Synthesis and Properties of Novel Triptycene-Containing
Segmented Polyurethanes and Semicrystalline Polysulfone-Polyester Multiblock Copolymers

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Segmented copolymers are important polymers with attractive properties and wide applications. In this dissertation, segmented polyurethanes containing triptycene units and multiblock copolymers containing poly(arylene ether sulfone) (PAES) and poly(1,4-cyclohexyldimethylene terephthalate) (PCT) segments were synthesized and systematically studied.

Investigation of the influence of the bulky triptycene structure on the morphologies and properties of segmented polyurethanes was carried out by using triptycene-1,4-hydroquinone bis(2-hydroxyethyl)ether (TD) as the chain extender. Segmented polyurethanes based on poly(tetramethylene glycol) (PTMG) of 1000 g/mol were synthesized using a two-step polymerization procedure. Hydroquinone bis(2-hydroxyethyl)ether (HQEE) was used for the purpose of comparison. Hard segments with different bulkiness and flexibility were prepared with hexamethylene diisocyanate (HDI) and 4,4'-methylenebis(phenyl isocyanate) (MDI), and HQEE or TD as chain extenders. The incorporation of bulky TD and less flexible MDI significantly inhibited hydrogen bonding based on the Fourier transform infrared (FTIR) results. In addition, the microphase separation was also disturbed by the bulky and less flexible hard segments with confirmation from tapping mode atomic
force microscopy (AFM) and small angle X-ray scattering (SAXS). The flexible HDI can be used to overcome the bulkiness of triptycene, promote microphase separation, and enhance mechanical properties.

Novel PTMG based soft segments containing triptycene units were also prepared with number average molecular weight (M_n) around 2500 g/mol. Then this soft segment was reacted with MDI and HQEE to prepare segmented polyurethanes. Soft segments such as hydroquinone (HQ) containing PTMG (M_n = 2100 g/mol), and pure PTMGs (M_n = 1000 and 2000 g/mol) were used for comparison. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) results demonstrated that triptycene units led to an increased glass transition temperature (T_g) and an elimination of the crystallization of the soft segments. The absence of strain hardening for the triptycene-containing sample suggested a suppressed strain induced crystallization of soft segments, which was also confirmed by the analysis of wide-angle X-ray diffraction (WAXD) on the films strained to 370 %.

Crystallizable PCT segments were copolymerized with PAESs to enhance solvent resistance and mechanical properties. PAES oligomers (M_n = 2000 g/mol) were first synthesized, and then reacted with dimethyl terephthalate (DMT) and 1,4-cyclohexanediol (CHDM). Weight percentages of PCT segments were gradually changed from 20 wt% to 80 wt%. With PCT content greater than 50 wt%, crystallinity was observed by DSC, DMA, and WAXD. The extent of crystallinity of the copolymers was dependent on the wt% of PCT. Furthermore, crystallization behavior of copolymers based on two CHDMs with different isomer ratios (cis/trans
30/70 and all *trans* were studied. Due to their more symmetric structure, copolymers based on all *trans* CHDM exhibited a higher extent of crystallization.
DEDICATION

To my grandparents, Yuanke Chang, Lanxiu Gong

and grandparents in-law, Fuyuan He, Aizhi Fan

Thank you for all the love you gave me
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# Table of Contents

**Chapter 1. Literature Review on Segmented Polyurethanes** .................. 1

1.1 Introduction of polyurethanes .......................................................... 1

1.2 History of polyurethanes ........................................................................ 1

1.3 Polyurethane chemistry ......................................................................... 3

1.4 Chemical structure of segmented polyurethanes .................................... 5

1.5 Basic polyurethane raw materials ......................................................... 7

1.5.1 Polyols ............................................................................................... 7

1.5.2 Isocyanates ......................................................................................... 8

1.5.3 Chain extenders ................................................................................. 11

1.6 Preparation of polyurethanes ................................................................. 12

1.7 Microphase separation in segmented polyurethane ............................... 15

1.8 Modification of segmented polyurethanes ............................................. 19

1.8.1 Modification of segmented polyurethanes with novel chain extenders ................................................................. 19

1.8.2 Modification of segmented polyurethanes with novel isocyanates .. 20

1.8.3 Modification of segmented polyurethanes with novel polyols ........ 21

1.9 Triptycene and applications in polymers ............................................... 22

1.10 Applications ......................................................................................... 28
Chapter 2. Literature Review on Poly(arylene ether sulfone)s and Poly(1,4-cyclohexyldimethylene terephthalate) (PCT) ................................................................. 36

2.1 Literature review of poly(arylene ether sulfone)s .................................. 36
2.1.1 Overview of poly(arylene ether sulfone)s ........................................... 36
2.1.2 Chemistry .......................................................................................... 39
2.1.3 Properties and Applications of Poly(arylene ether sulfone)s ............. 45
2.1.4 Modification of PAESs .................................................................... 48
2.1.5 Semi-crystalline PAESs .................................................................... 53

2.2 Literature review of poly(1,4-cyclohexyldimethylene terephthalate) (PCT) .............................................................................................................. 57
2.2.1 Structures and properties of PCT ....................................................... 57
2.2.2 Polymers modified by PCT ............................................................... 60

2.3 Summary .............................................................................................. 61
2.4 References ............................................................................................ 61

Chapter 3. Synthesis and Properties of Segmented Polyurethanes with Triptycene Units in the Hard Segment ................................................................. 68

3.1 Abstract ............................................................................................... 68
3.2 Introduction ........................................................................................... 69
Chapter 4. Synthesis and Properties of Segmented Polyurethanes with Triptycene Units in the Soft Segment ............................................. 106

4.1 Abstract .................................................................................. 106
4.2 Introduction...........................................................................................................107
4.3 Experimental.........................................................................................................110
  4.3.1 Materials.........................................................................................................110
  4.3.2 Synthesis of PTMG-based Polyol Containing Aromatic Units ......111
  4.3.3 Synthesis of Segmented Polyurethanes.........................................................113
  4.3.4 Film Preparation..............................................................................................114
  4.3.5 Instrumentation ..............................................................................................115
4.4 Results and Discussion ..........................................................................................118
  4.4.1 Synthesis of Soft Segments Containing Aromatic Structures and Polyurethanes........................................................................................................................................................................................................118
  4.4.2 Thermal Properties..........................................................................................120
  4.4.3 Thermomechanical Analysis ..........................................................................125
  4.4.4 Tensile Properties ..........................................................................................127
  4.4.5 Morphological Features ..................................................................................131
4.5 Conclusions ...........................................................................................................136
4.6 Acknowledgement ..................................................................................................137
4.7 Supporting information..........................................................................................138
4.8 Supplementary Materials ......................................................................................144
  4.8.1 Synthesis and properties of PUs based on Soft Segments Containing Aromatic Structures ........................................................................................................................................................................................................144
4.8.2 Synthesis and characterizations of novel PTMG650 soft segments containing aromatic structures..........................................................154

4.9 Appendix: ........................................................................................................159

4.10 References ........................................................................................................163

Chapter 5. Synthesis and Properties of Semicrystalline Poly(arylene ether sulfone)s Containing Polyester Segments .........................................................166

5.1 Abstract: ..............................................................................................................166

5.2 Introduction .........................................................................................................166

5.3 Experimental .......................................................................................................170

5.3.1 Materials .........................................................................................................170

5.3.2 Synthesis of biphenyl based poly(arylene ether sulfone)s oligomer with phenol end groups .........................................................................................170

5.3.3 Synthesis of PAES2K with hydroxy ethoxy end groups .........................171

5.3.4 Melt-phase polymerization of PAES-PCT multiblock copolymers .172

5.3.5 Preparation of polymer film ..............................................................................174

5.3.6 Instrumentation ................................................................................................174

5.4 Results and Discussion .......................................................................................176

5.4.1 Synthesis of PAES oligomers and multiblock copolymers .................176

5.4.2 \(^1\)H NMR analysis .........................................................................................177

5.4.3 Thermal Stability .............................................................................................178
5.4.4 DSC analysis ................................................................................................................. 179
5.4.5 Thermomechanical analysis ......................................................................................... 184
5.4.6 Tensile properties ......................................................................................................... 187
5.4.7 Morphology study ......................................................................................................... 188
5.5 Conclusion ....................................................................................................................... 189
5.6 Supporting information .................................................................................................. 190
5.7 References ..................................................................................................................... 193

Chapter 6.  **Suggested Future Work and Summary** ...................................................... 196

6.1 Introduction .................................................................................................................... 196
6.2 Segmented polyurethane containing triptycene units in the soft segments
............................................................................................................................................... 196
6.3 Segmented polyurethanes containing highly functionalized triptycene units
............................................................................................................................................... 197
6.4 Block copolymers with triptycene-containing polysulfone segments .... 198
6.5 Summary ......................................................................................................................... 199
6.6 References: ..................................................................................................................... 201
List of Figures

Figure 1.1 Typical reactions of diisocyanates with diols to form polyurethanes or with diamines to form polyureas ................................................................. 3

Figure 1.2 Resonance structures of the isocyanate group ........................................ 4

Figure 1.3 Mechanism of isocyanate reactions with alcohols and amines .......... 4

Figure 1.4 Secondary structure of polyurethanes: hard and soft block microdomain .............................................................................................................. 6

Figure 1.5 Typical polyols used in the syntheses of polyurethanes ..................... 7

Figure 1.6 Preparation of Novomer polyols ............................................................ 8

Figure 1.7 Typical isocyanates used in the synthesis of polyurethanes .......... 10

Figure 1.8 Typical chain extenders used in the synthesis of polyurethane ....... 12

Figure 1.9 Representation of structure of polyurethane prepared via one-step method .................................................................................................................. 14

Figure 1.10 Representation of the structure of polyurethanes prepared via the prepolymer method ........................................................................................................ 15

Figure 1.11 Hard and soft segments in PUs .......................................................... 16

Figure 1.12 Phase separation of polyurethanes .................................................... 17

Figure 1.13 Calix[4]arene with para t-butyl substituent ................................ .... 20

Figure 1.14 TMXDI (meta) aliphatic isocyanate ................................................. 21

Figure 1.15 Siloxane-carbonate soft segments ..................................................... 22

Figure 1.16 Structure of basic triptycene unit (1,4-Connection and bridgehead connection) .................................................................................................................. 23

Figure 1.17 Molecular threading and molecular interlocking mechanism ........ 24
Figure 1.18 3-Dimensional and 2-Dimensional schemes of the triptycene unit...25
Figure 1.19 Minimization of internal molecular free volume (IMFV) for polymers
with triptycene units ........................................................................................................25
Figure 1.20 Synthesis of triptycene-containing sulfonated polysulfone............28
Figure 2.1 General chemical structure of PAESs.........................................................36
Figure 2.2 Bond angle of aromatic ether linkage ........................................................38
Figure 2.3 Bond angle of aromatic ether linkage ........................................................38
Figure 2.4 Typical synthesis of bisphenol-A-based PAES ........................................39
Figure 2.5 Nucleophilic aromatic substitution mechanism .........................................42
Figure 2.6 Typical polysulfonylation synthesis of PAESs...........................................43
Figure 2.7 Friedel-Crafts sulfonylation mechanism....................................................44
Figure 2.8 Resonance structure of bisphenol-A-based PAES ..................................46
Figure 2.9 Synthesis of PTMG-PAES copolymers via melt transesterification....52
Figure 2.10 Synthesis of PEG-PAES block copolymers ...........................................53
Figure 2.11 Diblock and multiblock copolymers at the interface between two
immiscible polymers.....................................................................................................55
Figure 2.12 Modification of PCT by isophthalic acid ...............................................57
Figure 2.13 DMT, CHDM and PCT general structure ............................................58
Figure 2.14 Conformations of CHDMs ...................................................................58
Figure 2.15 PCT melting temperature of polyesters dependence on the molar ratio
of cis/trans CHDM.......................................................................................................59
Figure 2.16 General structure for PCTG and PETG .................................................60
Figure 3.1 Appearance of the PU films ...................................................................78
Figure 3.2 FTIR spectra in the carbonyl region for the PU samples at ambient conditions..........................................................................................................................81
Figure 3.3 FTIR spectra in the N-H region for the PU samples at ambient conditions ..................................................................................................................................................82
Figure 3.4 Variable temperature FTIR spectra in the carbonyl region for the PU materials ..............................................................................................................................................83
Figure 3.5 DMA storage modulus responses of the PU samples with different hard segments ..............................................................................................................................................87
Figure 3.6 DMA Tan delta profiles of the PU samples with different hard segments ..............................................................................................................................................87
Figure 3.7 Tensile properties of the PUs based on different chain extenders .......90
Figure 3.8 SAXS curves for the PU samples ..................................................................................................................................................................................92
Figure 3.9 AFM images of the PUs based on HQEE and TD ................................94
Figure 3.10 $^1$H NMR spectrum of biphenol bis(2-hydroxyethyl)ether (BHEE) ....98
Figure 3.11 $^1$H NMR spectrum of triptycene-1,4-hydroquinone-bis(2-hydroxyethyl) ether (TD) .......................................................................................................................99
Figure 3.12 FTIR spectrum of HDI-HQEE .................................................................................100
Figure 3.13 FTIR spectrum of HDI-TD ...................................................................................100
Figure 3.14 FTIR spectrum of MDI-HQEE .............................................................................101
Figure 3.15 FTIR spectrum of MDI-TD ..................................................................................101
Figure 3.16 TGA curves of the PU samples ..........................................................................102
Figure 3.17 DSC curves of the PU samples ..........................................................................102
Figure 4.1 DSC traces of the pure soft segments .................................................................124
Figure 4.2 DSC traces of the segmented polyurethanes based on different soft segments ........................................................................................................124
Figure 4.3 Storage modulus and Tan delta of segmented polyurethanes based on different soft segments ........................................................................................127
Figure 4.4 Stress-strain curves of polyurethanes based on different soft segments ........................................................................................................128
Figure 4.5 Hysteresis of the polyurethane samples stretched to 300% ............131
Figure 4.6 WAXD profiles of segmented polyurethanes at strains ...............133
Figure 4.7 WAXD patterns of segmented polyurethanes at strains ..........133
Figure 4.8 SAXS profiles of the polyurethane samples ................................134
Figure 4.9 AFM phase images of the PU samples ........................................136
Figure 4.10 Thermal degradation of polyurethanes with different soft segments ........................................................................................................138
Figure 4.11 $^1$H NMR spectrum of PTMG1K-diMs ........................................139
Figure 4.12 $^1$H NMR spectrum of PTMGHQ diol ........................................140
Figure 4.13 $^1$H NMR spectrum of PTMGTH diol .........................................140
Figure 4.14 Variable temperature FTIR spectra of segmented polyurethane samples ........................................................................................................141
Figure 4.15 WAXD profile of PTMG2K pure soft segment ..........................141
Figure 4.16 DMA profiles comparison between solvent cast and compression molded PTMG1K-PU .................................................................142
Figure 4.17 DMA profiles comparison between solvent cast and compression molded PTMG2K-PU .................................................................142
Figure 4.18 DMA profiles comparison between solvent cast and compression molded PTMGHQ-PU ................................................................. 143
Figure 4.19 DMA profiles comparison between solvent cast and compression molded PTMGTH-PU ........................................................................ 143
Figure 4.20 $^1$H NMR spectrum of acetylated PTMG-HQ-diol .................. 147
Figure 4.21 $^1$H NMR spectrum of acetylated PTMG-TH-diol .................... 147
Figure 4.22 Synthesis of PUs with different soft segments ......................... 150
Figure 4.23 FTIR spectra of PUs with different SSs .................................. 151
Figure 4.24 Thermal degradation of PU samples ....................................... 152
Figure 4.25 DSC traces of PU samples ..................................................... 153
Figure 4.26 DMA storage modulus profiles of PU samples ....................... 154
Figure 4.27 $^1$H NMR spectrum of PTMG650-TH-diMs .......................... 157
Figure 4.28 $^1$H NMR spectrum of PTMG650-HQ-diMs ........................... 157
Figure 4.29 WAXS scattering pattern of PTMG1K-PU ............................. 159
Figure 4.30 WAXS scattering pattern of PTMG2K-PU .............................. 160
Figure 4.31 WAXS scattering pattern of PTMGHQ-PU ............................ 161
Figure 4.32 WAXS scattering pattern of PTMGTH-PU ............................. 162
Figure 5.1 Isomerization of cis/trans CHDA ........................................... 169
Figure 5.2 Thermal degradation behaviors of PAES-PCT copolymers .......... 179
Figure 5.3 Thermal transitions of PAES-PCT copolymers ....................... 182
Figure 5.4 Thermal transitions of PAES-tPCT copolymers ...................... 183
Figure 5.5 DMA profiles of PAES-PCT copolymers .................................. 185
Figure 5.6 DMA profiles of PAES-tPCT copolymers ............................... 186
Figure 5.7 Representative stress-strain curves of PAES-PCT-50 and PCT......187
Figure 5.8 WAXS profiles of annealed PAES-PCT copolymers.........................188
Figure 5.9 ¹H NMR spectrum of PAES2K.................................................................190
Figure 5.10 ¹H NMR spectrum of HEPAES2K.......................................................191
Figure 5.11 ¹H NMR spectrum of PAES-PCT-50.....................................................192
Figure 5.12 ¹H NMR spectrum of PAES-tPCT-50....................................................193
Figure 6.1 Soft segments prepared based on different molecular weights of PTMG .................................................................................................................................197
Figure 6.2 Polyurethane ionomers containing sulfonated triptycene units in soft segments ..........................................................................................................................198
**List of Tables**

Table 1.1 Applications, properties and processing method of polyurethanes .....29
Table 2.1 Common commercially available PAESs ........................................37
Table 2.2 Common names and structures of diphenol monomers ..................40
Table 2.3 Selected chemical and physical properties of the typical commercially available polysulfones .................................................................47
Table 2.4 Various diphenol monomers used in PAES preparation ...............49
Table 2.5 PAESs based on novel dihalide monomers ..................................50
Table 3.1 Composition and SEC results of the PUs based on different hard segments ..................................................................................................................78
Table 3.2 Thermal properties of the PUs based on the various chain extenders studied ..................................................................................................................85
Table 3.3 Comparison of tensile properties of PUs based on various chain extenders ..................................................................................................................89
Table 3.4 SAXS of PUs based on various chain extenders ............................92
Table 4.1 Structure and number average molecular weight of soft segments ..119
Table 4.2 Composition and SEC results of the segmented polyurethanes based on different soft segments .................................................................120
Table 4.3 Thermal transitions of pure soft segments ....................................123
Table 4.4 Thermal properties of the four segmented polyurethanes ..........123
Table 4.5 Tensile properties of polyurethanes based on different soft segments ..................................................................................................................129
Table 4.6 Hysteresis behavior of polyurethane samples stretched to 300%.....130
Table 4.7 SAXS of polyurethanes based on different soft segments ..............135
Table 4.8 Novel Soft segments used in the PUs synthesis..............................149
Table 4.9 Averaged hydroxyl numbers and $M_n$ of different soft segments ....158
Table 5.1 Thermal transitions of PAES-PCT and PAES-tPCT samples............181
List of Schemes

Scheme 3.1 Structure of triptycene-1,4-hydroquinone bis(2-hydroxyethyl) ether 72
Scheme 3.2 Synthesis of the PUs based on different diisocyanates and chain extenders .................................................................................................................... 77
Scheme 3.3 Synthesis of biphenol bis(2-hydroxyethyl) ether (BHEE) and triptycene-1,4-hydroquinone-bis(2-hydroxyethyl) ether (TD) ........................................ 97
Scheme 4.1 Structure of 1,4-dihydroxy triptycene (molecular weight: 286 g/mol) ................................................................................................................................. 110
Scheme 4.2 Synthesis of soft segments containing aromatic units ........................ 113
Scheme 4.3 Synthesis of segmented polyurethanes with different soft segments ................................................................................................................................. 114
Scheme 4.4 Acetylation of PTMG-TH-diol ................................................................ 146
Scheme 4.5 Synthesis of soft segments based on PTMG650 .................................. 156
Scheme 5.1 Synthesis of PAES2K with hydroxyl end groups ............................... 172
Scheme 5.2 Synthesis of PAES-PCT multiblock copolymers ................................. 174
Chapter 1. Literature Review on Segmented Polyurethanes

1.1 Introduction of polyurethanes

Polyurethanes (PU)s are versatile polymeric materials with applications including foams, elastomers, coatings, adhesives, fibers, etc, and have been studied for more than 70 years.¹

The chemical structures of PUs mainly consist of three basic components: oligomer diols, multifunctional isocyanates, and chain extenders. One of the most important advantages of polyurethane materials is the ability to tune morphologies and properties. With the selection of the three basic components and their composition, a range of properties can be achieved, which enables them to be widely used in various applications.²,³ Thus, controlling the chemical structure of polyurethane, in order to obtain useful properties, has resulted in large efforts devoted in developing key monomers for polyurethanes, diisocyanates and diols.⁴,⁵

1.2 History of polyurethanes

Bayer conducted the pioneering research on polyurethane chemistry in 1937.⁶ One of the earliest polyurethane product, Perlon U, was prepared by reacting 1,6-hexanediisocyanate (HDI) with 1,4-butandiol (BDO).¹ Since then, more polymers containing urethane and urea linkages were synthesized via step-growth polymerization.⁷ Although some of these polyurethanes were not practically useful, this was the initial work and foundation of polyurethane science. In the 1940s, the reactions between diisocyanates and diols were further explored by the Bayer Company, and products such as rigid foams, coatings and adhesives were
manufactured and introduced into the market. American companies such as DuPont and Goodyear Aircraft also started their research on polyurethanes around 1945.\textsuperscript{1,5}

In the 1950s, polyurethane products, especially polyester-based polyurethane soft foams, with excellent mechanical properties were commercialized by Bayer. 4,4′-Methylene diphenyl diisocyanate (MDI) was developed by ICI, and used to produce soft and hard polyurethane foams. These studies significantly expanded the applications of polyurethane foams, and made them commercially available on a large scale. In the meantime, the raw materials, production machinery, and technical expertise were also studied and developed by the Bayer and Hennecke Companies. With these advancements, the applications of polyurethanes were greatly expanded.\textsuperscript{6}

In the two decades that followed, to meet the growing demand of urethane materials, numerous efforts were made to improve synthesis methods, processing conditions, and development of new raw materials. However, limitations of polyurethane products also gradually appeared, and more studies were conducted to overcome these drawbacks. First, a large challenge of the polyurethane industry is the environmental impact of the processing for the materials. For example, chlorofluorocarbons (CFCs), which were the most efficient blowing agents in the manufacture of polyurethane foams, were replaced by other environmentally friendlier blowing agents such as hydrochlorofluorocarbons (HCFCs), hydrofluorocarbons (HFCs), and water. These blowing agents are less hazardous to the environment. Second, polyurethane materials were competing with other
polymeric materials during this period. For example, polyethylene (PE) with reduced cost and enhanced properties became very competitive in the market in 1980s. Studies on property modifications of polyurethanes were constantly proceeding, and the feature of adaptability make polyurethanes one of the most important polymeric materials today.

1.3 Polyurethane chemistry

The development of the synthesis of isocyanates has enabled the introduction and growth of polyurethanes in the commercial marketplace. Hentschel synthesized isocyanates by using amine salts and phosgene in 1884. His effort established the foundation for the industrialization of polyurethane because the cost of isocyanate raw materials was greatly reduced.

\[
	ext{HO-R_1- OH} + \text{OCN-R-NCO} + \text{H}_2\text{N-R_2-NH}_2
\]

\[
\text{Polyol} \quad \text{Diisocyanate} \quad \text{Chain extenders}
\]

\[
\left(\text{O-\text{C-N-R-N-C-O-R_1-O}}\right)_n \quad \left(\text{O-\text{C-N-R-N-C-N-R_2-N}}\right)_m
\]

Polyurethanes Polyureas

Figure 1.1 Typical reactions of diisocyanates with diols to form polyurethanes or with diamines to form polyureas
Typical chemical reactions that form polyurethanes or polyureas are shown in Figure 1.1. Urethane linkages are obtained by reacting hydroxyl groups and isocyanate groups (\(-\text{NCO}\)).

The high reactivity of isocyanate groups arises from the unsaturated structure. Figure 1.2 illustrates the resonance structures of the isocyanate group, due to the electron-induction effect, the carbons in \(-\text{NCO}\) groups are electron deficient and react with nucleophiles. The mechanism of an isocyanate reaction is illustrated in Figure 1.3.

Figure 1.2 Resonance structures of the isocyanate group

\[
\begin{align*}
\text{R}^{-} & \text{N}^{-} \text{C}^{-} \text{O} & \quad & \text{R}^{-} \text{N}^{-} \text{C}^{-} \text{O} & \quad & \text{R}^{-} \text{N}^{-} \text{C}^{-} \text{O}^{-}
\end{align*}
\]

Figure 1.3 Mechanisms of isocyanate reactions with alcohols and amines

Alcohols and amines, both containing active hydrogens, are common nucleophiles in isocyanate reactions. By reacting with isocyanates, alcohols will be
converted to a urethane linkage while amines yield a urea linkage. Referring to Figure 1.3, the difference between the urethane and urea linkages is that the urea linkage has one more N-H group. The hydrogen on this N-H group is an extra hydrogen donor, and the stronger resonance effect from both sides of the urea carbonyl makes it highly polarized, which eventually gives higher hydrogen bonding density.

