

Modified Poly(arylene ether sulfone) Compositions and their Segmented Block Copolymers

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ABSTRACT

A series of modified poly(arylene ether sulfone)s (PAES) incorporating hexafluoroisopropylidene units and co-monomers, bisphenol A (BA), 4,4'-dihydroxyterphenyl (DHTP) and triptycene-1,4-hydroquinone (TPDH), were synthesized using a polyetherification synthetic method. These thermoplastic PAES were copolymerized with the elastomer, polydimethylsiloxane (PDMS) to form segmented block copolymers. The segmented block copolymers with diverse PAES structures were studied and investigated for their thermal, tensile, and morphological properties. These multiphase segmented block copolymer materials have the potential to impart useful combinations of optical transparency, thermal stability, and enhanced tensile properties, and enhanced environmentally resistant properties for various high impact, high performance applications.

In Chapter 2, hexafluoroisopropylidene bisphenol PAES (BAF PAES) segmented block copolymers containing various volume fraction of PDMS were synthesized. Analysis of the segmented block copolymer films by atomic force microscopy (AFM) and small angle x-ray scattering (SAXS) show the materials are microphase separated. Further analysis of the BAF PAES segmented block copolymers by transmission electron microscopy (TEM) show an increased morphological order with decreasing PDMS content, with lamellar morphologies formed at higher or near equal PAES and PDMS volume fractions. Comparatively, the morphological properties of the BAF PAES

segmented block copolymers are considerably different from the isopropylidene bisphenol PAES (BA PAES) segmented block copolymer of similar PDMS volume percents.

In this document, segmented block copolymers prepared from BA PAES incorporating 4,4'-dihydroxyterphenyl (DHTP) and triptycene-1,4-hydroquinone (TPDH) co-monomers were characterized by proton nuclear magnetic resonance spectroscopy (^1H NMR). Films of these materials, prepared from THF solution, were tested for thermal and tensile properties. These materials provide higher thermal stabilities over the BA PAES segmented block copolymers with thermal degradation ranging 380–435 °C under nitrogen at 5%-wt. loss. Similarly, the PAES incorporating co-monomers gave higher T_g (200 °C) than the BA PAES (183 °C) synthesized in our labs. Previously synthesized BA PAES segmented block copolymers showed plastic to elastomeric tensile properties upon increasing addition of PDMS content. These new segmented block copolymers, incorporating co-monomers, provided comparable results with the reported BA PAES segmented block copolymers analogues.

The last research topic discussed in this dissertation covers the preparation of blends from 5% of segmented block copolymer and 95% of Udel[®], donated by Solvay Advanced Polymers. The preparation of blends from the segmented block copolymers containing random copolymers led to materials with higher moduli than Udel[®] as observed by dynamic mechanical analysis (DMA). Tensile measurements performed by Instron also show the blends have high moduli, though no changes in the tensile elongation comparable to Udel[®].

DEDICATION

*To my great-grandparents, Estella K. Cureton and the late Howard W. Cureton, Sr.
Thank you for teaching us the best things in life: to love, to pray, and to believe in
God's amazing grace and mercy.*

With All My Love

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ATTRIBUTION

Chapter 2 (Synthesis and Characterization of Hexafluoroisopropylidene Bisphenol Poly(arylene ether sulfone) and Polydimethylsiloxane Segmented Block Copolymers) of this dissertation was co-authored with Dr. Frederick Beyer and Dr. S. Richard Turner. Dr. Beyer is a researcher at the U.S. Army Research Laboratory at the Aberdeen Proving Ground in Aberdeen, Maryland. Dr. Beyer attributed to this research by performing the initial small angle x-ray scattering (SAXS) measurements on the hexafluoroisopropylidene bisphenol poly(arylene ether sulfone) and polydimethylsiloxane segmented block copolymers and the isopropylidene bisphenol poly(arylene ether sulfone) and polydimethylsiloxane segmented block copolymers (Fig. 2.6) and allowed use of the SAXS instrument for further measurements of the hexafluoroisopropylidene bisphenol poly(arylene ether sulfone) and polydimethylsiloxane segmented block copolymers (Fig. 2.7). Dr. Beyer provided data analysis and discussion of the results for publication. Dr. Turner is a research professor at Virginia Polytechnic Institute and State University. Dr. Turner served as the research advisor and point of contact for publication.

Modified Poly(arylene ether sulfone) Compositions and their Segmented Block Copolymers

TABLE OF CONTENTS

Chapter	Page
Abstract.....	ii
Dedication.....	iv
Acknowledgements.....	v
Attribution.....	viii
List of Schemes	xiii
List of Figures	xiv
List of Tables	xvi
List of Equations	xvii
1.0. LITERATURE REVIEW	1
1.1. INTRODUCTION TO POLY(ARYLENE ETHER SULFONE)S.....	1
1.1.1. Overview	1
1.1.2. Synthesis of PAES	3
1.1.3. Properties of PAES	7
1.1.3.1. Mechanical Properties.....	7
1.1.3.2. Chemical Properties.....	9
1.1.3.3. Thermal Properties.....	10
1.2. INTRODUCTION TO POLYDIMETHYLSILOXANES.....	13
1.2.1. Overview	13
1.2.2. Preparation of Linear and Cyclic PDMS	13
1.2.3. Ring-Opening Polymerization of Cyclic Siloxanes	16
1.2.3.1. Living Anionic Polymerization	16
1.2.3.2. Acid-Catalyzed Reactions	18
1.2.3.3. Basic-Catalyzed Reactions	19
1.2.4. Properties.....	25
1.3. INTRODUCTION TO SEGMENTED BLOCK COPOLYMERS.....	26
1.3.1. Overview	26
1.3.2. Properties.....	29
1.3.2.1. Morphological Properties	29
1.3.2.2. Mechanical Properties.....	32
1.3.2.3. Thermal Properties.....	33
1.3.2.4. Optical Properties.....	37
1.4. RESEARCH OBJECTIVES	38
1.5. REFERENCES	41

2.0. SYNTHESIS AND CHARACTERIZATION OF HEXAFLUOROISOPROPYLIDENE BISPHENOL POLY(ARYLENE ETHER SULFONE) AND POLYDIMETHYLSILOXANE SEGMENTED BLOCK COPOLYMERS	46
2.1. ABSTRACT	46
2.2. INTRODUCTION	47
2.3. EXPERIMENTAL	49
2.3.1. General Methods and Materials	49
2.3.2. Preparation of Hydroxyl-Terminated PAES Oligomers	50
2.3.2.1. Hexafluoroisopropylidene Bisphenol PAES (BAF PAES)	50
2.3.2.2. Isopropylidene Bisphenol PAES (BA PAES)	51
2.3.3. Preparation of Dimethylamino-Terminated PDMS (PDMS) Oligomers.....	51
2.3.4. Preparation of Segmented Block Copolymers	52
2.3.4.1. Hexafluoroisopropylidene Bisphenol PAES Segmented Block Copolymers (BAF PAES- <i>b</i> -PDMS).....	52
2.3.4.2. Isopropylidene Bisphenol PAES Segmented Block Copolymers (BA PAES- <i>b</i> -PDMS)	52
2.3.5. Film Preparation of the Segmented Block Copolymers	52
2.4. CHARACTERIZATION METHODS	53
2.4.1. Thermogravimetric Analysis (TGA)	53
2.4.2. Tensile Analysis	53
2.4.3. Tapping Mode Atomic Force Microscopy (TP-AFM)	53
2.4.4. Small-Angle X-Ray Scattering (SAXS)	53
2.4.5. Transmission Electron Spectroscopy (TEM).....	54
2.5. RESULTS AND DISCUSSION	55
2.5.1. Synthesis of Segmented Block Copolymers	55
2.5.2. Thermal Stability of Segmented Block Copolymers.....	57
2.5.3. Tensile Analysis of Segmented Block Copolymers.....	59
2.5.4. Morphological Characteristics of Segmented Block Copolymers	63
2.6. CONCLUSIONS	69
2.7. ACKNOWLEDGMENTS	70
2.8. REFERENCES	71
3.0. MOLECULAR WEIGHT ANALYSIS OF SEGMENTED BLOCK COPOLYMERS ...	73
3.1. ABSTRACT	73
3.2. INTRODUCTION	73
3.3. NOMENCLATURE AND STRUCTURES	75
3.4. CHARACTERIZATION METHODS	77
3.4.1. Size Exclusion Chromatography (SEC) with Light Scattering Detection	77
3.4.2. Size Exclusion Chromatography (SEC) with Differential Refractive Index Detection	77
3.4.3. Dynamic Light Scattering (DLS).....	77
3.4.4. Intrinsic Viscosity, $[\eta]$	78
3.5. RESULTS AND DISCUSSION	78
3.5.1. Analysis by SEC.....	78
3.5.2. Analysis by Dynamic Light Scattering	84
3.5.3. Analysis by Intrinsic Viscosity, $[\eta]$	87

3.6. CONCLUSIONS	88
3.7. ACKNOWLEDGMENTS	89
3.8. REFERENCES	89
4.0. SYNTHESIS AND PROPERTIES OF BISPHENOL A-TERPHENOL POLY(ARYLENE ETHER SULFONE) AND POLYDIMETHYLSILOXANE SEGMENTED BLOCK COPOLYMERS	91
4.1. ABSTRACT	91
4.2. INTRODUCTION	91
4.3. EXPERIMENTAL	93
4.3.1. General Methods and Materials	93
4.3.2. Synthesis of 4, 4'-dihydroxyterphenyl (DHTP)	94
4.3.3. Synthesis of BA–DHTP PAES Random Copolymers (BA–DHTP PAES)	95
4.3.4. Preparation of Dimethylamino-Terminated PDMS (PDMS) Oligomers	96
4.3.5. Preparation of Bisphenol A–Terphenol PAES Segmented Block Copolymers (BA–DHTP PAES– <i>b</i> –PDMS)	97
4.3.6. Film Preparation of the Segmented Block Copolymers	98
4.3.7. Polymer Acronyms	98
4.4. CHARACTERIZATION METHODS	100
4.4.1. Nuclear Magnetic Resonance Spectroscopy (NMR)	100
4.4.2. Thermogravimetric Analysis (TGA)	100
4.4.3. Differential Scanning Calorimetry (DSC)	100
4.4.4. Tensile Analysis	100
4.5. RESULTS AND DISCUSSION	101
4.5.1. Synthesis and Characterization of the PAES Random Copolymers and Segmented Block Copolymers	101
4.5.2. Thermal Properties of Polymers	103
4.5.3. Tensile Analysis of Segmented Block Copolymers	109
4.6. CONCLUSIONS	113
4.7. ACKNOWLEDGMENTS	114
4.8. REFERENCES	114
5.0. SYNTHESIS AND CHARACTERIZATION OF TRIPTYCENE POLY(ARYLENE ETHER SULFONE)S	117
5.1. ABSTRACT	117
5.2. INTRODUCTION	117
5.3. EXPERIMENTAL	119
5.3.1. General Methods and Materials	119
5.3.2. Synthesis of TPDH PAES	120
5.3.3. Synthesis of BA–TPDH PAES Random Copolymers (BA–TPDH PAES)	121
5.3.4. Synthesis of BA–TPDH PAES Segmented Copolymer	122
5.3.5. Preparation of Dimethylamino-Terminated PDMS (PDMS) Oligomers	124
5.3.6. Preparation of Segmented Block Copolymers (BA–TPDH PAES– <i>b</i> –PDMS)	125
5.3.7. Film Preparation of the Segmented Block Copolymers	128
5.3.8. Polymer Acronyms	128
5.4. CHARACTERIZATION METHODS	128

5.4.1. Nuclear Magnetic Resonance Spectroscopy (NMR)	128
5.4.2. Size Exclusion Chromatography (SEC)	128
5.4.3. Thermogravimetric Analysis (TGA)	129
5.4.4. Differential Scanning Calorimetry (DSC)	129
5.4.5. Tensile Analysis	129
5.5. RESULTS AND DISCUSSION	130
5.5.1. Synthesis of Polymers.....	130
5.5.2. Solubility of TPDH PAES	132
5.5.3. Thermal Properties of Polymers.....	133
5.5.4. Tensile Analysis of Segmented Block Copolymers.....	136
5.6. CONCLUSIONS	139
5.7. ACKNOWLEDGMENTS	140
5.8. REFERENCES	140
6.0. TENSILE AND THERMAL CHARACTERISTICS OF SEGMENTED BLOCK COPOLYMER BLENDS	142
6.1. ABSTRACT	142
6.2. INTRODUCTION	143
6.3. EXPERIMENTAL	145
6.3.1. General Methods and Materials	145
6.3.2. Preparation of Segmented Block Copolymer Blends.....	145
6.4. CHARACTERIZATION METHODS	146
6.4.1. Thermogravimetric Analysis (TGA)	146
6.4.2. Dynamic Mechanical Analysis (DMA)	146
6.4.3. Tensile Analysis	146
6.5. RESULTS AND DISCUSSION	146
6.5.1. Thermal Stability of Segmented Block Copolymer Blends.....	146
6.5.2. Dynamic Mechanical Analysis of Segmented Block Copolymer Blends.....	147
6.5.3. Tensile Analysis of Segmented Block Copolymer Blends	153
6.6. CONCLUSIONS	157
6.7. ACKNOWLEDGMENTS	157
6.8. REFERENCES	158
7.0. FUTURE WORK	160
REFERENCES	168

List of Schemes

Scheme 1.1: Synthesis of PAES.	3
Scheme 1.2: Synthesis of PAES.	6
Scheme 1.3: Production of linear and cyclic siloxanes ²⁸	14
Scheme 1.4: Polycondensation reactions of linear siloxanes.....	15
Scheme 1.5: Living anionic polymerization of D ₃ ⁵¹	17
Scheme 1.6: Linear and cyclic chains from polymerization of D ₄	18
Scheme 1.7: Acidic-catalyzed reactions of D ₄	19
Scheme 1.8: Basic-catalyzed reaction with potassium hydroxide catalyst of D ₄	21
Scheme 1.9: Synthesis of tetramethylammonium disiloxanolate catalyst.	22
Scheme 1.10: Synthesis of hexamethyldisiloxane-terminated PDMS using tetramethylammonium disiloxanolate catalyst.	24
Scheme 1.11: Siloxane back-biting ⁵³	25
Scheme 1.12: Bisphenol A-polycarbonate–PDMS segmented block copolymer.	29
Scheme 1.13: PAES–bisphenol A-polycarbonate segmented block copolymer.	32
Scheme 1.14: Reaction between hydroxyl-terminated polycarbonate oligomer and dimethylamino-terminated PDMS.	35
Scheme 1.15: Reaction between hydroxyl-terminated PAES and dimethylamino- terminated PDMS.	39
Scheme 2.1: Synthesis of segmented block copolymers.	56
Scheme 4.1: Synthesis of DHTP.	95
Scheme 4.2: Synthesis of BA–DHTP PAES– <i>b</i> –PDMS.	99
Scheme 5.1: Synthesis of TPDH PAES.....	121
Scheme 5.2: Synthesis of BA–TPDH PAES random copolymer.	122
Scheme 5.3: Synthesis of BA–TPDH PAES segmented copolymer.	124
Scheme 5.4: Synthesis of BA–TPDH PAES– <i>b</i> –PDMS.	127
Scheme 7.1: Proposed synthesis of 4,4'-(hexafluoroisopropylidene)bis[(4- hydroxyphenyl)hydroquinone].....	162
Scheme 7.2: Proposed synthesis of segmented block copolymers containing fluorine groups.	163
Scheme 7.3: Proposed synthesis of segmented block copolymers containing DP <i>m</i> -T.	167

List of Figures

Figure 1.1: Structure of Udel [®]	1
Figure 1.2: a) D ₃ cyclic siloxane and b) D ₄ cyclic siloxane.	16
Figure 1.3: Structure of PDMS.....	16
Figure 1.4: Block copolymer phase morphology. (Adaptation of Figs. 1-2, Bates and co-workers ⁸⁰)	30
Figure 1.5: Stress-strain plots for a fiber, plastic, flexible plastic, and an elastomer. (Adaptation of Fig. 1-10, Odian ⁸⁹).....	33
Figure 1.6: Temperature-modulus phase behavior of segmented block copolymers. (Recreation of Fig. 1, McGrath et al. ⁹⁴).....	37
Figure 1.7: Three bisphenol monomers studied in this research.....	40
Figure 2.1: TGA thermograms of PAES segmented block copolymers, at 10 °C/min.	58
Figure 2.2: TGA thermograms of BAF PAES- <i>b</i> -PDMS and homopolymers.	59
Figure 2.3: AFM images of PAES segmented block copolymers BAF-72 and BA-71 showing the surface of the film.	63
Figure 2.4: TEM images of BAF PAES- <i>b</i> -PDMS (BAF-72) 5400–10,000, (BAF-55) 6800–5800, (BAF-44) 5400–4100, (BAF-41) 9700–4700, and (BAF-22) 5400–1600....	65
Figure 2.5: TEM images of BA PAES- <i>b</i> -PDMS (BA-71) 5500–10,000, (BA-52) 10,000–10,000, and (BA-20) 10,000–1600.	65
Figure 2.6: SAXS data for PAES segmented block copolymers BAF-72 and BA-71. ..	67
Figure 2.7: SAXS data for BAF PAES- <i>b</i> -PDMS of various PDMS volume fractions. The data have scaled vertically for clarity of presentation.	68
Figure 3.1: Degree of polymerization over time.....	79
Figure 3.2: Molecular weight measurements from light scattering detection of BA PAES- <i>b</i> -PDMS (10,000–5600) over time.....	82
Figure 3.3: Representative auto-correlation function for the segmented block copolymers measured by DLS.....	86
Figure 3.4: Size distribution by intensity of BAF PAES- <i>b</i> -PDMS (A) 9700–4700, (B) 5400–4100, (C) 6800–5800, and (D) 5400–10,000.....	86
Figure 4.1: ¹ H NMR of hydroxyl-terminated BA-DHTP PAES random.	102
Figure 4.2: ¹ H NMR of BA-DHTP PAES- <i>b</i> -PDMS.....	103
Figure 4.3: TGA thermograms of BA PAES and BA73-DHTP27 PAES random copolymer, at 10 °C/min.	104
Figure 4.4: Thermal stability of BA-DHTP PAES- <i>b</i> -PDMS (4500–4500) compared to BA PAES- <i>b</i> -PDMS (4300–4500), at 10 °C/min.....	105
Figure 4.5: DSC profile BA PAES and BA73-DHTP27 PAES random copolymer, at 10 °C/min.	106
Figure 4.6: AFM images of BA-DHTP PAES- <i>b</i> -PDMS (BA-DHTP-1) 5900–1300, (BA-DHTP-2) 4500–4500, and (BA-DHTP-3) 8500–20,400 showing the surface of the film.	109
Figure 4.7: Stress-Strain curve for BA PAES- <i>b</i> -PDMS (5500–1300) and BA-DHTP PAES- <i>b</i> -PDMS (5900–1300).	113
Figure 4.8: Stress-Strain curve for BA PAES- <i>b</i> -PDMS (5500–10,000) and BA-DHTP PAES- <i>b</i> -PDMS (4500–9300).	113

Figure 5.1: ^1H NMR of TPDH PAES in THF- d_8	130
Figure 5.2: SEC MALLS trace of the TPDH PAES in THF.	131
Figure 5.3: Thermal stability of BA PAES and PAES containing TPDH, at 10 $^\circ\text{C}/\text{min}$	134
Figure 5.4: Thermal stability of BA94–TPDH6 PAES– <i>b</i> –PDMS, at 10 $^\circ\text{C}/\text{min}$	135
Figure 5.5: DSC profile of BA PAES and PAES containing TPDH at 10 $^\circ\text{C}/\text{min}$	136
Figure 5.6: Stress–Strain curve for BA94–TPDH6 PAES– <i>b</i> –PDMS materials with varying PDMS content.	139
Figure 6.1: Thermal stability profile of Udel [®] and blends.	147
Figure 6.2: Storage modulus and temperature profile of Udel [®] in comparison with (A) BA–DHTP PAES– <i>b</i> –PDMS blends and (B) BA–TPDH PAES– <i>b</i> –PDMS blends.	149
Figure 6.3: Tan δ spectra of blends in comparison of Udel [®] in comparison with (A) BA– DHTP PAES– <i>b</i> –PDMS blends and (B) BA–TPDH PAES– <i>b</i> –PDMS blends.	152
Figure 7.1: Fluorinated monomers of interest.	161
Figure 7.2: Structure of 4,4''-dihydroxy-5'-phenyl- <i>m</i> -terphenyl (DPM-T) monomer.	165
Figure 7.3: Structures of DPM-T containing a) polyester and b) polyether.....	166
Figure 7.4: Proposed structure of DPM-T poly(arylene ether sulfone).	167

List of Tables

Table 1.1: Properties of amorphous high impact and engineering thermoplastics ^{a,b}	2
Table 1.2: Bisphenol derivatives and common names (trade name).....	6
Table 1.3: Thermal and mechanical properties of polyarylethers and polycarbonate.	8
Table 1.4: Solubility character of bisphenol A PAES at room temperature ^a	10
Table 1.5: Reduced viscosity and T_g values for various PAES ^a	12
Table 1.6: Most common block copolymer architectures.....	27
Table 2.1: Thermal stabilities of BAF PAES and PDMS homopolymers and BAF PAES- <i>b</i> -PDMS.	58
Table 2.2: Tensile properties of BAF PAES- <i>b</i> -PDMS.	61
Table 2.3: Tensile properties of BA PAES- <i>b</i> -PDMS.	62
Table 2.4: Interdomain (ID) spacing between scattering domains from SAXS for BAF PAES- <i>b</i> -PDMS.....	69
Table 3.1: Segmented block copolymers investigated in this study.	76
Table 3.2: Molecular weight values of segmented block copolymers.....	81
Table 3.3: Molecular weight comparison of BAF PAES- <i>b</i> -PDMS.	85
Table 3.4: Intrinsic viscosities for segmented block copolymers.	88
Table 4.1: Thermal properties of BA-DHTP PAES- <i>b</i> -PDMS.....	108
Table 4.2: Tensile properties of BA-DHTP PAES- <i>b</i> -PDMS compared to BA PAES- <i>b</i> -PDMS.	112
Table 5.1: Solubility of TPDH PAES.....	133
Table 5.2: Tensile properties of BA PAES and PAES containing TPDH.....	138
Table 6.1: 95% Udel P-3500/5% Bisphenol A PAES- <i>b</i> -PDMS Blend Tensile Properties.	155
Table 6.2: 95% Udel P-3500/5% PAES- <i>b</i> -PDMS Blend Tensile Properties.	156

List of Equations

$$\Delta c = (n_s - n_r) / (d_n / d_c)$$

Equation 3.1.....82

Chapter 1:

LITERATURE REVIEW

1.1. INTRODUCTION TO POLY(ARYLENE ETHER SULFONE)S

1.1.1. Overview

Poly(arylene ether sulfone)s (PAES) are widely used amorphous, engineering thermoplastics based on their high T_g , good chemical stability, and excellent mechanical properties¹. The first member of the PAES family of thermoplastics was prepared from bisphenol A and 4,4'-dichlorodiphenyl sulfone (Fig. 1.1). This PAES was marketed in the early 1960's by Union Carbide Corporation/Amoco under the commercial trade name, Udel[®]. Farnham and Johnson et al.²⁻⁴ extensively explored the synthetic procedure, based on the catalyzed nucleophilic aromatic substitution reaction of 4,4'-dichlorodiphenyl sulfone and bisphenol A. They also studied the mechanical and other properties of the bisphenol A PAES.

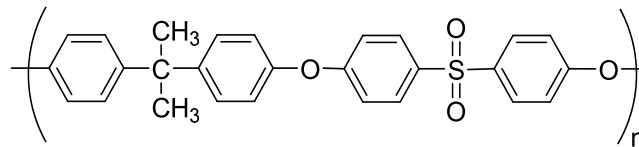


Figure 1.1: Structure of Udel[®].

Since that time, other PAES have been explored and this family of engineering thermoplastics has excellent mechanical strength, high T_g , and high hydrolytic and

thermal stabilities like other well studied engineering thermoplastic, including polycarbonate, polyetherimide, and PMMA (Table 1.1).

Table 1.1: Properties of amorphous high impact and engineering thermoplastics^{a,b}.

Amorphous Polymer	T_g, °C	Specific Properties
Bisphenol A Poly(arylene ether sulfone)	185	Rigid, Thermally Stable, Oxidative Resistant and Fair Chemical Resistance
Polycarbonate	150	Impact Resistant, Tough, Moderately Chemically Resistant, Biocompatible
PMMA	100	Brittle, Good Chemical Resistance and Weathering
Modified polyphenylene ether	100-135	High Stiffness, Low Moisture Absorption, Good Electrical Properties and Chemical Resistance
PCTG/PETG	85	Tough, Good Chemical Resistance
Thermoplastics urethane ^c	--	Chemically and Environmental Resistant, High Tensile Strength, Tear Resistant

^aAdaptation of IAPD Thermoplastic Rectangle ⁵.

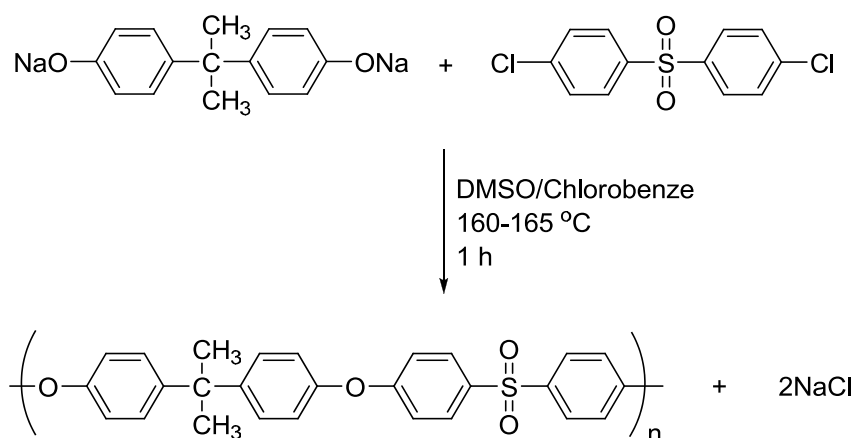
^bData taken from Charrier ⁶ unless stated otherwise.

^cData taken from Handbook of Thermoplastic Elastomers ⁷.

1.1.2. Synthesis of PAES

The main synthetic route for preparing PAES is polyetherification via a base catalyzed nucleophilic aromatic substitution mechanism. Polyetherification of PAES (3) can be done using many polycondensation polymerization processes; however, the two most common processes are the caustic and the carbonate processes ⁸.

The caustic process was the original method for synthesizing PAES ⁹. An example (Scheme 1.1) of the process employs the disodium salt of bisphenol A and an activated halide, such as dichlorodiphenylsulfone, in a dipolar aprotic solvent system, DMSO with chlorobenzene as an azeotroping agent. Within 1 h of adding dichlorodiphenylsulfone to the polymerization, the reduced viscosity was 1.0 (0.2 g/dl in chloroform at 25 °C).



Scheme 1.1: Synthesis of PAES.

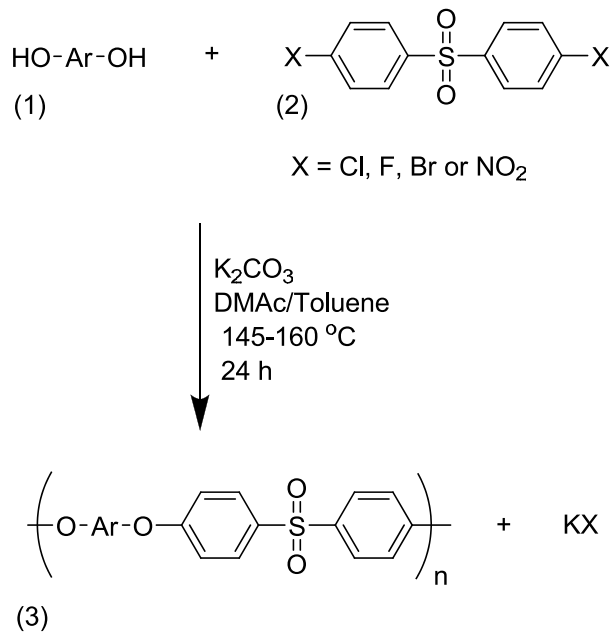
The carbonate process is the preferred method for polymerization of PAES ¹⁰. This process (Scheme 1.2) involves several components, monomers: a bisphenol

derivative (1) (Table 1.2) and an activated halide (2); a weak or a strong base such as potassium carbonate (K_2CO_3) or sodium carbonate (Na_2CO_3); and a polar aprotic solvent system such as *N*-methylpyrrolidinone (NMP), dimethylacetamide (DMAc), or sulfolane with toluene as an azeotroping agent. Under the protection of a gas such as argon or nitrogen, the polymerization typically produces high molecular weight polymer within 24 h at temperatures ranging 140–250 °C. The by-product is a metal halide ⁴. Other alternative routes have been proposed producing comparable results ¹¹. Attwood and co-workers described three alternative synthetic methods: (a) melt polycondensation of halogenophenylsulphonyl phenoxides under vacuum, (b) polycondensation of halogenophenylsulphonyl phenoxides conducted in solution, and (c) polycondensation of halogenophenylsulphonyl and hydroxyphenyl in the presence of potassium fluoride as a base.

The halogen substituted (X) on (2) can have a large effect on the rate of the polymerization. It is well known the leaving group reactivity in the nucleophilic aromatic substitution reaction is in the order of $F^- > Cl^- > Br^- \sim I^-$ ¹². Aromatic fluorides are faster in terms of reactivity; however, they are too expensive for large scale commercial use. Typically, aromatic chlorides are frequently used in this reaction and high molecular weight polymers are readily achieved ⁹.


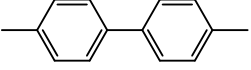
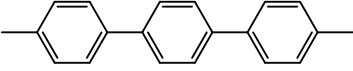
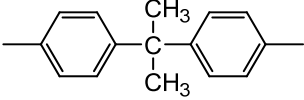
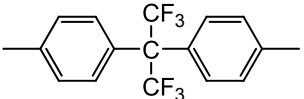
Molecular weight and chain ends can be controlled by the stoichiometry between the bisphenate and the dihalide reactants. For preparing a polymer with the highest molecular weight, the reaction conditions should have a 1:1 stoichiometry between the bisphenate and the dihalide reactants. Additionally, the reaction must be charged with pure reactants, reagents, and solvents ¹³⁻¹⁵. The elimination of water and oxygen from

the reaction is also absolutely necessary to prohibit the polymerizing functional groups from undergoing side reactions that can change the stoichiometric co-monomer charge ratio and affect the molecular weight and chain ends. For instance, water can neutralize the phenolate salt generating phenol and a hydroxide ion, followed by the free hydroxide ion attacking the aromatic dihalide to form an excess of phenol endgroup. The presence of oxygen can oxidize the phenolate and offset the stoichiometry ¹⁶.



Scheme 1.2: Synthesis of PAES.

Table 1.2: Bisphenol derivatives and common names (trade name).

Ar	Monomer	Ref
	Hydroquinone, HQ	4
	Biphenol, BP (Radel [®] R)	17, 18
	Terphenol	19
	Bisphenol A, Bis A (Udel [®])	4, 20
	Bisphenol AF, Bis AF, 6F	4

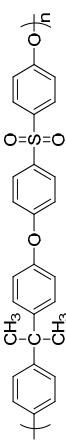
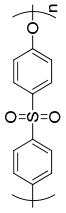
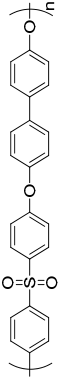
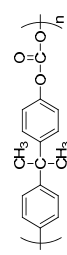
1.1.3. Properties of PAES

1.1.3.1. Mechanical Properties

PAES have outstanding mechanical properties which enable their applications in many engineering thermoplastic markets. The mechanical properties of polyarylethers and PAES are often compared to other thermoplastics including bisphenol A polycarbonate (Table 1.3). Research has suggested the comparison of bisphenol A PAES to bisphenol A polycarbonate relies heavily on their free volume size, which impacts their T_g and mechanical properties ²¹. From the table, it can be seen that bisphenol A polycarbonates display similar high thermal stability and good mechanical properties compared to PAES.

Bisphenol A PAES has high tensile and flexural moduli, but demonstrates reduced elongation to break and notched Izod values when compared to bisphenol A polycarbonate. It is well known these values suggest that both PAES and bisphenol A polycarbonate have rigidity and strength to impede failure. While these analyses were done at ambient conditions, the tendency of these mechanical properties to change under several factors including temperature, environmental exposure, and chemical interaction is likely. For instance, at increased temperature, tensile modulus and tensile strength are expected to decrease. DMA has shown that PAES have a low temperature loss at -100 °C, which also accounted for impact strength and toughness ².

Table 1.3: Thermal and mechanical properties of polyarylethers and polycarbonate.

Material	Density g/cm ³	Tensile Mod. MPa	Tensile Stren. MPa	Ten. Elon. (Break) %	Flexural Mod. MPa	Flexural Stren. MPa	Notched Izod Impact J/m	Tensile Impact Stren. kJ/m ²
ASTM method	D792	D638	D638	D638	D790	D790	D256	D1822
Udel® P-1700^a 	1.24	2480	70.3	50-100	2690	106	69.4	420
Veradel® A-201^a 	1.37	2690	88.9	6.5 (Yield)	2620	125	53.4	Not Listed
Radel® R-5000^a 	1.29	2340	69.6	60-120	2410	91.0	694	399
Lexan® Resin 101^b 	1.19	2250	62	135	2340	97	907	630

^aData taken from Solvay Advanced Polymers, material datasheets.

^bData taken from SABIC (Saudi Basic Industries Corp), Lexan® Resin 101 datasheet.

Also, studies on PAES with varying molecular weights have shown that impact strength increases as a function of molecular weight^{22, 23}. Still, major deficiencies of PAES, particularly bisphenol A, are brittleness and low ductility, which can be mediated or increased by adding plasticizers and elastomers to the polymer composition²⁴. However, compared to bisphenol A polycarbonate, certain mechanical properties of bisphenol A PAES, such as the tensile and flexural modulus, are higher.

1.1.3.2. Chemical Properties

PAES are usually non-crystalline and because of the amorphous character; they generally have only fair chemical resistance which can lead to mechanical failure on exposure to various solvents. However, PAES are often used in various applications where bisphenol A polycarbonates show substandard effectiveness, especially those that require exposure to chemicals at high temperatures or even high temperature environments²⁵. The amorphous character of PAES also determines their transparency because there are no crystalline regions within the polymer to scatter light. The solubility of bisphenol A PAES at room temperature is listed in Table 1.4. Information from the table shows bisphenol A PAES is insoluble in non-polar organic solvents and is only soluble in polar aprotic solvents.

Table 1.4: Solubility character of bisphenol A PAES at room temperature^a.

Class of solvent	Solubility^b
Inorganic acids	N
Alkalies	N
Aliphatic alcohols	N
Aliphatic esters	PS
Aliphatic ketones	PS
Aliphatic hydrocarbons	N
Aromatic hydrocarbons	PS
Polar aromatics compounds	S-PS
Chlorinated hydrocarbons	S
DMF, DMAc	S
NMP	S
DMSO, Sulfolane	PS

^a Adaptation of data from Table XII in Johnson et al.⁴.

^b N = not soluble; PS = partly soluble or swells; S = soluble.

1.1.3.3. Thermal Properties

PAES display exceptional thermal properties. These thermoplastics have high thermal stability under various atmospheres. Li et al.²⁶ showed that the onset of degradation under nitrogen and argon atmospheres at various heating rates was between 520–525 °C. The thermal degradation of bisphenol A polycarbonate is similar

to bisphenol A PAES in the region of 420–540 °C under nitrogen and air atmospheres²⁷.

One particular contrast is bisphenol A polycarbonate has a T_g of 150 °C¹, lower than bisphenol A PAES, which is 185 °C. Several PAES tested by Attwood et al.²³ showed increased T_g with the incorporation of additional *p*-phenylene rings in the PAES unit due to the increased chain rigidity (Table 1.5). The results listed also include the reduced viscosities of the polymers.

Table 1.5: Reduced viscosity and T_g values for various PAES^a.

PAES Types	T_g (°C)	RV ^b
	228-240	0.45-2.3
	185	0.42
	207	1.88 ^c
	224	0.65
	289	0.47
	251 ^d	--

^a Adaptation of data from Table 4 in Attwood et al. ²³.

^b Reduced viscosity for 1% solutions measured in DMF at 25°C, unless stated otherwise.

^c Measured on 1% solution in sulfuric acid.

^d Value taken from Staniland ¹⁹.

