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SEMIFLUORINATED AROMATIC ETHER POLYMERS SEGMENTED WITH POLYETHYLENE GLYCOL (PEG)

Dakarai Brown
Clemson University, dakarab@clemson.edu

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SEMIFLUORINATED AROMATIC ETHER POLYMERS SEGMENTED WITH
POLYETHYLENE GLYCOL (PEG)

A Dissertation
Presented to
the Graduate School of
Clemson University

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

by
Dakarai K. Brown
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Accepted by:
Dr. Dennis W. Smith, Jr., Co-Chair
Dr. Kenneth A. Christensen, Co-Chair
Dr. Karl R. Dieter, Committee Member
Dr. Rhett C. Smith, Committee Member
ABSTRACT

Aromatic trifluorovinyl ether (TFVE) monomers are the precursors for perfluorocyclobutyl (PFCB) aryl ether polymers and fluoroethylene/vinylene alkyl/aryl ether (FAE) polymers. PFCB aryl ether polymers are prepared by $2\pi + 2\pi$ cycloaddition of aromatic TFVE monomers. FAE polymers are prepared by nucleophilic addition of dual functional aryl or alkyl alcohols to aryl TFVE monomers. PFCB aryl ether and FAE polymers are amorphous, have excellent processability, high thermal stability, optical clarity, and tunability using a variety of (co)monomers. In this dissertation several novel monomers, polymers, and blends were prepared by incorporation of polyethylene glycol (PEG) or PEG precursors.

Chapter 1 contains the introduction to fluoropolymers and exceptional properties of PFCB aryl ether, FAE, and PEG polymers.

Chapter 2 describes the one step synthesis of macromonomers using diethylene glycol (DEG) and a series of polyethylene glycols (PEGs). Macromonomers were homopolymerized and copolymerized using commercially available TFVE monomers and a PFCB prepolymer. All macromonomers and copolymers were characterized by $^1$H and $^{19}$F Nuclear magnetic resonance (NMR) and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. Thermal properties of all polymers were determined by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC).

Chapter 3 explores the compatibilization of PEG and a commercial polymer bis(trifluorovinylxyloxy) biphenyl ether (BPVE) using a copolymer from chapter 2. Reduced
interfacial tension was observed by scanning electron microscope (SEM) and phase homogeneity (miscibility) was studied by DSC.

After the one step synthesis of polyethylene glycol (PEG) functionalized with TFVE, a unique crystallization was discovered and is discussed in Chapter 4. DSC analysis and wide angle X-ray diffraction (WAXD) were used to characterize the crystallization of macromonomers.

Chapter 5 details the preparation of a series of PEG-PFCB aryl ether segmented copolymers. Copolymers were polymerized by nucleophilic addition of polyethylene glycol (PEG) to trifluorovinyl ether (TFVE) end-groups of PFCB aryl ether oligomers. Copolymers were linked through a hydrofluoroethane (-CHFCF₂⁻) ether bond. All polymers were well characterized as above. $T_g$s were studied by DSC analysis and compared to calculated values using the Fox equation.

Polymerization and characterization of novel segmented semifluorinated polyaryl ether (PAEs) were discussed in chapter 6. In addition, thermal properties were explored by DSC and TGA analysis. Surface morphology of semi-crystalline polymers were studied by atomic force microscopy (AFM). Phase images show needlelike crystals. Chapter 7 outlines experimental information.

Publications obtained from this work:

1. Iacono, Scott T.; Brown, Dakarai; Smith, Dennis W., Jr. Functionalized Semifluorinated Aryl Ether Polymers Polymer Preprints (American Chemical Society, Division of Polymer Chemistry) 2010, 51(1), 155.

2. Brown, Dakarai; Park, Jiyoun; Verma, Rajneesh; Tomar, Neetu; Jayasinghe, Rahula; Colon-Mercado, Hector; Elvington, Mark; Hobbs, David; Sharif, Iqbal; DesMarteau, Darryl; et al Phase Separation of TFVE Base Block Copolymers and
Their Applications Polymer Preprints (American Chemical Society, Division of Polymer Chemistry) 2009, 50(2), 626.


DEDICATION

This work is dedicated to my mom, dad, my sister, and my fiancée Laura.
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Thanks are not enough to be given to those who have helped and supported me in my endeavors here at Clemson University. First, I sincerely thank my advisor Prof. Dennis W. Smith Jr. Through his knowledge, support and guidance, I have developed into an organic chemist capable of creating new innovative ideas, conducting valuable research, and evaluating my work. He has helped me to realize my potential and motivated me to finish my research to the best of my abilities. I also extend thanks to past members of the Smith group. In particular, thanks to Ken Tackett and Dr. Scott Ianaco for your friendship. They helped me in my studies and research at Clemson. In particular, I would like to thank Jean-Marc Crakowicz, a post-doctorial mentor. As my mentor, he played an important role in my research, and helped me to develop my writing abilities.

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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>TITLE PAGE</td>
<td>.................................................................</td>
<td>i</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>..............................................................</td>
<td>ii</td>
</tr>
<tr>
<td>DEDICATION</td>
<td>..............................................................</td>
<td>v</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>..................................................</td>
<td>vi</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>..................................................</td>
<td>ix</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>..................................................</td>
<td>x</td>
</tr>
<tr>
<td>LIST OF SCHEMES</td>
<td>..................................................</td>
<td>xiii</td>
</tr>
<tr>
<td><strong>CHAPTER</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>BACKGROUND AND INTRODUCTION TO POLYMERS FROM AROMATIC TRIFLUOROVINYL ETHERS AND POLYETHYLENE GLYCOL</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Fluoropolymers</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Perfluorocyclobutyl (PFCB) Aryl Ether polymer</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>Synthesis of Trifluorovinyl Aryl Ethers (TFVE)</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>PFCB polymers Degradation</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>PFCB polymers Applications</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>Preparation and Applications of Fluoroethylene/vinylene Aryl Ether (FAE) Polymers</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>Perfluorocyclopentenyl (PFCP) Aryl Ether Polymers</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Introduction to Polyethylene glycol (PEG)</td>
<td>26</td>
</tr>
<tr>
<td></td>
<td>Preparation of PEG</td>
<td>28</td>
</tr>
<tr>
<td></td>
<td>Properties of PEG</td>
<td>33</td>
</tr>
<tr>
<td>2.</td>
<td>PERFLUOROCYCLOBUTYL ARYL ETHER POLYMERS WITH POLYETHYLENE GLYCOL ENCHAINMENT</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Introduction</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>Polymerization of PEG-PFCB Polymers by Polycondensation</td>
<td>37</td>
</tr>
<tr>
<td></td>
<td>Synthesis and Characterization of PEG Macromonomer</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>Polymerization of PEG Macromonomer</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>Copolymerization of Random PFCB-PEG copolymer</td>
<td>46</td>
</tr>
<tr>
<td></td>
<td>Thermal Properties of Copolymers</td>
<td>48</td>
</tr>
<tr>
<td></td>
<td>Conclusion</td>
<td>51</td>
</tr>
<tr>
<td>3.</td>
<td>COMPATIBILITIZATION OF PEG AND BIPHENYL VINYL ETHER (BP-PFCB) POLYMER BLENDS</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>Introduction</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td>Reduction of Interfacial Tension</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>Blend Optical Properties</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Blend Thermal Properties</td>
<td>61</td>
</tr>
</tbody>
</table>
Conclusion ................................................................................................................................. 63

4. SELF-ASSEMBLY POLYETHYLENE GLYCOL END-CAPPED WITH AROMATIC TRIFLUOROVINYL ETHER
   Introduction ................................................................................................................................. 64
   Thermal Properties of PEG End-Capped with TFVE .......................................................... 66
   Wide Angle X-ray Diffraction (WAXD) of Telechomers .................................................. 70
   Scanning Electron Microscope Images ............................................................................... 73
   Conclusion ................................................................................................................................. 74

5. STEP-GROWTH POLYMERIZATION OF AROMATIC TFVE WITH POLYETHYLENE GLYCOL
   Introduction ................................................................................................................................. 75
   Polymerization of Segmented BP-PFCB PEG Copolymers ............................................. 78
   Segmented BP-PFCB PEG Copolymer Characterization and Composition ..................... 81
   Thermal Properties of BP-PFCB PEG Copolymers .......................................................... 84
   Conclusion ................................................................................................................................. 89

6. PREPARATION OF SEMIFLUORINATED POLYARYL (ETHER)S FROM WELL DEFINED AROMATIC TRIFLOROVINYL ETHERS AND DIOLS
   Introduction ................................................................................................................................. 90
   Polymerization ......................................................................................................................... 92
   Characterization ...................................................................................................................... 93
   Thermal Properties .................................................................................................................. 96
   Degradation Analysis .............................................................................................................. 98
   Surface Morphology ............................................................................................................... 100
   Conclusion ................................................................................................................................. 102

7. EXPERIMENTAL DETAILS
   Materials .................................................................................................................................... 103
   Calculated Section .................................................................................................................. 104
   Instrumentation ...................................................................................................................... 105
   Optical Spectroscopy .............................................................................................................. 108
   Polymer Processing ............................................................................................................... 108
   Synthesis and Characterization of (Co)polymers and Macromonomers ......................... 109

APPENDICES ............................................................................................................................. 125

REFERENCES ............................................................................................................................ 141
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Tables</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Selected Properties of PEG</td>
</tr>
<tr>
<td>2.1</td>
<td>Polycondensation conditions of PFCB-PEG</td>
</tr>
<tr>
<td>2.2</td>
<td>Selected properties of macromonomers (3.7a-e)</td>
</tr>
<tr>
<td>2.3</td>
<td>Copolymer properties and polymerization conditions</td>
</tr>
<tr>
<td>4.1</td>
<td>Composition, $T_g$s, and $T_m$s of macromonomers (3.6a-e)</td>
</tr>
<tr>
<td>5.1</td>
<td>Selected properties of Copolymers</td>
</tr>
<tr>
<td>5.2</td>
<td>Summary of thermal decomposition of copolymers</td>
</tr>
<tr>
<td>6.1</td>
<td>Selected properties of 7.6 to 7.9</td>
</tr>
<tr>
<td>6.2</td>
<td>Summary of thermal decomposition of polymers 7.6 to 7.9</td>
</tr>
<tr>
<td>Figures</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>------</td>
</tr>
<tr>
<td>1.1. Commerically available amorphous fluoropolymers. 1 = Teflon AF from Dupont, 2 = Fomblins Z from Solvay Solexis, 3 = Cytop from Asahi, and 4 Fluoroacrylates from Solvay Solexis, Daikin, and Allied Signal</td>
<td>2</td>
</tr>
<tr>
<td>1.2. Sample of PFCB polymers synthesized by organolithium or Grignard synthetic strategy</td>
<td>11</td>
</tr>
<tr>
<td>1.3. One-pot synthesis of aryl bistrifluorovinyl ether (BTFVE) monomers By Grignard chemistry</td>
<td>12</td>
</tr>
<tr>
<td>1.4. Thermal and oxidative degradation mechanism of polymers prepared from 1,1,1-tris(4-trifluorovinylxyloxyphenyl)ethane</td>
<td>13</td>
</tr>
<tr>
<td>1.5. Design, structure-property relationship, and properties of PFCB aryl ether polymers</td>
<td>14</td>
</tr>
<tr>
<td>1.6. Refractive indices of PFCB aryl ether polymers based on fluorine content of the corresponding monomer (Reported at 1550 nm)</td>
<td>16</td>
</tr>
<tr>
<td>1.7. TEM images of nanocomposites prepared with 0.5 mol % of (left) CaF₂:Er³⁺ and (right) LaF₃:Nd</td>
<td>17</td>
</tr>
<tr>
<td>1.8. Scanning electron micrographs (SEM) of waveguide gratings fabricated by transfer molding using silicon master</td>
<td>18</td>
</tr>
<tr>
<td>1.9. Scanning electron micrographs of waveguide gratings fabricated by dry etching photolithography</td>
<td>18</td>
</tr>
<tr>
<td>1.10. Polarized optical microscope (POM) images displaying birefringence of 28 (n=1) at 190 °C (left) for 15 min and (right) 2 h.</td>
<td>21</td>
</tr>
<tr>
<td>1.11. Structure-property relationship of PEG</td>
<td>26</td>
</tr>
<tr>
<td>2.1. ¹H NMR (in CDCl₃) of trifluorovinyl aryl ether-functionalized PEG(49d)</td>
<td>41</td>
</tr>
<tr>
<td>2.2. ¹⁹F NMR (in CDCl₃) overlay of trifluorovinyl aryl ether-functionalized PEG 400, 49d (top), and 50d (bottom)</td>
<td>43</td>
</tr>
<tr>
<td>2.3. Gel permeation chromatogram overlay in CHCl₃ of 50a-e</td>
<td>44</td>
</tr>
<tr>
<td>2.4. DSC thermograms of homopolymers 50a-e</td>
<td>48</td>
</tr>
<tr>
<td>2.5. TGA comparison of PEG 400, 50d, 51-co2-49d, and 51-co2-49d in air</td>
<td>50</td>
</tr>
</tbody>
</table>
3.1. SEM images of PEG/BP-PFCB polymer (1:1, w/w) blend cross-sections with the addition of 51-co2-49d at: (a) 0 wt %; (b) 1 wt %; (c) 2 wt %; (d) 3 wt %; (e) 4 wt %;and (f) 5 wt % ................................................................. 55

3.2. SEM images of PEG/BP-PFCB polymer (1:1, w/w) blend surface with the addition of 51-co2-49d at: (a) 0 wt % and (b) 5 wt % ......................................................... 57

3.3. SEM image (left) and EDS results (right) on a dispersed phase (sphere) of uncompatibilized (0 wt % of 51-co2-49d) PEG/BP-PFCB polymer (1:1, w/w) blend ................................................................. 58

3.4. SEM image (left) and EDS results (right) on the continuous phase (nonspheric) of uncompatibilized (0 wt % of 51-co2-49d) PEG/BP-PFCB polymer (1:1, w/w) blend ................................................................. 58

3.5. SEM image (left) and EDS results (right) on a cross-section of compatibilized (5 wt % of 51-co2-49d) PEG/BP-PFCB polymer (1:1, w/w) blend ................................................................. 59

3.6. Effect of wt % of PEG on BP-PFCB polymer (Mn of 20000 g/mol) refractive indices (All samples contain 5 wt % of 51-co2-49d) ................................................................. 60

3.7. DSC thermograms of (a) BP-PFCB polymer, (b) 51-co2-49d:PEG:BP-PFCB polymer (5:1:99; w/w/w), (c) 51-co2-49d:PEG:BP-PFCB polymer (5:2:98; w/w/w), (d) 51-co2-49d:PEG:BP-PFCB polymer (5:3:97; w/w/w), (e) 51-co2-49d:PEG:BP-PFCB polymer (5:4:96; w/w/w), and (f) 51-co2-49d:PEG:BP-PFCB polymer (5:5:95; w/w/w). ................................................................. 61

3.8. DSC thermograms of 51-co2-49d:PEG: BP-PFCB polymer at: (a) (5:10:90; w/w/w) and (b) (5:20:80; w/w/w) ................................................................. 62

4.1. Structure description of 49a-e were n = av of 2.0 to 13.2, respectively ............... 66

4.2. DSC first cycle at 10°C per minute from -70 to 140 °C of: (a) 49a, (b) 49b, (c) 49c, (d) 49d, and (e) 49e ................................................................. 67

4.3. DSC thermograms of 49e: (a) first heating, (b) second cooling, and (c) third heating cycles ................................................................. 68

4.4. Wide-angle diffraction patterns of: (a) 49c, (b) 49d, and (c) 49e. ...................... 70

4.5. WAXD at 2θ = 0.8 to 2θ = 4.0 for: (a) 3.6c, (b) 3.6d, and (b) 3.6e. ...................... 71

4.6. SEM images at high and low magnification (mag) of: (a) 49c (low mag), (b) 49c (high mag), (c) 49d (low mag), (d) 49d (high mag), (e) 49e (low mag), and (f) 49e (high mag)................................. 73
5.1. $^1$H NMR of 53c-co-54c in acetone-$d_6$. ................................................................. 82
5.2. $^{19}$F NMR of 53c-co-54c in acetone-$d_6$. ................................................................. 83
5.3. DSC thermo-grams of copolymers at 10 °C/min. ......................................................... 84
5.4. Experimental and theoretical $T_g$s values of copolymers as a function of weight faction of PEG. ................................................................. 86
5.5. TGA thermo-gram overlay of 53c-co-54c and BP-PFCB oligomer (53c) in nitrogen and air. ................................................................. 87
6.1. Structural description of semifluorinated polyaryl ethers (PAEs) prepared from well defined from 4,4’-bis(4-trifluorovinyloxy)biphenyl and diols monomers. ... 91
6.2. Gel permeation chromatogram of polymer (57a) prepared in: (a) 0.2 wt %, (b) 0.1 wt %, and (c) 0.08 wt % of DMF to 4,4’-bis(4-trifluorovinyloxy)biphenyl (55) and ethylene glycol (56a) monomers. ........................................ 93
6.3. $^1$H NMR spectrum of 57b in DMSO-$d_6$ ................................................................. 94
6.4. $^{19}$F NMR spectrum of 57b in DMSO-$d_6$. ................................................................. 95
6.5. DSC thermo-grams of (a) 57a, (b) 57b, (c) 57c, and (d) 57d. ..................................... 97
6.6. DSC thermo-grams of 57a before (a) quench cool, after (b) quench cool, and after (c) second quench cool. ......................................................... 97
6.7. TGA thermo-gram overlay of 57a and 57d in nitrogen and air. ................................. 99
6.8. AFM phase images of solution cast films of 57a (left) and 57b (right). ............... 100
6.9. AFM height images of solution cast films of 57a (left) and 57b (right). ............... 101
LIST OF SCHEMES

Scheme                                    Page

1.1. Synthetic pathways to functionized PFCB polymers: Path 1 shows PFCB formation of brominated TFVE followed by chain extension via step-growth; Path 2 shows synthesis of a difunctional TFVE monomer followed by step-growth cyclopolymerization .................................. 4

1.2. Synthetic routes to aryl TFVE monomers. (1) Reaction of phenol with 1,2-dibromotetrafluoroethane, followed zinc mediated elimination. (2) Reaction of phenol with tetrafluoroethene (TFE) in the presence of CO₂ and thermally induced elimination. (3) Reaction of phenol with TFE in the presence of water followed by elimination utilizing lithium diisopropyl amide (LDA) (4) Reaction of phenol with TFE at elevated temperature and pressure .......................................................................................................................... 6

1.3. Proposed mechanism for fluoroalkylation of phenols with BrCF₂CF₂Br.............. 7

1.4. Functionalization of 4-bromo(trifluorovinylxylo)benzene, 5 ................................. 9

1.5. Routes to different products from nucleophilic addition of perfluorinated olefins .......................................................................................................................................................................................... 22

1.6. Preparation of fluoroethylene (bottom) aryl ether polymers (FAE) or fluorovinylene (top) aryl ether polymers (FAE) ............................................................... 23

1.7. Modular family of FAE polymers (36-40) and potential applications .................. 24

1.8. Preparation of PFCP Aryl Ether Polymers (43a-c) ................................................ 25

1.9. Initial PEG Polymerization strategies. (1) Thermally induced S_N2 of ethylene bromide by ethylene glycol. (2) Ring-opening polymerization (ROP) of ethylene oxide by ethylene glycol. (3) ROP initiated by water or acetic acid. (4) ROP initiated by zinc chloride or sodium hydroxide .............. 28

1.10. Polymerization steps of low molecular weight (1000 and below) PEG by anionic ROP ......................................................................................................................... 30

1.11. Activated chain end (ACE) mechanism for ethylene oxide............................... 31

1.12. Polymerization of EO by cationic coordination ROP: (1) Activation of EO by metal coordination. (2) Initiation by nucleophilic attack of neighboring alkoxide of the catalyst. (3) Propagation by activation of EO followed continuous nucleophilic attack ................................................................................................................................. 32
1.13. Mechanism for oxidative degradation of PEG by: (1) Oxidation of PEG and the formation of hydroperoxide. (2) Homolytic cleavage leading to radical hydroxide ion and radical on PEG backbone. (3) Chain cleavage and formation of aldehyde.

2.1. Synthetic pathways to PEG-PFCB polymers: Path 1 shows PFCB formation followed by polycondensation.; Path 2 shows synthesis of PEG end-capped with trifluorovinyl ether (TFVE) followed by Step-growth polymerization via thermal induced [2+2] cycloaddition.

2.2. Synthesis of PFCB-PEG copolymer (46) by polycondensation.

2.3. Polymerization of PEG-PFCB copolymer (46) utilizing stannous chloride (SnCl₂) as a Lewis acid.

2.4. Synthesis of PEG macromonomers 49a-e.

2.5. Polymerization of macromonomers 50a-e.

2.6. Copolymerization of TFVE functionalized PEG 400 (50d) with 51, 51b, and 52.

5.1. Synthetic routes to semi-fluorinated aryl ether polymers from TFVE monomers by thermal [2+2] cycldimeration to produce PFCB aryl ether polymers and nucleophilic addition to TFVE monomers to afford FAE polymers.