1.4 Chemical structure of segmented polyurethanes

Segmented polyurethanes (SPU) are the most important polyurethane materials. They normally possess alternating hard and soft segments along the backbone. Due to their short and rigid structures, hard segments normally have a higher T_g (typically above 80 °C), while flexible soft segments have a lower T_g (typically below -40 °C). These two segments segregate from each other and form hard and soft domains, respectively. The segmented structures and the induced domain morphologies of polyurethanes play essential roles in their properties.

Polyurethanes typically consist of three components, polyols, isocyanates and chain extenders as shown in Figure 1.1. Polyols act as the soft segments due to the chain flexibility of their long linear chains. Polyester and polyether oligomers are the most common polyols employed in the synthesis of polyurethanes. Diisocyanates are used to form the urethane with hydroxyl groups or urea linkage with amines. Chain extenders are normally bi- or multifunctional-alcohols or amines. They are much shorter than the polyols, and used to obtain longer chains by coupling prepolymer.
Primarily due to thermodynamic compatibility, hard segments tend to aggregate to form hard domains. In addition, hydrogen bonds among the hard segments also promote their aggregation. Polyols that are more flexible form the soft domains and demix from the hard domains. As shown in Figure 1.4, with such a phase-separated system, the hard domains behave as physical crosslinks, which can be thermally reversible with a temperature range of 80 to 200 °C. These thermal and mechanical properties are important for applications like thermoplastic elastomers. The domain structure induced from the differences in polarity of the segments is the critical feature of segmented polyurethane materials. Varying the polyurethane structure by changing the chemical nature of the hard and soft segments is the most common approach to adjust the properties, such as tensile strength, ductility, and shape-memory properties, etc.

Figure 1.4 secondary structure of polyurethanes: hard and soft block microdomain
1.5 Basic polyurethane raw materials

1.5.1 Polyols

Common polyols are listed in Figure 1.5. Polyethers consisting of oxyethylene, oxybutylene, and/or oxypropylene chains with relatively low $T_g$s can benefit physical properties at low temperature. In addition, the ether linkage possesses higher hydrolytic stability than the ester linkage. The length of polyols also have an influence on the morphologies and properties of polyurethanes; for the same series of polyols, an increase of the chain length normally leads to a higher degree of microphase separation. Poly (tetramethylene glycol) (PTMG), poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG) are the most widely used polyethers for segmented polyurethanes. Studies have revealed that crystallized soft domains based on PTMG or PEG act as physical crosslinkers, and provide enhancement of the mechanical strength.

![Polyols](image)

Figure 1.5 Typical polyols used in the syntheses of polyurethanes
Polyester diols are generally prepared with dicarboxylic acids and glycols via esterification with an excess of diols. The most commonly used polyester diols are the polyadipates of ethylene glycol, di(ethylene glycol) and propylene glycol. In recent years, an increasing number of interests are focused on one specific type of polyester, the polycaprolactone (PCL) polyols, which are prepared by ring-opening polymerization. PCL based polyurethanes exhibit excellent properties in many aspects including biodegradability, hydrolytic stability, oil resistance, chemical resistance, exterior durability and flexibility at low temperatures.\textsuperscript{11} However, the costs of raw materials are high and the processing methods are complicated, which hinder the applications of polycaprolactone polyols. In addition to the polyether and polyester soft segments, other attempts have been made to use polycarbonate (PC) or siloxane diols. These soft segments can elevate the resistance towards hydrolytic and oxidation degradation, as well as the mechanical performance at low temperatures.\textsuperscript{12} Recently, novel polycarbonate diols using carbon dioxide as one of the starting materials (Novomer) have attracted increasing interest in preparation of polyurethanes (Figure 1.6).\textsuperscript{13,14}

![Figure 1.6 Preparation of Novomer polyols](image)

1.5.2 Isocyanates

Polyurethanes are prepared by the reaction of isocyanates and diols or polyols. Some typical isocyanates such as 4,4′-ethylenediphenyl diisocyanate (MDI), 2,4
and 2,6-toluene diisocyanate (TDI), 1,6-hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI) are shown in Figure 1.7.

The isocyanate group acts as an electrophile in polyurethane chemistry. Relative to the aliphatic isocyanates, the electron density of the carbonyl carbon in the aromatic isocyanate is decreased by the inductive effect and conjugation of the aromatic ring. Therefore, aromatic isocyanates generally have a higher reactivity to nucleophiles than aliphatic isocyanates. Furthermore, the rigidity of aromatic diisocyanates, like MDI and TDI, can impart strength to the polymers as well. In contrast, polyurethanes based on aliphatic isocyanates generally have lower mechanical properties but better resistance to UV light degradation and thus better outdoor weathering properties. Crosslinking agents can be used to generate chemically linked networks with enhanced mechanical performance (elastic strength, adhesion, etc.) for applications in foams or coatings.⁶
It has been reported that polyurethanes prepared from symmetric diisocyanates have increased regularity of polymer chains, which improve the mechanical strength.\textsuperscript{15-17} Recently, more novel isocyanates have been developed. For instance, Kojio and coworkers used 1,2-bis(isocyanato)ethoxyethane (TEGDI), and the resulting polyurethanes exhibited excellent elongation, which can potentially be utilized as highly softened polyurethane elastomers.\textsuperscript{18}
1.5.3 Chain extenders

Chain extenders are diols or diamines with low molecular weights. They react with isocyanates to form hard segments. Some commonly used chain extenders are listed in Figure 1.8.

Utilization of different chain extenders can regulate various aspects of the hard segments in polyurethanes. The chain extender controls the chemical structures, the extent of hydrogen bonding, the mass ratio between the hard segment and the soft segment, the microphase separation, etc. The most commercially important chain extenders are shown in Figure 1.8. 1,4-Butanediol (BDO) is the most commonly used chain extender in polyurethane products such as rubbers and adhesives. Other aliphatic diols used as chain extenders have also been investigated.\textsuperscript{19,20} It is observed that by increasing the length of the aliphatic diol, the $T_g$ of the hard segment decreases accordingly. This is reasonable because as the length of the linear aliphatic diol is increased, the chain flexibility is increased.\textsuperscript{21} Hydroquinone bis(2-hydroxyethyl) ether (HQEE) is an aromatic chain extender. Compared to the aliphatic diols, polyurethanes based on HQEE exhibit excellent physical properties, especially at elevated temperatures.\textsuperscript{22} The aromatic structures increase the cohesion and the order of the hard domains, which leads to a better microphase separation.\textsuperscript{22} Another study investigated the rate of microphase separation for various polyurethanes based on different hard segments. By measuring the heat capacity of soft segments $T_g$ by differential scanning calorimetry (DSC), the sample based on HQEE showed a heat capacity of 0.388
J/g, which is higher than the BDO sample (0.356 J/g), suggesting a faster domain segregation rate.\textsuperscript{23}

As briefly discussed in Figure 1.3, alcohols and amines lead to urethane and urea linkages, respectively. In general, due to the strong bidentate hydrogen bonds in the urea moiety, polyureas are more rigid than polyurethanes, and possess higher mechanical strength but lower flexibility.\textsuperscript{24,25} For example, with 60 wt% of hard segment content, the tensile modulus of segmented polyureas based on ethylene diamine (20 MPa) is much greater than polyurethane analog prepared by BDO (2 MPa).\textsuperscript{26} Choosing diols or diamines as the chain extender depends on the intended application of the final materials. Modification of polyurethanes with novel chain extenders will be discussed in a later section.

Figure 1.8 Typical chain extenders used in the synthesis of polyurethane

1.6 Preparation methods for polyurethanes

The general structure of polyurethanes was illustrated in Figure 1.1. However, the segmented chain structure is influenced by many factors. For example, different preparation approaches lead to polymer chains with different distributions.
of segments. Today, two well-known methods, “one-step” and “two-step” are utilized.

The one-step method refers to the technique in which all the raw materials, including polyols, isocyanates, chain extenders and other additives, are added into the reaction system all at once. It is a simple and effective way to prepare polyurethanes with a low cost. This technique is mostly utilized in the manufacturing industry, especially for the polyurethane products without high performance requirements. However, the disadvantage is also obvious, the reactions and chain structures cannot be precisely controlled. The products based on this technique have a relatively random distribution of segment lengths, which leads to a microphase separation with broad size distribution of domains (Figure 1.9).
The two-step preparation method is also called the prepolymer method. Polyols are first reacted with diisocyanates, which generates the prepolymer end-capped with isocyanate groups. These isocyanate groups further react with the chain extender in the second step to form the polyurethanes (Figure 1.10). The preparation process and molecular structure are well controlled via this technique. Due to the narrow size distribution of hard domains, the products prepared based on the prepolymer method normally exhibit well-defined phase separation and excellent mechanical performance. It was also reported that the one-step method resulted in a higher hard segment $T_m$, comparing to the two-step method; and the
tensile properties were governed by the interactions between the hard and soft domains.\textsuperscript{28}

Figure 1.10 Representation of the structure of polyurethanes prepared via the prepolymer method

1.7 Microphase separation in segmented polyurethane

As stated earlier, the alternating hard and soft segments along the backbone of segmented polyurethanes possess different polarity and thermodynamic nature.\textsuperscript{29} As shown in Figure 1.11, the hard segments, which include diisocyanate and chain extenders, are mostly rigid hydrocarbon structures, while the soft segments are derived from flexible polyether or polyester oligomers with much
lower glass transition temperatures ($T_g$) relative to the hard segments. Due to their thermodynamic incompatibility, these segments tend to segregate and form domain structures; the sizes of these domains are normally in the range of 5-100 nm.\(^3\) This behavior is similar to polymer blends, but the domains are chemically linked; thus, the segmented polyurethanes act as physically crosslinked networks (Figure 1.12). Moreover, among the polar urethane linkages, intermolecular and intramolecular hydrogen bonding also occurs, which facilitates aggregation and formation of hard domains. In most cases, hard domains have a lower volume fraction and disperse in the soft matrix, and they play the role of physical crosslinkers that reinforce the strength and ductility of the materials.\(^{30}\) Additionally, either one of the hard or soft segments, or both of them are crystallizable, which results in a multi-phase system.

![Diagram of hard and soft segments in PUs](image)

**Figure 1.11** Hard and soft segments in PUs
At ambient conditions, the thermodynamically incompatible polyurethane segments separate into hard domains with rigidity and high polarity and soft domains with flexibility and low polarity. The soft domains are responsible for the elasticity and physical properties at low temperatures, while the hard domains primarily contribute to the strength of the material. These materials also possess excellent processing capability. When the temperature increases, the hard domain softens. Such reduced hard segment interactions at elevated temperature enable the polyurethanes to be thermally processable.

Since physical properties of segmented polyurethanes are strongly influenced by morphological behavior, considerable efforts have been made to study and control the phase separation behavior. Chu and coworkers reported a series of kinetic studies of phase separation of polyurethanes in the early 1990s. They prepared polyurethanes based on hard segments and soft segments with varying
flexibility and molecular weight. The experimental results demonstrated that even with segments that possess similar solubility parameters, the corresponding polyurethanes exhibit dramatically different phase separation behaviors. This is because the kinetic factors greatly affect the process of phase separation. The segments mobility, viscosity, and the segments interactions were reported as the most important controlling factors.

Runt and coworkers used DSC, temperature-controlled Fourier Transform infrared (FTIR) and small-angle X-ray scattering (SAXS) to study the temperature dependence of microphase separation and mixing behavior. They studied segmented polyurethanes based on MDI-BDO hard segments and various soft segments including aliphatic polycarbonate, PTMG, hydroxyl-terminated poly(dimethylsiloxane) (PDMS) and poly(hexamethylenoxide) (PHMG). They found that there was gradual dissolution of the hard domains with increasing temperature. In addition, the SAXS and DSC results suggested that phase separation disappearance at high temperature is related to the softening of hard domains.

Wilkes and his coworkers have systematically probed the effect of hard segment symmetry on the microphase separations and properties of segmented polyurethanes.\textsuperscript{15-17,35} By comparing “symmetric” diisocyanates like para-phenylene diisocyanate (p-PDI) and HDI to “asymmetric” diisocyanate meta-phenylene diisocyanate (m-PDI) and TDI, it was observed that the symmetric diisocyanate based hard segments pack more effectively, which promotes a high level of microphase separation, and results in enhanced mechanical performance.
1.8 Modification of segmented polyurethanes

As stated earlier, one of the most significant advantages of polyurethane materials is their adaptability. By utilizing new components to replace the traditional polyols, isocyanates and chain extenders, polyurethanes can be modified to achieve a wide range of desirable properties.

1.8.1 Modification of segmented polyurethanes with novel chain extenders

Theoretically, polyurethanes can be prepared with only oligomeric polyols and isocyanates, but the addition of chain extenders can help achieve a high molecular weight and increase their hard segment contents. Due to the wide availability of chain extenders, it is considered the most adaptable component in polyurethanes.

Recently, new bulky chain extenders have attracted interest. Zheng et al. prepared polyurethanes using calixarene derivatives as the chain extenders. Calixarenes are a class of molecular host compounds, which are usually used in host-guest chemistry. Calix[4]arene diol is a typical example of calixarene compounds. According to the unique three dimensional basket structure (Figure 1.13), intrinsic receptor properties can be improved by taking advantage of the internal volume of the calixarene structure. It is found that the introduction of calix[4]arene diol into the backbone of polyurethane leads to an improvement of thermal resistance and elongation with less sacrifice of Young’s modulus. The calix[4]arenes in the hard segment of polyurethanes increase the hard segment content and enhance the thermal stability. In addition, the residual hydroxyl groups in calix[4]arenes serve as radical acceptors which also contribute to resistance to thermal degradation. However, the bulky structure of calixarene likely decreases
the intermolecular interactions and leads to decreased tensile strength and Young’s modulus. The utilization of calixarene derivatives for the improvement of polyurethanes can be further investigated. For example, the incorporation of a bulky chain extender with large free volume into polyurethanes is a rarely explored area and has the potential to impart polyurethanes with new properties in host-guest chemistry.

![Calix[4]arene with para t-butyl substituent](image)

**Figure 1.13** Calix[4]arene with para t-butyl substituent

### 1.8.2 Modification of segmented polyurethanes with novel isocyanates

The modification of diisocyanate monomers is not as extensively studied as the chain extenders. One reason is that the isocyanate groups are very reactive towards water, hydroxyl and amine groups at ambient conditions. To reduce the sensitivity, a specially designed tertiary isocyanate was synthesized, which is called TMXDI®. Cody synthesized waterborne polyurethanes with TMXDI aliphatic isocyanate (Figure 1.14). The resulting polyurethanes exhibited excellent toughness and flexibility. The reactivity of isocyanate groups in TMXDI is drastically reduced due to the steric hindrance, which prevent them from reacting with water at room temperature. This feature make TMXDI® a good candidate for water-borne polymers.
1.8.3 Modification of segmented polyurethanes with novel polyols

The most common polyols used in polyurethanes have been discussed in the previous sections. In the last decades, growing attention was paid to the development of new polyols.

Tonelli et al. synthesized perfluoropolyether (PFPE) macrodiols (molecular weight ranging from 1200 g/mol to 2260 g/mol), and incorporated them into polyurethanes with different diisocyanates like MDI and 4,4’-methylenbis(cyclohexyl isocyanate) (HMDI) along with chain extenders such as BDO and 2-ethyl-2-(hydroxymethyl)-1,3-propanediol (TMP). The flexibility of PFPE offers a relatively low $T_g$ ($-120 \, ^\circ\text{C}$), which benefits low temperature properties. For example, the resulting polyurethane material exhibited good dimensional recovery even at $-75 \, ^\circ\text{C}$. Furthermore, the PFPE soft segments enhance the thermal stability by 100 °C in air or nitrogen conditions.

Polycaprolactone (PCL) is widely used as a biodegradable material. Eceiza and coworkers reported the utilization of PCL-PTMG-PCL copolymers (total 2100 g/mol; PTMG block = 1100 g/mol; each PCL block = 500 g/mol) as novel soft segments. They studied the morphological behavior and physical properties by varying the HDI-BDO hard segment content (18-42 wt%). The polyurethanes...
based on these novel soft segments showed excellent biocompatibility and controllable microphase separation. Studies of polyurethanes based on PCL soft segments have also been reported by other researchers.\textsuperscript{40}

Using 1,3-bis(4-hydrobutyl) tetramethyldisiloxane (BHTD) and diethylcarbonate, Runt et al. prepared novel soft segments containing alternating silicone and carbonate blocks (Figure 1.15).\textsuperscript{41} It was found that this soft segment provided good oxidative stability relative to other PDMS-based segmented polyurethanes. Furthermore, the elastic strength and ductility can be tuned by adjusting the MDI-BDO hard segment content.

![Siloxane-carbonate soft segments](image)

**Figure 1.15** Siloxane-carbonate soft segments

### 1.9 Triptycene and applications in polymers

Triptycenes are a series of paddlewheel-shaped molecules with arene units fused to bicycle[2.2.2]octatriene structures (Figure 1.16). Triptycene is the most common member of the iptycene family of molecules, which have the [2,2,2]-ring structures with connected aromatic rings. The initial study was conducted by Bartlett who first synthesized triptycene diol in 1942.\textsuperscript{42} Hart et al. summarized the syntheses of a series of iptycene derivatives and partially demonstrated the nomenclature system of itpcyene monomers (tri-, penta-, etc.).\textsuperscript{43}
Figure 1.16 Structure of basic triptycene unit (1,4-Connection and bridgehead connection)

The initial attempt to synthesize triptycene-containing polymers was in 1969; Hoffmeister et al. synthesized a series of polymers containing bridgehead-substituted triptycene units, including polyurethanes, polyesters, polyamides, and polyoxadiazoles, etc. Clear and colorless triptycene-containing films were obtained with a thermal stability (5% weight loss) around 450 °C. In the last decade, the applications of triptycene and its derivatives have been extensively explored in polymeric materials, with special focuses on high performance polymers and microporous polymers. Swager and coworkers systematically studied the utilization of 1,4-connection iptycene units in the design of high performance polymers. It was found that these triptycene-containing polyesters exhibited enhancement for both stiffness and ductility, which is not commonly observed for polymer modifications since these two properties are typically mutually exclusive.

A new mechanism named “molecular threading and molecular interlocking” was proposed as an explanation for this phenomenon (Figure 1.17). Referring to the structure of triptycene (Figure 1.18), a large internal molecular free volume is present, which is called Internal Molecular Free Volume (IMFV).
With this special configuration, polymers with the triptycene units in the backbone tend to move through the cavities of the triptycene units from adjacent polymer chains and minimize the IMFV. When the triptycene-containing polymer films are stretched, triptycene units gradually approach each other, and eventually are interlocked. The interlocking acts as a physical crosslinker, and enhances the strength and ductility. This interlocking mechanism was described as “molecular barbed wire”, which suggests that the polymer chains tend to minimize the IMFV and provide the driving force for the movement of polymer chains (Figure 1.19).\textsuperscript{51}

Figure 1.17 Molecular interlocking mechanism, adapted from Tsui, N.; Torun, L.; Pate, B.; Paraskos, A.; Swager, T.; Thomas, E. *Adv. Funct. Mater.* **2007**, *17*, 1595-1602. Used with permission of John Wiley and Sons, 2007
The triptycene structure was also introduced into polycarbonates via either physical blending or chemical reaction. The tensile modulus, and yield strength of
commercial lupilon® polycarbonate were enhanced by blending with a low molecular weight, low triptycene content polycarbonate (2 wt%). It was also found that incorporation of 26 wt% of triptycene into polycarbonates improved Young’s modulus, and compressive and tensile strength without an apparent sacrifice of ductility.\textsuperscript{52}

Swager and Wagener et al. synthesized triptycene-containing polyetherolefins via acyclic diene metathesis (ADMET) polymerization.\textsuperscript{53} Their study showed that the $T_g$ of polyoctenamer was increased with higher triptycene content. They also found that adjustment of the amount and orientation of the triptycene units could lead to the enhancement of certain properties, such as stiffness, toughness, or ductility. By comparing polymers containing bridgehead triptycene units or 1,4-connection triptycene units, it appeared 1,4-connection triptycene unit inhibit crystallization of polyethylene chains more efficiently than the bridgehead analog.

However, some recent work suggested that the “molecular interlocking” mechanism and the simultaneous enhancement of strength and ductility are not applied to all of the linear triptycene-containing polymers. Turner et al. incorporated triptycene diol into the copolyesters via melt-phase polymerization. They found the rigidity of triptycene structure increased thermal stability, glass transition temperature and Young’s modulus, but there was a decrease of ductility.\textsuperscript{54}

In addition to the focus on the improvement of mechanical performance, triptycene units are also used for preparation of ion-containing materials. Since there are three aromatic rings in each of the triptycene monomer, it is possible to achieve high sulfonation efficiency with polymers containing sulfonated triptycene
units. Zhang et al. reported a strategy of introducing the triptycene structure into the poly(arylene ether sulfone)s (Figure 1.20).\textsuperscript{55} By taking advantage of highly sulfonated triptycene units, the polysulfones possess high ion exchange capacity (IEC) and proton conductivity in a wide range of humidity at 80 °C. They also showed that the degree of sulfonation can be tuned by gradually varying the ratio between 2,5-triptycenediol (TPD) and bis(4-hydroxyphenyl) sulfone (BHPS). In subsequent work, Zhang prepared polysulfones containing a quaternized ammonium salt of triptycene units.\textsuperscript{56} The resulting polymers were used to obtain flexible and tough membranes via solvent casting, and the high hydroxide conductivity of these membranes suggested their potential application in alkaline fuel cells.
Polyurethane materials offer excellent physical properties including elastic modulus, flexibility, and abrasion resistance, etc. With these properties, polyurethanes are very versatile for a wide spectrum of applications (Table 1.1). The global consumption of urethane products ranging from foams to coatings, etc. is tremendous; it was 9.25 million metric tons in 2000 according to Bayer Corporation statistics. This number increased to 12 million metric tons in 2007, with an average annual growth of 5%.
Among the many applications for polyurethanes, foam has the largest consumption in terms of volume. Despite a decrease in recent years, foams still account for about three quarters of all polyurethane products.\textsuperscript{6,58} There are three main categories for foams including rigid foam, semi-rigid foam and flexible foam, which have different applications.\textsuperscript{59} Rigid foams are usually used as paving materials and water-proof materials in the building and construction industry. Because of their low thermal conductivity, polyurethane foams are also used for heat preservation materials for manufacture of refrigerators. Most of the flexible and semi-rigid foams are utilized as cushions and in packaging material for furniture, as well as for automotive interior specifically in the seats.
Polyurethanes are also used as protective coatings on a large scale. Common applications include furniture and automotive body coatings. Recently, there has been a trend for polyurethane coatings focusing on environmentally friendly coatings, for example, aqueous dispersible polyurethane coatings containing ionic groups.\(^6\)

Although they do not account for a large percentage of product sales in urethane products, elastomers are one of the most common applications for polyurethanes, especially linear segmented polyurethanes.\(^3,31\) Because of the segmented backbones and phase separation behavior, polyurethane elastomers exhibit good elastomeric performance thanks to the physical crosslinking and low \(T_g\) soft segments, and maintain excellent strength due to the contribution from hard segments. Moreover, properties of the elastomers can be easily tailored by changing the type and composition of monomers, which makes them versatile for numerous practical applications. Based on these features, linear polyurethanes are utilized as thermoplastic elastomers, cast elastomers, gels, and elastomeric fibers. Although the quantity is not as enormous as foams or coatings, polyurethane elastomers may be the most versatile product in urethane materials.

Polyurethanes are also used as adhesives, sealants, and binders. Polyurethane adhesives can be applied on a variety of substrates (metal, glass, wood, etc.) because of their excellent adhesion; this feature mostly arises from the hydrogen bonding between the urethane groups in the polymers and the substrates.\(^61\) More recently, waterborne polyurethane ionomers are widely used as environmentally friendly adhesives.\(^62\)
1.11 Summary

The synthesis, processing, microphase separation and structure-property relationship have been extensively studied for the segmented polyurethanes. Many modification methods have been used to control the morphology of segmented polyurethanes, and desirable properties can be obtained for practical applications. Triptycene was used in polymers to achieve increased $T_g$ and enhanced mechanical properties. With bulky structure, the triptycene unit has its potential to modify either the hard segment or soft segment of polyurethanes to provide controllable morphologies such as microphase separation, and crystallization. A fundamental investigation of triptycene-containing segmented polyurethanes is important to broaden the modification of polymers with triptycene moities.

