = 1.92 (s, H$^3$), $\delta$ = 3.98 (t, H$^4$), $\delta$ = 4.12 (t, H$^2$), $\delta$ = 4.24 (t, H$^2$), $\delta$ = 5.57 (s, H$^1$), $\delta$ = 6.13 (s, H$^1$)

2-methyl-acrylic acid (dibuthoxy-phosphoryloxy)-alkyl ester or phosphate ester based defoamer was successfully synthesized and was confirmed its structure by FT-IR and $^1$H-NMR. % yield was around 70 % by gravimetric method. This phosphate ester based defoamer acting as an in-situ defoaming agent in polycarboxylate superplasticizer was then used to copolymerize with other monomers (e.g. methacrylic acid and MPEGMAs) in order to synthesize a new polycarboxylate admixture for the concrete via RAFT polymerization (CHAPTER V).
3.5.3 Characterization of water soluble RAFT agent: CPADB

This CPADB RAFT agent was synthesized in three step-process as stated in previous part. $^1$H-NMR was a main characterization method to characterize the product in each step after purification.

*Characterization of diethyl ammonium dithiobenzoate*

![NMR Spectrogram](image)

**Figure 3-13 $^1$H-NMR of diethyl ammonium dithiobenzoate**

This sample was dissolved in CDCl$_3$. In the spectrum, at $\delta$ 1.31 ppm it shows triplet of $\text{–CH}_3\text{-CH}_2$- and at $\delta$ 2.90 – 3.00 represents quartet of $\text{–CH}_3\text{-CH}_2$-. Hydrogen atoms of the aromatic ring appears at $\delta \sim 7 – 8$ ppm.
Characterization of bis (thiobenzoyl) disulfide

This sample was dissolved in CDCl$_3$. In the spectrum, at $\delta \sim 7$ – 8 ppm it shows H from aromatic ring. However, at $\delta \sim 1.20$ and 3.70 ppm it may also represent the resonances of residual ethanol.

Characterization of 4-cyanopentanoic acid dithiobenzoate

Figure 3-14 $^1$H-NMR of bis (thiobenzoyl) disulfide

Figure 3-15 $^1$H-NMR of 4-cyanopentanoic acid dithiobenzoate
This sample was dissolved in CDCl₃. It can be noticed that at δ 1.95 ppm, it represents –CH₃ and at δ 2.40 – 2.80 ppm it shows multiplet –CH₂CH₂-. Aromatic protons appear at δ 7.42 – 7.91 ppm {7.42 (m, 2H, m-ArH); 7.60 (m, 1H, p-ArH); 7.91 (m, 2H, o-ArH)}. 

After three steps process, RAFT agent, CPADB was successfully synthesized and was confirmed the structure by ¹H-NMR. % yield for the synthesis of CPADB was around 40 - 50 % by gravimetric method. % yield was quite low may be because of the purification through column chromatography.

3.6 Conclusions

All starting materials including series of MPEGMs, 2-methyl-acrylic acid (dibuthoxy-phosphoryloxy)-alkyl ester or phosphate ester based defoamer, and water-soluble RAFT agent were successfully synthesized. Many characterization methods e.g. FT-IR, ¹H-NMR, and Mass spectrometry (MALDI-TOF) were used to confirm the chemical structures. These materials were further used to synthesize polycarboxylate admixtures via conventional radical polymerization/esterification process and RAFT polymerization in CHAPTER IV and CHAPTER V respectively. They were also used to synthesize amphiphilic block copolymers for mesoporous materials and a new fatty acid-based rheology modifier application in CHAPTER VII and CHAPTER VIII respectively.
CHAPTER IV

THE SYNTHESIS OF POLYCARBOXYLATE ADMIXTURES FOR CONCRETE VIA CONVENTIONAL RADICAL POLYMERIZATION AND ESTERIFICATION PROCESS

4.1 Overview

Traditional comb-shaped polycarboxylate copolymers used in this study were synthesized in two different ways. The first synthesis method was performed by conventional radical copolymerization between methoxy poly (ethylene glycol) methacrylate (MPEGMA) and methacrylic acid (MAA) in the presence of persulfate initiators or 2, 2’-azobis (isobutryonitrile) (AIBN) initiator. The second pathway was performed by esterification reaction of poly (methacrylic acid) (PMAA) with methoxy (poly ethylene glycol) (MPEG) in the presence of acid catalyst. GPC was a characterization method used to determine molecular weights and molecular weight distribution of these polycarboxylate copolymers. $^1$H-NMR was used to confirm the chemical structures of all prepared polycarboxylate copolymers used in this study. These prepared polycarboxylate copolymers in this study could then be compared to polycarboxylate copolymers synthesized via RAFT polymerization (CHAPTER V) in order to investigate the concrete properties affected by various copolymers (CHAPTER VI).
4.2 Introduction

Polycarboxylate superplasticizers have been used in concrete filed for many years in order to improve flowability in concrete processing. In addition, they provide a high strength and durability of concrete due to a very low used water/cement ratio $^{104}$.

In general, there are two different pathways to synthesize comb-shaped polycarboxylate copolymers: (i) pre-fabrication of macromonomers between (meth)acrylic acid and alkyl-PEGs through esterification process, followed by radical copolymerization between those macromonomers and (meth)acrylic acid. Other comonomers are alternatives in the copolymerization and (ii) radical polymerization of (meth)acrylic acid and other comonomers to first create the backbone, followed by an esterification process of alkyl poly (ethylene glycol) or “alkyl-PEG” $^{104}$.

For the first pathway, persulfate initiators [e.g. sodium persulfate (Na$_2$S$_2$O$_8$), ammonium persulfate ((NH$_4$)$_2$S$_2$O$_8$, or potassium persulfate (K$_2$S$_2$O$_8$)] have been widely used to initiate a copolymerization reaction by generating free radicals by means of thermally induced chain scission of O-O bonds $^{105}$. However, pH in the reaction medium plays an important role for creating or suppressing the radical species. At a lower pH, no radicals from a persulfate ion ($S_2O_8^{2-}$) are formed, leading to a suppression in polymerization in acidic medium. On the other hand, two radical anions are generated from a persulfate ion in a basic or neutral media $^{105-107}$.

$$\text{pH} < 7: \, S_2O_8^{2-} + H_2O^+ \rightarrow HSO_4^- + HSO_5^- \quad (4-1)$$

$$\text{pH} \geq 7: \, S_2O_8^{2-} \rightarrow 2SO_4^{2-} \quad (4-2)$$
In most practical polymerization with persulfate initiator, it is very common that this initiator is normally used together with a reducing agent such as bisulfite anion \( (\text{HSO}_3^-) \) in a redox-initiating system. This results in producing bisulfate anion and two radical anions, which can further initiate polymerization reaction\(^{107}\).

\[
\text{S}_2\text{O}_8^{2-} + \text{HSO}_3^- + \frac{1}{2}\text{O}_2 \rightarrow \text{HSO}_4^- + 2\text{SO}_4^{2-}
\]  

(4-3)

For suitable monomers, the radical anions (shown above) will act as initiators to initiate polymerization and produce polymer molecules\(^{107}\).

\[
\text{SO}_4^{2-} + n\text{CH}_2 = \text{CH(R)} \rightarrow \text{O}_3\text{SO}((\text{CH}_2\text{CH(R)})_{n-1}(\text{CH}_2\text{CH(R)})
\]  

(4-4)

In some cases, free radical species can also be formed in the presence of a chain transfer agent e.g. mercaptans:

\[
\text{S}_2\text{O}_8^{2-} + 2\text{RSH} \rightarrow 2\text{HSO}_4^- + 2\text{RS}.
\]  

(4-5)

The second pathway is an esterification process between PMAA and MPEGMA in the presence of a catalyst in order to create polycarboxylate copolymers\(^{14}\). The polycarboxylate copolymers synthesized by these two methods act as controls, which would be further compared to polycarboxylate copolymers synthesized via RAFT polymerization (CHAPTER V). This gives of the opportunity of investigating the concrete properties under the effects of different polycarboxylate copolymers (CHAPTER VI).
4.3 Materials

Methoxy poly (ethylene glycol) methacrylate (MPEGMA, 950 and 2,000 g mol\(^{-1}\)) were used from the synthesis in Chapter III. Methoxy poly (ethylene glycol) (MPEG 750 and 2,000 g mol\(^{-1}\), Aldrich), methacrylic acid (MAA) (Aldrich, 99%), methanesulfonic acid (MSA) (Sigma-Aldrich, ≥ 99.5%), sodium persulfate (Na\(_2\)S\(_2\)O\(_8\)) (Sigma-Aldrich, reagent grade, ≥ 98%), ammonium persulfate (NH\(_4\))\(_2\)S\(_2\)O\(_8\) (Sigma-Aldrich, ACS reagent, ≥ 98%), 2-mercaptoethanol (Aldrich, ≥ 99%), sodium hydroxide (NaOH) (Aldrich), sodium azide (NaN\(_3\)) (Sigma-Aldrich, ≥ 99.5%), potassium phosphate monobasic (KH\(_2\)PO\(_4\)) (Sigma-Aldrich, ACS reagent, ≥ 99%), sodium phosphate dibasic dodecahydrate (Na\(_2\)HPO\(_4\)-12H\(_2\)O) (Sigma-Aldrich, puriss. p.a., crystallized, ≥ 99%), sodium sulfate (Na\(_2\)SO\(_4\)) (Sigma-Aldrich, ACS reagent, ≥ 99%), toluene (Aldrich, anhydrous, 99.8%), tetrahydrofuran (THF) (Sigma-Aldrich, HPLC, ≥ 99.9%), diethyl ether (EMD Millipore, anhydrous), and deuterium oxide (D\(_2\)O) (Cambridge Isotope Laboratories, Inc.) were used as received. 2,2’-Azobis(isobutyronitrile) (AIBN) (Aldrich, 98%) was purified by recrystallization from methanol.
4.4 Instrumentation

\textit{\textsuperscript{1}H-NMR Analysis}. \textsuperscript{1}H-NMR Analysis was recorded on Varian NMRS-500 nuclear magnetic resonance instrument (500 MHz) using deuterium oxide (D\textsubscript{2}O) as a solvent.

\textit{Gel Permeation Chromatography (GPC)}. Molecular weights and molecular weight distribution of these polycarboxylate copolymers were measured by using Bryce-type differential refractometer (RI) as a detector equipped with TSKgel SuperMultipore PW-H (TOSOH) column, and polyethylene oxide (PEO) and polyethylene glycol (PEG) as standards for the calibration. The samples were analyzed by using 75 wt. % aqueous solution of these salts: sodium azide (NaN\textsubscript{3}), potassium phosphate monobasic (KH\textsubscript{2}PO\textsubscript{4}), sodium phosphate dibasic dodecahydrate (Na\textsubscript{2}HPO\textsubscript{4}·12H\textsubscript{2}O), and sodium sulfate (Na\textsubscript{2}SO\textsubscript{4}). The flow rate was 0.5 ml min\textsuperscript{-1} and polymer concentration was 1 mg ml\textsuperscript{-1} solvent.

4.5 Synthesis

This section concentrates on the synthesis of polycarboxylate copolymers via two different methods, conventional radical polymerization and esterification process.

4.5.1 Synthesis of polycarboxylate copolymers \textit{via} conventional radical polymerization

There are many research groups who used free radical polymerization method for preparing polycarboxylate copolymers. The most popular initiators that has been used for these syntheses are persulfate initiators e.g. ammonium persulfate ((NH\textsubscript{4})\textsubscript{2}S\textsubscript{2}O\textsubscript{8})\textsuperscript{108-110}, sodium persulfate (Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8})\textsuperscript{106,111,112}, and AIBN.

First, we followed the method used by Liu et al.\textsuperscript{111} in which they used (Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}) as an initiator and sodium bisulfite (NaHSO\textsubscript{3}) as an activator in a redox-initiating system.
Run 1 in Table 4-1, methacrylic acid (MAA) (2.58 g, 0.03 mol) and methoxy poly (ethylene glycol) methacrylate, $M_w$ 950 g mol$^{-1}$ (MPEGMA950) (9.50 g, 0.01 mol) were mixed with deionized (DI) water in a three-neck round bottom flask, equipped with a condenser, a gas inlet, a gas outlet, and a rubber septum (for adding chemicals). NaOH solution was then added to this mixture in order to adjust the pH around 7-9. Each reaction mixture was gently stirred by magnetic stir bar under a streaming of nitrogen gas. After 30 min, the polymerization was initiated by an aqueous solution of Na$_2$S$_2$O$_8$ (10 wt. %) and NaHSO$_3$ (10 wt. %) via syringe pump through the rubber septum within 3.5 h and continued for another 20 h. After that, the polymerization was terminated via immediate exposure to air and quenching with an ice bath. Then, the water was isolated through rotary evaporator. The residual mixture was purified by precipitation in diethyl ether for three times in order to remove unreacted materials. Finally, it was dried overnight in a vacuum oven at room temperature.

In the second method for the synthesis of polycarboxylate copolymers via conventional radical polymerization, AIBN was used as the initiator, which is as same as the initiator used in the synthesis of polycarboxylate copolymers via RAFT polymerization (CHAPTER V). MPEGMA molecular weights 950 g mol$^{-1}$ (MPEGMA950), methacrylic acid (MAA), NaOH as a pH adjuster, 2-mercapto ethanol as a chain transfer agent, and deionized (DI) water as solvent were introduced into a three-neck round bottom flask, equipped with a condenser, a gas inlet, a gas outlet, and a rubber septum (for adding chemicals).
Run 2 in Table 4-1 was performed by mixing methacrylic acid (2.58 g, 0.03 mol), MPEGMA950 g mol⁻¹ (9.50 g, 0.01 mol), and DI water (7.00 g) as a solvent in a reaction flask.

Run 3 in Table 4-1 was performed by mixing methacrylic acid (2.58 g, 0.03 mol), MPEGMA950 g mol⁻¹ (9.50 g, 0.01 mol), and DI water (7.00 g) as a solvent in a reaction flask.

In run 2 and run 3 (Table 4-1), pH was adjusted around 7-9 by sodium hydroxide (NaOH) solution. Then, the mixture solution was gently stirred by magnetic stir bar under the nitrogen ambient in an oil bath at 65 °C. After 30 min, the polymerization was initiated by adding AIBN and 2-mercaptop ethanol which were solubilized in 4 mL of THF via syringe pump within 3.5 h and continued for another 20 h. Polymerization was finished by exposure to air and quenching with an ice bath. After cooling, the mixture was washed with diethyl ether (100 mL) for three times in order to remove unreacted reactants. Finally, it was dried overnight in a vacuum oven.

Table 4-1 Summary of the synthesis of polycarboxylate copolymers synthesized via conventional radical polymerization between MPEGMA950 and MAA monomer

<table>
<thead>
<tr>
<th>Run</th>
<th>Initiator</th>
<th>2-Mecapto ethanol</th>
<th>MAA/MPEGMA950</th>
<th>DI water (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Na₂S₂O₈ / NaHSO₃</td>
<td>-</td>
<td>3/1</td>
<td>7.00</td>
</tr>
<tr>
<td>2</td>
<td>AIBN (164 mg, 10⁻³ mol)</td>
<td>0.125 g, 1.6 x 10⁻³ mol</td>
<td>3/1</td>
<td>7.00</td>
</tr>
<tr>
<td>3</td>
<td>AIBN (164 mg, 10⁻³ mol)</td>
<td>0.0625 g, 8.0 x 10⁻⁴ mol</td>
<td>3/1</td>
<td>7.00</td>
</tr>
</tbody>
</table>
4.5.2 Synthesis of polycarboxylate copolymers via esterification process

This is a two-step process. The first step was to synthesize poly (methacrylic acid) in different molecular weights (as shown in Figure 4-2). Those series of poly (methacrylic acid) were then esterified with methoxy poly (ethylene glycol) in a presence of catalyst in order to generate polycarboxylate copolymers (as shown in Figure 4-3)\textsuperscript{14}.

*Synthesis of poly (methacrylic acid) or PMAA*

Methacrylic acid (MAA) as a monomer, AIBN as an initiator, and toluene as a solvent were introduced into a three-neck round bottom flask, equipped with a condenser and a dean-stark trap, nitrogen gas inlet and outlet. The amount of MAA (21.00 g, 2.44 x 10\textsuperscript{-1} mol) and toluene (70 g) were fixed constant, but changing the amount of AIBN in three different quantities: [AIBN (0.115 g, 6.99 x 10\textsuperscript{-4} mol), AIBN (50.4 mg, 3.07 x 10\textsuperscript{-4} mol), and AIBN (20.8 mg, 1.27 x 10\textsuperscript{-4} mol)]. Thus, there would be three different molecular weights of poly (methacrylic acid) or PMAA.
Each reaction mixture was gently stirred by magnetic stir bar under the nitrogen at room temperature. After 30 min, the polymerization was initiated by immersing the reaction flask into an oil bath at 80 °C for 24 h. Polymerization was finished by exposure to air and quenching with an ice bath. After cooling, toluene was evaporated by rotary evaporator. The white powder was collected and then washed with hexane 50 mL for three times in order to remove unreacted MAA monomer. Finally, it was dried overnight in a vacuum oven.

![Chemical structures of methacrylic acid, AIBN as an initiator, and toluene as a solvent used for synthesis of polycarboxylate admixtures](image)

**Figure 4-2 Chemical structures of methacrylic acid, AIBN as an initiator, and toluene as a solvent used for synthesis of polycarboxylate admixtures**

**Esterification reaction for the synthesis of polycarboxylate copolymers**

Methoxy poly (ethylene glycol) or MPEG as a monomer, methanesulfonic acid as a catalyst, and deionized water as a solvent were introduced into a three-neck round bottom flask, equipped with a condenser, nitrogen gas inlet and outlet. Each reaction mixture was gently stirred by magnetic stir bar under the nitrogen ambient at 120 °C. After 30 min, the polymerization was initiated by adding PMAA (synthesized in previous step) solubilized in deionized water via syringe pump within 1 h and continued for another 23 h. After that, the mixture was washed with diethyl ether for three times in order to remove unreacted reactants. Finally, it was dried overnight in a vacuum oven.
The amount of methanesulfonic acid catalyst was 1.4 wt. % of total weight of monomers. The total amount of deionized water was kept to provide the concentration of total materials around 40 wt. %.

Run 1 in Table 4-2 was performed by mixing PMAA-1 (\(M_n = 3.9 \times 10^3 \text{ g mol}^{-1}\)) (1.22 g, 3.12 \times 10^{-4} \text{ mol}), MPEG750 (\(M_n = 750 \text{ g mol}^{-1}\)) (5.62 g, 7.50 \times 10^{-3} \text{ mol}), methanesulfonic acid (96 mg, 9.98 \times 10^{-4} \text{ mol}), and DI water (10 g) in a reaction flask.

Run 2 in Table 4-2 was performed by mixing PMAA-2 (\(M_n = 6.2 \times 10^3 \text{ g mol}^{-1}\)) (1.93 g, 3.12 \times 10^{-4} \text{ mol}), MPEG750 (\(M_n = 750 \text{ g mol}^{-1}\)) (5.62 g, 7.50 \times 10^{-3} \text{ mol}), methanesulfonic acid (0.11 g, 1.17 \times 10^{-3} \text{ mol}), and DI water (12 g) in a reaction flask.

Run 3 in Table 4-2 was performed by mixing PMAA-3 (\(M_n = 1.2 \times 10^4 \text{ g mol}^{-1}\)) (3.74 g, 3.12 \times 10^{-4} \text{ mol}), MPEG750 (\(M_n = 750 \text{ g mol}^{-1}\)) (5.62 g, 7.50 \times 10^{-3} \text{ mol}), methanesulfonic acid (0.13 g, 1.36 \times 10^{-3} \text{ mol}), and deionized water (14.00 g) in a reaction flask.

Run 4 in Table 4-2 was performed by mixing PMAA-3 (\(M_n = 1.2 \times 10^4 \text{ g mol}^{-1}\)) (3.74 g, 3.12 \times 10^{-4} \text{ mol}), MPEG2000 (\(M_n = 2000 \text{ g mol}^{-1}\)) (15.00 g, 7.50 \times 10^{-3} \text{ mol}), methanesulfonic acid (0.26 g, 2.73 \times 10^{-3} \text{ mol}), and deionized water (28.00 g) in a reaction flask.
Table 4-2 Summary of esterification reaction for the synthesis of polycarboxylate copolymers

<table>
<thead>
<tr>
<th>Run</th>
<th>Material 1</th>
<th>Material 2</th>
<th>MPEG/PMAA</th>
<th>Methanesulfonic acid (g)</th>
<th>DI water (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PMAA-1</td>
<td>MPEG750</td>
<td>24/1</td>
<td>0.09</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>PMAA-2</td>
<td>MPEG750</td>
<td>24/1</td>
<td>0.11</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>PMAA-3</td>
<td>MPEG750</td>
<td>24/1</td>
<td>0.13</td>
<td>14</td>
</tr>
<tr>
<td>4</td>
<td>PMAA-3</td>
<td>MPEG2000</td>
<td>24/1</td>
<td>0.26</td>
<td>15</td>
</tr>
</tbody>
</table>

Figure 4-3 Esterification process of PMAA with MPEG for the synthesis of polycarboxylate copolymers

4.6 Results and discussion

GPC and $^1$H-NMR were the main characterization methods to analyze PMAA homopolymers and polycarboxylate copolymers synthesized via conventional radical polymerization and esterification process. GPC was method used to determine molecular weights and molecular weight distribution. $^1$H-NMR was used to confirm the chemical structures used in this study.
4.6.1 Characterization of polycarboxylate copolymers via conventional radical polymerization

There were different initiators including sodium persulfate (Na$_2$S$_2$O$_8$) and AIBN used to synthesize polycarboxylate copolymers via conventional radical polymerization.

Table 4-3 Molecular weights and PDI of polycarboxylate copolymers via conventional radical copolymerization

<table>
<thead>
<tr>
<th>Run</th>
<th>Initiator</th>
<th>Monomers</th>
<th>Molecular Weight (g mol$^{-1}$)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$M_n$</td>
<td>$M_w$</td>
</tr>
<tr>
<td>1</td>
<td>Na$_2$S$_2$O$_8$</td>
<td>MPEGMA950/MAA</td>
<td>21,000</td>
<td>56,000</td>
</tr>
<tr>
<td>2</td>
<td>AIBN</td>
<td>MPEGMA950/MAA</td>
<td>19,500</td>
<td>103,800</td>
</tr>
<tr>
<td>3</td>
<td>AIBN</td>
<td>MPEGMA950/MAA</td>
<td>69,700</td>
<td>288,000</td>
</tr>
</tbody>
</table>

Figure 4-4 $^1$H-NMR of polycarboxylate copolymer via conventional radical polymerization
Figure 4-4 shows $^1$H-NMR of polycarboxylate copolymer via conventional radical copolymerization between MPEGMA and MAA with the adjusted pH of $\approx 7 - 9$ by NaOH. Each copolymer was dissolved in D$_2$O, which shows the chemical shift ($\delta$) at 4.79 ppm. Two broad distinct chemical shifts: -CH$_2$-C(CH$_3$)$_2$- (copolymer main chain) at $\delta = 0.80 - 1.50$ ppm and -CH$_2$-C(CH$_3$)$_2$- (copolymer main chain) at $\delta = 1.70 - 2.30$ ppm were observed. -O-CH$_3$ (methoxy group in MPEGMA) shows proton resonances at $\delta = 3.45$ ppm. -CO$_2$-CH$_2$-CH$_2$-O- (PEO unit next to the ester group in MPEGMA) shows proton resonances at $\delta = 4.24$ ppm. This confirmed the successful synthesis of polycarboxylate copolymers (PMPEGMA - random - PMAA). The reason that these polycarboxylate copolymers were assumed to be random is based on the previous study by Smith et al. $^{92}$ in which they studied the monomer reactivity of MAA and MPEGMA in different media. They found that in aqueous medium, reactivity of MAA and MPEGMA were $r_1 = 1.03$ and $r_2 = 1.02$, respectively. This means two monomers have similar reactivities towards both propagating species (homo-propagating and cross-propagating species). Although the prepared copolymers will have the compositions as same as the monomers feeds, but the compositional distribution of each monomer in the polymer backbone will be random.

4.6.2 Characterization of polycarboxylate copolymers via esterification process

As described in section 4.5.2, there were three molecular weights for PMAA (as shown in Table 4-4 below) synthesized according to the radical polymerization using AIBN as an initiator. The molecular weights were measured with water GPC using PEO and PEG as standards.
For the polycarboxylate copolymers via esterification reaction, there were four copolymers in this study. The molecular weights were measured with water GPC using PEO and PEG as standards.