5.2. Polymerization of PFCB aryl ether and PEG copolymers.

6.1. Structural description of semifluorinated polyaryl ethers (PAEs) prepared from well defined from 4,4'-bis(4-trifluorovinyloxy)biphenyl and diols monomers.
CHAPTER 1
PERFLUOROCYCLOBUTYL (PFCB) ARYL ETHER POLYMERS

Fluoropolymers

Polytetrafluoroethylene (PTFE), better known as Teflon, was accidentally discovered in 1938 by Roy J. Plunkett, a DuPont chemist. Teflon is inert to acids, bases, heat, and is insoluble in organic solvents. Today, it is utilized in a broad range of applications, for example, to separate Uranium isotopes\(^1\) and to coat non-stick pans.\(^2\) Its chemical and thermal stability are due to the high bond dissociation energy of 116 kcal/mol for C-F, compared with 98 kcal/mol for C-H. Fluoropolymers typically exhibit high chemical and thermal stability, low refractive index, low coefficient of friction, low surface energy, low relative permittivity, and are water and oil repellent.\(^3\) These properties makes fluoropolymers highly valued materials.

Unfortunately, the value of fluoropolymers are somewhat undermined by the difficulty of processing them. Most fluoropolymers are highly crystalline, insoluble in common organic solvents, and have high melt transition temperatures (\(T_{ms}\)). As a result, many fluorine-containing polymers are only melt-processible and are thus more expensive. Significant research aims to develop solution-processible amorphous fluoropolymers. Examples of commercially available amorphous fluoropolymers are shown in Figure 1.1.
Figure 1.1. Commercially available amorphous fluoropolymers. 1 = Teflon AF from DuPont; 2 = Fomblins Z from Solvay Solexis; 3 = Cytop from Asahi; and 4 = poly(fluoroacrylates) from Solvay Solexis, Daikin, and Allied Signal.

These amorphous fluoropolymers arose for specific applications. Teflon AF (Figure 1.1, 1) was polymerized from perfluoro(2,2-dimethyl-1,3-dioxole) (PDD) and tetrafluoroethane (TFE) to develop a high-performance material for microelectronics.\(^4\) Cytop (Figure 1.1, 3) was produced by Asahi via radial intramolecular cyclization of CF\(_2\)=CF-O-CF\(_2\)-CF\(_2\)=CF\(_2\). Both polymers are known for low dielectric constants and low refractive indices. Fomblins (Figure 1.1, 2) are utilized as lubricants for mechanical devices and compact disc (CD) coatings and sulfonated Fomblins are employed by DuPont as ion-conducting membranes.\(^5\)
**Perfluorocyclobutyl (PFCB) Aryl Ether Polymers**

The ability of fluoroolefins to cyclodimerize to fluorinated cyclobutyl rings is a remarkable reaction in organofluorine chemistry. The dimerization of tetrafluoroethene (CF$_2$CF$_2$) to a perfluorocyclobutyl (PFCB) ring was originally discovered in 1947 from thermal decomposition products of PTFE.$^6$ Cyclodimerization of tetrafluoroethene (TFE) is thermodynamically favored by 38.0 kJ/mol compared with the endothermic dimerization of ethene which requires 13.4 kJ/mol.$^7,8$ The major forces contributing to cyclodimerization of TFE reaction are pi bond strain due to the presence of the fluoroolefins.$^4$

Further research by Dupont produced an perfluororoalkyl trifluorovinyl ether (TFVE) monomer and the first PFCB polymers.$^9$ A well known class of fluorinated polymers are semifluorinated perfluorocyclobutyl (PFCB) aryl ether polymers. Babb and coworkers initially synthesized 3-trifluorovinylxyloxy-$\alpha,\alpha,\alpha$-trifluorotoluene, 1,3-bis(trifluorovinylxyloxy) benzene, 4,4'-bis(trifluorovinylxyloxy) biphenyl, and 1,1,1-tris(4-trifluorovinylxyloxyphenyl) ethane monomers for the preparation of low dielectric thin films for microelectronics.$^{10}$ Polymers prepared from 4,4'-bis(trifluorovinylxyloxy) biphenyl were amorphous, possessed glass transition temperatures ($T_g$s) between 160 and 165 °C, and were soluble in common organic solvents.

To date PFCB aryl ether polymers are usually prepared by step-growth [2+2] cyclodimerization of aryl trifluorovinyl ether (TFVE) monomers (Scheme 1.1, Path 2). PFCB ring formation was considered to follow the same nonconcerted biradical mechanism of TFE, which was later confirmed by electron magnetic resonance (EPR)
analysis. In addition, cycloaddition kinetics have been studied by differential scanning calorimetry (DSC) and Raman spectroscopy. Scheme 1.1, Path 1 details formation of PFCB monomer and chain extension via step-growth polymerization. For example, condensation polymerization was performed using 1,2,3,3,4,4-Hexafluoro-1,2-bis(4-bromophenoxy)cyclobutane and 4-phenyl-azoaniline as monomers. Poly (alkyl aryl) ether containing 1,2,3-triazolyl and PFCB components were polymerized via Huisgen’s (3+2) cycloaddition using polyethylene glycol diazides and 1,2-bis(4-ethynylphenoxy)perfluorocyclobutane. Both pathways employ a functional spacer designed for a specific application.

Scheme 1.1. Synthetic pathways to functionalized PFCB polymers: Path 1 shows PFCB formation from brominated TFVE followed by chain extension via step-growth polymerization; Path 2 shows synthesis of a difunctional TFVE monomer followed by step-growth cyclopolymerization.
PFCB aryl ether polymers are amorphous, in part, due to their stereo-random PFCB linkage. Isomers of 1,2-bis(4-bromophenoxy)hexafluorocyclobutane were isolated by selective crystallization, identified by X-ray diffraction, and characterized by nuclear magnetic resonance (NMR).\textsuperscript{16} In addition to being amorphous, PFCB polymers are known for thermal stability, excellent optical clarity, and ease of processability. As a result, PFCB aryl ether polymers have been investigated for many applications including fuel cells membranes, liquid crystals, composites, photonics, and atomic oxygen (AO) resistant coating materials.
Synthesis of Aryl Trifluorovinyl Ether Monomers and PFCB Polymers

Scheme 1.2 illustrates the synthetic routes to aryl TFVE monomers. All routes start with deprotonation of the phenolic precursor by potassium hydroxide. The preferred route (Scheme 1.2, 1) involves the use of dibromotetrafluoroethane, followed by zinc-mediated elimination.\(^\text{10}\) Although this route is preferred, dibromotetrafluoroethane is known to deplete the ozone layer and is only available in limited commercial quantities.\(^\text{17}\) Other synthetic routes (Scheme 1.2, 2-4) utilize the more environmentally friendly TFE. Route 2 entails the addition of the phenolic to TFE in the presence of carbon dioxide, followed by thermally-induced decarboxylation and elimination.\(^\text{18}\) Route 3 also involves the addition to TFE, followed by quenching with water and dehydrohalogenation using lithium diisopropyl amide (LDA).\(^\text{19,20}\) The product can be synthesized directly by addition to TFE at elevated temperature and pressure, scheme 1.2, 4.\(^\text{21,22}\) While synthetic routes 2 through 4 do not involve the difficulty of acquiring dibromotetrafluoroethane and arduous azeotropic distillation of deprotonated phenol, TFE is well known to be carcinogenic and detonates in the presence of oxygen. Other synthetic routes are currently being explored.

Scheme 1.2. Synthetic routes to aryl TFVE monomers. (1) Reaction of phenolic precursor with 1,2-dibromotetrafluoroethane, followed by zinc mediated elimination.\(^\text{10}\) (2) Reaction of phenolic precursor with tetrafluoroethene (TFE) in the presence of CO\(_2\) and thermally-induced elimination.\(^\text{18}\) (3) Reaction of phenolic precursor with TFE in the
presence of water followed by elimination utilizing lithium diisopropyl amide (LDA)\textsuperscript{19,20} 

(4) Reaction of phenolic precursor with TFE at elevated temperature and pressure.\textsuperscript{21,22}

Importantly, fluoroalkylation and zinc-mediated elimination must be performed under anhydrous conditions to prevent formation of the by-product, ArOCF\textsubscript{2}CF\textsubscript{2}H. Azotropic distillation of DMSO and water is essential to prevent the formation of ArOCF\textsubscript{2}CF\textsubscript{2}H. The formation of ArOCF\textsubscript{2}CF\textsubscript{2}H can be understood by exploring the proposed mechanistic details (Scheme 1.3).\textsuperscript{23} In the two-electron process the phenoxide attacks the bromine on dibromotetrafluor ethane. This results in elimination and the formation of TFE and a hypohalite. Another phenoxide attacks TFE to form a new carbanion. In the presence of water the carbanion can protonate to form ArOCF\textsubscript{2}CF\textsubscript{2}H. The hydrogen by-product is difficult to separate from the desired product and can result in chain termination during polymerization. In the absence of water, carbanion attacks the hypohalite formed earlier and yields the desired product.

\textbf{Scheme 1.3.} Proposed mechanism for fluoroalkylation of phenols with BrCF\textsubscript{2}CF\textsubscript{2}Br.\textsuperscript{23}
Although there are many commercially available phenols, a new strategy was developed to synthesize more diverse monomers. This strategy was based on formation of a Grignard reagent from 4-bromo(trifluorovinyl)benzene (5) to later synthesize 4-(trifluorovinyl)phenyldimethylsilane.\textsuperscript{24} Calculations performed on $p$-carbanion of phenyl TFVE showed a decrease in electrophilicity. The decrease in electrophilicity leaves the fluoroolefin less susceptible to nucleophilic attack by the carbanion.\textsuperscript{25} Starting from 5, a variety of functional groups derivatives can be synthesized (Scheme 1.4) These include carboxylic acid (6), acid chloride (7), amine (10), aldehyde (19), alcohol (20), and isocyanate (9).\textsuperscript{26} Suzuki coupling can be performed on boronic acid TFVE (Scheme 1.4, 13) to construct new monomers. Utilizing the aldehyde TFVE (Scheme 1.4, 19), Wittig condensation can also be performed.
Scheme 1.4. Functionalization of 4-bromo(trifluorovinyl)oxybenzene, 5.²⁶
Figure 1.2 displays a sample of PFCB polymers employing a 4-bromo(trifluorovinloxy)benzene intermediate strategy. Siloxane-containing TFVE monomer (Figure 1.2, 30) was prepared in three steps starting from 1-bromo(trifluorovinloxy)benzene and forming a Grignard TFVE intermediate. Addition of dimethylchlorosilane (Si(CH₃)₂ClH) followed by condensation via dehydrogenative hydrolysis/methanolysis resulted in the isolation of a new monomer in high yield and, finally, the preparation of first PFCB aryl ether fluorosiloxane (Figure 1.2, 30).²⁴ Aryl TFVE carboxylic acid was coupled with polyhedral oligomeric silesquioxanes (POSS) to construct a pendent POSS PFCB aryl ether copolymer (Figure 1.2, 23).²⁷ The polymerization of tris(4-trifluorovinloxy)phenyl ethane with aryl TFVE benzoic acid led to network materials (Figure 1.2, 24) capable of chelating rare earth metals for the production of fiber amplifiers.²⁸ Incorporation of crown ethers (Figure 1.2, 26) was achieved by condensation of TFVE benzyl chloride with diamine crown ethers.²⁹ Utilizing a lithium intermediate, a sulfonyl chloride precursor was synthesized and later aminated to the sulfonimide aryl TFVE (R=SO₂NH₂). Coupling of the sulfonimide with the sulfonyl chloride precursor, followed by counterion exchange, and polymerization led to a new polymer (Figure 1.2, 27) that could potentially be used in fuel cell and electrochemical applications.³⁰ After palladium-mediated Suzuki cross-coupling of 4-bromo(trifluorovinloxy)benzene with a series of oligophenylene boronic acids, oligophenylene segmented monomers and polymers (Figure 1.2, 28) were afforded with thermotropic liquid crystalline properties.³¹ Suzuki cross-coupling was also utilized for preparation of pyrimidine PFCB polymers (Figure 1.2, 29).³² Additional network
polymers were constructed using triarylamine (Figure 1.2, 31) and triphenylphosphine oxide (Figure 1.2, 32) for hole transport layers (HTLs) and space durable materials, respectively.\textsuperscript{33,34}

\textbf{Figure 1.2.} Sample of PFCB polymers synthesized by 1-bromo(trifluorovinyloxy) benzene strategy.\textsuperscript{26-34}
Although the Grignard or lithiated strategy has been successfully utilized for the majority of functionalized TFVE monomers, new and simplistic strategies are still under development. One exciting approach is based on the one-pot synthesis of tertiary alkyl carboxylates and sulfonates from ketones. Figure 1.3 illustrates the synthesis of new aryl bistrifluorovinyl ether (BTFVE) monomers, 35a-e. Starting with 1-bromo(trifluorovinyloxy)benzene (Figure 1.3, 5), a Grignard reagent (32) is formed, the reaction is quenched with methyltrifluoroacetate, and finally a monomer specific acid chloride (34a-e) is added to form a new BTFVE monomers (35a-e). Polymers produced from monomer 35a were optically transparent, and direct lithography was performed with similar results as PFCB polymers. This strategy may be more cost effective method to obtain TFVE from which bisphenolic precursors are not available.

**Figure 1.3.** One-pot synthesis of aryl bistrifluorovinyl ether (BTFVE) monomers (35a-e) by Grignard chemistry.36
Degradation of polymers prepared from 1,1,1-tris(4-trifluorovinylxyloxyphenyl)ethane was studied by thermal-gravimetric analysis (TGA) coupled with mass spectrometry (MS) and Fourier-transform infrared. Results show that in an anaerobic environment polymers exhibit a single process of degradation. In an air environment, MS results show formation of hexafluorocyclobutene, 1,3-hexafluorobutadiene, phenol, and oxidation of the methyl group as major decomposition products (Figure 1.4).

**PFCB Polymer Applications**

As previously discussed, the ability to functionalize TFVE monomers has been utilized for a multitude of polymer-specific applications. Design, structure-property relationships of high performance PFCB aryl ether polymers are shown in Figure 1.5. Polymers are typically thermally polymerized from 150 to 200 °C. The aromatic ether linkages provide thermal stability and mechanical properties. The stereorandom PFCB linkage imparts typical amorphous character, solubility, chemical and oxidation resistance, low dielectric constant / refractive index, and processability. After polymerization, PFCB polymers retain reactive TFVE end-groups. This characteristic allows for further modification toward crosslinked networks or copolymers via copolymerization with other PFCB oligomers and/or monomers.

![Figure 1.5. Design, structure-property relationship of PFCB aryl ether polymers.](image)

Figure 1.5. Design, structure-property relationship of PFCB aryl ether polymers. 

14
Aromatic PFCB polymers were initially developed by The Dow Chemical company as a low dielectric constant to replace the passive layer of microelectronics.\textsuperscript{39,40} However, aryl PFCB ether polymers have a unique set of qualities that make them attractive for other applications. Among these desired qualities is the ability to tune the refractive index by controlling the aromatic and fluorine content (Figure 1.6).\textsuperscript{37} Wong and coworkers demonstrated this phenomenon with a variety of semifluorinated to highly fluorinated polymers.\textsuperscript{41} In addition, $T_g$'s are also tunable from 110 to 350 °C for low to high temperature applications. Thin films of PFCB copolymers exhibit low birefringence (<0.003), low optical loss (<0.25 dB/cm), and broad extinction of coefficients (0.2 to 33 μm).\textsuperscript{42} These properties make PFCB copolymers interesting for electroluminescence, liquid crystals, photonic, and nonlinear optical applications. In fact, many fluoropolymers have been utilized in optical applications due to their inherent toughness, long term chemical and thermal stability, and oxygen resistance. For example, Dupont AF and Asahi’s Cytop also have similar low optical losses and have been utilized in optical applications.\textsuperscript{43}
Nanocrystal quantum dots (NQDs) are nanometer-sized materials that alter the modes of propagating light and in some cases are able to suppress propagation of light in certain directions. These NQDs typically have broad absorption, narrow emission, and are resistant to photobleaching. To utilize these crystals, particles must be dispersed in a low optical loss and low birefringence matrix. CaF$_2$:Er$^{3+}$ particles can easily be dispersed in hexafluoropropyl (6F) PFCB polymers by a solvothermal method. This method was also useful in preparation of 6F PFCB polymer doped with LaF$_3$:Nd. Based on quantum efficiencies, 95% for LaF$_3$:Nd and 51% for CaF$_2$:Er$^{3+}$, 0.5 mol % of particles was determined to be ideal. Transmission electron microscopy (TEM) images prove that the particles were well dispersed (Figure 1.7). Although this provides a method for preparing nanocomposites, current research focuses on preparing structured polymers for
doping with a variety of particles, for example, copolymerization of trifunctional monomer with erbium TFVE acid.\textsuperscript{28}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{TEM_images}
\caption{TEM images of nanocomposites prepared with 0.5 mol \% of (left) CaF\textsubscript{2}:Er\textsuperscript{3+} and (right) LaF\textsubscript{3}:Nd. (Reprinted with permission from Kumar, G.A., et al. \textit{Chem. Mater.} \textbf{2007}, \textit{19}, 1523, ©2007 American Chemistry Society).}
\end{figure}

Fuch and coworkers fabricated waveguides using 1,1,1-tris(4-trifluorovinyloxyphenyl) ethane and PbS, InAs/ZnSe, CdSe/ZnS, and InAs.\textsuperscript{49} Nanocrystals maintained infrared-emitting properties and were unaffected by the aryl PFCB environment.

Waveguides have been prepared by transfer molding using a silicon master.\textsuperscript{50} This method was more simplistic than conventional lithography in producing submicrometer size gratings (Figure 1.8). For compact wavelength-division multiplexers (CWDM), dry etching photolithography was performed (Figure 1.9).\textsuperscript{51} The same technique was used to fabricate waveguide planes with single air interface bends (SAIBs).\textsuperscript{52}
**Figure 1.8.** SEM images of waveguide gratings fabricated by transfer molding using silicon master. (Images reprinted with permission from D.W. Smith, Jr., et al. *Adv. Mater.* **2002**, *14*, 1585, ©2002 Wiley-VCH verlag GmbH & Co. KGaA.)

**Figure 1.9.** SEM images of waveguide gratings fabricated by dry etching photolithography. [Images reprinted with permission from J. Jiang, et al., *J. Lightwave Tech.* **2006**, *24*, 3227, ©2006 Institute of Electrical and Electronics Engineers (IEEE).]
The growing market for high contrast images has led to growing research interest in organic or polymeric light emitting diodes (OLEDs or PLEDs). While inorganic materials dominate this market, PLEDs have some competing advantages. PLEDs are light-weight, consume less power, and have a better cost to contrast ratio. The main disadvantages of PLEDs are low quantum efficiencies and poor lifetime due to photobleaching. Fluoropolymers are known to operate at the required high operating temperatures, enhance luminance, and resist photobleaching. Further, PFCB polymers are known for tunability, thermal stability, and processability. Andrew R. Neilson and coworkers synthesized some of the first emissive monomers by utilizing 1-bromo(trifluorovinyl)benzene intermediate synthetic strategy. Suzuki coupling was performed with 9,9-dihexylfluorene-2,7-diboronic acid and 4-trifluorovinylxyphenylboronic acid to synthesized a new fluorescent TFVE monomer. Thiophene and thiadiazole based monomers were also synthesized by Suzuki coupling. After thermal polymerization, all polymers exhibited quantum efficiencies (Φs) between 0.23 and 0.58. Aryl PFCB polymers containing phenylene vinylene were prepared by Wittig conditions with much higher Φs between 0.68 and 0.78. Based on the success of Hexa-peri-hexabenzocoronene and triaryl amines as hole transport layers (HTLs), network polymers were prepared form TFVE hexabenzocoronene and triaryl amine monomers. Polymers produced from TFVE hexabenzocoronene monomer showed similar photoluminescent properties of hexabenzocoronene.
Synthesis of hyperpolarizable chromophores with a high dipole donor was achieved using vinylene thiophene bridges and triaryl amine as donors. Monomers could be polymerized anionically or thermally and showed high thermal stability.

The thermal and chemical stability of fluoropolymers led to the introduction of fluoropolymers as proton exchange membranes. Similarly, sulfonated aryl PFCB polymers have been extensively studied for the same application. Recent conductivity values are highly competitive with Dupont’s Nafion, the current industry standard. Current work focuses on sulfonation of aryl PFCB copolymers to create hydrophobic and hydrophilic domains in the membrane and sulfonated aryl PFCB polymers blended with Nafion.

PFCB polymers with liquid crystalline (LC) properties were prepared by thermal polymerization of TFVE monomer with a mesogenic α-methylstilbene unit. Results show the formation of lyotrophic lamellar mesophases and birefringence by polarized optical microscope. PFCB polymers containing oligophenylene also displayed LC properties (Figure 1.10). Before polymerization, monomers exhibited no birefringence by polarized optical microscopy (Figure 1.10 left). After polymerization, birefringence was observed as a Schlieren texture (Figure 1.10 right).
Figure 1.10. Polarized optical microscope (POM) images displaying birefringence of 28 (n=1) at 190 °C (left) for 15 min and (right) 2 h. (Reprinted with permission from J. Jin, et al., Macromolecules 2006, 39, 4646, ©2006 American Chemical Society.)
Fluoroalkenes are more prone to attack by nucleophiles than electrophiles due to high electronegativity of the fluorines. Nucleophilic attack on the fluoroolefin leads to the formation of a carbanionic intermediate, Scheme 1.5. The intermediate can be trapped by any available electrophile, but in the absence of an electrophile, the intermediate can lead to the elimination of the fluoride ion and substitution product, Scheme 1.5.