1.12 References


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Chapter 2. Literature Review on Poly(arylene ether sulfone)s and Poly(1,4-cyclohexyldimethylene terephthalate) (PCT)

2.1 Literature review of poly(arylene ether sulfone)s

2.1.1 Overview of poly(arylene ether sulfone)s

Poly(arylene ether sulfone)s (PAES)s are a class of high performance thermoplastic polymers with excellent thermal stability, strength, and high T<sub>g</sub>s.<sup>1-3</sup> The general chemical structure of PAES chains, with the characteristic sulfonyl group, is shown in Figure 2.1. These polymers have exceptional thermal stability up to 500°C or higher. With high glass transition temperatures (normally higher than 180°C), PAESs offer good mechanical properties at ambient or elevated temperatures.<sup>3</sup> PAESs also have excellent hydrolytic stability, which makes them good candidates for medical applications and membranes. In addition, due to their amorphous morphology, they have better processability relative to structurally similar semi-crystalline poly(arylene ether ketone)s (PEEK).<sup>2,4</sup> Thanks to these properties, PAES materials find applications in many different fields such as flame retardant materials, and engineering thermoplastics.<sup>5-11</sup>

![General chemical structure of PAESs](image)

Figure 2.1 General chemical structure of PAESs
Table 2.1 Common commercially available PAESs, adapted from Dizman, C.; Tasdelen, M. A.; Yagci, Y. *Polym. Int.* **2013**, 62, 991-1007. Used with permission of John Wiley and Sons, 2013

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<thead>
<tr>
<th>Structure of PAES</th>
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<th>Trade name (Company)</th>
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<td>Udel (Solvay) Ultrason S (BASF)</td>
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<tr>
<td><img src="image2" alt="Poly(phenyl sulfone)" /></td>
<td>220</td>
<td>Radel (Solvay) Ultrason P (BASF)</td>
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<tr>
<td><img src="image3" alt="Poly(ether sulfone)" /></td>
<td>225</td>
<td>Veradel (Solvay) Ultrason E (BASF)</td>
</tr>
</tbody>
</table>

PAES prepared from bisphenol-A (BPA) and 4,4’-dichlorodiphenyl sulfone (DCDPS) is one of the earliest commercialized polysulfones, marketed in 1966 by Union Carbide under the trade name Udel®. Continued development led to the introduction of biphenol-based Radel® into the market in the early 1970s, by ICI and Union Carbide. The most commonly commercialized PAESs today are listed in Table 2.1.

Due to the absence of crystallinity, most polysulfones suffer from lack of solvent resistance and low dimensional stability at elevated temperatures. These properties restrict their use in certain applications. The low tendency for crystallization in polysulfones primarily arises from incompatible bond angles.
The two major bond linkages in the backbone of polysulfones, the sulfonyl group and the aromatic ether group, have bond angles of 106˚ and 121˚, respectively (Figure 2.2 and Figure 2.3). These linkages result in irregular chain geometry and inhibit efficient packing among the polymer chains, leading to an amorphous morphology. As a comparison, the carbonyl groups in poly(arylene ether ketone)s have bond angles of 121˚, which are close to the bond angles of the aromatic ether groups. Such regularity allows the backbones to adopt an effective conformation to promote crystallization.
2.1.2 Chemistry

2.1.2.1 Polyetherification

Polyetherification, which is a nucleophilic aromatic substitution (S\textsubscript{n}Ar) reaction, is the most widely used approach to prepare polysulfones.\textsuperscript{14} Typical polyetherifications involve reactions between diphenol and dihalide monomers, such as BPA and DCDPS, in the presence of dry potassium carbonate (K\textsubscript{2}CO\textsubscript{3}) in a polar aprotic solvent like dimethylacetamide (DMAc) (Figure 2.4).

![Figure 2.4 Typical synthesis of bisphenol-A-based PAES](image)

Figure 2.4 Typical synthesis of bisphenol-A-based PAES
**Table 2.2 Common names and structures of diphenol monomers**

<table>
<thead>
<tr>
<th>Diphenol monomer (Abbreviation)</th>
<th>Structure</th>
<th>Reference</th>
</tr>
</thead>
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<td>Hydroquinone (HQ)</td>
<td><img src="image" alt="Structure" /></td>
<td>15-17</td>
</tr>
<tr>
<td>4,4’-Dihydroxyl biphenyl (DHBP)</td>
<td><img src="image" alt="Structure" /></td>
<td>18,19</td>
</tr>
<tr>
<td>4,4’-Dihydroxyl ρ-terphenyl (DHTP)</td>
<td><img src="image" alt="Structure" /></td>
<td>20</td>
</tr>
<tr>
<td>4,4’-Isopropylidene diphenol (Bisphenol-A)</td>
<td><img src="image" alt="Structure" /></td>
<td>15,21</td>
</tr>
<tr>
<td>4,4’-Sulfonyldiphenol (Bisphenol-S)</td>
<td><img src="image" alt="Structure" /></td>
<td>22</td>
</tr>
</tbody>
</table>

The feed ratio between diphenol and dihalide can be varied to control the molecular weight of PAESs and end groups. Various diphenol monomers have been developed for the preparation of PAESs for specific applications. The most common ones are summarized in the Table 2.2. The choice of diphenol monomers enables the adjustment of the properties of polysulfones, and makes them adaptable to a wide range of applications.
A strong base like aqueous sodium hydroxide can be used to obtain the diphenolate anion (called strong base approach), but this method is not favored because strong bases cause hydrolysis of dihalides, which can prevent the polymer from achieving high molecular weights, and some hydroquinone and biphenol salts are not completely soluble during the reactions. In addition, the stoichiometry between the monomers and bases needs to be controlled strictly to obtain high molecular weight polymers. Limitations of the strong base approach prompted researchers to develop alternative methods. McGrath and coworkers systematically studied the synthesis of polysulfone with K$_2$CO$_3$.\textsuperscript{18,24,25} A comparison between potassium hydroxide (KOH) and K$_2$CO$_3$ revealed that, as a weak base, K$_2$CO$_3$ minimizes the occurrence of side reactions and hydrolysis without sacrificing the ability to facilitate polymerization reactions.\textsuperscript{24} Furthermore, control of the end groups and molecular weight is also feasible. However, there are still a few disadvantages with this method. For example, the slow reaction rates of this method can be a concern when employed in industrial production of the polymer.\textsuperscript{3}

The mechanism of nucleophilic substitution has been well studied.\textsuperscript{26} As illustrated in Figure 2.5, the nucleophilic aromatic substitution mechanism consists of two steps. In the first step, the electron-withdrawing effect from the halide and activating sulfonyl group makes the carbon next to the halide susceptible to the nucleophilic attack, and a Meisenheimer complex is formed as an intermediate.\textsuperscript{27} This step is reversible and much slower than the following step, which make it the rate-determining step. The halide is then released in the second step. The effect
of halides on the rate of polymerization is not based on the basicity, but instead, on the electron-withdrawing ability.\textsuperscript{28} The reactivity of halide substituents is in the order $\text{F}^-$ >> $\text{Cl}^-$ > $\text{Br}^-$ > $\text{I}^-$. Although $\text{F}^-$ is a poor leaving group, it stabilizes the Meisenheimer intermediate with a strong inductive electron-withdrawing effect and facilitates the rate-determining step.

![Diagram of nucleophilic aromatic substitution mechanism](image)

Figure 2.5 Nucleophilic aromatic substitution mechanism

**2.1.2.2 Polysulfonylation**

Polysulfonylation occurs via electrophilic aromatic substitution (Friedel-Crafts sulfonylation). With Friedel-Crafts catalysts like $\text{AlCl}_3$, $\text{FeCl}_3$, $\text{AlBr}_3$, etc., a reaction can occur, either between aromatic sulfonyl chloride and phenyl ether monomers (Figure 2.6.a) or between monomers containing two different functional groups (Figure 2.6.b). Jennings and coworkers reported that when using elevated temperatures, high molecular weight polysulfones can be obtained with minimal
amounts of the Lewis acid (1-5 mol%). This method has a decreased chance of side reactions.

Figure 2.6 Typical polysulfonylation synthesis of PAESs, adapted from Dizman, C.; Tasdelen, M. A.; Yagci, Y. Polym. Int. 2013, 62, 991-1007. Used with permission of John Wiley and Sons, 2013
Figure 2.7 Friedel-Crafts sulfonylation mechanism

The mechanism of sulfonylation reactions is illustrated in Figure 2.7. The Lewis acid, AlCl₃ for example, is used to produce the sulfonylium cation ArSO₂⁺. The cation can be subsequently attacked by the π electrons in the aromatic ring and generate an intermediate. The aromatic ring then eliminates one of the protons to regain aromaticity. As a result, one proton is substituted by the sulfonylium cation and then a sulfonylated product is obtained. However, this mechanism suggests a possibility of irregularity. A para position substitution is normally favored, but not guaranteed, since the sulfonylium cation can substitute protons at different
positions on the aromatic ring. If an electron-donating group is present on the phenyl monomer, ortho and para positions will be directed in the substitution reaction, even though para is favored due to steric hindrance. Regardless of substitution, high reaction temperature, high catalyst concentration or highly reactive monomers can increase the chance of ortho substitution, in addition to other side reactions that can cause irregularity in the polymer chain.\textsuperscript{30,31}

The polysulfonylation approach found early success in commercial polysulfone products as engineering polymers. The 3M company introduced Astrel\textsuperscript{®} into the market in 1967.\textsuperscript{32} However, this method is limited for industrial manufacturing due to several reasons. The side reaction problem was discussed above, for example, undesirable substitution or branching at ortho positions of nucleophilic aromatic units may occur. Moreover, unlike polyetherification, this approach is only applied to a few monomers, further restricting its utilization.

2.1.3 Properties and Applications of Poly(arylene ether sulfone)s

PAESs are well-known for their excellent thermal stabilities. Although there are a number of monomers used in the preparation of PAESs, most of them show little degradation below 420 \textdegree C, even in the presence of air.\textsuperscript{2} They also possess high oxygen indices and low smoke emission during burning, which makes them good candidates for flame-retardant materials.\textsuperscript{33}

The high T\textsubscript{g} of this class of polymers imparts good mechanical properties within a wide temperature window, normally from -100 \textdegree C to 175 \textdegree C.\textsuperscript{24} The high T\textsubscript{g} is ascribed to the chain rigidity.\textsuperscript{34,35} Because of the delocalization effect, the \(\pi\) electrons in the aromatic rings of PAESs can be induced towards the sulfonyl
groups. Consequently, each of the carbon sulfur bonds bear more than one pair of electrons and obtains a partial double bond character, which increases the rotational barrier of the carbon sulfur bond (Figure 2.8). In addition, the aromatic structures along the backbone also contribute to the chain rigidity. A low temperature relaxation was observed at around -100 °C for polysulfone based on bisphenol-A. Previous studies suggest that this behavior corresponds to the motion of the aromatic units, combined with oscillational motion of the nearby polar linkages such as sulfonyl or aromatic ether groups.\textsuperscript{36,37} This low temperature relaxation can benefit the impact strength, since energy can be partially absorbed by bond rotation.

![Figure 2.8 Resonance structure of bisphenol-A-based PAES](image)

Table 2.3 summarizes the selected properties of some typical commercially available polysulfones. PAESs also possess excellent electrical properties, which allows them to find applications for electric and electronic parts. As shown in Table 2.3, many of the common PAES materials exhibit good dielectric strength. Polysulfones can be melt processed due to their excellent thermal stability and amorphous morphology. They can also be solution processed because they are
generally soluble in organic solvents such as chloroform, dimethylformamide (DMF), etc.

Table 2.3 Selected chemical and physical properties of the typical commercially available polysulfones*

(Data adapted from Solvay Advanced Polymers, material datasheet)

<table>
<thead>
<tr>
<th></th>
<th>Udel® P-1700</th>
<th>Radel® R-5000</th>
<th>Acudel® 22000</th>
<th>Veradel® AG-320</th>
<th>ASTM Test method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g/cm³)</td>
<td>1.24</td>
<td>1.29</td>
<td>1.51</td>
<td>1.28</td>
<td>D792</td>
</tr>
<tr>
<td>Water Absorption at 24 hr (%)</td>
<td>0.3</td>
<td>0.4</td>
<td>0.4</td>
<td>0.3</td>
<td>D570</td>
</tr>
<tr>
<td>Glass Transition Temperature (°C)</td>
<td>185</td>
<td>220</td>
<td>220</td>
<td>220</td>
<td>DSC</td>
</tr>
<tr>
<td>Heat Deflection Temperature at 1.84 MPa (°C)</td>
<td>174</td>
<td>207</td>
<td>214</td>
<td>197</td>
<td>-</td>
</tr>
<tr>
<td>Tensile Strength (GPa)</td>
<td>70</td>
<td>70</td>
<td>105</td>
<td>77</td>
<td>D638</td>
</tr>
<tr>
<td>Tensile Modulus (GPa)</td>
<td>2.48</td>
<td>2.34</td>
<td>5.70</td>
<td>2.69</td>
<td>D638</td>
</tr>
<tr>
<td>Tensile Elongation at break (%)</td>
<td>50-100</td>
<td>60-120</td>
<td>3.2</td>
<td>25-75</td>
<td>D638</td>
</tr>
<tr>
<td>Flexural Modulus (GPa)</td>
<td>2.69</td>
<td>2.41</td>
<td>5.17</td>
<td>2.76</td>
<td>D790</td>
</tr>
<tr>
<td>Tensile Impact (kJ/m²)</td>
<td>420</td>
<td>400</td>
<td>65</td>
<td>-</td>
<td>D1822</td>
</tr>
<tr>
<td>Dielectric Strength (kV/mm)</td>
<td>17</td>
<td>15</td>
<td>17</td>
<td>18</td>
<td>D149</td>
</tr>
</tbody>
</table>

* See Table 2.1 for some representative structures of polysulfones
2.1.4 Modification of PAESs

Despite the wide range of excellent properties, some drawbacks limit the practical applications of PAESs. For instance, due to their amorphous morphology, the PAES materials have poor solvent resistance and dimensional stability at elevated temperature. The hydrophobicity of PAESs also limits their blood compatibility, and inhibits their use in blood filtration membranes.\textsuperscript{38-40}

Considerable efforts have been made to alter or adjust the properties of PAESs for specific applications. Many studies focus on the chemical modification of the backbones using three routes: (1) new diphenol monomers; (2) new dihalide monomers; and (3) the post-functionalization of preformed polymers.\textsuperscript{3}

2.1.4.1 Modification of diphenol and dihalide monomers

Modification of PAES properties by incorporation of new monomers can provide precise control of the backbones of PAESs. However, the added functional groups can potentially affect the polymerization process, or induce some side reactions.\textsuperscript{3} To achieve successful PAES modification with new monomers, the chemical structure and the functional groups should be carefully chosen or designed. Table 2.4 and

Table 2.5 list a group of examples of diphenol and dihalide monomers and their derivatives used in PAESs. The table also suggests diphenols that can be possibly used in PAES preparation. A comprehensive compilation of diphenol and dihalide monomers used in PAESs was summarized by Cotter.\textsuperscript{41}
Table 2.4 Various diphenol monomers used in PAES preparation, adapted from Dizman, C.; Tasdelen, M. A.; Yagci, Y. *Polym. Int.* **2013**, *62*, 991-1007. Used with permission of John Wiley and Sons, 2013

<table>
<thead>
<tr>
<th>Diphenols</th>
<th>Representative chemical structure</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluoro</td>
<td><img src="image" alt="Fluoro chemical structure" /></td>
<td>42,43</td>
</tr>
<tr>
<td>Acid</td>
<td><img src="image" alt="Acid chemical structure" /></td>
<td>44-47</td>
</tr>
<tr>
<td>Allyl</td>
<td><img src="image" alt="Allyl chemical structure" /></td>
<td>48-51</td>
</tr>
<tr>
<td>Phenyl</td>
<td><img src="image" alt="Phenyl chemical structure" /></td>
<td>52-55</td>
</tr>
<tr>
<td>Triptycene</td>
<td><img src="image" alt="Triptycene chemical structure" /></td>
<td>56,57</td>
</tr>
<tr>
<td>Cyclohexylidene</td>
<td><img src="image" alt="Cyclohexylidene chemical structure" /></td>
<td>58</td>
</tr>
<tr>
<td>Diphenols</td>
<td>Representative chemical structure</td>
<td>Reference</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>-----------------------------------</td>
<td>-----------</td>
</tr>
<tr>
<td>Trimethylcyclohexylidene</td>
<td><img src="image" alt="Structure" /></td>
<td>59</td>
</tr>
<tr>
<td>Fluorenylidene</td>
<td><img src="image" alt="Structure" /></td>
<td>60,61</td>
</tr>
<tr>
<td>Diphenylethylene</td>
<td><img src="image" alt="Structure" /></td>
<td>62</td>
</tr>
<tr>
<td>Cyclohexane-diylbis(methylene)</td>
<td><img src="image" alt="Structure" /></td>
<td>63</td>
</tr>
</tbody>
</table>

Table 2.5 PAESs based on novel dihalide monomers, adapted from Dizman, C.; Tasdelen, M. A.; Yagci, Y. *Polym. Int.* **2013**, *62*, 991-1007. Used with permission of John Wiley and Sons, 2013

<table>
<thead>
<tr>
<th>Dihalides</th>
<th>Representative chemical structure</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfone</td>
<td><img src="image" alt="Structure" /></td>
<td>64-68</td>
</tr>
<tr>
<td>Amine</td>
<td><img src="image" alt="Structure" /></td>
<td>69</td>
</tr>
</tbody>
</table>
2.1.4.2 Block copolymers with PAES segments

In addition to using modified monomers, introduction of oligomer blocks into the PAES backbone is another method to adjust the properties to meet requirements for certain applications. In order to implement this approach, the preparation of oligomers with functional end-groups is necessary in controlling the structure and properties of final product.

A considerable number of studies have focused on incorporation of flexible segments in the PAESs to obtain block copolymers. Early copolymerization work was done by Noshay et al.\textsuperscript{70} Utilizing the reaction between the silylamines of polydimethylsiloxane (PDMS) and the hydroxyl end groups of PAES oligomers, PDMS-b-PAES can be obtained with good hydrolytic stability. Such copolymers also display desirable properties within a wide temperature window thanks to the combination of flexible PDMS segments and rigid PAES segments. To further improve the mechanical properties, Cureton and Turner developed similar segmented polymers with terphenol monomers in the PAES segment.\textsuperscript{71} The rigid terphenol monomers were found to increase $T_g$ and tensile strength when compared to the similarly structured commercial product Udel\textsuperscript{®} product.

Poly(tetramethylene glycol) (PTMG) is another oligomer widely used to enhance properties, especially low temperature properties for copolymers. Pospiech et al. investigated the synthesis of PTMG-PAES block copolymers via melt transesterification (Figure 2.9), resulting in improved hydrophilicity.\textsuperscript{72} They reported that the copolymer was water soluble or swellable only when the molecular weight of the PTMG blocks was higher than polysulfone blocks. In
another paper, they found that the phase separation behavior of these copolymers depended on the molecular weight of the blocks. With a low molecular weight PTMG block (1150 g/mol), only one $T_g$ was observed, suggesting a phase mixing morphology. When the molecular weights of both PAES and PTMG were above 2000 g/mol, the polymers segregated into amorphous PAES and PTMG domains along with crystallized PTMG domains.

![Figure 2.9 Synthesis of PTMG-PAES copolymers via melt transesterification](image)

With a structure similar to the PTMG blocks, poly(ethylene glycol) (PEG) is also used to modify polysulfones. Due to its excellent biocompatibility, PEG has attracted widespread interest for biomaterial applications. Ting and Hancock studied the synthesis of tri-block copolymers with a central polysulfone block end-capped by monomethylpoly(ethylene glycol) (Me-PEG). Synthesis of the PEG-PAES copolymer was illustrated in Figure 2.10. In their following work, segmented PAES-$b$-PEG copolymers with 33-35 wt% of PEG were synthesized. By comparing the dynamic water contact angles of PAES-$b$-PEG ($33 \pm 2$) and PAES ($111^\circ \pm 3$), they suggested the hydrophilicity of PAES-$b$-PEG was enhanced by the
incorporation of PEG segments, which can be useful for fabrication of membranes for medical devices.

\[
\begin{align*}
\text{HO-(CH}_2\text{CH}_2\text{O)}_n\text{Me} & \quad + \quad \text{Cl-}\text{SO-}\text{Cl} \quad + \quad \text{HO-}\text{CH}_2\text{OH} \\
\text{165-190}\degree\text{C} & \quad \text{K}_2\text{CO}_3 \\
& \quad \text{NMP/Toluene} \\
\text{Me(OCH}_2\text{CH}_2\text{O)}_n\text{SO-}\text{O} & \quad \text{O} \quad \text{SO-} \quad \text{O} \quad \text{O} \quad \text{O} \quad \text{SO-} \quad \text{O} \quad \text{O} & \quad \text{CH}_2\text{CH}_2\text{O)}_n\text{Me}
\end{align*}
\]

Figure 2.10 Synthesis of PEG-PAES block copolymers

Unlike the flexible low \( T_g \) PDMS, PTMG and PEO oligomers, other segments with high \( T_g \)s are also incorporated into the PAES, such as polycarbonates (PC) and polyesters.\(^{76}\) Since this topic is closely related to our project, we will discuss these block copolymers in more detail in the next section.

### 2.1.5 Semi-crystalline PAESs

PAESs are widely used as high performance engineering thermoplastic materials due to their high \( T_g \), excellent thermal stability and mechanical properties. However, some negative aspects such as low organic solvent resistance limit the applications of PAES.

One common method to compensate the drawbacks of PAES is blending with other materials to impart desirable chemical and physical properties. Blending crystallizable polymers, such as poly(ether ether ketone) (PEEK) and polyesters, with PAES have previously been reported in the literature.\(^{20,77}\) This is a viable
approach to introduce crystallinity into the polymer mixtures and reinforcing polysulfones, making it of great interest to the industry. Nevertheless, compatibility between two polymers can dramatically influence the morphologies and properties of the blended system. Many efforts have been made to study the compatibility and phase separation behavior of polymer blends between crystallizable polymers and polysulfones.\textsuperscript{78-81} Dai et al. reported that the use of long random copolymers can enhance the compatibility of two immiscible homopolymers.\textsuperscript{82} Noolandi et al. also studied the difference between using di-block or tri-block, and multiblock copolymers as the compatibilizer in binary polymeric systems (Figure 2.11). Based on this work, Häußler et al. used polysulfone-polyester multiblock copolymers to increase compatibility of the binary blend of polysulfone and liquid crystalline polyester (LCP).\textsuperscript{83} They found that, when the molecular weight of the copolymer segments was above a critical value, the multiblock copolymers offer improvement to the compatibility of two immiscible polymers, and the resulting blend exhibited enhanced mechanical strength.

Although polymer blending is a convenient method for mixing two or more polymers, incompatibility between the components can cause some level of phase separation and lead to a decrease in mechanical properties. In contrast, chemically linked multiblock copolymers not only provide the ability to combine the properties of different polymers, but also enable more controllable property tailoring through variation of the block structure and length. Therefore, the preparation of multiblock copolymers containing polysulfone and other polymers has attracted growing interest.
Due to its similar structure, PEEK is a desirable candidate to copolymerize with PSU. Because of the regular chain architecture, PEEK is one of a class of semicrystalline polymers, which can be used to improve the solvent resistance of PSU. Moreover, the relatively low $T_g$ of PEEK can also be increased by copolymerizing with the rigid polysulfones. Kricheldorf et al. and Wu et al. conducted early work synthesizing PSU-PEEK.\textsuperscript{86,87} It is also reported that transesterification may occur if monomers or oligomers containing hydroxyl groups present, which can cause molecular weight decrease or rearrangement.\textsuperscript{88,89}

In recent years, other crystallizable moieties have been inserted into the backbone of PSU to prepare semicrystalline PAES. Turner and coworkers reported that the replacement of 4,4$'$-dihydroxybiphenyl (BP) by 4,4$'$-dihydroxyterphenyl (DHTP) can be used to impart crystallinity into the PAES system. The segmented PSU containing 50 mol\% of BP and 50 mol\% of DHTP exhibited a melting peak at 320°C in the first heating cycle when analyzed by DSC.\textsuperscript{13} Gaymans et al. incorporated monodisperse amide segments into a copolymer based on PAES via both solution and melt polymerization.\textsuperscript{12} High crystallinity can be obtained from the amide segments (92\%-97\%), along with improved dimensional and solvent resistance relative to the polysulfone homopolymers. Dennis et al. prepared multiblock copolymer based on PAES and poly(butylene terephthalate) (PBT), tunable crystallinity was achieved by incorporation of PBT segments when the composition of PAES segment was lower than 50 wt\%.\textsuperscript{90}
2.2 Literature review of poly(1,4-cyclohexyldimethylene terephthalate) (PCT)

2.2.1 Structures and properties of PCT

PCT is a polyester widely used in packaging materials, food containers, precision electronic components, etc. PCT possesses a higher heat deflection temperature (HDT) around 260 °C when compared to similar polymers such as PBT (213 °C) and poly(ethylene terephthalate) (PET) (224 °C). This feature makes PCT a good candidate for high-temperature applications. However, due to high $T_m$, a high processing temperature of PCT is required. In order to improve the processability of PCT materials, isophthalic acid (IPA) is added to modify the crystallization temperature (Figure 2.12).\textsuperscript{91}

\begin{center}
\includegraphics[width=0.5\textwidth]{figure212.png}
\end{center}

Figure 2.12 Modification of PCT by isophthalic acid

PCT is normally prepared with dimethyl terephthalate (DMT) and 1,4-cyclohexanediol (CHDM); the monomers and general structure of PCT are shown in Figure 2.13.\textsuperscript{92}
There are two configurations of CHDM, \textit{cis} and \textit{trans}. Both configurations can experience ring flips and adopt boat or chair conformations that manifest as a secondary relaxation detected by dynamic mechanical analysis (DMA) (Figure 2.14).\textsuperscript{93,94}
The symmetry difference between cis- and trans-CHDM can affect the polymer chain packing and crystallization. It is reported that varying the molar ratio of the two isomers can adjust crystallization behavior and melting temperature of the CHDM-containing polyesters.\textsuperscript{95} As shown in Figure 2.15, the melting temperature of PCT proportionally increases with an increase of the molar ratio of trans-CHDM from 251°C to 315°C. Isomerization of cis- and trans-CHDM has been studied and disclosed in patents.\textsuperscript{96,97} The most common commercially available CHDM, which is a mixture of 30/70 cis/trans produced by Eastman Chemical Company.