Table 4-5 Molecular weights and PDI of polycarboxylate copolymers via esterification reaction between PMAA and MPEG

<table>
<thead>
<tr>
<th>Run</th>
<th>Material 1</th>
<th>Material 2</th>
<th>Molecular Weight (g mol⁻¹)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PMAA-1</td>
<td>MPEG750</td>
<td>13,400</td>
<td>43,500</td>
</tr>
<tr>
<td>2</td>
<td>PMAA-2</td>
<td>MPEG750</td>
<td>16,600</td>
<td>60,800</td>
</tr>
<tr>
<td>3</td>
<td>PMAA-3</td>
<td>MPEG750</td>
<td>20,600</td>
<td>65,500</td>
</tr>
<tr>
<td>4</td>
<td>PMAA-3</td>
<td>MPEG2000</td>
<td>23,300</td>
<td>80,100</td>
</tr>
</tbody>
</table>
Figure 4-5 $^1$H-NMR of poly (methacrylic acid) or PMAA

Figure 4-5 shows $^1$H-NMR of PMAA synthesized by conventional radical polymerization (as shown in section 4.5.2). Each PMAA was dissolved in deuterium oxide (D$_2$O), which shows the chemical shift ($\delta$) at 4.79 ppm. $\delta$ 1.00 - 1.50 ppm represents the methyl group of -CH$_2$-CCH$_3$ repeating units in the PMAA main chain. $\delta$ around 1.89 - 2.40 ppm shows the methylene group of -CH$_2$-CCH$_3$ repeating units in the polymer main chain. The integral area of the methyl group to the methylene group is 3:2, which indicates the successful synthesis of PMAA. In addition, there are no proton resonances around 5 - 6 ppm, corresponding to the chemical shift of protons from alkene group from methacrylic monomer. This further confirmed the preparation of PMAA $^{114, 115}$. 
Figure 4-6 $^1$H-NMR of polycarboxylate copolymer via esterification process

Figure 4-6 illustrates the $^1$H-NMR of polycarboxylate copolymer prepared via step-growth polymerization between PMAA and MPEG in a presence of catalyst. Each copolymer was dissolved in D$_2$O. Two chemical shifts: $-\text{CH}_2$-$\text{C}$(CH$_3$)- (polymer main chain) at $\delta = 0.80$ - 1.50 ppm and $-\text{CH}_2$-$\text{C}$(CH$_3$)- (polymer main chain) at $\delta = 1.70$ - 2.30 ppm were from polymer main chain of PMAA. In addition, new resonances were observed: $\text{CH}_3$-$(\text{O}–\text{CH}_2–\text{CH}_2)$–O-CO$_2$ (PEO repeating units in MPEG) at $\delta = 3.60$ - 3.92 ppm, $-\text{O}–\text{CH}_3$ (methoxy group in MPEG) at $\delta = 3.45$ ppm, and $-\text{CO}_2$-$\text{CH}_2$-$\text{CH}_2$-O- (PEO unit next to the ester group) at $\delta = 4.24$ ppm. The proton resonance at 4.24 ppm is very important to prove the successful esterification reaction between PMAA and MPEG.
4.7 Conclusions

Polycarboxylate copolymers (MPEGMA/MAA) were successfully synthesized by both conventional radical polymerization and esterification process. GPC were used to characterized molecular weights and molecular weight distributions of all synthesized polymers. $^1$H-NMR was used to confirm the chemical structures of all polymers used in this study. These polycarboxylates copolymers synthesized via conventional radical polymerization and by esterification were further used as concrete admixtures to compare the concrete properties (CHAPTER VI) with the polycarboxylates copolymers synthesized via RAFT polymerization (CHAPTER V).
CHAPTER V

THE SYNTHESIS OF NEW POLYCARBOXYLATE ADMIXTURES FOR CONCRETE VIA RAFT POLYMERIZATION

5.1 Overview

A series of polycarboxylate copolymers, PMPEGMA - random - PMAA and PMPEGMA - block - PMAA were successfully synthesized via RAFT polymerization with different molar ratios of the polycarboxylate copolymers and different chain lengths of PEO repeating units. In addition, a new polycarboxylate terpolymer was also created via RAFT polymerization. 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester monomer (modified defoaming agent) was another monomer in addition to MPEGMA and MAA monomers in the reaction mixture. $^1$H-NMR, GPC, and MALDI-TOF mass spectrometry were used to characterize these polycarboxylate copolymers and a new polycarboxylate terpolymer. These prepared copolymers in this chapter could then be compared to polycarboxylate copolymers synthesized via conventional radical polymerization and esterification process (CHAPTER IV) in order to investigate the concrete properties affected by various copolymers (CHAPTER VI).
5.2 Introduction

High performance concretes provide a high strength and durability. This is probably the aid of added additives. Among them, polycarboxylate superplasticizers as dispersing agents have played a big role for years. They not only help to enhance the flow ability during concrete processing, but also increase the mechanical properties due to a very low used of water/cement ratio\textsuperscript{109, 116, 117}.

Generally, these polycarboxylate superplasticizers are synthesized by two different ways (as mentioned in CHAPTER IV): (i) radical copolymerization of methacrylic acid (MAA) and alkyl-PEGs macromonomers and (ii) post-grafting of alkyl poly (ethylene glycol) on to a preformed PMAA backbone\textsuperscript{104}.

Previously, many research groups have synthesized polycarboxylate superplasticizers based on the methods mentioned above. Liu et al.\textsuperscript{111} created a series of comb-like copolymers with different side chain lengths of PEO repeating units. Acrylic acid (AA) instead of methacrylic acid (MAA) was used in their study. Sodium persulfate (Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8}) was used as an initiator and NaHSO\textsubscript{3} as an activator. Plank et al.\textsuperscript{106} synthesized and studied the performance of methacrylate ester based polycarboxylate superplasticizers. They used radical copolymerization to create those copolymers by using Na\textsubscript{2}S\textsubscript{2}O\textsubscript{8} as an initiator, methallyl sulfonic acid (sodium salt) as a chain transfer agent. MAA, methoxy poly (ethylene glycol) methacrylate (MPEGMA), and hydroxy termination of poly (ethylene glycol) methacrylate (PEGMA) were used as monomers. They found the similar performance in concrete between using MPEGMA or hydroxy termination of PEGMA. Rongguo et al.\textsuperscript{42} also fabricated and studied the effect of molecular structure on the performance of polyacrylic acid superplasticizer in cement.
Similar to other research groups, they synthesized those superplasticizers through radical polymerization. The basic monomers are very much the same, but using ammonium persulfate \((\text{NH}_4)_2\text{S}_2\text{O}_8\) as an initiator. Whatever the method used, the synthesized polycarboxylate copolymers usually show a broad molecular weight distribution. Furthermore, the molar composition between MAA and alkyl-PEG units along the copolymer chains is barely controlled.

To overcome a broad molecular weight distribution and have more control of monomer composition, living/controlled radical polymerization techniques have brought into attention. Among living radical processes, reversible-addition fragmentation chain transfer (RAFT) polymerization has been reported to be useful for diverse monomers \(^{97}\). Moreover, RAFT polymerization is very similar to free radical polymerization. The only difference between those reactions is added RAFT agent. Therefore, if any monomer is able to be polymerized by conventional radical polymerization, it should be able to establish the condition for RAFT polymerization. For the polycarboxylate copolymers in concrete industry, there were not so many research groups using RAFT polymerization technique. Rinaldi et al. \(^{118}\) used a water soluble RAFT agent together with MAA and MPEGMA to synthesize polycarboxylate copolymers. They did only one chain length of PEO repeating units in MPEGMA and did not use those synthesized copolymers to investigate the interaction with cement and cement properties. In addition, only random copolymers were synthesized. For these reasons; in this present study, a series of polycarboxylate copolymers, PMPEGMA - random - PMAA with various charge densities of the polycarboxylate copolymers and different chain lengths of PEO repeating units were synthesized and characterized. A series of polycarboxylate block copolymers,
PMPEGMA - *block* - PMAA were also created due to the benefit of using RAFT polymerization. Moreover, a new polycarboxylate terpolymer was also synthesized via RAFT polymerization. 2-methyl acrylic acid (dibutoxy-phosphoryloxy) – alkyl ester monomer (modified defoaming agent) acts as an *in-situ* defoaming agent in a polycarboxylate terpolymer. These synthesized polycarboxylate copolymers and terpolymer would be further compared to polycarboxylate copolymers synthesized via conventional radical polymerization and esterification process (CHAPTER IV). This gives the opportunity of investigating the concrete properties under the effects of different polycarboxylate copolymers (CHAPTER VI).

5.3 Materials

Methoxy poly (ethylene glycol) methacrylates (MPEGMA 550, 950, and 2000 g mol⁻¹) and 4-cyanopentanoic acid dithiobenzoate (CPADB) were used from the synthesis in CHAPTER III. MPEGMA 350 g mol⁻¹ (Aldrich), Methacrylic acid (MAA) (Aldrich, 99%), *N,N*-Dimethylformamide (DMF) (Aldrich, anhydrous, 99.8%), deuterated chloroform (CDCl₃) (Cambridge Isotope Laboratories, Inc.), deuterium oxide (Cambridge Isotope Laboratories, Inc.), sodium hydroxide (NaOH) (Aldrich), tetrahydrofuran (THF) (Aldrich, anhydrous >99%), sodium azide (NaN₃) (Sigma-Aldrich, ≥ 99.5%), potassium phosphate monobasic (KH₂PO₄) (Sigma-Aldrich, ACS reagent, ≥ 99%), sodium phosphate dibasic dodecahydrate (Na₂HPO₄·12H₂O) (Sigma-Aldrich, puriss. p.a., crystallized, ≥ 99%), sodium sulfate (Na₂SO₄) (Sigma-Aldrich, ACS reagent, ≥ 99%), dithranol matrix (Alfa Aesar, >97%), and sodium trifluoroacetate (Aldrich, >98%), and poly (methyl methacrylate) standard (Fluka) were used as
received. 2,2’-Azobis(isobutyronitrile) (AIBN) (Aldrich, 98%) was purified by recrystallization from methanol.

5.4 Instrumentation

*Gel Permeation Chromatography (GPC).* Molecular weights and molecular weight distribution of these polycarboxylate copolymers were measured by using Bryce-type differential refractometer (RI) as a detector equipped with TSKgel SuperMultipore PW-H (TOSOH) column, and polyethylene oxide (PEO) and polyethylene glycol (PEG) as standards for the calibration. The samples were analyzed by using 75 wt. % aqueous solution of these salts; sodium azide (NaN₃), potassium phosphate monobasic (KH₂PO₄), sodium phosphate dibasic dodecahydrate (Na₂HPO₄•12H₂O), and sodium sulfate (Na₂SO₄). The flow rate was 0.5 ml min⁻¹ and polymer concentration was 1 mg ml⁻¹ solvent.

*¹H and ¹³C NMR analysis.* ¹H and ¹³C-NMR Analysis of these materials were recorded on Varian NMRS-500 nuclear magnetic resonance instrument (500 MHz) using deuterated chloroform (CDCl₃) or deuterium oxide (D₂O) as a solvent.

*Mass spectrometry analysis.* Mass spectral experiments were performed to assist in determining the chemical structure of starting materials, using a Bruker ULTRAFLEX-III time-of-flight matrix-assisted laser desorption ionization mass spectrometer (Bruker Daltonics, Billerica, MA) equipped with a pulsed Nd:YAG, a two-stage gridless reflector and a single stage pulsed ion extraction source. Separate THF (Aldrich, anhydrous >99%) solutions of dithranol matrix (20 mg mL⁻¹) (Alfa Aesar, >97%), sodium trifluoroacetate (10 mg mL⁻¹) (Aldrich, >98%) and polymer (10 mg mL⁻¹) were mixed in a ratio of matrix: cationizing salt: polymer (10:1:2), and 0.5 μL of the resulting mixture was
introduced onto the MALDI target plate. The spectra were obtained in the reflection mode. The attenuation of the laser was adjusted to minimize unwanted polymer fragmentation and to maximize the sensitivity. The calibration of mass scale was carried out externally using poly (methyl methacrylate) standard (Fluka) with a similar molecular weight as the sample.

5.5 Synthesis

Different types of PMPEGMA - co – PMAA (polycarboxylate copolymers) and a polycarboxylate terpolymer were successfully synthesized via RAFT polymerization

5.5.1 Synthesis of PMPEGMA - random – PMAA via RAFT polymerization

MPEGMA in different molecular weights (550, 950, and 2000 g mol\(^{-1}\)), methacrylic acid (MAA), CPADB as a RAFT agent, sodium hydroxide as a pH adjuster, and deionized (DI) water as a solvent were introduced into a three-neck round bottom flask, equipped with a condenser, nitrogen gas inlet and outlet, and a rubber septum (for adding chemicals).

Run 1 in Table 5-1 was performed by mixing methacrylic acid (1.232 g, 1.43 \times 10^{-2} \text{ mol}), MPEGMA550 g mol\(^{-1}\) (6.79 g, 1.43 \times 10^{-2} \text{ mol}), CPADB (0.10 g, 3.58 \times 10^{-4} \text{ mol}) as a RAFT agent, and deionized water (20.00 g) as a solvent in a reaction flask.

Run 5 in Table 5-1 was performed by mixing methacrylic acid (1.232 g, 1.43 \times 10^{-2} \text{ mol}), MPEGMA950 g mol\(^{-1}\) (6.80 g, 7.16 \times 10^{-3} \text{ mol}), CPADB (0.05 g, 1.79 \times 10^{-4} \text{ mol}) as a RAFT agent, and deionized water (10.00 g) as a solvent in a reaction flask.
Table 5-1 Copolymers synthesized via RAFT polymerization between MPEGMA (550, 950, and 2000) and MAA monomer

<table>
<thead>
<tr>
<th>Run</th>
<th>Monomers</th>
<th>MPEGMA / MAA / CPADB</th>
<th>CPADB/AIBN</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MPEGMA550/MAA</td>
<td>40 / 40 / 1</td>
<td>3.3</td>
</tr>
<tr>
<td>2</td>
<td>MPEGMA950/MAA</td>
<td>40 / 40 / 1</td>
<td>3.3</td>
</tr>
<tr>
<td>3</td>
<td>MPEGMA2000/MAA</td>
<td>40 / 40 / 1</td>
<td>3.3</td>
</tr>
<tr>
<td>4</td>
<td>MPEGMA550/MAA</td>
<td>40 / 80 / 1</td>
<td>3.3</td>
</tr>
<tr>
<td>5</td>
<td>MPEGMA950/MAA</td>
<td>40 / 80 / 1</td>
<td>3.3</td>
</tr>
<tr>
<td>6</td>
<td>MPEGMA2000/MAA</td>
<td>40 / 80 / 1</td>
<td>3.3</td>
</tr>
<tr>
<td>7</td>
<td>MPEGMA350/MAA</td>
<td>40 / 120 / 1</td>
<td>3.3</td>
</tr>
<tr>
<td>8</td>
<td>MPEGMA550/MAA</td>
<td>40 / 120 / 1</td>
<td>3.3</td>
</tr>
<tr>
<td>9</td>
<td>MPEGMA950/MAA</td>
<td>40 / 120 / 1</td>
<td>1.1</td>
</tr>
<tr>
<td>10</td>
<td>MPEGMA950/MAA</td>
<td>40 / 120 / 1</td>
<td>3.3</td>
</tr>
<tr>
<td>11</td>
<td>MPEGMA950/MAA</td>
<td>40 / 120 / 1</td>
<td>6.6</td>
</tr>
<tr>
<td>12</td>
<td>MPEGMA2000/MAA</td>
<td>40 / 120 / 1</td>
<td>3.3</td>
</tr>
<tr>
<td>13</td>
<td>MPEGMA550/MAA</td>
<td>40 / 160 / 1</td>
<td>3.3</td>
</tr>
<tr>
<td>14</td>
<td>MPEGMA950/MAA</td>
<td>40 / 160 / 1</td>
<td>3.3</td>
</tr>
<tr>
<td>15</td>
<td>MPEGMA2000/MAA</td>
<td>40 / 160 / 1</td>
<td>3.3</td>
</tr>
</tbody>
</table>
Each mixture in Table 5-1 was adjusted the pH to be around 7-9 by sodium hydroxide (NaOH). Then, the mixture solution was gently stirred by magnetic stir bar under the nitrogen ambient in an oil bath at 65 °C. After 30 min, the polymerization was initiated by adding AIBN that was solubilized in 4 mL of THF via syringe pump through a rubber septum within 3.5 h and continued for another 20 h. Polymerization was finished by exposure to air and quenching with an ice bath. After cooling, the mixture was washed with diethyl ether (100 mL) for three times in order to remove unreacted reactants. Finally, it was dried overnight in a vacuum oven.

Figure 5-1 shows chemical structures and reaction condition used for synthesis of random copolymers of PMPEGMA - random - PMAA. There were many ratios between methoxy poly (ethylene glycol) methacrylate (MPEGMA) monomer and methacrylic acid (MAA) monomer ranging from 1:1, 1:2, 1:3, and 1:4 used in this study. Moreover, the length of side chain of poly (ethylene oxide) (PEO) repeating units in the MPEGMA are different as MPEGMA550 (n = 12), MPEGMA950 (n = 24), and MPEGMA2000 (n = 48). In addition, molar ratio of MPEGMA / MAA / CPADB was kept constant in Run 8 - Run 10, but the ratio of CPADB/AIBN was varied in Table 5-1. This was performed in order to study the effect of molecular weight of polycarboxylate copolymers. Therefore, there would be many combination reactions for these syntheses (as can be seen in Table 5-1). These polycarboxylate copolymers were then used in the study of concrete properties in terms of various charge densities of the polycarboxylate copolymers and different chain lengths of PEO repeating units. This section will focus only on the synthesis and characterization of those series of polycarboxylate copolymers. The
Concrete properties from these polycarboxylate random copolymers will be explained and discussed in Chapter VI (Concrete tests for new polycarboxylate admixtures).

Figure 5-1 Chemical structures of methoxy poly (ethylene glycol) methacrylate (n= 12, MPEGMA550; n = 24, MPEGMA950, and n = 48, MPEGMA 2000), Methacrylic acid (MAA), and CPADB RAFT agent used for synthesis random copolymers of PMPEGMA - random - PMAA

5.5.2 Synthesis of PMPEGMA - block – PMAA via RAFT polymerization

A series of PMPEGMA950 - b - PMAA were synthetized by using RAFT polymerization method. There were two steps in these syntheses. First stage was to synthesize 950 macro RAFT agents. These resulting macro RAFT agents were further polymerized with methacrylic acid to create a series of block copolymers, PMPEGMA950 – b – PMAA.
Homopolymerization of MPEGMA950 via RAFT polymerization

MPEGMA having the molecular weight of 950 g mol\(^{-1}\), DMF as a solvent, AIBN as an initiator, and CPADB as a RAFT agent were introduced into a three-neck round bottom flask, equipped with a condenser, nitrogen gas inlet and outlet.

Run 1 in Table 5-2 was performed by mixing MPEGMA950 (21.00 g, 2.21 \(\times\) 10\(^{-2}\) mol), CPADB (0.248 g, 8.85 \(\times\) 10\(^{-4}\) mol), AIBN (29.5 mg, 1.77 \(\times\) 10\(^{-4}\) mol), and DMF (10.00 g) in a reaction flask.

Run 2 in Table 5-2 was performed by mixing MPEGMA950 (21.00 g, 2.21 \(\times\) 10\(^{-2}\) mol), CPADB (0.124 g, 4.42 \(\times\) 10\(^{-4}\) mol), AIBN (14.5 mg, 8.80 \(\times\) 10\(^{-5}\) mol), and DMF (10.00 g) in a reaction flask.

Table 5-2 Synthesis summary of macro RAFTs PMPEGMA 950

<table>
<thead>
<tr>
<th>Run</th>
<th>Monomer (Monomer)</th>
<th>MPEGMA/CPADB (wt. %)</th>
<th>CPADB/AIBN (Molar ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MPEGMA950</td>
<td>67.14</td>
<td>25/1</td>
</tr>
<tr>
<td>2</td>
<td>MPEGMA950</td>
<td>67.44</td>
<td>50/1</td>
</tr>
</tbody>
</table>

The mixture from Table 5-2 was gently stirred by a magnetic stir bar under the nitrogen purge. After 30 min, the polymerization was initiated by placing the reaction flask into an oil bath at 65 °C and continued for 20 h. The polymerization was terminated via immediate exposure to air and quenching in an ice bath. After termination, the PMPEGMA macro RAFT was purified by precipitation in diethyl ether for three times in order to remove unreacted MPEGMA950, AIBN, and CPADB. Finally, it was dried overnight in a vacuum oven at room temperature.
Block copolymerization of PMPEGMA950 - b - PMAA via RAFT Polymerization

A series of block copolymers of PMPEGMA950 – b – PMAA were successfully synthesized. DMF as a solvent, AIBN as an initiator, and PMPEGMA950 from previous step as macro RAFT agents were introduced into a three-neck round bottom flask, equipped with a condenser, a nitrogen gas inlet and outlet.

Run 3 in Table 5-3 was performed by mixing PMPEGMA950 (M_n = 1.10 x 10^4 g mol^{-1}) (3.00 g, 2.70 x 10^{-4} mol), MAA (1.34 g, 1.56 x 10^{-2} mol), AIBN (8.80 mg, 5.36 x 10^{-5} mol), and DMF (6.50 g) in a reaction flask.

Run 5 in Table 5-3 was performed by mixing PMPEGMA950 (M_n = 1.75 x 10^4 g mol^{-1}) (3.00 g, 1.70 x 10^{-4} mol), MAA (0.43 g, 5.0 x 10^{-3} mol), AIBN (5.60 mg, 3.40 x 10^{-5} mol), and DMF (7.50 g) in a reaction flask.

Table 5-3 Summary of block copolymerization of PMPEGMA and PMAA via RAFT polymerization

<table>
<thead>
<tr>
<th>Run</th>
<th>First block</th>
<th>M_n of the First block (g mol^{-1})</th>
<th>Second block</th>
<th>Second block / First block (Molar ratio)</th>
<th>First block/AIBN (Molar ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>PMPEGMA950-1</td>
<td>11,000</td>
<td>MAA</td>
<td>1/57</td>
<td>5/1</td>
</tr>
<tr>
<td>4</td>
<td>PMPEGMA950-1</td>
<td>11,000</td>
<td>MAA</td>
<td>1/114</td>
<td>5/1</td>
</tr>
<tr>
<td>5</td>
<td>PMPEGMA950-2</td>
<td>17,500</td>
<td>MAA</td>
<td>1/29</td>
<td>5/1</td>
</tr>
<tr>
<td>6</td>
<td>PMPEGMA950-2</td>
<td>17,500</td>
<td>MAA</td>
<td>1/58</td>
<td>5/1</td>
</tr>
<tr>
<td>7</td>
<td>PMPEGMA950-2</td>
<td>17,500</td>
<td>MAA</td>
<td>1/79</td>
<td>5/1</td>
</tr>
</tbody>
</table>
The mixture from Table 5-3 was gently stirred by a magnetic stir bar under the nitrogen purge. After 30 min, the polymerization was initiated to fabricate the block copolymer by immersing the reaction flask into the oil bath at 65 °C and proceeded for 20 h. Polymerization was terminated via immediate exposure to air and quenching with an ice bath. After cooling, the block copolymer, PMPEGMA950 - b - PMAA was precipitated by 100 mL diethyl ether for three times in order to remove unreacted reactants. Finally, it was dried overnight in a vacuum oven at room temperature.

Scheme 5-1 Chemical structures of methoxy poly (ethylene glycol) methacrylate (n = 24, MPEGMA950), Methacrylic acid (MAA), CPADB RAFT agent, and macro RAFT agents (PMPEGMA950) used for synthesis block copolymers of PMPEGMA950 - b – PMAA
5.5.3 Synthesis of polycarboxylate terpolymer via RAFT polymerization

Methacrylic acid (3.67 g, $4.30 \times 10^{-2}$ mol), MPEGMA 950 g mol$^{-1}$ (13.60 g, 1.43 x $10^{-2}$ mol), 2-methyl acrylic acid (dibutoxy-phosphoryloxy) – alkyl ester (0.24 g, 7.45 x $10^{-4}$ mol), AIBN (17.8 mg, 1.08 x $10^{-4}$ mol), CPADB (0.10 g, 3.58 x $10^{-4}$ mol) as a RAFT agent, and deionized water (20.00 g) as a solvent were mixed in a three-neck round bottom flask. Sodium hydroxide (NaOH) (1.00 g, 0.025 mol) was then added to the flask. The mixture was gently stirred by magnetic stir bar under the nitrogen purge in an oil bath at 85 °C. After 30 min, the polymerization was initiated by dropping AIBN (0.0178 g, 1.84 x $10^{-4}$ mol) as an initiator solubilized in 4 mL of THF via syringe pump within 3.5 h and continued for another 20 h. Polymerization was terminated via immediate exposure to air and quenching with an ice bath. After cooling, the mixture was washed with diethyl ether 100 mL for three times in order to remove unreacted reactants. Finally, it was dried overnight in a vacuum oven.

Scheme 5-2 Chemical structures of MPEGMA950 (n = 24), Methacrylic acid (MAA), 2-methyl acrylic acid (dibutoxy-phosphoryloxy) – alkyl ester, and CPADB RAFT agent, used for synthesis polycarboxylate terpolymer via RAFT polymerization
5.6 Results and discussion

GPC, $^1$H-NMR, and MALDI-TOF (Mass spectrometry) were the main characterization methods to analyze polycarboxylate copolymers and polycarboxylate terpolymer synthesized via RAFT polymerization.