Scheme 1.5. Routes to different products from nucleophilic addition of perfluorinated olefins.

Here we employ the above method (Scheme 1.5) to produce fluoroethylene/vinylene aryl ether (FAE) polymers by step-growth polymerization of commercially available, TFVE monomers. Initial polymers (Scheme 1.6) involved the deprotonation of a diol monomer utilizing NaH as a base to produce an alkoxide. Next, addition of stoichiometric amounts of dual-functional TFVE monomer was added to produce vinylene (-CF2=CF-) enriched polymer via elimination of fluoride (Scheme 1.6, top). Fluoroethylene (-CHFCF2-) enriched polymer was polymerized by using Cs2CO3 (50 mol %) as a base (Scheme 1.6, bottom).
Telechelomers were prepared using excess sodium hydride to deprotonate commercial bisphenols and an excess of dual-functional TFVE monomer. Further chain extension was achieved thermally at 210 °C via [2+2] cyclodimerization of TFVE end-groups. The internal fluoroolefin (CF=CF) of fluorovinylene aryl ether is tolerant to common anionic and PFCB cycloaddition polymerization conditions. The fluoroolefin can be thermally activated above 250 °C to produce an insoluble, crosslinked fluoropolymer. Utilizing this thermal crosslinking ability, fluorovinylene aryl ether polymers can be solution casted then thermally crosslinked without the use of post-curing agents.
Additionally, FAE polymers can be modularly functionalized with chromophore segments providing tunable photoluminescence properties (Scheme 1.7). These chromophore enriched semifluorinated FAE polymers were utilized for ion sensing. For example, thiophene-modified FAE polymers (Scheme 1.7, 38) have shown strong binding affinity for CN⁻ and F⁻ ions over other anions. In addition, bipyridine-modified FAE polymers (Scheme 1.7, 40) have displayed noticeable red-shifts upon addition of transition and lanthanide ions (Co²⁺, Cu²⁺, Zn²⁺, Cd²⁺, and Hg²⁺), with the largest shift observed for Cu²⁺. Other polymers included fluorenylidene (36), p-phenylene vinylene (37), and thiadiazole (39) as chromophores.

Scheme 1.7. Modular family of FAE polymers (36-40) and potential applications.
Perfluorocyclopentenyl (PFCP) Aryl Ether Polymers

Octafluorocyclopentene (OFCP) is a cyclic perfluorinated olefin. OFCP has been employed in multiple photochromic molecules, but has limited adaptation in polymeric materials.\textsuperscript{73,74} Attempts to radically polymerize OFCP with styrene and vinyl acetate led to low molar ratios of perfluorocyclopentane in the copolymer.\textsuperscript{75} OFCP is well known to undergo nucleophilic addition by phenoxides,\textsuperscript{76-79} amines,\textsuperscript{80-82} organolithium reagents,\textsuperscript{83-85} and other nucleophiles.\textsuperscript{86,87} Recently, the condensation polymerization of OFCP (Scheme 1.8, 41) was achieved utilizing commercial bisphenols (42a-c) to produce the first perfluorocyclopentenyl (PFCP) aryl ether polymers (Scheme 1.8, 43a-c).\textsuperscript{88} These conjugated semifluorinated polyaryl ethers have the potential to modularly functionalize similar to FAE polymers. Current research focuses on this hypothesis and other high performance material applications.

\begin{equation}
\begin{array}{c}
\text{41} + \text{HO-}R-\text{C}_{\text{Ph}}-\text{OH} \\
\text{NEt}_3 \\
\text{DMF} \\
10 \text{ h, 80 °C} \\
\text{43a-c}
\end{array}
\end{equation}

\textbf{Scheme 1.8.} Preparation of PFCP Aryl Ether Polymers (43a-c).\textsuperscript{88}
Polyethylene glycol (PEG) is a polyether with the general formula (–CH₂–CH₂–O–)ₙ, where n is the repeat unit. PEG has a rare solubility pattern: It is soluble in common organic solvents like methylene chloride, toluene, and dimethyl sulfoxide, but also in water. These properties result from its unique structure (Figure 1.11); PEG has a hydrophobic hydrocarbon with an oxygen that is capable of hydrogen bonding. \(^{89}\)

**Figure 1.11. Amphiphillic structure of PEG.** \(^{89}\)

PEG is commercially available in a wide range of molecular weights and properties. PEG with number average molecular weights (\(M_n\)) of 200 to 600 g/mol are liquids at room temperature. At \(M_n\)s of 1000 to 1500 g/mol, PEG is a semicrystalline semisolid. Higher molecular weights are semicrystalline wax-like solids. \(^{90}\) These properties, along with its low price and reactive end-groups, have yielded a variety of PEG applications.
PEG has been utilized in fields from materials science to biology. In material science, PEG has been used as a plasticizer, an electrolyte in lithium batteries, an optical waveguide, and a curing agent. Addition of PEG as a copolymer has led to applications in elastomeric fibers, and hydrogels. In biology, covalent attachment of PEG to pharmaceutical drugs is known to lower immune response and increase solubility. Additionally, attachment of PEG to the cell membrane is known to cause cell fusion. Attachment to proteins increases the serum lifetime of the protein. Indeed, addition of PEG to any surface results in a decrease in cell absorption. PEG is also known for the purification and crystallization of proteins through competitive interactions. These major breakthroughs have subsequently led to the commercial success of PEG and thousands of publications that utilized PEG.
The first polymerization of PEG was reported in 1859. Lourenco and coworkers heated ethylene glycol with ethylene dibromide to 120 °C and found PEG units as high as six (Scheme 1.10, 1).106,107 Wurtz reported the polymerization of PEG from heating ethylene oxide (EO) with ethylene glycol for several weeks (Scheme 1.9, 2).108 This method resulted in oligomeric product. Wurtz later developed an alternative approach by heating EO in the presence of water or acetic acid (Scheme 1.9, 3).109 Polymerization of PEG using this strategy resulted in low molecular weight oligomers. Higher molecular weight was achieved utilizing zinc chloride or sodium hydroxide.110 In the 1920s Staudinger and Lohmann obtained higher molecular weights, 100,000 and above, by employing sodium hydroxide or zinc chloride as an initiator with EO (Scheme 1.9, 4).111,112 Yields as high as 50 % were reported. In the 1950s commercialized high molecular weight polymers were reported via ring-opening polymerization (ROP) of EO.90

Scheme 1.9. Initial PEG polymerization strategies. (1) Thermally-induced S_N2 of ethylene bromide by ethylene glycol.106,107 (2) Ring-opening polymerization (ROP) of ethylene oxide by ethylene glycol.108 (3) ROP initiated by water or acetic acid.109 (4) ROP initiated by zinc chloride or sodium hydroxide.111,112
Today the most common polymerization of PEG is achieved by ring-opening polymerization of EO. EO is utilized as a monomer due to a high reactivity caused by strain of the three-membered ring.\textsuperscript{90} Polymerization of EO is classified in two major mechanistic pathways, anionic ROP polymerization and cationic ROP polymerization induced by a Lewis acid.

Low molecular weight polymers, 1000 and below, are polymerized by anionic ROP using sodium hydroxide as a base and ethylene glycol or diethylene glycol as an initiator (Scheme 1.10, 1).\textsuperscript{90} After initiation, propagation is accomplished by additional ring-opening of EO (Scheme 1.10, 2). Polymerization is terminated by neutralization with a strong acid, like hydrochloric acid (Scheme 1.10, 3). Anionic polymerization usually produces polymers with narrow polydispersity ($M_w/M_n$).\textsuperscript{113-115} Attempts to achieve higher molecular weight using this method resulted in dehydration of the PEG end-group, regeneration of alkali hydroxide, and formation of unsaturated end-groups.\textsuperscript{90} Although low amounts of high molecular weight polymers were reported, this approach ultimately caused chain termination before the higher molecular weight was obtained. Ptitsyna and coworkers acquired molecular weight higher than 10000 by using cesium hydroxide as the base and increasing the pressure, resulting in higher EO concentration.\textsuperscript{116} Interest in this method of polymerizing EO remains. Recent publications utilized cryptates or $N$-heterocyclic carbenes as initiators resulting in high to low molecular weights, respectively.\textsuperscript{117,118}
The first report of high molecular weight PEG was reported in 1958. Hill and coworkers discovered that anionic ROP of EO could be accomplished using alkaline earth carbonates and water. Initially, an equilibrium is established between the carbonate, bicarbonate, water, and hydroxide ions. Available hydroxide ions initiate the polymerization via ring-opening of ethylene oxide and the anionic polymerization continues in a similar chain growth fashion, as described in Scheme 1.10. Although polymerization rates were low, this method was more efficient than any previous reports.

Cationic ROP of EO is achieved by addition of a strong Lewis acid to ethylene oxide. Lewis acids include organic acids and inorganic salts. Depending on the Lewis acid and polymerization conditions a variety of counterions are utilized as cationic initiators. Mechanistic details of cationic ROP can be seen in Scheme 1.11. Cationic ROP is initiated by the formation of an oxonium ion (Scheme 1.11, 1). Depending on
oxonium ion stability, the counterion can be attacked by an available EO monomer or available glycol end-group (Scheme 1.11, 2). This reaction is often referred to as active chain end propagation (ACE).\textsuperscript{120}

\begin{center}
\includegraphics[width=\textwidth]{scheme_11.png}
\end{center}

**Scheme 1.11.** Activated chain end (ACE) mechanism for ethylene oxide.\textsuperscript{120}

ACE has a major drawback: the possibility of intermolecular and intramolecular nucleophilic attack during polymerization.\textsuperscript{121,122} Although this polymerization occurs rapidly, a variety of nucleophiles coexists and competes with EO monomer as a nucleophile. As a result, cyclic oligomers are produced, reducing the molecular weight and broadening polydispersity ($M_w/M_n$). A low molecular weight PEG is added to reduce cyclization and lower polydispersity. This method, known as activated monomer propagation (AM), utilizes PEG as the nucleophile during propagation and localizes the charge to end-groups of the polymer.\textsuperscript{123} Another strategy to reduce cyclization is reducing EO concentration.\textsuperscript{120} These reactions are carried out by slow dropwise addition of the monomer to an initiator solution. This strategy also successfully produces high molecular weight PEG.
Most high molecular weight PEGs are prepared under milder conditions by coordinate anionic polymerization.\textsuperscript{124} Based on the polymerization of propylene oxide by Pruitt and Bagget, an EO monomer is activated by coordination with metal catalyst (Scheme 1.12, 1). Next, the newly activated monomer is attacked by a metal alkoxide (Scheme 1.12, 2). Propagation then begins with the new anionic species proceeding to attack the next coordinated ethylene oxide monomer (Scheme 1.12, 3). Of course, the exact transition states depend on the catalyst utilized.\textsuperscript{120} Industrial interest in this method of polymerization continues. A recent publication by researchers at The Dow Chemical company demonstrates polymerization of ethylene oxide using aluminum tetraphenoxide catalysts.\textsuperscript{125}

\textbf{Scheme 1.12.} Polymerization of EO by cationic coordination ROP.\textsuperscript{125} (1) Activation of EO by metal coordination. (2) Initiation by nucleophilic attack of neighboring alkoxide of the catalyst. (3) Propagation by activation of EO followed by continuous nucleophilic attack.\textsuperscript{120}
Properties of PEG

The thermal properties of PEG have been well studied by differential scanning calorimetry (DSC). Work by Read and Faucher showed that $T_g$s do not increase proportionally with molecular weight. $T_g$s increase from -72 °C for PEG 200 to a maximum of -17 °C for PEG 6000, which displays the greatest degree of crystallinity by DSC. Molecular weights higher than PEG 6000 exhibit lower $T_g$s values. Quenching molten polymers with liquid nitrogen resulted in lower $T_g$s, but samples gave inconsistent values due to crystallization. While $T_g$ values can change with molecular weight, other melt and crystalline transition temperatures can be affected by molecular weight and polydispersity. These transitions are due to changes in polymer morphology. Properties of PEG are shown in Table 1.1.

<table>
<thead>
<tr>
<th>Number-average molecular weight ($M_n$)</th>
<th>200</th>
<th>600</th>
<th>1500</th>
<th>6000</th>
<th>20000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point (°C)</td>
<td>supercools</td>
<td>20-25</td>
<td>4-8</td>
<td>60-63</td>
<td>50-55</td>
</tr>
<tr>
<td>Glass Transition Temperatures, $T_g$s (°C)</td>
<td>-72</td>
<td>-68</td>
<td>-65</td>
<td>-17</td>
<td>-66$^{126}$</td>
</tr>
</tbody>
</table>

Like many ethers, PEG is prone to thermo-oxidative attack, sometimes termed autoxidation. Although the purely thermal degradation of PEG is backbiting from alcohol endgroups, autoxidation mechanistic details can be seen in Scheme 1.13. First, PEG is attacked by oxygen and forms hydroperoxide (Scheme 1.13, 1). Hydroperoxide
then undergoes homolytic cleavage leaving to a hydroxyl radical and a radical on the polymer chain (Scheme 1.13, 2). The radical on the polymer chain causes chain cleavage and results in the formation of aldehyde (Scheme 1.13, 3). This process has been studied kinetically and is known to increase with heat.\textsuperscript{129,130} Degradation can be catalyzed in the presence of chromium (III), iron (III), strong acids, and ultraviolet light.\textsuperscript{90,131} Further, PEG can be stabilized with the addition of antioxidants.\textsuperscript{132,133} Recently, miscible blends of PEG with poly(L-lactic acid) (PLLA), show a reduction of autoxidation of PEG without chain cleavage or transesterification of the PLLA.\textsuperscript{134}

Scheme 1.13. Mechanism for oxidative degradation of PEG by: (1) Oxidation of PEG and the formation of hydroperoxide. (2) Homolytic cleavage leading to radical hydroxide ion and radical on PEG backbone. (3) Chain cleavage and formation of aldehyde.\textsuperscript{90,129,130}

The chemistry of oxidative degradation is important to the fluoropolymer PEG hybrids discussed in the following chapters.
CHAPTER 2
PERFLUOROCYCLOBUTYL (PFCB) ARYL ETHER POLYMERS WITH
POLYETHYLENE GLYCOL (PEG) ENCHAINMENT

Introduction

Polymers have been used as an electrolyte for lithium-based electrochemical devices. For a polymer to be utilized as an electrolyte, several requirements must be satisfied: 135,136

1. The polymer must be stable to the power density and the polarization effect of the electrochemical device.
2. It must promote ion conductivity.
3. It must possess thermal stability due to a device’s range of operating temperatures.
4. It must be chemically stable against corrosion.

Fulfilling these requirements will produce a stable electrochemical device with the possibility for product development.

Fluoropolymers have been little explored as polymer electrolytes due to high crystallinity. One exceptional class of fluoropolymer is the perfluorocyclobutyl (PFCB) aromatic ether polymer. While thermally and chemically stable, remarkably, PFCBs are also amorphous. 38 Indeed, PFCB sulfonamide and crown ether polymers show promising adaptability to lithium ion batteries. 16,30 Although these advances are encouraging, glass transition temperatures ($T_g$s) are high and this tends to lower ionic conductivity. 135,136
Lower glass transition temperatures increase segmental motions, ionic mobility, and promote ion transport. As a result, lower $T_g$ increases ionic conductivity. Thus, an advance that lowers $T_g$ in PFCBs would enhance the usefulness of these polymers.

Polyethylene glycol (PEG) is the most widely studied polymer for lithium ion conductivity, because of low $T_g$'s and an ability to coordinate with metal cations. A review of PEG polymerization and properties is presented in Chapter 1. Incorporation of PEG in PFCB to create a copolymer should decrease the glass $T_g$'s and promote further research toward PFCB applications. PFCB polymers are typically synthesized by two divergent synthetic pathways, Scheme 2.1. Both pathways will be explored for the synthesis of PEG-PFCB copolymers.

**Scheme 2.1.** Synthetic pathways to PEG-PFCB polymers: **Path 1** shows PFCB formation followed by polycondensation; **Path 2** shows synthesis of PEG end-capped with trifluorovinyl ether (TFVE) followed by step-growth polymerization via thermal induced [2+2] cycloaddition.
Polymerization of PEG-PFCB Polymers by Polycondensation

Whinfield and Dickson discovered polyethylene terephthalate, commonly referred to as PET.\textsuperscript{138} PET has a high melting point (265 °C) and good hydrolytic stability. Synthesis of PET occurs through polycondensation of difunctional monomers. These include the esterification of diacids with diols, condensation of diacid chlorides with diols (Schotten-Baumann reaction), or transesterification of diester and diols.\textsuperscript{139} PET is typically produced by polycondensation of terephthalic acid with ethylene glycol (EG). The second most common method is transesterification of terephthalic diester. Both methods produce many side reactions, including thermal degradation, hydrolysis, and cyclization of the polymer.\textsuperscript{140} To synthesize a perfluorocyclobutyl (PFCB) polymer with a flexible polyethylene glycol (PEG) linker, two synthetic strategies were devised based on previous PFCB and polyester work (Scheme 2.1).

![Scheme 2.2](image)

\textbf{Scheme 2.2.} Synthesis of PFCB-PEG copolymer (46) by polycondensation.

The initial polycondensation strategy was based on condensation polymerization of bis-acid chloride (Scheme 2.2, \textit{44a}) and bis-carboxylic acid monomers (Scheme 2.2, \textit{44b}). In addition, a traditional PFCB strategy was also devised to construct the corresponding polymer. The first attempt was carried out using bis-acid chloride (\textit{44b}). Triethylamine (NEt\textsubscript{3}) was utilized to neutralize the HCl liberated during the reaction (Table 2.1). The amine is also capable of performing a nucleophilic attack on the acid
chloride, producing an acylammonium salt.\textsuperscript{139} The salt can be attacked by PEG (45) to form a new ester bond. The polydispersity index (PDI), a ratio of weight-average molecular weight ($M_{\text{w}}$) to number-average molecular weight ($M_{\text{n}}$), was between 1.25 and 1.81, indicating some step-growth polymerization.\textsuperscript{141} The solvent was varied to find the right conditions for higher $M_{\text{n}}$ values. Although reaction 1 produced the highest $M_{\text{n}}$, it was still considered oligomeric product.

<table>
<thead>
<tr>
<th>Rxn\textsuperscript{a}</th>
<th>X=</th>
<th>Conditions</th>
<th>Solvent</th>
<th>PEG (45)</th>
<th>Reagent(s)</th>
<th>$M_{\text{n}}$\textsuperscript{c}</th>
<th>PDI\textsuperscript{c}</th>
<th>$M_{\text{w}}/M_{\text{n}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1\textsuperscript{d}</td>
<td>Cl</td>
<td>65 °C 12hr</td>
<td>THF</td>
<td>400\textsuperscript{b}</td>
<td>NEt\textsubscript{3}</td>
<td>2267</td>
<td>1.81</td>
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<tr>
<td>2\textsuperscript{d}</td>
<td>Cl</td>
<td>70 °C 12hr</td>
<td>DMF</td>
<td>400\textsuperscript{b}</td>
<td>NEt\textsubscript{3}</td>
<td>1677</td>
<td>1.56</td>
<td></td>
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<tr>
<td>3\textsuperscript{d}</td>
<td>Cl</td>
<td>70 °C 12hr</td>
<td>DMSO</td>
<td>400\textsuperscript{b}</td>
<td>NEt\textsubscript{3}</td>
<td>1522</td>
<td>1.25</td>
<td></td>
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<tr>
<td>4\textsuperscript{d}</td>
<td>OH</td>
<td>160 °C 24hr</td>
<td>Mesitylene</td>
<td>400\textsuperscript{b}</td>
<td>SnCl\textsubscript{2}</td>
<td>2822</td>
<td>1.89</td>
<td></td>
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<tr>
<td>5\textsuperscript{d}</td>
<td>OH</td>
<td>160 °C 24hr</td>
<td>Mesitylene</td>
<td>400\textsuperscript{b}</td>
<td>H\textsubscript{2}SO\textsubscript{4}</td>
<td>2972</td>
<td>1.92</td>
<td></td>
</tr>
<tr>
<td>6\textsuperscript{d}</td>
<td>OH</td>
<td>160 °C 24hr</td>
<td>Mesitylene</td>
<td>400\textsuperscript{b}</td>
<td>H\textsubscript{2}SO\textsubscript{4}</td>
<td>2158</td>
<td>2.28</td>
<td></td>
</tr>
<tr>
<td>7\textsuperscript{a}</td>
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<td>160 °C 24hr</td>
<td>Neat</td>
<td>400\textsuperscript{b}</td>
<td>HCl</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>8\textsuperscript{a}</td>
<td>OH</td>
<td>160 °C 24hr</td>
<td>Neat</td>
<td>400\textsuperscript{b}</td>
<td>H\textsubscript{2}SO\textsubscript{4}</td>
<td>------</td>
<td>------</td>
<td>------</td>
</tr>
<tr>
<td>9\textsuperscript{a}</td>
<td>OH</td>
<td>160 °C 24hr</td>
<td>Mesitylene</td>
<td>200\textsuperscript{b}</td>
<td>H\textsubscript{2}SO\textsubscript{4}</td>
<td>1004</td>
<td>1.65</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Reactions performed under nitrogen atmosphere. \textsuperscript{b}PEG number-average molecular weight ($M_{\text{n}}$) in g/mol \textsuperscript{c}Determined by gel permeation chromatography (GPC) using polystyrene standards (PDI: polydispersity index). \textsuperscript{d}Performed in the presence of 3Å-molecular sieves.
Further polymerizations were carried out using bis-carboxylic acids (44a). These reaction conditions were based on dimer fatty acid and polyethylene glycol polyesterification research. Mesitylene was used as the solvent, and the reaction mixture was heated at reflux. The bis-carboxylic acid (Scheme 2.3, 44a) to PEG (Scheme 2.3, 45) ratio was changed to 1/1.2, and stannous chloride (SnCl₂) was used at 0.3 weight percent (wt %) to that of 44a. Using this method, $M_n$ was improved to ~2800 and PDI indicated the reaction was closer to a step-growth. In the presence of H₂SO₄, the molecular weight showed only slight improvement. Precise control of chain length was not obtained due to the inability to facilitate ester formation at high yields.

