

SYNTHESIS AND CHARACTERIZATION OF PERFECTLY ALTERNATING
SEGMENTED COPOLYMERS COMPRISED OF POLY(DIMETHYLSILOXANE)S
AND ENGINEERING THERMOPLASTICS

by

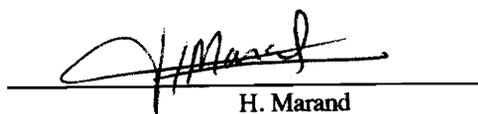
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Thesis submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of
MASTER OF SCIENCE
in
Chemistry

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August, 1991

Blacksburg, Virginia

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(ABSTRACT)

Novel perfectly alternating segmented copolymers containing imide junction points were synthesized via terminal amine-anhydride coupling from poly(dimethylsiloxane)s and either poly(arylene ether)s or polyimides. The copolymers were characterized in solution and the solid state. The $-(-A-B)-_n$ architecture and molecular design of these linear systems afforded thermodynamically microphase separated systems which gave rise to interesting copolymer properties.

Each controlled molecular weight oligomeric segment, or homopolymer, was initially synthesized with reactive endgroups and fully characterized prior to copolymerization. Thus, anhydride-terminated poly(dimethylsiloxane)s were prepared via cationic ring-opening polymerization in the presence of a "monofunctional" bis-norbornane anhydride disiloxane endcapping species. Aromatic amine-terminated engineering thermoplastics were synthesized through either nucleophilic aromatic substitution in the presence of a "monofunctional" aminophenol endcapper (as for poly(arylene ether ketone)s and poly(arylene ether sulfone)) or by solution imidization using a controlled excess of the diamine monomer.

A solution imidization method was developed for the segmented copolymerization that simplified the typically two-step, two-solvent method into a one-step approach with a

single solvent. Thus, a previously described condensation catalyst, 2-hydroxypyridine, was utilized which was demonstrated to be essential in obtaining high molecular weight copolymers.

These segmented copolymers generally were fibrous and highly soluble in many common organic solvents. Creasable, transparent, solution-cast films were readily prepared. Thermal and morphological analyses demonstrated that the copolymers exhibited phase separation, and displayed lower and upper Tg's as a result of the two components employed. At short hard block lengths, upper Tg's were somewhat depressed, implying partial miscibility.

Acknowledgements

Much appreciation is extended to Prof. McGrath for his support and suggestions throughout the two years of research represented in this thesis. Thanks also to Prof. Riffle and Prof. Marand for the helpful "Saturday morning group meeting" discussion sessions.

To all the "Characterization Staff" that worked so hard on helping me, thanks: David DeSante, Dan Woodie and Ross Zirkle for intrinsics; Paul Vail, George Dallas and Raji Jayaraman for thermal data; Martin Rogers, Paul Wood and Greg Lyle for helpful discussions and polymers; Dr. Milos Netopilik for GPC analysis; Tom Glass for Solid State NMR analyses; Steve McCartney for TEM analyses; Saikat Joardar for Stress-Strain measurements, and Dr. Dave Rodriques for SAXS analyses.

Special gratitude to my family --Mom, Dad and Lydia, and Laura and David-- for emotional support and pretending to understand and be interested in what I was doing for two years here. Also to Mary Joseph and Phyllis Moy, great friends and chemistry wives who listened to my complaining with the right ear and their husbands' with the left.

My most grateful and understated thanks goes to my husband and colleague, Carrington, for everything mentioned above and more. Wearing all hats, I thank him for help in his area of synthetic expertise (poly(arylene ether)s), obtaining and deciphering many, many results, classwork, encouragement, my sanity, and doing the dishes.

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Introduction

Siloxane-containing blends and copolymers have introduced into many thermodynamically dissimilar systems added processability, oxidative stability and water repellency [40,70-72]. Blends, unlike copolymers, have no chemical bonds between the segments, and therefore tend to fall short in applicability due to macrophase separation of the components. Copolymers, although more costly and preparatively time-consuming, generally can only phase separate on a microscopic level because of the covalent bond that physically disallows gross separation.

Several forms of copolymers exist that have utilized siloxanes and engineering thermoplastics including block and segmented architectures. Similar in structure, these types are differentiated by the length of each component. Generally, block copolymers consist of very long homopolymer "blocks" and may have only one or two chemically combined unions. Segmented copolymers are made from shorter homopolymer "segments" and are usually composed of greater than two unions. Both randomly and perfectly alternating segmented copolymers have been made from poly(dimethylsiloxane)s and thermoplastics [45, 47, 56, 78, 79], and similar properties and characteristics have been observed. For example, microphase separation occurred in these systems, giving rise to two glass transitions due to each component. All siloxane-containing copolymers displayed siloxane-rich surfaces, which when oxidized formed silicate "crusts" and increased char yields when compared to the hard homopolymer segment.

Research for this thesis dealt with the synthesis and characterization of perfectly alternating segmented copolymers prepared from anhydride-terminated poly(dimethylsiloxane)s and aromatic amine-terminated engineering polymers. Preparation of starting materials, both monomeric and oligomeric forms, were essential aspects of the work carried out. Furthermore, methods for characterization of monomeric and oligomeric

siloxane species were developed prior to copolymerization.

The major goals of this work were to prepare high molecular weight perfectly alternating segmented copolymers via established solution imidization techniques. Silicon elemental analysis and solid state ^{13}C NMR indicated that copolymerizations were successfully accomplished with all poly(arylene ether) and polyimide oligomers through a catalyzed, one-step solution imidization route that was devised.

Comparable to past findings in our labs [61, 71, 79, 86], these perfectly alternating segmented copolymers exhibited microphase separation which was observed by DMTA, DSC and TEM analyses. Additionally, unique lamellar structures were noticed in some TEM micrographs, indicating some phase mixing.

Not observed in previous randomly segmented copolymer systems was the highly surface active nature of all the copolymers synthesized, proved by solution ^1H NMR spectra. For this reason, other means of characterization (elemental analysis, solid state NMR) were necessary to deduce siloxane incorporation and extent of reaction.

The introduction of siloxane segments into the copolymer increased solubility, especially noticed in the polyimide-based systems. As siloxane segment was increased to approximately 50 weight percent or higher, copolymers were noted to become soluble in room temperature toluene for at least 30 minutes, after which time micelles formed. Tough, translucent-to-transparent films were easily prepared from a variety of common organic solvents at room temperature, including chloroform, NMP and *o*-dichlorobenzene.

The development of synthetic procedures utilized throughout this research are discussed herein. Moreover, extensive characterization results are presented regarding the perfectly alternating poly(dimethylsiloxane)-engineering thermoplastic segmented copolymers prepared.

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Background

A. Engineering Thermoplastics

Engineering thermoplastics comprise a class of linear polymer systems that possess good mechanical properties, high temperature serviceability and dimensional stability. Developed in the 1950's for applications in the electronics and aerospace industries [1], they are steadily replacing typically metal or ceramic materials. The term *thermoplastic* is used to express the ability of a polymer to flow and/or melt upon heating. Thermoplastics that can withstand fairly elevated temperatures and/or high impacts are usually regarded for rugged applications, thus designating those systems *engineering thermoplastics*.

In order to be usable in high-temperature environments, gross physical change cannot occur. For this reason, these systems are tailored to possess glass transition temperatures (T_g) or melting temperatures (T_m) in excess of 100°C . In addition to their excellent thermal and dimensional stabilities, they are often accompanied by hydrolytic and oxidative stability.

Common examples of this class of polymer include poly(arylene ether)s, polyimides, polyamides and polycarbonates, all produced through polycondensation, or step-growth, reactions. From combinations of the numerous monomers available, the structures shown in Figure 1 reveal only a very small fraction of the engineering thermoplastics existing today. Because there is a very broad array, only those polymers directly related to this thesis research will be discussed in the following history.

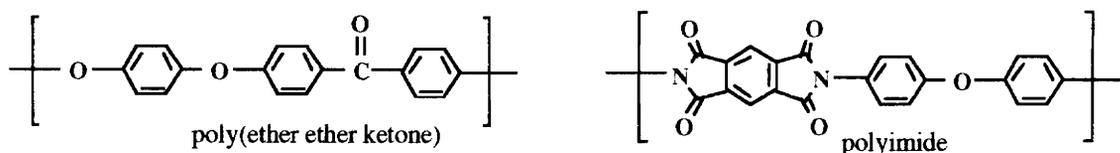


Figure 1. Common engineering thermoplastics.

1. Poly(arylene ether)s

Those macromolecules which contain the aromatic ether bond are appropriately labeled poly(arylene ether)s. These systems can include many other connecting groups, as evidenced by several structures in Figure 2. Unlike the aliphatic polyethers, these phenyl-containing polyethers are thermally stable and thus exhibit high temperature serviceability.

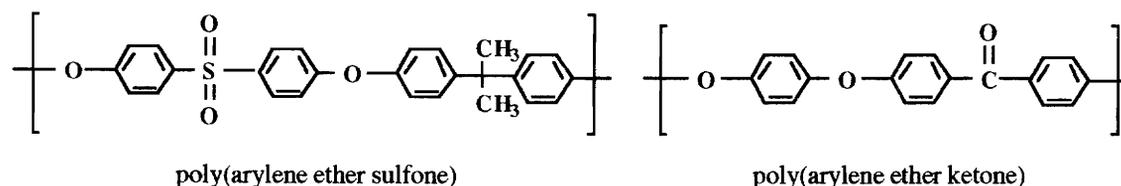
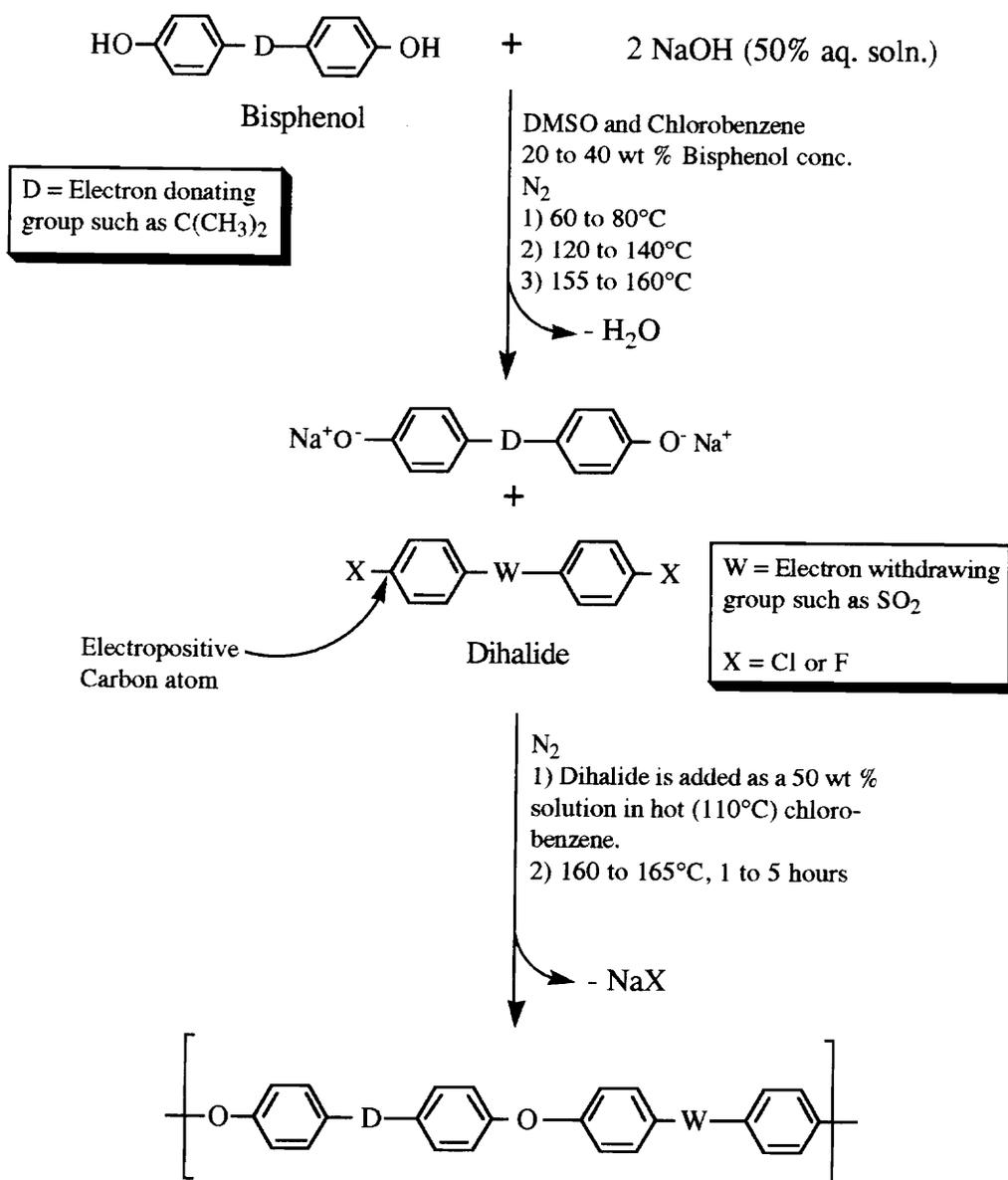


Figure 2. Common poly(arylene ether)s.

The majority of poly(arylene ether)s have large regions of physically unordered chains and so are amorphous. Tg values are usually 130°C or above and are dependent on both chemical structure and molecular weight. Because they display good mechanical properties along with high thermal stability, poly(arylene ether)s are generally excellent candidates for demanding applications.

Some of the first research in poly(arylene ether) synthesis was reported by Johnson, *et al.* [2] in 1967. By a polycondensation route, a dialkali metal salt of a bisphenol and an aromatic dihalide activated with an electron withdrawing group produced a linear, high molecular weight polymer (see Scheme 1). The reaction was noted to be quick and clean, provided that it was carried out under dry conditions in an anhydrous, dipolar, aprotic solvent at temperatures near 150°C. If water was present in the reaction, it could act as a nucleophile and revert the bisphenate to unreactive bisphenol, as well as hydrolyze the dihalide and convert it to the corresponding unreactive bisphenol. Dipolar,



Scheme 1. Poly(arylene ether) synthesis via nucleophilic aromatic substitution reported by Johnson, *et al.* [2].

aprotic solvents, such as dimethyl sulfoxide (DMSO) and tetrahydrothiophene 1,1-dioxane (Sulfolane), were employed to solvate the sodium or potassium cations, making the corresponding bisphenate more nucleophilic.