5.6.1 Characterization of RAFT PMPEGMA - random - PMAA

![Figure 5-2 A series of GPC chromatogram of RAFT PMPEGMA550 - r - PMAA](image)
Figure 5-3 A series of GPC chromatogram of RAFT PMPEGMA950 - r - PMAA

Figure 5-4 A series of GPC chromatogram of RAFT PMPEGMA2000 - r - PMAA
Figure 5-2 to Figure 5-4 show GPC chromatograms of polycarboxylate copolymers of PMPEGMA550 - \textit{r} - PMAA, PMPEGMA950 - \textit{r} - PMAA, and PMPEGMA2000 - \textit{r} - PMAA respectively synthesized via RAFT polymerization method. For PMPEGMA550 - \textit{r} - PMAA in Figure 5-2, the number average molecular weights ($M_n$) of those four copolymers are in the same range around 13,000 - 14,000 g mol$^{-1}$ and a little broad PDI from 1.38 - 1.78. In case of PMPEGMA950 - \textit{r} - PMAA as shown in Figure 5-3, the number average molecular weights ($M_n$) of those four copolymers are close to each other as 19,000 - 22,000 g mol$^{-1}$ and represent PDI around 1.38 - 1.71. A series of PMPEGMA2000 - \textit{r} - PMAA (as shown in Figure 5-4) show number average molecular weights ($M_n$) almost equivalent to each other around 28,000 - 32,000 g mol$^{-1}$ and their PDIs are very narrow as of $\sim$1.20. By fixing molar ratio of CPADB RAFT agent to AIBN initiator as 3.3 and changing only the molar ratios between MPEGMA monomer and MAA monomer (ranging from 1:1, 1:2, 1:3, and 1:4), the obtained molecular weights were in the same range as seen in GPC chromatograms in Figure 5-2 to Figure 5-4. Furthermore, it can also be noticed that when the molar ratios of MPEGMA/MAA and CPADB/AIBN were kept constant, but varying the side chain lengths of PEO repeating units in MPEGMA; MPEGMA 550 ($n = 12$), MPEGMA950 ($n = 24$), and MPEGMA2000 ($n = 48$), the molecular weights in those series increased systematically.
Figure 5-5 A series of GPC chromatogram of RAFT PMPEGMA950 - r - PMAA (molar ratio = 1:3) with different ratios of CPADB/AIBN

Figure 5-5 shows GPC chromatograms of RAFT PMPEGMA950 - r - PMAA (molar ratio = 1:3) with different ratios of CPADB/AIBN (as shown in Run 9 - Run 11 in Table 5-1). The molar ratio between MPEGMA monomer and MAA monomer was kept constant at 1:3, but varying the molar ratio of CPADB RAFT agent to AIBN initiator (ranging from 1:1/1, 3.3/1, and 6.6/1). With a lower CPADB/AIBN ratio, the molecular weight seems to be higher. Run 9 in Table 5-1, the number average molecular weight (\(M_n\)) of PMPEGMA950 - r - PMAA is around 38,000 g mol\(^{-1}\) with PDI = 1.82. Run 10 and Run 11 in Table 5-1, the number average molecular weights of PMPEGMA950 - r - PMAA are 22,000 g mol\(^{-1}\) (PDI = 1.71) and 5,300 g mol\(^{-1}\) (PDI = 1.45) respectively.
which corresponded to the CPADB/AIBN ratio = 3.3 and 6.6. It is very obvious that the CPADB/AIBN ratio plays a big role for tailoring the molecular weight of these polycarboxylate copolymers. Therefore, those polycarboxylate copolymers were successfully synthesized and were then used to be added in the concrete mixture to study the relationship between copolymer structures and concrete properties. This will be demonstrated and discussed in CHAPTER VI. To better understand, Figure 5-6 depicts the synthesized polycarboxylate copolymers as summarized in Table 5-1.

Figure 5-6 Molecular images of synthesized polycarboxylate copolymers via RAFT polymerization
Figure 5-7 $^1$H-NMR spectra of (a) sodium methacrylate monomer, (b) MPEGMA950 monomer, and (c) PMPEGMA950 - random - PMAA

Sodium methacrylate monomer, MPEGMA, and series of PMPEGMA - random - PMAA were dissolved in deuterium oxide for $^1$H ($\text{D}_2\text{O, } \delta = 4.79$ ppm) and $^{13}$C NMR analysis. According to the Table 5-1, there were totally 15 reactions in this study. $^1$H and $^{13}$C NMR spectra of those series of polycarboxylate copolymers via RAFT polymerization are very similar to each other e.g. chemical shift. The only difference is the integration area due to the chain length of PEO repeating units and different molar ratios of starting monomers. Thus, Figure 5-7 is a representative of other 14 polycarboxylate copolymers to be explained in this section. According to reaction Figure 5-1, when sodium hydroxide (NaOH) was added in the solution mixture prior to initiate the reaction, methacrylic acid (MAA) monomer would transform to sodium methacrylate salt. For this reason, sodium methacrylate salt was used to compare proton resonances with synthesized polycarboxylate copolymers. This can be seen at the chemical shift 5.40
ppm and 5.71 ppm of CH$_2$=C(COONa)CH$_3$) between Figure 5-7 (a) and (c) that there was little unreacted sodium methacrylate monomer mixed with PMPEGMA950 - random - PMAA.

Table 5-4 $^1$H resonance assignments of (a) sodium methacrylate monomer, (b) MPEGMA monomer, and (c) PMPEGMA - random - PMAA

<table>
<thead>
<tr>
<th>Chemical Structural Group</th>
<th>Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Sodium methacrylate</td>
<td></td>
</tr>
<tr>
<td>CH$_2$=C(COONa)CH$_3$</td>
<td>1.94</td>
</tr>
<tr>
<td>CH$_3$=C(COONa)CH$_3$</td>
<td>5.40 and 5.71</td>
</tr>
<tr>
<td>(b) MPEGMA</td>
<td></td>
</tr>
<tr>
<td>CH$_2$=CR-CH$_3$</td>
<td>1.80 - 2.00</td>
</tr>
<tr>
<td>R-O-CH$_3$</td>
<td>3.46</td>
</tr>
<tr>
<td>-(CH$_2$CH$_2$O)$_n$</td>
<td>3.60 - 3.92</td>
</tr>
<tr>
<td>-OCO-(CH$_2$CH$_2$O)$_n$</td>
<td>4.20 - 4.40</td>
</tr>
<tr>
<td>CH$_2$=CR-CH$_3$</td>
<td>5.82 and 6.24</td>
</tr>
<tr>
<td>(c) PMPEGMA950 - random - PMAA</td>
<td></td>
</tr>
<tr>
<td>-CH$_2$-C(CH$_3$)$_n$- (polymer main chain)</td>
<td>0.80 - 1.50</td>
</tr>
<tr>
<td>-CH$_2$-C(CH$_3$)$_n$- (polymer main chain)</td>
<td>1.70 - 2.30</td>
</tr>
<tr>
<td>R-O-CH$_3$</td>
<td>3.45</td>
</tr>
<tr>
<td>-(CH$_2$CH$_2$O)$_n$</td>
<td>3.60 - 3.92</td>
</tr>
<tr>
<td>-OCO-(CH$_2$CH$_2$O)$_n$</td>
<td>3.66 - 4.24</td>
</tr>
</tbody>
</table>

Table 5-4 shows $^1$H assignments of sodium methacrylate monomer, MPEGMA monomer, and PMPEGMA - random - PMAA. The polymerization started and both monomers were consumed showing decrease in the intensity at $\delta = 5.40$ and 5.71 ppm for sodium methacrylate and $\delta = 5.82$ and 6.24 ppm for MPEGMA. In addition, there were two new chemical shifts: -CH$_2$-C(CH$_3$)$_n$- (polymer main chain) at $\delta = 0.80 - 1.50$ ppm and
-CH₂-C(CH₃)⁻ (polymer main chain) at δ = 1.70 - 2.30 ppm. Both of them showed broad resonances and multiplet splitting pattern. This is due to the sequence of repeating units derived from both starting monomers [119]. In addition, it can be observed in Figure 5-7 (c) that there was also little intensity of proton resonances of unreacted sodium methacrylate monomer of (CH₂=C(COONa)CH₃) at δ = 5.40 and 5.71 ppm and (CH₂=C(COONa)CH₃) at δ = 1.94 ppm compared to Figure 5-7 (a). At the chemical shift 1.94 ppm, there was a sharp proton resonance showing among a broadly new proton resonance of CH₂-C(CH₃)⁻ (polymer main chain) at δ = 1.70 - 2.30 ppm. Thus from this ¹H-NMR interpretation it can be referred that the conversion of sodium methacrylate monomer did not reach 100%. The method and measurement of monomer conversion in RAFT copolymerization will be discussed in the following section. Moreover, after purification with diethyl ether (100 mL, three times), unreacted monomers were not removed completely. This infers that those monomers were quite hard to remove from the copolymer solution mixture. These observations were also found by other groups e.g. Yamada et al. [14].
Figure 5-8 $^{13}$C-NMR spectra of (a) sodium methacrylate monomer, (b) MPEGMA950 monomer, and (c) PMPEGMA950 - random - PMAA

Comparing the $^{13}$C NMR spectra between monomers (Figure 5-8 (a) and (b)) and PMPEGMA950 - random - PMAA (Figure 5-8 (c)), there were some resonances showing some unreacted monomers still existed in the polycarboxylate copolymer solution; $^{13}$C NMR resonances of sodium methacrylate monomer of ($\text{CH}_2=\text{C}($COONa)$\text{CH}_3$) at $\delta = 142$ and 178 ppm. In Figure 5-8 (c) proved that both these monomers were difficult to remove from the copolymer solution mixture.
Table 5-5 $^{13}$C resonance assignments of (a) sodium methacrylate monomer, (b) MPEGMA monomer, and (c) PMPEGMA - random - PMAA

<table>
<thead>
<tr>
<th>Chemical Structure</th>
<th>Structural Group</th>
<th>Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Sodium methacrylate</td>
<td>$\text{CH}_2=\text{C(COONa)CH}_3$</td>
<td>18 - 19</td>
</tr>
<tr>
<td></td>
<td>$\text{CCH}_2=\text{C(COONa)CH}_3$</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_2=\text{C(COONa)CH}_3$</td>
<td>142 - 143</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_2=\text{C(COO\text{Na})CH}_3$</td>
<td>177-178</td>
</tr>
<tr>
<td>(b) MPEGMA</td>
<td>$\text{CH}_2=\text{CR-CH}_3$</td>
<td>17 - 18</td>
</tr>
<tr>
<td></td>
<td>$\text{R-O-CH}_3$</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>-(C\text{H}_2\text{C}_2\text{O})- (PEO repeating units)</td>
<td>68 - 72</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_2=\text{CR-CH}_3$</td>
<td>127</td>
</tr>
<tr>
<td></td>
<td>$\text{CH}_2=\text{CR-CH}_3$</td>
<td>135 - 136</td>
</tr>
<tr>
<td></td>
<td>$\text{R-\text{COO-(CH}_2\text{CH}_2\text{O)}_n-CH}_3$</td>
<td>169 - 170</td>
</tr>
<tr>
<td>(c) PMPEGMA950 - random - PMAA</td>
<td>$\text{-CH}_2=\text{C(\text{CH}_3)}$- (polymer main chain)</td>
<td>16 - 19</td>
</tr>
<tr>
<td></td>
<td>$\text{-CH}_2=\text{C(\text{CH}_3)}$- (polymer main chain)</td>
<td>45 - 47</td>
</tr>
<tr>
<td></td>
<td>$\text{-CH}_2=\text{C(\text{CH}_3)}$- (polymer main chain)</td>
<td>54 - 56</td>
</tr>
<tr>
<td></td>
<td>$\text{R-O-CH}_3$</td>
<td>58</td>
</tr>
<tr>
<td></td>
<td>-(C\text{H}_2\text{C}_2\text{O})- (PEO repeating units)</td>
<td>68 - 72</td>
</tr>
<tr>
<td></td>
<td>$\text{R-\text{COO-R'}}$</td>
<td>185 - 190</td>
</tr>
</tbody>
</table>

Table 5-5 illustrates $^{13}$C NMR assignments of sodium methacrylate monomer, MPEGMA monomer, and PMPEGMA - random - PMAA. There were three new chemical shifts: a primary carbon of $\text{-CH}_2=\text{C(\text{CH}_3)}$- (polymer main chain) at $\delta = 16 - 19$ ppm, a secondary carbon of $\text{-CH}_2=\text{C(\text{CH}_3)}$- (polymer main chain) at $\delta = 45 - 47$ ppm, and a quaternary carbon of $\text{-CH}_2=\text{C(\text{CH}_3)}$- (polymer main chain) at $\delta = 54 - 56$ ppm (as also be seen in Figure 5-8). These indicated the formation of polycarboxylate copolymers.
Therefore, $^{13}$C-NMR results supported the $^1$H-NMR interpretation and confirmed the formation of PMPEGMA950 - random - PMAA in this study.

5.6.2 Characterization of RAFT PMPEGMA950 - b - PMAA

![Chemical structure and NMR spectrum]

Figure 5-9 $^1$H-NMR of PMPEGMA950 by RAFT polymerization

This sample was dissolved in deuterium oxide (D$_2$O), which shows the chemical shift ($\delta$) at 4.77 ppm. At $\delta$ 0.88 - 1.11 ppm represents $\text{-CH}_2\text{-CCH}_3$ repeating units of the main chain. At $\delta$ around 1.60 - 1.72 ppm shows $\text{-CH}_2\text{-CCH}_3$ repeating units of the polymer main chain. The sharp singlet of $\text{-O-CH}_3$ can be noticed at $\delta$ 3.38 ppm. The most intensive resonances are at $\delta$ around 3.50 - 3.80 ppm representing the multiplet of $\text{-}(\text{CH}_3\text{CH}_2\text{O})\text{-}$, the repeating units of PEO side chains. Furthermore, a resonance of ethylene oxide group that locates between ester group of the main chain and other
ethylene oxide groups, \(-\text{OCO-(CH}_2\text{CH}_2\text{O)}\)-, shifts at a higher resonance at around 3.98 - 4.05 ppm.

![Diagram of chemical structure (PMPEGMA950 - b - PMAA)]

Figure 5-10 \(^1\text{H-NMR of PMPEGMA950 - b - PMAA by RAFT polymerization}\)

A series of block copolymers; PMPEGMA950 - b - PMAA were then polymerized from the homopolymer, PMPEGMA950. \(^1\text{H-NMR was used to characterize these copolymers. Each sample of the block copolymer was analyzed by dissolving in deuterium oxide (D}_2\text{O), which shows the chemical shift (\(\delta\)) at 4.77 ppm. When methacrylic acid (MAA) monomer was attached to create the block copolymer, its \(^1\text{H-NMR spectrum looks similar to that of homopolymer, PMPEGMA950. At }\delta 0.88 - 1.11 \text{ ppm represents methyl group (-CCH}_3\text{) repeating units of the main chain from both PMPEGMA950 and PMAA. At }\delta \text{ around 1.60 - 1.72 ppm shows -CH}_2\text{-CCH}_3\text{ repeating units of the polymer main chain from both PMPEGMA950 and PMAA. The singlet of } -\)
O-CH₃ can be discovered at δ 3.38 ppm. In addition, the most intensive resonances are still at δ around 3.50 - 3.80 ppm representing the multiplet of -(CH₂CH₂O)- at the side chains. At δ around 3.98 - 4.05 ppm, a resonance of ethylene oxide group that locates between ester group of the main chain and other ethylene oxide groups, -OCO-(CH₂CH₂O)- can be found.

From ¹H-NMR spectrum of PMPEGMA950 and PMPEGMA950 - b - PMAA, it is clearly seen that there was no proton resonances around 5 - 6 ppm, which correspond to the chemical shift of protons from alkene group. Usually proton resonances at the double bond of MPEGMA950 will show up at δ 5.68 and 6.11 ppm and for MAA at δ 5.27 and 5.58 ppm. For this reason it can be assumed that there were no unreacted monomers left once the purification was performed after the polymerization either homopolymerization or block copolymerization. However, to prove that each block copolymer, PMPEGMA950 - b - PMAA, was really created, another characterization method is needed. This is because proton resonances of methacrylic acid (MAA) monomer added into the block copolymerization show the same chemical shifts as PMPEGMA950 either the methyl group (-CCH₃) or alkene group (-H₂C=CH₂). In the following section, GPC chromatograms of PMPEGMA950 and PMPEGMA950 will be shown. This will provide more evidences to the achievement of this block copolymerization.
Table 5-6 Summary of synthesized block copolymers PMPEGMA950 - b - PMAA: molecular weights and their poly dispersity index (PDI)

<table>
<thead>
<tr>
<th>Run</th>
<th>First block</th>
<th>Second block</th>
<th>$M_n$ (g mol$^{-1}$)</th>
<th>$M_w$ (g mol$^{-1}$)</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>PMPEGMA950-1 MAA</td>
<td></td>
<td>20,600</td>
<td>32,100</td>
<td>1.55</td>
</tr>
<tr>
<td>4</td>
<td>PMPEGMA950-1 MAA</td>
<td></td>
<td>31,600</td>
<td>53,800</td>
<td>1.70</td>
</tr>
<tr>
<td>5</td>
<td>PMPEGMA950-2 MAA</td>
<td></td>
<td>22,500</td>
<td>41,200</td>
<td>1.83</td>
</tr>
<tr>
<td>6</td>
<td>PMPEGMA950-2 MAA</td>
<td></td>
<td>27,700</td>
<td>47,600</td>
<td>1.72</td>
</tr>
<tr>
<td>7</td>
<td>PMPEGMA950-2 MAA</td>
<td></td>
<td>42,200</td>
<td>81,000</td>
<td>1.92</td>
</tr>
</tbody>
</table>

![Chart showing retention time versus RI (mV) for different copolymers](chart.png)
A series of block copolymers; RAFT PMPEGMA950 – $b$ – PMAA were done by two steps. First was to synthesize PMPEGMA950 macro RAFT agents. Then methacrylic acid (MAA) monomer was added to create block copolymers. For this study, there were two molecular weights of the first block: PMPEGMA950 (M\(_n\) = 11,000, PDI = 1.26), which will be named PMPEGMA950-1 and PMPEGMA950 (M\(_n\) = 17,500, PDI =1.32), which will be named PMPEGMA950-2. In Figure 5-11 (a) shows GPC chromatograms of PMPEGMA950-1 and series of PMPEGMA950-1 - $b$ - PMAA. The homopolymer of PMPEGMA950-1 was eluted from GPC at a highest retention time, corresponds to the lowest molecular weight size of its series. When MAA was added in the second step of polymerization to this PMPMEGMA950-1 homopolymer, the block copolymer of
PMPEGMA950-1 - b - PMAA was obtained. This was because new polymer peaks from GPC chromatograms in Figure 5-11 (a) shifted toward lower retention time, which correspond to higher molecular weight size. The similar results can be seen in Figure 5-11 (b) illustrating GPC chromatograms of PMPEGMA950-2 and series of PMEGMA950-2 - b - PMAA. The differences between chromatograms in Figure 5-11 (a) and Figure 5-11 (b) are not only molecular weights of PMPEGMA950 homopolymers, but also the length of MAA monomer that was added to the homopolymers to fabricate PMPEGMA950 - b - PMAA. Depend on the ratio between macro RAFT agent and methacrylic acid, different molecular weights of PMPEGMA950 - b - PMAA were achieved. These GPC results confirm the $^1$H-NMR results in previous part that series of block copolymers of PMPEGMA950 - b - PMAA were successfully synthesized. The summary in terms of molecular weight and poly dispersity index (PDI) of those block copolymers PMPEGMA – b - PMAA can be seen in Table 5-7.

5.6.3 Characterization of polycarboxylate terpolymer via RAFT polymerization

Different characterization techniques were performed to prove the structure of polycarboxylate terpolymer. However, the chemical structure of this terpolymer is quite complicated. Thus, $^1$H-NMR, $^{13}$C-NMR, GPC, and mass spectrometry (MALDI-TOF) were utilized in this analysis.
The components to synthesize polycarboxylate terpolymer via RAFT polymerization in this section was similar to the synthesis of polycarboxylate copolymer in Table 5-1 (Run 10). The molar ratio of MPEGMA 950 and MAA was kept same as 1:3. The molar ratio between RAFT agent and AIBN was also fixed at 3.3:1. The only difference in the synthesis of polycarboxylate terpolymer was adding 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester (M$_w$ = 322 g mol$^{-1}$) around 1.4 wt. % of total weight of all monomers. The synthesis and characterization for this new monomer can be again seen in Chapter III. Figure 5-12 shows GPC chromatogram of polycarboxylate copolymer and polycarboxylate terpolymer synthesized via RAFT polymerization. There was just a slightly increase in molecular weight of polycarboxylate terpolymer compared with polycarboxylate copolymer. This was expected because the third monomer was added in the reaction was just a small molecule and very miniscule quantity in overall reaction mixture. However, only GPC result cannot prove all three
monomers were consumed to be a polycarboxylate terpolymer. NMR spectroscopy plays an important role to verify the preparation of this terpolymer.

Figure 5-13 $^1$H-NMR of polycarboxylate terpolymer by RAFT polymerization
Table 5-7 $^1$H resonance assignments of polycarboxylate terpolymer (PMPEGMA - co - PMAA - co - poly [2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester]) synthesized via RAFT polymerization

<table>
<thead>
<tr>
<th>Structural Group</th>
<th>Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH$_2$-C(CH$_3$)$_2$- (polymer main chain)</td>
<td>0.80 - 1.40</td>
</tr>
<tr>
<td>P-O(CH$_2$-CH$_2$-CH$_2$-CH$_3$)</td>
<td>1.40 - 1.62</td>
</tr>
<tr>
<td>-CH$_2$-C(CH$_3$)$_2$- (polymer main chain)</td>
<td>1.70 - 2.40</td>
</tr>
<tr>
<td>R-O-CH$_3$</td>
<td>3.45</td>
</tr>
<tr>
<td>-(CH$_2$CH$_2$O)$_n$- (PEO repeating units)</td>
<td>3.60 - 4.00</td>
</tr>
</tbody>
</table>

Figure 5-13 illustrates proton resonances of polycarboxylate terpolymer by RAFT polymerization. In addition, its proton resonance assignments can be seen in Table 5-7. After purification, there was still unreacted sodium methacrylate as shown at chemical shift 5.40 ppm and 5.71 ppm of (-CH$_2$=C(COONa)CH$_3$). In this terpolymer synthesis, there were at least three new chemical shifts comparing to starting monomers: -CH$_2$-C(CH$_3$)$_2$- (polymer main chain) at $\delta$ = 0.80 -1.40 ppm showing broad proton resonances, P-O(CH$_2$-CH$_2$-CH$_2$-CH$_3$) at $\delta$ = 1.40 - 1.62 showing multiplet splitting pattern of methylene groups from 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester, and -CH$_2$-C(CH$_3$)$_2$- (polymer main chain) at $\delta$ = 1.70 - 2.40 ppm showing broad proton resonances. Therefore, $^1$H-NMR can confirm that 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester was successfully polymerized into the polycarboxylate terpolymer backbone. These are for the reasons that there were no proton resonances from carbon-carbon double bond from either MPEGMA950 or 2-methyl acrylic acid
(dibuthoxy-phosphoryloxy) – alkyl ester; and there were proton multiplet showing at $\delta = 1.40 - 1.62$, which corresponds to methylene groups in P-O(CH$_2$-CH$_2$-CH$_2$-CH$_3$). These multiplet intensities were very weak comparing to other resonances due to the less amount added to the reaction mixture. To confirm again that there was no unreacted of 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester monomer left in the reaction, mass spectrometry (MALDI-TOF) was used to help for this analysis. This will be explained and discussed in the following section.

Figure 5-14 MALDI-TOF mass spectrum of polycarboxylate terpolymer before purification
Figure 5-15 MALDI-TOF mass spectrum of polycarboxylate terpolymer before purification + 1 wt. % of 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester monomer

Figure 5-16 MALDI-TOF Mass spectrum of polycarboxylate terpolymer before purification + 5 wt. % of 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester monomer
It was observed from $^1$H and $^{13}$C NMR that within 20 h reaction for polycarboxylate copolymer synthesis, the conversion of both monomer MPEGMA950 and sodium methacrylate did not reach 100 %. Therefore, purification was performed for getting rid of those unreacted monomers. The same analogy was applied to polycarboxylate terpolymer synthesis. Thus, to prove that 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester monomer was consumed during polymerization process, the polycarboxylate terpolymer before purification was analyzed by MALDI-TOF mass spectrometry. There were three samples for mass spectrometry analysis including polycarboxylate terpolymer before the purification and polycarboxylate terpolymer before purification + 1 wt. % or 5 wt. % of 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester monomer that was added to reaction mixture (as shown in section 5.5.3). The reason to add very little amount of 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester monomer to polycarboxylate terpolymer for MALDI-TOF mass spectrometry was to see the sensitivity of the instrument and to prove whether or not 2-methyl acrylic acid (dibuthoxy- phosphoryloxy) – alkyl ester monomer still existed in the polycarboxylate terpolymer solution mixture.

Polycarboxylate terpolymer before purification in Figure 5-14 and polycarboxylate terpolymer before purification with 1 wt. % or 5 wt. % of 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester monomer in Figure 5-15 and Figure 5-16 respectively were mixed with dithranol matrix solution and sodium trifluoroacetate at 2:10:1 ratio. Mass spectrometer was operated in reflection mode. The mass spectra in Figure 5-14 to Figure 5-16 illustrate two polymer distributions with a mass difference between each peak corresponding in each distribution to the molecular weight of the PEO
repeating unit (44.0262 Da). The first distribution was related to methoxy poly (ethylene glycol) methacrylate (MPEGMA) cationized by sodium [CH₂CH(CH₃)-COO-(PEO)ₙ-CH₃, Na]⁺. The second distribution corresponded to methoxy poly (ethylene glycol) (MPEG) cationized by sodium [HO-(PEO)ₙ-CH₃, Na]⁺. The latter distribution was probably a result of the synthesis of methoxy poly (ethylene glycol) methacrylate macromonomer that was mentioned in CHAPTER III. Therefore, MALDI-TOF mass spectrometry technique in reflection mode is an effective method to detect unreacted starting materials e.g. MPEGMA and MPEG.

