Synthesis and Characterization of *trans*-1,4-Cyclohexylene Ring Containing Poly(arylene ether sulfone)s

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ABSTRACT

Poly(arylene ether sulfone)s (PAES) are important commercial polymers and have been extensively studied due to their excellent thermal and mechanical properties. However, some applications are still limited when good solvent resistance and low thermal expansion coefficient are required. There has been a continuous interest in developing new PAES based on new monomers or polymer modifications to obtain new properties or to enhance existing properties. In this dissertation, the synthesis, characterization and structure-property relationship of new 1,4-cyclohexylene ring containing PAESs were comprehensively studied. Different polymerization techniques were used to synthesize polymers with different segmental lengths.

The monomer, 4,4'-[*trans*-1,4-cyclohexanebis(methylene)] bisphenol (CMB), was synthesized and fully characterized. Based on 4,4’-dihydroxy-*p*-terphenyl (DHTP), 4,4’-dihydroxybiphenyl (DHBP) and the CMB monomer, homopolymer and random copolymers of PAES were prepared with high molecular weights and high glass transition temperatures. Dynamic mechanical analysis (DMA) on these polymers showed multiple sub-T_g relaxations. A large increase in the ultimate elongation was obtained with the CMB and DHTP containing sample, which could be due to the strong sub-T_g relaxations observed from the DMA results.

A series of four acid chloride monomers were synthesized and polymerized with phenol terminated PAES oligomers. Solution polymerization and pseudo-interfacial polymerization techniques were used to prepare both bisphenol-A (bis-A) based and DHBP based PAES oligomers. With the incorporation of the *trans*-1,4-cyclohexylene units, decreases in the glass transition temperatures were observed from both the bis-A based and the DHBP based polymers. However, melting transitions were only observed in the DHBP based *trans*-1,4-cyclohexylene containing PAESs. Crystallinity was confirmed by differential scanning calorimetry (DSC) and wide angle X-ray diffraction (WAXD). A mechanical property study of the high molecular weight *trans*-1,4-cyclohexylene containing polymer samples showed moderate ultimate elongation enhancements.

A series of PAES-polyester multiblock copolymers were synthesized with both solution method and melt polymerization. In the solution method, phenol terminated PAES oligomers and the acid chloride terminated poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) oligomers were presynthesized and coupled in solution. The molecular weights of the polymer products obtained from the solution method were limited by solubility issues. Melt phase polymerization was employed to obtain high molecular weight polymers. Hydroxy ethoxy terminated PAES oligomers were synthesized and polymerized with 1,4-cyclohexanedimethanol (CHDM) and dimethyl terephthalate (DMT) in the melt. Polymers with high molecular weights were obtained. Tensile test results suggested that the mechanical properties of these polymers were dominated by the PAES components with polyester contents up to 20 wt%. Melting transitions were observed from polymers with higher polyester contents, and these polymers exhibited limited solubility in common organic solvents.

DEDICATION

To my grandparents, Rong Zhang, Shuqin Li,

and grandparents in-law, Shude Wang, Guo Lu

Thank you so much for loving me and giving me everything to make me who I am!

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Chapter 1 Dissertation Overview

The research described in this dissertation is focused on poly(arylene ether sulfone) (PAES) backbone modification with 1,4-cyclohexylene ring containing units based on polycondensation polymerizations. A roadmap for the dissertation is configured in **Figure 1.1**. **Chapter 2** presents a comprehensive review. The first part describes synthetic methods, characterization, applications, and commercially available products. The second part of the review is on cyclohexylene ring containing polymers. Monomers and polymers of two major classes of cyclohexylene ring are reviewed. The two classes are 1,1-cyclohexylene ring and 1,4-cyclohexylene ring. The reviews start with the common monomer synthesis and modifications followed by polymer synthesis, properties, and effects of cyclohexylene ring incorporation. Due to the limited amount of research on cyclohexylene ring containing PAES, the polymers reviewed in this part are focused on polyesters, polyamides, etc..

Chapters 3, **4**, and **5** describe the synthesis and properties of different cyclohexylene ring containing polymer systems based on new cyclohexylene ring containing monomers and oligomers. The thermal properties, mechanical properties, and relaxation behavior were evaluated with their aromatic analogues or commercial products with comparable structures. Some preliminary research on the segmented polysulfone-polyurethane work is presented in **Chapter 6**. **Chapter 7** summarizes the whole dissertation and conclusions are drawn based on the overall findings and trends.

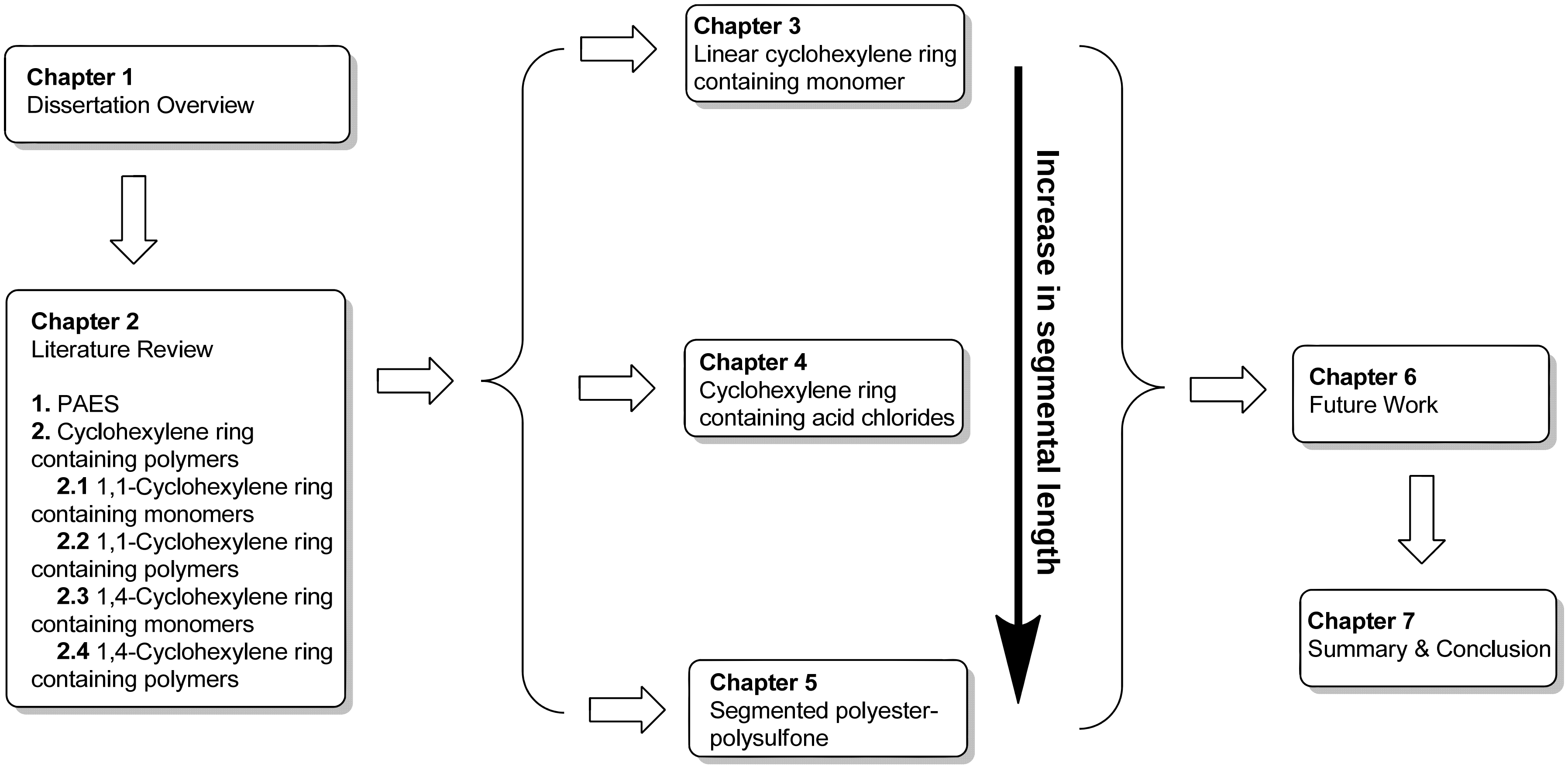


Figure 1.1 Overview of the dissertation structure

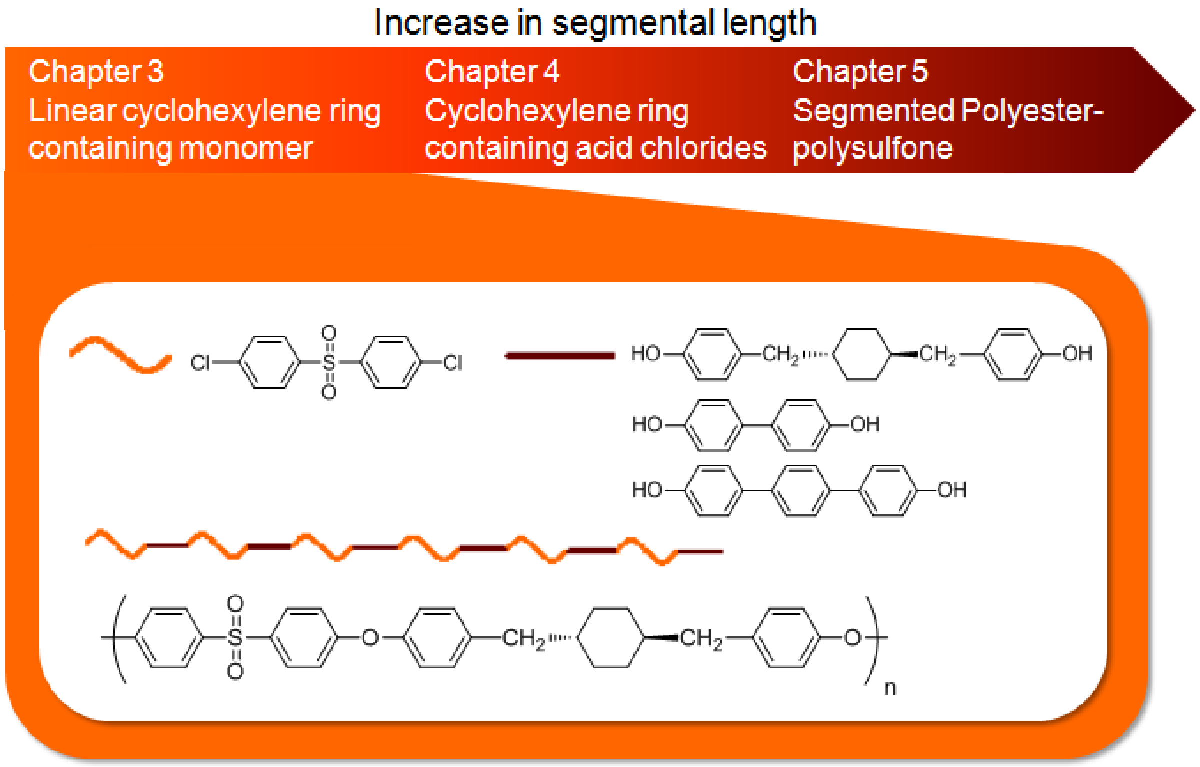


Figure 1.2 Chapter 3 Linear cyclohexylene ring containing monomer

The research described in **Chapters 3**, **4**, and **5** was organized systematically in a sequence where the segmental length was increased.

As shown in **Figure 1.2**, **Chapter 3** describes polymers derived from a series of linear diphenol monomers (short maroon straight lines) and 4,4’-dichlorodiphenylsulfone (DCDPS, short orange waves, it is shown as a wave due to the kinked sulfone unit). The linear monomers include 4,4’-dihydroxylbiphenyl (DHBP), 4,4’-dihydroxyl-*p*-terphenyl (DHTP), and 4,4'-[*trans*-1,4-cyclohexanediylbis(methylene)] bisphenol (CMB). DHBP and DHTP are two rigid aromatic linear monomers. CMB is a new cyclohexylene ring containing diphenol monomer that was synthesized in the lab. We define homopolymer as a polymer from DCDPS and a single biphenol and random copolymers as ones based on two biphenols. Both homopolymer and the random copolymers of DHBP, DHTP, and CMB were synthesized and characterized. The thermal properties, mechanical properties and the relaxation behaviors were studied.

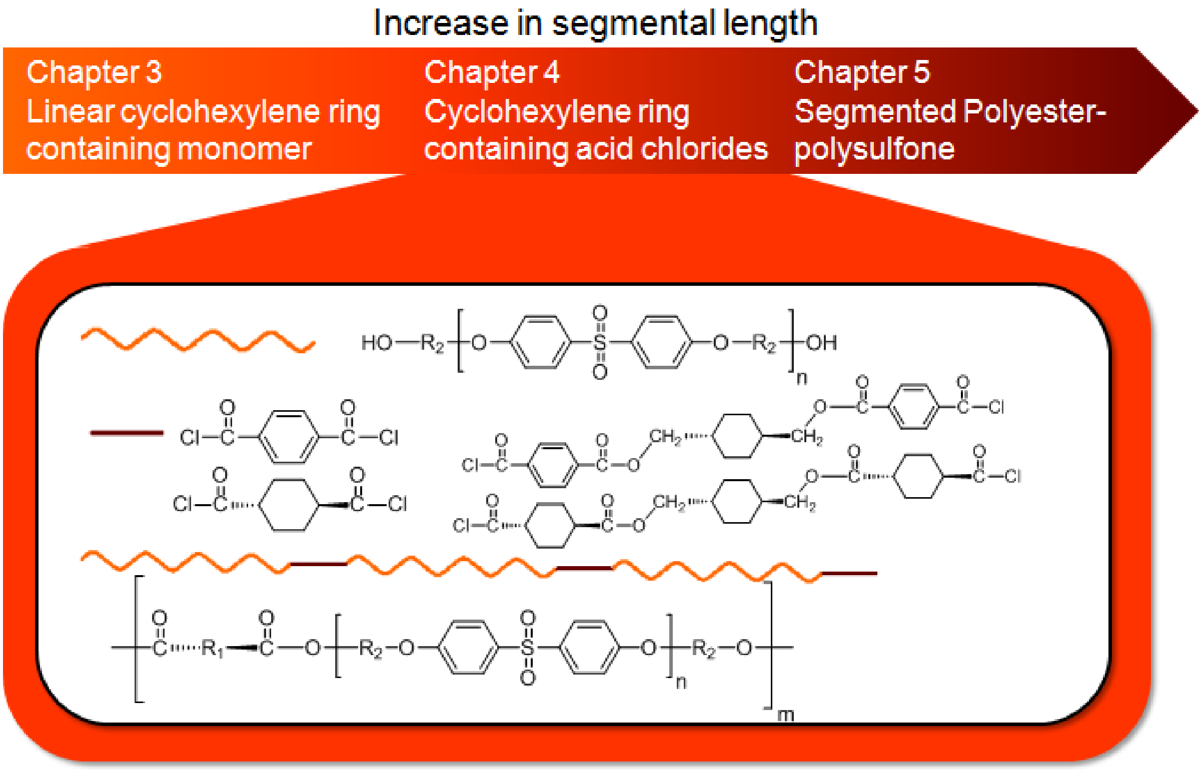


Figure 1.3 Chapter 4 Cyclohexylene ring containing acid chlorides

In **Chapter 4**, the length of one of the components was increased (shown in **Figure 1.3**). Instead of using the sulfone containing DCDPS monomer, we first synthesized phenol terminated PAES oligomers (long orange waves) with target molecular weights using stoichiometry imbalance technique. In the synthesis of the PAES oligomers, two classes of diphenols, DHBP and 4,4'-(propane-2,2-diyl)diphenol (bisphenol-A or bis-A), were used. The number average molecular weights of the oligomers were determined by end group analysis. Then we synthesized a series of cyclohexylene ring containing acid chloride monomers (short maroon straight lines). Taking advantage of the acid chloride chemistry that has been used widely in polyarylate and polyester synthesis, the polymerization was done in solution. The crystallization behavior, thermal properties, mechanical properties and the relaxation behaviors were studied.

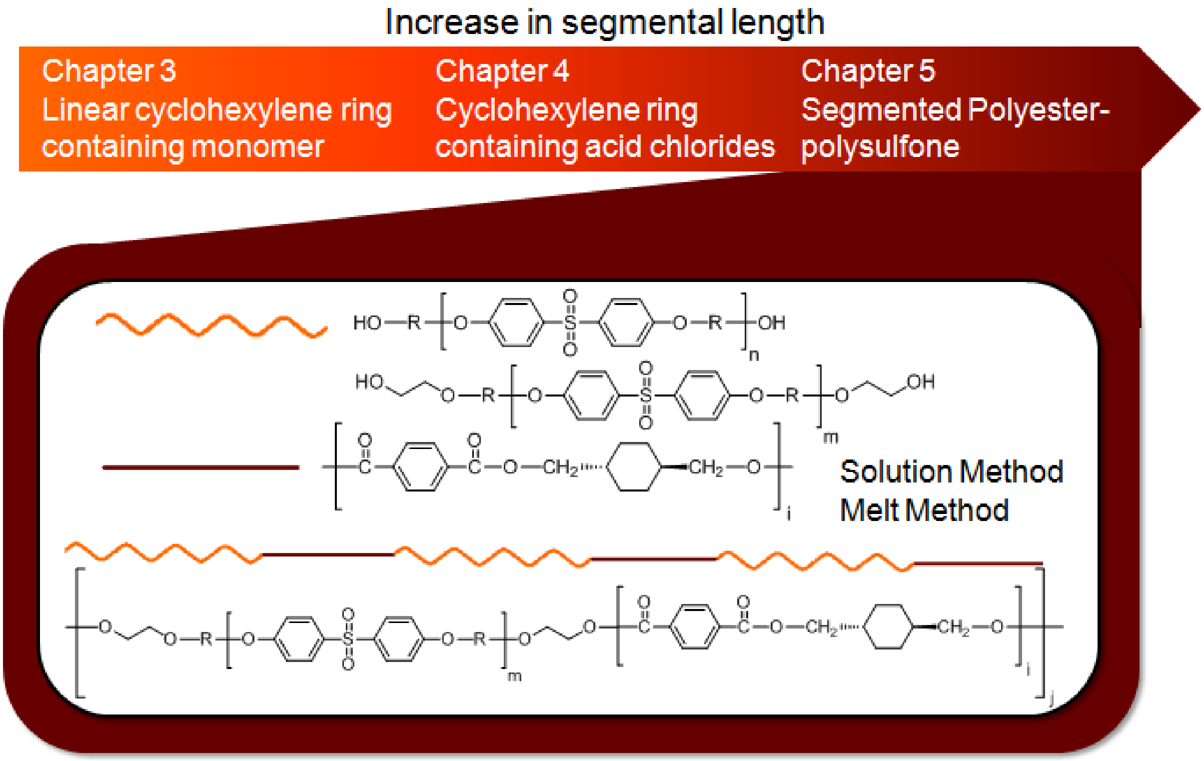


Figure 1.4 Chapter 5 Segmented polyester-polysulfone

To extend our research ideas in **Chapter 4**, we took a further step to increase the length of the second component in the polymerization increased. In the study described in **Chapter 5** (shown in **Figure 1.4**), we synthesized the sulfone containing segments (long orange waves) in two ways. One way is to synthesize the phenol terminated PAES oligomers as used in **Chapter 4**. In this way, we can do the solution polymerization with these phenol terminated PAES oligomers and pre-synthesized acid chloride terminated poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) oligomers which were made by reactions of terephthalic chloride and *trans*-1,4-cyclohexanedicarboxylic acid (CHDA). However in this approach, the molecular weight and reaction kinetics were limited by the solubility of both the starting materials and the products. In an alternative approach, the phenol terminated PAES oligomers were reacted with ethylene carbonate and potassium carbonate to convert the phenol groups to primary hydroxyl groups. In this approach, high reactivity can be achieved in melt polymerization due to the higher reactivity of the aliphatic OH groups compared to the phenols. Both bis-A and DHBP based PAES were used to synthesize the hydroxy ethoxy terminated PAES oligomers. In the melt polymerization, the hydroxy ethoxy terminated PAES oligomers, dimethyl terephthalate (DMT), and 1,4-cyclohexanedimethanol (CHDM) with different stereochemistry were used. The crystallization behavior, thermal properties, mechanical properties and the relaxation behaviors of the block systems were studied.

Chapter 2 Literature Review on Poly(arylene ether sulfone)s and 1,4-Cyclohexylene Ring Containing Polymers

2.1 Introduction

In this chapter, the history of poly(arylene ether sulfone)s (PAESs) is briefly introduced and followed by a discussion of common synthetic methods, important commercially available products, and areas of applications. Previous research on the modification of the PAES backbone with cyclohexylene rings is reviewed. The chapter concludes with a discussion of the research objectives and synthetic approaches for incorporation of cyclohexylene units and study of the properties of the new PAESs.

2.2 Reviews on Poly(arylene ether sulfone)s

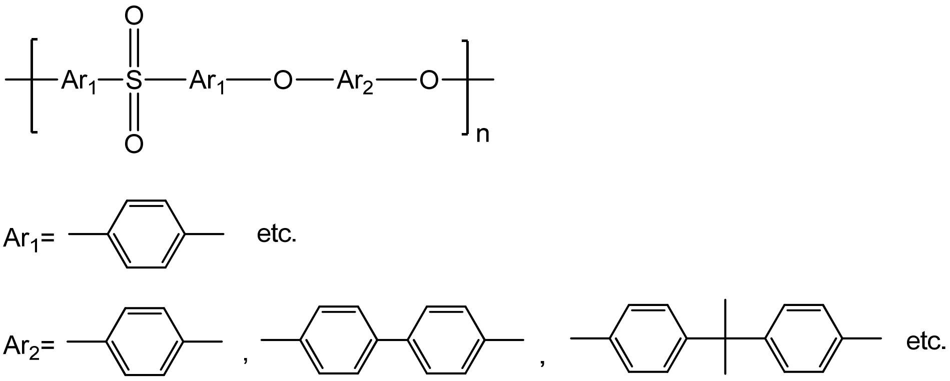


Figure 2.1 General structure of poly(arylene ether sulfone)s

Poly(arylene ether sulfone)s (PAESs) are extremely important amorphous engineering thermoplastics due to physical properties such as high T_g, outstanding thermal stability, high modulus, inherent flame-retardancy and so on. The general structure of PAESs is demonstrated in **Figure 2.1**. In the structure, Ar_1 and Ar_2 are the aromatic components. The bridging units of the aromatic components are the sulfone groups and ether units. In PAESs, the rigid arylenes, resonance structures, and strong interchain dipole-dipole interactions contribute to the high glass transition temperature.[1] Aromatic C-S bonds have partial double-bond characteristics, and there are strong dipole-dipole interactions between sulfone units on adjacent polymer chains, restricting the chain segmental movement and resulting in high T_gs. Fundamental research of polysulfones can be traced back to 1930s-1940s.[2-6] In the following decades, there was a tremendous amount of research on polysulfones focused on new monomers, synthetic methods, structure property studies, and different kinds of applications, such as electronic substrates and separation membranes.[7-13] In the late 60s and early 70s, three different companies, Union Carbide, 3M, and Imperial Chemical Industries (ICI), independently developed PAES based commercial products.[14-20] From then on, PAES based commercial products were continuously developed by different companies for different applications. Some details of commercially available products will be discussed later in this chapter.

2.2.1 Poly(arylene ether sulfone)s Synthetic Methods

The synthesis of poly(arylene ether sulfone)s (PAESs) has been documented in the literature.[21-27] The two major synthetic approaches are nucleophilic aromatic substitution (S_NAr) and electrophilic aromatic substitution (AES). The majority of PAESs have been synthesized by these two methods. Other approaches requiring specially designed monomers include radical polymerization,[28-30] ring opening polymerization,[31-35] and the Ullmann ether synthesis.[36,37] Given the relevance to the research in this dissertation and the generality of the methods, only nucleophilic aromatic substitution and electrophilic aromatic substitution will be discussed in detail.

2.2.1.1 Nucleophilic Aromatic Substitution (S_NAr)

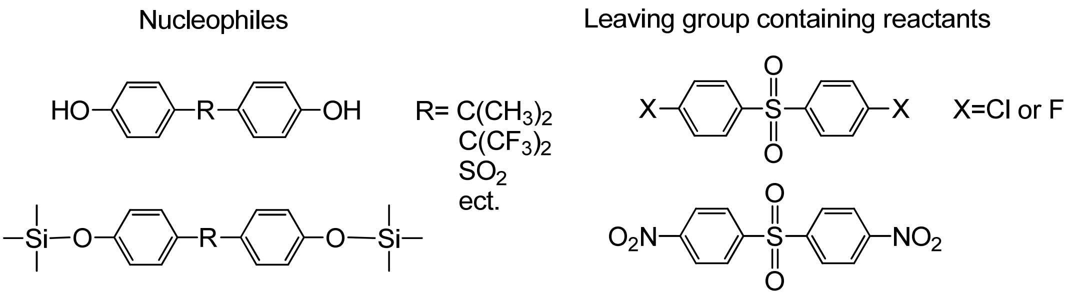
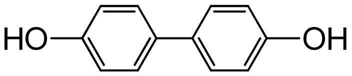
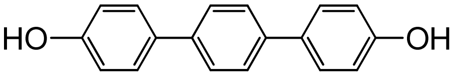
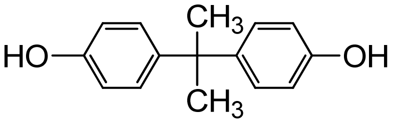
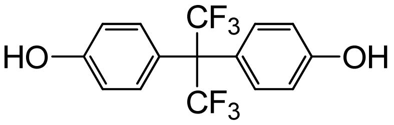
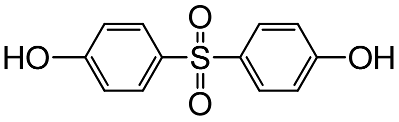


Figure 2.2 Structures of common nucleophiles and leaving group containing reactants in S_NAr PAES synthesis[17,38-40]

A wide variety of PAESs can be synthesized by nucleophilic aromatic substitution (S_NAr). S_NAr PAES synthesis reactions generally are two-monomer (A-A, B-B) reactions involving a difunctional nucleophile and a difunctional leaving group containing reactant. The common nucleophiles are diphenols or silylated diphenols as shown by the structures in **Figure 2.2**.[17,38-40] **Table 2.1** summarizes commonly used diphenol structures with their abbreviations. Typical leaving group containing compounds are halogenated or nitrated aromatic sulfones.[17,40]

The sulfone groups in the leaving group containing compounds highly activate the reactants with the resonance structures shown in **Figure 2.3**. With different leaving groups (electron donating groups or electron withdrawing groups), the resonance structures can be different which result in different electron densities on the *ipso* carbons. Because of the electronegative nature of the sulfone groups, the aromatic carbon on the *para* or *ortho* position relative to the sulfone group is electron deficient which increases the reactivity.

Table 2.1 Structures and abbreviations of common diphenols in S_NAr PAES synthesis

Name (abbreviation)	Structure	Ref
Hydroquinone (HQ)		17
4,4'-Dihydroxylbiphenyl (DHBP)		41
4,4'-Dihydroxyl-*p*-terphenyl (DHTP)		42
4,4'-Isopropylidene Diphenol (Bisphenol A, Bis-A or BPA)		17
4,4'-(Hexafluoroisopropylidene) Diphenol (Bisphenol AF or 6F-BPA)		17
4,4'-Sulfonyldiphenol (Bisphenol S)		43

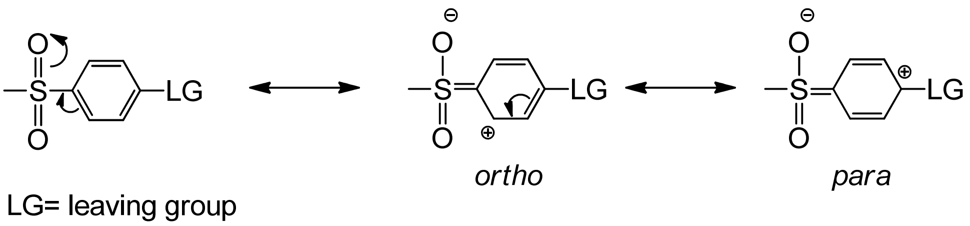
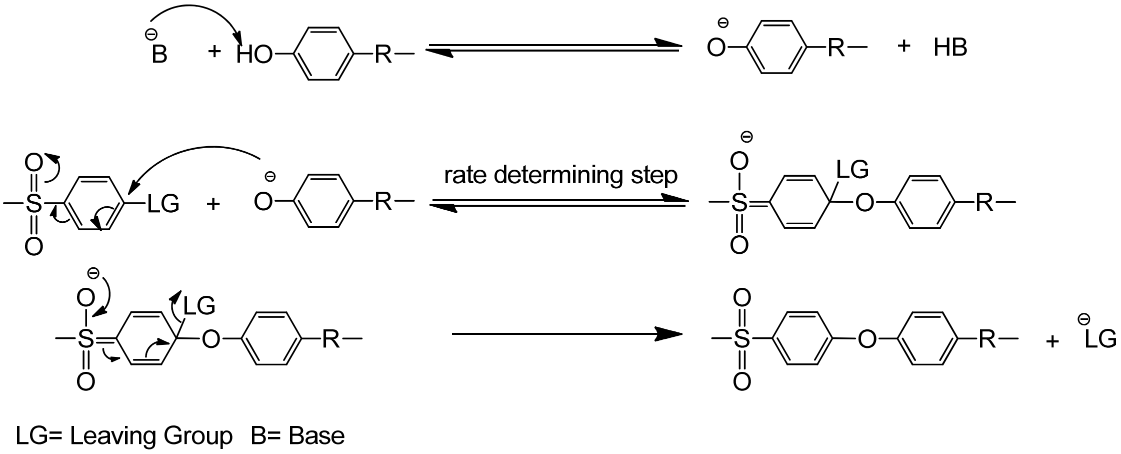


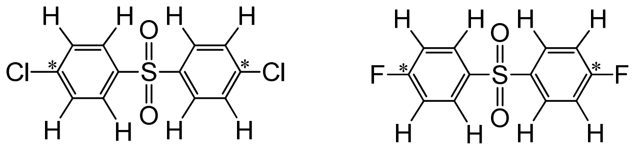
Figure 2.3 Resonance structures due to the electron withdrawing effect of the sulfonyl group



Scheme 2.1 The general mechanism for S_NAr PAES synthesis

The mechanism of S_NAr PAES polymerization involves several steps. An example of one ether linkage formation is shown in **Scheme 2.1**. The first step is usually the activation of the nucleophile. In the scheme, base-promoted activation of a phenol is used as an example. The second step is the rate determining step wherein the nucleophile adds to the electrophilic carbon to form the Meisenheimer complex. The last step is the elimination of the leaving group. There are several critical factors for a successful polymerization including the nucleophilicity of the nucleophile, the property of the leaving group, the thermal stability of the nucleophile and the intermediate, the overall solubility, and the base.

The nucleophilicity of the nucleophile can have major effects on the reaction kinetics. For example, bisphenol-A exhibits much higher reactivity than bisphenol-S (structures shown in **Table 2.1**).[44] The electron-withdrawing resonance effects of the sulfone units in bisphenol-S stabilize the phenolate. With different leaving groups, the reactivity of the reactant is indicated by the electronegativity of the aromatic carbon where the leaving group is bonded. With structure shown in **Figure 2.4,** 4,4'-dichlorodiphenyl sulfone (DCDPS), where the leaving group is chloride, is a common monomer used in S_NAr polymerization for PAES synthesis. When the chlorine atoms are replaced with more electron withdrawing fluorine atoms, the resulting compound 4,4'-difluorodiphenyl sulfone (DFDPS) is more reactive than DCDPS due to the fact that the *ipso* carbons (shown as star labeled carbons in the structures in **Figure 2.4**) are more electronegative.[45]



4,4'-Dichlorodiphenyl Sulfone 4,4'-Difluorodiphenyl Sulfone

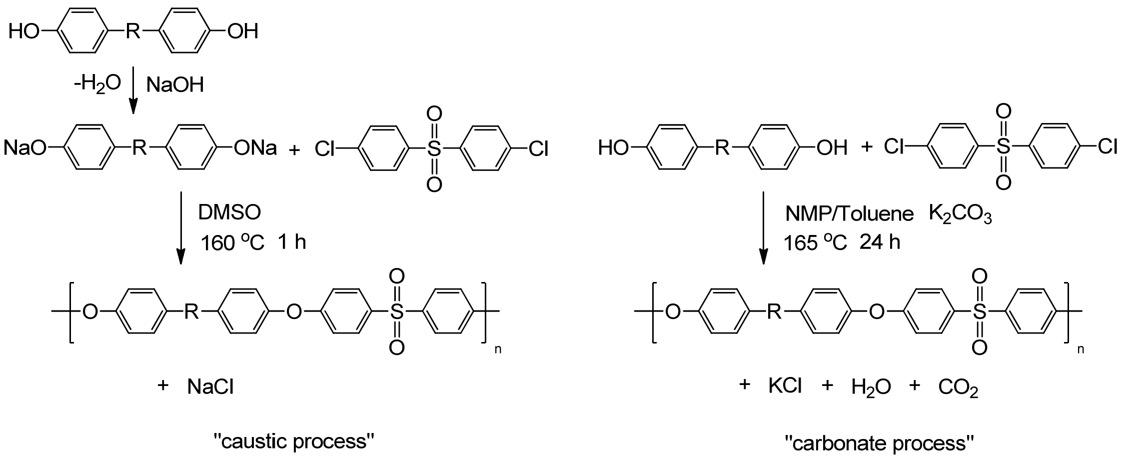
Figure 2.4 Structures of 4,4'-dichlorodiphenyl sulfone and 4,4'-difluorodiphenyl sulfone

Based on the systematic NMR study on the reactivity of the leaving group in the literature,[46-48] in general, the reactivity can be indicated by the chemical shift of the protons on the phenol ring (as shown as examples in **Figure 2.4**).[48] The larger chemical shift to lower fields, the higher the reactivity.

High boiling point polar aprotic solvents are good candidates for S_NAr PAES synthesis because of the solubility of the reactants, the intermediate, and the catalyst. Common solvents are N,N-dimethylacetamide (DMAc), N-methyl pyrrolidone (NMP), dimethyl sulfoxide (DMSO), and N,N-dimethyl formamide (DMF), etc. Aprotic solvents are required to prevent major side reactions from occurring. The phenolate reactants, the charged intermediates, and the polymer product all have good solubility in those solvents. Furthermore, the solvents can stabilize the non-aromatic intermediate in the solution. Mixed solvent systems have also been used to provide better solubility. Because in some cases water is one of the major impurities and can cause side reactions during the polymerization, azeotropic distillation is commonly used to dry the solvent in a preliminary step. In these cases, a mixed solvent system is usually composed of a high boiling point polar aprotic solvent and an azeotroping solvent, typically toluene.

Common bases and catalysts used in S_NAr PAES synthesis are strong bases such as sodium hydroxide,[49] weak bases such as potassium carbonate,[17] salts such as potassium fluoride,[40] and phase transfer catalysts[50-54] such as crown ethers in solid-liquid diphase polymerization and quaternary ammonium salts in interfacial and pseudo-interfacial polymerization. The basic catalysts are generally used to react with phenol to produce phenolate which is a good nucleophile.[49,55] Potassium fluoride is believed to form a very strong hydrogen bond with phenol to dramatically increase the nucleophilicity of the nucleophile.[40] The stability of the nucleophile and intermediate are also crucial for the polymerization. To prevent thermal and oxidative decompositions, the reaction temperature should be carefully controlled and the reaction should be performed in an oxygen-free environment.

The two important nucleophilic aromatic substitution reactions are known as “caustic process”[17] and “carbonate process”.[49] The reaction schemes for both processes are shown in **Scheme 2.2** and the comparison of the reaction parameters is listed in **Table 2.2**. In the caustic process, the diphenol is first treated with strong base such as sodium hydroxide to yield the sodium salt which is the activated monomer. The polymerization is performed at an elevated temperature in anhydrous polar aprotic solvents for a very short period of time to yield high molecular weight polymer. A strictly stoichiometric amount of sodium hydroxide is critical to an efficient polymerization reaction. Excess strong based can cause depolymerization reactions at high temperature.



Scheme 2.2 Synthetic schemes of “caustic process” and “carbonate process”[17,49]

Table 2.2 Reaction parameter comparison between “caustic process” and “carbonate process”[17,49]

	“Caustic process”	**“Carbonate process”**
Base used	Sodium hydroxide	Potassium carbonate
Amount of base	Strictly 1 molar equivalent	Typically 2-3 molar equivalents
Solvent	High b. p. polar aprotic solvent	High b. p. polar aprotic solvent with an azeotroping solvent
Reaction time	Short, usually 1-2 h	Long, typically over 20 h
Reaction temp.	~ 160 ^{o}C	~ 160 ^{o}C
Side reactions	Some	Few

Instead of using sodium hydroxide, a metal carbonate is used in the “carbonate process”. In this approach, the polymerization is performed at an elevated temperature in a one-pot reaction in a mixed solvent system. Toluene is used as the azeotroping solvent to remove water. Different types of carbonates have been studied including Na_2CO_3, K_2CO_3, and $NaHCO_3$.[56-58] K_2CO_3 is found to be the best because it has a combination of the highest basicity with better solubility in the solvent system over the other carbonate compounds.[58-60] Furthermore, the resulting potassium phenolate is also more reactive than the sodium salt due to a less intimate ion pair. In comparison to the sodium hydroxide used in the “caustic process”, the stoichiometry of the carbonate is not critical for a successful polymerization. The absence of the strong base in the carbonate process can prevent undesirable side reactions such as hydrolysis caused by sodium hydroxide residue. However due to the fact that carbonates are less basic than hydroxides, the reaction rate of the “carbonate process” is significantly slower than that of the “caustic process”. Therefore synthesis of PAES by the carbonate process requires longer polymerization time.

2.2.1.2 Electrophilic Aromatic Substitution (AES) Synthetic Method

Electrophilic aromatic substitution (AES) is another very important PAES synthesis method that has been widely reported in the literature.[61-66] In an AES reaction, an electrophile attacks an electron rich aromatic reactant. Generally in PAES synthesis, AESs are polysulfonation reactions because the sulfonylium cation is a good electrophile. Some monomer structures from the literature are shown in **Figure 2.5**.

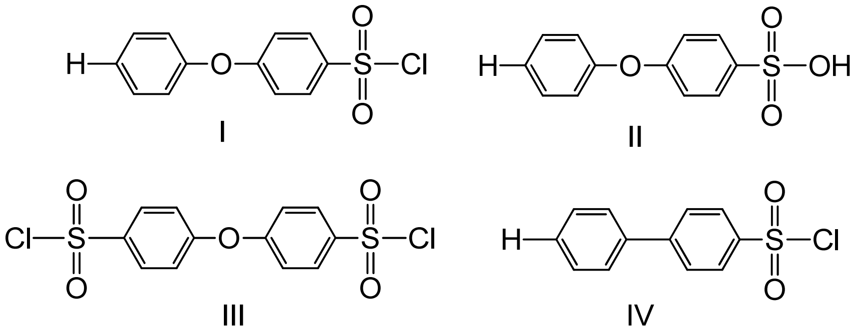
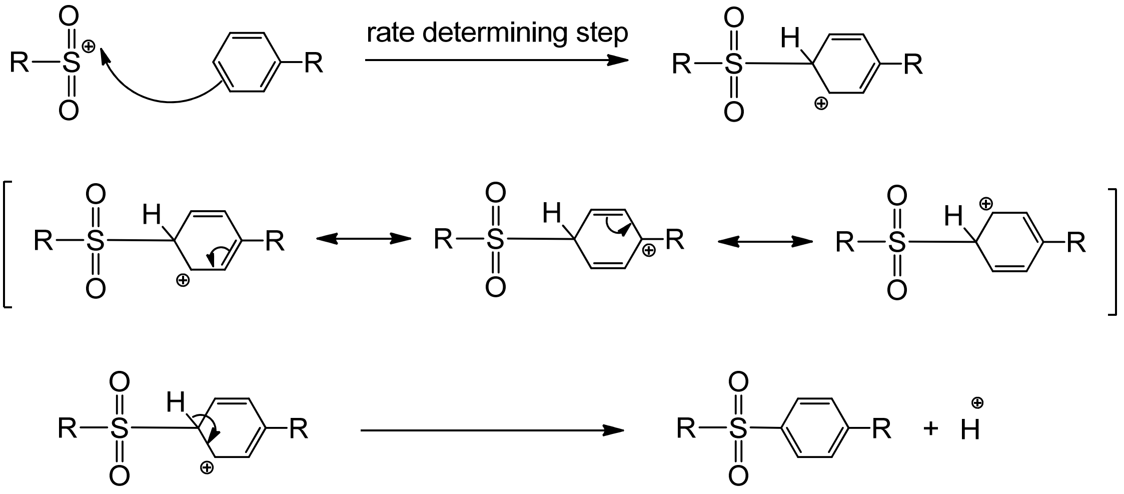


Figure 2.5 Examples of monomers for AES PAES synthesis[44,67]

The general mechanism for formation of one repeat unit by AES method is shown in **Scheme 2.3**. Depending on the nature of the monomers, the formation mechanism of the electrophile can be different; however, it all starts with the attack of the sulfonylium cation on an aromatic carbon, forming an intermediate stabilized by several resonance structures. The formation of the arenium cation is the rate determining step because aromaticity is lost, which requires high energy of activation. The stability of the arenium cation is critical for a successful polymerization because it is involved in the rate determining step. An electron donating group, such as an ether group, on the *para* or *ortho* position relative to the aromatic carbon attacked is helpful to stabilize the arenium cation. This is the reason why the second monomers used in AES PAES method are usually phenol ethers. The last step is the elimination reaction yielding a proton and the final sulfonation product which retains the aromaticity.



Scheme 2.3 The general mechanism for AES PAES synthesis

As a typical polycondensation reaction, PAES synthesis by AES method can be accomplished with A-A, B-B type bifunctionalized monomer pairs or with an A-B type self-polycondensation monomer. In **Figure 2.5**, monomer I and II, shown on the top, are used in self-polysulfonation or A-B type step growth polymerization. Monomer IV is also used in self-polysulfonation polymerization, however, the absence of oxygen on the *para* position of the phenyl ring results in lower reactivity than that of monomer I and II. The difunctional monomer III that contains the potential sulfonylium cations is used in the two-monomer reaction. As mentioned above, the second monomers in the two-monomer reactions are usually phenyl ethers such as diphenyl ether.

With controlled monomer structures, the theoretical repeat unit of the polymer yielded from the single-monomer method and the two-monomer method can be the same. The structures, however, can be a lot different due to branching reactions. It has been well studied in the literature that the single-monomer method gives low degree of branching. On the other hand, the degree of branching can be as high as 20 % in two-monomer method.[43,62,63-66] This is because the two-monomer method offers more than one target carbon available for the electrophilic attack. As shown in **Figure 2.6**, in the example for diphenyl ether, the *ortho* and *para* carbons shown in the structure are electron rich due to resonance. The multiple electron rich carbons, as the active sites for the Friedel-Crafts addition, result in considerable amount of branching. The one-monomer route not only yields products with low branching level, but also provides easy stoichiometry control for the polymerization reaction. As long as high purity monomer is used, the stoichiometry for the self-polysulfonation reaction is not a concern. However because the target aromatic group is in the same structure with the sulfone group, the reactivity of self-polysulfonation monomers is low due to the low electron density on the aromatic ring caused by the electron withdrawing effect of the sulfone group. The electron donating group on the target aromatic ring can enhance the reactivity. As mentioned above, with electron donating oxygen on the phenyl ring, monomer I in **Figure 2.5** has a higher reactivity than that of monomer IV. However, in general the single-monomer method requires high reaction temperatures due to low monomer reactivity. For examples, a reaction temperature of 175 ^{o}C is required for the self-condensation of sodium 4-halobenzenesulfonate in dimethylsulfoxide and only moderate molecular weights were achieved.[68] As in the S_NAr reaction, the thermal stability of the reactant and the intermediate is an important factor for a successful polymerization especially when a high reaction temperature is required. For example, the thermal decomposition temperature of sulfonylium cation is about 250 ^{o}C.[69] The reaction temperature of AES PAES synthesis should be well controlled at a temperature lower than 250 ^{o}C.[69]

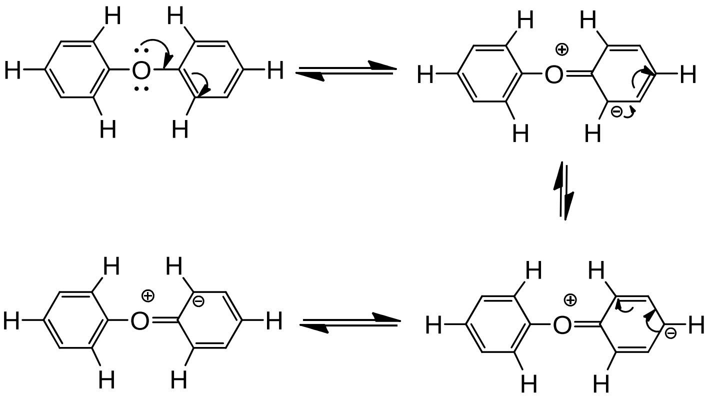
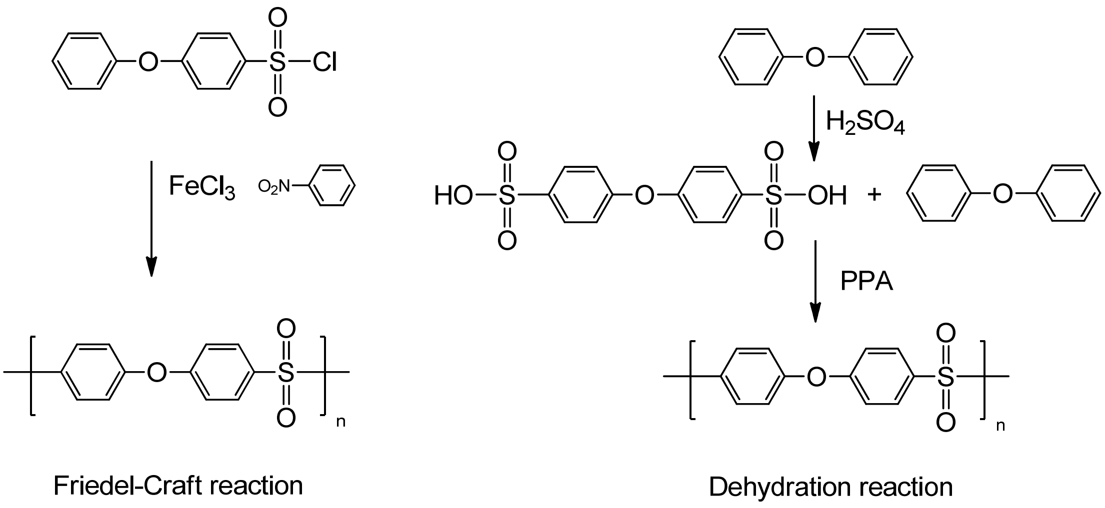


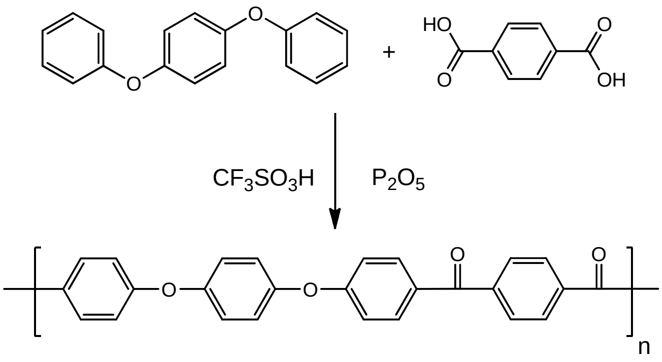
Figure 2.6 Multiple reaction sites in diphenyl ether as the second monomer in two-monomer polymerization via Friedel-Crafts mechanism

Two important AES reactions in PAES synthesis that will be discussed are Friedel-Crafts reactions[66,69] and dehydration reactions.[70,71] The reaction schemes are shown in **Scheme 2.4**. Similar to Friedel-Crafts alkylation reaction, the cation, in this case the sulfonylium cation, is formed as a result of the reaction with Lewis-acid catalyst such as

$AlCl_3$ and $FeCl_3$.[72] However, the amount of catalyst required for Friedel-Crafts sulfonation and alkylation is quite different. Unlike Friedel-Crafts alkylation where stoichiometric amount of metal chloride is usually required, Friedel-Crafts sulfonation can be performed successfully at elevated temperature with a low concentration of catalyst, typically 1-5 mol%.[70,72] Due to the high temperature, the reaction should be well protected with inert gas atmosphere. Usually in the final stage of the reaction, vacuum is applied to help remove the byproduct hydrochloric acid in order to yield high molecular weight product.[72] A critical step in AES PAES synthesis is to completely remove the Lewis-acid catalyst. The removal of the residual Lewis-acid, for example, can be done by adding an amine.[73] Even a small amount of metal containing catalyst residue such as $FeCl_3$ can dramatically affect the color, mechanical properties, and electric properties of the final product.



Scheme 2.4 Examples of a Friedel-Crafts reaction and a sulfonation-dehydration reaction in AES PAES synthesis



Scheme 2.5 Reaction example of a dehydration reaction in polyketone synthesis[74]

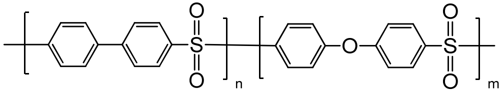
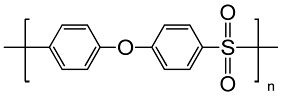
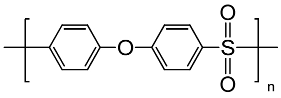
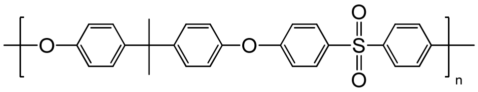
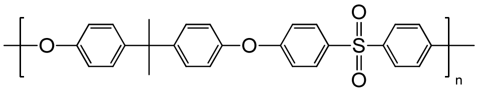
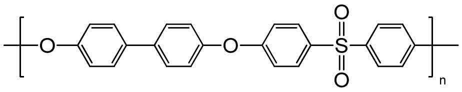
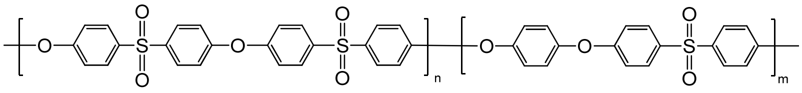
An example of dehydration reaction with sulfonic acid group containing monomers is shown in **Scheme 2.4**. In this reaction, the sulfonic acid group is formed from *in-situ* diphenyl ether with treatment of sulfuric acid. It is believed that the bifunctionalized sulfonic acid is generated and later reacts with diphenyl ether to form low molecular weight oligomers.[70] Further dehydration reaction is promoted at an elevated temperature with strong acid catalyst such as polyphosphoric acid (PPA) to give a product with high molecular weight.[71] Other than sulfonic acid containing monomers, carboxylic acid containing monomers have been reported in the literature[74] in polyketone synthesis. In this work, with terephthalic acid and 4-phenoxyphenyl monomers, high molecular weight polyketone products were obtained at low temperature using trifluoromethanesulfonic acid and phosphorus(V) oxide as shown in **Scheme 2.5**.

Although the AES method has been widely studied in the literature[66,69,75] and some commercial products have been produced with AES method,[44,70,71] The AES method suffers from branching, and crosslinking reactions as well as the formation of non-*para* isomers.[66,69] Complete removal of the catalyst can also be technically challenging. The polymer structural irregularity and the impurities significantly decrease the toughness and other properties of the products.[62,63,65] There are the most important reasons why AES method is not used as widely as S_NAr reaction in PAES synthesis and is not practically applied to commercial production.

2.2.2 Poly(arylene ether sulfone) based Commercial Products, Properties, and Areas of Applications

Table 2.3 shows selected commercial PAES based products with their trade names, PAES structures and manufacturers.

Table 2.3 Trade names and structures of selected commercially available PAESs[44,67,76-80]

Trade Name	Structure	Manufacturer
Astrel®		3M
Victrex® PES		ICI
Ultrason® E		BASF
Ultrason® S		BASF
Udel®		Solvay Advanced Polymer L.L.C.
Radel® R		Solvay Advanced Polymer L.L.C.
Radel® A		Solvay Advanced Polymer L.L.C.

The first commercial PAES based materials were developed independently by 3M, ICI and Union Carbide in late 60s to early 70s. The PAES based product from 3M was developed under the trade name of Astrel® (structure shown in **Table 2.3**) which is a copolymer made with an AES process through a two-monomer route. The product was discontinued around 1976 partially due to the melt processing difficulty as a result of branching.[44,67] Victrex® PES (structure shown in **Table 2.3**) is the PAES based polymer commercialized by ICI. It was also made with AES methods either through the one-monomer route or the two-monomer route. The product from the two-monomer route is brittle with poorer mechanical properties than that of the one-monomer route product. In 1992, ICI decided to withdraw from the polysulfone business and later licensed their polysulfone technology to a Japanese company.[76] Udel® (structure shown in **Table 2.3**) was developed by Union Carbide about the same time the previous two products were developed. In some references,[77,78] it is considered as the first commercial PAES based product. It has been used widely in different type of applications such as food service containers, filters, etc. Later Udel® was marketed by Amoco Performance Products. Inc. which ultimately was sold to Solvay Advanced Polymer L.L.C. in 2001.[79]

Since the first PAES based commercial product was introduced, many other products have been developed. About two decades ago, BASF commercialized their PAES materials under the trade names of Ultrason® (structures of Ultrason® E and Ultrason® S are shown in **Table 2.3**). Many different types of derivative products have been developed under the Ultrason® trade name for a series of applications ranging from sterilizable baby bottles to filters.[80]

Table 2.4 Summary of Udel® and Radel® R polymer properties[81-83]

	Udel®	**Radel® R**
Heat Deflection Temperature	170 °C	205 °C
Hydrolytic Stability (in 96 °C water)	Over 2200 h	Over 2200 h
Tensile Strength	> 10 kpsi	> 10 kpsi
Acid and Base Resistance	Good	Excellent
Limiting Oxygen Index	30 %	45 %

Recently,[81] Radel® PAES based products were commercialized by Solvay Advanced polymer L.L.C.. Radel® A and Radel® R structures are shown in **Table 2.3**. The Udel® and Radel® R backbone structures are of importance to the research in this dissertation. Because of the structural similarity, these two commercial products provided by Solvay Advanced polymer L.L.C. were used as property controls in Chapters 3, 4, 6. Some of the property parameters of Udel® and Radel® R are summarized in

Table 2.4.[82] They show excellent thermal and hydrolytic properties. The heat deflection temperatures (HDT; it is defined as the deformation temperature under a specific load. In case of the ASTM D648, load=264 psi; 1.8 MPa.) are 170 and 205 °C respectively with the ASTM D648 test method.[83] They are stable in hot water or steam for a long period of time and exhibit high tensile strength and good acid base resistance. Limiting oxygen index (LOI), expressed as a percentage, has been widely used as a quantitative analysis tool to measure the flammability of various materials such as polymers, composites, paper products, coating materials, etc. LOI is defined as the minimum oxygen concentration to support the burning of a specimen. Based on the definition, the

higher the LOI number the better the flame retardancy. As listed in the

Table 2.4, both Udel® and Radel® R exhibit very low flammability. Compared to polystyrene whose LOI is 19 %, Udel® and Radel® R have LOI values 30 % and 45 % respectively.

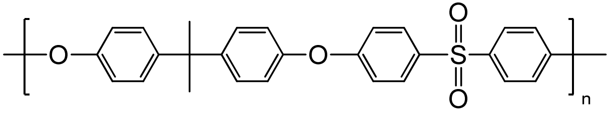
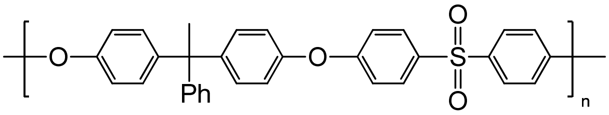
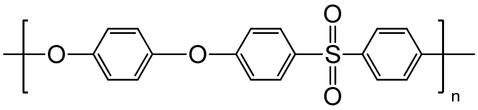
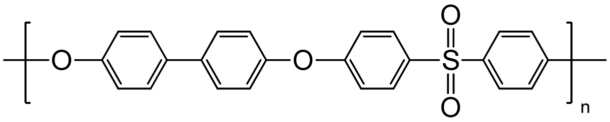
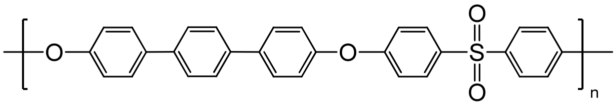
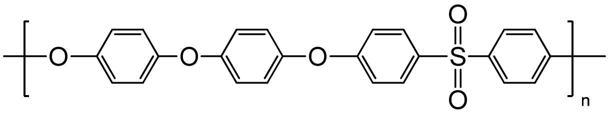
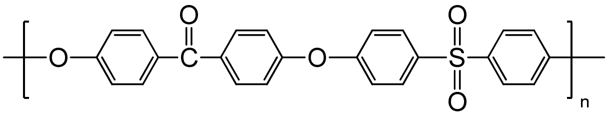
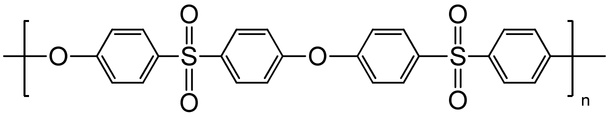
PAES based materials are used in many different applications based on a combination of properties listed below:

- High glass transition temperature
- Outstanding thermal stability
- Low flammability
- Good chemical resistance
- Excellent mechanical properties such as modulus, toughness
- Good dielectric properties
- Good transparency

The high glass transition temperature is due to the high rigidity of the polymer chain. The strong dipole-dipole interaction in the polymer limits the chain rotation resulting in increased chain rigidity. The thermal properties are related with the glass transition temperature, the functionality and the chemical composition. The glass transition temperatures and thermal properties of PAES polymers with different functional groups are listed in

Table 2.5. PAES based materials can generally be used at the temperature range from 110 – 200 °C for extended time periods without significant decline of other important properties such as mechanical properties and light transmission in visible range.

Table 2.5 Thermal properties of selected PAES materials

Structure	**T_g (^oC)**		**Ref**
	185		84
	216		85
	207		84
	221		86
	251		42,87
	180		88
	205		88
	230		75

PAESs show excellent acid base resistance, but only moderate solvent resistance due to the amorphous nature. The general PAES solubility with selected chemicals at room temperature is summarized in **Table 2.6**.[17,89] PAESs are not soluble in water, acidic and basic aqueous solutions, alcohols, and aliphatic hydrocarbons, etc, but have poor resistance to halogenated solvents, phenols, ketones, and high boiling aprotic solvents such as DMSO, DMF, etc.

Table 2.6 PAES solubility in selected chemicals at room temperature[17,89]

Chemical	**PAES solubility**	**Chemical**	**PAES solubility**
H_2O	Not soluble	Ethyl acetate	Not soluble
10 % HCl	Not soluble	Chloroform	Soluble
10 % HNO_3	Not soluble	Tetrachloroethane	Soluble
Acetic acid	Not soluble	N,N-dimethylacetamide	Soluble
10 % NaOH	Not soluble	N-methyl pyrrolidone	Soluble
Acetone	Swell	Dimethyl sulfoxide	Soluble
Methyl ethyl ketone	Swell	N,N-dimethyl formamide	Soluble
Methanol	Not soluble	Sulfolane	Soluble
Isopropanol	Not soluble	Cyclohexylpyrrolidone	Soluble

Other than the excellent mechanical properties mentioned above, good optical properties and excellent dielectric properties of PAES based polymers are critical for electronics applications. Transparency is often required for some electronics applications. For example, a total light transmission (TLT) > 85 % over the wavelength range of 400-700 nm is typically required for use as a substrate for bottom-emissive displays.[90] Generally PAES based polymers can provide a TLT > 90 %.[89] The dielectric properties are also critical for some electronic applications. PAES based polymers generally exhibit stable dielectric constant values within a large temperature range from -200 ^{o}C to +200 ^{o}C and a large frequency range from 0.1 kHz to 100 kHz.[85]

Table 2.7 General property comparison of selected amorphous polymers with PAES[91,92]

	PAES (BisAPAES)	**PC (BisAPC)**	**PMMA**
Glass transition temp.	185 ^{o}C	145 ^{o}C	100 ^{o}C
Deflection Temp.	181 ^{o}C	143 ^{o}C	95 ^{o}C
Chemical resistance	Good resistance to acidic and basic aqueous solution, alcohols. Not resistance to polar organic solvents.	Very limited chemical resistance. Resistant to hydrocarbons. Swollen or soluble in most of other solvents.	Stable to weak acids and bases. Attached by strong acids and bases. Resistant to oxidation. Limited resistance to organic solvents.
Notched Izod	80 Jm^{-1}	800 Jm^{-1}	16 Jm^{-1}
Tensile Modulus	2480 MPa	2410 MPa	2241 MPa
Transparent	Yes	Yes	Yes
Cost	High	Medium	Low

PAES based materials have been widely been used in many different applications, primarily in a high temperature area where other amorphous polymeric materials use is limited. A property comparison of PAES and traditional amorphous polymer polycarbonate (PC) and poly(methyl methacrylate) (PMMA) is listed in **Table 2.7**.[91,92] As shown in **Table 2.7**, compared to the properties of PAES, the limitation of traditional amorphous polymers is due to low thermal stability, low hydrolytic stability and poor chemical resistance, particularly at elevated temperatures. The impact resistance of PMMA is also significantly lower than that of the PAES.

Table 2.8[85] summarizes the commercial applications of PAES based materials with some examples. The required properties of those applications are also listed in the table. With its excellent thermal property, hydrolytic stability and good chemical resistance at high temperatures, PAES has been commercially used in electronics applications, automobile industry, medical industry, filters, and household appliances. The wide commercial application is also due to high processbility of PAES. Even though high temperatures are required for injection molding and extrusion, PAES structures have sufficient stabilities to tolerant these processes. To increase the processbility at high temperatures, end group protection is usually used in PAES industry. End capping can minimize oxidation processes and enhance stability. For example, in “carbonate process”, the polymers with phenol end groups are typically treated with methyl chloride or a strong base such as sodium methoxide to form methoxy end groups or metal salts which have been reported to be much more chemically stable than the phenol end group.[62,93] In general, PAES can be melt processed at a temperature in the vicinity of 300 ^{o}C and can be molded at a temperature range from 180 to 200 ^{o}C without major thermal decomposition. The outstanding properties of the PEAS backbone, especially in regard to hydrolytic and oxidative stability have rendered them outstanding candidates for modification into membranes.[94-99] For example, the sulfonated PAES containing hydrophilic-hydrophobic multiblock system[100,101] has been used in proton exchange membrane, anion exchange membrane, and direct methanol fuel cell study due to the good nanophase separation, good water uptake, and low methanol permeability, etc. It is also believed that these PAES based ionized polymers are promising membrane materials for desalination membranes because it has high salt rejection, good hydrolytic stability, resistance to chlorine ions, and good oxidative stability.[99,100]

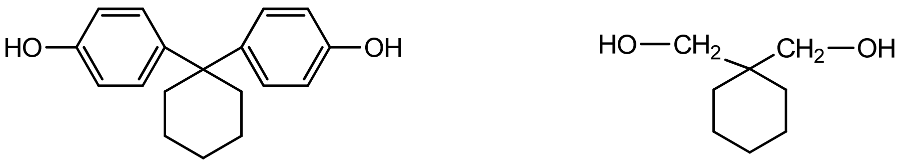
Table 2.8 Applications of PAES[85]

Application area	Example	Important Properties
Electrical/electronics sector	Chip trays and carriers, circuit boards, connectors, circuit breaker parts.	Thermal stability, directional stability, constant electrical properties, rigidity.
Auto parts	Bearing cages, head lamp reflectors, engine compartment parts, sensor housings.	Thermal stability, high rigidity and toughness, chemical resistance, transparency.
Medical parts and technology	Secretion bottles, dialysis parts, inhaler components, trays, instrument part.	Resistance to high sterilization temperatures, transparency, chemical resistance.
Filters	Membranes for dialysis, ultra and micro filtration	Chemical resistance, chemically modifiable, good pore size control.
Hot water fittings	Pump rotors, water meters, thermostat parts, pipe fittings, faucet parts.	Hydrolysis resistance, temperature-stability, good mechanical properties.
Food and household appliances	Handles, cooker parts, transparent covers, hairdryer parts.	Temperature stability, hydrolysis resistance, transparency, toughness.
Coatings	Non-Stick coatings (with PTFE)	Metal adhesion, thermal stability.

2.3 Reviews on Backbone Cyclohexylene Ring Containing Polymers

Incorporation of cyclohexylene rings into polymers by using cyclohexylene ring containing monomers is widely studied in the literature. In this section of the dissertation, the synthesis, characterization, and properties of the polymers with cyclohexylene ring units in the backbone is reviewed. The cyclohexylene ring incorporation is reviewed according to the substitution positions on the ring. Two major substitution patterns are 1,1 and 1,4 which are reviewed separately. Based on the review, the research objectives and synthetic approaches of the research work in this dissertation will be discussed in detail.

2.3.1 1,1-Cyclohexylene Ring Containing Monomers

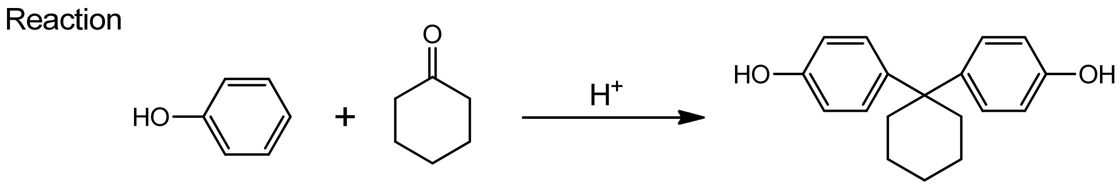


A
1,1-bis(4-hydroxyphenyl)cyclohexane
(BHPC)

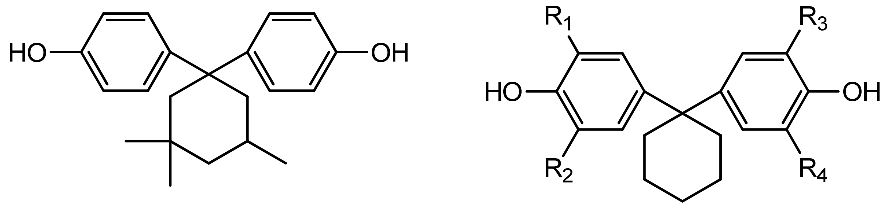
B
1,1-cyclohexanedimethanol

Figure 2.7 The structures of 1,1-cyclohexanedimethanol and 1,1-bis(4-hydroxyphenyl)cyclohexane (BHPC)

As the name describes, 1,1-cyclohexylene ring containing monomer is a molecule where two hydrogens on the same carbon of the cyclohexylene ring are substituted. Examples are shown in **Figure 2.7**, **Figure 2.9** and **Figure 2.10**. 1,1-Cyclohexylene ring containing polymers are a widely studied group of polymers with cyclohexylene rings in the backbone. The most common monomers are 1,1-cyclohexanedimethanol and 1,1-bis(4-hydroxyphenyl)cyclohexane (BHPC) whose structures are shown in **Figure 2.7**. With the primary hydroxyl groups, 1,1-cyclohexanedimethanol can be directly used in my polyester and polyurethane chemistry. BHPC is a very important 1,1-cyclohexylene ring containing monomer with phenol functionalities. It is synthesized by using phenol and cyclohexanone. The reaction scheme is shown in **Scheme 2.6.**



Scheme 2.6 The synthetic scheme of 1,1-bis(4-hydroxyphenyl)cyclohexane (BHPC) monomer



1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane (BHTC)

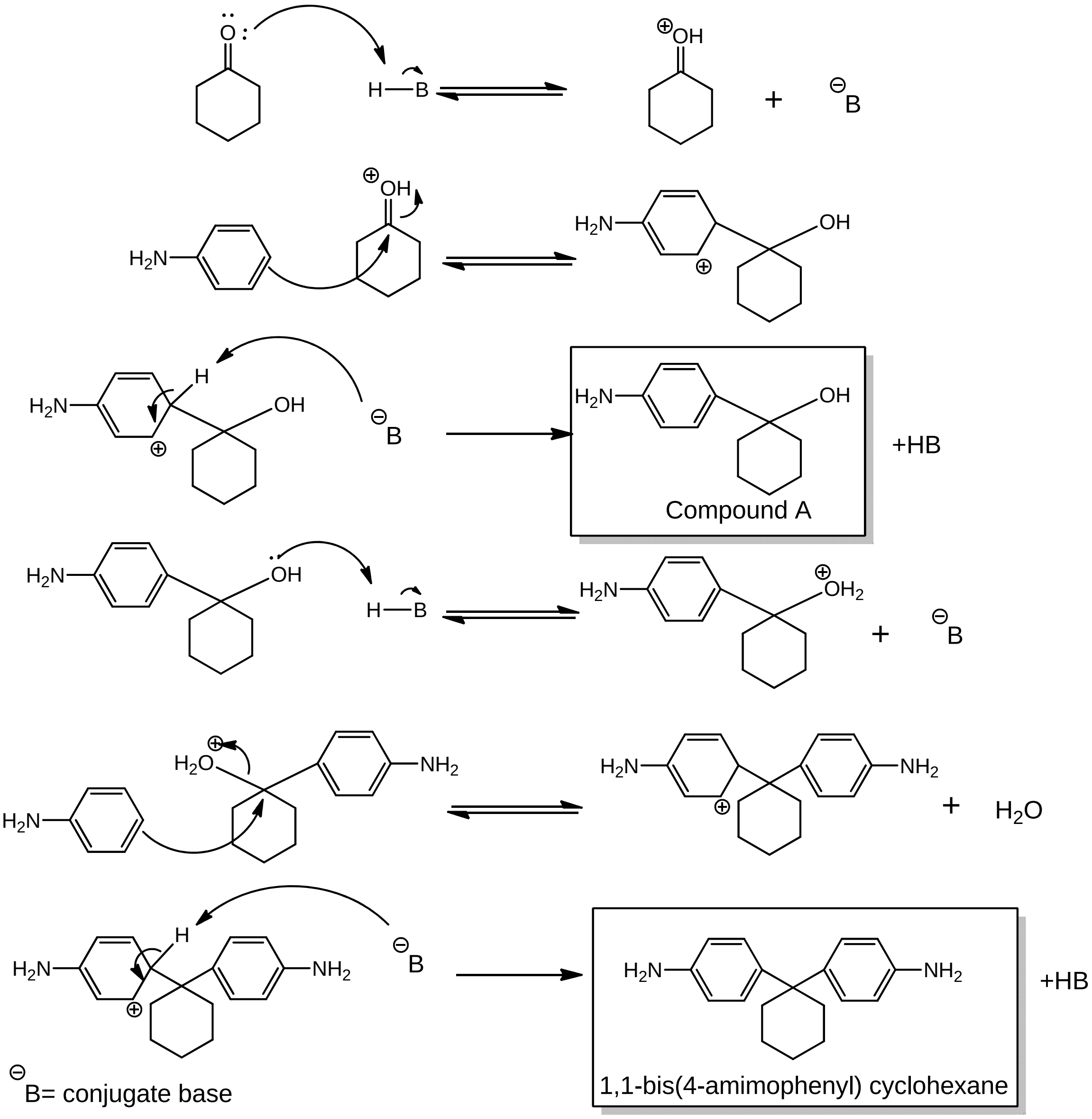
R_1, R_2, R_3, R_4 = H, CH_3, Br, Cl

Figure 2.8 Structure of 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane (BHTC) and BHPC based monomers with substitution groups on the phenol rings

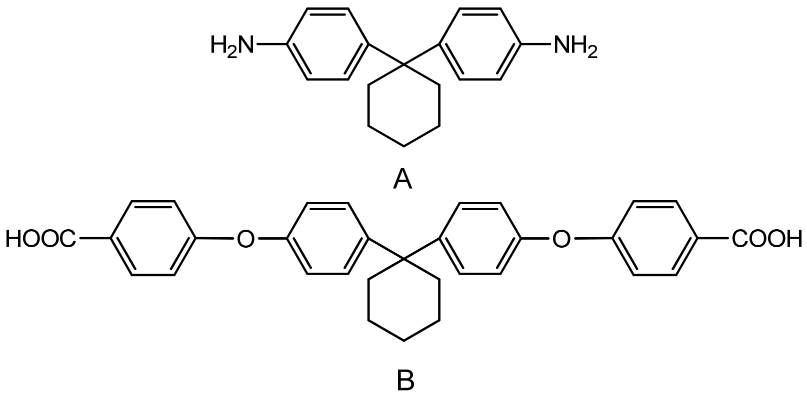
The derivative monomers based on BHPC structures are very important and greatly studied in the synthesis of different type of polymers. One of the major modifications is to use substituted starting materials (substituted phenols and cyclohexanones). 1,1-bis-(4-hydroxyphenyl)-3,3,5-trimethylcyclohexane (BHTC) is one of the most important BHPC derivative monomers (structure shown in **Figure 2.8**). When the BHTC monomer is incorporated into polymer backbone, due to the steric effect of the three methyl groups, the glass transition temperature of the resulting polymer will be increased. Using substituted phenols as starting materials, functional groups can be placed on the phenol rings on the BHPC monomers. Those substitution groups include Cl, Br, CH_3 etc.. The halogenated and alkylated BHPC monomers are used in polymer mechanical property and electronic property studies. The phenolic hydroxyl groups in those monomers allowed those monomers to be incorporated into polycarbonates, polysulfones, etc. and the properties of these polymers were studied.