The reaction, represented in Scheme 1, involved a two-step, two-pot process. Reaction conditions --solvent, time and temperature-- were investigated, and optimized conditions were reported. A solvent was needed to dissolve both the dihalide and bisphenol salt, in the form of either a sodium or potassium bisphenate. DMSO was considered to be the the most effective solvent for these polymerizations as extents of reaction greater than 99% were achieved when polymerizations were run at 165°C. Furthermore, viscosity data proved that high molecular weights could be obtained in as little as one hour reaction time. Bisphenol reactivity was based on the connecting group of the monomer. Electron-withdrawing groups like the sulfone linkage cause the bisphenol to be more acidic, which in turn decreases its reactivity towards nucleophilic aromatic substitution. Sulfolane's allowance of higher reaction temperatures by approximately 60°C overcame this problem. As a result, high molecular weights were achieved for less reactive bisphenols in approximately six hours.

The attack by the nucleophile (bisphenol salt) onto the activated site of the dihalide was the rate determining step for this reaction (and not the expulsion of the halogen atom). For the dihalide monomer, the presence of a strong electronegative atom (such as fluorine or chlorine) in combination with the electron-withdrawing connecting group (such as sulfone or acyl) creates a highly susceptible electropositive carbon atom. This point of attack can be readily observed by reviewing Scheme 1. Although there are few purely unimolecular or bimolecular nucleophilic substitution reactions, evidence has shown that poly(arylene ether)s synthesized in the manner described by Johnson and coworkers have reacted by a mostly bimolecular mechanism [2]. This was concluded from the fact that the dihalide did not react with DMSO or Sulfolane at elevated reaction temperatures since any halide dissociation prior to nucleophilic attack would surely have resulted in reaction between the carbocation intermediate and the sulfonated solvent had the

mechanism been unimolecular.

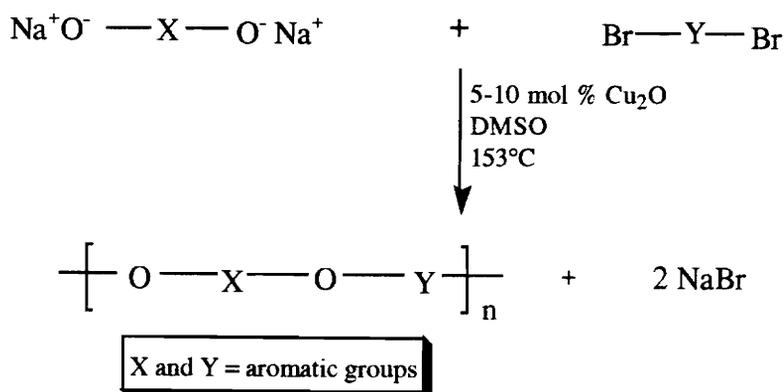
Through their extensive research, the relationship between electron-withdrawing group of the bisphenol and Tg was established: bulkier groups yielded higher Tg values. Also investigated was the nature of the reactivity of the dihalide; a fluoride group was easier to displace than its chloride counterpart. And lastly, the influence on Tg of the connecting moiety in various dihalides was studied. Controlled largely by the polarity of the connecting group, Tg values were found to increase as more highly polar units were incorporated. The predominance of these three variables can be seen in Table 1 which lists some of the poly(arylene ether)s reported by Johnson and coworkers in their 1967 publication.

Table 1. Poly(arylene ether)s prepared by Johnson, *et al.* by nucleophilic aromatic substitution [2].

Polymer Structure (repeat unit)	Bisphenol	Dihalide	Tg(°C)
			195
			230
			155
			—
only very low molecular weight achieved			

At nearly the same time, Jennings, *et al.* [3, 4] published results regarding the synthesis of poly(arylene ether)s via electrophilic aromatic substitution, or Friedel-Crafts

polycondensation reactions. This group also attempted nucleophilic aromatic substitution methods. But, unlike Johnson, *et al.*, Jennings and coworkers found the nucleophilic substitution route less suitable. Based on work reported in 1962, a cuprous salt catalyst (Cu_2O) was utilized. Along with dibromo monomers, their rationale was that Ullman-type reaction conditions were applicable to poly(arylene ether) synthesis [3] (see Scheme 2).

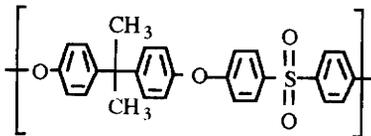
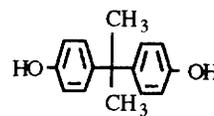
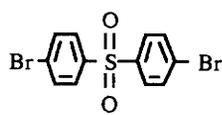
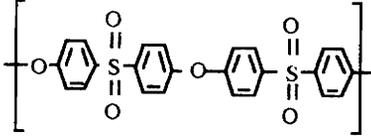
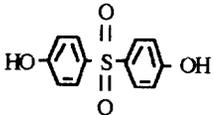
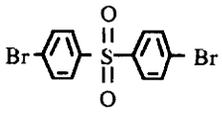
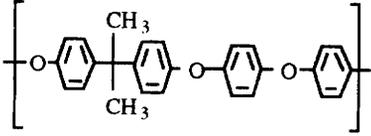
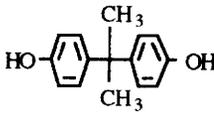
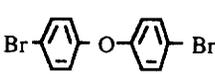
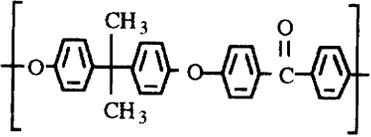
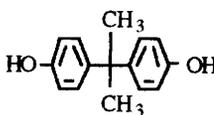
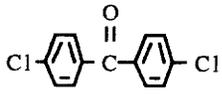


Scheme 2. Poly(arylene ether) synthesis via Ullman-type nucleophilic aromatic substitution by Jennings, *et al.* [3].

However, only low molecular weight poly(ether sulfone)s and poly(ether ketone)s were prepared, the structures of which are shown in Table 2.

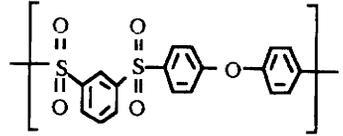
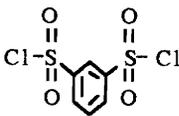
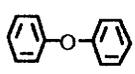
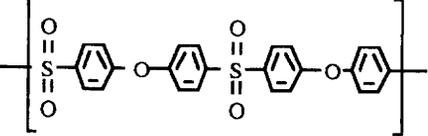
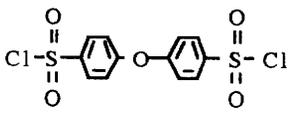
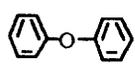
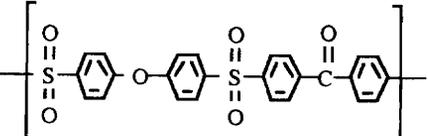
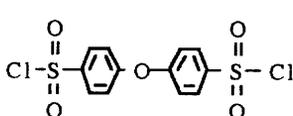
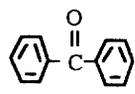
Briefly mentioned above, Jennings and coworkers developed a successful electrophilic aromatic substitution route to preparing poly(arylene ether)s structurally similar to those prepared by Johnson, *et al.*, which can be noted by comparison of Tables 1 and 3. By employing a catalytic quantity of a Friedel-Crafts halide, such as ferric chloride, polysulfonylation and polyacylation of the appropriate monomers were made possible; however, fairly harsh reaction conditions were necessary. These polymerizations were carried out under melt conditions, with temperatures of up to 320°C being used. Due to the elevated temperatures, some crosslinking was experienced which could be calculated

Table 2. Poly(arylene ether)s prepared by Jennings, *et al.* by nucleophilic aromatic substitution using Ullman-type conditions [3].

Polymer Structure (repeat unit)	Bisphenol	Dihalide	DP*
			40
			19
			2
			21

* Degree of polymerization; roughly the number of repeat units per polymer chain

Table 3. Poly(arylene ether sulfone)s prepared by Jennings, *et al.* via Friedel-Crafts electrophilic aromatic substitution [3].

Polymer Structure (repeat unit)	Disulfonyl chloride	Diphenyl monomer
		
		
		

by measuring the amount of product that did not redissolve. Usually this was around 20 to 40 percent. Glass transition temperatures of these poly(sulfone)s were upwards of around 280°C [5]. Although slightly different poly(ether sulfone)s and poly(ether ketone)s were prepared, reaction extents and molecular weights were not as impressive as data published by Johnson, *et al.* Nonetheless, Jennings and his colleagues provided the chemical field with novel polymers that exhibited high thermal stability and high performance potential.

Hashimoto, *et al.* [6] reported some of the first phosphorus-containing poly(arylene ether)s in 1977. Through the utilization of sodium hydroxide and DMSO, the reaction of the phosphorus-containing activated dihalide with a bisphenol was very similar to Johnson, *et al.*[2]. Table 4 shows the resulting poly(arylene ether phosphine oxide)s along with the

Table 4. Poly(arylene ether phosphine oxide)s prepared by Hashimoto, *et al.* [6].

Polymer Structure (repeat unit)	Dihalide	Bisphenol

necessary monomers. Incorporation of the bulky phosphorus group could lead to increased solubility. Such a group would also inhibit crystallinity and provide high thermal stability along with increased T_g. Unfortunately, these workers did not obtain high molecular weight polymers.

By 1980, many variations of the work by Johnson, *et al.* were developed. Other polar, aprotic solvents such as dimethylformamide (DMF), dimethylacetamide (DMAc), and 1-methyl-2-pyrrolidinone (NMP) were employed along with alkali metal bases such as potassium fluoride (KF) and potassium carbonate (K_2CO_3) [6-11]. In 1984, Mohanty and McGrath [10, 11] published a modified procedure to prepare poly(arylene ether)s via nucleophilic aromatic substitution based on earlier work carried out in that lab. This method was applied to both poly(arylene ether sulfone)s and poly(arylene ether ketone)s successfully. Table 5 shows the chemical structures of these two types of engineering thermoplastics prepared by this group.

Table 5. Poly(arylene ether)s prepared by potassium carbonate procedure [10, 11].

Polymer Structure (repeat unit)	Bisphenol	Dihalide

Instead of using a strong base like Johnson, potassium carbonate was employed as the weak alkali metal base in this procedure. A mixture of NMP and toluene was utilized instead of DMSO or Sulfolane. The procedure by Johnson required extreme caution in

measuring an exact 1:1 stoichiometry of base to bisphenol so that high polymer and clean products were obtained, thus avoiding halide hydrolysis. Potassium carbonate utilization allowed up to 50 % excess base without shifting the 1:1 stoichiometry of dihalide to bisphenol (or bisphenate). The use of NMP afforded the opportunity to solvate some bisphenol salts that were otherwise insoluble in DMSO; moreover, it offered a higher boiling point (202°C) than DMSO. Reaction times were approximately 12 to 16 hours at temperatures from 120°C to 160°C for this two-step procedure.

By the potassium carbonate route, two proposed reaction schemes were described, as contrasted in Scheme 3. One possibility involved formation of a bisphenate which then went on to react with the dihalide. The other more acceptable route involves formation of a monophenate which then reacts with one site of a dihalide molecule. This A-B type intermediate (one phenol and one halide functionality per intermediate molecule) then continues to react and form polymeric species. As can be seen from the reaction scheme, water is a byproduct in this polycondensation. Therefore, it is apparent that toluene is used as a cosolvent to azeotropically distill the water formed. Water remaining in the system alters the stoichiometry and can form KOH (by reaction with the bisphenol potassium salt), which can then attack the dihalide and reduce its reactivity. A third modification by this group was the reduction from a two-pot to a one-pot process in which all reactants were combined in the initial step.

By the mid-1980's, several poly(arylene ether)s were made commercially available under names such as ICI's PEEK® [poly(ether ether ketone)] and Victrex® PES [poly(ether sulfone)], and Amoco's Udel® [poly(ether sulfone)], Radel® [poly(ether sulfone)] and Kadel® [poly(ether ketone)] [12]. During this time, continued work on the poly(arylene ether phosphine oxide)s that were introduced by Hashimoto, *et al.* in 1977 [6] brought about further achievements. With reaction conditions reported by Mohanty and McGrath

[10], German [13,14] and Japanese [15] chemists were able to successfully synthesize fairly high polymer from various bisphenols and the difluoro analog of the phosphorus-containing dihalide utilized by Hashimoto. Thus, it was concluded that the phosphine oxide group does not possess as strong electron-withdrawing effects as the sulfone moiety. Table 6 shows the monomers and resulting poly(arylene ether phosphine oxide)s obtained by the Japanese group. Most recently, Smith, *et al.* [16-18] have prepared high molecular

Table 6. Poly(arylene ether phosphine oxide)s prepared by Japanese chemists using difluorophosphine oxide monomer [15].

Polymer Structure (repeat unit)	Dihalide	Bisphenol

weight poly(arylene ether phosphine oxide)s by the potassium carbonate nucleophilic aromatic substitution route [10]. Also utilizing the difluoro analog of the phosphine oxide, Smith incorporated two additional bisphenols besides those used by the Japanese. The monomers used and resulting poly(arylene ether phosphine oxide)s prepared by Smith are shown in Table 7 on the following page.