![Figure 2.15 PCT melting temperature of polyesters dependence on the molar ratio of cis/trans CHDM, adapted from Kibler, C. J.; Bell, A.; Smith, J. G. J. Polym. Sci. Part A: Gen. Papers 1964, 2, 2115-2125. Used with permission of John Wiley and Sons, 2003](image-url)
2.2.2 Polymers modified by PCT

Early utilization of CHDM monomer involved partially replacing the ethylene glycol (EG) in the PET backbones to adjust the crystallization of PET\textsuperscript{98}. It is reported that even low levels of CHDM, less than 5 mol\%, improve the stretch blow molding properties of PET and make it more widely useful for container applications.\textsuperscript{92}

Based on the study of PET and PCT, modifications have been implemented to combine or tune the properties of these two polymers, resulting in glycol modified PCTG and PETG. These polymers have the same general structure but different EG and CHDM content (Figure 2.16).

![Figure 2.16 General structure for PCTG (EG mol\%<50) and PETG (EG mol\%>50)](image)

Blending PCT with other polymers for modification has also been studied, for example, with polyvinylphenol (PVPh) and PC.\textsuperscript{99} It was reported the cyclohexylene structure in PCT should be reduced to a low content to achieve desirable miscibility.\textsuperscript{100,101}
2.3 **Summary**

Chemical structure, preparation and modification of high performance PAES materials have been studied previously. Introduction of crystallinity into amorphous PAESs improves chemical resistance and dimensional stability at high temperature. Semicrystalline PAESs can be prepared by either polymer blending or copolymerization with crystallizable polymer segments. PCT has excellent crystallizability. It also possesses low temperature relaxation, which can potentially enhance impact strength of polymers. Study of synthesis and properties of PAES-PCT multiblock copolymer are promising to obtain tunable crystallinity of PAES based polymers, and achieve desirable properties for applications as engineering plastics and more.

2.4 **References**


(51) Qi, Y.; Ding, J.; Day, M.; Jiang, J.; Callender, C. L. Polymer 2006, 47, 8263.


(56) Zhao, Z.; Gong, F.; Zhang, S.; Li, S. J. Power Sources 2012, 218, 368.


3.1 Abstract

Segmented polyurethanes based on poly(tetramethylene glycol) (PTMG) of 1000 g/mol were synthesized using a two-step procedure. Various hard segments were obtained using hexamethylene diisocyanate (HDI) or 4,4'-methylenedibis(phenyl isocyanate) (MDI) as the diisocyanates and hydroquinone bis(2-hydroxyethyl)ether (HQEE) or triptycene-1,4-hydroquinone bis(2-hydroxyethyl)ether (TD) as the chain extenders. The effect of rigidity and bulkiness of the hard segments on morphology, thermal and mechanical properties were studied. Fourier transform infrared (FTIR) suggested that hydrogen bonding interactions were weakened in the presence of the bulky triptycene-containing hard segments compared to HQEE-based hard segments. Variable temperature FTIR demonstrated that hydrogen bonds completely dissociate at around 170 °C for polyurethanes chain extended by HQEE compared to around 110°C for their TD analogues. Polyurethanes based on MDI and TD displayed microphase mixing behavior based on atomic force microscopy (AFM) and small angle X-ray scattering (SAXS). When HDI was used as the diisocyanate in the TD chain extended polyurethane, enhanced microphase separation was observed with mechanical properties comparable to those of the MDI analogues with HQEE.
3.2 Introduction

Polyurethanes (PU) constitute a broad class of polymers for various applications such as elastomers, adhesives, foams, etc. Among different types of polyurethanes, linear segmented polyurethanes are of importance since their physical and chemical properties can be easily tailored by changing the chemical composition, segment molecular weight, etc.\(^1\) The segmental structure of these polyurethanes, with alternating hard and soft segments along the backbone, offers control of unique morphologies and properties. The hard segments, which are of relatively low content, can organize to form domains. These hard domains are dispersed in the soft matrix and act as physical or virtual crosslinks. The soft segment regions can benefit mechanical properties at low temperature.\(^2\) Despite numerous studies focusing on preparation and characterization of new polyurethanes, improvements in polyurethane properties, such as mechanical properties, still receive considerable attention since their scientific implications and commercial applications keep expanding.\(^3\) The most common approach to prepare high performance polyurethanes is incorporating unique chemical structures into the polymer chains to tailor various properties for specific applications.\(^4\)-\(^6\)

The effect of the hard segment on morphology and properties of segmented polyurethanes has been widely studied. Polyurethanes derived from various diisocyanates and chain extenders can result in different morphological structures and physical properties. Chu and coworkers investigated the dependence of microphase separation on the flexibility of diisocyanates.\(^7\),\(^8\) They observed that
4,4'-methylenebis(phenyl isocyanate) (MDI) gave rise to a partially microphase-mixed morphology while 1,6-hexamethylene diisocyanate (HDI) resulted in increased microphase separation. Due to the larger solubility parameter difference between MDI and soft segments such as poly(tetramethylene glycol) (PTMG) or polycaprolactone (PCL), thermodynamic effects suggest a more distinct microphase separation for the MDI based polyurethane. However, greater mobility introduced by the incorporation of flexible HDI can enhance microphase separation, which suggests that microphase separation is at least also greatly influenced by kinetic factors such as hard segment mobility rather than purely thermodynamic factors. Lee and coworkers studied polyurethanes based on a series of diisocyanates. They found that the hard segments containing aromatic diisocyanates such as toluene diisocyanate (TDI) and MDI were normally more miscible with the PTMG soft segments than aliphatic diisocyanates such as isophorone diisocyanate (IPDI) and HDI. It is also reported that chain extenders can be specially designed to impart particular chemical and physical properties to the polyurethanes. Gong et al. synthesized polyurethanes with calix[4]arene derivatives as new types of chain extenders. These large bulky chain extenders provide potential applications as metal ion sequestrants and ion selective substrates. Polyurethanes containing calix[4]arene derivatives exhibited lower tensile strength and modulus when compared to polyurethanes chain extended by 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA). It was proposed that this behavior was due to the bent chain conformation of the calix[4]arene structure which introduced free volume and decreased the intermolecular forces, especially
hydrogen bonding interactions. Polyhedral oligomeric silsesquioxanne (POSS) was also introduced into the hard segments of polyurethanes either along the backbone or as the side chains.\textsuperscript{13,14} It was found that the polyurethanes containing POSS in the hard segments as side chains exhibited a wider rubbery plateau regime than the non-POSS analogue. It was proposed that the crystallized POSS hard blocks acted as physical crosslinks and provided further reinforcements.

Previous research has reported that triptycene and its derivatives can be introduced into various polymers to prepare new functional materials.\textsuperscript{15-19} The study of triptycene-containing polymers started in the 1960s, for the purpose of preparing thermally stable polymers; a variety of polymers based on triptycene units were synthesized and characterized.\textsuperscript{20} In this early research, bridgehead substituted triptycene derivatives were used to prepare polyesters, polyurethanes, and polyamides. Polyurethane films obtained in this initial work were brittle due to stiffness of polymer chains and the relatively low molecular weight indicated by the inherent viscosity. Recently, Swager and his coworkers incorporated triptycenes into polyesters, polycarbonates, and other polymers.\textsuperscript{21-25} In most of their work, 1,4-benzene substituted triptycene rather than bridgehead substituted triptycene was used to increase free volume. Due to the three-dimensional propeller shape of triptycene units with large mass (254.11 g/mol), polymers with the triptycene structures are proposed to allow the flexible chains to move through the clefts in the triptycene units for the purpose of reducing free volume. Simultaneous enhancement of strength and ductility can also be obtained when triptycene units interlock with each other in polyesters and other polymer systems.\textsuperscript{26} In our group,
a new triptycene primary diol, triptycene-1,4-hydroquinone-bis(2-hydroxyethyl) ether (TD) (Scheme 3.1), was prepared and incorporated into copolyesters via melt polymerization. It was found that there were increases in thermal stability and glass transition temperature in comparison to the non-triptycene controls. These results suggested that the highly aromatic content of triptycene units impart rigidity and bulkiness into the copolyester system.

Scheme 3.1 Structure of triptycene-1,4-hydroquinone bis(2-hydroxyethyl) ether (molecular weight: 374.43 g/mol)

To our knowledge, triptycene-containing segmented polyurethanes have not been explored. In this paper, TD is utilized as a chain extender for polyurethanes in an effort to understand the effect of the bulky triptycene unit on the morphologies and properties of segmented polyurethanes with triptycene units being part of the hard segments. Polyurethanes using hydroquinone bis(2-hydroxyethyl)ether (HQEE) as a chain extender were also synthesized for the purpose of comparison. It is worth mentioning that the large molecular weight of the triptycene unit can increase hard segment content significantly when compared to the non-triptycene analogues. Two types of diisocyanates, HDI and MDI, were also used to prepare the hard segments. FTIR was used to investigate the hydrogen bonding
interactions. TGA, DSC, DMA, SAXS and AFM were employed to study the properties and morphologies of the DMF solution cast polyurethane films.

3.3 Experimental

3.3.1 Materials

Poly(tetramethylene glycol) oligomer (Terathane, DuPont) with a number average molecular weight of 1000 g/mol, and hydroquinone bis(2-hydroxyethyl)ether (HQEE, 98%) were purchased from Aldrich. 4,4’-methylenebis(phenyl isocyanate) (MDI, 99.5%) was kindly provided by Bayer MaterialScience and used as received. 1,6-Hexamethylene diisocyanate (HDI, 98%) was purchased from Alfa Aesar and used as received. 1,4-dihydroxy triptycene was kindly provided by ICx technologies, Inc (now FLIR Systems, Inc). A new triptycene diol (TD), triptycene-1,4-hydroquinone bis(2-hydroxyethyl)ether was previously synthesized in our group.27 PTMG, HQEE and TD were dried under vacuum for 12 h at 60 °C before use. Anhydrous dimethylformamide (DMF, Aldrich, ≥99.9%) and anhydrous tetrahydrofuran (THF, Aldrich, ≥99.9%) were used as received. Dibutyltin dilaurate (DBTDL, 95%), purchased from Aldrich, was dissolved in anhydrous THF to prepare a 1 wt% solution.

3.3.2 Instrumentation.

$^1$H NMR spectra were recorded on a Varian INOVA 400 MHz spectrometer at room temperature using deuterated dimethyl sulfoxide ($d$-DMSO) and deuterated chloroform ($d$-CDCl$_3$) as the solvents. $^1$H NMR spectra were used to confirm the structure and molecular weight of prepolymer which were PTMG end-capped by diisocyanates. FTIR data were obtained on a Varian 670-IR spectrometer (DTGS
detector) equipped with a Pike Technologies variable temperature GladiATR™ attachment (diamond crystal). The spectra were collected at ambient condition with a resolution of 4 cm⁻¹, and 32 scans were averaged. For variable temperature FTIR experiments, the spectra were collected every 10 °C starting from 30 to 160 °C with a temperature ramp of 1 °C/min. The molecular weights and molecular weight distributions were measured by size exclusion chromatography (SEC) in N-methyl-2-pyrrolidone (NMP) with 0.05 LiBr at 30 °C on a Waters Alliance model 2690 chromatograph equipped with a Waters HR 0.5+ HR2+ HR3+ HR 4 styrage column set. Mono-disperse polystyrene standards were used to construct a universal molecular weight calibration curve. A Viscotek refractive index detector and a viscometer were used for the molecular weight determination.

Thermogravimetric analysis (TGA) was performed using a TA Instrument TGA 2950 with a heating ramp of 10 °C/min under nitrogen. Differential scanning calorimetry (DSC) data were obtained on a TA Instruments Q 2000 with a nitrogen flow of 40 mL/min with a heating rate of 10 °C/min. Glass transition temperatures (Tg) were determined as the midpoint of transition in the second heating cycle after the samples were quenched at 50 °C/min during the cooling cycle. Tensile analysis was performed on an Instron Model 4400 Universal Testing System at ambient conditions. The film samples were stamped into dog bone shape specimens with dimension of 40 × 4 × 0.4 mm (length × width × thickness) with a die according to ASTM D3368 specifications. Specimens were tested with a cross-head rate of 50 mm/min at ambient conditions using an initial grip-to-grip separation of 15 mm. The repeated tensile test results were an average value of at least five specimens.
Dynamic mechanical analysis (DMA) were performed on a TA Instruments Q800 dynamic mechanical analyzer in the film tension mode at a frequency of 1 Hz and a temperature ramp of 2 °C/min over the range from -130 to 130°C. Atomic force microscopy (AFM) measurements were conducted on a Veeco MultiMode AFM in a tapping mode at room temperature on the free air surface of films. SAXS experiments were performed using a Rigaku S-Max 3000 3 pinhole SAXS system, equipped with a rotating anode emitting X-ray with a wavelength of 0.154 nm (Cu Kα). The sample-to-detector distance was 1603 mm, and the q-range was calibrated using a silver behenate standard. Two-dimensional SAXS patterns were obtained using a fully integrated 2D multiwire, proportional counting, gas-filled detector, with an exposure time of 1 hour. The SAXS data were corrected for sample thickness, sample transmission and background scattering. All the SAXS data were analyzed using the SAXSGUI software package to obtain radically integrated SAXS intensity versus scattering vector $q$, where $q=(4\pi/\lambda)\sin(\theta)$, $\theta$ is one half of the scattering angle and $\lambda$ is the wavelength of X-ray.

3.3.3 Synthesis of Polyurethanes.

Polyurethanes were prepared by the prepolymer method which creates uniform and small size hard domains. All of the polyurethanes were synthesized in the same manner, and the synthesis of the polyurethane based on MDI and TD is given here as an example. In the first step, PTMG (2.5 g, 2.5 mmol) and MDI (1.31 g, 5.25 mmol) were charged in a 100 mL three-necked round bottom flask under argon. The flask was equipped with a water condenser, an overhead mechanical stirrer, and an addition funnel. The flask was heated to 70°C with stirring until all
solids had melted to give a clear liquid. Stirring was continued for 3 h. \( ^1 \text{H NMR} \) spectra were used to confirm the complete consumption based on the disappearance of hydroxyl group peak around 2.5 ppm in the \( ^1 \text{H NMR} \) spectra. In the second step, TD (0.94 g, 2.5 mmol) was dissolved in 24 mL anhydrous DMF and added dropwise into the reaction system. The chain extension proceeded at 80°C for 24 h. FTIR was used to confirm that the isocyanate groups were completely reacted. Polyurethanes based on HDI followed the same procedure. A solution with 1 wt% DBTDL in THF was used as the catalyst in the synthesis of the HDI based polyurethanes; it was added into the reaction system at the beginning of the first step.
Scheme 3.2 Synthesis of the PUs based on different diisocyanates and chain extenders
Table 3.1 Composition and SEC results of the PUs based on different hard segments

<table>
<thead>
<tr>
<th>Polyurethane code</th>
<th>Hard segment content (wt%)</th>
<th>Molecular weight (kg/mol)</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$M_n$</td>
<td>$M_w$</td>
</tr>
<tr>
<td>HDI-HQEE</td>
<td>34.8</td>
<td>27.3</td>
<td>64.5</td>
</tr>
<tr>
<td>HDI-TD</td>
<td>41.5</td>
<td>23.5</td>
<td>51.8</td>
</tr>
<tr>
<td>MDI-HQEE</td>
<td>41.1</td>
<td>13.5</td>
<td>24.2</td>
</tr>
<tr>
<td>MDI-TD</td>
<td>46.7</td>
<td>14.0</td>
<td>25.8</td>
</tr>
</tbody>
</table>

* The nomenclature of polyurethane samples is based on the selection of diisocyanates and chain extenders since the identical molar ratio and soft segments, PTMG, are used for all the samples. Therefore, HDI-HQEE is the designation for those polyurethanes synthesized using PTMG, HDI and HQEE with the molar ratio of 1:2:1.
3.3.4 Preparation of Polyurethane films.

Films were obtained by casting a homogeneous DMF solution (20 wt%) of the segmented polyurethanes directly into a leveled Teflon® mold at 60 °C. After 24 h, the films were removed from the mold and dried under vacuum (125 torr) at 60 °C for 24 h. The samples were stored in a dessicator at room temperature, and dried again under vacuum at 60°C for 12 h before any of the analyses. It is noted that in all cases, transparent films with some variations were obtained (Figure 3.1). Films were also stamped into dog-bone shaped specimens of roughly 40 mm in length and 4 mm in width for tensile measurements. The thickness of the specimens was in the range of 0.4 ± 0.1 mm.

3.4 Results and discussion

3.4.1 Hydrogen bonding behavior.

Hydrogen bonding interactions are important driving forces for microphase separation of polyurethanes and significantly affect the thermal and mechanical properties. Hydrogen bonds are formed in the polyurethanes between the active hydrogen atom in the urethane group and the oxygen atom of the carbonyl group in the hard segments or the ether oxygens in the soft segments, such as PTMG, in this study. With such interactions, the stretching vibration of the carbonyl groups and N-H groups can be observed by FTIR. The stretching vibration bands of the carbonyl groups split into two peaks which correspond to non-hydrogen bonded carbonyl groups and hydrogen bonded carbonyl groups, respectively. The hydrogen bonded carbonyl peak appears at lower wavenumbers, which is attributed to a reduction in the electron density of the carbonyl groups due to
hydrogen bonds. With the split peak, it is possible to use FTIR to evaluate the strength of hydrogen bonding interactions.\textsuperscript{29} As shown in Figure 3.2, the HDI-HQEE sample displays the lowest wavenumber absorption and highest intensity of hydrogen bonded carbonyl peak, and then followed by MDI-HQEE and HDI-TD, while the MDI-TD sample has the highest wavenumber absorption and lowest intensity peak. This behavior can be readily explained by the structure of the hard segments. Since the hard segments of HDI-HQEE contain the more flexible HDI species and relatively less bulky HQEE component, they pack more efficiently and promote the highest level of hydrogen bond interaction. By contrast, the bulkiness of the triptycene units and the lower flexibility of MDI in the MDI-TD material limit the formation of the hydrogen bonds dramatically, which leads to the higher wavenumber absorption and lowest intensity of the hydrogen bonded carbonyl peak. Hydrogen bonding is inhibited in both the MDI-HQEE and HDI-TD samples because the hard segments contain the less flexible MDI in the former and the bulky TD in the latter. As a result, the wavenumbers for hydrogen bonded carbonyl peaks of MDI-HQEE and HDI-TD are between that of HDI-HQEE and the MDI-TD materials. The shoulder of the hydrogen bonded carbonyl peak of the MDI-HQEE sample at 1704 cm\textsuperscript{-1} is attributed to disordered hydrogen bonded carbonyl groups when compared with the peak at 1696 cm\textsuperscript{-1} for the ordered hydrogen bonded carbonyl groups.\textsuperscript{29,30} The N-H stretching vibration bands of PU samples offer additional evidence for hydrogen bonding. It is reported that PUs with a higher extent of hydrogen bonding exhibit narrower N-H peaks.\textsuperscript{5}
In our work, HDI-HQEE shows the sharpest peak, while the N-H peak of MDI-TD is much broader (Figure 3.3). These observations are consistent with the hydrogen bonding results from the carbonyl peaks.

Figure 3.2 FTIR spectra in the carbonyl region for the PU samples at ambient conditions (Curves were stacked by constant offset on the vertical axis and thus no numerical absorption values are shown)
Figure 3.3 FTIR spectra in the N-H region for the PU samples at ambient conditions (Curves were stacked by constant offset on the vertical axis and thus no numerical absorption values are shown)
Figure 3.4 Variable temperature FTIR spectra in the carbonyl region for the PU materials (Curves were stacked by constant offset on the vertical axis and thus no numerical absorption values are shown).

Variable temperature FTIR was performed to understand the dissociation behavior of the hydrogen bonds in the various polyurethanes. As shown in Figure 3.4, the dissociation process is not complete until around 170 °C for HQEE-based PUs and 110 °C for TD-based PUs. Higher temperatures are generally needed to dissociate hydrogen bonding in the stronger hydrogen bonded polymers. Thus, the HQEE-based PUs have a higher dissociation temperature due to stronger
hydrogen bonding than TD based PUs, considering the significant difference between their hard segment chemistry.

3.4.2 Thermal properties.

Thermal properties of the PU samples were investigated by TGA and DSC. It is generally accepted that the thermal degradation process in polyurethanes is a two-stage or three-stage decomposition, which primarily depends on the chemical structure, and the composition of polyols, diisocyanates, and chain extenders.\textsuperscript{31} The first stage is normally attributed to the cleavage of urethane bonds, and followed by the degradation of soft segments as the second and third stage.\textsuperscript{32} The four polyurethane samples in our work display typical two-stage degradation. Since PTMG was used as the soft segment for all of these samples, the major difference in the thermal degradation comes from the hard segment decomposition. By comparing the thermal degradation temperature at 5% weight loss in Table 3.2, we found the addition of triptycene units into the hard segments increase the initial thermal stability of these polyurethanes. Although there are no references showing the effect of triptycene structure on the thermal stability of polyurethanes, polyesters containing triptycene units exhibit increased thermal stability when compared to their non-triptycene analogues.\textsuperscript{22,27} According to Table 3.2, the degradation temperature of the HDI-HQEE film is 10°C lower than that of the MDI-HQEE material, which also agrees with the results reported in the literature.\textsuperscript{33}

The thermal transition behaviors of the polyurethane materials were examined by DSC. The HDI-HQEE material showed a lower T\textsubscript{g} at -67 °C relative to the value of -41 °C observed for the MDI-HQEE and -31 °C for HDI-TD based materials.
(Table 3.2). It is believed that with more well-defined microphase separated morphology, the motion of the soft segments is less hindered in HDI-HQEE. The MDI-TD sample possesses a much higher \( T_g \) than the other samples, which is indicative of microphase mixing. The DSC curves did not show a distinct \( T_g \) for any of the hard segments in any of the samples; this is commonly observed for other segmented polyurethanes.\(^{34}\) Melting endotherms of the hard segments were only observed in the HQEE based polyurethanes, which strongly implies the triptycene units, because of their bulkiness, inhibit crystallization of the hard segments. Such melting endotherms correlate with the hydrogen bonding dissociation temperature as previously discussed. This correlation can also be found in the literature.\(^{35}\)

Table 3.2 Thermal properties of the PUs based on the various chain extenders

<table>
<thead>
<tr>
<th>Polyurethane samples</th>
<th>TGA ( T_d ) 5% weight loss ((^{\circ})C)</th>
<th>DSC ( T_g ) (soft segment) ((^{\circ})C)</th>
<th>DSC ( T_m ) (hard segment) ((^{\circ})C)</th>
<th>( \Delta H_m ) (hard segment) (J/g)</th>
<th>DMA ( T_g ) (soft segment) ((^{\circ})C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDI-HQEE</td>
<td>282</td>
<td>-67</td>
<td>162</td>
<td>9.37</td>
<td>-46</td>
</tr>
<tr>
<td>HDI-TD</td>
<td>306</td>
<td>-31</td>
<td>-</td>
<td>-</td>
<td>-28</td>
</tr>
<tr>
<td>MDI-HQEE</td>
<td>294</td>
<td>-41</td>
<td>181</td>
<td>8.73</td>
<td>-25</td>
</tr>
<tr>
<td>MDI-TD</td>
<td>305</td>
<td>17</td>
<td>-</td>
<td>-</td>
<td>22</td>
</tr>
</tbody>
</table>

3.4.3 Thermomechanical behavior.

DMA analysis is a sensitive method to study the thermomechnical behavior of polymers. The major dissipation peak in the Tan delta profiles is usually used to designate \( T_g \). In addition, the storage modulus and the broadness of the rubbery plateau obtained from the DMA are also important indicators that aid in the
evaluation of the structure-property relationship of the materials. As shown in the
DMA analysis (Figure 3.5 and Figure 3.6), the MDI-TD material showed a much
higher \( T_g \) than the other samples, which is in accordance with the DSC results. It
is very likely that some of the hard segments mix with the soft segments to a high
degree, reducing the mobility of the soft segments, and resulting in a higher \( T_g \). A
decrease in the storage modulus can be observed around 70 °C for the PU
materials, and this is affected by the annealing treatment which can cause some
further rearrangement of the hydrogen bonds in the hard segments.\(^{34}\) It is observed
that annealing the same samples at 80 °C and 100 °C shifts the transitions to
somewhat higher temperatures.