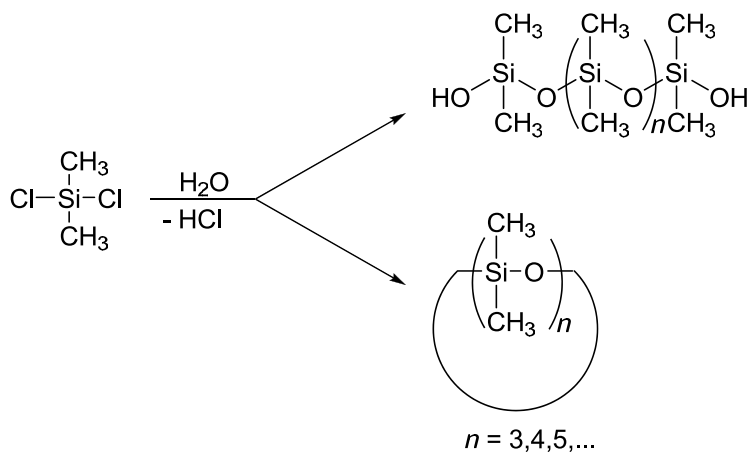
1.2. INTRODUCTION TO POLYDIMETHYLSILOXANES

1.2.1. Overview

Siloxanes were first synthesized in 1872²⁸. Commercial manufacturing of siloxanes began in the 1940's with the linear dimethyldichlorosilane²⁹. From the production of linear siloxanes, a variety of cyclic siloxanes have been produced and later used for the polymerization of polydimethylsiloxane (PDMS) materials. Today, PDMS is widely used in many elastomer applications. PDMS has been copolymerized with many other polymers including polycarbonates³⁰⁻³², bisphenol A PAES³³, polyurethanes^{34, 35}, polyimides³⁶, polystyrenes^{37, 38}, poly(ether ketone sulfone)³⁹ and polyetheretherketone⁴⁰.

1.2.2. Preparation of Linear and Cyclic PDMS

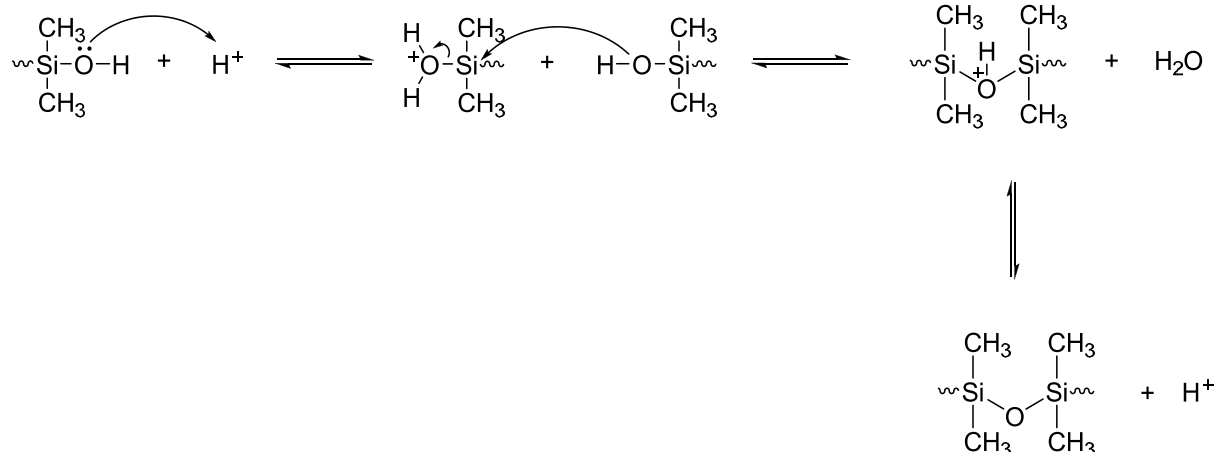
Linear and cyclic siloxanes are prepared through the hydrolysis of methylchlorosilanes⁴¹. The traditional method for preparing methylchlorosilanes is through a direct synthesis, commonly known as the Rochow Synthesis, which uses a copper catalyst^{42, 43}. Linear and cyclic siloxanes are produced by the hydrolysis, then by condensation of dichlorodimethylsilane as shown in Scheme 1.3.



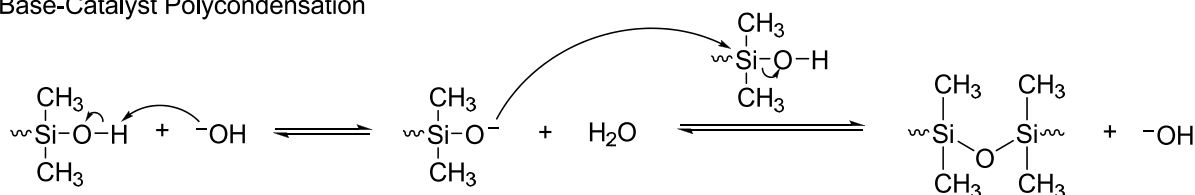
Scheme 1.3: Production of linear and cyclic siloxanes ²⁸.

The linear siloxanes can be further polymerized to produce high molecular weight PDMS through a polycondensation reaction with a strong acid catalyst, such as HCl or via a strong base catalyst, such as KOH (Scheme 1.4).

Acid-Catalyst Polycondensation



Base-Catalyst Polycondensation



Scheme 1.4: Polycondensation reactions of linear siloxanes.

The cyclics, specifically 4–6, can be isolated by fractional distillation. While this is the most common technique, another synthetic route was also investigated⁴⁴. The two most common types of cyclic siloxanes (Fig. 1.2) used for polymerization are hexamethylcyclotrisiloxane (D₃) and octamethylcyclotetrasiloxane (D₄)²⁸. Both cyclic siloxanes can be polymerized into PDMS by ring-opening polymerization illustrated by the repeat unit in Fig. 1.3.

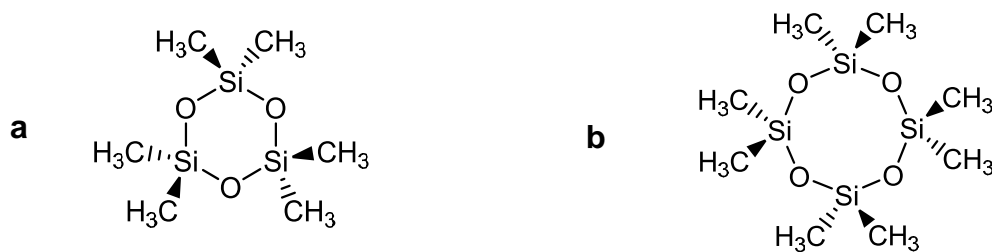


Figure 1.2: a) D₃ cyclic siloxane and b) D₄ cyclic siloxane.

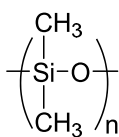


Figure 1.3: Structure of PDMS.

1.2.3. Ring-Opening Polymerization of Cyclic Siloxanes

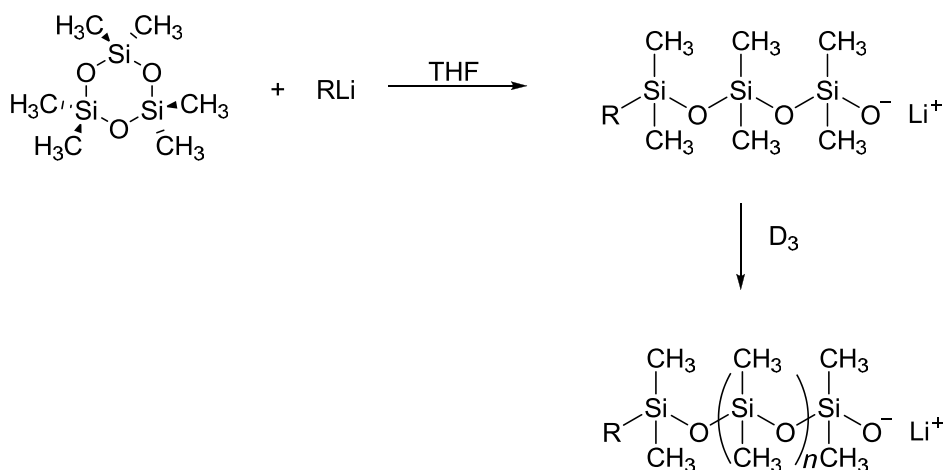
Bauer et al.⁴⁵ reported ring-opening polymerization for D₃ cyclic siloxanes occurs more rapidly and polymerization rates are larger than for D₄ cyclic siloxanes because of the increased reactivity of the siloxane bond due to the ring strain of D₃. D₃ cyclic siloxane is less stable due to a larger degree of ring strain, 3.2 kcal/mole. D₄ cyclic siloxane is more stable and virtually has no ring strain^{46, 47}.

The strained ring in D₃ makes the polymerization a kinetically controlled process and represents an exothermic reaction, whereas D₄ polymerizes by a thermodynamically controlled route¹³.

1.2.3.1. Living Anionic Polymerization

D₃ cyclic siloxanes are typically polymerized by living anionic polymerization. Organolithium compounds, such as *n*-Bu-Li, and tetrahydrofuran (THF) solvent are used

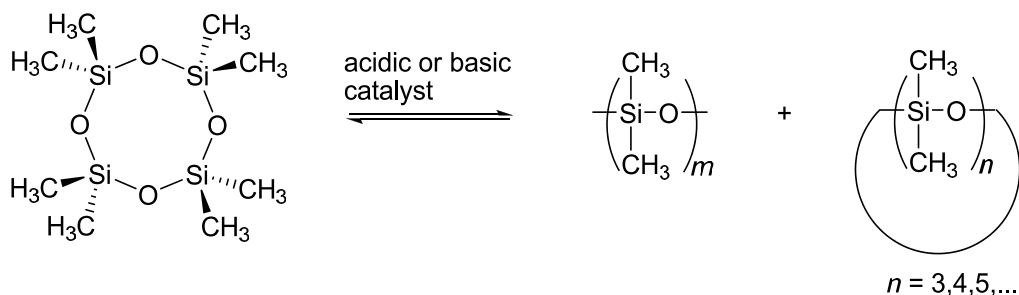
to initiate the reaction and also to prevent the ion-ion interaction between the lithium (cation) and the silanoate (anion) as shown in Scheme 1.5. The reaction can be completed at room temperature and requires no chain transfer agent. Under these reaction conditions, the degree of polymerization increases with the percent conversion. The polymerization of D_3 produces no residual cyclic chains and achieves a narrow molecular weight distribution upon completion⁴⁸. Successful polymerization of D_3 substituted monomer including those with vinyl substituent groups has been reported^{14, 15, 48-50}.



Scheme 1.5: Living anionic polymerization of D_3 ⁵¹.

As aforementioned, D_4 polymerizes by a thermodynamically controlled route. Thermodynamically controlled polymerizations occur when the reaction is allowed to reach equilibrium conditions. For D_4 , the polymerization results in a distribution of both linear and cyclic chains (Scheme 1.6). The ring-opening polymerizations of D_4 cyclic

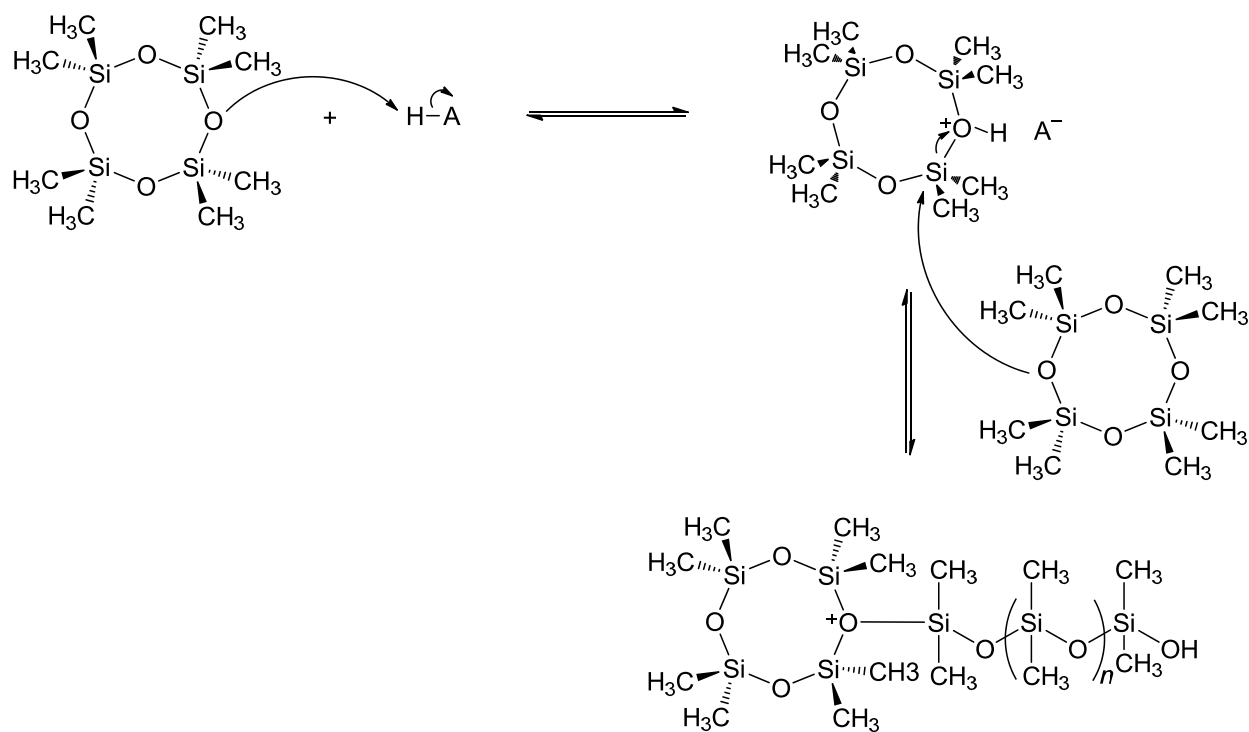
siloxanes are traditionally commenced by acidic or basic catalysts. The catalysts are chosen based on the reaction conditions.



Scheme 1.6: Linear and cyclic chains from polymerization of D₄.

1.2.3.2. Acid-Catalyzed Reactions

The ring-opening polymerization of cyclic siloxanes can also use acid catalysts. Common catalysts are sulfuric acid, anhydrous hydrogen chloride, and stannic chloride. Though, this method of polymerization is intended to yield high molecular polymer, little research has investigated the exact reaction mechanism. Wilczek et al.⁵² proposed the ring-opening polymerization in Scheme 1.7. The reaction occurs by using an acid to protonate the cyclic siloxane. After the cyclic siloxane is protonated, nucleophilic attack on the silicon-oxygen bond promotes ring-opening of the cyclic siloxane.

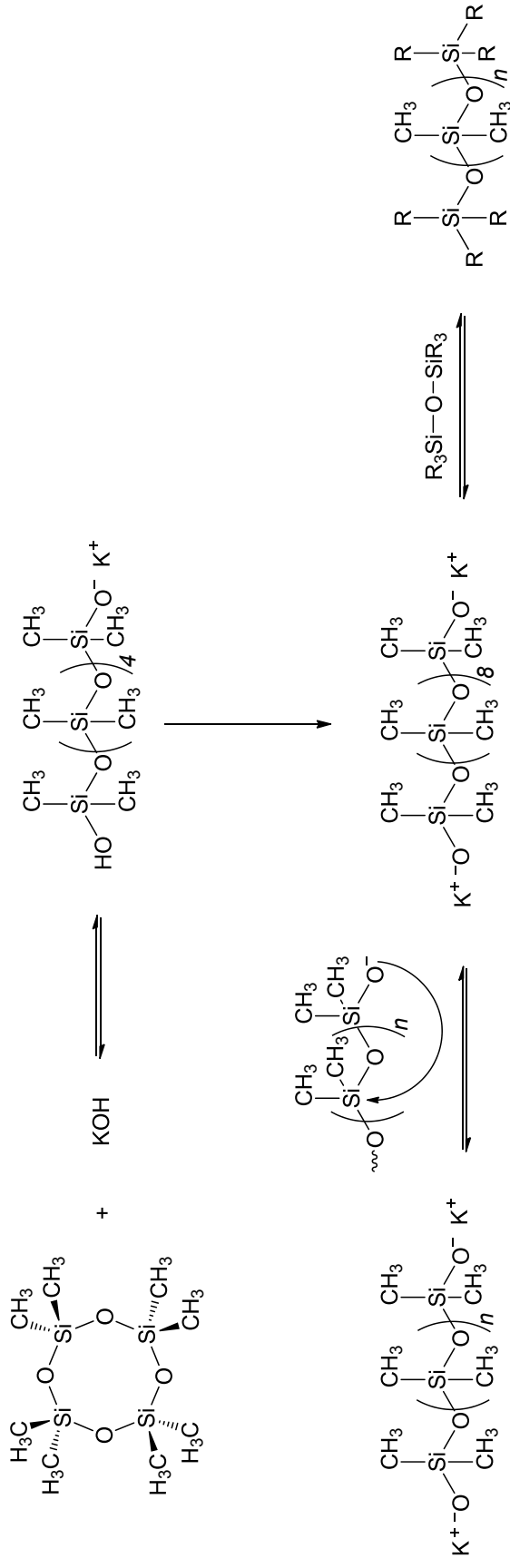


Scheme 1.7: Acidic-catalyzed reactions of D₄.

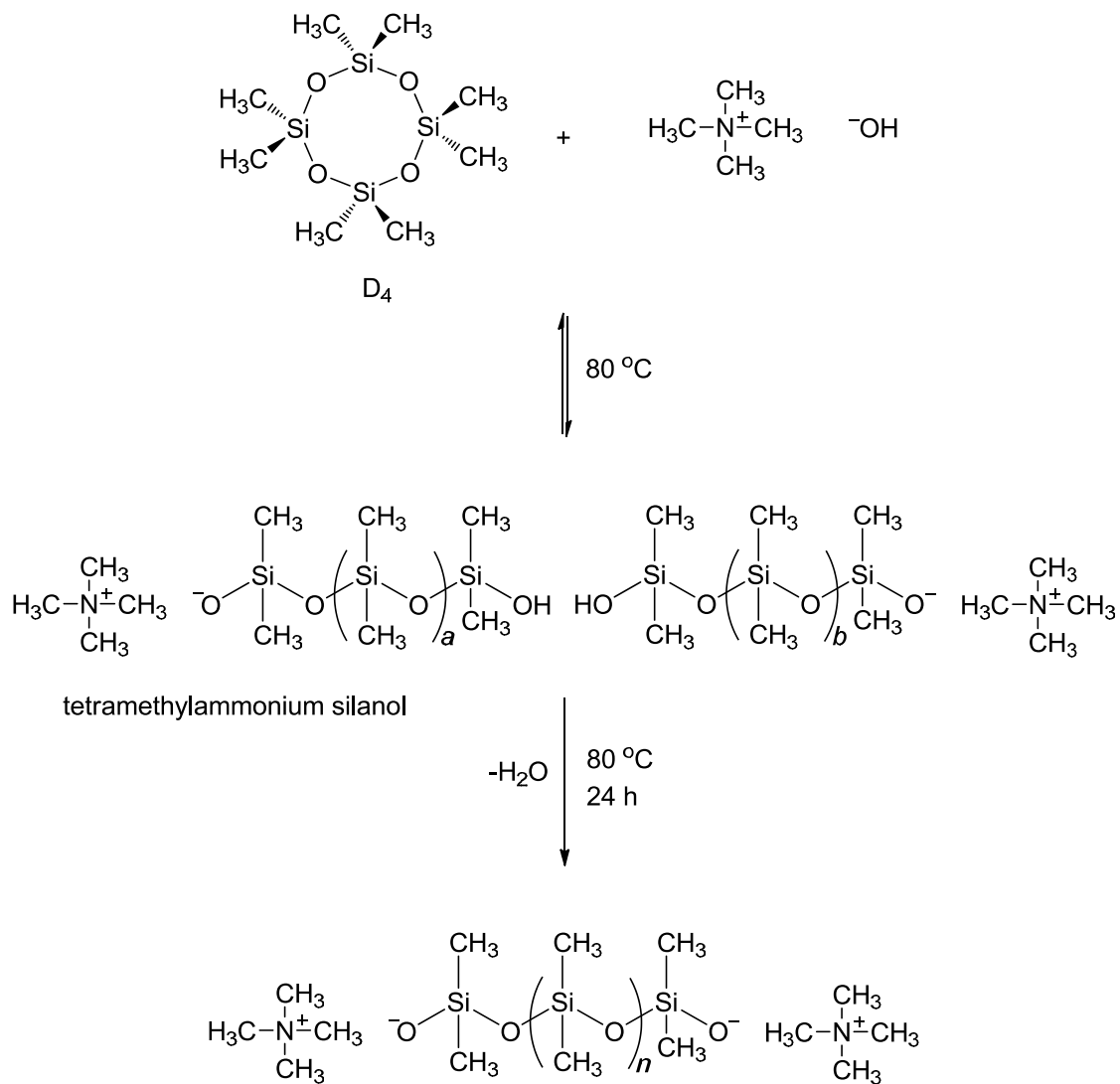
1.2.3.3. Basic-Catalyzed Reactions

Several basic-catalysts including alkali metal hydroxides, phenolates, and siloxanates of phosphonium or quaternary ammonium, and an end-capping agent can be used to synthesize PDMS. Reactivity of the alkali metal hydroxide catalysts increases in the order of CsOH > KOH > NaOH > LiOH²⁸. A simple reaction using potassium hydroxide catalyst (KOH) is shown in Scheme 1.8⁵¹. KOH catalyst leads to a high polymerization rate with an activation energy of 18 kcal/mole, Sormani et al.⁵³ explain that KOH is a non-transient catalyst because it has to be neutralized or removed from the reaction to avoid depolymerization at high temperatures. Thus, transient catalysts like quaternary ammonium are commonly used to polymerize D₄⁵⁴. Above a specific temperature, transient catalysts readily decompose into products that are not

catalytically reactive towards siloxanes. For instance, tetramethylammonium siloxanolate catalyst (Scheme 1.9) readily polymerizes D_4 at temperatures up to 130 °C and has an activation energy of 42 kcal/mole⁵⁵.



Scheme 1.8: Basic-catalyzed reaction with potassium hydroxide catalyst of D₄.

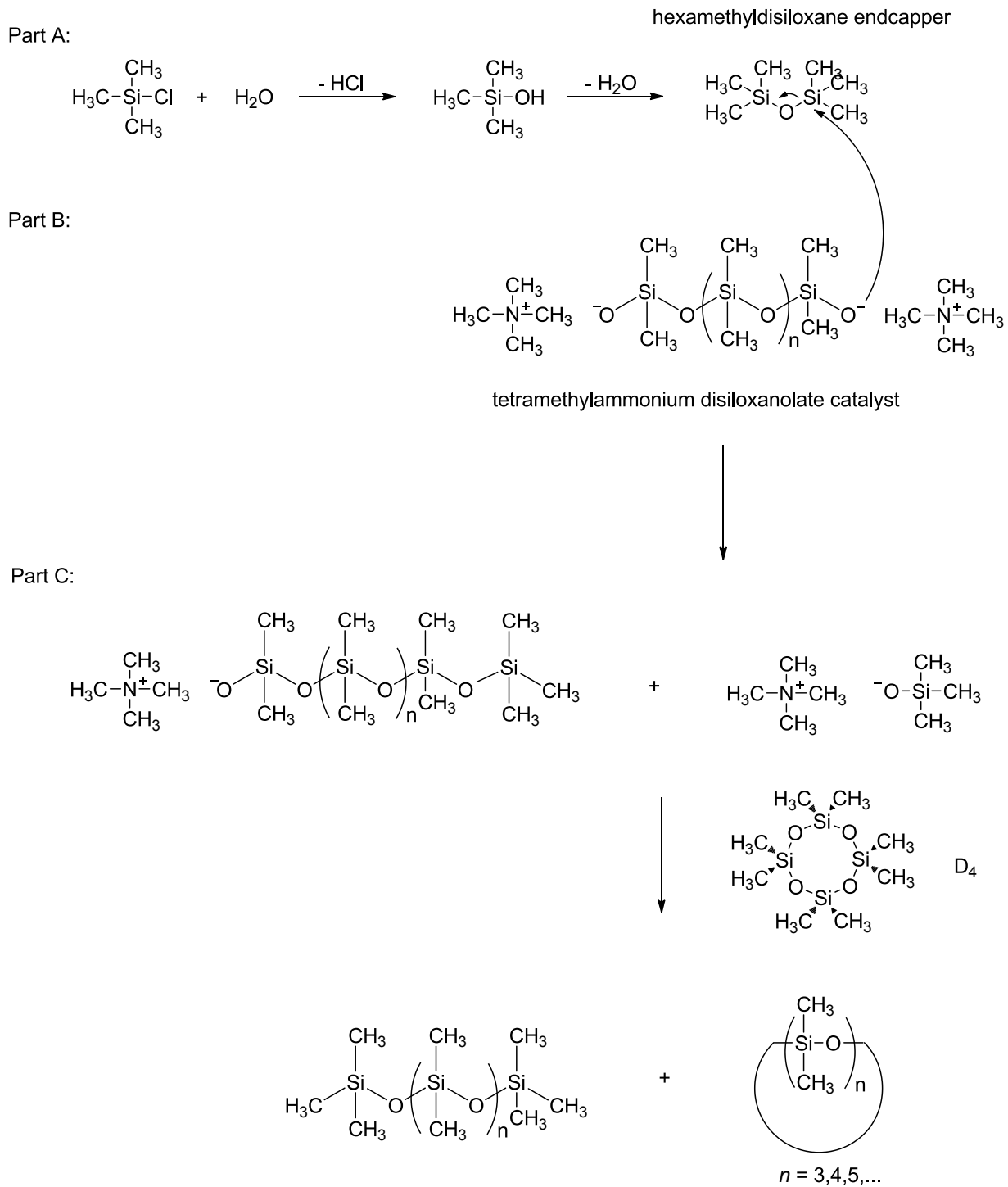


Scheme 1.9: Synthesis of tetramethylammonium disiloxanolate catalyst.

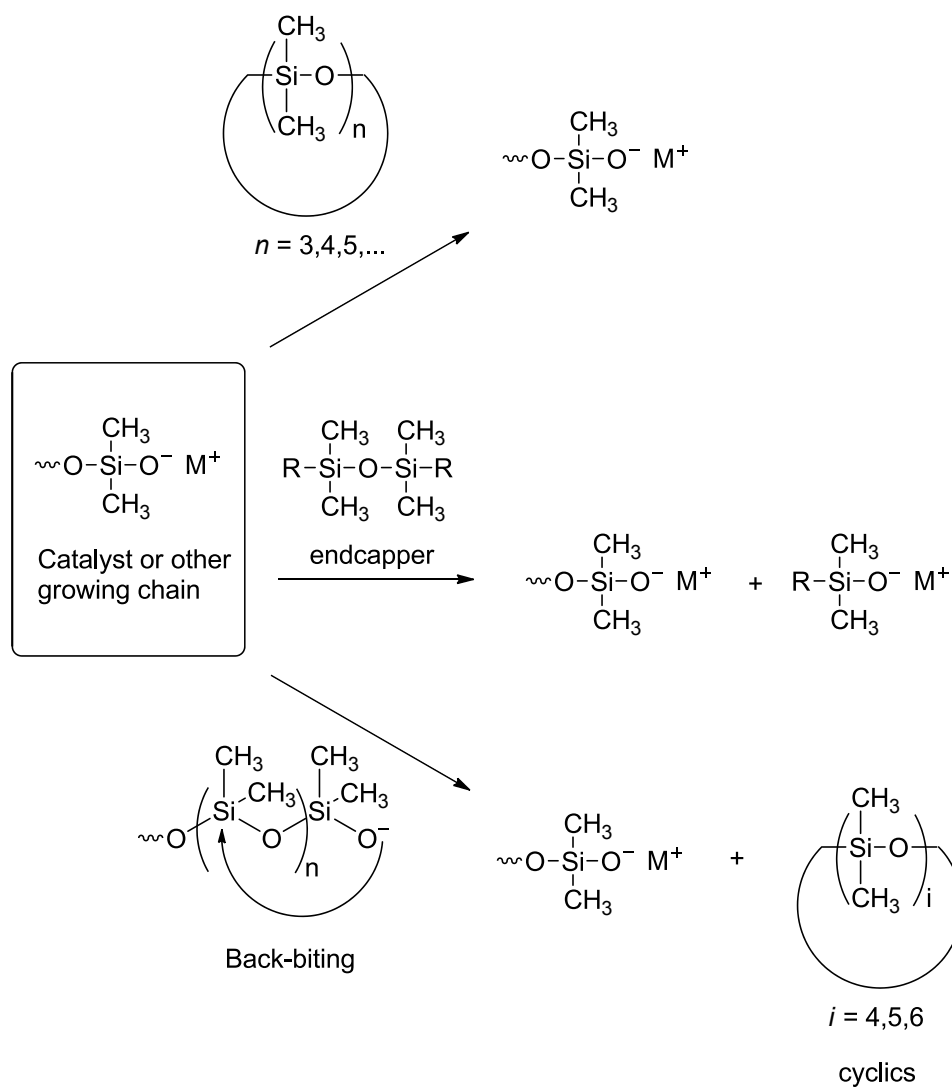
An example polymerization of PDMS that utilizes an endcapping agent to control the molecular weight of the siloxane polymer is illustrated in Scheme 1.8⁵⁶. In part A, the endcapper, hexamethyldisiloxane, is prepared by reacting trimethylchlorosilane with water to form an unstable silanol that is dehydrated to form the dimer⁵⁷. Part B illustrates the reaction between the hexamethyldisiloxane and tetramethylammonium

disiloxanolate catalyst (from Scheme 1.10) to yield a base catalyzed initiator. Equilibration of the base catalyzed initiator with D_4 results in a PDMS linear chain and various cyclic species. The anions couple, by-products, and remaining cyclics can be easily removed by vacuum distillation⁵⁸. Other commonly used endcapping agents include aminopropyl-1,3-tetramethyldisiloxane or a silylamine. During the equilibration, the viscosity and molecular weight are increased steadily over time until the D_4 is consumed. At that point, the viscosity reaches equilibrium. The rate of polymerization does depend on the catalyst type and reaction conditions.

While the equilibration of D_4 appears unproblematic, the solvent can have a major affect on the polymerization rate and the amount of cyclics formed, which is attributed to back-biting. Typically in the polymerization the amount of cyclics are determined by the solvent. Siloxanolate anion attacks the silicon-oxygen bond and hinders the formation of cyclics. However, during back-biting shown in Scheme 1.11, siloxanate anions on the silicon-oxygen bond are hindered by the increased solvent concentration and cannot attack the cyclics to form polymer—thus, after prolonged back-biting, cyclics are only formed in the polymerization and little to no polymer is present.



Scheme 1.10: Synthesis of hexamethyldisiloxane-terminated PDMS using tetramethylammonium disiloxanolate catalyst.



Scheme 1.11: Siloxane back-biting⁵³.

1.2.4. Properties

PDMS elastomers exhibit excellent oxidative stability, high gas permeability, and high chain flexibility. They typically exhibit a very low T_g , $-125\text{ }^\circ\text{C}$, have a melting temperature, T_m , $-55\text{ }^\circ\text{C}$ ⁶. Particularly, they are thermally stable at high temperatures and possess wide temperature use ranges, $-100\text{--}250\text{ }^\circ\text{C}$. PDMS elastomers also have low surface energy of approximately 21 mN/m and a low solubility parameter (7.5–9.6)

depending on the siloxane units ²⁹. These features give PDMS many of the properties that make it an attractive material for incorporation into polymer compositions for many elastomer applications ⁵⁹.

1.3. INTRODUCTION TO SEGEMENTED BLOCK COPOLYMERS

1.3.1. Overview

Segmented block copolymers have been studied for their mechanical, chemical, and thermal properties. Most reports call these materials perfectly alternating block copolymers or multiblock copolymers because their formation is from a condensation reaction of two polymers with reactive end-groups versus the traditional termination-free anionic polymerization route to block copolymers. Table 1.6 outlines the various block copolymer types that have synthesized and studied.

Di-block copolymers have been studied extensively in the literature. In terms of preparing materials with high resilience, high tensile strength and modulus, and high reversible elongation, tri-block and segmented block copolymers have been the copolymers of choice in the literature. Such well-defined copolymers that incorporate phase-separated hard and soft segments with outstanding properties have put materials of these types in a unique class, thermoplastic elastomers ⁶⁰.

Table 1.6: Most common block copolymer architectures.

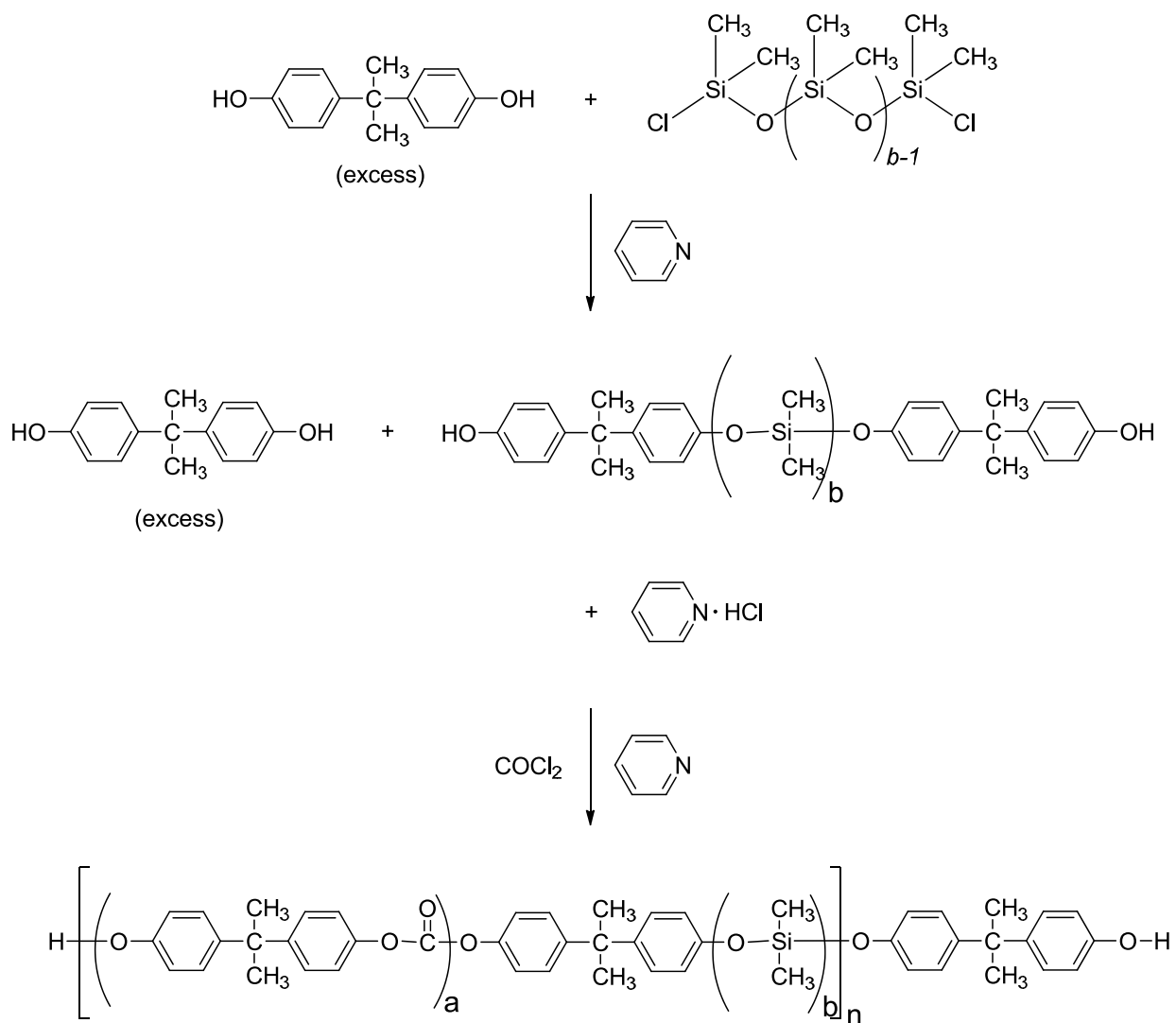
Block Copolymer	Structure	Polymerization Method	Example Ref
Di-block $\sim\text{A}-\text{B}\sim$		Macro-monomer coupling; Living polymerization	61-63
Tri-block $\sim\text{A}-\text{B}-\text{A}\sim$		Living polymerization; Step-growth polymerization	64-66
Perfectly Alternating (Segmented Block) $\left(\sim\text{A}-\text{B}\sim\right)_n$		Step-growth polymerization	67, 68

Considerable research conducted on segmented block copolymers has gone into developing polymeric structure-property relationships. The resulting materials have been found to have a combination of impact resistance and toughness, resulting from the hard and soft segments, that can serve in high impact applications^{69, 70}. In order to achieve high impact and toughness, segmented block copolymers typically encompass oligomers with well-defined properties—good thermal stabilities and excellent mechanical properties. Materials that possess many of the properties include high performance thermoplastic polymers such as polycarbonates, polyimides, polyketones, and PAES^{71, 72}.