Other advances in poly(arylene ether) research included the use of functionalized endgroups which subsequently brought about molecular weight control and future

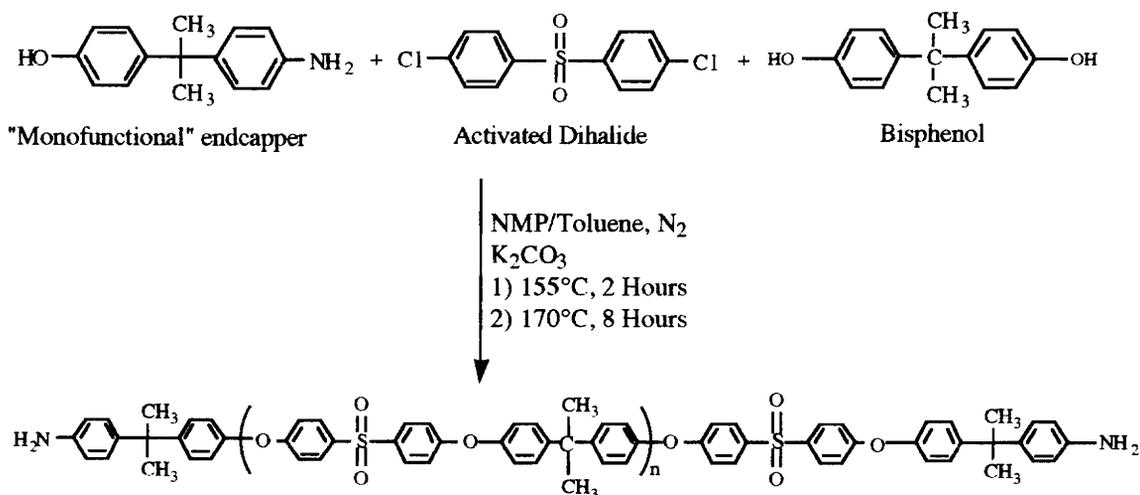
reactivity. One of the most easily produced telechelic polymers was the hydroxyl terminated poly(arylene ether sulfone). Prepared by adding an excess of bisphenol in a

Table 7. Recent poly(arylene ether phosphine oxide)s prepared by Smith, *et al.* from the difluorophosphine oxide monomer [16,17].

Polymer Structure (repeat unit)	Dihalide	Bisphenol

nucleophilic aromatic substitution polymerization, it was first reported by Noshay, *et al.* [19] in 1971 and later repeated by McGrath, *et al.*[20] for both novelty and post-polymerization into segmented copolymers. Utilizing forms of the Carothers equations like those detailed in *Molecular Weight Control via the Carothers Equation* in this chapter, preformed hydroxyl-terminated bisphenol A-based poly(ether sulfone)s were prepared, and molecular weight data was easily obtained by titration of the phenolic groups from a

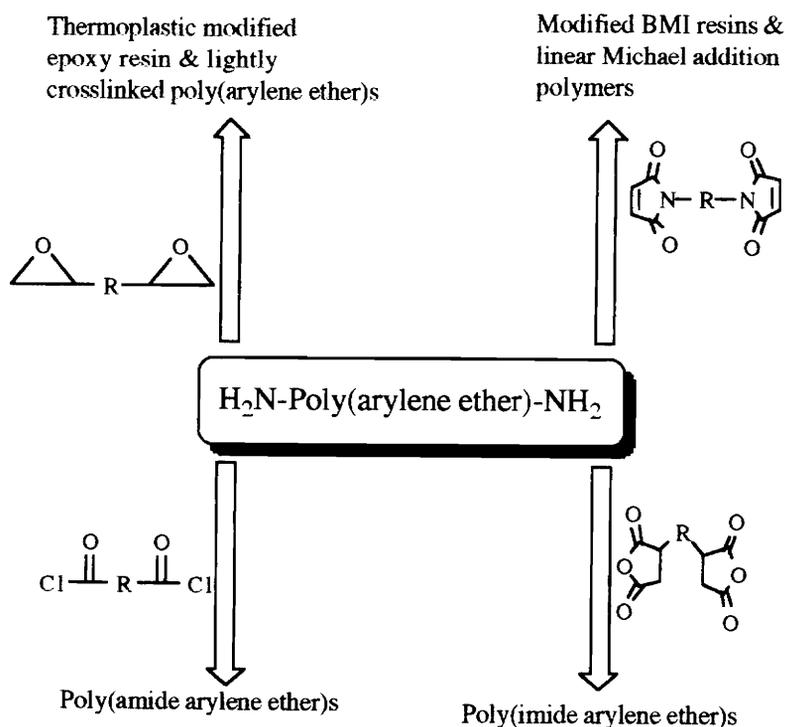
procedure developed by Wnuk, *et al.* [21]. Utilizing a synthetic procedure developed by Noshay, *et al.* [22], perfectly alternating segmented copolymers of poly(ether sulfone)s and poly(dimethylsiloxane)s were synthesized. The preparation of functionalized poly(arylene ether)s was further expanded when several chemists introduced primary aromatic amine-terminated oligomers [20, 24] made from addition of a "monofunctional" endcapper in the initial stage of poly(arylene ether sulfone) synthesis. The endcappers employed contained both a "functional" hydroxyl group that was reactive in polysulfone synthesis and a "non-functional" amine group that was not reactive in nucleophilic aromatic substitution polymerization. Scheme 4 more clearly provides an example of this reaction.



Scheme 4. Synthesis of an amine functionalized poly(arylene ether sulfone) [17, 21].

The resulting amine terminated poly(ether sulfone) was now functionalized for further reactions such as imidizations, amidizations, and other types of reactions like those shown in Scheme 5. As with the hydroxyl-terminated polymers, McGrath *et al.* used known techniques to potentiometrically titrate the amine endgroups in order to obtain molecular

weight information [24]. Additionally, proton nuclear magnetic resonance and Fourier transform infrared spectroscopies were used to confirm product identification.



Scheme 5. Possible post-polymerizations for amine-terminated poly(arylene ether)s [24].

Due to the early interest in poly(arylene ether)s, the need for continued research has been established. The past few decades have given rise to optimization of reaction conditions. Increased T_gs and solubilities have been achieved through the use of different monomers, while varied endgroups have been utilized to grant the opportunity for many different post-polymerizations. From these functional oligomers, novel copolymers (thermoplastics and thermosets) are continuously being synthesized for applications in numerous fields.

2. Polyimides

Historically, the first reported polyimide was made in 1908 from 3,4-diaminophthalic acid [26]. It was not until DuPont marketed the first commercial polyimide, Kapton® (originally H-Film®), that thermal stability was intensively investigated [5]. Currently synthesized primarily from dianhydrides and diamines, reaction of these monomers yields linear polymers comprised of thermally stable imide connecting groups. As in the case of poly(arylene ether)s, polyimides can contain other linking groups within the polymer backbone, as seen in Figure 3. While some aliphatic diamines have been employed [26], most polyimides today are wholly aromatic since higher thermal stability is achieved from the aromatic diamines.

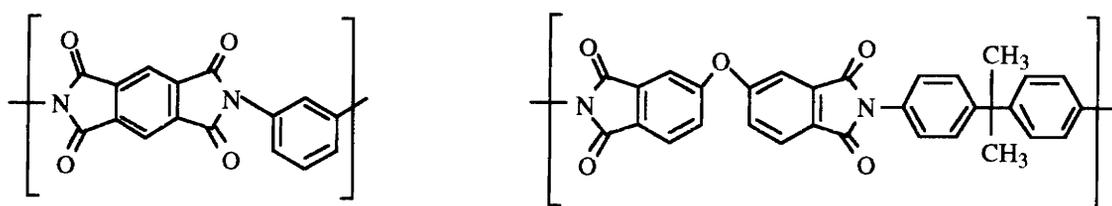


Figure 3. Two polyimides containing various functional groups.

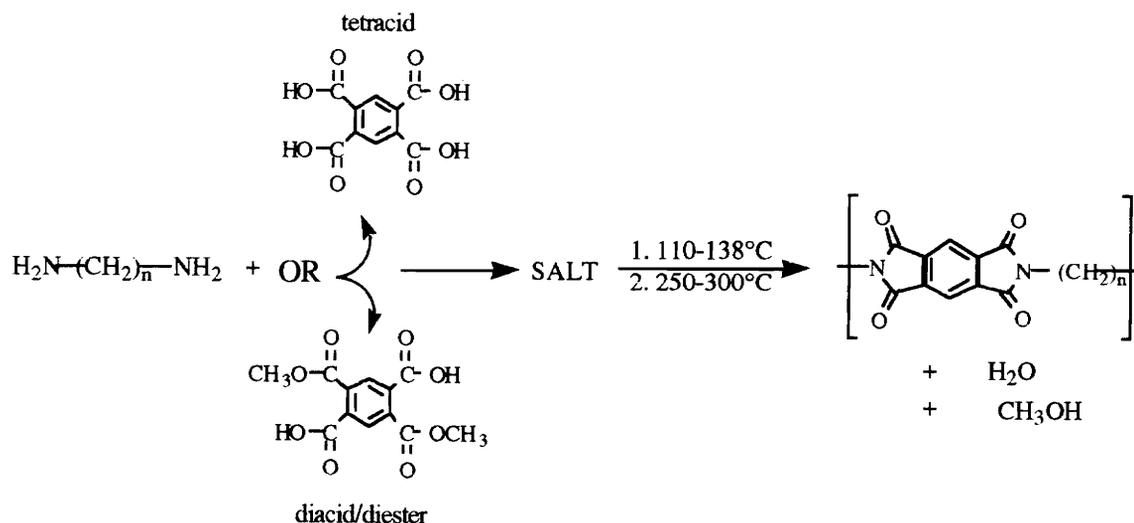
These systems have high T_g values --usually above 200°C -- which like poly(arylene ether)s show some molecular weight and compositional dependence. They are resistant to many common solvents and have been classically considered insoluble and infusible. Thermal and oxidative durability are also noted by the observed stability and only mild decomposition experienced in oxygen-containing environments at temperatures in excess of 300°C . Moreover, they are tough --displaying good mechanical properties-- and have excellent adhesive ability. Some additional examples of polyimides are shown in Table 8 along with reported thermal transitions.

Table 8. Several polyimides and their glass transition temperatures [78].

Polymer Structure (repeat unit)	T _g (°C)
	222
	290
	361

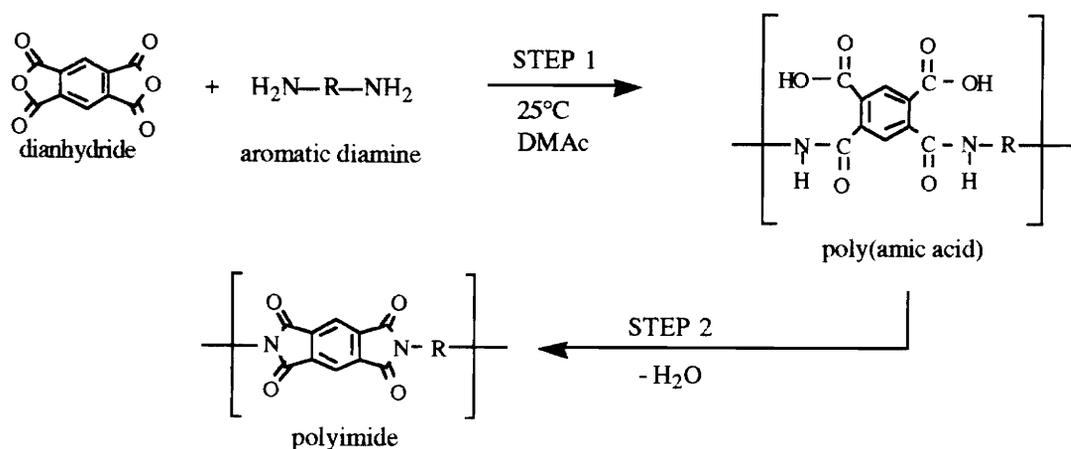
From 1955 to 1959, preliminary development on polyimides was performed by Edwards and Robinson in the United States [26]. The basic synthetic method involved melt fusion of the salt of an aliphatic diamine and a tetracid or diacid/diester monomer and was carried out as a two-step process, initially heated to about 110°C, then increased to 300°C. The reactants and process can be more easily understood from Scheme 6. By this method, it is apparent that relatively low melting polyimides were necessary in order to achieve high polymer. Thus, long aliphatic chains in the diamine were usually a requirement for the melt fusion reaction.

Through the development of a second method which incorporated a solvent, aromatic diamines were applicable in polyimide synthesis. In the early 1960's, Edwards and Endrey independently patented the route which involved reaction of an aromatic diamine with an

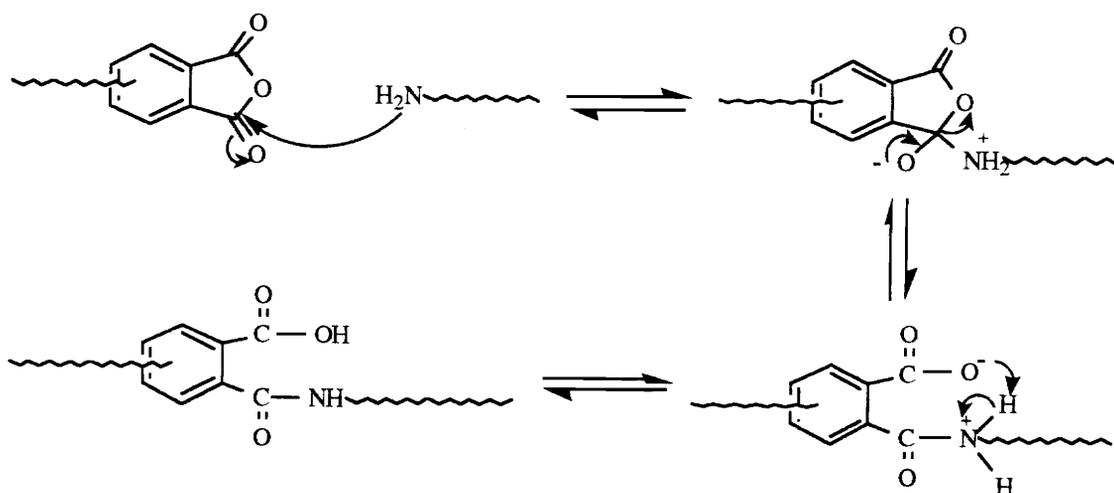


Scheme 6. Polyimide synthesis via melt fusion by Edwards and Robinson [26].

aromatic dianhydride [26]. Again a two-step process (see Scheme 7), a soluble prepolymer called a poly(amic acid) was initially produced at ambient temperatures and then converted to the polyimide by cyclodehydrating the system. Scheme 8 shows the proposed mechanistic pathway of poly(amic acid) formation.