Another major structure modification based on BHPC is on the functional end groups. The structures of selected 1,1-cyclohexylene ring containing monomer with different functional groups are shown in **Figure 2.9**. With the chemical modification on the phenol hydroxyl group, the functional end groups can be controlled. The examples given are amino groups and carboxylic acid groups. The amino end group containing monomer (monomer A in **Figure 2.9**) can be synthesized by using aniline and cyclohexanone. This synthetic approach to control the functional end groups are limited due to mechanism of the reaction shown in **Scheme 2.7.**

Mechanism



Scheme 2.7 Reaction mechanism of 1,1-bis(4-aminophenyl)cyclohexane monomer



A

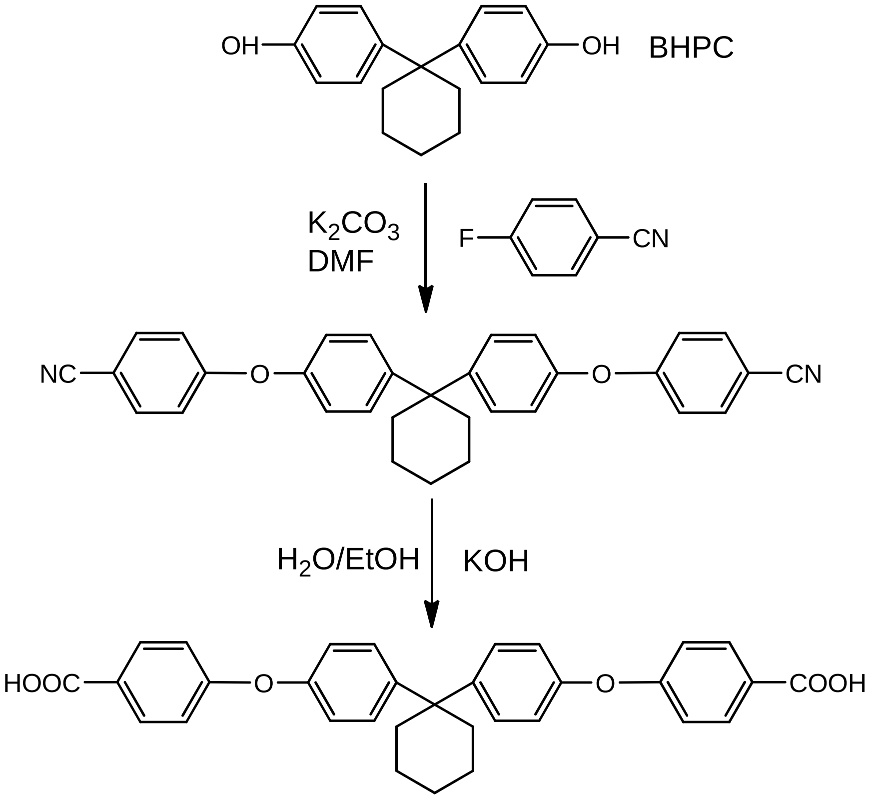
B

Figure 2.9 Structures of selected 1,1-cyclohexylene ring containing monomer with different functional groups

The reaction mechanism starts with the protonation of the cyclohexanone carbonyl group in acidic condition to make the carbonyl carbon more reactive in the following electrophilic aromatic substitution reaction. Due to the electron donating effect of the amino groups, the phenyl ring attacks the carbonyl group in cyclohexanone to form the charged intermediate which later converts into the first substitution product (Compound A in **Scheme 2.7**) to retain the aromaticity in the presence of conjugate base. The same electrophilic aromatic substitution reaction takes place again on the same target carbon to yield 1,1-bis(4-aminophenyl)cyclohexane monomer.

This synthetic approach to control the functional end groups is limited electron donating functional groups. Electron donating functional groups such as hydroxyl group, amine group, and halogen groups can enhance the nucleophilicity of the phenol ring to facilitate the aromatic substitution reaction and direct the substitution reaction at para position. The monomers containing halogen atoms can be further modified taking advantages of halogen related chemistry. The amine functionalized monomers can be readily used in polyurea, polyamide, polyimide, and epoxy chemistry.[102-107]

In order to incorporate functional groups without electron donating effect, further chemical modification needs to be performed. The example given in **Figure 2.9** is the monomer with carboxylic acid groups (monomer B in **Figure 2.9**). One of the common ways to introduce carboxylic acid groups is to modify the phenol hydroxyl groups on BHPC monomers. An example reaction is shown in **Scheme 2.8.**



Scheme 2.8 Reaction scheme of BHPC monomer modification with 4-fluorobenzonitrile

The modification reaction on BHPC monomer can be done with *para*-fluorophenyl compounds. In the example shown in **Scheme 2.8,** 4-fluorobenzonitrile was used. In the present of the potassium carbonate as the base, a Williamson reaction can give a high yield of the dicyano products. With the subsequential treatment of strong base such as potassium hydroxide and acidification, the cyano groups can be readily converted to carboxylic acid functional groups.[108] Other functional groups can be introduced in a similar fashion. The monomers with carboxylic acid functionalities in place of the phenolic hydroxyl groups can be used to prepare polyamides, polycarbonates, and polyesters.[108-110]

2.3.2 1,1-Cyclohexylene Ring Units Containing Polymers

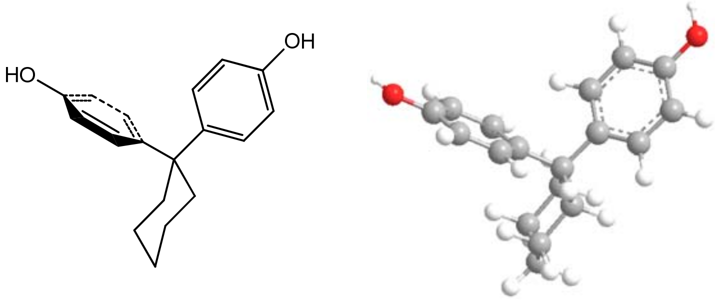


Figure 2.10 3D structure simulation of 1,1-bis(4-hydroxyphenyl)cyclohexane (BHPC)

Polymer backbones based on 1,1-cyclohexylene ring units are classified as cardo group containing polymers – a name defined from the Latin word “cardo” (a loop).[111] The 3D structure simulation is shown in **Figure 2.10**. With the presence of the pendent 1,1-cyclohexylene ring unit as a cardo group in the backbone, the free volume of the polymer is increased which leads to a decreased glass transition temperature when compared with the all-aromatic analogues.[108] The glass transition temperatures of the

BHTC containing polymers are generally higher than that of the BHPC containing polymers because of the steric effect of the trimethyl groups on the 1,1-cyclohexylene ring. Due to the internal plasticizing effect of the 1,1-cyclohexylene, the planarity of the phenyl rings are disrupted resulting in low packing efficiency. Intermolecular interactions such as the π-π stacking of the phenyl rings are, as a result, decreased. Decreased crystallinity, increased solubility, increased transparency, and increased processbility can be obtained because of the combination of decreased chain packing efficiency, glass transition temperature, and intermolecular interactions.[108,112-114] With halogen atom substitution, such as the examples shown in **Figure 2.8**, the thermal stability can also be enhanced. Even with enhanced thermal stability, the 1,1-cyclohexylene containing polymers are generally reported to have lower thermal stability than their aromatic analogues.

Figure 2.11 shows the structures of the polymer series that reported by Chuang and coworkers.[108] The 1,1-cyclohexylene ring units were incorporated into the backbone of polyamide-polysulfone, polyamide-polyether. Improved solubility of the 1,1-cycloehexylene ring containing polyamides was observed compared to conventional aromatic polyamides. The main structural difference between the two series polymers shown in **Figure 2.11** is they are made from 1,1-cyclohexylene ring containing diamine monomer and 1,1-cyclohexylene ring containing dicarboxylic acid monomer respectively.

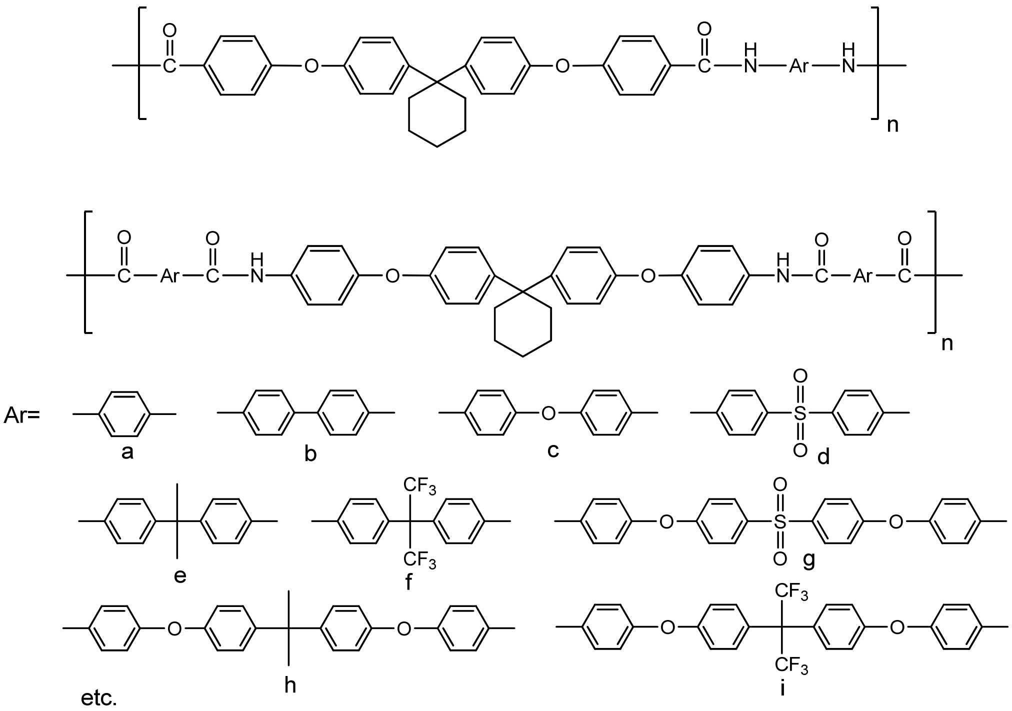


Figure 2.11 Structures of the polymer series with 1,1-cyclohexylene ring units in backbone

Within the two series of polymers, no or little difference in solubility was observed indicating that the 1,1-cyclohexylene ring in diamine and dicarboxylic acid units both can enhance the solubility independent of the regiochemistry of the amide bonds. Polymers with b, c aromatic units showed lower solubility in DMF,DMSO, m-cresol, and THF than that of the polymer with other aromatic units which indicated that the b, c units showed good packing characteristics and, subsequently, promoted strong intermolecular hydrogen bonding. For the same reason of the decreased packing efficiency, all the polyamides were determined as amorphous materials. The incorporation of the pendent cyclohexylene group resulted in the loss of crystallinity. The glass transition temperatures of the pendent cyclohexylene group containing polyamides were reported ranging from 190 °C to 220 °C. The glass transition temperatures were significantly lower than the all aromatic polyamide known as polyaramide. The 10 wt% weigh loss temperatures were reported to characterize the thermal stabilities. The 10 wt% weigh loss temperatures of the polyamides shown in **Figure 2.11** were reported in the range of 450 °C to 500 °C both in air and nitrogen atmosphere. It need to be noted that in almost all cases the 10 wt% weigh loss temperatures in air were reported higher than that in nitrogen, due to possible thermal crosslinking and/or the weight-gain oxidation of the aliphatic units at the early stage.

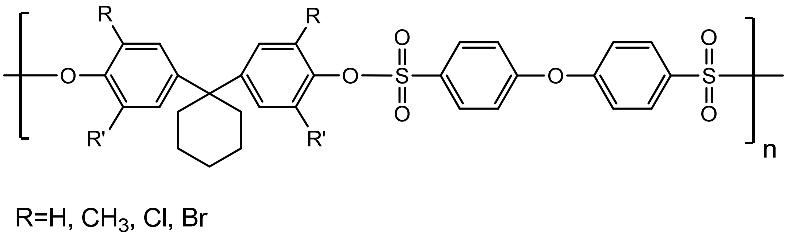
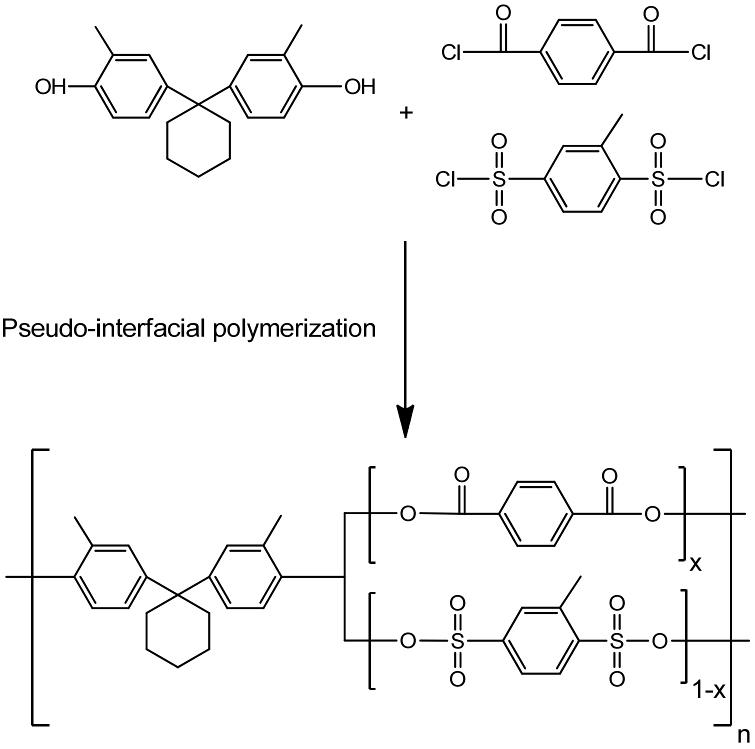


Figure 2.12 Structure of polysulfonates with 1,1-cyclohexylene ring units in the backbone

In the work reported by Parsania and Patel,[115] the mechanical properties, and the electrical properties of 1,1-cyclohexylene ring containing poly(aryl ether sulfone)s were evaluated as shown in **Figure 2.12**. Polymers were reported to be thermally stable up to 350 °C and exhibited low tensile strength of 6.2-21.1 N/mm^2 comparing to the tensile strength of 62.6 N/mm^2 for Udel®. This relatively poor stability and mechanical properties were probably due to the low molecular weights. The polymers with methyl and halogen substitution groups exhibited good electric breakdown properties of 7.4-16.2 kV/mm.



Scheme 2.9 Reaction scheme and the structure of polyester sulfonates with 1,1-cyclohexylene ring units in the backbone

Poly(ester-sulfone)s with similar structures were reported in another paper by the same research group. The polymers were synthesized from 1,1-bis(3-methyl 4-hydroxyphenyl)cyclohexane with toluene-2,4-disulfonyl and terephthaloyl chlorides. The polymer synthesis and structure are shown in **Scheme 2.9**. The successful polymerization was confirmed by FT-IR and viscosity measurements. Many polymer properties were dependent on the terephthalate contents. Properties such as density, glass transition temperature, thermal stability, volume resistivity, breakdown voltage, tensile strength were reported to be increased with increasing terephthalate content.

To summarize, because of the pendant structure of the 1,1-cyclohexylene units, the incorporation of 1,1-cyclohexylene ring into the polymer backbone can possibly decrease the crystallinity, glass transition temperature and increase solubility when compared with the all aromatic analogues. Polymers based on 1,1-bis(4-hydroxyphenyl)cyclohexane (BHPC) also exhibit good electric breakdown properties with substituent groups on the phenyl rings.[115]

2.3.3 1,4-Cyclohexylene Ring Units Containing Monomers

Polymers with 1,4-cyclohexylene ring units in the backbone are of great interest both from a fundamental and a practical point of view. They have been widely reported in the literature ranging from synthesis, mechanical properties to understanding the macroscopic properties at molecular weight level. Many studies concerned with the synthesis and property evaluation of the 1,4-cyclohexylene ring containing structures has been reported.

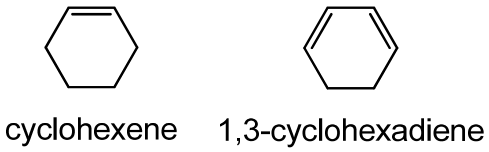
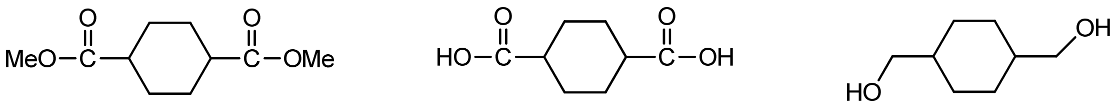


Figure 2.13 Structures of cyclohexene and 1,3-cyclohexadiene

Pioneering research on 1,4-cyclohexylene ring containing polymers can be traced back to 1930s-1940s. At the early stage of the studies on polymers with 1,4-cyclohexylene ring, important monomers are cyclohexene, cyclohexadiene, and their derivatives. The structure of cyclohexene and cyclohexadiene are shown in **Figure 2.13**. These monomers are generally polymerized with liquid sulfur dioxide via a radical procedure in the presence of a radical initiator such as hydrogen peroxide under pressure.

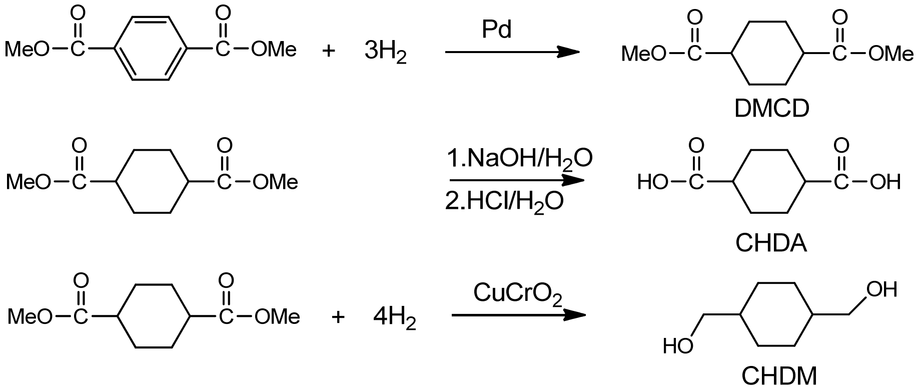

dimethyl 1,4-cyclohexane dicarboxylate (DMCD)

1,4-cyclohexane dicarboxylic acid (CHDA)

1,4-cyclohexane dimethanol (CHDM)

Figure 2.14 Structures of common 1,4-cyclohexylene ring containing monomers

As shown in **Figure 2.14**, the most widely used 1,4-cyclohexylene ring containing monomers are 1,4-cyclohexane dimethanol (CHDM), dimethyl 1,4-cyclohexane dicarboxylate (DMCD), and 1,4-cyclohexane dicarboxylic acid (CHDA). They are commercially available. Millions pounds of the three monomers are produced commercially. With the hydroxyl group, ester group, and carboxylic acid group, they can be used in the synthesis of many different types of polymers such as polyesters, polycarbonates etc.



Scheme 2.10 Synthesis of dimethyl 1,4-cyclohexane dicarboxylate (DMCD), 1,4-cyclohexane dicarboxylic acid (CHDA), and 1,4-cyclohexane dimethanol (CHDM)[116,117]

The synthesis of DMCD, CHDA, and CHDM are depicted in **Scheme 2.10**. DMCD can be obtained by the selective reduction of the phenyl ring in dimethyl terephthalate by using hydrogen over platinum catalyst. With further reduction of DMCD or subsequent hydrolysis of DMCD, CHDM and CHDA can be obtained.[116,117] One important characteristic of 1,4-cyclohexylene ring is the six member ring can undergo low energy transitions between chair conformation and boat conformation. This characteristic is believed to be critical to the polymer mechanical properties. Another very important characteristic about the 1,4-cyclohexylene ring is the ring isomers. There are two ring isomers shown in **Figure 2.15**. The 1,4-*trans*- and *cis*-cyclohexylene rings are different in 3 directional structures due to the difference in substitution positions. These two ring structure isomers behavior differently in the polymer backbone thus play an important role in polymer crystallinity and crystallization kinetics. It is very important to control and determine the ring isomer content. The commercial DMCD product consists of the *cis*-isomer to *trans*-isomer ratio of about 30:70. Pure isomers are commonly separated and used in polymerizations in order to study the effect of the ring structures.

1,4-*trans*-cyclohexylene ring 1,4-*cis*-cyclohexylene ring

Figure 2.15 Structures of 1,4-*trans*- and *cis*-cyclohexylene ring

Some selected 1,4-cyclohexylene ring containing monomers based on secondary diols and amines are shown in **Figure 2.16.** Those monomers are not as well studied as DMCD, CHDA, and CHDM monomers, but have been the topics of several reports.[118-124] The variety of different functional group enables them to be used in the backbone of many types of polymers.

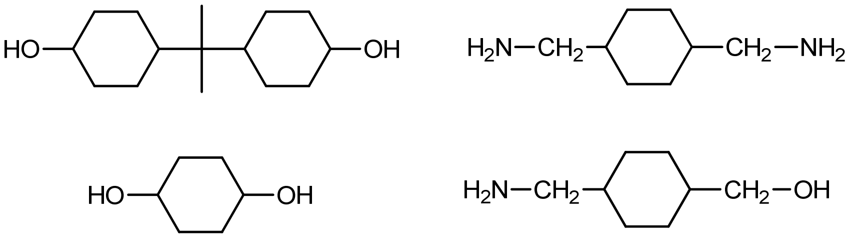
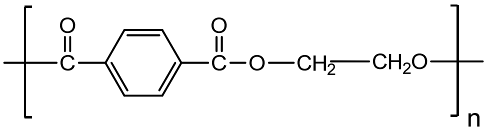


Figure 2.16 Structures of 1,4-cyclohexylene ring containing monomers with secondary diols and amines

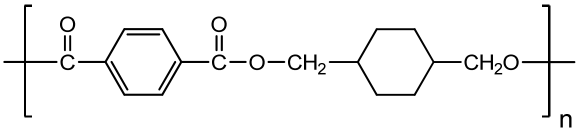
2.3.4 1,4-Cyclohexylene Ring Units Containing Polymers

With cyclohexene and 1,3-cyclohexadiene monomer, polymerization reactions for

1,4-cyclohexylene ring units containing polymers are limited to the addition route and tough reaction conditions. For example, reported by Key and coworkers in 1974,[125] a bromo-substituted 1,4-cyclohexylene ring containing polysulfone were synthesized by using 1,3-cyclohexadiene and liquid sulfur dioxide with hydrogen peroxide. The polymer was reported to show rapid weight loss at 170 ^oC however no distinct T_g was observed and no solubility results were reported. These sulfone copolymers have low ceiling temperatures and have been studied as e-beam resists.[126]



Poly(ethylene terephthalate) (PET)



Poly(1,4-cyclohexylenedimehylene terephthalate) (PCT)

Figure 2.17 Structures of poly(ethylene terephthalate) (PET) poly(1,4-cyclohexylenedimethylene terephthalate) (PCT)

The structure of poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) shown in **Figure 2.17**. PCT is one the most important and well studied 1,4-cyclohexylene ring containing polymers. It can be synthesized by conventional polyester melt polymerization by using dimethyl terephthalate or terephthalic acid and CHDM with metal containing catalysts. Many properties of PCT are highly dependent on the *cis*-isomer to *trans*-isomer ratio. **Figure 2.18**[127] shows the effect of *cis*-isomer to *trans*-

isomer ratio on the melting point of PCT. PCT with 100 % *trans*-1,4-cyclohexylene ring exhibits a melting transition about 315 °C. Decreasing T_ms were reported with increasing *cis*-1,4-cyclohexylene ring content. The T_m of 30:70 *cis*-isomer to *trans*-isomer ratio PCT is about 290 °C; the melting transition temperature drops to around 255 °C for PCT with 100 % *cis*-isomer. The gas permeability also exhibits strong correlation with isomer ratios. Higher oxygen permeability was observed with PCT with higher *trans*-isomer content. The difference in permeability indicates a much different free volume of the *cis* and *trans* isomers.[128]

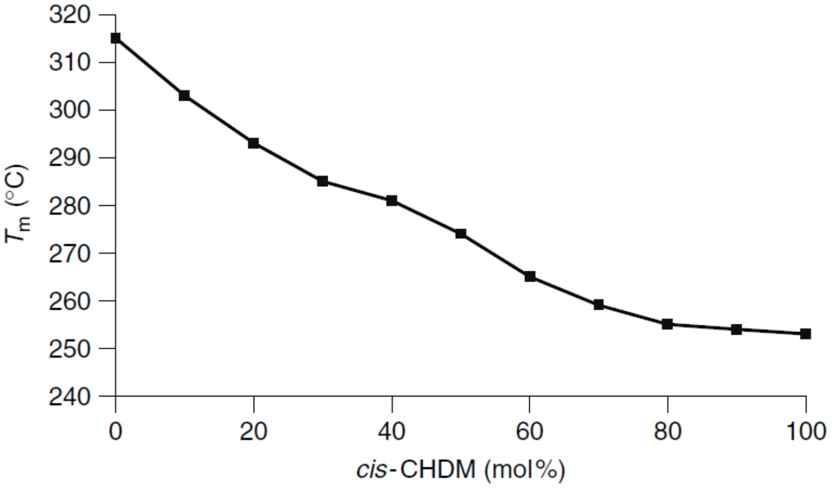


Figure 2.18 Effect of CHDM *cis*/*trans* ratio on the melting points of poly(1,4-cyclohexylenedimethylene terephthalate)[127]

The incorporation of 1,4-cyclohexylene ring units via CHDM into a terephthalate based polyester backbone imparts significant property change. Because PCT (T_g ~ 90 °C) has a higher glass transition temperature than that of the PET (T_g ~80 °C, structure shown in **Figure 2.17**), the temperature where the maximum crystallization rate of PCT is observed is reported to be higher than that of the PET. At low temperature range around -50 ^{o}C, PCT shows a stronger sub-T_g relaxation peak in dynamic mechanical loss curves than PET.[129] A correlation has been reported between this low temperature relaxation and the mechanical properties of PCT and PET.[129] There is a good agreement in the literature that the origin of this sub-T_g relaxation is a conformational transition of the cyclohexane ring. It is believed that the conformational transition can facilitate the cooperative motion to reduce the barrier of polymer chain slippage which increases the ductility of the material. The enhanced ductility phenomenon was similarly observed the in the copolyesters PETG and PCTG which contain 1,4-cyclohexylene rings.[109] As shown in **Table 2.9** and **Figure 2.19**, with close stress-at-yield values and modulus values, PCTG shows an enhanced ultimate elongation and enhanced toughness in amorphous state. This relaxation also increases the toughness in the polymer in the amorphous state. Amorphous PCT has a much higher Notched Izod impact strength than PET.

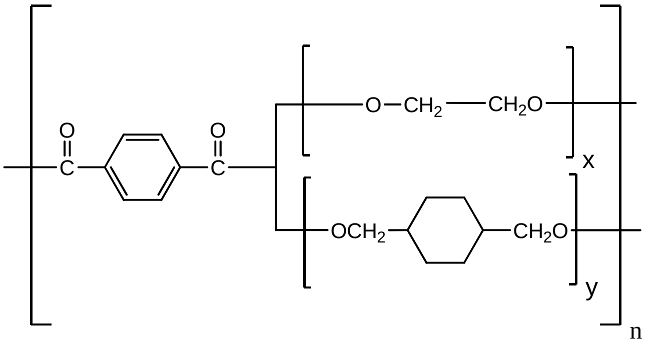
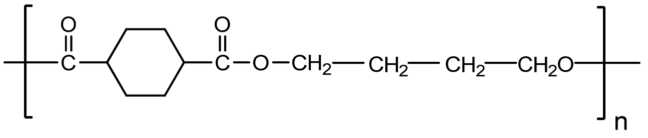


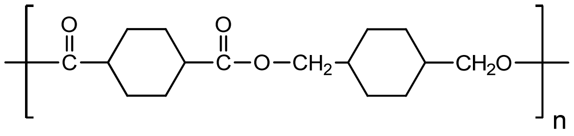
Figure 2.19 The structure of PCTG (when y>x) and PETG (when x>y)

Table 2.9 Mechanical property comparison of amorphous PETG and PCTG[109]

Property	PETG	PCTG
Stress at yield (MPa)	50	45
Elongation at break (%)	110	330
Flexural modulus (MPa)	2100	1900
Flexural yield strength (MPa)	70	66
Notched Izod at 23 °C (J/m)	101	No break



Poly(butylene 1,4-cyclohexanedicarboxylate) (PBCHD)



Poly(1,4-cyclohexylenedimethylene 1,4-cyclohexanedicarboxylate) (PCCD)

Figure 2.20 Structure of poly(butylene 1,4-cyclohexanedicarboxylate) (PBCHD) and poly(1,4-cyclohexylenedimethylene 1,4-cyclohexanedicarboxylate) (PCCD)

This distinct low temperature relaxation is widely reported in 1,4-cyclohexylene ring containing polycarbonates, polyesters. In the paper by Credico and coworkers,[130] the synthesis, characterization and crystallization behavior of poly(butylene 1,4-cyclohexanedicarboxylate) (PBCHD) and poly(1,4-cyclohexylenedimethylene 1,4-cyclohexanedicarboxylate) (PCCD) were reported (shown in **Figure 2.20**). The authors concluded that the sub-T_g relaxation was beneficial for the improvement of impact resistance. The relaxation observed at around -50 ^oC was assigned to the chair-boat-chair conformational change of the 1,4-cyclohexylene ring. It was also found that the *trans*-cyclohexylene ring improved chain packing due to high symmetry resulting in a subsequent increase in crystallinity. Similar crystallization behavior was also reported in copolyesters and polyimides which contain 1,4-cyclohexylene rings. It needs to be noted that slightly higher thermal stability was achieved when a phenyl ring is replaced by 1,4-cyclohexylene ring.[130] For examples, the degradation temperature of the PBCHD polymer was reported 13 degrees higher than that of the PBT polymer. The results were also observed in the reference reported and mentioned above in this dissertation.[108,131]

A whole family of 1,4-cyclohexylene ring polycarbonates, polyesters, polyester-carbonates were systematically studied in a series of papers published by Yee and coworkers.[113,132-135] Selected polymer structures are listed in **Figure 2.21**. In the polycarbonate and polyester-carbonate, the 1,4-cyclohexylene ring not only showed conformational change but also activated the corporative motion of the linked carbonate group to further facilitate the local chain motion. In bis-A (or substituted bis-A) polycarbonate with 1,4-cyclohexylene ring units (polymer BC and TC in **Figure 2.21**), the polymer showed ductile yield behavior and promoted ultimate elongation. Further investigation showed that an increase in chain motion caused by incorporation of 1,4-cyclohexylene ring is beneficial for the craze resistance of the polymers. In their later study on 1,1-bis(4-hydroxyphenyl)cyclohexane (BHPC) or spirobiindane bisphenol (SBI) monomers with 1,4-cyclohexylene rings (polymer SCBC, ZCBC in **Figure 2.21**), many polymer properties exhibited good correlations with the 1,4-cyclohexylene ring content.

With increasing 1,4-cyclohexylene ring content, an increase in thermal expansion coefficient and a decrease in Young's modulus, yield stress, and post-yield stress drop and were all observed.

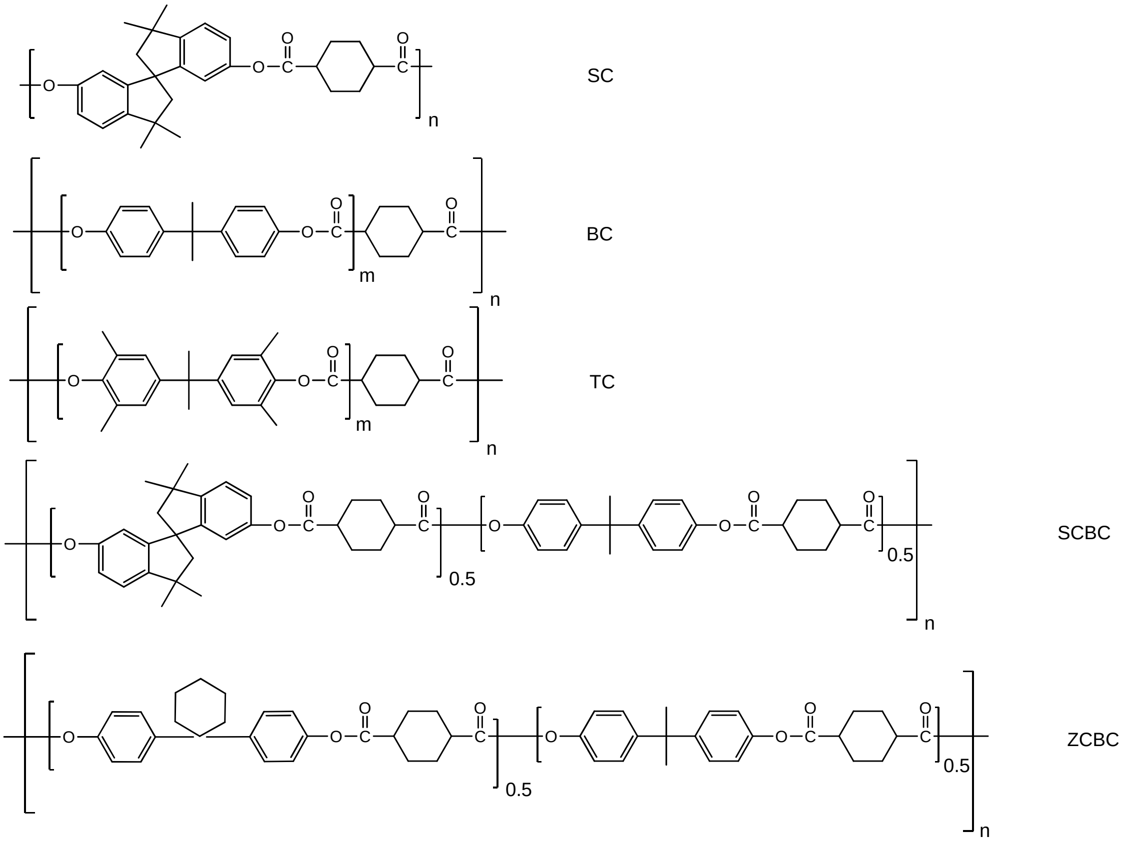


Figure 2.21 Structures of selected 1,4-cyclohexylene ring containing polymer reported by Yee and coworkers

2.4 The Research Objectives and Synthetic Approaches

As reviewed previously, due to the excellent thermal stability, anti-oxidation and mechanical properties, poly(arylene ether sulfone)s (PAES), commonly known as polysulfones, have been extensively studied and used as important thermoplastics in the past decades. However some applications of PAES are limited by poor solvent resistance and large thermal dimensional changes resulting from the amorphous nature of the polymer.

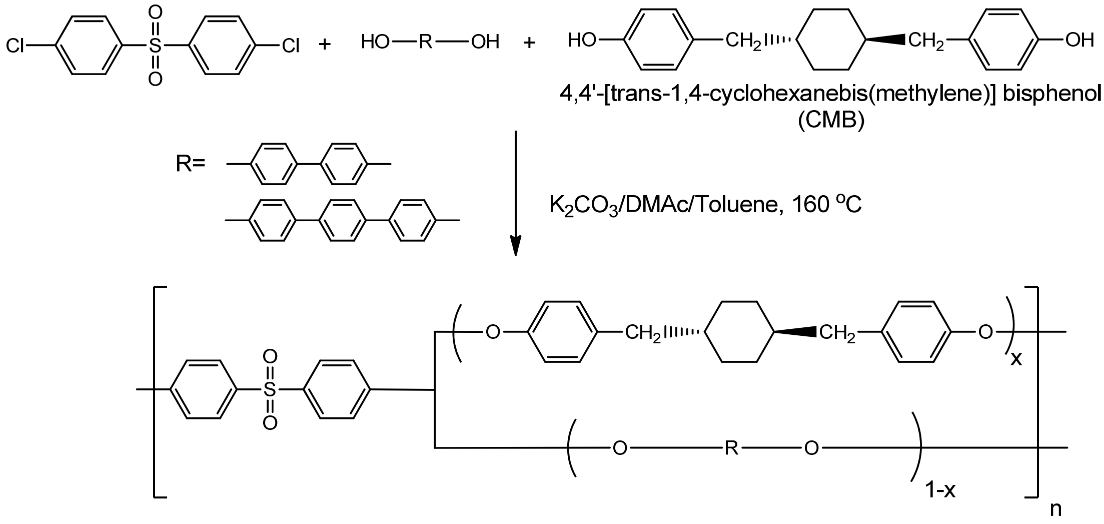
Our strategy is to modify the polymer backbone by incorporating new monomers designed to impart specific structural change and properties. One of our research focuses has been to enchain monomers to enhance the crystallinity of the PAES backbone. Previous work in our group showed that incorporation of linear terphenyl and biphenyl unit gave a semicrystalline polymer but the crystallization rate was extremely slow due to the narrow crystallization window (about 60 ^oC in this case). The crystallization window is defined as the temperature difference between glass transition temperature (T_g) and melting temperature (T_m). Crystallization window which provides the driving force is critical to the crystallization process.[136]

A major goal of the research described is this dissertation is to incorporate *trans*-1,4-cyclohexylene ring units into PAES backbones for the following reasons:

- Maintain linearity with *trans*-isomer that can potentially promote crystallinity
- Conformational freedom to potentially enlarge crystallization window
- Mechanical property enhancement

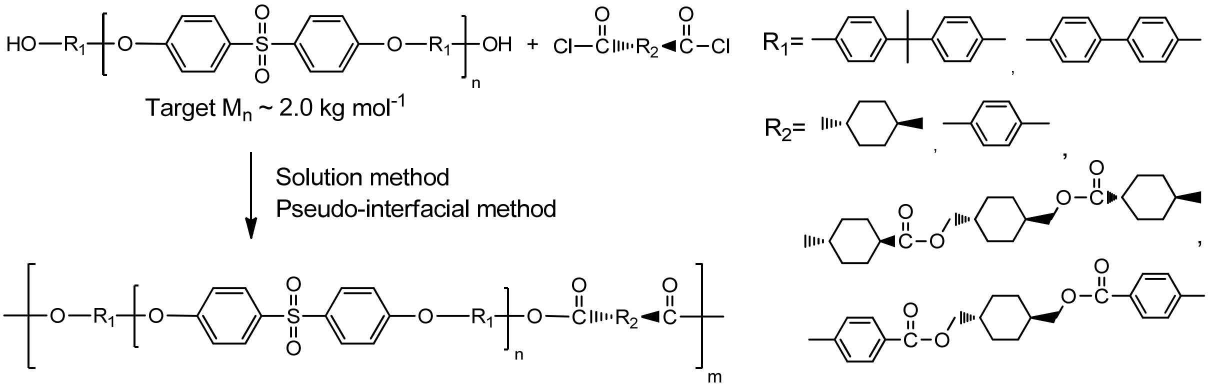
Inspired by 1,4-cyclohexylene ring containing polymers, incorporation of *trans*-1,4-cyclohexylene ring in to PAES backbone can possibly promote crystallinity because the *trans*-isomer can maintain the linearity of the polymer backbone. At the same time, 1,4-cyclohexylene ring can undergo conformational changes with low energy barrier and provide flexibility to increase chain mobility. As mentioned above in the literature, another very important reason that incorporation of 1,4-cyclohexylene ring can potentially promote toughness and impact resistance enhancement.

In this dissertation, several different approaches were established to introduce crystallinity into PAES.



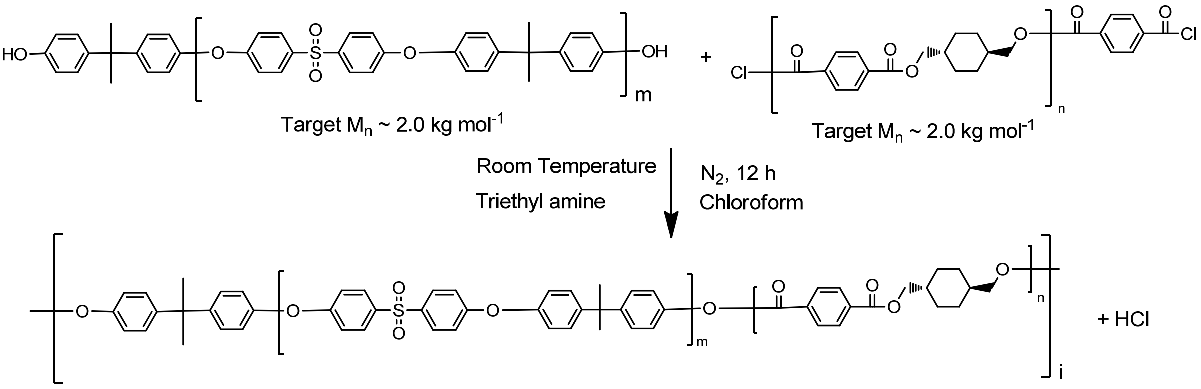
Scheme 2.11 Synthetic scheme of linear monomers approach

The linear monomer approach is based on a novel linear *trans*-1,4-cyclohexylene containing monomer, 4,4'-[*trans*-1,4-cyclohexanebis(methylene)] bisphenol (CMB). CMB was synthesized in a four-step synthesis with an overall yield about 77 % and used to synthesize homopolymer and copolymers with DHBP and 4,4’-dihydroxyl-*p*-terphenyl (DHTP) (shown in **Scheme 2.11**). The polymers showed mechanical property enhancement and interesting sub-T_g relaxations results in dynamic mechanical analysis (DMA); however all the random copolymers were amorphous. This research is described in **Chapter 3**.



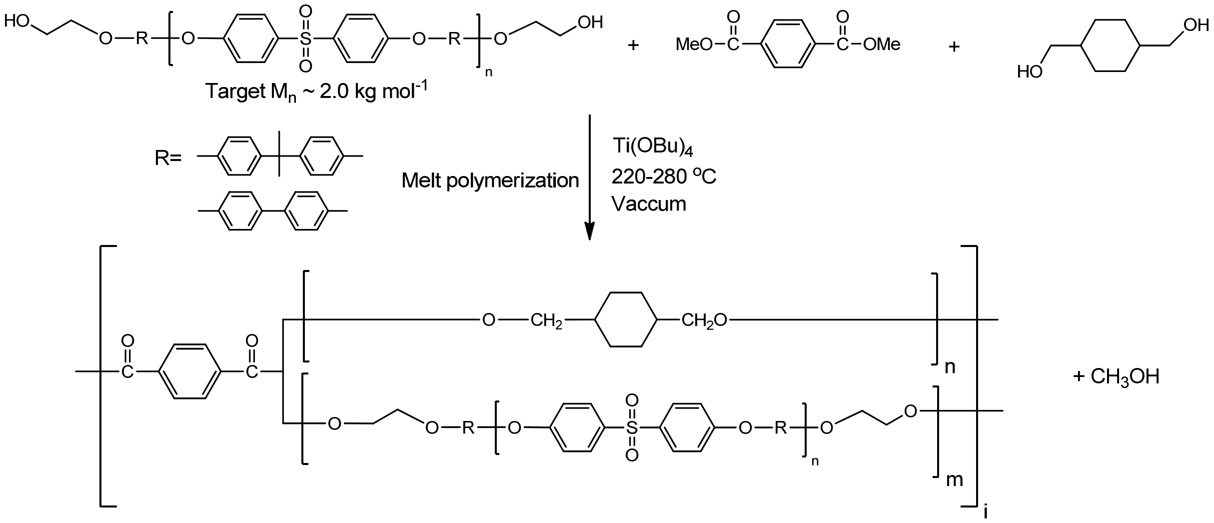
Scheme 2.12 Synthetic scheme of acid chloride monomers approach

In the second approach, *trans*-1,4-cyclohexylene ring containing acid chloride monomers were prepared and used to chain extend bis-A based and 4,4'-dihydroxylbiphenyl (DHBP) based PAES oligomers with phenolic hydroxyl groups (shown in **Scheme 2.12**).[137] The polymers were synthesized by a solution method and a pseudo-interfacial method. This research is described in **Chapter 4**.



Scheme 2.13 Synthetic scheme of block copolymer systems by solution method

Attempts to extend the acid chloride monomers approach to higher molecular weight polymers proved to be problematic. The acid chloride monomers approach was extended to the block systems (shown in **Scheme 2.13**). The solution method of block systems is limited due to solubility issues and it was very difficult to achieve high molecular weights. An alkylation approach was explored where the PAES oligomers were chemically modified with hydroxy ethoxy groups. The PAES oligomers with primary alcohol groups were suitable for the synthesis of polyester-sulfone with conventional melt polymerization with metal based catalyst at elevated temperature under vacuum (shown in **Scheme 2.14**). The thermal properties and mechanical properties of the block copolymer systems were evaluated. This research is described in **Chapter 5**.



Scheme 2.14 Synthetic scheme of block copolymer systems by melt polymerization method

2.5 References

(1) Kroschwitz, J. I.; Mark, H. F. *Encyclopedia of Polymer Science and Technology: , v. 1. A to Coatings*; Wiley-Interscience, 2003.

(2) Kharasch, M. S.; Friedlander, H. N. *J Org Chem* **1948**, *13*, 882.

(3) Marvel, C. S.; Glavis, F. J. *J. Am. Chem. Soc.* **1938**, *60*, 2622.

(4) Ryden, L. L.; Marvel, C. S. *J. Am. Chem. Soc.* **1936**, *58*, 2047.

(5) Kharasch, M. S.; Sternfeld, E. *J. Am. Chem. Soc.* **1940**, *62*, 2559.

(6) Marvel, C. S.; Dunlap, L. H. *J. Am. Chem. Soc.* **1939**, *61*, 2709.

(7) Desaulniers, C. W.; Baker, R. W. Application: FR 1969-9936 2005334 1969 12 pp

(8) Rozelle, L. T.; Cadotte, J. E.; Corneliussen, R. D.; Erickson, E. E. *Development of new reverse osmosis membranes for desalination*, North Star Res. and Develop. Inst.,Minneapolis,MN,USA., 1968.

(9) Rozelle, L. T.; Cadotte, J. E.; McClure, D. J. *Development of new reverse osmosis membranes for desalination*, North Staar Res. and Develop. Inst.,Minneapolis,MN,USA., 1970.

(10) Caldwell, J. R.; Hill, E. H. Application: US 2899412 1959

(11) Fanning, R. J. Application: US 1952-319788 2721851 1955

(12) Kreuchunas, A. Application: US 1955-550805 2822351 1958

(13) Noether, H. D. *Text. Res. J.* **1958**, *28*, 533.

(14) Bringer, R. P.; Morneau, G. A. *Appl. Polym. Symp.* **1969**, *11*, 189.

(15) Vogel, H. A.; Oien, H. T. Application: FR 1559971 1969 8 pp

(16) Bugel, T. E.; Walton, R. K. *Tech. Papers, Reg. Tech. Conf., Soc. Plast. Engrs., Detroit Sect.* **1965**, 82.

(17) Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F.; Merriam, C. N. *J. Polym. Sci., Part A-1 Polym. Chem.* **1967**, *5*, 2375.

(18) Staub, R. B. *Tech. Papers, Reg. Tech. Conf., Soc. Plastics Engrs., Newark Sect.* **1965**, 94.

(19) Leslie, V. J.; Rose, J. B. Application: DE 1970-2038166 2038166 1971 24 pp

(20) Dewing, J. Application: GB 1960-15717 927822 1963 2 pp

(21) Johnson, R. N., Farnham, A.G. *Journal of Polymer Science, Part A* **1967**, *5*, 2415.

(22) Gatham, K. V., Turner, S. *Polymer* **1974**, *15*, 665.

(23) Attwood, T. E., King, T., Leslie, V.J., Bose, J.B. *Polymer* **1977**, *18*, 369.

(24) Viswanathan, R., Johnson, B.C., McGrath, J.E. *Polymer* **1984**, *25*, 1827.

(25) Lakshmana, R. V. *Polymer Reviews* **1999**, *39*, 655.

(26) Harrison, W. L., Hickner, M.A., Kim, Y.S., McGrath, J.E. *Fuel Cells* **2005**, *5*, 201.

(27) Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F.; Merriam, C. L. *J. Polym. Sci., Polym. Chem. Ed.* **1967**, *5*, 2375.

(28) Kitamura, T.; Tanaka, N.; Mihashi, A.; Matsumoto, A. *Macromolecules (Washington, DC, U. S.)* **2010**, *43*, 1800.

(29) Percec, V.; Wang, J. H.; Oishi, Y. *J. Polym. Sci., Part A Polym. Chem.* **1991**, *29*, 949.

(30) Percec, V.; Wang, J. H.; Oishi, Y.; Feiring, A. E. *J. Polym. Sci., Part A Polym. Chem.* **1991**, *29*, 965.

(31) Cella, J. A.; Talley, J. J.; Fukuyama, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1989**, *30*, 581.

(32) Kricheldorf, H. R.; Boehme, S.; Schwarz, G.; Krueger, R.-P.; Schulz, G. *Macromolecules* **2001**, *34*, 8886.

(33) Guo, Q.; Xiao, Y.; Yu, X.; Cheng, Z.; Chen, T. *Gaofenzi Xuebao* **2010**, 536.

(34) Imai, Y.; Hirukawa, H.; Okuyama, K.; Ueda, M. *Makromol. Chem.* **1979**, *180*, 25.

(35) Jiang, H.; Chen, T.; Bo, S.; Xu, J. *Polymer* **1998**, *39*, 6079.

(36) Unroe, M. R.; Hedberg, F. L. *Acetylene-terminated sulfone resin precursors of tailored length via a modified Ullmann ether synthesis*, Air Force Wright Aeronaut. Lab.,Wright-Patterson AFB,OH,USA., 1985.

(37) Weil, A. *Compt. Rend.* **1962**, *254*, 3674.

(38) Kricheldorf, H. R.; Jahnke, P. *Makromol. Chem.* **1990**, *191*, 2027.

(39) Kricheldorf, H. R.; Schmidt, B.; Delius, U. *Eur. Polym. J.* **1990**, *26*, 791.

(40) Imai, Y.; Ueda, M.; Ii, M. *Makromol. Chem.* **1978**, *179*, 2989.

(41) Roovers, J.; Toporowski, P. M.; Ethier, R. *High Perform. Polym.* **1990**, *2*, 165.

(42) Staniland, P. A. *Bull. Soc. Chim. Belg.* **1989**, *98*, 667.

(43) Danilina, L. I.; Muromtsev, V. I.; Pravednikov, A. N. *Vysokomol. Soedin., Ser. A* **1975**, *17*, 2592.

(44) Seymour, R. B.; Kirshenbaum, G. S. *High Performance Polymers: Their*

Origin and Development. ; Elsevier Science Publishing Co. Inc: New York, 1986.

(45) Carey, F. A. *Organic Chemistry, 4th edition*; Mcgraw-Hill, 2000.

(46) Attwood, T. E.; Newton, A. B.; Rose, J. B. *Brit. Polym. J.* **1972**, *4*, 391.

(47) Newton, A. B.; Rose, J. B. *Polymer* **1972**, *13*, 465.

(48) Hedrick, J. L.; Labadie, J. W. *Macromolecules* **1990**, *23*, 1561.

(49) Clendinning, R. A.; Farnham, A. G.; Zutty, N. L.; Priest, D. C. Canad. Pat. 847, 963 1970

(50) Cameron, G. G.; Buchan, G. M.; Law, K.-S. *Polymer* **1981**, *22*, 558.

(51) Gerbi, D. J.; Dimotsis, G.; Morgan, J. L.; Williams, R. F.; Kellman, R. *J. Polym. Sci., Polym. Lett. Ed.* **1985**, *23*, 551.

(52) Mathias, L. J.; E., C. J. C. *Crown Ethers and Phase Transfer Catalysis in Polymer Science.*; Plenum Press: NewYork, 1984.

(53) Banthia, A. K.; Webster, D. C.; McGrath, J. E. *Org. Coat. Plast. Chem.* **1980**, *42*, 127.

(54) Imai, Y.; Ueda, M.; Ii, M. *Kobunshi Ronbunshu* **1978**, *35*, 807.

(55) Clayden, N. J.; Parker, D. G.; Thorogood, A. S.; Rose, J. B. *Polym. Int.* **1994**, *33*, 335.

(56) Ishikura, M.; Omori, H. Application: JP 1989-30158 02209926 1990 5 pp

(57) Hoover, K. C.; Scoggins, L. E.; Nesheiwat, A. M.; Shang, W.-t. W. Application: EP 1988-112313 301566 1989 11 pp

(58) Hedrick, J. L.; Dumais, J. J.; Jelinski, L. W.; Patsiga, R. A.; McGrath, J. E. *J. Polym. Sci., Part A Polym. Chem.* **1987**, *25*, 2289.

(59) Hedrick, J. L.; Mohanty, D. K.; Johnson, B. C.; Viswanathan, R.; Hinkley, J.

A.; McGrath, J. E. *J. Polym. Sci., Part A Polym. Chem.* **1986**, *24*, 287.

(60) Viswanathan, R.; Johnson, B. C.; McGrath, J. E. *Polymer* **1984**, *25*, 1827.

(61) Vogel, H. A. *J. Polym. Sci., Part A-1 Polym. Chem.* **1970**, *8*, 2035.

(62) Rose, J. B. *Chimia* **1974**, *28*, 561.

(63) Berg, A. A.; Monakov, Y. B.; Salazkin, S. N.; Rafikov, S. R.; Budtov, V. P.; Grigor'eva, V. P.; Filatova, E. S.; Egorov, A. E. *Vysokomol. Soedin., Ser. A* **1983**, *25*, 2048.

(64) Iojoiu, C.; Marechal, M.; Chabert, F.; Sanchez, J. Y. *Fuel Cells (Weinheim, Ger.)* **2005**, *5*, 344.

(65) Kozlov, V. G.; Filatova, E. S.; Egorov, A. E. *Khimiya i Fiz.-khimiya Vysokomolekul. Soed., Ufa* **1988**, 68.

(66) Verko, N.; Stropnik, C. *Kovine, Zlitine, Tehnol.* **1995**, *29*, 233.

(67) Fontanille, M.; Guyots, A. *Recent Advances in Mechanicstic and Syntheic Aspects of Polymerisation*; D. Reidel Publishing Co., : Bandol, France, 1987.

(68) Robello, D. R.; Ulman, A.; Urankar, E. J. *Macromolecules* **1993**, *26*, 6718.

(69) Cudby, M. E. A.; Feasy, R. G.; Jennings, B. E.; Jones, M. E. B.; Rose, J. B. *Polymer* **1965**, *6*, 589.

(70) Jones, M. E. British Patent 1166624 1969

(71) Rose, J. B. British Patent 2099006 1982

(72) Jennings, B. E.; Jones, M. E. B.; Rose, J. B. *J. Polym. Sci., Polym. Symp.* **1967**, *16*, 715.

(73) Yamazaki, S.; Yamada, K.; Yamabe, S.; Yamamoto, K. *Journal of Organic Chemistry* **2002**, *67*, 2889.

(74) Darnell, W. R.; Jackson, W. J. Application: US 1988-240642 4861856 1989 6 pp

(75) Rose, J. B. *Polymer* **1974**, *15*, 456.

(76) Craver, C. D.; Carraher, C. E. *Applied polymer science: 21st century*; Elsevier, 2000.

(77) Harper, C. A. *Handbook of plastics, elastomers, and composites*; McGraw-Hill Professional, 2002.

(78) Black, J. *Handbook of biomaterial properties*; Springer, 1998.

(79) Platt, D. *Engineering and High Performance Plastics*; iSmithers Rapra Publishing, 2003.

(80) http://iwww.plasticsportal.com/products/ultrason.html.

(81) Olabisi, O. *Handbook of thermoplastics*; CRC Press, 1997.

(82) http://www.solvayplastics.com/sites/solvayplastics/EN/specialty_polymers/SulfonePolymers/Pages/Overview.aspx.

(83) http://www.solvayplastics.com/sites/solvayplastics/EN/specialty_polymers/SulfonePolymers/Pages/Sulfone_Polymers.aspx.

(84) Attwood, T. E.; King, T.; Leslie, V. J.; Rose, J. B. *Polymer* **1977**, *18*, 369.

(85) Salamone, J. C. *Polymeric Materials Encyclopedia*; CRC Press, 1996; Vol. 8.

(86) Attwood, T. E.; Cinderey, M. B.; Rose, J. B. *Polymer* **1993**, *34*, 2155.

(87) Mao, M.; Das, S.; Turner, S. R. *Polymer* **2007**, *48*, 6241.

(88) Rose, J. B. *Chem. Ind.* **1968**, 461.

(89) *Dupont Teijin Films Report*, 2004.

(90) Crawford, G. P. *Flexible flat panel displays*; John Wiley and Sons, 2005.

(91) Bloch, D. R. *Polymer handbook*; New York : John Wiley, 1999.

(92) Charrier, J. M. *Polymeric Materials and Processing: Plastics, Elastomers, and Composites.*; Oxford University Press: New York, 1991.

(93) Brzozowski, Z. K.; Rokicki, G.; Wolkiewicz, S. *Polimery (Warsaw)* **1975**, *20*, 429.

(94) Paul, M.; Park, H. B.; Freeman, B. D.; Roy, A.; McGrath, J. E.; Riffle, J. S. *Polymer* **2008**, *49*, 2243.

(95) Friedrich, C.; Driancourt, A.; Noel, C.; Monnerie, L. *Desalination* **1981**, *36*, 39.

(96) Riley, R. L.; Case, P. A.; Lloyd, A. L.; Milstead, C. E.; Tagami, M. *Desalination* **1981**, *36*, 207.

(97) Geise, G. M.; Freeman, B. D.; Paul, D. R. *Polymer* **2010**, *51*, 5815.

(98) Xie, W.; Park, H.-B.; Cook, J.; Lee, C. H.; Byun, G.; Freeman, B. D.; McGrath, J. E. *Water Sci. Technol.* **2010**, *61*, 619.

(99) Badami, A. S.; Lane, O.; Lee, H.-S.; Roy, A.; McGrath, J. E. *J. Membr. Sci.* **2009**, *333*, 1.

(100) Guo, R.; Lane, O.; Van Houten, D.; McGrath, J. E. *Ind. Eng. Chem. Res.* **2010**, *49*, 12125.

(101) Lee, H.-S.; Roy, A.; Lane, O.; Lee, M.; McGrath, J. E. *J. Polym. Sci., Part A Polym. Chem.* **2010**, *48*, 214.

(102) Choi, K.-Y.; Yi, M. H. *Macromol. Symp.* **1999**, *142*, 193.

(103) Yi, M. H.; Huang, W.; Jung, J. T.; Kwon, S. K.; Choi, K.-Y. *J. Macromol. Sci., Pure Appl. Chem.* **1998**, *A35*, 843.

(104) Krasnov, E. P.; Khar'kov, S. N.; Vorob'ev, E. A.; Gribov, R. N.; Zakharov, V. S.; Grechushnikova, L. P. *Khim. Volokna* **1972**, *14*, 12.

(105) Khar'kov, S. N.; Grechushnikova, L. P.; Chegolya, A. S.; Krasnov, E. P.; Preobrazhenskii, K. K.; Gribov, R. N.; Vorob'ev, E. A. *Vysokomol. Soedin., Ser. A* **1972**, *14*, 817.

(106) Petryakova, T. N.; Lapitskii, V. A. *Zh. Prikl. Khim. (Leningrad)* **1989**, *62*, 2393.

(107) Nishikubo, Y. Application: JP 2008-17387 2009179649 2009 17pp

(108) Hsiao, S.-H.; Yang, C.-P.; Wang, S.-W.; Chuang, M.-H. *J. Polym. Sci., Part A Polym. Chem.* **1999**, *37*, 3575.

(109) Yang, H.; Moskala, E.; Jones, M. *J. Appl. Med. Polym.* **1999**, *3*, 50.

(110) Nielinger, W.; Mayska, P. J.; Freitag, D.; Idel, K. J.; Fengler, G. Application: EP 1990-115121 413233 1991 13 pp

(111) Korshak, V. V.; Vinogradova, S. V.; Vygodskii, Y. S. *Polymer Reviews* **1974**, *11*, 45

(112) Huang, W.; Xu, H.; Yin, J. *Eur. Polym. J.* **2006**, *42*, 946.

(113) Li, X.; Yee, A. F. *Macromolecules* **2004**, *37*, 7231.

(114) Yi, M. H.; Huang, W.; Jin, M. Y.; Choi, K.-Y. *Macromolecules* **1997**, *30*, 5606.

(115) Patel, Y. V.; Parsania, P. H. *Polym. Test.* **2002**, *21*, 711.

(116) Aiken, G. A.; Lewis, H. J.; Reid, T. F. Br. Patent 879 264 1961

(117) Hasek, R. H.; Knowles, M. B. US Patent 2 917 549 1958-707462 2917549 1959

(118) Mozdzen, E. C. Application: US 1982-427219 4503273 1985 4 pp

(119) Zhao, Z. Application: CN 2010-10616421 102093161 2011 6pp

(120) Ohmae, T.; Sakurai, H.; Ohnishi, S.; Kuwata, K.; Nitta, I. *J. Phys. (Moscow)* **1967**, *46*, 1865.

(121) Prince, F. R.; Fredericks, R. J. *Macromolecules* **1972**, *5*, 168.

(122) Yoshimura, S.; Kiyono, S.; Kunihiro, T.; Tsuruta, M.; Hamada, T.; Watabe, E.; Morooka, S. Application: JP 2010-89861 2011006382 2011 17pp

(123) Grashof, H. R.; Kan, H. C.; Sandhu, M. A.; Wright, J. F.; Yacobucci, P. D. Application: US 1985-688386 4601966 1986 9 pp

(124) Davis, T. G.; Weaver, M. A. Application: DE 1980-3005223 3005223 1980 23 pp

(125) Ballard, D. G. H.; Key, J. M. *Eur. Polym. J.* **1975**, *11*, 565.

(126) Gozdz, A. S.; Craighead, H. G.; Bowden, M. J. *Polym. Eng. Sci.* **1986**, *26*, 1123.

(127) Kibler, C. J.; Bell, A.; Smith, J. G. *J. Polym. Sci.* **1964**, *2*, 2115.

(128) Turner, S. R.; Seymour, R. W.; Smith, T. W. *Cyclohexanedimethanol Polyesters*; John Wiley & Sons, Inc., 2001.

(129) Chen, L. P.; Yee, A. F.; Moskala, E. J. *Macromolecules* **1999**, *32*, 5944.

(130) Berti, C.; Celli, A.; Marchese, P.; Marianucci, E.; Barbiroli, G.; Di Credico, F. *Macromol. Chem. Phys.* **2008**, *209*, 1333.

(131) Sun, Y.-M.; Wang, C.-S. *Eur. Polym. J.* **1999**, *35*, 1087.

(132) Li, X.; Yee, A. F. *Macromolecules* **2003**, *36*, 9421.

(133) Li, X.; Yee, A. F. *Macromolecules* **2003**, *36*, 9411.

(134) Liu, J.; Yee, A. F. *Macromolecules* **1998**, *31*, 7865.

(135) Liu, J.; Yee, A. F. *Macromolecules* **2000**, *33*, 1338.

(136) Abadie, M. J. M.; Sillion, B. *Polyimides and other high-temperature polymers : proceedings of the 2nd European Technical Symposium on Polyimides and High-Temperature Polymers (STEPI 2)*; Amsterdam ; New York : Elsevier, 1991.

(137) Zhang, B.; Turner, S. R. *J. Polym. Sci., Part A: Polym. Chem.,* **2011**, *49*, 4316

Chapter 3 Synthesis, Characterization, and Property Study of Poly(arylene ether sulfone)s based on 4,4'-[*trans*-1,4-Cyclohexanebis(methylene)] Bisphenol

(Manuscript submitted)

3.1 Abstract

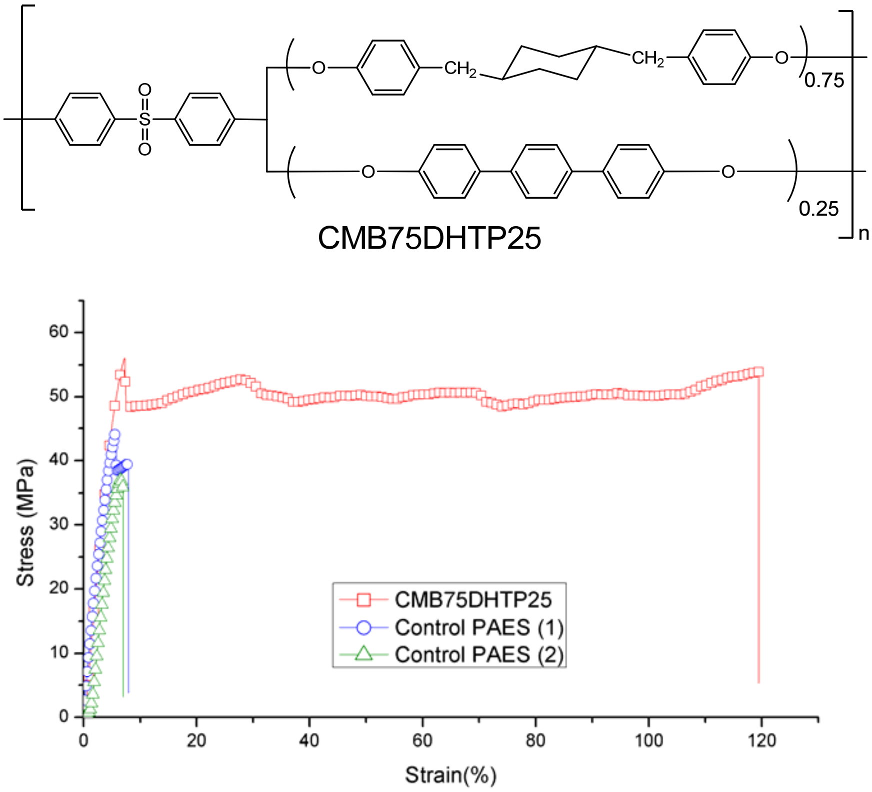


Figure 3.1 Large strain at failure enhancement obtained in the CMB75DHTP25 polymer sample vs. control PAESs

A new bisphenol monomer, 4,4'-[*trans*-1,4-cyclohexanebis(methylene)] bisphenol (CMB), was designed, synthesized and fully characterized with NMR, HRMS, and elemental analysis. Two series of poly(arylene ether sulfone)s (PAESs) containing *trans*-1,4-cyclohexylene units based on the new CMB monomer and 4,4'-dihydroxyl-*p*-terphenyl (DHTP) and 4,4'-dihydroxylbiphenyl (DHBP) were synthesized and studied. The cyclohexylene containing monomer and polymers were carefully analyzed by 1d ^{1}H NMR and 2d H-H correlation spectroscopy (COSY) confirming that the cyclohexylene units were in the *trans*-conformation. Moderate strain at failure enhancement was observed in CMB/DHBP copolymers with slightly reduced moduli when compared with commercial DHBP based PAES. As shown in **Figure 3.1**, a large strain at failure enhancement was obtained in the CMB75DHTP25 polymer sample. Some preliminary dynamic mechanical analysis (DMA) results suggest that the strain at failure enhancement is related to the strong intensity in both the β and γ-relaxations.