Nevertheless, the mass spectrometry (MALDI-TOF) analysis did not show any polymer distribution above 1,700 Da. This is unexpected because during the polymerization of polycarboxylate terpolymer via RAFT polymerization, the molecular weight increased significantly up to around 23 kDa (from GPC results in Figure 5-12). Apparently, the detection of high molecular weight of polycarboxylate terpolymer is limited by the MALDI-TOF technique as long as the product still contains low molecular weight reactants. The same phenomenon was also observed by Guerandel et al. They used MALDI-TOF spectroscopic method to analyze copolymeric superplasticizer traces in cement leachates. They found only MPEG traces in a mixture with polycarboxylate superplasticizer and they concluded that MALDI-TOF mass spectrometry cannot provide polycarboxylate copolymer detection in this analysis.

At the low region of the MALDI-TOF spectra, the peak at m/z 345.22 is related to 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester monomer cationized by sodium [CH₂CH(CH₃)-COO-(CH₂)₂-O-PO-(CH₂CH₂CH₂CH₃)₂, Na⁺]. The MALDI-TOF mass spectrum of polycarboxylate terpolymer before purification in Figure 5-14 does not
contain such a peak at all. However, the MALDI-TOF mass spectrum of the mixture of polycarboxylate terpolymer before purification plus 1 wt. % of 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester monomer in Figure 5-15 does contain a peak at m/z = 345.22 Da corresponding to 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester monomer cationized by sodium. The same observation was noticed when 5 wt. % of 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester monomer was mixed with polycarboxylate terpolymer before purification (as shown in Figure 5-16).

Even though MALDI-TOF mass spectrometry is not an appropriate tool to analyze a high molecular weight polycarboxylate copolymer/terpolymer, it is still very sensitive to small molecules. In this case, MALDI-TOF mass spectrometry was used to detect the 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester monomer that was added during the synthesis of polycarboxylate terpolymer via RAFT polymerization. From the above results, it can be concluded that before purification, there was none of this monomer left once the reaction was completed. This infers that 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester monomer was totally consumed during the polymerization process. Hence, the MALDI-TOF mass spectra provide evidence for the successful fabrication of polycarboxylate terpolymer.
5.7 Conclusions

A series of polycarboxylate copolymers, PMPEGMA - random - PMAA, were successfully synthesized via RAFT polymerization with various charge densities of the polycarboxylate copolymers and different chain lengths of PEO repeating units. In addition, a series of polycarboxylate block copolymers, PMPEGMA - block - PMAA, were successfully synthesized via RAFT polymerization. $^1$H-NMR and GPC were used to confirm the preparation of these polycarboxylate copolymers. A new polycarboxylate terpolymer was also synthesized via RAFT polymerization. 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester monomer (modified defoaming agent) was the third monomer in addition to MPEGMA and MAA monomers in the reaction mixture. $^1$H-NMR, GPC, and MALDI-TOF mass spectrometry were used to characterize this polycarboxylate terpolymer. They confirmed that 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester monomer was completely consumed during the polymerization process and was successfully attached to the polycarboxylate terpolymer.

All of those polycarboxylate copolymers either random copolymer or block copolymers and polycarboxylate terpolymer were then used in the study of concrete properties in terms of various charge densities of the polycarboxylate copolymers, different chain lengths of PEO repeating units, and types of copolymer. The concrete properties using all of these samples will be explained and discussed in CHAPTER VI (Concrete tests for new polycarboxylate admixtures).
6.1 Overview

Various polycarboxylate admixtures either synthesized by RAFT polymerization or conventional radical polymerization / esterification process were tested with cement/concrete system in order to investigate the effects of side chain lengths of PEO repeating units inside copolymers, monomer molar ratios, amount of unreacted monomers, molecular weight / molecular weight distribution, and the copolymer structures on fluidity of fresh cement. In addition, it was found that RAFT polycarboxylate terpolymer (containing \textit{in-situ} defoaming groups) not only able to provide a reasonable cement fluidity over a long period of time, but also able to control the amount of generated bubbles at the same time. In case of actual concrete tests, RAFT polycarboxylate terpolymer (blended with air entraining agents) in the concrete system effectively reached a good concrete slump compared to polycarboxylate 1 (commercially available) at the same dosage. Although the compressive strength of concrete system at 7 and 28 days using RAFT polycarboxylate terpolymer was less than that of concrete system using polycarboxylate 1, the stability of an air-void system (\% air content \(\sim 7.0\%\)) of harden concrete was achieved. This may probably lead to a new candidate admixture for an outdoor concrete structural application that requires freeze-thaw stability without adding separate defoaming agents.
6.2 Introduction

When water is added to cement, cement hydration happens instantaneously. Without the dispersing admixture e.g. superplasticizer, cement particles are likely to form small flocs, which limit fluidity of cement paste. Generally, cement particles have irregular shapes with positive and negative charged within their crystal lattice. The electrostatic attraction between these opposite charges on the surface of fine cement particles causes this flocculation (as seen in Figure 6-1 (a)). These small flocs trap water inside them causing the cement mix to be less fluid with conglomerate formation and quick sedimentation.\textsuperscript{27, 121} In chemistry point of view, added water will normally absorb into the surface of the cement particles, dissolving calcium ions (\(\text{Ca}^{2+}\)) and hydroxide ions (\(\text{HO}^-\)) (main product of cement hydration reaction), which will subsequently move out into the surrounding water. This causes a calcium-depleted hydrosilicate layer carrying more negative charges on the surface of cement particles. Some of the calcium ions in the solution may adsorb back onto the hydrosilicate surface, resulting in positive charges as investigated by Zeta potential. This is the reason why many literatures mentioned that there are positively charged calcium ions on the cement surface when cement hydration happens. Later on, water continues diffuse into cement particles, releasing more calcium ions and hydroxide ions into the solution and further increasing the hydrosilicate layer thickness.\textsuperscript{31}

To overcome the flocculation of cement particles in order to enhance the fluidity of cement paste, dispersing admixture such as polycarboxylate superplasticizer is needed. This type of superplasticizer is generally a copolymer between carboxylic group and poly(ethylene glycol) based monomer. The negative charges on the polymer will adsorb onto
the positively charged calcium ions on the surface of cement particles (as seen in Figure 6-1 (b)). The dispersion is caused by the poly (ethylene glycol) based monomer through steric hindrance effect. This leads to the cement particles to repel each other, which breaks up the flocculation and releases the trapped water. These actions then improve the fluidity of cement paste.

![Diagram](image)

Figure 6-1 Flocs formation by cement particles (a) without dispersing admixture e.g. superplasticizers and (b) dispersion of flocs after addition of dispersing admixture.

Nevertheless, this type of superplasticizer has a drawback which is generating uncontrolled bubbles, which required additional defoaming agents in the system in order to get rid of those bubbles. Air entraining agents are also added to the cement system to promote good bubbles. This has to be balanced to achieve the amount of good bubbles in the cement system. Therefore, a new polycarboxylate superplasticizer has been established, which is polycarboxylate terpolymer synthesized via RAFT polymerization in CHAPTER V. This new polycarboxylate admixture is expected to give the fluidity to the cement system and eradicate those uncontrolled bubbles at the same time.

Up to now, there are plenty of literatures that have studied the cement or concrete properties affected by polycarboxylate copolymers based on conventional radical
polymerization and esterification process \(^\text{106, 108, 111}\). Surprisingly, there is no research group synthesizing polycarboxylate copolymers \(\text{via RAFT polymerization}\) and study their properties with the cement system. In particular, polycarboxylate terpolymer (contain \textit{in-situ} defoaming agent group) is considered to be a very new polycarboxylate admixture for cement and concrete field.

For these reasons, this chapter aims to compare the cement/concrete properties e.g. slump test, \% air content, and concrete compressive strength by using different polycarboxylate admixtures for example; the synthesized polycarboxylate copolymers (\(\text{via conventional radical polymerization and esterification process in CHAPTER IV}\) and \(\text{via RAFT polymerization in CHPATER V}\)) and polycarboxylate terpolymer (\(\text{via RAFT polymerization in CHAPTER V}\)).

Many variables were studied in order to understand more fresh cement behavior i.e. fresh cement fluidity (measured by cement slump tests) when mixed with water and polycarboxylate superplasticizers. These variables include the effect of different side chain lengths of PEO repeating units inside copolymers, the effect of molar ratio between carboxylic acid groups and poly (ethylene glycol) based monomer (MPEGMA), the effect of unreacted monomers, the influences of molecular weight and molecular weight distribution, and the copolymer structures (random copolymers vs. block copolymers). In addition, defoaming characteristic test was performed by simple shaking test to verify polycarboxylate terpolymer.
6.3 Materials

Methacrylic acid (MAA) (Aldrich, 99%) and tributyl phosphate (Chemprec) were used as received. MPEGMA 950, MPEGMA 2000, and 2-methyl-acrylic acid (dibuthoxy-phosphoryloxy)-alkyl ester were received from the synthesis in CHAPTER III. Portland cement Type I, coarse aggregate (rocks), fine aggregate (sand), and air mix 200 (air entraining agent) were received from Euclid Chemical Company. A polycarboxylate 1 (received from Euclid Chemical Company), which is a commercially available superplasticizer product in a market. A series of polycarboxylate admixtures including copolymers and terpolymers both by conventional radical polymerization/esterification process and RAFT polymerization were received from previous sections (CHAPTER IV and CHAPTER V).

6.4 Instrumentation

There were various cement/concrete tests including slump test, air content measurement in concrete, concrete compression test, and defoaming characteristic test. They can be either the lab scale tests or the actual concrete tests at Euclid Chemical Company. Each instrument will be explained in the following section.

6.4.1 Cement/Concrete slump test

The slump test is a test used to determine the workability or fluidity of fresh concrete. It is an indirect measurement of concrete consistency or concrete stiffness. It is also used to certify regularity of similar concrete with different batches under field conditions and used to investigate the effects of plasticizers in the concrete mixes. In addition, this test is very beneficial for an on-site qualitative control check on the hour-to-hour or day-to-day variation in the materials being fed into the concrete mixer. For
instance; the slump increases may be because the moisture content of aggregate has unpredictably increases. The test is widely used because of the easiness of apparatus used (e.g. slump cone, scale of measurement, and temping rod (steel)) and straight forward protocol.

Lab scale: cement slump test

This was a pre-screening of the cement slump in a lab scale. It was performed to screen out ineffective polycarboxylate admixtures before testing in a large scale at Euclid Chemical Company. Cement paste was mixed at room temperature at 0.4 water/cement ratio, using Hamilton Beach blender. First, 300 g of Portland cement type I was placed into a blender. 1.2 g of each polymer admixture at the same concentration (40 wt. %) dissolved in 120 g of water (depends on the water/cement ratio) was poured into the blender and initially mixed for 30 seconds. The cement paste was also mixed another 30 seconds prior to the slump test. The slump of cement paste was evaluated by measuring its diameter after pulling out spread of cement paste from a cylinder of 5.08-cm inner diameter and 5.08-cm height (as shown below in Figure 6-2 (a)). The slump tests (diameter of spread cement paste) were measured with different mixing times (5 min, 10 min, 30 min, and 60 min).
Actual slump test at Euclid Chemical Company

Polycarboxylate admixtures that had a good slump in fresh cement at different times compared with a commercial (polycarboxylate 1) in the lab scale test then were further tested for a large scale at Euclid Chemical Company.

The differences between the slump test in a lab scale and the actual slump test at Euclid Chemical Company were not only the quantity of materials, but also the ingredients e.g. rocks and sands. There were no rocks and sands in the slump test in a lab scale. However, rocks and sands were put in the actual concrete slump test in order to simulate the real construction situation. As stated in CHAPTER II, rocks and sands contribute to a stronger final hardened concrete. They are bound in a concrete together by calcium silicate hydrate in a cement paste, which acts as a main glue.

Two polycarboxylate admixtures were tested. One was the control, polycarboxylate 1 and the other was RAFT polycarboxylate terpolymer [PMPEGMA - co - PMAA - co - poly [2-methyl acrylic acid (dibutoxy-phosphoryloxy) – alkyl ester]), molar ratio = 1:3:0.05, $M_n = 23,900$ g mol$^{-1}$, PDI = 1.90]. 2-methyl-acrylic acid
(dibuthoxy-phosphoryloxy)-alkyl ester \( (M_w = 322 \text{ g mol}^{-1}) \) is the \textit{in-situ} modified defoaming agent that was added during the terpolymer synthesis around 1.4 wt. \% of the weight of the other two monomers.

In this actual concrete test, there were two categories of testing: 1) polycarboxylate admixtures without air-entraining agent and 2) polycarboxylate admixtures with air-entraining agent. For the actual slump test without air-entraining agent; 30.32 kg of rocks and 24.68 kg of sands were initially put a concrete mixer (shown in Figure 6-3) and then mixed for 1 min. 10 kg of cement, 4.34 kg of water, and 35.5 g of polycarboxylate admixture (concentration was 40 wt.\%) were then put in the mixer. The slump test in different times (5 min, 30 min, and 60 min) were measured. For the actual slump test with air-entraining agent; 2.7 g of air entraining agent (air mix 200) was placed in a concrete mixer together with 30.32 kg of rocks and 22.86 kg of sands and then mixed for 1 min. 10 kg of cement, 3.69 kg of water, and 35.5 g of each polycarboxylate admixtures (concentration were 40 wt. \%) were then put in the mixer. The slump test in different times (5 min, 30 min, and 60 min) were measured. Amount of water was adjusted comparing to the test without air-entraining agent. This was because adding the air entraining agent would cause more bubbles in the concrete system, leading to improper slump characterization.
Figure 6-3 (a-c) Sands, rocks, and cement used in an actual concrete test at Euclid Chemical Company, and (d) a concrete mixer

Figure 6-4 Actual slump test at Euclid Chemical Company
A fresh concrete mix in different times was placed in a mold for the slump test. The mold is a frustum of a cone with 30 cm of height. The base is 20 cm in diameter and a smaller diameter at the top of 10 cm. The base was placed on an even floor and the cone was filled with concrete in three layers. Each layer was temped about 25 times with a steel rod of 16 mm in diameter. After the mold was entirely filled with concrete, the top surface was then smoothen and leveled. The cone was subsequently lifted vertically and an unsupported concrete would slump (Figure 6-4 (a-b)). The slump was measured by placing the mold next to the slumped concrete. The steel rod was placed both over the mold and over the area of slumped concrete (Figure 6-4 (c)). The decrease in height of the center of the slumped concrete is called slump (usually in inch unit).

6.4.2 Concrete air content measurement

Several techniques are available for measuring the air content of fresh concrete like pressure method (ASTM C231), volumetric method (ASTM C173), and gravimetric method (ASTM C138). The test method covers the determination of the air content of freshly mixed concrete exclusive of any air that may exist inside voids within aggregate particles. Thus, it is applicable to concrete made with relatively dense aggregate particles. However, the pressure method is frequently preferred because it is relatively fast.

The air meter used in this studied was American Cube Mold - Type B air meter (as seen in Figure 6-5). The pressure method is based on Boyle’s law, which states that the volume occupied by air is proportional to the applied pressure. The pressure meter has an upper chamber filled with air and a lower chamber that the operator fills with concrete (Figure 6-5 (a)). To measure the air content of the concrete, with the valve
closed: the upper chamber is pressurized to a predetermined operating pressure (Figure 6-5 (b)). When the valve is opened, the air is released into the lower chamber. And the pressure drops in proportion to the air contained within the concrete sample.

![Figure 6-5 Air content measurement by pressure method](image)

6.4.3 Concrete compression test

The compression test shows the compressive strength of hardened concrete. It is a measure of the concrete’s ability to resist loads which tend to crush it. The compression machine used in this study was Forney QC-410-CS100-2A. After the concrete mixing (cement + water + admixtures + aggregates), approximately 60 min, the concrete mix was prepared in a concrete cylinder with 4 inches of diameter and 8 inches of length (shown in Figure 6-6 (a)). The cylinder was filled with concrete mix in three layers. Each layer was temped about 25 times with a steel rod of 16 mm in diameter. After the cylinder was completely filled, the top surface was then smoothen and leveled (shown in Figure 6-6 (b)).
The compressive strength for the harden concrete in each cylinder was measured in different times (7 and 28 days). ASTM C39/C39 M was a standard method to measure the compressive strength in this study. A compressive axial load was applied to molded cylinders at a rate which was within a prescribed range until failure occurred. The compressive strength of the sample was calculated by dividing the maximum load attained during the test by the cross-sectional area of the sample. The strength is commonly specified as a characteristic strength of a harden concrete. The testing was performed at Euclid Chemical Company.
6.4.4 Defoaming characteristic test

To investigate defoaming characteristic of each samples, it was simply performed by shaking test. Three polycarboxylate admixtures (concentration = 40 wt. %) including RAFT polycarboxylate copolymer [PMPEGMA 950 – co – PMAA (molar ratio = 1:3), \( M_n = 22,400 \text{ g mol}^{-1}, \text{PDI} = 1.71 \)], RAFT polycarboxylate terpolymer [PMPEGMA - co - PMAA - co - poly [2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester] (molar ratio 1:3:0.05), \( M_n = 23,900 \text{ g mol}^{-1}, \text{PDI} = 1.90 \)], polycarboxylate 1 (commercial polycarboxylate admixture) were used in this study. Tributyl phosphate (commercial defoaming agent) and 2-methyl-acrylic acid (dibuthoxy-phosphoryloxy)-alkyl ester (\( M_w = 322 \text{ g mol}^{-1} \), modified defoaming agent) were also employed in this study. First, 1 g (40 wt. %) of each polycarboxylate admixture was added to 20 mL vial. 10 g of water was subsequently added. Then all of samples were shaken for 1 min by a vortex mixer at the same speed in order to observe the amount of bubbles and defoaming characteristic for each samples. Tributyl phosphate and a modified defoaming agent were added couple drops in some mixtures or added after shaking. The ingredients and observation after shaking were described in Table 6-3.

6.5 Results and discussion

There were various tests to verify the efficiency of polycarboxylate copolymers in cement or concrete including slump test, defoaming characteristic test, concrete air content measurement, and concrete compression test.
6.5.1 Cement slump test (lab scale)

Various types of polycarboxylate admixtures including copolymers and terpolymers either synthesized by conventional radical polymerization/esterification process or RAFT polymerization were used to mix with water and cement in order to evaluate the fluidity of fresh cement mix by cement slump test. There are many interesting factors, which are included in this study, can affect the fluidity of fresh cement mix. Each factor on the impact of fresh cement fluidity will be explained in the following section.

The effect of side chain lengths on the cement slump test

To study the effect of side chain lengths on the cement slump test, a series of polycarboxylate copolymers PMPEGMA - random - PMAA synthesized via RAFT polymerization (CHAPTER V) were used in this consideration. During the synthesis of these polycarboxylate copolymers, many variables were kept constant including molar ratio between MPEGMA and MAA (1:3), the molar ratio between CPADB (RAFT agent) and AIBN (initiator) (3.3:1), reaction temperature, reaction time, and solution concentration. The only difference was the side chain length of MPEGMA macromonomer. There were four different chain lengths of MPEGMA in this study depending on the number of PEO repeating units (n) inside MPEGMA including MPEGMA350 (n~7), MPEGMA550 (n~12), MPEGMA950 (n~24), and MPEGMA2000 (n~48).
The effect of polycarboxylate superplasticizers with different side chain lengths of PEO repeating units in different MPEGMA monomer on the cement slump test is shown in Figure 6-7.

![Figure 6-7 Cement slump tests on the effect of polycarboxylate superplasticizers synthesized via RAFT polymerization with different side chain lengths](image)

From the cement slump test, it can be noticed that all superplasticizers improved workability or cement fluidity compared to the plain cement. The slump diameter of fresh cement containing polycarboxylate superplasticizer decreased overtime. This was probably due the competitive effects between dispersion effect of polycarboxylate superplasticizer and cement hardening effect of cement particles via hydration process. Depending on how effective of polycarboxylate superplasticizer, this will dictate how fast/slow flocculation of cement particles, which results in the stiffness of cement mix. In this study, the slump diameter of fresh cement (related to the cement fluidity) increased with the increment of the length of PEO repeating units in MPEGMA macromonomer at
the same mixing time. When the mixing was greater than 5 min, the cement paste mixed with PMPEGMA350-random-PMAA was too stiff to be measured the slump diameter. This cement stiffness could also be observed at 30 and 60 min mixing time for PMPEGMA550-random-PMAA and PMPEGMA2000-random-PMAA. Only PMPEGMA950-random-PMAA could retain the cement fluidity until 60 min mixing time.

In this study, it was also observed that the slump diameter of fresh cement paste increased almost systematically according to the PEO repeating unit side chain lengths (n) in polycarboxylate copolymers at the same mixing time. The slump diameter at the same mixing time of fresh cement containing polycarboxylate copolymers with side chain length (n) of 7 was less than (n) of 12 and 48 respectively. This was expected due to the steric hindrance effect. But PMPEGMA2000-random-PMAA containing PEO repeating unit side chain length (n) of 48 did not show greater slump diameter of fresh cement at the same dosage than the others. This was contradictory to steric hindrance effect 112.

According to stereoscopic point of view of superplasticizer mechanism, it is believed that the performance of better cement dispersion is correlated with the steric hindrance of PEO repeating units (n) side chain in MPEGMA macromonomer. Polycarboxylate copolymers with longer PEO side chain having heavier molecular weights, should provide better dispersion effect and fluid-retaining ability as a result of the stronger steric hindrance. Nevertheless, if the length of PEO repeating units (n) side chain is too long, the main back bone chain is too short correspondingly, the adsorption of polycarboxylate copolymers can be reduced 108. Long side chain length of PEO in
polycarboxylate copolymers may have the polymer mass concentrating on the non-adsorbing copolymer backbone. Therefore, the coverage of the cement particle surfaces may be lesser than the polycarboxylate copolymers with shorter side chain length. This statement will be true if it is assumed that the total amount of copolymer adsorbed is the same in both cases. Cement particles with less surface coverage by polycarboxylate copolymers should experience faster cement hardening $^{104}$.

*The effect of molar ratio between MPEGMA and MAA on the cement slump test*

To study the effect of molar ratio between MPEGMA and MAA on the cement slump test, a series of polycarboxylate copolymers PMPEGMA - random - PMAA synthesized via RAFT polymerization (CHAPTER V) were used in this study. During the synthesis of these polycarboxylate copolymers, different molar ratios between MPEGMA (n ~ 12, 24, and 48) and MAA were used including 1:1, 1:2, 1:3, and 1:4. The molar ratio between RAFT agent and initiator was kept constant at 3.3:1. The reaction temperature, reaction time, and solution concentration were all the same for every synthesis of these polycarboxylate copolymers.

The effects of polycarboxylate superplasticizers with different molar ratios between MPEGMA and MAA on the cement slump test are shown in Figure 6-8 to Figure 6-10. Figure 6-8 shows the cement slump test of fresh cement mixed with PMEGMA550 (n~12) – random – PMAA. Figure 6-9 depicts the cement slump test of fresh cement mixed with PMEGMA950 (n~24) – random – PMAA. Figure 6-10 illustrates the cement slump test of fresh cement mixed with PMEGMA2000 (n~48) – random – PMAA.
Figure 6-8 Cement slump tests on the effect of polycarboxylate superplasticizers (PMPEGMA550 - random - PMAA) with different molar ratios of monomers
Figure 6-9 Cement slump tests on the effect of polycarboxylate superplasticizers (PMPEGMA950 - random - PMAA) with different molar ratios of monomers
Figure 6-10 Cement slump tests on the effect of polycarboxylate superplasticizers (PMPEGMA2000 - random - PMAA) with different molar ratios of monomers

In this study, it was observed that the slump diameter of fresh cement paste increased almost systematically with the increment of the molar ratio between MPEGMA and MAA at the same mixing time. In most cases, the slump diameter at the same mixing time of fresh cement containing polycarboxylate copolymers with molar ratio between MPEGMA and MAA 1:1 was less than the molar ratios of 1:2 and 1:3 respectively. When this molar ratio was 1:4, the slump diameter of fresh cement in every series of PMPEGMA (550,950, and 2000) – random – PMAA decreased significantly. Thus, it infers that the molar ratio between MPEGMA and MAA is another important factor affecting the fluidity of fresh cement.
In chemistry point of view, the PMAA as a part of polycarboxylate copolymers in a strongly basic medium can form anions with negatively charges like the carboxyl group. These negatively charges from carboxyl groups as part of polycarboxylate copolymers were anticipated to straightforwardly adsorb to the positive charges on the surfaces of cement particles. The key functions were to establish and increase the adsorption anchorage on to the surfaces of cement particles. Therefore, it was expected that the increment of molar ratio between MPEGMA and MAA or the relative amount of carboxyl groups in the polycarboxylate copolymers would be contributed to the efficiency of adsorption anchorage between polycarboxylate copolymers and surfaces of cement particles. According to the slump tests, adsorption variation of different series of PMPEGMA-random-PMAA on the surfaces of cement particles caused different dispersion effects of fresh cement.

There are two explanations why the higher molar ratio between MPEGMA and MAA (e.g. 1:4) in PMPEGMA-random-PMAA copolymers caused less slump diameter in fresh cement over time. The first reason was probably because of the differences in conformations. In an aqueous solution with high ionic strength, the polycarboxylate copolymers may change the shape to mushroom-like conformation (as shown in Figure 6-11). When this conformation occurs, the dispersion effect would be diminished. Uchikawa et al. observed this phenomenon with similar type of polycarboxylate copolymers at a high concentration of sulfate ion. The second reason was probably due to the competitive adsorption between hydroxide ions and anions from polycarboxylate copolymer. Increasing hydroxide concentration reduced the amount of adsorbed polycarboxylate copolymer and consequently the cement paste flow. During the
copolymer synthesis, pH of the solution was adjusted to be around 9. Thus, the more amount of MAA, the more NaOH solution was added. This led to have more hydroxide ions in the solution.