Scheme 7. Two-step polyimide synthesis of Edwards and Endrey [26].



Scheme 8. Proposed mechanistic pathway of poly(amic acid) formation [60].

A number of solvents, mostly amide-containing, were suitable for obtaining high molecular weight poly(amic acid) in the first step. These included NMP, N,N-dimethylformamide (DMF), N,N-methylcaprolactam, and dimethyl sulfone [26]. Although the solution method will work with some aliphatic diamines, it was noted by Endrey that the wholly aromatic poly(amic acid) remains solvated throughout the entire two-step process, but the aliphatic diamine will precipitate and redissolve slowly only when vigorously agitated [26].

To convert the prepolymer to the thermally stable polyimide, two methods were known to drive off water formed, and subsequently cyclize the poly(amic acid). The *thermal* method involved gradual heating of poly(amic acid) film to 300°C in a vacuum oven. Following the cyclodehydration by IR, these elevated temperatures and reduced pressures were used to strip water formed and push the reaction toward polyimide conversion. *Chemical imidization* was carried out by submerging prepolymer film in a dehydration solution composed of acetic anhydride and pyridine in benzene. After several hours of soaking, the converted films was removed and dried. A variation of the chemical

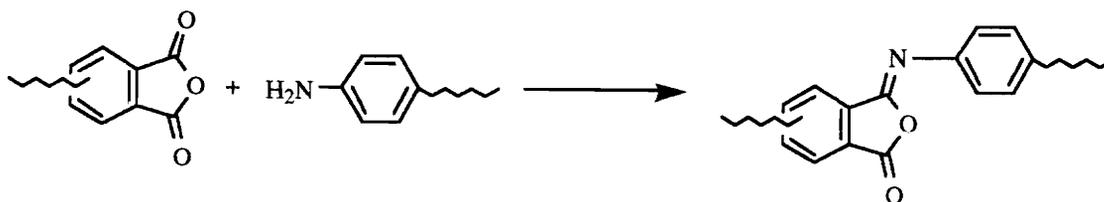
method, acetic anhydride and pyridine could be added directly to the reaction vessel containing the poly(amic acid)/NMP solution. However, its application was limited to the few cases where the final polyimide was soluble and could be removed from the flask.

During the 1970's and 1980's, active academic and industrial research produced a great many aromatic polyimides through the recruitment of new monomers and novel routes. Tricyclic fused ring-containing polyimides [28-30], which gave highly thermally and oxidatively stable products, resulted in T_g values as high as 364°C. Fluorinated systems [31] allowed ease of solvation in solvents such as chloroform and DMF. Through a novel reaction approach, poly(ether imide)s [32-36] were prepared with sulfone, ketone and sulfide functionalities along the polymer backbone.

More recent advances in polyimide research include the development of a third imidization technique. Takekoshi, *et al.* [32, 33] reported work on a solution imidization method that converted the poly(amic acid) to the polyimide via cyclodehydration through the use of moderate temperatures and appropriate reaction and azeotroping solvents. At 160°C to 180°C in the presence of a phenolic reaction medium and chlorobenzene azeotroping solvent, a high molecular weight poly(ether imide) was synthesized. Similarly, Summers, *et al.* [38] published results on a solution imidization for the synthesis of segmented copolymers in which siloxane blocks were incorporated into polyimides via imide bonds. In this case, the hot poly(amic acid) solution was poured into a separate vessel containing an azeotroping solvent mixture of hot NMP and N-cyclohexyl pyrrolidinone (CHP) and cyclodehydrated for an additional 24 hours at 160°C to 180°C to yield high copolymer. Most recently, Waldbauer, *et al.* [39] modified Summer's method by eliminating the separate NMP/CHP pot. Controlled molecular weight polyimides were successfully prepared in a one-pot approach by adding room temperature CHP or *o*-dichlorobenzene to the hot poly(amic acid) in the reaction vessel and heating for 24 hours

at reflux temperatures.

With the expanding production of soluble polyimides, the solution imidization techniques were attractive. By converting the prepolymer to the polyimide in the reaction vessel, high temperatures (300°C) in a vacuum oven were omitted, and therefore, greater control of side reactions (e. g. crosslinking) was achieved. Utilization of an azeotropic solvent eliminated expensive anhydride dehydrating agents, and again limited side reactions such as isoimides (see Scheme 9) that could occur. Furthermore, large batches of prepolymer could be quantitatively converted in a single flask.

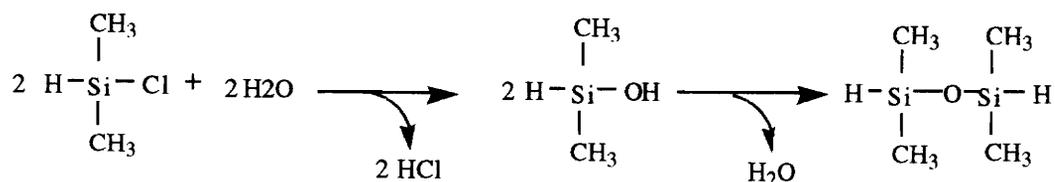


Scheme 9. Isoimide side reaction and product.

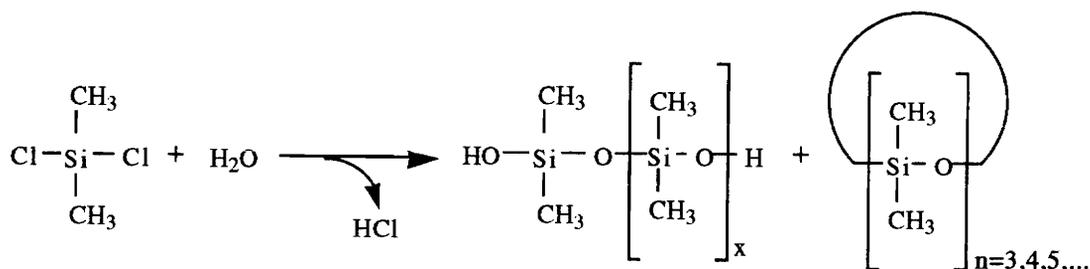
Presently, polyimide research is among the most active areas under exploration. Great interest is taken in both optimizing synthetic conditions and studying properties. Because of their noted insolubility, trends are favoring modified polyimides which display increased solubility for easier processing. The many current uses of polyimides, ranging from strong adhesives to electrical wire coverings, have demonstrated the necessity of future research efforts.

B. Poly(dimethylsiloxane)s

Since the introduction of poly(dimethylsiloxane) in the 1940's, it has been considered the most important of the semi-organic polymers [40, 41]. Polyorganosiloxanes, as this type of polymer is often classified, are made from the hydrolysis of organochlorosilanes, as can be seen in Scheme 10. The flexibility of the Si-O backbone is due to free rotation



a. Hydrolysis of dimethylchlorosilane to form tetramethyldisiloxane.



b. Hydrolysis of dimethyldichlorosilane to form poly(dimethylsiloxane), or PDMS.

Scheme 10. Hydrolyses of some organochlorosilanes [42].

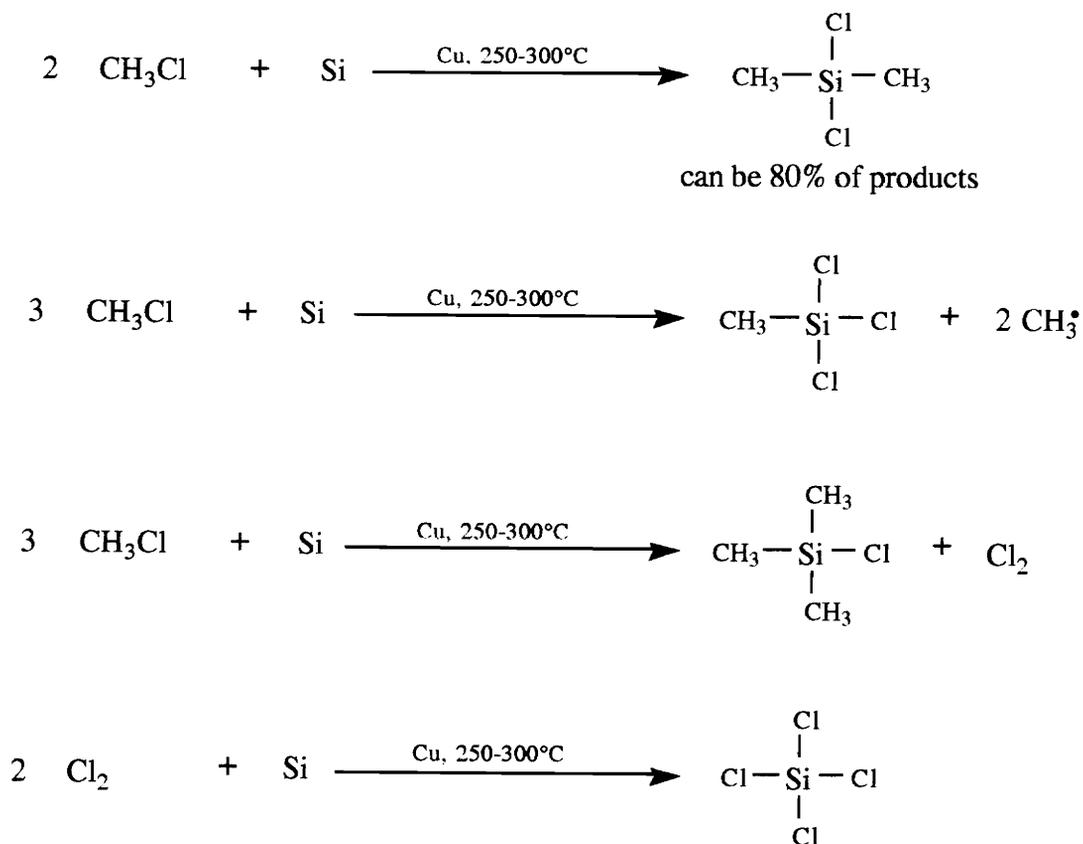
about that axis, giving rise to low intermolecular forces which allow the relatively small methyl groups that flank the backbone to easily rotate [42]. This rotation induces the unique characteristics observed in poly(dimethylsiloxane), or PDMS. Among these are the low surface energy, which in turn yields hydrophobicity, low dielectric constant, low viscosity, and low T_g (-123°C). Other qualities include biocompatibility, elasticity, and thermal, oxidative and UV stabilities. Commodities, such as sealants, lubricants, insulating

materials, prosthetics and implants, release agents, and heating fluids, have been developed to take advantage of those desirable properties. However, due to the extremely high molecular weights necessary to render this polymer useful, various techniques have been used to incorporate poly(dimethylsiloxane)s into other polymer systems in which only moderate molecular weights of PDMS segments are needed. For example, PDMS has been used as a "soft" reactant in copolymerizations with "hard" species like polyimides or poly(arylene ether)s [40, 41, 56-59]. While copolymerization *may* lower the T_g of the "hard" coreactant, it is often seen as a little sacrifice for the benefits of processability, hydrophobicity, and oxidative stability. (Aspects of copolymerization will be discussed in the next section of this chapter.)

Some of the earliest reported investigations on polyorganosiloxanes were undertaken by Friedel, Crafts, and Landenburg, but not until the early 1900's did Kipping, *et al.* detail the structure of polysiloxane [40]. Kipping indeed named the monomeric structure a "silicone" because he believed it was analogous in structure to the ketone moiety [42], and this term is still used interchangeably with siloxane.

Polymeric siloxanes were not of interest until the 1940s, after the process for making organochlorosilanes was patented by Rochow [40]. By reaction of an organic halide with a metallic silicon in the presence of a copper catalyst [42], Scheme 11 shows this "direct process", which is still the standard industrial method used today. Then, by a hydrolytic route, these small molecules could be polymerized to form polyorganosiloxanes of two architectures: linear and cyclic. Linear polysiloxanes are of various molecular weights with silanol ends, while cyclic structures are usually comprised of three to five siloxane units-- but larger rings exist-- with the major product having four units [42]. These cyclic siloxanes are often used as the sole monomer in linear, high molecular weight polysiloxane synthesis. Scheme 10 outlines the reactions that occur in both the preparations of a

disiloxane from a chlorosilane and polysiloxane (linear and cyclic) from a dichlorosilane.



Scheme 11. Synthesis of organochlorosilanes: possible reactions that occur during "direct process" as exemplified in the preparation of dimethyldichlorosilane [43].