Polycarbonate-siloxane structures have been one the most studied segmented block copolymer materials in the literature. Reports of these materials date as far back

as the early 1960s and still are being reported ³¹. Several researchers ⁷³⁻⁷⁶ have studied a series of segmented block copolymers of bisphenol A-polycarbonate incorporating PDMS. In one example synthesis of bisphenol A-polycarbonate-PDMS (Scheme 1.12), bisphenol A reacts with dichloro-terminated PDMS oligomer in the presence of pyridine to form bisphenol A-capped polydimethylsiloxane oligomer and a pyridine hydrochloride by-product. The second step involves the reaction between bisphenol A-capped polydimethylsiloxane oligomer, phosgene, and bisphenol A to form a carbonate-polydimethylsiloxane linkage. The polymerization produced high weight average molecular weight polymers ranging 50,000-100,000. These materials were shown to have a two-phase morphology, demonstrated thermal stability to 390 °C, and exhibit good mechanical properties including tensile strength from 6000-10000 psi and tensile moduli corresponding to elastomers to rigid materials depending on the polysiloxane content. Holub and co-workers patented work on polycarbonate-PDMS segmented block copolymer derivatives producing similar results ⁷⁷.

Similarly, Hamciuc et al. and Fitzgerald et al. ^{78, 79} synthesized materials using fluorinated polyimide as the engineering thermoplastic with PDMS. These segmented block copolymers possessed good processability, low water absorption, atomic oxygen resistance, low dielectric constants, and excellent adhesion. These materials have the potential to be used for applications in the microelectronics, automobiles, and aerospace areas.



Scheme 1.12: Bisphenol A-polycarbonate–PDMS segmented block copolymer.

1.3.2. Properties

1.3.2.1. Morphological Properties

The morphological profile of polymeric materials is extremely important on the basis of polymer properties and is therefore, one of the most widely researched topics in polymer science. For materials that microphase separate due to the incompatibility of the units copolymerized to form a block, various morphologies can be produced. For

diblock copolymers, the phase separated morphology can be predicted based on the phase diagram (Fig. 1.5). Two variables are defined, f , volume fraction of each unit, A and B, and the Flory-Huggins interaction parameter, χN , where N is the overall degree of polymerization of the copolymer. While these morphologies are attributed specifically to diblock copolymer systems, they can also be observed in segmented block copolymers. Segmented block copolymers prepared from two incompatible polymers likely results in microphase separation between the units forming blocks.

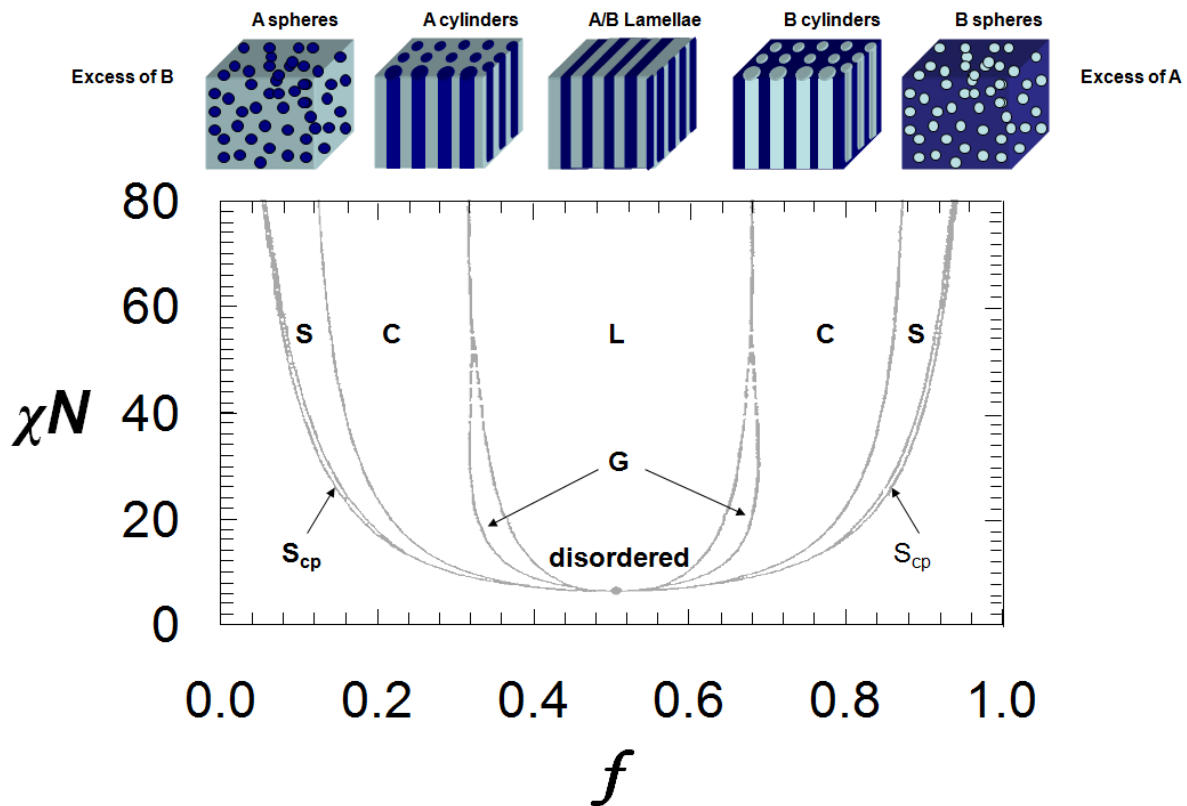


Figure 1.4: Block copolymer phase morphology. (Adaptation of Figs. 1-2, Bates and co-workers⁸⁰)

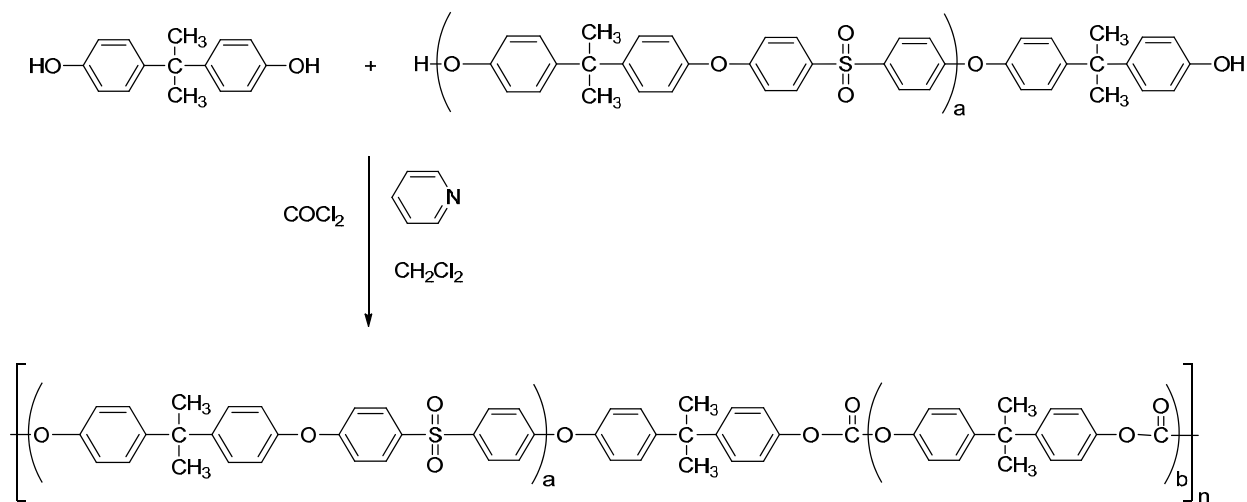
Bercea et al.⁸¹ explained the phase separation as shown in segmented block copolymers on the basis of interfacial adhesion between the two segments. An increase in the segment content leads to the lack of interfacial adhesion between the two segments. Phase separation in segmented block copolymers can be investigated theoretically, by means of using the Flory-Huggins interaction parameter or experimentally, by using microscopy and x-ray scattering techniques⁸².

Kricheldorf and co-workers^{83, 84} published work on the phase separation of a series of PAES segmented block copolymers. In that work the onset of phase separation was examined by DSC, i.e. at what volume fractions of PAES does phase separation occur? SAXS showed the extent of phase separation based on the domain size in the segmented block copolymers.

PAES–PDMS segmented block copolymers also exhibit phase separation which increases as the PDMS content increases⁸⁵. Tyagi et al.⁸⁶ also studied the phase separation of PAES–PDMS segmented block copolymers and determined that the segment with the highest content is continuous and is predominate on the surface as shown under the transmission electron microscope (TEM).

McGrath and co-workers⁸⁷ synthesized the segmented block copolymers incorporating PAES and bisphenol A polycarbonate via a phosgenation reaction in chloroform (Scheme 1.13). In contrast to the phase separated materials, these segmented block copolymers produced transparent, single phase materials due to the similarity in the chemical properties of PAES and bisphenol A polycarbonate. The rationale to this single phase profile is the small difference in the solubility parameters,

PAES and bisphenol A polycarbonate which produces no phase separation because of similar solubility.



Scheme 1.13: PAES–bisphenol A-polycarbonate segmented block copolymer.

1.3.2.2. Mechanical Properties

The mechanical properties of the segmented block copolymers vary, depending on the content and type of each unit, the molecular weight of the oligomers, and the overall molecular weight of the block copolymer⁸⁸. A series of mechanical properties can be produced when segmented block copolymers are microphase separated (Fig. 1.4 depicts the stress-strain behavior of materials). When there is a larger volume fraction or weight percent of the hard segment over the soft segment, the material can act as a physical cross-link to reinforce the soft segment that will lead to excellent mechanical and thermal properties for many thermoplastic elastomeric applications¹⁶. On the opposite end, at higher soft segment volume fractions or weight percent, the

hard segment is segregated and dispersed within soft segment continuous phase. The material behaves like an elastomer while maintaining thermoplastic processability.

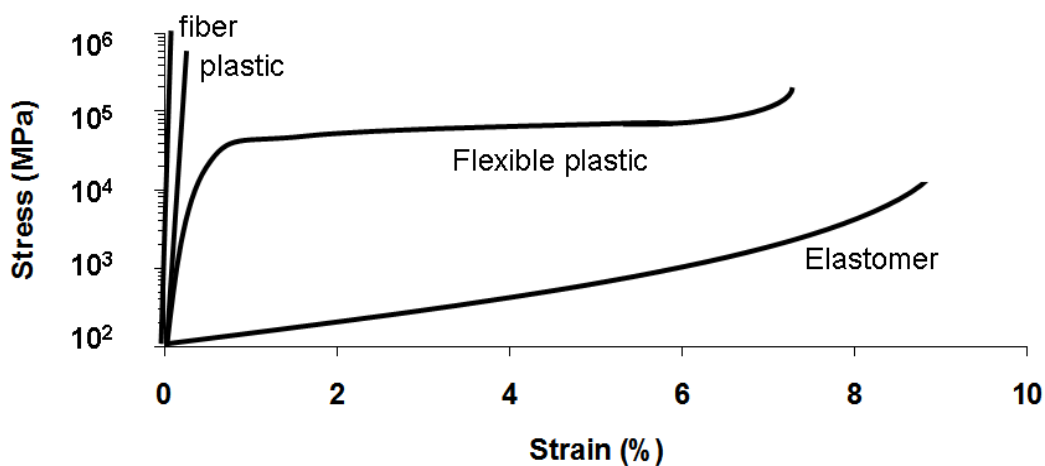


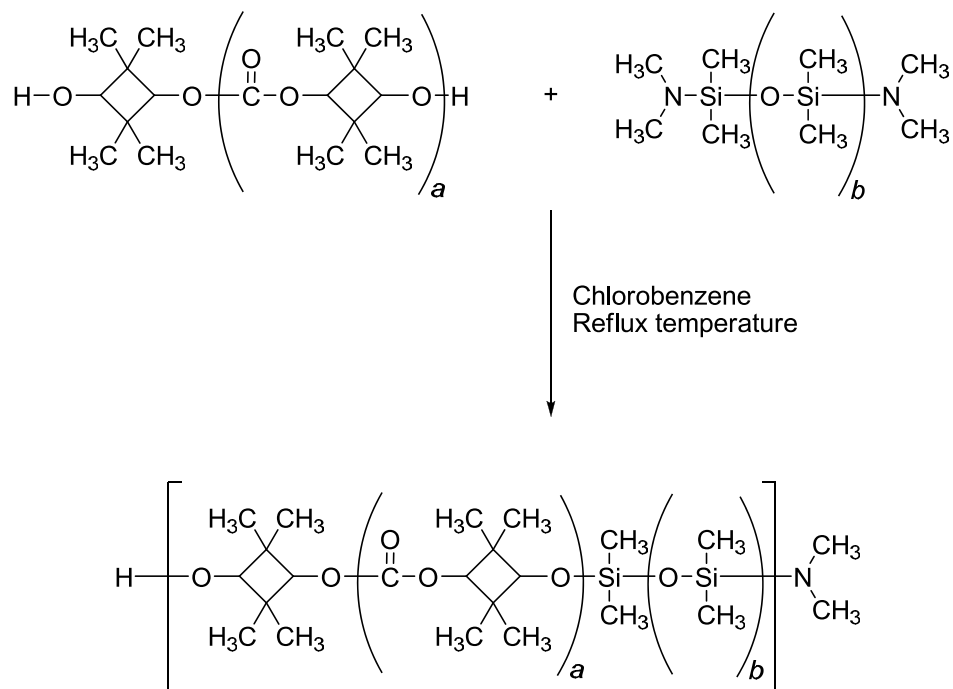
Figure 1.5: Stress-strain plots for a fiber, plastic, flexible plastic, and an elastomer. (Adaptation of Fig. 1-10, Odian ⁸⁹)

When the units forming the segmented block copolymer are of equal volume fractions or weight percent, the mechanical property of the material behaves like both a thermoplastic and elastomer at the same time—flexible plastic. These mechanical characteristics were observed in PAES–PDMS segmented block copolymers synthesized by Robeson et al. ⁹⁰. In that study, higher siloxane weight percents produced highly elastomeric materials with strain values as high as 600%.

1.3.2.3. Thermal Properties

Separated block copolymers that are microphase separated exhibit outstanding thermal properties. Matzner and co-workers ⁹⁰ synthesized segmented block

copolymers with segments of cycloaliphatic polycarbonate based on tetramethylcyclobutane-1,3-diol with PDMS by a polycondensation reaction between the hydroxyl-terminated polycarbonate and the dimethylamino-terminated PDMS (Scheme 1.14). The materials showed good thermal stability in nitrogen and in air. Temperature-modulus studies of the materials by DMA gave two T_g values at $-120\text{ }^\circ\text{C}$ due the PDMS unit and at $40\text{-}80\text{ }^\circ\text{C}$ for the polycarbonate unit, proving microphase separation. The mechanical properties of these materials included tensile modulus (190,000 psi), tensile strength (5200 psi), and low elongation (5%) at 7% siloxane content. At siloxane content of 63%, the elongation increased to 600%. The research also concluded under thermal age heating at $170\text{ }^\circ\text{C}$ for more than 1000 h studies, these materials retained their tensile strength.



Scheme 1.14: Reaction between hydroxyl-terminated polycarbonate oligomer and dimethylamino-terminated PDMS.

Segmented block copolymers illustrate a temperature-modulus profile depicted in Fig. 1.6. Measuring the T_g of microphase separated materials can be done by various methods, such as differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA), though DMA provides greater sensitivity to determining the thermal transitions.

Polyisobutylene–polyamide thermoplastic elastomers were synthesized incorporating various polyisobutylene derivatives and showed T_g values for the soft and hard segments indicative of the microphase separation existing between the segment⁹¹. Similar microphase separation was observed in copoly(imide siloxane)s synthesized

by Ghosh and co-workers ⁹². The copolymers showed two T_g values were observed, one for the siloxane soft block between 2-12 °C and the other for the polyimide hard block between 173-194 °C. The materials also showed thermal stability at 5% weight loss around 470 °C in nitrogen and 412 °C in air. In the research done by Noshay et al. ⁹³, results showed that at low molecular weight of PDMS, a single-phase T_g was observed at 125 °C. However, at molecular weight values ≥ 5000 , the materials were microphase separated and produced T_g at -120 °C and 160 °C associated with the PAES and PDMS, respectively.

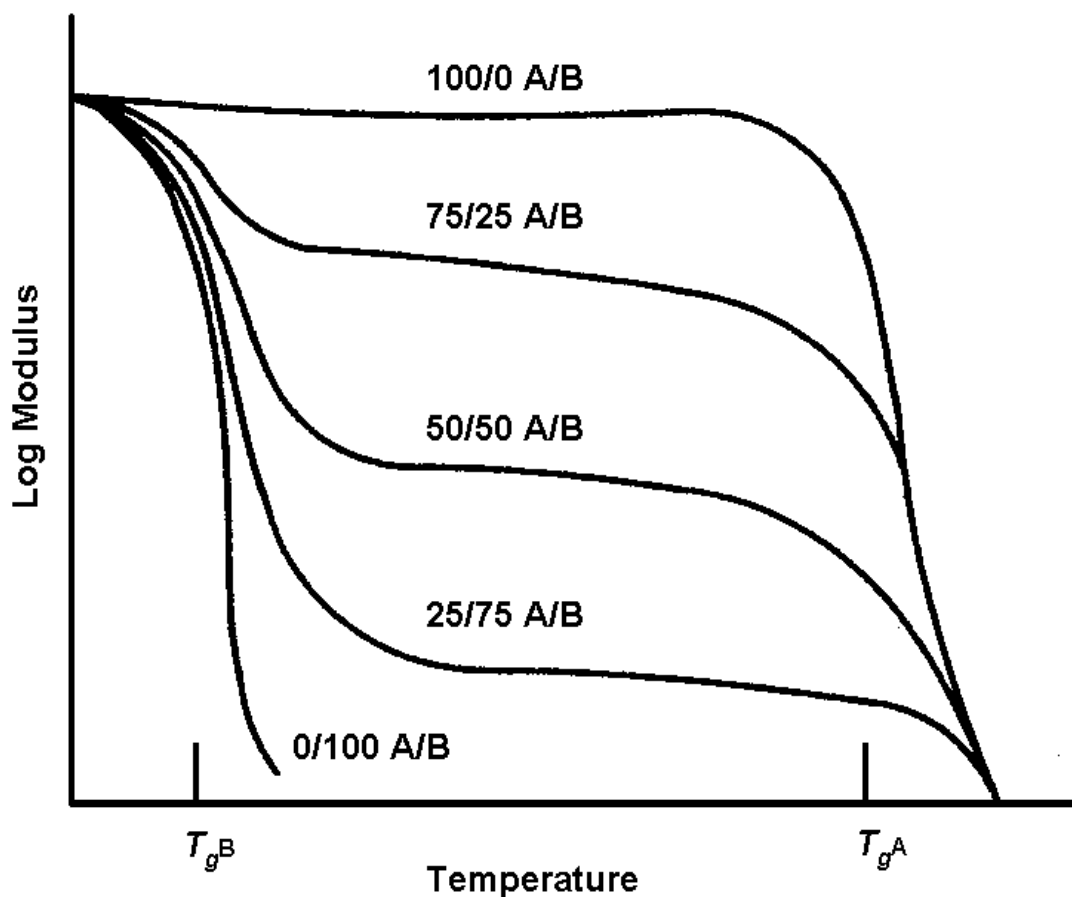


Figure 1.6: Temperature-modulus phase behavior of segmented block copolymers. (Recreation of Fig. 1, McGrath et al. ⁹⁴)

1.3.2.4. Optical Properties

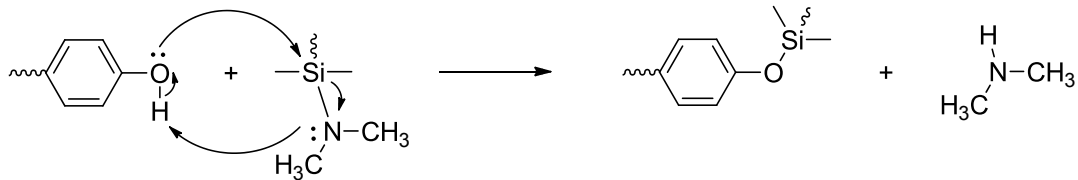
Noshay and McGrath ⁹⁵ suggest the optical properties of segmented block copolymers are influenced by the microphase separation. In synthesizing segmented block copolymers, it is important to control the size and distribution of the segments. When segments form large-sized domains, larger than the wavelength of visible light, they can scatter visible light, and result in hazy or opaque materials. Small-sized

domains formed from the individual segments can lead to optical transparency. For this, segmented block copolymer materials not only possess good mechanical and thermal properties, but optical properties for advanced applications, including automotive, electronics, packaging, and the biomedical industry.

1.4. RESEARCH OBJECTIVES

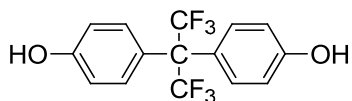
PAES and PDMS polymers have been shown to have outstanding mechanical, chemical, and thermal properties. As previously discussed in detail, PAES and PDMS have large differences in their physical properties for example, the T_g ($-125\text{ }^\circ\text{C}$ for PDMS versus $185\text{ }^\circ\text{C}$ for PAES) and solubility parameters $\{\delta \approx 7.3\text{--}7.5\text{ (cal cm}^{-3})^{0.5}\}$ for PDMS as compared with $\delta \approx 10.3\text{ (cal cm}^{-3})^{0.5}$ for PAES³³. This combination of property differences are responsible for materials with a unique combination of enhanced tensile, chemical, and thermal properties to be used in many high performance applications.

Segmented block copolymers from bisphenol A PAES and PDMS were first synthesized and studied by Noshay et al.⁹⁶⁻⁹⁸. Noshay and coworkers showed the copolymerization between hydroxyl-terminated PAES and dimethylamino-terminated PDMS worked well in chlorobenzene solvent (Scheme 1.15). Chlorobenzene was the solvent of choice over THF because THF would likely hydrogen bond to the hydroxyl-terminated group thus making the hydrogen less available for attack by the amine group. The research also demonstrated the phenolic end-group reacted rapidly over aliphatic end-groups and formed a stable Si–O–C bond that had once been theorized as an unstable bond^{99, 100}. This copolymerization has since been duplicated using different reaction techniques and parameters yet showing similar results⁴.

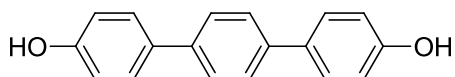


Scheme 1.15: Reaction between hydroxyl-terminated PAES and dimethylamino-terminated PDMS.

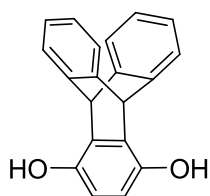
This work intends to further investigate various PAES compositions copolymerized with PDMS. The hydroxyl-terminated PAES oligomers will be synthesized according to the literature using hexafluoroisopropylidene bisphenol (BAF, bisphenol AF) and co-monomers, 4,4'-dihydroxyterphenyl (DHTP) and triptycene-1,4-hydroquinone (TPDH) with bisphenol A. The structures of the bisphenol monomers to be used in this work are shown in Fig. 1.7.



hexafluoroisopropylidene bisphenol (BAF)



4,4'-dihydroxyterphenyl (DHTP)



tritycene-1,4-hydroquinone (TPDH)

Figure 1.7: Three bisphenol monomers studied in this research.

Preparation of segmented block copolymers incorporating units with varying molecular weights will produce materials with diverse thermal, tensile, and morphological properties that could lead to the development of thermoplastic elastomers. The segmented block copolymers will be analyzed by size-exclusion chromatography (SEC) to determine the weight average molecular. Thermal analysis by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) will provide thermal stability profiles of the segmented block copolymers as well as the thermal transitions, respectively. Measurements from DSC will provide results on the microphase separation in the materials. Results should show two T_g values indicative of the segments forming blocks, i.e. PAES and PDMS, depending on the percent composition of the segments. Other evaluations of the segmented block copolymers include measurement of the tensile properties using Instron. The measurements will

specifically provide information on the effect of increasing the PDMS content and the addition of the co-monomer in bisphenol A PAES segment on the tensile modulus and elongation of the segmented block copolymer. The segmented block copolymers will also be investigated for the morphological properties by atomic force microscopy (AFM), transmission electron microscopy, and small-angle X-ray scattering (SAXS). These techniques will not only examine the segmented block copolymer morphology, but they will also qualitatively describe the microphase separation resulting from modifying the bisphenol A PAES segment. A further study will measure the tensile properties of blends prepared from 95% of Udel[®] blended with 5% of the new PAES–PDMS segmented block copolymers.

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Chapter 2:

SYNTHESIS AND CHARACTERIZATION OF HEXAFLUOROISOPROPYLIDENE BISPHENOL POLY(ARYLENE ETHER SULFONE) AND POLYDIMETHYLSILOXANE SEGMENTED BLOCK COPOLYMERS

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2.1 ABSTRACT

A series of hexafluoroisopropylidene bisphenol poly(arylene ether sulfone) (BAF PAES) segmented block copolymers with varying fractions of polydimethylsiloxane (PDMS) were synthesized by a condensation reaction of hydroxyl-terminated BAF PAES and dimethylamino endcapped PDMS. The segmented block copolymers have high thermal stability. The BAF PAES homopolymer exhibits a tensile modulus of 1700 MPa and an elongation at break of 16%. Copolymerizing BAF PAES with increasing molecular weight amounts of PDMS results in tensile properties ranging from plastic to elastomeric where the elongation is 417% for a segmented block copolymer with 64 wt% PDMS incorporated. The morphological properties of these segmented block copolymers were characterized by atomic force microscopy (AFM), small-angle X-ray scattering (SAXS), and transmission electron microscopy (TEM). AFM and TEM images show the segmented block copolymers were microphase separated, and comparison with bisphenol A (BA) PAES-*b*-PDMS segmented block copolymers revealed complex differences between the morphological behavior of the two systems. SAXS data of the

segmented block copolymers supports AFM and TEM images, indicating microphase separation but little long-range order.

KEYWORDS: poly(arylene ether sulfone); segmented block copolymer; morphology

2.2. INTRODUCTION

Segmented block copolymers have been long studied for their mechanical, chemical, and thermal properties. Considerable research that has been conducted on segmented block copolymers has gone into developing polymeric structure-property relationships. The resulting materials based on high performance thermoplastics have been found to have a combination of impact resistance and toughness that can serve in high impact applications^{1,2}. In order to achieve high impact and toughness, segmented block copolymers typically encompass oligomers with well-defined properties—good thermal stabilities and excellent mechanical properties. These high performance thermoplastics include polycarbonates, polyimides, polyketones, and poly(arylene ether sulfone)s³.

Vaughn et al.⁴ reported the synthesis of segmented block copolymers with bisphenol A–polycarbonate–polydimethylsiloxane (PDMS) in the late 1960s. This research showed these materials had a two-phase morphology, demonstrated thermal stability to 390 °C, and had mechanical properties ranging from elastomeric to rigid depending on the polysiloxane content. Holub et al.⁵ also synthesized similar materials using polyimide as the thermoplastic with PDMS. These segmented block copolymers possessed good processability, low water absorption, atomic oxygen resistance, low dielectric constants, and excellent adhesion. These materials have the potential to be used for applications in the microelectronics, automobiles, and aerospace areas.

Segmented block copolymers with polyetheretherketone and polystyrene have also provided promising results for high performance applications⁶⁻⁸.

Poly(arylene ether sulfone) (PAES) has been one of the most studied thermoplastics to be incorporated into segmented block copolymers. PAESs are amorphous thermoplastics that have exceptional thermal, mechanical, and chemical properties that have been studied for their use in medical applications, substrates for cookware, and tubing for pump housings³. PAESs have also been modified by sulfonation or by chloromethylation for their use in reverse osmosis⁹, materials for environmental applications^{10, 11}, and extensively for their use in proton exchange membranes (PEMs) in fuel cell applications¹²⁻¹⁴. However, the most common PAES based on bisphenol A is a relatively brittle polymer which limits its use in many applications. Previous research by Noshay et al.^{15, 16} showed that incorporating an elastomer like PDMS improves the impact resistance of the polymer because the soft domains can inhibit crack propagation in the material. Tensile properties of these materials suggested that as more polysiloxane was added into the PAES, the materials became more elastic and the elongation increased. Further research by McGrath and Wilkes et al.¹⁷ studied the phase separation of bisphenol A PAES–PDMS segmented block copolymers (BA PAES–*b*–PDMS) and determined the polymer segment with the highest content was the continuous phase and predominated on the film surface as shown by transmission electron microscopy (TEM).

While these materials and other segmented block copolymers often produce transparent films, it is important to control the size and distribution of the elastomeric domains as transparency is dependent on the size of the domains. Elastomeric

domains with sizes larger than the wavelength of visible light can scatter visible light and result in hazy or opaque materials. We have interest in exploring these properties of PAES–PDMS segmented block copolymers where the bisphenol in the PAES is changed from bisphenol A to bisphenol AF. It is well known that incorporation of fluorine into a polymer backbone can improve the T_g of the polymer, enhance the thermal stability, and optimize the tensile properties such as modulus, yield stress and strain at break¹⁸. Our desire is to understand the tensile, thermal, and the morphological properties of segmented block copolymer systems. In this report, we synthesize and characterize hexafluoroisopropylidene bisphenol poly(arylene ether sulfone) (BAF PAES) segmented block copolymers with PDMS (BAF PAES–*b*–PDMS) by varying the molecular weight of the two segments. This report will summarize our work on studying the morphological properties of BAF PAES–*b*–PDMS in comparison with BA PAES–*b*–PDMS. Morphology was studied by small-angle X-ray scattering (SAXS), atomic force microscopy (AFM), and transmission electron microscopy (TEM). We have also evaluated the tensile and thermal properties of the segmented block copolymers.

2.3. EXPERIMENTAL

2.3.1. General Methods and Materials

Anhydrous dimethylacetamide (DMAc), chlorobenzene, tetramethylammonium hydroxide pentahydrate (TMAH • 5H₂O), and toluene were purchased from Aldrich and used as received. Anhydrous potassium carbonate (K₂CO₃) and isopropylidene bisphenol monomer (BA) were purchased from Aldrich in highly pure monomer grade and dried overnight under vacuum at 60 °C before use. Hexafluoroisopropylidene bisphenol monomer (BAF) and dichlorophenylsulfone (DCDPS) were graciously

provided by Solvay Advanced Polymers and dried overnight under vacuum at 60 °C before use. Udel[®] was also provided by Solvay Advanced Polymers. Octamethylcyclotetrasiloxane (D₄), purchased from Aldrich, was vacuum distilled before use. 1,5-Bis(dimethylamino)hexamethyltrisiloxane was purchased from Silar Laboratories.

2.3.2. Preparation of Hydroxyl-Terminated PAES Oligomers

2.3.2.1. Hexafluoroisopropylidene Bisphenol PAES (BAF PAES)

Hydroxyl-terminated BAF PAES oligomer was prepared following a previous literature method¹⁹. Synthesis of the oligomers was conducted in a three-neck, 250-mL round-bottom flask equipped with a mechanical stirrer, gas inlet, Dean–Stark trap, and condenser. The polymerization was carried out in a metal bath capable of high temperature reactions. For preparation of a 5400 g/mol oligomer, the round-bottom flask was charged with BAF (10.00 g, 37.84 mmol), DCDPS (7.67 g, 26.71 mmol), and K₂CO₃ (10.71 g, 77.50 mmol) as a base. DMAc (80 mL) was added to the flask in a 2:1 v:v ratio with toluene as an azeotroping agent.

The reaction was started at 140 °C for 1–2 h. The temperature of the reaction was increased gradually from 140 to 152 °C over 3–4 h to allow the toluene to reflux. Within 5 h of reaction, all toluene/water had been removed. The temperature was increased to 160 °C and maintained for 20–24 h. Upon completion, the polymer was coagulated by pouring the reaction mixture gradually into a stirred solution of 10% aqueous HCl (800 mL). The polymer was filtered and dried overnight under vacuum at 90–110 °C. The polymer was dissolved in dichloromethane, precipitated into methanol, and dried under vacuum overnight at 80 °C.

2.3.2.2. Isopropylidene Bisphenol PAES (BA PAES)

For preparation of a 5000 g/mol oligomer, the round-bottom flask was charged with BA (5.06 g, 22.16 mmol), DCDPS (3.83 g, 13.34 mmol), and K_2CO_3 (5.40 g, 39.07 mmol) as a base. DMAc was added in a 2:1 ratio with toluene as an azeotroping agent. Reaction conditions were identical to the preparation of BAF PAES oligomers.

2.3.3. Preparation of Dimethylamino-Terminated PDMS (PDMS) Oligomers

The dimethylamino-terminated PDMS oligomers were prepared following a previous literature method^{17, 20-22}. To synthesize the tetramethylammonium disiloxanolate catalyst, D_4 (13.30 g, 44.84 mmol) and TMAH • 5H₂O (0.71 g, 3.92 mmol) were added to a reactor with an attached Dean–Stark trap with condenser linked to a drying tube equipped with an overhead mechanical stirrer. The mixture was heated to 80 °C in a silicone oil bath for 24 h under a rapid stream of Argon bubbled through the reaction mixture. The solution became homogenous within 2 h. The reaction was conducted for 24 h.

For the synthesis of a 10,000 g/mol PDMS oligomer, D_4 (60.3 g, 6.03 mmol) and 1,5-bis(dimethylamino)hexamethyltrisiloxane (1.78 g, 6.03 mmol) were added to a 250-mL round-bottom flask equipped with a magnetic stir bar and condenser, and stirred under Argon. The catalyst (3.73 g, 10.51 mmol) was removed from the reactor and was added to the reaction mixture using a clean, dry 12-gauge needle. The reaction was allowed to proceed at 80 °C for 2–3 days. The temperature was increased to 150 °C under Argon for 2–3 h to remove any residual catalyst. The solution was vacuum distilled at 70 °C to remove any residual end-capping reagent.

2.3.4. Preparation of Segmented Block Copolymers

2.3.4.1. Hexafluoroisopropylidene Bisphenol PAES Segmented Block Copolymers (BAF PAES-*b*-PDMS)

Segmented block copolymers were prepared with BAF PAES and PDMS in a 1:1 molar ratio following a modified previous literature method ¹⁵. BAF PAES oligomer 5400 g/mol (1.04 g, 0.193 mmol) and chlorobenzene (40 mL) were charged to a three-neck, 100-mL round-bottom flask equipped with a magnetic stir bar, gas inlet, Dean–Stark trap, and condenser in a silicone oil bath. The solution was stirred for 1 h at 125–132 °C. The PDMS oligomer 10,000 g/mol (1.93 g, 0.200 mmol) were added to the reaction mixture using a clean, dry 18-gauge needle in increments. The reaction was allowed to proceed at 125–132 °C for 8–12 h. The reaction was cooled and the product was precipitated into methanol (800 mL). The product was dried overnight under vacuum at 90–110 °C.

2.3.4.2. Isopropylidene Bisphenol PAES Segmented Block Copolymers (BA PAES-*b*-PDMS)

Identical preparation conditions were used for the segmented block copolymers prepared with BA PAES and PDMS. Segmented block copolymers were prepared in a 1:1 molar ratio, using BA PAES oligomer 5500 g/mol (1.50 g, 0.273 mmol) and PDMS oligomer 10,000 g/mol (2.79 g, 0.279 mmol).

2.3.5. Film Preparation of the Segmented Block Copolymers

The segmented block copolymers were dissolved in THF to afford transparent solutions with 5, 10, or 15 wt-% solids, and the solutions were filtered through a 25 mm diameter syringe filter (0.45 µm pore) and cast onto clean glass substrates. The films

were dried for 2–3 days at ambient temperature, and then dried overnight under vacuum at 90–110 °C.

2.4. CHARACTERIZATION METHODS

2.4.1. Thermogravimetric Analysis (TGA)

Measurements were conducted by TA Instruments Thermogravimetric Analysis Q500 at temperatures from 35 °C to 600 °C under nitrogen at a heating rate of 10 °C/min.

2.4.2. Tensile Analysis

Stress-strain tests were performed on an Instron Model 1123 Universal Testing system with a Bluehill software package using a 20-lb load cell at room temperature at a rate of 10 mm/min. Tests were done on dog-bone-shaped specimens (15 mm gauge length and 3.93 mm width) cut by a standard bench-top die from films (0.09 mm thickness). Prior to testing, specimens were dried under vacuum overnight at 90–110 °C.