3.2 Introduction

Poly(arylene ether sulfone)s (PAESs) are important commercial polymers and have been extensively studied due to their excellent thermal and mechanical properties.[1,2] PAESs are commonly synthesized through aromatic nucleophilic substitution based on dichlorodiphenyl sulfone and various diphenols. There has been a continuous interest in developing new PAESs based on new monomers to obtain new properties or to enhance existing properties.

In this paper, we describe new PAES polymer systems with *trans*-1,4-cyclohexylene incorporated into the backbone based on a new bisphenol monomer 4,4'-[*trans*-1,4-cyclohexanebis(methylene)] bisphenol (CMB). Polymers with 1,4-cyclohexylene ring units in backbone are of great interest from both a fundamental and a practical point of view. The most explored areas of cyclohexylene containing polymers are polyesters, polycarbonates, and polyketones.[3-11] Yee and coworkers comprehensively studied the properties of cyclohexylene containing polyketone, polycarbonates and polyester polycarbonates.[5-9] It was generally found that incorporation of cyclohexylene units in the backbone enhanced the local chain motion and showed enhanced craze resistance behavior. Poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) is an important commercial polyester. The cyclohexylene units in PCT impart a high melting point and significant toughness to these polyesters.[12] Credico and coworkers[10] did a systematic study on the dynamic mechanical behavior of a group of cyclohexylene containing polyesters with different *trans/cis* ratio. A series of relaxations were observed and attributed to the flexible components of methylene groups and cyclohexylene groups.

To the best of our knowledge, little research has been done in cyclohexylene containing polysulfones. We have recently reported a series of PAESs synthesized from *trans*-1,4-cyclohexylene ring containing acid chloride monomers.[13] In this paper we report new PAESs that contain cyclohexylene ring units in the backbone. The conformations of the cyclohexylene rings in the polymer backbones were carefully monitored to ensure the all *trans*-conformations were obtained. This feature provides a simplified polymer system to study the relaxation behaviors without complication from a mixture of *cis*-, *trans*-cyclohexylene ring conformation as a result of the starting materials or isomerization side reactions.[4,5,10]

3.3 Experimental

3.3.1 Materials

All chemicals were purchased from Aldrich with the exception of *trans*-1,4-cyclohexane dicarboxylic acid (CHDA) which was donated by the Eastman Chemical Company. Radel® R sample was provided by Solvay Advanced Polymers L.L.C.. All reagents were used without further purification.

3.3.2 Instrumentation

Size Exclusion Chromatography (SEC) was used to determine molecular weights and molecular weight distributions. With a flow rate of 0.500 mL/min, data were obtained in N-methyl-2-pyrrolidone (NMP) solvent at 30 ^{o}C on a Waters Alliance model 2690 chromatograph equipped with a Waters HR 0.5+ HR 2+ HR 3+ HR 4+ styragel column set. A Viscotek refractive index detector and a viscometer were used for molecular weight determination. Polystyrene standards were utilized to construct a universal molecular weight calibration curve.

FT-IR data were obtained on an M2004 FTIR spectrometer from the MIDAC Corporation from 4000 cm^{-1} to 650 cm^{-1} with 4 cm^{-1} resolution. ^{1}H and ^{13}C NMR spectra were obtained by a JEOL 500 (500 MHz) spectrometer at room temperature with chemical shifts relative to tetramethylsilane (TMS). High Resolution Mass Spectrum

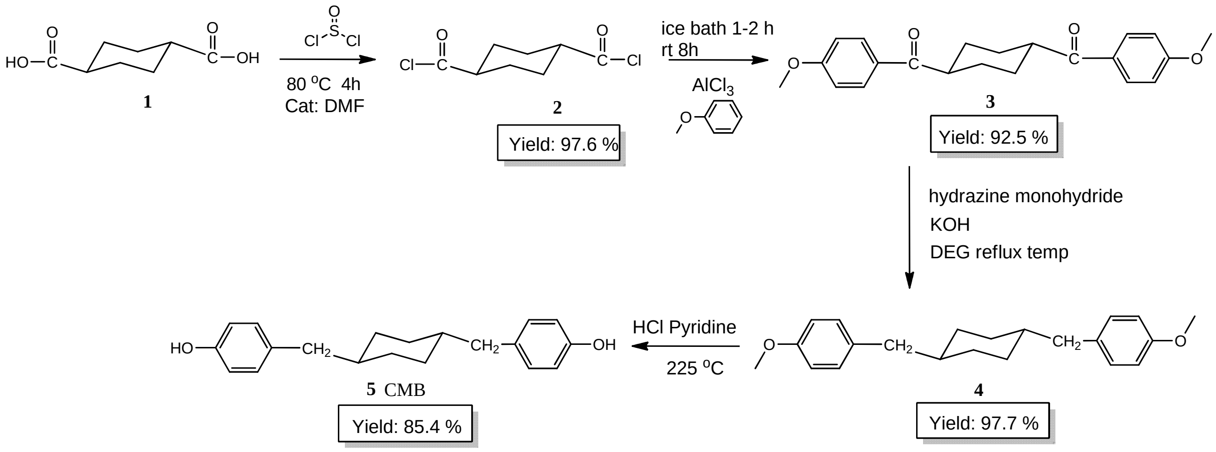
(HRMS) was obtained from an Agilent 6220 LC/MS mass spectrometer with time of flight (TOF) analyzer. The elemental analysis was done by the Atlantic Microlab, Inc (Norcross, Georgia).

T_gs and T_ms were determined by Differential Scanning Calorimetry (DSC). Data were obtained by using a TA Instruments™ Q2000. Nitrogen was used as the carrying gas with a sample flow rate of 20 mL/min and a heating rate of 10 ^oC/min. T_gs were determined in the second heating cycle after the samples were quenched at nominally 100 ^oC/min in the cooling cycle. Thermogravimetric analysis (TGA) was carried out by a TA Instruments™ Q10 from 25 ^oC to 600 ^oC under nitrogen at a heating rate of 10 ^oC /min. Dynamic mechanical analysis (DMA) was performed on a TA Instruments™ Q800 in nitrogen atmosphere from -150 ^oC to 200 ^oC with a rate of 2 ^oC/min. The DMA parameters were Mode: Multi-Freq-Strain Tension Film; Amplitude: 10 μm; Preload force: 0.01 N. The tensile properties were obtained on an Instron Model 4400 Universal Testing System with a rate of 2 mm/min at room temperature. All the DMA results were averaged over at least 5 samples.

3.3.3 Monomer Synthesis

3.3.3.1 Synthesis of *trans*-1,4-Cyclohexane Dicarbonyl Dichloride (Compound 2 in Scheme 3.1)

With a Teflon coated magnetic stir bar, a condenser, and an argon inlet, a pre-dried 250 mL three-necked round bottom flask was charged with 16.00 g (93.02 mmol) of CHDA, 120.0 mL of thionyl chloride and 0.1 mL of DMF. After heating at 60 ^oC under argon for 4 h, excess thionyl chloride was removed under vacuum at 60 °C. A white crystalline product was obtained and dried in vacuum oven (-80 kPa) at room temperature for 12 h. The product was used directly in the next step without any further purification. Yield 97.6 %. No melting point was observed due to the thermal instability of this compound. ^{1}H NMR ($CDCl_3$, ppm): δ 2.73 (m, 2H), δ 2.30 (m, 4H), δ 1.58 (m, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 188.4, 50.6, 30.0.



Scheme 3.1 Synthesis of 4,4'-[*trans*-1,4-cyclohexanebis(methylene)] bisphenol (CMB)

3.3.3.2 Synthesis of *trans*-1,4-Cyclohexanebis[(4-hydroxyphenyl) Methanone (Compound 3 in Scheme 3.1)

A 250 mL one-necked round bottom flask was charged with 8.000 g (38.28 mmol) *trans*-1,4-cyclohexane dicarbonyl dichloride and 100.0 mL of anisole as the solvent and the reactant. The flask was equipped with a Teflon coated magnetic stir bar and a condenser. After a homogenous solution was obtained, the system was placed in an ice bath and cooled to 0 °C. Aluminum chloride (12.76 g, 95.69 mmol) was then slowly added to the solution with vigorous stirring. The reaction mixture was kept at 0 °C for 2 h followed by another 8 h at room temperature. After the reaction, 400.0 mL of deionized water was added to the light orange suspension. The mixture was vigorously stirred at room temperature for 1 h then filtered. The white solid product was added to 200.0 mL of methanol and stirred at room temperature for another 3 h to remove residual anisole. The suspension was filtered to obtain the final product as a white solid which was thoroughly dried in vacuum oven (-80 kPa) at 80 °C for 12 h. Yield: 92.5 %. m.p. : 153.5-159.3 °C . Elemental analysis: Found: C, 74.75, H, 6.90. Calc. for $C_{22}H_{24}O_4$: C, 74.98; H, 6.86; O, 18.16 %. ^{1}H NMR ($CDCl_3$, ppm): δ 7.95 (d, 4H), δ 6.95 (d, 4H), δ 3.87 (s, 6H), δ 3.31 (m, 2H), δ 2.03 (m, 4H), δ 1.69 (m, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 202.0, 163.5, 130.6, 129.1, 113.9, 55.6, 44.6, 28.9.

3.3.3.3 Synthesis of *trans*-1,4-bis(4-methoxybenzyl)cyclohexane (Compound 4 in Scheme 3.1)

To a 250 mL two-necked round bottom flask equipped with an argon inlet, a Teflon coated magnetic stir bar, and a condenser, 15.00 g (42.61 mmol) of **compound 3**, 19.18 g (38.35 mmol) of hydrazine monohydrate, 21.48 g (38.35 mmol) of potassium hydroxide and 100.0 mL of diethylene glycol were added. Under an argon gas atmosphere, the mixture was heated to 250 °C in a high temperature silicon oil bath under stirring. The reaction mixture was held at this temperature for 24 h then the system was cooled down to room temperature and poured into 300.0 mL of deionized water. The aqueous solution was extracted with 100.0 mL of chloroform three times. The chloroform solution then was combined and chloroform was removed by rotary evaporation to obtain a light yellow solid. The solid was extracted in a Soxhlet extractor with 400.0 mL of methanol to remove soluble side products followed by drying at 80 ^oC in vacuum oven (-80 kPa) for 12 h. Yield: 97.7 %. m.p.: 129.4-133.2 ^oC. Elemental analysis: Found: C, 81.39, H, 8.81. Calc. for $C_{22}H_{28}O_2$: C, 81.44; H, 8.70; O, 9.86 %. ^1H NMR ($CDCl_3$, ppm): δ 7.02 (d, 4H), δ 6.80 (d, 4H), δ 3.77 (s, 6H), δ 2.39 (d, 4H), δ 1.67 (m, 4H), δ 1.40 (m, 2H), δ 0.89 (m, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 157.7, 133.5, 130.0, 113.5, 55.3, 43.1, 40.1, 33.0.

3.3.3.4 Synthesis of 4,4'-[*trans*-1,4-Cyclohexanebis(methylene)] Bisphenol (CMB, Compound 5 in Scheme 3.1)

15.00 g (46.30 mmol) of **compound 4** and 53.47 g (46.30 mmol) of pyridine hydrochloric acid were added to a 250 mL two-necked round bottom flask equipped with an argon inlet, a Teflon coated magnetic stir bar, and a condenser. Under argon atmosphere, the system was heated in a high temperature silicon oil bath to 225 ^oC and allowed to react at this temperature for 12 h with stirring. Then the reaction mixture was cooled to room temperature and 200 mL of water was added. The suspension was allowed to vigorously stir at room temperature for 12 h then filtered to obtain the crude product with a beige color. Crystals with a slight beige color were obtained after recrystallization with methanol with a yield of 85.4 %. m.p.: 227.8-233.1 ^oC. Elemental analysis: Found: C, 80.35, H, 8.24. Calc. for $C_{20}H_{24}O_2$: C, 81.04; H, 8.16; O, 10.80 %. ^1H NMR (DMSO-d6, ppm): δ 9.08 (s, 2H), δ 6.89 (d, 4H), δ 6.63 (d, 4H), δ 2.30 (d, 4H), δ 1.58 (m, 4H), δ 1.32 (m, 2H), δ 0.83 (m, 4H). ^{13}C NMR (DMSO-d6, ppm): δ 155.7, 131.3, 130.3, 115.4, 42.9, 40.1, 32.9. HRMS (*m/z*): Found: 296.1776. Calcd for $C_{20}H_{24}O_2$: 296.1785. Diff: 2.80 ppm.

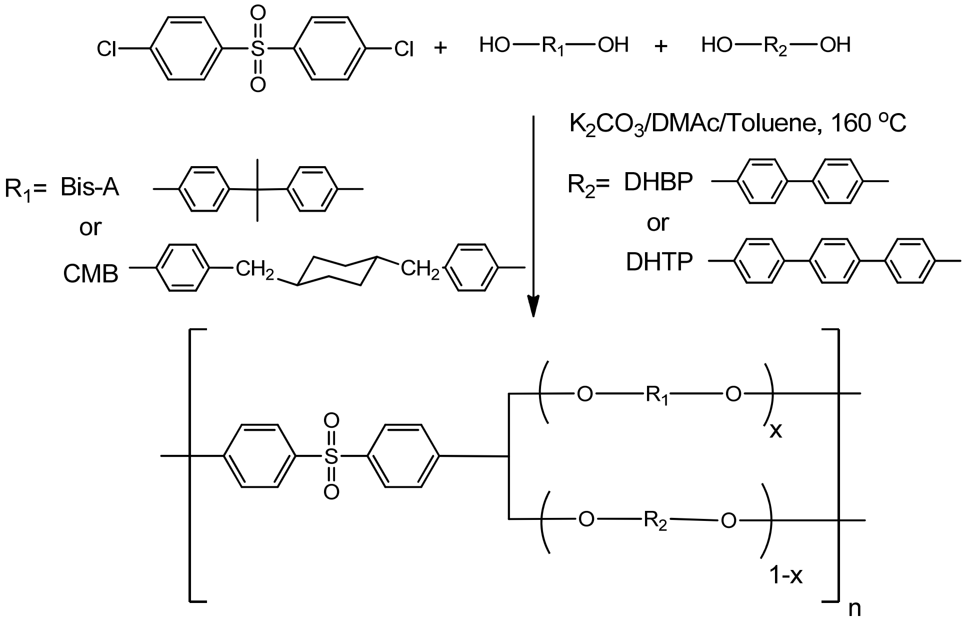
3.3.3.5 Synthesis of 4,4'-Dihydroxyl-*p*-terphenyl (DHTP)

4,4'-Dihydroxyl-*p*-terphenyl (DHTP) was synthesized according to a previously published procedure.[14] ^{1}H NMR (DMSO-d6 ppm): δ 7.56 (s, 4H), δ 7.46 (d, 4H), δ 6.80 (d, 4H). ^{13}C NMR (DMSO-d6 ppm): δ 157.1, 138.1, 130.5, 127.5, 126.3, 115.8.

3.3.4 Polymer Synthesis

3.3.4.1 Synthesis of 4,4'-[*trans*-1,4-Cyclohexanebis(methylene)] Bisphenol based Homopolymer and Random Copolymers

trans-1,4-Cyclohexylene ring containing poly(arylene ether sulfone)s based on CMB, 4,4'-dihydroxylbiphenyl (DHBP), and DHTP were synthesized by nucleophilic aromatic substitution with 4,4'-dichlorodiphenylsulfone (DCDPS) as shown in **Scheme 3.2**. The polymers based on bisphenol-A (bis-A), DHTP, and DCDPS was synthesized in a similar fashion with different starting materials. We define homopolymer as a polymer from DCDPS with a single biphenol and random copolymers as the ones with two biphenols.



Scheme 3.2 Synthesis of 4,4'-[*trans*-1,4-cyclohexanebis(methylene)] bisphenol based homopolymer (x=1) and random copolymers

The synthesis of random copolymers based on 0.5 molar equivalent of CMB, 0.5 molar equivalent of DHBP, and 1 molar equivalent of DCDPS is described here as an example. All the other homopolymer and copolymers were synthesized via similar technique. To a 100 mL round bottom flask equipped with a mechanical stirrer, an argon inlet and a Dean-Stark trap, 3.875 g (13.50 mmol) of DCDPS, 2.000 g (6.75 mmol) of CMB, 1.256 g (6.75 mmol) of DHBP, 4.842 g (35.09 mol) of K_2CO_3, 60.0 mL of DMAc and 30.0 mL of toluene were added. Under protection of argon, the reaction was allowed to dehydrate at 140 ^oC for 3 h by azeotropic distillation. Then the temperature was slowly increased to 160 ^oC over 2 h to remove toluene. After 20 h at 160 ^oC the reaction mixture was cooled to room temperature. The solution was precipitated in 5 weight percent HCl aqueous solution. The polymer product was obtained after filtration and subsequently washed three times with 200 mL of deionized water and three times with 200 mL of methanol. The polymer sample was obtained as a white solid and was dried thoroughly at 120 ^{o}C for 12 h in vacuum oven (-80 kPa). Yield: 92.5 %. ^{1}H NMR ($CDCl_3$, ppm): δ 7.86 (m), δ 7.58 (m, 3.90), δ 7.11 (m), δ 7.06 (m), δ 7.98 (m), δ 6.92 (m), δ 2.47 (d, 4.00), δ 1.70 (m), δ 1.46 (m), δ 0.93 (m). In proton NMR, the integration area ratio between protons with chemical shift δ 7.58 and δ 2.47 was used to determine actual monomer ratio in the polymer sample.

3.3.4.2 Synthesis of High Molecular Weight 4,4’-Dihydroxylbiphenyl (DHBP) based PAES as Property Control

The 4,4’-dihydroxylbiphenyl (DHBP) based PAES was synthesized with comparable high molecular weight to the Radel® R sample. Both of the Radel® R sample and the lab-synthesized high molecular weight DHBP based PAES sample were used as controls in thermal and mechanical property evaluation. The high molecular weight DHBP based PAES sample was synthesized in the same way as described in the polymer synthesis paragraph above but with a different stoichiometry imbalance to control the molecular weight.

3.3.4.3 Polymer Film Preparation

Film samples were obtained by solution casting. The polymers offered transparent tough films with no color or light yellow color. The film samples were prepared as follows. The solid polymer sample was dissolved at room temperature in chloroform, DMAc, or NMP to offer a homogeneous solution with a concentration of 10 wt%. The polymer solution was filtered through a 45 μm micro glass fiber filter and then was cast on a leveled glass substrate, dried at 80 ^oC for 12 h, and subsequently dried at 120 ^oC under vacuum (-80 kPa) for 12 h. Dog bone samples for mechanical property evaluation were prepared from the polymer films. The dimensions of the dog bone samples were 4.00 mm in width and about 15 mm in length. The thickness of the samples was in the range of 60-100 μm.

3.4 Results and Discussion

3.4.1 Synthesis of 4,4'-[*trans*-1,4-Cyclohexanebis(methylene)] Bisphenol (CMB) Monomer

The CMB monomer was successfully synthesized in four steps with an overall yield of 77 %. The key reaction step is the Wolff-Kishner-HuangMingLong reduction reaction[15] where strong base potassium hydroxide, hydrazine monohydrate as the reducing reagent, and high boiling point solvent diethylene glycol were used (shown in **Scheme 3.1**). The FT-IR spectra shown in **Figure 3.2** clearly show the characteristic adsorption of the carbonyl group at 1667 cm^{-1} was eliminated which is indicative of successful reduction of the carbonyl. The structures of **compound 3** and **4** were confirmed by ^1H NMR and ^{13}C NMR. They also exhibited sharp melting points.

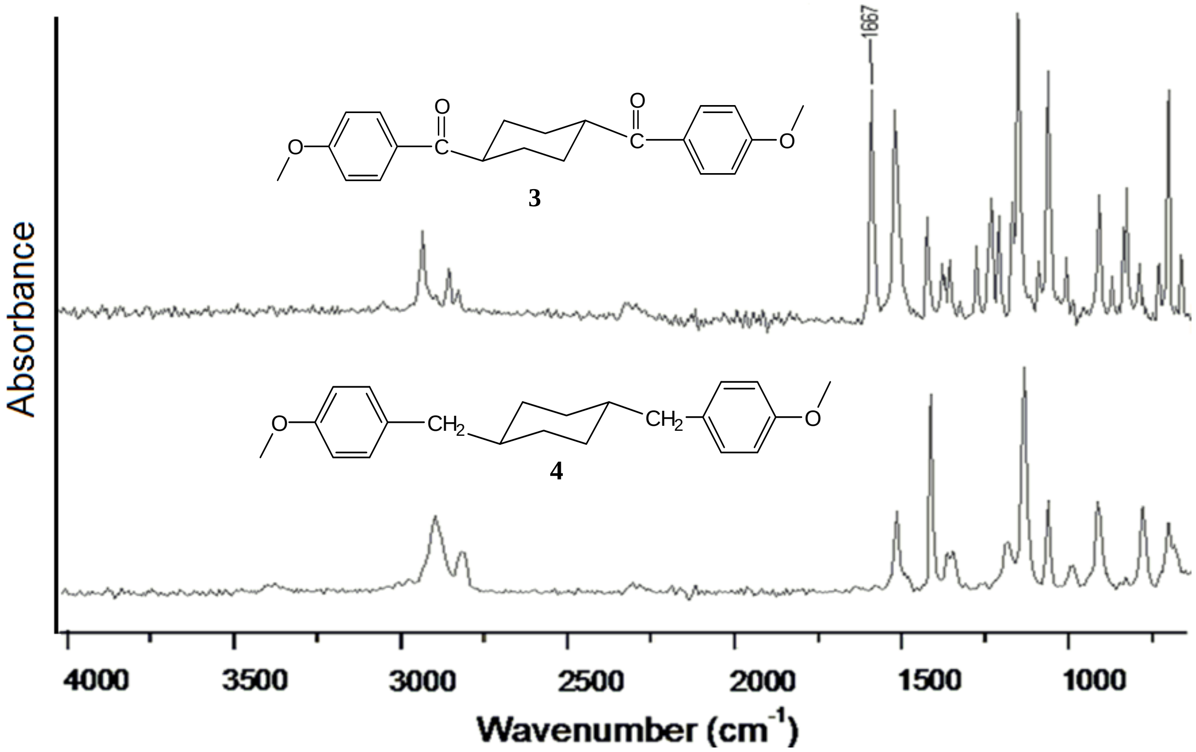


Figure 3.2 The FT-IR spectra monitoring the Wolff-Kishner-HuangMingLong reduction reaction

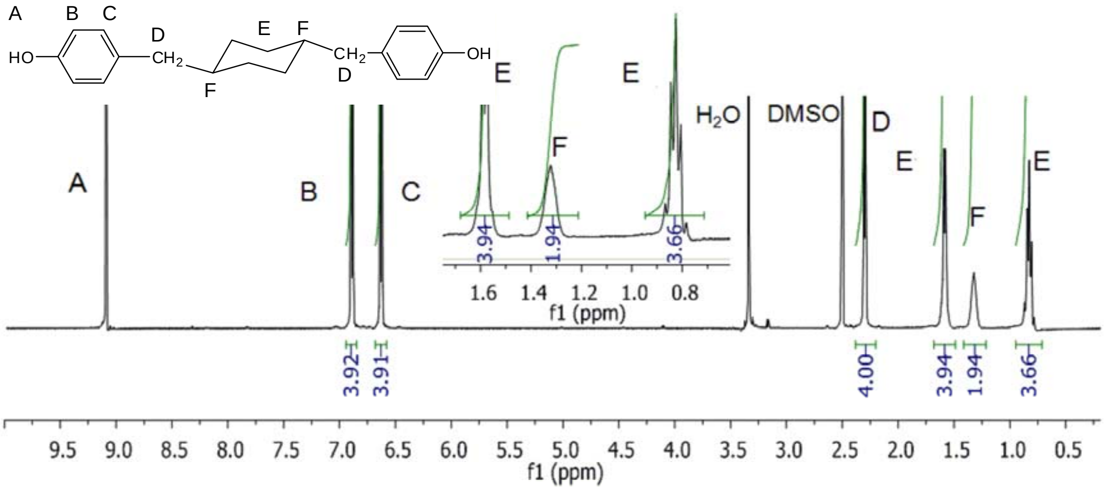


Figure 3.3 The 1d ^1H NMR spectrum of CMB monomer

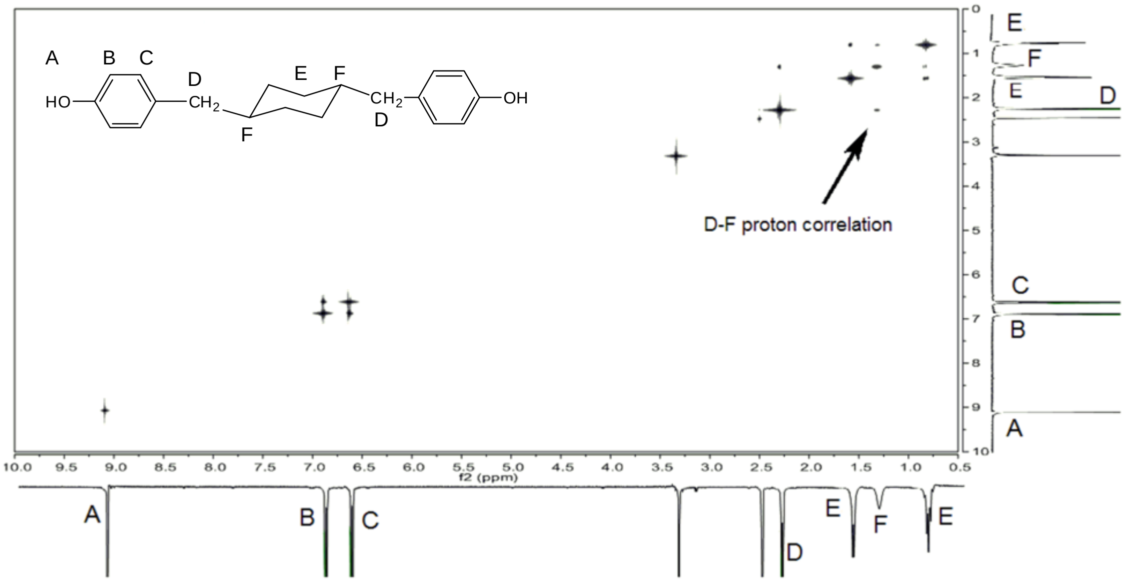


Figure 3.4 The 2d H-H COSY spectrum of CMB monomer

trans-CHDM was used as the starting material. In the synthesis **Scheme 3.1**, the conformation of the cyclohexylene rings in product compounds was carefully monitored by NMR. For example, the 1d ^{1}H NMR of CMB is shown in **Figure 3.3** with the 2d H-H Correlation Spectroscopy (COSY) NMR shown in **Figure 3.4**. The enlarged area in **Figure 3.3** shows the aliphatic ring protons. Based on the H-H COSY NMR spectra, the only H-H correlation of **D protons** was with the **F protons** which indicate that the **F protons** are the cyclohexyl protons shown in **Figure 3.3**. Due to the fact that only one signal (broadened by multiple splitting) was observed for **F protons**, the cyclohexylene ring in the CMB monomer is in *trans*-conformation. All the cyclohexylene ring containing compounds showed the same proton NMR pattern which confirmed the *trans*-conformation. The CMB monomer structure was further confirmed by ^{13}C NMR and

HRMS. The elemental analysis results of the CMB monomer were in good agreement with the theoretical values.

3.4.2 Homopolymer and Random Copolymers based on 4,4'-[*trans*-1,4-Cyclohexanebis(methylene)] Bisphenol (CMB) and 4,4’-Dihydroxylbiphenyl (DHBP)

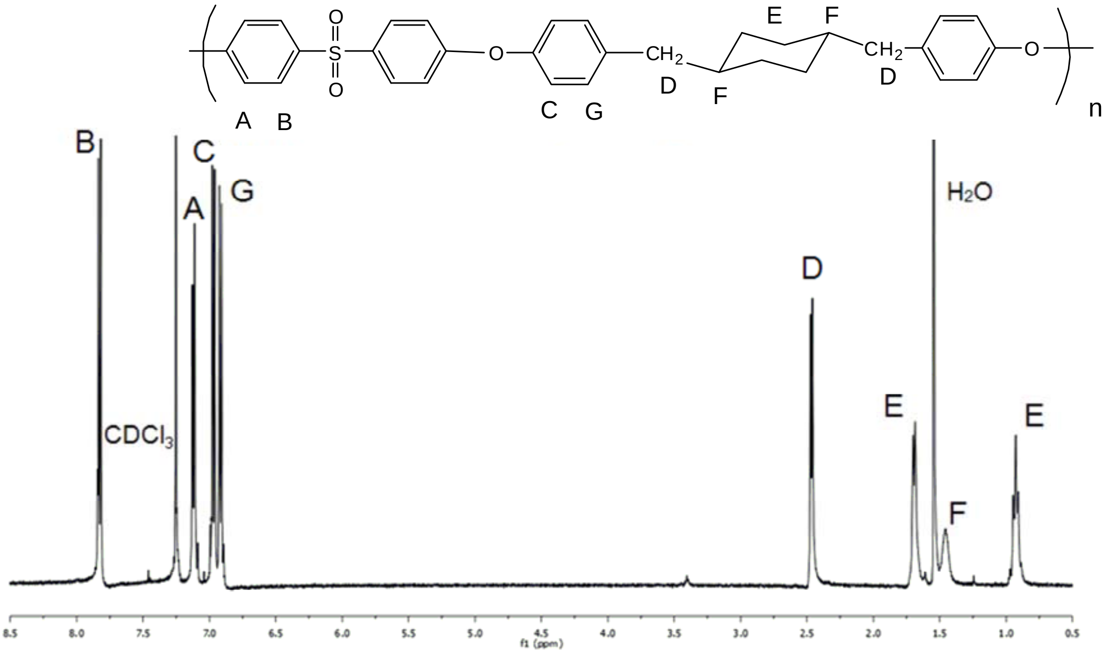


Figure 3.5 The 1d ^{1}H NMR CMB DCDPS homopolymer (CMB100)

The PAES homopolymer based on CMB as the only biphenol and random copolymers based on different ratios of CMB and DHBP (or DHTP) were all synthesized with high yield. In the random copolymer names, the numbers after the acronyms indicate the molar percentage of the phenol monomer. For example, CMB75DHBP25 is the random copolymer made with 75 molar percent of CMB, 25 molar percent of DHBP, and 100 molar percent of DCDPS. The conformation of the cyclohexylene ring units were carefully monitored by ^{1}H NMR. The ^{1}H NMR of the homopolymer based on CMB is shown in **Figure 3.5** as an example. The aliphatic ring proton area in all the polymer samples displayed the same sample pattern as shown in the CMB monomer in **Figure 3.3**. Only one signal was observed for **F protons** (broadened by multiple splitting) which indicated the cyclohexylene ring units were in the *trans*-conformation and no isomerization reactions occurred during the polymerizations. These polymer samples were readily soluble in chloroform, DMF, DMAc, NMP at room temperature but not in THF and methanol.

The monomer ratios in the random copolymers were determined by ^{1}H NMR. As shown in **Table 3.1**, the actual monomer ratios were very close to the monomer feed ratios. The SEC traces of the samples were all monomodal with no indication of branching. The homopolymer and random copolymers exhibited high molecular weights with number average molecular weight around 30 kg/mol and PDIs (Polydispersity Index) all close to 2. Similar high molecular weights of the new PAESs ensured that thermal properties and mechanical properties results were from structural differences not molecular weight based effects.

As expected, decreasing glass transition temperatures were observed in DSC with the increasing CMB contents. The decreasing glass transition is attributed to the flexibility provided by the *trans*-1,4-cyclohexylene ring units incorporated in the CMB monomer via low energy conformational changes. This result agreed very well with our results obtained in the series of PAES based on *trans*-1,4-cyclohexylene ring containing acid chloride monomers.[13] No melting points were observed in the CMB homopolymer

Table 3.1 Compositions, molecular weights, and thermal properties of CMB homopolymer and CMB/DHBP polysulfone random copolymers

Polymer	CMB mol[2] (%)	DHBP mol[2] (%)	CMB mol[2] (%)	DHBP mol[2] (%)	T_g[3] (°C)	T_d[3] (°C)	Molar Mass[4] (kg/mol) M_n	M_w	PDI
CMB100[1]	100	0	100	0	172	466	28.9	64.2	2.2
CMB75DHBP25	75.0	25.0	74.8	25.2	186	484	39.9	72.7	1.8
CMB50DHBP50	50.0	50.0	49.7	50.3	199	453	40.3	84.6	2.1
CMB25DHBP75	25.0	75.0	24.1	75.9	214	442	34.7	68.2	2.0

[1] The numbers indicate molar ratio of the diphenol monomers.

[2] The first two columns are the feed ratios of the monomers; the second two columns are the actual monomer ratios determined by ^{1}H NMR.

[3] The T_gs were determined in the 2nd heating cycle in DSC with a rate of 10 °C/min. The decomposition temperature is the 5 % weight loss temperature in nitrogen.

[4] NMP as the SEC solvent with a refractive index detector and a viscometer

and DHBP/CMB random copolymers. All the polymer samples exhibited high thermal stability. In nitrogen, the thermal degradation temperatures, defined as 5 % weight loss temperature, were all observed around 450 °C.

Table 3.2 Mechanical properties of CMB homopolymer and CMB/DHBP polysulfone random copolymers

Polymers[1]	Modulus (MPa)	Yield Stress (MPa)	Strain at Yield (%)	Strain at Failure (%)
Radel® R	1353±92	62.3 ±6.0	7.0±1.0	8.1±1.3
DHBP PAES	1498±140	82.3±5.7	7.8±0.7	7.9±0.8
CMB100[2]	1157±31	64.8±3.5	8.2±0.9	14.3±6.0
CMB75DHBP25	1132±110	55.6±5.7	6.6±0.8	9.9±3.8
CMB50DHBP50	1130±302	58.8±4.8	10.4±3.4	18.2±4.0
CMB25DHBP75	1063±51	50.2±5.0	9.4±5.7	21.1±4.0

[1] All the DMA results were averaged over at least 5 samples.

[2] The numbers indicate molar ratio of the diphenol monomers.

The excellent solubility of the homopolymer and DHBP/CMB copolymer system allowed us to cast films from homogeneous 10 weight percent DMAc solution. Transparent tough films with no color or a light yellow color were obtained. Mechanical properties were obtained from dog bone samples made from the films. The film samples of Radel® R provided by Solvay Advanced Polymers L.L.C. and the DHBP based PAES with comparable high molecular weight were used as the mechanical property controls with the same solvent casting technique. As the tensile results show in **Table 3.2**, the CMB containing polymers exhibited slightly reduced moduli when compared to the controls, however, independent of the monomer ratios in the copolymer, all CMB containing polymers showed similar moduli values. Moderate strain at failure enhancements were observed for CMB homopolymer and CMB/DHBP copolymers. The largest strain at failure value about 20 % was observed in CMB25DHBP75 sample.

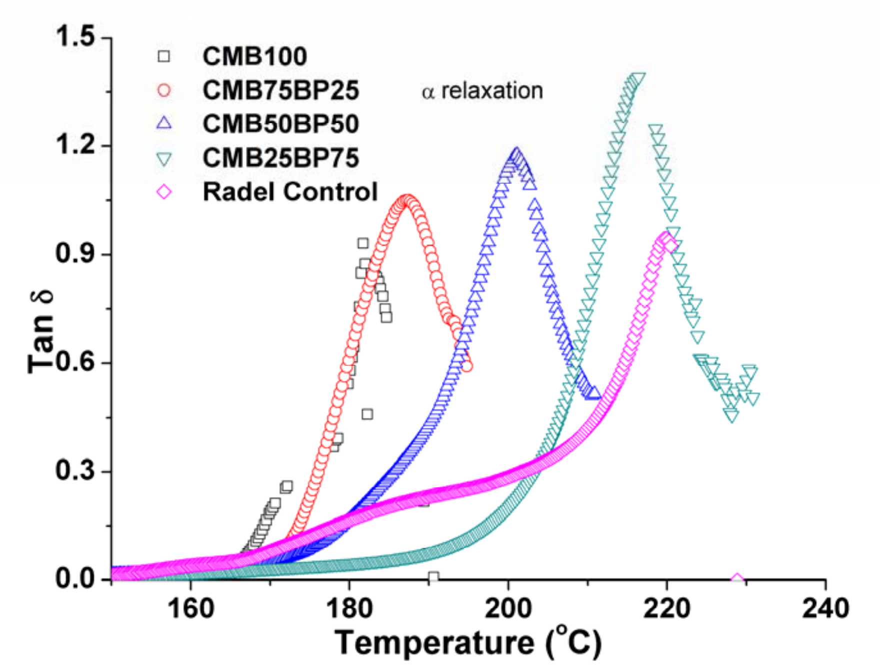


Figure 3.6 The dynamic mechanical analysis results of CMB/DHBP copolymers in high temperature region

Figure 3.6 and **Figure 3.7** show the dynamic mechanical analysis data of the tan δ curve from the same series of samples showing relaxations in the decreasing temperature sequence of α, β, γ peaks. The relaxations shown in high temperature region (**Figure 3.6**) are the α-relaxations which correspond to the relaxations at the glass transition. With increasing CMB content, a shift of the α-relaxation peak value to lower temperatures was observed. These results agree well with the glass transition values obtained from DSC measurements shown in **Table 3.1**. In the low temperature region, two series of relaxations, the β- and γ-relaxation were observed and are shown in **Figure 3.7**.

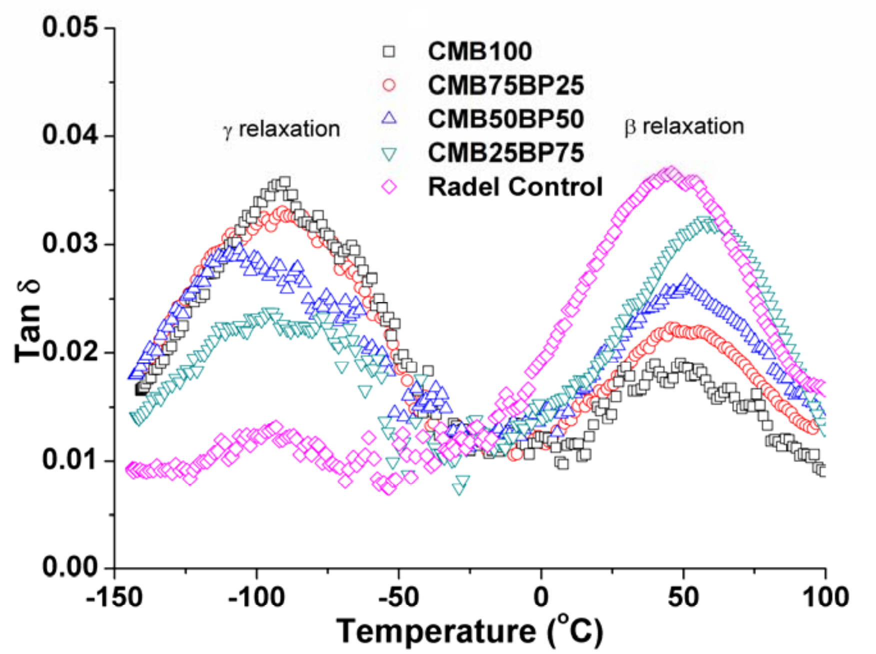


Figure 3.7 The dynamic mechanical analysis results CMB/DHBP copolymers in low temperature region

The γ-relaxation in DMA at 1 Hz has been widely reported in cyclohexylene ring containing polymers and non-cyclohexylene containing polysulfones. In a paper by McGrath and coworkers,[16] the dynamic mechanical behavior of non-cyclohexylene containing polysulfones was reviewed. The origin of the γ-relaxation was concluded to be combination motions of aryl ether bonds and sulfone-water complexes. In the work reported by Yee and coworkers,[6,8] Tomomi and coworkers,[17] and Credico and coworkers,[10] γ-relaxations have been observed in cyclohexylene ring containing polycarbonates, polyesters, and poly(1,4-cyclohexylene dimethylene phthalate)s reinforced epoxy resin in DMA studies. However the reported peak maximum values were all reported in the vicinity of -60 °C for these polymers. All the results listed above were reported for polymer samples containing *cis*-*trans*-mixed cyclohexylene rings. In relaxation studies on the all *trans*-conformation cyclohexylene ring incorporated poly(butylene 1,4-cyclohexanedicarboxylate) (PBCHD), enhanced γ-relaxations around -100 °C were observed which were attributed to the local motion of the methylene units enhanced by the less polar *trans*-enchained cyclohexylene units when compared to the *cis*-enchained units.[10]

As shown in **Figure 3.7**, with increasing CMB content, the intensity of the γ-relaxations at around -100 °C was observed to significantly increase. Similar γ-relaxations were also observed in a series of PAES based on *trans*-1,4-cyclohexylene ring containing acid chlorides which we recently reported.[13] Because of the amorphous nature of the polymers and the all *trans* conformation of the cyclohexylene units, the polymer relaxation behavior will not be affected by the difference in polymer backbone component polarity and polymer crystallinity which have been reported to play a significant role in γ-relaxations.[10,18] With the clear trend toward an increase in intensities of the γ-relaxation peak values with increasing *trans*-cyclohexylene content and the absence of the relaxation around -60 °C reported for cyclohexylene ring containing polyesters,[6,8,10,16] we assigned the γ-relaxation to the motion of *trans*-cyclohexylene ring units, probably chair boat conformational transitions, with cooperative motion of aryl ether bonds.

The β-relaxation was observed in the low temperature DMA Tan δ curve at around 50 °C (**Figure 3.7**). This has been reported in non-cyclohexylene containing polysulfones in the temperature range of 0 °C - 60 °C.[16] A decrease in intensity in β-relaxation with increasing *trans*-cyclohexylene content was observed CMB/DHBP copolymers shown in **Figure 3.7**. This result indicated that the β-relaxation is likely related to sulfone units or the aromatic units in the polymers and not the cyclohexylene group.

3.4.3 Homopolymer and Random Copolymers based on 4,4'-[*trans*-1,4-Cyclohexanebis(methylene)] Bisphenol (CMB) and 4,4’-Dihydroxyl-*p*-terphenyl (DHTP)

CMB/DHTP copolymers were prepared by a similar process as used for the CMB/DHBP copolymers. The compositions, molecular weights, thermal properties of CMB/DHTP polysulfone random copolymers are summarized in **Table 3.3**. The CMB50DHTP50 and CMB25DHTP75 polymer samples exhibited limited solubility in all

Table 3.3 Compositions, molecular weights, and thermal properties of DHTP/CMB polysulfone random copolymers

Polymer	CMB mol [2] (%)	DHTP mol [2] (%)	CMB mol [2] (%)	DHTP mol [2] (%)	T_g [3] (°C)	T_d [3] (°C)	Molar Mass[5] (kg/mol) M_n	M_w	PDI
CMB100[1]	100	0	100	0	172	466	28.9	64.2	2.2
CMB75DHTP25	75.0	25.0	74.8	25.2	186	472	35.1	68.5	1.9
CMB50DHTP50	50.0	50.0	-	-	207	490	NA[4]	NA	NA
CMB25DHTP75	25.0	75.0	-	-	222	510	NA	NA	NA

[1] The numbers indicate molar ratio of the diphenol monomers.

[2] The first two columns are the feed ratios of the monomers; the second two columns are the actual monomer ratios determined by ^{1}H NMR.

[3] The T_gs were determined in the 2nd heating cycle in DSC with a rate of 10 °C/min. The decomposition temperature is the 5 % weight loss temperature in nitrogen.

[4] The polymers with 50 and 75 molar percent of DHTP monomer are not soluble in SEC solvents.

[5] NMP as the SEC solvent with a refractive index detector and a viscometer

common organic solvents including chloroform, dichloromethane, DMAc, and NMP, etc even at 80 ^{o}C in contrast to the CMB/DHBP copolymers. Therefore molecular weight and monomer composition results were not obtained for these two samples. CMB75DHBT25 was soluble in DMAc and NMP.

Glass transition temperatures were observed to increase from 186 ^{o}C to 222 ^{o}C as the DHTP content increased. These results are expected due to the rigidity of the DHTP units and the trends are similar to our previous work on DHTP containing polysulfones.[14] The polymers all showed excellent thermal stability. The decomposition temperatures (defined as 5 % weight loss temperatures in nitrogen) were observed higher than 460 ^{o}C. Similar high thermal stability also has been reported in polymers with DHTP moiety.[19]

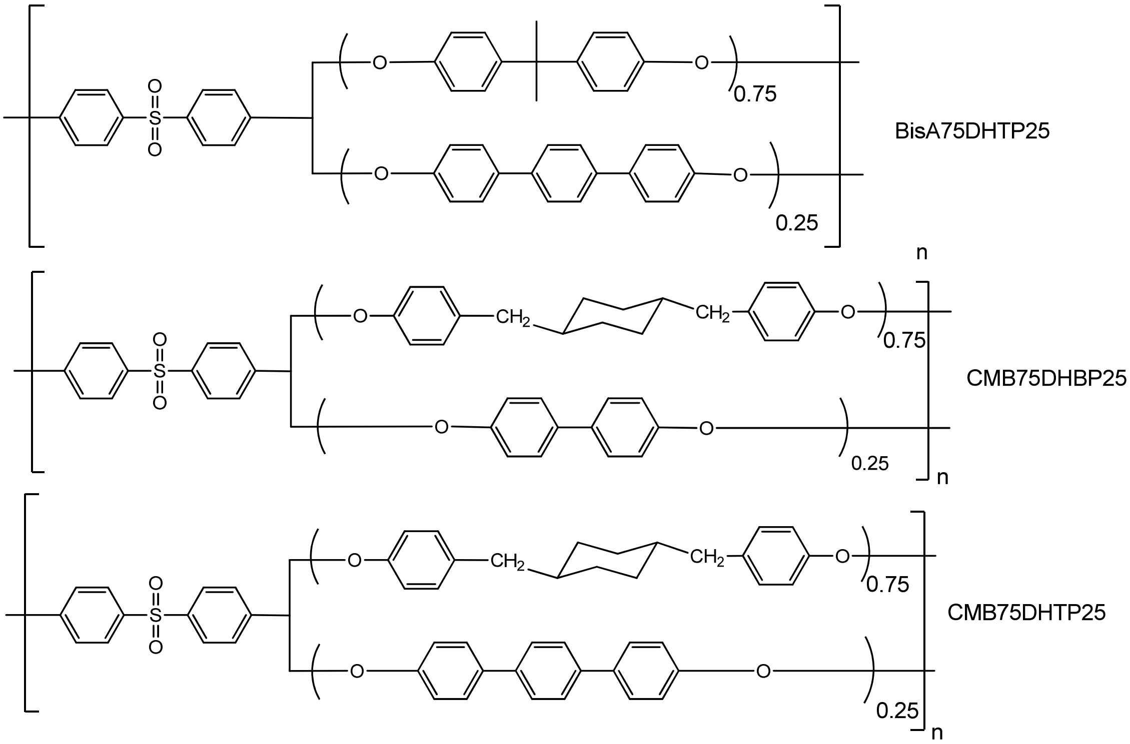


Figure 3.8 Structures of CMB or DHTP containing random copolymers

Table 3.4 Compositions, molecular weights, and thermal properties of CMB or DHTP containing polysulfone random copolymers

Polymer	CMB mol [2] (%)	Second monomer mol [2] (%)	CMB mol [2] (%)	Second monomer mol [2] (%)	T_g [3] (°C)	T_d [3] (°C)	Molar Mass[4] (kg/mol) M_n	M_w	PDI
BisA75DHTP25[1]	75.0	25.0	75.2	24.8	207	515	38.2	66.2	1.7
CMB75DHBP25	50.0	50.0	74.4	25.6	186	474	39.9	72.7	1.8
CMB75DHTP25	25.0	75.0	74.8	25.2	190	497	35.1	68.5	1.9

[1] The numbers indicate molar ratio of the diphenol monomers.

[2] The first two columns are the feed ratios of the monomers; the second two columns are the actual monomer ratios determined by ^{1}H NMR.

[3] The T_gs were determined in the 2nd heating cycle in DSC with a rate of 10 °C/min. The decomposition temperature is the 5 % weight loss temperature in nitrogen.

[4] NMP as the SEC solvent with a refractive index detector and a viscometer

The mechanical properties of CMB75DHTP25 were compared with its structural analogues as shown in **Figure 3.8**. The compositions, molecular weights, and thermal properties of these random polymers were summarized in **Table 3.4**. The actual monomer compositions determined by ^{1}H NMR spectrometry exhibited excellent agreement with the monomer feed ratios. The glass transition temperatures were all observed in the vicinity of 190 ^{o}C. They showed excellent thermal stability with decomposition temperatures higher than 470 ^{o}C and molecular weight higher than 35 kg/mol M_n with reasonable polycondensation PIDs. The high molecular weight ensured that the mechanical properties were not dependent on molecular weight.

Table 3.5 Mechanical properties of CMB or DHTP containing polysulfone random copolymers

Polymers[1]	Modulus (MPa)	Yield Stress (MPa)	Strain at Yield (%)	Strain at Failure (%)
BisA75DHTP25[2]	972±161	40.8±9.0	5.8±0.7	6.4±1.5
CMB75DHBP25	1132±110	55.6±5.7	6.6±0.8	9.9±3.8
CMB75DHTP25	1055±67	52.4±4.2	7.2±0.5	118±19

[1] All the DMA results were averaged over at least 5 samples. The original tensile curves are shown in **Figure 3.30**, **Figure 3.31**, and **Figure 3.32** in the **appendix**.

[2] The numbers indicate molar ratio of the diphenol monomers.

The polymers shown in **Figure 3.8** shared structural similarity exhibiting similar glass transition temperatures and comparable high molecular weights. However mechanically, they showed significantly different behaviors which are shown in **Table 3.5**. When DHTP was copolymerized with bisphenol-A (bis-A), the polymer exhibited brittle behavior where the polymer failed immediately after yield point. When CMB was copolymerized with DHBP, slight improvement was observed over the BisA/DHTP polymer. A tenfold strain at failure enhancement over the previous stated copolymers was observed in CMB/DHTP copolymer. The moduli results of the materials shown in **Table 3.5** indicate that the elongation enhancement was not obtained due to the loss of stiffness. The structural basis of this enhanced elongation is not clearly understood.

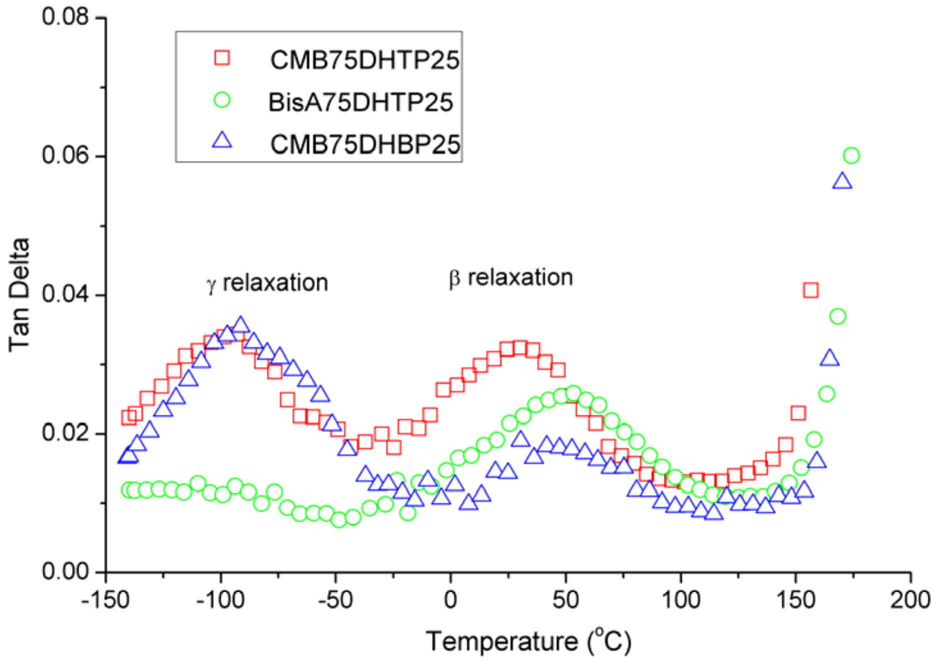


Figure 3.9 The dynamic mechanical analysis results of BisA75DHTP25 (circles) copolymer, CMB75DHBP25 copolymer (triangles), and CMB75DHTP25 (squares)

Our preliminary DMA results (**Figure 3.9**) show that the three copolymers have different relaxation behaviors. The CMB containing copolymers (CMB75DHTP25 (squares) and CMB75DHBP25 copolymer (triangles)) exhibited strong γ-relaxation due to the incorporation of the cyclohexylene units. In contrast, only β-relaxation which relates with aromatic sulfone units was observed in the BisA75DHTP25 polymer (circles). The γ-relaxation was absent due to the absence of the cyclohexylene ring. These results are consistent with the relaxation results from the CMB/DHBP copolymer systems described earlier. The CMB75DHTP25 copolymer (squares) exhibited a strong intensity in both β-relaxation and γ-relaxation which is possibly contributive to the elongation enhancement. In the cases of BisA75DHTP25 copolymer (circles) and CMB75DHBP25 copolymer (triangles), significantly lowered intensities in γ-relaxation and β-relaxation were observed respectively.

3.5 Conclusions

In this paper, we prepared 1,4-*trans*-cyclohexylene ring containing poly(arylene ether sulfone)s based on a new CMB bisphenol monomer with 4,4'-*trans*-1,4-cyclohexanebis(methylene) unit. The monomer and the polymers were carefully characterized. The mechanical properties and relaxation characteristics were studied. In the CMB/DHBP copolymers, multiple relaxations and moderate strain at failure improvement with reduced modulus were observed. The γ-relaxation was assigned to the combination motion of the cyclohexylene ring and the aryl ether bond. A large elongation to break enhancement, which may be a result of the strong sub-T_g relaxations, was observed in CMB75DHTP25 samples.

3.6 Acknowledgements

This research was sponsored by the Army Research Laboratory and was accomplished under Cooperative Agreement Number W911NF-06-2-0014. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing official policies, either expressed or implied, of the Army Research Laboratory or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation hereon. We acknowledge the assistance of the Department of Chemistry and the Macromolecules & Interfaces Institute at Virginia Tech. We are grateful to Solvay Advanced Polymers L.L.C. and Eastman Chemical Company for supplying chemicals. We appreciate the assistance of Professor Long's, Professor Riffle's, and Professor McGrath's groups at Virginia Tech.

3.7 Supplementary Materials

3.7.1 Polymerization Reaction Setup

The polymerizations described in section **3.3.4** were performed in the apparatus as shown in **Figure 3.10**. The polymerization reactions were protected by inert argon gas under vigorous mechanical stir. On the left of the Figure, the Dean-Stark trap connected with the condenser was used to achieve the azeotropic distillation to dehydrate the system.

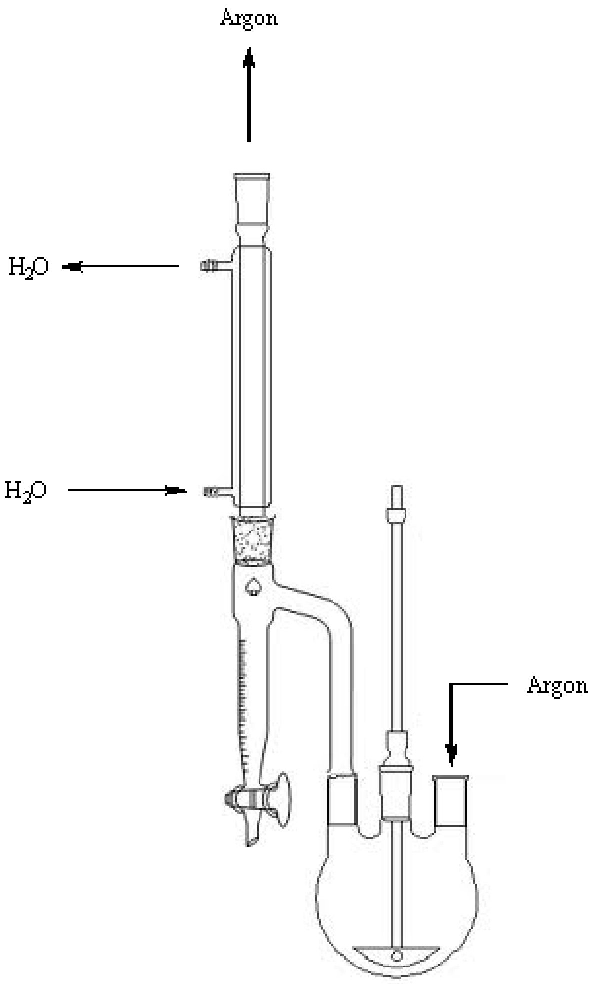


Figure 3.10 The reaction apparatus set up of PAES synthesis

3.7.2 Polymer Film Samples

As discussed in **3.3.4.3**, polymer film samples were prepared by solvent casting method. A typical CMB based PAES film sample by solvent casting is shown in **Figure**

3.11. In the picture, a piece of polymer film was held by a pair of tweezers. The film was covering a piece of paper with the name and logos of Virginia Tech and MII. As shown, the polymers offered transparent tough films with no color or light yellow color. The film thickness is typically in the range of 60-100 μm. The dog bone samples were prepared from these films with a dog bone mold. The dimensions of the dog bone samples are shown in **Figure 3.12**. The middle part of the dog bone sample with the same width was used for the tensile test.

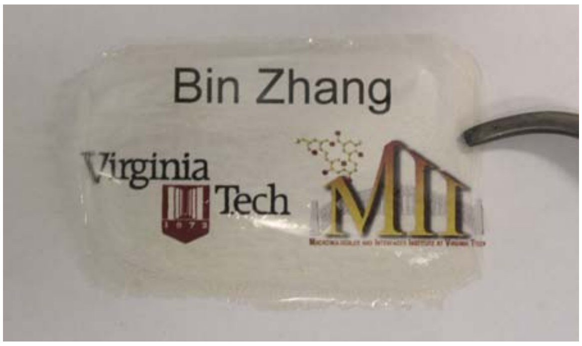


Figure 3.11 Picture of a typical CMB based PAES film sample by solvent casting

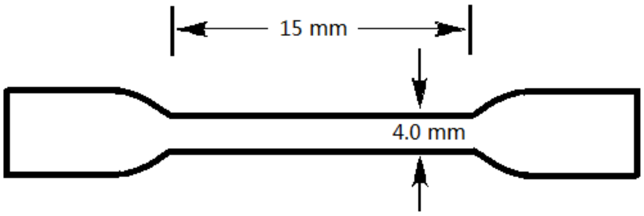


Figure 3.12 Dimension parameters of the dog bone sample

3.7.3 Biphenol Monomer with Ether Linkage

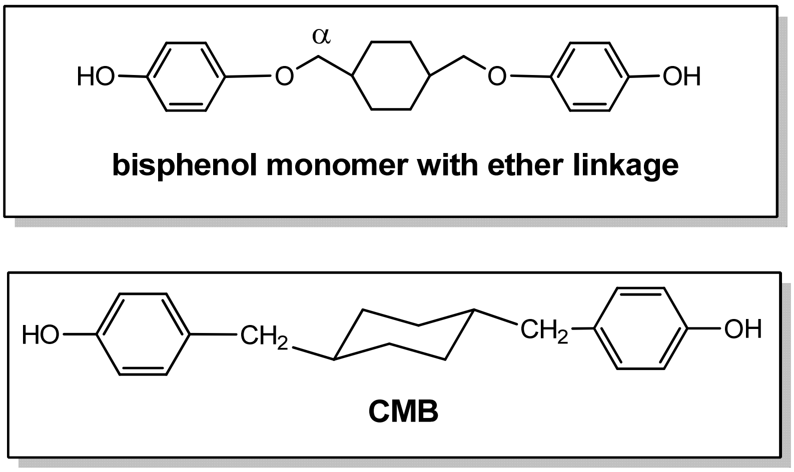
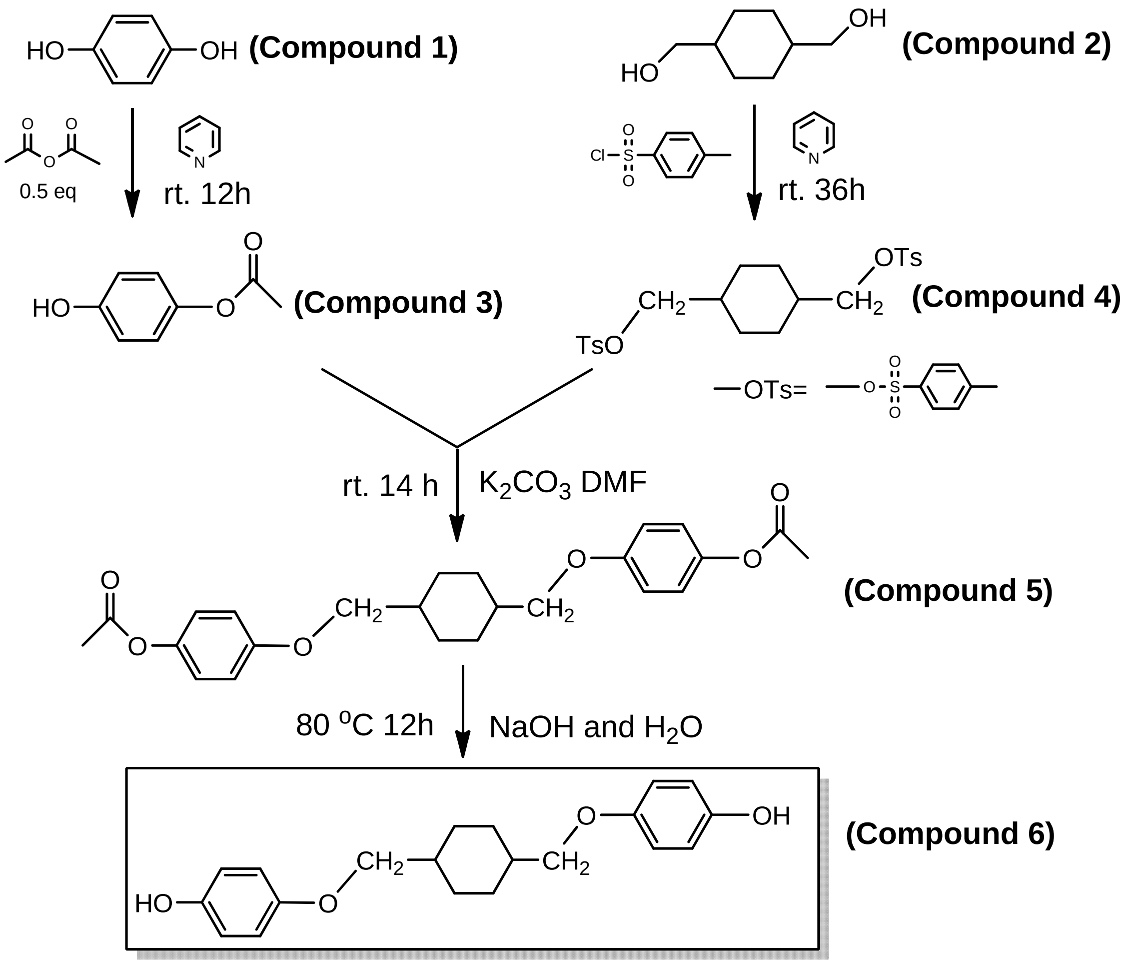


Figure 3.13 Structures of the target bisphenol monomer with ether linkage and the CMB monomer

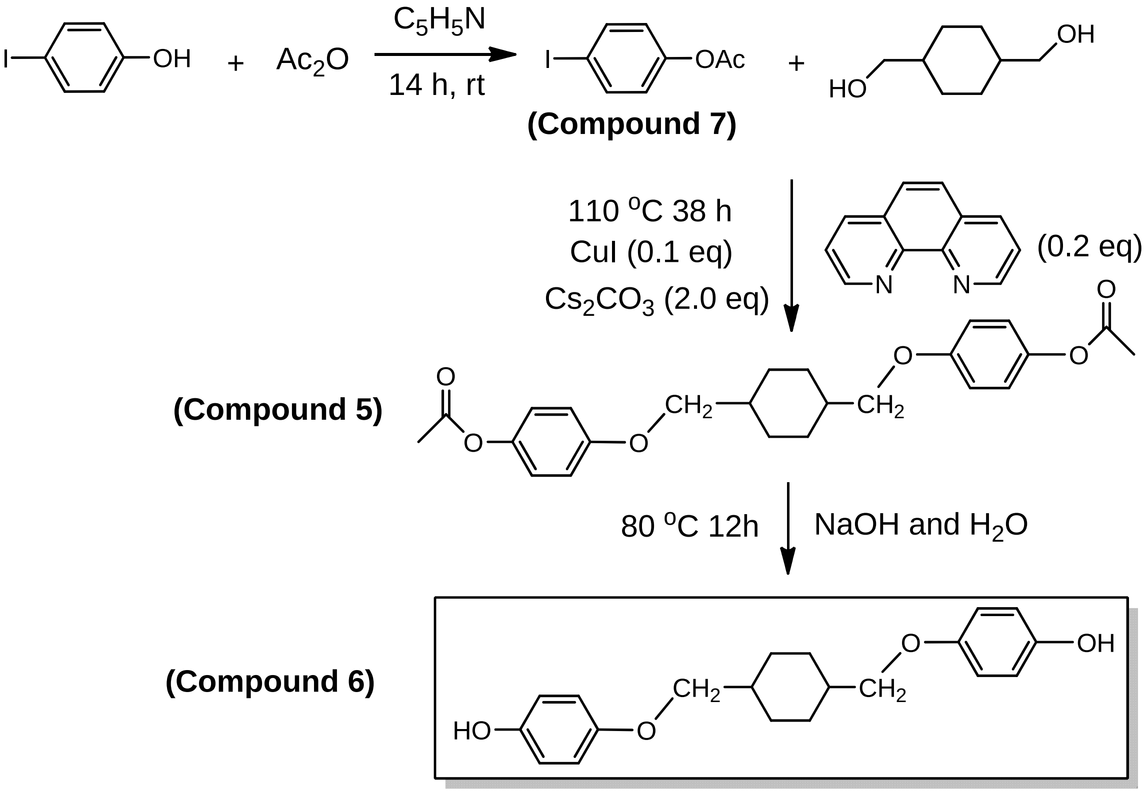
The initial target *trans*-1,4-cyclohexylene ring containing biphenol monomer was designed with the structure shown on the top of **Figure 3.13**. Comparing with the structure with the CMB monomer used in this chapter, instead of the methylene groups in CMB, it has an ether bond connected to a CH_2 group on the α position. This ether linkage containing structure resulted in a major side reaction in the final synthesis step and probably in the polymerization. The details will be discussed in this section.



Scheme 3.3 The first reaction scheme of the bisphenol monomer with ether linkage[20-23]

The total synthesis plan of this target monomer is shown in **Scheme 3.3**.[20-23] The NMR spectra of the successfully isolated compounds are provided in the Appendix**.** The reactions started with hydroquinone (HQ) and CHDM with *cis/trans* ratio of 30/70 (Compound 1 and 2 shown **Scheme 3.3** respectively). These compounds are commercially available starting materials. Compound 3 was obtained by reacting hydroquinone with 0.5 molar equivalent of acetic anhydride in the present of pyridine as the solvent at room temperature for 12 h. Compound 3 was isolated as a white crystal by column chromatography with hexane:ethyl acetate = 4:1 as the developing solution. The ^{1}H NMR and ^{13}C NMR are shown in **Figure 3.22** and **Figure 3.23** in the appendix. Compound 4 was obtained by reacting CHDM with 4-methylbenzene sulfonyl chloride in excess with pyridine as the solvent at room temperature for 36 h. After the reaction, the reaction solution was dissolved in 60 mL of water and extracted with 30 mL of Et_2O. The final product was obtained as white solid by Et_2O recrystallization of the crude product obtained by the extraction. The ^{1}H NMR and ^{13}C NMR are shown in **Figure 3.24** and **Figure 3.25** in the appendix. Compound 5 is the product of the reaction of compound 3 and 4. Compound 3 was used in excess to ensure the full substitution of the tosylate groups (OTs). Since the tosylate is a very good leaving group, the reaction was able to be performed at room temperature in DMF solvent with potassium carbonate as the base. The product was purified by dissolving the reaction solution in 60 mL water and extracted with hexane followed by column chromatography. The ^{1}H NMR and ^{13}C NMR of compound 5 are shown in **Figure 3.26** and **Figure 3.27** in the appendix.