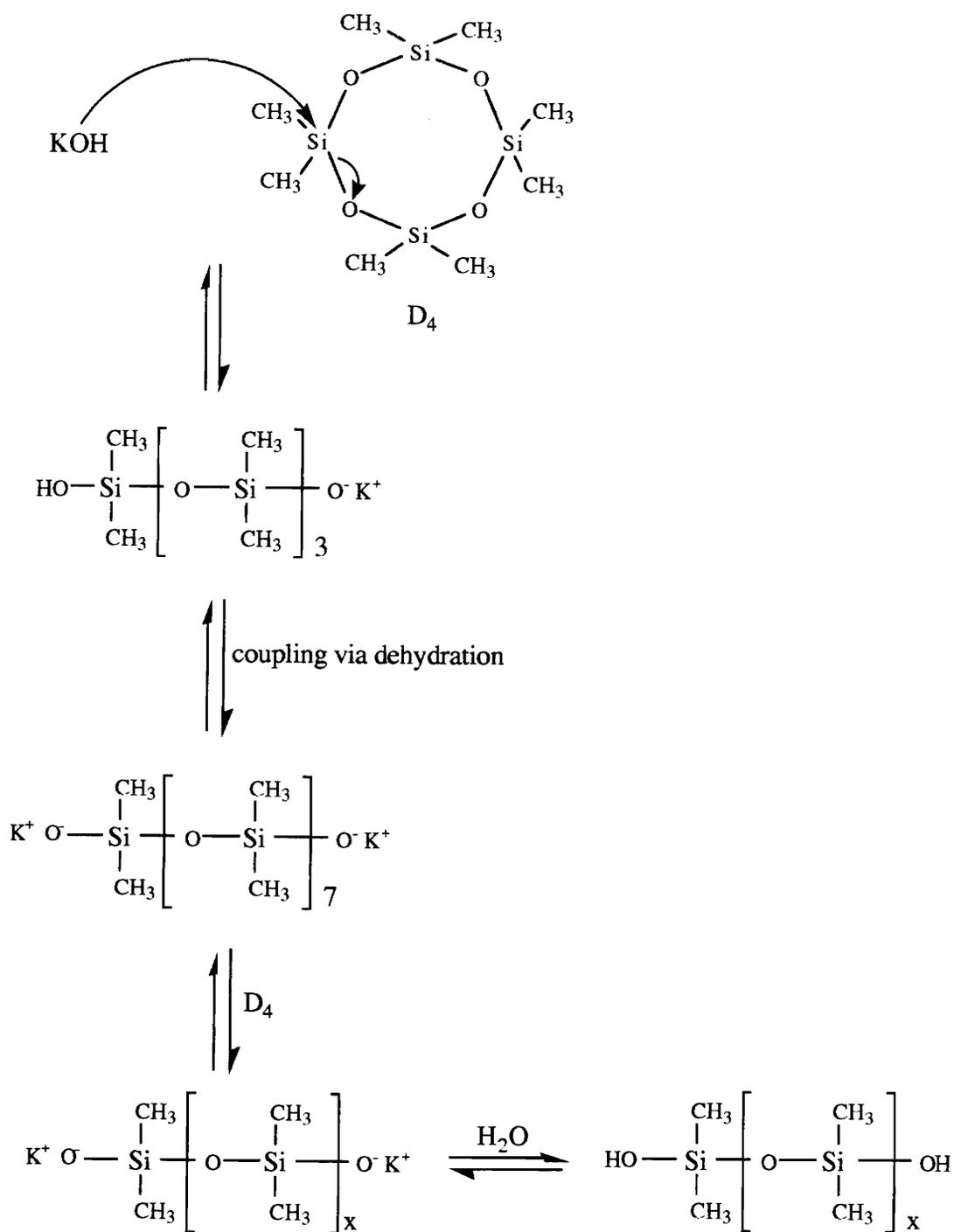
The most common polymer of this type is poly(dimethylsiloxane), PDMS, and is typically used as the major siloxane component in random and block copolymers [42]. Although it can be made from dimethyldichlorosilane, it is usually prepared by a base-catalyzed anionic ring-opening equilibration process. Highest molecular weights are obtained when a strong base such as potassium hydroxide is used to open and polymerize the cyclic tetramer, D₄, resulting in a gummy product [42]. The mechanism of this anionic equilibration process is

well documented [43-47] and is detailed in Scheme 12.

For later use in copolymerizations, PDMS is frequently prepared with reactive endgroups. By initially incorporating a reactant that will lend telechelcity to the siloxane, molecular weight is also controlled. For example, the addition of water in a ring-opening polymerization will offer silanol endgroups, which when stabilized in dry, neutral environments [42] can be post-polymerized. The "monofunctional" endcapper, water in this case, acts as both a chain transfer agent and an endgroup provider. Numerous reactive and unreactive endgroups are possible, as can be seen in Table 9.

Table 9. Poly(dimethylsiloxane)s of various endgroups prepared with "monofunctional" endcappers.

Endcapped PDMS	"Monofunctional" endcapper
$\text{HO}-\text{Si}\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}\right)-\left[\text{O}-\text{Si}\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}\right)\right]_x-\text{OH}$	H ₂ O
$\text{CH}_3-\text{Si}\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}\right)-\left[\text{O}-\text{Si}\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}\right)\right]_x-\text{CH}_3$	$\text{CH}_3-\text{Si}\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}\right)-\text{O}-\text{Si}\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}\right)-\text{CH}_3$
$\text{H}_2\text{N}-(\text{CH}_2)_3-\text{Si}\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}\right)-\left[\text{O}-\text{Si}\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}\right)\right]_x-(\text{CH}_2)_3-\text{NH}_2$	$\text{H}_2\text{N}-(\text{CH}_2)_3-\text{Si}\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}\right)-\text{O}-\text{Si}\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}\right)-(\text{CH}_2)_3-\text{NH}_2$
$\text{CH}_2=\text{CH}-\text{Si}\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}\right)-\left[\text{O}-\text{Si}\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}\right)\right]_x-\text{CH}=\text{CH}_2$	$\text{CH}_2=\text{CH}-\text{Si}\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}\right)-\text{O}-\text{Si}\left(\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}\right)-\text{CH}=\text{CH}_2$

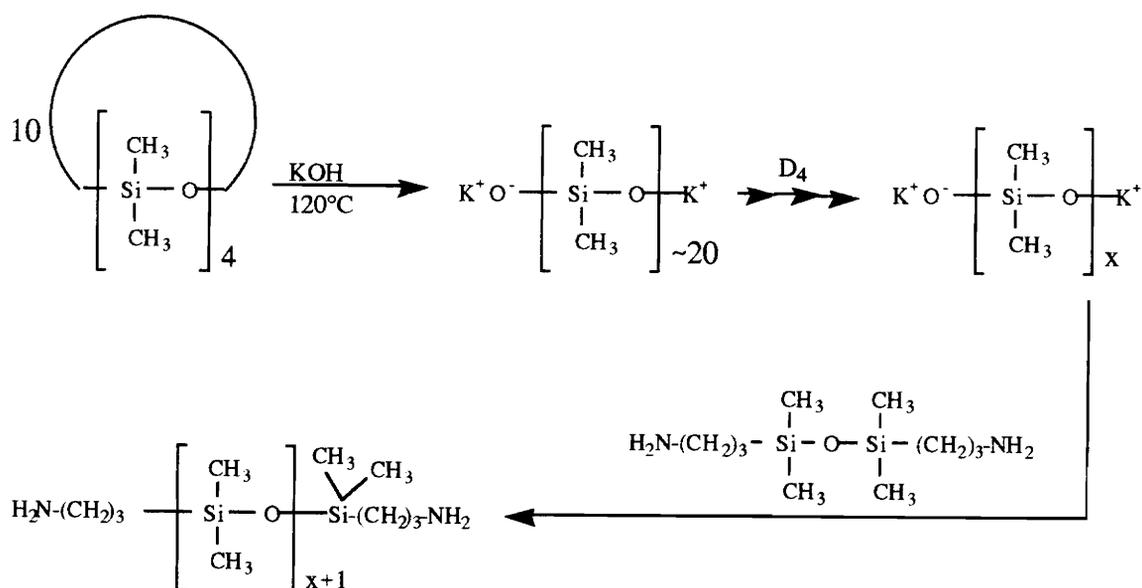


Scheme 12. Mechanism of anionic polymerization of D₄ to yield PDMS [44].

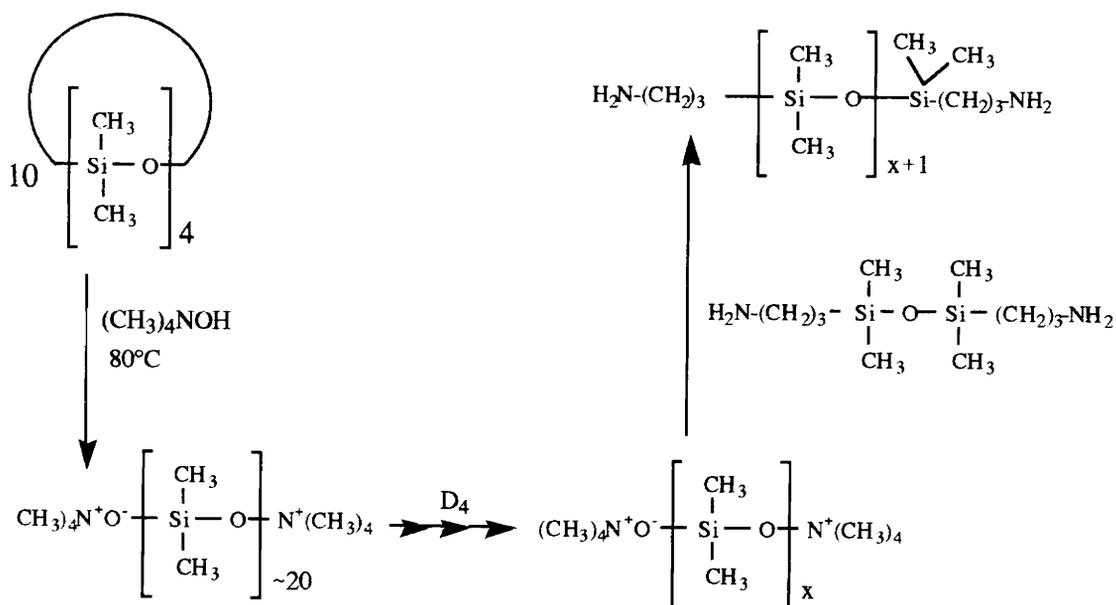
Several research chemists have comparably prepared amine-terminated PDMS from D₄ with α,ω -bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane as the endcapping species. Sormani, *et al.* [44, 45] and Elsbernd [43] employed a basic potassium siloxanolate catalyst in the ring-opening equilibration polymerization, shown in Scheme 13, prepared by reacting potassium hydroxide with the cyclic tetramer in a 1-to-10 molar ratio. The catalyst synthesis was run either neat, in which case the temperature was held at 120°C while the mixture was rapidly stirred and flushed with argon, or in toluene (50 % solution), in which case the temperature was initially 95°C for 12 hours then increased to 120°C for an additional 12 hours. Both methods yielded viscous potassium siloxanolate catalysts with roughly two weight percent KOH content, as predicted by theoretical calculations.

Riffle [47] used a tetramethylammonium siloxanolate catalyst prepared by Union Carbide. Similarly, Elsbernd [43] prepared the same catalyst from tetramethylammonium hydroxide pentahydrate (TMAH) and D₄ (see Scheme 14). With a 10-to-1 molar ratio of TMAH to D₄, the temperature of the reaction solution was stabilized at 80°C since decomposition of the catalyst began at 90°C. Due to the necessarily lower reaction temperature, toluene was not used to distill the condensed water.

For preparation of the aminopropyl-terminated PDMS, all followed the anionic route. Sormani and Elsbernd ran the ring-opening equilibration polymerization at 120°C in the presence of α,ω -bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane with the potassium siloxanolate catalyst. Under rigorously dry reaction conditions, telechelic PDMS molecular weights were controlled by the molar ratio of D₄ to endcapper. After 48 hours, the reaction was terminated by neutralizing the potassium catalyst with acetic acid, washing with water and finally, stripping the system of cyclics by vacuum distillation. Conversely, Elsbernd and Riffle, employing the transient tetramethylammonium siloxanolate catalyst, ran the equilibration polymerizations at only 80°C under a dry, inert atmosphere. Again controlling



Scheme 13. Preparation of potassium siloxanolate catalyst and subsequent polymerization of D_4 in the presence of α,ω -bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane.

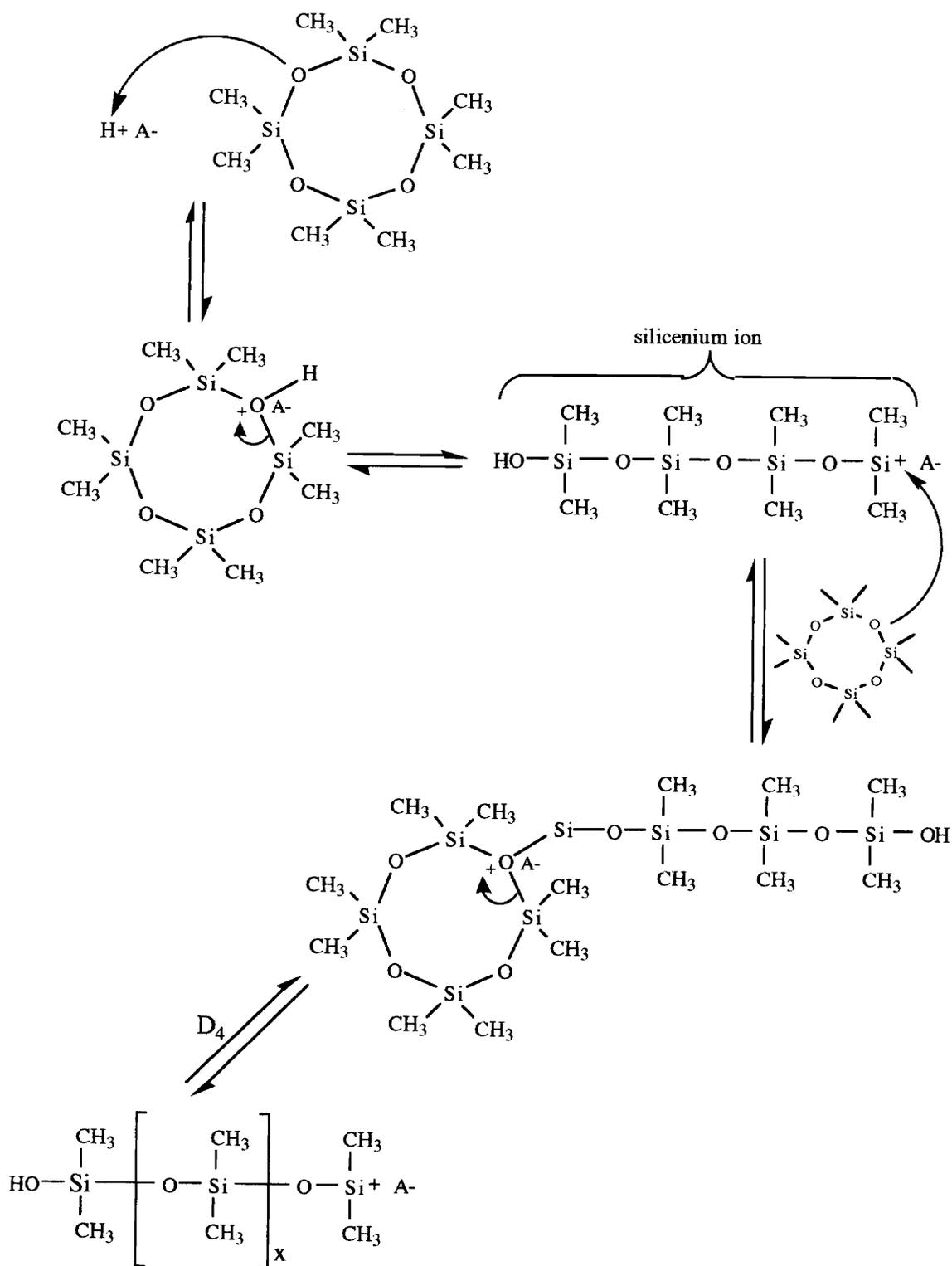


Scheme 14. Preparation of tetramethylammonium siloxanolate catalyst and subsequent polymerization of D_4 in the presence of α,ω -bis(3-aminopropyl)-1,1,3,3-tetramethyldisiloxane.