![Conformation model of polycarboxylate copolymer in water and in alkaline and high ion concentration liquid](image)

Figure 6-11 Conformation model of polycarboxylate copolymer in water and in alkaline and high ion concentration liquid \(^{123}\).

To comprehend the adsorption behavior of polycarboxylate copolymers on the cement particles, it is better to consider both molar ratio of MPEGMA/MAA and PEO repeating units \(n\) inside MPEGMA together. These two factors together dictate the charge density of polycarboxylate copolymers. It is important to mention the charge density of polycarboxylate copolymers because it is related to their adsorption behavior, possibly resulting in the fluidity of fresh cement \(^{104}\).

If the length of PEO side chain in MPEGMA is too long, the main chain is too short correspondingly, the adsorption efficiency on cement particles can be reduced \(^{108}\). The overall charge density of the polycarboxylate copolymers decreased with increasing PEO side chain length in MPEGMA. On the other hand, the overall charge density of
polycarboxylate copolymers increased with a decrease in the PEO side chain length in MPEGMA, and thus influencing the adsorption behavior. This may be the reason why the slump diameter of PMPEGMA950-random-PMAA at different monomer molar ratios were greater than PMPEGMA2000-random-PMAA at the same mixing time. This explanation also supported by the experimental data of Winnefeld et al.

In this present study, it was found that PMPEGMA950-random-PMAA (molar ratio = 1:3) showed the greatest slump tests for all different times of mixing. This was presumably due to two factors; the proper side chain length of MPEGMA950 and the high charge density of this polycarboxylate copolymer. The first factor can be contributed to the steric hindrance effect. The second factor can be contributed to a good adsorption of the copolymer on the surfaces of cement particles.

*The effect of unreacted monomers on the cement slump test*

A series of mixtures between unreacted monomers [MPEGMA and MAA] and polycarboxylate copolymers synthesized via RAFT polymerization were mixed in different weight ratios. A concrete slump test in the lab scale was performed in various time intervals; 30 sec, 5 min, and 10 min.
Table 6-1 Slump diameter in various mixing times of fresh cement with different ratios of unreacted monomers mixed with RAFT PMPEGMA-random-PMAA

<table>
<thead>
<tr>
<th>Group</th>
<th>wt. % MPEGMA</th>
<th>wt. % PMPEGMA-random-PMAA</th>
<th>wt.% MAA</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MPEGMA950</td>
<td>MPEGMA2000</td>
<td>PMPEGMA 950 – r – PMAA (1:3)</td>
</tr>
<tr>
<td>A</td>
<td>50 wt.%</td>
<td>48 wt.%</td>
<td></td>
</tr>
<tr>
<td>A1</td>
<td>25.00</td>
<td>25.00</td>
<td>7.20</td>
</tr>
<tr>
<td>A2</td>
<td>25.00</td>
<td>25.00</td>
<td>16.80</td>
</tr>
<tr>
<td>A3</td>
<td>25.00</td>
<td>25.00</td>
<td>26.40</td>
</tr>
<tr>
<td>A4</td>
<td>25.00</td>
<td>25.00</td>
<td>36.00</td>
</tr>
<tr>
<td>B</td>
<td>40 wt.%</td>
<td>58 wt.%</td>
<td></td>
</tr>
<tr>
<td>B1</td>
<td>20.00</td>
<td>20.00</td>
<td>8.70</td>
</tr>
<tr>
<td>B2</td>
<td>20.00</td>
<td>20.00</td>
<td>20.30</td>
</tr>
<tr>
<td>B3</td>
<td>20.00</td>
<td>20.00</td>
<td>31.90</td>
</tr>
<tr>
<td>B4</td>
<td>20.00</td>
<td>20.00</td>
<td>43.50</td>
</tr>
<tr>
<td>C</td>
<td>30 wt.%</td>
<td>68 wt.%</td>
<td></td>
</tr>
<tr>
<td>C1</td>
<td>15.00</td>
<td>15.00</td>
<td>10.20</td>
</tr>
<tr>
<td>C2</td>
<td>15.00</td>
<td>15.00</td>
<td>23.80</td>
</tr>
<tr>
<td>C3</td>
<td>15.00</td>
<td>15.00</td>
<td>37.40</td>
</tr>
<tr>
<td>C4</td>
<td>15.00</td>
<td>15.00</td>
<td>51.00</td>
</tr>
</tbody>
</table>

In group A, the amount of MAA, MPEGMA, and polycarboxylate copolymers were fixed at 2 wt. %, 50 wt. % and 48 wt. % respectively. However the amount of the polycarboxylate copolymers was varied between RAFT PMPEGMA950 – r - PMAA and RAFT PMPEGMA2000 - r - PMAA. This can be divided into four subgroups, A1, A2, A3, and A4. In group B, the amount of MAA, MPEGMA, and polycarboxylate copolymers were fixed at 2 wt. %, 40 wt. % and 58 wt. % respectively. In group C, the amount of MAA, MPEGMA, and polycarboxylate copolymers were fixed at 2 wt. %, 30 wt. % and 68 wt. % respectively. The amount of the polycarboxylate copolymers in group B and C was also varied between RAFT PMPEGMA950 - r - PMAA and RAFT PMPEGMA2000 – r - PMAA. Each group can also be divided into four subgroups; (Group B: B1, B2, B3, and B4) and (Group C: C1, C2, C3, and C4).
Figure 6-12 Slump diameter in various mixing times of fresh cement with different ratios of unreacted monomers mixed with RAFT PMPEGMA - random - PMAA

From Table 6-1 and Figure 6-12, it can be noticed that the more the unreacted monomer (MPEGMA), the less effective of fresh cement in terms of slump test (less cement spread diameter). In this case, group A had less spread cement diameter than group B and group C respectively. This was probably because the unreacted monomers may hinder the absorption process of polycarboxylate copolymers to the cement particles, leading to faster process of cement flocculation.

Comparing the slump test between A1, A2, A3, and A4 in specific mixing time; it was observed that when the amount of RAFT PMPEGMA950 – r - PMAA increased while the amount of RAFT PMPEGMA2000 - r - PMAA decreased (to keep polycarboxylate copolymers content ≈ 48 wt. %), there was an improvement of slump diameter of fresh cement. This trend was also noticed in (Group B: B1, B2, B3, and B4)
and (Group C: C1, C2, C3, and C4). These results agreed with the slump tests of purified RAFT PMPEGMA950 - r - PMAA and purified RAFT PMPEGMA2000 - r - PMAA in previous section (section 6.5.1). RAFT PMPEGMA950 - r - PMAA (molar ratio = 1:3) showed better spread cement diameter than that of RAFT PMPEGMA2000 - r - PMAA (molar ratio = 1:3) in different mixing times (30 sec, 5 min, 10 min, 30 min, and 60 min).

When a mixing time increased, the diameter of fresh cement decreased significantly and could not retain the spread cement diameter as much as it supposed to be compared to the purified polycarboxylate copolymers. Thus, it can be concluded that unreacted monomers will not give the positive effect on slump test of fresh cement. They played a crucial role in the fresh cement slump test. This may be because the raw materials may obstruct the adsorption process of superplasticizers onto the cement particles. Therefore, a good purification should be taken into account to reach the maximum potential of the polycarboxylate plasticizers. In some cases, post initiator addition is employed in order to reduce the purification cost.

*The effect of molecular weights and molecular weight distribution on the cement slump test*

To study the effect of molecular weight of polycarboxylate copolymers on the cement slump test, well-designed polycarboxylate copolymers PMPEGMA950 - random - PMAA synthesized via RAFT polymerization (CHAPTER V) were used in this consideration. During the synthesis of these polycarboxylate copolymers, many variables were kept constant including molar ratio of monomers between MPEGMA950 and MAA (1:3), reaction temperature, reaction time, and solution concentration. The only difference
was the molar ratio between CPADB (RAFT agent) and AIBN (initiator). There were three CPADB/AIBN molar ratios used in this study: 1.1:1, 3.3:1, and 6.6:1. These different CPADB/AIBN molar ratios contributed to PMPEGMA950 - *random* - PMAA with different molecular weights. The molecular weight demonstration of polycarboxylate copolymers according to the change in CPADB/AIBN molar ratio can be seen in Figure 6-13.

![Molecular images of PMPEGMA950 - random – PMAA with different CPADB/AIBN molar ratios](image.png)

Figure 6-13 Molecular images of PMPEGMA950 - *random* – PMAA with different CPADB/AIBN molar ratios [(1.1:1 in Run 9), (3.3:1 in Run 10), and (6.6:1 in Run 11) in Table 5-4]
Figure 6-14 Cement slump tests on the effect of polycarboxylate superplasticizers (PMPEGMA950 - random - PMAA) with different molecular weights

Figure 6-14 shows the increase of cement slump diameter with the increment of the molecular weight of polycarboxylate copolymers at the same molecular architecture. In specific mixing time of the cement paste, copolymer of the molecular weight around 22,000 g mol\(^{-1}\) provided much better cement fluidity than that of 5,300 g mol\(^{-1}\). This was probably because the higher molecular weight contained more negatively charges adsorb on the cement particles, resulting in the increment of cement adsorption efficiency. With a heavier molecular weight, it was expected to provide more PEO side chains, leading to an enhancement of the steric hindrance effect \(^{108}\). For these reasons, polycarboxylate copolymers with higher molecular weights had a greater slump diameter of fresh cement
and cement fluid-retaining ability due to more active adsorption points and stronger adsorption anchorage.

Nevertheless, PMPEGMA950 - random - PMAA at the molecular weight of 38,400 g mol\(^{-1}\) did not show a greater slump diameter of fresh cement and cement fluid-retaining ability in different mixing times compared to the same copolymer architecture of the molecular weight around 22,000 g mol\(^{-1}\). This was quite unexpected because the higher molecular weight should provide more active adsorption sites and stronger adsorption anchorage as mentioned earlier with the purpose of enhancement in fresh cement fluidity. From these results, it seems like there is a limitation of building up the molecular weight of polycarboxylate copolymers in order to improve the slump diameter and fluid-retaining ability of fresh cement.

E. Sakai et al.\(^{126}\) also observed the same phenomenon. If the molecular weight of polycarboxylate copolymer is too large, it is possibly causing a bridging effect (as shown in Figure 6-14). The bridging effect can probably occur when the chain length of a large molecular weight synthetic water-soluble polycarboxylate copolymer may be long enough for one chain end to adsorb onto the first cement particle and the other chain end onto a second cement particle. Each copolymer chians had a great chance to adsorb on several cement particles at once, resulting in a three-dimensional matrix. As a result of bridging effect, cement particles tend to flocculate easier, which affected in the dispersion efficiency of polycarboxylate copolymers in a cement mix\(^ {127}\). This may explain why PMPEGMA950 - random - PMAA of the molecular weight around 38,400 g mol\(^{-1}\) gave much less cement fluidity than that of 22,000 g mol\(^{-1}\) in different time of cement mixing.
In case of the effect of molecular weight distribution of polycarboxylate copolymers on the cement slump tests, polycarboxylate copolymers PMPEGMA950 - \textit{random} - PMAA synthesized \textit{via} conventional radical polymerization/esterification process (CHAPTER IV) and PMPEGMA950 - \textit{random} - PMAA synthesized \textit{via} RAFT polymerization (CHAPTER V) were used in this study. Table 6-2 shows a summary of molecular weights and PDI of PMPEGMA950 - \textit{random} - PMAA synthesized by different methods.
Table 6-2 Summary of molecular weights and PDI of polycarboxylate copolymers (PMPEGMA950 - random – PMAA) synthesized by different methods

<table>
<thead>
<tr>
<th>Synthesis Method</th>
<th>Copolymers</th>
<th>Molecular Weight (g mol(^{-1}))</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(M_n)</td>
<td>(M_w)</td>
</tr>
<tr>
<td>RAFT polymerization</td>
<td>PMPEGMA950 - r - PMAA (molar ratio = 1:3)</td>
<td>22,425</td>
<td>40,115</td>
</tr>
<tr>
<td>Conventional radical</td>
<td>PMPEGMA950 - r - PMAA (molar ratio = 1:3)</td>
<td>21,000</td>
<td>56,000</td>
</tr>
<tr>
<td>polymerization (Initiator = Na(_2)S(_2)O(_8)/NaHSO(_3))</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Conventional radical</td>
<td>PMPEGMA950 - r - PMAA (molar ratio = 1:3)</td>
<td>19,500</td>
<td>103,800</td>
</tr>
<tr>
<td>polymerization (Initiator = AIBN)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Esterification process</td>
<td>PMPEGMA950 - r - PMAA</td>
<td>20,600</td>
<td>65,500</td>
</tr>
</tbody>
</table>

Figure 6-16 Cement slump tests on the effect of molecular weight distribution of polycarboxylate copolymers (PMPEGMA950 - random – PMAA)
The synthesis conditions between RAFT polymerization and conventional radical polymerization were almost the same e.g. molar ratio between MPEGMA950 and MAA (1:3), solvent, reaction temperature, reaction time, and solution concentration. Figure 6-16 illustrates that at the same range of the molecular weight (~ 20,000 g mol\(^{-1}\)) of PMPEGMA950 - random – PMAA, polycarboxylate copolymers synthesized via RAFT polymerization provided a greater slump diameter of fresh cement in different mixing times than that of the same types of copolymers synthesized via conventional radical polymerization/esterification process. This was probably due to the differences in molecular weight distribution or poly dispersity index (PDI) of copolymers.

Polycarboxylate copolymers synthesized by RAFT polymerization had narrower PDI (~ 1.71). On the other hand, polycarboxylate copolymers synthesized by conventional radical polymerization/esterification process had much broader in molecular weight distribution (~ 2.67 – 5.32). As discussed earlier about the effect of molecular weight, too low or too high in the molecular weight of polycarboxylate copolymers will not give good results for an enhancement the fluidity of fresh cement. Thus, the optimum molecular weight of polycarboxylate copolymer is required for dispersion application in cement. The broader molecular weight distribution leads to more fractions of high and low molecular weight of polycarboxylate copolymers.

The less active adsorption points together with less adsorption anchorage by the low molecular weight of polycarboxylate copolymers and the bridging effect by the very large molecular weight of polycarboxylate copolymers may deteriorate the overall adsorption efficiency and dispersion effect to the cement particles, resulting in less cement fluidity and improvement of cement flocculation.
This phenomenon was also observed by Ridi et al. They measured the molecular weight distribution of filtered solution from the cement paste mixed with polycarboxylate superplasticizers. They found that the molecular weight distribution shifted toward a lower molecular weight compared to the original polycarboxylate superplasticizer solution. This indicated that a high molecular weight copolymer fractions adsorb favorably on the surface of cement particles.

Thus, to achieve the maximum potential of the polycarboxylate copolymers for enhancement of fresh cement fluidity, synthesized polycarboxylate copolymers should have optimal molecular weights and very narrower molecular weight distribution.

The effect of copolymer structures on the cement slump test

To study the effect of the structures of polycarboxylate copolymers on the cement slump test, well-designed polycarboxylate copolymers PMPEGMA950 - random - PMAA and a series of PMPEGMA950 - block - PMAA synthesized via RAFT polymerization (CHAPTER V) were used in this study. The molecular weight of PMPEGMA950 - random - PMAA was around 22,000 g mol\(^{-1}\). For a series of PMPEGMA950 - block - PMAA, the molecular weights of those copolymers were ranging from 20,000 to 42,000 g mol\(^{-1}\). Different structures of polycarboxylate copolymers are illustrated in Figure 6-17.
Figure 6-17 Molecular images of PMPEGMA950 - *random* - PMAA (Run 10 in Table 5-1) and a series of PMPEGMA950 – *block* – PMAA (Run 3 – Run 7 in Table 5-3)

Figure 6-18 shows the cement slump tests between PMPEGMA950 - *random* - PMAA and PMPEGMA950 - *block* - PMAA. It was found that every polycarboxylate block copolymer when mixed with cement did not provide cement fluidity compared to PMPEGMA950 - *random* - PMAA ($M_n = 22,425$, PDI = 1.71). Those block copolymers provided a slump diameter of fresh cement similar to the plain cement. Thus, it can infer that those polycarboxylate block copolymers almost had no effect on improvement the fluidity of fresh cement. This was probably because the block copolymer structure may directly affect the adsorption to cement particles. The poor adsorption leads to the flocculation of the cement particles, resulting in faster in cement hardening. Thus, the copolymer structure/architecture of polycarboxylate copolymers is another factor that will have a great impact on fresh cement fluidity.
Figure 6-18 Cement slump tests on the effect of polycarboxylate copolymer structures (PMPEGMA950 - random - PMAA and PMPEGMA950 - block - PMAA)
Cement slump test of polycarboxylate terpolymer synthesized via RAFT polymerization

After many variables e.g. side chain length of PEO units, monomer molar ratios between MPEGMA and MAA, molecular weight, molecular weight distribution, and polymeric structure of polycarboxylate copolymer were optimized in order to reach the full potential of fresh cement mix fluidity. It was found that PMPEGMA950 - random – PMAA (molar ratio = 1:3) and \((M_n = 22,425 \text{ g mol}^{-1}, \text{PDI} = 1.71)\) synthesized via RAFT polymerization provided the greatest fluidity of fresh cement over a long period of time. In addition to those fine-tuned starting materials and synthesis condition, 1.4 wt. % (in-situ defoaming agent group) of 2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester was added to create a new polycarboxylate terpolymer. Polycarboxylate terpolymer (PMPEGMA - co - PMAA - co - poly [2-methyl acrylic acid (dibuthoxy-phosphoryloxy) – alkyl ester]) was successfully synthesized via RAFT polymerization and the detail of synthesis and characterization can be found in CHAPTER V.

Figure 6-19 shows the results of cement slump tests between a new polycarboxylate terpolymer compared to a polycarboxylate copolymer with all fine-tuned conditions. It was found that those two polycarboxylate admixtures showing very similar slump diameter of fresh cement in different mixing time. Thus, it inferred that the in-situ defoaming group added to the polycarboxylate terpolymer did not interfere overall adsorption efficiency and dispersion effect to the cement particles. A great cement fluidity over a long time period of mixing can still be obtained by using this new polycarboxylate terpolymer.
6.5.2 Defoaming characteristic test

Shaking test was an easy method to examine the defoaming characteristic of each samples. Polycarboxylate 1 (commercially available), RAFT polycarboxylate copolymer [PMPEGMA 950 – random – PMAA (molar ratio = 1:3), $M_n = 22,400$ g mol$^{-1}$, PDI = 1.71], RAFT polycarboxylate terpolymer [PMPEGMA - co - PMAA - co - poly [2-methyl acrylic acid (dibutoxy-phosphoryloxy) – alkyl ester] (molar ratio = 1:3:0.05), $M_n = 23,900$ g mol$^{-1}$, PDI = 1.90], Tributyl phosphate (commercial defoaming agent) and 2-methyl-acrylic acid (dibutoxy-phosphoryloxy)-alkyl ester ($M_w = 322$ g mol$^{-1}$, modified defoaming agent) were used in this study.
Table 6-3 Lab shake test of different type of polycarboxylate admixtures with/without defoaming agent

<table>
<thead>
<tr>
<th>Run</th>
<th>Samples</th>
<th>Observation after shaking</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Polycarboxylate 1</td>
<td>Had lots of bubbles and stayed there at more than 15 min</td>
</tr>
<tr>
<td>2</td>
<td>Polycarboxylate 1, then tributyl phosphate was added</td>
<td>Those bubbles disappeared immediately after adding the tributyl phosphate</td>
</tr>
<tr>
<td>3</td>
<td>Polycarboxylate 1 with tributyl phosphate</td>
<td>Still had some bubbles</td>
</tr>
<tr>
<td>4</td>
<td>Polycarboxylate 1, then modified defoaming agent</td>
<td>Those bubbles disappeared immediately after adding the modified defoaming agent</td>
</tr>
<tr>
<td>5</td>
<td>RAFT polycarboxylate copolymer</td>
<td>Had some bubbles, mostly at the edge of vial at least 5 min</td>
</tr>
<tr>
<td>6</td>
<td>RAFT polycarboxylate copolymer, then tributyl phosphate was added</td>
<td>Those bubbles disappeared immediately after adding tributyl phosphate</td>
</tr>
<tr>
<td>7</td>
<td>RAFT polycarboxylate copolymer with tributyl phosphate</td>
<td>No bubbles, but got unclear solution (non-homogenous solution)</td>
</tr>
<tr>
<td>8</td>
<td>RAFT polycarboxylate copolymer, then modified defoaming agent was added</td>
<td>Those bubbles disappeared immediately after adding the modified defoaming agent</td>
</tr>
<tr>
<td>9</td>
<td>RAFT polycarboxylate copolymer, with modified defoaming agent</td>
<td>No bubbles, but got unclear solution (non-homogenous solution)</td>
</tr>
<tr>
<td>10</td>
<td>RAFT polycarboxylate terpolymer</td>
<td>Those bubbles disappeared within 20 sec</td>
</tr>
</tbody>
</table>

Figure 6-20 Defoaming characteristic test: (a) Polycarboxylate 1, (b) RAFT polycarboxylate copolymer, (c) RAFT polycarboxylate copolymer with tributyl phosphate, and (d) RAFT polycarboxylate terpolymer
When dealing with a concrete construction, normally concrete will be mixed with cement, water, rock, and sand. Without any special chemical aid, that concrete will be very stiff and hard to flow into any shape. The current product that solves this issue is called plasticizer (e.g. polycarboxylate 1). The problem with that existing material is it generates too many bubbles and different uncontrolled sizes of bubbles (as shown in Figure 6-20 (a)). This will cause a freeze-thaw problem especially in North America that have very severe climate, leading to lose the strength of the concrete. Currently, a defoaming agent is normally added to control or eliminate the foaming. In a separate step, an air entraining agent is used to promote good air once again into the concrete/cement in order to provide a freeze-thaw resistance.

Commercially, a package of plasticizer and defoaming agent will be mixed together. This package of admixtures is specifically for a high strength concrete construction. However, as mentioned in CHAPTER II, a defoaming agent will be insoluble in a continuous phase. In this case, a continuous phase is water. So, a defoaming agent always phase separates from polycarboxylate plasticizer. For a customer use, if it is not mixed or shaken properly before mixing with the concrete, it may affect the freeze-thaw resistance in a harden concrete. Figure 6-20 (c) shows the mixture of RAFT polycarboxylate copolymer with tributyl phosphate (commercial defoaming agent). After the mixture was shaken for 1 min, no bubbles were noticed. However, non-homogenous solution occurred and finally phase separated. Therefore, it is a great challenge to develop a new generation of concrete admixture to help the concrete be easy to flow in terms of processing and also able to get rid of those uncontrolled bubbles at the same time. Figure 6-20 (b) displays RAFT polycarboxylate copolymer [PMPEGMA 950
– random – PMAA (molar ratio = 1:3), $M_n = 22,400$ g mol$^{-1}$, PDI = 1.71] dissolved in water. After 1 min shaking, lots of bubbles were noticed throughout the top surface. Then some bubbles, mostly at the edge of vial were observed at least 5 min. In contrast to polycarboxylate 1 and RAFT polycarboxylate copolymer, the bubbles of RAFT polycarboxylate terpolymer dissolved in water after 1 min shaking disappeared within 20 sec (as shown in Figure 6-20 (d)). This suggests that the in-situ defoaming agent that was successfully polymerized in RAFT polycarboxylate terpolymer (CHAPTER V) and had a big impact on getting rid of bubbles. It was already confirmed by Mass spectrometry in CHAPTER V that after 20 h polymerization of RAFT polycarboxylate terpolymer, there was no 2-methyl-acrylic acid (dibuthoxy-phosphoryloxy)-alkyl ester ($M_w = 322$ g mol$^{-1}$) or modified defoaming agent left in the reaction. This is really important because the shaking tests of Run 8 and Run 9 in Table 6-3 showing that modified defoaming agent itself was also able to get rid of the bubbles. RAFT polycarboxylate terpolymer was then used in an actual concrete tests at Euclid Chemical Company compared with polycarboxylate 1, which will be discussed in the following section.

6.5.3 Actual concrete tests at Euclid Chemical Company

The actual concrete tests were comprised of three main tests; actual concrete slump test, concrete air content measurement, and concrete compression test. The first two tests were performed in different mixing times of concrete; 5 min, 30 min, and 60 min. Both tests were also performed at the same moment in each particular mixing time. After 60 min mixing of concrete, the fresh concrete mix was put in concrete cylinders. Each harden concrete in cylinders was then measured a compressive strength in different times (7 and 28 days).
Table 6-4 Actual concrete tests for polycarboxylate admixtures without air entraining agent

<table>
<thead>
<tr>
<th></th>
<th>Polycarboxylate 1</th>
<th>RAFT polycarboxylate terpolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dosage (% by weight of cement)</td>
<td>0.35 %</td>
<td>0.35 %</td>
</tr>
<tr>
<td>Slump Initial (inches)</td>
<td>8.00</td>
<td>7.75</td>
</tr>
<tr>
<td>Slump 30 min (inches)</td>
<td>6.00</td>
<td>5.50</td>
</tr>
<tr>
<td>Slump 60 min (inches)</td>
<td>1.50</td>
<td>2.50</td>
</tr>
<tr>
<td>Air Content Initial</td>
<td>4.2%</td>
<td>4.4%</td>
</tr>
<tr>
<td>Air Content 30 min</td>
<td>3.3%</td>
<td>4.2%</td>
</tr>
<tr>
<td>Air Content 60 min</td>
<td>2.8%</td>
<td>3.2%</td>
</tr>
<tr>
<td>Compressive Str. 7 days (MPa)</td>
<td>48.85 ± 0.68</td>
<td>45.08 ± 1.43</td>
</tr>
<tr>
<td>Compressive Str. 28 days (MPa)</td>
<td>59.64 ± 0.83</td>
<td>55.76 ± 0.92</td>
</tr>
</tbody>
</table>

The actual concrete tests in Table 6-4 shows that using RAFT polycarboxylate terpolymer in the concrete system successfully reached the slump compared to polycarboxylate 1 at the same dosage. It even had a higher slump diameter than polycarboxylate 1 after 60 min mixing. When the mixing time increased, the slump diameter decreased in both cases. This was probably because of the competitive effects between dispersion effect of polycarboxylate superplasticizer and solidification reaction of cement particles via hydration process. In case of % air content measurement, both of polycarboxylate admixtures showed similar results. The air did not spiral up in both cases, but went down from around 4% to 3% over a 60 min mixing time. This was what
expected without air entraining agent. The compressive strength for both polycarboxylate admixtures increased significantly from 7 days to 28 days due to the continuous concrete hardening.