As shown in **Scheme 3.4**,[24,25] a second reaction route was also used to synthesize the same compound 5 in **Scheme 3.3**. 4-iodophenyl acetate was obtained by reaction starting with 4-iodophenol and excess acetic anhydride which are commercially available. With pyridine as the solvent the reaction was allowed to be stirred at room temperature for 14 h. After the reaction the solvent was removed on a rotary evaporator. The remaining solid was dissolved in cyclohexane and the solution was thoroughly washed with Na_2CO_3 and NaCl aqueous solution in order to purify the product. The organic layers were isolation and dried with Na_2SO_4 anhydrous. The final product, a beige color crystal, was obtained by complete removing the cyclohexane (^{1}H NMR is shown in **Figure 3.28**). Compound 5 was obtained by reacting 4-iodophenyl acetate with CHDM. 2 equivalent of cesium carbonate was used as the base. 0.2 equivalent of 1,10-phenanthroline and 0.1 equivalent of copper iodide were used as catalysts. The mixture was reacted at 110 ^{o}C for 38 h under the protection of argon. After the reaction, the product was isolated by column chromatography using developing solution of hexane:ethyl acetate =20:1 then 10:1 and the subsequent removing of the solvent (^{1}H NMR is shown in **Figure 3.29**).



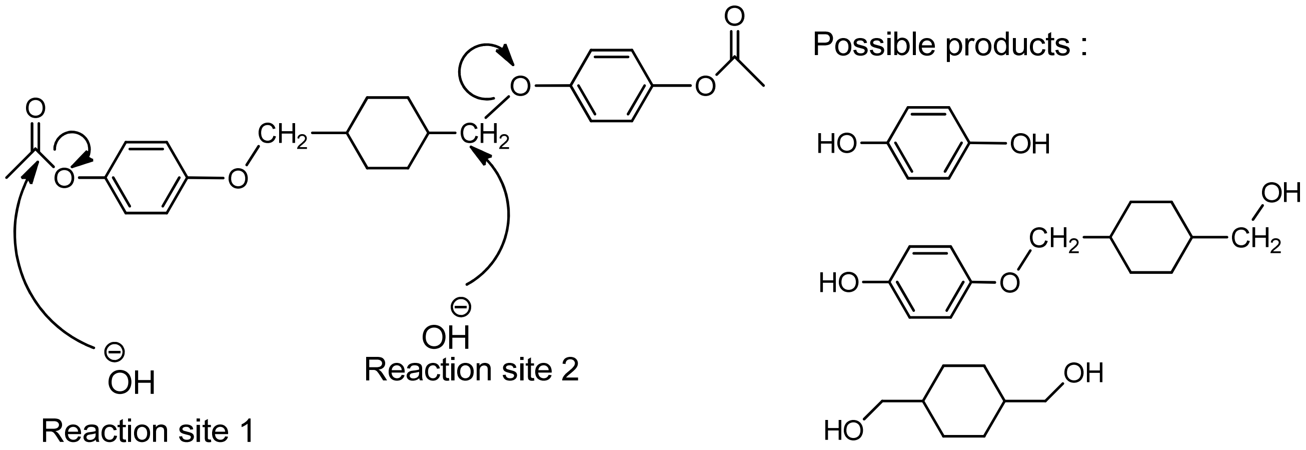
(Compound 7)

(Compound 5)

(Compound 6)

Scheme 3.4 The second reaction scheme of the bisphenol monomer with ether linkage[24,25]

The hydrolysis reaction of the acetate groups is the last step for both **Scheme 3.3** and **Scheme 3.4**. However, the formation of the compound 6 was problematic due to the ether linkage in the monomer. The common reaction condition to remove acetate protection group was to use sodium hydroxide aqueous solution at a temperature about 80 ^{o}C. The reaction performed at these conditions ended up with a mixture of many compounds due to a second reaction site shown in **Scheme 3.5**. In the present of the strong base, the hydroxyl group can attack the methylene group at the α position (shown as reaction site 2). This side reaction resulted in multiple possible products as listed on the right of **Scheme 3.5**. A similar reaction will also happen in the polymerization at the conditions shown in **3.3.4**.



Scheme 3.5 The reaction scheme of the side reaction due to ether linkage and possible products

3.7.4 Tensile Test of CMB/DHBP Copolymers in Controlled Environment

As discussed in **3.4.2**, in the CMB/DHBP copolymer series, multiple relaxations were observed below room temperature. A moderate ultimate elongation enhancement was also achieved at room temperature. An extension tensile study of the mechanical properties of this polymer series was performed at a temperature below room temperature aiming at understanding the influence of the sub room temperature relaxation on the mechanical properties.

In this study, the dog bone samples were used with the geometry as shown in **Figure 3.12**. The Instron instrument used was equipped with a customized chamber where temperature and moisture can be controlled by using liquid nitrogen and purging gas. The temperature for this test was set at -25 ^{o}C. This temperature was selected to be complimentary with the tensile test performed at room temperature. As shown in **Figure 3.7**, the β-relaxation was observed to start at a temperature in the vicinity of -25 ^{o}C. Tensile test results obtained at this temperature will only reflect the presence of the γ-relaxations. A typical test procedure can be described as follow. The dog bone samples were mounted on the Instron machine in the controlled chamber. Then the temperature was cooled to -25 ^{o}C and kept at this temperature for 5 min. The tensile test was performed with the experimental parameters as listed in **3.3.2**.

The tensile test results of the same series of polymer at different temperatures are shown in **Table 3.6**. No significant difference in toughness was observed based on the tensile date. Across the table, both the modulus and the strain at failure results were observed statistically the same at the two different temperatures. Based on these results, the tensile behavior of the CMB/DHBP copolymers were independent of the β-

relaxations. However, more designed experiments need to be performed to make this study conclusive. Some discussion will be provided in the future work section. I would like to acknowledge Dr. David Dillard's group in Engineering Science and Mechanics department at Virginia Tech for their help and allowing me to use their instrument.

Table 3.6 The tensile results at room temperature and -25 °C

Polymer[1]	Room Temperature		-25 °C	
	Modulus (MPa)	Strain at Failure (%)	Modulus (MPa)	Strain at Failure (%)
CMB100[2]	1157±31	14.3±6.0	1135±318	10.0±1.5
CMB75DHBP25	1034±98	6.9±1.9	1063±117	5.8±0.7
CMB50DHBP50	992±66	9.8±5.5	1129±302	18.2±4.1
CMB25DHBP75	1063±51	21.1±4.0	1336±233	12.4±3.6

[1] All the DMA results were averaged over at least 5 samples.

[2] The numbers indicate molar ratio of the diphenol monomers.

3.8 Future Work

3.8.1 Tensile Test of CMB/DHBP Copolymers in Controlled Environment

The preliminary results in **3.7.4** showed that the tensile properties of the CMB/DHBP polymers were independent of the β-relaxations. It will be very interesting to study the tensile properties of the CMB/DHBP copolymer series at 50 °C and -100 °C. These temperatures are the peak maximum temperatures of the β-relaxations and γ-relaxations respectively. These data will definitely help to have a better understanding of the low temperature relaxation influence on the mechanical properties.

3.8.2 The *trans*-1,4-Cyclohexylene Ring Containing Monomer with Ether Linkage

In **3.7.3**, a study on the *trans*-1,4-cyclohexylene ring containing monomer with ether linkage was described with a major side reaction. As shown in **Scheme 3.5**, the reaction conditions could be optimized to effect a selective deprotection of the acetate groups. With the side reaction at the ether linkage in the polymerization, the polymer product will not have a well defined structure, however, the *trans*-1,4-cyclohexylene units will be incorporation into the PAES backbone.

3.8.3 New *trans*-1,4-Cyclohexylene Ring Containing Monomer

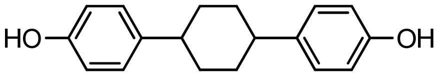


Figure 3.14 The structure of a new *trans*-1,4-cyclohexylene ring containing monomer

It always has been a research focus to develop new monomers with *trans*-1,4-cyclohexylene units. A bisphenol monomer with a structure very similar to the CMB monomer has appeared several times in the literature.[26-28] The structure is shown in **Figure 3.14**. It will be really interesting to study the use of this *trans*-1,4-cyclohexylene monomer to prepare PAES homopolymer and copolymers. Because of the structural similarity, the comparison of the thermal properties, mechanical properties, and relaxation behavior between these polymers and the CMB based polymers would be very interesting too.

3.9 Appendix

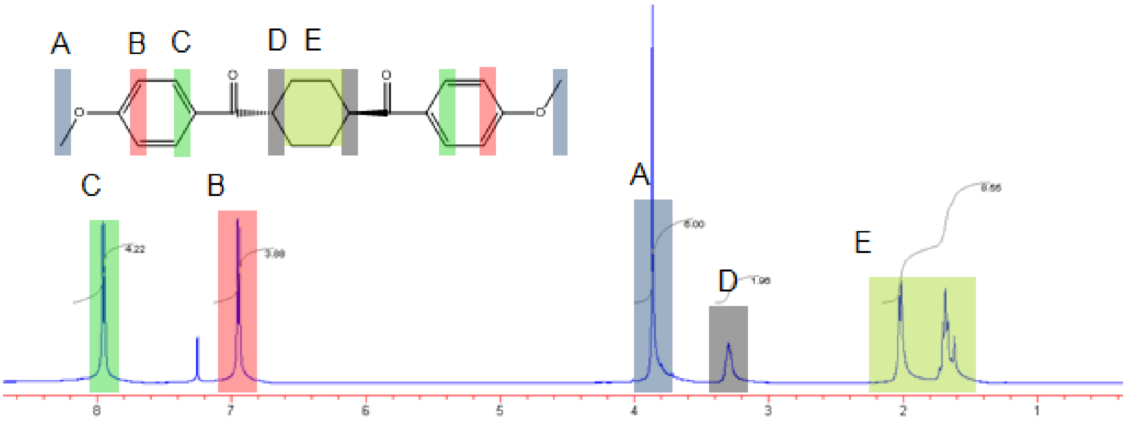


Figure 3.15 The ^1H NMR of *trans*-1,4-cyclohexanebis[(4-hydroxyphenyl) methanone (compound 3 in **Scheme 3.1**)

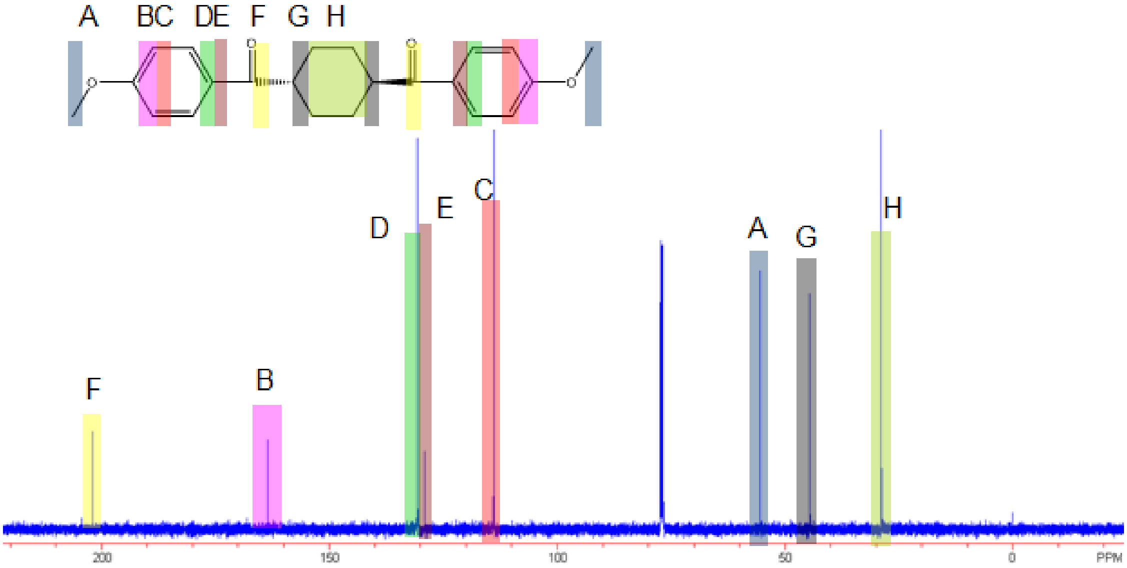


Figure 3.16 The ^{13}C NMR of *trans*-1,4-cyclohexanebis[(4-hydroxyphenyl) methanone (compound 3 in **Scheme 3.1**)

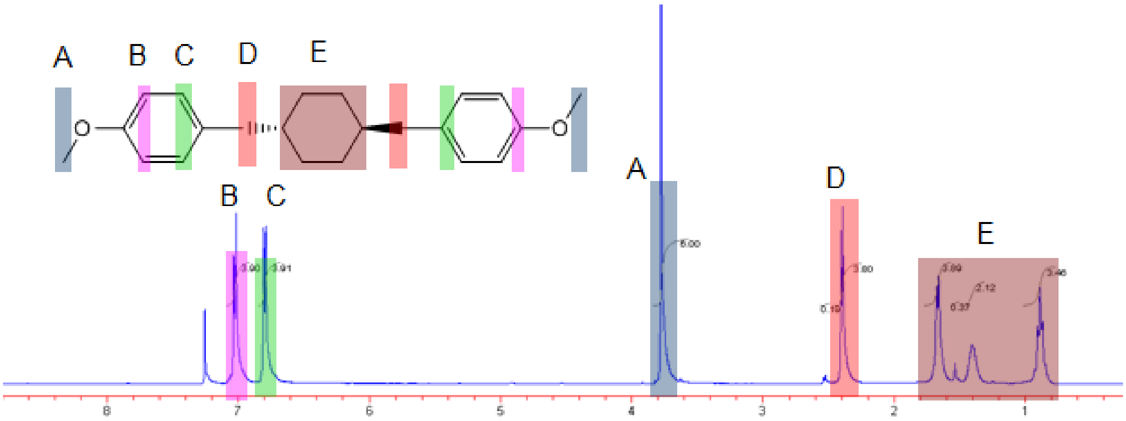


Figure 3.17 The ^{1}H NMR of *trans*-1,4-bis(4-methoxybenzyl)cyclohexane (compound 4 in **Scheme 3.1**)

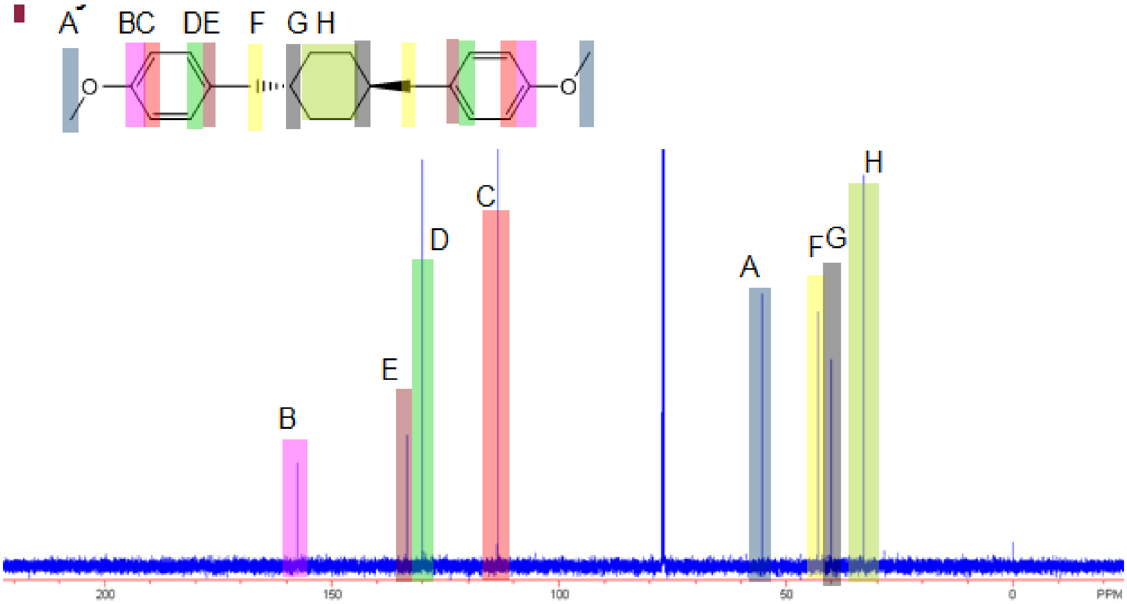


Figure 3.18 The ^{13}C NMR of *trans*-1,4-bis(4-methoxybenzyl)cyclohexane (compound 4 in **Scheme 3.1**)

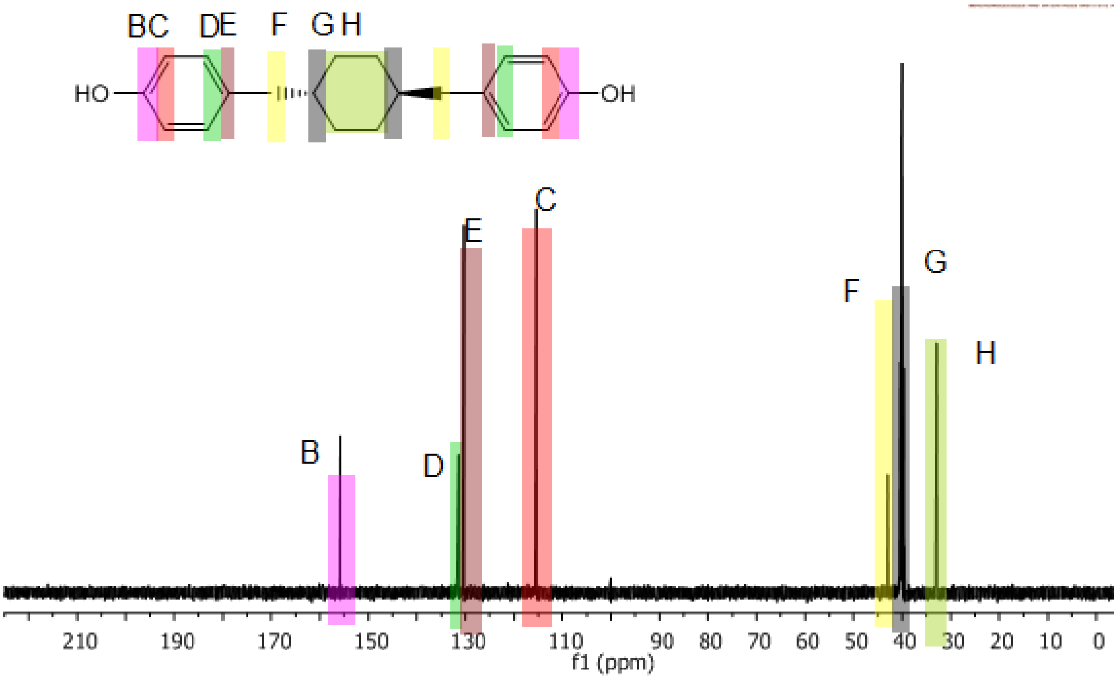


Figure 3.19 The ^{13}C NMR of 4,4'-[*trans*-1,4-Cyclohexanebis(methylene)] Bisphenol (CMB compound 5 in **Scheme 3.1**)

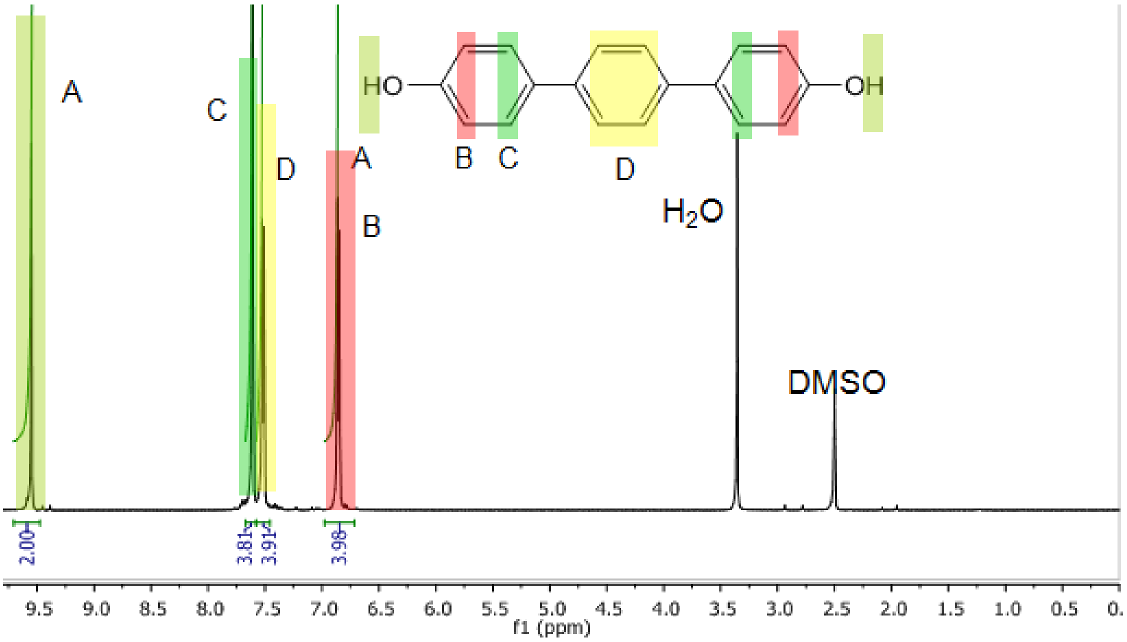


Figure 3.20 The ^{1}H NMR of 4,4'-dihydroxyl-*p*-terphenyl (DHTP in **3.3.3.5**)

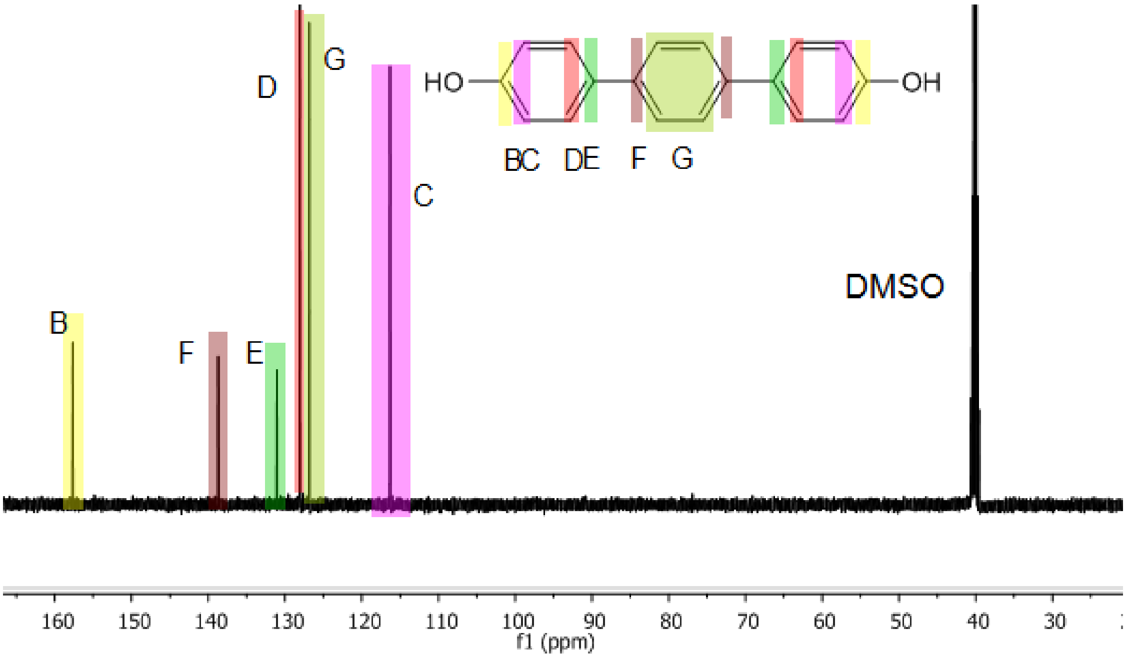


Figure 3.21 The ^{13}C NMR of 4,4'-dihydroxyl-*p*-terphenyl (DHTP in **3.3.3.5**)

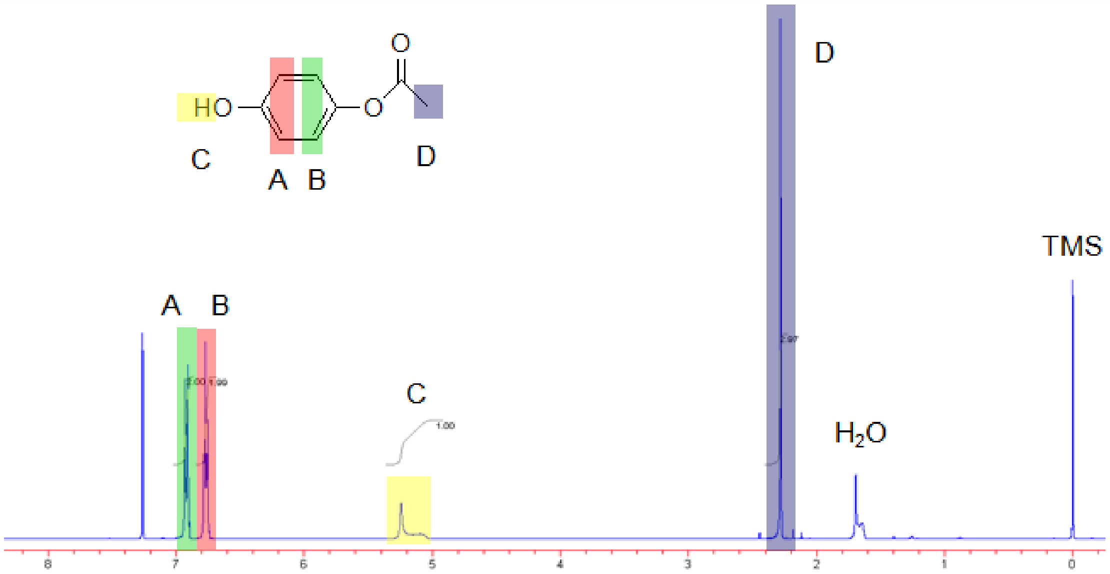


Figure 3.22 The ^{1}H NMR of 4-hydroxyphenyl acetate (compound 3 in **Scheme 3.3**)

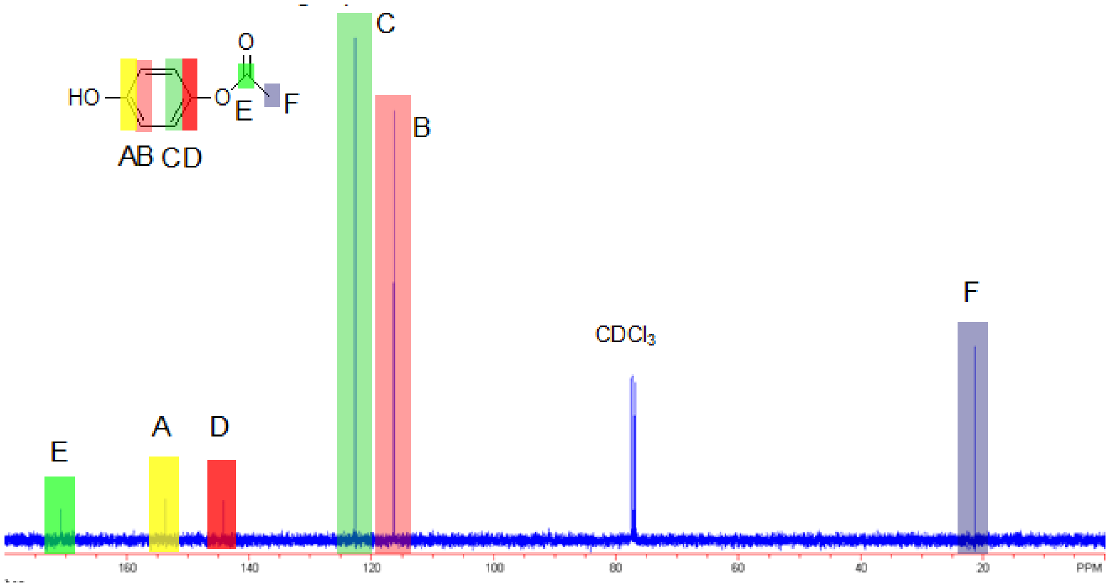


Figure 3.23 The ^{13}C NMR of 4-hydroxyphenyl acetate (compound 3 in **Scheme 3.3**)

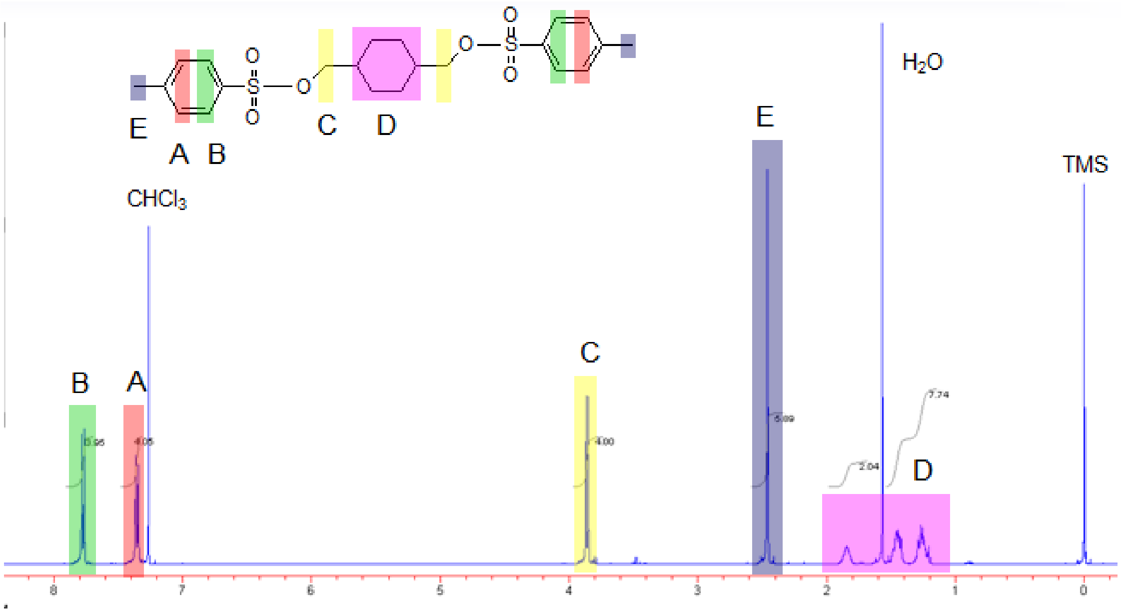


Figure 3.24 The ^{1}H NMR of cyclohexane-1,4-bis(methylene) bis(4-methylbenzenesulfonate) (compound 4 in **Scheme 3.3**)

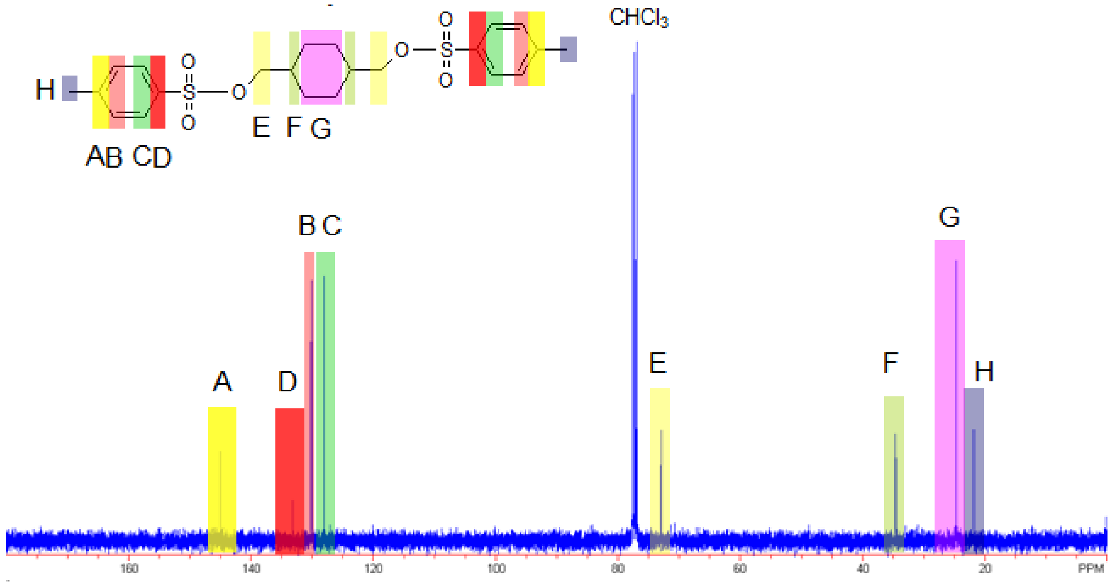


Figure 3.25 The ^{13}C NMR of cyclohexane-1,4-bis(methylene) bis(4-methylbenzenesulfonate) (compound 4 in **Scheme 3.3**)

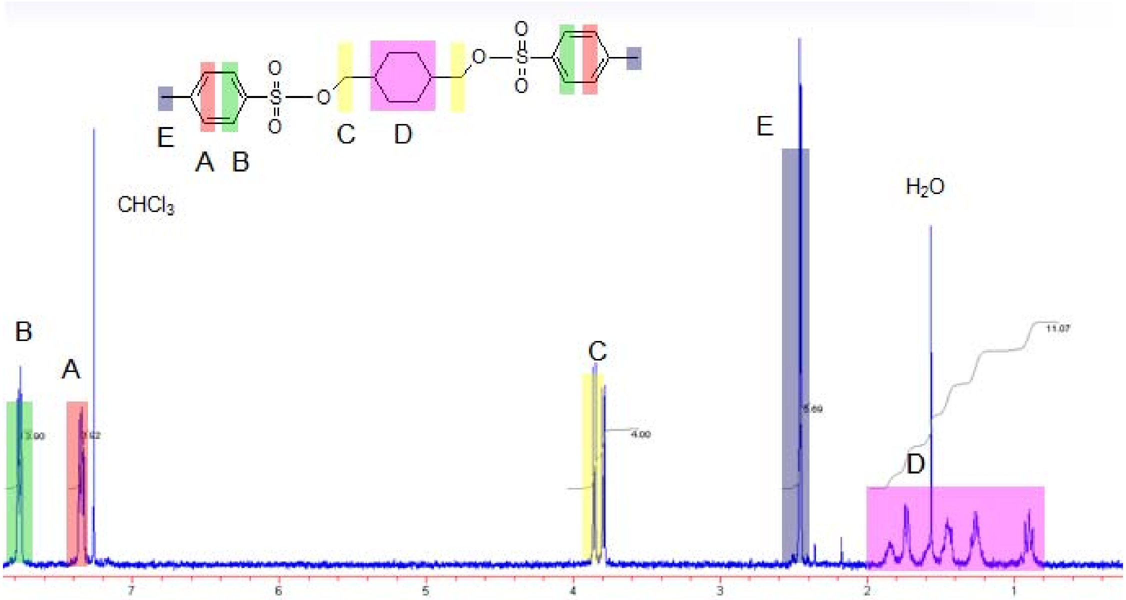


Figure 3.26 The ^{1}H NMR of ((cyclohexane-1,4-bis(methylene))bis(oxy))bis(4,1-phenylene) diacetate (compound 5 in **Scheme 3.3**)

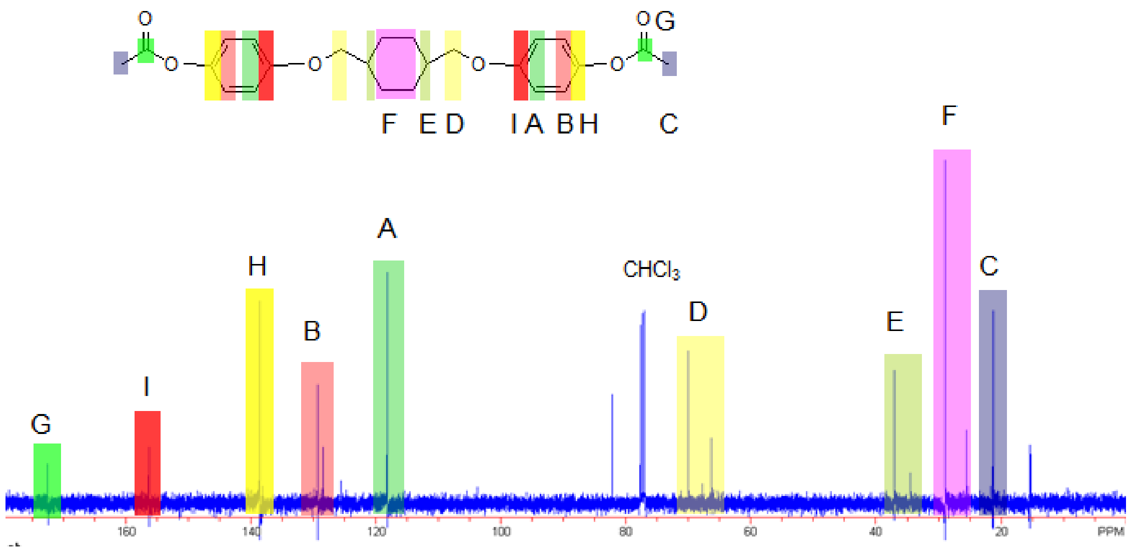


Figure 3.27 The ^{13}C NMR of ((cyclohexane-1,4-bis(methylene))bis(oxy))bis(4,1-phenylene) diacetate (compound 5 in **Scheme 3.3**)

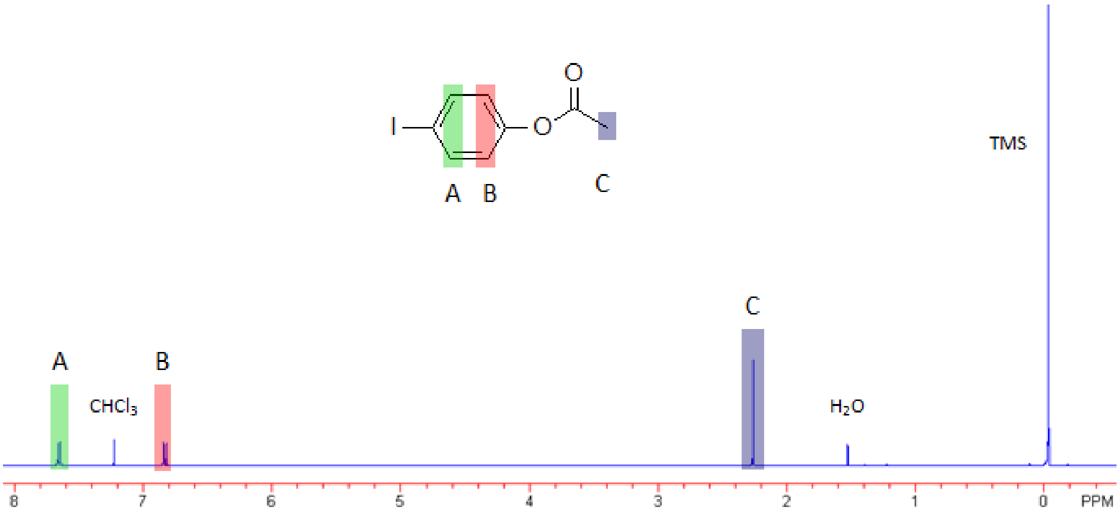


Figure 3.28 The ^{1}H NMR of 4-iodophenyl acetate (**Scheme 3.4**)

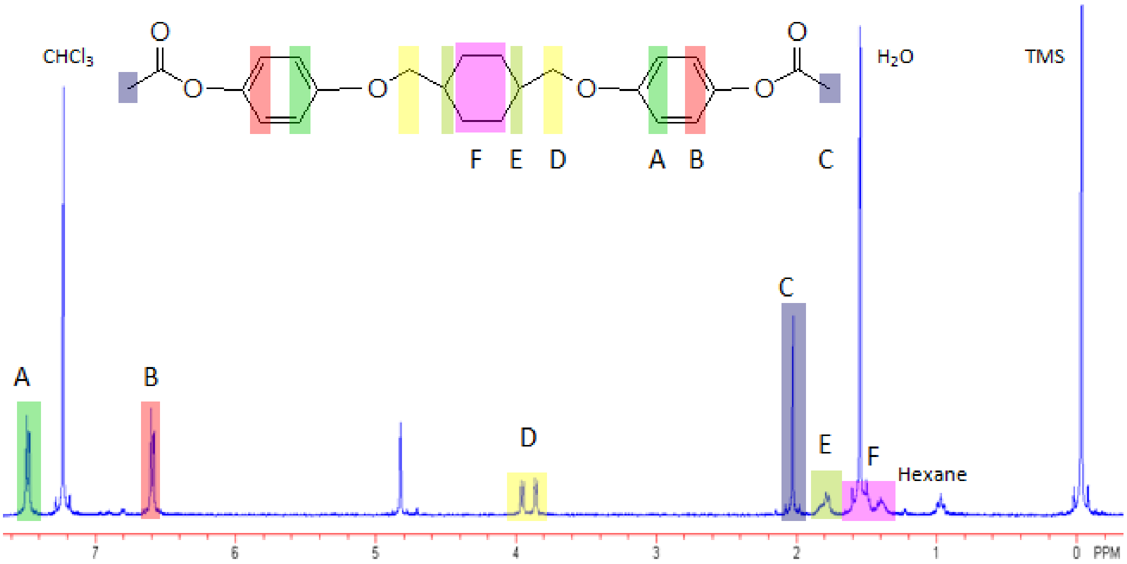


Figure 3.29 The ^{1}H NMR of ((cyclohexane-1,4-bis(methylene))bis(oxy))bis(4,1-phenylene) diacetate (compound 5 in **Scheme 3.4**)

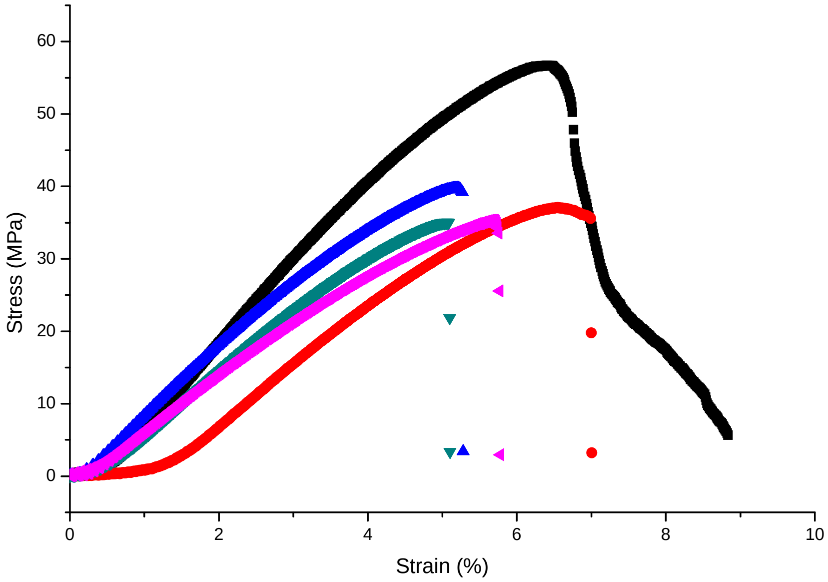


Figure 3.30 The tensile test curves for the BisA75DHTP25 polymer with mechanical data shown in **Table 3.5**

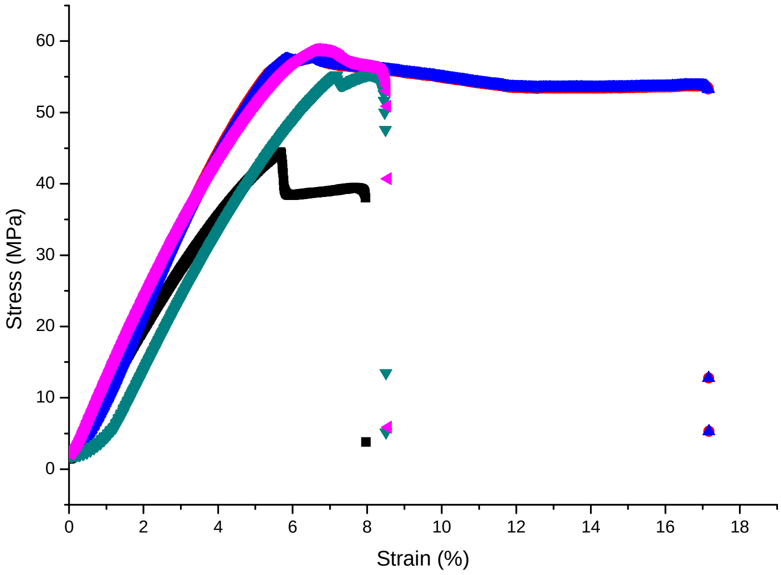


Figure 3.31 The tensile test curves for the CMB75DHBP25 polymer with mechanical data shown in **Table 3.5**

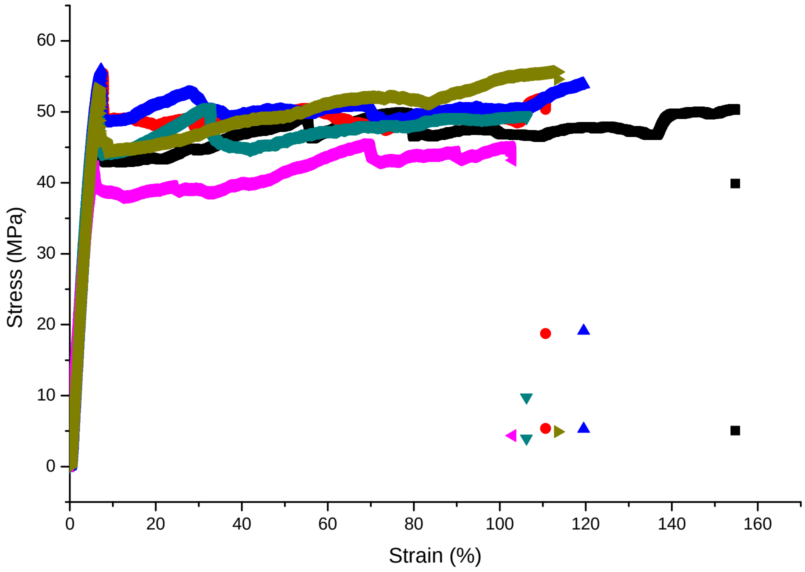


Figure 3.32 The tensile test curves for the CMB75DHTP25 polymer with mechanical data shown in **Table 3.5**

3.10 References

(1) Robeson, L. M.; Farnham, A. G.; McGrath, J. E. *Appl. Polym. Symp.* **1975**, *26*, 373.

(2) Rose, J. B. *Polymer* **1974**, *15*, 456.

(3) Rao, Y. Q.; Greener, J.; Avila-Orta, C. A.; Hsiao, B. S.; Blanton, T. N. *Polymer* **2008**, *49*, 2507.

(4) Osano, K.; Das, S.; Turner, S. R. *Polymer* **2009**, *50*, 1144.

(5) Li, X.; Yee, A. F. *Macromolecules* **2003**, *36*, 9421.

(6) Li, X.; Yee, A. F. *Macromolecules* **2003**, *36*, 9411.

(7) Li, X.; Yee, A. F. *Macromolecules* **2004**, *37*, 7231.

(8) Liu, J.; Yee, A. F. *Macromolecules* **1998**, *31*, 7865.

(9) Liu, J.; Yee, A. F. *Macromolecules* **2000**, *33*, 1338.

(10) Berti, C.; Celli, A.; Marchese, P.; Marianucci, E.; Barbiroli, G.; Di Credico, F. *Macromol. Chem. Phys.* **2008**, *209*, 1333.

(11) Berti, C.; Celli, A.; Marchese, P.; Marianucci, E.; Sullalti, S.; Barbiroli, G. *Macromol. Chem. Phys.* **2010**, *211*, 1559.

(12) Scheirs, J.; Long, T. E. *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters* 1ed.; Wiley, 2003.

(13) Zhang, B.; Turner, S. R. *J. Polym. Sci., Part A: Polym. Chem.,* **2011**, *49*, 4316

(14) Mao, M.; Das, S.; Turner, S. R. *Polymer* **2007**, *48*, 6241.

(15) Huang, M. *J. Am. Chem. Soc.* **1946**, *68*, 2487.

(16) Robeson, L. M.; Farnham, A. G.; McGrath, J. E. *Midl. Macromol. Monogr.* **1978**, *4*, 405.

(17) Lijima, T.; Ohnishi, K.; Fukuda, W.; Tomoi, M. *Polym. Int.* **1998**, *45*, 403.

(18) McCrum, M. G.; Read, B.; Williams, G. *Anelastic and Dielectric Effects in Polymeric Solid*; Wiley: London, 1967.

(19) Salunke, A. K.; Madhra, M. K.; Sharma, M.; Banerjee, S. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 55.

(20) Barton, D. H. R.; Boivin, J.; Gastiger, M.; Morzycki, J.; Hay-Motherwell, R. S.; Motherwell, W. B.; Ozbalik, N.; Schwartzentruber, K. M. *J. Chem. Soc., Perkin Trans. 1* **1986**, 947.

(21) Gajewski, J. J.; Jimenez, J. L. *J. Am. Chem. Soc.* **1986**, *108*, 468.

(22) Hansen, M. M.; Bertsch, C. F.; Harkness, A. R.; Huff, B. E.; Hutchison, D. R.; Khau, V. V.; LeTourneau, M. E.; Martinelli, M. J.; Misner, J. W.; Peterson, B. C.; Rieck, J. A.; Sullivan, K. A.; Wright, I. G. *Journal of Organic Chemistry* **1998**, *63*, 775.

(23) Thomas, H.; Spaniol, T. P.; Okuda, J. *Angew. Chem., Int. Ed.* **2006**, *45*, 7818.

(24) Adamski-Werner, S. L.; Palaninathan, S. K.; Sacchettini, J. C.; Kelly, J. W. *Journal of Medicinal Chemistry* **2004**, *47*, 355.

(25) Naidu, A. B.; Sekar, G. *Tetrahedron Lett.* **2008**, *49*, 3147.

(26) Kimura, K.; Yamashita, Y.; Okumura, Y.; Ito, S. Application: EP 2001-303894 1149853 2001 26 pp

(27) Kimura, K.; Tabuchi, Y.; Nishichi, A.; Yamashita, Y.; Okumura, Y.; Sakaguchi, Y. *Polym. J. (Tokyo, Jpn.)* **2001**, *33*, 290.

(28) Tanaka, H. Application: JP 1991-302672 05113677 1993 25 pp

Chapter 4 Synthesis and Characterization of Poly(arylene ether sulfone)s with *trans*-1,4-Cyclohexylene Ring Containing Ester Linkages

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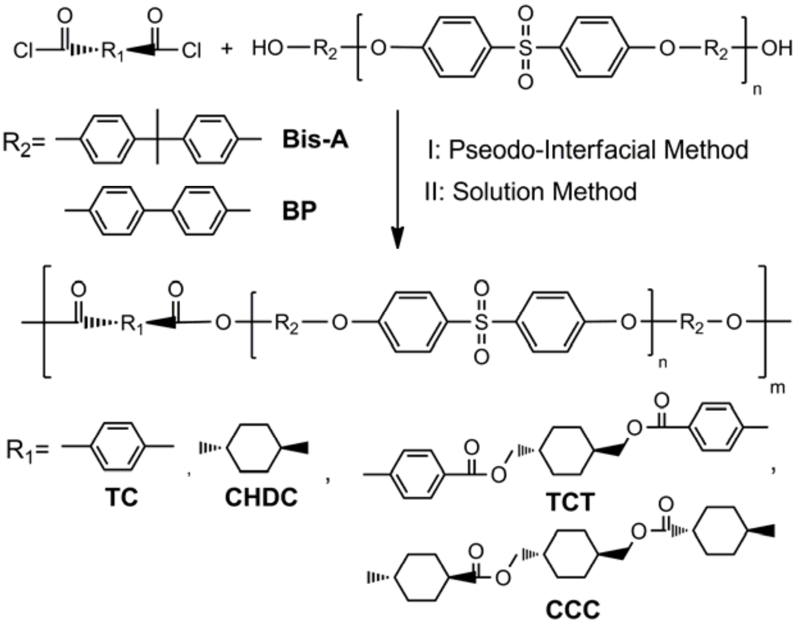
4.1 Abstract



Scheme 4.1 Reaction scheme of synthesis of poly(arylene ether sulfone)s with *trans*-1,4-cyclohexylene ring containing ester linkages

trans-1,4-Cyclohexylene ring containing acid chloride monomers were incorporated into poly(arylene ether sulfone) (PAES) backbones to study their effect on mechanical and thermal properties. The *trans*-1,4-cyclohexylene ring containing acid chloride monomers were synthesized and characterized by NMR and HRMS. *trans*-1,4-Cyclohexylene containing PAESs were synthesized from the acid chloride monomers and hydroxyl terminated polysulfone oligomers with a pseudo-interfacial method and a solution method. These PAESs, with *trans*-1,4-cyclohexylene ring containing ester linkages, were fully characterized by ^{1}H-NMR, ^{13}C NMR, TGA, DSC, SEC, and DMA. The tensile properties were also evaluated. The polymers made with the pseudo-interfacial method had relatively low molecular weights when compared to the solution method where much higher molecular weight polymers were obtained. Crystallinity was promoted in the low molecular weight biphenol-based PAES samples with the pseudo-interfacial method. The crystallinity was confirmed by both the DSC and the WAXD results. The tensile test results of the high molecular weight polymers suggested that incorporation of the *trans*-1,4-cyclohexylene ring containing linkage slightly improved the ultimate elongations while maintaining the Young’s moduli. The *trans*-1,4-cyclohexylene ring containing PAESs also showed higher sub-T_g relaxations in DMA when compared with their terephthaloyl containing analogues.

4.2 Introduction

Thermoplastic polyarylethers have been extensively studied since their initial discovery in early 1960s.[1] Poly(arylene ether sulfone)s (PAESs), commonly known as polysulfones, are important commercial polymers with wide applications due to their excellent thermal and mechanical properties.[2-5] The literature contains many studies of the PAES structures based on a variety of biphenols and diphenylsulfones. The most common PAES structure is based on the reaction of bisphenol-A and 4,4'-dichlorodiphenylsulfone. This polymer is commercially sold as Udel® (Solvay Advanced polymer L.L.C.). However, some applications of PAES are limited by drawbacks such as poor resistance to some solvents, moderate impact resistance, and unacceptable thermal dimensional changes especially near T_g due to the PAES amorphous nature.[1,6]

An important structure modification for property improvement of polysulfone is to incorporate ester segments into the backbone. There are many reports of the synthesis of polysulfone polyester segmented copolymers for different applications with different synthetic methods.[7-11] In the work reported by McGrath and coworkers,[12] a glass-crystal transition around 250 ^{o}C was observed with a narrow crystallization window about 30 ^{o}C in the biphenol based copolymer obtained by solution polymerization with terephthaloyl chloride. Recently, Gaymans and coworkers[13] reported their synthesis of the bisphenol-A based polysulfone polyester segmented copolymers by using the hydroxyl terminated PAES oligomer reacted with diphenyl terephthalate in melt or terephthaloyl chloride in solution. The reaction parameters, such as the reaction temperatures and the solvents, were systematically studied; no mechanical properties, however, were reported.

It is well known that the incorporation of *trans*-1,4-cyclohexylene rings into a polymer backbone can enhance the mechanical properties and affect the crystallization rate.[14,15] Poly(1,4-cyclohexanedimethylene terephthalate) (PCT) is an important commercial crystalline polyester and has a fast crystallization rate.[14] Increasing the *trans*/*cis* ratio of the cyclohexylene unit enhances the crystallization rate. Other 1,4-

cyclohexylene ring containing polycarbonates and polyesters, such as poly(1,4-cyclohexylenedimethylene 1,4-cyclohexanedicarboxylate) (PCCD) and poly(butylene 1,4-cyclohexanedicarboxylate) (PBCHD), have also been widely reported in the literature.[16-21] However, to the best of our knowledge, there are no reports of *trans*-1,4-cyclohexylene ring containing PAESs.

In this paper, we describe a systematic study of the effect of the incorporating *trans*-1,4-cyclohexylene ring containing polyester segments in the PAES backbones by acid chloride chemistry which has been widely used in polyarylate and polyester synthesis.[22,23] A series of acid chlorides was designed and used as the *trans*-1,4-cyclohexylene ring containing segments to react with the PAES oligomers to yield the final PAESs with solution polymerization and pseudo-interfacial polymerization.[12] In contrast to the interfacial polymerization technique where the reaction occurs at the interface, the reaction in pseudo-interfacial polymerization takes place in the organic phase and the side product is transferred into the aqueous phase with the assistance of the phase transfer reagent. Two classes of oligomers, bisphenol-A and biphenol based PAES oligomers, were chosen. The thermal and mechanical properties of the *trans*-1,4-cyclohexylene ring containing PAESs were evaluated by comparing with their terephthalic analogue and the commercially available PAES Udel® and Radel® R provided by Solvay Advance Polymer L.L.C.. A complementary study on the molecular dynamics using solid state NMR technique was also performed and described elsewhere.[24]

4.3 Experimental

4.3.1 Materials

All the chemicals were purchased from Aldrich with the exception of *trans*-1,4-cyclohexane dicarboxylic acid (CHDA) and *trans*-1,4-cyclohexane dimethanol (CHDM) which were provided by Eastman Chemical Company. The Udel® and Radel® R samples were provided by Solvay Advanced Polymers L.L.C.. Tetrahydrofuran (THF) was dried by PURE SOLV purification system from Innovative Technologies, Inc.. Triethylamine (TEA), chloroform, N,N-dimethylacetamide (DMAc), and N-methyl-2-pyrrolidone (NMP) were treated with calcium hydride then purified by the vacuum distillation and stored over molecular sieves. All the other reagents were used as received without further purification.

4.3.2 Instrumentation

The ^{1}H and ^{13}C NMR spectra were obtained by a JEOL 500 (500 MHz) spectrometer at room temperature with chemical shifts relative to tetramethylsilane (TMS). The FT-IR data were obtained on an M2004 FTIR spectrometer from MIDAC Corporation from 4000 cm^{-1} to 650 cm^{-1} with a resolution of 4 cm^{-1}. The T_gs and T_ms were determined by Differential Scanning Calorimetry (DSC). The data were obtained by using a TA Instruments™ Q2000. Nitrogen was used as the carrier gas with a sample flow rate of 20 mL/min and a heating rate of 10 ^{o}C/min. The T_gs were determined in the second heating cycle after the samples were quenched at nominally 100 ^{o}C/min during the cooling cycle. The thermogravimetric analysis (TGA) was carried out by a TA

Instruments™ Q10 from 25 ^{o}C to 600 ^{o}C under nitrogen at a heating rate of 10 ^{o}C/min. The dynamic mechanical analysis (DMA) was performed on a TA Instruments™ Q800 in nitrogen from -150 ^{o}C to 200 ^{o}C with a rate of 2 ^{o}C/min. The DMA parameters are Mode: Multi-Freq-Strain Tension film; Amplitude: 10 μm; Preload force: 0.01 N. All the DMA results were averaged over at least 5 samples. The tensile test was performed on an Instron Model 4400 Universal Testing System with a rate of 2 mm/min at room temperature. Size exclusion chromatography (SEC) was used to determine the molecular weights and the molecular weight distributions. The data were obtained in the SEC solvent at 30 ^{o}C on a Waters Alliance model 2690 chromatograph equipped with a Waters HR 0.5+ HR 2+ HR 3+ HR 4+ styragel column set. Viscotek refractive index detector and a viscometer were used for the molecular weight determination. Polystyrene standards were utilized to construct a universal molecular weight calibration curve. Chloroform and NMP were used as the SEC solvents with a flow rate of 0.500 mL/min. The high resolution mass spectrum (HRMS) was obtained from an Agilent LC/MS (liquid chromatography/mass spectrometry) mass spectrometer with a time of flight (TOF) analyzer. The wide angle X-ray diffraction was performed using a Rigaku S-Max 3000 3 pinhole SAXS/WAXD system. The X-ray source is the Cu Kα radiation, and the wavelength is 0.154 nm. Silver behenate is used to calibrate the sample-to-detector distance and the sample-to-detector distance is 82.5 mm. The WAXD two-dimensional images were obtained using an image plate, with an exposure time of 1 h and analyzed using the SAXSGUI software package.

4.3.3 Monomer Synthesis

The structures and the abbreviations of the *trans*-1,4-cyclohexylene ring containing acid chloride monomers are shown in **Figure 4.1**. Terephthaloyl chloride (TC) is commercially available and used as the aromatic analogue.

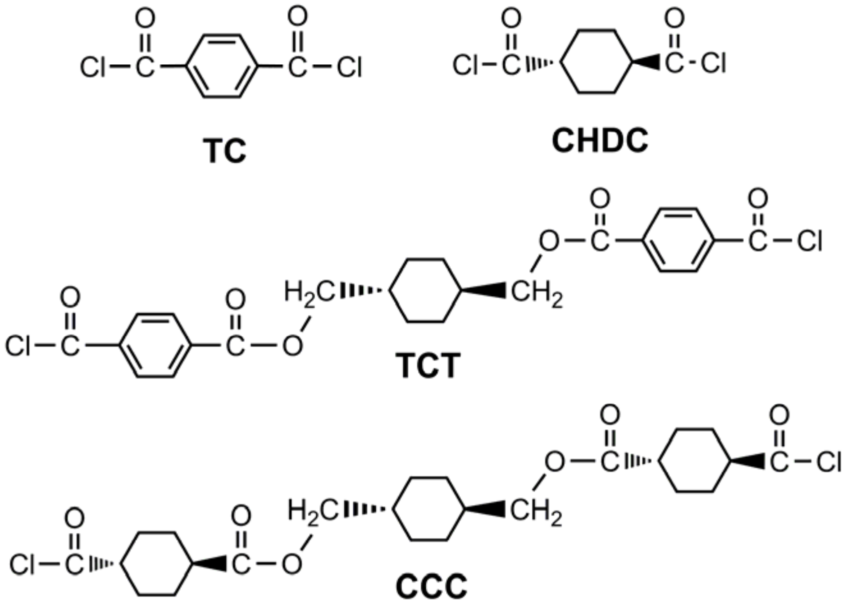


Figure 4.1 Structures of the acid chloride monomers

4.3.3.1 Synthesis of *trans*-1,4-Cyclohexanedicarbonyl Chloride (CHDC)

The glassware and the stir bar were pre-dried in an oven at 80 ^oC for 12 h. To a 250 mL three-necked round bottom flask equipped with a Teflon coated magnetic stir bar, a condenser and an argon inlet, 16.00 g (93.02 mmol) of CHDA, 120.0 mL of thionyl chloride and 0.1 mL of N,N-dimethylformamide (DMF) were added. The reaction was stirred in the presence of argon at 60 ^oC for 4 h. Then the excess amount of thionyl chloride was distilled out at 60 ^oC with vacuum. The white crystals were obtained and dried in a vacuum oven (-80 kPa) at room temperature for 12 h and then kept under argon atmosphere. The product was used directly in the next step without any further purification. Yield 94.4 %. No melting point was observed due to instability. ^{1}H NMR ($CDCl_3$, ppm): δ 2.73 (m, 2H), δ 2.30 (m, 4H), δ 1.58 (m, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 188.4, 50.6, 30.0.

4.3.3.2 Synthesis of *trans*-1,4-Cyclohexane-diylbis(methylene) Bis(4-(chlorocarbonyl)benzoate) (TCT)

10.00 g (49.26 mmol) of terephthaloyl chloride (TC) was dissolved in 80.0 mL of dry THF in a three-necked round bottom flask with a magnetic stir bar, an addition funnel and an argon inlet. A dry THF solution of 1.773 g (12.32 mmol) of *trans*-1,4-CHDM and 4.975 g (49.26 mmol) TEA was added dropwise in a period of 1 h. The reaction mixture was stirred at room temperature for 12 h. Then excess water and triethylamine were added until a clear solution was obtained. After acidification, filtration was applied. The solid obtained was extracted with 600 mL of methanol twice and dried in a vacuum oven (-80 kPa) at 80 ^{o}C for 12 h. The white solid obtained after drying was identified as *trans*-1,4-cyclohexane-bis(methylene)bis(oxy)bis(oxomethylene) dibenzoic acid with a yield of 59.6 %. No melting point was observed due to thermal decomposition below melting point. ^{1}H NMR (DMSO-d6, ppm): δ 13.35 (s, 2H), δ 8.07 (s, 8H), δ 4.15 (d, 4H), δ 1.85 (d, 4H), δ 1.75 (s, 2H), δ 1.13 (m, 4H). ^{13}C NMR (DMSO-d6, ppm), δ 167.2, 165.7, 135.5, 133.8, 130.2, 129.9, 70.2, 37.1, 28.8. HRMS (m/z) Calcd for $C_{24}H_{24}O_8$: 440.1471; Found: 440.1469; Diff: 0.51 ppm.

The glassware and stir bar were pre-dried in an oven at 80 ^{o}C for 12 h. To a 250 mL three-necked round bottom flask equipped with a Teflon coated magnetic stir bar, a condenser and an argon inlet, 2.000 g *trans*-1,4-cyclohexane bis(methylene) bis(oxy) bis(oxomethylene)dibenzoic acid, 120.0 mL of thionyl chloride and 0.1 mL of DMF were added. The reaction was stirred in the presence of argon at 60 ^{o}C for 4 h. Then the excess amount of thionyl chloride was distilled out at 60 ^{o}C with vacuum. The fresh product (TCT) was used directly in the next step without any further purification. A light yellow solid with a yield of 97.6 % was obtained. No melting point was observed due to instability. ^{1}H NMR ($CDCl_3$, ppm): δ 8.18 (m, 8H), δ 4.22 (d, 4H), δ 1.96 (d, 4H), δ 1.84 (s, 2H), δ 1.18 (m, 4H). ^{13}C NMR (DMSO-d6, ppm), δ 168.0, 165.2, 136.7, 136.2, 131.3, 130.0, 70.5, 37.2, 29.0. HRMS (m/z) Calcd for $C_{24}H_{22}O_6Cl_2$: 476.0793; Found: 476.0762; Diff: -6.70 ppm.

4.3.3.3 Synthesis of *trans*-1,4-Cyclohexane-diylbis(methylene) Bis(4-(chlorocarbonyl)cyclohexanecarboxylate) (CCC)

The compound CCC was synthesized in a similar way as compound TCT shown above. *trans*-Cyclohexane-1,4-diylbis(methylene)) bis(oxy)) bis(carbonyl))cyclohexane dicarboxylic acid was obtained as white powder with a yield of 50.9 %. No melting point was observed due to thermal decomposition below melting point. ^{1}H NMR ($CDCl_3$, ppm): δ 3.89 (d, 4H), δ 2.5 - δ 1.0 (m, 30H). ^{13}C NMR ($CDCl_3$, ppm), δ 177.0, 175.3, 68.9, 42.3, 42.2, 37.2, 28.8, 28.2, 26.1. HRMS (m/z) Calcd for $C_{24}H_{36}O_8$: 452.2410; Found: 452.2429; Diff 4.14 ppm.

CCC was obtained with a yield of 95.7 % and used directly in the next step without any further purification. No melting point was observed due to instability. ^{1}H NMR

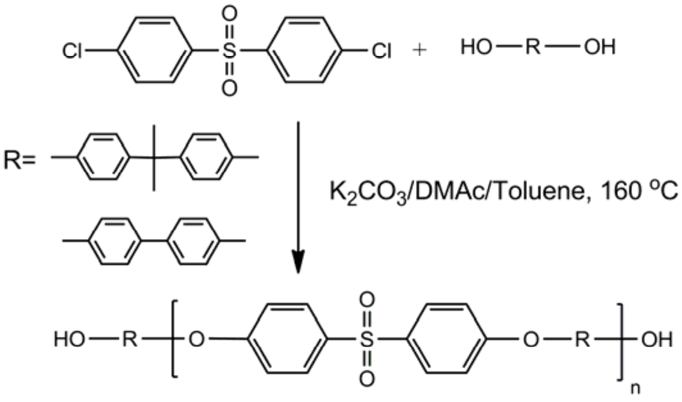
($CDCl_3$, ppm): δ 3.84 (d, 4H), δ 2.5 - δ 1.0 (m, 30H). **^{13}C** NMR ($CDCl_3$, ppm), δ 175.7, 175.2, 69.0, 51.9, 42.1, 37.2, 28.2, 28.1, 26.0. HRMS (m/z) Calcd for $C_{24}H_{34}O_6Cl_2$: 488.1732; Found: 488.1720; Diff: -2.52 ppm.

4.3.4 Polymer Synthesis

4.3.4.1 Synthesis of Hydroxyl-terminated PAES Oligomers with Controlled Molecular Weight

The reaction scheme is shown in **Scheme 4.2**. The hydroxyl-terminated bisphenol (bis-A) and the biphenol (BP) based PAES oligomers with 2.0 kg/mol target molecular weight were synthesized by using the stoichiometry imbalance technique based on the Carothers equation. The bis-A based PAES oligomer with 2.0 kg/mol target molecular weight is shown as an example. The BP based oligomer was synthesized in a similar fashion. 5.036 g (17.54 mmol) of dichlorodiphenyl sulfone (DCDPS), 5.000 g (21.90 mmol) of bis-A, 7.870 g (56.95 mmol) of K_2CO_3, 80.0 mL of DMAc and 40.0 mL of toluene were added to a flask equipped with a mechanical stirrer, an argon inlet and a Dean-Stark trap. The reaction was heated to 140 ^{o}C for 3 h to remove water by azeotropic distillation. Then toluene was distilled out by increasing the temperature slowly to 160 ^{o}C in 2 h. After 20 h at 160 ^{o}C the reaction mixture was cooled to room temperature. White solid was obtained by the precipitation of the reaction mixture in a 5 weight percent HCl aqueous solution and filtration. The product was washed three times each with 200 mL of deionized water and with methanol. After drying at 120 ^{o}C for 12 h in a vacuum oven (-80 kPa), the product was obtained with a yield of 92.4 %. ^{1}H NMR

($CDCl_3$, ppm): δ 8.18 (m, 16.38), δ 7.21 (m), δ 7.06 (m), δ 6.96 (m), δ 6.91 (m), δ 6.72 (m, 4.00), δ 1.66 (m). In the proton NMR, the integration area ratio between the protons with the chemical shift of δ 6.72 and δ 8.18 was used to determine the number average molecular weights. The actual molecular weights of the oligomers were very close to the target. For this specific bis-A PAES oligomer, the number average molecular weight was 2.0 kg/mol from the ^{1}H NMR end group analysis.