**Scheme 2.3.** Polymerization of PEG-PFCB copolymer (46) utilizing stannous chloride (SnCl₂) as a Lewis acid.
Synthesis and Characterization of PEG Macromonomer

The new TFVE functionalized PEG macromonomers (49a-e) are shown in Scheme 2.4. A macromonomer is a polymer or oligomer with a functional group capable of further polymerization.\textsuperscript{138} Macromonomers (49a-e) were synthesized from commercially available DEG (diethylene glycol) (49a), PEG with a $M_n$ of 200 g/mol (49b), PEG with a $M_n$ of 300 g/mol (49c), PEG with a $M_n$ of 400 g/mol (49d), and PEG with a $M_n$ of 600 g/mol (49e). All ethers were thoroughly dried before usage and are illustrated as 3.5a-e. Esterification was achieved under mild acidic conditions using 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) and dicyclohexylcarbodiimide (DCC) as a coupling agent at room temperature. This method is useful to functionalize thermally and chemically sensitive TFVE monomers, and was previously used in well defined mono-TFVE functionalized polyhedral oligomeric silesquioxanes (POSS) macromonomers.\textsuperscript{27}

![Scheme 2.4. Synthesis of PEG macromonomers 49a-e.](image)

After column chromatography, macromonomers (49a-e) were isolated in low to good yields (26 to 70 %). Monomers were characterized by $^1$H nuclear magnetic resonance (NMR), $^{19}$F NMR, attenuated total reflectance Fourier transform infrared
(ATR-FTIR), and elemental analysis. The $^1$H NMR spectrum of macromonomer 49d is shown in Figure 2.1. Doublets reported at 7.01 (D) and 8.01 (C) ppm are attributed to hydrogen atoms on the aromatic ring. Signals at 4.34 (A) and 3.70 (B) ppm are attributed to $\alpha$ and $\beta$ hydrogen atoms to the ester bond linkage. $^1$H NMR analysis agreed with molar ratios. All macromonomers (49a-e) were soluble in CHCl$_3$, acetone, DMSO, and methanol, but were insoluble in diethyl ether and hexane.

![Figure 2.1. $^1$H NMR spectrum (in CDCl$_3$) of trifluorovinyl aryl ether-functionalized PEG (49d).]
Polymerization of PEG Macromonomers

Step-growth polymerizations of macromonomers (49a-e) were performed neat by heating at 180 °C for 24 h (Scheme 3.4).

**Scheme 2.5.** Polymerization of macromonomers (49a-c).

The $^{19}$F NMR spectrum of 49d is shown in Figure 3.2 (top). The AMX pattern associated with vinyl fluorines of TFVE monomers can be observed at -118 ppm, -125 ppm, and -135 ppm. By using $^{19}$F NMR spectroscopy as a diagnostic tool during polymerization, the disappearance of vinyl fluorine signals can be observed and the appearance of PFCB absorptions can be seen as a multiplet from -127 to -132 ppm (Figure 3.2 bottom). The cis- and trans- stereoisomeric ratios for the 1,2-disubstituted PFCB rings ranged from 48 to 52 %, respectively, consistent with literature reports.\(^\text{16}\)
Figure 2.2. $^{19}$F NMR (in CDCl$_3$) overlay spectra of 49d (top) and 50d (bottom).
The homopolymers (50a-e) were contaminated with a small fraction of oligomeric product, as evidenced by gel permeation chromatography (GPC) analysis. After precipitation in hexane, the polymers were reanalyzed by GPC. The gel permeation chromatogram indicated a monomodal distribution as shown in Figure 2.3.

![Gel permeation chromatogram overlay of 50a-e using CHCl₃ as an eluent.](image)

**Figure 2.3.** Gel permeation chromatogram overlay of 50a-e using CHCl₃ as an eluent.

Number-average molecular weight ($M_n$) was between 4400 and 13400 g/mol, and polydispersity ($M_w/M_n$) between 3.0 and 4.2 was observed (Table 2.2). This large molecular weight distribution may indicate probable macrocyclization during
polymerization. no visible end groups are observed by $^{19}$F NMR for this relatively low $M_n$ mixture and also supports oligocyclization. As further confirmation, the hexane supernatant from the precipitation of 50d was concentrated and revealed a polymer with a $M_n$ of 1000, polydispersity of 1.1, and only the presence of PFCB by $^{19}$F NMR. GPC analysis and $^{19}$F NMR of hexane supernatant from polymerization 50d are shown in Appendices A and B, respectively. An analysis by $^{19}$F NMR revealed only the presence of PFCB and further confirmed the presence of macrocycles. While macrocycle formation in many step growth polymerizations are common, the inherent rigidity of the aryl groups in typical PFCB polymers apparently reduces this occurrence. The Flory-Huggins statistical model illustrated twenty three dipole conformers of PEG at high temperature.\(^{142}\)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n$(^{a}) (g/mol)</th>
<th>$M_w$(^{a}) (g/mol)</th>
<th>$M_w/M_n$(^{a})</th>
<th>$T_g$(ºC)(^{b})</th>
<th>$T_d$ºC N(_2) (air)(^{c})</th>
</tr>
</thead>
<tbody>
<tr>
<td>50a</td>
<td>9200</td>
<td>39000</td>
<td>4.2</td>
<td>52</td>
<td>338 (293)</td>
</tr>
<tr>
<td>50b</td>
<td>4400</td>
<td>13000</td>
<td>3.0</td>
<td>9</td>
<td>355 (320)</td>
</tr>
<tr>
<td>50c</td>
<td>13400</td>
<td>40000</td>
<td>3.0</td>
<td>-8</td>
<td>421 (262)</td>
</tr>
<tr>
<td>50d</td>
<td>6500</td>
<td>20000</td>
<td>3.0</td>
<td>-24</td>
<td>342 (233)</td>
</tr>
<tr>
<td>50e</td>
<td>5000</td>
<td>20000</td>
<td>4.0</td>
<td>-33</td>
<td>260 (207)</td>
</tr>
</tbody>
</table>

\(^{a}\)Determined by GPC in chloroform using polystyrene standards. \(^{b}\)Determined by DSC under nitrogen (10 ºC min\(^{-1}\)). \(^{c}\)TGA onset determined at 5 wt % lost (10 ºC/min).
Copolymerization of Random PEG PFCB Copolymers

Copolymerization of macromonomer (49d) with commercial 4,4’-bis(4-trifluorovinylxyloxy)biphenyl (51), 4,4’-bis(4-trifluorovinylxyloxy)biphenyl prepolymer (51b with a $M_n$ of 13000 g/mol), and 2,2-bis(4-trifluorovinylxyloxyphenyl) 1,1,1,3,3,3-hexafluoropropane (52) are shown in Scheme 2.6. Selected polymer properties are presented in Table 2.2. All step-growth polymerizations were performed at 160 °C in vacuum-sealed ampoules between 24-48 h neat or with mesitylene as needed to maintain stirring. Purification was achieved by dissolving the polymer in DMF and precipitation in water. Copolymerization of 49d with 51b produced a segmented copolymer with a $M_n$ of 17000 with a monomodal distribution ($M_w/M_n$) of 2.5. Copolymers exhibited the same excellent solubility as the homopolymers polymerized from 51, 51b, and 52; and no amphiphilic behavior was observed.

Scheme 2.6. Copolymerization of TFVE-functionalized PEG (50d) with 51, 51b, and 52.
The $^{19}$F NMR spectra for all copolymers showed multiplets representing PFCB formation from -127 and -132 ppm. Full conversion of trifluorovinyl ether end groups were observed for all polymers, except for **51-co-49d**, which displayed vinyl end groups associated with the **49d** macromonomer. Polymer composition can be determined by $^{19}$F NMR for copolymers polymerized with monomer **52** due to the presence of the hexafluoro-i-propylidine (6F) signal at -65 ppm. Compositions agreed well with feed ratios (Table 2.3). Analysis of the aromatic proton signals from $^1$H NMR spectra revealed that encheded units of **51**, **51b**, and **52** agreed with feed ratios provided in Table 2.3.

### Table 2.3. Copolymer properties and polymerization conditions.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>mol% $^b$</th>
<th>$M_n$ c (g/mol)</th>
<th>$M_w/M_n$ c</th>
<th>$T_g$ (°C)$^d$</th>
<th>$T_d$ /°C $^e$</th>
<th>Rxn. Time$^f$</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>51-co-49d</strong></td>
<td>50</td>
<td>11000</td>
<td>1.8</td>
<td>-14</td>
<td>417(228)</td>
<td>24 h</td>
<td>Mesitylene</td>
</tr>
<tr>
<td><strong>51-co2-49d</strong></td>
<td>55</td>
<td>12000</td>
<td>2.0</td>
<td>-1</td>
<td>421(241)</td>
<td>48 h</td>
<td>Mesitylene</td>
</tr>
<tr>
<td><strong>51-co3-49d</strong></td>
<td>55</td>
<td>11000</td>
<td>3.0</td>
<td>-5</td>
<td>426(240)</td>
<td>48 h</td>
<td>None</td>
</tr>
<tr>
<td><strong>52-co-49d</strong></td>
<td>50</td>
<td>11000</td>
<td>2.0</td>
<td>5</td>
<td>425(238)</td>
<td>24 h</td>
<td>Mesitylene</td>
</tr>
<tr>
<td><strong>52-co2-49d</strong></td>
<td>55</td>
<td>13000</td>
<td>2.0</td>
<td>9</td>
<td>422(240)</td>
<td>48 h</td>
<td>Mesitylene</td>
</tr>
<tr>
<td><strong>52-co3-49d</strong></td>
<td>55</td>
<td>9000</td>
<td>2.5</td>
<td>-5</td>
<td>425(307)</td>
<td>48 h</td>
<td>None</td>
</tr>
<tr>
<td><strong>51b$^a$-co-49d</strong></td>
<td>20.0</td>
<td>17000</td>
<td>2.5</td>
<td>51</td>
<td>480(339)</td>
<td>24 h</td>
<td>Mesitylene</td>
</tr>
</tbody>
</table>

$^a$**51b** is a prepolymer of **51** with a $M_n$ of 13000 g/mol. $^b$mol % of **51**, **51b**, or **52**. $^c$Determined by GPC in chloroform using polystyrene standards. $^d$Determined by differential scanning calorimetry (DSC) under nitrogen (10 °C/ min). $^e$Thermal gravimetric analysis (TGA) onset determined at 5% weight lost (10 °C/min). $^f$Performed at 160 °C.
Thermal Properties of (Co)polymers

As shown in Figure 2.4, the glass transition temperature ($T_g$s) of homopolymers (50a-e) were expectedly higher than the corresponding value for PEG (-72 to -68 °C) and ranged from -33 °C to 52 °C. All $T_g$ values correspond with the length of polyether enchainment (Table 2.1.).

![Graph showing DSC thermograms of homopolymers 50a-e.](image)

**Figure 2.4.** DSC thermograms of homopolymers 50a-e. All DSC samples were prepared under nitrogen and performed at 10 °C/min.
Selected thermal properties of the copolymers are shown in Table 2.2. The copolymers were polymerized using 49d to investigate the effect of the PEG linker with commercially available monomers (51 and 52) and prepolymer 51b. Copolymer 51-co-49d (50/50 mol %) resulted in a $T_g$ of -14 °C. An increase from 50 mol % to 55 mol % of 51 resulted in a higher $T_g$ of -1 °C (51-co2-49d). The increase was also observed for copolymers 52-co-49d and 52-co2-49d, but was not observed in 52-co3-49d, possibly due to lower molecular weight and higher polydispersity. The polymerization of 49d with 51b resulted in a lower $T_g$ (51 °C) as expected when compared to the $T_g$ of 51b homopolymer at 140 °C. Surprisingly, this segmented copolymer gave a single $T_g$ suggesting a homogeneous morphology. Surprisingly, this segmented copolymer gave a single $T_g$ suggesting a homogeneous morphology. DSC thermograms of copolymers can be seen in Appendix C.

Thermal stability was studied in nitrogen and air using thermo-gravimetric analysis (TGA), and the data were reported at 5% wt lost (Tables 2.1 and 2.2). Homopolymers 50a-e showed 5% weight loss between 207 and 320 °C in air and 260 and 421 °C in nitrogen. Copolymers showed a step-wise decomposition in nitrogen and air equal to their weight percentage of PEG to 51, 51b, and 51. A TGA comparison of PEG with a $M_n$ of 400 g/mol, 50d, 51-co2-49d, and 52-co2-49d in air is shown in Figure 2.5. PEG is prone to free-radical oxidative attack when heated in the presence of air. The more thermally labile PEG units undergo oxidation and bond cleavage in the presence of air. PEG degradation is discussed in Chapter 1. The PFCB linkage typically decomposes above 350 °C through homolytic bond dissociation at the oxygen-to-perfluorocyclobutyl
bond (see chapter 1). As expected, a significant increase in thermal stability was observed from PEG $M_n$ of 400 g/mol, to homopolymer Poly 3d, and copolymers 4-co2-3d and 5-co2-3d (Figure 2.5).

![Figure 2.5. TGA comparison of PEG with a $M_n$ of 400 g/mol, 50d, 51-co2-49d, and 52-co2-49d in air. All TGA samples were performed at 10 °C/min.](image-url)
Conclusion

New PEG macromonomers functionalized with aryl TFVE groups, and their polymers and copolymers, were synthesized. Thermal polymerization resulted in a new PFCB-PEG polymers and copolymers which exhibited moderate molecular weight, tailorable $T_g$s based on PEG composition, and increased thermal stability compared to PEG homopolymer. Copolymers were prepared from TFVE functionalized PEG (400 g/mol) macromonomer and commercially available monomers and prepolymer. Copolymers displayed lower $T_g$s compared to homopolymers prepared from commercial TFVE monomers. Surprisingly, the segmented copolymer prepared from PEG macromonomer and PFCB prepolymer ($M_n$ of 13000) gave a single $T_g$ suggesting a homogeneous morphology. These new semifluorinated polymers are soluble in most organic solvents and may have applications for new fluoroelastomers and hydrophilic/hydrophobic polymer blend compatibilizers.
CHAPTER 3
COMPATIBILIZATION OF PEG AND BIPHENYL VINYL ETHER (BP-PFCB) POLYMER BLENDS

Introduction

Polymer blends are a mixture of two or more macromolecular substances, generally polymers or copolymers. The advantage of preparing polymeric blends is the ability to combine polymeric properties in a cost-effective manner. Typically, polymeric blends can be prepared faster than a new monomer or (co)polymer with the desired properties can be synthesized. Blends are classified as miscible (co-continuous) or immiscible (dispersed) according to their homogeneity at the molecular level. Most polymers are immiscible and require some degree of compatibilization to create a co-continuous blend.Compatibilization is a process of modifying the interfacial properties, formation, and stabilization of the morphology of blend. Immiscibility of blends can result in a decrease in product performance and reliability. The result of compatibilization is the molecular miscibility of all components and facilitation of combined properties. Properly executing this compatibilization process is the key to the success of a co-continuous blend. Three main goals exist for the compatibilization process: (1) optimization of interfacial tension; (2) stabilization of morphology against high stresses during formation; and (3) enhancement of adhesion between the phases in the solid state.
Compatibilization is achieved by utilizing an array of methods: (1) end-group reactions; (2) compatible graft or block copolymer (most common); (3) ionic complexes; and (4) mechano-chemical blend. Addition of graft or block copolymers as compatibilizing agents has led to the commercialization of many polymeric blends. For example, blends of polyamide (PA) with polycarbonate of bisphenol-A (PC) were compatibilized by a polyesteramide currently called Dexcarb. To date, there is no successful strategy for the compatibilization of available commercial polymers with PFCB aryl ether polymers. In this chapter, 51-co2-49d copolymer, which was discussed in Chapter 2, is used to reduce interfacial tension and stabilize the morphology of blends of PEG ($M_n$ of 20000 g/mol) and 4,4’-bis(4-trifluorovinloxy)biphenyl perfluorocyclobutyl (BP-PFCB) polymer ($M_n$ of 20000 g/mol).
Reduction of Interfacial Tension

BP-PFCB polymer (\(M_n\) of 20000 g/mol) and PEG (\(M_n\) of 20000 g/mol) in a 1:1 weight ratio, with 1 to 5 wt percent of compatibilizer (51-co2-49d), were dissolved in chloroform and stirred overnight. Films were solution-casted and annealed in a vacuum at 120 °C for 30 minutes. All cross-sections were cryofractured with liquid nitrogen. Scanning electron microscope (SEM) was utilized to determine reduction of interfacial tension (Figure 3.1).
Addition of 51-co2-49d copolymer should reduce the interfacial tension between BP-PFCB polymer and PEG and polymeric adhesion interactions at the interface, which can be observed by SEM. In a compatibilized blend, a single macroscopically homogeneous morphology would be observed. Addition of the compatibilizer reduces dispersion of the two polymers and increases solubility. SEM images of PEG/BP-PFCB
polymer (1:1, w/w) showed a discontinuous phase and sphere morphology, Figure 3.1 (a). This morphology is common with incompatible polymer blends. The size of the dispersed phased is typically influenced by concentration during formation conditions. This sphere shape is caused by the affinity of the polymer for itself and by minimizing surface area to the other polymer. Measurements of their sizes showed a broad distribution from 7.0 to 23.0 μms. Further, 1, 2, and 3 wt % of 51-co2-49d showed little to no changes in morphology. However, at 4 wt % a clear reduction in sphere morphology was observed. Specifically, sphere size was smaller and more dispersed. At 5 wt %, no spheres were observed, making this amount of 51-co2-49d ideal for lowering the interfacial tension, Figure 3.1 (f). Of note, the majority of compatibilized polymer blends use between 0.5 and 2 wt % of the compatibilizing agent.
Surface morphology of blends was also observed by SEM. SEM images of 0 wt % and 5 wt % of **51-co2-49d** are shown in Figure 3.2. Sphere shape morphology was observed for 0 wt % of **51-co2-49d**, indicating incompatibility of PEG and BP-PFCB polymer at the surface. Addition of 5 wt % of **51-co2-49d** resulted in homogeneous surface morphology. These observation further confirms that 5 wt % of **51-co2-49d** is ideal for reduction of interfacial tension of 1:1 blend of PEG ($M_n$ of 20000 g/mol) and BP-PFCB polymer ($M_n$ of 20000 g/mol).

**Figure 3.2.** SEM images of PEG/BP-PFCB polymer (1:1, w/w) blend surface with the addition of **51-co2-49d** at: (a) 0 wt % and (b) 5 wt %.

Energy-Dispersive X-ray Spectroscopy (EDS) experiments were performed on compatibilized (5 wt % **51-co2-49d**) and uncompatibilized (0 wt % **51-co2-49d**) cross-sections of cryofractured films to determine atomic composition. SEM images and EDS results for uncompatibilized and compatibilized blends are shown Figure 3.3, Figure 3.4, and Figure 3.5. Figure 3.3 shows EDS results on a sphere of the uncompatibilized blend. The sphere displayed a fluorine carbon ratio comparable to that of BP-PFCB polymer. EDS experiments conducted on nonspheric domain showed little fluorine content and carbon hydrogen ratio similar to PEG. The EDS results from compatibilized blends,
Figure 4.5 right, identified a fluorine content consistent with 1:1 blend ratio of PEG ($M_n$ of 20000 g/mol) and BP-PFCB polymer ($M_n$ of 20000 g/mol).

Figure 3.3. SEM image (left) and EDS results (right) on a sphere of uncompatibilized (0 wt % of 51-co249d) PEG/BP-PFCB polymer (1:1, w/w) blend.

Figure 3.4. SEM image (left) and EDS results (right) on the continuous phase (nonspheric) of uncompatibilized (0 wt % of 51-co2-49d) PEG/ BP-PFCB polymer (1:1, w/w) blend.
Figure 3.5. SEM image (left) and EDS results (right) on a cross-section of compatibilized (5 wt % of 51-\textit{co2}-\textit{49d}) PEG/ BP-PFCB polymer (1:1, w/w) blend.
Blend Optical Properties

Optical properties of PFCB aryl ether polymers are discussed in Chapter 1. Addition of a chelating polymer, like PEG, could aid in the dispersion of nanocrystals to PFCB polymers. The change in optical properties of BPVE thin films as a function of the wt % of PEG was assessed and is illustrated in Figure 3.6. Addition of 5 wt % of 51-co2-49d to BP-PFCB polymer produced no measurable change in refractive index of BPVE. Refractive indices remained similar at 1 to 3 wt % of PEG. At 4 wt % of PEG the refractive index increased by 0.040. Finally, 5 wt % of PEG was determined to be the maximum amount of PEG before BP-PFCB polymer optical properties were compromised.