2.4.3. Tapping Mode Atomic Force Microscopy (TP-AFM)

Images of the BAF PAES-*b*-PDMS were obtained using a Digital Instruments MultiMode scanning probe microscope with a NanoScope Iva controller. A silicon probe (Veeco) with an end radius of <10 nm and a force constant of 5 N m⁻¹ was used to image samples.

2.4.4. Small-Angle X-Ray Scattering (SAXS)

Small-angle X-ray scattering profiles of films of various thicknesses were collected using a Molecular Metrology multiwire area detector. X-rays having wavelength of 1.542 Å were generated using a Rigaku Ultrax18 rotating anode X-ray

generator operated at 45 kV and 100 mA, with a Cu anode and a Ni filter. Data collected at camera lengths of 1.5 m and 0.5 m were combined to span an effective q -range of 0.007 \AA^{-1} to 0.45 \AA^{-1} , where q is the magnitude of the scatter vector defined by $q = 4\pi \cdot \sin(\theta)/\lambda$ for scattering angle, 2θ , and wavelength, λ . Camera length and beam center were determined using a silver behenate calibration standard. The data were corrected for background noise and transmission before azimuthal averaging. The azimuthally averaged data were placed on an absolute scale using type-2 glassy carbon as a secondary intensity standard. For samples where thickness and transmission measurements were thought to be inaccurate, data were scaled to a background level of 0.1 cm^{-1} and subsequently presented with intensity in arbitrary units (a.u.). The average interdomain spacing, d , of the segmented block copolymers was calculated as $d = 2\pi/q_{max}$, where q_{max} is the position of maximum intensity for a given scattering peak. All data manipulation, data evaluation, and scattering calculations were done in WaveMetrics IGOR Pro v. 6 using data analysis packages written by Jan Ilavsky, Argonne National Laboratory²³.

2.4.5. Transmission Electron Spectroscopy (TEM)

Non-equilibrium segmented block copolymers films were observed and imaged using a Philips EM 420 TEM equipped with a tungsten filament, 100 kV maximum accelerating voltage, single and double axis sample tilt, and a CCD camera for recording images. Staining of the segmented block copolymer films was not necessary due to the sufficient contrast between the PAES and PDMS phases.

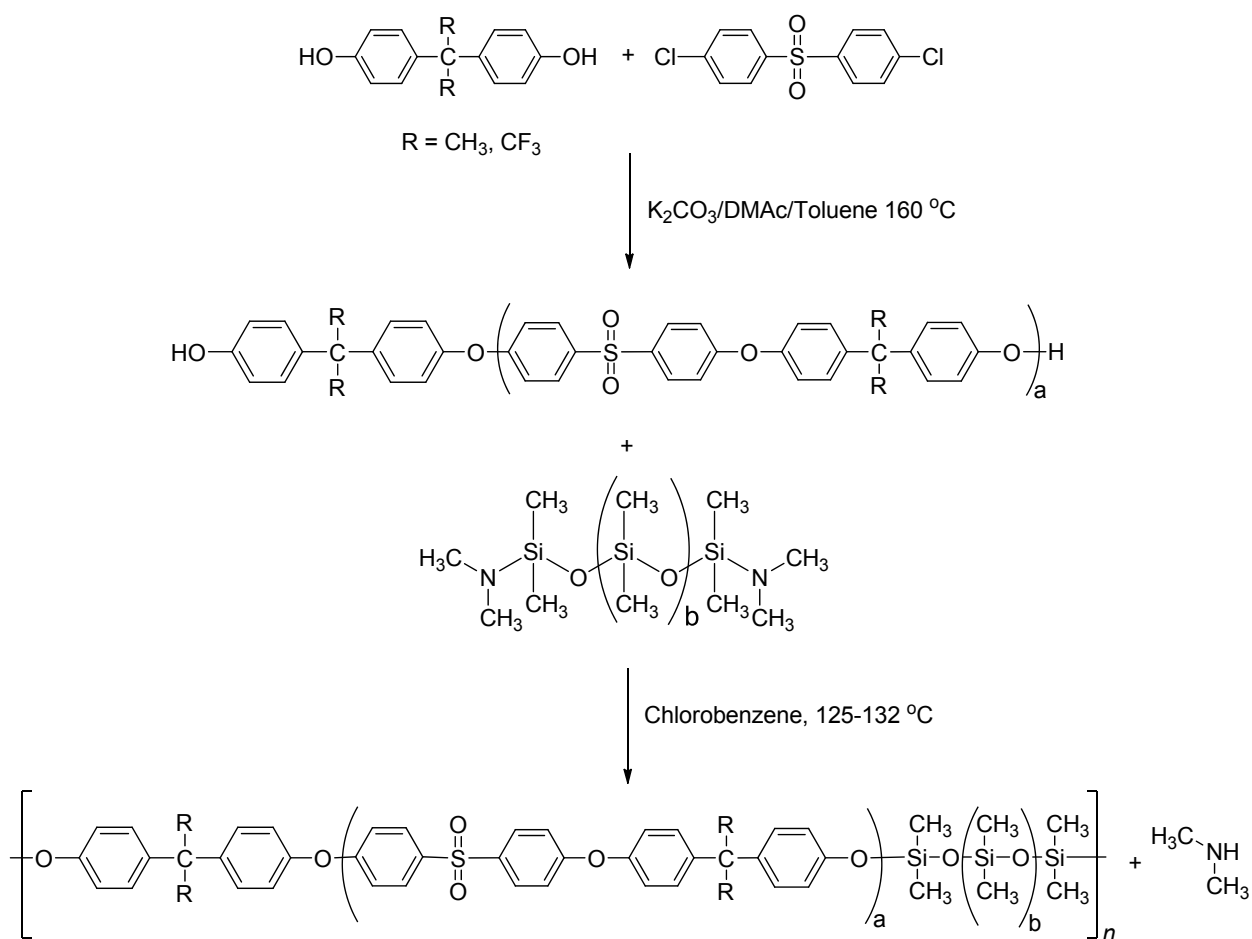
Finally, in this report, the nomenclature used for these materials will refer to the PAES type (BA or BAF) followed by the volume fraction of PDMS incorporated in the segmented block copolymer.

2.5. RESULTS AND DISCUSSION

2.5.1. Synthesis of Segmented Block Copolymers

The synthesis of the segmented block copolymers is shown in Scheme 2.1. Segmented block copolymers were achieved by a nucleophilic aromatic substitution reaction between the phenol (BA or BAF) and DCDPS monomers with a molar excess of phenol (BA or BAF) to afford hydroxyl end-groups on the PAES oligomers. Systematically varied molecular weights of these oligomers were prepared. The hydroxyl-terminated BAF PAES structure was determined by ^1H NMR and their molecular weights were determined by SEC. The dimethylaminosilyl-terminated PDMS oligomers were synthesized by an equilibrium reaction as described in detail by Kantor et al.²⁰. The dimethylaminesilyl end-groups and molecular weights of these oligomers were determined by NMR end-group analysis. Synthesis of the segmented block copolymers was done by a condensation reaction in chlorobenzene between the hydroxyl-terminated PAES oligomers and the silylamine end-groups of the PDMS at a 1:1 molar ratio with the release of the dimethylamine by-product. Noshay et al.¹⁵ synthesized BA PAES-*b*-PDMS in both chlorobenzene and THF. Their work determined that chlorobenzene was a better reaction solvent as high molecular weight copolymers could be synthesized in a shorter reaction time¹⁵. With slow and gradual addition of PDMS to the PAES solution the viscosity increased. This addition process is also described by Noshay in order to gradually reach a stoichiometric end-point to

achieve high molecular weight segmented block copolymers. Precipitation into methanol provided fluffy white material characterized by ^1H NMR to determine their structural compositions and functional groups. ^1H NMR also provided a measure of the molecular weight content and volume fraction of PDMS which was incorporated into the segmented block copolymer. Intrinsic viscosity measurements (in chloroform at 25 °C) for these segmented block copolymers were as high as 0.4 dL/g. We also note the silicon-oxygen-carbon linkage in these segmented block copolymers is hydrolytically stable under various conditions as described by previous studies ²⁴.



Scheme 2.1: Synthesis of segmented block copolymers.

2.5.2. Thermal Stability of Segmented Block Copolymers

The TGA profile, in Fig. 2.1, shows thermal stability of two segmented block copolymer systems. The BA PAES-*b*-PDMS (5500-4700) has a thermal decomposition at 5% weight loss at 320 °C. The BAF PAES-*b*-PDMS (5400-4100) showed thermal stability to 439 °C at 5% weight loss. This increased stability for these fluorinated segmented block copolymer systems can be attributed to the higher bond strength of the C-F bond relative to the C-H bond and the shielding effect of the high electronegativity of the fluorine atoms in the polymer^{25, 26}.

We also show the thermal decomposition temperatures of several other BAF PAES-*b*-PDMS in Table 2.1. The thermal stabilities range from 400 to 467 °C, these values are also consistent with many other fluorinated-based polysulfones^{27, 28} copolymers and polyimides siloxane copolymers^{18, 29, 30} that are in the range of 400-500 °C. The influence of the BAF PAES oligomer on the thermal stability of the segmented block copolymer is illustrated in Fig. 2.2. The thermal stability of the segmented block copolymer at 5% weight loss is 467 °C. This high stability is resultant of the BAF PAES 9700 g/mol oligomer incorporated, which has a T_d of 491 °C rather than the PDMS oligomer which has a T_d at 5% weight loss of 343 °C.

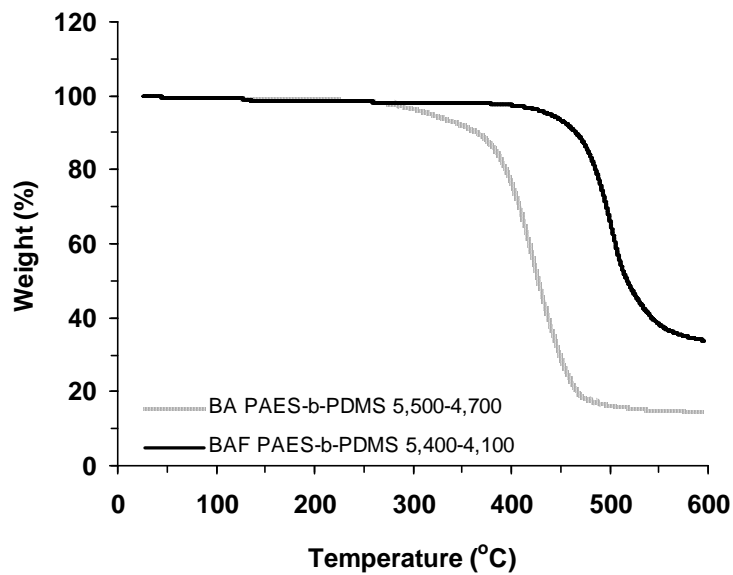


Figure 2.1: TGA thermograms of PAES segmented block copolymers, at 10 °C/min.

Table 2.1: Thermal stabilities of BAF PAES and PDMS homopolymers and BAF PAES-*b*-PDMS.

Segmented Block Copolymers		
BAF PAES	PDMS	<i>T_d</i>-5% wt. loss (°C)
5400	1600	410
5400	4100	439
5400	10,000	406
9700	4100	467

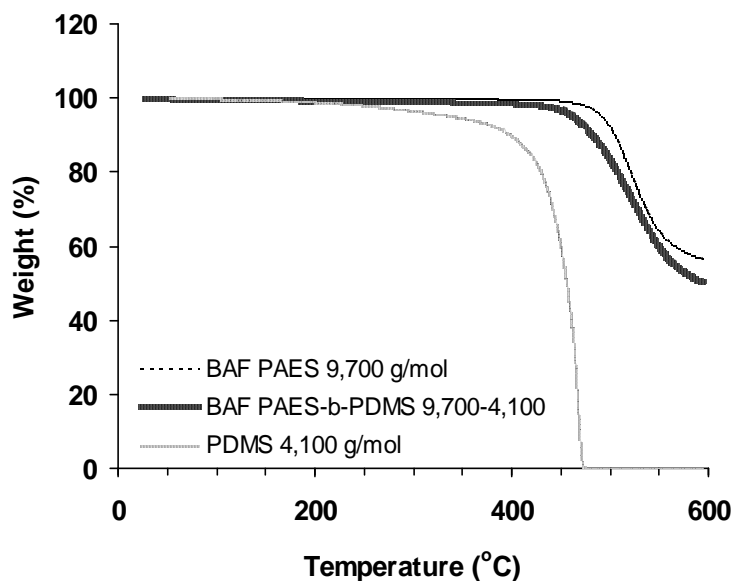


Figure 2.2: TGA thermograms of BAF PAES–*b*–PDMS and homopolymers.

2.5.3. Tensile Analysis of Segmented Block Copolymers

Segmented block copolymers are unique in that excellent properties can result from their multiphase structures. We synthesized BAF PAES homopolymer (41,000 g/mol) and then prepared films cast from THF. The tensile properties of the homopolymer and segmented block copolymers are presented in Table 2.2. The data show the homopolymer had a modulus of 1700 MPa. BAF PAES–*b*–PDMS, with increasing PDMS content from 35 wt-% to 64 wt-%, showed a decrease in the modulus from 520 MPa to 36 MPa. The material properties transition from being plastic to more elastomeric. The segmented block copolymers also showed an increase in the tensile strain at break from 16% to 420% with increase in PDMS content. These tensile properties were consistent with the BA PAES–*b*–PDMS materials synthesized in our labs as well as to the original work by Noshay et al.¹⁵

Similarly, Udel[®] homopolymer obtained from Solvay Advanced Polymers was cast from THF and the tensile properties were determined. The homopolymer had a modulus of 1200 MPa compared to the 1700 MPa for the fluorinated analog. BA PAES-*b*-PDMS was prepared and films cast from THF gave tensile properties ranging from plastic to elastomeric upon increasing the amount and molecular weight of PDMS in the segmented block copolymer.

The tensile properties of segmented block copolymers were also explained by Noshay and McGrath in their review. They suggested that at a certain M_n of PDMS (correlating to a high PDMS composition) incorporated into the segmented block copolymer system, PAES no longer influences the modulus and merely acts as a “pseudo crosslink,” and the PAES oligomer only reinforces the copolymers^{1, 31}. These values are consistent with other segmented block copolymers. Therefore, incorporating fluorine into the bisphenol unit has only a moderate effect on the modulus of the homopolymer and the segmented block copolymer (Table 2.3).

Table 2.2: Tensile properties of BAF PAES-*b*-PDMS.

Segmented Block Copolymers		BAF PAES	PDMS	Siloxane (wt-%) ^a	Intrinsic Viscosity ^b (dL/g)	Tensile stress at Break (MPa)	Tensile strain at Break (%)	Tensile stress at Yield (MPa)	Young's Modulus (MPa)
40,000	0	0	0	0.215	16 ± 3	16 ± 4	38 ± 6	1700 ± 62	
5400	4100	35	35	0.194	15 ± 3	16 ± 14	16 ± 3	520 ± 98	
6800	5800	46	46	0.289	9 ± 3	170 ± 54	13 ± 0.61	245 ± 21	
5400	10,000	64	64	0.367	8 ± 0.9	420 ± 67	8 ± 0.96	36 ± 3	

^aCalculated by ¹H NMR

^b0.2 dL/g in chloroform at 25 °C

Table 2.3: Tensile properties of BA PAES-*b*-PDMS.

Segmented Block Copolymers		BA PAES	PDMS	Siloxane (wt-%) ^a	Intrinsic Viscosity ^b (dL/gm)	Tensile stress at Break (MPa)	Tensile strain at Break (%)	Tensile stress at Yield (MPa)	Young's Modulus (MPa)
Udel		0		0	0.342	28 ± 20	6 ± 1	48 ± 12	1200 ± 350
P-3500		5600		36	0.197	15 ± 8	8 ± 7	24	800 ± 7
		7800		47	0.340	9 ± 4	135 ± 49	12 ± 2	355 ± 25
		5500		65	0.307	14 ± 0.8	630 ± 170	14 ± 0.6	8 ± 2

^aCalculated by ¹H NMR

^b0.2 dL/gm in chloroform at 25 °C

2.5.4. Morphological Characteristics of Segmented Block Copolymers

AFM was used to show that these materials form phase-separated morphologies. Images of the as cast, non-equilibrium PAES segmented block copolymers BAF-72 (BAF PAES-*b*-PDMS 5400-10,000) and BA-71 (BA PAES-*b*-PDMS 5500-10,000) in Fig. 2.3 showed that these materials were microphase separated. In these phase (surface) images, dark features are representative of the soft material (PDMS) and light features are indicative of the hard material (PAES). BA-71 showed finer dimensions than the BAF-72.

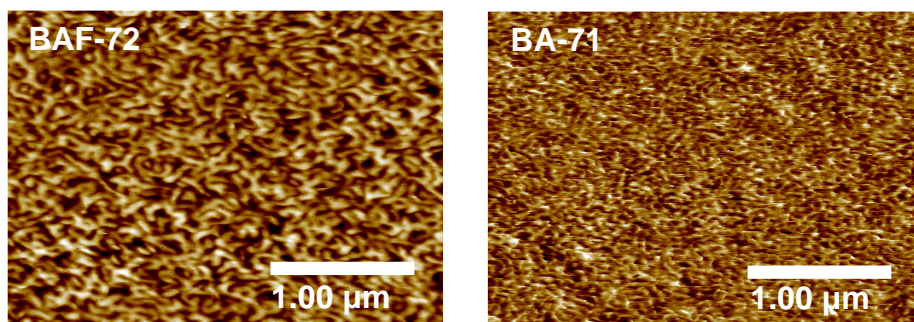


Figure 2.3: AFM images of PAES segmented block copolymers BAF-72 and BA-71 showing the surface of the film.

The microphase separation that is evident in these segmented block copolymers is indicative of the incompatibility between the PAES, an amorphous thermoplastic, and PDMS, an elastomer. The phase separation of polysulfone segmented block copolymers incorporating various flexible units such as poly(tetramethylene oxide) and polyester was studied by Pospiech et al.³². Their research showed that phase separation is enhanced by the incorporation of flexible units due to their higher mobility

and incompatibility between the two phases. Segmented block copolymers with highly amorphous segments show a high degree of intermixing and no phase separation³³.

We further analyzed the morphology of a series of segmented block copolymers using TEM. Images were obtained from cryosections of un-stained, non-equilibrium films solution-cast from THF at room temperature over 3 days. The BAF PAES-*b*-PDMS micrographs, in Figs. 2.4 and 2.5, show microphase separation, with the PDMS domains appearing dark because of their higher electron density than BAF PAES. BAF-72 showed a disordered morphology. In the samples where the composition is approximately balanced between the two polymers, BAF-55 and BAF-44, the formation of small, weakly ordered lamellar domains was observed. Surprisingly, BAF-41 showed the most well-ordered lamellar morphology despite being more asymmetric in composition than BAF-55. Where the composition heavily favored either constituent, BAF-72 and BAF-22, the morphology was disordered.

In comparison with selected BAF PAES-*b*-PDMS micrographs, Fig. 2.5 shows the TEM micrographs for BA PAES-*b*-PDMS with PDMS volume fractions of 71, 52, and 20%. The BA PAES-*b*-PDMS all exhibited microphase separation. As was seen for BAF-72, the micrograph of BA-71 shows a disordered, microphase-separated morphology. The roughly equal volumes of BA PAES and PDMS in BA-52 give rise to the development of lamellar-like morphology with some order, roughly equivalent to that found for BAF-55.

Unlike the fluorinated analog, the morphology for the sample with the lowest PDMS volume fraction, BA-20, was clearly microphase separated, and appears to show the formation of spherical domains of PDMS. Previous work by McGrath and Wilkes et

al.¹⁷ and follow-up research by Patel et al.³⁴ on the bulk morphology of a series of BA PAES-*b*-PDMS found spherical microdomain structures where the interdomain spacing increased as the molecular weight percent of the PDMS segments increased. The morphologies also illustrated continuity for both phases where the segment compositions were nearly equal.

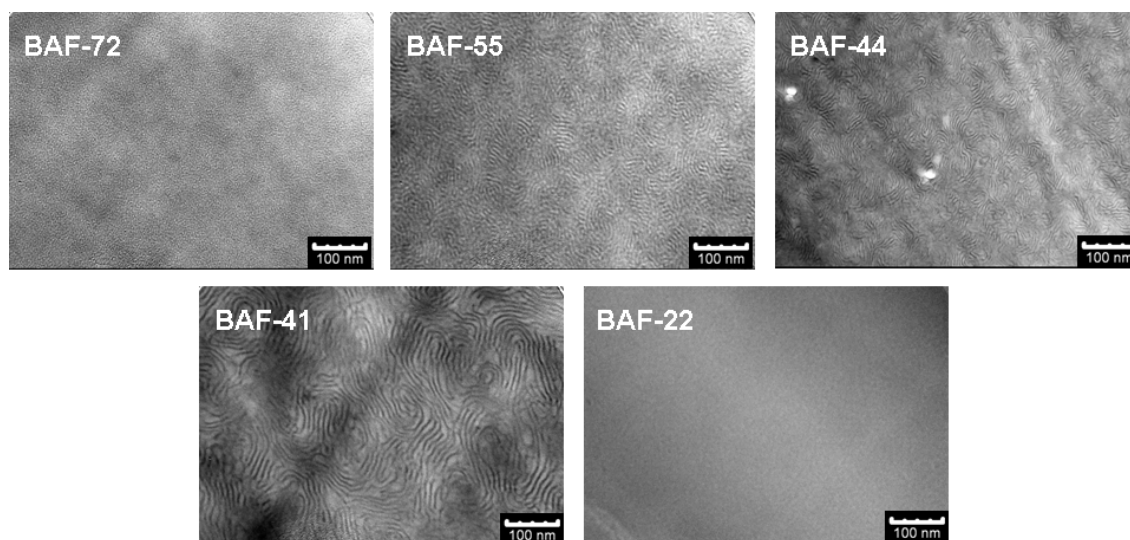


Figure 2.4: TEM images of BAF PAES-*b*-PDMS (BAF-72) 5400–10,000, (BAF-55) 6800–5800, (BAF-44) 5400–4100, (BAF-41) 9700–4700, and (BAF-22) 5400–1600.

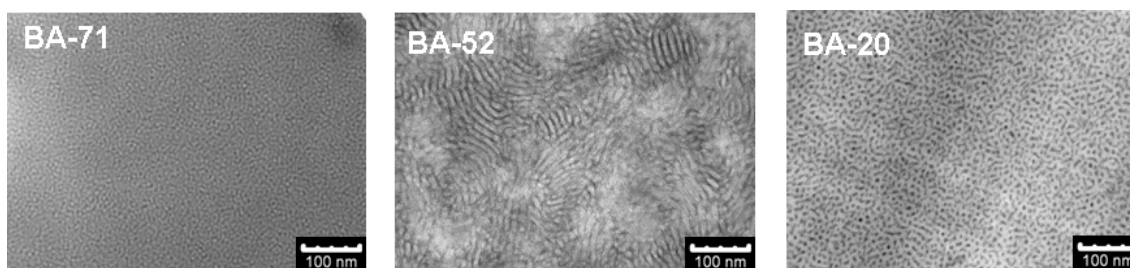


Figure 2.5: TEM images of BA PAES-*b*-PDMS (BA-71) 5500–10,000, (BA-52) 10,000–10,000, and (BA-20) 10,000–1600.

Based on the AFM and TEM results of the BAF PAES-*b*-PDMS, we further evaluated these materials by SAXS in Figs. 2.6 and 2.7. Well-defined peaks in the SAXS data for BAF-72 and BA-71, shown in Fig. 2.6, indicate microphase separation, consistent with the AFM and TEM images. The lack of second-order Bragg reflections indicates no long-range ordering, also consistent with microscopy data. The data also indicate that the incorporation of fluorine into the PAES unit led to an increase in the scattered intensity for BAF PAES-*b*-PDMS, due in part to the higher electron density of BAF PAES over BA PAES. The scattering term $(\Delta\rho)^2$, a measure of the X-ray scattering contrast in a two-phase material, is increased approximately 40% by the substitution of fluorine for hydrogen in the bisphenol A. Sample BAF-72 has an interdomain spacing of 21.9 nm, while BA-71 has an interdomain spacing of 19.3 nm.

The remaining BAF PAES-*b*-PDMS materials were also characterized by SAXS, as shown in Fig. 2.7. The interdomain spacings of the segmented block copolymers were determined and are given in Table 2.4. The data agree well with the microscopy data for the disordered samples, with at most a single characteristic scattering maximum. Sample BAF-41, which was clearly lamellar by TEM, does not show the characteristic Bragg diffraction peaks one would expect for a strongly lamellar morphology. This discrepancy may be the result of preferential orientation of the lamella in the plane of the cast films, a likely result of the very low surface tension of the PDMS constituent. Attempts to collect SAXS data with the specimen geometry rotated such that the incident beam of photons would be parallel to the lamellae were unsuccessful due to minimal film thickness (22 μm).

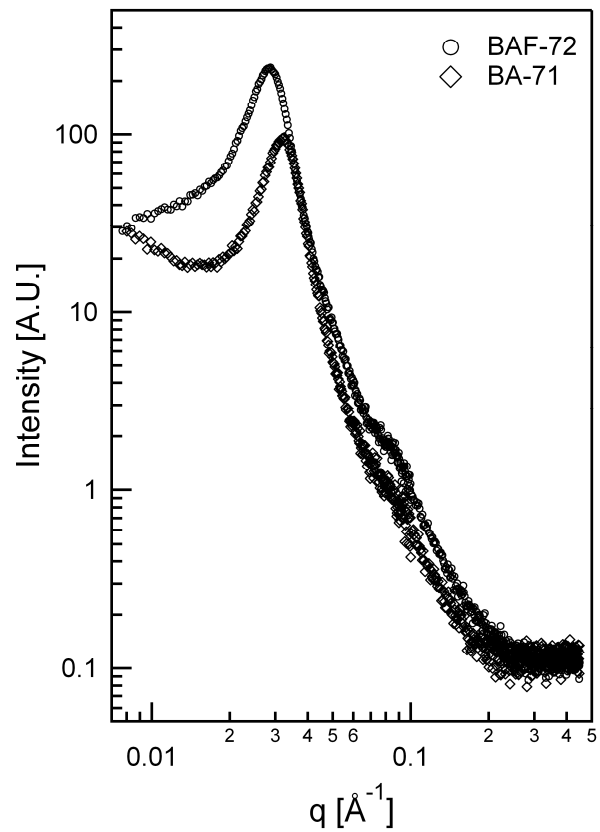


Figure 2.6: SAXS data for PAES segmented block copolymers BAF-72 and BA-71.

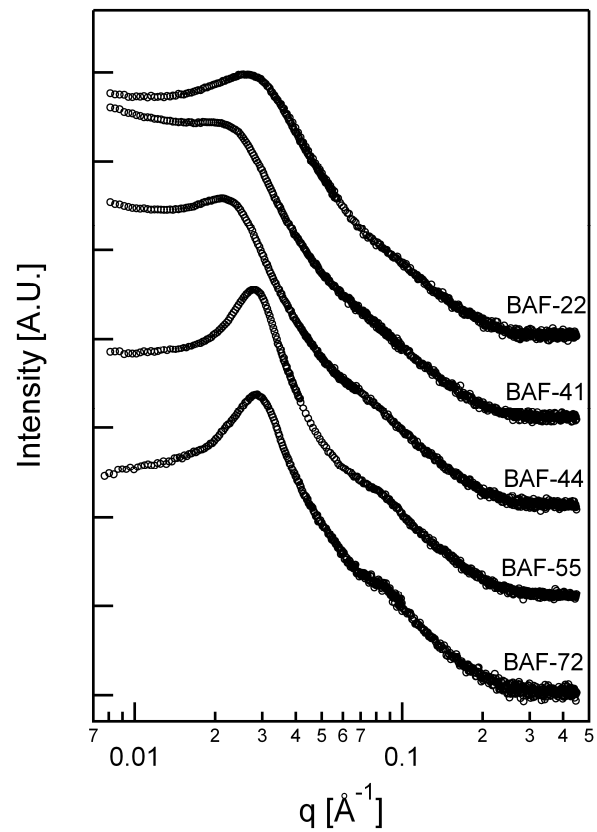


Figure 2.7: SAXS data for BAF PAES-*b*-PDMS of various PDMS volume fractions. The data have scaled vertically for clarity of presentation.

Table 2.4: Interdomain (ID) spacing between scattering domains from SAXS for BAF PAES-*b*-PDMS.

Image	BAF PAES	PDMS	ID Spacing (SAXS Bragg, nm)
BAF-72	5400	10,000	21.9
BAF-55	6800	5800	25.9
BAF-44	5400	4100	29.9
BAF-41	9700	4700	26.6
BAF-22	5,400	1,600	24.7

The exact effect of fluorination on morphology in these materials remains unclear. The BAF PAES-*b*-PDMS materials appear to show stronger microphase separation behavior, with BAF-41 forming well-defined lamellae. However, where direct comparisons are possible the effects are not clearly discernable. While BAF-55 and BA-52 have very similar morphologies, BA-20 is more strongly phase separated than BAF-22. A number of complex explanations for the observed morphological behaviors are possible, but outside the scope of this work. It is worth noting that many parameters play an important role in determining bulk morphology, including molecular weight^{35, 36}, casting solvent^{37, 38}, annealing temperature and time³⁹⁻⁴².

2.6. CONCLUSIONS

We have synthesized and characterized a new family of BAF PAES-*b*-PDMS and compared them to BA PAES-*b*-PDMS synthesized in our lab. The incorporation of

fluorinated methyl groups in the PAES unit gives these segmented block copolymers thermal stability to nearly 500 °C, which is greater than the BA PAES-*b*-PDMS. The BAF PAES homopolymer has a higher tensile modulus than the Udel[®] homopolymer, 1700 MPa compared to 1200 MPa. The tensile properties of the two families of segmented block copolymers were similar with properties ranging from elastomeric and plastic depending on the molecular weight composition of the oligomer. Both segmented block copolymer systems were transparent and colorless. They were also microphase separated, as indicated by AFM, SAXS, and TEM. There were distinct differences in the morphological properties of these segmented block copolymers analyzed by TEM. The BA PAES-*b*-PDMS materials formed weakly ordered lamellae at a symmetric composition and were disordered at asymmetric compositions, but were thought to have characteristics in agreement with those reported previously for this class of segmented block copolymers. The BAF PAES-*b*-PDMS displayed increased morphological order with decreasing PDMS content, with a clearly lamellar morphology formed by the sample with 41 vol-% PDMS. Without a direct comparison to BAF-41, these results do not conclusively reveal the effect of fluorination on the driving force for microphase separation in these segmented block copolymers.

2.7. ACKNOWLEDGMENTS

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Chapter 3:

MOLECULAR WEIGHT ANALYSIS OF SEGMENTED BLOCK COPOLYMERS

3.1. ABSTRACT

A series of PAES–PDMS segmented block copolymers have been synthesized. The materials incorporate PAES and PDMS oligomers of various molecular weights. Measurements were made to determine the molecular weight of the segmented block copolymers in order to be able to understand structure, property, and composition relationships for the phase separated materials. The data shows the molecular weight of the segmented block copolymers could not accurately be determined using chromatographic measurements such as size exclusion chromatography because of the interaction with some of units in the segmented block copolymer sticking to the column. Additionally, d_n/d_c values calculated on-line lead to inaccurate molecular weight measurements of the segmented block copolymers. Measurements by dynamic light scattering show the segmented block copolymers are non-aggregated and have particle sizes lower than 100 d.nm. Intrinsic viscosities of a series segmented block copolymers measured in chlorobenzene range 0.19 dl/g to 0.64 dl/g.

KEYWORDS: molecular weight, light scattering, copolymers

3.2. INTRODUCTION

The most common chromatographic technique used to measure polymer molecular weight is size exclusion chromatography (SEC) or gel permeation chromatography (GPC) ¹⁻³. The separation technique works by separating molecular

species based on their hydrodynamic radius in solution. Molecular species with a large hydrodynamic radius do not diffuse into the porous column and are eluted first or unretained, while species of smaller hydrodynamic radius penetrate the porous column and eluted later or retained. Molecular species that are between the two extremes penetrate into the pores based upon their hydrodynamic radius and exhibit fractionation related to molecular size and shape. Separation of the molecular species is described based on elution time or volume as a function of molecular size^{4,5}.

The molecular weights can be determined by several detection systems though the most common are differential refractive index (DRI) detection and light scattering detection. DRI detection responds linearly to polymer concentration and molecular weight is determined relative to a standard calibration of polystyrene of known molecular weight (reference against the sample). Molecular weights are generally relative values. On the other hand, light scattering detection provides absolute molecular weight values, as no calibration or reference standards are required for determination of molecular weight. However, light scattering detection requires the concentration and the d_n/d_c value of the molecular species in solution. The d_n/d_c value is the change in the solution refractive index as it relates to the change in concentration of a material in the polymer solution^{2,6}.





Determining the molecular weight of polymer materials provides the basis for anticipating and establishing their T_g , mechanical, thermal, and viscoelastic properties⁷⁻⁹. Specifically for copolymers of various architectures, determining the molecular weight can be difficult and can result in unreliable or inaccurate data¹⁰. In this study, the molecular weight of segmented block copolymers between PAES and PDMS has been

evaluated through chromatographic and analytical techniques. The first technique was SEC, in which the molecular weights were obtained from light scattering and RI detection in THF and chloroform solvents, respectively. Intrinsic viscosities of the segmented block copolymers were determined in chlorobenzene polymer solutions. Another analytical technique used to analyze the association of species in the segment block copolymer in THF solvent was dynamic light scattering (DLS). This work will provide a summary of the results obtained from the various techniques and discuss the accuracy of the measurements.

3.3. NOMENCLATURE AND STRUCTURES

The segmented block copolymers used in this study are listed in Table 3.1. The PAES unit contains bisphenol A (BA), bisphenol AF (BAF), or random copolymers of BA and co-monomers, biphenol (DHBP) or terphenol (DHTP).

Table 3.1: Segmented block copolymers investigated in this study.

Structure	PAES Type	Segmented Block Copolymer Abbreviation
	Bisphenol A	BA PAES- <i>b</i> -PDMS
	Bisphenol AF	BAF PAES- <i>b</i> -PDMS
	Bisphenol A-DHBP	BA-DHBP PAES- <i>b</i> -PDMS
	Bisphenol A-DHTP	BA-DHTP PAES- <i>b</i> -PDMS

3.4. CHARACTERIZATION METHODS

3.4.1. Size Exclusion Chromatography (SEC) with Light Scattering Detection

Molecular weights were determined by SEC using light scattering detection. BAF PAES were analyzed in approximately 0.25% solution of tetrahydrofuran (THF) at 40 °C with a flow rate of 1.00 mL/min. using a Waters Liquid Chromatography 717 Autosampler. Microstryogel columns of 500, 1000, 10,000, 100,000 Å pore size with a Waters 410 Refractive Index detector, an in-line Wyatt miniDAWN multiple angle laser light scattering (MALLS) detector, and a Viscotek 270 dual Viscosity detector. The d_n/d_c values were determined on-line using the calibration constant for the RI detector and the mass of the polymer sample. For all samples, it was assumed that 100% of the polymer eluted from the column during the measurement.

3.4.2. Size Exclusion Chromatography (SEC) with Differential Refractive Index Detection

Number-average molecular weights were determined using a Waters 1515 isocratic HPLC pump, Waters Autosampler and Waters 2414 refractive index detector calibrated using polystyrene standards with very narrow polydispersities and an online differential viscometric detector (Viscotek T60A) coupled in parallel to detect the copolymers as they eluted from the separation column. The oven temperature of the column set containing two Styragel HT 6E and one Styragel HT 3 was constant at 30 °C. Chloroform with a 1.00 mL/min flow rate was used as the mobile phase.

3.4.3. Dynamic Light Scattering (DLS)

DLS, also known as quasi-elastic light scattering, was used to study particle association of the segment block copolymer in THF solutions (0.05–0.1 wt-%). The

samples were sonicated for 2-3 minutes and filtered using a 25 mm diameter (0.2 μm pore) syringe filter. DLS measurements were conducted with a Malvern Zetasizer ZS compact scattering spectrometer (Malvern Instruments Ltd, Malvern, UK) at a wavelength of 633 nm from a 4.0 mW, solid-state He-Ne laser at a scattering angle of 170° at room temperature. A total of 3 measurements were taken per sample solution with no delay between the measurements. Intensity average diameters were calculated using Malvern's Zetasizer Nano 4.2 software utilizing an algorithm, based upon Mie theory, which transforms time-varying intensities to particle size calculations ¹¹.