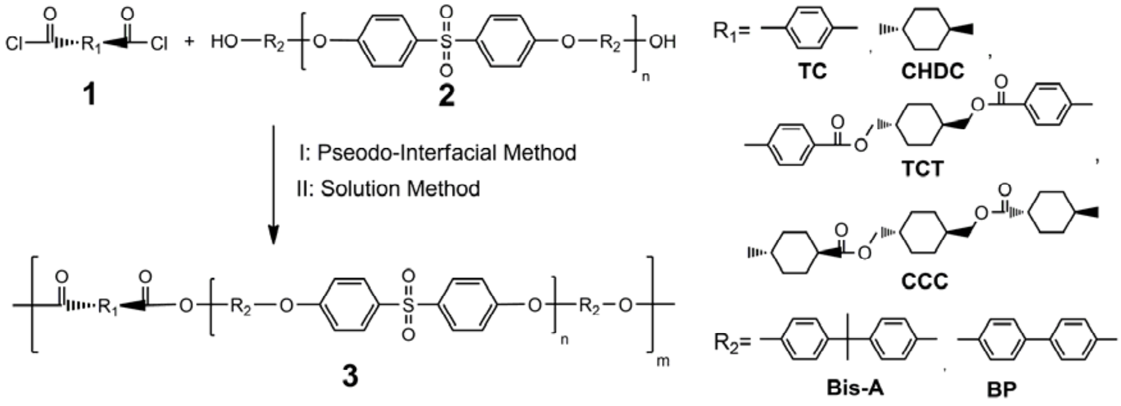
Scheme 4.2 Synthesis of the bis-A based and biphenol based PAESs

4.3.4.2 Synthesis of the High Molecular Weight Bis-A Based and Biphenol based PAESs

Bis-A based and biphenol based PAESs were both synthesized with comparable molecular weights to the Udel®, Radel® R samples and used as our lab-synthesized polymer controls in the thermal and the mechanical property evaluation. These high molecular weight samples were synthesized in the same way as the hydroxyl-terminated PAES oligomers shown above but with a different stoichiometry imbalance to control the molecular weights.

4.3.4.3 Synthesis of the *trans*-1,4-Cyclohexylene Ring Containing PAES (Polymer 3 in Scheme 4.3)

The *trans*-1,4-cyclohexylene ring containing PAES polymers were synthesized from the PAES oligomers and the diacid chloride monomers by pseudo-interfacial polymerization and solution polymerization.



Scheme 4.3 Synthesis of the *trans*-1,4-cyclohexylene ring containing PAES

4.3.4.3.1 Pseudo-Interfacial Polymerization

A typical polymerization for the copolymers is described below. 3.015 g (1.478 mmol) bis-A based PAES oligomer was dissolved in 20.0 mL of chloroform in a two-necked round bottom flask equipped with an argon inlet. Then a 5.0 mL aqueous solution of 1.020 g (7.389 mmol) K_2CO_3 was added along with 0.038 g (0.150 mmol) tetraethylammonium iodide (TEAI) which worked as the phase transfer reagent. Under vigorous stirring, 0.300 g (1.478 mmol) terephthaloyl chloride in 20.0 mL of chloroform was added. The reaction mixture was stirred at room temperature for 8 h. After precipitation in methanol and filtration, the polymer was washed three times with 100 mL of water and 100 mL of methanol respectively. With a yield of 81.2 %, the solid product was dried at 120 ^{o}C in a vacuum oven (-80 kPa) for 12 h.

4.3.4.3.2 Solution Polymerization

High molecular weight materials were prepared with the solution method when dry chloroform or dry 1,1,2,2-tetrachloroethane was used as the solvent. A typical polymerization for the copolymers is described below. 3.015 g (1.478 mmol) bis-A based PAES oligomer was dissolved in 20.0 mL of chloroform with addition of 0.373 g (3.695 mmol) TEA in a two-necked round bottom flask equipped with an argon inlet. Under vigorous stirring, 0.300 g (1.478 mmol) terephthaloyl chloride in 20.0 mL of chloroform was added slowly in 1 h. A viscous solution was obtained after the reaction was performed at 100 ^{o}C for another 8 h. After precipitation in methanol and filtration, the polymer was washed three times with 100 mL of water and 100 mL of methanol respectively to remove TEA hydrochlorides. With a yield of 91.9 %, the solid product was dried at 120 ^{o}C in a vacuum oven (-80 kPa) for 12 h.

4.3.4.4 Polymer Film Preparation

The film samples were obtained by the solution casting method. The solid polymer sample was dissolved at room temperature under stirring in chloroform, DMAc, or NMP depending on the results of solubility test to offer a homogeneous solution with concentration of 10 % wt. After the filtration through a 45 μm micro glass fiber filter, the polymer solution was cast on a leveled glass substrate dried at 80 ^{o}C for 12 h and subsequently dried at 120 ^{o}C under vacuum (-80 kPa) for 12 h. The dog bone samples for the mechanical property evaluation were prepared from the polymer films. The dimension parameters of the dog bone sample were 4.00 mm in width and about 15 mm in length. The thickness of the samples was in the range of 60-100 μm. The polymers offered transparent tough films with no color or light yellow color.

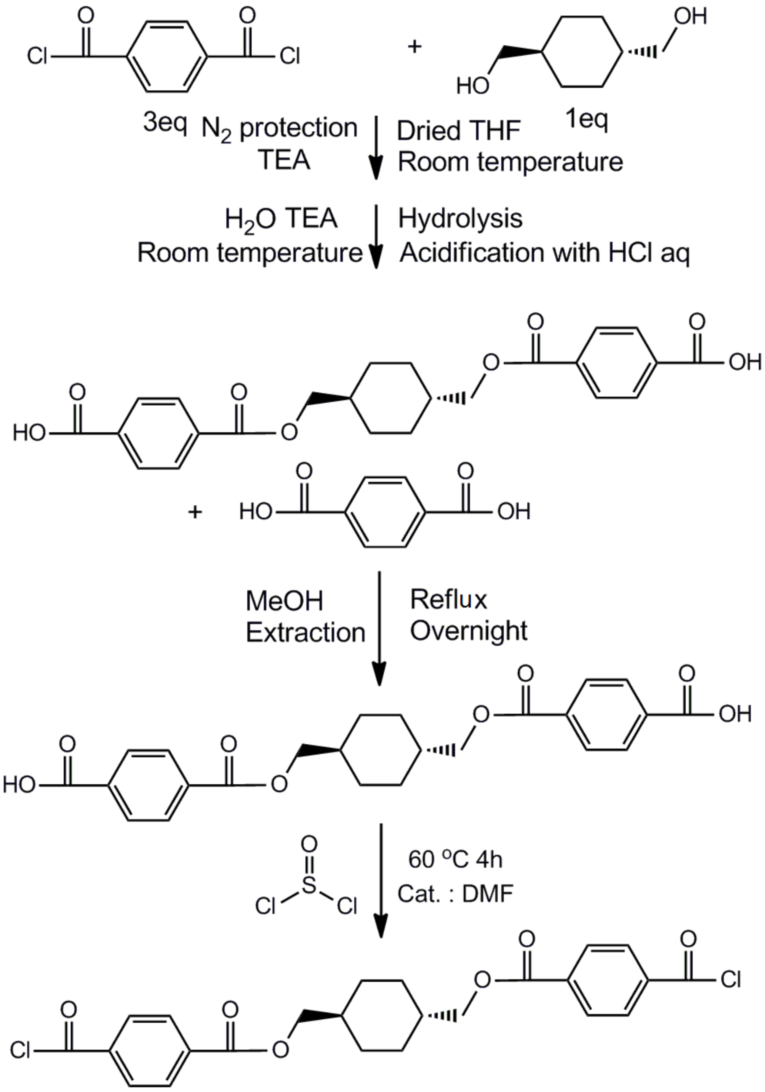
4.4 Results and Discussion

4.4.1 Solubility Results of the *trans*-1,4-Cyclohexylene Containing PAES

Solubility tests were performed at room temperature in chloroform, DMSO, DMAc, and NMP. The bis-phenol A based polymers were readily dissolved in all the solvents listed. Enhanced solvent resistance was observed in biphenol based materials. Biphenol based polymers showed low solubility in chloroform and DMSO and were soluble in DMAc and NMP. No solubility differences were found between the *trans*-1,4-cyclohexylene-containing and the 1,4-phenyl-containing polymers in the solvents studied.

4.4.2 Synthesis of New *trans*-1,4-Cyclohexylene Ring Containing Diacid Chloride Monomers

Terephthaloyl chloride is commercially available and was used as the aromatic analogue. CHDC monomer (structure shown in **Figure 4.1**) was obtained from the high conversion reaction of *trans*-CHDA with thionyl chloride.



Scheme 4.4 Synthesis of *trans*-1,4-cyclohexane bis(methylene) bis(4-(chlorocarbonyl)benzoate) (TCT)

In the synthesis of new TCT and CCC trimer diacid chloride monomers, the corresponding diacid monomers were first synthesized by using an excess amount of terephthaloyl chloride (in case of TCT) or CHDC (in case of CCC). The synthesis scheme of TCT is shown in **Scheme 4.4** as an example. After the hydrolysis and acidification, the excess of terephthaloyl chloride ensured that only the trimer diacid monomer was formed in the first step with the terephthalic acid. The diacid monomer mixtures required a purification step to obtain the pure trimer diacid compound. This was accomplished by extraction twice with 600 mL of methanol to remove the terephthalic acid. The obtained diacid monomer structure was confirmed by ^{1}H NMR, ^{13}C NMR and HRMS. With subsequent treatment of the trimer diacid with the thionyl chloride, the desired trimer diacid chlorides TCT and CCC were obtained. This synthetic route was designed due to the difficulty to fully characterize the TCT and CCC diacid chloride monomers which are highly reactive. No melting points were observed for both the diacid monomers and diacid chloride monomers because they degrade below melting point.

4.4.3 Bis-A and BP Based *trans*-1,4-Cyclohexylene Ring Containing PAES by Pseudo-Interfacial Polymerization

Bis-A and BP based *trans*-1,4-cyclohexylene ring containing PAES polymers were synthesized from PAES oligomers with 2.0 kg/mol target number average molecular weights and the diacid chloride monomer (structures shown in **Figure 4.1)** at stoichiometry ratio. In the pseudo-interfacial polymerization, the reaction took place in the organic phase and side product HCl was transferred across the interface under the assistance of the phase transfer reagent TEAI. The polymer samples were characterized with FT-IR and typical spectra are shown in **Figure 4.2**. The appearance of the peak at 1738 cm^{-1} which is a characteristic peak of an ester carbonyl group showed up in the polysulfone with ester linkage; while in the polysulfone oligomer sample, no peak was observed in this range. This result combined with the disappearance of the hydroxyl characteristics peak at 3455 cm^{-1} in bis-A PAES with ester segments confirmed the formation of the ester linkage and the successful polymerization. The molecular weight results shown later in this paper also confirmed the successful polymerization.

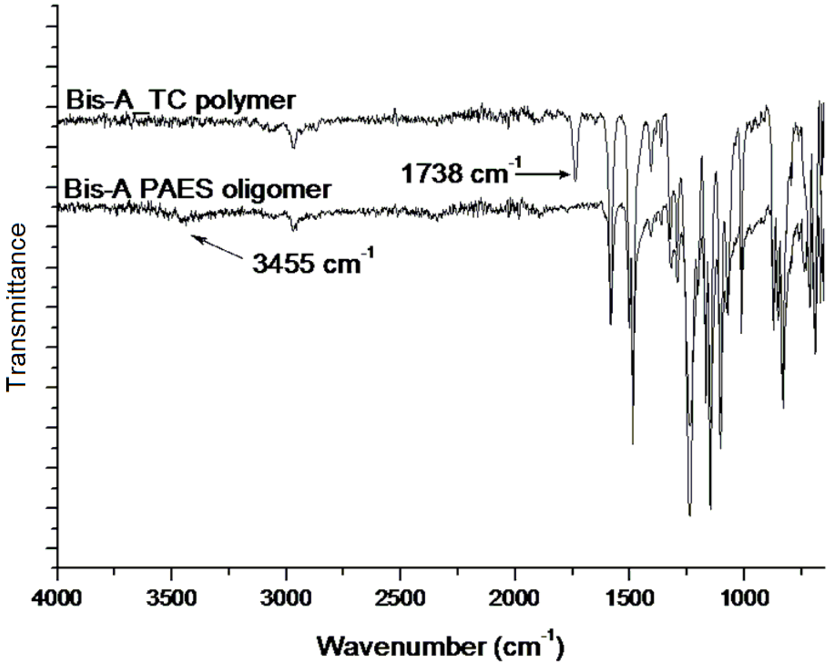


Figure 4.2 FT-IR spectra of bis-A PAES oligomer and bis-A based PAES with ester segments

The samples were characterized by ^{1}H NMR in order to determine *trans*-1,4-cyclohexylene ring conformation in the polymer backbone. A typical ^{1}H NMR spectrum of *trans*-1,4-cyclohexylene ring containing PAES is shown in **Figure 4.3** with the polymer structure. The enlarged area in the middle of **Figure 4.3** shows the peak of the protons A which are the cyclohexyl protons next to the carbonyl groups. Only one signal was observed for proton A which indicated that no isomerization reaction occurred during the polymerization. Isomerization was not expected since the polymerizations were performed at low temperatures.

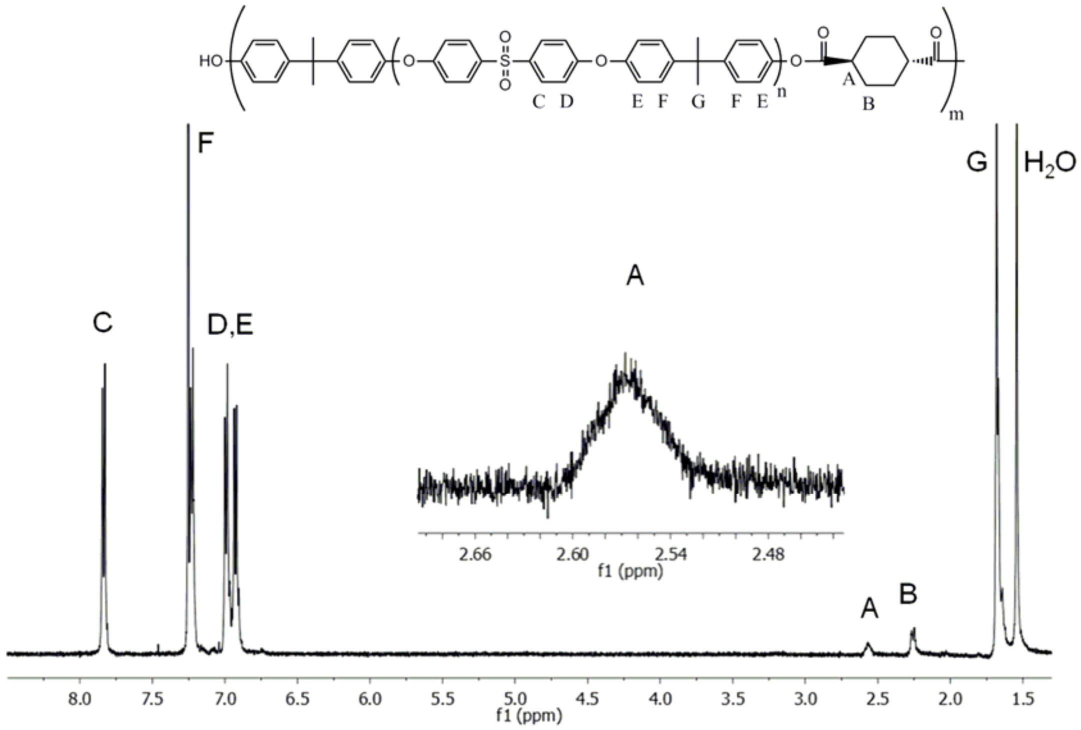


Figure 4.3 ^{1}H NMR spectrum of a typical *trans*-1,4-cyclohexylene ring containing PAES

The molecular weights and thermal properties of the pseudo-interfacial polymerization products were characterized (summarized in **Table 4.1)**. All the polymer samples were dried in a vacuum oven thoroughly before characterization. Independent of polysulfone oligomer used, pseudo-interfacial polymerization yielded polymers with number average molecular weights lower than 10 kg/mol. Polydispersity values of the polymers were all lower than the ideal value of 2.0. The low polydispersity results from the loss of some low molecular weight fractions during the precipitation isolation procedure.

Table 4.1 Components, molecular weights, T_gs and T_ms of bis-A and BP based *trans*-1,4-cyclohexylene ring containing PAES by pseudo-Interfacial polymerization

Polymers	Molar Mass (kg/mol)		PDI	T_g	T_m	ΔT
	M_n	M_w		^oC	^oC	^oC
Bis-A_TC	11.5	22.7	1.9	182	-	-
Bis-A_CHDC	10.5	16.3	1.5	168	-	-
Bis-A_TCT	6.9	10.9	1.6	160	-	-
Bis-A_CCC	10.8	17.4	1.6	155	-	-
BP_TC	6.2	9.2	1.5	200	247	47
BP_CHDC	5.2	8.4	1.6	186	244	48
BP_TCT	3.6	7.7	2.1	177	241	64
BP_CCC	4.2	5.6	1.3	167	244	77

In both bis-A PAES and BP PAES series, the terephthaloyl containing polymers (Bis-A_TC and BP_TC) had the highest glass transition temperatures. With the incorporation of the *trans*-1,4-cyclohexylene ring, the glass transition temperature decreased in the monomer sequence of CHDC > TCT > CCC. This T_g trend was as expected because the cyclohexylene ring incorporated in the polymer backbone can provide flexibility and facilitate the chain segment motion resulting in a decreased T_g. Bisphenol-A containing PAES polymers did not show melting transitions due to the tetrahedral isopropylidene units.

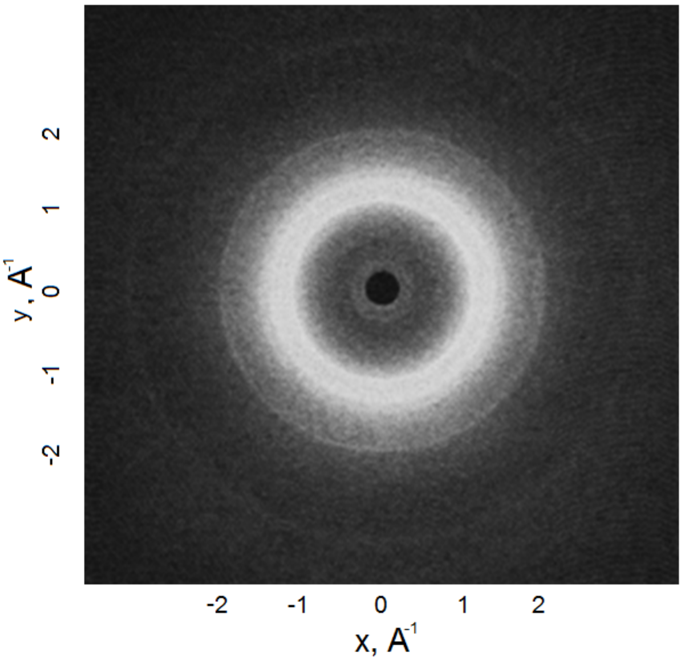


Figure 4.4 Wide angle X-ray diffraction pattern of BP_TC sample

When bis-A PAES oligomers were replaced by BP PAES oligomers, crystallinity was found in all four polymer samples. Independent of the acid chloride monomers, the melting transitions of the polymers were all in the vicinity of 240 ^{o}C. The melting transition data of the BP_TC sample we observed is in close agreement with the reported value.[12] The DSC melting transition results were further confirmed by the wide angle X-ray diffraction (WAXD) measurements. All four biphenol based PAESs showed similar WAXD pattern. An example pattern of BP_TC is shown in **Figure 4.4**. Similar to the bis-A system, decreasing glass transition temperatures in the monomer sequence of TC > CHDC > TCT > CCC were found. Because of the structure independency of the melting transition, the decreasing glass transition temperatures enlarged the crystallization window defined as the temperature difference between T_g and T_m (shown as ∆T in **Table 4.1**).

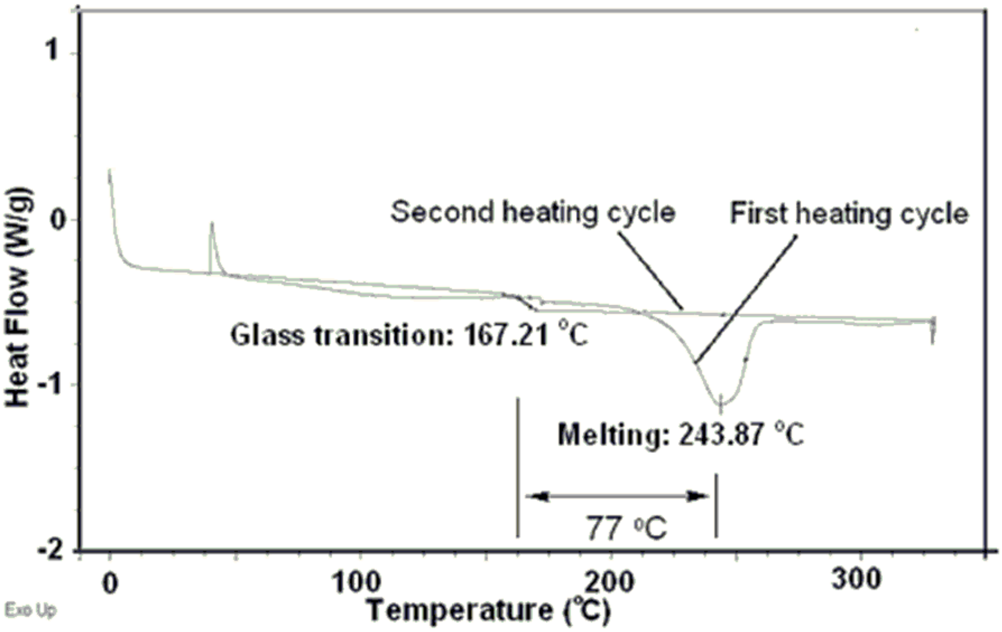


Figure 4.5 DSC curves of the BP based *trans*-1,4-cyclohexylene ring containing PAES synthesized from CCC (BP_CCC sample)

The DSC curve of samples BP_CCC is shown in **Figure 4.5** with a crystallization window of 77 °C. In the DSC study, the samples were quenched at nominally 100

^{o}C/min or cooled at a rate of 2 ^{o}C/min in the cooling cycles. It needs to be noted that neither recrystallization nor melting transition were observed in the cooling cycle and the second heating cycle of the DSC curves in all the polymers. These results indicated that the semi-crystallinity was a result of solvent-induced crystallization with relatively low molecular weight samples. A slow crystallization rate in the melt inhibits polymer recrystallization.

4.4.4 Bis-A and BP Based *trans*-1,4-Cyclohexylene Ring Containing PAES by Solution Polymerization

Attempts to cast films from the *trans*-1,4-cyclohexylene ring containing polymers with pseudo-interfacial polymerization resulting in brittle films due to the low molecular weights. In order to obtain high quality films for mechanical property characterizations, *trans*-1,4-cyclohexylene ring containing PAESs were prepared by the solution method using the same starting materials at the stoichiometric ratio. For the bisphenol-A series, chloroform was chosen because it is easy to dehydrate and the oligomer and the product are both soluble. Chloroform was not used for biphenol series, because the solubility of the starting oligomer is too low to provide a high concentration for solution polymerization. Furthermore, the solubility of the polymer product is limited. Different solvent systems including DMAc, DMF, NMP and DMAc/Chloroform have been used. In agreement with a previous report,[13] the solvents listed above resulted in low molecular weight products probably due to small amount of water which hydrolyzed some of the diacid chloride and disrupted the stoichiometry balance. Successful solution polymerization was obtained in 1,1,2,2-tetrachloroethane which provided good solubility to the starting materials and the products. The polymer products from the solution method were also characterized by FT-IR and ^{1}H NMR. The results were similar to the results from the polymers by pseudo-interfacial polymerization as shown in **Figure 4.2** and **Figure 4.3**. The successful polymerization was confirmed by the appearance of the ester carbonyl peak in the FT-IR of the products. The *trans*-1,4-cyclohexylene ring conformation was confirmed by the ^{1}H NMR peak of the cyclohexyl protons next to the carbonyl groups.

The molecular weights and thermal properties of polymer products with solution polymerization are summarized in **Table 4.2**. For both of the bis-A and BP based PAES, the solution method yielded polymers with higher molecular weights than those of products with pseudo-interfacial polymerization. The molecular weights of cyclohexylene ring containing polymers were comparable to the molecular weight of the Udel® and Radel® R control so that the mechanical properties of these polymers can be evaluated without having molecular weight as a factor. The SEC traces of the polymers from the solution method were all observed with monomodel peaks with no sign of branching or crosslinking.

No crystallinity was found in biphenol based PAES samples listed in Error! Not a valid bookmark self-reference.. The loss of crystallinity could be due to the combination of higher molecular weights and slightly larger PDI with the solution method than those with pseudo-interfacial methods. The fact that higher molecular weight results in lower crystallinity has been reported in PE and PEEK.[25-27] Similar to the results in pseudo-interfacial polymerization, in both series, the terephthaloyl containing polymers had the highest glass transition temperatures and the glass transition temperature decreased in the sequence of TC > CHDC > TCT > CCC as expected.

Table 4.2 Components, molecular weights, T_gs and T_ms of bis-A and BP based *trans*-1,4-cyclohexylene ring containing PAES by solution polymerization with controls

Polymers	Molar Mass (kg/mol)		PDI	T_g	T_m	T_d
	M_n	M_w		^oC	^oC	^oC
Udel®	22.8	41.7	1.8	189	-	498
BisA PAES	20.8	36.0	1.7	186	-	537
Bis-A_TC	24.6	49.9	2.0	189	-	480
Bis-A_CHDC	23.2	36.1	1.5	181	-	466
Bis-A_TCT	11.0	28.7	2.6	163	-	429
Bis-A_CCC	9.6	18.4	1.9	159	-	450
Radel® R	14.2	28.8	2	220	-	526
BP PAES	21.6	37.4	1.7	227	-	565
BP_TC	10.8	32.5	3.0	220	-	541
BP_CHDC	9.3	24.7	2.6	211	-	497
BP_TCT	8.6	17.8	2.1	196	-	448
BP_CCC	10.5	28.9	2.7	185	-	469

Table 4.3 Tensile test results of bis-A and BP based *trans*-1,4-cyclohexylene ring containing PAES by solution polymerization with controls

Polymers	Modulus (MPa)	Strain at Failure (%)
Udel® control	1304±86	6.4 ±0.5
Bis-A PAES	N/A*	N/A
Bis-A_TC	1550±106	15.4±3.9
Bis-A_CHDC	1504±108	13.9±3.6
Bis-A_TCT	1318±73	17.5±8.6
Bis-A_CCC	1417±169	14.4±2.4
Polymers	Modulus (MPa)	Strain at Failure (%)
Radel® R control	1353±92	8.1±1.3
BP PAES	1498±140	7.9±0.8
BP_TC	1758±137	8.4±0.8
BP_CHDC	1175±92	34.9±11
BP_TCT	1216±100	8.2±1.2
BP_CCC	1329±315	9.9±1.5

* N/A, not available, the sample resulted in brittle film in solution casting.

The bis-A based and biphenol based PAESs were both synthesized with comparable high molecular weights to the Udel®, Radel® R samples and used as our lab-synthesized polymer controls in mechanical property evaluation. The film tensile test results summarized in **Table 4.3** suggested that *trans*-1,4-cyclohexylene ring containing PAES exhibited approximately the same Young's moduli as their aromatic analogue and the property controls. Moderate ultimate elongation improvements were observed in *trans*-1,4-cyclohexylene ring containing polymers. This result is in agreement with similar moderate elongation enhancement in *trans*-1,4-cyclohexylene containing polyketone polysulfone results previously published.[28]

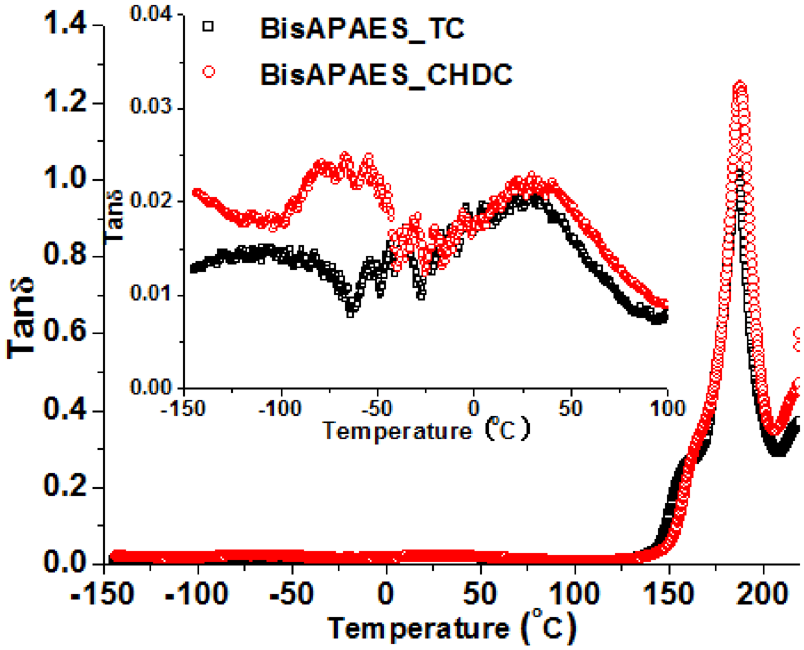


Figure 4.6 DMA curves of the bis-A based *trans*-1,4-cyclohexylene ring containing PAES and its aromatic analogue

In DMA tests, *trans*-1,4-cyclohexylene ring containing PAES showed a higher relaxation, with the peak temperature value in the vicinity of -70 °C, than their aromatic analogue. Typical DMA curves of *trans*-1,4-cyclohexylene containing PAES and the terephthaloyl containing PAES are shown in **Figure 4.6**. The enlarged area is the DMA low temperature region. At the peak value in the vicinity of -60 ^{o}C, *trans*-1,4-cyclohexylene ring containing PAES showed a large low temperature relaxation which was absent in the aromatic analogue. The observed sub T_g relaxation has been well reported in the literature. Similar relaxations were observed in a series of *trans*-1,4-cyclohexylene ring containing polyesters with a peak value at around -55 ^{o}C.[17] In the secondary relaxation study reported by Chen and Yee,[15] a low temperature relaxation with the peak value about -75 ^{o}C was observed in PCT. Based on the references, we propose that the origin of the secondary relaxations in our PAESs samples is the conformation transition of the backbone *trans*-1,4-cyclohexylene ring.[29] This enhanced low temperature relaxation suggested that the incorporation of the *trans*-1,4-cyclohexylene ring can potentially enhance the impact strength without sacrificing modulus.

4.5 Conclusion

The incorporation of the *trans*-1,4-cyclohexylene rings into a polymer backbone is well known to have a dramatic influence on the polymer properties such as crystallinity, thermal property and mechanical properties. In this paper, *trans*-1,4-cyclohexylene ring units were successfully introduced into the poly(arylene ether sulfone) (PAES) backbones by the reactions of a series of diacid chloride monomers and the hydroxyl-terminated PAES oligomers. Crystallinity was achieved in the biphenol based *trans*-1,4-

cyclohexylene ring containing PAESs with the pseudo-interfacial method but not in the bisphenol-A based polymers. Recrystallization was not observed in the second heating cycle of the DSC measurement likely due to the slow crystallization rate of the copolymer in the melt state. The mechanical properties of the high molecular weight *trans*-1,4-cyclohexylene ring polymers from the solution polymerization were evaluated. Both the tensile properties and the DMA results suggested that the incorporation of *trans*-1,4-cyclohexylene ring ester linkages improves the ultimate elongation and promotes sub-T_g relaxations while maintaining the moduli of the polymers.

4.6 Acknowledgement

This research was sponsored by the Army Research Laboratory and was accomplished under Cooperative Agreement Number W911NF-06-2-0014. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing official policies, either expressed or implied, of the Army Research Laboratory or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation hereon. We acknowledge the assistance of the Department of Chemistry and the Macromolecules & Interfaces Institute at Virginia Tech. We are grateful to Solvay Advanced Polymers L.L.C. and Eastman Chemical Company for supplying chemicals. We appreciate the assistance of Professor Long's, Professor Riffle's, and Professor McGrath's groups at Virginia Tech. We also appreciate

assistance from Professor Moore’s group at Virginia Tech for WAXD measurements on the Rigaku S-Max 3000 3 pinhole SAXS/WAXD system from NSF DMR-0923107.

4.7 Supplementary Materials

The publication which is the first part of this chapter was condensed from considerable amount of other work on using the acid chloride techniques. This section of the chapter provides further supplemental details and results in this area.

4.7.1 Solvent Purification

The polymer described in this chapter is based on acid chloride chemistry. It is well known that the compound containing acid chloride functional groups are very sensitive to moisture. The compounds used in the polymer synthesis need to be dried prior to use. Any water residue in the polymerization will affect the 1:1 stoichiometry ratio, resulting in low molecular weight.

The two main chemicals used are triethylamine as the base and dichloromethane as the solvent. Triethylamine was purified with the following procedure. 5.0 weight percent of calcium hydride was added with 300 mL of triethylamine in a two necked round bottom flask with an argon inlet, a condenser and a magnetic stir bar. The solution was heated to reflux and kept at reflux temperature overnight under stirring. Then distillation at atmospheric pressure was performed under argon protection. The fraction from 87-88 ^{o}C was collected as a clear colorless liquid. Dichloromethane was purified with the same procedure but instead of 88 ^{o}C fraction, the fraction from 32-34

^{o}C was collected as a clear colorless liquid. The dried chemicals were used freshly.

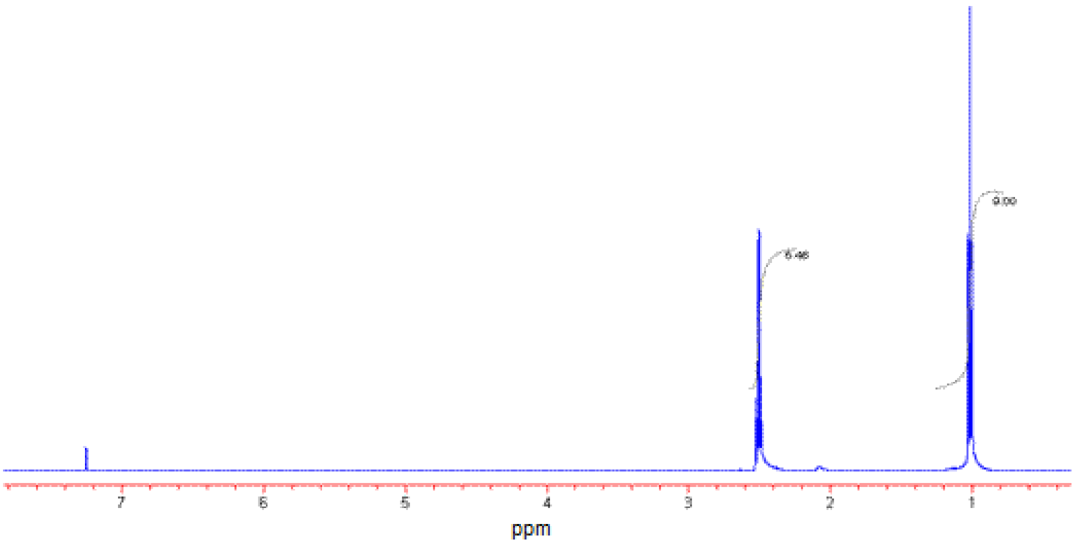


Figure 4.7 ^{1}H NMR spectrum of triethylamine in $CDCl_3$ after purification

The ^{1}H NMR spectra of the two compounds in $CDCl_3$ after purification are shown in **Figure 4.7** and **Figure 4.8**. After treatment with calcium hydride, no water peak or only a very small water peak (could be trace amounts of water in $CDCl_3$) was observed in the vicinity of 1.5 ppm chemical shift which indicated a successful solvent purification. The reactions including the polymerization reactions were all performed in the presence of dry argon protection gas to prevent any moisture during the reactions. The thoroughly dried PAES oligomers are also critical to obtain high molecular weight polymer products. The drying conditions and other properties of the PAES oligomers will be discussed in the following section.

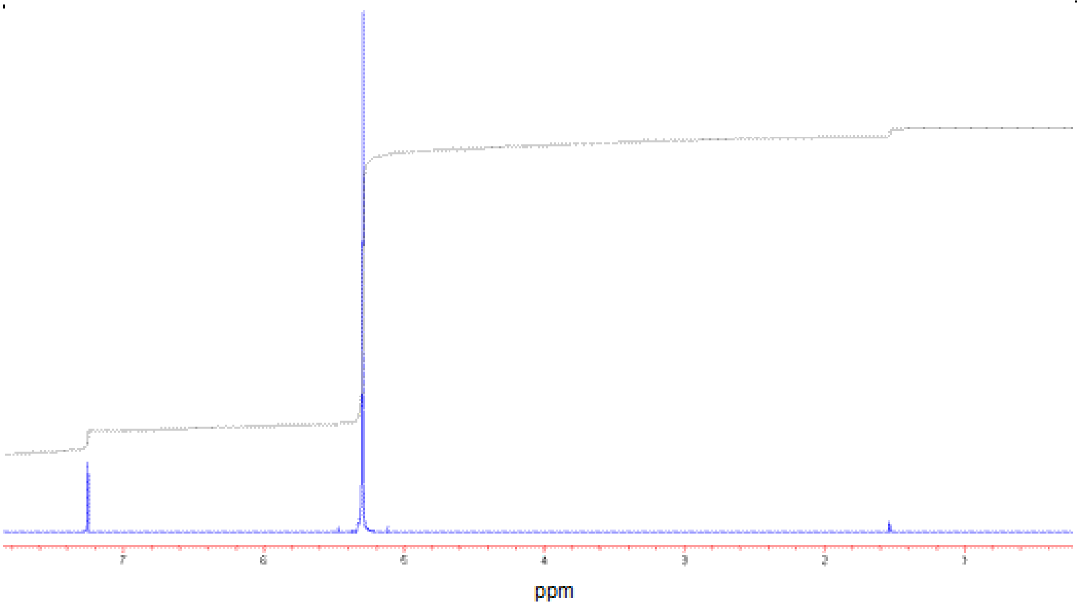


Figure 4.8 ^{1}H NMR spectrum of dichloromethane in $CDCl_3$ after purification

4.7.2 The Drying Condition and Thermal Properties of the PAES Oligomers

The PAES oligomer is another compound that needs to be thoroughly dried. The polar sulfone groups in the oligomer can interact with water molecules which makes it hard to obtain very dry samples. The synthesis of the PAES oligomers is described in **4.3.4.1**. The reaction apparatus is shown in **Figure 4.9**. After the synthesis, the oligomers were isolated by precipitation in acid aqueous solution. The precipitation step introduced water in the oligomer products which were subsequently dried in a vacuum oven (-80 kPa) for 12 h.

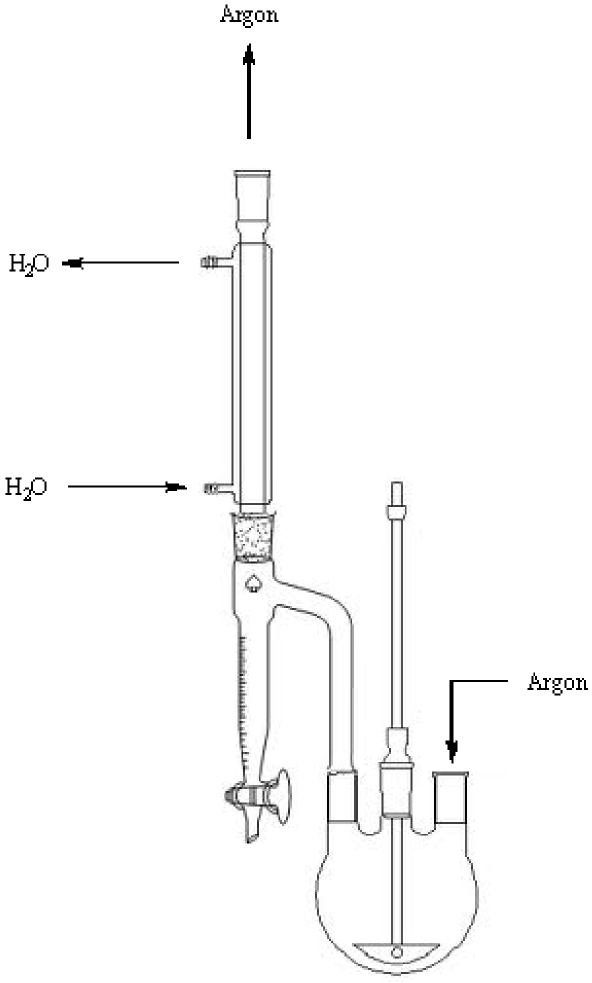


Figure 4.9 The reaction apparatus set up of PAES synthesis

Figure 4.10 and **Figure 4.11** are the ^{1}H NMR spectra of a bisphenol-A based PAES oligomer dried in a vacuum oven at 80 ^{o}C and 120 ^{o}C respectively for 12 h. As indicated by the water proton peak at around 1.5 ppm, drying at 120 ^{o}C can further reduce the amount of water in the oligomer sample. It needs to be noted that high drying temperature may result in a slight increase in molecular weight probably due to the loss of a small amount of unreacted monomers and low molecular weight oligomers.

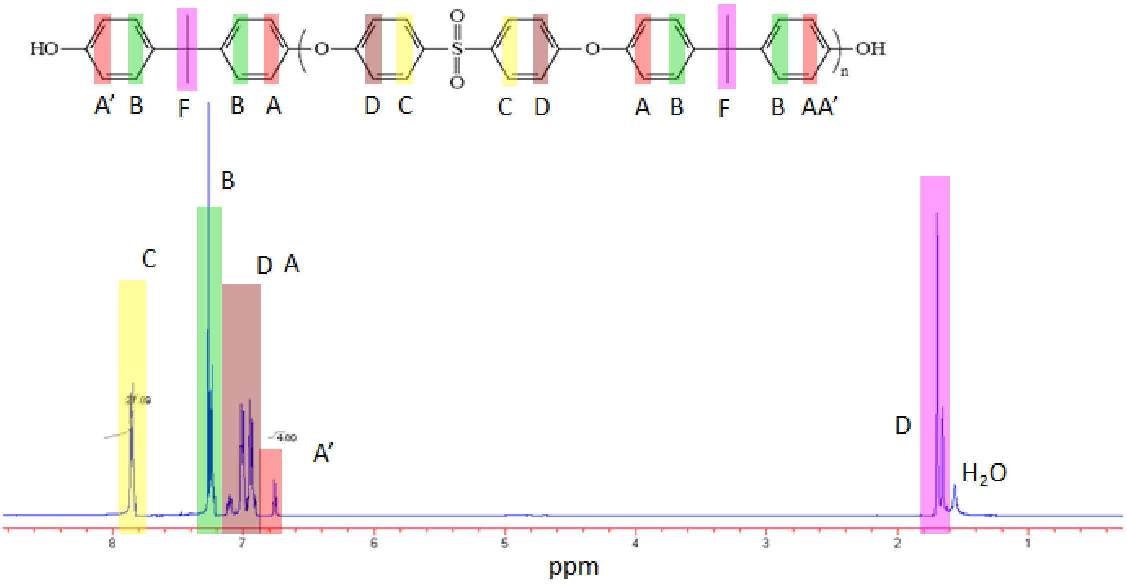


Figure 4.10 ^{1}H NMR spectrum of a bisphenol-A based PAES oligomer dried in a vacuum oven at 80 °C for 12 h (in $CDCl_3$)

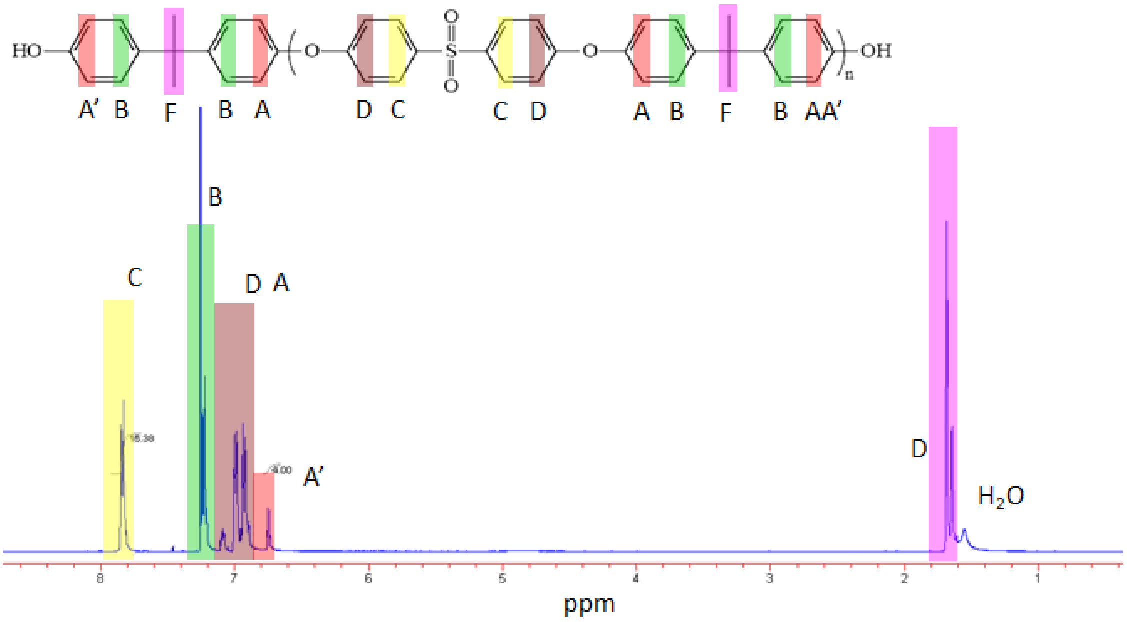


Figure 4.11 ^{1}H NMR spectrum of a bisphenol-A based PAES oligomer dried in a vacuum oven at 120 °C for 12 h (in $CDCl_3$)

Table 4.4 The thermal properties and molecular weights of the bisphenol-A and biphenol based polysulfone oligomers

Polymers	Molar Mass (kg/mol)		PDI	T_g[2]	T_m	T_d[3]
	M_n[1]	M_w		°C	°C	°C
BisA PAES	2.7	-	-	137	-	457
BP PAES	2.4	-	-	143	-	482

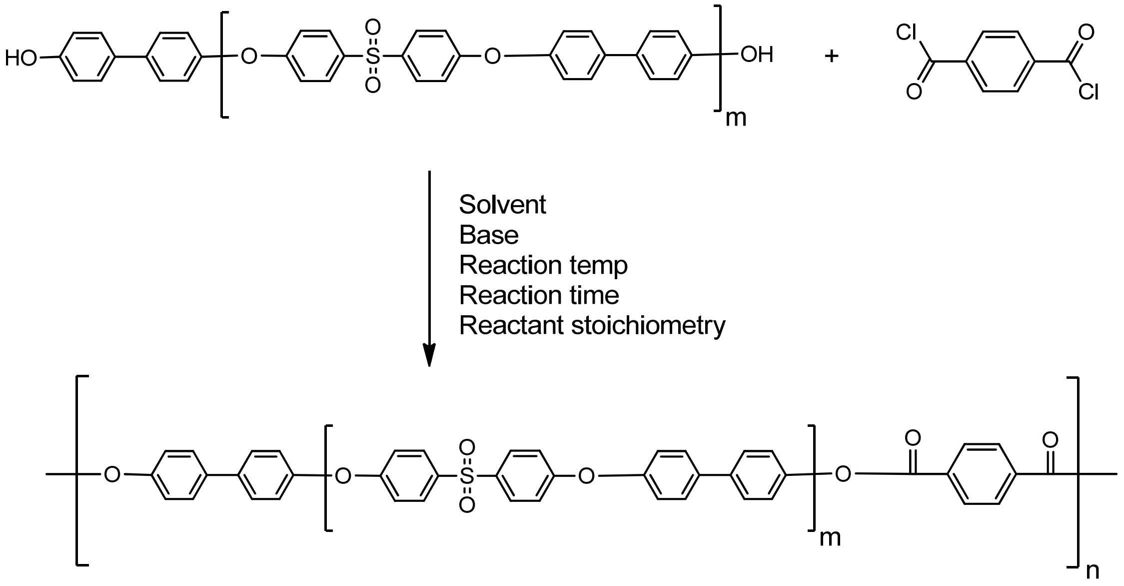
[1] Determined by ^{1}H NMR

[2] T_gs were observed on a TA Q2000 heating rate 10 °C/min; cooling quench

[3] T_d was defined as 5 % weight loss temperature and obtained on a TA Q500 with a heating rate of 10 °C/min

The thermal properties and number average molecular weight information are summarized in **Table 4.4**. The glass transition temperature and the decomposition temperature of the biphenol based oligomer were higher than those of the bisphenol-A based oligomer due to the stiffer and more thermally stable structure of biphenol. The number average molecular weights were determined by the ratio of A' protons and C protons in ^{1}H NMR as shown in **Figure 4.10** and **Figure 4.11**. Due to the loss of low molecular weight oligomers in both the precipitation and drying procedure, the M_ns of the bisphenol-A based and biphenol based oligomers were slightly higher than 2.0 kg/mol, the target molecular weight. Comparing these molecular weights with the data in **Table 4.2**, final polymers exhibited much higher molecular weights which indicated that the step-growth polymerizations were successful. As expected, with the increase in molecular weights, the final polymers in **Table 4.2** also showed increased glass transition temperatures and higher decomposition temperatures than the oligomers.

4.7.3 Solution Polymerization of Biphenol based PAESs



Scheme 4.5 The reaction scheme of the selected model reaction for reaction parameter study

The main reason why solution polymerization was investigated in this chapter is that only low molecular weight polymer products were obtained with the pseudo-interfacial method. This is due to the limited solubility of the final products and possible side reactions mentioned in section **4.4.4**. High molecular weight bisphenol-A based *trans*-1,4-cyclohexylene ring containing PAESs were easily obtained with the solution method (as shown in the middle section of **Table 4.2**), however, reactions with biphenol based oligomers were not straightforward.

Table 4.5 Reaction parameter study of biphenol (BP) based PAES based on terephthaloyl chloride (TC) by solution method

Polymers	Solvent	Base	Reaction Temp. (^oC)	Reaction Time	M_n[1] (x10^3 g mol^{-1})	M_w (x10^3 g mol^{-1})	PDI
BP_TC	DMAc	5eqDMAP	100	12h	3.3	5.5	1.7
BP_TC	DMAc	10eqDMAP	165	12h	3.9	7.2	1.8
BP_TC	NMP	No base	100	12h	4.1	7.6	1.8
BP_TC	NMP	2eq TEA	100	12h	3.9	7.0	1.8
BP_TC	NMP	2eq TEA	100	24h	3.4	5.9	1.7
BP_TC	1,1,2,2-tetrachloroethane	2eq TEA	100	12h	15.1	33.1	2.2

[1] NMP as the SEC solvent with a refractive index detector and a viscometer

The reaction shown in **Scheme 4.5** was selected as the model reaction to study the reaction parameters (listed in the scheme) that can potentially affect molecular weight. This reaction was selected because terephthaloyl chloride is commercially available with high purity.

A systematic study of the reaction parameters was performed and the conditions and molecular weight results are listed in **Table 4.5**. The reaction parameters studied are base used, reaction solvent, reaction temperature and reaction time. As shown, the reactions with TEA and 4-dimethylaminopyridine (DMAP) were studied. The base used has little effect on the final molecular weight. When the solvents were DMAc and NMP, only low molecular weight products were obtained independent of the type of base used, the reaction time and temperature. These results agreed well with the observation that has been previously published.[11] High molecular weight products were obtained when 1,1,2,2-tetrachloroethane was used as the solvent. This is because 1,1,2,2-tetrachloroethane offers good solubility for both the starting materials and final polymer products. It is also hydrophobic so that it can be easily dried, which prevents the side reaction of the acid chloride compounds with water.

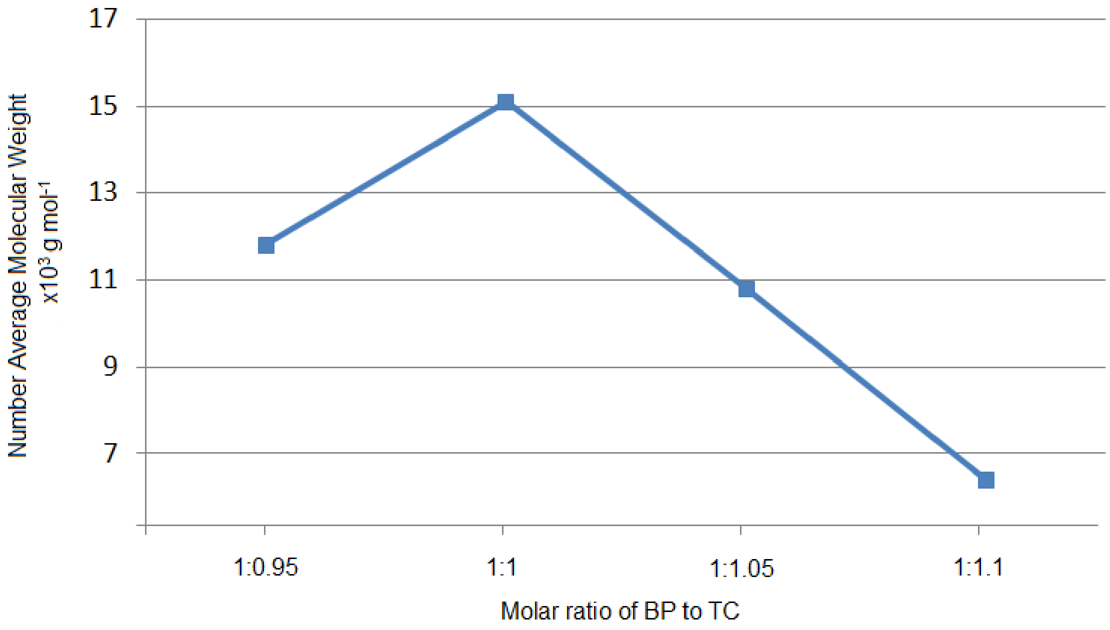


Figure 4.12 The relationship between the molar ratio of the starting materials and the final product number average molecular weight of the model reaction

Table 4.6 The reaction stoichiometry ratio study of biphenol (BP) based PAES and terephthaloyl chloride (TC) by solution method

Polymers[1]	Molar ratio[2] BP to TC	M_n[3] ($x10^3$ g mol^{-1})	M_w ($x10^3$ g mol^{-1})	PDI
BP_TC	1.00:0.95	11.8	24.2	2.0
BP_TC	1.00:1.00	15.1	33.1	2.2
BP_TC	1.00:1.05	10.8	32.5	3.0
BP_TC	1.00:1.10	6.4	15.6	2.4

[1] Reaction conditions were solvent: 1,1,2,2-tetrachloroethane; base: TEA; reaction temp: 100 ^oC; reaction time: 12h

[2] feed ratio

[3] NMP as the SEC solvent with a refractive index detector and a viscometer

A further studied was performed on the 1,1,2,2-tetrachloroethane system where the molar ratio between the biphenol based oligomer (BP) and terephthaloyl chloride (TC) was controlled. It is well known that to obtain high molecular weight in polycondensation polymerization, a 1:1 molar ratio is required. In the model reaction shown in **Scheme 4.5**, it is a concern that because of the possible side reactions of the diacid chloride monomers, mainly hydrolysis, a 1:1 reactant molar ratio may not be the optimum stoichiometry. A series of reaction with different reactant molar ratios were performed. The results shown in **Table 4.6** suggested that the 1:1 stoichiometry ratio still resulted in the polymer product with the highest molecular weight. Polymers with lower molecular weights were obtained with molar ratio imbalance (either excess of BP or excess of TC). **Figure 4.12** shows the relationship between molar ratio of the starting materials and the number average molecular weight of the final product. A clear maximum value was obtained in the curve at the 1:1 stoichiometry ratio.

4.7.4 Crystallinity Study

As shown in **Table 4.1**, melting points were observed by DSC in the biphenol based *trans*-1,4-cyclohexylene ring containing PAESs with the pseudo-interfacial method (described in **4.3.4.3.1**) but not in the bis-A based polymers. **Figure 4.13** and **Figure 4.14** summarize the T_g and T_m data (in **Table 4.1**) of bis-A based polymers and biphenol based polymer respectively. When bis-A was used (**Figure 4.13**), only glass transition temperatures were observed. With the incorporation of the *trans*-1,4-cyclohexylene ring units, a clear trend of the decreasing glass transition temperatures can be clearly observed.

When biphenol was used, both glass transition temperatures and melting temperatures were observed. As shown in **Figure 4.14**, the T_g and T_m of the biphenol based PAESs were described by the solid line and the dashed line respectively. A similar decreasing trend of the glass transition temperatures was observed. With little difference in the melting transition temperatures as described by the dash line, the temperature differences (ΔT) between T_g and T_m showed a clear sequence of BP_TC > BP_CHDC > BP_TCT > BP_CCC.

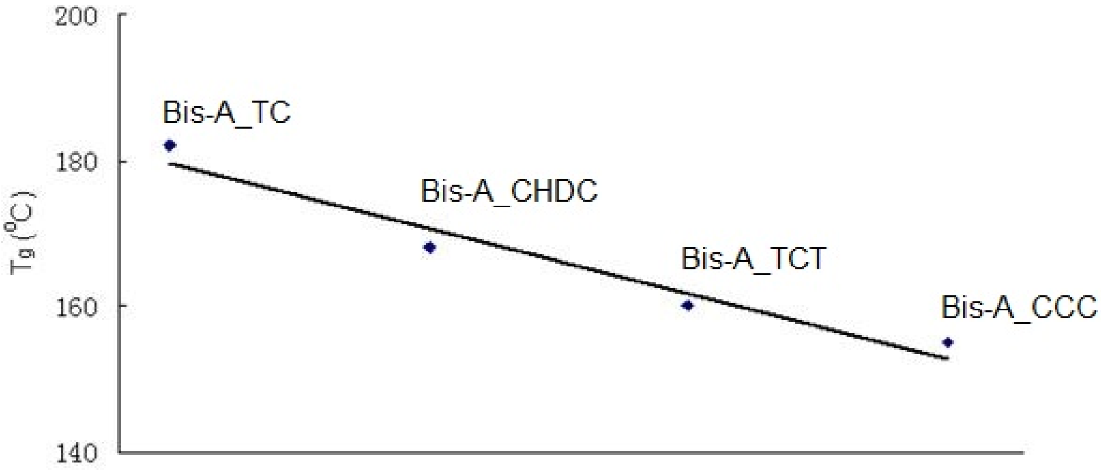


Figure 4.13 The glass transition temperatures (T_g) of the bisphenol-A based *trans*-1,4-cyclohexylene ring containing PAESs by pseudo-interfacial polymerization

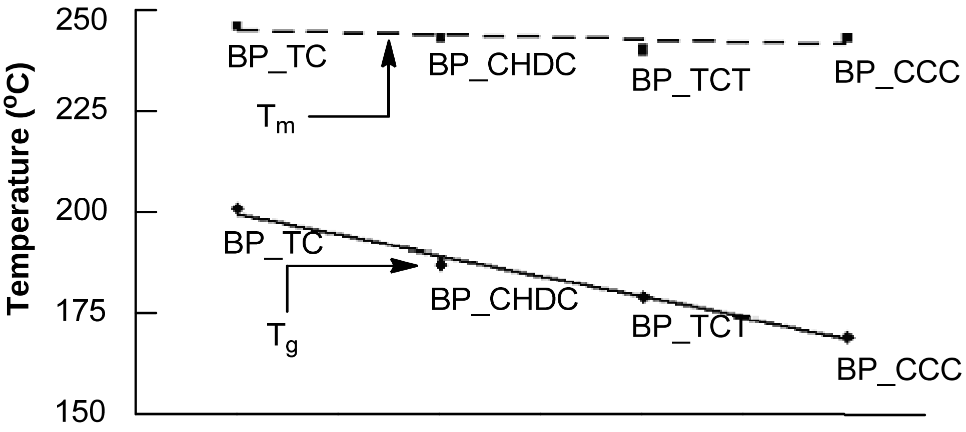


Figure 4.14 The glass transition temperatures (T_g, solid line) and melting temperatures (T_m, dashed line) of the biphenol based *trans*-1,4-cyclohexylene ring containing PAESs by pseudo-interfacial polymerization

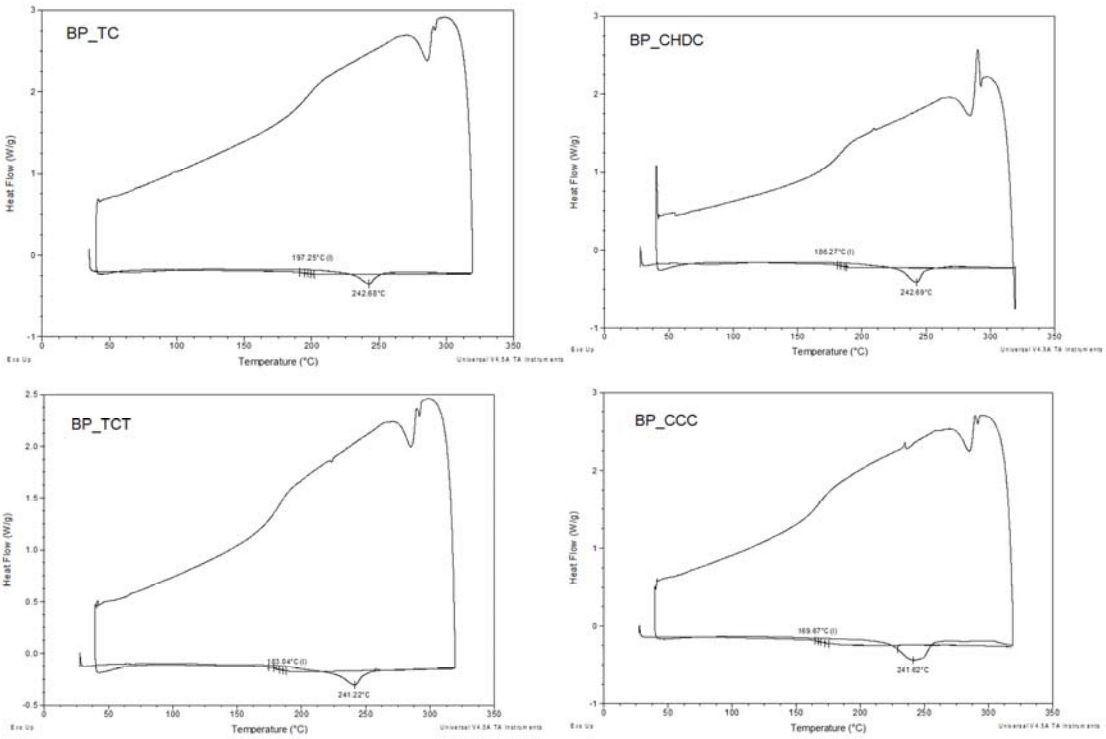


Figure 4.15 DSC curves of the biphenol based *trans*-1,4-cyclohexylene ring containing PAESs with the pseudo-interfacial method (TA Q2000 heating rate 10 °C/min, cooling quench)

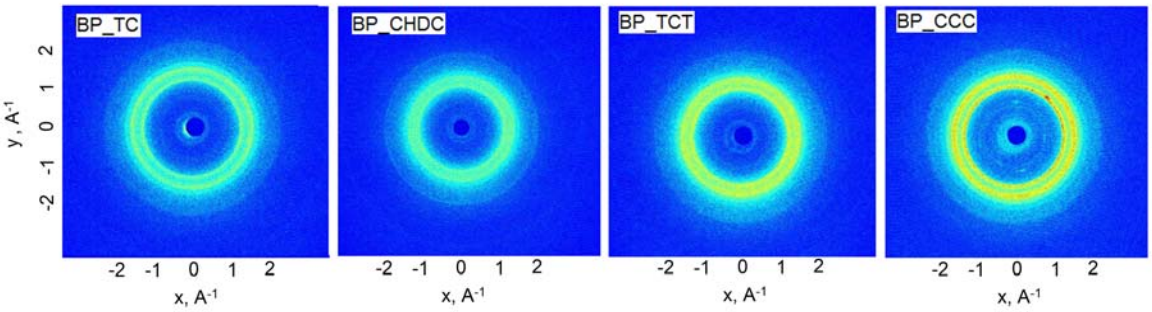


Figure 4.16 The wide angle X-ray diffraction patterns of biphenol based *trans*-1,4-cyclohexylene ring containing PAESs with the pseudo-interfacial method

The crystallinity of the biphenol based PEASs was confirmed by the WAXD results. The DSC curves and WAXD patterns are shown in **Figure 4.15** and **Figure 4.16**. In the DSC curves, distinct glass transition temperatures and melting transition temperatures were observed. The four polymers showed similar WAXD patterns, which indicated semi-crystallinity in the samples.

Table 4.7 The enthalpy of melting for biphenol based *trans*-1,4-cyclohexylene ring containing PAESs with the pseudo-interfacial method

Polymers	BP_TC	BP_CHDC	BP_TCT	BP_CCC
Enthalpy of melting (J/g)	16.6	26.1	26.3	41.3

With the DSC curves in **Figure 4.15**, the values for the enthalpy of melting for the biphenol based *trans*-1,4-cyclohexylene ring containing PAESs were calculated based on the integral area of the melting transition. The results are shown in **Table 4.7**. For these polymers, it is not possible to calculate the percentage of crystallinity from the enthalpy of melting data since biphenol based PAES oligomers may or may not participate in the crystallization. However, simple comparison can be made with other semi-crystalline polymers that have similar structures. The enthalpy of fusion of polyethylene terephathalate is 140 J/g; the enthalpy of fusion of polybutylene terephathalate is 145 J/g; and the enthalpy of fusion of polyetheretherketone is 130 J/g (with a percentage of crystallinity of 30-35 %).[30,31] Compared to those semi-crystalline polymers, the biphenol based *trans*-1,4-cyclohexylene ring containing PAESs obtained by the pseudo-interfacial method exhibited low percentage of crystallinity.

4.7.5 Poly(arylene ether sulfone)s with *trans*-1,4-Cyclohexylene Ring Containing Ester Linkages based on Bisphenol-A PAES Oligomers with 2.0, 4.0, 6.0 kg/mol Molecular Weights

In this section, the tensile properties of the poly(arylene ether sulfone)s with *trans*-1,4-cyclohexylene ring containing ester linkages were studied based on bisphenol-A PAES oligomers with different molecular weights. In the **4.3.4.1** section, the oligomers were synthesized with target number average molecular weights of 2.0 kg/mol. With a similar synthetic method, the bisphenol based PAES oligomers with 4.0 kg/mol and 6.0 kg/mol of target molecular weights were synthesized. The ^{1}H NMR and end group analysis are shown in **Figure 4.17** and **Figure 4.18**. In the end group analysis the protons A' and C were used to determine the number average molecular weights. The M_ns were 3.8 kg/mol and 5.3 kg/mol which were close to the targets.