Table 6-5 Actual concrete tests for polycarboxylate admixtures with air entraining agent

<table>
<thead>
<tr>
<th></th>
<th>Polycarboxylate 1</th>
<th>RAFT polycarboxylate terpolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dosage (% by weight of cement)</td>
<td>0.35 %</td>
<td>0.35 %</td>
</tr>
<tr>
<td>Slump Initial (inches)</td>
<td>8.25</td>
<td>7.75</td>
</tr>
<tr>
<td>Slump 30 min (inches)</td>
<td>3.75</td>
<td>3.50</td>
</tr>
<tr>
<td>Slump 60 min (inches)</td>
<td>1.50</td>
<td>2.25</td>
</tr>
<tr>
<td>Air Content Initial</td>
<td>7.5%</td>
<td>7.4%</td>
</tr>
<tr>
<td>Air Content 30 min</td>
<td>5.7%</td>
<td>7.0%</td>
</tr>
<tr>
<td>Air Content 60 min</td>
<td>4.9%</td>
<td>6.9%</td>
</tr>
<tr>
<td>Compressive Str. 7 days (MPa)</td>
<td>45.55 ± 0.53</td>
<td>39.87 ± 2.12</td>
</tr>
<tr>
<td>Compressive Str. 28 days (MPa)</td>
<td>55.11 ± 2.34</td>
<td>45.70 ± 1.71</td>
</tr>
</tbody>
</table>

The amount of air entraining agent used for these concrete mixes was around 2.7 g and the amount of water was reduced from 4.34 kg to 3.69 kg compared with the concrete system without the air entraining agent. This was because when air entraining agent was used together with superplasticizer, the amount of air will increase drastically, leading to an enormously increase in concrete slump. So, the water adjustment was
necessary to make the concrete slump containing the air entraining agent and superplasticizer measurable.

This concrete testing in Table 6-5 shows that using RAFT polycarboxylate terpolymer in the concrete system successfully reached the slump compared to polycarboxylate 1 at the same dosage. Although it had slightly less slump initially, it showed a greater slump than polycarboxylate 1 after 60 min mixing. By using polycarboxylate 1 in the concrete system, the % air content decreased significantly from 7.5 % to 4.9 % over a 60 min mixing. On the other hand, % air content of the concrete by using RAFT polycarboxylate terpolymer was quite stable around 7.0 % over 60 min mixing time, which reached expectation. This probably happened because of the competition process between the air entraining agent and \textit{in-situ} defoaming agent inside RAFT polycarboxylate terpolymer. The air entraining agent increased % air content and the \textit{in-situ} defoaming agent in the RAFT polycarboxylate terpolymer might suppress or burst the generated air bubbles from the air entraining agent; leading to an expected air stable content. To have the % air content in the concrete around 6.0 – 8.0 %, the amount of the air entraining agent and amount of \textit{in-situ} defoaming inside the RAFT polycarboxylate terpolymer should be taken into account. Thus, by using the RAFT polycarboxylate terpolymer together with air entraining agents in the concrete system possibly be a good candidate for an outdoor concrete structural application that requires freeze-thaw stability provided by stable air-void system of harden concrete.

When the air-entraining agents were added in the concrete system, the compressive strength decreased\textsuperscript{38}. Compressive strength at 7 days of concrete system blended with polycarboxylate 1 decreased from 48.85 ± 0.68 MPa (without air entraining
agents) to 45.55 ± 0.53 MPa (with air entraining agents). Similarly, when blended with RAFT polycarboxylate terpolymer, the compressive strength also decreased from 45.08 ± 1.43 MPa (without air entraining agents) to 39.87 ± 2.12 MPa (with air entraining agents). The same trend for the concrete compressive strength at 28 days was also observed the decrease in strength when the air entraining agents were added (as seen in Table 6-4 and Table 6-5).

6.6 Conclusions

The effects of different polycarboxylate copolymers either synthesized by RAFT polymerization or conventional radical polymerization / esterification process based on varying (side chain lengths of PEO repeating units inside copolymers, monomer molar ratios, amount of unreacted monomers, molecular weight / molecular weight distribution, and the copolymer structures) on fresh cement fluidity were investigated.

It was found that all mentioned variables were inter-related on the effect of fresh cement fluidity. The length of PEO repeating units in MPEGMA macromonomer should be long enough for better dispersion of cement particles though steric hindrance effect. The molar ratios between MPEGMA and MAA should be high enough for better adsorption on cement particles. A good purification is important to reach the maximum potential of the polycarboxylate copolymers. Molecular weights of polycarboxylate copolymers should be in an optimal range and the molecular weight distribution should be very narrow to obtain a good fluidity of fresh cement.

In addition, it was found that RAFT polycarboxylate terpolymer not only able to provide a reasonable cement slump test, but also able to get rid of the generated bubbles at the same time base on defoaming characteristic test.
In case of actual concrete tests, RAFT polycarboxylate terpolymer (blended with air entraining agents) in the concrete system successfully reached the slump compared to polycarboxylate 1 at the same dosage. Although the compressive strength of concrete system using RAFT polycarboxylate terpolymer was less than that of concrete system using polycarboxylate 1, the stability of an air-void system (% air content ~ 7.0 %) of harden concrete was obtained. This may possibly lead to a good candidate admixture for an outdoor concrete structural application that requires freeze-thaw stability without adding separate defoaming agents.
CHAPTER VII

POLY (METHOXY POLY (ETHYLENE GLYCOL) METHACRYLATE) – BLOCK – POLY (BUTYL ACRYLATE) VIA RAFT POLYMERIZATION ON THE APPLICATION OF MESOPOROUS MATERIALS

7.1 Overview

A new series of block copolymers, poly (methoxy poly (ethylene glycol) methacrylate) - block - poly (butyl acrylate) [PMPEGMA – b – PBA], with different chain lengths of MPEGMA (Mw = 475 and 950 g mol\(^{-1}\)) and different chain lengths of butyl acrylate were successfully synthesized via reversible addition-fragmentation chain transfer (RAFT) polymerization. 4-cyanopentanoic acid dithiobenzoate (CPADB) was a RAFT agent used for the synthesis. \(^1\)H-NMR was used to identify the chemical structures of the first block (PMPEGMA) and second block (PBA) of these copolymers. GPC chromatograms showed narrow polydispersity index (PDI) of PMPEGMA and PMPEGMA - b - PBA.

In a mesoporous fabrication process; copolymer dissolved in THF, cobalt nitrate and/or nickel nitrate and citric acid dissolved in ethanol and were casted on a silicon wafer substrate. The temperature was raised to 120-250 °C (depending on the mole fraction between cobalt and nickel nitrate) to form “micelle-structured metal carbonate”.

166
After that, the temperature increased again to 250 – 350 °C to remove micelles and formed “mesoporous metal oxide”. The processing temperatures for metal carbonate and oxide formation of were determined by TGA. FT-IR was used to track the compositional changes that occurred in the films throughout the processing. AFM showed the surface morphology with a spherical microphase separated structure after metal carbonate and oxide formation obtained by soft-templating method using PMPEGMA – b – PBA as a micelle.

7.2 Introduction

Amphiphilic block copolymers have received considerable attention in terms of their ability to form numerous types of nanoparticles and mesoporous materials. These block polymers are usually comprised of more than one type of monomer. It is predominantly fascinating when their chemical natures are not quite compatible with each other e.g. hydrophilic/hydrophobic. Those block polymers can be considered as “macro-surfactants” because their chemical structures are similar to low molar mass surfactants.

There are many advantages from these amphiphilic block copolymers. In recent years, the use of block copolymers as stimuli-responsive materials has had significant progress. Either chemical stimuli (i.e. electrochemical reaction, acid-base reaction, photochemical reaction, etc.) or physical stimuli (e.g. changes of temperature, pressure, pH, magnetic field, etc.) can be used for the purpose of changing the hydrophilic characteristic of functional groups into a hydrophobic one, or vice versa in an aqueous system. Another application is the use of copolymers as templates for the mesoporous metal oxide materials. For instance, alumina is extensively used as a
catalyst support, cobalt oxide can be used as an electrode material for lithium-ion batteries, and nickel oxide is broadly used in electro-chromic display devices, fuel cell electrodes, etc.\textsuperscript{17} Evaporation induced self-assembling (EISA) is a common soft-templating method that employs micelles of amphiphilic block copolymers as the porous templates\textsuperscript{18,19}.

Due to the benefits of amphiphilic block copolymers, various polymerization techniques have been extensively used especially controlled free radical polymerization (CFRP) techniques. They have received interest because of their versatility in engineering complex materials with controlled molecular weights, controlled block locations, and narrow molecular weight distribution\textsuperscript{4-9}. There are three CFRP techniques to polymerize vinyl monomers which include nitroxide mediated polymerization (NMP), atom transfer radical polymerization (ATRP), and reversible-addition fragmentation chain transfer (RAFT) polymerization\textsuperscript{3,94-96}. Among these living radical processes, RAFT has been reported to be useful for diverse monomers\textsuperscript{97}. For example, Chaduc et al. employed a one-pot strategy to synthesize poly (methacrylic acid) - $b$ - poly [methoxy poly (ethylene glycol) methacrylate] \textit{via} RAFT polymerization\textsuperscript{62}. In addition, Mertoglu et al. synthesized various types of amphiphilic block copolymers for stimuli-responsive materials \textit{via} RAFT polymerization. Those block copolymers included poly (butyl acrylate) – $b$ – poly (N-acryloyl pyrrolidine), poly [methoxy poly (ethylene glycol) acrylate] – $b$ – poly (4-(2-sulfoethyl)-1-(4-vinyl-benzyl) pyridinium betain), etc\textsuperscript{3}.

Up to now, a number of amphiphilic block copolymers have been synthesized, not only varying block combinations, but also varying the lengths of hydrophilic and hydrophobic blocks\textsuperscript{61}. This is a great advantage for the fabrication of mesoporous
materials with possible fine tuning of mesopore size by changing the polymer concentrations and the block lengths \(^1\).

Therefore, in the present work a new series of amphiphilic block copolymers, PMPEGMA – b – PBA, with different chain lengths of MPEGMA (M\(_n\) = 475 and 950 g mol\(^{-1}\)) and different chain lengths of n-butyl acrylate were synthesized via RAFT polymerization. \(^1\)H-NMR was used to identify the chemical structures of both homopolymers (PMPEGMA) and block copolymers (PMPEGMA - b - PBA). Molecular weight, polydispersity index (PDI), and molecular weight growth in different reaction time interval were investigated by GPC technique. In addition, TGA was used to determine decomposition temperatures for a series of amphiphilic block copolymers, PMPEGMA - b - PBA.
7.3 Materials

Materials used in this chapter can be divided into two parts. The first part is contributed to the materials for synthesis of block copolymer templates. The latter part is related to materials for synthesis of cobalt and/or nickel mesoporous materials.

7.3.1 Materials for block copolymer templates

Methoxy poly (ethylene glycol) methacrylate (MPEGMA, 475 and 950 g mol\(^{-1}\), Aldrich), butyl acrylate (Aldrich, >99%), \(N, N\)-Dimethylformamide (DMF) (Aldrich, anhydrous, 99.8%), tetrahydrofuran (THF) (Sigma-Aldrich, HPLC, >99.9%), hexane (Sigma-Aldrich, anhydrous, 95%), diethyl ether (EMD Millipore, anhydrous), and deuterated chloroform (CDCl\(_3\)) (Cambridge Isotope Laboratories, Inc.) were used as received. 2,2'-Azobis(isobutynitrite) (AIBN) (Aldrich, 98%) was purified by recrystallization from methanol. 4-cyanopentanoic acid dithiobenzoate (CPADB) was synthesized according to the literature\(^{86,101}\).

![](image)

(a) MPEGMA  (b) BA  (c) CPADB

Figure 7-1 Chemical structures of monomers (a) Methoxy poly (ethylene glycol) methacrylate \((n = 11, \text{MPEGMA 475}; n = 24, \text{MPEGMA 950})\), (b) Butyl acrylate (BA), and RAFT agent (c) CPADB
7.3.2 Materials for synthesis of cobalt and/or nickel mesoporous materials

PMPEGMA 475 – b – PBA (M_n = 5.9 x 10^4 g mol^-1) was received from previous section. Nickel (II) nitrate hexahydrate (puriss. p.a., \( \geq 98.5\% \) (KT)), cobalt (II) nitrate hexahydrate (reagent grade, 98%), , citric acid (ACS reagent, \( \geq 99.5\% \)), ethanol (ACS reagent, \( \geq 99.5\% \) (200 proof), absolute), tetrahydrofuran (THF) (ACS reagent, \( \geq 99.0\% \), containing 250 ppm BHT as inhibitor), mercaptosuccinic acid (97%), sodium perchlorate (ACS reagent, \( \geq 98.0\% \)), ethylene carbonate (anhydrous, 99%), and propylene carbonate (reagent plus, 99%) were purchased from Sigma-Aldrich and used as received. H_2SO_4, Hydrogen peroxide (30%) was purchased from Fisher Scientific.

There were three substrates used in these studies for different purposes: 1) single side polished silicon wafers (Silicon, Inc.) were used for general studies; 2) high resistivity (1-10 \( \Omega \cdot \text{cm} \)), 600 \( \mu \text{m} \) thick double side polished Si wafers were used for FTIR measurements in order to track changes in functional groups of chemical transformation during the construction of mesoporous materials; and 3) 250 \( \mu \text{m} \) thick quartz slides (GM Associates Inc.) sputter coated with gold were used for electrochemical measurements. All types of silicon wafers employed in these studies were carefully cleaned with Piranha solution (H_2SO_4 : H_2O_2 = 3:1 V/V) at 90 °C for 45 min. Subsequently, deionized water was used to rinse those silicon wafers for multiple times. These silicon wafers were further dried in a nitrogen ambient prior to the film casting. In case of the quartz slides coated with gold, they were treated with 10 mM ethanoic mercaptosuccinic acid for 24 h in order to create a hydrophilic surface. After that, ethanol was used to rinse these quartz
substrates for several times. Finally, they were further dried in a nitrogen ambient prior to use as current collectors.

7.4 Synthesis of amphiphilic block copolymer templates

A series of PMPEGMA - $b$ - PBA were synthetized by using RAFT polymerization method. There were two steps in these syntheses (shown in Scheme 7-1). First was creating PMPEGMA 475 or PMPEGMA 950 macro RAFT agents. These resulting macro RAFT agents were then polymerized with butyl acrylate to create a new series of amphiphilic block copolymers, PMPEGMA 475/950 – $b$ – PBA.

7.4.1 The Synthesis of the first block [RAFT poly (MPEGMA)]

MPEGMA in different molecular weights (475 and 950 g mol$^{-1}$), DMF as a solvent, AIBN as an initiator, and CPADB as a RAFT agent were introduced into a three-neck round bottom flask, equipped with a condenser, nitrogen gas inlet and outlet.

Run 1 in Table 7-1 was performed by mixing MPEGMA 475 g mol$^{-1}$ (21.00 g, $4.42 \times 10^{-2}$ mol), CPADB (0.49 g, $1.75 \times 10^{-3}$ mol), AIBN (58 mg, $3.53 \times 10^{-4}$ mol), and DMF (10.00 g) in a reaction flask.

Table 7-1 Synthesis summary of RAFT poly (MPEGMA)

<table>
<thead>
<tr>
<th>Run</th>
<th>Monomer</th>
<th>(Monomer) (wt. %)</th>
<th>MPEGMA/CTA (Molar ratio)</th>
<th>CTA/AIBN (Molar ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>MPEGMA 475</td>
<td>66.56</td>
<td>25/1</td>
<td>5/1</td>
</tr>
<tr>
<td>2</td>
<td>MPEGMA 950</td>
<td>67.14</td>
<td>25/1</td>
<td>5/1</td>
</tr>
</tbody>
</table>
The mixture from Table 7-1 was gently stirred by magnetic stir bar under the nitrogen purge. After 30 min, the polymerization was initiated by immersing the reaction flask into the oil bath at 65 °C for 20 h. Polymerization was terminated via immediate exposure to air and quenching with an ice bath. After termination, the PMPEGMA was purified by precipitation in diethyl ether for three times in order to remove unreacted MPEGMA, AIBN, and CPADB. Finally, dried it overnight in a vacuum oven at room temperature.

7.4.2 Block copolymerization of PMPEGMA and PBA via RAFT Polymerization

A series of amphiphilic block copolymers of PMPEGMA – b – PBA were successfully synthesized. DMF as a solvent, AIBN as an initiator, and PMPEGMAs from previous step as macro RAFT agents, were introduced into a three-neck round bottom flask, equipped with a condenser, a nitrogen gas inlet and outlet.

Run 3 in Table 7-2 was performed by mixing poly (MPEGMA 475) (M<sub>n</sub> = 2.50 x 10<sup>4</sup> g·mol<sup>-1</sup>) (5.00 g, 2.00 x 10<sup>-4</sup> mol), butyl acrylate (BA) (4.66 g, 3.64 x 10<sup>-2</sup> mol), AIBN (0.03 g, 1.86 x 10<sup>-4</sup> mol), and DMF (10.00 g) in a reaction flask.

Run 7 in Table 7-2 was performed by mixing poly (MPEGMA 950) (M<sub>n</sub> = 5.20 x 10<sup>4</sup> g·mol<sup>-1</sup>) (5.00 g, 1.15 x 10<sup>-4</sup> mol), butyl acrylate (BA) (4.38 g, 3.41 x 10<sup>-2</sup> mol), AIBN (14.3 mg, 8.75 x 10<sup>-5</sup> mol), and DMF (12.00 g) in a reaction flask.
Table 7-2 Summary of Block Copolymerization of PMPEGMA and PBA via RAFT polymerization

<table>
<thead>
<tr>
<th>Run</th>
<th>First block</th>
<th>Second block</th>
<th>First block/Second block</th>
<th>First block/AIBN (Molar ratio)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>PMPEGMA 475</td>
<td>BA</td>
<td>1/182</td>
<td>1.08/1</td>
</tr>
<tr>
<td>4</td>
<td>PMPEGMA 475</td>
<td>BA</td>
<td>1/364</td>
<td>1.08/1</td>
</tr>
<tr>
<td>5</td>
<td>PMPEGMA 475</td>
<td>BA</td>
<td>1/728</td>
<td>1.08/1</td>
</tr>
<tr>
<td>6</td>
<td>PMPEGMA 475</td>
<td>BA</td>
<td>1/1456</td>
<td>1.08/1</td>
</tr>
<tr>
<td>7</td>
<td>PMPEGMA 950</td>
<td>BA</td>
<td>1/296</td>
<td>1.32/1</td>
</tr>
<tr>
<td>8</td>
<td>PMPEGMA 950</td>
<td>BA</td>
<td>1/592</td>
<td>1.32/1</td>
</tr>
<tr>
<td>9</td>
<td>PMPEGMA 950</td>
<td>BA</td>
<td>1/1184</td>
<td>1.32/1</td>
</tr>
</tbody>
</table>

The mixture was gently stirred by magnetic stir bar under the nitrogen purge. After 30 min, the polymerization was initiated to fabricate the copolymer by immersing the reaction flask into the oil bath at 65 °C for 20 h. Polymerization was terminated via immediate exposure to air and quenching with an ice bath. After cooling, DMF in the mixture was evaporated by rotary evaporator. The crude solid product was dissolved in a 5 mL of THF. The block copolymer was precipitated by 100 mL hexane three times, and filtered. Finally, the precipitate was dried overnight in a vacuum oven at room temperature.
Scheme 7-1 Chemical structures of methoxy poly (ethylene glycol) methacrylate (n = 11, MPEGMA 475; n = 24, MPEGMA 950), n-Butyl acrylate (BA), CPADB RAFT agent, and macro RAFT agents (PMPEGMA 475/950) used for synthesis block copolymers of PMPEGMA - b - PBA
7.5 Sample preparation for fabrication of cobalt and/or nickel mesoporous materials

There are three major steps to fabricate cobalt and/or nickel mesoporous materials. 1) Film casting process: Run 1 in Table 7-3, a film was prepared by a flow casting method. This was done by dissolving 188 mg of cobalt (II) nitrate hexahydrate [Co(NO₃)₂.6H₂O] in 0.6 g ethanol solution. After 15 min mixing, 62 mg citric acid was introduced to the cobalt (II) nitrate hexahydrate solution and further stirred at room temperature for 1 h. In another vial, 50 mg of a block copolymer (PMPEGMA 475 – b – PBA, Mn = 5.9 x 10⁴ g mol⁻¹) was dissolved in 1.8 g of THF. After 1 h mixing, the cobalt (II) nitrate hexahydrate nitrate solution prepared in a previous step was added dropwise via a syringe pump to the block copolymer solution. A mixture was then stirred for 12-14 h at a room temperature before film casting. In Table 7-3, it shows other precursor compositions (Run 2 – Run 5) of cobalt oxide, nickel oxide and their mixed metal oxide (NiₓCo₁₋ₓOᵧ) composites to fabricate the films in this work. Films were casted on the silicon wafer substrates by a flow coating at 40 mm/s and at a relative humidity (RH) of ~ 40-50%. The casted films were subsequently dried at a room temperature for 30 min prior to calcination to create a metal carbonate. 2) Calcination towards carbonate: The casted films in previous step were placed in a preheated furnace (Ney Vulcan 3-130) and then heated at 200 °C for 60 min in order to fabricate the metal carbonate. After that, the furnace was cooled to a room temperature. 3) Calcination towards oxide: The metal carbonate films obtained from the previous step were subsequently subjected to additional calcination in a preheated furnace and then heated at 300 °C for 30 min in order to fabricate the metal oxide. Then the films were immediately taken out from the furnace and quenched to a room temperature. The calcination processing conditions
toward carbonate and toward oxide were different based on the precursor compositions as presented in Table 7-3.

Table 7-3 Precursor compositions and processing conditions for fabrication of cobalt oxide, nickel oxide and their mixed metal oxide (Ni\textsubscript{x}Co\textsubscript{1-x}O\textsubscript{y}) composites

<table>
<thead>
<tr>
<th>Run</th>
<th>Sample</th>
<th>Co(NO\textsubscript{3})\textsubscript{2},6H\textsubscript{2}O (mg)</th>
<th>Ni(NO\textsubscript{3})\textsubscript{2},6H\textsubscript{2}O (mg)</th>
<th>Citric acid (mg)</th>
<th>PMPEGMA 475-b-PBA (mg)</th>
<th>Calcination towards carbonate</th>
<th>Calcination towards oxide</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Co\textsubscript{3}O\textsubscript{4}</td>
<td>188</td>
<td>-</td>
<td>62</td>
<td>50</td>
<td>60 min at 200 °C</td>
<td>30 min at 300 °C</td>
</tr>
<tr>
<td>2</td>
<td>Ni\textsubscript{0.25}Co\textsubscript{0.75}O\textsubscript{2}</td>
<td>143</td>
<td>51</td>
<td>63</td>
<td>53</td>
<td>60 min at 220 °C</td>
<td>30 min at 325 °C</td>
</tr>
<tr>
<td>3</td>
<td>Ni\textsubscript{0.5}Co\textsubscript{0.5}O\textsubscript{2}</td>
<td>96</td>
<td>94</td>
<td>63</td>
<td>52</td>
<td>60 min at 240 °C</td>
<td>30 min at 350 °C</td>
</tr>
<tr>
<td>4</td>
<td>Ni\textsubscript{0.75}Co\textsubscript{0.25}O\textsubscript{2}</td>
<td>42</td>
<td>148</td>
<td>62</td>
<td>55</td>
<td>60 min at 255 °C</td>
<td>30 min at 365 °C</td>
</tr>
<tr>
<td>5</td>
<td>NiO</td>
<td>-</td>
<td>191</td>
<td>66</td>
<td>53</td>
<td>60 min at 265 °C</td>
<td>30 min at 375 °C</td>
</tr>
</tbody>
</table>

7.6 Instrumentation

Instruments used in this chapter can be categorized into two parts. The first part is contributed to the instruments for synthesis of block copolymer templates. The latter part is related to instruments for fabrication of cobalt and/or nickel mesoporous materials.

7.6.1 Instrumentation for synthesis of block copolymer templates

_Gel Permeation Chromatography (GPC)._ Three Waters system was used for gel permeation chromatography (GPC) with a HR4, HT2, HR1, HR0.5 styrigel, and 500 Å ultrastyrigel columns connected in series. GPC analyses were performed at 35 °C on 0.1% (w/v) sample solutions in distilled tetrahydrofuran (THF). Solutions were filtered with 0.45 μm membrane syringe filters and 200 μL was injected into the chromatograph.
with an eluent flow rate set at 1.0 mL min\(^{-1}\). The molecular weight and poly dispersity index (PDI) of these homopolymers and series of amphiphilic block copolymers were measured by using light scattering detector. The molecular weight development was examined by using refractive index detector and data were interpreted by Omnisec software v.4.7.0.406.