The transition from the rubbery state to the viscous flow of polyurethanes in
DMA analysis generally corresponds to hard segment softening.\(^{36}\) It is interesting
to note that polyurethanes based on HQEE exhibit a higher flow temperatures than
their TD analogues, which is attributed to the stronger hydrogen bonding
interactions and partially crystallized hard segments. As additional evidence, these
observations suggest stronger hydrogen bonding in the HQEE based
polyurethanes, and subsequently lead to higher temperature for the onset of flow
in their DMA profiles. Furthermore, the crystallization of hard segments for HDI-
HQEE and MDI-HQEE enable their hard domains to act as effective physical
crosslinks which increase moduli as well as softening temperatures.
Figure 3.5 DMA storage modulus responses of the PU samples with different hard segments.

Figure 3.6 DMA Tan delta profiles of the PU samples with different hard segments.
3.4.4 Tensile properties.

The mechanical properties of polyurethanes were studied by uniaxial tensile tests at 25 °C. The results are summarized in Table 3.3, and the representative stress-strain behavior of each of the samples is shown in Figure 3.7. When comparing the results, there is no dramatic difference in the elongation at break for the samples; they are all in the range of 750 % to 1050 %. But it is noted that the MDI-TD sample has a much lower Young’s modulus (~ 2MPa) than the other samples, even though its hard segment weight percent is the highest (Table 3.1), while the HDI-HQEE sample exhibits the highest Young modulus (~27 MPa). These results are consistent with the results from DMA at 25 °C. The different extent of microphase separation among samples can be used to help explain this phenomenon. With a greater hard segment connectivity and microphase separation, the hard domains in HDI-HQEE, HDI-TD, and MDI-HQEE act as more effective “fillers”, which increase the tensile strength and Young’s modulus. As discussed in the DMA results, the crystallization of HQEE based hard segments also increases the modulus of their corresponding polyurethanes, which results in the higher Young’s modulus for HDI-HQEE and MDI-HQEE when compared to their triptycene analogues. On the other hand, the hard segments in MDI-TD fail to efficiently aggregate and reinforce the stiffness of the material, which leads to a much lower Young’s modulus. In addition, the insufficient hydrogen bonding interaction in MDI-TD also contributes to the low tensile modulus. However, there is a clear upturn in stress at elongations greater than 700% for the MDI-TD sample. It is reported that polyurethanes with PTMG as the soft segments may exhibit strain
hardening due to some partial strain-induced crystallization behavior of the PTMG soft matrix.\textsuperscript{38} Wide angle X-ray diffraction (WAXD) was used to observe the strain-induced crystallization with a uniaxial stretched MDI-TD film (800%). The WAXD pattern (not shown) does not reveal any crystal reflections, which suggests that the upturn of MDI-TD stress-strain curve does not arise from the strain-induced crystallization.

Table 3.3 Comparison of tensile properties of PUs based on various chain extenders

<table>
<thead>
<tr>
<th>Polyurethane samples</th>
<th>Tensile stress at break (MPa)</th>
<th>Elongation (%)*</th>
<th>Young’s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDI-HQEE</td>
<td>22.6 ± 1.2</td>
<td>1036 ± 37</td>
<td>26.5 ± 1.7</td>
</tr>
<tr>
<td>HDI-TD</td>
<td>18.2 ± 0.6</td>
<td>809 ± 14</td>
<td>11.5 ± 2.0</td>
</tr>
<tr>
<td>MDI-HQEE</td>
<td>21.6 ± 0.6</td>
<td>771 ± 35</td>
<td>17.5 ± 0.8</td>
</tr>
<tr>
<td>MDI-TD</td>
<td>9.4 ± 0.6</td>
<td>959 ± 41</td>
<td>2.1 ± 0.3</td>
</tr>
</tbody>
</table>

* Elongation values were corrected by excluding the films slide out from the fixture.
Figure 3.7 Tensile properties of the PUs based on different chain extenders

3.4.5 Morphological characterization.

As stated earlier, microphase separation of the segmented polyurethanes is a very important feature, which significantly influences the polymer’s mechanical properties. In order to study the microphase separation behavior of our samples and understand the structure-property relationships, atomic force microscopy (AFM) and small angle X-ray scattering (SAXS) were employed. AFM and SAXS have been widely used in characterizing surface and bulk morphology of polyurethanes.\textsuperscript{39,40} The SAXS results are plotted in Figure 3.8 as log intensity versus log scattering vector $q$ (nm\textsuperscript{-1}). As expected from the FTIR results, MDI-TD does not exhibit a clear interference maximum, and this is attributed to the high level of microphase-mixing. The other three samples show scattering profiles that are typical for microphase separated system with a scattering maximum observed
around 0.5 nm<sup>-1</sup>.<sup>39</sup> Bragg’s law \((d=2\pi/q_{\text{max}})\) was used to estimate the average interdomain spacings of the separated microphases in the polyurethane samples based on the maximum intensity positions of the peaks, \(q_{\text{max}}\), and the results are shown in Table 3.4. Furthermore, it is observed that the peak for MDI-HQEE is slightly broader than the other two peaks and this may suggest that microphase separation is less defined in MDI polyurethanes relative to that in the HDI polyurethanes.
Table 3.4 SAXS of PUs based on various chain extenders

<table>
<thead>
<tr>
<th>Polyurethane samples</th>
<th>Scattering vector $q_{\text{max}}$ (nm$^{-1}$)</th>
<th>Interdomain spacings $d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDI-HQEE</td>
<td>0.437</td>
<td>14.4</td>
</tr>
<tr>
<td>HDI-TD</td>
<td>0.393</td>
<td>16.0</td>
</tr>
<tr>
<td>MDI-HQEE</td>
<td>0.419</td>
<td>15.0</td>
</tr>
<tr>
<td>MDI-TD</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Figure 3.8 SAXS curves for the PU samples

(HDI-HQEE $d$=14.4 nm; HDI-TD $d$=16.0 nm; MDI-HQEE $d$=15.0 nm)

To gain further insight into the nature of the microphase morphology of these materials, tapping mode AFM was used to study the surface features of the PU samples. The analysis of AFM imaging upon microphase separation is limited by
several factors such as tapping strength and frequency, film preparation, conditions, etc., which prevent AFM from providing precise quantitative information about hard and soft domains.\(^3\) However, AFM phase images may provide direct visual representation of the microphase separation of PUs with the hard domains appearing as bright regions and the dark regions resulting from the soft segment rich regions. As shown in Figure 3.9, we observed distinct images for the four samples. Well-defined microphase separation could be observed for the HDI-HQEE, HDI-TD and MDI-HQEE samples, while the MDI-TD sample showed a greater microphase-mixed morphology. The MDI-TD sample which contains both bulky triptycene units and the less flexible MDI dramatically inhibits microphase separation, which results in a much less featured AFM phase image. With the more flexible diisocyanates, HDI-HQEE and HDI-TD, these each displayed “ribbon-like” hard domains with some degree of long range order. This indicates that the hard segments of these PUs can effectively pack with each other. There is also microphase separation noted for the MDI-HQEE material, but the hard domains lengths are much shorter than those in the HDI samples. The structure of MDI is not as flexible as HDI which inhibits the long range connectivity of its hard segments. Overall, the AFM images strongly support the earlier FTIR, DMA and SAXS results.
3.5 Conclusions

Four segmented polyurethanes based on PTMG (1000 g/mol) with MDI or HDI were successfully chain extended with HQEE or TD. The incorporation of the bulky triptycene structure in the hard segment was found to disrupt the hydrogen bonding, which resulted in a significant influence on the thermal and mechanical properties. SAXS measurements showed little microphase separation for the MDI-TD polyurethane sample from the information of the scattering vector $q$ vs intensity plot. The HDI-TD showed improvement of microphase separation with the more flexible HDI, which was confirmed by DSC, DMA, AFM, and SAXS analysis. As a
result, comparable thermal and mechanical properties of HDI-TD were obtained relative to its HQEE analogs even with the presence of bulky triptycene units.

3.6 Acknowledgements

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3.7 Supplementary Materials

3.7.1 Monomer synthesis

Modification of monomers was carried out to obtain chain extenders in polyurethane synthesis. For example, the reactivity of phenol groups on 4,4’-biphenol and 1,4-dihydroxy triptycene was limited due to the electron delocalization effect from nearby benzene rings. To prepare more reactive monomers, primary hydroxyl groups were obtained by reacting these monomers with ethylene carbonate, which converted phenol groups into primary alcohols. Unlike ethylene oxide, ethylene carbonate is less toxic, which is a good candidate to prepare the hydroxy ethoxy groups. Below is the procedure of monomer modifications (Scheme 3.3).
Scheme 3.3 Synthesis of biphenol bis(2-hydroxyethyl)ether (BHEE) and triptycene-1,4-hydroquinone-bis(2-hydroxyethyl)ether (TD)

Biphenol bis(2-hydroxyethyl)ether (BHEE) and triptycene-1,4-hydroquinone-bis(2-hydroxyethyl)ether (TD) were synthesized and used as chain extenders in future synthesis of segmented polyurethanes. The synthetic scheme for these two monomers followed the method described by Liu et al.²⁷ Synthesis of BHEE was used as representative example here. A 100 mL two-necked round bottom flask was charged with 1.86 g (0.01 mol) 4,4’-biphenol and 0.14 g (0.001 mol) of K₂CO₃ in 25 mL of N,N-dimethylformamide (DMF). The reaction mixture was heated to 165 °C under argon. 1.76 g (0.02 mol) of ethylene carbonate was dissolved in 10 mL of DMF, and then added into the flask dropwise (~1 h). After that, the reaction proceeded for another 2 h and then the mixture was cooled to room temperature.
The reaction mixture was poured into deionized water and the white precipitate was collected by filtration. The white solid recrystallized from methanol was dried at 60°C under vacuum. Yield: 1.83 g, 67%, m.p. 215.9-217.1°C. For TD, yield: 2.62 g, 70%, m.p. 239.3-240.4°C. ¹H NMR was used to characterize the structures of two monomers, and the spectra are shown in Figure 3.10 and Figure 3.11.

BHEE: ¹H NMR (400 MHz, d-DMSO) δ 7.50 (d, J = 8.4 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 4.91 – 4.82 (m, 1H), 3.99 (t, J = 4.9 Hz, 2H), 3.70 (q, J = 5.1 Hz, 2H).

TD: ¹H NMR (400 MHz, d-DMSO) δ 7.40 (dd, J = 5.1, 3.2 Hz, 4H), 6.96 (dd, J = 5.2, 3.1 Hz, 4H), 6.62 (s, 2H), 5.93 (s, 2H), 4.93 (t, J = 5.6 Hz, 2H), 3.93 (t, J = 5.0 Hz, 4H), 3.73 (dd, J = 10.4, 5.2 Hz, 5H).

Figure 3.10 ¹H NMR spectrum of biphenol bis(2-hydroxyethyl)ether (BHEE)
Figure 3.11 $^1$H NMR spectrum of triptycene-1,4-hydroquinone-bis(2-hydroxyethyl)ether (TD)
3.8 Appendix

Figure 3.12 FTIR spectrum of HDI-HQEE

Figure 3.13 FTIR spectrum of HDI-TD
Figure 3.14 FTIR spectrum of MDI-HQEE

Figure 3.15 FTIR spectrum of MDI-TD
Figure 3.16 TGA curves of the PU samples

Figure 3.17 DSC curves of the PU samples
3.9 References


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Chapter 4. Synthesis and Properties of Segmented Polyurethanes with Triptycene Units in the Soft Segment

(Accepted by *Macromolecular Chemistry and Physics*)

4.1 Abstract

Segmented polyurethanes based on poly(tetramethylene glycol) (PTMG) soft segments containing aromatic units were synthesized. Hydroquinone bis (2-hydroxyethyl) ether (HQEE) and 4,4’-methylenebis(phenyl isocyanate) (MDI) were used as the chain extender and the diisocyanate, respectively. Effects of incorporation of hydroquinone and 1,4-dihydroxy triptycene (also called triptycene hydroquinone) (TH) into the soft segments on the morphology and properties of the undeformed segmented polyurethanes were investigated. Differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) indicated that the incorporation of triptycene units led to an increased glass transition temperature \( T_g \) and an elimination of the crystallization of soft segments. The tensile analysis showed there was no strain hardening for the polymer films with triptycene-containing soft segments. Wide-angle X-ray diffraction (WAXD) demonstrated that the absence of strain hardening in triptycene-containing segmented polyurethane likely arose from the suppressed strain induced crystallization. In contrast, the less bulky hydroquinone units showed little effect on either thermally or strain induced crystallization of the soft segments. Morphology studies, including small angle X-ray scattering (SAXS) on the compression molded film and atomic force microscopy (AFM) on the solvent cast film revealed that polyurethanes with
hydroquinone and triptycene containing soft segments maintained distinct microphase separation.

4.2 Introduction

Segmented polyurethanes exhibit properties that enable a broad spectrum of applications ranging from thermoplastic elastomers to coatings.\textsuperscript{1-3} This diverse adaptability originates from the segmented structure and microphase separated morphology. The chain structure of thermoplastic polyurethanes normally consists of alternating hard and soft segments. Due primarily to thermodynamic incompatibility at ambient conditions, the hard and soft segments tend to phase separate and form micro domains or matrixes.\textsuperscript{4,5} The morphological structure of these domains plays a critical role on the properties. Thus, it is possible to control the morphology of segmented polyurethanes by tailoring the chemical structure and compositions of hard and soft segments, and consequently achieve desirable properties for a variety of potential applications.

The effect of soft segments on the morphology and properties has been widely studied in many aspects such as the type, symmetry and molecular weight.\textsuperscript{6-10} Crystallization of soft segments, which is influenced primarily by the molecular symmetry, can dramatically influence the microphase separation and mechanical properties.\textsuperscript{10,11} Hammond and coworkers have studied how the crystallization and domain ordering of the polyether soft matrix affect the morphology and the mechanical properties at ambient conditions.\textsuperscript{11,12} In their work, 1,4-butanediol (BDO) and 1,6-hexamethylene diisocyanate (HDI) were used as the chain extender and diisocyanate to maximize the efficient packing of hard segments and
microphase separation. Crystallizable poly(ethylene oxide) (PEO) with different molecular weights (1000 g/mol and 4600 g/mol) were used as the soft segments. For comparison, non-crystallizable poly(propylene oxide) (PPO) was introduced into the soft segments to prepare less crystallizable PEO-PPO-PEO that are of a tri-block structure with a central PPO segment (total 1900 g/mol, PPO block = 950 g/mol, each PEO block = 475 g/mol). It appeared that microphase separation was improved by the crystallization of the PEO soft segments. Moreover, the crystalline domains of the PEO soft segment act as the load-bearing component during deformation and provide further reinforcement. Efforts have also been made to understand the crystallization behavior of segmented polyurethanes containing polyester soft segments.\textsuperscript{10,13-16} It is reported that the crystallization of polycaprolactone (PCL) and poly(butylene adipate glycol) soft segments are enhanced by increasing the molecular weight of the oligomeric diol.\textsuperscript{14,15} Similar to the PEO-based segmented polyurethanes discussed above, enhanced crystallinity in the PCL soft segments also led to an increase in tensile strength. Xu et al. probed the molecular weight dependence of the PCL crystallization behavior. They found the molecular weight of PCL soft segments needed to be above a minimum value of 2000 to 3000 g/mol to obtain crystallizability at ambient conditions; MDI and BDO were used as the diisocyanate and the chain extender in the study.\textsuperscript{10}

To obtain desirable transparency and mechanical properties, tailoring the degree of crystallization has also attracted considerable interest in different segmented polyurethane systems.\textsuperscript{17-19} Li and coworkers investigated the restriction of PEO soft segment crystallization using hard segment contents greater
than 50 wt.%. With crystallizable hard segments consisting of HDI and BDO, they found that increasing hard segment content and hard segment crystallinity suppressed the crystallinity of the PEO soft segments. Kojio et al. synthesized a series of segmented polyurethanes using PTMG and polycarbonate (PC) soft segments and MDI-BDO hard segments. For comparison, PTMG-based soft segments containing different content of methyl and dimethyl side groups on the backbone were prepared, from which they obtained a range of crystallizabilities. By incorporating these soft segments, they were able to vary the mechanical properties by restricting soft segment crystallinity.

Introduction of triptycene structures into different polymeric backbones has been widely studied in the past. It was reported that the paddle-wheel shaped structure of triptycene (Scheme 4.1) effectively improved the thermal stability and tensile strength in homopolymers such as polyesters, polycarbonates and polyimides. Moreover, triptycene units have been suggested to offer simultaneous enhancement of tensile strength and ductility in certain polyesters. This unique behavior was explained by a “molecular threading and interlocking mechanism”. Previously, we studied PTMG (1000 g/mol)-based segmented polyurethanes. MDI and HDI were used as the diisocyanates, and triptycene-1,4-hydroquinone bis(2-hydroxyethyl)ether (TD), and HQEE were used as the chain extenders. By preparing four types of hard segments with the chain extenders and diisocyanates described above, we assessed the effect of bulkiness and flexibility of hard segments on morphologies and properties of these segmented polyurethanes.
Various novel soft segments have been prepared to study their effect on the morphologies and properties of polyurethanes.\textsuperscript{21,33,34} However, segmented polyurethanes based on soft segments containing bulky aromatic units have never been explored. Due to the bulky structure, triptycene units are expected to inhibit crystallinity when introduced into otherwise symmetric soft segments. In this work, we synthesized novel soft segments containing the aromatic units of hydroquinone or 1,4-dihydroxy triptycene. These soft segments were subsequently end-capped by MDI and chain extended by HQEE to obtain segmented polymers. By comparing these materials with pure poly(tetramethylene glycol) (PTMG) soft segments (PTMG1K, PTMG2K) and PTMG-based polyether soft segments containing aromatic structures, we determined the influence of these aromatic units on the soft segment crystallization, as well as the morphologies and physical properties.

4.3 Experimental

4.3.1 Materials

Poly(tetramethylene glycol) oligomer (Terathane, DuPont) with a number average molecular weight of 1000 g/mol (PTMG1K) and 2000 g/mol (PTMG2K),
hydroquinone (HQ) and hydroquinone bis(2-hydroxyethyl)ether (HQEE, 98%), potassium carbonate (K$_2$CO$_3$), and methanesulfonyl chloride (MsCl, ≥99.5%) were purchased from Aldrich. 4,4'-methylenebis(phenyl isocyanate) (MDI, 99.5%) was kindly provided by Bayer MaterialScience and used as received. 1,4-dihydroxy triptycene (TH) was kindly provided by ICx technologies, Inc (now FLIR Systems, Inc). PTMG1K, PTMG2K, HQ, TH, HQEE and K$_2$CO$_3$ were dried under vacuum (125 torr) for 12 h at 60 °C before use. Acetonitrile (HPLC Grade) and methylene chloride (DCM) (HPLC Grade) were purchased from Fisher and distilled before use. Anhydrous dimethylformamide (DMF, Aldrich, ≥99.9%) and anhydrous triethylamine (TEA, Aldrich, ≥99.5%) were used as received.

4.3.2 Synthesis of PTMG-based Polyol Containing Aromatic Units

PTMG-based polyols containing hydroquinone or 1,4-dihydroxy triptycene were synthesized in a manner similar to a method described in the literature.$^{35}$ A typical procedure is shown below using 1,4-dihydroxy triptycene (TH) as an example (Scheme 4.2). PTMG1K (100.00 g, 100 mmol), triethylamine (TEA) (69.74 ml, 500 mmol) and dichloromethane (DCM) (150 ml) were added to a 500 mL three-necked round bottom flask. Methanesulfonyl chloride (23.22 ml, 300 mmol) was first dissolved in 25 ml DCM, and then added into the flask dropwise over 30 min at 0 °C. The reaction mixture was stirred at room temperature under argon for 12 h. The mixture was then poured into ice water to quench the reaction. A separatory funnel was used to remove the aqueous layer. The remaining organic layer was washed with 1 M HCl three times, and then washed with brine three times. Magnesium sulfate was used to dry the organic layer for 1 h after the wash.
DCM was evaporated and the characteristic yellow oily product was obtained. The product was methanesulfonyl end-capped PTMG1K (PTMG1K-diMs) (yield: 95.13 g, 82.3%). $^1$H NMR (500 MHz, CDCl$_3$) δ 4.28 (t, $J = 6.5$ Hz, 1H), 3.45 (dd, $J = 14.0$, 5.8 Hz, 14H), 3.02 (s, 1H), 1.86 (dt, $J = 14.9$, 6.5 Hz, 1H), 1.80 – 1.51 (m, 15H). (Figure 4.11).

A 500 mL three-necked round bottom flask was charged with PTMG1K-diMs (34.68 g, 30 mmol), 1,4-dihydroxy triptycene (4.29 g, 15 mmol), anhydrous potassium carbonate (5.53 g, 40 mmol) and freshly distilled acetonitrile (100 ml). The reaction mixture was stirred at 60 °C under argon for 24 h. Subsequently, K$_2$CO$_3$ (5.53 g, 40 mmol), H$_2$O (5 ml) and acetonitrile (50 ml) were added to the flask. The reaction mixture was stirred at 80 °C for another 24 h, and the reaction mixture was cooled to room temperature and poured into water. This mixture was extracted with DCM. The organic layer was washed with saturated NaCl solution three times and dried over magnesium sulfate. A dark brown viscous oil was obtained by evaporating the DCM followed by vacuum drying (125 torr) at 80 °C for 24 h. (yield: 25.58 g, 75.6%). $^1$H NMR (500 MHz, CDCl$_3$) δ 7.39 (dt, $J = 7.2$, 3.6 Hz, 6H), 6.98 (dd, $J = 5.3$, 3.2 Hz, 6H), 6.49 (s, 3H), 5.87 (s, 3H), 4.16 (t, $J = 6.5$ Hz, 1H), 3.96 (t, $J = 6.1$ Hz, 6H), 3.72 – 3.32 (m, 169H), 2.58 (t, $J = 5.7$ Hz, 2H), 1.96 – 1.80 (m, 13H), 1.74 – 1.56 (m, 163H) (Figure 4.13). The four different soft segments were acetylated by acetic anhydride. In $^1$H NMR spectra, the integration of methyl end groups on the acetylated oligomers were used as the standard peak to calculated the number average molecular weight of the soft segments. Each of the samples were characterized for three times to calculate the
average values and standard deviation of number average molecular weights (Table 4.1).

![Chemical reaction diagram]

Scheme 4.2 Synthesis of soft segments containing aromatic units

### 4.3.3 Synthesis of Segmented Polyurethanes

Polyurethanes were prepared by the conventional prepolymer method. PTMG1K, PTMG2K, PTMG-HQ-diol and PTMG-TH-diol were used as the soft segments, and hard segments consisted of MDI as the diisocyanate and HQEE as the chain extender. All of the polyurethanes were synthesized in the same manner. The synthesis of the polyurethane based PTMG-TH-diol is given here as an example (Scheme 4.3). In the first step, PTMG-TH-diol (2.60 g, 1 mmol) and MDI (0.58 g, 2.3 mmol) were charged to a 100 mL three-necked round bottom flask under argon. The flask was equipped with a water condenser, an overhead mechanical stirrer, and an addition funnel. The flask was heated to 70 °C with
stirring, which continued for 4 h. \(^1\)H NMR was used to confirm the complete consumption of hydroxyl groups based on the disappearance of hydroxyl group peak around 2.5 ppm. In the second step, HQEE (0.20 g, 1 mmol) was dissolved in 17 mL anhydrous DMF and added dropwise into the reaction system. The chain extension was carried out at 75˚C for 24 h. The other segmented materials synthesized with other soft segments followed the same procedure.

Scheme 4.3 Synthesis of segmented polyurethanes with different soft segments

4.3.4 Film Preparation

Films of the respective materials were obtained by casting a homogeneous DMF solution (20 wt%) directly into a leveled Teflon® mold at 60˚C. After 24 h, the
films (thickness: ca. 0.4 ± 0.1 mm) were removed from the mold and subsequently
dried under vacuum (125 torr) at 60 °C for another 24 h. For DSC, DMA, tensile
and hysteresis analysis, samples were compression molded at 220 °C for 5 min
and rapidly cooled on stainless steel plate at ambient temperature. The samples
were stored in a desiccator at room temperature for two weeks before testing.
Films were stamped into dog-bone shaped specimens with a die for tensile and
hysteresis measurements. Specimens were 40 mm long, 4 mm wide and 0.4 ± 0.1
mm thick.