3.4.4. Intrinsic Viscosity, $[\eta]$

Intrinsic viscosities were determined in 0.2 g/dl chlorobenzene 25 °C using a Cannon Ubbelohde viscometer.

3.5. RESULTS AND DISCUSSION

3.5.1. Analysis by SEC

Segmented block copolymers were synthesized using a polycondensation reaction between hydroxyl-terminated PAES and the dimethylamino-terminated PDMS oligomers in a 1:1 stoichiometric ratio according to previous research ¹². Increased viscosity during the reaction assumes successful incorporation of PDMS. The assumption is that the initial molecular weight of segmented block copolymers is a distribution or an “average” of the molecular weights of the starting PAES and PDMS oligomers. The molecular weight of the segmented block copolymer increases as a result of the polymerization over time ¹³. This basic depiction is illustrated (Fig. 3.1) by the *number-average degree of polymerization*, \overline{X}_n over the reaction time. This

demonstrates the molecular weight steadily increases over time where long reaction times are needed to produce high molecular weight polymer ¹⁴.

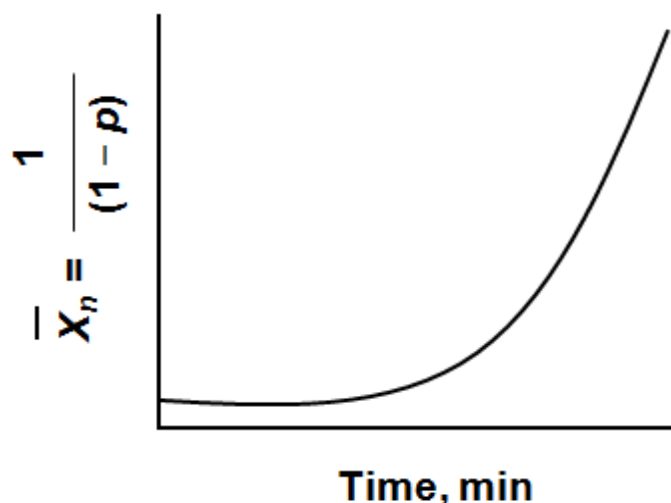


Figure 3.1: Degree of polymerization over time.

The segmented block copolymers synthesized were analyzed by SEC using a light scattering detector in order to determine the absolute molecular weights (Table 3.1). According to the results, the segmented block copolymers polymerized to produce segments of only $n < 3$, where n is the number of repeats units per polymer chain. Weight-average molecular weights of the segmented block copolymers ranged 31,900 to 142,900 g/mol. However, the results also showed that within a series of measurements, the on-line calculated d_n/d_c values varied significantly between a series of segmented block copolymers (Table 3.2). In a review by Wyatt, the author explained that in order to accurately determine the absolute molecular weight using light scattering detection, the measured d_n/d_c value should be accurate. Further, the variation in d_n/d_c value for a homopolymer below 10,000 g/mol and a copolymer is significant to

establishing results ⁶. Thus, while absolute molecular weights were established, the segmented block copolymers cannot be compared to one another since there is about a 3% deviation in the d_n/d_c values.

The inconsistency in the d_n/d_c values and the lower molecular weight results prompted an investigation on the influence of the d_n/d_c value on the calculated molecular weight of the segmented block copolymer. A molecular weight–time study was conducted on a BA PAES–*b*–PDMS incorporating PAES of 10,000 g/mol and PDMS of 5600 g/mol. During the reaction, a series of samples were taken from the reaction and analyzed by SEC using light scattering detection. The results plotted in a graph (Fig. 3.2) show that over a 48 h period, the segmented block copolymer molecular weight varied and did not increase gradually over the reaction period. The plot of this reaction is contrary to Fig. 3.1 and to the theory that there should be a significant increase in the molecular weight over time. Based on this information, the variation in the d_n/d_c value does affect the molecular weight. The final molecular weight is 14,600 g/mol, which suggests the reaction only produced one repeat unit.

Table 3.2: Molecular weight values of segmented block copolymers.

Segmented Block Copolymer	PAES (M_n)	PDMS (M_n)	Siloxane wt-% ^a	SEC M_n	SEC M_w	PDI	d_n/d_c
BA PAES- <i>b</i> -PDMS	10,000	1600	14	15,800	31,900	2.02	0.145
BA PAES- <i>b</i> -PDMS	10,000	5600	36	24,500	39,800	1.62	0.119
BA PAES- <i>b</i> -PDMS	5500	4700	46	21,400	33,900	1.59	0.103
BA PAES- <i>b</i> -PDMS	10,000	10,000	50	30,600	63,100	2.06	0.130
BA-DHBP PAES- <i>b</i> -PDMS	6400	5800	45	62,600	110,700	1.77	0.117
BA-DHBP PAES- <i>b</i> -PDMS	5500	10,000	61	77,600	142,900	1.84	0.076
BA-DHTP PAES- <i>b</i> -PDMS	4500	9300	67	69,800	124,500	1.78	0.071
BA-DHTP PAES- <i>b</i> -PDMS	3000	9300	76	40,800	55,900	1.37	0.051

^aCalculated by ¹H NMR

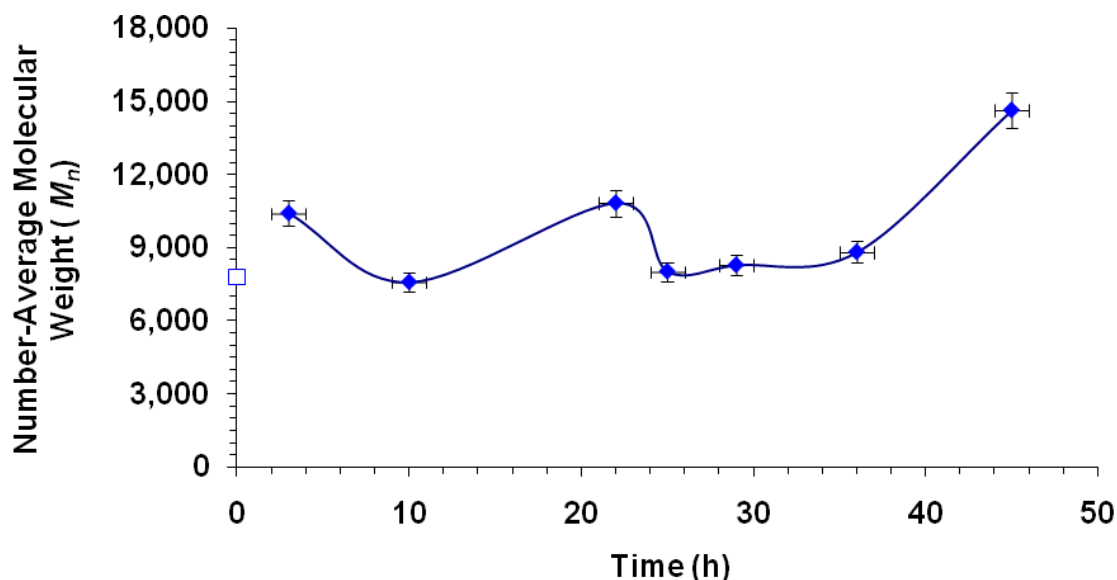


Figure 3.2: Molecular weight measurements from light scattering detection of BA PAES-*b*-PDMS (10,000–5600) over time.

There are two reasons to explain the d_n/d_c value inconsistency that can be deduced from this analysis. The refractive index differences between the PAES and PDMS in THF solvent contribute to the inaccuracy of the d_n/d_c value. PAES has a refractive index of 1.633 and PDMS has a refractive index of 1.430¹⁵. Wyatt⁶ explains the d_n/d_c value is related to the refractive index in that each polymer solution at a specific concentration produces a different refractive index, this case is simply represented by the relation:

$$\Delta c = (n_s - n_r) / (d_n / d_c) \quad \text{Equation 3.1}$$

where Δc is the change in concentration, n_s is the solution refractive index, n_r is the refractive index of the solvent, and d_n/d_c is determined by calibration of the solution and solvent. During the detection, if there are inequalities in on-line calculated d_n/d_c value, then the concentrations may be inaccurate. Similarly, differences in the refractive indices can produce inaccurate values as well.

Secondly, there was an idea that the PDMS, at higher molar concentrations, was sticking to the column and not eluting with the bulk of the segmented block copolymer, which would also affect the measurement on the d_n/d_c value and polymer concentration. However, recent reports have shown good chromatographic elution and measurement of PDMS^{16, 17}.

A second approach to determining molecular weights of the segmented block copolymers by SEC was done by using the DIR detector. The second molecular weight study consisted of comparing the molecular weights obtained by light scattering detection and by RI detection of BAF PAES-*b*-PDMS materials (Table 3.3). The two major differences between the SEC systems are the detectors and the solvent systems. The DIR detector uses chloroform solvent and the light scattering detector uses THF solvent. As previously discussed, the DIR detector provides relative data and the light scattering detector provides absolute molecular weights.

The results showed the molecular weights obtained correlate well to some degree. Specifically for the BAF PAES-*b*-PDMS (9700-4700), the molecular weight values do not vary between detection types or solvent types. However, for the BAF PAES-*b*-PDMS (5400-10,000), there was a huge discrepancy in the molecular weights between both the detection types and the solvent types. This further enhances the

original assumption that the PDMS, at higher molar concentrations, is sticking to the column and not eluting with the bulk of the segmented block copolymer. As well, the BAF PAES-*b*-PDMS (5400–10,000) material produced a lower d_r/d_c value relative to the other BAF PAES-*b*-PDMS samples.

From these experiments using SEC with both the DIR and light scattering detectors, it can be concluded that this chromatographic technique is not proficient in establishing the molecular weight of segmented block copolymers with diverse architectures or those incorporating oligomers of different refractive index values.

3.5.2. Analysis by Dynamic Light Scattering

With the inconsistencies from SEC results, it was of interest to study the particle association of the segment block copolymers by DLS. THF solutions of 0.05–0.1 wt-% BAF PAES-*b*-PDMS were prepared for measurement, which was determined to be the best concentration based on the initial auto-correlation function (Fig. 3.3). The auto-correlation function shows no rough features or “bumps” in the curve that would suggest the samples were too dilute or too concentrated. The intensity and size distribution plots (Fig. 3.4) illustrate the particles sizes of the segmented block copolymers. The Z-average ranges 14.1 to 90.4 d.nm for all samples. The Z-average is the intensity weighted mean size of the particle distribution. Plots A through C showed multimodal distribution, in which there are some large particles in the solutions, which suggests there is aggregation occurring in the polymer solutions. Plot D showed that particle sizes are equally sized and a very low amount of large particles exist in the solution. This particular sample incorporated more PDMS in the segmented block copolymer although particles are well dispersed in THF.

Table 3.3: Molecular weight comparison of BAF PAES-*b*-PDMS.

		Light Scattering Detection THF SEC Absolute Analysis			DIR Detection THF SEC Relative Analysis			DIR Detection Chloroform SEC Relative Analysis			
BAF PAES (M_n)	PDMS (M_n)	SEC M_n (kg/mol)	SEC M_w (kg/mol)	PDI	d_p/d_c	SEC M_n (kg/mol)	SEC M_w (kg/mol)	PDI	SEC M_n (kg/mol)	SEC M_w (kg/mol)	PDI
9700	4700	16	26	1.59	0.086	14	30	2.20	13	22	1.74
5400	4100	20	32	1.63	0.088	17	38	2.21	12	18	1.55
6800	5800	29	64	2.21	0.091	47	92	1.94	29	46	1.59
5400	10,000	85	187	2.19	0.048	22	55	2.47	114	137	1.21

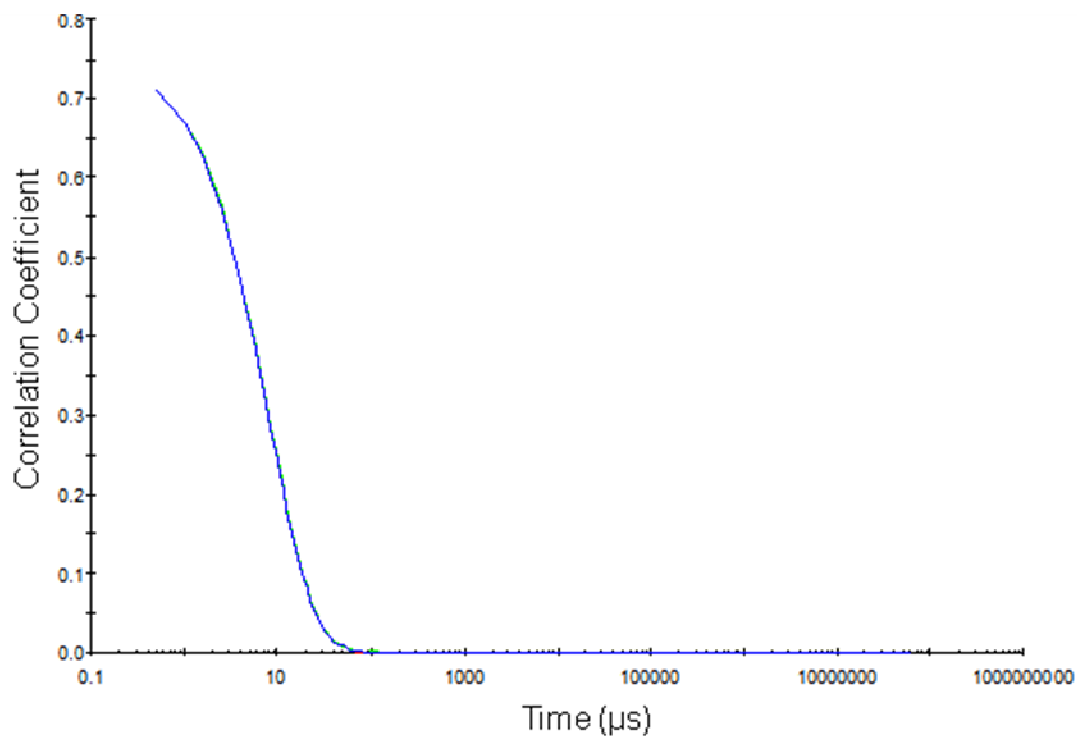


Figure 3.3: Representative auto-correlation function for the segmented block copolymers measured by DLS.

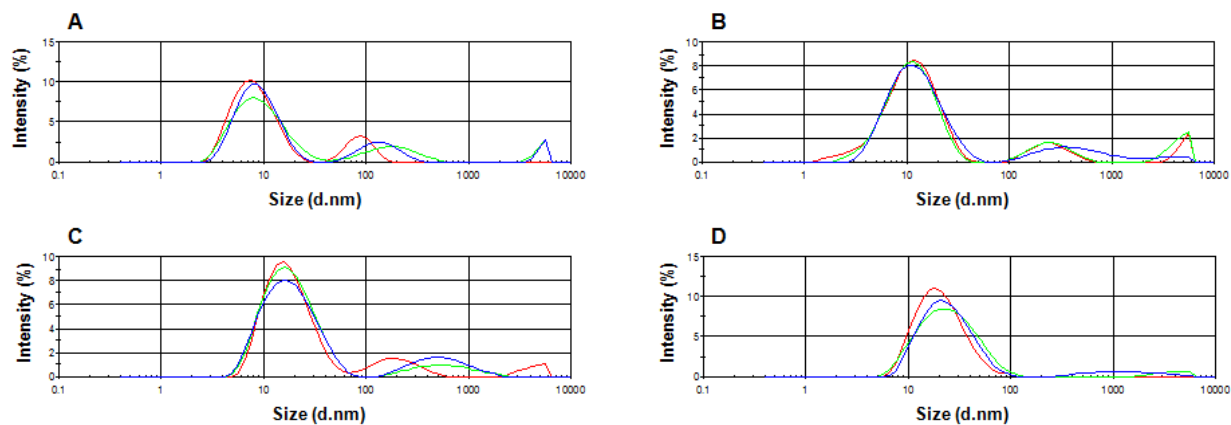


Figure 3.4: Size distribution by intensity of BAF PAES-*b*-PDMS (A) 9700–4700, (B) 5400–4100, (C) 6800–5800, and (D) 5400–10,000.

3.5.3. Analysis by Intrinsic Viscosity, $[\eta]$

Previous research by Noshay and co-workers¹⁸ showed high molecular weight BA PAES-*b*-PDMS could be obtained within 3 h of the reaction in chlorobenzene. Segmented block copolymers synthesized in a 1:1 stoichiometric ratio produced “reduced viscosities (0.2 g/dl in methylene chloride at 25 °C) as high as 1.60 dl/g” correlating to “a weight-average molecular weight of about 238,000 (determined by ultracentrifugation in THF solution).” McGrath and co-workers¹⁹ also synthesized BA PAES-*b*-PDMS according to Noshay’s work. The segmented block copolymers produced intrinsic viscosities (in THF at 25 °C) in the range of 0.60 dl/g to 0.78 dl/g. Additionally, Rusu and co-workers²⁰ reported reduced viscosities (0.2 g/dl in dichloroethane at 25 °C) of 0.12 dl/g to 0.37 dl/g. These studies suggest similar viscosities could be produced within the current segmented block copolymer materials

Intrinsic viscosities were measured in 0.05M chlorobenzene at 25 °C. The intrinsic viscosities ranged 0.19 dl/g to 0.64 dl/g for a series segmented block copolymers (Table 3.4). These viscosities are consistent with the values reported in the previous literature. However, there is no direct correlation to the molecular weight of the segmented block copolymer.

Table 3.4: Intrinsic viscosities for segmented block copolymers.

Segmented Block Copolymer	PAES (M_n)	PDMS (M_n)	Siloxane wt-% ^a	[η] (dl/g)
BA PAES- <i>b</i> -PDMS	10,000	1600	14	0.19
BA PAES- <i>b</i> -PDMS	10,000	5600	36	0.27
BA PAES- <i>b</i> -PDMS	5500	4700	46	0.28
BA PAES- <i>b</i> -PDMS	4600	5600	55	0.34
BAF PAES- <i>b</i> -PDMS	5400	4100	43	0.23
BAF PAES- <i>b</i> -PDMS	9700	4700	33	0.64
BAF PAES- <i>b</i> -PDMS	5400	10,000	65	0.40
BA-DHBP PAES- <i>b</i> -PDMS	6400	5800	45	0.57

^aCalculated by ¹H NMR

3.6. CONCLUSIONS

The molecular weights of a series of segmented block copolymers have been measured by SEC and viscosity techniques. The results suggest the differences in the d_n/d_c values obtained from SEC light scattering detection produce inaccurate results. When compared to measurements obtained from SEC DRI detection, the two sets of results are inconsistent. Based on the SEC studies, it is concluded that the best way to determine molecular weight of polymers with diverse arrangements using chromatographic methods is to use a SEC system that uses a third detector such as UV or FTIR. This will help avoid relying solely on d_n/d_c values and the variation in concentration and refractive indices. DLS results suggest there is aggregation

occurring in the polymer solutions, even though the solutions were sonicated prior to measuring.

Outside of SEC analysis, the segmented block copolymers have intrinsic viscosities ranging 0.19 dl/g to 0.64 dl/g in chlorobenzene. These results are consistent with previous literature values and seemingly the most reliable of all the results.

3.7. ACKNOWLEDGMENTS

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CHAPTER 4:

SYNTHESIS AND PROPERTIES OF BISPHENOL A- TERPHENOL POLY(ARYLENE ETHER SULFONE) AND POLYDIMETHYLSILOXANE SEGMENTED BLOCK COPOLYMERS

4.1. ABSTRACT

We have synthesized new poly(arylene ether sulfone) (PAES) and polydimethylsiloxane (PDMS) segmented block copolymers where the PAES segments contain 20–30% of 4,4'-dihydroxyterphenyl (DHTP) and 70–80% of bisphenol A (BA) units. The tensile and thermal properties of the materials were measured and were compared to those of existing bisphenol A PAES–PDMS segmented block copolymers (BA PAES-*b*-PDMS). Also, a high molecular weight BA–DHTP PAES random copolymer containing 80% BA and 20% DHTP was prepared and its properties were compared to Udel[®], a commercial PAES based on bisphenol A. The BA–DHTP PAES random copolymer had a significantly higher modulus (1800 MPa) and T_g (196 °C) when compared to Udel[®]. In the segmented block copolymer materials, increased modulus and tensile strain at break (elongation) were also found when DHTP was incorporated into the PAES segments.

KEYWORDS: poly(arylene ether sulfone); terphenol; thermal properties

4.2. INTRODUCTION

Poly(arylene ether sulfone)s (PAES) are tough amorphous thermoplastics that have exceptional thermal and mechanical properties ¹. While PAES are tough

amorphous polymers with good thermal stability, many studies have been devoted to modifying the PAES structure in order to enhance not only the mechanical²⁻⁴ and thermal⁵, but also the adhesive⁶ and gas transport properties⁷⁻⁹. In addition, incorporation of 4,4'-biphenol and hydroquinone in the PAES polymer backbone has been shown to yield polymers with higher thermooxidative properties and higher T_g ^{10, 11} than the bisphenol A (BA) PAES analogs. Another structural unit incorporated into polymer backbones and explored in the literature is *p*-terphenyl. A major property that makes the *p*-terphenyl group an exceptionally unique monomer is its high rigidity. Reports^{12, 13} have shown that incorporation of the *p*-terphenyl group has led to the formation of materials with outstanding thermal and mechanical properties.

An early study was based on the incorporation of 4,4'-dihydroxyterphenyl (DHTP) into poly(aryl ether)³. The researchers investigated the thermo-mechanical properties in various poly(aryl ether)s and PAES and showed the DHTP poly(aryl ether) had a high T_g of 182 °C and a low temperature relaxation at -100 °C associated with the relaxation of the aryl ether group. The materials also had a water absorption value of 0.18 wt-%. Similarly, Staniland¹⁴ synthesized polysulfone containing DHTP in order to produce a crystalline polymer while maintaining a high T_g . The DHTP polymers had 41% crystallinity, a T_g of 251 °C and a T_m of 389 °C. Most recently, Mao and Turner¹⁵ prepared PAES copolymers that incorporated bisphenol A (BA) and DHTP. These materials exhibited good thermal properties, such as T_g of 250 °C and T_m of 370 °C and T_d -5% weight loss between 490 and 500 °C under N₂. The BA–DHTP PAES random copolymers were soluble in dimethylacetamide (DMAc) at room temperature when DHTP incorporation was < 70%.

The purpose of this research is to enhance the tensile and thermal properties of BA PAES–PDMS segmented block copolymers by modifying the backbone structure with the addition of DHTP. The tensile and thermal properties of the DHTP containing segmented block copolymers will be investigated. By incorporating the rigid DHTP comonomer into the polymer backbone, we expect the thermal stability and T_g to increase as well as an enhancement of the modulus of the segmented block copolymers over the analogous BA PAES–PDMS structures.

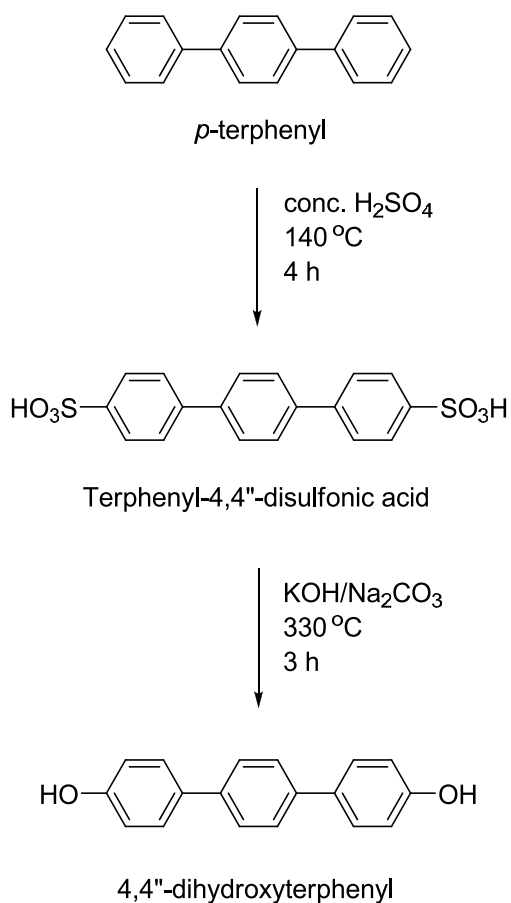
4.3. EXPERIMENTAL

4.3.1. General Methods and Materials

Anhydrous dimethylacetamide (DMAc), chlorobenzene, tetramethylammonium hydroxide pentahydrate (TMAH • 5H₂O), *p*-terphenyl, potassium hydroxide (KOH), sodium carbonate (Na₂CO₃), and toluene were purchased from Aldrich and used as received. Bisphenol A (BA) and anhydrous potassium carbonate (K₂CO₃) was purchased from Aldrich in highly pure monomer grade and dried overnight under vacuum at 60 °C before use. Sulfuric acid and hydrochloric acid (HCl) was purchased from Fisher Scientific. Dichlorodiphenylsulfone (DCDPS) and Udel[®] were donated by Solvay Advanced Polymers. Monomers were dried overnight under vacuum at 60 °C before use and the polymers were used as received. Octamethylcyclotetrasiloxane (D₄), purchased from Aldrich, was vacuum distilled before use. 1,5-Bis(dimethylamino)hexamethyltrisiloxane was purchased from Silar Laboratories, and used as received.

4.3.2. Synthesis of 4, 4'-dihydroxyterphenyl (DHTP)

Synthesis of DHTP (Scheme 4.1) was performed according to the previous literature ¹⁶. Concentrated sulfuric acid (130.72 g, 71.00 mL) was heated to 110 °C, and *p*-terphenyl (40.00 g, 173.67 mmol) were added to a 250-mL round-bottom flask. The temperature was raised to 140 °C and maintained for 4 h. After cooling to 100 °C, water (120 mL) was added dropwise, and the mixture was allowed to cool and then filtered under reduced pressure to give a crude product. The crude product (11.65 g, 29.84 mmol) was added to a stainless steel vessel in a Parr reactor and charged with KOH (27.96 g, 498.35 mmol) and Na₂CO₃ (2.80 g, 26.38 mmol). The reaction temperature was raised to 330 °C and the mixture was stirred for 3 h under argon. The mixture was then cooled to 100 °C and the pressure was released. The yellow crude product was removed by the addition of water (270 mL) and was filtered under reduced pressure. The crude product was suspended in a 1000 mL beaker of 10% aqueous HCl (300 mL), heated to 90 °C and vacuum filtered while hot. The crude product was dried and recrystallized twice from DMAc. Yield: 65% white solid, m.p. 371 °C (literature values, 375 °C ¹⁷ and 378 °C ¹⁸). Characterization by ¹H NMR (DMSO-*d*₆ 400 MHz) δ ppm: 9.50 (s, 2H, OH), 7.57 (s, 4H, Ar-H), 7.47 (d, 4H, Ar-H), 6.81 (d, 4H, Ar-H).



Scheme 4.1: Synthesis of DHTP.

4.3.3. Synthesis of BA–DHTP PAES Random Copolymers (BA–DHTP PAES)

The BA–DHTP PAES random copolymers were prepared in a three-neck, 250-mL round-bottom flask equipped with a mechanical stirrer, gas inlet, Dean-Stark trap, and condenser. The polymerization was carried out in a metal bath capable of high temperature reactions. For preparation of a 3500 g/mol oligomer, the round bottom flask was charged with BA (1.83 g, 8.02 mmol), DHTP (0.53 g, 2.02 mmol), DCDPS (2.39 g, 8.32 mmol), and K₂CO₃ (3.59 g, 9.99 mmol). To the monomers, DMAc (35 mL) was added in a 2:1 ratio with toluene (17 mL) as an azeotroping agent. The reaction

was started at 140 °C for 1–2 h. The temperature of the reaction was raised to 145 °C and then 152 °C within 3–4 h. Within 5 h, all toluene/water was removed, which is vital for formation of the polymer and the targeted molecular weight. The temperature was increased to 160 °C for 20–24 h. Upon completion, the polymer was coagulated in a 10% aqueous HCl (800 mL). The polymer was then filtered and dried overnight under vacuum at 90–110 °C, giving 3.7 g of a white solid. The same procedure was used to prepare other polymer samples.

4.3.4. Preparation of Dimethylamino-Terminated PDMS (PDMS) Oligomers

The dimethylamino-terminated PDMS oligomers were prepared following a literature method¹⁹⁻²². To synthesize the tetramethylammonium disiloxanolate catalyst, D₄ (13.30 g, 44.84 mmol) and TMAH • 5H₂O (0.71 g, 3.92 mmol) were added to a reactor with an attached Dean-Stark trap with condenser linked to a drying tube equipped with an overhead mechanical stirrer. The mixture was heated at 80 °C for 24 h under a rapid stream of Argon bubbled through the reaction mixture. The solution became homogenous within 2 h. The reaction was conducted for 24 h. At the end of the reaction the catalyst was used directly in the next step.

For the synthesis of a 4500 g/mol PDMS oligomer, D₄ (58.90 g, 198.57 mmol) and 1,5-bis(dimethylamino)hexamethyltrisiloxane (3.50 g, 11.88 mmol) were added to a 250-mL round-bottom flask equipped with a magnetic stir bar and condenser, and stirred under Argon. The tetramethylammonium disiloxanolate catalyst (3.82 g, 10.77 mmol) was removed from the reactor and added to the reaction mixture using a clean, dry 12-gauge needle. The reaction was allowed to proceed at 80 °C for 2–3 days. The temperature was increased to 150 °C under Argon for 2–3 h to remove any residual

catalyst and cyclics. The solution was vacuum distilled at 70 °C to remove any residual end-capping reagent. The reaction yield 100 mL of clear, viscous liquid at room temperature. Characterization by ^1H NMR ($\text{CHCl}_3\text{-}d_6$ 500 MHz) δ ppm: 2.47 (s, 12H, N- CH_3), 0.06 (m, 6H, Si- CH_3). ^{13}C NMR ($\text{CHCl}_3\text{-}d_6$ 500 MHz) δ ppm: 77.09 (t, 2C, N- CH_3), 1.09 (s, 6C, Si- CH_3). ^{29}Si NMR ($\text{CHCl}_3\text{-}d_6$ 400 MHz) δ ppm: -10.41 (s, 2Si, N-Si), -22.70 (s, 1Si, Si-O).

4.3.5. Preparation of Bisphenol A-Terphenol PAES Segmented Block Copolymers (BA-DHTP PAES-*b*-PDMS)

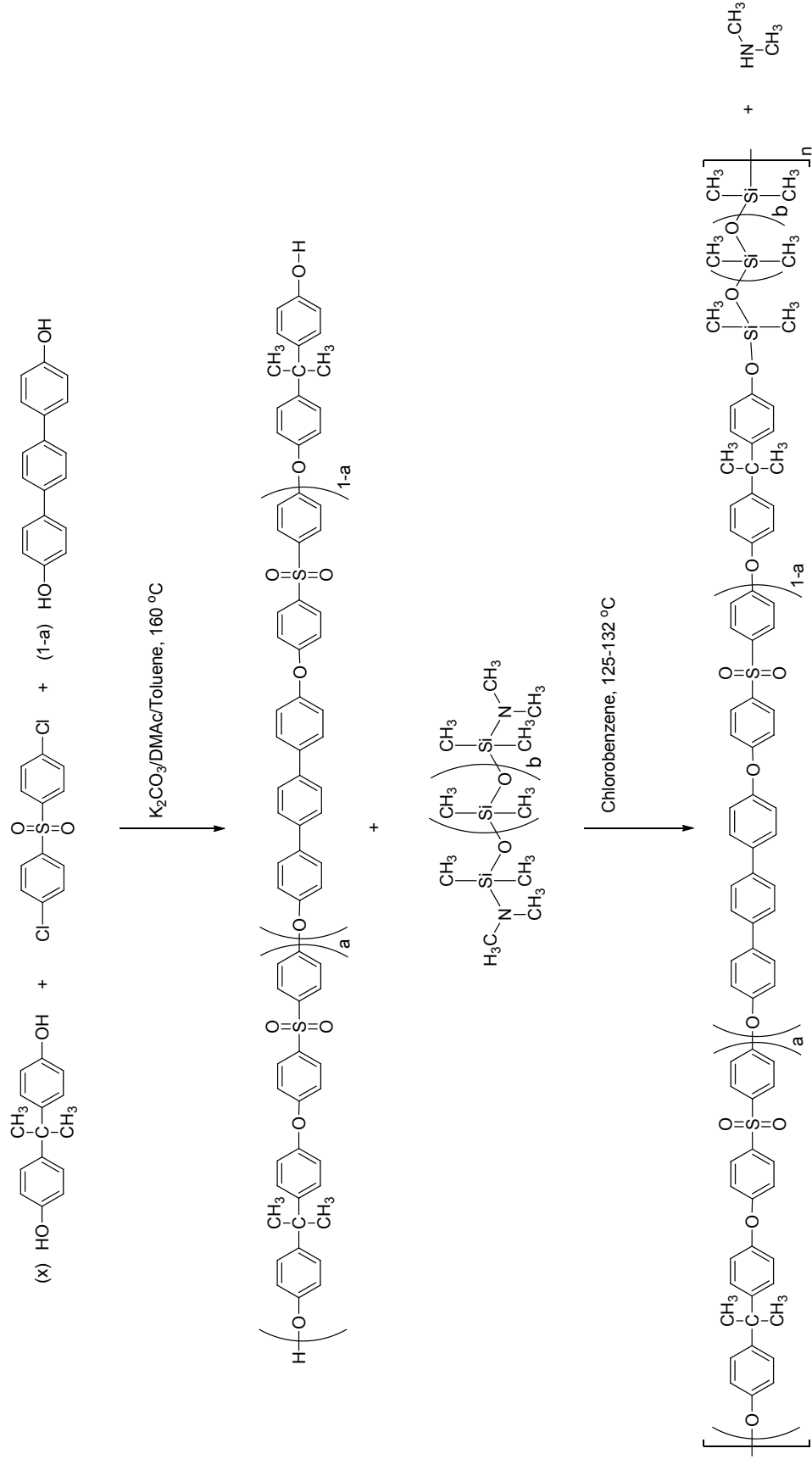
Segmented block copolymers (Scheme 4.2) were prepared with BA-DHTP PAES and PDMS in a 1:1 molar ratio following a modified literature method²³. BA-DHTP PAES random copolymer 4500 g/mol (1.19 g, 0.26 mmol) and chlorobenzene (40 mL) were charged to a 100-mL three-neck, round-bottom flask equipped with a magnetic stir bar, gas inlet, Dean-Stark trap, and condenser. The polymerization was carried out in a silicon oil bath heated on a hot plate. The solution was stirred at reflux temperature (132 °C) for 1 h. The PDMS oligomer 45 00 g/mol (1.18 g, 0.26 mmol) were added to the reaction mixture using a clean, dry 18-gauge needle in increments. The reaction was heated at reflux for 8–12 h. At the end of 12 h, the reaction formed a viscous solution. The solution was cooled and the product was precipitated from methanol (800 mL). The fluffy, white product was dried under vacuum at 90–110 °C overnight, giving a water solid (2.1 g). The same procedure was used to prepare other segmented block copolymer samples. The segmented block copolymers containing high PDMS were isolated as a white elastomeric gum.

4.3.6. Film Preparation of the Segmented Block Copolymers

The segmented block copolymers were dissolved in THF to afford transparent solutions with 5 wt-% solids. The solutions were filtered through a 25 mm diameter syringe filter (0.45 μm pore) and cast onto clean glass substrates. The films were covered to minimize evaporation and dried at room temperature for 2–3 days, and then dried under vacuum at 90–110 $^{\circ}\text{C}$ overnight.

4.3.7. Polymer Acronyms

In this report, we have given the PAES random copolymers descriptive acronyms in order to identify the mole ratio between BA and DHTP. For a PAES random copolymer that incorporates 80% BA and 20% DHTP, the name is BA80–DHTP20. For the segmented block copolymers, the PAES random copolymer acronym will be used in conjunction with PDMS followed the molecular weight of each segment (PAES and PDMS) in parentheses, such as, BA80–DHTP20 PAES–*b*–PDMS (4500–4500).



Scheme 4.2: Synthesis of BA-DHTP PAES-*b*-PDMS.

4.4. CHARACTERIZATION METHODS

4.4.1. Nuclear Magnetic Resonance Spectroscopy (NMR)

¹H NMR spectra were obtained using a JEOL 500 MHz spectrometer at 25 °C. Spectra were obtained in a 10 w/v-% deuterated chloroform without TMS solution for BA–DHTP PAES random copolymers and BA–DHTP PAES–*b*–PDMS.

4.4.2. Thermogravimetric Analysis (TGA)

Measurements were conducted by TA Instruments thermogravimetric analysis (TGA) Q500 at temperatures from 35 °C to 600 °C under nitrogen at a heating rate of 10 °C/min.