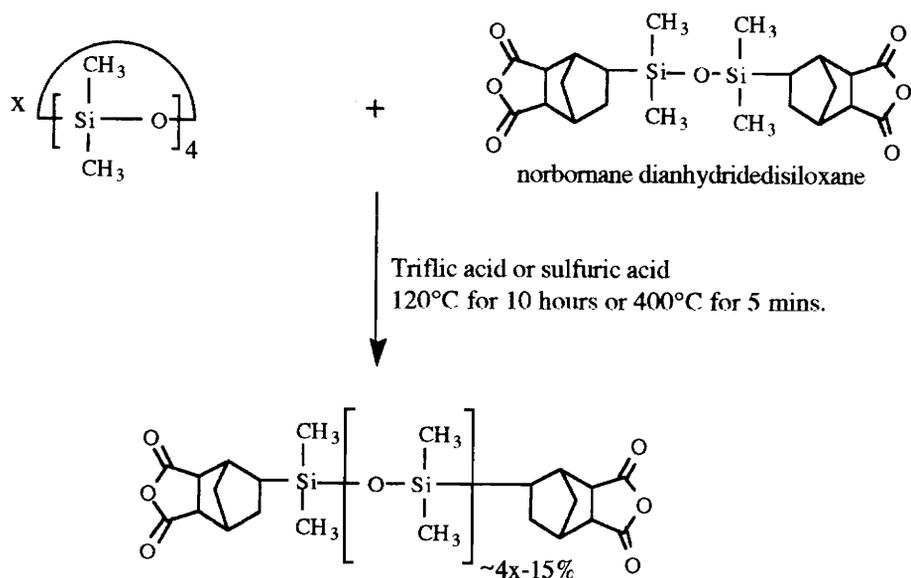
the molecular weight by the molar ratio of cyclic tetramer to endcapper, amine-terminated PDMS was obtained in 24 to 48 hours, after which time the catalyst was decomposed into trimethylamine and methanol or methoxysiloxane by increasing the reaction temperature to 150°C for at least 30 minutes. Lastly, the PDMS was purified by vacuum removal of the cyclic and decomposition byproducts

A less common route to PDMS synthesis utilizes acid catalysts which have also proven to polymerize cyclic siloxanes. Work patented in 1948 stated poly(dimethylsiloxane)s were prepared using ferric chloride, a Lewis acid [40]. Other acids more recently used include sulfuric [48-50], triflic [51-53] and trifluoroacetic [54], all protic acids. The mechanism of cationic ring-opening equilibration of PDMS is not fully understood. It has been suggested that PDMS is formed by a step-growth process, a free radical process, or a cationic polymerization [43]; most research has supported the latter mechanism which is represented in Scheme 15. This suggestion proposes that a tertiary oxonium ion is formed and then rearranges to a silicenium ion; however, no proof has been found to validate the existence of the silicenium ion [46].

Recently, workers at General Electric Co. [55-58] have used the cationic method to produce norbornane anhydride terminated oligomeric PDMS since a basic catalyst would not allow such acidic endgroups. A dianhydride-disiloxane was used as the endcapper in their equilibration polymerizations, shown in Scheme 16. Reactions were carried out in dry and inert atmospheres. Both sulfuric acid and triflic acid were separately employed as acidic catalysts to cationically polymerize D₄, with temperatures and times varying from 120°C for several hours to 400°C for five minutes. Molecular weights were diverse, and no anhydride terminated PDMS greater than 52 siloxane repeat units (this corresponds to a polymer molecular weight of 4200 g/mol) was reported. A major aspect of this research was the preparation of norbornane anhydride-functionalized PDMS in molecular weights from



Scheme 15. Proposed mechanism of cationic ring-opening polymerization of D₄ [46].



Scheme 16. Cationic ring-opening polymerization of D_4 and endcapping with anhydride endgroups (General Electric Co.) [55-58].

1000 g/mol to 10,000 g/mol .

As with any reactive endgroups, further polymerization is potentially possible. In the same literature cited above, G. E. also prepared copolymers from the anhydride-terminated PDMS and monomeric diamines. Another major topic of this thesis was the synthesis of perfectly alternating segmented copolymers prepared from the anhydride-terminated poly(dimethylsiloxane)s and oligomeric diamines.

For both anionic and cationic routes, molecular weight is determined by the ratio of cyclic monomer to endgroup. Though it may seem that the amount of catalyst used would effect the molecular weight as well, this was not found to be the case [42]. Most PDMS polymerizations utilize the cyclic tetramer octamethylcyclotetrasiloxane, or D_4 . Each molecule of D_4 will open to give a linear chain of four dimethylsiloxane units. When initiation occurs and a molecule of the cyclic tetramer is opened, the ionic charge is transferred to the linear tetramer (refer to Schemes 12 and 15) which can then act as the

initiator and attack more D₄. As propagation continues, the active chain end can "backbite" and attack a siloxane unit within its own backbone, thus resulting in a cyclic species. Equally possible is the attack of this newly formed cyclic species by the catalyst to yield a linear siloxane once again. This redistribution in ring-opening polymerizations of D₄ is the cause of equilibration between cyclics and chains. The reader is referred to the in-depth kinetic studies performed and reported by Elsbernd [43].

The use of a solvent plays a very important role in the ring-chain equilibration. It has been found that as the system is diluted with solvent, cyclic structures are favored; beyond a critical dilution point, 100 percent cyclics can be formed [43]. To promote linear polysiloxanes, ring-opening polymerizations are carried out in bulk, using D₄ dually as the solvent and monomer. In the absence of an endcapper, bulk polymerization of D₄ generally yields approximately 85 to 90 percent linear PDMS, with the remainder being cyclic siloxanes [42, 43]. It has also been found that depending on the desired molecular weight, cyclic products increase as the ratio of D₄ to endcapper increases [42], thus higher proportions of cyclic species result.

Interestingly, the enthalpy of polymerization is almost zero. One may tend to think that the polymerization would not occur due to this fact. But, because the entropy of polymerization is positive, D₄ will polymerize. It is thought that the entropy increase is a result of increased flexibility when the cyclic structure is made linear [46].

Polyorganosiloxanes, mainly PDMS, are commonly used in many chemical-related disciplines today. Their simple and inexpensive commercial preparation has brought about many applications in industrial, academic, biomedical, and domestic settings. They are easily functionalized to give telechelic polymers, which when copolymerized offer their unique properties to aid in processability and add ductility.

C. Segmented Copolymers Containing Poly(dimethylsiloxane)s

The term copolymer, originally used to indicate the reaction between two monomers, is used to classify those macromolecules resulted from a union between two homopolymers. Several subclasses of copolymers exist which are based on the overall architecture, specifically *graft*, *block*, and *segmented* copolymers, represented in Figure 4.

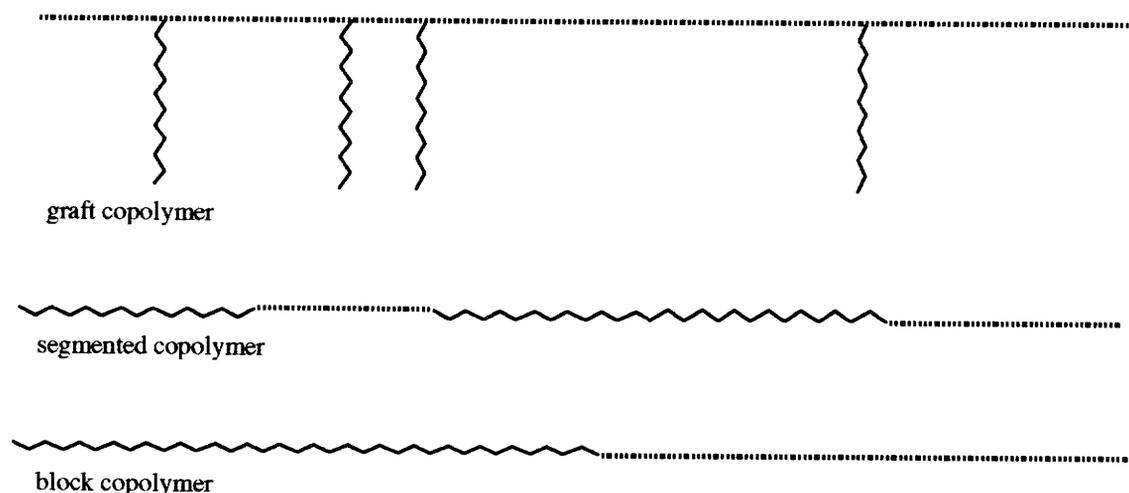
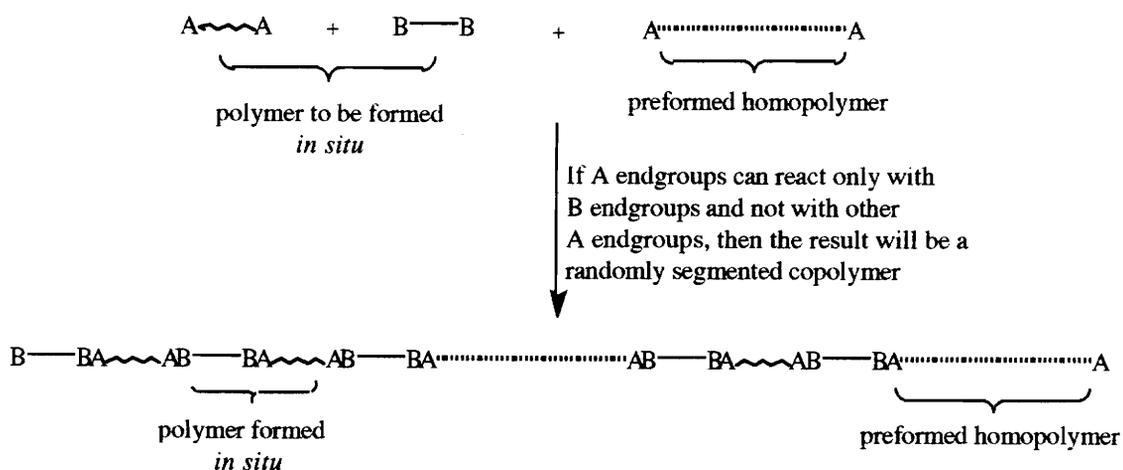


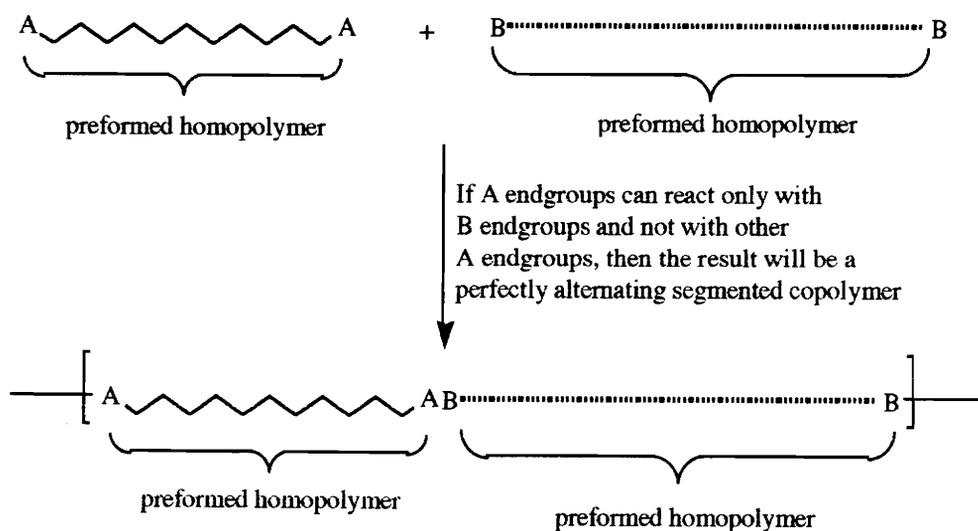
Figure 4. Types of copolymer architectures.

Because the interest in this project was with segmented copolymers, only these types of copolymers will be reviewed. Segmented copolymers, also referred to as multiblock copolymers, can be again divided into another two groups, namely *randomly* and *perfectly alternating* copolymers. Randomly segmented systems are generally made from one preformed homopolymer and one prepared *in situ*. An example of this type of copolymerization is depicted in Scheme 17. Perfectly alternating segmented copolymers are made from two preformed telechelic homopolymers via essentially a coupling reaction; a representation is shown in Scheme 18.

A number of variables are involved in the production of segmented copolymers. Along with method of preparation, as just described, are segment lengths and segment



Scheme 17. Pictorial representation of a randomly segmented copolymerization between two monomers and one telechelic homopolymer.



Scheme 18. Pictorial representation of copolymerization of perfectly alternating fashion between two telechelic homopolymers.

components. Segments are usually oligomeric in molecular weight, ranging from 1000 g/mol to 15,000 g/mol. Polyimides, polyamides, poly(arylene ethers), polycarbonates, polystyrenes and polymethacrylates are only a few of the homopolymers utilized in copolymerizations as segmental components [40]. Provided the appropriate reaction conditions are met and reactive endgroups are introduced, the possibilities of segmented copolymers may be endless. For this reason, the perfectly alternating copolymers reviewed next will be closely related to the work involved in this research; only PDMS-containing copolymers prepared by a step-growth (polycondensation) process will be discussed.