4.3.5 Instrumentation

$^1$H NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer at
room temperature using deuterated dimethyl sulfoxide (d-DMSO) and deuterated
chloroform (CDCl$_3$) as the solvents. $^1$H NMR spectra were used to confirm the
structure of the prepolymer that was diisocyanate end-capped PTMG. FTIR
spectra were obtained on a Varian 670-IR spectrometer (DTGS detector) equipped
with a Pike Technologies variable temperature GladiATR™ attachment (diamond
crystal). The spectra were collected at a resolution of 4 cm$^{-1}$, and 32 scans were
averaged. The molecular weight and molecular weight distribution of each sample
were measured by size exclusion chromatography (SEC) in N-methyl-2-
pyrrolidone (NMP) with 0.05 LiBr at 30 °C on a Waters Alliance model 2690
chromatograph equipped with a Waters HR 0.5+ HR2+ HR3+ HR 4 styragel
column set. Mono-disperse polystyrene standards were used to construct a
universal molecular weight calibration curve. A Viscotek refractive index detector
and a viscometer were used for molecular weight determination.
Thermogravimetric analysis (TGA) was performed using a TA Instrument TGA Q500 from room temperature to 600 °C with a heating ramp of 10°C/min under nitrogen. Differential scanning calorimeter (DSC) data were obtained on a TA Instruments Q2000 equipped with refrigerated cooling system (RCS) with a nitrogen flow of 40 mL/min. Pure soft segment samples were initially heated to 30 °C for elimination of thermal history, and then equilibrated at -90 °C for 5 min, followed by another scan from -90 °C to 30 °C with a heating rate of 10 °C/min. For segmented polyurethanes, samples were equilibrated at -90 °C for 5 min, and then heated to 230 °C with a heating rate of 10 °C/min. Thermal transitions such as the glass transition temperature \( (T_g) \) and melting temperatures \( (T_m) \) were determined from the second heating cycle for pure soft segments and from the first heating cycle for segmented polyurethane samples. Tensile analysis was performed on an Instron Model 4400 Universal Testing System at ambient conditions. The film samples were stamped into dog bone shaped specimens \((40 \times 4 \times 0.4 \text{ mm})\) with a die according to ASTM D3368 specifications. Specimens were tested with a cross-head rate of 50 mm/min at ambient conditions using an initial gauge length of 15 mm. The tensile test results were an average value of at least five specimens. For determining the actual elongation value, two lines were marked on the specimens next to the grips, and the elongation of each sample was calculated based on the distance between the two marks divided by the initial gauge length. Mechanical hysteresis experiments were also conducted using an Instron Model 4400 Universal Testing System at ambient conditions. Each sample was tested with five full cycles. For one full cycle, specimens were initially stretched to a
maximum strain of 300% at a constant rate of 15 mm/min, and immediately returned to original length at the same rate and held there for 3 min before the next cycle. Dynamic mechanical analysis (DMA) was performed on a TA Instruments Q800 dynamic mechanical analyzer using the film tension mode at a frequency of 1 Hz and a temperature ramp of 3 °C/min from -130 to 150°C. Atomic force microscopy (AFM) measurements were conducted on a Veeco MultiMode AFM in a tapping mode at room temperature on the free air surface of the solution cast films. Small angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) experiments were performed using a Rigaku S-Max 3000 3 pinhole SAXS system, equipped with a rotating anode emitting X-ray with a wavelength of 0.154 nm (Cu Kα). The sample-to-detector distance was 1603 mm for SAXS and 82.5 mm for WAXD, and the q-range was calibrated using a silver behenate standard. Two-dimensional SAXS patterns were obtained using a fully integrated 2D multiwire, proportional counting, gas-filled detector, with an exposure time of 1 h. WAXD two-dimensional diffraction patterns were obtained using an image plate with an exposure time of 1 h. The SAXS and WAXD data were corrected for sample thickness, sample transmission and background scattering, and the WAXD profiles were vertically shifted to facilitate a comparison of peak positions. All the SAXS and WAXD data were analyzed using the SAXSGUI software package to obtain radically integrated SAXS and WAXD intensity versus the scattering vector q (SAXS) or 2θ (WAXD), where q=(4π/λ)sin(θ), θ is one half of the scattering angle and λ is the wavelength of X-ray. WAXD profiles were integrated along the Bragg's
angle around equatorial with 30° in azimuthal direction. WAXD patterns of the films at strains were obtained by stretching the films in vertical direction.

4.4 Results and Discussion

4.4.1 Synthesis of Soft Segments Containing Aromatic Structures and Polyurethanes

To prepare PTMG based soft segments containing aromatic units, PTMG1K was first end-capped with methanesulfonyl chloride to give dimesylate PTMG1K, which was then reacted with the 1,4-dihydroxy triptycene (TH). The molar ratio between dimesylate PTMG1K and TH was 2:1 to ensure a mesylate end-capped product. This product was then hydrolyzed to obtain the hydroxyl end groups. The four different soft segments were acetylated by acetic anhydride. In 1H NMR spectra, the integration of methyl end groups on the acetylated oligomers were used as the standard peak to calculated the number average molecular weight of the soft segments. As summarized in Table 4.1, each modified soft segment contains, on average, slightly more than one aromatic unit in the chain.
Table 4.1 Structure and number average molecular weight of soft segments

<table>
<thead>
<tr>
<th>Soft segments</th>
<th>Structure</th>
<th>( ^{\text{a}}M_n , (\text{g/mol}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMG1K</td>
<td><img src="image1.png" alt="Structure" /></td>
<td>1100</td>
</tr>
<tr>
<td>PTMG2K</td>
<td><img src="image2.png" alt="Structure" /></td>
<td>2000</td>
</tr>
<tr>
<td>PTMGHQ</td>
<td><img src="image3.png" alt="Structure" /></td>
<td>2400</td>
</tr>
<tr>
<td>PTMGTH</td>
<td><img src="image4.png" alt="Structure" /></td>
<td>2600</td>
</tr>
</tbody>
</table>

* Number average molecular weight data were determined by \(^1\)H NMR.

As stated earlier, synthesis of the segmented polyurethanes utilized the well-known prepolymer method. These prepolymers were synthesized by soft segments reacting with excess of MDI in the first step, and then HQEE was dissolved in DMF and added dropwise to achieve a high level of chain extension. FTIR was used to confirm that all isocyanate groups were completely reacted (disappearance of isocyanate stretching vibration peak at 2260 cm\(^{-1}\)).\(^{37}\) The calculated hard segment content and molecular weight of the polyurethane samples are listed in Table 4.2.
Table 4.2 Composition and SEC results of the segmented polyurethanes based on different soft segments

<table>
<thead>
<tr>
<th>Polyurethane code</th>
<th>Hard segment content (wt%)</th>
<th>Molecular weight (kg/mol)</th>
<th>$M_n$</th>
<th>$M_w$</th>
<th>$M_w/M_n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMG1K-PU</td>
<td>43.6</td>
<td>42.3</td>
<td>115.6</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>PTMG2K-PU</td>
<td>27.9</td>
<td>28.2</td>
<td>51.8</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>PTMGHQ-PU</td>
<td>24.4</td>
<td>29.5</td>
<td>54.4</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>PTMGTH-PU</td>
<td>22.9</td>
<td>27.9</td>
<td>59.3</td>
<td>2.1</td>
<td></td>
</tr>
</tbody>
</table>

* The nomenclature is based on the selection of soft segment since the identical molar ratio and hard segment were used for all the samples. Therefore, PTMGTH-PU is the designation for those polyurethanes synthesized using PTMGTH soft segment, MDI and HQEE with the molar ratio of 1:2:1.

4.4.2 Thermal Properties

The thermal properties of the final segmented copolymers were analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Under an $N_2$ atmosphere, all of the samples showed a two-stage thermal degradation with 5% weight loss at around 300 °C (Table 4.4 and Figure 4.10). For the thermal transitions, segmented polyurethanes typically display glass transitions, which depend on the flexibility and molecular weight of either the soft or the hard segments. Melting peaks can be observed if there is any crystallinity in the soft or hard segments. In our study, four types of soft segments with or without aromatic units were chosen to understand the effect of molecular symmetry and bulky units on the crystallization behaviors. The thermal transitions of the pure soft segments were determined by DSC. As shown in Table 4.3 and Figure 4.1, no glass transition was detected. This is believed due to the high crystallinity of each
sample. The melting temperatures ($T_m$) of PTMG2K, PTMG1K, PTMGHQ and PTMGTH were reduced from 25 °C to 16 °C, and a decrease from 123 J/g to 77 J/g was determined for the normalized enthalpy of the melting endotherm based on the pure PTMG content. In addition, the shape of the melting peaks varied from a sharp single peak (PTMG2K) to a broader double peak (PTMGTH). These results implied that the crystallization of the soft segments is inhibited by the aromatic units, with bulky triptycene units disrupting the crystallization more.

DSC results are summarized in Table 4.4 and Figure 4.2. By comparing the melting endotherms of the pure soft segments and the soft segments incorporated into the polymers (Figure 4.1 and Figure 4.2), the crystallization of the soft segments in the polymer samples appears to be significantly depressed by restrictions from the chemically linked hard segments. Only PTMG2K-PU and PTMGHQ-PU showed a soft segment melting peak. Nevertheless, each of these melting endotherm enthalpies was greatly reduced relative to the pure PTMG2K and PTMGHQ soft segments. It is surprising that the enthalpy of the melting endotherm of PTMGHQ-PU is larger than PTMG2K-PU, which demonstrates that PTMGHQ-PU has a higher degree of crystallinity. This might be attributed to the higher molecular weight of PTMGHQ (~2400 g/mol), but this needs to be further studied. No soft segment melting behavior was detected in PTMG1K-PU or PTMGTH-PU. As discussed above, the triptycene units in PTMGTH-PU inhibited soft segment crystallization. The PTMG1K-PU sample possessed relatively low molecular weight soft segment and high hard segment content. The soft segment crystallization was prevented by a lack of sufficient soft segment mobility and the
restriction imposed by the hard segments. Each sample exhibited a hard segment melting peak except PTMGTH-PU. PTMG1K-PU possessed the highest enthalpy of melting, which is due to the 43.6 wt% hard segment content (Table 4.2).

The samples exhibited soft segment T_g s ranging from -74 °C to -52 °C (Table 4.4). Since the mobilities of the soft segments were restricted by the high hard segment content, PTMG1K-PU showed a higher soft segment T_g than the other three samples. We also observed that PTMGTH-PU had a higher T_g than PTMG2K-PU and PTMGHQ-PU, which was attributed to the rigidity introduced by the triptycene units. Without any major inhibition effects, both PTMG2K-PU and PTMGHQ-PU exhibited a low T_g (-71°C and -74°C), which were close to the T_g of pure PTMG homopolymers (-79°C).38
Table 4.3 Thermal transitions of pure soft segments\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>SS molecular weight</th>
<th>PTMG molecular weight</th>
<th>Normalized $\Delta H_m$ (J/g)\textsuperscript{c}</th>
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</thead>
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<tr>
<td>PTMG2K</td>
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<td>2000</td>
<td>2000</td>
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<td>1100</td>
<td>1100</td>
<td>99</td>
</tr>
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<td>PTMGHQ</td>
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<td>85</td>
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<td>2300</td>
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<tr>
<td>PTMGTH</td>
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<td>2600</td>
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</tbody>
</table>

\textsuperscript{a} Thermal transition data obtained from the 2nd heating cycle of the DSC experiment;
\textsuperscript{b} The mass of aromatic units are excluded;
\textsuperscript{c} Normalized enthalpy was calculated only based on the PTMG component

Table 4.4 Thermal properties of the four segmented polyurethanes\textsuperscript{a}

<table>
<thead>
<tr>
<th></th>
<th>TGAT\textsubscript{d} 5% weight loss (°C)</th>
<th>DSC SS $T_g$ (°C)</th>
<th>DSC SS $T_c$ (°C)</th>
<th>DSC SS $T_m$ (°C)</th>
<th>$\Delta H_m$ SS (J/g)\textsuperscript{b}</th>
<th>$\Delta H_m$ SS (J/g)\textsuperscript{c}</th>
<th>DSC HS $T_m$ (°C)</th>
<th>$\Delta H_m$ HS (J/g)</th>
<th>DMA SS $T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMG1K-PU</td>
<td>297</td>
<td>-52</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>191</td>
<td>13.6</td>
</tr>
<tr>
<td>PTMG2K-PU</td>
<td>300</td>
<td>-71</td>
<td>-28</td>
<td>2</td>
<td>4.5</td>
<td>4.5</td>
<td>186</td>
<td>3.3</td>
<td>-49</td>
</tr>
<tr>
<td>PTMGHQ-PU</td>
<td>304</td>
<td>-74</td>
<td>-28</td>
<td>3</td>
<td>9.4</td>
<td>9.8</td>
<td>187</td>
<td>4.4</td>
<td>-50</td>
</tr>
<tr>
<td>PTMGTH-PU</td>
<td>281</td>
<td>-63</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-35</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a} Thermal transition data obtained from 1st heating cycle of the DSC experiment.
\textsuperscript{b} Normalized based on the total soft segment weights which include HQ or TH.
\textsuperscript{c} Normalized based on the PTMG portion.
Figure 4.1 DSC traces of the pure soft segments (PTMG2K, PTMG1K, PTM GHQ, PTMGTH)

Figure 4.2 DSC traces of the segmented polyurethanes based on different soft segments (PTMG2K-PU, PTMG1K-PU, PTM GHQ-PU, PTMGTH-PU)
4.4.3 Thermomechanical Analysis

The dynamic mechanical behavior of the four segmented systems was investigated by DMA using the film tension mode at a frequency of 1 Hz and a temperature ramp of 3 °C/min from -130 to 150°C. As shown in Figure 4.3, both PTMG2K-PU and PTMGRHQ-PU displayed shoulders in the storage modulus profiles at the later stages of the glass transition region (-30°C). As stated earlier, PTMG2K-PU and PTMGRHQ-PU are the only two samples that displayed soft segment crystallization as evidenced by their DSC traces (T_c = -28 °C). The observation from DMA and DSC suggests that the slight increases in storage modulus of PTMG2K-PU and PTMGRHQ-PU are the result of soft segment crystallization.\textsuperscript{21,39} The T_g values were measured according to the peak positions of the tan delta curves (Table 4.4). Due to differences between the two techniques, T_g values measured by DMA are typically higher than the ones measured by DSC; however, the trends agree with each other.\textsuperscript{40}

As illustrated in Figure 4.3, all of the samples showed a well-defined rubbery plateau ranging from 0 °C to 100 °C or higher. In addition, the storage modulus of PTMG1K-PU is higher than the other samples in the region of the rubbery plateau. This is likely because the hard segment content of PTMG1K-PU is the highest of the four materials studied (43.6%), and its molecular weight is also much greater than other samples which can provide further entanglement (Table 4.2). Moreover, comparison of the storage modulus in the rubbery plateau regions for the four samples reveals that the order of the storage modulus values are in agreement with the hard segment content given earlier in Table 4.2. As temperature
increased further, the rubbery plateau extended up to 100 °C and above, followed by the viscous flow region. The onset of this latter behavior is associated with hard segment softening, which may either result from hard segment T_g transitions or its potential melting. As shown in Figure 4.3, the trend of the flow onset temperatures are consistent with the hard segment melting temperatures as measured by DSC.

To study the influence of processing methods on the morphologies and properties of the studied segmented polyurethanes, a series of comparisons have been made between the solvent cast samples and compression molded samples. As shown in Figure 4.16 to Figure 4.19, each pair of DMA curves exhibits similar profiles. It is worth mentioning that the viscous flow of compression molded samples occurred about 20°C lower than the solvent cast analogs. It is believed that these observations were due to possible thermal degradation caused by compression molding at 220°C. However, for each pair of the four samples obtained by compression molding or solvent casting, the glass transitions and crystallization behavior measured by the tan delta curves showed no significant differences. In addition, the storage modulus curves of each two samples processed by the two methods almost overlapped with their analog (Figure 4.16 to Figure 4.19), which strongly suggested the two processing methods for the studied materials did not drastically change the eventual phase separation.
Figure 4.3 Storage modulus and Tan delta of segmented polyurethanes based on different soft segments

(Compression molded films; Film tension mode; 3˚C/min; 1Hz)

4.4.4 Tensile Properties

Tensile properties of the polyurethane samples were studied. Due to microphase separation, the hard segments aggregate to form microdomains and act as reinforcing fillers.\textsuperscript{37} This behavior imparts strength, extensibility and toughness to segmented polyurethanes and makes them widely adaptable for a variety of practical applications.
The tensile properties of the segmented polymer samples are tabulated in Table 4.5, and their corresponding representative stress-strain curves are illustrated in Figure 4.4. PTMG1K-PU showed a higher Young’s modulus and a lower elongation (~660%), which is in agreement with the DMA results. On the other hand, despite the lower Young’s modulus, PTMG2K-PU exhibited a greater strength and elongation at break. The better elongation arises from a higher soft matrix content in this sample, which is consistent with expectation and other studies.\textsuperscript{43} The higher tensile strength of PTMG2K-PU is promoted by the high tendency of this material to undergo strain-induced crystallization. The crystallinity formed during elongation can act as a stress-bearing component and reinforce the mechanical performance of PTMG2K-PU.\textsuperscript{11} It is noted that an upturn appears
in the tensile curves of PTMG1K-PU and PTMG2K-PU, and PTMGHQ-PU also showed some sign of an upturn. But there is no obvious strain hardening in PTMGTH-PU (Figure 4.4). The bulky triptycene units along the backbone prevented PTMGTH-PU from strain-induced crystallization or ordering of the soft segments, which led to a lower ultimate tensile stress and elongation at break relative to the other three materials. The occurrence of strain-induced crystallization of soft segments was further investigated by wide-angle X-ray diffraction (WAXD), and these results will be discussed in the next section that addresses the morphological aspect of these materials.

Table 4.5 Tensile properties of polyurethanes based on different soft segments

<table>
<thead>
<tr>
<th>Polyurethane samples</th>
<th>Tensile stress at break (MPa)</th>
<th>Elongation (%)*</th>
<th>Young`s modulus (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMG1K-PU</td>
<td>28.5 ± 14.2</td>
<td>658 ± 128</td>
<td>7.6 ± 2.8</td>
</tr>
<tr>
<td>PTMG2K-PU</td>
<td>36.8 ± 7.3</td>
<td>998 ± 123</td>
<td>3.7 ± 0.1</td>
</tr>
<tr>
<td>PTMGHQ-PU</td>
<td>19.9 ± 2.4</td>
<td>960 ± 74</td>
<td>2.2 ± 0.6</td>
</tr>
<tr>
<td>PTMGTH-PU</td>
<td>8.2 ± 0.7</td>
<td>679 ± 39</td>
<td>4.3 ± 0.2</td>
</tr>
</tbody>
</table>

* E elongation values were corrected for compensating the films slide out in the fixtures

Hysteresis behavior of the polyurethanes was also investigated by applying five deformation cycles to each segmented copolymer. For one cycle, a specimen was stretched to 300% at a crosshead speed of 15 mm/min and then immediately returned to its initial position at the same rate and held there for 3 min before the next cycle. The mechanical hysteresis percentage of each sample was calculated using the area under the loading and unloading curves as described in the
As shown in Figure 4.5 and Table 4.6, no sample achieved full recovery immediately after the first stretch. The cycles that took place after the initial loading/unloading cycle are similar in that each showed a decreased mechanical hysteresis with respect to that obtained from the first cycle as expected. It is generally accepted that significant mechanical hysteresis after the first loading cycle arise from the disruption of the connectivity of the hard segments.9,45 Also, it is noted that the mechanical hysteresis of PTMG1K-PU is higher than the other samples whose soft segments have a higher molecular weight, which enhances the incompatibility of the hard and soft segments, and contributes to a higher extent of microphase separation. Similar behavior has been reported in the study of polydimethylsiloxane (PDMS) and PPO segmented polyurethanes.43,45

Table 4.6 Hysteresis behavior of polyurethane samples stretched to 300%

<table>
<thead>
<tr>
<th>Polyurethane samples</th>
<th>Mechanical hysteresis (%)</th>
<th>Instantaneous permanent set after first cycle (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>PTMG1K-PU</td>
<td>69</td>
<td>39</td>
</tr>
<tr>
<td>PTMG2K-PU</td>
<td>55</td>
<td>27</td>
</tr>
<tr>
<td>PTMGHQ-PU</td>
<td>61</td>
<td>30</td>
</tr>
<tr>
<td>PTMGTH-PU</td>
<td>69</td>
<td>37</td>
</tr>
</tbody>
</table>
4.4.5 Morphological Features

Wide-angle X-ray diffraction (WAXD) was used to further confirm the crystallization of the soft segments. It was proposed that strain induced crystallization can partially contribute to strain hardening and consequently enhance the mechanical properties for crystallizable thermoplastic polymers.\textsuperscript{44,46,47} In our study, all samples except PTMGTH-PU showed some sign of hardening behavior (Figure 4.4). As previously discussed in the thermal properties section, the bulky triptycene units minimizes thermally induced crystallization. This prompted us to therefore also investigate the effect of these same bulky aromatic structures upon strain induced crystallization of the soft segments. WAXD was used to analyze the unstrained samples and the samples that were uniaxially stretched to 150%, 300% and 370% (PTMGTH-PU). None of
the unstrained samples exhibited diffraction peaks characteristic of PTMG crystallization (Figure 4.6). This is because the soft segment crystal structure of four of the samples melt below room temperature, as demonstrated by the earlier DSC results. At strains of 150%, PTMG2K-PU and PTMGHQ-PU started to show a sharp peak at $2\theta = 19.9^\circ$ and a shoulder at $2\theta = 24.2^\circ$, which are typical characteristic peaks for PTMG crystallinity (Figure 4.6).\textsuperscript{21} The intensity of both peaks also increased as the strain increased to 300%. Although overlapping with the broad amorphous peak, the peak around 19.9° was observed to become sharper and more intense when the strain increased from 150% to 300%. However, no diffraction peak was observed from the PTMGTH-PU sample, even when the strain was increased to 370% (Figure 4.6 and Figure 4.7). This is evidence that the triptycene units prevent strain induced crystallization at strains up to at least 370% under these conditions. In addition, the PTMG1K-PU sample lacks the ability to promote strain induced crystallization at strains of 300% due to the short soft segments.
Figure 4.6 WAXD profiles of segmented polyurethanes at strains (films were stretched in vertical direction)

Figure 4.7 WAXD patterns of segmented polyurethanes at strains (films were stretched in vertical direction)
Small angle X-ray scattering (SAXS) was also used to probe the morphology of the compression molded films. The scattering intensities and the scattering vector $q$ values are plotted in Figure 4.8. All SAXS profiles display a single interference peak that strongly supports the presence of microphase separation in the four samples. As expected, the interference peak of PTMG1K-PU appears at a higher $q$ value than other samples, which indicates a shorter interdomain spacing around 10.1 nm (Table 4.7). With soft segment molecular weights higher than 2000 g/mol, the interdomain spacings of PTMG2K-PU, PTMGHQ-PU and PTMGTH-PU increased to 13.3 nm, 16.0 nm and 16.2 nm, and the order is consistent with their soft segment molecular weights.43

![SAXS profiles of the polyurethane samples](image)

Figure 4.8 SAXS profiles of the polyurethane samples
Unlike the bulk morphologies studied by SAXS, tapping mode AFM provides a direct view of morphology on the surface of the materials. It is worth mentioning that the free air surface of the solution cast films were used in the AFM analysis, while the compression molded films were used in other characterizations. As shown in Figure 4.9, all of the samples exhibit a distinct microphase separation with well-defined bright regions (hard domains) dispersed in the dark regions (soft domains), which confirms that the microphase separation is not significantly reduced by the presence of the aromatic units in the soft segments. The triptycene containing PTMGTH-PU sample even showed a long range order of hard segment connectivity.

Table 4.7 SAXS of polyurethanes based on different soft segments

<table>
<thead>
<tr>
<th>Polyurethane samples</th>
<th>$q_{max}$ (nm(^{-1}))</th>
<th>Interdomain spacings $d$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMG1K-PU</td>
<td>0.621</td>
<td>10.1</td>
</tr>
<tr>
<td>PTMG2K-PU</td>
<td>0.472</td>
<td>13.3</td>
</tr>
<tr>
<td>PTMGHQ-PU</td>
<td>0.393</td>
<td>16.0</td>
</tr>
<tr>
<td>PTMGTH-PU</td>
<td>0.389</td>
<td>16.2</td>
</tr>
</tbody>
</table>
4.5 Conclusions

PTMG-based soft segments containing hydroquinone and 1,4-dihydroxy triptycene were synthesized and incorporated into segmented polyurethanes. Hydroxyl end-capped PTMG with molecular weights of 1000 g/mol and 2000 g/mol were also used as the soft segment for comparison. DSC and DMA analyses showed that the incorporation of hydroquinone units had no major impact on the mobility and crystallizability of soft segments. In contrast, when triptycene units were introduced into the soft segments, an increase in the soft
segment \( T_g \) and suppression of the thermally induced crystallization of the soft segment were observed. WAXD profiles of the uniaxially deformed samples revealed that the triptycene units also suppressed strain induced crystallization and prevented the films from strain hardening. However, morphology studies carried out with SAXS and AFM showed that polyurethanes with triptycene units in the soft segments still maintained a distinct microphase separation.

### 4.6 Acknowledgement

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4.7 Supporting information

Figure 4.10 Thermal degradation of polyurethanes with different soft segments
Figure 4.11 $^1$H NMR spectrum of PTMG1K-diMs
Figure 4.12 $^1$H NMR spectrum of PTMGHQ diol

Figure 4.13 $^1$H NMR spectrum of PTMGTH
Figure 4.14 Variable temperature FTIR spectra of segmented polyurethane samples

Figure 4.15 WAXD profile of PTMG2K pure soft segment
Figure 4.16 DMA profile comparison between solvent cast and compression molded PTMG1K-PU (Conditions: 3°C/min; 1Hz; film tension mode)

Figure 4.17 DMA profile comparison between solvent cast and compression molded PTMG2K-PU (Conditions: 3°C/min; 1Hz; film tension mode)
Figure 4.18 DMA profile comparison between solvent cast and compression molded PTMGHQ-PU (Conditions: 3°C/min; 1Hz; film tension mode)

Figure 4.19 DMA profile comparison between solvent cast and compression molded PTMGTH-PU (Conditions: 3°C/min; 1Hz; film tension mode)
4.8 Supplementary Materials

Several series of novel soft segment containing aromatic units were prepared and incorporated into the segmented polyurethanes. One series of such soft segments was based on PTMG1K. For instance, 2500 g/mol for PTMG-HQ-diol and 3000 g/mol for PTMG-TH-diol. Another series was based on PTMG650 (650 g/mol) with overall 2400 g/mol for the number average molecular weight of soft segments. In this case, more aromatic units were introduced into a single chain of soft segments. Properties of these novel soft segments and their polyurethane products were investigated as discussed in the following sections.