\(^{1}H\)-NMR analysis. \(^{1}H\)-NMR Analysis of all starting materials was recorded on Varian NMRS-500 nuclear magnetic resonance instrument (500 MHz) using deuterated chloroform (CDCl\(_{3}\)) as a solvent\(^{118,132}\).

Thermogravimetric analysis (TGA, TA Instruments, TGA-Q50) was used to determine the decomposition temperatures for these series of amphiphilic block copolymers (PMPEGMA 475/950 – b - PBA). TGA was performed under an air purge with 10 °C/min ramp rate. The operation temperature was ranging from room temperature to 700 °C.

7.6.2 Instrument for fabrication of cobalt and/or nickel mesoporous materials

Thermogravimetric analysis (TGA, TA Instruments, TGA-Q50) was used to determine the processing temperatures for both the carbonate and oxide formation of (Ni\(_{x}\)Co\(_{1-x}\)O\(_y\)) mixed metal oxides (MMOs). Metal nitrate and citric acid were placed in an ethanol / THF mixture without the block copolymer (PMPEGMA 475 - b - PBA) template. The mixture was subsequently allowed to dry at 22 °C for 8-10 h, followed by heating under vacuum at 50 °C for additional 10 h. Eventually, powders of the metal nitrate and citric acid were obtained for the TGA. TGA was performed under an air purge
with 5 °C/min ramp rate. The onset temperature of metal carbonate or oxide formation was determined by the derivative of the temporal mass with respect to temperature.

*Fourier Transform Infrared (FT-IR)* (Thermo Scientific, Nicolet iS50 FT-IR) was used to determine characteristics of chemical bond stretching/bending for various functional groups. The spectra were obtained in transmission mode on the thin films by collecting 512 scans with a resolution of 8 cm⁻¹ using a Deuterated TriGlycine Sulfate (DTGS) detector. The baseline of the FTIR spectra and functional group assignment were corrected and interpreted by using OMNIC software.

*Atomic Force Microscopy* (AFM, Dimension ICON, Veeco) was used to explore the surface morphology of mixed metal composite thin films throughout the processing (including as cast, carbonate formation, and metal oxide formation).

7.7 Results and discussion

There are two parts for results and discussion. The first part is about the characterization of block copolymer templates. GPC, ¹H-NMR, and TGA were used for this characterization. The latter part is related to the characterization of fabrication of cobalt and/or nickel mesoporous materials. TGA, FT-IR, and AFM were used for this characterization.
7.7.1 Characterization of RAFT PMPEGMA – block – PBA Templates

Figure 7-2 GPC chromatograms of samples withdrawn during RAFT homopolymerization of PEGAMA 475 (run 1 in Table 7-1)

Figure 7-3 GPC chromatograms of samples withdrawn during RAFT homopolymerization of PEGAMA 950 (run 2 in Table 7-1)
Figure 7-2 demonstrates molecular weight development of samples regularly withdrawn from the RAFT polymerization medium of the run 1 (Table 7-1). It can be seen that the intensity of MPEGMA 475, at the retention volume \( \approx 28 \) mL, decreased significantly. It completely disappeared at the reaction time of 6 h. When the reaction was going on, new peaks at higher elution volume appeared, which corresponds to the formation of polymer chains, PMPEGMA 475. The new polymer peaks shifted toward lower elution volume with continuity of MPEGMA 475 consumption, indicating the growth of the polymer chains. Figure 7-3 also shows the evolution of GPC chromatograms of samples regularly withdrawn from the RAFT polymerization medium of the run 2 (Table 7-1). Similar to homopolymerization of MPEGMA 475, the consumption of MPEGMA 950, at the retention volume \( \approx 26.8 \) mL, was obviously observed. The intensity diminished significantly and almost disappeared at the reaction time of 6 h and completely disappeared at 20 h. New peaks at higher elution volume were seen instantaneously with the consumption of MPEGMA 950. A slightly dissymmetric polymer peak can be observed in Figure 7-2 and Figure 7-3, which is possibly because of an irreversible polymer adsorption onto the GPC columns operating during the analyses for longer polymer chain. From the homopolymerization MPEGMA 475 and MPEGMA 950, the monomer consumption rate was quite different. MPEGMA 475 was completely consumed within 6 h. On the other hand, MPEGMA 950 at the reaction time of 6 h, there was still some unreacted monomers left. The reason for this is probably because the MPEGMA 950 has longer side chain, which creates more steric hindrance than MPEGMA 475. The more steric hindrance might impede the rate of monomer consumption.
Figure 7-4 GPC chromatograms of PMPEGMA 475 and series of PMPEGMA 475 - b - PBA

Figure 7-5 GPC chromatograms of PMPEGMA 950 and series of PMPEGMA 950 - b - PBA
Figure 7-4 shows GPC chromatograms of PMPEGMA 475 and series of PMEGMA 475 - b - PBA. The homopolymer of PMPEGMA 475 was eluted from GPC at a highest retention volume, corresponds to the lowest molecular weight size of its series. However, when BA was attached to this PMPMEGMA 475 homopolymer, the block copolymer of PMPEGMA 475 - b - PBA was established. The new polymer peaks shifted toward lower elution volume which corresponds to higher molecular weight. Based on the ratio between macro RAFT agent and butyl acrylate, different molecular weights of PMPEGMA 475 - b - PBA were obtained. Figure 7-5 illustrates the GPC chromatograms of PMPEGMA 950 and series of PMPEGMA 950 – b - PBA. As shown, the similar trend was observed in which a lower retention volume corresponds to the higher molecular weight. This confirmed the successful fabrication of series block copolymers of PMPEGMA 475/950 - b - PBA.

![Figure 7-6 ¹H-NMR of PMPEGMA 475/950](image-url)
Table 7-4 $^1$H resonance assignments of PMPEGMA 475/950

<table>
<thead>
<tr>
<th>Structural Group</th>
<th>Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH$_2$-CCH$_3$ (main chain)</td>
<td>0.88 - 1.11</td>
</tr>
<tr>
<td>-CH$_2$-CCH$_3$ (main chain)</td>
<td>1.58 - 2.04</td>
</tr>
<tr>
<td>-O-CH$_3$</td>
<td>3.39</td>
</tr>
<tr>
<td>-(CH$_2$CH$_2$O)- (PEO region)</td>
<td>3.42 - 3.80</td>
</tr>
<tr>
<td>-OCO-(CH$_2$CH$_2$O)-</td>
<td>3.98 - 4.08</td>
</tr>
</tbody>
</table>

Figure 7-7 $^1$H-NMR of PMPEGMA 475/950 – b – PBA
Table 7-5 $^1$H resonance assignments of PMPEGMA 475/950 - $b$ - PBA

<table>
<thead>
<tr>
<th>Structural Group</th>
<th>Chemical Shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-CH$_2$-CCH$_3$ (MPEGMA) and -O-CH$_2$-CH$_2$-CH$_2$-CH$_3$ (BA)</td>
<td>0.80-1.10</td>
</tr>
<tr>
<td>-COO-CH$_2$-CH$_2$-CH$_2$-CH$_3$ (BA)</td>
<td>1.35 - 1.37</td>
</tr>
<tr>
<td>-COO-CH$_2$-CH$_2$-CH$_2$-CH$_3$ (BA)</td>
<td>1.57 - 1.62</td>
</tr>
<tr>
<td>-CH$_2$-CCH$_3$ (MPEGMA) and -CH$_2$-CH$_2$ (BA)</td>
<td>1.89 - 2.30</td>
</tr>
<tr>
<td>-O-CH$_3$</td>
<td>3.39</td>
</tr>
<tr>
<td>-(CH$_2$CH$_2$O)$_n$ (PEO region)</td>
<td>3.54 - 3.78</td>
</tr>
<tr>
<td>-COO-(CH$_2$CH$_3$O)$_n$ (MPEGMA) and -COO-CH$_2$-CH$_2$-CH$_2$-CH$_3$ (BA)</td>
<td>3.97 - 4.15</td>
</tr>
</tbody>
</table>

Figure 7-6 shows the $^1$H-NMR of homopolymers of PMPEGMA 475 and 950. These two homopolymers show the same resonances in $^1$H-NMR. The only difference between these homopolymers is the integration area of -(CH$_2$CH$_2$O)$_n$, corresponds to (PEO region). PMPEGMA 950 has higher integration area than that of PMPEGMA 475 due to greater number of PEO units. It also shows the completion of homo RAFT polymerization because there were no protons from double bonds left for MPEGMA monomer in the chemical shift between 5.50 - 6.50 ppm of $^1$H-NMR. $^1$H-NMR assignments of PMPEGMA 475/950 can be seen in Table 7-4. Figure 7-7 shows $^1$H-NMR of PMPEGMA 475/950 – $b$ – PBA. New chemical shifts e.g. from 1.35 - 1.62 ppm, corresponding to $^1$H resonances of -COO-CH$_2$-CH$_2$-CH$_2$-CH$_3$ in BA part. In addition, there were no protons from double bonds left of BA monomer in the chemical shift between 5.50 - 6.50 ppm of $^1$H-NMR, which indicated the success of fabrication PMPEGMA 475/950 - $b$ - PBA. $^1$H-NMR assignments of PMPEGMA 475/950 - $b$ - PBA can be seen in Table 7-5.
Figure 7-8 TGA of (a) PMPEGMA 475 and a series of PMPEGMA 475 - b - PBA, (b) PMPEGMA 950 and a series of PMPEGMA 950 - b - PBA
From Figure 7-8, it can be seen that by fixing the molecular weight of PMPEGMA 475 and varying the lengths of PBA, TGA thermograms of these block copolymers were different. The length of PBA plays an important role for this thermogravimetric analysis. For the longer chain length of PBA (corresponding to higher molecular weight), the onset decomposition temperature shifted towards higher temperature. This also happened in the similar fashion as the block copolymer series PMPEGMA 950 - b - PBA. Knowing the onset decomposition of each block copolymer will offer the advantage for fabrication of mesoporous materials via soft template method that uses micelles of amphiphilic block copolymers as the porous templates.
Mole fraction of PBA can be calculated from integration area of methyl group in PMPEGMA block and methylene group in PBA block. This can be seen in Table 7-6. By increasing mole fraction of PBA, decomposition temperature of both block copolymer series of PMPEGMA 475 - b - PBA and PMPEGMA 950 - b - PBA shifted towards higher temperature (as seen in Figure 7-9). The decomposition temperatures of these block copolymer series PMPEGMA 475/950 - b - PBA were determined by the intersection of two tangent lines of the temporal mass and temperature in TGA.
Table 7-6 Calculation of mole fraction of PBA in block copolymer series PMPEGMA 475/950 - b - PBA by using $^1$H-NMR

<table>
<thead>
<tr>
<th>Polymer Name</th>
<th>Integral area of methyl gr. (3.39 ppm)</th>
<th>Integral area of CH$_2$ from PBA (1.89 - 2.30)</th>
<th>Relative mole PMPEGMA 475</th>
<th>Relative mole PBA</th>
<th>% mole of PBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMPEGMA 475</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>PMPEGMA 475</td>
<td>1.11</td>
<td>1.89</td>
<td>0.37</td>
<td>0.95</td>
<td>0.72</td>
</tr>
<tr>
<td>- b - PBA 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMPEGMA 475</td>
<td>0.99</td>
<td>5.01</td>
<td>0.33</td>
<td>2.50</td>
<td>0.88</td>
</tr>
<tr>
<td>- b - PBA 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMPEGMA 475</td>
<td>1.01</td>
<td>8.99</td>
<td>0.33</td>
<td>4.50</td>
<td>0.93</td>
</tr>
<tr>
<td>- b - PBA 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMPEGMA 475</td>
<td>1.05</td>
<td>18.22</td>
<td>0.35</td>
<td>9.11</td>
<td>0.96</td>
</tr>
<tr>
<td>- b - PBA 4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Polymer Name</th>
<th>Integral area of methyl gr. (3.39 ppm)</th>
<th>Integral area of CH$_2$ from PBA (1.89 - 2.30)</th>
<th>Relative mole PMPEGMA 950</th>
<th>Relative mole PBA</th>
<th>% mole of PBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMPEGMA 950</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
<tr>
<td>PMPEGMA 950</td>
<td>0.93</td>
<td>4.07</td>
<td>0.31</td>
<td>2.04</td>
<td>0.87</td>
</tr>
<tr>
<td>- b - PBA 1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMPEGMA 950</td>
<td>0.94</td>
<td>6.06</td>
<td>0.32</td>
<td>3.03</td>
<td>0.91</td>
</tr>
<tr>
<td>- b - PBA 2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMPEGMA 950</td>
<td>0.98</td>
<td>18.02</td>
<td>0.33</td>
<td>9.01</td>
<td>0.96</td>
</tr>
<tr>
<td>- b - PBA 3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
% mole of PBA in block copolymer series PMPEGMA 475/950 - b - PBA can be calculated by using equations shown below:

\[
\text{Relative mole PMPEGMA} = \frac{\text{Integral area of methyl gr. (at 3.39 ppm)}}{\# \text{ of protons in methyl gr.}}
\] (7-1)

\[
\text{Relative mole PBA} = \frac{\text{Integral area of } -\text{CH2 from BA side chain (at 1.89 - 2.30 ppm)}}{\# \text{ of protons in methylene gr. in BA}}
\] (7-2)

\[
\text{Mole % of PBA} = \frac{\text{Relative mole PBA} \times 100\%}{\text{Relative mole PBA} + \text{Relative mole PMPEGMA}}
\] (7-3)

Table 7-7 Summary of synthesized amphiphilic block copolymers PMPEGMA 475/950 - b - PBA; molecular weight, decomposition temperature, and mole fraction of PBA

<table>
<thead>
<tr>
<th>Run</th>
<th>Polymer</th>
<th>(M_w)</th>
<th>(M_n)</th>
<th>PDI</th>
<th>Decomposition Temperature (°C)</th>
<th>Mole fraction of PBA</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PMPEGMA 475</td>
<td>(3.3 \times 10^4)</td>
<td>(2.5 \times 10^4)</td>
<td>1.3</td>
<td>216.33 ± 3.51</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>PMPEGMA 475 - b - PBA 1</td>
<td>(4.4 \times 10^4)</td>
<td>(3.7 \times 10^4)</td>
<td>1.2</td>
<td>248.67 ± 1.53</td>
<td>0.72</td>
</tr>
<tr>
<td>4</td>
<td>PMPEGMA 475 - b - PBA 2</td>
<td>(7.7 \times 10^4)</td>
<td>(5.9 \times 10^4)</td>
<td>1.3</td>
<td>270.00 ± 4.00</td>
<td>0.88</td>
</tr>
<tr>
<td>5</td>
<td>PMPEGMA 475 - b - PBA 3</td>
<td>(12.1 \times 10^4)</td>
<td>(10.1 \times 10^4)</td>
<td>1.2</td>
<td>314.00 ± 9.54</td>
<td>0.93</td>
</tr>
<tr>
<td>6</td>
<td>PMPEGMA 475 - b - PBA 4</td>
<td>(19.6 \times 10^4)</td>
<td>(15.1 \times 10^4)</td>
<td>1.3</td>
<td>340.00 ± 6.24</td>
<td>0.96</td>
</tr>
<tr>
<td>2</td>
<td>PMPEGMA 950</td>
<td>(6.3 \times 10^4)</td>
<td>(5.2 \times 10^4)</td>
<td>1.2</td>
<td>232.67 ± 2.08</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>PMPEGMA 950 - b - PBA 1</td>
<td>(9.5 \times 10^4)</td>
<td>(7.9 \times 10^4)</td>
<td>1.2</td>
<td>273.33 ± 3.05</td>
<td>0.87</td>
</tr>
<tr>
<td>8</td>
<td>PMPEGMA 950 - b - PBA 2</td>
<td>(10.4 \times 10^4)</td>
<td>(8.7 \times 10^4)</td>
<td>1.2</td>
<td>296.00 ± 2.65</td>
<td>0.91</td>
</tr>
<tr>
<td>9</td>
<td>PMPEGMA 950 - b - PBA 3</td>
<td>(16.2 \times 10^4)</td>
<td>(13.5 \times 10^4)</td>
<td>1.2</td>
<td>312.33 ± 2.08</td>
<td>0.96</td>
</tr>
</tbody>
</table>
Table 7-7 shows the summary of new series of amphiphilic block copolymers PMPEGMA 475/950 - b - PBA that are present in this paper. The molecular weight of homopolymers PMPEGMA 475 and PMPEMGA 950 were fixed, but varying the amount of added BA. The results were PMPEGMA - b - PBA with different chain lengths of PBA. The different mole fraction of PBA will affect the decomposition temperatures as mentioned earlier.

7.7.2 Characterization of fabrication of cobalt and/or nickel mesoporous materials

Metal nitrate-citric acid complexes typically degrade in a two-step process when heating in air atmosphere. Firstly, they form a metal carbonate, which decomposes into the corresponding metal oxide at higher temperatures. Figure 7-10 demonstrates the compositional dependence on these transformations by TGA.

![Figure 7-10 TGA of mixed metal-citric acid complexes for finding the processing temperature of their carbonate and oxide formation](image)
Regardless of nickel/cobalt composition, it is obvious in Figure 7-10 that the decomposition of metal nitrate-citric acid complexes occurred in two distinct steps. The first decomposition step corresponded to a loss of the metal nitrate and its derivatives e.g. H$_2$O, CO$_2$, CO, NO$_x$\textsuperscript{135, 136} with the citric acid. This instantaneously formed the metal carbonate (yellow region). The second decomposition step at a higher temperature corresponded to a transformation of metal carbonate into the metal oxide (orange region). Further heating led to a near constant mass after formation of the metal carbonate. A decrease in weight in the latter step was probably due to the release of CO$_2$ (g) during the metal oxide formation. In addition, it can be seen that the onset temperature for metal carbonate formation and decomposition into metal oxide shifted towards higher temperature with increasing nickel content in the nickel/cobalt composite.

![Figure 7-11 Summary of onset temperature for carbonate and oxide formation of mixed metal-citric acid complexes for fabrication of mesoporous materials](image-url)

\textbf{Figure 7-11} Summary of onset temperature for carbonate and oxide formation of mixed metal-citric acid complexes for fabrication of mesoporous materials
The onset temperatures were determined from the derivative of TGA trace obtained on calcination of the metal nitrate-citric acid complexes as illustrated in Figure 7-11. Only a single plateau region following the carbonate onset was observed for these mixed metal nitrate-citric acid complexes, which suggested that there was a formation of single phase mixed metal carbonates (MMCs) (Ni\textsubscript{x}Co\textsubscript{(1-x)}(CO\textsubscript{3})\textsubscript{y}) across the full composition window. As can be seen in Figure 7-11 the onset temperature of cobalt carbonate occurred around 135 °C, while that of nickel carbonate occurred at much higher temperature of 260 °C.

At higher temperatures, a second drop in weight was observed, indicating the decomposition of the metal carbonate into its corresponding metal oxide (orange region in Figure 7-10). Similar to the trend of the onset temperature of metal carbonate formation, the onset temperature of oxide formation was primarily based on the metal (nickel/cobalt) compositions. It also shifted towards higher temperature with increasing nickel content. For instance, the onset temperature for cobalt oxide was around 245 °C, but this increased to approximately 375 °C for nickel oxide. Furthermore, it can be noticed in Figure 7-11 that the gap of the onset temperature between carbonate formation and oxide formation for each metal composition was around 100 °C. The increase in both onset temperature of carbonate formation and oxide formation with increasing nickel content implies that the nickel has more activation energy required for carbonate or oxide formation than cobalt. The TGA in Figure 7-10 suggests that this fabrication route can generate single phase Ni\textsubscript{x}Co\textsubscript{(1-x)}O\textsubscript{y} composites.
FT-IR was used to determine characteristics of chemical bond stretching/bending for various functional groups, leading to additional insight into the compositional changes that occurred in the films throughout the processing (including as cast, carbonate formation, and metal oxide formation). Figure 7-12 shows an example of the FTIR spectra for micelle templated thin film using 50:50 mole:mole cobalt and nickel nitrate through the processing. At the beginning of the process, a peak at 1740 cm\(^{-1}\), shown in Figure 7-12 (a), (corresponding to the C=O vibration from the acrylate group in PMPEGMA 475 – b – PBA template) was used to follow the degradation of the copolymer template. When the thin film was heated at 240 °C for 1 h, the peak at 1740 cm\(^{-1}\) considerably decreased (shown in Figure 7-12 (b)), but full template degradation...
had not occurred. In addition to the decomposition of the template in this stage, the carbonate was formed. This was because of the appearance of peaks at 1412 cm\(^{-1}\) and 1587 cm\(^{-1}\) (corresponding to C-O bonds in Ni\(_{0.5}\)Co\(_{0.5}\)(CO\(_3\))\(_y\)) (shown in Figure 7-12 (b)). This peak position was slightly shifted from pure cobalt carbonate\(^{134}\). Additional heating at 350 °C for another 30 min (shown in Figure 7-12 (c)), this template was completely decomposed. The peak at 1740 cm\(^{-1}\) totally disappeared. Furthermore, the peaks associated with the carbonate peaks at 1412 cm\(^{-1}\) and 1587 cm\(^{-1}\) also thoroughly disappeared, representing the decomposition of Ni\(_{0.5}\)Co\(_{0.5}\)(CO\(_3\))\(_y\). The new peaks occurred at 634 cm\(^{-1}\) and 475 cm\(^{-1}\) in the spectra corresponding to M-O vibrations from Co-O and Ni-O in Ni\(_{0.5}\)Co\(_{0.5}\)O\(_2\)\(^{137}\). These FTIR spectra were consistent with the expected carbonate and oxide phases suggested by TGA. Other FTIR spectra of micelle templated mesoporous including Co\(_3\)O\(_4\), Ni\(_{0.25}\)Co\(_{0.75}\)O\(_2\), Ni\(_{0.5}\)Co\(_{0.5}\)O\(_2\), Ni\(_{0.75}\)Co\(_{0.25}\)O\(_2\), and NiO fabricated by first forming the carbonate (heating for 1 h) and subsequently the oxide (heating for 30 min) using the temperatures specified in Table 7-7 can be found in this manuscript\(^{138}\).
Figure 7-13 AFM images of micelle templated (a) Ni(CO$_3$)$_y$, (b) Ni$_{0.25}$Co$_{0.75}$(CO$_3$)$_y$, (c) Ni$_{0.50}$Co$_{0.50}$(CO$_3$)$_y$, (d) Ni$_{0.75}$Co$_{0.25}$(CO$_3$)$_y$, and (e) Co(CO$_3$)$_y$, (Scale bar = 200 nm in all micrographs)

Figure 7-13 shows the surface morphology after carbonate formation of these block copolymer (PMPEGMA 475-b-PBA) micelle templated thin films. These MMCs with different mole contents of nickel and cobalt exhibited a microphase separated structure that appeared to have ordered spherical of block copolymer micelles. According to the FT-IR results (as shown in Figure 7-12 (b)), it is suggested that a microphase spherical separated structure had not shown mesopore yet, but the contrast of the block copolymer micelles. These films show an average length-scale of 33.2 nm associated with the center-to-center packing for cobalt carbonate.
Figure 7-14 AFM images of PMPEGMA 475 – b - PBA micelle templated mesoporous (a) NiO, (b) Ni$_{0.25}$Co$_{0.75}$O$_2$, (c) Ni$_{0.50}$Co$_{0.50}$O$_2$, (d) Ni$_{0.75}$Co$_{0.25}$O$_2$, and (e) Co$_3$O$_4$. (Scale bar = 200 nm in all micrographs)

Figure 7-14 demonstrates the surface morphology due to the creation of the oxide structure of these films after further heating at a higher temperature. The metal carbonate decomposition appeared to degrade all of block copolymer micelle templates in general, leading to the mesoporous structure. This is consistent with the FT-IR results (as illustrated in Figure 7-12 (c)). Moreover, some small cracks can be seen in the films, especially at higher nickel content films (also subjected to high calcination temperatures). These cracks are attributed to the shrinkage of the confined inorganic framework in these films, which initiated an anisotropic shrinkage$^{139, 140}$. These cracks can also result in a loss in the ordered nanostructure due to the stresses present$^{141}$. 

197
This shrinkage caused decrease in an average length-scale associated with the center-to-center of a microphase spherical separated structure from 33.2 nm (from cobalt carbonate, due to the copolymer micelles) to 28.6 nm (from cobalt oxide, representing the porous structure). The diameter of these mesopores are $15 \pm 3$ nm obtained from AFM. Although a large amount of stresses were applied due to the shrinkage during copolymer template removal and transformation to oxide, the inorganic structure still held in all the films (as shown in Figure 7-14) at the surface.

7.8 Conclusions

The RAFT polymerization is a powerful pathway to prepare block copolymers that have different nature in chemical characteristic i.e. hydrophilic/hydrophobic. Series of amphiphilic diblock copolymers PMPEGMA 475/950 - $b$ - PBA become conveniently reachable. $^1$H-NMR was used to identify the chemical structures of these series of copolymers. $^1$H-NMR analysis together with GPC confirmed that the second block (PBA) was attached to the first block (PMPEGMA 475/950). GPC also showed a molecular weight and narrow PDI of those copolymers. This will be a benefit in an area of fabrication of mesoporous materials in soft-templating method, which concerns the well-defined templated size distribution. TGA illustrates the decomposition temperature of each block copolymer in this series as the higher PBA content, the higher onset decomposition temperature.