![Figure 3.6](image)

**Figure 3.6.** Effect of wt % of PEG ($M_n$ of 20000 g/mol) on BP-PFCB polymer ($M_n$ of 20000 g/mol) refractive indices. All samples contain 5 wt % of 51-co2-49d and were performed on a Metricon 2010 using prism coupled reflectometry.
Blend Thermal Properties

Thin films were then studied by dynamic scanning calorimetry (DSC) to determine miscibility and phase behavior at 0 to 5 wt % of PEG with 5 wt % of 51-co2-49d. Thermograms of all samples are shown in Figure 3.7. In a compatibilized blend the glass transition temperatures ($T_g$s) vary proportionally with blend composition. DSC studies showed lower single $T_g$ values, from 133 to 124 °C, compared to BP-PFCB polymer. One glass transition indicated compatibilization of BP-PFCB polymer and PEG. PEG melt transitions ($T_m$s) were present at 3, 4, and 5 wt % of PEG. The heat required to melt the crystalline phase increased from 1.593 J/g to 7.346 J/g for 3 to 5 wt % of PEG, respectively. DSC thermograms of the blend with 5 wt % of PEG and no compatibilizer are available in Appendix D.

**Figure 3.7.** DSC thermograms of (a) BP-PFCB polymer, (b) 51-co2-49d:PEG: BP-PFCB polymer (5:1:99; w/w/w), (c) 51-co2-49d:PEG: BP-PFCB polymer (5:2:98; w/w/w), (d) 51-co2-49d:PEG: BP-PFCB polymer (5:3:97; w/w/w), (e) 51-co2-49d:PEG: BP-PFCB polymer (5:4:96; w/w/w), and (f) 51-co2-49d:PEG: BP-PFCB polymer (5:5:95; w/w/w). All DSC samples were prepared under nitrogen and performed at 10 °C/min.
Blends with 10 and 20 wt % of PEG were prepared and studied by DSC and the resulting thermograms are shown in Figure 3.8. Thermograms prepared with 10 wt % PEG showed a single $T_g$ at 101 °C, while a thermogram of the blend prepared with 20 wt % of PEG exhibits two $T_g$s at 88 °C and 144 °C. These two $T_g$s indicate an immiscible blend at 20 wt % of PEG using 5 wt % of 51-co2-49d.

Figure 3.8. DSC thermograms of 51-co2-49d:PEG:BP-PFCB polymer at: (a) (5:10:90; w/w/w) and (b) (5:20:80; w/w/w). All DSC samples were prepared under nitrogen at 10 °C/min.
Conclusion

PEG/ BP-PFCB polymer blends were successfully compatibilized using 51-co2-49d as a compatibilizing agent. SEM images showed that PEG and BP-PFCB polymers at a 1:1 ratio are immiscible. Based on SEM images, 5 wt % 51-co2-49d was able to improve miscibility of 1:1 blend of PEG ($M_n$ of 20000 g/mol) to BP-PFCB polymer ($M_n$ of 20000 g/mol). EDS experiments further confirmed this result. 5 wt % of PEG and compatibilizer to BP-PFCB polymer resulted in a loss in optical clarity and a higher refractive index. DSC thermograms showed an increase in crystallization phase in the blends at 3, 4, and 5 wt % of PEG. DSC thermograms also showed a single glass transition at 10 wt % of PEG and two glass transitions at 20 wt % of PEG.
CHAPTER 4
CRYSTALLIZATION OF POLYETHYLENE GLYCOL (PEG) END-CAPPED
WITH AROMATIC TRIFLUOROVINYL ETHER (TFVE)

Introduction

Self-assembly is the process by which a disordered system becomes ordered. This process can either be described as static or dynamic. Static self-assembly occurs in an ordered state where the system is approaching equilibrium, thereby reducing its free energy. Dynamic self-assembly requires energy and is better described as induced organization. Both types are based on noncovalent interactions (van der Waals, electrostatic, hydrophobic, hydrogen bonding) that form micro- to nano-sized structures.

Self-assembly plays a significant role in nature, leading to a wide array of intricate structures such as cell membranes and folded proteins. Further, this process has a broad range of applications in materials science and nanotechnology. For example, self-assembled monolayers (SAMs) have been utilized in sensors and nanoelectronics. Additionally, ordered mesogenic units of copolymers, known as liquid crystals, have applications in optical displays.

PEGylation has been used as a successful strategy for drug delivery, crystallization of proteins, and implantable biotechnology. Covalent attachment of hydrophobic end groups to PEG has produced molecular building blocks for new nanostructures. The synthesis of these new amphiles requires a delicate balance of hydrophobicity and hydrophilicity. Molecular phase separation results in the self-
assembly of a wide variety of intricate supramolecular structures. In water these hydrophobic structures form flowerlike micelles. For example, ABA triblock copolymers of polyrotaxane led to pH-sensitive micelle structures in aqueous solution. Recently the synthesis of diblock copolymers of poly(ethylene glycol)-poly(ε-caprolactone) displayed new and exciting spherulitic crystallization properties. End-capping PEG with polyhedral oligosilesquioxane (POSS) resulted in new POSS-PEG telechelics. Hydrophobic-hydrophobic interactions of the POSS were observed by wide-angle x-ray diffraction (WAXD) and were determined to depend on PEG length.

In Chapter 3, a series of new telechelic macromonomers (TFVE-PEG$_n$-TFVE) were synthesized by end-capping low molecular weight PEG and DEG with aryl trifluorovinyl ether. These new dumbbell-shaped polymers exhibited phase separation of end-groups resulting in rod like crystals. This crystallization will be discussed.
Thermal properties of PEG End-capped with TFVE

Addition of hydrophobic end-groups as an AB or ABA type polymer is well known to cause phase separation.\textsuperscript{154} Low molecular weight liquid PEG should allow a flexible medium for phase transitions while also providing an environment to promote self-assembly. Figure 4.1 illustrates the structure description of macromonomers synthesized in Chapter 2.

![Structure of 49a-e](image)

**Figure 4.1.** Structure description of 49a-e were n = av of 2.0 to 13.2, respectively.

Thermal properties of 49a to 49e were studied by differential scanning calorimetry (DSC). All DSC thermograms were performed under nitrogen at a scan rate of 10 °C/min from -70 °C to 140 °C to prevent PFCB formation. All transitions were measured at the midpoint. The first cycle of DSC analysis for 49a to 49e is shown in Figure 4.2. Thermograms from the first cycle are shown in Figure 4.3 and indicate $T_g$s between -33 and -52 °C for 49a to 49e, respectively. Initial $T_g$s for DEG, and PEG $M_n$ of 200 g/mol, 300 g/mol, 400 g/mol, and 600 g/mol were from -76 to -68 °C.\textsuperscript{90} These higher glass transition temperatures indicates that functionalization of these glycols with TFVE decreased chain mobility. However, this result was expected due to introduction of a rigid
aromatic ring. Further analysis revealed $T_m$s at 84, 111, and 127 °C for 49c, 49d, and 49e, respectively; DSC analysis of 49a and 49b indicated no melt transitions.

**Figure 4.2.** DSC thermograms from -70 to 140 °C of (a) 49a ($n = \text{av of } 2.0$), (b) 49b ($n = \text{av of } 4.5$), (c) 49c ($n = \text{av of } 6.8$), (d) 49d ($n = \text{av of } 8.7$), and (e) 49e ($n = \text{av of } 13.2$). All DSC samples were prepared under nitrogen, at 10 °C/min, and were the first cycle.

These $T_m$s do not correspond with the well known melt temperature of PEG; further, low molecular weight PEG is amorphous. Results from DSC thermograms suggest that TFVE and PEG ratios played a critical role in crystallization. $T_m$s increased with increasing PEG constant, possibly due to a better aryl TFVE/PEG separation, and may be a result of different crystallization structures and domains. Further examination of DSC thermograms revealed no crystallization of telechelomers in the cooling cycle. A second heating cycle revealed little change in $T_g$s and no crystallization or melt transitions. Crystallization of PEG is well known as an exothermic transition at 45 °C by
DSC. Little PFCB formation occurred at these temperatures, but the formation increases at 150 °C and higher. Large amounts of PFCB formation would lower chain mobility and increase the $T_g$. Since the $T_g$s remained unchanged and no exothermic event indicative of PFCB dimerization was detected by DSC, very little formation occurred. The absence of crystallization indicates the self-assembly process was not thermally induced and may be driven by the thermodynamics of the telechelomers. Three cycles of 49e are shown in Figure 4.3 as an example. The compositions, glass transition temperatures ($T_g$s), and melt temperatures ($T_m$s) of all macromonomers are shown in Table 4.1.

![DSC thermograms](image)

**Figure 4.3.** DSC thermograms of 49e: (a) first heating, (b) second cooling, and (c) third heating cycles.
Table 4.1. Composition, $T_g$s, and $T_m$s of macromonomers (49a-e).

<table>
<thead>
<tr>
<th>Macromonomers</th>
<th>n$^a$</th>
<th>wt % of TFVE$^b$</th>
<th>wt % of PEG$^b$</th>
<th>TFVE/PEG$^b$</th>
<th>$T_m$(°C)$^c$</th>
<th>$T_g$(°C)$^d$</th>
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<tr>
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<td>2.0</td>
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<td>20.4</td>
<td>3.9</td>
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<td>-33</td>
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<td>66.7</td>
<td>33.3</td>
<td>2.0</td>
<td>---</td>
<td>-49</td>
</tr>
<tr>
<td>49c</td>
<td>6.8</td>
<td>56.2</td>
<td>43.8</td>
<td>1.3</td>
<td>84</td>
<td>-48</td>
</tr>
<tr>
<td>49d</td>
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<td>49.9</td>
<td>50.1</td>
<td>1.0</td>
<td>111</td>
<td>-52</td>
</tr>
<tr>
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<td>13.2</td>
<td>40.1</td>
<td>59.9</td>
<td>0.7</td>
<td>127</td>
<td>-52</td>
</tr>
</tbody>
</table>

$^a$Report unit based on $^1$H NMR spectrum of 49a to 49e (0.2% of calculated values).

$^b$Calculations based on integrations of $^1$H NMR spectrum of aromatic hydrogen atoms to ethylene oxide (EO) repeat units of 49a to 49e (0.2% of calculated values).

$^c$Determined by DSC thermograms of first heating cycle (performed under nitrogen at 10 °C/min).

$^d$Determined by DSC thermograms of second heating cycle (performed under nitrogen at 10 °C/min).
Wide-angle X-ray diffraction (WAXD) of Telechelomers

Wide-angle x-ray diffraction (WAXD) was used to determine characteristics of the crystalline phases. WAXD patterns for 49c, 49d, and 49e are presented in Figure 4.4.

Results from WAXD showed an intense sharp curve at $2\theta = 6.5^\circ$ ($\theta = $ diffraction angle). A less intense peak was also detected at $2\theta = 8.0^\circ$ for 49c and 49d. Atomic distance ($d$) in angstroms (Å) can be calculated by using Bragg’s Law (Eq. 4.1), $n\lambda = 2dsin \theta$ where $n$ is the order of reflection (1), $\lambda$ is the wavelength of the incident wave in angstroms (Å), and $\theta$ is the angle between the incident rays in degrees. Calculations showed that the initial peak ($2\theta = 6.5^\circ$) corresponded to 13.6 Å, and a less intense peak at $2\theta = 8.0^\circ$ corresponded to 11.04 Å. These two distances suggest a crystallization of two TFVE end groups and are in very good agreement with the calculated distances (~ 12.6 Å) already described in the literature. The diffraction pattern that is characteristic of PEG forming a 7/2 helix structure was not present. Instead, a broad phase with very
little order was detected at $2\theta = 15.0^\circ$ to $2\theta = 30.0^\circ$. This observation provides evidence that crystallization was driven by the hydrophobic-hydrophobic interactions of TFVE end groups and their incompatibility with low molecular weight PEG. WAXD performed at a lower angle, $2\theta = 0.8^\circ$ to $2\theta = 4.0^\circ$, showed no diffraction pattern (Figure 4.5), indicating no other ordered domains.

Figure 4.5. WAXD at $2\theta = 0.8^\circ$ to $2\theta = 4.0^\circ$ for: (a) 49c, (b) 49d, and (b) 49e.
To obtain surface topography scanning electron microscopy (SEM) was performed using an SEM with back-scattering (BSE) to contrast differences. SEM images of 49c, 49d, and 49e are shown in Figure 4.6. Images of 49c and 49d showed distinct dark phases at low magnification. At higher magnification distinctive rod-like crystals could be observed on the surface of these dark phases. These rods aggregated into a shape that, due to their varied orientations, resembled a spherulite. Research using low molecular weight liquid PEG end-capped with hydrophobic groups showed segregation of the hydrophobic groups because of more favorable interactions with the air. Based on SEM observations, WAXD patterns, and DSC data, the darker regions appeared to be a result of slow static self-assembly of the TFVE end group. Crystals (rod-shaped) were observed on the surface, but some of the polymer remained in an amorphous state.
Figure 4.6. SEM images at high and low magnification (mag). (a) 49c (low mag), (b) 49c (high mag), (c) 49d (low mag), (d) 49d (high mag), (e) 49e (low mag), and (f) 49e (high mag).
Conclusion

In this chapter, the synthesis, properties, and self-assembly of unique PEG end-capped telechelomers are described. These telechelomers exhibit a higher $T_g$s compared to corresponding ether. $49c$, $49d$, and $49e$ exhibited distinctive $T_m$s by DSC. Although $T_m$s were observed with a TFVE/PEG ratio of 1.3 and lower, no thermally-induced crystallization (dynamic crystallization) was observed by DSC. Crystalline phases were studied by WAXD and confirmed phase separation of TFVE end-groups and PEG, and crystallization of TFVE groups in a broad amorphous PEG phase. SEM images showed rod-like crystals located in dark phases of the polymers, evidence of the polymer at various stages of static self-assembly. These rods aggregated to form spherulite type structures. Further applications are currently being explored.
CHAPTER 5
STEP-GROWTH POLYMERIZATION OF AROMATIC TRIFLUOROVINYL ETHER WITH POLYETHYLENE GLYCOL

Introduction

Polyethylene glycol (PEG) is commonly utilized in segmented block copolymers because of its flexibility and reactive end-groups. For example, addition of PEG to aromatic isocyanates produced the well known elastomer Spandex. Addition of many hydrophobic segments to the polymer backbone causes phase separation and ultimately produced a new exciting, semi-crystalline copolymer. PEG copolymers containing poly(ε-caprolactone), poly(lactic acid), and poly(β-benzyl-L-aspartate) are notorious for their spherulite formation. Perfluorocyclobutyl (PFCB) aryl ethers are a unique class of semi-fluorinated polymer with many desirable properties, such as melt and solution processability. PFCB aryl ether polymers are commonly prepared without catalyst or condensate by thermal-initiated [2+2] cycloaddition of dual-functional trifluorovinyl ether (TFVE) monomers (Scheme 5.1). Synthesis, properties, and applications are reviewed in Chapter 1.
Scheme 5.1. Synthetic routes to semi-fluorinated aryl ether polymers from TFVE monomers by thermal [2+2] cyclodimerization to produce PFCB aryl ether polymers or nucleophilic addition to TFVE monomers to yield FAE polymers.

In addition to PFCB aryl ether polymers, step-growth nucleophilic addition to TFVE monomers produces a new class of fluoroethylene/vinylene aryl ether (FAE) polymers (Scheme 5.1). Using sodium hydride or cesium carbonate as a base, the backbone of the polymer can be selectively enriched with difluorovinylene (CF=CF) or hydrofluoroethylene (CHFCF₂). Functionalization of the aryl group has lead to the construction of difluorovinylene enriched telechelomers, proton electrolyte membranes (PEMs), polymeric chemical sensors, and polymer light emitting diodes (PLEDs), as reviewed in chapter 1.

Although the synthesis of new FAE and PFCB monomers has lead to a variety of new FAE an PFCB polymers for specific applications, little work has been done to include commercially available polymers and oligomers. PFCB aryl ether polymers contain an active TFVE end group capable of further polymerization by thermally induced [2+2] cycloaddition or FAE addition. Numerous polymers (e.g. PEG) with a reactive end group can be added to the PFCB backbone by simple FAE addition to the
TFVE end groups. To date no report describes the preparation of an amorphous PFCB random block copolymer by FAE addition to PFCB oligomers. This opportunity has led to the present study of FAE addition as a route to PFCB copolymers. In this chapter we have studied FAE addition of PEG to 4,4’-bis(4-trifluorovinyl oxy)biphenyl perfluorocyclobutyl (BP-PFCB) oligomers, an amorphous commercially-available prepolymer. The copolymer compositions and thermal properties were characterized by an assortment of techniques.
Polymerization of Segmented BP-PFCB PEG Copolymers

Fluoroethylene/vinylene alkyl/aryl ether (FAE) polymers were previously demonstrated on step-growth polymerization of aliphatic alcohols with fluoroolefins performed by Feiring and coworkers at Dupont.\textsuperscript{158} FAE polymers can be enriched with difluorovinylene (CF=CF) by employing an excess of sodium hydride as a base.\textsuperscript{19} F NMR spectroscopy reveals a 1:1 cis:trans isomeric ratio consistent with Feiring’s observations.\textsuperscript{158,159} However, the addition of catalytic amounts of cesium carbonate as a base results in a stereorandom hydrofluoroethylene (-CHFCF\textsubscript{2}-) linkage, due to the protonation of an anion intermediate (-CFCF\textsubscript{2}-) and the regeneration of cesium carbonate.

\begin{figure}
\begin{center}
\includegraphics[width=\textwidth]{Scheme5.2.png}
\end{center}
\end{figure}

\textbf{Scheme 5.2.} Polymerization of BP-PFCB PEG copolymers.
Polymerizations of copolymers are shown in Scheme 5.2. All polymerizations were achieved using estimated stoichiometric 1:1 amounts of hydroxytelechelic PEGs (54a-c) and 4,4’-bis(4-trifluorovinyloxy)biphenyl perfluorocyclobutyl (BP-PFCB) oligomers (53a-c). Polymerizations were preformed in flame-dried glassware at 80 °C using Cs₂CO₃ as a base in a minimum amount of DMF. All copolymers were precipitated in water to remove oligomers. 53c-co-54c required additional precipitation in hexanes after gel permeation chromatography (GPC) analysis. This additional precipitation was required due to the high PEG content (74.1 mol %) of this copolymer. All copolymers were isolated in moderate to high yields (74-94 %), were film-forming, and soluble in DMF, DMSO, DCM, chloroform, and acetone.

Initial polymerization was attempted using BP-PFCB oligomer 53a (Mₙ of 8000 g/mol) and PEG 54a (Mₙ of 600 g/mol). This approach resulted in a polymer with an increased Mₙ of 14000 g/mol with a moderately lower polydispersity (Mₘ/Mₙ) of 2.1 (Table 5.1). To further probe the scope of copolymerization and properties, PEGs with higher Mₙ of 1000 g/mol (54b) and 1500 g/mol (54c) were employed. Upon addition of 54b and 54c to oligomer 53a, an increase in Mₙ was observed along with a similar polydispersity. Copolymers 53b-co-54c and 53c-co-54c were prepared to study the effects of using lower molecular BP-PFCB oligomers, 53b (Mₙ of 4000 g/mol) and 54c (Mₙ of 2000 g/mol), on copolymerization and copolymer properties. GPC analysis revealed Mₙs of 9000 g/mol and 12000 g/mol for copolymers 53b-co-54c and 53c-co-54c, respectively. Polydispersities for these copolymers were similar to step-growth polymerization values and corresponded to literature values (Table 5.1).⁶⁹,¹⁴¹
<table>
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<tr>
<th>Polymer</th>
<th>Calcd mol % of PEG&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Found mol % of PEG&lt;sup&gt;b&lt;/sup&gt;</th>
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<th>$M_w$&lt;sup&gt;c&lt;/sup&gt; (g/mol)</th>
<th>$M_w$/$M_n$&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Calcd $T_g$°C&lt;sup&gt;d&lt;/sup&gt;</th>
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<td>-26</td>
</tr>
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</table>

<sup>a</sup>Calculations based $M_n$ of BP-PFCB oligomer and PEG.
<sup>b</sup>Measured by $^1$H NMR using the ratio of aryl to PEG repeat unit.
<sup>c</sup>Determined by gel permeation chromatography (GPC) using polystyrene standards.
<sup>d</sup>Calculated using the Fox equation.
<sup>e</sup>Determined by DSC under nitrogen (10 °C/min).
Segmented BP-PFCB PEG Copolymer Characterization and Composition

After isolation, polymers were characterized by attenuated total reflectance Fourier transform infrared (ATR-FTIR), $^{19}$F nuclear magnetic resonance (NMR), and $^1$H NMR. The $^1$H NMR spectrum of 53c-co-54c in acetone-$d_6$ is shown in Figure 5.1. $^1$H NMR illustrates signals at 7.20 to 7.42 (Figure 5.1, B) and 7.59 to 7.82 (Figure 5.1, A) ppm, which correlate with aromatic hydrogen atoms of BP-PFCB aryl ether oligomers (53c). Signals of hydrogen atoms associated with hydrofluoroethylene (CHFCF$_2$) (Figure 5.1, C) and revealed no stereoselectivity upon addition of PEG. Distinctive peaks at 4.14 to 4.24 (Figure 5.1, D) and 3.72 to 3.85 (Figure 5.1, E) ppm are attributed to $\alpha$ and $\beta$ hydrogen atoms of –CH$_2$-CH$_2$-O- to the hydrofluoroethylene, respectively. All other hydrogen atoms of (–CH$_2$-CH$_2$-O–)$_n$ repeat units are shown as a multiplet at 3.47 to 3.71 ppm (Figure 5.1, F). $^1$H NMR integration of signals corresponding to hydrogen atoms (–CH$_2$-CH$_2$-O–)$_n$ of PEG units and to the aromatics hydrogen atoms of BP-PFCB aryl ethers were utilized to determine the compositions of all copolymers. Compositions of all copolymers were determined and are shown in mol % and wt % in Tables 5.1 and 5.2, respectively.
Figure 5.1. $^1$H NMR spectrum of 53c-co-54c in acetone-$d_6$. 
F$^{19}$ NMR spectrum of 53c-co-54c in acetone-$d_6$ is shown in Figure 5.2. Signals of fluorine atoms associated with BP-PFCB linkages were observed as a multiplet between -126.7 and -132.4 ppm. Hydrofluoroethylene fluorine atom signals (CHFCF$_2$) were shown as a singlet at -84.2 ppm (s, CHFCF$_2$) and a doublet at -142.5 ppm (d, $J = 57.4$, CHFCF$_2$) ppm. Integration of a hydrofluoroethylene moiety to PFCB is not useful in revealing the copolymer composition because the addition product can be of a variety of PEG molecular distributions. F$^{19}$ NMR also revealed the consumption of the TFVE end-group.