4.8.1 Synthesis and properties of PUs based on Soft Segments Containing Aromatic Structures

A series of novel soft segments containing aromatic units were synthesized. They were structurally similar to the PTMGHQ and PTMGTH discussed in the previous sections, but with higher number average molecular weights (2500 to 3000 g/mol). Thus, PTMG2900 (~2900 g/mol) was used for comparison. The syntheses of the two novel soft segments followed the same route of PTMGHQ and PTMGTH described before.

4.8.1.1 Characterizations of novel soft segments containing aromatic structures

Novel polyurethane soft segments based on PTMG (1000 g/mol) with hydroquinone (HQ) and 1,4-dihydroxy triptycene (TH) were successfully
synthesized and denoted as PTMG-HQ-diol (2500 g/mol) and PTMG-TH-diol (3000 g/mol).

Acetylation of these two soft segments provided acetylated products for $^1$H NMR characterization. A typical procedure for acetylation of novel soft segments was as follows (Scheme 4.4). PTMG-TH-diol (1 g) and anhydrous pyridine (1 mL) were charged to a 100 mL round bottom flask. Acetic anhydride (0.45 mL) was then dropwise added into the flask. The reaction mixture was stirred at 100 ºC for 12 h. The mixture was poured into ice water to quench the reaction. Dichloromethane (DCM) was used to extract the products from aqueous layer, and the aqueous layer was removed by a separatory funnel. The remaining organic layer was washed with 1 M HCl three times, and then brine three times. Magnesium sulfate was utilized to dry the organic layer for 1 hour after the wash. DCM was evaporated by rotovap and a yellow oil was obtained. The four different soft segments were acetylated by acetic anhydride. In $^1$H NMR spectra, the integration of methyl end groups on the acetylated oligomers were used as the standard peak to calculated the number average molecular weight of the soft segments. Each of the samples were characterized for three times to calculate the average values and standard deviation of number average molecular weights (Table 4.8).

PTMG-HQ-diol: $^1$H NMR (500 MHz, CDCl3) $\delta$ 6.80 – 6.67 (m, 1H), 4.01 (t, $J = 6.5$ Hz, 1H), 3.85 (t, $J = 6.3$ Hz, 1H), 3.52 – 3.23 (m, 35H), 1.98 (s, 1H).
PTMG-TH-diol: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.38 (dt, $J = 7.1$, 3.5 Hz, 1H), 6.97 (dd, $J = 5.3$, 3.2 Hz, 1H), 6.48 (s, 1H), 5.86 (s, 1H), 4.09 (t, $J = 6.5$ Hz, 1H), 3.95 (t, $J = 6.2$ Hz, 1H), 3.58 – 3.34 (m, 29H), 2.91 (s, 1H), 2.05 (s, 1H), 1.95 – 1.51 (m, 31H).

Scheme 4.4 Acetylation of PTMG-TH-diol
Figure 4.20 $^1$H NMR spectrum of acetylated PTMG-HQ-diol

Figure 4.21 $^1$H NMR spectrum of acetylated PTMG-TH-diol
4.8.1.2 Synthesis of PUs containing different soft segments

Segmented polyurethanes were prepared by the prepolymer method. PTMG1000, PTMG2900, PTMG-HQ-diol and PTMG-TH-diol (Table 4.8) were used as the soft segments; MDI and HQEE were used as the diisocyanate and chain extender, which provide hard segment aggregation and thus phase-separated morphologies. The PU samples were denoted such as PTMG1000-PU or PTMG-HQ-diol-PU, which indicates the soft segments in the PU samples.

All of the polyurethanes were synthesized in the same manner, and the synthesis of the polyurethane based PTMG-HQ-diol is given here as an example. In the first step, PTMG-HQ-diol (2.5 g, 1 mmol) and MDI (0.576 g, 2.3 mmol) were charged to a 100 mL three-necked round bottom flask under argon. The flask was equipped with a water condenser, an overhead mechanical stirrer, and an addition funnel. The flask was stirred at 70 °C. Stirring was continued for 4 h. $^1$H NMR spectra were used to confirm the complete consumption of hydroxyl groups in the polyols based on the disappearance of hydroxyl group peak around 2.5 ppm. In the second step, HQEE (0.20 g, 1 mmol) was dissolved in anhydrous DMF and added dropwise into the reaction system. The chain extension proceeded at 75 °C for 24 h. FTIR was used to confirm that the isocyanate groups were completely reacted (no obvious peak appears around 2260 cm$^{-1}$). Polyurethanes based on other soft segments were made by the same procedure. Films were obtained by casting a clear, homogeneous DMF solution (0.2 g/ml) of the segmented polyurethanes directly into a leveled Teflon® mold at 60 °C and then removed
from the mold after 24 h, The films were subsequently dried under vacuum (125 torr) at 60 °C for 24 h and then stored in desiccator for further characterizations.

Table 4.8 Novel Soft segments used in the PUs synthesis

<table>
<thead>
<tr>
<th>Soft segments</th>
<th>Structure</th>
<th>*Molecular Weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMG1000 (Control)</td>
<td><img src="image" alt="Structure" /></td>
<td>1139 ± 61</td>
</tr>
<tr>
<td>PTMG2900 (Control)</td>
<td><img src="image" alt="Structure" /></td>
<td>2940 ± 53</td>
</tr>
<tr>
<td>PTMG-HQ-diol</td>
<td><img src="image" alt="Structure" /></td>
<td>2530 ± 158</td>
</tr>
<tr>
<td>PTMG-TH-diol</td>
<td><img src="image" alt="Structure" /></td>
<td>3028 ± 210</td>
</tr>
</tbody>
</table>
4.8.1.3 Properties of PUs containing different soft segments

PU samples were characterized by FTIR; thermal properties were studied by TGA and DSC; and the thermomechanical behaviors were analyzed by DMA.

FTIR spectra demonstrated that the isocyanate groups were completely consumed in the reactions since there was no sign of N=C=O peak around 2260 cm\(^{-1}\) (Figure 4.23). The carbonyl peak for each of the sample was split, which is attributed to hydrogen bonding interactions. The wavenumber of hydrogen bonded carbonyl peak is slightly lower than the free carbonyl peak due to the lower electron density within the carbonyl groups.
Thermal properties were analyzed by TGA and DSC. According to the TGA results (Figure 4.24), The PTMG1000-PU exhibited a relatively less stable profile than the other three samples, which resulted from the higher content of hard segment relative to other samples. This dependence of polyurethanes’ initial thermal stability on the hard segment content is also reported in the literature.\textsuperscript{49,50} The DSC results were summarized in Figure 4.25, which illustrates the effect of aromatic structures on crystallization behavior of the soft segments in PUs. The PTMG-HQ-diol-PU showed a series of thermal transitions of the SS, which included T\textsubscript{g} at -34 °C, T\textsubscript{c} at -24 °C and T\textsubscript{m} at 10 °C (\(\Delta H_m = 16.02\) J/g). While the PTMG2900-PU exhibited a SS melting endotherm at 16 °C (\(\Delta H_m = 21.76\) J/g). By comparing these two samples, the low T\textsubscript{m} and melting enthalpies of PTMG-HQ-diol-PU suggest that the HQ units slightly disrupt the crystallization of the SS. The
PTMG-TH-diol-PU showed no obvious $T_g$ and $T_m$. No obvious $T_m$ was detected, which strongly implied the inhibition effect of bulky triptycene units on the crystallization of SS. The absence of $T_g$ is probably because of the limitation of the DSC equipment for cooling, which is also the case for PTMG1000-PU and PTMG2900-PU.

Figure 4.24 Thermal degradation of PU samples
The thermomechanical properties of two polyurethane samples (PTMG-HQ-diol-PU and PTMG-TH-diol) are shown in Figure 4.26. It was found that PTMG-HQ-diol-PU exhibited an increase of storage modulus around -20 °C, followed by a decrease around 0 °C. These two transitions correlated well with the crystallization and melting behaviors of PTMG-HQ-diol detected by DSC. The PTMG-TH-diol-PU did not show any increase of storage modulus, which demonstrated that the triptycene units in the SS significantly disrupt the formation of crystallinity, which is also consistent with the DSC results.
4.8.2 Synthesis and characterizations of novel PTMG650 soft segments containing aromatic structures

4.8.2.1 Synthesis of PTMG650 SS containing aromatic structures

Novel polyurethane soft segments based on PTMG (650 g/mol) with HQ and TH were successfully synthesized, and denoted as PTMG650-HQ-diol and PTMG650-TH-diol (Scheme 4.5). The syntheses of these two soft segments are similar to the syntheses of soft segments based on PTMG1000 with HQ and TH, which are described in previous sections. Compared to the PTMG1K based soft segments, PTMG650-based soft segments have high concentration of aromatic units in the chains, which may increase the chances of triptycene interlocking and affecting the crystallization behavior.
The number average molecular weights \( (M_n) \) of these two soft segments were characterized by \(^1\text{H} \) NMR as described in Table 4.1. PTMG soft segments were end-capped by methanesulfonate groups, and the end methyl groups were used as the standard peak for integration and calculation of molecular weight values. Structures of end-capped soft segments and corresponding spectra are shown in Figure 4.27 and Figure 4.28.

PTMG650-TH-diMs: \(^1\text{H} \) NMR (500 MHz, CDCl\(_3\) \( \delta \) 7.31 (dd, \( J = 5.0, 3.4 \) Hz, 1H), 6.89 (dd, \( J = 5.2, 3.1 \) Hz, 1H), 6.40 (s, 1H), 5.78 (s, 1H), 4.19 (t, \( J = 6.5 \) Hz, 1H), 3.87 (t, \( J = 6.0 \) Hz, 1H), 3.52 – 3.26 (m, 20H), 2.93 (s, 1H), 1.90 – 1.44 (m, 23H).

PTMG650-HQ-diMs: \(^1\text{H} \) NMR (500 MHz, CDCl\(_3\) \( \delta \) 6.74 (s, 1H), 4.19 (t, \( J = 6.5 \) Hz, 1H), 3.85 (t, \( J = 6.3 \) Hz, 1H), 3.61 (s, 1H), 3.43 – 3.28 (m, 20H), 2.94 (s, 1H), 1.82 – 1.47 (m, 25H).
Scheme 4.5 Synthesis of soft segments based on PTMG650
Figure 4.27 $^1$H NMR spectrum of PTMG650-TH-diMs

Molecular Weight ($^1$H NMR): ≈ 2426 g/mol

Figure 4.28 $^1$H NMR spectrum of PTMG650-HQ-diMs

Molecular Weight ($^1$H NMR): ≈ 2414 g/mol
4.8.2.2 Titration of PTMG650 SS containing aromatic structures

Titration was carried out to determine the hydroxyl numbers of the soft segments. Samples were first reacted with acetic anhydride in pyridine for 24 h, and then back titrated with 1 N potassium hydroxide standard solution in ethanol. PTMG1K (1000 g/mol) and PTMG2K (2000 g/mol) were also titrated. Hydroxyl numbers were calculated as follows:

\[ OH \text{ value} = \frac{(B - S) \times N \times 56.1}{W} \]

Where B is the volume of KOH solution consumed in blank titration (mL), S is the volume of KOH solution consumed in sample titration, N is the normality of the KOH solution and W is the weight of sample (grams).

According to the results from both \(^1\)H NMR and titration, soft segments based on HQ and TH have comparable molecular weight and chain length.

Table 4.9 Average hydroxyl numbers and M\(_n\) of soft segments

<table>
<thead>
<tr>
<th>Soft segments</th>
<th>OH value (mg KOH/g)</th>
<th>Molecular Weight (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMG650-HQ-diol</td>
<td>50.6 ± 6.6</td>
<td>2240 ± 293</td>
</tr>
<tr>
<td>PTMG650-TH-diol</td>
<td>50.5 ± 8.8</td>
<td>2267 ± 405</td>
</tr>
<tr>
<td>PTMG1K</td>
<td>121.6 ± 6.5</td>
<td>925 ± 51</td>
</tr>
<tr>
<td>PTMG2K</td>
<td>61.4 ± 1.5</td>
<td>1830 ± 45</td>
</tr>
</tbody>
</table>
4.9 Appendix:

Figure 4.29 WAXS scattering pattern of PTMG1K-PU
Figure 4.30 WAXS scattering pattern of PTMG2K-PU
Figure 4.31 WAXS scattering pattern of PTMGHQ-PU
Figure 4.32 WAXS scattering pattern of PTMGTH-PU
4.10 References


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Chapter 5. Synthesis and Properties of Semicrystalline Poly(arylene ether sulfone)s Containing Polyester Segments

5.1 Abstract:

Multiblock copolymers of poly(arylene ether sulfones) (PAESs) and poly(1,4-cyclohexyldimethylene terephthalate) (PCT) were synthesized via melt-phase polymerization. PAES oligomers \( M_n = 2000 \text{ g/mol} \) were synthesized with hydroxyethoxyl end groups, and then reacted with dimethyl terephthalate (DMT) and 1,4-cyclohexanediethanol (CHDM) to obtain segmented copolymers with the goal of introducing semi-crystallinity into the PAES segmented block copolymers. Two CHDM (\textit{all trans} and \textit{cis/trans} = 30/70) were used for comparison. Weight percentages of PCT segments varied from 20 wt% to 80 wt%. According to the results measured by DSC, DMA and WAXD, the copolymers crystallized when the content of PCT segment above 50 wt%, and the crystallinity of the copolymers exhibited a proportional dependence was on the weight percentage of PCT segments. Segmented copolymers with \textit{trans}-CHDM as the polyester segment exhibited a higher level of crystallinity than the 30/70 CHDM mixture.

5.2 Introduction

Poly(arylene ether sulfones) (PAESs) are high performance polymers with high glass transition temperatures \( T_g \), thermal and hydrolytic stabilities, and excellent mechanical properties.\textsuperscript{1-3} With these attractive features, PAESs have found extensive applications in the field of engineering plastics, membrane materials and biomaterials. However, due to the different bond angles of the aromatic ether (121˚) and the sulfonyl (106˚) groups, PAES chains cannot pack effectively, which
prevents crystallization. Thus, when compared to semi-crystalline polymers, PAESs exhibit relatively low chemical resistance and dimensional stability at elevated temperature, etc. Efforts have been made to introduce crystallinity into the PAES systems, and expand applications by chemical structure modification.

Polymer blending is well known as an economical and convenient approach to combine desired properties from different polymer systems. PAESs are often blended with other polymers to improve physical and chemical properties; however, most PAESs are immiscible with other polymers and these immiscible blends have reduced mechanical properties. To solve this problem, multiblock copolymer compatibilizers have attracted growing interest for their ability to reinforce the polymer interface in blended systems.

Chemical structure modification can also impart crystallinity to amorphous PAESs. Kwiatkowski et al. prepared poly(ether ketone ketone)/poly(ether sulfone) (PEKK/PES) block copolymers via nucleophilic polycondensation. The copolymers were semi-crystalline when PEKK composition exceeded 65 wt%, and had $T_m$s above 300 °C, which increased with PEKK content. Recently, Gaymans developed triblock and multiblock semi-crystalline PAESs with monodisperse amide segments by both solution and the melt methods. As a result, crystallinity was introduced with $T_m$s ranging from 220 °C to 270 °C. The $T_m$s increased linearly with amide segment content. The crystallization windows of semicrystalline polymers were defined by the temperature region between $T_g$ and $T_m$. For these PAES copolymers, crystallization windows are relatively small to obtain fast crystallization. Dennis et al. synthesized multiblock copolymers containing
alternating PAES and poly(butylene terephthalate) (PBT) segments.\textsuperscript{17} Semicrystalline morphology was obtained by copolymerizing amorphous PAES oligomers ($M_n = 6000$ g/mol) with crystallizable PBT, when the composition of PAES was below 80 wt\% in the copolymer.

Poly(1,4-cyclohexyldimethylene terephthalate) (PCT) is semicrystalline polyester. Due to the rigidity of cyclohexylene ring, PCT has a higher $T_m$ than PBT (222 °C) and poly(ethylene terephthalate) (PET) (260 °C) in most cases. $T_m$ of PCT is dependent on the $cis/trans$ ratio of CHDM, ranging from 250 °C (all cis-CHDM) to 315 °C (all trans-CHDM).\textsuperscript{17-19} The PCT structure has also been modified by copolymerizing with other comonomers such as isophthalic acid to adjust physical and chemical properties.\textsuperscript{19,20} The cyclohexylene moieties introduced by 1,4-cyclohexanediol (CHDM) provide sub $T_g$ relaxations, that enhance the impact strength. Yee and coworkers studied the secondary relaxations of PET, PCT, and their copolymers. They found the presence of cyclohexylene rings to correspond with secondary relaxations observed at low temperatures using DMA. They attributed the relaxations to interconversion between chair and twist-boat conformations adopted by the cyclohexane rings.\textsuperscript{21,22} They also stated that the combined movements of multiple cyclohexane units result in relatively large-scale translational motions, which increase volume fluctuations and improve the impact properties of the materials. The configuration of cyclohexylene rings also affects the chain packing and crystallization behavior. The melting temperatures of PCT range from 250 °C (all cis-CHDM) to 315 °C (all trans-CHDM), which significantly influences the properties and applications of the material. Thus, the $cis/trans$ ratio
of CHDM is important for the polyester properties, and the cis/trans CHDM does not isomerize during the polymerization. On the other hand, it was observed that cis-trans isomerization occurs for polymers containing 1,4-cyclohexanedicarboxylic acid (CHDA), and acid groups catalyze this process (Figure 5.1).\(^{23,24}\)

![Figure 5.1 Isomerization of cis/trans CHDA](image)

In our group, we synthesized semi-crystalline PAESs by different methods. Terphenyl groups were incorporated into the backbone in both a random and segmented fashion. The segmented copolymer with 50 mol% of 4,4'-dihydroxybiphenyl (DHBP) and 50 mol% of 4,4'-dihydroxyterphenyl (DHTP), showed a melting peak at 320 °C with a relatively narrow crystallization window.\(^4\) Another series of semi-crystalline PAESs were synthesized containing trans-1,4-cyclohexylene rings. These polymers were synthesized from PAES oligomers and trans-1,4-cyclohexylene acid chloride monomers via pseudo-interfacial and solution methods. Crystallinity was increased for biphenyl based PAESs, but the crystallization rate was still slow.\(^{25,26}\) In the present work, we synthesized 2000 g/mol PAES oligomers from biphenyl (BP). Hydroxyl end-capped PAES oligomers were reacted with dimethyl terephthalate (DMT) and two different racemic mixtures of CHDM (all trans and cis/trans = 30/70) to yield segmented copolymers via melt-phase polymerization. The compositions were varied to produce a series of
copolymers, with each having a different PCT segment content. The polymers were characterized to investigate the effect of the ester segments on the morphology and properties. For both all-trans and 30/70 cis/trans mixture of CHDM, crystallization was observed when ester content exceeded 50 wt%.

5.3 Experimental

5.3.1 Materials

Dichlorodiphenyl sulfone (DCDPS, 98%), 4,4’-biphenol (BP, 97%), potassium carbonate (K$_2$CO$_3$, ≥99%), ethylene carbonate (EC, ≥99%), dimethyl terephthalate (DMT, ≥99%), 1,4-cyclohexylenedimethonal (cis/trans = 30/70, 99%), trans-1,4-cyclohexylenedimethanol (all trans, 99%) were purchased from Aldrich, and dried before use. Dimethylacetamide (DMAc, ≥99%) was purchased from Aldrich and used with no further purification. Titanium(IV) butoxide (97%) was purchased from Aldrich and dissolved in n-butanol (Aldrich, 99.8%) with 0.02 g/mol concentration. Toluene, dimethylformamide (DMF, 99.9%), and trifluoroacetic acid (TFA, 99%) were purchased from Fisher Scientific, and used as received.

5.3.2 Synthesis of biphenyl based poly(arylene ether sulfone)s oligomer with phenol end groups

As illustrated in the first step of Scheme 5.1, PAES oligomer synthesis was carried out with an excess of 4,4’-biphenol. The target molecular weight of the product was 2000 g/mol, and controlled based on the stoichiometry imbalance technique.

A typical procedure is shown as follows. BP (20.48 g, 110 mmol), DCDPS (25.84 g, 90 mmol), K$_2$CO$_3$ (37.32 g, 270 mmol), DMAc (300 mL) and toluene (150
mL) were charged to a 1 L three-necked round bottom flask equipped with a mechanical stirrer, an argon inlet, and a Dean-stark trap. The reaction mixture was stirred at 140 °C under argon for 3 h to remove water by azeotropic distillation. The reaction temperature was then increased to 160 °C to distill toluene for 2 h. After the polymerization proceeded at 160 °C for another 22 h, the reaction mixture was cooled to room temperature and poured into a 5 wt% of HCl aqueous solution. A white solid was obtained by precipitation and filtration. The solid was washed with deionized water and methanol three times, respectively. The product was first air dried to remove most of methanol and water, and then dried in a vacuum oven (125 torr) at 100 °C for 18 h. (Yield: 35.5 g, 89.3%) (1H NMR spectrum is shown in Figure 5.9 in supporting information)

5.3.3 Synthesis of PAES2K with hydroxy ethoxy end groups

The PAES2K obtained from BP and DCDPS can be further converted into hydroxy ethoxy end-capped oligomers.27,28 The procedure is illustrated in the second step of Scheme 5.1. PAES2K (20.00 g, 10 mmol), ethylene carbonate (2.64 g, 30 mmol), K₂CO₃ (0.42 g, 3 mmol) and DMF (150 mL) were added into a 250 mL three-necked round bottom flask equipped with a mechanical stirrer, an argon inlet, and a water condenser. The reaction was stirred at 100 °C under argon for 24 h. White solid gradually precipitated from the reaction solution. After cooling to room temperature, the reaction mixture was poured into deionized water. A white solid precipitated and was isolated by filtration. The product was washed with deionized water three times and dried in a vacuum oven (125 torr) at 100 °C for 18
h. (Yield: 19.52 g, 93.5%) (\(^1\)H NMR spectrum is shown in Figure 5.10 in supporting information)

![Chemical structures and reactions](attachment:image.png)

Scheme 5.1 Synthesis of PAES2K with hydroxyl end groups

### 5.3.4 Melt-phase polymerization of PAES-PCT multiblock copolymers

A series of PAES-PCT multiblock copolymers with varying compositions were synthesized in the similar manner. A typical procedure is shown below with PAES-PCT-50 as an example (Scheme 5.2). PAES2K (6.30 g, 3 mmol), DMT (4.76 g, 24.5 mmol), and CHDM (\textit{cis/trans} = 30/70, 3.89 g, 27 mmol) were added to a 100 mL single-necked round bottom flask. Titanium(IV) butoxide (100 ppm) was used as the catalyst. Before the reaction was started, the flask was purged with nitrogen.
for 5 min and then evacuated (~0.2 mmHg) for 5 min. These two steps were repeated for three cycles to remove residual moisture and oxygen in the flask. The reaction flask was lowered into a 220 °C molten metal bath and the melting reaction mixture was stirred at 200 rpm. As soon as the reaction mixture formed a clear liquid (~5 min), the reaction temperature was increased from 220 °C to 270 °C within 30 min. The reaction proceeded at 270 °C under nitrogen for another 2 h. Then the stirring rate was reduced to 30 rpm, a vacuum (0.1-0.2 mmHg) was slowly applied, and the temperature was increased to 290 °C over 15 min. The reaction proceeded with slow stirring (15 rpm) for another 2 h. The reaction mixture was cooled to room temperature over 15 min and turned opaque; crystallization was allowed in this step. The reaction flask was then lowered into the metal bath again to melt any polymer directly in contact with the inside of the flask. The stirring rod was then pulled to separate the polymer from the flask. The polymer was isolated by breaking the flask. The product was chiseled from the stirring rod and cut into small pieces. These product pieces were washed by deionized water, and then dried in vacuum oven (125 torr) at 80 °C for 18 h. (¹H NMR spectrum is shown in Figure 5.11 in supporting information)
Scheme 5.2 Synthesis of PAES-PCT multiblock copolymers

5.3.5 Preparation of polymer films

Polymers were cut into small pieces with a chisel, and compression molded into polymer films. Before the compression molding, polymer samples were dried at 100 °C in a vacuum oven (125 torr) for 18 h to eliminate any residual moisture, which may cause potential degradation at elevated temperatures. Then, the samples were sandwiched between Kapton® polyimide films and compression molded at 270 °C with a pressure of 500 PSI for 5 min and immediately quenched in an ice water bath. The films were dried at 60 °C in a vacuum oven (125 torr) for 18 h, and then stored in a desiccator at room temperature.