4.4.3. Differential Scanning Calorimetry (DSC)

Glass transition temperatures were measured on a TA Instruments differential scanning calorimetry (DSC) Q1000 using a custom method with a heat/cool/heat cycle. A temperature ramp at 10 °C/min from 35 °C to 300 °C was applied for the homopolymers. For the segmented block copolymers a temperature ramp from -150 °C to 300 °C at 20 °C/min was employed in order to resolve all transitions.

4.4.4. Tensile Analysis

Stress-strain tests were performed on an Instron Model 1123 Universal Testing system with a Bluehill software package using a 20-lb load cell at room temperature. Tests were performed on dog-bone-shaped specimens (15 mm gauge length and 3.93 mm width) cut by a standard bench-top die from films (0.09 mm thickness), prepared as described above. Prior to testing, specimens were dried under reduced pressure at 90–110 °C overnight.

4.5. RESULTS AND DISCUSSION

4.5.1. Synthesis and Characterization of the PAES Random Copolymers and Segmented Block Copolymers

A polycondensation polymerization was done using BA, DHTP, and DCDPS for preparation of the BA–DHTP PAES random copolymers containing approximately 80% BA and 20% DHTP. This synthetic procedure has been well established in the literature^{3, 24, 25}. We used a stoichiometric imbalance with an excess of BA monomer in order to achieve hydroxyl-terminated end-groups and target molecular weights. The presence of the hydroxyl-terminated end-groups is especially important in the next step where the reaction between hydroxyl-terminated PAES and dimethylamino-terminated PDMS is employed to form the segmented block copolymers^{21, 23}. The ¹H NMR spectrum (Fig. 4.1) illustrates the position of the hydroxyl-terminated end-groups at 5.15 ppm and the phenyl rings located between 6.80 ppm and 8.00 ppm.

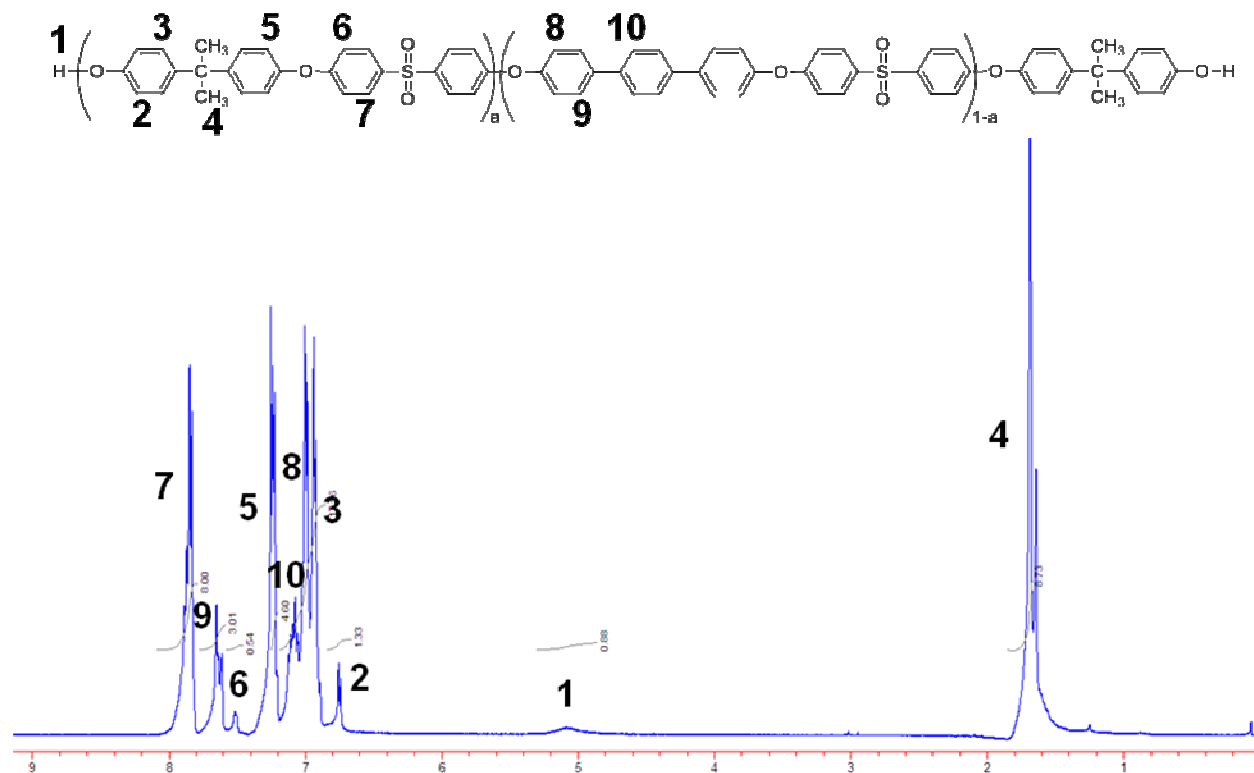


Figure 4.1: ^1H NMR of hydroxyl-terminated BA–DHTP PAES random.

Copolymerization with various molecular weights of PDMS produced fluffy, white materials. In the ^1H NMR spectrum (Fig. 4.2) of hydroxyl-terminated BA–DHTP PAES random copolymer, the peak at 0 ppm correlates to the $-\text{CH}_3$ groups in the PDMS oligomer. The disappearance of the peak at 5.15 ppm indicated a successful reaction between the hydroxyl-terminated BA–DHTP PAES random copolymer and the dimethylamino-terminated PDMS oligomer to form the segmented block copolymer. The segmented block copolymer materials were cast from THF solution to produce transparent films as previously described.

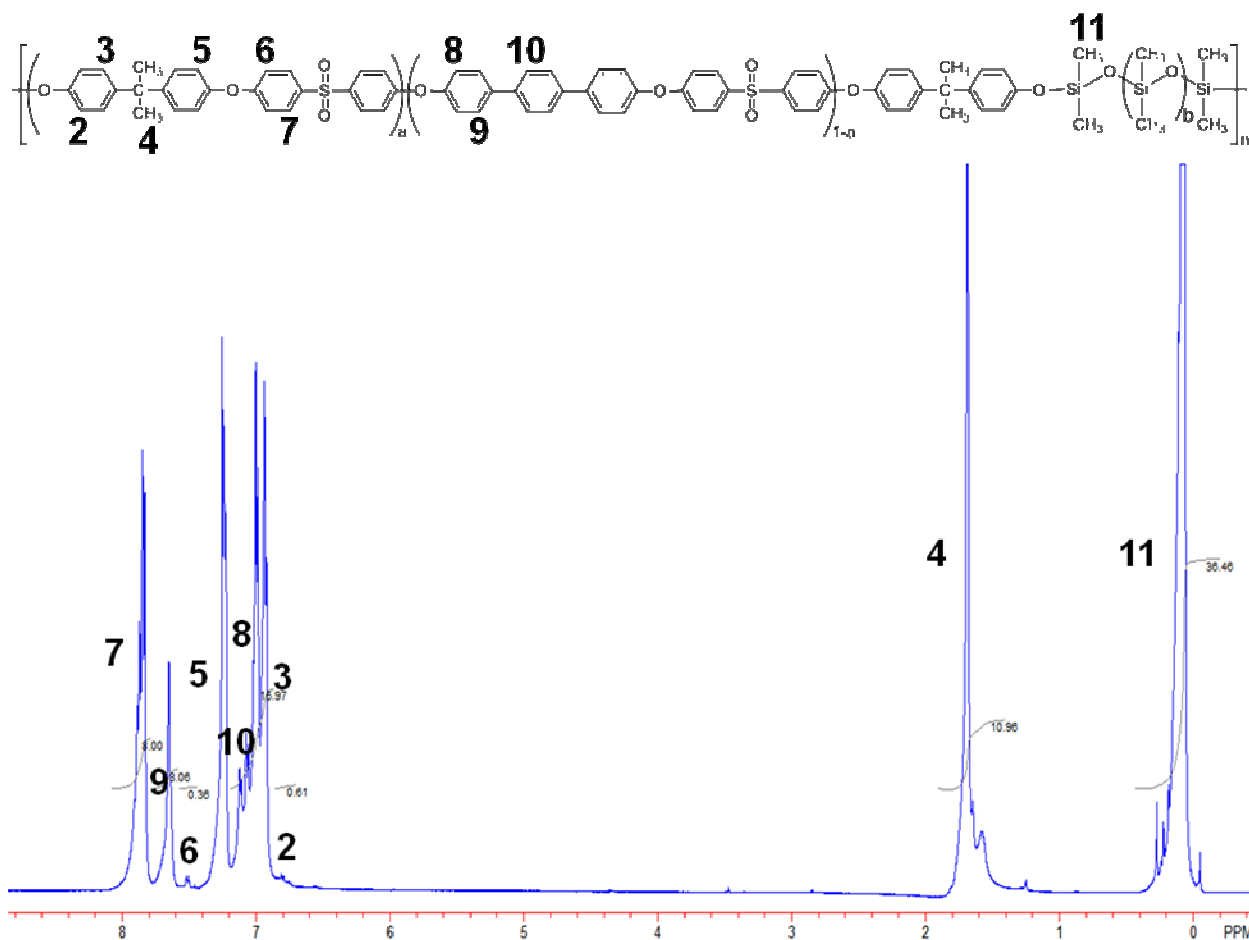


Figure 4.2: ^1H NMR of BA-DHTP PAES-*b*-PDMS.

4.5.2. Thermal Properties of Polymers

The thermal properties of the segmented block copolymers incorporating various amounts of PDMS were measured. In order to understand the thermal stability of the segmented block copolymers, it was important to establish the profile of the BA-DHTP PAES random copolymer. The thermal stability of the BA73-DHTP27 PAES random copolymer was measured by TGA (Fig. 4.3) and showed a T_d -5% weight loss of 393 °C under N_2 . Comparatively, BA PAES only showed thermal stability to 358 °C at 5%

weight loss, which infers the incorporation of 27% DHTP does improve the thermal stability of the PAES.

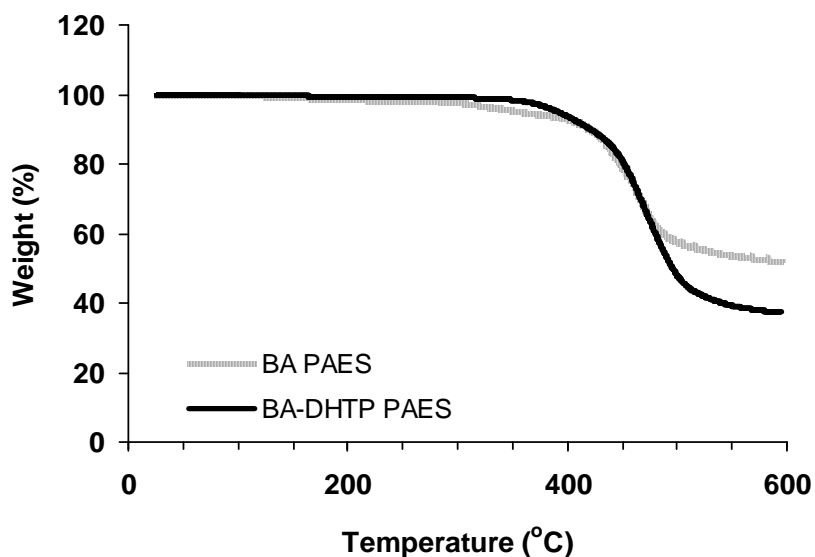


Figure 4.3: TGA thermograms of BA PAES and BA73–DHTP27 PAES random copolymer, at 10 °C/min.

The segmented block copolymers showed high thermal stability at 5% weight loss under N_2 . The thermal stability of BA80–DHTP20 PAES–*b*–PDMS (4500–4500) had a $T_{d-5\%}$ weight loss of 385 °C under N_2 (Fig. 4.4). Other segmented block copolymers synthesized from BA–DHTP PAES random copolymers and PDMS were stable from 348 °C to 446 °C (Table 4.1).

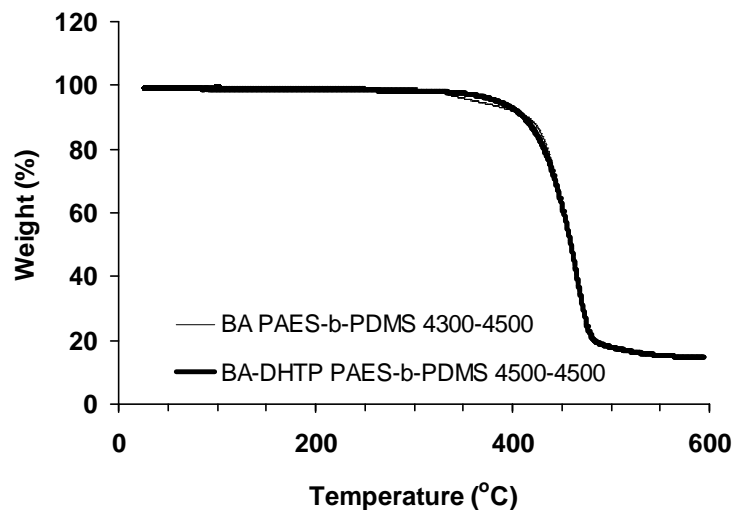


Figure 4.4: Thermal stability of BA–DHTP PAES–*b*–PDMS (4500–4500) compared to BA PAES–*b*–PDMS (4300–4500), at 10 °C/min.

The T_g 's of the PAES random copolymers were determined by DSC. The BA73–DHTP27 PAES random copolymer had a T_g of 196 °C compared to the BA PAES, which had a T_g of 183 °C (Fig. 4.5). This T_g value is consistent with the value Mao and Turner¹⁵ observed in the BA–DHTP PAES random copolymers synthesized with various DHTP percentages. The authors suggested the incorporation of higher percentages of DHTP raises the T_g of the PAES.

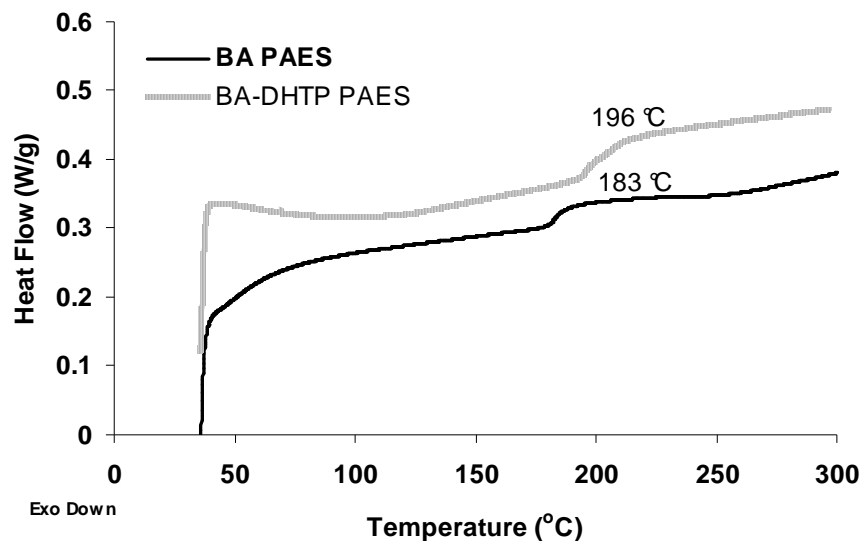


Figure 4.5: DSC profile BA PAES and BA73–DHTP27 PAES random copolymer, at 10 °C/min.

In Table 4.1, the T_g values of the segmented block copolymers are listed. The segmented block copolymer with less than 20 wt-% PDMS showed one T_g at 189 °C. Increasing the wt-% of PDMS in the segmented block copolymer to nearly 50 wt-%, the DSC trace showed two T_g s at –122 °C and 161 °C, indicative of phase separation of the blocks. Similarly, BA80–DHTP20 PAES–*b*–PDMS (4500–9300) having the highest PDMS wt-%, showed two T_g s, i.e. at –122 °C and 143 °C. This data set suggests that the segmented block copolymers are microphase separated like other PDMS segmented block copolymer materials that have been studied previously reported in the literature²⁶⁻²⁸. The T_g values are influenced by the amount of PDMS in the segmented block copolymer and of DHTP in the PAES unit. The segmented block copolymers, as discussed earlier, incorporate 20–30% DHTP co-monomer and have T_g s range from

173 °C to 187 °C. A slight reduction in the T_g was observed with increasing addition of PDMS, which results in the segmented block copolymer material becoming more microphase separated.

Table 4.1: Thermal properties of BA-DHTP PAES-*b*-PDMS.

Segmented Block Copolymers									
PAES	DHTP mol-% in PAES unit	PDMS	Siloxane wt%^a	<i>T</i>_d^{5% wt. loss} (°C)	Lower <i>T</i>_g (°C)	Upper <i>T</i>_g (°C)			
5900	25	1300	17	349	--	189			
8500	26	4500	33	446	-125	192			
4500	20	4500	46	385	-122	161			
4500	20	9300	62	414	-122	143			

^aCalculated by ¹H NMR

Microphase separation in the segmented block copolymers is indicative of the incompatibility between the PAES unit and the PDMS unit and was analyzed by AFM (Fig. 4.6). Phase (surface) images of the as cast, non-equilibrium BA–DHTP PAES segmented block copolymers illustrated light and dark features. The dark features represented the soft material (PDMS) and the light features were indicative of the hard material (PAES). The amount of PDMS in the BA–DHTP PAES segmented block copolymers increased from 17% to 64%. From image BA–DHTP–1 to BA–DHTP–3, the microphase separation became more pronounced.

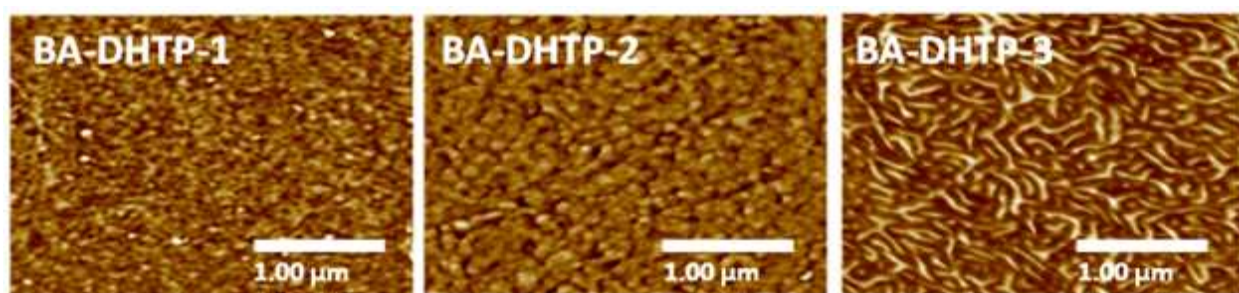


Figure 4.6: AFM images of BA–DHTP PAES–*b*–PDMS (BA–DHTP–1) 5900–1300, (BA–DHTP–2) 4500–4500, and (BA–DHTP–3) 8500–20,400 showing the surface of the film.

4.5.3. Tensile Analysis of Segmented Block Copolymers

PAES is an excellent high performance amorphous thermoplastic with a high T_g and excellent modulus²⁹. In previous studies^{21, 23, 27}, the BA PAES–*b*–PDMS materials gave tensile properties ranging from plastic to elastomeric upon increasing the amount and molecular weight of PDMS in the segmented block copolymer. The purpose of incorporating DHTP in the BA PAES segmented block copolymer material

was to evaluate the effect of the rigid *p*-terphenyl group on the segmented block copolymer properties. BA73–DHTP27 PAES random copolymer had a modulus of 1770 MPa (Table 4.2). The BA–DHTP PAES–*b*–PDMS materials displayed decreasing moduli from 1660 MPa to 9 MPa and increasing elongation from 5% to 195% with increasing PDMS content. The trend in this data set is consistent with the previous measurements of BA PAES–*b*–PDMS where the tensile properties range from plastic to elastomeric upon increased wt-% of PDMS incorporated^{23, 27}.

Comparatively, the BA73–DHTP27 PAES random copolymer had a higher modulus than Udel[®] and the BA–DHTP PAES–*b*–PDMS had a higher modulus than the BA PAES–*b*–PDMS. Udel[®] had a tensile modulus and elongation of 1200 MPa and 6%, respectively. Adding DHTP co-monomer into the PAES backbone improved the tensile modulus by 30% while the elongation was unchanged. The BA75–DHTP25 PAES–*b*–PDMS (5900–1300) prepared from low PDMS content give a 65% improvement in the tensile modulus over the BA PAES–*b*–PDMS (5500–1300), which was 580 MPa. Again, there was no significant change in the elongation from BA PAES–*b*–PDMS to BA–DHTP PAES–*b*–PDMS. Both segmented block copolymer materials with high PDMS content afforded materials with greater elasticity and more elastomeric properties. The elongation for the BA PAES–*b*–PDMS was 630%, which was higher than the BA–DHTP PAES–*b*–PDMS, 195%. The modulus values for these segmented block copolymer materials were the same.

The stress–strain plots of the data discussed are depicted in Figs. 4.7 and 4.8. The BA–DHTP PAES–*b*–PDMS curve illustrated in Fig. 4.7 suggested the material was stiff, ductile, and strong compared to the BA PAES–*b*–PDMS of similar PDMS content.

In contrast, segmented block copolymers with high PDMS is elastomeric. The BA-DHTP PAES-*b*-PDMS shown in Fig. 4.8 was also stiff, ductile, and strong compared to the BA PAES-*b*-PDMS.

Table 4.2: Tensile properties of BA-DHTP PAES-*b*-PDMS compared to BA PAES-*b*-PDMS.

Segmented Block Copolymers		PDMS	Siloxane wt%^a	Intrinsic Viscosity^b (dL/gm)	Tensile stress at Break (MPa)	Tensile strain at Break (%)	Tensile stress at Yield (MPa)	Modulus (MPa)
21,400	0	0	0.187	37 ± 22	5 ± 0.8	63 ± 13	1770 ± 238	
Udel [®] , 27,000	0	0	0.342	28 ± 20	6 ± 1	48 ± 12	1200 ± 350	
5900	1300	17	0.225	60 ± 8	5 ± 0.8	66 ± 6	1660 ± 218	
BA, 5500	1300	19	0.135	10 ± 7	8 ± 3	18 ± 4	590 ± 196	
8500	4500	33	0.177	18 ± 7	130 ± 59	24 ± 3	540 ± 49	
4500	4500	46	0.228	9 ± 2	55 ± 17	19 ± 2	100 ± 20	
4500	9300	62	0.441	7 ± 1	195 ± 53	8 ± 1	9 ± 1	
BA, 5500	10,000	65	0.307	14 ± 0.8	630 ± 170	14 ± 0.6	8 ± 2	

^aCalculated by ¹H NMR

^b0.2 dL/gm in chloroform at 25 °C

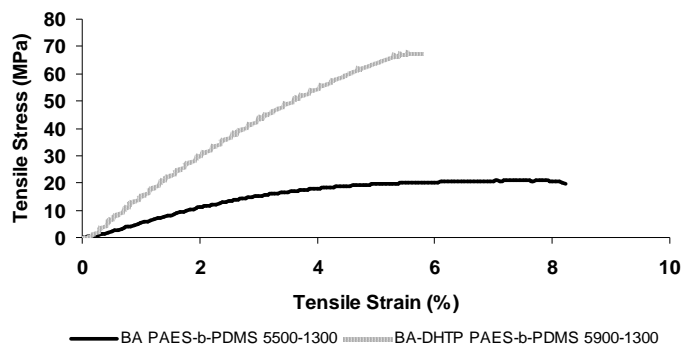


Figure 4.7: Stress–Strain curve for BA PAES–*b*–PDMS (5500–1300) and BA–DHTP PAES–*b*–PDMS (5900–1300).

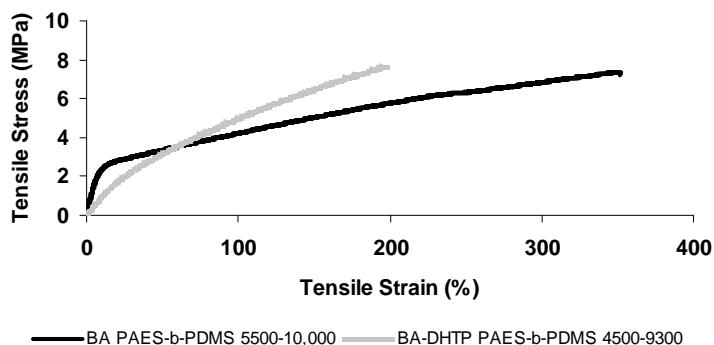


Figure 4.8: Stress–Strain curve for BA PAES–*b*–PDMS (5500–10,000) and BA–DHTP PAES–*b*–PDMS (4500–9300).

4.6. CONCLUSIONS

In this research study, a series of segmented block copolymers incorporating PAES with DHTP co-monomer was synthesized and characterized by ^1H NMR, TGA, and DSC. Transparent and colorless films were obtained by casting from THF solution. The materials gave high thermal stabilities to approximately 450 °C. Incorporation of

the rigid DHTP into the PAES unit enhanced T_g from 183 °C to 196 °C. Thermal analysis of the BA–DHTP PAES–*b*–PDMS afforded two T_g values, one corresponding to the PAES unit and corresponding to the PDMS unit.

The tensile analysis showed the BA–DHTP PAES random copolymer had a 30% higher modulus than Udel[®]. The BA–DHTP PAES–*b*–PDMS showed plastic to elastomeric properties depending on the composition in a manner similar to BA PAES–*b*–PDMS materials. The stress–strain plots of BA–DHTP PAES–*b*–PDMS illustrated the materials were stiff, ductile, and produced a higher modulus than the BA PAES–*b*–PDMS.

4.7. ACKNOWLEDGMENTS

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CHAPTER 5:

SYNTHESIS AND CHARACTERIZATION OF TRIPTYCENE POLY(ARYLENE ETHER SULFONE)S

5.1. ABSTRACT

Poly(arylene ether sulfone)s (PAES) incorporating triptycene-1,4-hydroquinone (TPDH) have been synthesized. The different PAES polymers compositions synthesized were TPDH PAES homopolymers, bisphenol A-TPDH PAES random and segmented copolymers, and bisphenol A-TPDH PAES-polydimethylsiloxane segmented block copolymers (BA-TPDH PAES-*b*-PDMS) showed diverse thermal, tensile, and morphological properties. The novel TPDH PAES homopolymer was thermally stable to 468 °C and formed a brittle, colored film cast from THF solution. BA-TPDH PAES random copolymers were thermally stable to 459 °C at T_d -5% weight loss and displayed high T_g values. Segmented block copolymers copolymerized from PDMS with BA-TPDH PAES random and segmented copolymers showed enhanced thermal properties over BA PAES-*b*-PDMS. The BA-TPDH PAES-*b*-PDMS had moduli ranging from 1550 to 1 MPa depending on the amount of PDMS incorporated into the segmented block copolymers. At increased amounts of PDMS, the modulus decreased as observed for other PAES-*b*-PDMS materials.

KEYWORDS: poly(arylene ether sulfone); triptycene; tensile properties

5.2. INTRODUCTION

Triptycene containing polymers have been investigated by several scientists in the recent years. Bartlett and Cohen first synthesized the triptycene monomer in the

early 1940's by reacting anthracene and 1,4-benzoquinone followed by hydrogenation ¹. Swager and co-workers synthesized triptycene-based polymers where derivatives were studied for their ability to fluoresce and provide good optical properties ². Other analogues of triptycene materials have also been reported in the literature and have been shown to produce materials with outstanding properties ³⁻⁶.

Swager and co-workers have extensively explored the free volume in various triptycene derivatives as it relates to the improving mechanical, optical, electronic, and thermal properties in polymers ⁷⁻¹¹. One such study that incorporated the triptycene monomer into polyesters showed that the monomer enhanced the polymer tensile strength, strain stiffness, and ductility. These materials also produced increased thermal properties over the non-triptycene polyesters, the T_g increased from 25 °C to 55 °C and the thermal stability in air improved slightly from 375 °C to 382 °C ⁸. Swager and co-workers ⁹ also completed a similar study in which triptycene-polycarbonate (PC) copolymers of various molecular weights were blended into commercial polycarbonate, Lupilon[®]. A blend incorporating triptycene-PC (7/93) copolymer and Lupilon[®] (total triptycene content of 1.9 wt-% in the blend) produced an increase in the tensile modulus by 20%, an increase in the tensile yield strength by 17%, and an enhancement in the elongation by 80% over commercial polycarbonate, Lexan PC.

Swager and co-workers ⁴ also investigated triptycene as building blocks for triptycene conjugated polymers. Triptycene in polymers, such as poly(aryl ether)s and polyesters provided materials with low dielectric constants, high thermal stability, and high T_g values. The polymers also had enhanced ductility and a high tensile modulus. MacLachlan and Chong ¹² reviewed the free volume in triptycene that includes two

bridgehead triptycenes. The structural arrangement provided enhanced rigidity and free-volume that allowed variations of the system to be in various supramolecular chemistries.

In this work, we expanded the work done by previous researchers by exploring the properties of poly(arylene ether sulfone) (PAES) random copolymers and PAES–polydimethylsiloxane (PDMS) segmented block copolymers associated with incorporating triptycene monomer into PAES polymer backbone. The PAES unit was composed of bisphenol A (BA) and triptycene (TPDH) monomers to make random and segmented copolymers. The PAES random copolymers were copolymerized with PDMS of varying molecular weights to form the segmented block copolymers of interest. The TPDH PAES homopolymer was also synthesized. The tensile and thermal properties of these materials were measured.

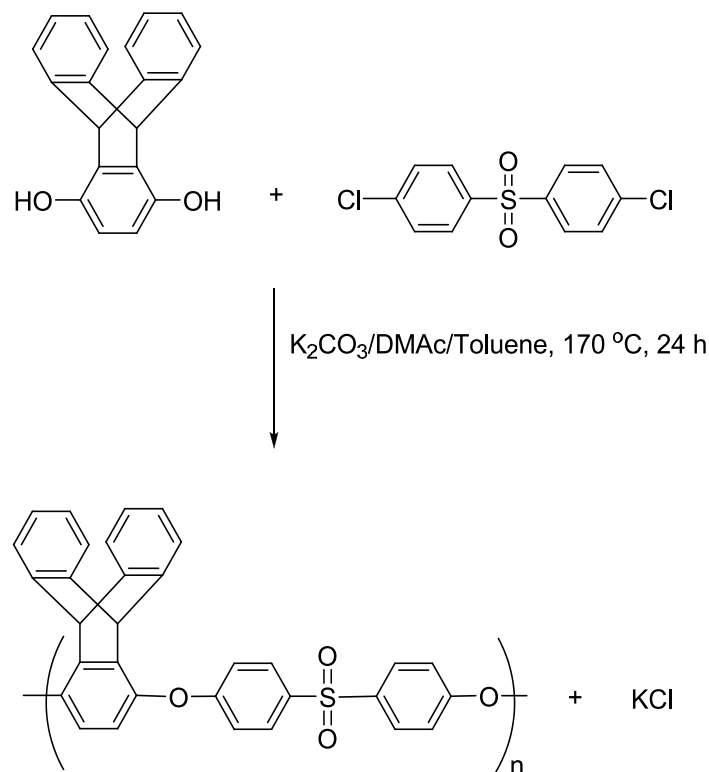
5.3. EXPERIMENTAL

5.3.1. General Methods and Materials

Anhydrous dimethylacetamide (DMAc), chlorobenzene, tetramethylammonium hydroxide pentahydrate (TMAH • 5H₂O), toluene were purchased from Aldrich and used as received. Bisphenol A (BA) and anhydrous potassium carbonate (K₂CO₃) were purchased from Aldrich in highly pure monomer grade and dichlorophenylsulfone (DCDPS) were obtained from Solvay and dried overnight under vacuum at 60 °C before use. Triptycene-1,4-hydroquinone (TPDH) monomer was donated by ICX Nomandics. Octamethylcyclotetrasiloxane (D₄), purchased from Aldrich, was vacuum distilled before use. 1,5-Bis(dimethylamino)hexamethyltrisiloxane was purchased from Silar Laboratories.

5.3.2. Synthesis of TPDH PAES

The TPDH PAES (Scheme 5.1) was prepared in a three-neck, 250 mL round bottom flask equipped with a mechanical stirrer, gas inlet, Dean-Stark trap, and condenser. The polymerization was carried out in a silicon oil bath heated on a hot plate controlled by a high temperature controller. The round bottom flask was charged with TPDH (5.00 g, 17.46 mmol), DCDPS (5.02 g, 17.46 mmol), and K_2CO_3 (2.95 g, 18.56 mmol). To the monomers, DMAc (35 mL) was added in a 2:1 v:v ratio to toluene (17 mL) as an azeotroping agent. The reaction was started at 140 °C for 1–2 h, after which the temperature of the reaction was raised to 155 °C and then to 160 °C over a 3–4 h period. Within 5 h of the reaction, all toluene/water was removed, which is vital for formation of the polymer and the targeted molecular weight. The temperature was increased to 170 °C for 20–24 h. Upon completion, the polymer was poured slowly into a 1000 mL beaker containing 10% aqueous HCl (800 mL) with a magnetic stir bar stirring at medium speed. The polymer was then filtered and dried overnight under vacuum at 90–110 °C, giving a white solid (9.7 g).

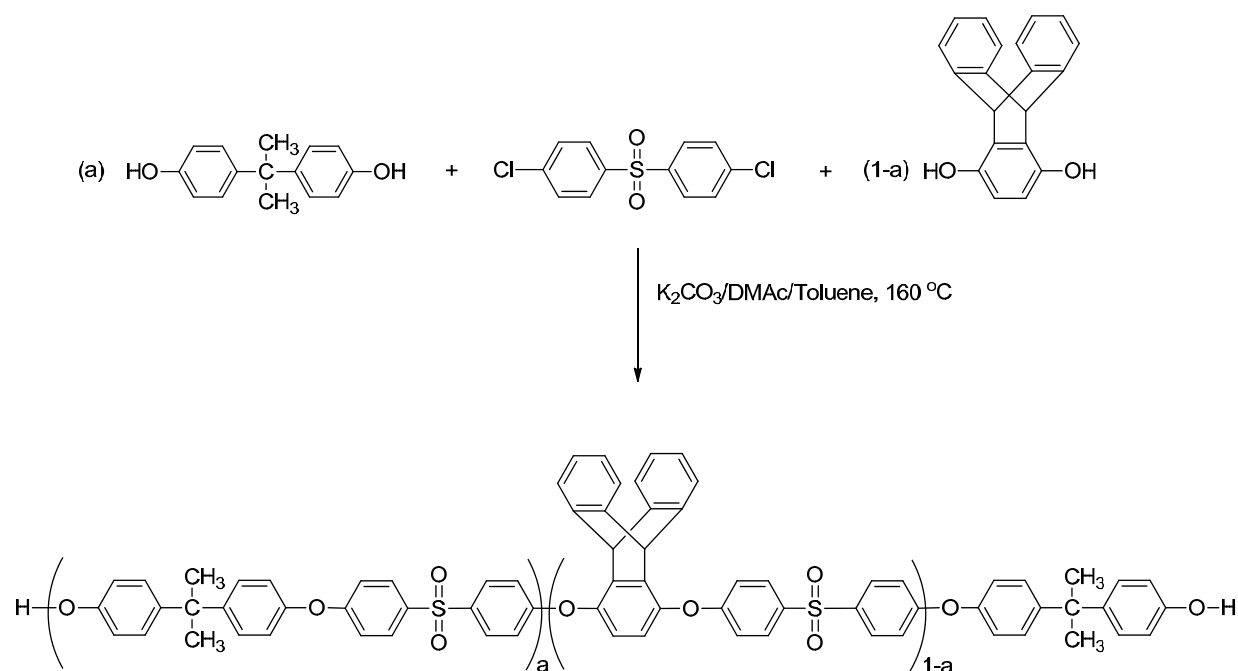


Scheme 5.1: Synthesis of TPDH PAES.

5.3.3. Synthesis of BA–TPDH PAES Random Copolymers (BA–TPDH PAES)

The PAES random copolymers (Scheme 5.2) containing BA and TPDH were prepared in a three-neck, 250 mL round bottom flask equipped with a mechanical stirrer, gas inlet, Dean-Stark trap, and condenser. The polymerization was carried out in a silicon oil bath heated on a hot plate controlled by a high temperature controller. For preparation of a 8200 g/mol oligomer, the round bottom flask was charged with BA (1.87 g, 8.18 mmol), TPDH (0.57 g, 2.01 mmol), DCDPS (2.75 g, 9.56 mmol), and K_2CO_3 (3.63 g, 10.10 mmol). To the monomers, DMAc (35 mL) was added in a 2:1 v:v ratio with toluene (17 mL) as an azeotroping agent. The reaction was started at 140 °C for 1–2 h. The temperature of the reaction was raised to 145 °C and then to 152 °C

over a 3–4 h period. Within 5 h of the reaction, all toluene/water was removed, which is vital for formation of the polymer and the targeted molecular weight. The temperature was increased to 160 °C for 20–24 h. Upon completion, the polymer was poured slowly into a 1000 mL beaker of 10% aqueous HCl (800 mL) with a magnetic stir bar stirring at medium speed. The polymer was then filtered and dried overnight under vacuum at 90–110 °C, giving 4.3 g of a white solid.