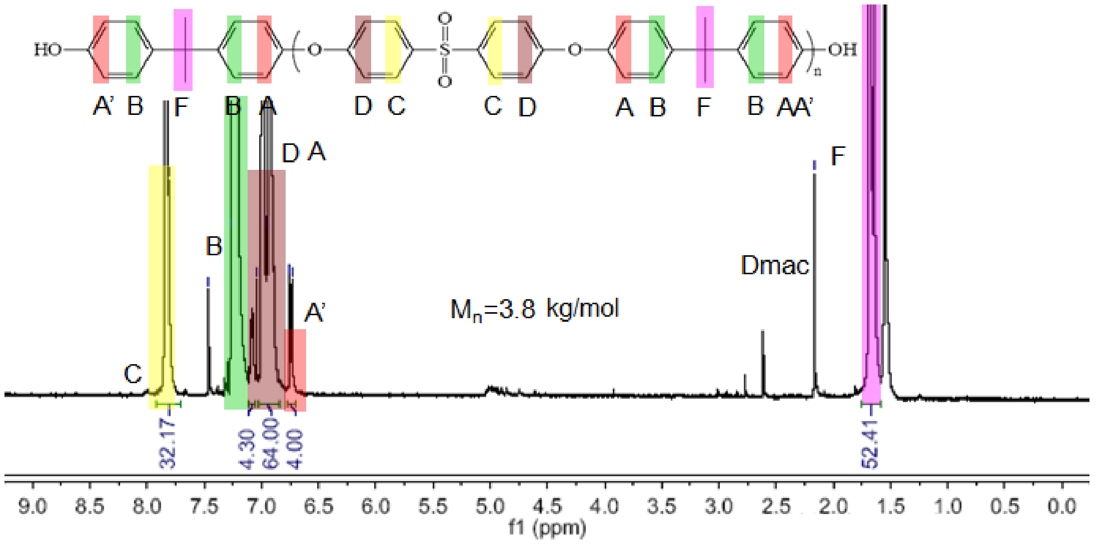


Figure 4.17 ^{1}H NMR spectrum of a bisphenol-A based PAES oligomer with 4.0 kg/mol target number average molecular weight (in $CDCl_3$)

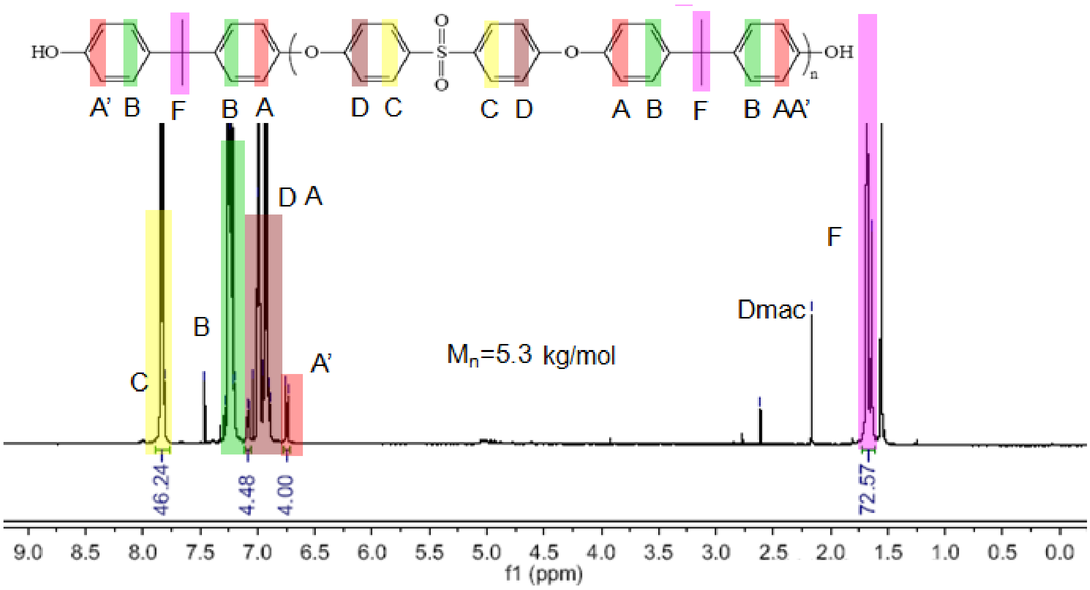


Figure 4.18 ^{1}H NMR spectrum of a bisphenol-A based PAES oligomer with 6.0 kg/mol target number average molecular weight (in $CDCl_3$)

Table 4.8 The molecular weights and thermal properties of bisphenol-A based PAESs with ester linkages

Polymers	M_n[1] ($\times10^3$ g mol^{-1})	M_w ($\times10^3$ g mol^{-1})	PDI	Ester groups per sulfone repeat unit
2KBis-APAES_TC	24.6	49.9	2.0	5.6
4KBis-APAES_TC	40.6	61.1	1.5	9.2
6KBis-APAES_TC	36.9	54.7	1.5	8.3
2KBis-APAES_CHDC	17.7	39.8	2.2	4.0
4KBis-APAES_CHDC	28.2	48.0	1.7	6.4
6KBis-APAES_CHDC	42.9	63.2	1.5	9.7

[1] NMP as the SEC solvent with a refractive index detector and a viscometer

After the oligomers were characterized, the solution polymerization was performed as described in **4.3.4.3.2**. Given the ease of obtaining the two monomers, terephthaloyl chloride (TC) and *trans*-1,4-cyclohexanedicarbonyl chloride (CHDC) were selected. The molecular weights of the two PAES series are shown in **Table 4.8**. The main purpose of making PAES oligomers with higher molecular weights is to study their effect on the mechanical properties. It is important to obtain high molecular weight samples. The PAES samples in **Table 4.8** showed high molecular weights, which ensure that there is no molecular weight effect on the mechanical properties.

Table 4.9 The tensile test results of bisphenol-A based PAESs with ester linkages

Polymers	Modulus (MPa)	Yield Stress (MPa)	Yield Stress (MPa)	Strain at Failure (%)
2KBis-APAES_TC	973±96	54.6±2.8	11.7±3.1	14.0±3.3
4KBis-APAES_TC	1155±34	61.7±5.8	12.7±1.5	15.4±3.9
6KBis-APAES_TC	829±25	65.6±4.0	13.5±0.9	14.8±1.1
2KBis-APAES_CHDC	953±43	65.8±2.4	13.1±0.5	14.1±1.3
4KBis-APAES_CHDC	975±56	61.2±4.7	11.8±1.8	13.9±3.6
6KBis-APAES_CHDC	-	-	-	-

The tensile test results of ester linkage containing PAES based 4.0 kg/mol and 6.0 kg/mol oligomers, TC, and CHDC are shown in

Table 4.9. Independent of the oligomer molecular weights and the acid chlorides used, the polymer samples exhibited very similar modulus, yield stress, yield stress, and strain at failure values. No further study was done with TCT, CCC, and BP based PAES oligomers due to the mechanical property independency of the oligomer molecular weight.

4.7.6 Molecular Weight Analysis based on Film Preparation Method

The film samples of the ester linkage containing PAESs were prepared by casting film from solution. Compression molded films were also prepared. A series of film samples from high molecular weight ester linkage containing PAESs were prepared by compression molding method. The typical procedure is described below. A PHI compression molding press was used and preheated to 50 ^{o}C above the glass transition temperature for amorphous polymers or 50 ^{o}C above melting temperature for semi-crystalline polymers. The polymer sample was evenly dispersed in a small area between two stainless steel plates which were later compressed by the machine at a pressure of 600 psi for 10 min at the set temperature. Then the set of plates was cooled to room temperature and the film sample was separated from the plates.

Figure 4.19 shows a picture of a typical film sample by compression molding. In the picture, there was a piece of polymer film covering some handwriting on a piece of paper. A clear film was obtained with light yellow color. A series of ester linkage containing polymers based on bisphenol-A PAES oligomers, TC, and CHDC was made and the film samples of these polymers were prepared with the compression molding method and the solution method described in **4.3.4.4.** The film samples were then submitted for molecular weight analysis. The molecular weight results are shown in

Table 4.10. All the polymers were predried in a vacuum oven (-80 kPa) at 120 ^{o}C for 12 h. The compression molding temperatures were in the vicinity of 250 ^{o}C for these high glass temperature amorphous polymers. Examination of the table showed a significant molecular decrease for all the polymer samples listed. This indicated even with predried polymer samples, the elevated temperature of the compression molding can cause significant molecular weight decrease probably due to the hydrolysis reaction of the backbone ester groups with residual water in the polymers.

Figure 4.19 A typical film sample by compression molding

Table 4.10 The film sample molecular weight data of bisphenol-A based PAESs with ester linkages with solution casting and compression molding

Polymers[1]	Solution Method			Compression Molding		
	M_n[2]	M_w	PDI	M_w	M_w	PDI
2KBis-APAES_TC	24.6	49.9	2.0	15.6	32.6	2.1
4KBis-APAES_TC	40.6	61.1	1.5	25.1	44.3	1.3
6KBis-APAES_TC	36.9	54.7	1.5	26.2	38.3	1.5
2KBis-APAES_CHDC	17.7	39.8	2.2	17.3	33.8	2.0
4KBis-APAES_CHDC	28.2	48.0	1.7	22.2	37.6	1.7
6KBis-APAES_CHDC	42.9	63.2	1.5	22.9	33.7	1.5

[1] NMP as the SEC solvent with a refractive index detector and a viscometer

[2] the unit of the molecular weights are kg/mol

Figure 4.20 Picture of a typical *trans*-1,4-cyclohexylene containing PAES film sample by solvent casting

Due to this failure of film making with compression molding method, all the film samples were prepared with solution casting method. A typical *trans*-1,4-cyclohexylene containing PAES film sample by solvent casting is shown in **Figure 4.20**. In the picture, a piece of polymer film is coving a piece of paper with the name and logos of Virginia Tech and MII. As shown, the polymers offered transparent tough films with no color or light yellow color.

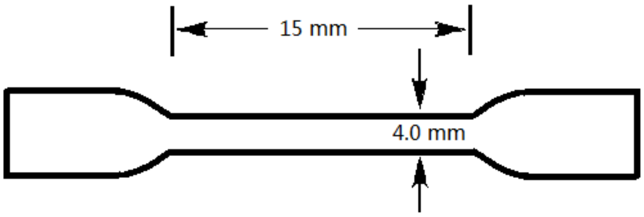


Figure 4.21 Dimension parameters of the dog bone sample

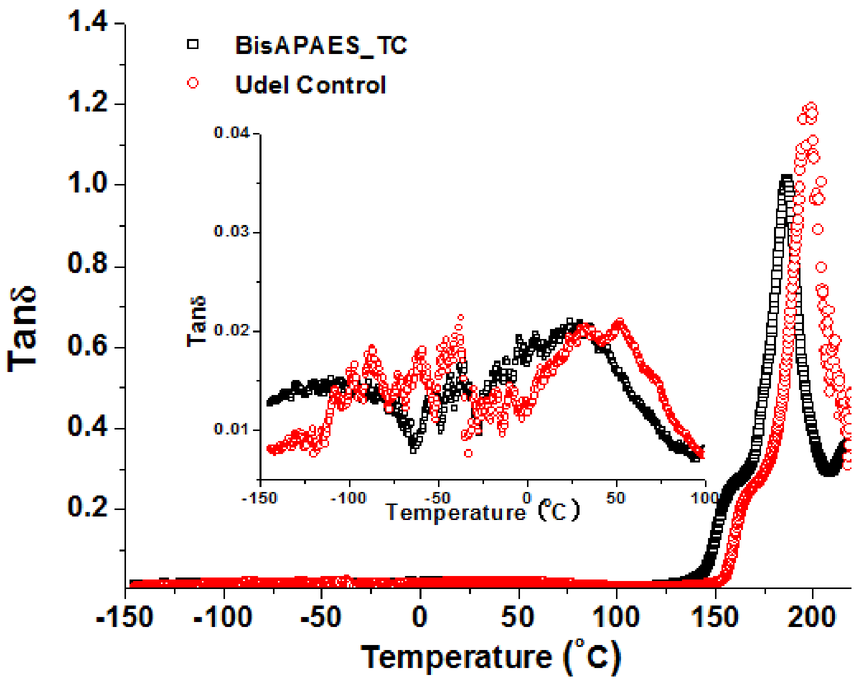


Figure 4.22 DMA curves of the bis-A based terephthaloyl containing PAES and the Udel® control

Dog bone samples were made from the film samples with a mold. As shown in **Figure 4.21**, the dimension parameters of the dog bone sample were 4.00 mm in width and about 15 mm in length. The thickness of the samples was in the range of 60-100 μm.

Figure 4.6 shows the DMA comparison of the terephthaloyl containing PAES and the 1,4-*trans*-cyclohexylene ring containing PAES. It can be clearly observed that at low temperature range, 1,4-*trans*-cyclohexylene ring containing PAES exhibited a larger relaxation. Neither terephthaloyl containing PAES nor the Udel® control showed significant low temperature relaxations (shown in **Figure 4.22**). This result is a strong support information which indicated that the sub-T_g relaxation was due to the incorporation of the 1,4-*trans*-cyclohexylene ring units.

4.7.7 Solid State NMR Study on the Biphenol based *trans*-1,4-Cyclohexylene Ring Containing PAESs

By using solid state NMR (SSNMR) technique**,** the T_1 relaxation time was studied for the biphenol based *trans*-1,4-cyclohexylene ring containing PAESs listed in **Table 4.1**. The method of T_1 relaxation measurement will be introduced and the results will be discussed in the following two sections.

4.7.7.1 Inversion Recovery Method for T_1 Relaxation Measurement

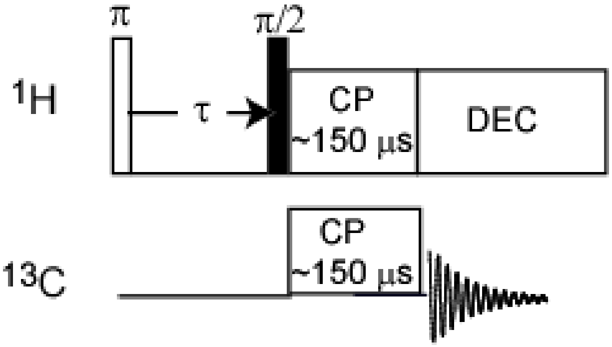


Figure 4.23 Pulse sequence of inverse recovery method for T_1 relaxation measurement

The inverse recovery method in SSNMR was used to measure the T_1 relaxations. The pulse sequence is shown in **Figure 4.23**. Both the proton channel and carbon channel were used. A π pulse is initially applied on the proton channel to direct the initial magnetization to the negative z direction. A delay time τ follows the π pulse. During the delay time, the magnetization recovers back to the original z direction with intensity as a function of delay time τ. Then a $\pi/2$ pulse is applied to redirect the magnetization to the analyzer. After crosspolarization, the proton channel is decoupled and the proton T_1 relaxation signal is detected along the carbon channel.

A series of experiments was performed for each polymer sample with different delay time τ. An illustration is shown in **Figure 4.24**. On the left of **Figure 4.24** is the demonstration of the magnetization magnitude. A series of NMR spectra is shown on the right. Since the magnetization magnitude is a function of the delay time τ, the signal observed (peak intensity on the right of **Figure 4.24**) in the NMR spectra is also a function of it. According to the **Equation 4.1**, the value of $\ln(1-M_z(\tau))$ is a linear function of τ where $1/T_1$ is the slope. Then the T_1 relaxation can be calculated from the peak intensity $M_z(\tau)$ and delay time τ.

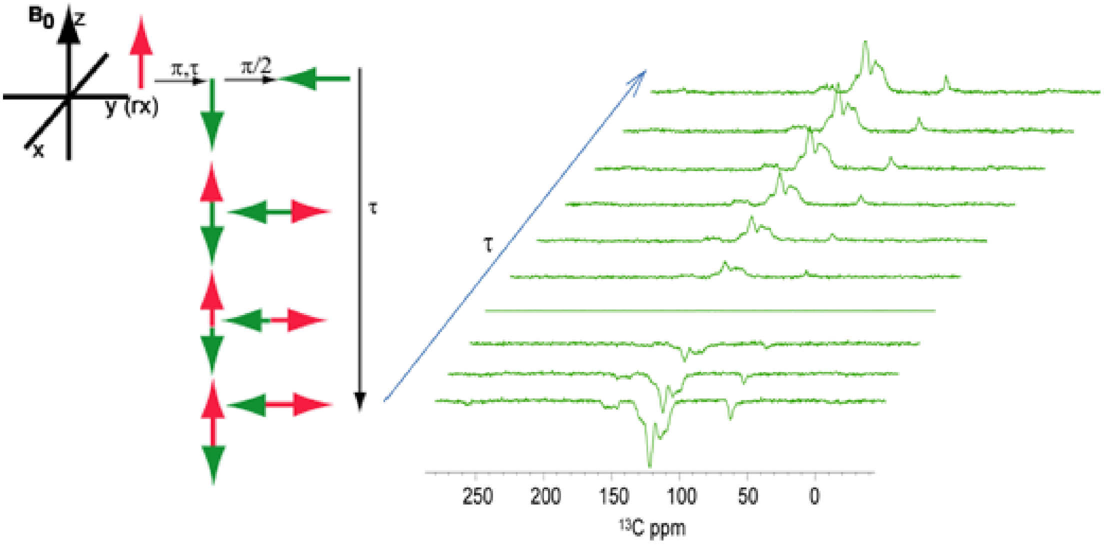


Figure 4.24 A series of NMR spectra for T_1 relaxation measurement

$$\text{Ln}\ (\ 1\text{-}M_z(\tau)\ ) = \text{Ln}(2) - (\tau/T_1)$$

Equation 4.1 Calculation of T_1 relaxations

4.7.7.2 T_1 Relaxation Results of Biphenol based *trans*-1,4-Cyclohexylene Ring Containing PAESs

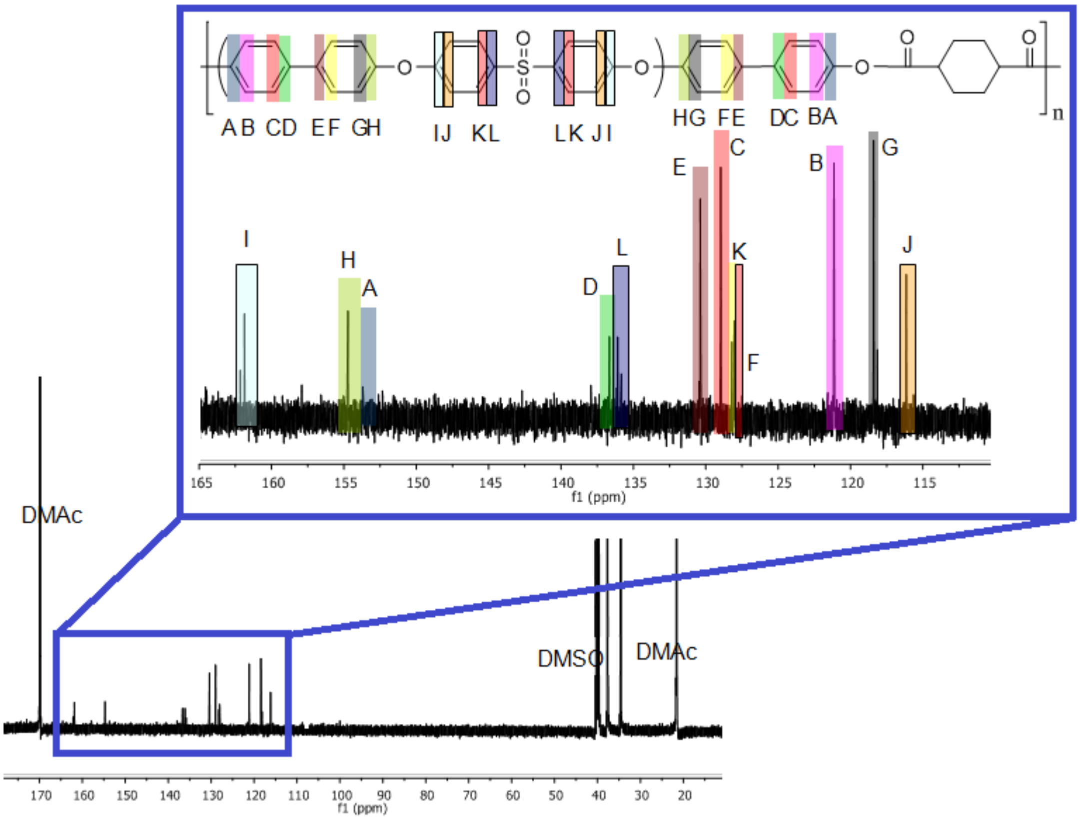


Figure 4.25 ^{1}H NMR spectrum of biphenol based CHDC containing PAES (in DMSO-d6 and non deuterated DMAc)

The T_1 relaxation time was studied on the biphenol based *trans*-1,4-cyclohexylene ring containing PAESs listed in **Table 4.1**. In this series, crystallinity was obtained. The T_1 relaxation analysis is a complimentary study on the molecular dynamics to support some of the results obtained in the DSC experiments.

Solution NMR and peak assignments are required for SSNMR analysis. In **Figure 4.25**, a ^{1}H NMR example of the biphenol based *trans*-1,4-cyclohexylene ring containing PAESs is shown. Because of the crystallinity and rigidity, the polymer samples were not soluble in all common deuterated solvents. The mixed solvents of DMSO-d6 and non deuterated DMAc were used. The enlarged area in **Figure 4.25** is the aromatic area with peak assignments. Two protons with the chemical shift of 118 and 127 ppm (proton G and K) were selected because their signals were well isolated in the SSNMR.

Table 4.11 The T_1 relaxation data of biphenol based PAESs with the pseudo-interfacial method

Polymers	^{1}H{^{13}C T_1 (ns) of BP based PAES			
	BP_TC	BP_CHDC	BP_TCT	BP_CCC
127 ppm (K)	0.42	0.66	0.45	0.27
118 ppm (G)	0.48	0.66	0.43	0.27

The T_1 relaxation data of biphenol based PAESs with the pseudo-interfacial method are summarized in **Table 4.11**. The T_1 relaxation was measured to give information about the local motion.

The glass transition temperatures decreased in the monomer sequence of

TC>CHDC>TCT>CCC (monomer structures and thermal properties are shown in **Figure 4.1** and **Table 4.1**). The T_1 relaxations decreased in the monomer sequence of CHDC>TC~TCT>CCC. They did not show exact correlation. There were two different factors from the 1,4-*trans*-cyclohexylene ring units. One was the chain flexibility effect.[32,33] The 1,4-*trans*-cyclohexylene ring can undergo conformational transition which results in a more flexible backbone when compared to the aromatic analogue. The other factor was the packing improvement effect. Due to the linearity of the 1,4-*trans*-cyclohexylene ring, it has been reported that it can improve the chain packing when compared to the aromatic analogue.[20]

The hypothesis is based on the chain flexibility effect and the packing improvement effect. In the glass transition sequence, the TC monomer, which is the whole aromatic one, gave highest T_g because no 1,4-*trans*-cyclohexylene ring was incorporated, there is less chain flexibility. As the 1,4-*trans*-cyclohexylene ring was incorporated, a decreasing glass transition was found as expected.

The T_1 results are strongly affected by both the chain flexibility effect and the packing improvement effect. When the TC and CHDC containing polymers were compared, the CHDC did have a more flexible backbone, however the chain local motion was largely restricted by the strong packing improvement effect which resulted in a larger T_1 value. In the case of TCT, the two factors balanced out resulting in a similar T_1 value to the TC containing samples. When three continuous 1,4-*trans*-cyclohexylene was incorporated in the monomer CCC, the chain flexibility effect dominated and ended up with the smallest T_1 value.

4.7.8 Dynamic Light Scattering Study of Biphenol based *trans*-1,4-Cyclohexylene Ring Containing PAESs

A dynamic light scattering (DLS) was employed to determine the hydrodynamic radium of the various PAESs by the polymer solution analysis. The hydrodynamic radius can be directly measured by DLS in a certain solvent. Assuming in the same solvent, the same polymer chains have the same geometry in the diluted solution, the hydrodynamic radius is in direct proportion to the radius of gyration which is related to the rigidity indicator α (the Mark-Houwink constant).

Table 4.12 Dynamic light scattering study results of Biphenol based *trans*-1,4-cyclohexylene ring containing PAESs[1]

Polymers	Hydrodynamic Diameter (nm)	Volume %
BP_TC	59.2	100
BP_CHDC	40.2	72
BP_TCT	34.9	80
BP_CCC	25.9	78

[1] DLS was perform in dilute DMF solutions with concentrations of 5 mg/mL

The DLS experiment was performed at room temperature on a ZETA SIZER Nano ZS instrument from MALNERN instruments. Quartz cells were used to hold the diluted polymer solution. The polymer solutions were prepared as follows. With a concentration of 5 mg/mL, polymers were dissolved in DMF at room temperature with vigorous stirring until a clear solution was obtained. To remove any aggregates, the polymer solutions were filtered through a 0.45 mm micro glass filter before testing.

The DLS results are listed in **Table 4.12**. When multiple hydrodynamic diameter values were observed (as shown in **Figure 4.30**, **Figure 4.31**, and **Figure 4.32** in the Appendix), the one with the highest volume percentage was selected. The volume fractions are listed in the last column in **Table 4.12**. As shown, the volume fraction values were observed to be higher than 70 % which indicated that the hydrodynamic diameter values were true for the major population of the polymer particles in the dilute solution.

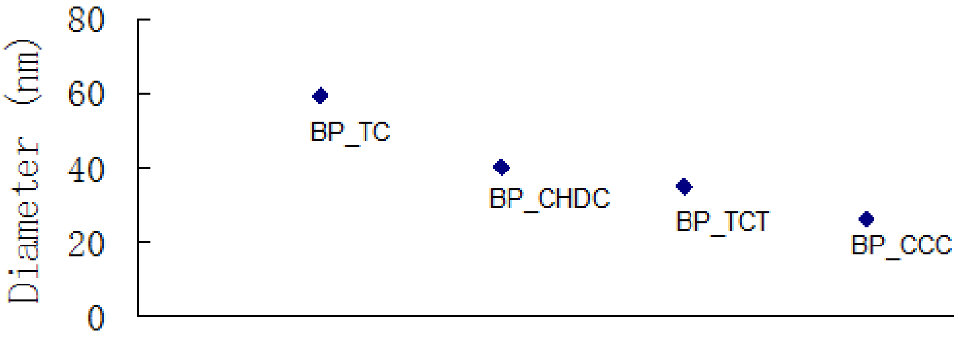


Figure 4.26 Hydrodynamic diameter values of biphenol based *trans*-1,4-cyclohexylene ring containing PAESs

A plot of the hydrodynamic diameter values is shown in **Figure 4.26**. Clear decreases in hydrodynamic diameter values were observed in the monomer sequence of TC>CHDC>TCT>CCC which is the same as the decreasing sequence of the glass transition temperatures (**Table 4.1** and **Figure 4.14**). Given the fact that the molecular weights of the polymer samples were very similar, higher hydrodynamic diameter may indicate a higher Mark-Houwink constant, thus a more rigid polymer conformation in the dilute solution. The hydrodynamic diameter decreasing sequence of TC>CHDC>TCT>CCC may lead to rigidity decreasing in the same sequence. This preliminary statement agrees with the glass transition results very well. However, the Mark-Houwink constant calculated by SEC measurements (as shown in **Table 4.13**) showed a slightly different sequence of CHDC>TC>TCT>CCC. This sequence if the same as the T_1 relaxation sequence observed in **Table 4.11**. Further investigation is needed.

Table 4.13 Mark-Houwink constants of the biphenol based *trans*-1,4-cyclohexylene ring containing PAESs calculated by SEC measurements

Polymer	BP_TC	BP_CHDC	BP_TCT	BP_CCC
Mark-Houwink constant	0.63	0.70	0.56	0.52

4.8 Future Work

In this part of the dissertation, some research ideas that can potentially expand the current research will be introduced. These ideas are independent but may overlap with the literature.

4.8.1 New Monomers with Cyclobutane Ring and Amide Linkages

A natural extension of the current research is to make new monomers with the current methodology. **Figure 4.27** lists three very interesting monomers. The first is based on 2,2,4,4-tetramethylcyclobutane-*trans*-1,3-diol (TMCD). This monomer led to a very successful commercialization of the Tritan^{TM} polyester by Eastman Chemical Company. TMCD is believed to provide very good toughness to the polymer. The second and third monomers are based on diamine monomers (1,4-phenylenedimethanamine and 1,4-phenylenediamine respectively). The idea of introducing the amine starting material is to form amide linkages to provide strong intermolecular interaction between polymer chains. This strong intermolecular interaction may further promote crystallinity in the PAES based systems.[13,34-37] However, the synthesis and isolation of these monomers can be challenging due to the limited solubility of the starting materials.

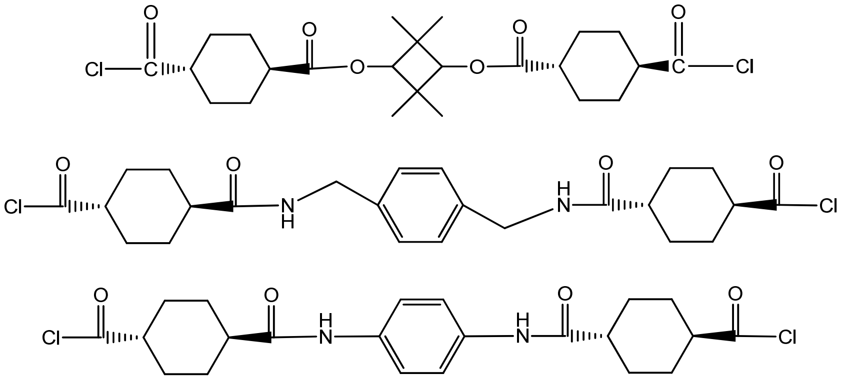
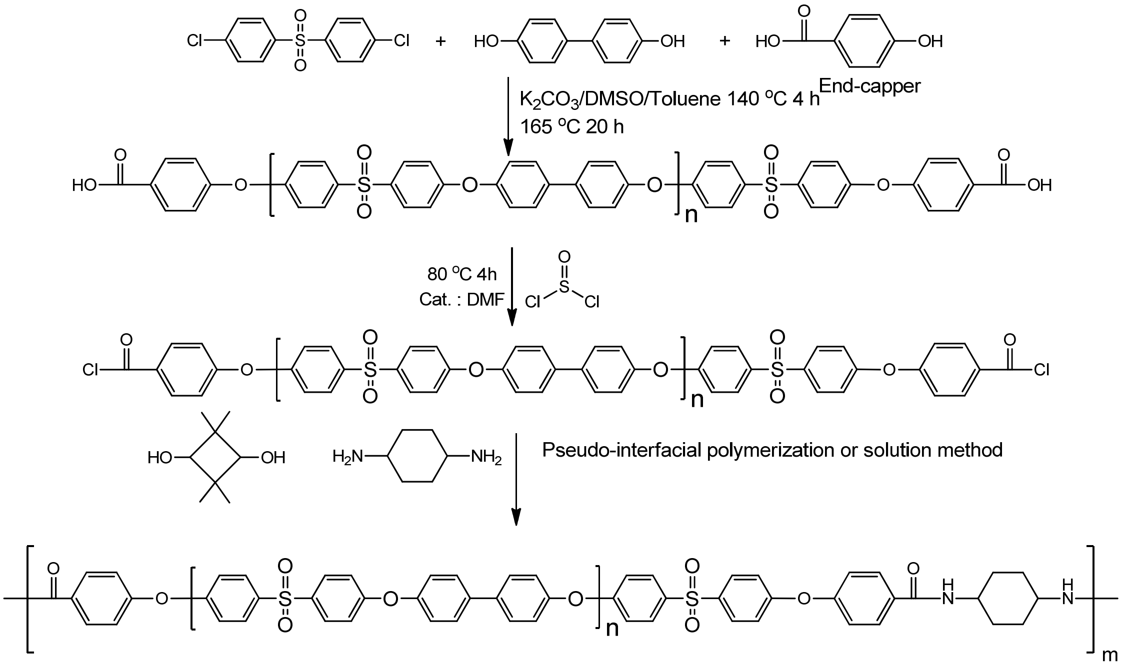


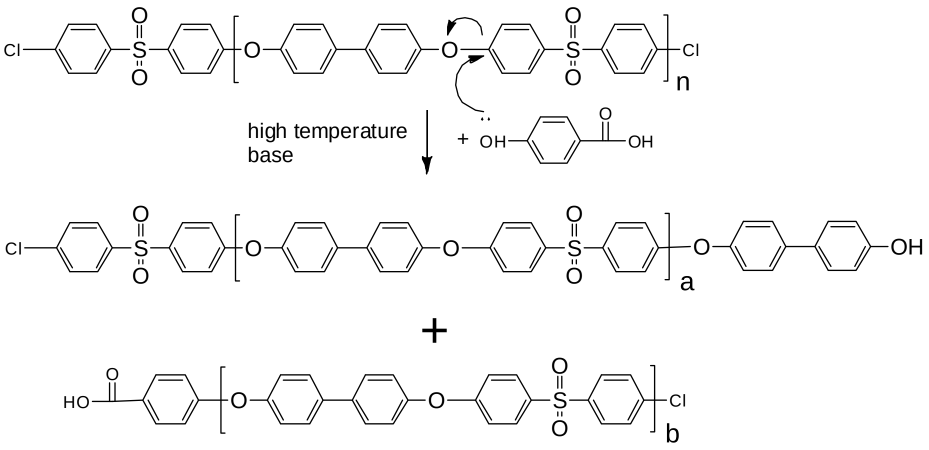
Figure 4.27 The structure of cyclobutane ring containing acid chloride monomer and cyclohexylene ring containing monomer with amide linkages

4.8.2 Polymer Modification with Acid Chloride End Groups

If the monomers shown in **Figure 4.27** are too hard to either synthesis or isolate, an alternative way to achieve a similar chemistry is proposed in **Scheme 4.6**. The PAES oligomers will be endcapped with acid functionality which can be later converted to acid chloride by treatment of thionyl chloride. Due to the high reactivity the PAES oligomer with acid chloride groups can easily react with diols and diamines. Examples given in **Scheme 4.6** are TMCD and -1,4-cyclohexanediamine. The polymerization reaction can be done in solution or in pseudo-interfacial fashion. In this way, both the cyclobutane ring units and the amide linkages can be incorporated into the backbone of the polymers.



Scheme 4.6 Polymer modification with acid chloride end groups and the subsequent aliphatic ring incorporation



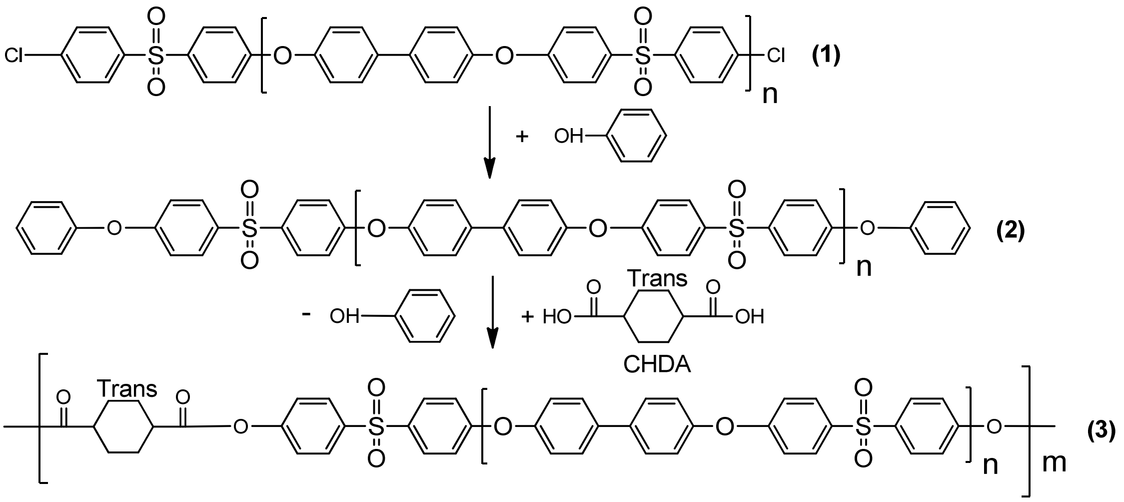
Scheme 4.7 A side reaction that can reduce the oligomer molecular weight (a<n and b<n)

The end capping reaction shown in **Scheme 4.6** may introduce side reactions as shown in **Scheme 4.7** if it is done in two separate steps. This side reaction can reduce the molecular weight of the oligomer. A careful model reaction study and carefully molecular weight determination based on NMR end group analysis need to be performed.

4.8.3 Polymer Modification with Chlorine End Groups

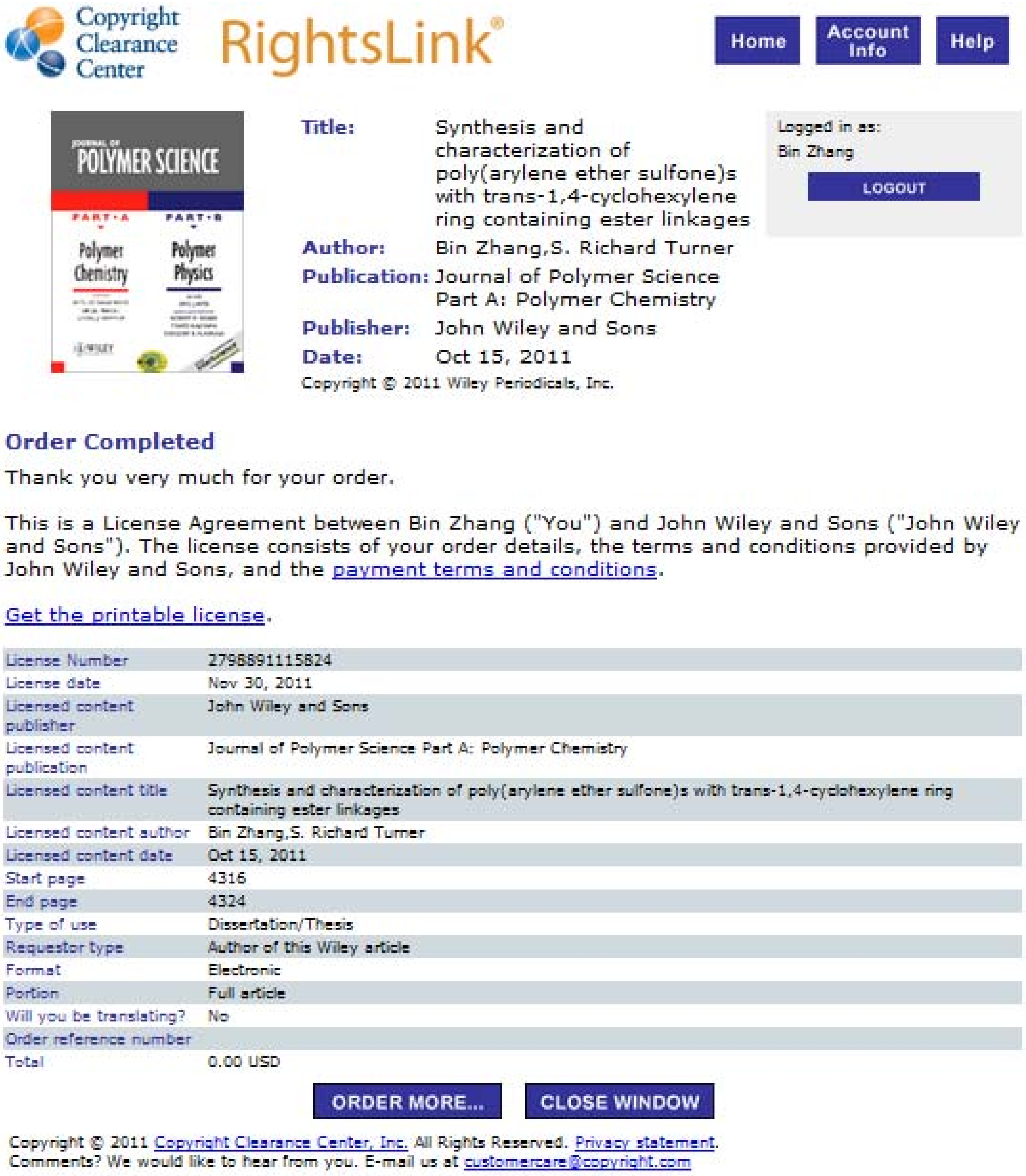
Most the research documented in this chapter is based on hydroxyl terminated PAES oligomers or polymers. The incorporation of *trans*-1,4-cyclohexylene ring can also be achieved by designing PAES oligomers with chlorine end groups. A reaction scheme is shown in **Scheme 4.8**. The chlorine end groups in the PAES oligomers with controlled molecular weights can be achieved by using excess amount of DCDPS based on the Carothers equation. The reaction conditions will be similar to the ones reported early in

4.3.4.1. Then the end chlorine groups can be further modified into oxyphenyl groups by reacting with phenol under the same conditions. The incorporation of *trans*-1,4-cyclohexylene ring units can be achieved by high temperature melt polymerization with CHDA. The condensed small molecule in this reaction would be phenol which may require fairly high reaction temperature and high vacuum. A side reaction can occur to possibly reduce the oligomer molecular weight in a similar way as shown in **Scheme 4.7**.



Scheme 4.8 Polymer modification with chlorine end groups and the subsequent cyclohexylene ring incorporation

4.9 Copyright Authorization



Title: Synthesis and characterization of poly(arylene ether sulfone)s with trans-1,4-cyclohexylene ring containing ester linkages
Author: Bin Zhang,S. Richard Turner
Publication: Journal of Polymer Science Part A: Polymer Chemistry
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4.10 Appendix

Some key spectra and original data will be presented in this section.

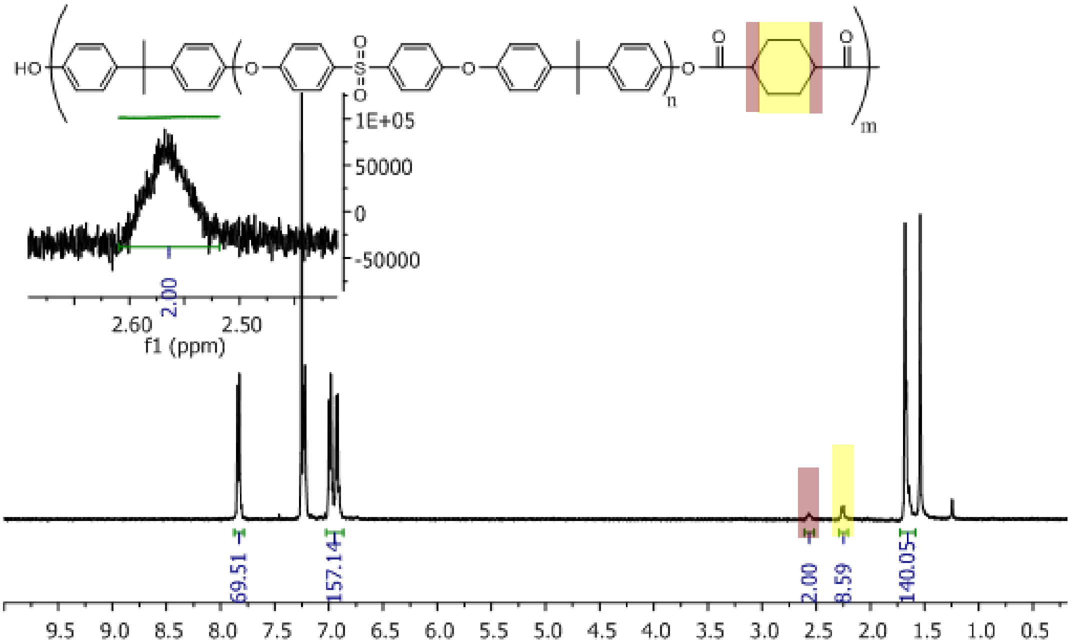
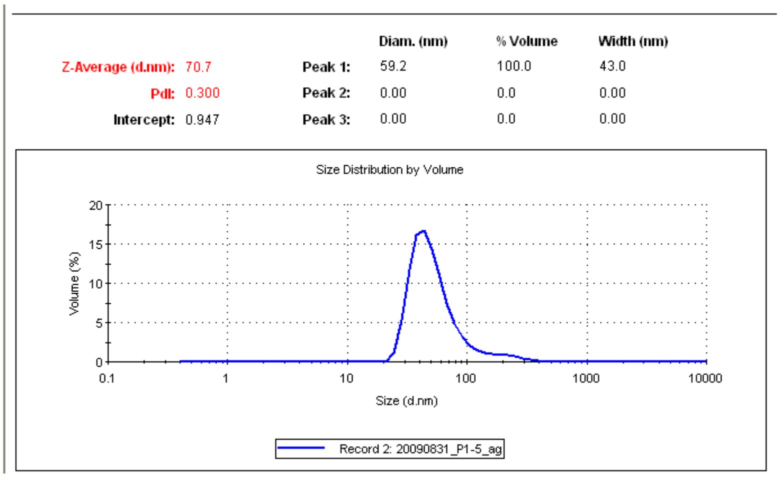
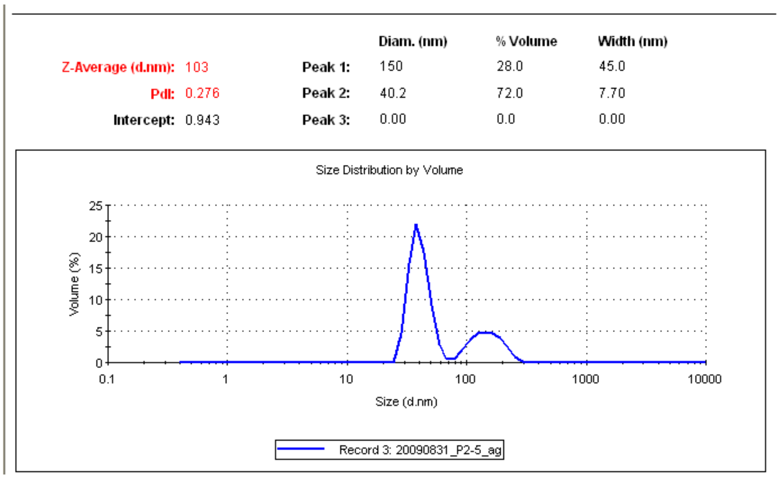


Figure 4.28 A typical ^{1}H NMR of structure of soluble poly(arylene ether sulfone)s with *trans*-1,4-cyclohexylene ring containing ester linkages (confirm the *trans*-conformation)



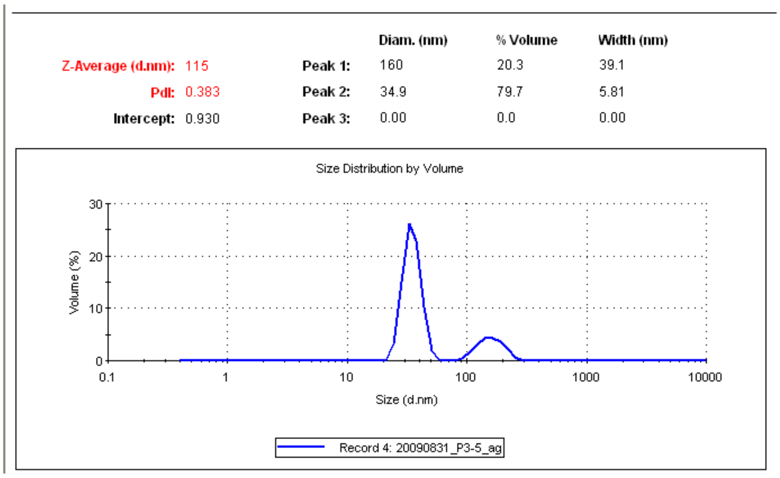
			Diam. (nm)	% Volume	Width (nm)
Z-Average (d.nm):	70.7	Peak 1:	59.2	100.0	43.0
PdI:	0.300	Peak 2:	0.00	0.0	0.00
Intercept:	0.947	Peak 3:	0.00	0.0	0.00

Figure 4.29 The dynamic light scattering curve of BP_TC polymer sample in **4.7.8**



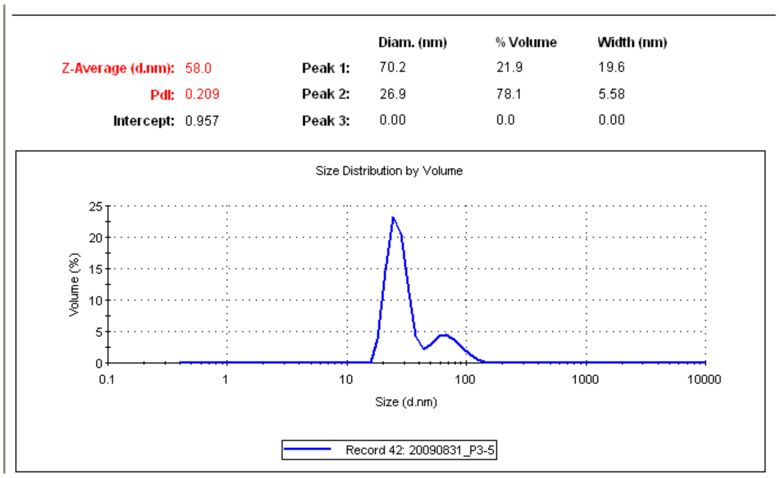
			Diam. (nm)	% Volume	Width (nm)
Z-Average (d.nm):	103	**Peak 1:**	150	28.0	45.0
PdI:	0.276	**Peak 2:**	40.2	72.0	7.70
Intercept:	0.943	**Peak 3:**	0.00	0.0	0.00

Figure 4.30 The dynamic light scattering curve of BP_CHDC polymer sample in **4.7.8**



			Diam. (nm)	% Volume	Width (nm)
Z-Average (d.nm):	115	**Peak 1:**	160	20.3	39.1
PdI:	0.383	**Peak 2:**	34.9	79.7	5.81
Intercept:	0.930	**Peak 3:**	0.00	0.0	0.00

Figure 4.31 The dynamic light scattering curve of BP_TCT polymer sample in **4.7.8**



			Diam. (nm)	% Volume	Width (nm)
Z-Average (d.nm):	58.0	Peak 1:	70.2	21.9	19.6
PdI:	0.209	Peak 2:	26.9	78.1	5.58
Intercept:	0.957	Peak 3:	0.00	0.0	0.00

Figure 4.32 The dynamic light scattering curve of BP_CCC polymer sample in **4.7.8**

4.11 Reference

(1) Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F.; Merriam, C. N. *J. Polym. Sci., Part A-1 Polym. Chem.* **1967**, *5*, 2375.

(2) Rose, J. B. *Polymer* **1974**, *15*, 456.

(3) Robeson, L. M.; Farnham, A. G.; McGrath, J. E. *Applied Poly. Symp.* **1975**, *26*, 373.

(4) Matsumoto, K.; Nakagawa, T.; Higashihara, T.; Ueda, M. *Journal of Polymer Science Part a-Polymer Chemistry* **2009**, *47*, 5827.

(5) Lee, H. S.; Roy, A.; Lane, O.; Lee, M.; McGrath, J. E. *Journal of Polymer Science Part a-Polymer Chemistry* **2010**, *48*, 214.

(6) Zoller, P. *J. Polym. Sci., Polym. Phys. Ed.* **1978**, *16*, 1261.

(7) Haussler, L.; Pospiech, D.; Eckstein, K.; Janke, A.; Vogel, R. *Journal of Applied Polymer Science* **1997**, *66*, 2293.

(8) Grundke, K.; Pospiech, D.; Kollig, W.; Simon, F.; Janke, A. *Colloid and Polymer Science* **2001**, *279*, 727.

(9) Cozan, V.; Avram, E. *European Polymer Journal* **2003**, *39*, 107.

(10) Pospiech, D.; Haussler, L.; Jehnichen, D.; Kollig, W.; Eckstein, K.; Grundke, K. *Macromol. Symp.* **2003**, *198*, 421.

(11) Pospiech, D.; Komber, H.; Voigt, D.; Jehnichen, D.; Haussler, L.; Gottwald, A.; Kollig, W.; Eckstein, K.; Baier, A.; Grundke, K. *Macromol. Symp.* **2003**, *199*, 173.

(12) Lambert, J. M.; Webster, D. C.; McGrath, J. E. *Polymer Science and Technology (Plenum)* **1985**, *31*, 93.

(13) Stephen, R.; Gibon, C. M.; Weber, M.; Gaymans, R. J. *J. Polym. Sci., Part A Polym. Chem.* **2009**, *47*, 3904.

(14) Turner, S. R. *J Polym Sci Part A Polym Chem* **2004**, *42*, 5847.

(15) Chen, L. P.; Yee, A. F.; Moskala, E. J. *Macromolecules* **1999**, *32*, 5944.

(16) Scheirs, J.; Long, T. E. *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters*; John Wiley & Sons, Inc.,NY,, 2003.

(17) Berti, C.; Celli, A.; Marchese, P.; Marianucci, E.; Barbiroli, G.; Credico, F. D. *Macromol. Chem. Phys.* **2008**, *209*, 1333.

(18) Kibler, C. J.; Bell, A.; Smith, J. G. *J. Polym. Sci., Part A: Polym. Chem.,* **1964**, *2*, 2115.

(19) Li, X.; Yee, A. F. *Macromolecules* **2004**, *37*, 7231.

(20) Li, X.; Yee, A. F. *Macromolecules* **2003**, *36*, 9421.

(21) Liu, Y. C.; Turner, S. R. *Journal of Polymer Science Part a-Polymer Chemistry* **2010**, *48*, 2162.

(22) Dean, B. D.; Matzner, M.; Tibbitt, J. M. In *Comprehensive Polymer Science*; Geoffrey, A., Bevington, J. C., Eds.; Pergamon Press: Oxiford: 1989; Vol. 5, p 317.

(23) McGrath, J. E.; Matzner, M.; Robeson, L. M.; Barclay, R., Jr. *J. Polym. Sci., Polym. Symp.* **1977**, *60*, 29.

(24) Spano, J.; Zhang, B.; Chen, Y.; Turner, S. R.; Wi, S. *Polymer* **2011**, submitted.

(25) Hoffman, J. D.; Miller, R. L. *Polymer* **1997**, *38*, 3151.

(26) Day, M.; Deslandes, Y.; Roovers, J.; Suprunchuk, T. *Polymer* **1991**, *32*, 1258.

(27) Deslandes, Y.; Sabir, F. N.; Roovers, J. *Polymer* **1991**, *32*, 1267.

(28) Osano, K.; Das, S.; Turner, S. R. *Polymer* **2009**, *50*, 1144.

(29) Chen, L. P.; Yee, A. F.; Goetz, J. M.; Schaefer, J. *Macromolecules* **1998**, *31*.

(30) Bloch, D. R. *Polymer handbook*; New York : John Wiley, 1999.

(31) Wunderlich, B. *Thermal Analysis*; Academic Press, 1990.

(32) Zhang, B.; Turner, S. R. *J. Polym. Sci., Part A: Polym. Chem.,* **2011**, *49*, 4316

(33) Liu, J.; Yee, A. F. *Macromolecules* **2000**, *33*, 1338.

(34) Gibon, C.; Weber, M.; Gaymans, R. J.; Stephen, R. Application: WO

WO 2010-EP57521

2010142548 2010 25pp

(35) Stephen, R.; Gibon, C. M.; Weber, M.; Gaymans, R. J. *J. Polym. Sci., Part*

A Polym. Chem. **2010**, *48*, 63.

(36) Gaymans, R. J. *Prog. Polym. Sci.* **2011**, *36*, 713.

(37) Gaymans, R. J.; van Swaaij, A. W. *J. Appl. Polym. Sci.* **2011**, *119*, 23.

Chapter 5 Poly(arylene ether sulfone)-polyester Multiblock Copolymers with Solution Polymerization and Melt Polymerization Method

5.1 Abstract

Poly(arylene ether sulfone)-polyester multiblock copolymers were synthesized with solution and melt polymerization. In order to incorporate the poly(arylene ether sulfone) (PAES) blocks, the PAES oligomers with phenol end groups and hydroxy ethoxy groups were synthesized. In solution polymerization, PAES oligomers with phenol groups were used to react with polyester oligomers with acid chloride end groups. The molecular weights of the multiblock copolymers with the solution method were limited by the solubility. The melt polymerization was introduced due to this solubility issue where hydroxy ethoxy terminated PAES oligomers were used to react with dimethyl terephthalate and 1,4-cyclohexanedimethanol at high temperature. Multiblock copolymers obtained by the melt reaction with low polyester content (up to 20 wt% polyester content) were soluble and exhibited high molecular weights. The mechanical properties of these polymers were dominated by the PAES blocks resulting in the similar moduli and ultimate elongations as the Udel® control. The multiblock copolymer with polyester weight percentage higher than 20 % exhibited limited solubility and no molecular weight data were obtained. Crystallization was obtained from the multiblock

copolymer with high polyester content. Two melting peaks were observed, which may suggest that the PAES blocks can participate in the polymer chain crystallization.

5.2 Introduction

Multiblock copolymers are important architectures for polymer backbone and have been extensively studied. There block copolymers have structures of $(AB)_n$ where A and B are chemically bonded blocks.[1] One of the major reasons to build the multiblock chain structures is to combine the desirable properties of the A and B blocks.[2-5] The compatibility of the A and B blocks can also significantly affect the properties of the multiblock copolymers.[3,6-11]

PAESs and polyesters are two classes of very important thermoplastics with extremely wide applications.[12-16] The research described in this chapter is to build multiblock copolymers based on PAES blocks and polyester blocks. These two blocks both exhibited glass transition temperatures a lot higher than room temperature. The main intention of the research was to significantly promote crystallinity and enhance the solvent resistance of the PAES containing multiblock copolymers by incorporation of cyclohexylene ring containing polyester blocks without sacrificing the mechanical properties. The property profile of the multiblock copolymers was studied.

The PAES-polyester multiblock copolymers were successfully synthesized via two methods, a solution polymerization method and by melt polymerization. The molecular weight, crystallinity, solubility, thermal properties, and mechanical properties were determined.

5.3 Experimental

5.3.1 Materials

1,4-Cyclohexanedimethanol (CHDM) (all *trans* or *cis/trans* = 30/70) and poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) were donated by Eastman Chemical Company. Udel® sample was provided by Solvay Advanced Polymers L.L.C.. All the other chemicals were purchased from Aldrich. Triethylamine (TEA) and N-methyl-2-pyrrolidone (NMP) were treated with CaH_2 to remove moisture. All the other reagents were used without further purification.

5.3.2 Instrumentation

The ^1H and ^{13}C NMR spectra were obtained on a JEOL 500 (500 MHz) spectrometer at room temperature with chemical shifts relative to tetramethylsilane (TMS). Size exclusion chromatography (SEC) was used to determine the molecular weights and the molecular weight distributions. The data were obtained in either chloroform or NMP at 30 ^{o}C on a Waters Alliance model 2690 chromatograph equipped with a Waters HR 0.5+ HR 2+ HR 3+ HR 4+ styragel column set. The flow rate is 0.500 mL/min. A Viscotek refractive index detector and a viscometer were used for molecular weight determination. Polystyrene standards were utilized to construct a universal molecular weight calibration curve.

The T_gs and T_ms were determined by Differential Scanning Calorimetry (DSC). The data were obtained by using a TA Instruments™ Q2000. Nitrogen was used as the carrier gas with a sample flow rate of 20 mL/min and a heating rate of 10 ^{o}C/min. The

T_gs were determined in the second heating cycle after the samples were quenched at nominally 100 ^{o}C/min during the cooling cycle. The thermogravimetric analysis (TGA) was carried out by a TA Instruments™ Q10 from 25 ^{o}C to 600 ^{o}C under nitrogen at a heating rate of 10 ^{o}C/min. With dog bone samples, tensile properties were obtained from an Instron Model 4400 Universal Testing System with a rate of 2 mm/min at room temperature. All the DMA results were averaged over at least 5 samples.

5.3.3 Synthesis and Modification of Monomer, Oligomers and Polymers

5.3.3.1 Monomer Synthesis

5.3.3.1.1 Synthesis of *trans*-1,4-Cyclohexanedicarbonyl Chloride (CHDC)

The glassware and the stir bar were pre-dried in an oven at 80 ^{o}C for 12 h. To a 250 mL three-necked round bottom flask equipped with a Teflon coated magnetic stir bar, a condenser and an argon inlet, 16.00 g (93.02 mmol) of CHDA, 120.0 mL of thionyl chloride and 0.1 mL of N,N-dimethylformamide (DMF) were added. The reaction was stirred in the presence of argon at 60 ^{o}C for 4 h. Then the excess amount of thionyl chloride was distilled out at 60 ^{o}C with vacuum. White crystals were obtained and dried in a vacuum oven (-80 kPa) at room temperature for 12 h and then kept under argon atmosphere. The product was used directly in the next step without any further purification. The yield was 94.4 %. No melting point was observed due to instability. ^{1}H NMR ($CDCl_3$, ppm): δ 2.73 (m, 2H), δ 2.30 (m, 4H), δ 1.58 (m, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 188.4, 50.6, 30.0.

5.3.3.2 Oligomer Synthesis

5.3.3.2.1 Synthesis of Phenol Terminated Poly(arylene ether sulfone)s Oligomer with Controlled Molecular Weight

The reaction scheme is shown in **Scheme 5.1** and the reaction apparatus set up is shown in **Figure 5.1**.

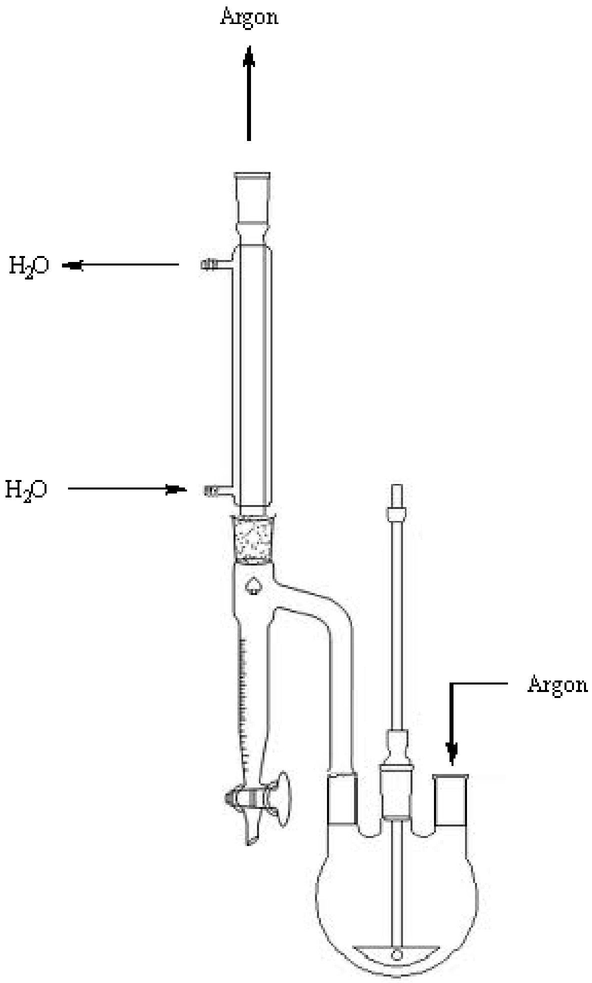
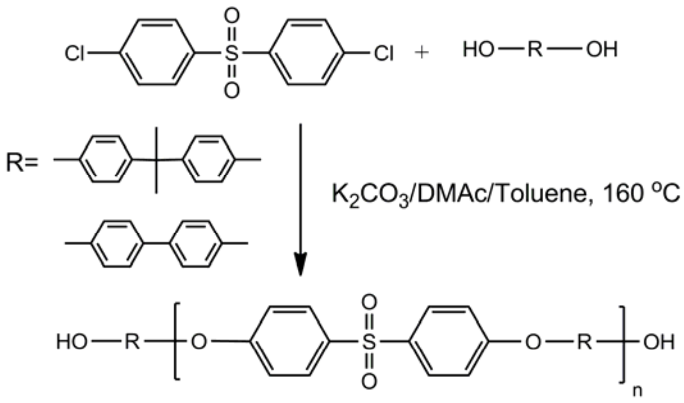


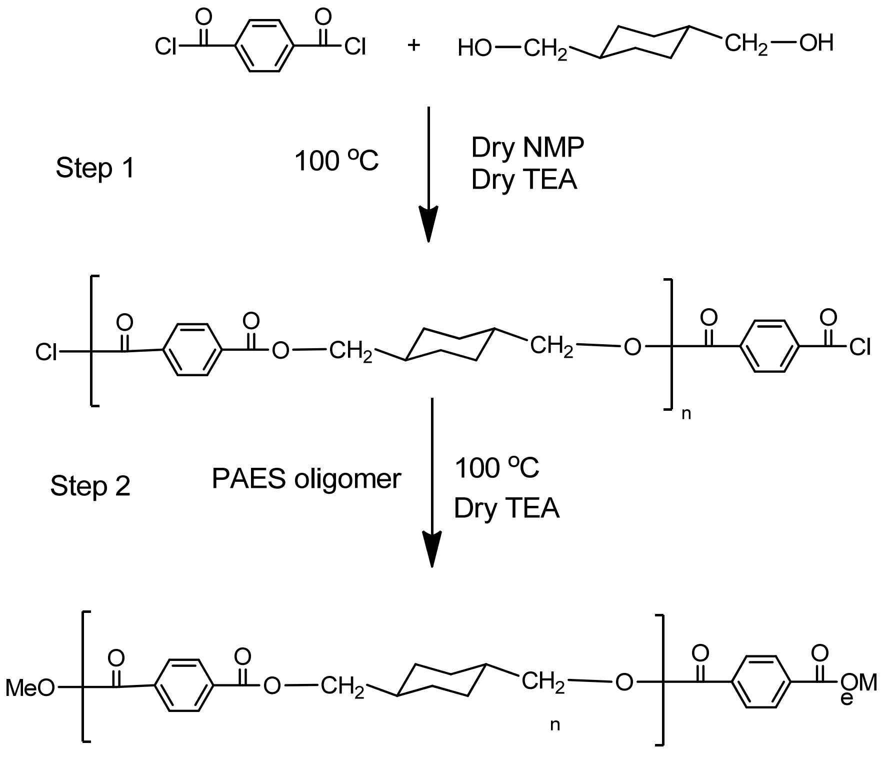
Figure 5.1 The reaction apparatus set up of PAES synthesis



Scheme 5.1 Synthesis of the bis-A based and biphenol based PAESs

The phenol terminated bisphenol (bis-A) and the biphenol (BP) based PAES oligomers with 2.0 kg/mol target molecular weight were synthesized by using the stoichiometry imbalance technique based on the Carothers equation. The bis-A based PAES oligomer with 2.0 kg/mol target molecular weight is shown as an example. The BP based oligomer was synthesized in a similar fashion. 5.036 g (17.54 mmol) of dichlorodiphenyl sulfone (DCDPS), 5.000 g (21.90 mmol) of bis-A, 7.870 g (56.95 mmol) of K_2CO_3, 80.0 mL of DMAc and 40.0 mL of toluene were added to a flask equipped with a mechanical stirrer, an argon inlet and a Dean-Stark trap. The reaction was heated to 140 ^oC for 3 h to remove water by azeotropic distillation. Then toluene was distilled out by increasing the temperature slowly to 160 ^oC in 2 h. After 20 h at 160 ^oC the reaction mixture was cooled to room temperature. White solid was obtained by the precipitation of the reaction mixture in a 5 weight percent HCl aqueous solution and filtration. The product was thoroughly washed three times with 200 mL of deionized water and methanol respectively. After drying at 120 ^oC for 12 h in a vacuum oven (-80 kPa), the product was obtained with a yield of 92.4 %. ^{1}H NMR ($CDCl_3$, ppm): δ 8.18 (m, 16.38), δ 7.21 (m), δ 7.06 (m), δ 6.96 (m), δ 6.91 (m), δ 6.72 (m, 4.00), δ 1.66 (m). In the proton NMR, the integration area ratio between the protons with the chemical shift of δ 6.72 and δ 8.18 was used to determine the number average molecular weights. The actual molecular weights of the oligomers were very close to the target.

5.3.3.2.2 Synthesis of Poly(1,4-cyclohexylenedimethylene terephthalate) Oligomer with Acid Chloride End Groups



Scheme 5.2 The endcapping reaction of poly(1,4-cyclohexylenedimethylene terephthalate) oligomer with acid chloride end groups

As shown in the first step in **Scheme 5.2**, with a condenser and an argon inlet, a 150 mL three-necked round bottom flash was charged with 2.000 g (9.661 mmol) freshly prepared CHDC (as the synthesis described in **5.3.3.1.1**), 1.212 g (8.404) *trans*-CHDM, 2.542 g (25.12 mmol) dry triethylamine (TEA), and 80 mL of dry NMP. Under argon protection, the mixture was reacted at room temperature for 12 h. Without isolation, the product was directly used in the following poly(arylene ether sulfone)s-polyester blocks copolymers synthesis in solution**.** The product was only isolated in a model endcapping reaction to determine the molecular weight of the PCT oligomer. This model reaction is described in section **5.3.3.2.3**.

5.3.3.2.3 Endcapping Reaction of Poly(1,4-cyclohexylenedimethylene terephthalate) Oligomer for End Group Analysis

As shown in the second step in **Scheme 5.2**, a procedure is described here for a model reaction to determine the molecular weight information of the PCT oligomer as synthesized in **5.3.3.2.2**. To the reaction solution from **5.3.3.2.2**, 20 mL of anhydrous methanol and 5 mL of dry TEA were added. The reaction solution was heated to 80 ^{o}C under vigorous magnetic stirring for 12 h. Then the reaction mixture was precipitated in 600 mL of deionized water and stirred overnight. After filtration, the white powder was washed with 200 mL of deionized water three times and dried in a vacuum oven (-80 kPa) at 100 ^{o}C for 12 h.

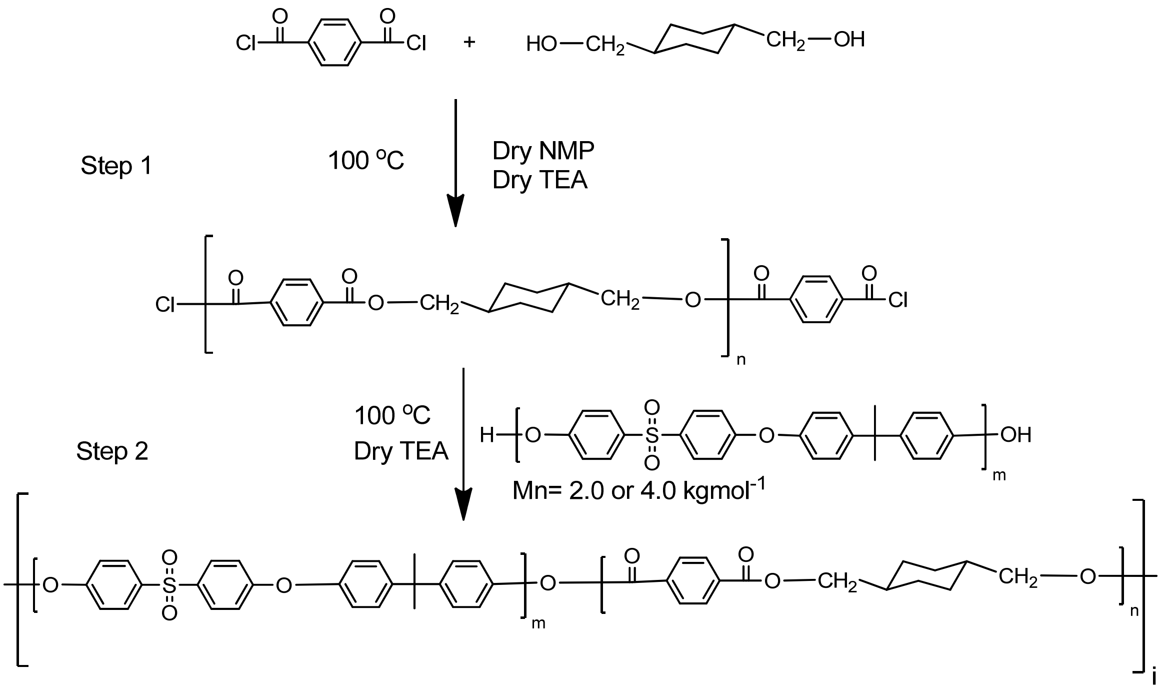
5.3.3.2.4 Synthesis of Poly(arylene ether sulfone)s Oligomer with Hydroxy Ethoxy End Groups

The bisphenol-A and the biphenol based hydroxy ethoxylated PAES oligomers were synthesized in the same way with either bisphenol-A or biphenol as starting material. The synthesis of bisphenol-A based terminated PAES oligomer is shown as an example. 15.00 g (5.484 mmol) of bisphenol-A based phenol terminated PAES oligomer, 4.826 g (54.84 mmol) of ethylene carbonate, 0.7568 g (5.484 mmol) of potassium carbonate and 120.0 mL of DMF were charged to a 250 mL round bottom flask equipped with an argon inlet, a condenser and a Teflon coated mechanical stir bar. In the presence of argon, the reaction was conducted at 80 ^{o}C for 24 h with stirring. After cooling to room temperature, the reaction solution was precipitated in 600 mL of water and then filtered. The white powder obtained was washed with 200 mL of water three times and dried in a vacuum oven (-80 kPa) at 100 ^{o}C for 12 h. Final product was obtained as white powder with a yield of 90.8 %. ^{1}H NMR (DMSO-d6, ppm): δ7.88 (m), δ7.26 (m), δ7.06 (m), δ6.96 (m), δ6.83 (m), δ4.83 (t), δ3.92 (m), δ3.67 (m), δ1.62 (m).