All polymers were studied by contact ATR-FTIR spectroscopy. Analysis revealed the presence of C-O-C in PEG at 1109 cm$^{-1}$. Aryl C-C stretching was present at 1606 and 1495 cm$^{-1}$. Peaks at 1198 and 821 cm$^{-1}$ confirmed the existence of a PFCB ring. A CF$_2$ signal associated with hydrofluoroethylene (CHFCF$_2$) was seen at 723 cm$^{-1}$.

**Figure 5.2.** $^{19}$F NMR spectrum of 53c-co-54c in Acetone-$d_6$. 
**Thermal Properties of BP-PFCB PEG Copolymers**

All glass transition temperatures ($T_g$s) were obtained from DSC analysis of the second heating cycle at 10 °C/min and are shown in Figure 5.3. All copolymers exhibited a single $T_g$ and no crystallization transition ($T_c$) or melt transition ($T_m$) was detected. This result is notable due to the known semi-crystalline nature of 54b (PEG with a $M_n$ of 1000 g/mol and a $T_m$ at 65 °C) and 54c (PEG with a $M_n$ of 1500 g/mol and a $T_m$ at 65 °C). This finding is a clear indication that addition to BP-PFCB oligomers has resulted in an amorphous copolymer. Copolymer $T_g$ values ranged from -25 to 127 °C for 53c-co-54c to 53a-co-54c, respectively. $T_g$s showed an increase with mol % PFCB aryl ether content and a decrease with mol % PEG content (Table 5.1).

![DSC thermograms of BP-PFCB PEG copolymers at 10 °C/min and were prepared under nitrogen.](image)

**Figure 5.3.** DSC thermograms of BP-PFCB PEG copolymers at 10 °C/min and were prepared under nitrogen.
The Fox equation (Eq. 5.1) was used to study theoretical copolymers $T_g$ values compared to experimental values.\textsuperscript{160,161}

\begin{equation}
\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}
\end{equation}

As shown in Eq. 5.1, $T_g$ is the theoretical glass transition temperature of the copolymer. $T_{g1}$ and $w_1$ are the glass transition temperature and the weight fraction of the PEG homopolymers (54a-c), respectively. $T_{g2}$ and $w_2$ are the glass transition temperature and the weight fraction of the BP-PFCB homopolymers (53a-c), respectively. All calculated theoretical $T_g$s are reported in Table 5.1. Figure 5.4 shows theoretical and experimental $T_g$ values as a function of PEG and BP-PFCB oligomer weight fraction.
Results showed that the experimental $T_g$ values do not always fit values calculated from the Fox equation, but they are agreeable at the lowest and highest PEG weight fractions of copolymers (53a-co-54c and 53c-co-54c have $T_g$s within 2 °C of theoretical values). Other copolymers showed a much lower value than the Fox equation predicts. The Fox equation is considered a display of uniform mixture and reflects randomness in a two-component mixture. Deviations from the Fox equation are common.$^{160,161}$

Thermal degradation ($T_d$) of the copolymers and BP-PFCB homopolymers was studied by thermal gravimetric analysis (TGA). $T_d$ values are reported in Table 5.2 at the
initial weight loss and weight loss %. All copolymers exhibited a two step degradation in nitrogen and air. An overlay of TGA thermograms of 53c-co-54c and BP-PFCB oligomer (53c) in nitrogen and air is displayed as Figure 5.5. $T_d$ temperatures ranged from 343 to 360 °C for copolymers in air and from 333 to 343 °C for copolymers in nitrogen, in all cases lower than the initial $T_d$ of PFCB aryl ether homopolymers (53a-e). Initial weight loss corresponds closely to PEG weight percent and therefore is attributed to degradation of PEG. Degradation temperatures and mechanisms of degradation have been fully studied for both homopolymers. Further, PEG is known to undergo autoxidation in the presence of air. BP-PFCB oligomers initially exhibit homolytic bond dissociation at the ether linkage resulting in the formation of hexafluorocyclobutene and polymer chain scission. The observed increase in initial degradation of PEG can be attributed to the presence of BP-PFCB in the copolymer.

![Figure 5.5. TGA thermogram overlay of 53c-co-54c and BP-PFCB oligomer (53c) in nitrogen and air. All TGA samples were perform under at 10 °C/min.](image-url)
<table>
<thead>
<tr>
<th>Polymer</th>
<th>Wt % PEG&lt;sup&gt;a&lt;/sup&gt;</th>
<th>in N&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Initial weight loss (%)</th>
<th>in air</th>
<th>Initial weight loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>53a</td>
<td>---</td>
<td>477</td>
<td>---</td>
<td>473</td>
<td>---</td>
</tr>
<tr>
<td>53b</td>
<td>---</td>
<td>471</td>
<td>---</td>
<td>458</td>
<td>---</td>
</tr>
<tr>
<td>53c</td>
<td>---</td>
<td>456</td>
<td>---</td>
<td>441</td>
<td>---</td>
</tr>
<tr>
<td>53a-co-54a</td>
<td>1.3</td>
<td>360, 465</td>
<td>1.5</td>
<td>335, 455</td>
<td>1.7</td>
</tr>
<tr>
<td>53a-co-54b</td>
<td>3.6</td>
<td>343, 465</td>
<td>4.0</td>
<td>340, 462</td>
<td>4.7</td>
</tr>
<tr>
<td>53a-co-54c</td>
<td>1.0</td>
<td>368, 460</td>
<td>1.2</td>
<td>343, 454</td>
<td>1.4</td>
</tr>
<tr>
<td>53b-co-54c</td>
<td>21.5</td>
<td>360, 473</td>
<td>19.1</td>
<td>321, 461</td>
<td>20.0</td>
</tr>
<tr>
<td>53c-co-54c</td>
<td>68.2</td>
<td>364, 470</td>
<td>50.1</td>
<td>333, 453</td>
<td>52.7</td>
</tr>
</tbody>
</table>

<sup>a</sup>Measured by 'H NMR using the ratio of aryl to PEG repeat unit.
<sup>b</sup>Determined by TGA at 10 °C/min. Initial refers to onset of degradation and second refers to second onset of degradation.
Conclusion

Semifluorinated aryl ether polymers segmented with PEG were successfully prepared from commercially available PEG and BP-PFCB oligomers. Copolymers were synthesized by nucleophilic addition to TFVE end groups of BP-PFCB aryl ether oligomers to form a new hydrofluoroethylene aryl ether (FAE) linkage. GPC results revealed an increase in molecular weight compared to the BP-PFCB corresponding oligomers. DSC thermograms showed that copolymers exhibited no melting transition ($T_m$), no crystallization transition ($T_c$), and a copolymer specific glass transition temperature ($T_g$). Comparisons of theoretical $T_g$s, calculated from the Fox equation, and experimental $T_g$s showed that values were agreeable at the lowest and highest PEG weight fractions. TGA thermograms exhibited two-step decompositions that closely corresponded with PEG and BP-PFCB aryl ether weight percent in the copolymer. Utilizing this method, commercial polymers with adequate functionally can be added by simple FAE addition to PFCB aryl ether oligomers, and a variety of segmented PFCB aryl ether copolymers can be prepared for a variety of applications.
CHAPTER 6
PREPARATION OF SEMIFLUORINATED POLYARYL (ETHER)S FROM
WELL DEFINED AROMATIC TRIFLOROVINYL ETHERS AND DIOLS

Introduction

Poly (aryl ether)s (PAEs) attained a lot of commercial success due to their high thermal stability, hydrolytic stability, and superior compatibility with commodity polymers such as polystyrene. This led to a multitude of engineered plastics such as poly(phenylene oxides) (PPOs), poly(ether ether ketone)s (PEEKs), and poly(ether sulfones) (PESs). Despite these attractive features, PPOs have a high melt viscosity and high melt temperatures \( T_m \), which leads to oxidation and gelation during processing.\(^{138,162}\) Although there are few reports on improving the processability of these materials, recent structural modifications have led to solution processable polymers with high glass transition temperatures and excellent thermal stability. For example, PAEs containing naphthyl moieties produced an amorphous polymer that was soluble in common organic solvents.\(^{163}\)

Perfluoropolyethers (PFPEs) are an interesting commercial class of fluorinated materials. PFPEs are viscous liquids at room temperature and are well known for their high thermal and chemical stability, low coefficient of friction, and low glass transition temperatures \( T_g \). These unique properties have led to specialized applications in biomedical devices, lubricants, and low dielectric fluids. Many commercial PFPEs are currently available under the names Fomblin Z, Demnum, and Krytox.\(^{164}\)
Introduction of a semifluorinated ether segment to PAEs should render them solution processable. Recently synthesized semifluorinated poly(aryl ethers) from 9,10-bis-(4-fluoro-3-trifluoromethylphenyl)anthracene and 2,7-bis-(4-fluoro-3-trifluoromethylphenyl)fluorene monomers showed high thermal stability, high glass temperatures, and were solution processable. Feiring and coworkers developed a facile step-growth polymerization using an aliphatic alcohol addition to fluoroolefins that produced an alternative route to PFPEs. This previous work by step-growth polymerization of bisphenols and aromatic trifluorovinyl ethers (TFVE) has led to processable, thermally stable, and optically transparent semifluorinated polyaryl ethers (PAEs) polymers. These polymers have been tailored for proton electrolyte membranes (PEMs) and ion sensing. These polymers and applications are discussed in chapter 1. In this chapter, semifluorinated polyaryl ethers (PAEs) with were prepared and investigated as thermally stable and solution processible polymers (Figure 6.1, 57a-e).

Figure 6.1. Structural description of semifluorinated polyaryl ethers (PAEs) prepared from well defined from 4,4'-bis(4-trifluorovinyloxy)biphenyl and diols monomers.
**Polymerization**

Step-growth polymerization of polyaryl (ether)s (PAEs) was achieved using commercially available diols (Scheme 6.1, 56a-d) and 4,4’-bis(4-trifluorovinloxy)biphenyl (Scheme 6.1, 55) in 1:1 molar ratios. Polymerization was performed using 50 mol % anhydrous cesium carbonate and anhydrous DMF at 80 ºC for 24 h. All copolymers were precipitated in water and washed with hexanes. Polymers were dried by high vacuum and isolated as a white powder (57a) to a white semi-solid (57d) in moderate yields from 73 to 89 %.

Gel permeation chromatography (GPC) revealed number average molecular weights ($M_n$) from 9000 to 13000 g/mol and polydispersities ($M_w/M_n$) from 2.16 to 1.67. All polymers were soluble in DMF, DMSO, and THF; polymers 57c and 57d showed additional solubility in DCM, chloroform, acetone, and methanol. All polymers were film-forming by solution casting.

![Diagram](attachment:image.png)

**Scheme 6.1.** Preparation of semfluorinated polyaryl ethers (PAEs).

Optimization of polymerization was achieved using ethylene glycol (56a) and 4,4’-bis(4-trifluorovinyloxy)biphenyl (55) as a model compound. Initial polymerizations had low yields and higher polymer dispersities ($M_w/M_n$) by GPC analysis. Further drying of 56a led to higher yield and lower polydispersities. Polymerization conditions were
further improved by varying amounts of DMF to maximize the $M_n$ and lower oligomeric product. Figure 6.2 displays gel permeation chromatograms (GPCs) using 0.2 wt %, 0.1 wt %, and 0.08 wt % of DMF to 4,4'‐bis(4‐trifluorovinyl oxy)biphenyl (55) and ethylene glycol (56a) monomers. GPC analysis showed that an increase in DMF led to a bimodal distribution and more oligomeric product as expected. All other polymers were performed using a minimum amount of DMF during polymerization.

**Figure 6.2.** Gel permeation chromatogram of polymer (57a) prepared in: (a) 0.2 wt %, (b) 0.1 wt %, and (c) 0.08 wt % of DMF to 4,4'‐bis(4‐trifluorovinyl oxy)biphenyl (55) and ethylene glycol (56a) monomers.
Characterization

All polymers were characterized by attenuated total reflectance Fourier transform infrared (ATR-FTIR), $^{19}$F nuclear magnetic resonance (NMR), and $^1$H NMR. $^1$H NMR spectrum of 7.7 in DMSO-$d_6$ is shown in Figure 7.3. Aromatic protons are illustrated as doublets at 7.19 to 7.22 (Figure 6.3, A) and 7.66 to 7.63 (Figure 6.3, B). Doublet at 6.50 ppm (Figure 6.3, C) are from hydrofluoroethylene (CHFCF$_2$) proton. Ether protons $\alpha$ and $\beta$ to hydrofluoroethylene are shown as 4.11-4.12 (Figure 6.3, D) and 3.65-3.71 (Figure 6.3, E) ppm, respectively. All other protons of ($-\text{CH}_2-\text{CH}_2-\text{O}-)_n$ are seen as a multiplet at 3.48 to 3.64 ppm. Integrations ratio of aromatic protons to protons diols agree with 1:1 feed ratios for all monomers.

Figure 6.3. $^1$H NMR spectrum of 57b in DMSO-$d_6$. 
$^{19}$F NMR spectrum of 57b in DMSO-$d_6$ is shown as Figure 6.4. Hydrofluoroethylene fluorines can be seen as a AB pattern at 88.3 and 87.8 ($J = 141.5$ Hz, CHF$CF_2$) ppm and as a doublet at -141.0 ppm ($J = 56.6$, CHF$CF_2$). $^{19}$F NMR spectrum also revealed the slight appearance of AMX pattern associated 4,4’-bis(4-trifluorovinyl oxy)biphenyl monomer (55), indicating high consumption of trifluorovinyl ether (TFVE). This method is known to produce low amounts of 1,2-difluoroethylene (CF=CF) from the elimination of sodium fluoride. The absence of CF=CF may be an induction of the presence of water inherently associated with most diols.

Figure 6.4. F$^{19}$ NMR spectrum of 57b in DMSO-$d_6$. 
Thermal Properties

Table 6.1 shows differential scanning calorimetry (DSC) analysis of polymers 57a to 57d. Figure 6.5 shows thermograms of polymers 57a to 57d. Glass transition temperatures (T_g)s for amorphous, semifluorinated PAEs were from 11 to -1 °C. Although an increase of ether units from three to four led to a decrease in T_g, this trend was not exhibited in 57a to 57d. Polymer 57a exhibited no T_g by initial DSC analysis. To observe the T_g of 57a a quench-cooling method was applied. Polymer 57a was heated to 200 °C in a DSC pan, removed, and quickly add to liquid nitrogen to maximize amorphous structure and slow crystallization. The quench-cooling method was unsuccessful in obtaining a T_g value. Thermograms obtained from this analysis can be seen in Figure 6.6.

Polymer 57a exhibited a melt transition temperature (T_m) of 189 °C by DSC. No thermally induced crystallization was observed on the heating cycle of 57a, but upon cooling a crystallization transition (T_c) was observed at 185 °C. 57b displayed a T_c at 27 °C and a T_m at 63 °C. Thermograms of all other polymers demonstrated no T_ms or T_cs. Increasing the ether units resulted in less crystalline polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>x</th>
<th>M_n</th>
<th>M_w/M_n</th>
<th>T_g(°C)</th>
<th>T_m(°C)</th>
<th>T_c(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>57a</td>
<td>1</td>
<td>9000</td>
<td>2.2</td>
<td>---</td>
<td>189</td>
<td>185</td>
</tr>
<tr>
<td>57b</td>
<td>2</td>
<td>10000</td>
<td>1.7</td>
<td>11</td>
<td>63</td>
<td>27</td>
</tr>
<tr>
<td>57c</td>
<td>3</td>
<td>12000</td>
<td>1.6</td>
<td>11</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>57d</td>
<td>4</td>
<td>13000</td>
<td>1.7</td>
<td>-1</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>

^aGPC in DMF using polystyrene standards.
^bDetermined by DSC under nitrogen (10 °C/min).
Figure 6.5. DSC thermograms of (a) 57a, (b) 57b, (c) 57c, and (d) 57d performed at 10 °C/min under nitrogen.

Figure 6.6. DSC thermograms of 57a before (a) quench cool, after (b) quench cool, and after (c) second quench cool.
Degradation Analysis

Polymer thermal stability was studied by thermal gravimetric analysis (TGA) in air and nitrogen. Initial and second thermal degradation ($T_d$) values are reported in Table 6.2. All polymers displayed a two step weight loss in air by TGA analysis and a one step weight loss in nitrogen. Polymer 57a has an onset of degradation 363 °C in nitrogen. In air 57a has an onset of degradation of 320 °C for initial weight loss followed by a second weight loss at 452 °C. Initial degradation in this case corresponds to the weight percent of semifluorinated ether unit (SFE). Polymers 57b to 57d showed an initial weight loss in air that closely corresponds to thermal degradation of SFE and then degradation of aromatic portion. An overlay of TGA thermograms of 57a and 57d in nitrogen and air can be seen in Figure 6.7. Semifluorinated polyethers are well known for thermal stability due to the high bond dissociation energy of the C-F bond (116 kcal/mol) compared to the bond dissociation energy of the C-H bond (98 kcal/mol). Polymers still degrade by autoxidation of ether units in air, which explains the two step weight loss of polymers 57a-d in air and is consistent with polymers discussed in previous chapters.

Table 6.2. Summary of thermal decomposition of polymers.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Wt % SFE$^a$</th>
<th>$T_d$(°C)$^b$</th>
<th>Initial weight loss(%)</th>
<th>$T_d$(°C)$^b$</th>
<th>Initial weight loss(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>in N₂</td>
<td>in air</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>57a</td>
<td>62</td>
<td>363, ---</td>
<td>---</td>
<td>320,452</td>
<td>62</td>
</tr>
<tr>
<td>57b</td>
<td>66</td>
<td>334, ---</td>
<td>---</td>
<td>333,475</td>
<td>61</td>
</tr>
<tr>
<td>57c</td>
<td>70</td>
<td>325, ---</td>
<td>---</td>
<td>313,450</td>
<td>64</td>
</tr>
<tr>
<td>57d</td>
<td>72</td>
<td>326, ---</td>
<td>---</td>
<td>316,441</td>
<td>67</td>
</tr>
</tbody>
</table>

$^a$Semifluorinated ether (SFE) was measured by $^1$H NMR using the ratio of aryl to ether repeat unit.

$^b$Determined by TGA at 10 °C/min. Initial refers to onset of degradation and second refers to second onset of degradation.
Figure 6.7. TGA thermogram overlay of 57a and 57d in nitrogen and air.
**Surface Morphology**

Surface morphology of polymers 57a and 57b were studied by atomic force microscopy (AFM) due to their crystalline nature. AFM phase and height images are shown in Figure 6.8 and Figure 6.9, respectively. Needle-like crystallites of 50 to 150 nm were observed for 57a and 57b. This formation may be due to crystallization of hard-segment. Needle or ribbon morphologies are commonly reported with many segmented polyurethanes and poly (ether amides).\textsuperscript{166-168} Crystallization of these polymers are reported to be due to aggregation of the hard chain segments as suspect is occurring with these new semifluorinated PAEs.

![AFM phase images of solution cast films of 57a (left) and 57b (right).](image)

**Figure 6.8.** AFM phase images of solution cast films of 57a (left) and 57b (right).
Figure 6.9. AFM height images of solution cast films of 57a (left) and 57b (right).
Conclusion

Semifluorinated polyaryl ethers (PAEs) were successfully prepared by nucleophilic addition of commercial glycols to \(4,4'\)-bis(4-trifluorovinyloxy)biphenyl to produce a novel polymer containing a new fluoroethylene alkyl bond. DSC thermograms showed that crystallinity dramatically depends on the diol utilized during polymerization and in one case a high melting point of 189 °C were obtained. In addition, glass transition temperatures from 11 to -1 °C were observed. TGA analysis displayed a step-wise degradation corresponding to less thermally stable ether units and then the more stable aromatic. AFM phase and height images showed needle-like crystalline morphologies.
CHAPTER 7
EXPERIMENTAL DETAILS

Materials

Chemicals and solvents were obtained from Sigma-Aldrich. THF and Et₂O were dried with a Pure-Solv solvent purification system. All other solvents dried according to well established procedures unless otherwise noted. 169 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) was synthesized according to published method. 170 Ethylene glycol (56a), diethylene glycol (48a or 56b), triethylene glycol (56c), tetraethylene glycol (56d), PEG $M_n$ of 200 g/mol (48b), PEG $M_n$ of 300 g/mol (48c), PEG $M_n$ of 400 g/mol (48d) and PEG $M_n$ of 600 g/mol (48e or 54a) was stirred for 30 minutes in magnesium sulfate. The suspensions were filtered using 0.45 μm filter, and further dried at 65 °C under high vacuum for 6 h. Diols were then stored with 3Å molecular sieves. PEG $M_n$ of 1,000 g/mol (54b), $M_n$ of 1,500 g/mol (54c), and $M_n$ of 20,000 g/mol were dried under high vacuum for 6 h before usage. All reactions were carried out in flamed dried glassware under a constant nitrogen purge. All polymers were dried at 65 °C under high vacuum before any analysis.