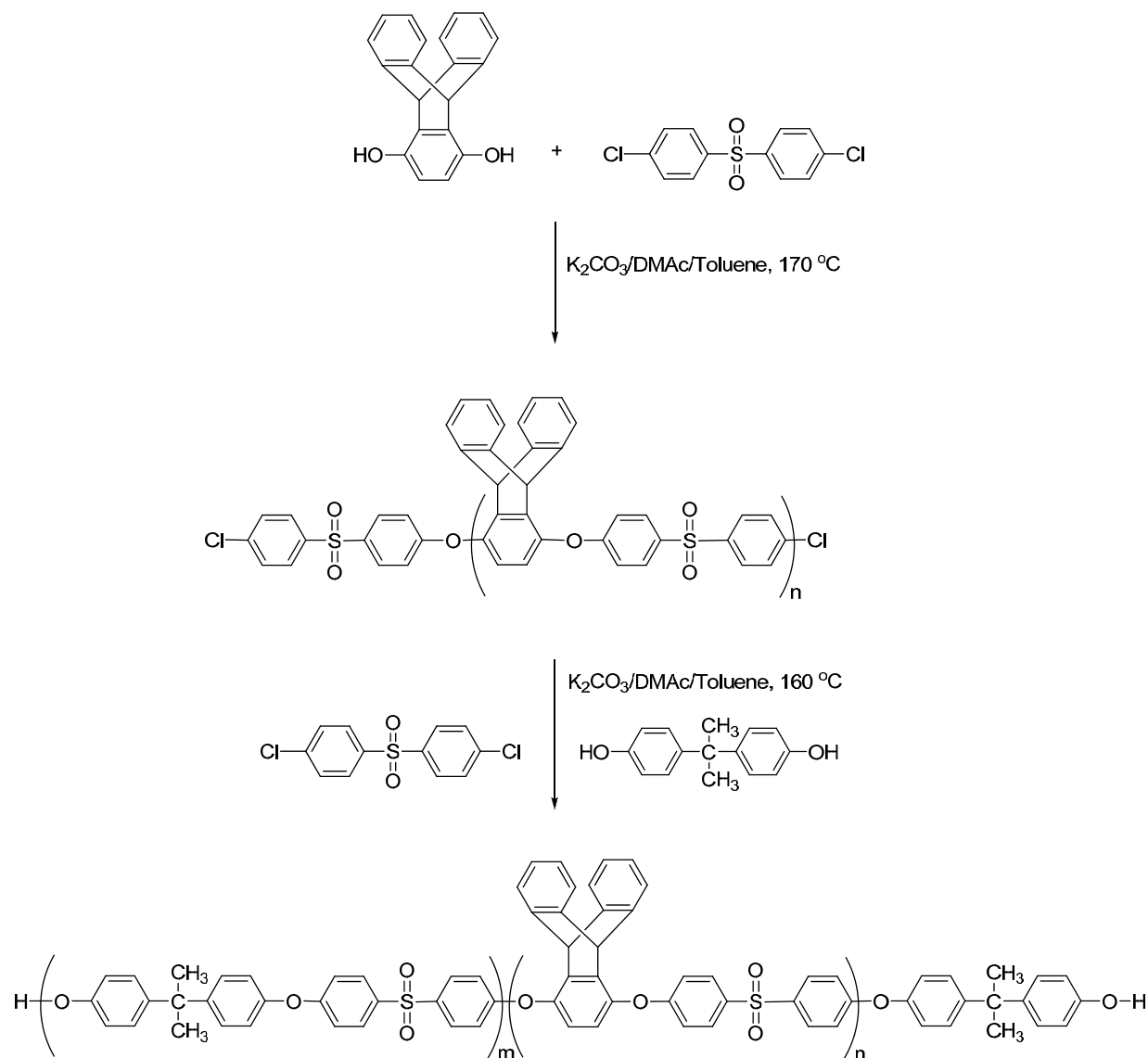


Scheme 5.2: Synthesis of BA–TPDH PAES random copolymer.

5.3.4. Synthesis of BA–TPDH PAES Segmented Copolymer

The BA–TPDH PAES segmented copolymer (Scheme 5.3) containing BA and TPDH was prepared in a three-neck, 250 mL round bottom flask equipped with a mechanical stirrer, gas inlet, Dean-Stark trap, and condenser. The polymerization was carried out in a silicon oil bath heated on a hot plate controlled by a high temperature

controller. The round bottom flask was charged with TPDH (1.99 g, 6.95 mmol), DCDPS (2.00 g, 6.98 mmol), and K_2CO_3 (1.95 g, 12.27 mmol). To the monomers, DMAc (30 mL) was added in a 2:1 v:v ratio with toluene (15 mL) as an azeotroping agent. The reaction was started at 140 °C for 1–2 h. The temperature of the reaction was raised to 155 °C and then to 160 °C over a 3–4 h period. Within 5 h of the reaction, all toluene/water was removed. The temperature was increased to 170 °C for 20–24 h. To the same reaction flask described previously, BA (2.01 g, 8.82 mmol), DCDPS (2.40 g, 8.36 mmol), and K_2CO_3 (3.20 g, 20.13 mmol) were introduced. DMAc (40 mL) was added in a 2:1 v:v ratio with toluene (19 mL) as an azeotroping agent. The reaction temperature was reduced 140 °C for 1–2 h. The temperature of the reaction was raised to 145 °C and then to 150 °C within 1 h. Within 3 h of the reaction, all toluene/water was removed. The temperature was increased to 160 °C for 20–24 h. Upon completion, the polymer was poured slowly into a 1000 mL beaker of 10% aqueous HCl (800 mL) with a magnetic stir bar stirring at medium speed. The polymer was then filtered and dried overnight under vacuum at 90–110 °C, giving 6.9 g of a white solid.



Scheme 5.3: Synthesis of BA-TPDH PAES segmented copolymer.

5.3.5. Preparation of Dimethylamino-Terminated PDMS (PDMS) Oligomers

The dimethylamino-terminated PDMS oligomers were prepared following a previous literature method¹³⁻¹⁶. To synthesize the tetramethylammonium disiloxanolate catalyst, D_4 (13.30 g, 44.84 mmol) and TMAH \cdot $5H_2O$ (0.71 g, 3.92 mmol) were added to a reactor with an attached Dean-Stark trap with condenser linked to a drying tube

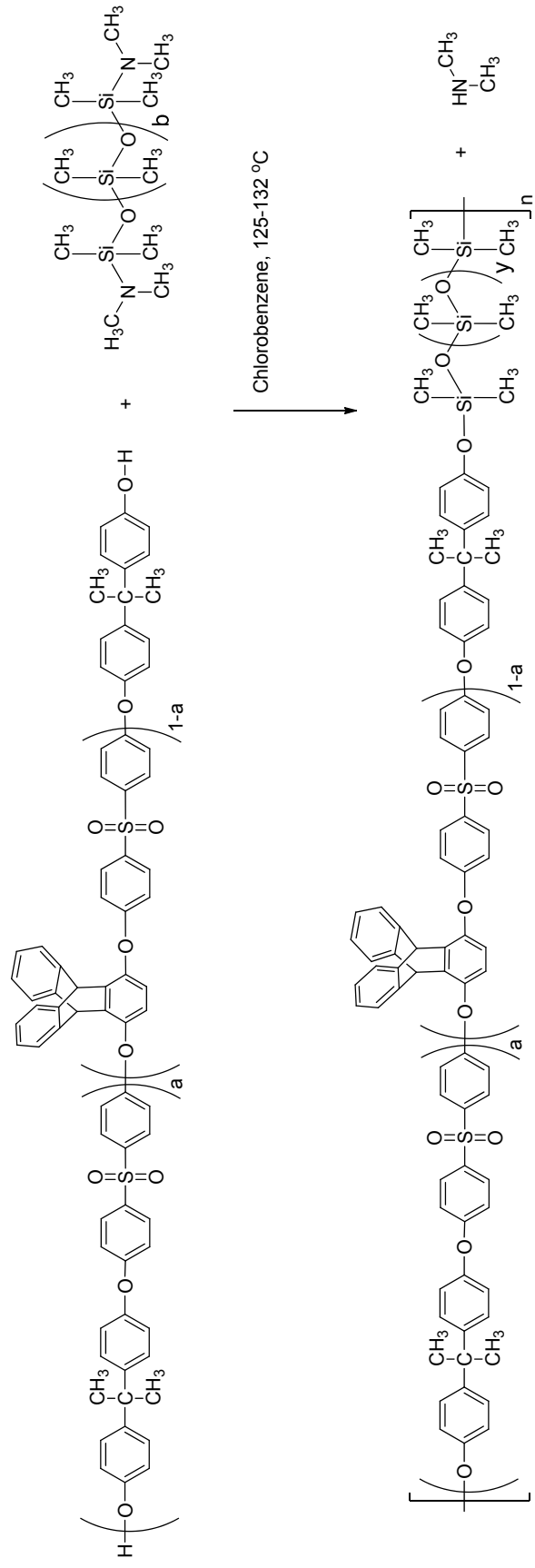
equipped with an overhead mechanical stirrer. The mixture was heated to 80 °C in a silicone oil bath for 24 h under a rapid stream of Argon bubbled through the reaction mixture. The solution became homogeneous within 2 h. The reaction was conducted for 24 h.

For the synthesis of a 4500 g/mol PDMS oligomer, D₄ (58.90 g, 198.57 mmol) and 1,5-bis(dimethylamino)hexamethyltrisiloxane (3.50 g, 11.88 mmol) were added to a 250-mL round-bottom flask equipped with a magnetic stir bar and condenser, and stirred under Argon. The tetramethylammonium disiloxanolate catalyst (3.82 g, 10.77 mmol) was removed from the reactor and added to the reaction mixture using a clean, dry 12-gauge needle. The reaction was allowed to proceed at 80 °C for 2–3 days. The temperature was increased to 150 °C under Argon for 2–3 h to remove any residual catalyst and cyclics. The solution was vacuum distilled at 70 °C to remove any residual end-capping reagent. The reaction yield 100 mL of clear, viscous liquid at room temperature. Characterization by ¹H NMR (CHCl₃-d₆ 500 MHz) δ ppm: 2.47 (s, 12H, N-CH₃), 0.06 (m, 6H, Si-CH₃). ¹³C NMR (CHCl₃-d₆ 500 MHz) δ ppm: 77.09 (t, 2C, N-CH₃), 1.09 (s, 6C, Si-CH₃). ²⁹Si NMR (CHCl₃-d₆ 400 MHz) δ ppm: -10.41 (s, 2Si, N-Si), -22.70 (s, 1Si, Si-O).

5.3.6. Synthesis of Segmented Block Copolymers (BA-TPDH PAES-*b*-PDMS)

Segmented block copolymers (Scheme 5.3) were prepared with BA-TPDH PAES and PDMS in a 1:1 molar ratio following a modified previous literature method ¹⁷. BA-TPDH PAES random copolymer oligomers 8200 g/mol (0.51 g, 0.06 mmol) and chlorobenzene (25 mL) were charged to a three-neck, 100-mL round-bottom flask equipped with a magnetic stir bar, gas inlet, Dean-Stark trap, and condenser in a

silicone oil bath. The solution was stirred for 1 h at reflux temperature (132 °C). The PDMS oligomer 4500 g/mol (0.29 g, 0.07 mmol) were added to the reaction mixture using a clean, dry 18-gauge needle in increments. The reaction was allowed to proceed at reflux temperature (132 °C) for 8–12 h. The reaction was cooled and the product was precipitated into methanol (800 mL). The fluffy, white product was dried overnight under vacuum at 90–110 °C, giving 0.8 g of materials. The same procedure was used to prepare other segmented block copolymer samples. The segmented block copolymers containing high PDMS were isolated as a white elastomeric gum.



Scheme 5.4: Synthesis of BA-TPDH PAES-*b*-PDMS.

5.3.7. Film Preparation of the Segmented Block Copolymers

The segmented block copolymers were dissolved in THF to afford transparent solutions with 5 wt-% solids. The solutions were filtered through a 25 mm diameter syringe filter (0.45 μm pore) and cast onto clean glass substrates. The films were covered to control evaporation and dried for 2–3 days at ambient temperature, and then dried overnight under vacuum at 90–110 $^{\circ}\text{C}$. The resulting films were transparent and colored.

5.3.8. Polymer Acronyms

In this report, we have given the PAES random copolymers descriptive acronyms in order to identify the mole ratio between BA and TPDH. For the PAES copolymers that incorporate 90% BA and 10% TPDH, for example, the name is BA90–TPDH10 PAES RC or BA90–TPDH10 PAES SC. For the segmented block copolymers, the PAES random copolymer acronym will be used in conjunction with PDMS followed the molecular weight of each segment (PAES and PDMS) in parentheses, for example, BA90–TPDH10 PAES–*b*–PDMS (8200–4500).

5.4. CHARACTERIZATION METHODS

5.4.1. Nuclear Magnetic Resonance Spectroscopy (NMR)

^1H NMR spectra were obtained using a JEOL 500 MHz spectrometer at 25 $^{\circ}\text{C}$. Spectra were obtained in a 10% deuterated tetrahydrofuran (THF) solution.

5.4.2. Size Exclusion Chromatography (SEC)

TPDH PAES and BA–TPDH PAES random copolymers were analyzed in approximately 0.25% solution of THF at 40 $^{\circ}\text{C}$ with a flow rate of 1.00 mL/min. using a Waters Liquid Chromatography 717 Autosampler. Microstryogel columns of 500, 1000,

10,000, 100,000 Å pore size with a Waters 410 Refractive Index detector, an in-line Wyatt miniDAWN multiple angle laser light scattering (MALLS) detector, and a Viscotek 270 dual Viscosity detector. The d_n/d_c values were determined on-line using the calibration constant for the RI detector and the mass of the polymer sample. For all samples, it was assumed that 100% of the polymer eluted from the column during the measurement.

5.4.3. Thermogravimetric Analysis (TGA)

Measurements were conducted by TA Instruments Thermogravimetric Analysis Q500 at temperatures from 35 °C to 600 °C under nitrogen at a heating rate of 10 °C/min.

5.4.4. Differential Scanning Calorimetry (DSC)

Glass transition temperatures were obtained by TA Instruments differential scanning calorimetry (DSC) Q1000 using a heat/cool/heat method. Temperature ramp at 10.00 C/min from 35 °C to 350 °C.

5.4.5. Tensile Analysis

Stress-strain tests were performed on an Instron Model 1123 Universal Testing system with a Bluehill software package using a 20-lb load cell at room temperature at a rate of 10 mm/min. Tests were done on dog-bone-shaped specimens (15 mm gauge length and 3.93 mm width) cut by a standard bench-top die from films (0.09 mm thickness). Prior to testing, specimens were dried under vacuum overnight at 90–110 °C.

5.5. RESULTS AND DISCUSSION

5.5.1. Synthesis of Polymers

Swager and co-workers⁵ first synthesized TPDH PAES using difluorodipheylsulfone (DFDPS) to afford porous materials for nanoparticle formation. In our study, TPDH PAES was synthesized by a 1:1 stoichiometric ratio between TPDH and DCDPS to afford high molecular weight polymer. The ¹H NMR spectra (Fig. 5.1) confirmed the structure of the TPDH PAES. The peak indicated at 7.9 ppm was representative of the protons near the sulfone group; the peaks shown around 7.0 ppm were representative of the protons in the aromatic rings. The -CH₂ protons on the triptycene bridgehead were assigned at 5.8 ppm. SEC analysis of the polymer provided a weight average molecular weight of 98,000 g/mol (Fig. 5.2).

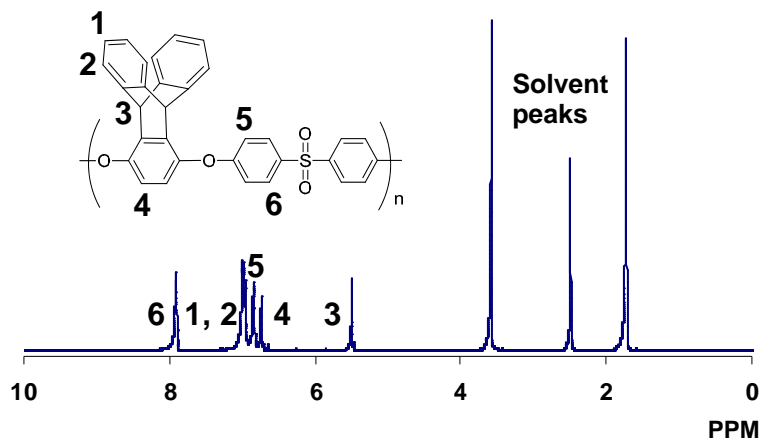


Figure 5.1: ¹H NMR of TPDH PAES in THF-*d*₈.

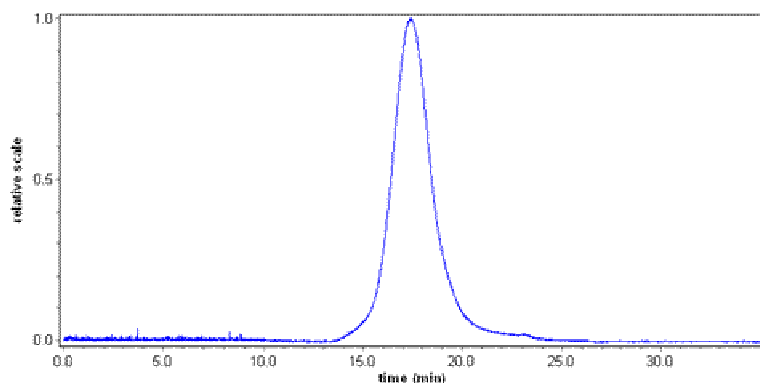


Figure 5.2: SEC MALLS trace of the TPDH PAES in THF.

Further exploration of TPDH PAES materials extended to BA–TPDH PAES random copolymers, synthetically described in Sections 5.3.3 using a stoichiometric imbalance where BA monomer was used in excess to control the molecular weight and to also establish hydroxyl-terminated end-groups that would enable a further reaction with dimethylamino-terminated PDMS oligomers to form segmented block copolymers. The BA–TPDH PAES random copolymer ($M_n = 8200$ g/mol) used for the synthesis of segmented block copolymers incorporated a low molar amount of TPDH monomer, 6%. Previous literature⁹ suggests only low amount amounts of TPDH monomer is required in the polymer to give provide enhanced thermal and tensile properties. Analysis of the segmented block copolymers incorporating the BA PAES random copolymers with TPDH co-monomer were used to determine the influence the rigid, high free-volume co-monomer has on the thermal and tensile properties. These results were be compared to the BA PAES–*b*–PDMS previously investigated^{15, 17, 18}.

BA–TPDH PAES segmented copolymers were prepared as described in Sections 5.3.4. The chlorine-terminated TDPH PAES oligomers were synthesized first.

Oligomers showed no precipitation from the reaction mixture. The BA and DCDPS monomers were mixed with the chlorine-terminated TDPH PAES oligomers for the second polycondensation step. High molecular weight segmented copolymer (weight average molecular weight of 54,000 g/mol) was formed with a higher molar amount of TPDH monomer (19%) incorporated into the copolymer. The BA–TPDH PAES segmented copolymers were compared to the TPDH PAES and BA–TPDH PAES random copolymers on the basis of thermal properties by TGA and DSC.

5.5.2. Solubility of TPDH PAES

The solubility properties of TPDH PAES were tested by a series of solvents using a concentration of 0.1 g/mL (Table 5.1). The polymer was extremely soluble in polar aprotic solvents at room temperature. The material was partially soluble in acetone and benzene only upon heating. The TPDH PAES was insoluble in hexane, methanol, and xylene before and after heating.

Table 5.1: Solubility of TPDH PAES.

Solvent	Solubility ^a
Acetone	(±)
Benzene	(±)
Chlorobenzene	+
Chloroform	+
<i>N,N</i> -dimethylacetamide	+
<i>N,N</i> - dimethylformamide	+
Dimethyl sulfoxide	+
N-methylpyrrolidone	+
Hexane	-
Methanol	-
Tetrahydrofuran	+
Xylene	-

^aNotation: Soluble: +; Partially Soluble: ±; Insoluble: -; On Heating: ().

5.5.3. Thermal Properties of Polymers

The thermal stabilities of the TPDH containing polymers were measured by TGA and shown in Fig. 5.3. BA PAES was stable to 358 °C at $T_{d-5\%}$ weight loss. Incorporating bulky TPDH into the PAES unit enhanced the thermal stability of the polymer, TPDH PAES was stable to 468 °C and BA94–TPDH6 PAES random copolymer was stable to 459 °C at $T_{d-5\%}$ weight loss. The BA81–TPDH19 PAES

segmented copolymer was thermally stable to 442 °C at T_d -5% weight loss. These results are consistent with previously studied TPDH containing polymers^{5,9}.

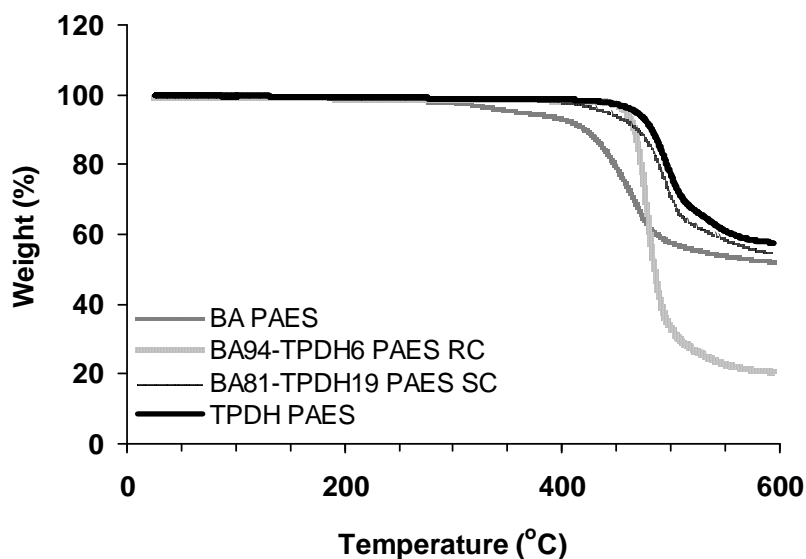


Figure 5.3: Thermal stability of BA PAES and PAES containing TPDH, at 10 °C/min.

The thermal stability of the segmented block copolymers was also determined by TGA. The segmented block copolymers show increasing thermal stability with increasing PDMS content from 345 °C to 416 °C in Fig. 5.4. Adding 70% PDMS to the segmented block copolymer (BA94-TPDH6 PAES-*b*-PDMS 8200-20,400) resulted in a material with a thermal stability profile similar to PDMS homopolymers.

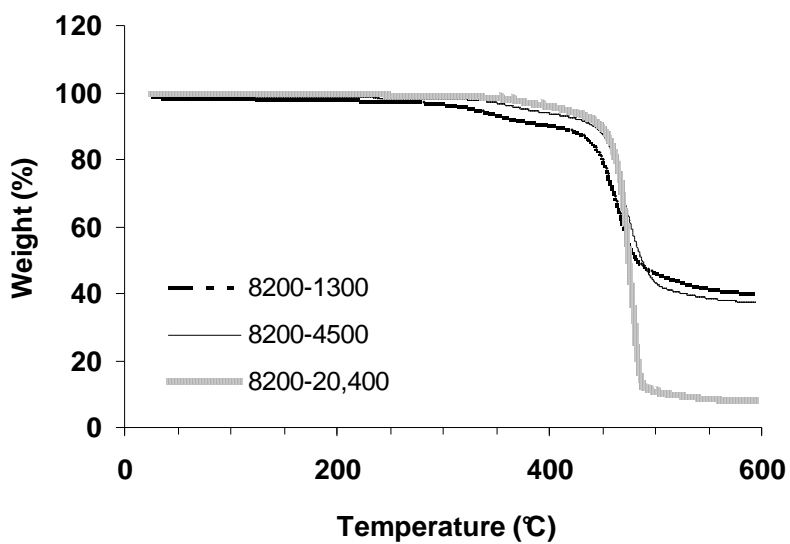


Figure 5.4: Thermal stability of BA94-TPDH6 PAES-*b*-PDMS, at 10 °C/min.

DSC was used to measure the T_g of the PAES materials. The polymer prepared from the rigid, high free-volume TPDH unit had a T_g of 276 °C, a T_g higher than the reported values of Udel® (185 °C), Radel® (224 °C)¹⁹, and terphenol PAES (251 °C)²⁰. Swager and co-workers⁵ previously synthesized TPDH PAES and reported a T_g value of 267 °C, consistent with the value observed in this current research. The T_g of TPDH PAES is also equivalent to the T_g of polyimides (221–296 °C) prepared from TPDH-containing dianhydride polymerized with various aromatic diamines²¹. A report on aromatic polyamides incorporating TPDH and a sulfone linkage gave a T_g as high as 370 °C²². The BA81-TPDH19 PAES segmented copolymer had a T_g of 226 °C. The BA94-TPDH6 PAES random copolymer (8200 g/mol) had an enhanced T_g of 196 °C over BA PAES, which had a T_g of 183 °C. The TPDH-based polymer and copolymers

glass transition occurs at a higher temperature because the addition of bulky TPDH comonomer into the copolymers interferes with the polymer chain mobility and flexibility.

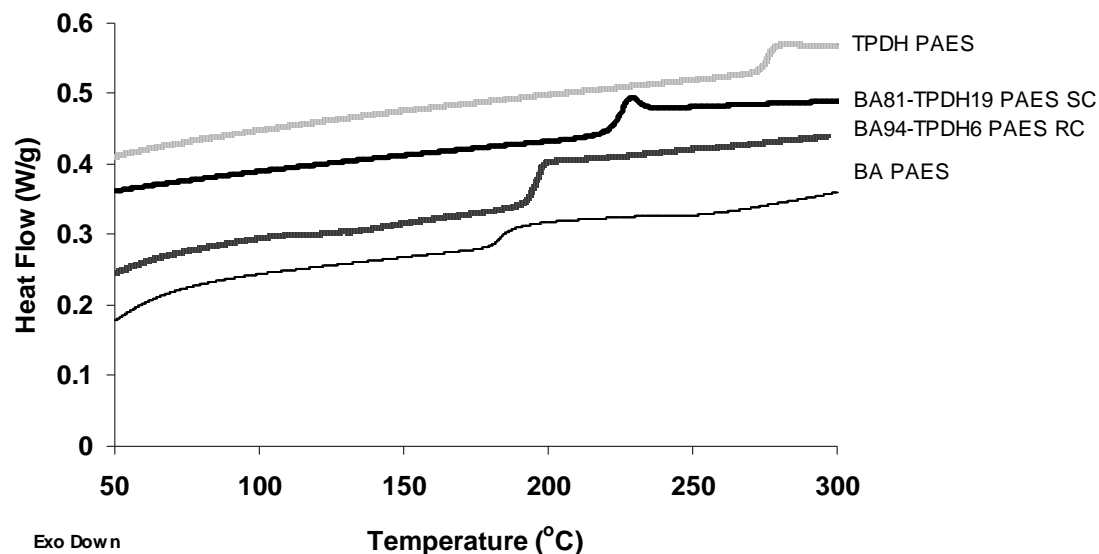


Figure 5.5: DSC profile of BA PAES and PAES containing TPDH at 10 °C/min.

5.5.4. Tensile Analysis of Segmented Block Copolymers

The tensile properties of the TPDH-based materials were also investigated. The tensile modulus of the BA–TPDH PAES random copolymer was 1900 MPa, approximately 40% higher than the Udel[®] film cast from THF solution (1200 MPa). However, the elongation of the BA–TPDH PAES random copolymer was lower than that of Udel[®]. These results suggested the random copolymer was stiffer than the Udel[®], but there was no enhancement in the ductility.

Segmented block copolymers prepared from BA94–TPDH6 PAES random copolymer (8200 g/mol) with various molecular weights of PDMS were expected to provide enhanced tensile properties. The results of BA94-TPDH6 PAES segmented

block copolymers (Table 5.2) were consistent with the previously synthesized BA PAES-*b*-PDMS, increased PDMS content from 0 wt-% to 70 wt-% produced materials that were initially stiff and brittle and changed to elastomeric as that PDMS content increased (Fig. 5.6). The modulus of the segmented block copolymers decreased from 1500 MPa to 1 MPa and the elongation increased from 5% to 240%. Similar to Swager and co-workers research on TPDH-polycarbonate blends ⁹, these values show the low molar content of TPDH in the segmented block copolymers provide little to no molecular threading resulting in no major enhancements in the tensile properties.

Table 5.2: Tensile properties of BA PAES and PAES containing TPDH.

Segmented Block Copolymers		PAES	PDMS	Siloxane (wt-%)^a	Intrinsic Viscosity^b (dL/gm)	Tensile stress at Break (MPa)	Tensile strain at Break (%)	Tensile stress at Yield (MPa)	Young's Modulus (MPa)
Udel [®] , 27,000	0	0	0	0.342	28 ± 20	6 ± 1	48 ± 12	1200 ± 350	
Segmented copolymer, 18,000	0	0	0	0.183	13 ± 9	2 ± 1	--	1210 ± 272	
Random Copolymer, 19,600	0	0	0	0.317	19 ± 14	2.3 ± 2	--	1900 ± 721	
8200	1300	13	13	0.208	57 ± 9	5 ± 0.5	--	1550 ± 149	
8200	4500	30	30	0.139	14 ± 11	40 ± 26	30 ± 3	750 ± 95	
8200	9500	46	46	0.340	11 ± 2	130 ± 33	12 ± 2	150 ± 25	
8200	20,400	70	70	0.484	3 ± 0.6	250 ± 38	3 ± 0.6	1 ± 0.3	

^aCalculated by ¹H NMR

^b0.2 dL/gm in chloroform at 25 °C

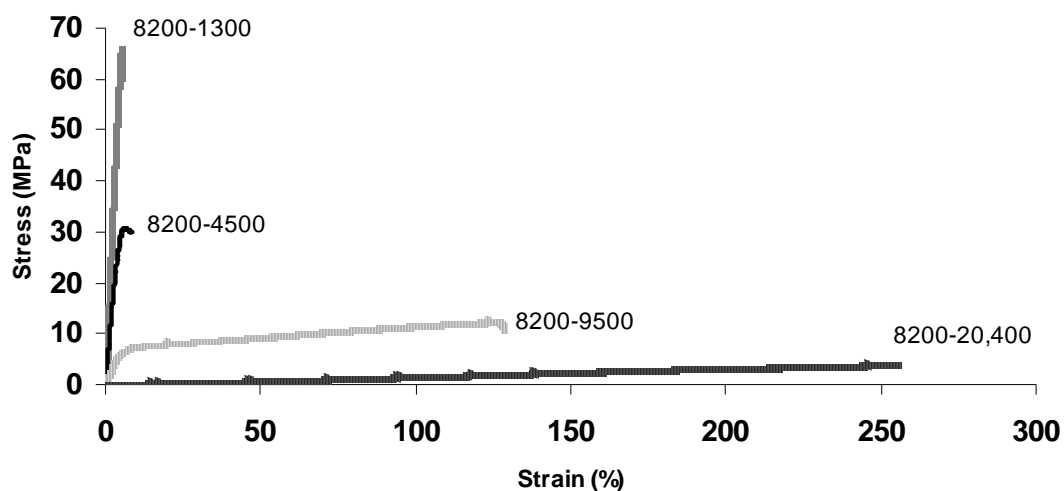


Figure 5.6: Stress–Strain curve for BA94–TPDH6 PAES–*b*–PDMS materials with varying PDMS content.

5.6. CONCLUSIONS

In this report, a series of segmented block copolymers incorporating bisphenols with co-monomer, TPDH was synthesized and the thermal and tensile properties were measured. The segmented block copolymer made transparent films cast from THF solutions. The materials provided higher thermal stability and high T_g than the BA PAES pervious synthesized. The tensile properties showed the incorporated rigid TPDH did stiffen the PAES unit due to the free volume associated with the co-monomer. This, therefore, influenced the properties of the segmented block copolymers, specifically the tensile modulus and elongation to break. Synthesis of TPDH PAES produced an extremely brittle polymer with high thermal stability and an enhanced T_g of 276 °C, which was higher than Udel[®], 185 °C. Polymers were soluble in most polar aprotic solvents and formed colored, brittle films when cast from THF and DMAc.

5.7. ACKNOWLEDGMENTS

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Chapter 6:

TENSILE AND THERMAL CHARACTERISTICS OF SEGMENTED BLOCK COPOLYMER BLENDS

6.1. ABSTRACT

Segmented block copolymers were used for impact modification of Udel[®] provided by Solvay Advanced Polymers. Solution mixed 95% of Udel[®] and 5% of poly(arylene ether sulfone)-*b*-polydimethylsiloxane (PAES-*b*-PDMS) blends were prepared by compression molding. The segmented block copolymers were previously synthesized in our labs by a polycondensation reaction between the hydroxyl-terminated PAES and the dimethylamino-terminated PDMS oligomers. The segmented block copolymer blends were analyzed by using tensile measurements to determine whether there is an enhancement in the tensile properties over Udel[®]. The data from these analyses suggested the segmented block copolymer blends have similar tensile properties as Udel[®] with no significant difference in the tensile modulus and elongation. The dynamic mechanical properties of these blends showed a low-temperature transition observed in the segmented block copolymer blends that has been commonly shown in other PAES materials and blends. The thermal stability of these segmented block copolymer blends were also analyzed and have high thermal stability to nearly 500 °C which is slightly higher than that of Udel[®].

KEYWORDS: poly(arylene ether sulfone); blends; dynamic mechanical analysis

6.2. INTRODUCTION

Blend materials prepared from high performance polymers have been of great commercial interest. These materials have been prepared on an industrial scale and used to enhance impact properties, elongation, tensile strength, thermal stability, processability, and solvent resistance ¹⁻³. One of the most common commercial polymer blends is high impact polystyrene (HIPS). HIPS is prepared by blending amorphous polystyrene (PS) with elastomeric polybutadiene (PB), as a rubber-toughening agent to form a graft copolymer ⁴⁻⁷.

Much research has focused on incorporating soft segments into polymers and copolymers to provide impact modification of thermoplastic blends ⁸⁻¹¹. Koval and co-workers ¹² were able to improve the impact strength of polycarbonate (PC) by blending with bisphenol A poly(arylene ether sulfone)–polydimethylsiloxane (PAES–PDMS) segmented block and triblock copolymers. The blends were phase separated especially for copolymers containing a PDMS content of >50 wt-%; they provided a high impact resistance over a wide temperature range. Noshay and co-workers ¹³ blended PAES–PDMS segmented block copolymers with PAES homopolymer. They observed improvement of the notched Izod impact strength of PAES from 1.3 ft-lbs/inch to 22.0 ft-lbs/inch by incorporating only 5% of bisphenol A PAES–PDMS segmented block copolymers in the blend. The researchers concluded that the elastomeric PDMS content and the thermal stability of the segmented block copolymer both contributed to its use as an impact modified in the blend.

Aside from the incorporation of segmented block copolymers in blends, other studies have incorporated polymers into blends, such as PAES ¹⁴⁻²⁰, polypropylene ²¹,

²², and poly(phenylene sulfide) ²³. Referring to the latter polymer, Lu and co-workers studied the effect of crystallinity on impact strength of blends. By blending poly(phenylene sulfide) into a series of polymers, the materials demonstrated the impact strength increased in a linear fashion as the crystallinity decreased.

Monomers with intermolecular free volume, such as triptycene ²⁴, have also been used in polymer blends to improve impact strength, enhance the tensile modulus, and explore morphological characteristics. Research conducted by Swager and co-workers on triptycene showed the minimization of high free volume through intermolecular threading improved stiffness and ductility in polyesters ²⁵. In the most recent research by Swager and co-workers ²⁴, triptycene-PC copolymers of various molecular weights were blended into commercial PC, Lupilon[®] to improve the stiffness and ductility. When compared to the commercial PC, at the lowest content of triptycene (1.9 wt-%) incorporated into the blend, the tensile modulus and the tensile yield strength increased by 20% and 17%, respectively, while the elongation was enhanced by 80%. However, there was no indication of improving the ductility of the commercial PC, Lupilon[®].