5.3.6 Instrumentation

$^1$H NMR spectra were recorded on a Varian INOVA 500 MHz spectrometer at room temperature using deuterated DMSO, and deuterated chloroform (CDCl$_3$)
with 5 vol% deuterated TFA as the solvents. ¹H NMR spectra were used to confirm the structure of PAES oligomers and PAES-PCT copolymers. The molecular weight and molecular weight distribution were measured by size exclusion chromatography (SEC) in N-methyl-2-pyrrolidone (NMP) with 0.05 LiBr at 30 °C on a Waters Alliance model 2690 chromatograph equipped with a Waters HR 0.5+ HR2+ HR3+ HR 4 styragel column set. Mono-disperse polystyrene standards were used to construct a universal molecular weight calibration curve. A Viscotek refractive index detector and a viscometer were used. Thermogravimetric analysis (TGA) was performed using a TA Instrument TGA Q500 from room temperature to 800 °C with a heating ramp of 10°C/min under nitrogen. Differential scanning calorimetric (DSC) data were obtained on a TA Instruments Q2000 equipped with refrigerated cooling system (RCS) with a nitrogen flow of 40 mL/min. Copolymer samples were initially equilibrated at 30 °C for 5 min, and then heated to 300 °C with a heating rate of 10 °C/min, and followed by a cooling cycle with a rate of 10 °C/min. The samples were equilibrated at 30 °C for 5 min, followed by the second heating cycle at 10 °C/min. Thermal transitions were determined from the second heating cycle, glass transition temperature (Tg) was determined by the temperature of midpoint of glass transition. Dynamic mechanical analysis (DMA) was performed on a TA Instruments Q800 dynamic mechanical analyzer using the film tension mode at a frequency of 1 Hz and a temperature ramp of 3 °C/min from -100 to 300°C. Tensile analysis was performed on an Instron Model 4400 Universal Testing System at ambient conditions. The film samples were stamped into dog bone shaped specimens (40 × 4 × 0.4 mm) with a die according to ASTM D3368.
specifications. Specimens were tested with a cross-head rate of 15 mm/min at ambient conditions using an initial gauge length of 15 mm. Small angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) experiments were performed using a Rigaku S-Max 3000 3 pinhole SAXS system, equipped with a rotating anode emitting X-ray with a wavelength of 0.154 nm (Cu Kα). The sample-to-detector distance was 1603 mm for SAXS and 82.5 mm for WAXD, and the q-range was calibrated using a silver behenate standard. Two-dimensional SAXS patterns were obtained using a fully integrated 2D multiwire, proportional counting, gas-filled detector, with an exposure time of 1 h. WAXD two-dimensional diffraction patterns were obtained using an image plate with an exposure time of 1 h. The SAXS and WAXD data were corrected for sample thickness, sample transmission and background scattering, and the WAXD profiles were vertically shifted to facilitate a comparison of peak positions. All the SAXS and WAXD data were analyzed using the SAXSGUI software package to obtain radically integrated SAXS and WAXD intensity versus the scattering vector q (SAXS) or 2θ (WAXD), where \( q = \frac{4\pi}{\lambda}\sin(\theta) \), θ is one half of the scattering angle and \( \lambda \) is the wavelength of X-ray.

5.4 Results and Discussion

5.4.1 Synthesis of PAES oligomers and multiblock copolymers

The PAES2K oligomers were synthesized with excess BP to control the molecular weight and end groups. Based on the Carothers equation, the feed ratio of BP and DCDPS was set at 11:9 to obtain PAES with number average molecular
weight around 2000 g/mol. For the purpose of comparison, PAES homopolymers were synthesized in a similar fashion with a 1:1 BP:DCDPS stoichiometry.

Because the phenolic groups of PAES2K are not reactive enough for transesterification and polycondensation reactions, PAES2K was converted into HEPAES2K to obtain hydroxyethoxy end groups. Turner reported the conversion of phenol group to hydroxyethyl group using ethylene carbonate for a series of diphenol monomers, and this method was applied to oligomers and polymers. Unlike the biphenol-A-based PAES, the BP-containing HEPAES2K was not soluble in chloroform or any other common organic solvents. As a result, melt-phase polymerization was chosen to copolymerize HEPAES2K with DMT and CHDM. The nomenclature of copolymer samples is based on the PAES and polyester segments and the weight percentage of polyester segment. Polyester segments from mixed CHDM (cis/trans = 30/70) are named as PCT, while tPCT refers to the polyester segments based on all trans CHDM. Therefore, PAES-tPCT-20 refers to PAES-PCT multiblock copolymers with 20 wt% of PCT based on all trans CHDM.

5.4.2 $^1$H NMR analysis

$^1$H NMR spectrum was used to analyze the structure of the oligomers and copolymers. PAES2K and HEPAES2K were characterized by $^1$H NMR, and the average number of repeat units were calculated by the ratio between the integration area of peak f and peak b (Figure 5.9). The number average molecular weight of PAES2K was 2060 g/mol as estimated by the $^1$H NMR results.
Reaction completion was confirmed by $^1$H NMR. As shown in Figure 5.10, the proton peaks of the hydroxyethoxy end groups in HEPAES2K appeared at 4.06 ppm and 4.14 ppm, and shifted to 4.70 ppm and 4.34 ppm, respectively, after polymerization. No obvious peaks were found around 4.06 ppm and 4.14 ppm after polymerization, suggesting that copolymerization between the HEPAES2K oligomers and DMT was complete. The two peaks observed at 4.18 ppm and 4.27 ppm are believed to correspond to the methylene groups next to the cyclohexylene rings from CHDM. The ratio of the integration areas between these two peaks was close to the expected ratio of CHDM mixture ($cis$/trans $= 30/70$). The $^1$H NMR spectrum of the copolymer containing tPCT segments (50 wt%) is also shown in Figure 5.12. A small peak from $cis$-PCT was observed, but concentration of the $cis$ isomer is expected to be fairly low (about 3 mol%).

The weight percent of PCT segments within the copolymer was also calculated using $^1$H NMR. As shown in Figure 5.11, the area of peak h divided by the area of peak d can be used to calculate the molar ratio between PAES segments and PCT segments. As a representative example, Figure 5.11 exhibits the spectrum of PAES-PCT-50 (50 wt% of PCT). The weight percentage of PCT calculated from the $^1$H NMR spectrum was 51.6%, which is in agreement with the theoretical value. The PAES-tPCT-50 (Figure 5.12) and other samples with different compositions also showed similar consistency.

5.4.3 Thermal Stability

The thermal stability of the copolymers was analyzed by thermogravimetric analysis (TGA). As shown in Figure 5.2, all the copolymers showed a two-stage
thermal degradation behavior under a nitrogen atmosphere, which corresponded to the PCT and PAES segments, respectively. All the copolymers showed an initial thermal degradation temperature around 400 °C. For all of the samples, as the content of PCT increased, the $T_d$ decreased.

![Graph showing thermal degradation behaviors of PAES-PCT copolymers](image)

Figure 5.2 Thermal degradation behaviors of PAES-PCT copolymers

(a.PCT; b.PAES-PCT-80; c.PAES-PCT-60; d.PAES-tPCT-50; e.PAES-PCT-40; f.PAES-tPCT-20; g.PAES)

5.4.4 DSC analysis

The thermal transitions of the multiblock copolymers were analyzed by DSC (Table 5.1). It is generally accepted that the $T_g$s of copolymers correspond to the percentage of the components and their morphologies. For phase-separated polymers, two or more glass transitions are possible; however, in this study there was only one glass transition observed for each of the samples (Figure 5.3 and
Figure 5.4), which suggested phase mixing in these segmented block copolymers. It should also be noted that the $T_g$ decreased with increasing PCT content. For PCT and PAES homopolymers, semi-crystalline PCT has a much lower $T_g$ (92 °C) compared to biphenol-based PAES (224 °C). Thus, the copolymers with lower PCT content exhibited higher $T_g$s.

The crystallization behavior of the materials was investigated by measuring the $T_m$ and $\Delta H_m$. $\Delta H_m$ was determined by area under melting peak of DSC curves. Melting peaks were not observable when the PCT content was below 50 wt%. However, each copolymer with more than 50 wt% of PCT exhibited melting peaks, and the $T_m$ and melting endotherm were proportional to the PCT wt%. From 100 wt% PCT ($cis/trans = 30/70$) to 60 wt% of PCT, the melting temperatures steadily dropped from 282 °C to 262 °C, and the melting endotherm decreased from 25.67 J/g to 10.67 J/g. Higher PCT content allows easier packing of the ester segments, resulting in a greater degree of crystallization.
Table 5.1 Thermal transitions of PAES-PCT and PAES-tPCT samples

<table>
<thead>
<tr>
<th></th>
<th>DSC $T_g$ (°C)</th>
<th>DSC $T_c$ (°C)</th>
<th>DSC $T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>DMA $T_g$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAES</td>
<td>231</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>225</td>
</tr>
<tr>
<td>PAES-PCT-20</td>
<td>174</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>178</td>
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<tr>
<td>PAES-PCT-40</td>
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<td>-</td>
<td>-</td>
<td>152</td>
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<tr>
<td>PAES-PCT-50</td>
<td>138</td>
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<td>-</td>
<td>-</td>
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<td>PAES-PCT-60</td>
<td>132</td>
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<tr>
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<td>93</td>
</tr>
<tr>
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<td>-</td>
<td>-</td>
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<tr>
<td>$^*_{tPCT}$</td>
<td>-</td>
<td>-</td>
<td>315</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* $T_m$ data was obtained from Kibler et al.\textsuperscript{18}
* $\Delta H_m$ was determined by area under melting peak of DSC curves
The thermal transitions of PAES-PCT copolymers prepared from all-trans CHDM were also studied by DSC. As evidenced in Figure 5.4, better regularity along the polymer backbone as a result of utilizing all-trans CHDM leads to a higher crystallinity relative to PAES-PCT analogs. This is demonstrated by the higher melting temperatures and melting endotherms. For example, the melting endotherm of PAES-tPCT-60 (21.1 J/g) is almost double the endotherm value of PAES-PCT-60 analog (10.8 J/g). In addition, the crystallization and melting behavior were detected for PAES-tPCT-50, while there was no sign of crystallization or melting for PAES-PCT-50.
Amide segments and PBT can be copolymerized with PAES to obtain semicrystalline PAES.\textsuperscript{15,17} In our study, semicrystalline PAESs containing PCT or tPCT segments exhibited higher glass transition temperatures, melting temperatures and wider crystallization windows (Table 5.1). Furthermore, biphenol-based PAES possesses a greater solvent resistance, when compared to the PAES prepared from bisphenol-A. Previous work in our group also demonstrated that the cyclohexylene ring introduced into the PCT segments provides sub-\(T_g\) relaxation, which is potentially useful for the enhancement of impact strength of the materials.\textsuperscript{25}
5.4.5 Thermomechanical analysis

DMA was utilized to characterize the thermodynamic properties of the PAES-PCT multiblock copolymers. As shown in Figure 5.5, the glass transition systematically increases from 93 °C to 225 °C as the PCT segment content decreases from 100 wt% to 0 wt%. The T\textsubscript{g}s measured by DMA were generally consistent with the values measured by DSC (Table 5.1).

Crystallization behavior was studied by DMA using initially amorphous samples. In order to obtain amorphous specimens for analysis, samples were prepared as follows. DMA specimens were compression molded at temperatures 10 °C higher than their T\textsubscript{m} (if they were semi-crystalline) or at 250 °C if they were amorphous. All films were immediately quenched in an ice bath to give each sample a similar thermal history. This method minimized crystallization and preserved the crystallizable PCT segments in an amorphous state before analysis. The samples were not thermally annealed before the DMA experiments. As a result, crystallization of the PCT segments can be observed around T\textsubscript{c}, as indicated by a rapid increase in the storage modulus. Unlike pure PAES, the copolymers containing PCT crystalline segments displayed a temperature independent plateau following the crystallization. The storage modulus and temperature range of this plateau were directly related to the crystallizable PCT segment content. The PCT homopolymer exhibited the widest plateau, ranging from 130 °C to 260 °C, and the highest storage modulus (~100 MPa). Both the plateau width and the storage modulus decreased when the PCT content decreased to 50 wt%. Interestingly, the PAES-PCT-50 also showed a hump between 200 °C to 250 °C. This appears to be
crystallization that was not detected by DSC, suggesting the copolymer with 50 wt% of PCT has the ability to crystallize under certain conditions. There was no sign of crystallization in the PAES-PCT-20 and PAES-PCT-40 samples. In these cases, the storage modulus of the PAES-PCT samples appears to be dominated by the PAES portion of the copolymers.

![DMA profiles of PAES-PCT copolymers](image)

Figure 5.5 DMA profiles of PAES-PCT copolymers

The PAES-tPCT multiblock copolymers were also analyzed using DMA. The Tgs of the materials increased with decreasing tPCT content (Figure 5.6). PAES-tPCT samples containing more than 40 wt% of tPCT showed an increased storage modulus, which we attribute to the crystallization of tPCT segments. Similar
crystallization behavior was observed in the PAES-PCT samples. This result further confirms that more than 40 wt% of ester segments are required to obtain crystallinity for both PCT and tPCT.

However, when compared to samples with 30/70 cis/trans PCT, PAES-tPCT samples showed a greater tendency toward crystallization. This is made evident by the width and storage modulus of the plateau after crystallization. The PAES-tPCT-50 exhibited a plateau with a similar width and storage modulus as PAES-PCT-50, but the plateau of PAES-tPCT-60 continued from 180 °C to 240 °C with a higher storage modulus, around 30 MPa, when compared to the PCT analog.

Figure 5.6 DMA profiles of PAES-tPCT copolymers
5.4.6 Tensile properties

Tensile testing was used to study the mechanical performance of PAES-PCT copolymers. All the polymers used in this test were quenched without annealing. Due to the defects in the specimens, like bubbles, most samples broke at low strains (10% to 20%). However, some samples elongated to 200% or more; representative stress-strain curves of PAES-PCT-50 and PCT are shown in Figure 5.7. Interestingly, both samples presented strain-hardening behavior above 120%, which suggested strain-induced crystallization or local orientation of polymer chains. Since the $T_g$ of PAES-PCT-50 is 138 °C (measured by DSC), this series of copolymers have the potential to be used as flexible substrates for electronics.

![Figure 5.7 Representative stress-strain curves of PAES-PCT-50 and PCT](image)

Figure 5.7 Representative stress-strain curves of PAES-PCT-50 and PCT
5.4.7 Morphology study

WAXS was used to characterize the crystallization and microphase separation of the copolymers. Before the analyses, the samples were annealed at 200 °C for 24 h to promote crystallization.

![WAXS profiles of annealed PAES-PCT copolymers](image)

Figure 5.8 WAXS profiles of annealed PAES-PCT copolymers

As shown in Figure 5.8, PAES-PCT samples exhibited a broad amorphous profile when the content of PCT segments was 20 wt% or lower. Sharp peaks started appearing at 16.1°, 18.5°, 23.2°, and 25.7° for the PAES-PCT-40 material. These peaks intensified as the PCT composition increases, which suggested a tunable crystallinity. This result confirmed the observation from previous DSC and DMA studies.
5.5 Conclusion

A series of semicrystalline polysulfone-polyester multiblock copolymers with varying composition was synthesized via melt-phase polymerization. Crystallizable PCT was copolymerized with amorphous PAES segments to obtain tunable crystallinity. PAES oligomers (Mn: 2000 g/mol) based on biphenol were synthesized to control the length of PAES segments in the copolymers. DMT and CHDM were used to form the PCT segments with varying weight percentage. For both PCT and tPCT, the composition of polyester segment needs to be above 50% to obtain observable crystallinity, studied by DSC, DMA and WAXS. The crystallinity of copolymers increases as the wt% of PCT or tPCT increases. Comparison of copolymer crystallization behavior was also made between two polyester segments. PCT prepared from all trans CHDM exhibited a greater degree of crystallization compared to the cis/trans 30/70 mixture.
5.6 Supporting information

PAES2K: $^1$H NMR (500 MHz, d-DMSO) δ 9.60 (s, 1H), 7.95 (s, 3H), 7.74 (s, 2H), 7.67 – 7.61 (m, 3H), 7.50 – 7.44 (m, 2H), 7.20 (dd, $J = 37.8, 15.1$ Hz, 23H), 6.86 (d, $J = 7.2$ Hz, 2H).

Figure 5.9 $^1$H NMR spectrum of PAES2K
HEPAES2K: $^1$H NMR (500 MHz, CDCl$_3$:TFA v/v 95:5) δ 7.80 (m, 18H), 7.58 – 7.39 (m, 22H), 7.09 – 6.96 (m, 37H), 6.92 (d, $J = 8.4$ Hz, 4H), 4.13 (t, 4H), 4.07 (t, 4H).

Figure 5.10 $^1$H NMR spectrum of HEPAES2K
PAES-PCT-50: $^1$H NMR (500 MHz, CDCl$_3$:TFA v/v 95:5) $\delta$ 8.21 – 8.07 (m, 33H), 7.97 – 7.82 (m, 18H), 7.69 – 7.51 (m, 22H), 7.12 (dt, $J = 13.5$, 7.7 Hz, 36H), 7.04 (d, $J = 8.4$ Hz, 4H), 4.79 (t, 4H), 4.43 (t, 4H), 4.38 – 4.34 (m, 8H), 4.26 (d, $J = 6.2$ Hz, 21H).

Figure 5.11 $^1$H NMR spectrum of PAES-PCT-50
PAES-tPCT-50: $^1$H NMR (500 MHz, CDCl$_3$:TFA v/v 95:5) $\delta$ 8.21 – 8.07 (m, 33H), 7.97 – 7.82 (m, 19H), 7.69 – 7.51 (m, 23H), 7.12 (dt, $J = 13.5$, 7.7 Hz, 38H), 7.04 (d, $J = 8.4$ Hz, 4H), 4.79 (t, 4H), 4.43 (t, 4H), 4.38 – 4.34 (m, 1H), 4.26 (d, $J = 6.2$ Hz, 29H).

Figure 5.12 $^1$H NMR spectrum of PAES-tPCT-50

5.7 References


Chapter 6. Suggested Future Work and Summary

6.1 Introduction

Triptycene-containing segmented polyurethanes and multiblock copolymers with polysulfone and polyester segments have been studied and discussed in the previous chapters. Future studies can be conducted in several directions based on these efforts. Possible modifications include functionalization of triptycene units in the polyurethane systems, introduction of triptycene into polysulfone segments in the copolymers, and so on.

6.2 Segmented polyurethane containing triptycene units in the soft segments

In Chapter 3, studies were performed relating to the synthesis of triptycene-containing PTMG based soft segments and their incorporation into the segmented polyurethanes. MDI and HQEE were used to prepare the hard segments. The obtained soft segments were synthesized with PTMG1K (1000 g/mol), and have a number average molecular weight of around 2500 g/mol; thus, it averaged one aromatic unit in one soft segment. To investigate the effect of triptycene structure on crystallization behavior and the interlocking effect of triptycene units, PTMG based soft segments containing aromatic units can be prepared with different molecular weights of PTMG, ranging from 650 g/mol to 2900 g/mol, and keeping the overall molecular weight of soft segment constant, for example, 6000 g/mol. (Figure 6.1). This method can vary triptycene unit concentration in the soft segment chains without drastically changing their molecular weights. Some preliminary results have been discussed in the supplementary materials from Chapter 3, in
which PTMG650 (650 g/mol) was utilized to prepare soft segments. Meanwhile, the effect of triptycene units on the crystallization behavior of the polyurethanes can also be investigated. It is possible that this work can offer an approach to control the soft segment crystallinity of segmented polymers and the corresponding physical properties such as mechanical strength and ductility.

Figure 6.1 Soft segments prepared based on different molecular weights of PTMG

6.3 Segmented polyurethanes containing highly functionalized triptycene units

Each of the triptycene units contains three phenyl groups. It is possible to attach at least one functional group to each phenyl group to convert the monomer into highly functionalized units. It has been reported that triptycene can be modified to prepare ion-containing poly(arylene ether sulfone)s for applications of anion or
proton exchange membranes.\textsuperscript{1,2} Based on these studies, it is feasible to synthesize sulfonated triptycene monomers and introduce them into the hard or soft segments of polyurethane systems for the potential application as water-dispersible polyurethane ionomers (Figure 6.2). Most of the previous efforts on polyurethane ionomers focused on the study of ion-containing hard segments polyurethanes,\textsuperscript{3-5} while a few studies have investigated polyurethanes based on ion-containing soft segments.\textsuperscript{6,7} By introducing sulfonated triptycene into polyurethanes, it is expected to impart enhanced conductivity, high dielectric constant and improve thermal and mechanical properties.

![Figure 6.2 Polyurethane ionomers containing sulfonated triptycene units in soft segments](image)

\textbf{6.4 Block copolymers with triptycene-containing polysulfone segments}

Poly(arylene ether sulfone)s are widely used as engineering plastics due to their high $T_g$, as well as excellent thermal and mechanical properties. However, most polysulfones are hydrophobic, which limits their use as membrane materials in aqueous conditions.\textsuperscript{8} Previous work showed the method to incorporate
sulfonated units or hydrophilic poly(ether oxide) (PEO) into the backbone of polysulfones.$^{9,10}$

As discussed in previous sections, it is possible to attach up to three sulfonyl groups onto one triptycene unit, which leads to a highly sulfonated structure. This approach provides the possibility of increased hydrophilicity and ion conductivity. On the other hand, investigations of block copolymers containing PAES segments reveal that flexible segments such as PEO or poly(tetrahydrofuran) (PTMG) can be used to increase hydrophilicity of PAESs.$^{9,11,12}$ Based on these studies, it is possible to copolymerize sulfonated triptycene-containing PAESs with low $T_g$ segments, and the composition and segment length of the blocky structure can be controlled to tune the morphologies and properties of resulting polymers.

### 6.5 Summary

In the scope of this dissertation, two polymer systems were discussed focusing on the synthesis, morphologies and properties of triptycene-containing segmented polyurethanes (Chapter 3 and Chapter 4), and semicrystalline polysulfone-polyester multiblock copolymers (Chapter 5).

In Chapter 3, a fundamental study was conducted on the synthesis and properties of segmented polyurethanes containing a triptycene chain extender. To systematically probe the effect of the hard segments on the morphologies and properties of segmented polyurethanes, four hard segments with varying bulkiness and flexibility were prepared from two diisocyanates and two chain extenders. Hexamethylene diisocyanate (HDI) or 4,4'-methylenebis(phenyl isocyanate) (MDI) were used as the diisocyanates, and hydroquinone bis(2-hydroxyethyl)ether
(HQEE) or triptycene-1,4-hydroquinone bis(2-hydroxyethyl)ether (TD) were used as the chain extenders. It was found that the bulky triptycene structure disturbs the hydrogen bonding interactions; microphase separation was also inhibited when the TD was coupled with less flexible MDI. However, flexible HDI was utilized to overcome the disturbance of bulky TD on the packing of hard segments, and lead to ribbon-like hard domains with long-range order. The interdomain spacings of the microphase-separated samples were around 15 nm, measured by SAXS.

Discussion in Chapter 4 demonstrated the effect of triptycene units on the crystallization behavior and microphase separation of segmented polyurethanes. Two new soft segments were synthesized containing either hydroquinone (HQ) or 1,4-dihydroxy triptycene (TH) in the chains. PTMG1K ($M_n$: 1100 g/mol) and PTMG2K ($M_n$: 2000 g/mol) were used for comparison. DSC and DMA measurements suggested that the bulky triptycene units inhibit the thermally induced crystallization of soft segments, while the soft segments with less bulky HQ did not exhibit a significant decrease of crystallinity. Tensile test results showed no sign of strain hardening for triptycene-containing soft segments, which implied that the triptycene units disturbed strain-induced crystallization. This result was supported by the wide angle X-ray scattering (WAXS) analysis with strained samples (up to 370% of elongation). Nevertheless, triptycene units in the soft segments showed little effect on the microphase separation. All of the polyurethane samples possessed well-defined microphase separation on the surface observed by tapping mode AFM phase images. Small angle X-ray scattering (SAXS) analysis also confirmed the existence of microphase separation.
in the bulk morphology. Moreover, the interdomain spacing of these samples, measured by SAXS, increases as the molecular weights of soft segments increase.

Study of semicrystalline polysulfone-polyester multiblock copolymers was discussed in Chapter 5. Crystallizable poly(cyclohexanedicarboxylate) (PCT) was copolymerized with amorphous poly(arylene ether sulfone) (PAES) segments to obtain tunable crystallinity for the multiblock copolymers. Polysulfone oligomers ($M_n$ 2000 g/mol) based on biphenol were synthesized to control the length of PAES segments, followed by phenol groups being converted into primary hydroxyl end groups to increase reactivity. Dimethyl terephthalate (DMT) and 1,4-Cyclohexanediol (CHDM) were used to form the PCT segments with varying weight percentage. It was found that the PCT wt% needs to be above 50% to obtain observable crystallinity, studied by DSC, DMA and WAXS, and the crystallinity of copolymers increases as the wt% of PCT increases. Comparison of PCT crystallization behavior was also made between two types of CHDMs with different cis/trans isomer ratio (cis/trans 30/70 and all trans). PCT prepared based on all trans CHDM exhibited a greater degree of crystallization compared to the cis/trans 30/70 mixture.

### 6.6 References