4,4’-((1,2,3,3,4,4-Hexafluorocyclobutane-1,2-diyldibis(oxy))-dibenzoic acid (44a), 4,4’-((1,2,3,3,4,4-Hexafluorocyclobutane-1,2-diyldibis(oxy))-dibenzoyl chloride (44b), 4-(1,2,2-trifluorovinyl)benzoic acid (47), 4,4’-bis(4-trifluorovinyl)benzoic acid (44c), 4,4’-bis(4-trifluorovinyl)benzoic acid (45), 4,4’-bis(4-trifluorovinyl)benzoic acid (46), 4,4’-bis(4-trifluorovinyl)benzoic acid (47), 4,4’-bis(4-trifluorovinyl)benzoic acid (48), 4,4’-bis(4-trifluorovinyl)benzoic acid (49), 4,4’-bis(4-trifluorovinyl)benzoic acid (50), 4,4’-bis(4-trifluorovinyl)benzoic acid (51), 4,4’-bis(4-trifluorovinyl)benzoic acid (52), 4,4’-bis(4-trifluorovinyl)benzoic acid (53), 4,4’-bis(4-trifluorovinyl)benzoic acid (54), 4,4’-bis(4-trifluorovinyl)benzoic acid (55), or 2,2-bis(4-
trifluorovinyloxyphenyl)-1,1,1,3,3,3-hexafluoropropane (52) were donated by Tetramer Technologies, L.L.C. and is commercially available through Oakwood Chemicals, Inc.

**Calculated Section**

*Fox Equation*

Glass transition temperatures ($T_g$s) of all copolymers were studied using the Fox equation (Eq. 1).

$$\text{Eq. 6.1} \quad \frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

Where $T_g$ is the theoretical glass transition temperature of the copolymer, $T_{g1}$ and $w_1$ are the glass transition temperature and the weight fraction of the PEG homopolymers, and $T_{g2}$ and $w_2$ are the glass transition temperature and the weight fraction of the PFCB homopolymers. All glass transition temperatures are reported in table 6.1.

*Bragg’s Law*

Atomic lattice were calculated by Bragg’s Law:

$$\text{Eq. 5.1} \quad n\lambda = 2d\sin \theta$$

Where $n$ is the order of reflection (1), $\lambda$ is the wavelength of incident wave in angstroms (Å), and $\theta$ is the angle between the incident ray in degrees.
Instrumentation

Nuclear Magnetic Resonance (NMR) Spectrometry

$^1$H and $^{19}$F Nuclear magnetic resonance (NMR) spectrums from chapter 7 were obtained from a Bruker 300. $^1$H and $^{19}$F Nuclear magnetic resonance (NMR) spectrums from all other chapters were obtained from a JOEL Eclipse+ 300. All spectrums were carbon decoupled. Chloroform-$d$ and Acetone-$d_6$ were used as solvent and all chemical shift are reported in parts per million (δ ppm). $^1$H and $^{19}$F NMR were internally referenced to tetramethylsilane and CFCl₃, respectively.

Infrared (IR) Spectroscopy

All IR spectrums were acquired neat from an attenuated total reflectance fourier transform infrared (ATR-FTIR) using a ThermoNicolet Magna IR 550 FTIR spectrophotometer.

Combustion Analysis

Combustion analysis (C, O, and F) were obtained from Atlantic Microlab, Inc. in Norcross, Georgia. Values are with 4 % of average calculated values.

Chromatography

All gel permeation chromatography (GPC) data from chapter 7 were performed using a Waters 2690 alliance system equipped using DMF containing 0.01% of lithium bromide.
Waters 2690 Alliance system were equipped with a Waters 2998 Photodiode Array Detector, Mixed-I low molecular weight and Mixed-I high molecular weight columns at 35 °C. Columns were obtained from viscotek. All data showed a monodispersed distribution. All polymers were compared to polystyrene standards.

All other gel permeation chromatography (GPC) data were performed in chloroform using a Waters 2690 Alliance system equipped with a 2410 refractive index, Mixed-D, and Mixed-E columns. Columns were obtained from polymer laboratories. All experiments were carried out at 35 °C. All data showed a monodispersed distribution and were compared to polystyrene standards.

**Thermal Analysis (DSC and TGA)**

Differential scanning calorimetry (DSC) analysis and thermal gravimetric analysis (TGA) were executed using a TA Q1000 instrument and Mettler-Toledo 851 instrument, respectively. The DSC were calibrated with indium standards. All samples were prepared under nitrogen. All crystallization temperatures ($T_c$s) were measured the maximum exothermic peak. Melting temperatures ($T_m$s) were taken at their endothermic minimum. Glass transition temperatures ($T_g$s) were determined from second heating cycle using DSC analysis rate of 10 °C/min, at the half-height of the heat capacity jump of the glass transitions. Quench-cool were performed by heating the 7.6 in a DSC pan to 200 °C. The pan were quenched in liquid nitrogen and reintroduced to the DSC at -50 °C and 0 °C for first and second quench-cool, respectively.
*Atomic Force Microscopy (AFM)*

AFM images were obtained by tapping mode from a Veeco dimension 3100 equipped with a Nanoscope IIIa controller (Veeco inc.) and 40 n/M tip with a radius of 10 nm (Mikromash, inc.). Scan rate was 1 Hz.

*Electron Microscopy*

Scanning Electron Microscope (SEM) micrographs for chapter 4 were obtained using a Hitachi S-4800 with a 20.0 kV and a mix detector. All images were taken between 1.10k to 1.20k and a working distance between 8.0 to 9.0 mm. All Energy-Dispersive X-ray Spectroscopy (EDS) experiments were carried out using an Oxford EDX Model 7200. Copper was used for optimization. SEM micrographs for chapter 5 were obtained using a Hitachi S-3400N with back-scatter (BSE). All images were taken between 500 and 100 μms.

*Powder X-Ray Diffraction*

All samples were performed 1 mg of sample spread evenly onto 1 cm² silicon wafer. Silicon wafer were cleaned and oxidized with a H₂SO₄/H₂O₂ solution to insure the absence of foreign particles. X-ray was carried out at room temperature for 5 h using a
Scintag 2000 with Cu Kα (λ = 1.54 Å) and was used to obtain one-dimensional X-ray patterns.

**Optical Spectroscopy**

All refractive index measures were completed using a Metricon 2010/M equipped with a silicon prism coupler at 632.8 nm. Thin films of PEG , \( M_n \) of 20000, and BPVE , \( M_n \) of 20000, covering a composition of 1/99, 2/98, 3/97, 4/96, and 5/99, w/w were prepared by dissolving both polymer in chloroform along with 5 wt % 51-co2-49d. Films were then solution casted and dried in dissicator. Films were annealed or 2 h at 120 °C in a vacuum oven. Film thickness were determined by a Metricon 2010/M and were between 3.3 to 4.2 μms.

**Polymer Processing**

*Preparation of Polymer Blends*

Blends were prepared by dissolving PEG (\( M_n \) of 20000), BPVE (\( M_n \) of 20000), and 51-co2-49d in chloroform at room temperature using the reported weight percentage. The solutions of blends were then solution casted and dried in dissicator overnight. Films were then annealed for 2 h at 120 °C under nitrogen. Films were slowly cooled down to room temperature. Cross-sections were prepared by cryofractured using liquid nitrogen.
Synthesis and Characterization of (Co)polymers and Macromonomers

*Synthesis of TFVE-DEG-TFVE (49a) (used for 50a).*

4-(1,2,2-trifluorovinyl oxy)benzoic acid (47) (1.36 g, 6.23 mmol), dicyclohexylcarbodiimide (DCC) (1.34 g, 6.51 mmol), and 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) (0.47 g, 1.70 mmol) were added to 25 mL round bottom flask containing 10 mL of DCM. The suspension was stirred at room temperature under slow nitrogen purge for 30 minutes. 48a, diethylene glycol, (0.30 g, 2.83 mmol) was then added via syringe to the stirring suspension. After stirring the reaction for 5 h at room temperature, the crude reaction mixture was concentrated under vacuum then dissolved in 10 mL of ethyl acetate. The suspension was filtered and the filtrate was concentrated under vacuum. The crude product was purified by flash chromatography using ethyl acetate as an eluent. After concentration, the macromonomer was dried in the vacuum oven for 24 to afford 49a as a yellow oil (1.0 g, 70%). ATR-FTIR (neat) ν 2956 (w), 1717 (s), 1606 (m), 1504 (w), 1453(s), 1095 (s), 851 (w) cm⁻¹; ¹H NMR (Chloroform-d, 300 MHz) δ 3.86-3.89 (m, 4H), 4.38-4.40 (m, 4H), 7.19 (d, J = 9.0 Hz, 4H), 7.09 (d, J = 9.0 Hz, 4H), 8.04 (d, J = 9.0 Hz, 4H); ¹⁹F NMR (Chloroform-d, 283 MHz, δ): -118.7 (dd, J = 95.5, 55.4 Hz, cis-CF=CF₂, 1F), -125.6 (dd, J = 111.9, 95.5 Hz, trans-CF=CF₂, 1F), -134.8 (dd, J = 111.9 52.4 Hz, CF=CF₂, 1F) -126.9 to -132.0 (m,cyclobutyl-F₆); Anal. Calcd for C₂₂H₁₆F₆O₇ (Found): C, 52.18 (52.78); H, 3.18 (3.40); F, 22.51 (21.43).
Synthesis of TFVE-PEG 200-TFVE (49b) (used for 50b).

Compound 48b, PEG with a $M_n$ of 200 g/mol, (0.40 g, 2.00 mmol) was used according to the procedure outlined in the synthesis of 49a. Compound 49b was isolated as a yellow oil (0.50 g, 42%). ATR-FTIR (neat): $\nu$ 2873 (s), 1718 (s), 1605 (m), 1504 (w), 1453(s), 1094 (s), 852 (w) cm$^{-1}$; $^1$H NMR (Chloroform-$d$, 300 MHz, $\delta$): 3.49-3.68 (m, 14H), 4.31-4.33 (m, 4H) 6.99 (d, $J = 9.0$ Hz, 4H), 7.94 (d, $J = 9.0$ Hz, 4H); Anal. Calcd for C$_{26}$H$_{24}$F$_6$O$_9$ (Found): C, 52.53 (53.22); H, 4.07 (4.52); F, 19.18 (17.75). $^{19}$F NMR (Chloroform-$d$, 283 MHz, $\delta$): -118.7 (dd, $J = 95.5, 55.4$ Hz, cis-CF=CF$_2$, 1F), -125.6 (dd, $J = 111.9, 95.5$ Hz, trans-CF=CF$_2$, 1F), -134.8 (dd, J=111.9 52.4 Hz, CF=CF$_2$, 1F) $\delta$ -127.0 to -132.0 (m,cyclobutyl-F$_6$); Avg. Anal. Calcd for C$_{26}$H$_{28}$F$_6$O$_{10}$ (Found): C, 52.67 (53.28); H, 4.42 (4.52); F, 17.85 (17.56).

Synthesis of TFVE-PEG 300-TFVE (49c) (used for 50c).

Compound 48c, PEG with a $M_n$ of 300 g/mol, (0.30 g, 1.00 mmol) was used according to the procedure outlined in the synthesis of 49a. Compound 49c was isolated as a yellow oil (0.18 g, 26 %). ATR-FTIR (neat): $\nu$ 2873 (s), 1718 (s), 1605 (m), 1504 (w), 1453(s), 1094 (s), 853 (w) cm$^{-1}$; $^1$H NMR (Chloroform-$d$, 300 MHz, $\delta$): 3.50-3.68 (m, 23H), 4.31-4.33 (m, 4H) 6.99 (d, $J = 9.0$ Hz, 4H), 7.94 (d, $J = 9.0$ Hz, 4H) $^{19}$F NMR (Chloroform-$d$, 283 MHz, $\delta$): -118.7 (dd, $J = 95.5, 55.4$ Hz, cis-CF=CF$_2$, 1F), -125.6 (dd, $J = 111.9, 95.5$ Hz, trans-CF=CF$_2$, 1F), -134.8 (dd, J=111.9 52.4 Hz, CF=CF$_2$, 1F) $\delta$ -126.9 to -132.0
(m,cyclobutyl-F$_6$); Avg. Anal. Calcd for C$_{32}$H$_{36}$F$_6$O$_{12}$ (Found): C, 52.90 (52.88); H, 4.99 (5.08); F, 15.69 (15.27).

**Synthesis of TFVE-PEG 400-TFVE (49d) (used for 50c and copolymers in chapter 2).**

Compound 48d, PEG with a $M_n$ of 400 g/mol, (2.50 g, 6.25 mmol) was used according to the procedure outlined in the synthesis of 49a. Compound 49d was isolated as a yellow oil (2.90 g, 58 %). ATR-FTIR (neat): $v$ 2872 (s), 1717 (s), 1606 (m), 1504 (w), 1453(s), 1094 (s), 852 (w) cm$^{-1}$; $^1$H NMR (Chloroform-$d$, 300 MHz, $\delta$): 3.51-3.62 (m, 28H), 3.69-3.71 (m, 4H), 4.33-4.35 (m, 4H), 7.01 (d, $J = 9.0$ Hz, 4H), 8.01 (d, $J = 9.0$ Hz, 4H); $^{19}$F NMR (Chloroform-$d$, 283 MHz, $\delta$): -118.6 (dd, $J = 95.5$, 55.4 Hz, cis-CF=CF$_2$, 1F), -125.3 (dd, $J = 111.9$, 95.5 Hz, trans-CF=CF$_2$, 1F), -134.5 (dd, $J = 111.9$, 52.4 Hz, CF=CF$_2$, 1F) $\delta$ -127.0 to -132.1 (m,cyclobutyl-F$_6$); Avg. Anal. Calcd for C$_{36}$H$_{44}$F$_6$O$_{14}$ (Found): C, 53.07 (53.19); H, 5.44 (5.61); F, 13.99 (12.42).

**Synthesis of TFVE-PEG 600-TFVE (49e) (used for 50e).**

Compound 48e, PEG with a $M_n$ of 600 g/mol, (0.30 g, 0.50 mmol) was used according to the procedure outlined in the synthesis of 49a. Compound 49e was isolated as a yellow oil (0.23 g, 45 %). ATR-FTIR (neat): $v$ 2871 (s), 1716 (s), 1605 (w), 1504 (w), 1453(s), 1095 (s), 852 (w) cm$^{-1}$; $^1$H NMR (Chloroform-$d$, 300 MHz, $\delta$): 3.56-3.61 (m, 46H), 3.73-3.75 (m, 4H), 4.37-4.39 (m, 4H) 7.06 (d, $J = 9.0$ Hz, 4H), 8.01 (d, $J = 9.0$ Hz, 4H) $^{19}$F NMR (Chloroform-$d$, 283 MHz, $\delta$): -118.7 (dd, $J = 95.5$, 55.4 Hz, cis-CF=CF$_2$, 1F), -125.6 (dd, $J = 111.9$, 95.5 Hz, trans-CF=CF$_2$, 1F), -134.8 (dd, $J = 111.9$, 52.4 Hz, CF=CF$_2$, 1F) $\delta$ -127.0 to -132.1 (m,cyclobutyl-F$_6$); Avg. Anal. Calcd for C$_{36}$H$_{44}$F$_6$O$_{14}$ (Found): C, 53.07 (53.19); H, 5.44 (5.61); F, 13.99 (12.42).
Preparation of 50a.

In a flame-dried round bottom flask equipped with a magnetic stirrer, 49a (0.50 g, 0.98 mmol) was added. The flask was stirred under nitrogen purge, and heated to 180 °C for 48 h. The crude polymer was then dissolved in DMF, precipitated in water. The polymer was then filtered, dissolved in chloroform, and precipitated in hexanes. Polymer 50a was then dried at 65 °C under vacuum for 24 h to afford a yellow solid with nearly quantitative yield. ATR-FTIR (neat): ν 2856 (s), 1718 (s), 1606 (s), 1505 (s), 1455(m), 851 (m) cm⁻¹; ¹H NMR (Chloroform-d, 300 MHz, δ): 3.85-3.87 (m, 4H), 4.47-4.63 (m, 4H), 7.08-7.21 (m, 4H), 8.03-8.09 (m, 4H); ¹⁹F NMR (Chloroform-d, 283 MHz, δ): -126.9 to -132.0 (m,cyclobutyl-F₆); Molecular weight and selected properties are reported in table 3.1.

Preparation of 50b.

Monomer 49b (0.30 g, 0.50 mmol) was used according to the procedure outlined in the preparation of 50a. Polymer 50b was isolated as a yellow solid in nearly quantitative yield. ATR-FTIR (neat): ν 2872 (s), 1718 (s), 1606 (s), 1505 (s), 1454(m), 852 (m) cm⁻¹; ¹H NMR (Chloroform-d, 300 MHz, δ): 3.61-3.81 (m, 14H), 4.44-4.46 (m, 4H), 7.12 (d, J = 9.0 Hz, 2H), 7.22 (d, J = 9.0 Hz, 2H), 8.03-8.09 (m, 4H); ¹⁹F NMR (Chloroform-d, 283
MHz, δ): -126.9 to -131.9 (m, cyclobutyl-F₆); Molecular weight and selected properties are reported in table 3.1.

**Preparation of 50c.**
Monomer 49c (0.18 g, 0.26 mmol) was used according to the procedure outlined in the preparation of 50a. Polymer 50c was isolated as a yellow solid in nearly quantitative yield. ATR-FTIR (neat): v 2871 (s), 1719 (s), 1606 (s), 1453 (m), 851 (m) cm⁻¹; ¹H NMR (Chloroform-d, 300 MHz, δ): 3.54-3.81 (m, 23H), 4.44-4.46 (m, 4H) 7.14 (d, J = 9.0 Hz, 2H), 7.22 (d, J = 9.0 Hz, 2H), 8.03-8.08 (m, 4H); ¹⁹F NMR (Chloroform-d, 283 MHz, δ): -126.3 to -131.9 (m, cyclobutyl-F₆); Molecular weight and selected properties are reported in table 3.1.

**Preparation of 50d.**
Monomer 49d (0.30 g, 0.37 mmol) was used according to the procedure outlined in the preparation of 50a. Polymer 50d was isolated as a yellow solid in nearly quantitative yield. ATR-FTIR (neat): v 2872 (s), 1718 (s), 1605 (s), 1453 (m), 851 (m); ¹H NMR (Chloroform-d, 300 MHz, δ): 3.56-3.65 (m, 28H), 3.79-3.81 (m, 4H), 4.44-4.46 (m, 4H), 7.13 (d, J = 9.0 Hz, 2H), 7.23 (d, J = 9.0 Hz, 2H), 8.03-8.08 (m, 4H); ¹⁹F NMR (Chloroform-d, 283 MHz, δ): -126.9 to -131.9 (m, cyclobutyl-F₆); Molecular weight and selected properties are reported in table 3.1.
Preparation of 50e.

Monomer 49e (0.23 g, 0.23 mmol) was used according to the procedure outlined in the preparation of 50a. Polymer 50e was isolated as a yellow solid in nearly quantitative yield. ATR-FTIR (neat): ν 2871(s), 1718 (s), 1606 (s), 1454(m), 853 (m); $^1$H NMR (Chloroform-$d$, 300 MHz, δ): 3.56-3.65 (m, 46H), 3.79-3.81 (m, 4H), 4.43-4.45 (m, 4H), 7.13 (d, $J = 9.0$ Hz, 2H), 7.23 (d, $J = 9.0$ Hz, 2H), 8.05-8.08 (m, 4H); $^{19}$F NMR (Chloroform-$d$, 283 MHz, δ): -126.9 to -131.9 (m, cyclobutyl-F$_6$); Molecular weight and selected properties are reported in table 3.1.

Preparation of copolymer 51-co-49d.

Monomer 49d (0.60 g, 0.75 mmol), 4,4'-bis(4-trifluorovinyloxy)biphenyl 51 (0.26 g, 0.75 mmol), and 0.5 mL of mesitylene was added to a flame-dried vacuum sealed ampoule. The ampoule was heated to 160 °C for 24 h. After cooling, the mixture was dissolved in DMF and precipitated in water. The polymer was washed with hexane and dried under vacuum at 65 °C for 24h. Copolymer 51-co-49d was isolated as a light brown solid in nearly quantitative yield. ATR-FTIR (neat): ν 2872(s), 1720 (s), 1606 (s), 1496 (s), 1453(m), 852 (m) 825 (m); $^1$H NMR (Acetone-$d$, 300 MHz, δ): 3.51-3.61 (m, 28H), 3.78-3.80 (m, 4H), 4.40-4.42 (m, 4H), 7.32-7.38 (m, 8H) 7.65-7.69 (s, 4H), 8.03-8.09 (m, 4H); $^{19}$F NMR (Acetone-$d$, 283 MHz, δ): -128.2 to -132.3 (m, cyclobutyl-F$_6$). Molecular weight and selected properties are reported in table 3.2.
Preparation of copolymer 51-co2-49d.