5.3.3.3 Polymer Synthesis

5.3.3.3.1 Poly(arylene ether sulfone)-polyester Multiblock Copolymers via Solution Polymerization

As shown in the second step in **Scheme 5.3**, to the reaction solution from **5.3.3.2.2**, 0.3307 g (3.268 mmol) TEA and 2.804 g (1.257 mmol) bis-A based phenol terminated PAES oligomer (number average molecular weight determined by ^{1}H NMR was 2.2 kg mol^{-1}) were added. In the presence of argon, the mixture was allowed to react at 100 ^{o}C with magnetic stirring for 12 h. Then the reaction mixture was precipitated in 600 mL of deionized water and stirred overnight. After filtration, the white powder was washed with 200 mL of deionized water three times and dried in a vacuum oven (-80 kPa) at 100 ^{o}C for 12 h.



Scheme 5.3 Synthesis of poly(arylene ether sulfone)-polyester multiblock copolymers with solution polymerization method with terephthaloyl chloride and CHDM based oligomer

5.3.3.3.2 Poly(arylene ether sulfone)-polyester Multiblock Copolymers with Melt Polymerization Method

To a 50 mL two-necked round bottle flask equipped with an argon inlet and a mechanical stirrer, 10.00 g (2.889 mmol) of hydroxy ethoxylated bisphenol-A based PAES (as the synthesis described in **5.3.3.2.4**), 1.121 g (5.779 mmol) of dimethyl terephthalate (DMT) and 0.4160 g (2.889 mmol) of 1,4-cyclohexane dimethanol (CHDM, *cis/trans* = 30/70) were added. Under the protection of nitrogen, 100 ppm titanium(IV) butoxide was carefully added. With a metal heating bath, the reaction was heated to 250 ^{o}C for 5 h at ambient pressure. A vacuum (0.2-0.4 mmHg) then was applied slowly and the reaction was allowed to further react at 250 ^{o}C for 1 h, 270 ^{o}C for 1 h and 290 ^{o}C for 1 h. At the last stage of the melt polymerization, a melt with high viscosity was observed which was indicative of high molecular weight product. After the reaction, the polymer melt was cooled to room temperature with argon protection. The polymer was dissolved in chloroform, precipitated in methanol, and then thoroughly washed with methanol. For insoluble polymer products, the reaction flasks were broken and the bulk polymers were collected.

5.3.3.3.3 Synthesis of High Molecular Bisphenol-A based Poly(arylene ether sulfone) Polymer for the Model Reaction in 5.3.3.3.4

High molecular weight PAES polymer was used in the model reaction to confirm the stability of the PAES block in the presence of a diol under melt polymerization condition. The synthesis of this high molecular weight PAES sample was the same as the synthesis of PAES oligomer described in **5.3.3.2.1** expect for the molar ratio of the starting materials. Instead of using the stoichiometry imbalance technique, a 1:1 molar ratio of bisphenol-A and DCDPS was applied to achieve high molecular weight.

5.3.3.3.4 Model Reaction of Poly(arylene ether sulfone) Polymer with 1,4-Cyclohexanedimethanol under Melt Polymerization Condition

A model reaction was performed to confirm if the PAES block was stable in the presence of a diol under melt polymerization condition. To a 50 mL round bottom flask, about 10 g high molecular weight PAES polymer (as described in **5.3.3.3.3**) was charged with about 0.4 g CHDM and 100 ppm titanium(IV) butoxide. The system was carefully protected by nitrogen gas. With a metal heating bath, the reaction mixture was heated at 250 ^{o}C for 5 h at ambient pressure. The vacuum (0.2-0.4 mmHg) then was applied slowly and the reaction was allowed to further react at 250 ^{o}C for 1 h, 270 ^{o}C for 1 h and 290 ^{o}C for 1 h. After the flask was cooled to room temperature, the polymer was obtained by breaking the reaction flask.

5.3.3.3.5 Preparation of Poly(arylene ether sulfone) and Poly(1,4-cyclohexylenedimethylene terephthalate) Blend

To a 50 mL two-necked round bottom flask, high molecular weight PAES and high molecular weight PCT were added with target weight percentage or molar ratio. The system was purged with nitrogen gas. The flask was put into a metal heating bath at a temperature of 250 ^{o}C. Then the temperature was raised to 290 ^{o}C in 5 min. The mixture was mechanically stirred at 290 ^{o}C, and 300 ^{o}C each for 1 h. Then the mixture was cooled to room temperature and the blend was obtained by breaking the blending flask.

5.3.3.4 Polymer Film Preparation

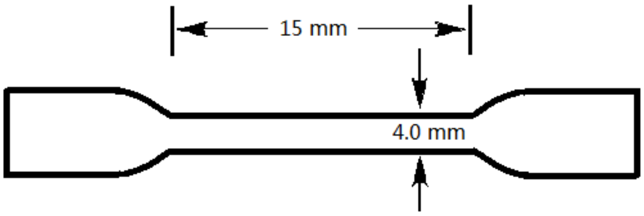


Figure 5.2 Dimension parameters of the dog bone sample

Figure 5.3 Picture of a typical *trans*-1,4-cyclohexylene containing PAES film sample by solvent casting

Polymer film samples were obtained by the solution casting method. The solid polymer sample was dissolved at room temperature under stirring in chloroform, DMAc, or NMP depending on the sample solubility to offer a homogeneous solution with concentration of 10 wt%. After filtration through a 45 μm micro glass fiber filter, the polymer solution was cast on a leveled glass substrate dried at 80 °C for 12 h and subsequently dried at 120 °C under vacuum (-80 kPa) for 12 h. Dog bone samples for the mechanical property evaluation were prepared from the polymer films.

As shown in **Figure 5.2**, the dimension parameters of the dog bone sample were 4.00 mm in width and about 15 mm in length. The thickness of the samples was in the range of 60-100 μm. A typical 1,4-cyclohexylene containing PAES-polyester multiblock polymer film sample by solvent casting is shown in **Figure 5.3**. In the picture, a piece of polymer film is coving a piece of paper with the name and logos of Virginia Tech and MII. The polymers were transparent tough films with no color or light yellow color.

5.4 Results and Discussion

5.4.1 Synthesis of Phenol Terminated Poly(arylene ether sulfone) Oligomer with Controlled Molecular Weight

The synthesis of the phenol terminated poly(arylene ether sulfone) (PAES) oligomer in this chapter is similar to the synthesis of the oligomers introduced in **Chapter 4**. Both bis-A based and BP based PAES oligomers with phenol end groups were synthesized. These PAES oligomers were used to synthesize PAES-polyester multiblock copolymers as the polysulfone blocks with solution polymerization method and melt polymerization method. In the solution method, only bis-A based PAES oligomers with 2.0 kg mol^{-1} and 4.0 kg mol^{-1} target number average molecular weights were used since the BP based

PAES oligomers were too insoluble to use in solution polymerization. The actual molecular weight was determined by NMR end group analysis. The ^{1}H NMR spectra of these two oligomers are shown in **Figure 5.13** and **Figure 5.14** in the Appendix. In both cases, the phenol end group proton signals were observed around 5 ppm as broad peaks. Because of the large error in the integral area of the phenol protons in ^{1}H NMR, A' protons and C protons were used to calculate the molecular weight. 2.2 and 3.8 kg mol^{-1} actual M_n were obtained for 2.0 and 4.0 kg mol^{-1} targets respectively. These results indicated that the stoichiometry imbalance technique successfully controlled the molecular weight and the functionality of the oligomers.

5.4.2 Synthesis of Poly(1,4-cyclohexylenedimethylene terephthalate) Oligomer with Acid Chloride End Groups

The synthesis of poly(arylene ether sulfone)s-polyester multiblock copolymers with solution polymerization method was accomplished by two major steps as shown in **Scheme 5.3**. First the acid chloride terminated PCT oligomer was synthesized by terephthaloyl chloride and *trans*-CHDM. Based on Carothers equation, a similar stoichiometry imbalance technique as applied in **5.3.3.2.1** was used to control the molecular weight. The target number average molecular weight of the PCT oligomer was 2.0 kg mol^{-1}. The second reaction was done *in-situ* with phenol terminated PAES oligomer without isolation of the PCT oligomer. In order to monitor the synthesis of the acid chloride terminated PCT oligomer, an endcapping reaction was performed to convert acid chloride end groups to methyl ester groups by treatment of methanol in the presence of TEA as the base.

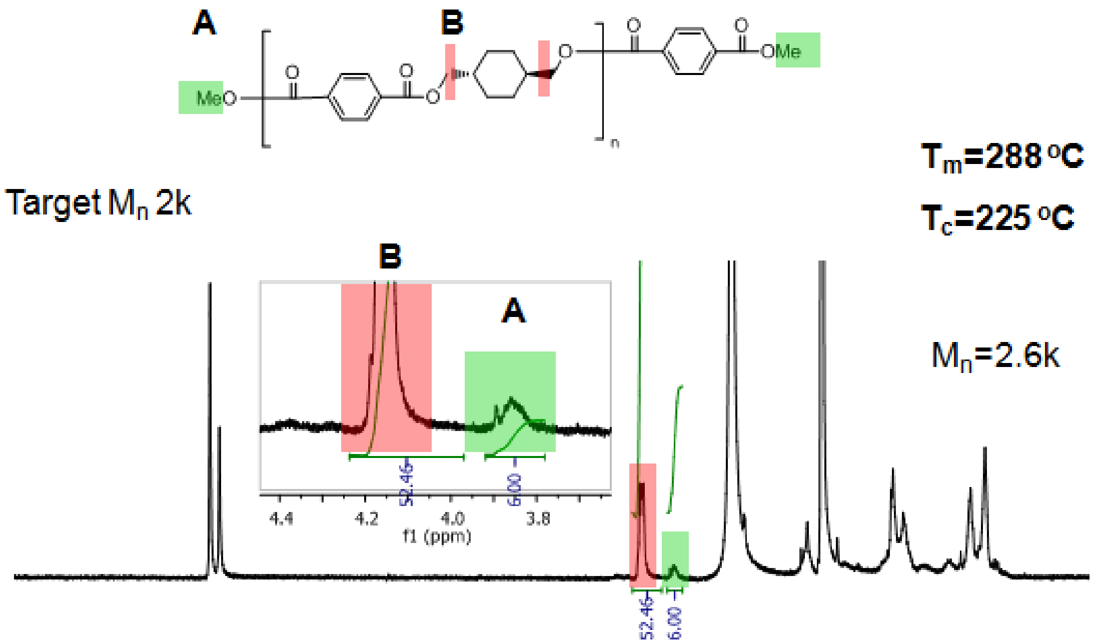


Figure 5.4 The ^{1}H NMR, number average molecular weight, and thermal properties of the PCT oligomer with methyl ester end groups

The reaction scheme and the ^{1}H NMR are shown in **Scheme 5.2** and **Figure 5.4** respectively. Due to the lack of the end groups that can be detected, the number average molecular weight of the acid chloride terminated PCT oligomer cannot be determined by NMR. However, after the conversion reaction, the methyl ester end groups were clearly detected and shown isolated in the NMR spectrum of **Figure 5.4**. As labeled, the methyl end group protons (A protons) and the methylene protons next to the cyclohexylene ring (B protons) were used to determine the molecular weight. The end group analysis results suggest that the number average molecular weight of this PCT oligomer with methyl ester groups was 2.6 kg mol^{-1} which was close to the target (2.0 kg mol^{-1}). This result indicated that the PCT oligomer was successfully prepared with expected molecular weight and function end groups. Because of the instability of the acid chloride end group, no thermal properties were obtained for the acid chloride terminated PCT oligomer. Both a melting transition temperature of 288 ^{o}C and a crystallization temperature of 225 ^{o}C were observed from the oligomer with methyl ester end groups. As described later, these thermal properties were used in comparison with the thermal properties of the multiblock copolymers.

5.4.3 Poly(arylene ether sulfone)s-polyester Multiblock Copolymers with Solution Polymerization Method

5.4.3.1 Synthesis and Characterization of Poly(arylene ether sulfone)s-polyester Multiblock Copolymers with Solution Polymerization Method

With the confirmation of the successful synthesis of the PCT oligomer with the acid chloride end groups, the PAES-polyester multiblock copolymers were synthesized from the acid chloride terminated PCT oligomer and phenol terminated PAES oligomers with solution method as shown in **Scheme 5.3**. Only bis-A based PAES was successfully used since the multiblock copolymers from BP based PAES oligomer and PCT oligomer exhibited very limited solubility in many common solvents such as DMAc, DMF, NMP, 1,1,2,2-tetrachloroethane, and chloroform. The limited solubility resulted in a major precipitation at the very early stage of the solution polymerization. The isolated products, probably with very low molecular weights, were insoluble and cannot be characterized by using solution techniques.

Table 5.1 The molecular weights and thermal properties of poly(arylene ether sulfone)-polyester multiblock copolymers with solution polymerization method

Polymers	Molecular Weights ($x10^3$ g mol^{-1})			T_g	T_m	T_c
	M_n[1]	M_w	PDI	(^oC)[2]	(^oC)	(^oC)
2kBisA2kPCT		insoluble		105, 171	247	180
4kBisA2kPCT	12.9	22.3	1.7	117,180	-	-
PCT homopolymer[3]		insoluble		100[4]	288	199

[1] NMP as the SEC solvent with a refractive index detector and a viscometer

[2] All the thermal properties were obtain by DSC

[3] Provided by the Eastman chemical company with *cis/trans* ratio of 30/70 (product # PCT 13787 Eastman (TM))

[4] Measured by the author

Even when bis-A based PAES oligomers were used, some reactions resulted in insoluble products. **Table 5.1** shows the molecular weights and thermal properties of the multiblock copolymers from PCT oligomer and bis-A based PAES oligomers with 2 or 4 kg mol^{-1} number average molecular weight (2kBis-A or 4kBis-A) with the PCT homopolymer control. The 4kBisA2kPCT sample was soluble in the SEC solvent and molecular weight results were obtained. The number average molecular weight was about 13 kg mol^{-1}, which indicated a successful solution polymerization. The PCT homopolymer is not soluble in the SEC solvent. However, because of the amorphous nature of the PAES block, the multiblock copolymer with 4kBisA oligomer was soluble.

When a PAES oligomer with short chain length (2kBisA) was used, as expected, the resulting polymer (2kBisA2kPCT) was insoluble, thus no molecular weight information was obtained. Due to the use of the PAES oligomer with short chain length, crystallinity was observed in DSC study. As shown in **Table 5.1**, both melting transitions and recrystallization transitions were observed with peak temperature at 247 °C and 180 °C respectively.

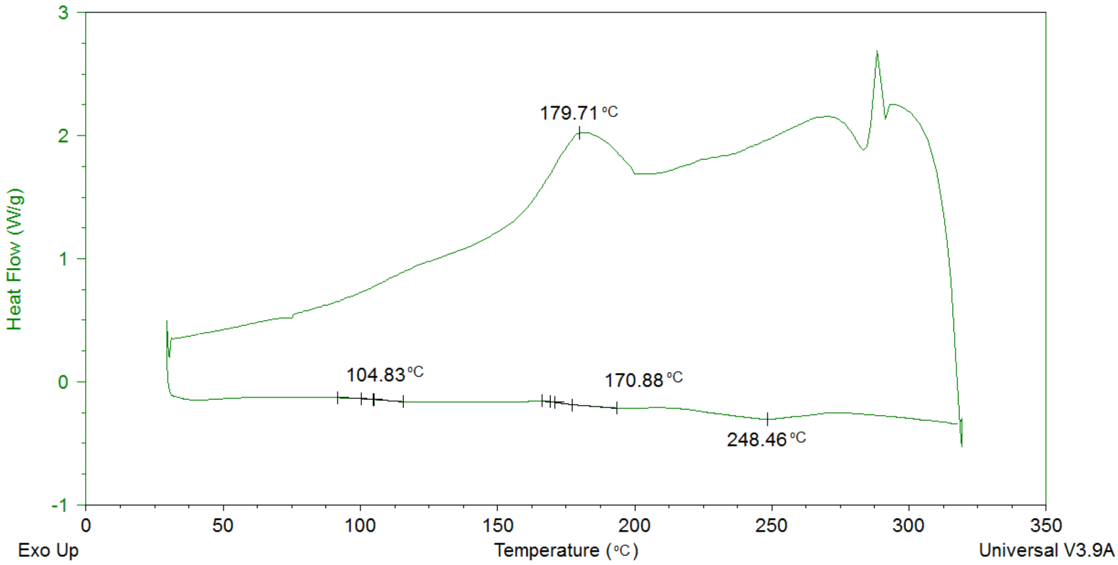


Figure 5.5 The DSC curve of the PAES-polyester multiblock copolymer from PCT oligomer and bis-A based PAES oligomers with 2 kg mol^{-1} number average molecular weight with solution method (cooling and 2nd heating cycle)

The DSC curve of this multiblock copolymer is shown in **Figure 5.5**. The DSC curve of the PCT homopolymer can be seen in **Figure 5.15** in the Appendix. As shown in **Figure 5.5**, a clear recrystallization peak at around 180 °C was observed in the cooling cycle. The melting transition observed was weak which indicated a low percentage of crystallinity. The details about the crystallinity will be discussed in the following section **5.4.3.2**. The PCT homopolymer showed a glass transition temperature at about 100 ^oC (listed in **Table 5.1;** it is generally reported that the glass transition temperature of PCT homopolymer is around 85 ^oC.[17] The glass transition temperature observed here may be enhanced by some additives unknown to the author); while the PAES homopolymer has a T_g of 181 ^oC. In the multiblock copolymer, two clear glass transition temperatures were also observed at round 105 ^oC and 171 ^oC which correspond to PCT blocks and PAES blocks. These results suggest that the multiblock copolymers with solution method were phase separated. The glass transition temperature observed for the PCT block (105 ^oC) is slightly higher than that of the PCT homopolymer (100 ^oC) while for the PAES block (171 ^oC) is lower than that of the PAES homopolymer (181 ^oC). This observation may indicate that there are interactions between these blocks. In other words, the PCT and PAES blocks were not completed phase separated.

5.4.3.2 Annealing DSC Study of Poly(arylene ether sulfone)-polyester Multiblock Copolymers with Solution Polymerization Method

The weak melting transition observed in **Figure 5.5** was obtained from the quenched sample in DSC study. An annealing DSC study will be discussed here in order to have a better understanding of the crystallization behavior of the PAES-PCT multiblock copolymer.

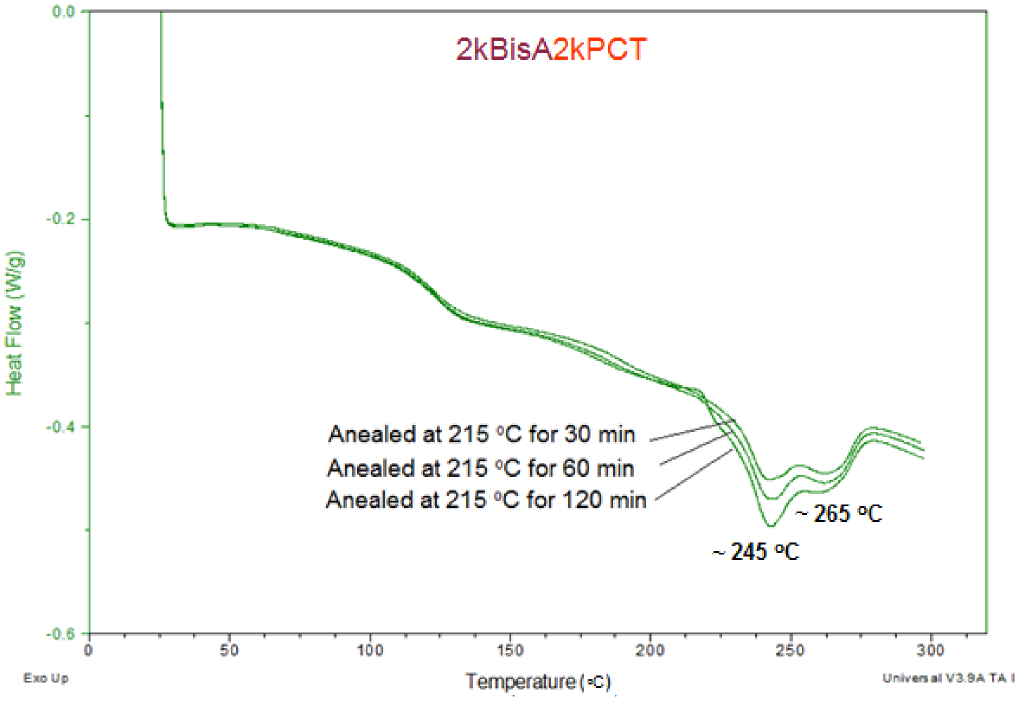


Figure 5.6 The annealing DSC curves of the PAES-polyester multiblock copolymer from PCT oligomer and bis-A based PAES oligomers with 2 kg mol^{-1} number average molecular weight with solution method

Figure 5.6 shows a series of the DSC curves of the same PAES-polyester multiblock copolymer from PCT oligomer and bis-A based PAES oligomers with 2 kg mol^{-1} number average molecular weight with the solution method. Based on the glass transition and melting transition temperatures observed with the quenched DSC sample the annealing temperature was selected at 215 ^{o}C. This temperature is lower than the melting temperature and significant higher than the glass transition of the PAES blocks, so that there is good driving force to form the crystalline domain. As shown in **Figure 5.6**, with the annealing time increased from 30 min to 120 min, a clear increase in the melting peak intensity was observed. Instead of only one melting peak with the quenched sample as shown in **Figure 5.5**, two well isolated melting peaks were observed with peak temperatures around 245 ^{o}C and 265 ^{o}C. With the increase of the annealing time, the intensity of both melting peaks increased.

Table 5.2 The enthalpy of melting for solution made PAES-polyester multiblock copolymer with different annealing time at 215 ^{o}C

2kBisA-b-2kPCT Polymers	Without annealing	215 ^{o}C[1] 30 min	215 ^{o}C 60 min	215 ^{o}C 120 min	PCT[2] without annealing
Enthalpy of melting (J/g)[3]	12.87	15.90	17.95	20.67	33.30

[1] The heating and cooling rate for the DSC annealing study are both 10 ^{o}C/min

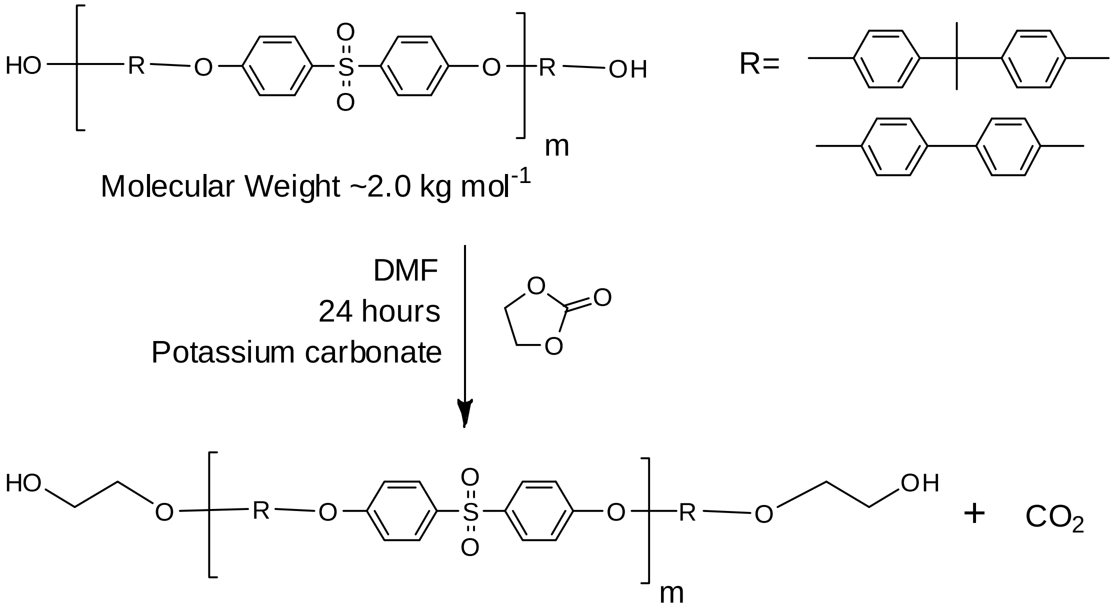
[2] Provided by the Eastman chemical company with *cis/trans* ratio of 30/70

[3] The DSC curves for the integral area calculation are shown in **Figure 5.16** – **Figure 5.19** in the Appendix

Table 5.2 shows the integral areas of the melting transitions of the PAES-polyester multiblock copolymer in the DSC curves, aka, enthalpy of melting with PCT homopolymer. As expected, with the annealing time increased from 0 min (without annealing) to 120 min, an increase in the enthalpy of melting values was also observed from 12.87 J/g to 20.67 J/g. The enthalpy of melting calculated for PCT oligomer without annealing was 33.30 J/g. Compared to this value, the PAES-PCT multiblock copolymer showed significant lower enthalpy of melting even after being annealed at 215 °C for 120 min, which indicated limited percentage of crystallinity.

5.4.4 Poly(arylene ether sulfone)s Oligomer with Hydroxy Ethoxy End Groups

5.4.4.1 Synthesis of Poly(arylene ether sulfone)s Oligomer with Hydroxy Ethoxy End Groups



Scheme 5.4 Reaction scheme of synthesis of hydroxy ethoxy terminated PAES oligomer based on bisphenol-A and biphenol

As described in **5.3.3.2.4**, the synthesis scheme of hydroxy ethoxy terminated PAES oligomer based on bisphenol-A and biphenol is shown in **Scheme 5.4**. In this synthesis all the PAES oligomers used had number average molecular weights about 2.0 kg mol^{-1}. The conversion of bisphenols to primary alcohol terminated monomers for incorporation in polyesters and polyurethanes is well documented.[18] Three reactants are reported for the reaction: 2-bromo ethanol, ethylene oxide and ethylene carbonate. Ethylene carbonate was found to be an effective, non-toxic reagent for the reaction.[18]

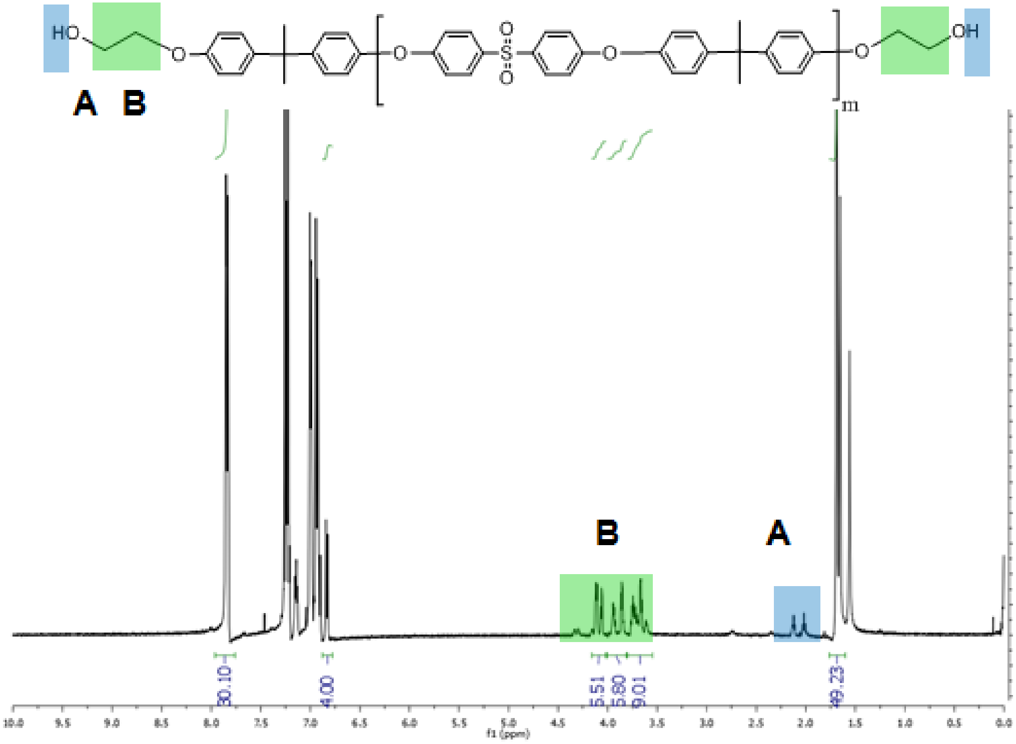


Figure 5.7 The ^{1}H NMR of the hydroxy ethoxy terminated PAES oligomer based on bisphenol-A, an indication of a multiple addition side reaction

The initial trials of the reaction based on the procedure reported in the literature[19] resulted in a major side reaction. With the expected structure and the new end groups labeled, the ^{1}H NMR spectrum of the reaction product based on bisphenol units is shown in **Figure 5.7**. However, in the area where the A and B end groups were expected, multiple A proton peaks and multiple groups of B proton peaks were observed. This is an indication of a side reaction, probably multiple addition of the ethylene carbonate. A similar result was also observed in the synthesis of the hydroxy ethoxy terminated PAES oligomer based on biphenol as shown in **Figure 5.20** in the Appendix.

To optimize the reaction condition and minimize side reactions, several reaction parameters were screened as listed in **Table 5.3**. The parameters include solvent, reaction temperature, and the amount of potassium carbonate and ethylene carbonate used. The optimized reaction conditions were found to be 100 °C in DMF with 1.0 molar equivalent of potassium carbonate and 4.0 equivalent of ethylene carbonate (shown as bold in **Table 5.3**).

Table 5.3 The parameter screened for reaction condition optimization of the hydroxy ethoxy terminated PAES oligomer synthesis

K_2CO_3 used	**Ethylene Carbonate Used**	**Solvent**	**Temperature**
0.2 molar eq	2.0 molar eq	**DMF**	150 °C
1.0 molar eq	**4.0 molar eq**	DMF(AH)	120 °C
2.0 molar eq	8.0 molar eq	-	**100 °C**
4.0 molar eq	10.0 molar eq	-	80 °C

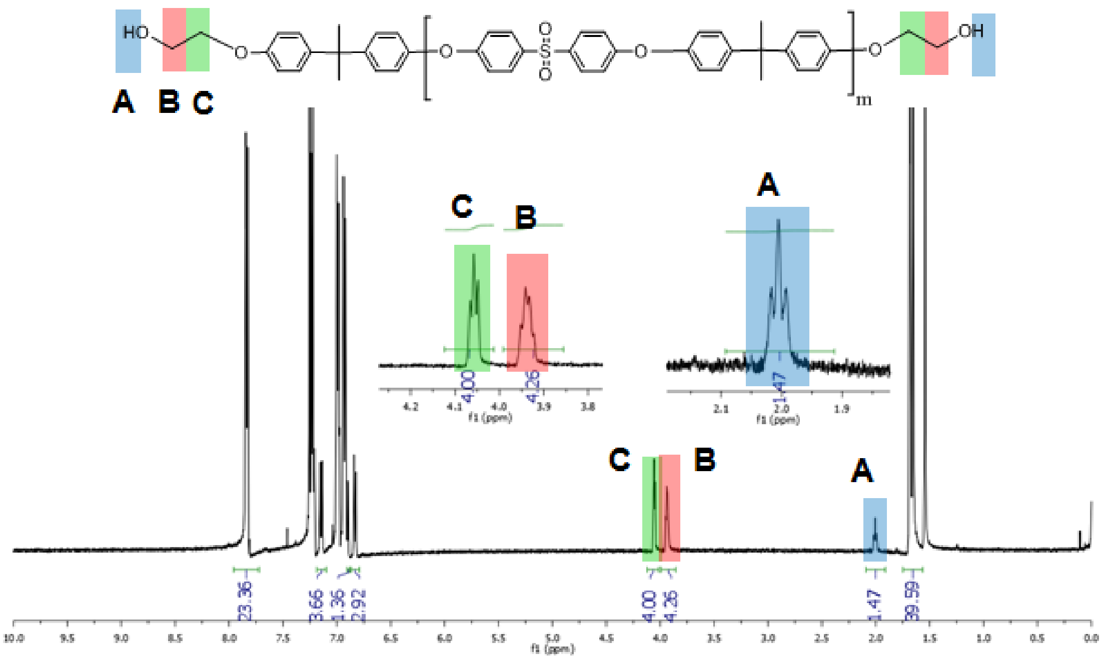


Figure 5.8 The ^{1}H NMR of the hydroxy ethoxy terminated PAES oligomer under optimized reaction condition

The product obtained under these optimized reaction conditions showed very clean ^{1}H NMR in **Figure 5.8**. In the middle of **Figure 5.8**, the enlarged areas are for the end group protons. The triplet peak of the primary hydroxyl groups (A protons) can be clearly observed at the chemical shift around 2.0 ppm. The ethylene protons in the end groups (B and C protons) were also observed with the correct integral area, the splitting pattern, and chemical shift.

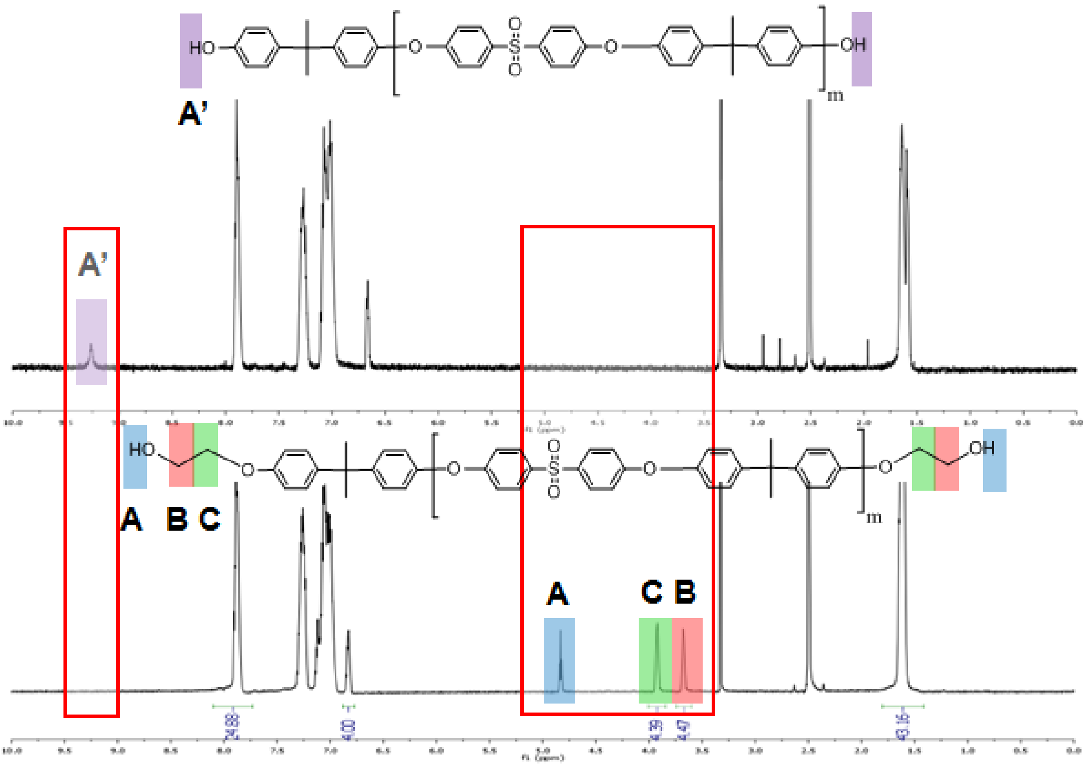


Figure 5.9 The ^{1}H NMR spectra showing the end group conversion of hydroxy ethoxy terminated PAES oligomer synthesis

A ^{1}H NMR spectra comparison to monitor the end group conversion of hydroxy ethoxy terminated PAES oligomer synthesis is shown in **Figure 5.9**. In the figure the ^{1}H NMR spectrum and the structure of the starting material and the product are shown on the top and the bottom respectively. The disappearance of the phenol end groups (A' protons) and the appearance of hydroxy ethoxy groups (A, B, and C protons) confirmed the successful end group modification.

5.4.4.2 Molecular Weights Determination of Poly(arylene ether sulfone) Oligomers with Hydroxy Ethoxy End Groups

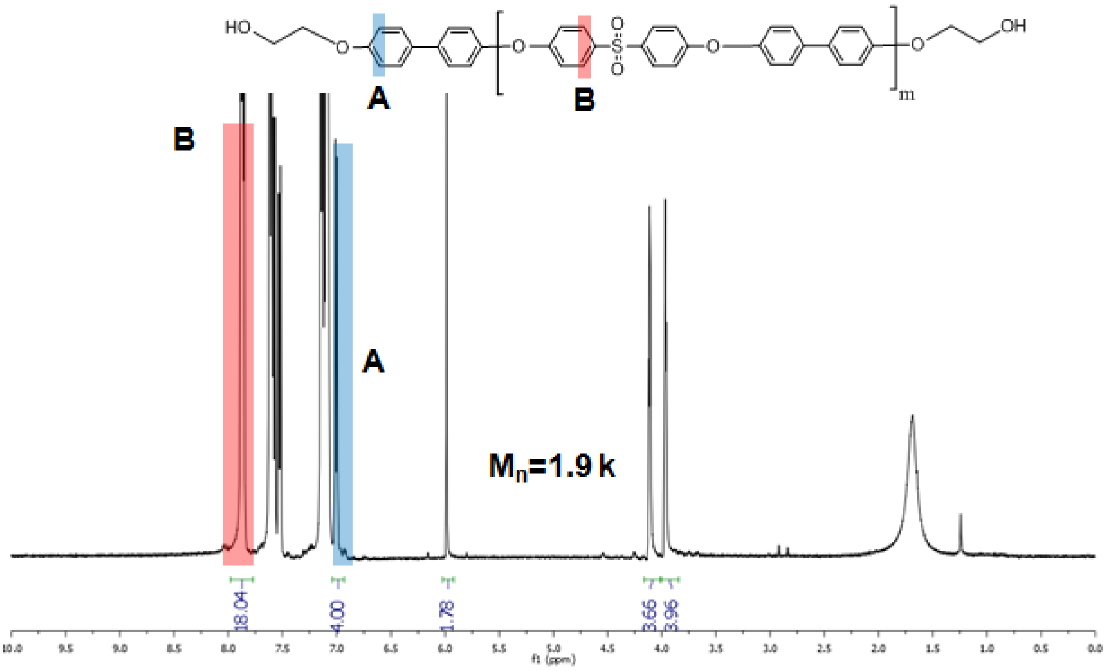


Figure 5.10 The ^{1}H NMR spectra showing resonance used for molecular weight determination of biphenol based PAES oligomer with hydroxy ethoxy end groups (in deuterated 1,1,2,2 tetrachloroethane)

The phenol terminated PAES oligomers used in the hydroxy ethoxy end group modification reaction had number average molecular weights about 2.0 kg mol^{-1} determined by ^{1}H NMR. The number average molecular weights of PAES oligomers with hydroxy ethoxy end groups were calculated in a similar way. The molecular weight determination for bisphenol-A based oligomer was straight forward because it showed good solubility in common NMR solvent such as DMSO-d6 and $CDCl_3$. A ^{1}H NMR spectrum example is shown in **Figure 5.22** in the Appendix. The number average for this sample is 2.8 kg mol^{-1}. The reason why the actual molecular weight was higher than the 2.0 kg mol^{-1} target is that the hydroxy ethoxy terminated PAES oligomer was obtained by two precipitation steps and was probably fractionated with loss of some low molecular soluble portions in the solution.

The molecular weight determination for biphenol based PAES oligomer with hydroxy ethoxy groups was different due to the solubility. The biphenol based PAES with phenol end groups can be easily dissolved in high boiling point aprotic solvent such as DMSO, DMF and DMAc. With the end group converted to hydroxy ethoxy groups, the oligomer exhibited limited solubility in DMSO, which made the molecular determination in DMSO problematic. Many NMR solvents and mix solvents were tested. The best result was obtained with deuterated 1,1,2,2 tetrachloroethane as shown in **Figure 5.10**. The number average molecular weight determined was 1.9 kg mol^{-1} which was very close to the target. In comparison to the bis-A system, it is likely the fractionation effect was limited due to the low solubility of the biphenol based PAES oligomer.

5.4.5 Poly(arylene ether sulfone)-polyester Multiblock Copolymers via Melt Polymerization Method

5.4.5.1 The Synthesis and Condition Optimization of Poly(arylene ether sulfone)s-polyester Multiblock Copolymers Melt Polymerization

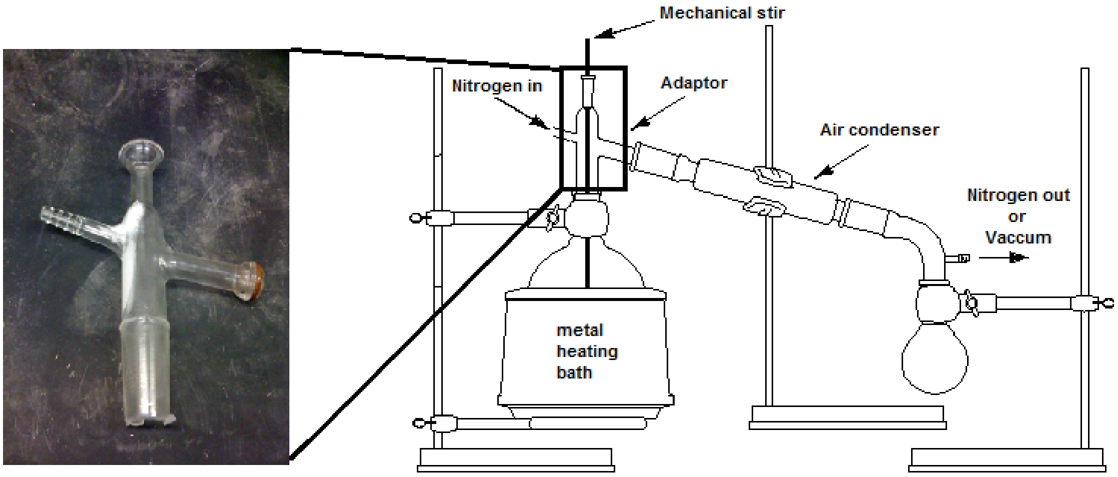
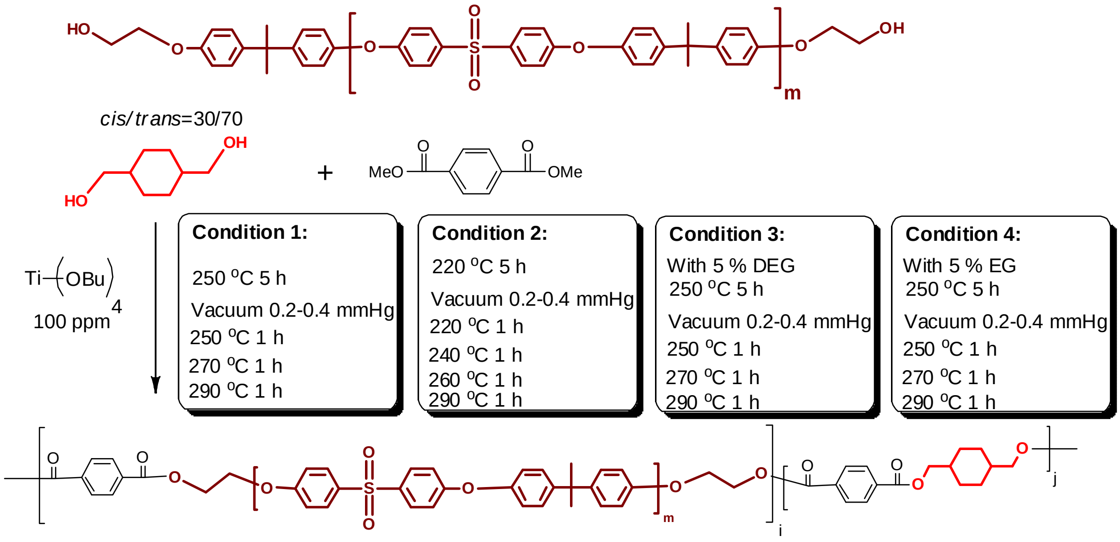


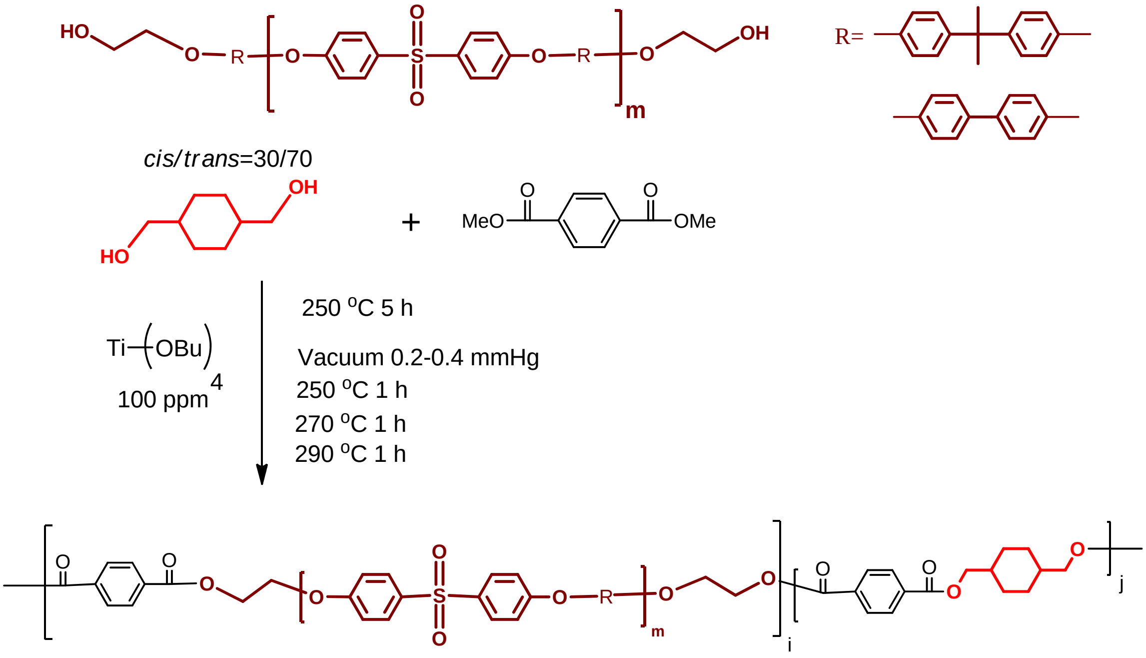
Figure 5.11 A demonstration of a typical melt polymerization apparatus with an actual picture of the adaptor

In comparison to the phenol terminated oligomer, the PAES oligomers with hydroxy ethoxy end groups can be easily used in melt polymerization for traditional polyester synthesis. Dimethyl terephthalate (DMT), CHDM (*cis/trans* = 30/70), and the PAES oligomer were used as starting materials. The typical melt polymerization apparatus is shown in **Figure 5.11** with an actual picture of the adaptor.

In the initial trials, white solid was condensed on the adaptor during the melt polymerization reaction as shown in the picture on the left of **Figure 5.11**. The white solid collected was analyzed by ^{1}H NMR (**Figure 5.23** in the Appendix). The corresponding proton signals from both DMT and CHDM were obtained. To optimize the reaction temperature and test additives, four different reaction conditions were screened as listed in **Scheme 5.5**. 220 °C and 250 °C were selected as the starting reaction temperatures. The reason why small amount of diethylene glycol or ethylene glycol was used in condition 3 and 4 was it has been reported in the literature that using of the diols can help to build up high molecular weight in polyester synthesis.[20]



Scheme 5.5 Reaction condition optimization of the synthesis of PAES-polyester multiblock copolymers with melt polymerization method



Scheme 5.6 Optimized melt polymerization scheme for PAES-PCT multiblock copolymers

The PAES-polyester multiblock copolymers were synthesized under these four different conditions with the same amount of starting materials. The molar ratio between bis-A based PAES oligomer and CHDM was 75 to 25. As the data show in **Table 5.4** the molecular weights of the PAES-polyester multiblock copolymers were independent of the starting temperature, the presence and the type of the additives. After the optimization, the reaction condition with the shortest reaction time and no additives was selected as shown in **Scheme 5.6**. Both the bisphenol-A and biphenol based PAES based PAES-polyester multiblock copolymers were synthesized in the same way.

Table 5.4 The molecular weight results for PAES-polyester multiblock copolymers synthesized under different conditions

Polymers[1]	Conditions[2]	M_n kg mol^{-1}	M_w kg mol^{-1}	PDI[3]
BisA75ctCHDM25DMT100	1	22.5	54.7	2.4
BisA75ctCHDM25DMT100	2	23.8	54.3	2.3
BisA75ctCHDM25DMT100	3	20.3	49.7	2.4
BisA75ctCHDM25DMT100	4	20.4	50.2	2.4

[1] The numbers indicate molar ratio of the monomers, ctCHDM stands for CHDM with *cis/trans* ratio of 30/70

[2] The condition details are listed in **Scheme 5.5**

[3] NMP as the SEC solvent with a refractive index detector and a viscometer

5.4.5.2 Model Reaction of Poly(arylene ether sulfone) Polymer with 1,4-Cyclohexanedimethanol under Melt Polymerization Condition

In the melt polymerization of PAES-polyester multiblock copolymers, the polyester blocks were built on to the presynthesized PAES blocks. It is important to know that under the melt polymerization reaction condition, the PAES block is maintained. To confirm this statement, this model reaction was performed with high molecular weight PAES polymer. Without DMT, the high molecular weight PAES polymer was mixed with CHDM and the titanium(IV) butoxide catalyst under the melt polymerization condition. The polymers before and after the model reaction were analyzed by SEC to monitor the molecular weight. As the results shown in **Table 5.5**, there was no significant difference in molecular weight between the polymer samples before and after the reaction. This result suggested that in the presence of a diol, the PAES block is stable under the melt polymerization condition.

Table 5.5 The molecular weight results for high molecular weight PAES under melt polymerization condition without the diester reactant

Polymers	M_n kg mol^{-1}	M_w kg mol^{-1}	PDI[1]
Bis-A PAES before the model reaction	39.9	72.7	1.8
Bis-A PAES after the model reaction	37.1	62.1	1.7

[1] $CHCl_3$ as the SEC solvent with a refractive index detector and a viscometer

5.4.5.3 Thermal Properties and Mechanical Properties of PAES-polyester Multiblock Copolymers with Different Block Weight Ratios

Using the optimized melt reaction condition, the bisphenol-A based PAES-polyester multiblock copolymers were synthesized. The molar ratio between bis-A based PAES oligomer and CHDM was 75:25, 50:50, and 25:75. The molecular weights and thermal properties of these multiblock copolymers are shown in **Table 5.6**.

Table 5.6 The block weight percentage, molecular weights, and thermal properties of bisphenol-A based PAES-polyester multiblock copolymer with melt polymerization method

Polymers[1]	PAES:PCT Weight ratio (PCT wt%)	M_n Kg mol^{-1}	M_w Kg mol^{-1}	PDI[2]	T_d[3] (°C)	T_g (°C)
BisA75ctCHDM25DMT100	36:1 (2.7 %)	22.8	42.3	1.8	433	161
BisA50ctCHDM50DMT100	12:1 (7.7 %)	26.2	42.6	1.6	418	155
BisA25ctCHDM75DMT100	4:1 (20 %)	28.9	64.2	2.2	393	146

[1] The numbers indicate molar ratio of the monomers, ctCHDM stands for CHDM with *cis/trans* ratio of 30/70

[2] NMP as the SEC solvent with a refractive index detector and a viscometer

[3] T_d is defined as 5 % weight loss temperature in N_2 in DSC study

With different monomer ratios, all the polymers exhibited high molecular weights and reasonable PIDs. The number average molecular weights of those multiblock copolymers were all above 20 kg mol^{-1}. Compared to PCT polyester, PAES has higher decomposition temperature and higher glass transition temperature. As expected, both the decomposition temperature and the glass transition temperature decrease with decreasing PAES contents (from 433 °C to 393 °C and from 161 °C to 146 °C respectively). To our surprise, in contrast to the results obtained with the solution method (listed in **Table 5.1**), only one T_g was observed for all the multiblock copolymers listed in **Table 5.6**. **Figure 5.12** shows the curve of the glass transition temperatures of the multiblock copolymers and their PCT weight percentages. A clear decrease in the glass transition temperature with increase PCT content was observed.

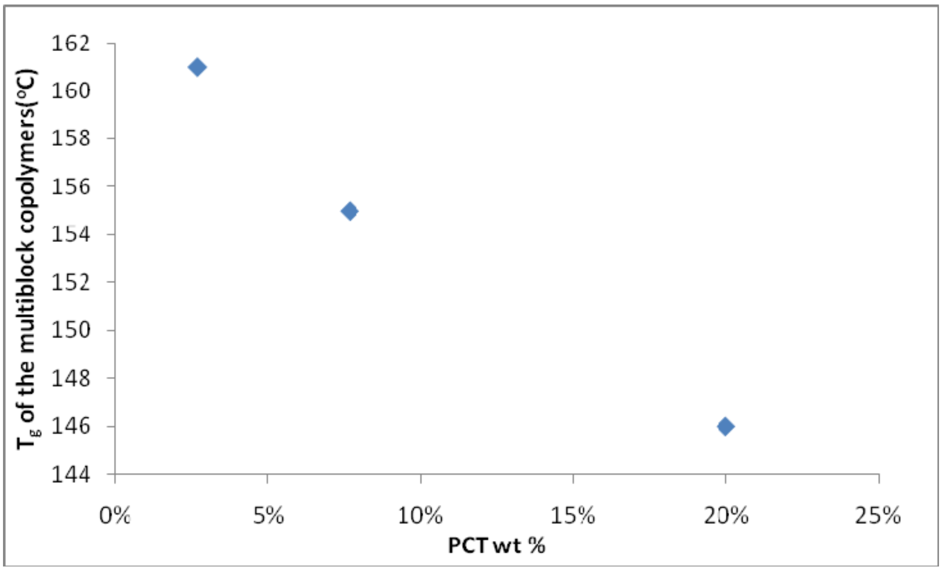


Figure 5.12 The plot of the glass transition temperatures of the multiblock copolymers and their weight percentages of PCT component

As shown by the results in **Table 5.7,** the mechanical properties of these multiblock copolymers with melt polymerization were essentially the same as the Udel® control. After careful analysis, these results may be due to the weight percentage. The second column in **Table 5.6** describes the weight ratio between PAES block and PCT block. Across the table, the PAES weight percentages were dominant. The highest PCT weight percentage value in the table is about 20 wt% (PAES weight percentage 80 %). This dominant weight faction of PAES blocks is probably the reason why the mechanical properties of these multiblock copolymers were dominated by the PAES blocks.

Table 5.7 The tensile test results of bisphenol-A based PAES-polyester multiblock copolymers with melt polymerization method

Polymers[1]	Modulus (MPa)	Yield Stress (MPa)	Strain at yield (%)	Strain at Failure (%)
Udel® Control	1304±86	62.6 ±6.2	6.0±0.3	6.4 ±0.5
BisA75ctCHDM25DMT100	1372±163	45.5±7.0	4.3 ±0.5	4.3 ±0.5
BisA50ctCHDM50DMT100	1377±110	52.4±7.0	4.7 ±0.8	4.7 ±0.8
BisA25ctCHDM75DMT100[2]	-	-	-	-

[1] The numbers indicate molar ratio of the monomers. All the DMA results were averaged over at least 5 samples.

[2] Due to the high polyester content, the polymer showed low solubility. The polymer solution with concentration of 1.0 g mL^{-1} cannot be obtained

Table 5.8 The block weight percentage and thermal properties of bisphenol-A based PAES-polyester multiblock copolymer with melt polymerization method with the thermal properties of the oligomers and PCT homopolymer

Polymers[1]	PAES:PCT Weight Ratio (PCT wt%)	T_g[6] (°C)	T_g[7] (°C)	T_m (°C)	T_c (°C)
BP oligomer[2]	-	-	160	-	-
PCT[3]	-	-	100	288	199
BP[2]25-PCT75 Blend[4]	0.48:1 (68 %)	114	116	278	180
BP25PCT75[4]	0.51:1 (66 %)	124	122	252,274	156,178
BisA25PCT75[5]	0.57:1 (64 %)	119	116	272	183

[1] The numbers indicate molar ratio of the polymer units

[2] Hydroxy ethoxy terminated PAES oligomers with M_n=1.9 kg mol^{-1}

[3] Provided by Eastman Chemical Company

[4] Insoluble in common solvents. Original DSC curves are shown in **Figure 5.28** - **Figure 5.31** in the **appendix**.

[5] Soluble in DMAc and resulted in brittle clear film

[6] The glass transition temperature predicted by the Fox equation

[7] The glass transition temperature, melting temperature, and recrystallization temperature observed by DSC study

In **Table 5.8**, PAES-polyester multiblock copolymers with higher PCT weight percentages were synthesized. The two polymers listed on the bottom are the PAES-polyester multiblock copolymers. The BP25-PCT75 blend was the mixture of hydroxy ethoxy terminated PAES oligomer and the PCT polymer provided by Eastman Chemical Company. The preparation of this blend was described in **5.3.3.3.5**. The blend was prepared to study the compatibility of the PAES and PCT segments. Under protection of nitrogen, the blending was performed at 300 ^{o}C due to the fact that below this temperature PCT does not melt. Unlike the synthesis of the multiblock copolymers, the blend was done in a shorter time (2 h) to minimize the transesterification. However, because of the high temperature applied, transesterification is inevitable. A better way to study the blending is to protect the primary alcohol groups or making the blend by using phenol terminated PAES oligomers with PCT.

In the synthesis of the multiblock copolymers, instead of monomer molar ratio, the PAES block to PCT block molar ratio of 75:25 was used resulting in a higher PCT weight percentage. As shown, PCT weight percentages of the blend and the multiblock copolymers were all around 66 wt%.

$$\frac{1}{T_g} = \frac{w_1}{T_{g,1}} + \frac{w_2}{T_{g,2}}$$

Equation 5.1 Fox equation

The Fox equation was used to estimate the glass transition temperatures of the blend and the multiblock copolymers. As described in **Equation 5.1**, The glass transition temperature of the polymer blend and the multiblock copolymers can be calculated by the glass transition temperature of the two components ($T_{g,1}$ and $T_{g,2}$) and the weight fractions of the two components (w_1 and w_2). The glass transition temperatures for high molecular weight bisphenol-A and biphenol based PAES polymers were observed at 181 ^oC and 234 ^oC which were used to calculate the multiblock copolymer glass transition temperatures. The glass transition temperature of the biphenol based PAES oligomer, 160 ^oC, was used to calculate the T_g of the blend. As the data suggest in **Table 5.8**, the predicted glass transition temperatures by the Fox equation agreed very well with the experimental results.

Similar to the results observed in **Table 5.6**, only one T_g was observed for the blend and the multiblock copolymers. These data indicated that the PAES segments with hydroxy ethoxy end groups were compatible with the PCT segments. The attempt to cast film from the BisA25PCT75 sample resulted in transparent film, which also suggested that the PAES and the PCT segments were compatible. However, due to the brittleness of the BisA25PCT75 film sample and the insolubility of the BP25PCT75 sample, no mechanical properties were obtained.

For both of the blend and the multiblock copolymers, melting transition and recrystallization were observed. The multiblock copolymer based on bisphenol-A units showed only one melting peak at 272 ^oC which was corresponding to the melting transition of the PCT blocks since the melting peak of the PCT homopolymer was observed at 278 ^oC. However, there were two melting temperatures observed for biphenol based multiblock copolymer. The additional melting peak at 252 ^oC may indicate that the biphenol based PAES block participated in the crystallization. The DSC curves of the blend and the multiblock copolymers can be seen in **Figure 5.24** – **Figure 5.27** in the Appendix.

5.5 Conclusions

Multiblock copolymers, composed of PAES blocks and polyester blocks, were described in this chapter focusing on the synthesis, thermal property, and mechanical property characterization. The phenol terminated PAES oligomers were coupled with cyclohexylene containing polyester blocks in solution. In the solution method, the molecular weights of the multiblock copolymers were limited by the solubility. As an alternative way, melt polymerization was used to avoid the solubility constraint. In order to incorporate the PAES blocks in the melt, the hydroxy ethoxy terminated PAES were synthesized by modification reaction of the PAES oligomer with phenol end groups. Multiblock copolymers were successfully obtained with the melt reactions. When the polyester content was lower than 20 wt%, the polymers showed good solubility, high molecular weights, and similar mechanical property as Udel®. When the polyester content was high, crystallinity was observed in the polymers, however, low solubility was also observed.

5.6 Acknowledgements

This research was sponsored by the Army Research Laboratory and was accomplished under Cooperative Agreement Number W911NF-06-2-0014. The views and conclusions contained in this document are those of the authors and should not be interpreted as representing official policies, either expressed or implied, of the Army Research Laboratory or the U.S. Government. The U.S. Government is authorized to reproduce and distribute reprints for Government purposes notwithstanding any copyright notation hereon. We acknowledge the assistance of the Department of Chemistry and the Macromolecules & Interfaces Institute at Virginia Tech. We are grateful to Solvay Advanced Polymers L.L.C. and Eastman Chemical Company for supplying chemicals. We appreciate the assistance of Professor Long's, Professor Riffle's, and Professor McGrath's groups at Virginia Tech.

5.7 Future Work

5.7.1 Multiblock Copolymers with Different PAES Block to PCT Block Molar Ratio

In **Table 5.8**, the only PAES block to PCT block molar ratio used was 25:75. To complete this study, it will be necessary to synthesize the multiblock copolymers with different block molar ratios in order to determine the relative effects of the two different segments on the properties.

5.7.2 Further Study on the Crystallinity of the Multiblock Copolymers

It has been our long-term goal to synthesize semi-crystalline PAES systems with a large difference between T_m and T_g. Crystallinity in the PAES-polyester multiblock copolymers, especially the double melting peak observed in BP25PCT75 sample in

Table 5.8, is of interest. Further study needs to be done to understand the crystallization behavior. Detailed wide angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) study of the multiblock copolymers and the PCT polymer could be really helpful.

5.7.3 Mechanical Properties of the PAES-polyester Multiblock Copolymers

It is shown in **Table 5.7** that the mechanical properties were dominated by the PAES blocks with a weight percentage value of 20 wt% of PCT and 80 wt% of PAES. From a polyester mechanical enhancement point of view, the mechanical properties of the high molecular weight PAES can be achieved by connecting short PAES blocks with 20 wt% of PCT blocks. It is essential to answer the question what the maximum PCT weight percentage is before the loss of PAES's mechanical properties. It is also important to expand the idea to synthesize hydroxy ethoxy terminated PAES polymer with molecular weight higher than the entangle molecular weight and incorporate this long block in to the PAES-polyester copolymers to study the mechanical properties.

5.7.4 The PAES-polyester Multiblock Copolymer based on *trans*-Cyclohexylene Ring Units

All the research described earlier in this chapter was based on *cis*/*trans* mixed cyclohexylene ring units. With the introduction and research documented in **Chapter 3** and **4**, it will be very interesting to study the multiblock copolymers based on all *trans*-cyclohexylene units. In **Table 5.9**, the molecular weights and thermal properties of multiblock copolymers based on bisphenol-A and CHDM (all *trans* or *cis/trans*) were listed. Compared with the same polymer sample made with *cis/trans* mixed CHDM (BisA25ctCHDM75DMT100), the all *trans* sample (BisA25tCHDM75DMT100) showed a 13 °C increase in the glass transition temperature. The extension and systematic study of the multiblock copolymers with all *trans*-cyclohexylene rings will be very important to the current research topic.

Table 5.9 The molecular weight and thermal properties of melt synthesized PAES-polyester multiblock copolymer based on bisphenol-A and all *trans*-CHDM

Polymers	M_n kg mol^{-1}	M_w kg mol^{-1}	PDI[3]	T_d[4] (°C)	T_g (°C)
BisA25tCHDM75DMT100[1]	10.5	22.6	2.2	429	159
BisA25ctCHDM75DMT100[2]	28.9	64.2	2.2	393	146

[1] The numbers indicate molar ratio of the monomers, tCHDM stands for all *trans*-CHDM

[2] The numbers indicate molar ratio of the monomers, ctCHDM stands for CHDM with *cis/trans* ratio of 30/70

[3] NMP as the SEC solvent with a refractive index detector and a viscometer

[4] T_d is defined as 5 % weight loss temperature in N_2 in DSC study

5.7.5 Incorporation of Other Ring Containing Units

The primary hydroxyl function groups in the hydroxy ethoxy terminated PAES oligomer makes it very easy to incorporate the PAES blocks into the PAES-polyester by reacting with diols and diesters. Other ring containing multiblock copolymer can be easily synthesized by using new diols or diesters. For examples, 2,2,4,4-tetramethylcyclobutane-*trans*-1,3-diol can be used along with the hydroxy ethoxy terminated PAES oligomer to make a new family of 1,3-cyclobutane ring containing multiblock copolymers. This methodology can be used to product an extremely wide variety of multiblock copolymers.