Characterization of copolymers is a major concern. Segmented copolymers which are comprised of two chemically different (thermodynamically incompatible) homopolymers generally show phase separation (basically, homopolymer attraction) above certain segment lengths [61]. Because the chemical bond between the two homopolymers exists, this phase separation may be reduced to microphase level [61]. Directly related is the property of *phase inversion*, a compositionally dependent characterization of a copolymer. Typically, the component of the highest weight percent of the copolymer will act as the *continuous phase*, with the other component dispersed throughout (*dispersed phase*). As the compositions favor the other component, the role of the phases normally will invert. Figure 5 will clarify this idea pictorially. Regardless of which phase was continuous, it was found that the low surface energy of the siloxane component caused its migration to the surface of the copolymer [62], resulting in hydrophobic films. Thus for copolymers even with low siloxane content, bulk portions of the film were siloxane-poor while surfaces were dense with siloxane.

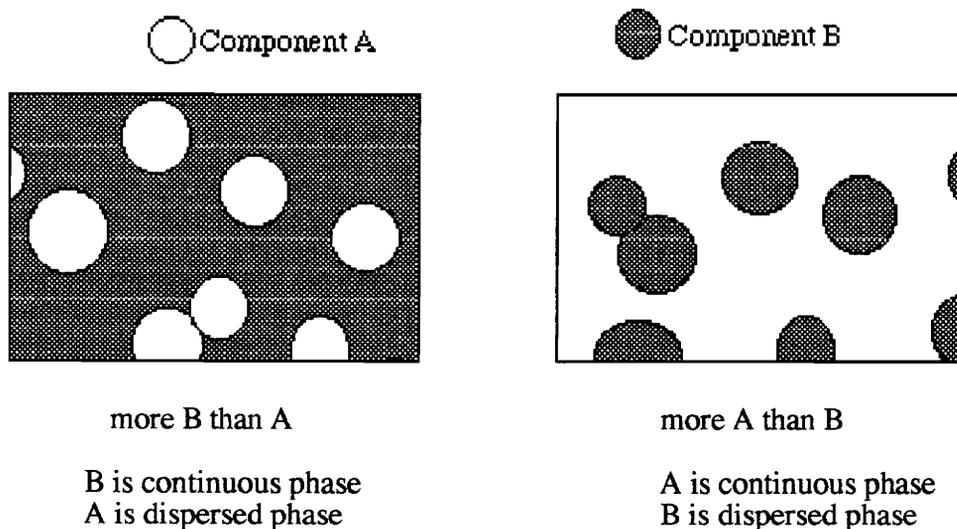
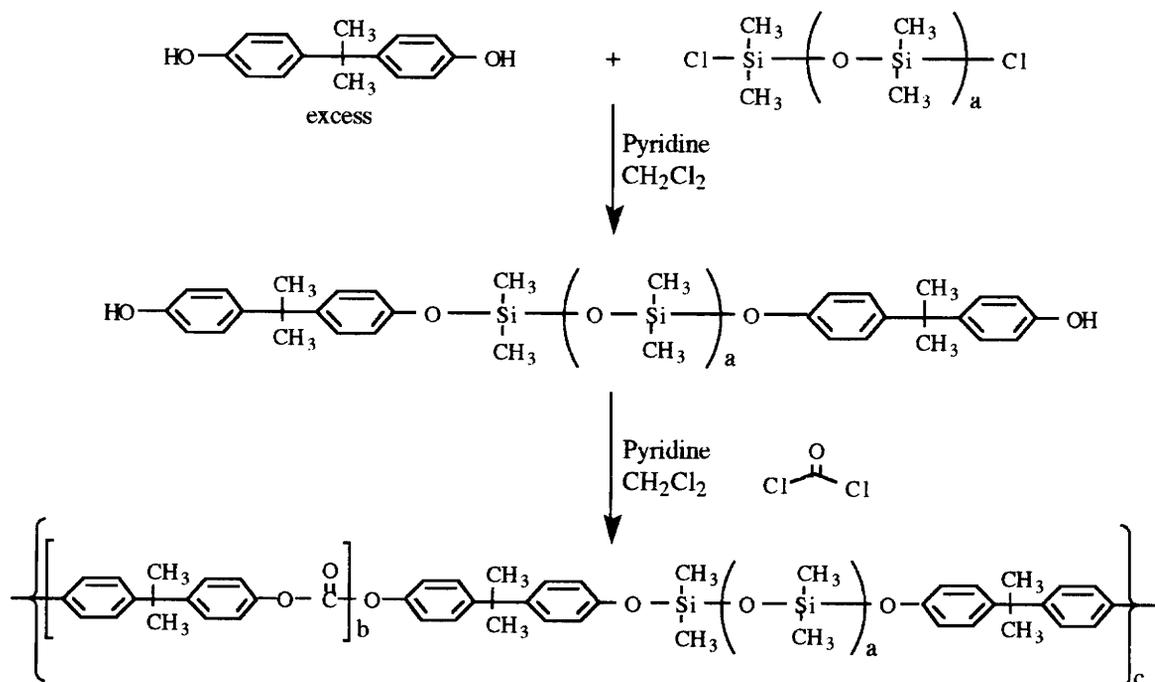


Figure 5. Pictorial representation of continuous and dispersed phases.

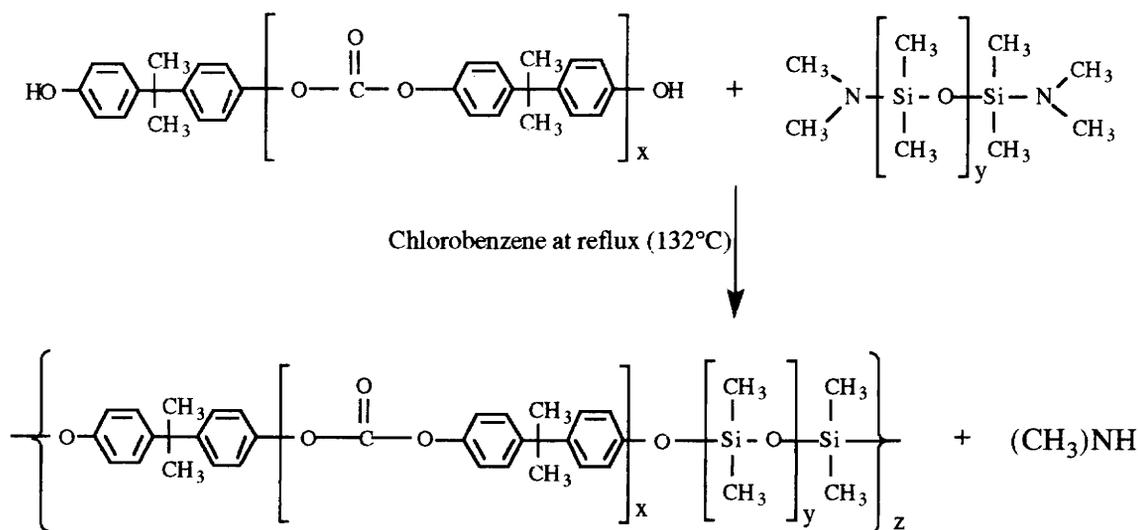
Poly(dimethylsiloxane)-polycarbonate segmented copolymers were first reported in 1965 by Vaughn [47]. These systems were random in structure, as the reaction in Scheme 19 indicates. The copolymerization was separated into two steps. Initially, chlorine-terminated PDMS was endcapped with bisphenol A to produce an α,ω -aromatic diol of PDMS, and then the polycarbonate was formed by reacting the PDMS diol with more bisphenol A and phosgene. The final copolymer, being randomly segmented, contained coupled bisphenol A units, coupled PDMS diol units, and coupled bisphenol A-PDMS diol units. Thus, pure polycarbonate segment lengths were completely varied, and PDMS segments, though characterized prior to copolymerization, were surely coupled as well. The resulting randomly segmented copolymers were generally ductile and rubber-like [61]. Mechanical property studies indicated that as polycarbonate quantity increased, modulus and tensile strength increased, but elongation at break decreased [61]. Further studies showed that much of the mechanical data was dependent on the amount of bisphenol A used in the initial endcapping step. As the amount of bisphenol A used to endcap the

dichloro-PDMS was decreased, and the molar ratio of bisphenol A to dichloro-PDMS approached unity, chain extension was more likely to occur. When chain extension of the PDMS did occur, tensile strength and modulus were improved [65] because the siloxane content was high.



Scheme 19. Synthesis of the first poly(carbonate-PDMS) randomly segmented copolymer [47].

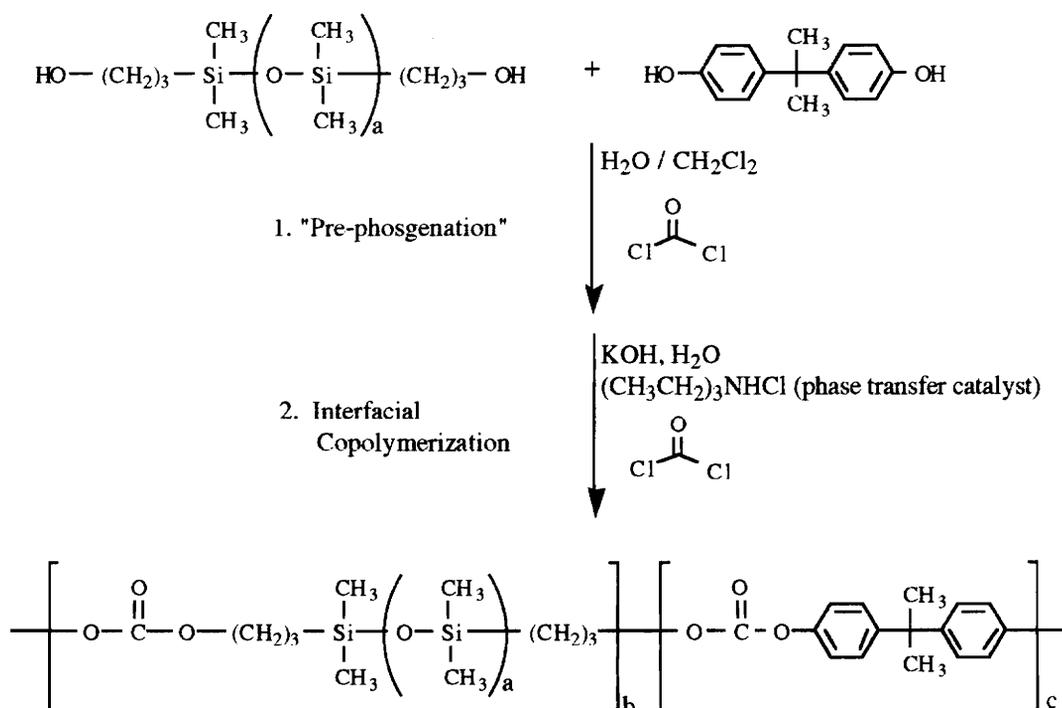
By the beginning of the 1980s, two methods to prepare PDMS-polycarbonate segmented copolymers were developed. The first method involved the reaction between disilylamine-terminated PDMS and phenolic-terminated polycarbonate (see Scheme 20), each preformed and characterized for molecular weight information. Developed by Noshay, *et al.* [22, 66] for phenolic-terminated poly(ether sulfone), the reaction conditions were successfully applied to polycarbonates. Because the telechelic homopolymers could only condense with each other, exclusively perfectly alternating copolymers resulted.



Scheme 20. Perfectly alternating polycarbonate-PDMS segmented copolymer prepared via silylamine/phenol reaction of Noshay, *et al.*

Additionally, compositional control (weight percent) depended only upon the segment lengths of the individual homopolymers. These copolymers were found to be microphase separated, and phase inversion occurred at 48 percent polycarbonate content (polycarbonate became the continuous phase) [61].

Riffle, *et al.* [47, 67, 68], utilized a room temperature interfacial technique to copolymerize carboxylpropyl-terminated PDMS with phosgene and bisphenol A (depicted in Scheme 21). This one-pot, two-step procedure first introduced α,ω -dicarboxypropyl-PDMS and phosgene/methylene chloride mixture in a "pre-phosgenation" step. Secondly, bisphenol A, potassium hydroxide, water and a phase transfer catalyst were added, along with intermittent additions of more phosgene. Formed in the organic phase, the randomly segmented copolymer was isolated and coagulated.

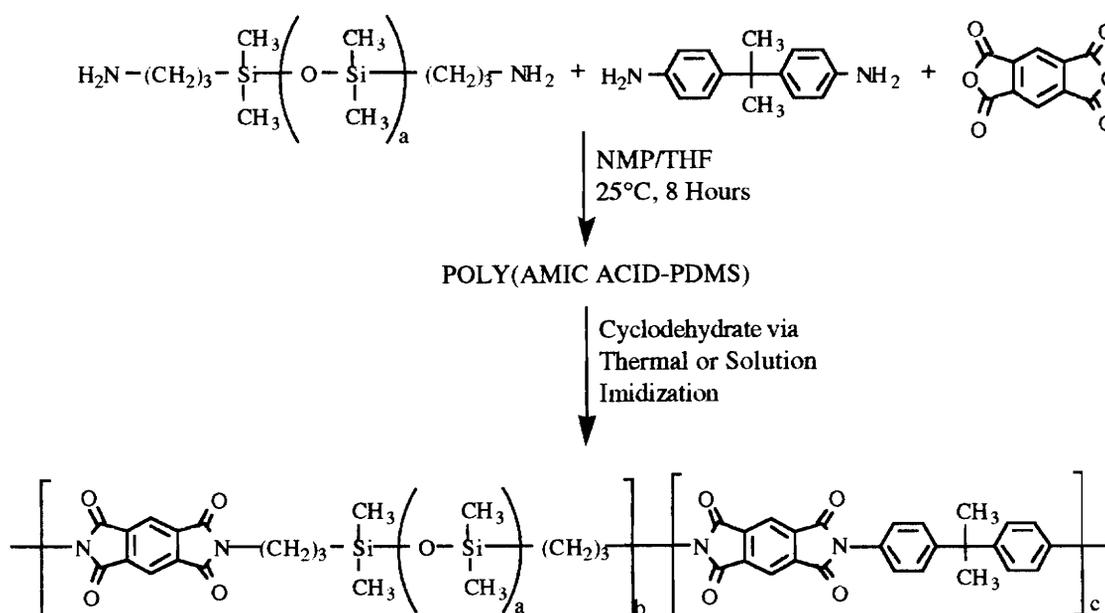


Scheme 21. Synthesis of polycarbonate-PDMS randomly segmented copolymer via interfacial copolymerization developed by Riffle [47].