Copolymer 51-co2-49d was prepared using 49d (0.25 g, 0.31 mmol), 4'-bis(4-trifluorovinylxylo)biphenyl 51 (0.13 g, 0.37 mmol), and 0.5 mL of mesitylene following to the procedure outlined for the preparation of 51-co-49d. Copolymer 51-co2-49d was isolated as a light brown solid in nearly quantitative yield. ATR-FTIR (neat): ν 2870(s), 1720 (s), 1606 (s), 1496 (s), 1453(m), 853 (m) 826(m); ¹H NMR (Acetone-d, 300 MHz, δ): 3.51-3.61 (m, 28H), 3.78-3.80 (m, 4H), 4.39-4.41 (m, 4H), 7.32-7.40 (m, 8H), 7.65-7.69 (s, 4H), 8.04-8.09 (m, 4H); ¹⁹F NMR (Acetone-d, 283 MHz, δ): -128.1 to -132.4 (m, cyclobutyl-F₆). Molecular weights are reported in table 3.2.

Preparation of copolymer 51-co3-49d.

Copolymer 51-co3-49d was prepared using 49d (0.25 g, 0.31 mmol) and 4,4'-bis(4-trifluorovinylxylo)biphenyl 51 (0.13 g, 0.37 mmol) following to the procedure outlined for the preparation of 51-co-49d. Copolymer 51-co3-49d was isolated as a light brown solid in nearly quantitative yield. ATR-FTIR (neat): ν 2870(s), 1720 (s), 1606 (s), 1496 (s), 1453(m), 852 (m) 825(m); ¹H NMR (Acetone-d, 300 MHz, δ): 3.51-3.61 (m, 28H), 3.78-3.80 (m, 4H), 4.39-4.41 (m, 4H), 7.32-7.40 (m, 8H), 7.65-7.69 (s, 4H), 8.03-8.09 (m, 4H); ¹⁹F NMR (Acetone-d, 283 MHz, δ): -120.0 (dd, J = 95.5, 55.4 Hz, cis-CF=CF₂, 1F), -127.1 (dd, J = 111.9, 95.5 Hz, trans-CF=CF₂, 1F), -136.0 (dd, J =111.9 52.4 Hz, CF=CF₂, 1F) -128.3 to -132.4 (m, cyclobutyl-F₆). Molecular weight and selected properties are reported in table 3.2.
Preparation of copolymer 51b-co-49d.

Copolymer 51b-co-49d was prepared using 49d (0.13 g, 0.16 mmol), 4,4’-bis(4-trifluorovinyl)oxy)biphenyl prepolymer 51b with $M_n$ of 13,000 g/mol (0.42 g, 0.03 mmol), and 0.5 mL of mesitylene following to the procedure outlined for the preparation of 51-co-49d. Copolymer 51b-co-49d was isolated as a light brown solid in nearly quantitative yield. ATR-FTIR (neat): v 2872(s), 1720 (s), 1606 (s), 1496 (s), 1453(m), 852 (m); $^1$H NMR (Acetone-$d$, 300 MHz, δ): δ 3.53-3.61 (m, 28H), 3.78-3.80 (m, 4H), 4.40-4.42 (m, 4H), 7.25-7.30 (m, 8H) 7.65-7.69 (m, 4H), 8.03-8.09 (m, 4H); $^{19}$F NMR (Acetone-$d$, 283 MHz, δ): -128.7 to -131.9 (m,cyclobutyl-$F_6$). Molecular weight and selected properties are reported in table 3.2.

Preparation of copolymer 52-co-49d.

Copolymer 52-co-49d was prepared using 49d (0.50 g, 0.62 mmol), 2,2-bis(4-trifluorovinyl)oxyphenyl) 1,1,3,3,3-hexafluoropropane 52 (0.31 g, 0.62 mmol), and 0.5 mL of mesitylene following to the procedure outlined for the preparation of 51-co-3.6d. Copolymer 52-co-49d was isolated as a light brown solid in nearly quantitative yield. ATR-FTIR (neat): v 2865(m), 1722 (m), 1606 (m), 1595 (s), 1453(m), 852 (m), 832 (s); $^1$H NMR (Acetone-$d$, 300 MHz, δ): 3.53-3.61 (m, 28H), 3 3.78-3.80 (m, 4H), 4.40-4.42 (m, 4H), 7.30-7.51 (m, 12H), 8.11 (m, 4H); $^{19}$F NMR (Acetone-$d$, 283 MHz, δ): -64.5 (6F), -127.2 to -133.2 (m,cyclobutyl-$F_6$). Molecular weight and selected properties are reported in table 3.2.
Preparation of copolymer 52-co2-49d.

Copolymer 52-co2-49d was prepared using 49d (0.25 g, 0.31 mmol), 2,2-bis(4-trifluorovinylxyloxyphenyl) 1,1,1,3,3,3-hexafluoropropane 52 (0.185 g, 0.37 mmol), and 0.5 mL of mesitylene following to the procedure outlined for the preparation of 51-co-49d. Copolymer 52-co2-49d was isolated as a light brown solid in nearly quantitative yield. ATR-FTIR (neat): ν 2872(s), 1721 (s), 1607 (s), 1507 (s), 1455(m), 852 (m), 832 (m); ^1^H NMR (Acetone-\(d\), 300 MHz, δ): 3.53-3.61 (m, 28H), 3.78-3.80 (m, 4H), 4.40-4.42 (m, 4H), 7.32-7.51 (m, 12H), 8.11 (m, 4H); ^19^F NMR (Acetone-\(d\), 283 MHz, δ): -64.5 (6F), -127.3 to -133.2 (m,cyclobutyl-\(F_6\)). Molecular weight and selected properties are reported in table 3.2.

Preparation of copolymer 52-co3-49d.

Copolymer 52-co3-49d was prepared using 49d (0.25 g, 0.31 mmol) and 2,2-bis(4-trifluorovinylxyloxyphenyl) 1,1,1,3,3,3-hexafluoropropane 52 (0.185 g, 0.37 mmol) following to the procedure outlined for the preparation of 51-co-49d. Copolymer 51-co3-49d was isolated as a light brown solid in nearly quantitative yield. ATR-FTIR (neat): ν 2872(s), 1721 (s), 1608 (s), 1508 (s), 1455(m), 852 (m), 832 (m); ^1^H NMR (Acetone-\(d\), 300 MHz, δ): 3.53-3.61 (m, 28H), 3.78-3.80 (m, 4H), 4.40-4.42 (m, 4H), 7.33-7.52 (m, 12H), 8.11 (m, 4H); ^19^F NMR (Acetone-\(d\), 283 MHz, δ): -64.5 (6F), -127.3 to -133.2 (m,cyclobutyl-\(F_6\)). Molecular weight and selected properties are reported in table 3.2.

Preparation of copolymer 53a-co-54a
53a, 4,4'-bis(4-trifluorovinylxy)biphenyl oligomer ($M_n$ of 8,000) (1.28 g, 0.16 mmol), and anhydrous Cs$_2$CO$_3$ (26 mg, 0.08 mmol) was added to a 5 mL flame dried round bottom flask containing a magnetic stir bar and 2.5 mL of anhydrous DMF. The agitated solution was heated to 80 °C under nitrogen purge for 24 h. 54a, PEG 600 (0.1g, 0.16 mmol) was added to the solution. The solution was precipitated in H$_2$O, filtered, and dried in vacuum at 65 °C for 24h to afford 53a-co-54a as a yellow solid (1.3g, 93 %).

ATR-FTIR (neat): $\nu$ 2870 (m), 1606 (s), 1495 (s), 1198 (s), 1109 (s) 821(m), 723(w);

$^1$H NMR (Acetone-$d$, 300 MHz, $\delta$): 3.48-3.68 (m, 45H), 3.73-3.95 (m, 4H), 4.14-4.23 (m, 4H), 7.08-7.45 (m, 92H), 7.48-7.86 (m, 92H); $^{19}$F NMR (Acetone-$d$, 283 MHz, $\delta$): -84.2 (s, CHFCF$_2$), -126.6 to -132.0 (m,cyclobutyl-$F_6$), -142.5 (d, $J$ = 57.9, CHFCF$_2$).

Molecular weight and selected properties are reported in table 6.1.

**Preparation of copolymer 53a-co-54b**

53a, 4,4'-bis(4-trifluorovinylxy)biphenyl oligomer ($M_n$ of 8,000 g/mol) (1.6g, 0.2 mmol), anhydrous Cs$_2$CO$_3$ (33 mg, 0.1 mmol), 3.1 mL of anhydrous DMF, and 54b, PEG with a $M_n$ of 1000 g/mol, (0.2g, 0.2 mmol) was used according to the procedure outlined in the preparation of 53a-co-54a. Copolymer 53a-co-54b was isolated as a white solid (1.7 g, 94 %). ATR-FTIR (neat): $\nu$ 2870 (m), 1606 (s), 1495 (s), 1198 (s), 1114 (s), 821(m), 722(w); $^1$H NMR (Acetone-$d$, 300 MHz, $\delta$): 3.41-3.67 (m, 81H), 3.69-3.88 (m, 4H), 4.11-4.27 (m, 4H), 6.17 (d, $J$=56.8 2H, CHFCF$_2$), 7.11-7.45 (m, 92H), 7.51-7.82 (m, 92H); $^{19}$F NMR (Acetone-$d$, 283 MHz, $\delta$): -84.2 (S,CHFCF$_2$), -126.0 to -132.3 (m,
cyclobutyl-$F_6$), -142.4 (d, $J = 57.4$, CHF\textsubscript{CF}$_2$). Molecular weight and selected properties are reported in table 6.1.

**Preparation of copolymer 53a-co-54c**

53a, 4,4’-bis(4-trifluorovinyloxy)biphenyl oligomer ($M_n$ of 8,000) (1.6g, 0.2 mmol), anhydrous Cs\textsubscript{2}CO\textsubscript{3} (33 mg, 0.1 mmol), 3.1 mL of anhydrous DMF, and 54b, PEG with a $M_n$ of 1500 g/mol, (0.3g, 0.2 mmol) was used according to the procedure outlined in the preparation of 53a-co-54a. Copolymer 53a-co-54c was isolated as a white fibrous solid (1.7 g, 74 %). ATR-FTIR (neat): $\nu$ 2870 (m), 1606 (s), 1494 (s), 1197 (s), 1107 (s), 821(m), 723(w); $^1$H NMR (Acetone-$d$, 300 MHz, $\delta$): 3.45-3.68 (m, 127H), 3.70-3.92(m, 4H), 4.14-4.23 (m, 4H), 6.18 (d, $J$=56.8 2H, CHF\textsubscript{CF}$_2$), 7.12-7.46 (m, 92H), 7.52-7.83 (m, 92H); $^{19}$F NMR (Acetone-$d$, 283 MHz, $\delta$): -84.2 (s,CHF\textsubscript{CF}$_2$), -126.1 to -132.1 (m,cyclobutyl-$F_6$), -142.5 (d, $J = 55.0$, CHF\textsubscript{CF}$_2$). Molecular weight and selected properties are reported in table 6.1.

**Preparation of copolymer 53b-co-54c**

53b, 4,4’-bis(4-trifluorovinyloxy)biphenyl oligomer ($M_n$ of 4,000) (0.8g, 0.2 mmol), anhydrous Cs\textsubscript{2}CO\textsubscript{3} (33 mg, 0.1 mmol), 1.5 mL of anhydrous DMF, and 54c, PEG with a $M_n$ of 1500 g/mol, (0.3g, 0.2 mmol) was used according to the procedure outlined in the preparation of 53a-co-54a. Copolymer 53b-co-54c was isolated as a white solid (1.0 g, 77 %). ATR-FTIR (neat): $\nu$ 2870 (m), 1606 (s), 1495 (s), 1198 (s), 1115 (s), 822(m), 722(w); $^1$H NMR (Acetone-$d$, 300 MHz, $\delta$): 3.47-3.72 (m, 127H), 3.72-3.93(m, 4H),
4.14-4.26 (m, 4H), 6.17 (d, J=56.8 2H, CHFCF₂), 7.18-7.44 (m, 46H), 7.60-7.78 (m, 46H); ¹⁹F NMR (Acetone-d, 283 MHz, δ): -84.2 (s, CHFCF₂), -126.7 to -132.4 (m,cyclobutyl-F₆), -142.5 (d, J = 57.4, CHFCF₂). Molecular weight and selected properties are reported in table 6.1.

Preparation of copolymer 53c-co-54c

54c, 4,4′-bis(4-trifluorovinloyoxy)biphenyl oligomer (Mₙ of 2,000) (0.26 g, 0.13 mmol), anhydrous Cs₂CO₃ (23 mg, 0.07 mmol), 0.4 mL of anhydrous DMF, and 54c, PEG with a Mₙ of 1500 g/mol, (0.20 g, 0.13 mmol) was used according to the procedure outlined in the preparation of 53a-co-54a with the exception of a final precipitation in hexanes. Copolymer 53c-co-54c was isolated after a final as a white solid (0.32 g, 81 %). ATR-FTIR (neat): ν 2870 (m), 1606 (s), 1495 (s), 1198 (s), 1109 (s), 821 (m), 723 (w); ¹H NMR (Acetone-d, 300 MHz, δ): 3.47-3.71 (m, 127H), 3.72-3.85(m, 4H), 4.14-4.24 (m, 4H), 6.17 (d, J=56.8 2H, CHFCF₂), 7.20-7.42 (m, 23H), 7.59-7.82 (m, 23H); ¹⁹F NMR (Acetone-d, 283 MHz, δ): -84.2 (s, CHFCF₂), -126.7 to -132.4 (m,cyclobutyl-F₆), -142.5 (d, J = 57.4, CHFCF₂). Molecular weight and selected properties are reported in table 6.1.

Preparation of 57a

Dried ethylene glycol, 56a, (1.6 mmol, 100 mg) was added to 5 mL round bottom flask containing 0.5 mL of anhydrous DMF and magnetic stir bar. 4,4′-bis(4-trifluorovinloyoxy)biphenyl, 55, (1.6 mmol, 558 mg) and anhydrous cesium carbonate
(0.8 mmol, 260 mg) was added to the agitated solution. The solution was heated to 80 °C under nitrogen purge for 24 h. The solution was precipitated in water, filtered, and washed with hexanes. Polymer 57a was dried in a vacuum oven at 65 °C for 24 h to afford a white powder (499 mg, 76 %). $^1$H NMR (DMSO-$d_6$, 300 MHz, $\delta$): 4.11-4.12 (m, 4H), 6.50 (broad dt, $J=56.8$ 2H, CHFCF$_2$), 6.59 (s, 1H), 7.19-7.22 (d, $J=9.0$ Hz, 4H), 7.59-7.63 (d, $J=9.0$ Hz, 4H); $^{19}$F NMR (DMSO-$d_6$, 283 MHz, $\delta$): -88.3 and 87.8 (AB pattern, $J = 141.5$ Hz CHFCF$_2$), -141.0 (d, $J = 56.6$, CHFCF$_2$). ATR-FTIR (neat): $\nu$ 2965 (m), 1607 (s), 1497 (s), 1124 (s), 739 (w). Molecular weight and selected properties are reported in table 7.1.

**Preparation of 57b**

4,4’-bis(4-trifluorovinyloxy)biphenyl, 55, (326 mg, 0.94 mmol), dried diethylene glycol, 56a, (100 mg, 0.94 mmol), anhydrous cesium carbonate (154 mg, 0.47 mmol), and 0.5 mL of anhydrous DMF were used according to the procedure outlined in the preparation of 57a. Polymer 57b were isolated as a white solid (349 mg, 82 %). $^1$H NMR (DMSO-$d_6$, 300 MHz, $\delta$): 3.65-3.71 (m, 4H), 4.11-4.12 (m, 4H), 6.50 (broad dt, $J=56.8$ 2H, CHFCF$_2$), 7.19-7.22 (d, $J=9.0$ Hz, 4H), 7.59-7.63 (d, $J=9.0$ Hz, 4H); $^{19}$F NMR (DMSO-$d_6$, 283 MHz, $\delta$): -88.3 and 87.8 (AB pattern, $J = 141.5$ Hz CHFCF$_2$), -141.0 (d, $J = 56.6$, CHFCF$_2$), ATR-FTIR (neat): $\nu$ 2877 (m), 1607 (s), 1497 (s), 1121 (s), 739(w). Molecular weight and selected properties are reported in table 7.1.

**Preparation of 57c**
4,4’-bis(4-trifluorovinyloxy)biphenyl, **55**, (231 mg, 0.666 mmol), dried triethylene glycol, **56c**, (100 mg, 0.666 mmol), anhydrous cesium carbonate (108 mg, 0.333 mmol), and 0.2 mL of anhydrous DMF were used according to the procedure outlined in the preparation of **57a**. Polymer **57c** were isolated as a white semi-solid (295 mg, 89%). $^1$H NMR (DMSO-$d_6$, 300 MHz, $\delta$): 3.48-3.56 (m, 8H), 4.08-4.10 (m, 4H), 6.50 (broad dt, $J$=56.8 Hz, $CHFCF_2$), 7.19-7.22 (d, $J$ = 9.0 Hz, 4H), 7.60-7.63 (d, $J$ = 9.0 Hz, 4H); $^{19}$F NMR (DMSO-$d_6$, 283 MHz, $\delta$): -88.3 and 87.8 (AB pattern, $J$ = 141.5 Hz $CHFCF_2$), -141.0 (d, $J$ = 56.6, $CHFCF_2$), ATR-FTIR (neat): $\nu$ 2875 (m), 1607 (s), 1497 (s), 1119 (s), 734(w). Molecular weight and selected properties are reported in table 7.1.

**Preparation of 57d**

4,4'-bis(4-trifluorovinyloxy)biphenyl, **55**, (178 mg, 0.51 mmol), dried tetraethylene glycol, **56c**, (100 mg, 0.51 mmol), anhydrous cesium carbonate (84 mg, 0.26 mmol), and 0.17 mL of anhydrous DMF were used according to the procedure outlined in the preparation of **56a**. Polymer **57d** were isolated as a white semi-solid (204 mg, 73%). $^1$H NMR (DMSO-$d_6$, 300 MHz, $\delta$): 3.48-3.64 (m, 12H), 4.08-4.10 (m, 4H), 6.50 (broad dt, $J$=56.8 Hz, $CHFCF_2$), 7.20-7.23 (d, $J$ = 9.0 Hz, 4H), 7.66-7.63 (d, $J$ = 9.0 Hz, 4H); $^{19}$F NMR (DMSO-$d_6$, 283 MHz, $\delta$): -88.3 and 87.8 (AB pattern, $J$ = 141.5 Hz $CHFCF_2$), -141.0 (d, $J$ = 56.6, $CHFCF_2$), ATR-FTIR (neat): $\nu$ 2875 (m), 1607 (s), 1496 (s), 1120 (s), 733(w). Molecular weight and selected properties are reported in table 7.1.
RECOMMENDED FUTURE WORK

Macromonomers should be copolymerized with sulfonamide monomer to create a copolymer capable of ion transport for lithium batteries. Values should be compared to polymerized macromonomers doped with lithium salts.

Other polymers should be blended with PFCB polymers using the strategy outlined in chapter 5. This can be directed toward many applications.

Macromonomers can also be used for micelle formation. Size vs concentration can be determined by GPC and cryo TEM.

Additional segmented polymers can be studied using TFVE monomers and other PFCB oligomers. Investigations into crystalline PFCB polymers like hexafluoropropane should be interesting.
LIST OF COMPOUNDS

\[
\text{49a } n=2.0 \\
\text{49b } n=\text{av of 4.5} \\
\text{49c } n=\text{av of 6.8} \\
\text{49d } n=\text{av of 8.7} \\
\text{49e } n=\text{av of 13.2}
\]

\[
\text{50a } n=2.0 \\
\text{50b } n=\text{av of 4.5} \\
\text{50c } n=\text{av of 6.8} \\
\text{50d } n=\text{av of 8.7} \\
\text{50e } n=\text{av of 13.2}
\]

\[
\text{51-co-49d } R = \text{BPVE} \\
\text{51b-co-49d } R = \text{BPVE} \\
\text{51-co2-49d } R = \text{BPVE} \\
\text{51-co3-49d } R = \text{BPVE} \\
^a\text{Prepolymer } M_n \approx 13,000
\]

\[
\text{53a-co-54a} \\
\text{53a-co-54b} \\
\text{53a-co-54c} \\
\text{53b-co-54c} \\
\text{53c-co-54c}
\]

\[
\text{57a } x = 1 \\
\text{57b } x = 2 \\
\text{57c } x = 3 \\
\text{57d } x = 4
\]
APPENDIX A

![Graph](image)

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APPENDIX B

![Graph](image)
51b\textsuperscript{a}-co-49\textsuperscript{d} \quad R = \text{BPVE}

\textsuperscript{a}Prepolymer $M_n \approx 13,000$
51b\textsuperscript{a}-co-50d \hspace{1em} R = BPVE
\textsuperscript{a}Prepolimer $M_n \sim 13,000$
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