5.8 Appendix

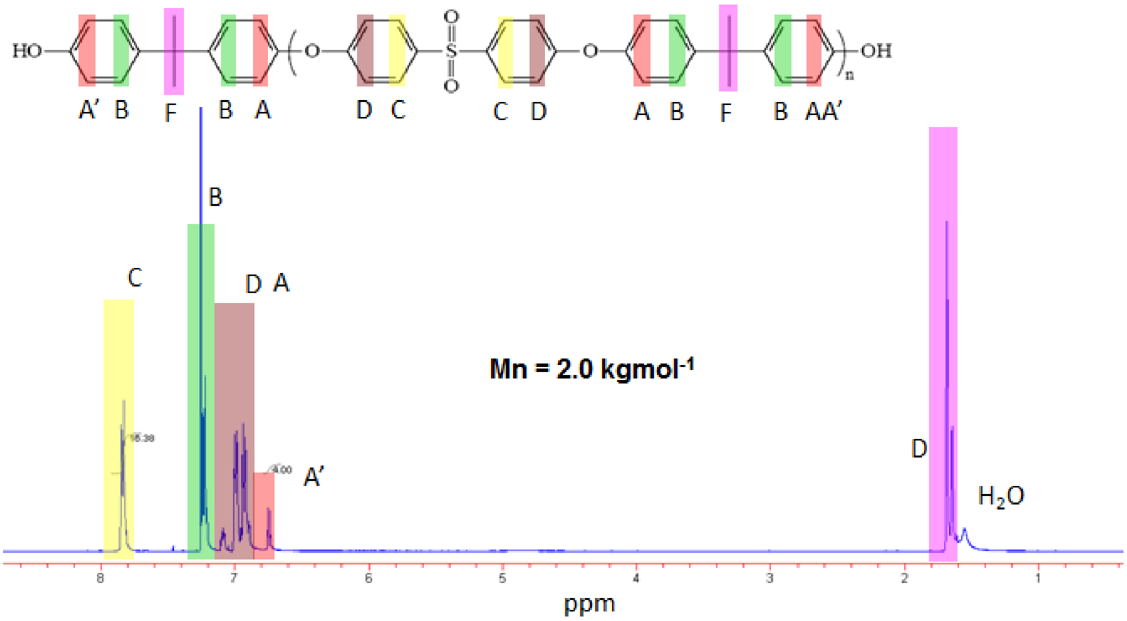


Figure 5.13 The ^{1}H NMR of bisphenol-A based PAES oligomer with phenol end groups (target molecular weight = 2.0 kg mol^{-1})

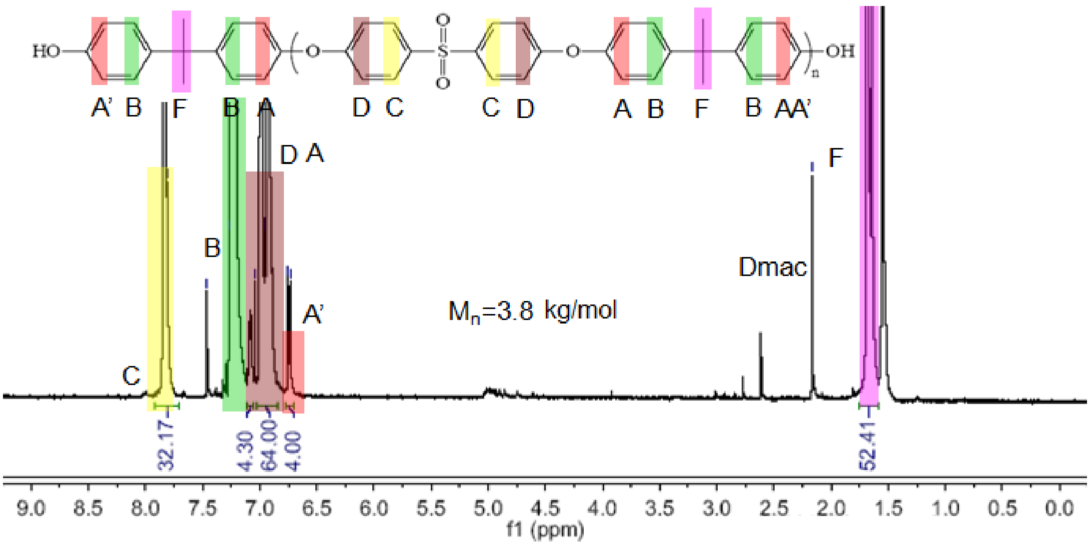


Figure 5.14 The ^{1}H NMR of bisphenol-A based PAES oligomer with phenol end groups (target molecular weight = 4.0 kg mol^{-1})

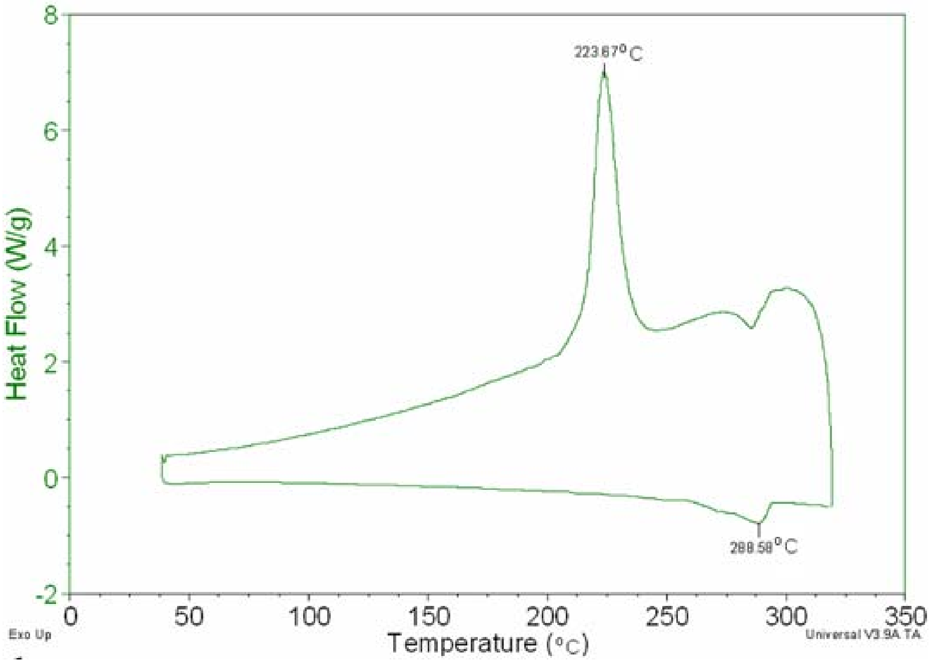


Figure 5.15 The DSC curve of the PCT oligomer with methyl ester end groups (structure shown in **Figure 5.4**)

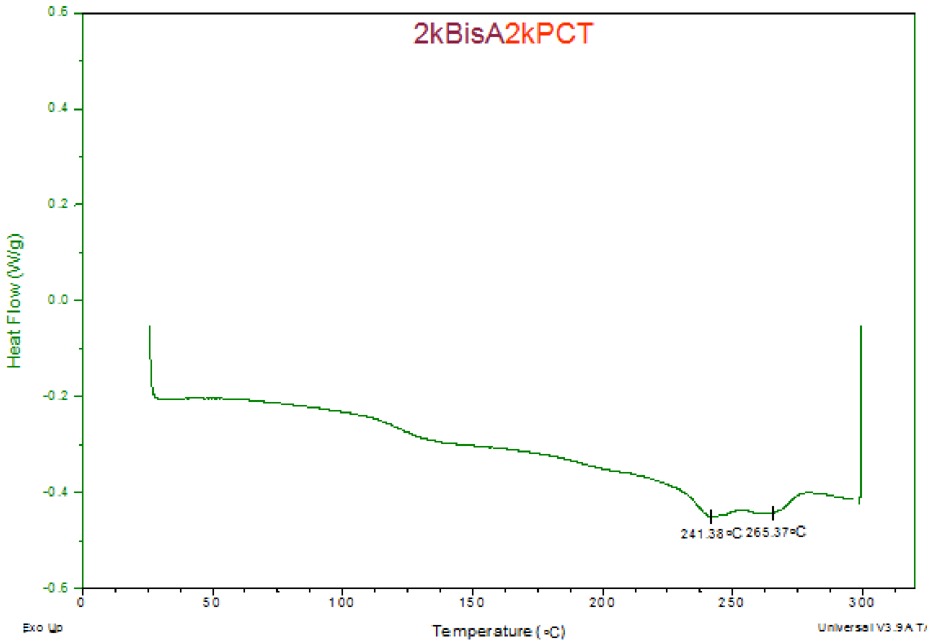


Figure 5.16 The DSC curve of the PAES-polyester multiblock copolymers annealed at 215 °C for 30 min

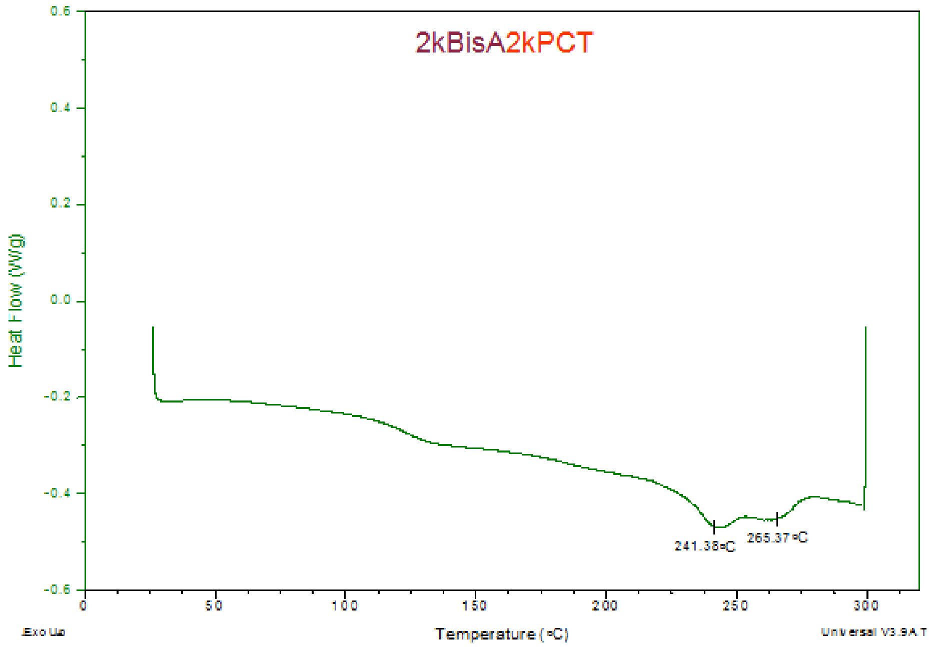


Figure 5.17 The DSC curve of the PAES-polyester multiblock copolymers annealed at 215 °C for 60 min

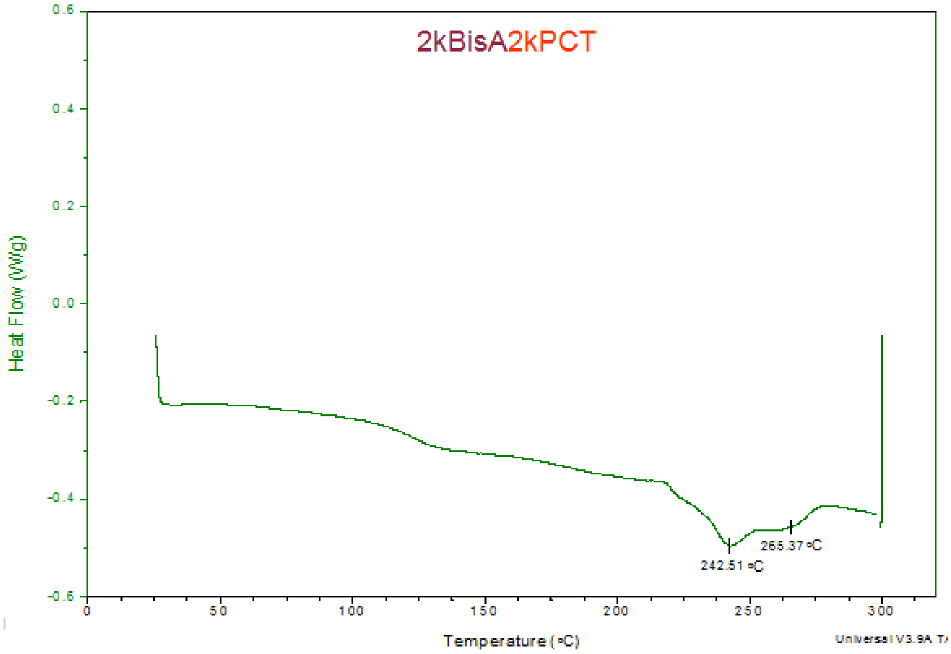


Figure 5.18 The DSC curve of the PAES-polyester multiblock copolymers annealed at 215 ^{o}C for 120 min

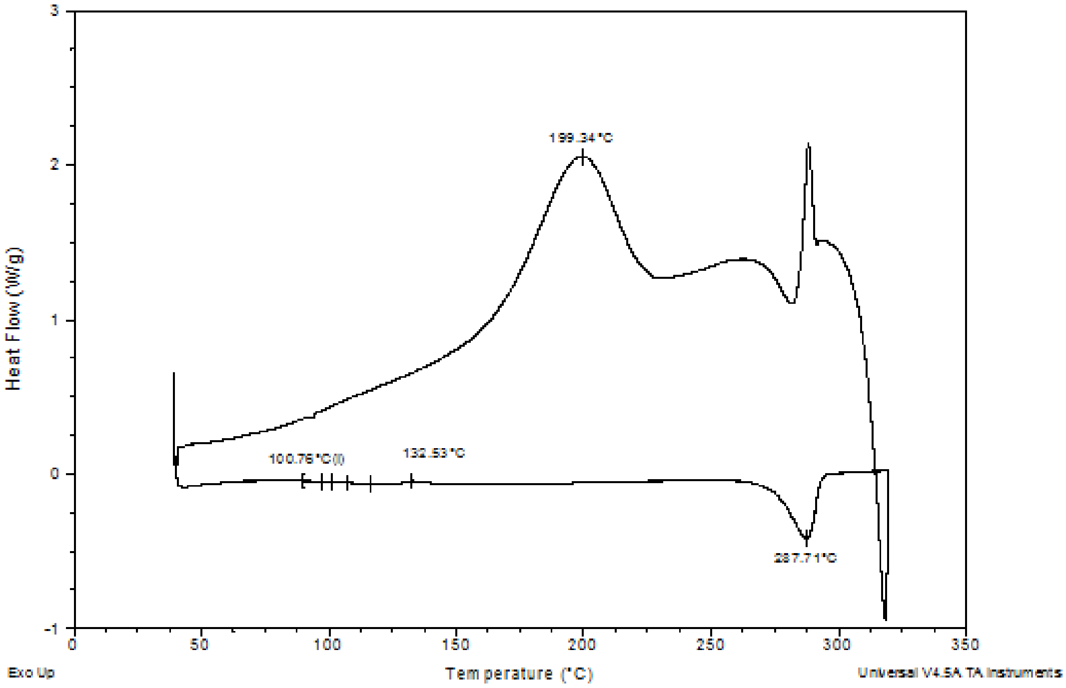


Figure 5.19 The DSC curve of the PCT homopolymer

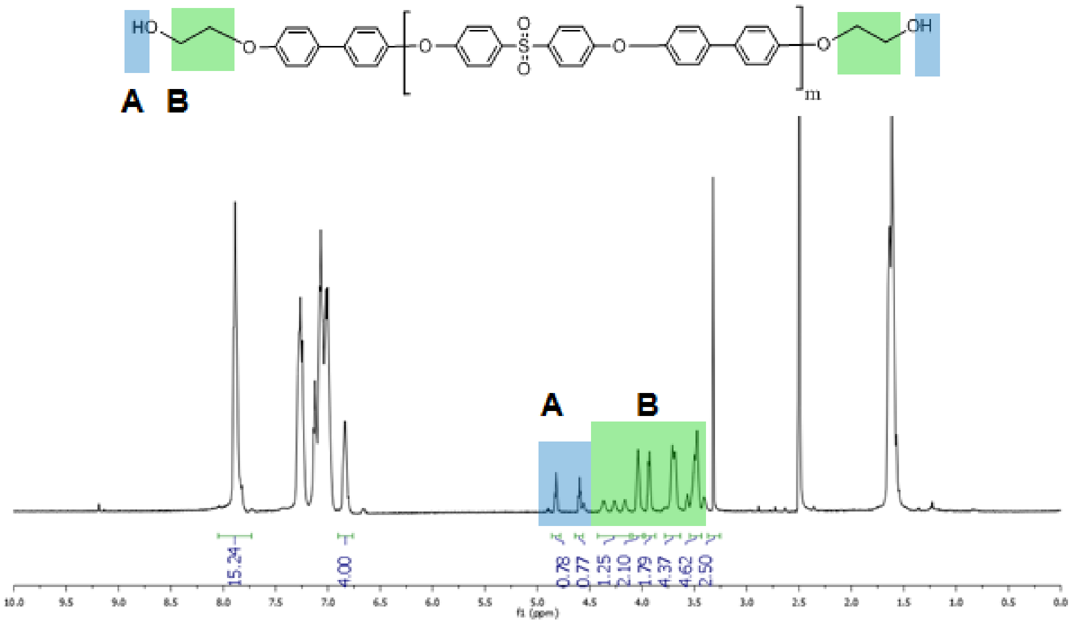


Figure 5.20 The ^{1}H NMR that indicated a multiple addition side reaction in the synthesis of biphenol based PAES oligomer with hydroxy ethoxy end groups

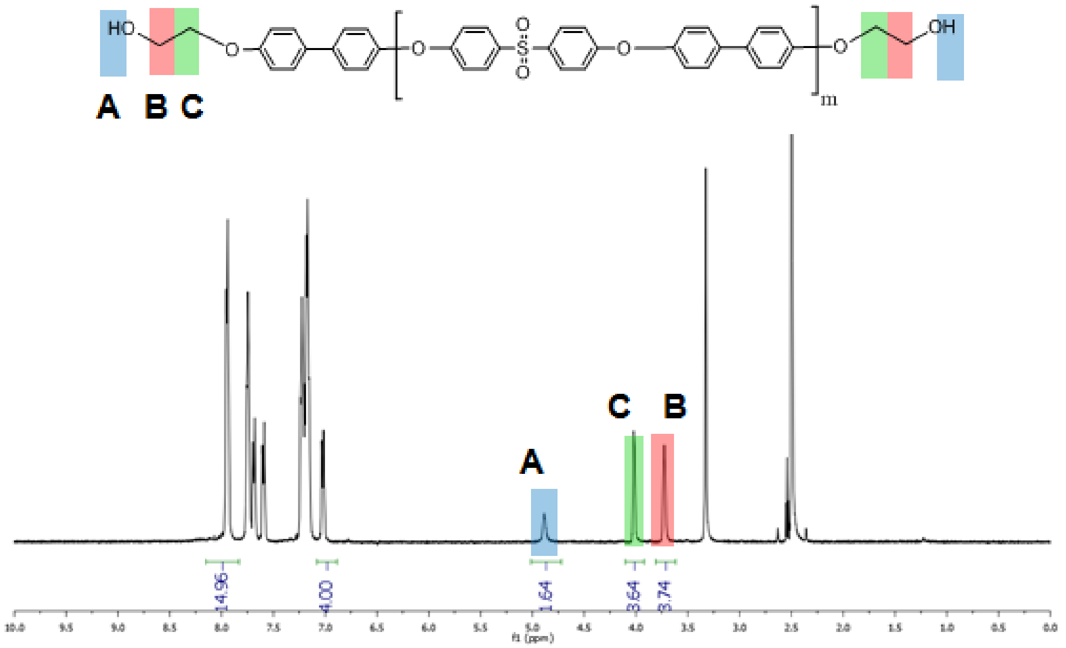


Figure 5.21 The ^{1}H NMR of the biphenol based PAES oligomer with hydroxy ethoxy end groups under optimized reaction condition

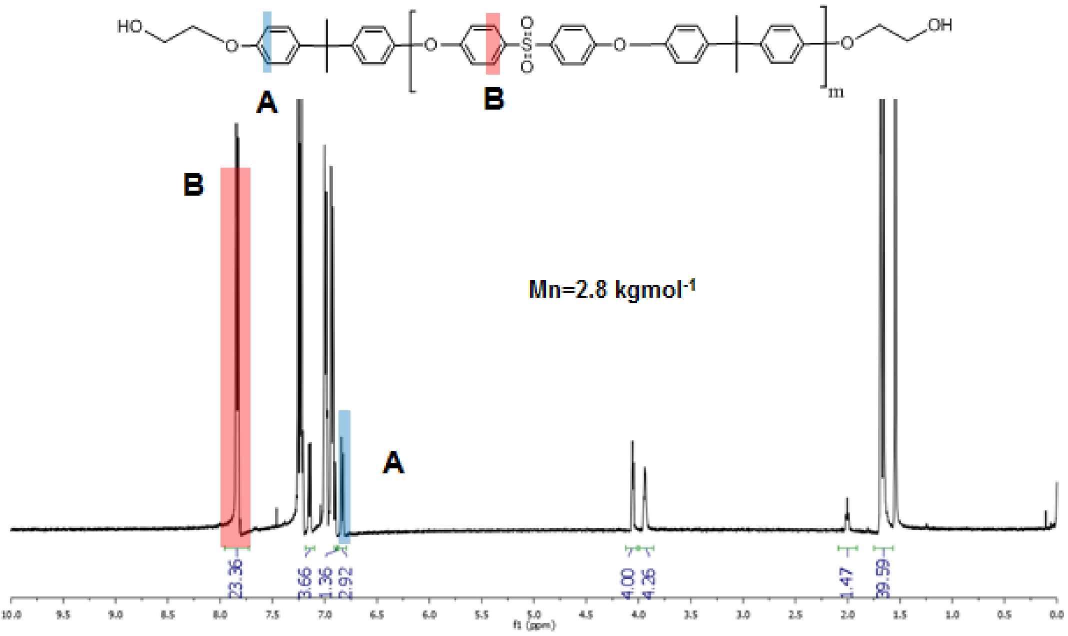


Figure 5.22 The ^{1}H NMR spectra showing molecular weight determination of bisphenol-A based PAES oligomer with hydroxy ethoxy end groups (in DMSO-d6)

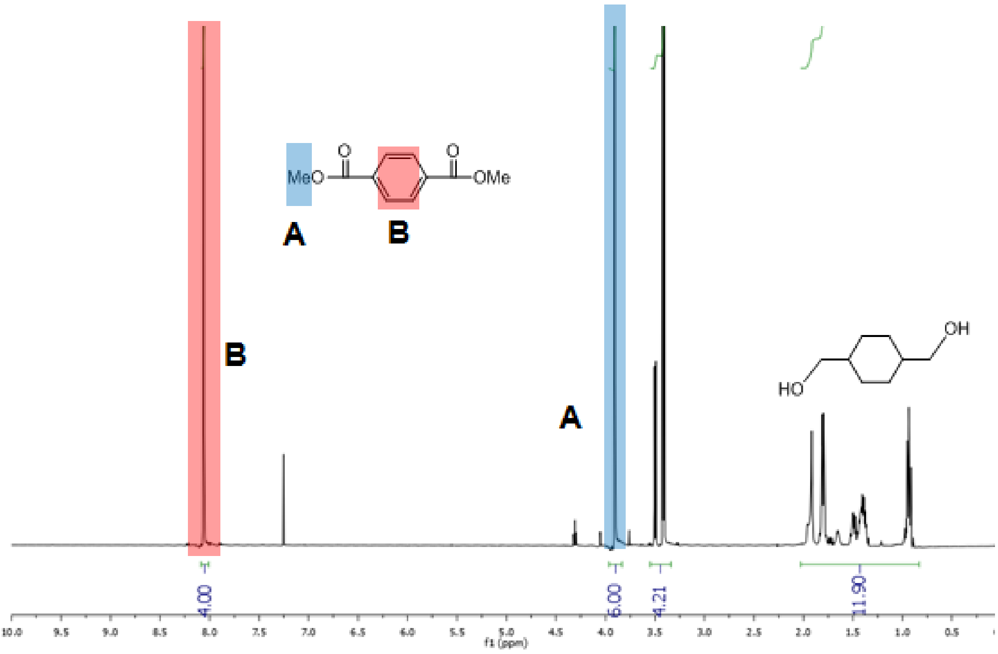


Figure 5.23 The ^{1}H NMR spectrum of the white solid collected in the adaptor during the melt polymerization of the multiblock copolymer synthesis

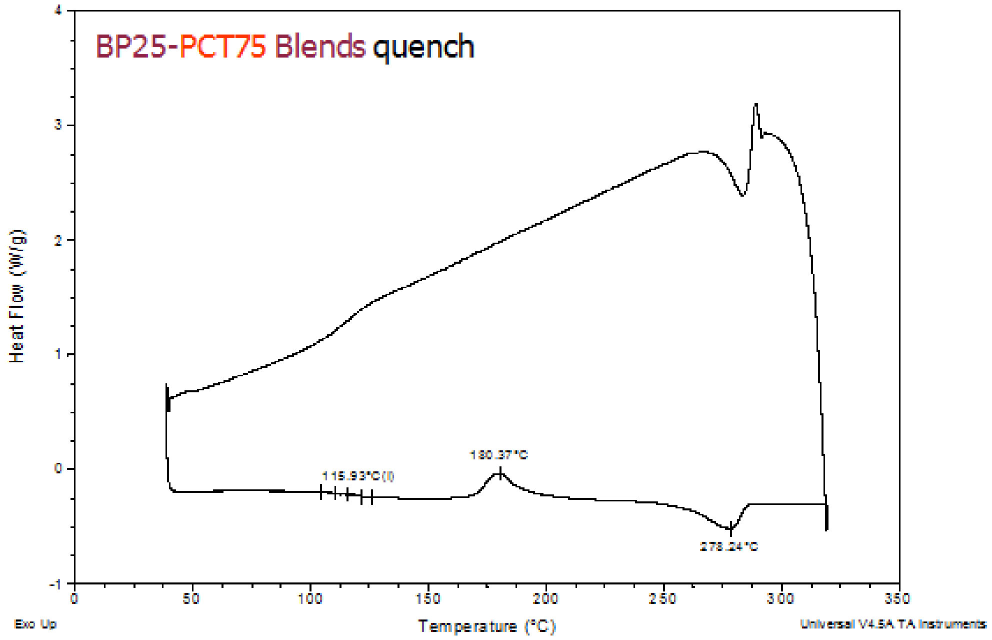


Figure 5.24 The quenching DSC curve of the biphenol based PAES oligomer and PCT homopolymer blend

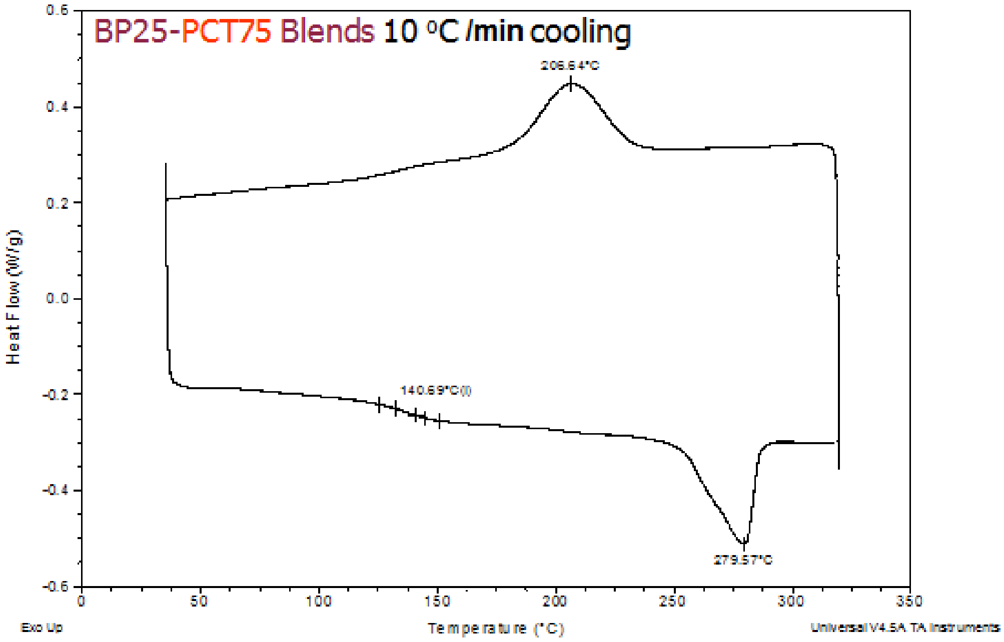


Figure 5.25 The DSC curve of the biphenol based PAES oligomer and PCT homopolymer blend with 10 ^{o}C/min cooling rate

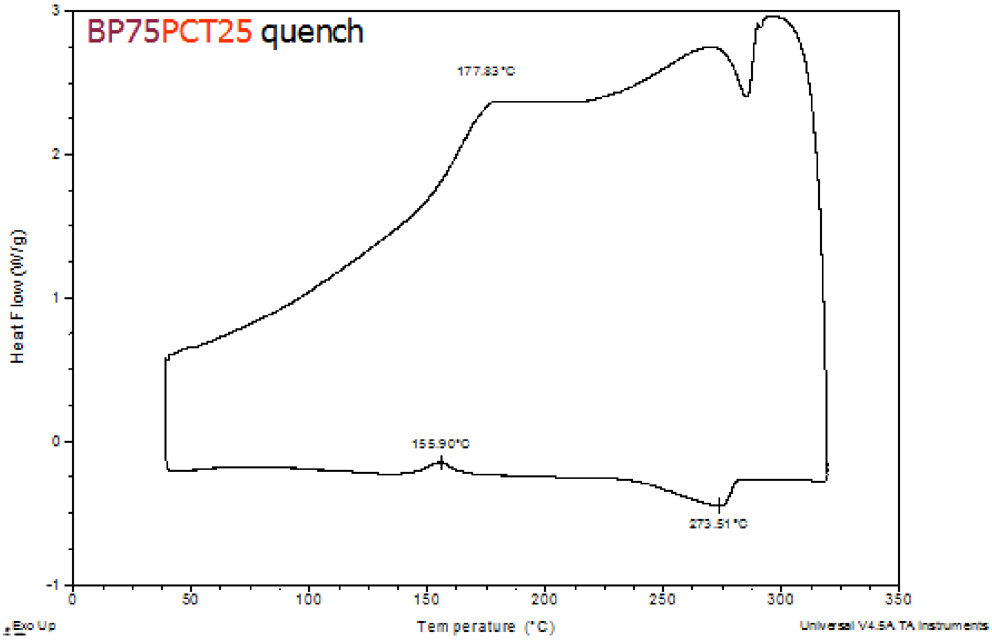


Figure 5.26 The quenching DSC curve of multiblock copolymers based on biphenol PAES oligomer

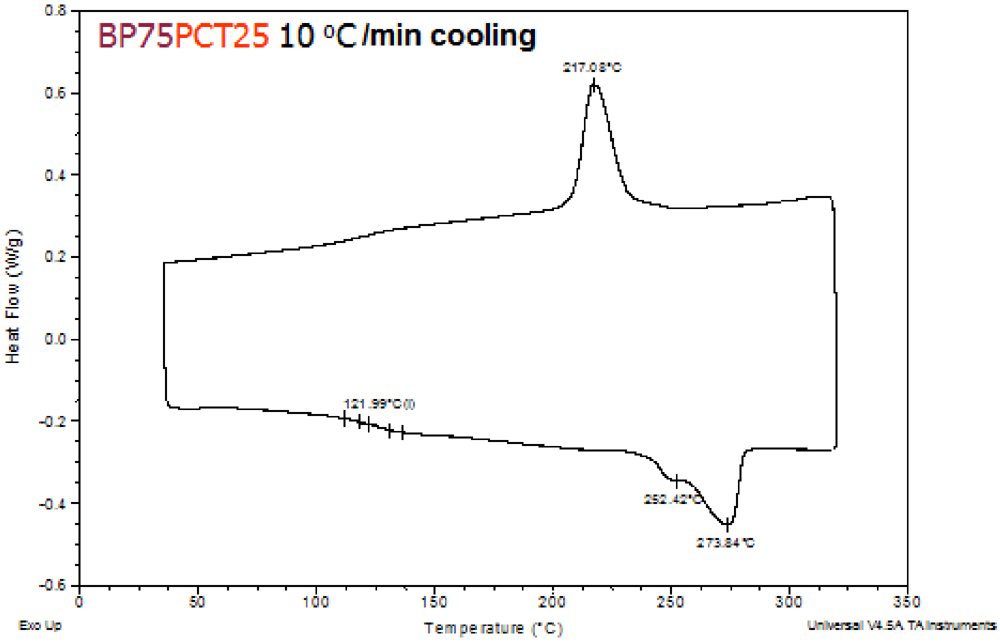


Figure 5.27 The DSC curve of the biphenol based PAES oligomer and PCT homopolymer blend with 10 ^{o}C/min cooling rate

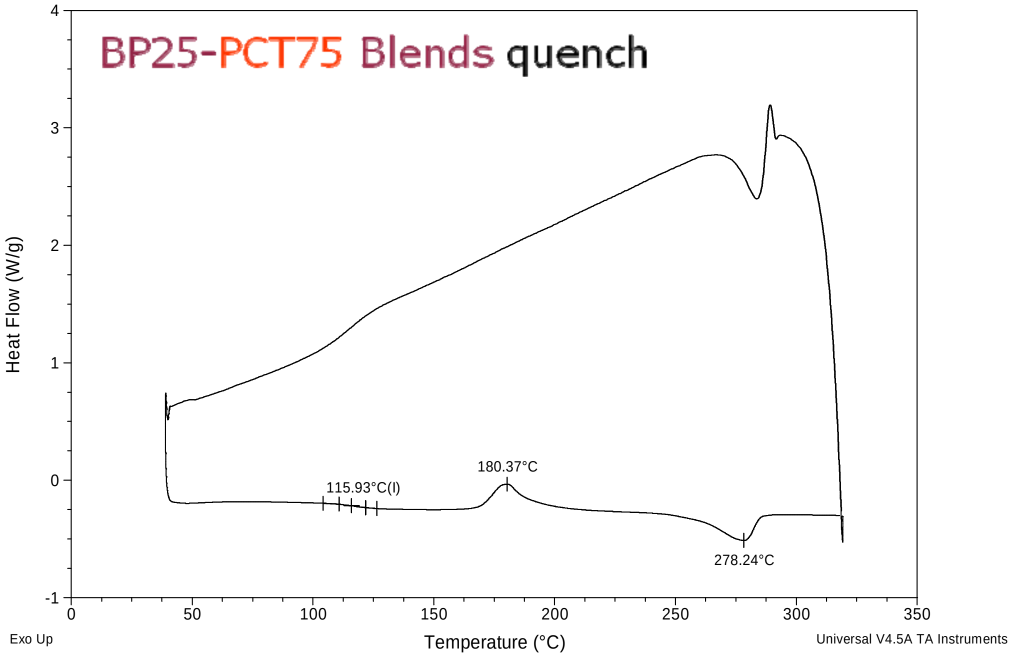


Figure 5.28 The original DSC curve of BP25-PCT75 Blends shown in **Table 5.8** (quenched in the cooling cycle and 10 ^{o}C/min in the heating cycles).

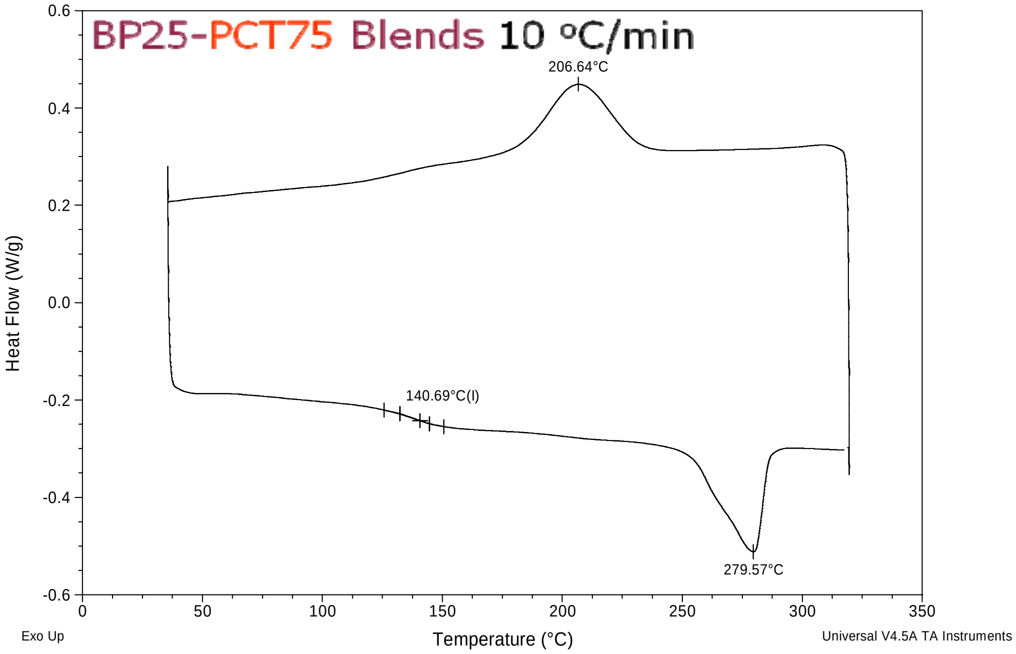


Figure 5.29 The original DSC curve of BP25-PCT75 Blends shown in **Table 5.8** (10 ^{o}C/min in both the cooling cycle and the heating cycles).

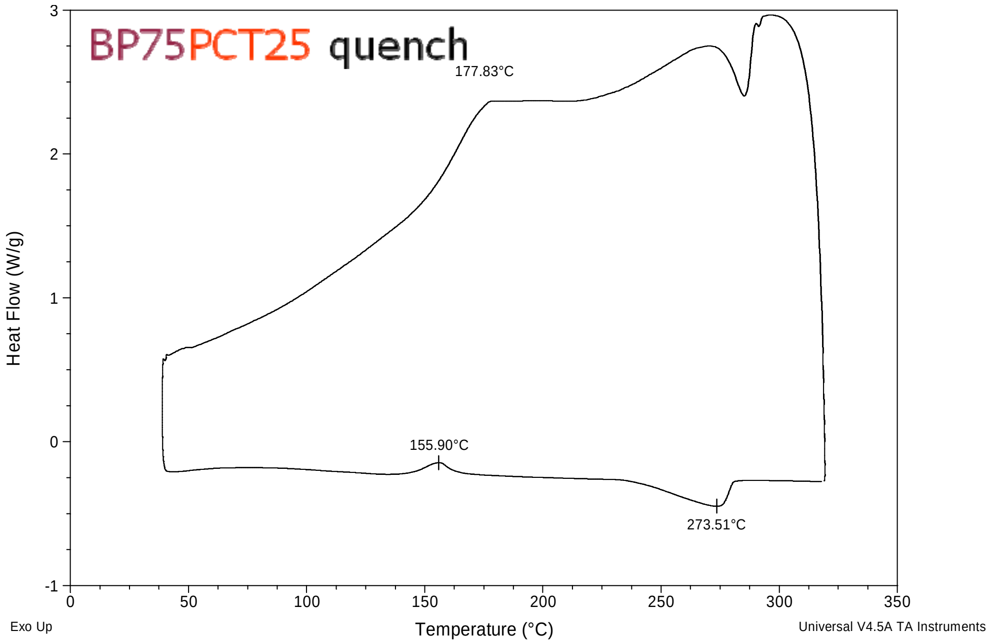


Figure 5.30 The original DSC curve of BP25PCT75 polymer shown in **Table 5.8** (quenched in the cooling cycle and 10 ^{o}C/min in the heating cycles).

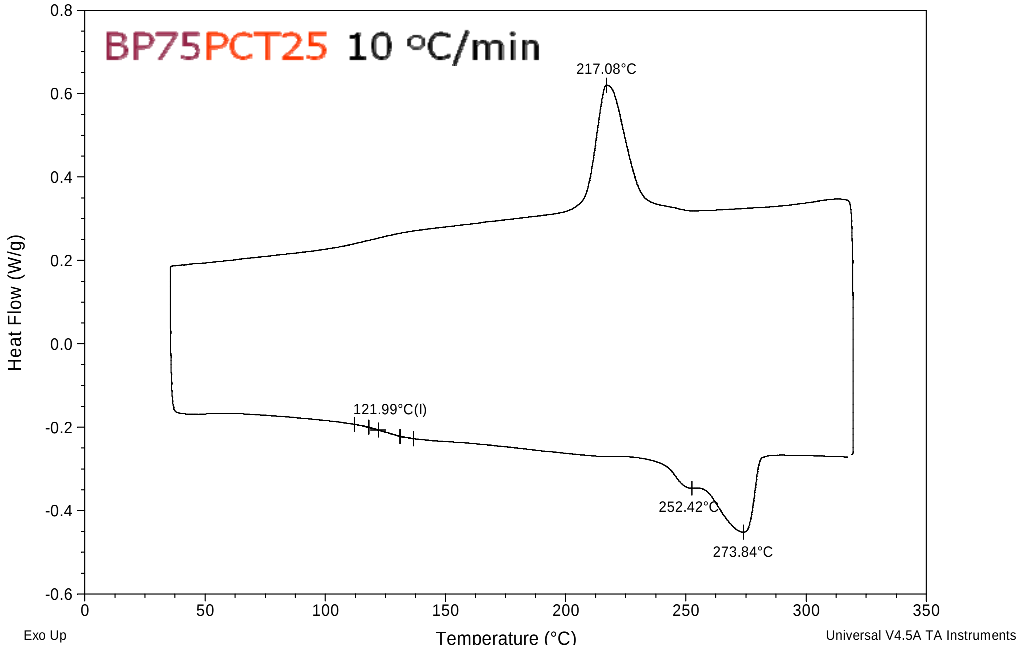


Figure 5.31 The original DSC curve of BP25PCT75 polymer shown in **Table 5.8** (10 ^{o}C/min in both the cooling cycle and the heating cycles).

5.9 Reference

(1) Odian, G. *Principles of Polymerization*; John Wiley and Sons, 2004.

(2) Haussler, L.; Pospiech, D.; Eckstein, K.; Jehnichen, D. *Thermochim. Acta* **1999**, *339*, 87.

(3) McGrath, J. E. *Abstracts of Papers, 242nd ACS National Meeting & Exposition, Denver, CO, United States, August 28-September 1, 2011* **2011**, PMSE.

(4) Pospiech, D.; Haeussler, L.; Komber, H.; Voigt, D.; Jehnichen, D.; Janke, A.; Baier, A.; Eckstein, K.; Boehme, F. *J. Appl. Polym. Sci.* **1996**, *62*, 1819.

(5) Pospiech, D.; Haussler, L.; Eckstein, K.; Komber, H.; Voigt, D.; Jehnichen, D.; Friedel, P.; Gottwald, A.; Kollig, W.; Kricheldorf, H. R. *High Perform. Polym.* **2001**, *13*, S275.

(6) Gottwald, A.; Jehnichen, D.; Pospiech, D.; Friedel, P.; Janke, A. *J. Macromol. Sci., Phys.* **1999**, *B38*, 549.

(7) Haussler, L.; Pospiech, D.; Eckstein, K.; Janke, A.; Vogel, R. *J. Appl. Polym. Sci.* **1997**, *66*, 2293.

(8) Jehnichen, D.; Friedel, P.; Kummer, S.; Haussler, L.; Eckstein, K.; Pospiech, D. *Mater. Sci. Forum* **2000**, *321-324*, 475.

(9) Pospiech, D.; Haeubler, L.; Meyer, E.; Janke, A.; Vogel, R. *J. Appl. Polym. Sci.* **1997**, *64*, 619.

(10) Pospiech, D.; Haussler, L.; Eckstein, K.; Komber, H.; Voigt, D.; Janke, A.; Gottwald, A.; Jehnichen, D.; Kricheldori, H. R. *EUROMAT 99, Biannu. Meet. Fed. Eur. Mater. Soc. (FEMS)* **2000**, *13*, 292.

(11) Pospiech, D.; Haussler, L.; Eckstein, K.; Komber, H.; Voigt, D.; Jehnichen, D.; Meyer, E.; Janke, A.; Kricheldorf, H. R. *Des. Monomers Polym.* **1998**, *1*, 187.

(12) Robeson, L. M.; Farnham, A. G.; McGrath, J. E. *Appl. Polym. Symp.* **1975**, *26*, 373.

(13) Rose, J. B. *Polymer* **1974**, *15*, 456.

(14) Cameron, D. J. A.; Shaver, M. P. *Chem. Soc. Rev.* **2011**, *40*, 1761.

(15) Malik, M.; Choudhary, V.; Varma, I. K. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **2000**, *C40*, 139.

(16) Papaspyrides, C. D. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1984**, *C24*, 325.

(17) Scheirs, J.; Long, T. E. *Modern Polyesters: Chemistry and Technology of Polyesters and Copolyesters* 1ed.; Wiley, 2003.

(18) Turner, S. R.; King, B.; Ponasik, J.; Adams, V.; Connell, G. *High Perform. Polym.* **2005**, *17*, 361.

(19) Liu, Y.; Turner, S. R.; Wilkes, G. *Macromolecules (Washington, DC, U. S.)* **2011**, *44*, 4049.

(20) Brunelle, D. J.; Jang, T. *Polymer* **2006**, *47*, 4094.

Chapter 6 Preliminary Results for Future Work

6.1 Abstract

The preliminary study of the synthesis and reaction kinetics of poly(arylene ether sulfone)-polyurethane multiblock copolymer is described in this chapter. The multiblock copolymers were obtained by a two-step polymerization based on hydroxy ethoxy terminated PAES oligomer. Only low molecular weight samples were obtained under the conditions studied. The kinetic study suggested that the reaction was done in the initial 3.5 h. Products obtained with longer reaction time showed lower molecular weights, which indicated possible side reactions. A systematic optimization needs to be performed to build up the molecular weight.

6.2 Introduction

Polyurethane (PU) is a class of very important thermoplastics that has extremely wide industrial applications including, but not limited to, synthetic fabric, fiber, shape memory foam, and adhesives.[1-3] It is a multiblock copolymer that is usually composed of soft segments and hard segments. The common soft blocks are polymeric glycols (eg. polytetramethylene glycol, polyethylene oxide) which are the low glass transition temperature components to provide flexibility. The hard segments are incorporated with the soft segments by the chain extender. The morphology and properties of PU are heavily dependent on the structure of the chain extender.[4-14] Convention chain extenders for linear PUs are diols such as 1,4-butanediol and 1,6-hexanediol. One major concern of the PU material made from the conventional chain extenders is the thermal stability. It has been reported that the conventional PU starts to lose its mechanical properties at a temperature around 90 ^{o}C.[15] Considerably research has been invested to explore using new materials to blend with or synthesize PU.[5-8,13-18]

The research discussed in this chapter is to use the hydroxy ethoxy terminated poly(arylene ether sulfone) (PAES) oligomer to synthesize the PU based material. PAES as a class of high glass transition temperature engineer thermoplastics shows excellent mechanical properties and thermal stability.[19-22] Some of the recent work in PU synthesis suggested that using high T_g hard segments can increase the thermal stability and enhance the nanophase separation.[15,18,23] In this research, the PAES-PU multiblock copolymer was synthesized through a two-step procedure based on hydroxy ethoxy terminated PAES oligomer and PTMG soft segments. Preliminary reaction kinetics was also studied.

6.3 Experimental

6.3.1 Materials

All the chemicals were purchased from Aldrich. Polytetramethylene glycol (PTMG) was dried in a vacuum oven (-80 kPa) at 100 ^{o}C for 12 h prior to the reaction. All the other reagents were used without further purification.

6.3.2 Instrumentation

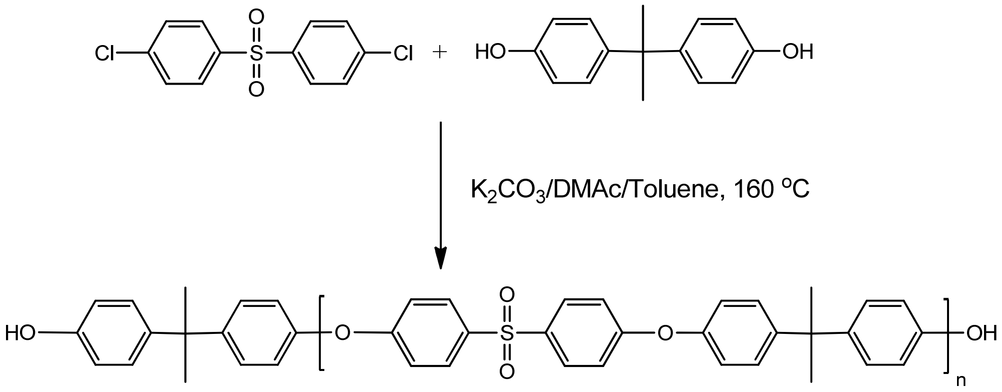
The ^1H and ^{13}C NMR spectra were obtained on a JEOL 500 (500 MHz) spectrometer at room temperature with chemical shifts relative to tetramethylsilane (TMS).

Size exclusion chromatography (SEC) was used to determine the molecular weights and the molecular weight distributions. The data were obtained in the SEC solvent at 30 ^oC on a Waters Alliance model 2690 chromatograph equipped with a Waters HR 0.5+ HR 2+ HR 3+ HR 4+ styragel column set. Viscotek refractive index detector and a viscometer were used for the molecular weight determination. Polystyrene standards were utilized to construct a universal molecular weight calibration curve. Chloroform and NMP were used as the SEC solvents with a flow rate of 0.500 mL/min.

6.3.3 Synthesis of Oligomers and Polymers

6.3.3.1 Synthesis of Bisphenol-A based Phenol Terminated Poly(arylene ether sulfone)s Oligomer with Controlled Molecular Weight

The reaction scheme is shown in **Scheme 6.1** and the reaction apparatus set up is shown in **Figure 6.1**. The phenol terminated bisphenol (bis-A) based PAES oligomer with 2.0 kg/mol target molecular weight was synthesized by using the stoichiometry imbalance technique based on the Carothers equation. A typical procedure is described as follows.



Scheme 6.1 Synthesis of the bis-A based PAESs with phenol end groups

5.036 g (17.54 mmol) of dichlorodiphenyl sulfone (DCDPS), 5.000 g (21.90 mmol) of bis-A, 7.870 g (56.95 mmol) of K_2CO_3, 80.0 mL of DMAc and 40.0 mL of toluene were added to a flask equipped with a mechanical stirrer, an argon inlet and a Dean-Stark trap. The reaction was heated to 140 ^{o}C for 3 h to remove water by azeotropic distillation. Then toluene was distilled out by increasing the temperature slowly to 160 ^{o}C in 2 h. After 20 h at 160 ^{o}C the reaction mixture was cooled to room temperature. White solid was obtained by the precipitation of the reaction mixture in a 5 weight percent HCl aqueous solution and filtration. The product was thoroughly washed three times with 200 mL of deionized water and methanol respectively. After drying at 120 ^{o}C for 12 h in a vacuum oven (-80 kPa), the product was obtained with a yield of 92.4 %. ^{1}H NMR ($CDCl_3$, ppm): δ 8.18 (m, 16.38), δ 7.21 (m), δ 7.06 (m), δ 6.96 (m), δ 6.91 (m), δ 6.72 (m, 4.00), δ 1.66 (m). In the proton NMR, the integration area ratio between the protons with the chemical shift of δ 6.72 and δ 8.18 was used to determine the number average molecular weights. The actual molecular weights of the oligomers were close to the 2.0 kg mol^{-1} target.

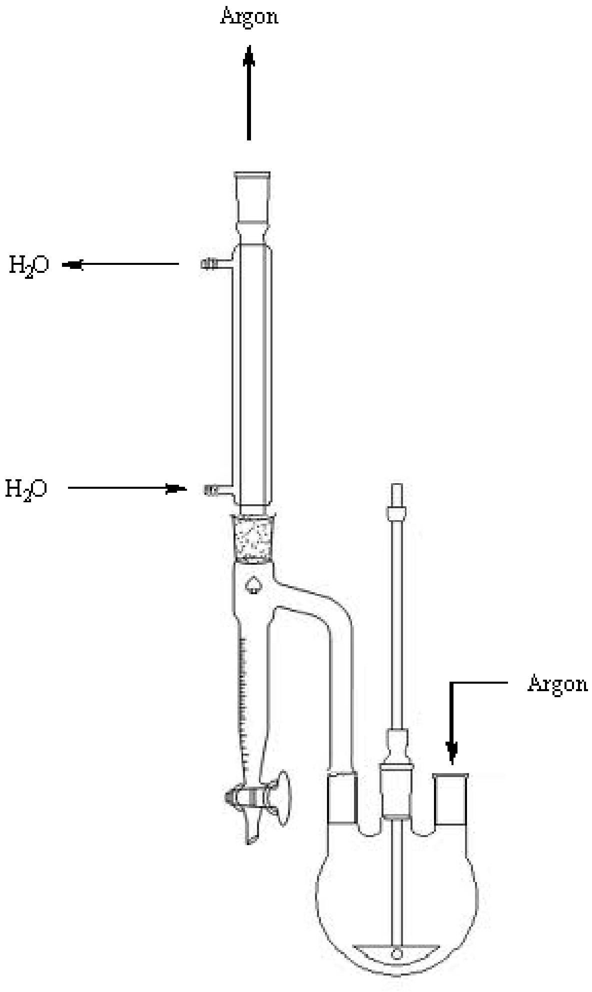
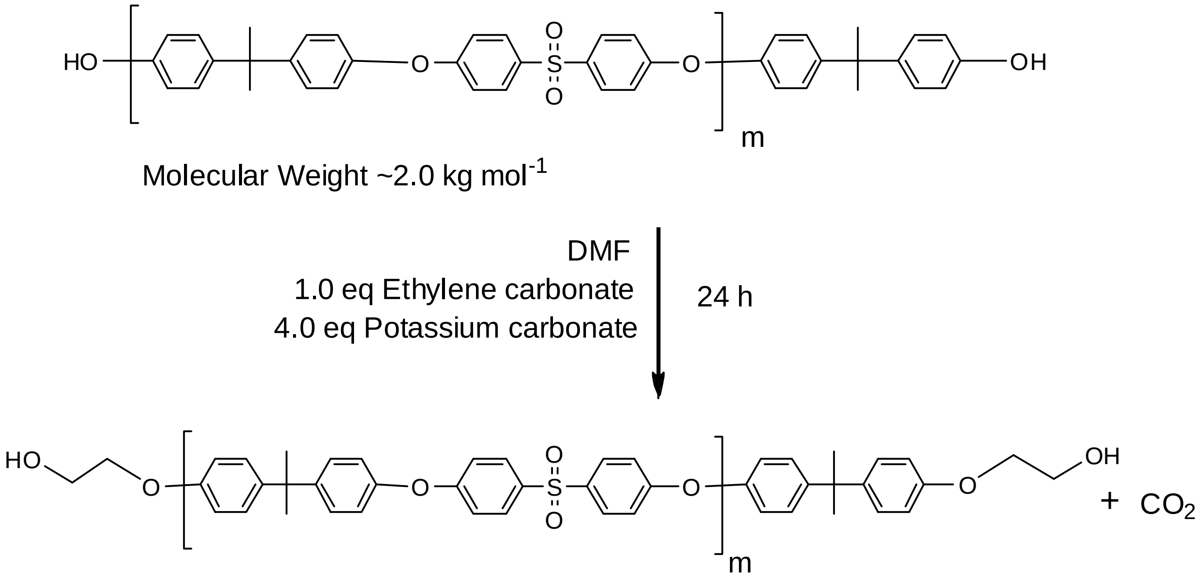


Figure 6.1 The reaction apparatus set up of PAES synthesis

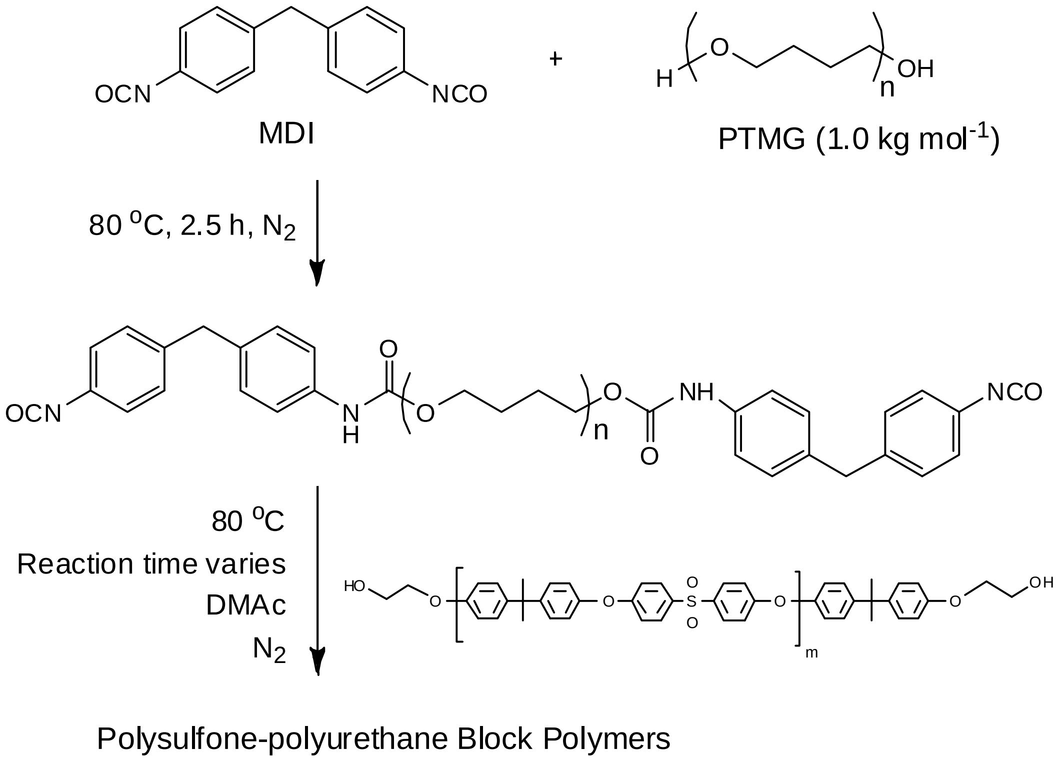
6.3.3.2 Synthesis of Bisphenol-A based Poly(arylene ether sulfone)s Oligomer with Hydroxy Ethoxy End Groups



Scheme 6.2 Synthesis of the bis-A based PAESs with hydroxy ethoxy end groups

The bisphenol-A based hydroxy ethoxylated PAES oligomer was synthesized as shown in **Scheme 6.2**. 15.00 g (5.484 mmol) of bisphenol-A based phenol terminated PAES oligomer, 4.826 g (54.84 mmol) of ethylene carbonate, 0.7568 g (5.484 mmol) of potassium carbonate and 120.0 mL of DMF were charged to a 250 mL round bottom flask equipped with an argon inlet, a condenser and a Teflon coated magnetic stir bar. In the presence of argon, the reaction was heated at 80 °C for 24 h with stirring. After cooled to room temperature, the reaction solution was precipitated in 600 mL of water and then filtered. The white powder obtained was washed with 200 mL of water three times and dried in a vacuum oven (-80 kPa) at 100 ^{o}C for 12 h. The final product was obtained as white powder with a yield of 90.8 %. ^{1}H NMR (DMSO-d6, ppm): δ 7.88 (m), δ 7.26 (m), δ 7.06 (m), δ 6.96 (m), δ 6.83 (m), δ 4.83 (t), δ 3.92 (m), δ 3.67 (m), δ 1.62 (m). In the proton NMR, the integration area ratio between the protons with the chemical shift of δ 6.96 and δ 7.88 was used to determine the number average molecular weights. The actual molecular weights of the oligomers were close to the 2.0 kg mol^{-1} target.

6.3.3.3 Synthesis of Poly(arylene ether sulfone)s-polyurethane Multiblock Copolymers



Scheme 6.3 Synthesis of the bis-A based PAESs with hydroxy ethoxy end groups

The synthesis of poly(arylene ether sulfone)s-polyurethane multiblock copolymers was done by two steps as shown in **Scheme 6.3**. The first step is the formation of the prepolymer (the soft segment of the polyurethane). The second step is the formation of the polysulfone-polyurethane multiblock copolymer based on the prepolymer and the PAES oligomer. The typical procedures of the two steps are described as follows.

2.000 g (2.0 mmol) PTMG with 1.0 kg mol^{-1} and 1.001 g (4.000 mmol) methylene diphenyl diisocyanate (MDI) were charged into a 100 mL three-necked round bottom flask equipped with a condenser, a magnetic stir bar, and a nitrogen inlet. The reaction mixture heated at 80 ^{o}C for 2.5 h in the presence of the inert gas. 5.400 g (2.000 mmol) bisphenol-A based PAES oligomer with hydroxy ethoxy end groups was added to the prepolymer with 50 mL of DMAc. The reaction solution was allowed to continuously react at 80 ^{o}C for up to 19 h. The polymer product was isolated as white solid by precipitation of the reaction solution in 600 mL of deionized water. After the filtration, the polymer was dried in a vacuum oven (-80 kPa) at 100 ^{o}C for 12 h.

6.4 Results and Discussion

6.4.1 Synthesis of the Oligomers and the Poly(arylene ether sulfone)-polyurethane Multiblock Copolymers

This chapter describes the preliminary work on the poly(arylene ether sulfone)s-polyurethane multiblock copolymers based on hydroxy ethoxy terminated PAES oligomers. Bisphenol-A based oligomer was selected for this initial study because it is inexpensive and offers very good solubility in various solvents. The reaction optimization was discussed in **Chapter 5**. Under the optimized reaction condition, the oligomer with hydroxy ethoxy end groups was carefully characterized and the molecular weight was determined as 2.7 kg mol^{-1} by ^{1}H NMR analysis.

6.4.2 Synthesis and Kinetic Study of the Poly(arylene ether sulfone)-polyurethane Multiblock Copolymers

As shown in **Scheme 6.3**, the first step of the poly(arylene ether sulfone)-polyurethane multiblock copolymer synthesis was the bulk polymerization of the soft segment prepolymer. MDI was stored in dry nitrogen atmosphere and reacted with predried PTMG with 1.0 kg mol^{-1} number average molecular weight. In the second step, the hydroxy ethoxy terminated PAES oligomer was used as a “macro chain extender” to form the hard segment. The molar ratio of PTMG, MDI, and PAES oligomer was 1:2:1 to achieve the 1:1 molar ratio of the functional groups.

A kinetic study was performed to monitor the multiblock copolymer synthesis reaction. The molecular weight and reaction time results are shown **Table 6.1**. The polymers listed in the table were synthesized from the same starting materials with the same reaction condition and molar ratio. The only different reaction parameter was the reaction time. From the top to the bottom of the table, the reaction time increases from 60 min (1 h) to 1140 min (19 h). Across the table, slight molecular weight increases over the oligomer molecular weight were observed. The highest molecular weight results were observed with the reaction time of 60 min. As the reaction time increased from 60 min to 1140 min, the molecular weights decreased.

Table 6.1 Reaction time and molecular weight results for the kinetic study of the poly(arylene ether sulfone)-polyurethane multiblock copolymer solution reaction

PAES-PU multiblock copolymers	Reaction time (min)	M_n $\times 10^3$ g mol^{-1}	M_w $\times 10^3$ g mol^{-1}	PDI[3]
PAES[1]	-	2.7[2]	-	-
PAES-PU 1	60	4.5	6.7	1.5
PAES-PU 2	150	4.1	6.6	1.6
PAES-PU 3	210	3.7	5.8	1.5
PAES-PU 4	330	3.8	5.9	1.5
PAES-PU 5	420	3.9	5.9	1.5
PAES-PU 6	1140	3.2	5.0	1.6

[1] Hydroxy ethoxy terminated PAES oligomers based on bisphenol-A units

[2] Determined by ^{1}H NMR end group analysis

Figure 6.2 describes the relationship between the molecular weight results and the reaction time. The decreasing of the molecular weight with the reaction time can be clearly observed. These results indicated that the multiblock copolymer reaction was done within the first hour and as the reaction time prolonged, a minor side reaction (possibly hydrolysis of polyurethane) happened resulting in the decrease of the molecular weight. To build up the molecular weight, further study should focus on the reactions with different starting material molar ratios and anhydrous solvents.

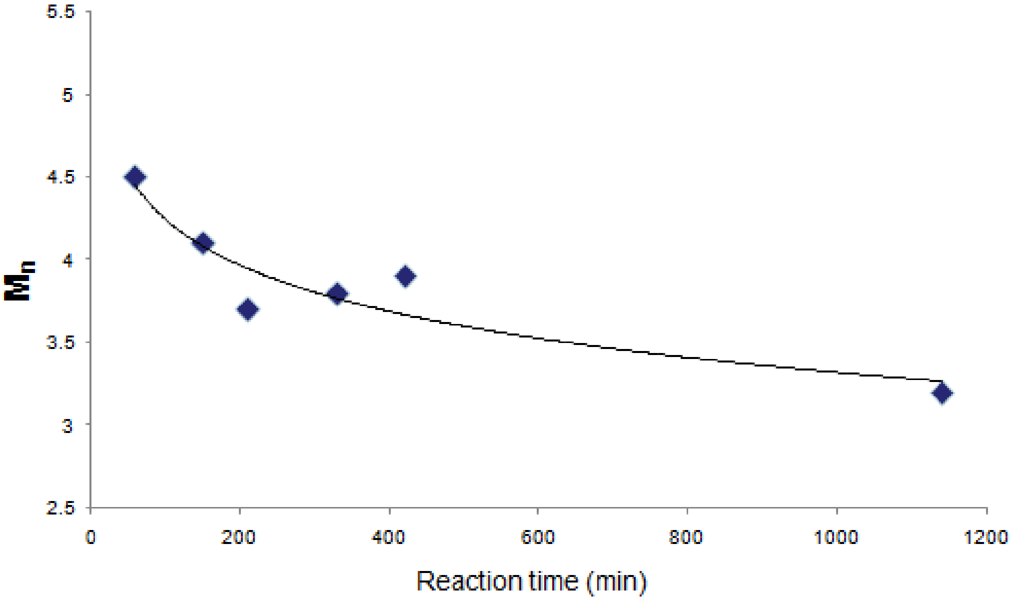


Figure 6.2 The molecular weight results of PAES-PU samples with different reaction times

6.5 Conclusions

The research discussed in this chapter is based on the idea of using the hydroxy ethoxy terminated PAES oligomer as a “macro” chain extender. The incorporation of a hard segment with high glass transition temperature is suggested in the literature to be able to enhance the thermal properties and the nanophase separation of polyurethane based materials. In this initial study, a two-step synthesis was applied to make the poly(arylene ether sulfone)-polyurethane multiblock copolymers. The kinetic study on the second reaction suggested that the chain extension reaction was achieved in the first hour. Longer reaction time resulted in slightly lower molecular weights possibly due to side reactions such as hydrolysis. To build up molecular weight and evaluate the thermal, mechanical properties of the multiblock copolymers, a comprehensive optimization of the reaction conditions should be performed.

6.6 Acknowledgements

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6.7 Reference

(1) Oectel, G. *Polyurethane Handbook*; Hanser Publishers: Munich, Germany, 1985.

(2) Woods, G. *The ICI Polyurethane Book, 2*; New York:Wiley, 1990.

(3) Hepbrun, C. *Polyurethane Elastomers*; Applied Science Publishers: London, 1982.

(4) Ishihara, H.; Kimura, I.; Yoshihara, N. *J Macromol Sci Phys* 1983, *B22*, 713.

(5) Wang, C. B.; Cooper, S. L. *Macromolecules* 1983, *16*, 775.

(6) Shibayama, M.; Kawauchi, T.; Kotani, T.; Nomura, S.; Matsuda, T. *Polym J* 1986, *18*, 719.

(7) Miller, C. E.; Edelman, P. G.; Ratner, B. D. *Appl Spectrosc* 1990, *44*, 576.

(8) Ishihara, H. *J Macromol Sci Phys* 1983, *22*, 763.

(9) Miller, C. E.; Edelman, P. G.; Ratner, B. D.; Eishinger, B. E. *Appl Spectrosc* 1990, *44*, 581.

(10) Yamamoto, T.; Shibayama, M.; Nomura, S. *Polym J* 1989, *21*, 895.

(11) Hu, C. B.; Ward, R. S. J.; Schneider, N. S. *J Appl Polym Sci* 1982, *27*, 2167.

(12) Petrovic, Z.; Zavargo, Z.; Flynn, J. H.; Mackingght, W. J. *J Appl Polym Sci* 1994, *51*, 1087.

(13) Born, L.; Hespe, H. *Colloid Polym Sci* 1985, *263*, 335.

(14) Filip, D.; Macocinschi, D. *Polym Int* 2002, *51*, 699.

(15) Qin, X.; Yang, X.; Wang, X.; Wang, M. *Journal of Polymer Science: Part A: Polymer Chemistry* 2005, *43*, 4469.

(16) Tyagi, D.; Yilgor, I.; J.E., M.; Wilkes, G. L. *Polymer* 1984, *25*, 1807.

(17) Ho, T.; Wynne, K. J.; Nissan, R. A. *Macromolecules* 1993, *26*, 7029.

(18) Qin, X.; Xiong, J.; Yang, X.; Wang, X.; Zheng, Z. *Journal of Applied Polymer Science* 2006, *104*, 3554.

(19) Rose, J. B. *Polymer* 1974, *15*, 456.

(20) Robeson, L. M.; Farnham, A. G.; McGrath, J. E. *Appl. Polym. Symp.* 1975, *26*, 373.

(21) Matsumoto, K.; Nakagawa, T.; Higashihara, T.; Ueda, M. *Journal of Polymer Science Part a-Polymer Chemistry* 2009, *47*, 5827.

(22) Lee, H.-S.; Roy, A.; Lane, O.; Lee, M.; McGrath, J. E. *J. Polym. Sci., Part A Polym. Chem.* 2010, *48*, 214.

(23) Wang, H.-H.; Yuen, U.-E. *Journal of Applied Polymer Science* 2006, *102*, 607.

Chapter 7 Summary and Conclusions

A systematic study, focusing on the synthesis, characterization, and property evaluation, of *trans*-1,4-cyclohexylene ring containing poly(arylene ether sulfone)s (PAES) was described.

Three polymer systems were discussed in great detail in **Chapters 3**, **4**, and **5**. These polymer systems were designed to have different segmental lengths by using different polymerization strategies.

In **Chapter 3**, a new *trans*-1,4-cyclohexylene ring containing linear monomer, 4,4'-[*trans*-1,4-cyclohexanebis(methylene)] bisphenol (CMB), was synthesized. PAES homopolymer and random copolymers were made based on this new monomer and another two aromatic linear monomers. Since the polymers were synthesized with monomers, there were essentially no segments. These PAES polymers showed characteristic sub-T_g relaxation behaviors. Generally, the incorporation of the *trans*-1,4-cyclohexylene ring units moderately enhanced the mechanical properties when compared to the structural analogues. A large ultimate elongation enhancement was observed from the polymer with CMB and terphenol, which may be due to the very strong sub-T_g relaxation of the polymer.

Instead of sulfone monomer, when PAES oligomers were used in **Chapter 4** to react with *trans*-1,4-cyclohexylene containing monomers to synthesize new polymers, the segmental length of the sulfone containing components was enlarged. The phenol end groups and molecular weights of the PAES oligomers were successfully controlled by the stoichiometry imbalance technique. Four *trans*-1,4-cyclohexylene containing acid chloride monomers were synthesized and used to react with the PAES oligomers with phenol function groups. Some crystallinity was observed in biphenol based *trans*-1,4-cyclohexylene containing PAES. With the incorporation of the *trans*-1,4-cyclohexylene ring units the crystallization temperature windows were also enlarged. Similar to the results observed in the previous chapter, the cyclohexylene containing polymer showed stronger sub-T_g relaxation than the aromatic analogue.

Multiblock PAES-polyester copolymers were synthesized in **Chapter 5**. With the PAES blocks and the polyester blocks, the segmental lengths of both the sulfone containing component and the cyclohexylene ring containing component were increased. The cyclohexylene ring containing polyester blocks were built onto the presynthesized PAES blocks with melt polymerization method. In the solution method, the two blocks were coupled by acid chloride chemistry. In order to achieve the solution reaction and the melt reaction, the phenol terminated and hydroxy ethoxy terminated PAES oligomers were made. The mechanical properties of these multiblock copolymers were dominated by the PAES blocks with up to 20 wt% of polyester incorporation. Multiblock copolymers with polyester weight percentage higher than 20 % exhibited very limited solubility. Crystallinity was achieved in the multiblock copolymers with high polyester contents. Two melting transitions were observed, which may indicate the PAES block participation of the crystallization.

In the future work chapter at the end, some preliminary research was performed as a natural extension of the research work in **Chapter 5**. In **Chapter 5** both the PAES block and the polyester block were glassy blocks with glass transition temperature much higher than room temperature. The PAES-polyurethane multiblock polymer described in **Chapter 6** was composed of a PAES glassy block and a PTMG rubbery block with glass transition temperature around -80 ^{o}C. The current results suggested that a comprehensive reaction optimization should be performed.