We were interested in the tensile properties of Udel[®] by blending new PAES–PDMS segmented block copolymers with the homopolymer. We have synthesized a series of segmented block copolymers incorporating bisphenol A PAES with co-monomers, biphenyl-4,4'-diol (DHBP), 4,4'-dihydroxyterphenyl (DHTP), and 1,4-triptycene dihydroxy (TPDH). The addition of the co-monomers should provide the enhanced tensile properties to the segmented block copolymer, which will, when blended into Udel[®], improve the impact strength of the homopolymer. We will also

investigate the thermal and dynamic mechanical properties of the PAES–PDMS segmented block copolymer blends.

6.3. EXPERIMENTAL

6.3.1. General Methods and Materials

Udel[®] was provided by Solvay Advanced Polymers. Segmented block copolymers were synthesized as described in previous chapters.

6.3.2. Preparation of Segmented Block Copolymer Blends

Blends were prepared with 95% of Udel[®] and 5% of PAES–PDMS segmented block copolymers. In a 100-mL round-bottom flask, PAES homopolymer (4.75 g) was dissolved in THF (90 mL) and stirred at room temperature overnight. In a 20-mL scintillation vial, segmented block copolymer (0.25 g) was dissolved THF (5 mL) solvent and stirred at room temperature overnight. The segmented block copolymer solution was poured into the PAES homopolymer solution and stirred at medium speed at room temperature overnight. The cloudy, inhomogenous mixture was coagulated in methanol (800 mL). Blends were then filtered, and dried under vacuum at 90-110 °C overnight. Blends were compression molded at 250 °C at 12 psi for 2 5-30 min resulting in opaque films.

6.4. CHARACTERIZATION METHODS

6.4.1. Thermogravimetric Analysis (TGA)

Measurements were conducted by TA Instruments thermogravimetric analysis (TGA) Q500 at temperatures from 35 °C to 600 °C under nitrogen at a heating rate of 10 °C/min.

6.4.2. Dynamic Mechanical Analysis (DMA)

Glass transition temperatures were obtained by TA Instruments dynamic mechanical analysis (DMA) Q800 in tension mode from –150 °C to 200 °C with a heating rate of 10 °C/min and 1 Hz frequency. The measurements were done on dog-bone-shaped specimens (3.93 mm width) cut by a standard bench-top die from compression molded films (0.40 mm thickness).

6.4.3. Tensile Analysis

Stress-strain tests were performed on an Instron Model 1123 Universal Testing system with a Bluehill software package using a 20-lb load cell at room temperature. Tests were done on dog-bone-shaped specimens (15 mm gauge length and 3.93 mm width) cut by a standard bench-top die from compression molded films (0.30 mm thickness).

6.5. RESULTS AND DISCUSSION

6.5.1. Thermal Stability of Segmented Block Copolymer Blends

The thermal properties of the PAES–PDMS segmented block copolymer blends were analyzed by TGA. By adding the Udel[®] to the PAES–PDMS segmented block copolymer, the thermal stability of the materials were expected to improved substantially

from the original segmented block copolymer^{16, 26}. The thermal stability profiles of the blend materials are illustrated in Fig. 6.1. The profiles showed the thermal stabilities improve with increasing PDMS molecular weight amount. Udel[®] was thermally stable to 455 °C at $T_{d-5\%}$ weight loss, while the thermal stability of the blend materials improved to 490 °C at $T_{d-5\%}$ weight loss.

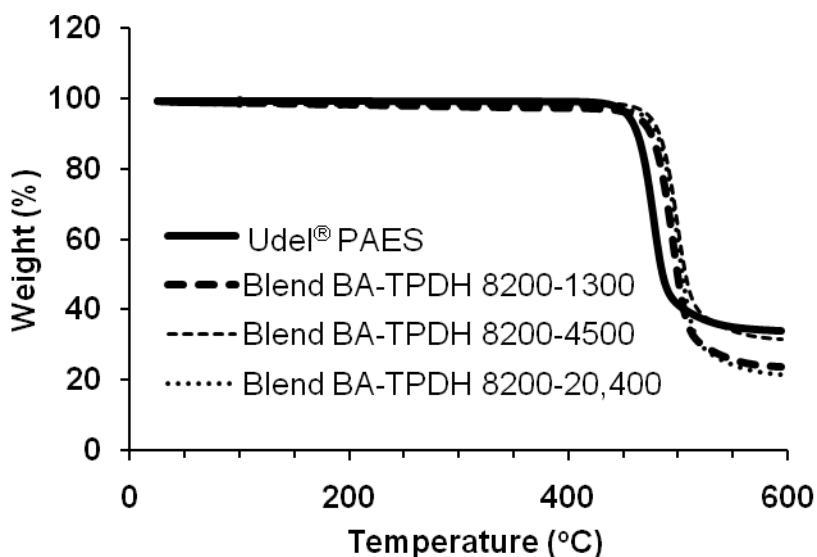


Figure 6.1: Thermal stability profile of Udel[®] and blends.

6.5.2. Dynamic Mechanical Analysis of Segmented Block Copolymer Blends

DMA was conducted on the blend materials. The storage modulus analysis for blends prepared from Udel[®] and segmented block copolymers containing BA–DHTP PAES or BA–TPDH PAES are presented in Fig. 6.2. The profiles clearly showed the storage moduli of the blends and of the Udel[®] were in the same range. No significant

increase in the storage modulus was shown as an effect of the type of co-monomer in the segmented block copolymer. There was also no trend observed in the modulus as a function of varying the PDMS content in the segmented block copolymer. This leads to the conclusion that the blends display similar stiffness at relatively low PDMS content in the segmented block copolymer. In comparison to Udel[®], all the blend materials had equal to slightly higher modulus values than Udel[®] throughout the experimental temperature range.

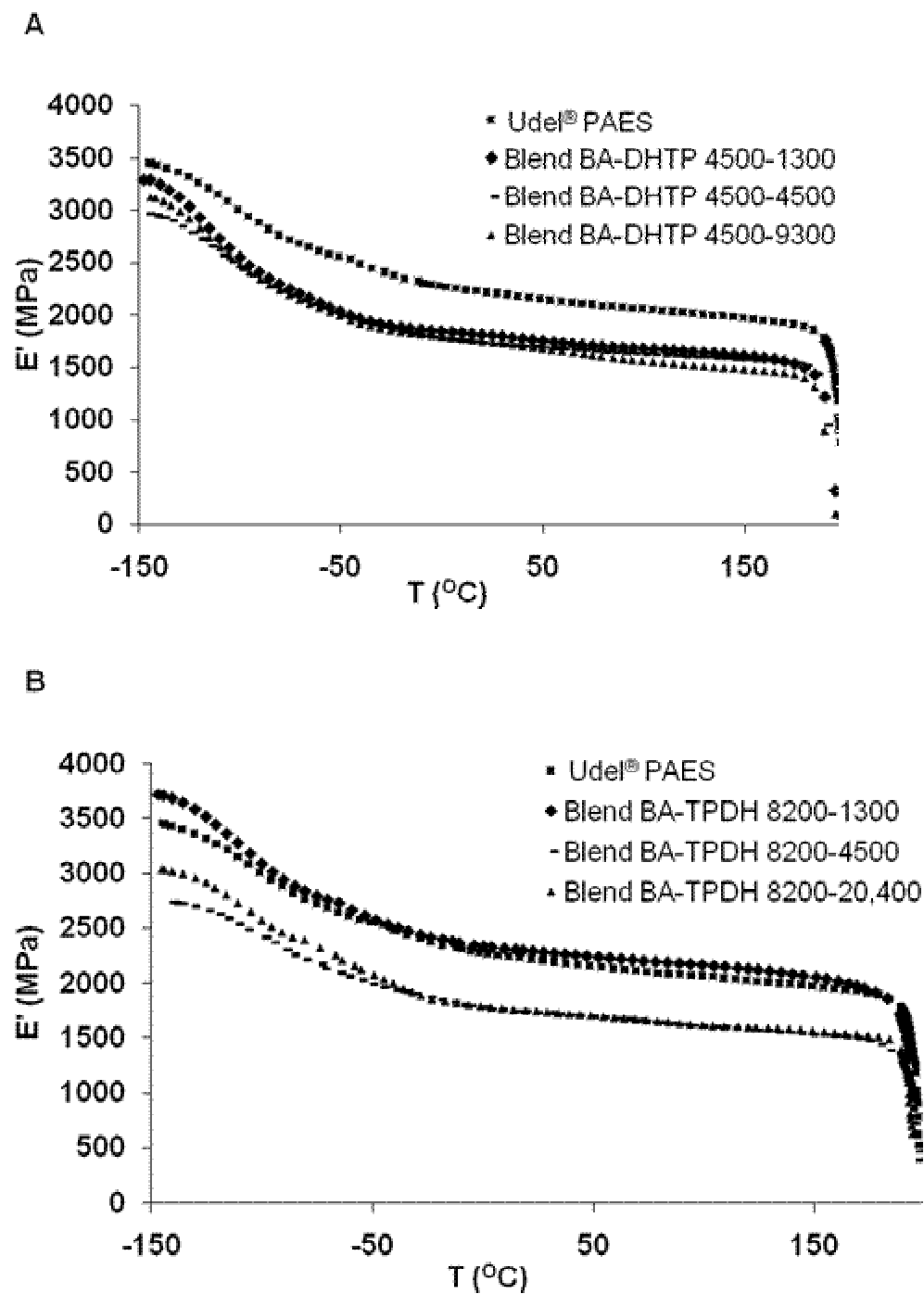


Figure 6.2: Storage modulus and temperature profile of Udel[®] in comparison with (A) BA-DHTP PAES-*b*-PDMS blends and (B) BA-TPDH PAES-*b*-PDMS blends.

In this same set of spectra, the profile also illustrated the intensity of the gamma relaxation occurring at about $-100\text{ }^{\circ}\text{C}$. Fig. 6.3 shows the $\tan \delta$ spectra for the blends. The γ relaxation occurring around $-100\text{ }^{\circ}\text{C}$ at 1 Hz is associated with the short-range motions in the polymer chains and possibly contributes to the impact resistance. Hale et al.²⁷ also studied poly(aryl ethers) thermoplastics extensively and showed their low-temperature transition was correlated to their toughness and impact strength. This relaxation observed in PAES and other poly(ether)s has been observed and noted in the literature^{17, 28-30}. Aikten and co-workers²⁹ conducted DMA measurements on various poly(arylene ether sulfone)s and attributed the transition to the motion of the phenylene rings in the polymer chain. Robeson and McGrath¹⁷ illustrated a low temperature transition, the β relaxation at $-100\text{ }^{\circ}\text{C}$, by DMA in various poly(arylene ether sulfone)s and polyethersulfones. However, the researchers attributed the transition to the aryl ether bond and the sulfone group in the polymer backbone where its polarity would strongly absorb water.

The blend materials containing BA-DHTP PAES-*b*-PDMS showed the γ -relaxation at relatively lower temperatures than that found in the blends containing BA-TPDH PAES-*b*-PDMS. The BA-DHTP PAES-*b*-PDMS and Udel[®] blends also showed more than one prominent sub- T_g relaxations, the second one appearing around $-25\text{ }^{\circ}\text{C}$. Since all the samples were compression molded, the higher temperature relaxation could be assigned to the non-equilibrium ordering defects or stresses due to the processing conditions. It could also be assigned to phenylene motions from the chain constituents in the PAES random copolymer, DHTP and TPDH. The bulky TPDH group is difficult to undergo ring flip; in contrast, the DHTP group is more likely to exhibit

such a motion, which is probably reflected in more than one sub- T_g relaxations. Hence, it is necessary to determine which of the sub- T_g relaxations actually contribute towards the impact resistance and assign the correct molecular group responsible for that particular relaxation.

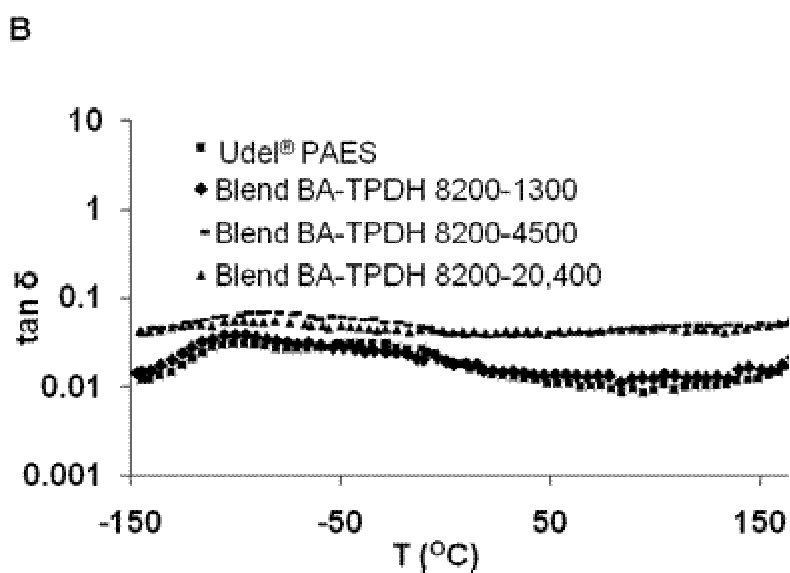
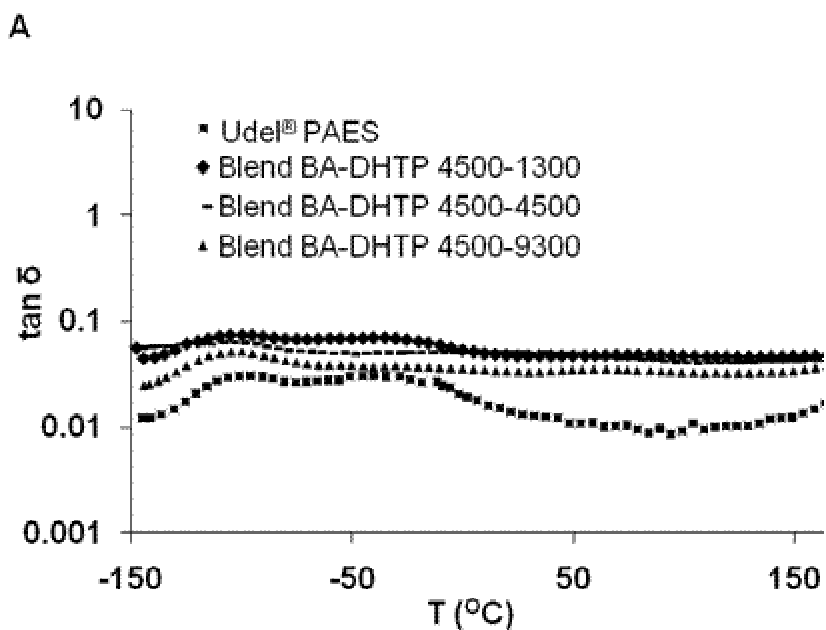


Figure 6.3: Tan δ spectra of blends in comparison of Udel[®] in comparison with (A) BA–DHTP PAES–*b*–PDMS blends and (B) BA–TPDH PAES–*b*–PDMS blends.

6.5.3. Tensile Analysis of Segmented Block Copolymer Blends

In a brief discussion on PAES, Robeson et al.³⁰ concluded that low temperature relaxations influence mechanical characteristics of polymer as it relates to “brittle-ductile behavior.” The tensile properties of segmented block copolymer blends with Udel[®] were evaluated on dog-bone specimens via standard tensile analysis. The capability for conducting notched Izod impact measurements was not available, so we have used tensile analysis to measure the changes in the tensile modulus and elongation and project enhanced elongation suggests higher impact strength. As a standard, the first set of blends was prepared from 5% of BA PAES–PDMS segmented block copolymers with 95% of Udel[®]. The tensile properties of the blends were measured by tensile analysis and the results of that analysis are presented in Table 6.1. The results suggested the blend materials provided no significant change in the tensile modulus or in the elongation over Udel[®]. These findings are consistent with the tensile results presented by Noshay et al.¹³, particularly for elongation which was unchanged.

Segmented block copolymers prepared from PAES random copolymers (BA–DHTP PAES, and BA–TPDH PAES) and PDMS were also used in the preparation of blends. Similarly, 5% of PAES–PDMS segmented block copolymers with 95% of Udel[®] were used to prepare the blends. The tensile measurements presented in Table 6.2 showed a combination of both segmented block copolymer types used to make the blends. Overall, the results are consistent with the observations in the BA PAES–*b*–PDMS blends previously measured and showed there was also no significant change in the tensile modulus or in the elongation. Additionally, neither the PAES bisphenol type

nor the amount of PDMS in the segmented block copolymers influenced the tensile properties.

Table 6.1: 95% Udel P-3500/5% Bisphenol A PAES-*b*-PDMS Blend Tensile Properties.

Segmented Block Copolymers									
BA PAES	PDMS	Siloxane wt%^a	Tensile stress at Break (MPa)	Tensile strain at Break (%)	Tensile stress at Yield (MPa)	Modulus (MPa)			
Udel [®] , 27,000	0	0	53 ± 5	--	61 ± 5	1270 ± 28			
10,000	5600	36	48 ± 11	6 ± 2	53 ± 8	1130 ± 71			
4300	4700	52	41 ± 8	7 ± 3	35 ± 25	900 ± 74			
5500	10,000	65	39 ± 13	5 ± 1	53 ± 4	1200 ± 120			
4300	10,000	70	43 ± 5	7 ± 1	45 ± 8	1120 ± 64			

^aCalculated by ¹H NMR

Table 6.2: 95% Udel P-3500/5% PAES-*b*-PDMS Blend Tensile Properties.

Segmented Block Copolymers							
Bisphenol	PAES	PDMS	Siloxane wt%^a	Tensile stress at Break (MPa)	Tensile strain at Break (%)	Tensile stress at Yield (MPa)	Modulus (MPa)
Udel [®]	27,000	0	0	53 ± 5	--	61 ± 5	1270 ± 28
BA-TPDH	8200	1300	13	39 ± 13	9 ± 2	41 ± 10	1180 ± 28
BA-DHBP	7500	4500	34	49 ± 4	28 ± 34	59 ± 4	1200 ± 58
BA-TPDH	8200	4500	30	52 ± 20	9 ± 1	62 ± 5	1190 ± 30
BA-DHTP	4500	4500	46	38 ± 21	8 ± 2	52 ± 6	980 ± 85
BA-DHTP	4500	9300	62	50 ± 12	6 ± 1	56 ± 7	1240 ± 66
BA-TPDH	8200	20,400	70	29 ± 14	6 ± 2	41 ± 10	1180 ± 108

^aCalculated by ¹H NMR

6.6. CONCLUSIONS

A series of blend material were prepared from Udel[®] and segmented block copolymers in THF solutions and compression molded to form opaque films. The rationale for this work was to prepare materials with enhanced impact strength. Measuring the impact strength by notched Izod analysis was not readily available, so DMA and tensile analysis studies were conducted in order to provide modulus and elongation data. Analysis by DMA and tensile tests suggested the incorporation of a small amount of PDMS chains (which is a low T_g polymer) in the segmented block copolymer did not significantly enhance the tensile properties of the blend material. There was no effect of varying the PDMS content in the segmented block copolymer on the modulus of the blend, but blends certainly resulted in materials with high modulus and impact strength. The segmented block copolymer blends demonstrate high thermal stability to nearly 500 °C at T_d -5% weight loss over Udel[®], which has a T_d of 455 °C at 5% weight loss.

6.7. ACKNOWLEDGMENTS

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Chapter 7:

FUTURE WORK

The research within this work consisted of measuring the thermal, tensile, and morphological properties of segmented block copolymers either with fluorinated-bisphenols or with the incorporation of co-monomers, 4, 4'-dihydroxyterphenyl (DHTP) and triptycene-1,4-hydroquinone (TPDH), into the bisphenol A (BA) PAES unit. For each research study, there were areas of interest that provided motivation for further investigation. In Chapter 2, a series of hexafluoroisopropylidene bisphenol poly(arylene ether sulfone) (BAF PAES) segmented block copolymers with varying fractions of polydimethylsiloxane (PDMS) show significant differences in the morphological properties over those of BA PAES-*b*-PDMS. The BAF PAES-*b*-PDMS displayed increased morphological order with decreasing PDMS content revealing the effect of fluorination on the driving force for microphase separation in the segmented block copolymers.

It is possible to further enhance microphase separation by incorporating bisphenol PAES with fluorine attached to the phenyl backbones into the segmented block copolymers. Two monomers have been identified to be incorporated into the PAES unit and compared to the previously studied BAF PAES-*b*-PDMS (Fig. 7.1). Monomer (1), prepared in 58% yield from BAF monomer and *N,N'*-difluoro-2,2'-bipyridinium bis(triflate) in 1,2-dichloroethane ¹, has been polymerized with an isocyanate group to make materials for electrophotographic photoreceptor applications. These materials were shown to have excellent mechanical strength and a durable

surface protective layer with photoelectric properties ². Monomer (2), is commercially available and has been used in various polycarbonates resins for transparent and heat resistant applications ³⁻⁵.

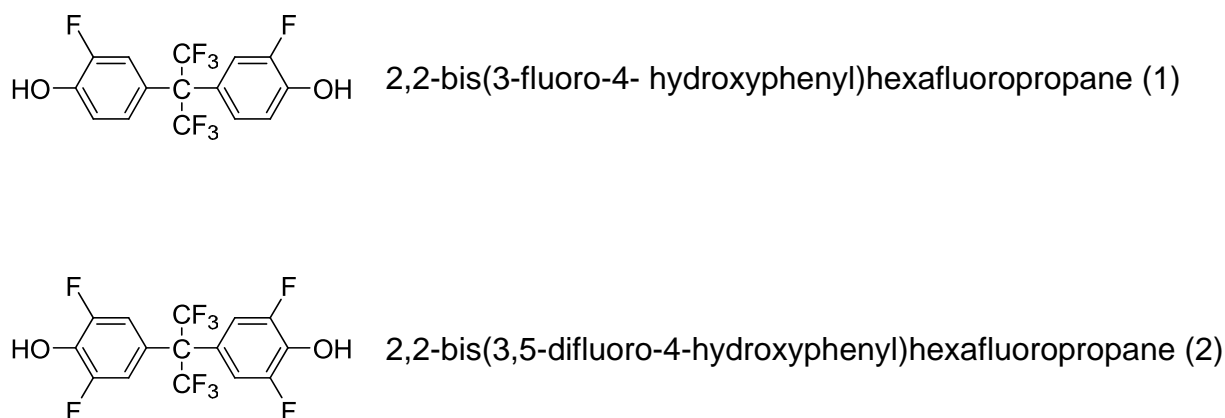
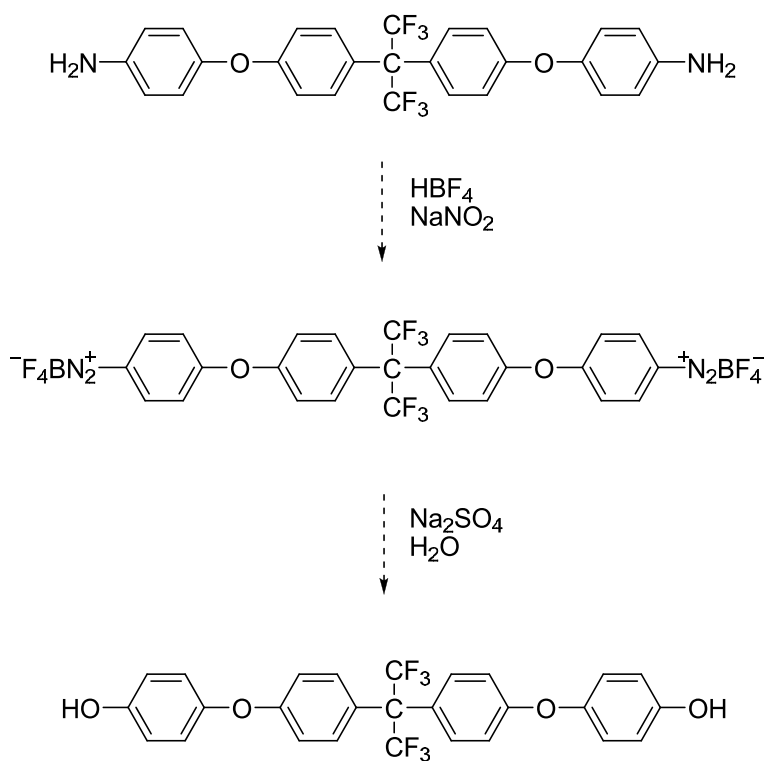


Figure 7.1: Fluorinated monomers of interest.

Both monomers share similar transparent and thermal stability properties as the BAF monomer, though they could potentially alter the morphology of segmented block copolymers. The 4,4'-(hexafluoroisopropylidene)bis[(4-hydroxyphenyl)hydroquinone] (BAFPh) monomer (Scheme 7.1) can be synthesized from the commercially available monomer, 4'',4'''-(hexafluoroisopropylidene)bis(4-phenoxyaniline). Mohr and co-workers ⁶ studied the gas transport properties of fluorinated poly(ether ketone)s (PEK) in comparison to non-fluorinated polymers. Because of the lower chain mobility and the larger free volume in the $-C(CF_3)_2-$ group in the polymer backbone, the fluorinated PEK had higher T_g , better gas selectivity, and lower permeability compared to those of the non-fluorinated PEK.

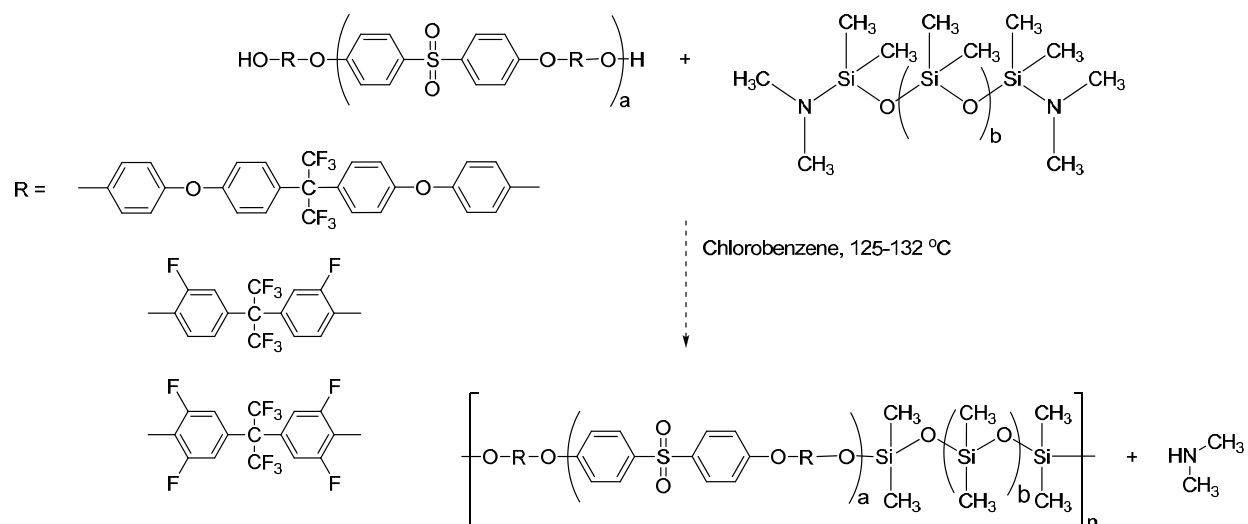


Scheme 7.1: Proposed synthesis of 4,4'-(hexafluoroisopropylidene)bis[(4-hydroxyphenyl)hydroquinone].

The $-\text{C}(\text{CF}_3)_2-$ group in the BAFPh monomer would provide higher thermal properties compared to the BAF monomer because of the additional phenyl rings. Additionally, with the additional phenyl rings in the backbone, the BAFPh monomer could improve the rigidity of the polymer backbone and enhance the tensile properties compared to the analogous BAF PAES.

To date, there is no current literature where the monomers have been incorporated into PAES. The monomers react with dichlorodiphenylsulfone (DCDPS) to

form the fluorinated PAES, which is then copolymerized with polydimethylsiloxane (PDMS) of various molecular weights ⁷ (Scheme 7.2). These materials could lead to specific morphological characteristics to be investigated by common techniques such as atomic force microscopy (AFM), transmission electron microscopy, and small-angle X-ray scattering (SAXS). These techniques would be able to qualitatively describe the morphological profile with the additional fluorine incorporated into the PAES segment.



Scheme 7.2: Proposed synthesis of segmented block copolymers containing fluorine groups.

In both Chapters 4 and 5, 4,4'-dihydroxyterphenyl (DHTP) and triptycene-1,4-hydroquinone (TPDH) co-monomers were employed in preparation of PAES random copolymers and segmented block copolymers with PDMS. These co-monomers are

both rigid and bulky, which improved the tensile modulus of the bisphenol A PAES. Swager and co-workers⁸ synthesized TPDH-based polyesters that produced enhanced polymer stiffness ductility compared to the non-TPDH-based polyesters. The tensile modulus improved from 0.58 GPa to 1.62 GPa and the strain had a 20-fold increase from the non-TPDH-based polyesters to the TPDH-based polyesters. The polymers also produced increased thermal properties over the non-TPDH polyesters, the T_g increased from 25 °C to 55 °C and the thermal stability in air improved slightly from 375 °C to 382 °C. The authors attributed the increase in the mechanical properties, specifically the enhanced stiffness and ductility, are attributed to the “molecular threading and molecular interlocking through the minimization of internal molecular free volume⁸.” These results were remarkable and confirmed that polymers which can provide enhanced stiffness without sacrificing ductility can be prepared.

Continuing the exploration of rigid and bulky monomers that have enhanced stiffness and ductility led to 4,4"-dihydroxy-5'-phenyl-*m*-terphenyl (DPM-T) (Fig. 7.2). Hay and co-workers⁹ incorporated this monomer into various polymers producing materials with excellent thermal properties, such as T_g values ranging 198 °C to 270 °C and thermal stability ranging 502 °C to 580 °C. The polymers were also soluble in dipolar aprotic solvents and show good UV-light emission around 380 nm.

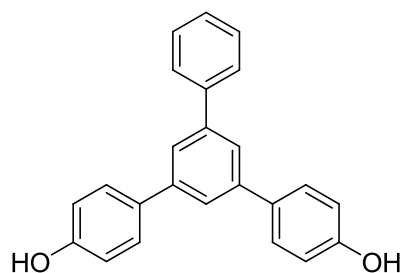


Figure 7.2: Structure of 4,4'-dihydroxy-5'-phenyl-*m*-terphenyl (DP*m*-T) monomer.

Mikroyannidis ¹⁰ synthesized polyesters and polyethers incorporating DP*m*-T (Fig. 7.3) to study the thermomechanical, optical, and solubility properties. The polymers were amorphous showing only a T_g , 146 °C for the polyester and 53–60 °C for the polyether. The polymers, particularly for the polyester, were thermally stable up to 340 °C. The polymers also showed good optical properties with fluorescence in the ultraviolet and violet-blue region with absorption maxima around 333–487 nm.

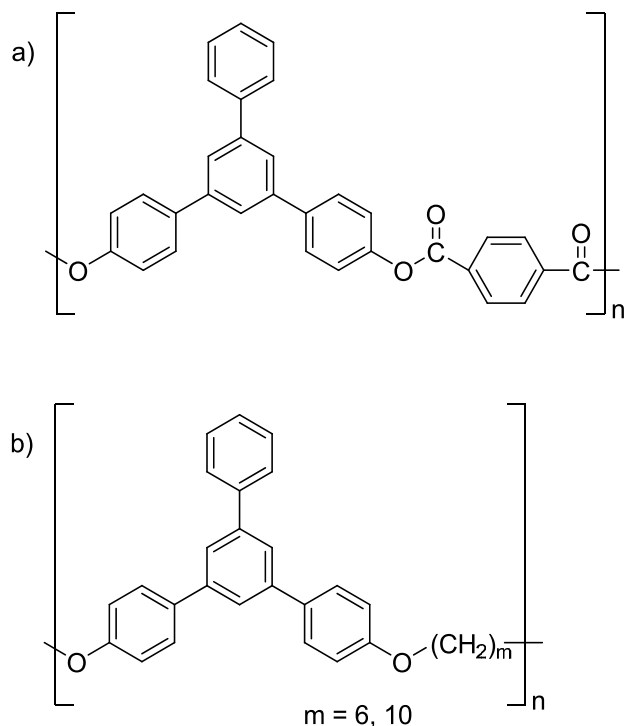


Figure 7.3: Structures of DP_m-T containing a) polyester and b) polyether.

The DP_m-T monomer can be polymerized with DCDPS to form a PAES (Fig. 7.4) corresponding to Hay and co-workers⁹ research specifically studying the affect of internal molecular free volume on polymer tensile properties in comparison with BA-TPDH PAES. Copolymerization with dimethylamino-terminated PDMS produces segmented block copolymers (Scheme 7.3) that could be compared to the previously synthesized segmented block copolymers incorporating DHTP and TPDH. The molecular structure of the segmented block copolymer should allow the PDMS unit of high molecular weight to fill the free volume regions of the bulky aromatic rings. Tailoring the PDMS weight content in the segmented block copolymer could lead to materials with enhanced tensile properties like stiffness and ductility.

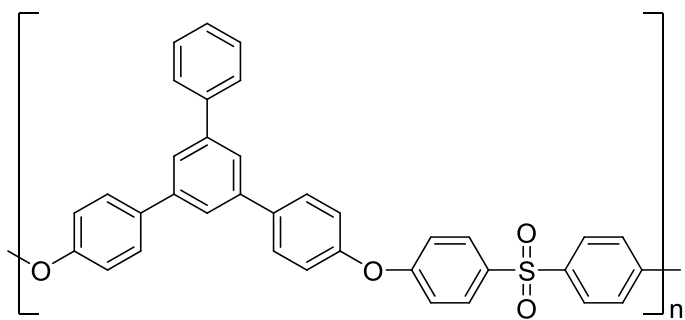
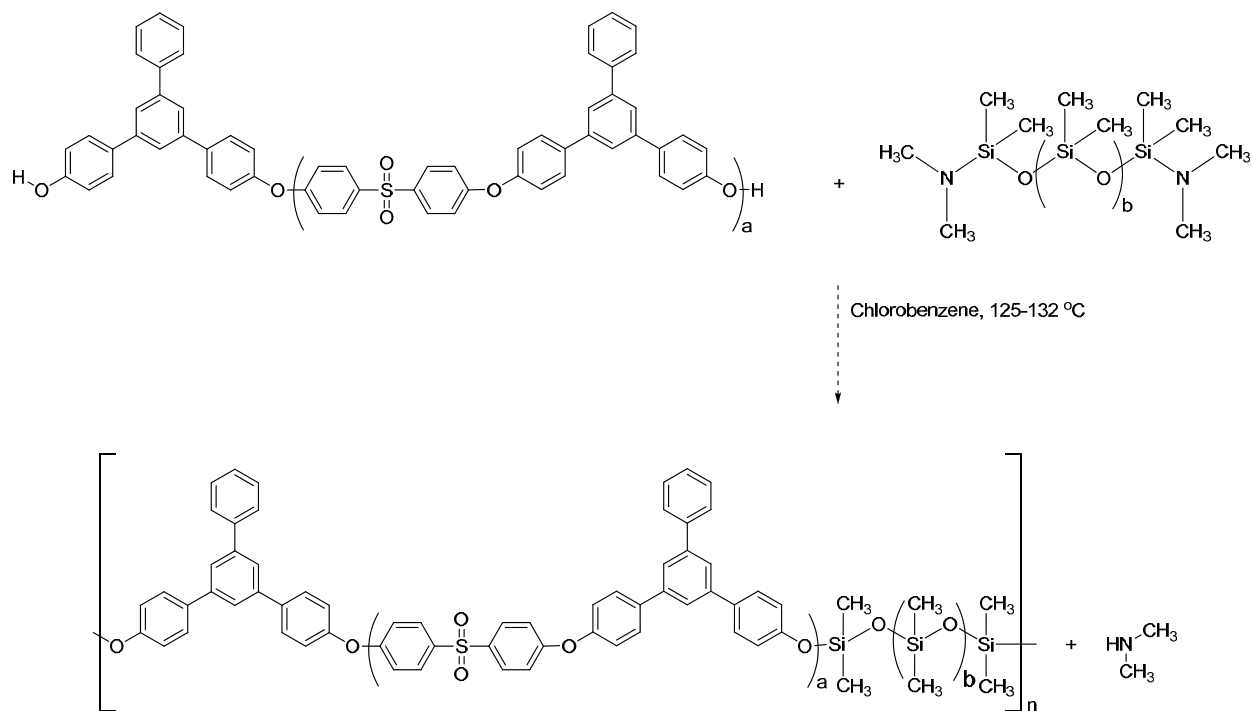


Figure 7.4: Proposed structure of DP*m*-T poly(arylene ether sulfone).



Scheme 7.3: Proposed synthesis of segmented block copolymers containing DP*m*-T.

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