In a mesoporous fabrication process; copolymer dissolved in THF, cobalt nitrate and/or nickel nitrate and citric acid dissolved in ethanol and were casted on a silicon wafer substrate. The temperature was raised to 120 - 250 °C (depending on the mole fraction between cobalt and nickel nitrate) to from “micelle-structured metal carbonate”.
After that, the temperature increased again to 250 – 350 °C to remove micelles and formed “mesoporous metal oxide”. FT-IR was used to track the compositional changes that occurred in the films throughout the processing. AFM showed the surface morphology with a spherical microphase separated structure after metal carbonate and oxide formation obtained by soft-templating method using PMPEGMA – b – PBA as a micelle. These mixed metal oxide mesoporous materials would be further used for battery performance. The detail of the battery performance by using these block copolymer templates can be seen in the literature, which will be published in the future in the title of *High Rate Sodium Ion Battery Anodes from Block Copolymer Templated Mesoporous Nickel-Cobalt Carbonates and Oxides* by Sarang M. Bhaway, Pattarasai Tangvijitsakul, Jeongwoo Lee, Mark D. Soucek, and Bryan D. Vogt.
CHAPTER VIII

A NEW FATTY ACID-BASED THICKENER: SYNTHESIS, CHARACTERIZATION, AND RHEOLOGICAL PROPERTIES

8.1 Overview

A novel fatty acid-based rheology modifier, poly[poly(ethylene glycol) methyl ether methacrylate]–block–poly(oleic acid) (PMPEGMA–b–POA), was designed and synthesized by the reversible addition–fragmentation chain-transfer (RAFT) polymerization of oleic acid (OA) and poly[methoxy poly(ethylene glycol) methacrylate] (PMPEGMA) macromonomer. The results showed well-controlled molar mass and the ability to chain extend by forming an AB block copolymer. The steady-shear properties of a well-characterized conventional latex, thickened with the different concentrations of the resulting rheology modifier, were measured at constant pH and temperature. The steady-shear data for the latex solutions with PMPEGMA homopolymer and the hydrophobically modified rheology modifier PMPEGMA–b–POA exhibited the expected thickening.
8.2 Introduction

Amphiphilic block copolymers (ABCs) are usually functional copolymers with several applications as thickeners, dispersants, emulsifiers, foamers, and compatibilizers. In recent years, interest in design, synthesis, and characterization of ABCs has extremely increased. Their unique chemical structure, which consists of two parts having different natures, can be designed such that interfaces between materials can be controlled to a broader range than those of low molecular weight surfactants.

The improvement of rheological properties of water-borne paints using polymers has been the object of interest during the last years. Associative thickeners (ATs) are a new class of hydrophobically modified water-borne ABCs which can increase viscosity through an association process. In general, these materials contain a backbone with hydrophilic nature and several hydrophobic segments as terminal groups or dispersed groups along the polymer chains. In fact, the reversible intermolecular associations resulting from the undesirable solvent conditions for the grafted hydrophobic segments in these systems are responsible for their thickening ability in aqueous solutions. An important class of ATs are polyacrylamide (PAM)-based copolymers such as hydrophobically modified poly(N-isopropylacrylamide) (HM-PNIPAM) and hydrophobically modified polyacrylamide (HM-PAM). These copolymers have recently received increasing attention due to their unique rheological characteristics and industrial applications in coatings, oil recovery, cosmetics, and drilling fluids.

Most of the non-ionic ABCs comprise poly(ethylene oxide) (PEO) as the hydrophilic block(s), whereas poly(propylene oxide) (PPO), poly(butylene oxide) (PBO), polystyrene (PS), etc. are typically used as the hydrophobic block(s).
The PEO is considered as a non-toxic, non-immunogenic, and water soluble polymer which also has the essential requirements for use in biocompatible surfaces and biomedical applications. The PEO-containing associative thickeners such as the hydrophobically modified ethoxylated urethanes (HEURs) have already been investigated by several research groups. The structure of HEUR-based ATs consists of a PEO as the hydrophilic segment and the hydrophobic hydrocarbon groups at the ends of hydrophilic segments. Despite the fact that these HEUR-based thickeners have been used for many years, there is still an ongoing debate on the detailed picture of the mechanism of thickening in latex/AT systems. In general, it is accepted that viscoelastic properties of latex in the presence of an AT are increased via volume restriction of the continuous phase or network formation in the continuous phase. AT can also associate to latex particles through ion–dipole interactions or through hydrophobic associations.

It is well-known that vegetable oils and their derivatives such as fatty acids are the most promising candidates for the preparation of polymers based on renewable resources. These materials have found applications in coatings because of their unique chemical structures and tendency to form films. Radiation curable coating formulations are ecologically compliant as no volatile organic compounds (VOCs) are required for such formulations. They show high curing efficiency and require low curing energy. Several UV curable coatings based on the chemically synthesized epoxies from vegetable oils have been already developed in our research group. Oleic acid (OA) is one of the most important fatty acids for production of bio-based polymers by different methods. For example, the methacrylate derivative of OA has been synthesized and polymerized to obtain poly(2-(methacryloyloxy)ethyl oleate) with controlled molecular weight and
narrow molecular weight distribution. The double bonds in the oleate side-chains were further utilized for various post-polymerization modifications. In addition, the double bond in OA has been used for the synthesis of a thermosensitive amphiphilic Y-shaped copolymer via free radical polymerization.

As part of our continuing efforts to extend the use of fatty acids in polymer coatings, the present work deals with the synthesis and characterization of a novel waterborne thickener, poly[poly(ethylene glycol) methyl ether methacrylate]–block–poly(oleic acid) (PMPEGMA–b–POA), through reversible addition–fragmentation chain transfer (RAFT) polymerization. The RAFT was chosen as the living polymerization technique because of its versatility with respect to choice of monomer and reaction conditions. In general, the PMPEGMA block provides desirable properties such as low toxicity and high biocompatibility, whereas the POA provides the hydrophobic characteristics. The resulting amphiphilic block copolymer was accurately characterized by FT-IR and NMR spectroscopies, which verified its chemical structure and molar composition. The molecular weight and polydispersity index (PDI) were investigated by gel permeation chromatography (GPC). Finally, the rheological properties of this amphiphilic block copolymer were investigated in a latex solution which is recently developed in our research group.

8.3 Materials

Methoxy poly(ethylene glycol) methacrylate (MPEGMA) (950 g mol⁻¹, Aldrich), oleic acid (Aldrich, technical grade, 90 %), N, N-dimethylformamide (DMF) (Aldrich, anhydrous, 99.8%), diethyl ether (EMD Millipore, anhydrous), tetrahydrofuran (THF) (Sigma-Aldrich, HPLC, >99.9%), hexane (Sigma-Aldrich, anhydrous, 95%), and
deuterated chloroform (CDCl₃) (Cambridge Isotope Laboratories, Inc.) were used as received. 2,2’-Azobis(isobutyronitrile) (AIBN) (Aldrich, 98%) was purified by recrystallization from methanol. 4-cyanopentanoic acid dithiobenzoate (CPADB) was synthesized according to the literature ⁸⁶,¹⁰¹. A well-characterized latex with 29.6 wt. % solids, an average particle size of 203 nm, surface tension of 46 mN/cm, and glass-transition temperature of 42 °C from differential scanning calorimetry (DSC) was used for rheological measurements. This latex consisted of 63.4 wt. % methyl methacrylate (MMA) and 36.6 wt. % butyl acrylate (BA). Figure 8-1 generally shows the chemical structure of this conventional latex. Details regarding the synthesis, properties, and characterization of this latex will be provided in a separate article. All other chemicals, unless otherwise discussed, were reagent grade and used as received.

![Figure 8-1 Chemical structure of the conventional latex](image-url)
8.4 Instrumentation

Fourier transform infrared (FT-IR) spectroscopy was performed on a NICOLET-380 FT-IR spectrophotometer. A series of 64 scans were taken for each run. NMR analyses were performed on a Varian NMRS-500 MHz apparatus using deuterated chloroform (CDCl$_3$) as the solvent. The molecular weight and poly dispersity index (PDI) of the prepared homopolymer and amphiphilic block copolymer were determined by gel permeation chromatography (GPC, Waters) with a HR4, HT2, HR1, HR0.5 styragel, and 500Å ultrastyragel columns connected in series. The GPC analyses in distilled tetrahydrofuran (THF) were performed at 35 °C using 0.1 % (w/v) polymer solutions. The solutions were filtered (0.45 μm) and 200 μL was injected into the column at an effluent flow rate of 1.0 mL min$^{-1}$. The chromatograph was collected by the light scattering detector and the data were interpreted using Omnisec software v.4.7.0.406. The viscosity of latex solution versus shear rate has a slope of −1 where viscosity ranges from 10 to ca. 0.005 Pas and shear rate varies from 0.01 to 250 s$^{-1}$. The steady shear viscosity measurements were performed with a TA Instruments ARES-G2 rheometer using cone and plate geometries. The cone angle and plate diameter were 2° and 50 mm, respectively. The temperature was set to 25 °C. The rheometer was utilized in two different modes, the steady state and the dynamic oscillatory modes. The time for the steady viscosity measurement was selected to ensure the steady state viscosity. The strain/stress for the dynamic test was chosen in such a way to produce data in the linear viscoelastic region for the applied frequencies. G' and G" were obtained and was converted to the complex viscosity. The dynamic and steady state viscosity were plotted in the same graph for the sake of comparison. The change in viscosity is also shown as
bar-graph for different concentrations (3, 5 and 10 wt. %) of the used fatty acid-based rheology modifier in the latex solution. The solution for rheological measurements was prepared by addition of the synthesized block copolymer to the latex at room temperature. The polymer was allowed to hydrate and swell for 24 h. Then, the solution was gently stirred magnetically for 24 h to form homogeneous solution. The polymer solutions were kept for another 24 h prior to measurement to remove air bubbles.

8.5 Synthesis of the fatty acid-based rheology modifier

A new block copolymer PMPEGMA–b–POA was synthetized using RAFT polymerization method. As shown in Scheme 8-1, the first step was the preparation of the poly [methoxy poly (ethylene glycol) methacrylate] (PMPEGMA) macro RAFT agent. At the second step, this homopolymer was polymerized with oleic acid monomer to create the new amphiphilic block copolymer PMPEGMA–b–POA. The procedure for the synthesis of the resulting homopolymer and block copolymer is described as follows.

**PMPEGMA homopolymer:** MPEGMA (21.00 g, 2.21 x 10⁻² mol), AIBN (58 mg, 3.53 x 10⁻⁴ mol) as an initiator, CPADB (0.49 g, 1.75 x 10⁻³ mol) as a RAFT agent, and DMF (10.00 g) as a solvent were introduced into a three-neck round bottom flask, equipped with a condenser, and nitrogen gas inlet and outlet. The mixture was gently stirred by a magnetic stir bar under the nitrogen atmosphere. After 30 min, the polymerization was initiated by immersing the reaction flask into an oil bath at 65 °C and continued for 20 h. The polymerization was terminated via immediate exposure to air and quenching in an ice bath. After termination, the PMPEGMA macro RAFT was purified by precipitation in diethyl ether for three times in order to remove unreacted MPEGMA,
AIBN, and CPADB. Finally, it was dried overnight in a vacuum oven at room temperature.

**PMPEGMA–b–POA**: PMPEGMA homopolymer \((M_n = 5.2 \times 10^4 \text{ g mol}^{-1})\) (5.00 g, 2.00 \times 10^{-4} \text{ mol}), oleic acid (OA) (4.46 g, 3.48 \times 10^{-2} \text{ mol}), AIBN (14.6 mg, 8.93 \times 10^{-5} \text{ mol}), and DMF (10.00 g) were introduced into a three-neck round bottom flask. The mixture was gently stirred by a magnetic stir bar under the nitrogen atmosphere. After 30 min, the polymerization was initiated by immersing the reaction flask into the oil bath at 65 °C for 48 h. The polymerization was terminated via immediate exposure to air and quenching with an ice bath. After cooling, DMF in the mixture was evaporated by rotary evaporator. The crude solid product was dissolved in 5 mL of THF. The block copolymer was precipitated by 100 mL of hexane (three times) and filtered. Finally, the precipitate was dried overnight in a vacuum oven at room temperature.
8.6 Results and discussion

There are two parts for results and discussion. The first part is about the characterization of fatty-acid based thickener. The latter part is related to the rheological properties of fatty-acid based thickener in a latex solution.

8.6.1 Characterization of fatty-acid based thickener

FT-IR, $^1$H-NMR, and GPC were utilized to characterize the chemical structures of PMPEGMA homopolymer and PMPEGMA-b-POA copolymer. In general, the FT-IR spectra of PMPEGMA and PMPEGMA-b-POA were similar to one another. The absorption bands at 1100 cm$^{-1}$, 1250 cm$^{-1}$, and 1720 cm$^{-1}$ were attributed to C–O stretching of ether bond, C–O stretching of ester bond, and C=O stretching of ester bond in PMPEGMA homopolymer and its corresponding copolymer. As shown in Figure 1 (a), there was a small broad peak in the range 3300–3600 cm$^{-1}$ which could be attributed to the O–H stretching of the carboxylic group of CPADB agent in the PMPEGMA homopolymer. Because of the presence of the oleic acid in the resulting PMPEGMA-b-
POA, an obvious broad band for O–H stretching appeared at 3200–3700 cm$^{-1}$ (Figure 1 (b)). In addition, there was no C=O stretching band at ~1640 cm$^{-1}$ which further confirmed the consumption of oleic acid and formation of PMPEGMA-$b$-POA.

Figure 8-2 shows the $^1$H NMR of PMPEGMA and the resonance assignments are summarized in Table 8-1. The signals at 0.88–1.11 ppm and 1.58–2.04 ppm were assigned to the –CH$_2$–CCH$_3$ and –CH$_2$–CCH$_3$ repeating units of the polymer main chain, respectively. The sharp singlet of the –O–CH$_3$ could be observed at 3.39 ppm. The most intensive signals were observed around 3.42–3.80 ppm representing the protons of –(CH$_2$CH$_2$O)$^-$ in the repeating units of PEO side chains. Moreover, the protons of ethylene oxide unit located between the ester group in the main chain and the ethylene oxide groups in the side chain (–OCO–(CH$_2$CH$_2$O)$^-$) were observed at a slightly higher chemical shift around 3.98–4.05 ppm.

Figure 8-2 FT-IR spectra of (a) the PMPEGMA and (b) the PMPEGMA-$b$-POA
Figure 8-3 $^1\text{H}$ NMR of the PMPEGMA in CDCl$_3$

<table>
<thead>
<tr>
<th>Polymer code</th>
<th>Structural group</th>
<th>Chemical shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMPEGMA</td>
<td>–CH$_2$–CCH$_3$ (main chain)</td>
<td>0.88–1.11</td>
</tr>
<tr>
<td></td>
<td>–CH$_2$–CCH$_3$ (main chain)</td>
<td>1.58–2.04</td>
</tr>
<tr>
<td></td>
<td>–O–CH$_3$</td>
<td>3.39</td>
</tr>
<tr>
<td></td>
<td>–(CH$_2$CH$_2$O)$^-$ (PEO)</td>
<td>3.42–3.80</td>
</tr>
<tr>
<td></td>
<td>–OCO–(CH$_2$CH$_2$O)$^-$</td>
<td>3.98–4.08</td>
</tr>
<tr>
<td>PMPEGMA-$b$-</td>
<td>–CH$_2$–CCH$_3$ (MPEGMA), –CH$^-$, –CH$_2$–(OA)</td>
<td>0.65–2.21</td>
</tr>
<tr>
<td>POA</td>
<td>–CH$_2$–CCH$_3$ (MPEGMA)</td>
<td>1.58–2.04</td>
</tr>
<tr>
<td></td>
<td>–O–CH$_3$</td>
<td>3.39</td>
</tr>
<tr>
<td></td>
<td>–(CH$_2$CH$_2$O)$^-$ (PEO)</td>
<td>3.42–3.80</td>
</tr>
<tr>
<td></td>
<td>–COO–(CH$_2$CH$_2$O)$^-$ (MPEGMA)</td>
<td>3.98–4.08</td>
</tr>
</tbody>
</table>
Due to the relatively small ratio of block POA in the resulting PMPEGMA-\textit{b}-POA, the $^1$H NMR spectrum of this copolymer was almost similar to that of PMPEGMA homopolymer (as shown in Figure 8-4). Most protons showed the same chemical shifts except the 0.65–2.21 ppm region, in which it not only showed the corresponding protons of methylene and methyl groups in the repeating units of the PMPEGMA main chain, but also exhibited the protons of methane (–CH–), methylene (–CH$_2$–), and methyl (–CH$_3$–) groups in the POA block. In addition, no resonances around 5–6 ppm corresponding to the chemical shift of protons attached to the carbon–carbon double bond of oleic acid were observed. Therefore, it could be assumed that no unreacted OA monomer remained after the polymerization of after purification. The mole fraction of hydrophobic
component (POA) in the copolymer was approximately 0.05 which was calculated from $^1$H NMR.

![Figure 8-5 GPC chromatograms of the PMPEGMA and PMPEGMA-b-POA](image)

The molecular weight and distribution of polymers were investigated by GPC. As shown in Figure 8-5, the GPC curves of both PMPEGMA and PMPEGMA-b-POA were unimodal and symmetric. The relative molecular weight ($M_n$) of PMPEGMA was measured to be 52000 g mol$^{-1}$ with PDI of 1.26, whereas the $M_n$ of PMPEGMA-b-POA was 54000 g mol$^{-1}$ with PDI of 1.43. PMPEGMA has a slightly longer retention time than that of PMPEGMA-b-POA. FT-IR, $^1$H NMR, and GPC results supported the successful formation of PMPEGMA-b-POA via RAFT polymerization method.
8.6.2 Steady-shear viscosity

Shear thinning behavior or pseudoplasticity is the decrease of apparent viscosity with shear rate. The shear thinning is a behavior which is displayed by paints, concentrated polymer solutions, and dispersed systems including inks, latex, and emulsions. This behavior occurs when a system has a structure which can be broken down reversibly as a stress is applied and then removed. In the present study, the effects of the synthesized homopolymer of PMEGMA and the new fatty acid-based associative thickener, PMPEGMA-\textit{b}-POA, on the rheological properties of their blends with the recently developed latex in our group was measured at low and high shear as is typical for industrial latex-based coatings. The steady-shear viscosity of the latex solution thickened with PMPEGMA in different concentrations (3, 5, and 10 wt. %) is shown in Figure 8-6. Non-Newtonian flow behavior was observed for the latex and its thickener blend. As shown, an increase in the concentration of homopolymer led to an increase in the shear rate viscosity. The PMPEGMA can be considered as a conventional rheology modifier that contains no strongly hydrophobic regions (macromonomers) and no strong hydrophobe–hydrophobe association.
Figure 8-6 Steady-shear viscosity for latex solutions thickened with homopolymer (PMPEGMA) in different concentrations

It is well-known that the introduction of hydrophobic macromonomers, referred to as the associative monomers, increases the thickening power with respect to unmodified polymers of similar molecular weight. Hence, the hydrophobically modified associative thickeners have been a good source of several studies in the last decades. Shear thinning is generally because of a transition from intermolecular (with other dispersed-phase particles and hydrophobes of other polymer chains) to intramolecular (with other hydrophobes on the same polymer chain) associations. This transient or associated physical network results from the “pull-out” and rearrangement of the hydrophobes. The specific rheological behavior given by these systems are a result of the mutual interaction of hydrophobic groups on the polymer chain with each other and with other hydrophobic segments such as latex particles dispersed in the aqueous phase. In fact, the associative
component has a dual character because of the formation of structure within the aqueous phase and the interaction with particle surfaces in the dispersed-phase systems.

In the present study, the steady-shear viscosities of the latex solution thickened with PMPEGMA-b-POA in different concentrations (3, 5, and 10 wt. %) are shown in Figures 8-7 to Figure 8-9. PMPEGMA-b-POA was expected that the addition of hydrophobic macromonomer POA as a second block onto the polymer chain would have a significant influence on the rheology behavior of the latex solution thickened with this rheology modifier. The resulting data supported that the PMPEGMA-b-POA resulted in comparatively higher thickening efficiency compared to that of the PMPEGMA when blended with the latex. Similar to that of homopolymer, an increase in the concentration of PMPEGMA-b-POA also led to an increase in the shear rate viscosity.

![Steady-shear viscosity for latex solutions thickened with 3 wt. % of homopolymer (PMPEGMA) and its block copolymer (PMPEGMA-b-POA)](image)

Figure 8-7 Steady-shear viscosity for latex solutions thickened with 3 wt. % of homopolymer (PMPEGMA) and its block copolymer (PMPEGMA-b-POA)
Figure 8-8 Steady-shear viscosity for latex solutions thickened with 5 wt. % of homopolymer (PMPEGMA) and its block copolymer (PMPEGMA-b-POA)

Figure 8-9 Steady-shear viscosity for latex solutions thickened with 10 wt. % of homopolymer (PMPEGMA) and its block copolymer (PMPEGMA-b-POA)
8.7 Conclusion

The steady-shear data for the latex solutions with PMPEGMA homopolymer and the hydrophobically modified rheology modifier PMPEGMA–b–POA exhibited the expected thickening. It is important to note that chain architecture, concentration, and molar mass of the polymers are main factors that influence the efficiency of thickeners. In addition, the thickening behavior of the rheology modifiers is a function of various parameters such as latex particle size, latex structure, and surfactant concentration. Hence, variations in thickening proficiency are expected when a thickener is individually blended with latexes that differ in particle size, composition, and solids.

The dynamic properties would be performed in the future in order to study the viscoelastic properties of this new fatty acid - based thickener with a latex system. Moreover, a reversible dynamic associative network by this new thickener with water-based coating system would be investigated.
CHAPTER IX

CONCLUSIONS

In this dissertation, MPEGMA-based copolymers were synthesized and used in three fascinating applications including new polycarboxylate admixtures for concrete, new amphiphilic block copolymers for mesoporous material templates, and a new fatty acid-based thickener for water-based coating system.

Numerous polycarboxylate MPEGMA-based admixtures either synthesized by RAFT polymerization or conventional radical polymerization/esterification process were tested with cement/concrete system. It was discovered that many variables provided a great impact on fresh cement fluidity. The length of PEO repeating units in MPEGMA macromonomer should be long enough for better dispersion of cement particles though steric hindrance effect. The molar ratios between MPEGMA and MAA should be high enough for better adsorption on cement particles. A good purification is important to reach the maximum potential of the polycarboxylate copolymers. Molecular weights of polycarboxylate copolymers should be in an optimal range and the molecular weight distribution should be very narrow to obtain a good fluidity of fresh cement. Based on the experiment results, PMPEGMA950-random-PMAA (Mn ~ 22,000 g mol⁻¹, PDI = 1.71) with the monomer molar ratio = 3:1 offered the best cement fluidity with a long period of time. Moreover, a new RAFT polycarboxylate terpolymer (containing in-
situ defoaming groups) not only able to provide a reasonable cement fluidity over a long period of time, but also able to get rid of the generated bubbles at the same time based on defoaming characteristic test. Although the compressive strength of concrete system using RAFT polycarboxylate terpolymer was less than that of concrete system using polycarboxylate 1 (commercially available), the stability of an air-void system (% air content ~ 7.0 %) of harden concrete was obtained. This may possibly lead to a good candidate admixture for an outdoor concrete structural application that requires freeze-thaw resistance without adding separate defoaming agents.

In mesoporous material template application, a new series of amphiphilic diblock copolymers PMPEGMA 475/950 - b - PBA were successfully synthesized and were carefully characterized by 1H-NMR and GPC. GPC showed a molecular weight and narrow PDI of those copolymers, resulting in well-defined templated size distribution for fabrication of mesoporous materials. In this present study, mesoporous mixed metal oxides between nickel and/or cobalt were successfully fabricated by using PMPEGMA – b – PBA as a micelle-template. The copolymer dissolved in tetrahydrofuran (THF) and cobalt nitrate and/or nickel nitrate with citric acid dissolved in ethanol were casted on a silicon wafer substrate. The temperature was raised to from “micelle-structured metal carbonate”. After that, the temperature increased again to remove micelles and formed “mesoporous metal oxide”. The processing temperatures for metal carbonate and oxide formation of were determined by TGA. FT-IR was used to track the compositional changes that occurred in the films throughout the processing. Atomic Force Microscopy (AFM) showed the surface morphology with a spherical microphase separated structure
after metal carbonate and oxide formation. These mixed metal oxide mesoporous materials would be further used for an electrode to explore the battery performance.

For a new type of thickener in water-based coating system, oleic acid was chosen to copolymerize with MPEGMA to obtain the copolymer of PMPEGMA–b–POA. This block copolymer was successfully synthesized by RAFT polymerization. The steady-shear data for the latex solutions with PMPEGMA homopolymer and the hydrophobically modified rheology modifier PMPEGMA–b–POA exhibited the expected thickening. Some dynamic properties have to be performed to study the viscoelastic properties and investigate a reversible dynamic associative network by this new thickener with water-based coating system.
REFERENCES


60. Kleitz, F.; Choi, S. H.; Ryoo, R. Cubic Ia3d large mesoporous silica: synthesis and replication to platinum nanowires, carbon nanorods and carbon nanotubes. *Chemical Communications* 2003, 2136-2137.


134. Eckhardt, B.; Ortel, E.; Bernsmeier, D.; Polte, J.; Strasser, P.; Vainio, U.; Emmerling, F.; Kraehnert, R. Micelle-Templated Oxides and Carbonates of Zinc, Cobalt,