Briefly mentioned above, Noshay, *et al.* [22, 66] developed poly(arylene ether sulfone)-PDMS copolymers prepared from a phenolic-terminated poly(arylene ether sulfone) reacted with a disilylamine-terminated PDMS in refluxing chlorobenzene (refer to Scheme 20). Like the polycarbonate analog, the perfectly alternating PDMS-poly(arylene ether sulfone) segmented copolymer was microphase separated.

Most recently, McGrath and coworkers [69-72] prepared randomly segmented polyimide-PDMS copolymers. The inclusion of soft PDMS into a rigid, infusible and insoluble system like the polyimide enables processability and solubility without significantly reducing the high T_g values of homopolyimides. Moreover, PDMS lends hydrophobicity and decreases the chance of hydrolysis that can occur in polyimides.

Utilizing a preformed primary amine-terminated PDMS oligomer along with monomeric diamines and dianhydrides, a randomly segmented copolymer was synthesized through a typical imidization reaction. As seen in Scheme 22, the dianhydride can react with either the α,ω -dipropylamino-PDMS or the monomeric diamine to form an imide bond. Thus, the polyimide is formed *in situ* and is of variable segment size. Morphological investigations indicated microphase separation, as expected.



Scheme 22. Synthesis of a poly(imide-PDMS) randomly segmented copolymer by Arnold, *et al.* [71, 72, 78].

Other "hard" reactants used in segmented copolymerizations involving an amine-terminated PDMS include isocyanates to yield polyurea-PDMS and aliphatic diacid chlorides to yield polyamide-PDMS [40]. Current research in our labs again is employing α,ω -dipropylamino-PDMS in a transimidization reaction with amine-terminated polyimide oligomers [72]. All aspects of characterization are still in progress. Many other similar cases have been reported in the literature; however, because roughly 95 percent of these

cases are Japanese patents, information is limited to brief, translated abstracts.

As proved by the polycarbonate copolymers, PDMS functionality is not limited to amines. As mentioned earlier, a primary goal in this research was to prepare anhydride terminated PDMS, which in turn was to be copolymerized with several engineering thermoplastics in a perfectly alternating fashion. The copolymerization technique (imidization) was used by Keohan and Hallgren [59] and by their colleagues in previous work [56, 74, 75] in the preparation of randomly segmented polyimide-PDMS. Utilizing a monomeric diamine, their copolymers contained high percentages of dimethylsiloxane and therefore, were elastomeric in behavior. Another goal of our research was to further investigate and extend this type of copolymerization to systems other than polyimides.

In most of the copolymer systems mentioned above, molecular weight of the copolymer was not controlled. In these cases, there were statistically two types of chain ends (from the two types of monomers or telechelic oligomers used) that were theoretically still reactive. Walbauer, *et al.* [39] and Arnold, *et al.* [76,78] utilized a monofunctional endcapper, phthalic anhydride, that controlled molecular weight and arrested further reactivity. Randomly segmented polyimide-PDMS copolymers of controlled molecular weight (25,000 g/mol to 45,000 g/mol) ensured processability and solubility in common organic solvents. Adhesive ability, a primary application of polyimide-PDMS copolymers, was enhanced for molecular weight controlled reaction batches [76].

The chemical modification of polymers with PDMS by copolymerization was undertaken for many reasons. PDMS incorporation offered processability, solubility, oxidative stability, ductility, as well as other useful properties without grossly effecting the high T_gs and tough characteristics of the "hard" segments. Both randomly and perfectly alternating structures have been easily synthesized. Microphase separation was observed for both randomly and perfectly alternating segmented copolymers in which the segments

were thermodynamically incompatible. For PDMS-containing systems, domain (phase) sizes were around 100 Å to 500 Å, and copolymer films had siloxane-rich surfaces [62]. The valuable information obtained from the segmented copolymers that have been synthesized is constantly being applied to novel systems that are currently developing. The advantages that PDMS offers have justified the great interest in such potentially useful polymers.

D. Molecular Weight Control via the Carothers Equation

On the assumption that only difunctional monomers will be used, molecular weight of a step-growth oligomer, polymer, or copolymer has been easily controlled through stoichiometric imbalance. Another means of molecular weight control is through incorporation of a monofunctional endcapper (a method of stoichiometric imbalance). Both cases of molecular weight control apply some form of the Carothers equation. Published in 1936 [77], Carothers proposed an equation relating the number-average degree of polymerization to the extent of reaction:

$$X_n = 1/(1-p) \quad \text{[Equation 1]},$$

where X_n is the number-average degree of polymerization and p is the extent of reaction. The number-average degree of polymerization is a relative or fractional amount based on the number of monomers that have linked together compared to the original number present. Therefore,

$$X_n = [\text{initial \# monomer molecules}] / [\text{\# monomer molecules at some time } t], \text{ or}$$

$$X_n = [M]_0 / [M]_t \quad \text{[Equation 2].}$$

The extent of reaction was equally called the extent of conversion. This is a fractional value, where

$p = 1$ implies 100 % conversion of reactants to products,
 $p = 0.95$ implies 95 % conversion of reactants to products, while the
 remaining 5 % reactants is unchanged, and
 $p = 0.50$ implies one-half reactants converted to product, while the
 other one-half reactants is unchanged, *etc.*

The extent of reaction, p , is a calculated value determined by the number of unreacted monomer molecules. This value is related to the equation

$$[M]_t = [M]_0 - p[M]_0, \text{ or rearranging to give } [\text{Equation 3}],$$

$$p = 1 - ([M]_t / [M]_0) \quad [\text{Equation 4}].$$

By substituting,

$$p = 1 - (1 / X_n), \text{ and by rearranging, } [\text{Equation 5}]$$

$$X_n = 1 / (1 - p), \text{ the Carothers equation.}$$

Odian [77] provides a more thoroughly detailed discussion of this equation.

The degree of polymerization, DP, is defined as the number of repeat units per polymer chain and is related to X_n by one of two ways. When one functional group of a monomer can react with another group of the same monomer, it is said to be an A-B monomer, examples of which include amino acids and "vinyl" monomers such as styrene. In the case of the polymerization of styrene,

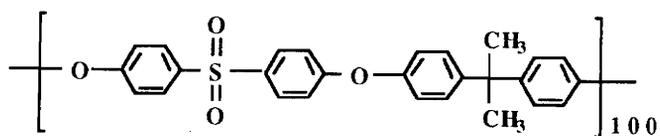
$$X_n = DP.$$

However, we must modify this equality in our case. Because our systems involve reaction between two monomers, we note that

$$X_n = 2DP \quad [\text{Equation 6}], \text{ or}$$

$$DP = 1/2 X_n.$$

Thus, for the poly(arylene ether sulfone) synthesized from bisphenol A and dichlorodiphenyl sulfone,



Molecular weight of repeat unit = 442.515 g/mol

DP = 100 because there are 100 repeat units, but

X_n = 200 because 200 monomer molecules (100 of each) have been linked together.

The monomers are said to be A-A and B-B monomers. In this situation, an A-A molecule cannot react with another A-A molecule, and a B-B molecule cannot react with another B-B molecule. For the poly(arylene ether sulfone) shown above, a molecule of bisphenol A cannot react with another bisphenol A (or any bisphenol) molecule; similarly, a molecule of dichlorodiphenyl sulfone cannot react with another dichlorodiphenyl sulfone (or any activated dihalide) molecule. The assignment of whether a monomer is an A-A or a B-B is completely arbitrary (provided it is difunctional).

Another important term in calculations for molecular weight control is the stoichiometric ratio of monomers used. The ratio or stoichiometric imbalance, r , of monomers A-A and B-B can simply be written as

$$r = \text{A-A} / \text{B-B} \quad [\text{Equation 7}].$$

If the amount of monomer A-A is the same as monomer B-B, then r is equal to the upper limit of 1, and the overall polymer molecular weight could, in principle, approach infinity. Statistically, this infinitely long chain will have one end of A and one end of B. Obviously, there is no molecular weight control in this case. If B-B is supplied in excess (stoichiometric imbalance), the ratio will decrease, and the overall molecular weight will be reduced. Statistically, the polymer chains will have B functionalities at both ends. If A-A is supplied in excess, the ratio will likewise decrease (since it can never exceed 1), but polymer chains will have A termini.

This ratio is not helpful at this stage and must be taken further. If one simplifies the symbols in Equation 7 and lets A represent the number of molecules of the A-A monomer and B represent the number of B-B molecules, then

$$r = A / B, \text{ or by rearranging} \quad [\text{Equation 7}],$$

$$A = rB.$$

One can say that the total number of A-A and B-B monomers can be represented by [M], such that

$$[A + B] = [M] \quad [\text{Equation 8}].$$

From Equation 2, one can say

$$X_n = [A+B]_0 / [A+B]_t .$$

The amount of monomer remaining at time t, $[A+B]_t$, is based on the extent of reaction, p. If one says that the amount of A-A molecules that have reacted is equal to the extent of reaction, then one must also say that the number of A-A molecules that have not reacted is equal to $(1-p)$. The fraction of B-B molecules that have reacted is dependent on the amount of A-A molecules reacted. Therefore, the fraction of reacted molecules of B-B is equal to (rp) . And, the fraction of unreacted B-B is $(1-rp)$. One can then note that

$$A(1-p) = \text{number of unreacted A-A molecules at time t, and}$$

$$B(1-rp) = \text{number of unreacted B-B molecules at time t.}$$

Recalling Equation 2, and now substituting, one obtains

$$X_n = [A+B] / [A(1-p) + B(1-rp)] \quad [\text{Equation 9}]$$

$$= [A+B] / [A-pA+B-rpB].$$

Equation 7 states that $A = rB$, so

$$X_n = [rB+B] / [rB-rpB+B-rpB] \quad [\text{Equation 10}]$$

$$= [rB+B] / [rB+B-2rpB].$$

Dividing all terms by B, one obtains

$$X_n = [r+1] / [r+1-2rp]. \quad \text{[Equation 11].}$$

As the polymerization proceeds, the extent of reaction increases, and eventually approaches the limit $p \rightarrow 1$. Therefore, at high extent of reaction,

$$\begin{aligned} X_n &= [r+1] / [r+1-2r] \\ X_n &= [r+1] / [1-r] \end{aligned} \quad \text{[Equation 12].}$$

Rearrangement will give Equation 13,

$$r = [X_n - 1] / [X_n + 1] \quad \text{[Equation 13].}$$

Equations 7 and 13 are equivalent, but the latter is more helpful in calculations for molecular weight control.

The equations needed to actually calculate a desired molecular weight for any step-growth polymerization involving two difunctional monomers are 6 and 13, as well as Equation 14,

$$DP \approx \text{desired molecular weight} / \text{mol. weight of repeat unit} \quad \text{[Equation 14].}$$

One can prepare the poly(arylene ether sulfone) (shown previously in this section) of any molecular weight with either hydroxyl or chloro endgroups. For example, if one desires a molecular weight of 10,000 g/mol and chloro endgroups, one can perform the following calculations:

$$\begin{aligned} DP &\approx 10,000 \text{ g/mol} / 442.515 \text{ g/mol} && \text{[Equation 14]} \\ &= 22.598. \end{aligned}$$

$$X_n = 2DP = (2)(22.598) = 45.196 \quad \text{[Equation 6].}$$

$$\begin{aligned} r &= [X_n - 1] / [X_n + 1] = [44.196] / [46.196] && \text{[Equation 13]} \\ &= 0.9567 = \text{bisphenol A/dichlorodiphenyl sulfone.} \end{aligned}$$

Note that because chloro endgroups are desired, an excess of the dihalide is needed. Since the ratio, r , cannot exceed 1, one must assign dichlorodiphenyl sulfone as the B-B

monomer (denominator in the ratio) and bisphenol A as the A-A monomer (numerator in the ratio). From this calculation, for every mole of dichlorodiphenyl sulfone used, only 0.9567 mole of bisphenol A is necessary. (See the *Experimental* for an actual calculation that involves other necessary variables.) To prepare hydroxyl endgroups, the A-A and B-B assignment is simply inverted.

As an aside, note that Equation 14 has is an inequality between the left and right hand sides of the statement. The two sides are only approximately equal because the equation does not account for the molecular weight due to the endgroups. This elimination of endgroup molecular weight has been undertaken to simplify the calculations. Thus for this example, DP is actually

$$DP = [10,000 \text{ g/mol} - \text{mol. wt. of endgroups}] / 442.515 \text{ g/mol} \quad [\text{Equation 14}']$$

As higher molecular weights are desired, the endgroup molecular weight factors into the equations less. For a desired molecular weight of 40,000 g/mol, 500 g/mol or so molecular weight due to the endgroups is not a large difference; therefore, the term can be eliminated. While most of the polymers for this research were desired to be 5000 g/mol, obtaining the exact size was not a major concern.

It was also stated that a monofunctional endcapper could be included to provide molecular weight control. The monofunctional endcapper will react with the polymer chain as it is growing. The reasons for adding this third reactant vary. If one wants completely unreactive endgroups on the poly(arylene ether sulfone), phenol can be added as the monofunctional endcapper. Thus the final endgroups will be phenyl rings. If one wants amine endgroups, aminophenol can be introduced into the reaction. The amine functionality will be inactive in this nucleophilic aromatic substitution, leaving the phenolic group reactive. A modification of Equation 7 is needed in order to accommodate for this third reactive species. The modification of Equation 7, which is used only to determine the

amount of endcapper needed, yields

$$r = B / (A + 2A'), \text{ or}$$

$$2A' = (B - rA) / r \quad \text{[Equation 15],}$$

where $2A'$ is the amount of monofunctional endcapper. This notation assumes that the reactive group of the endcapper is the same moiety as for the A-A monomer. Here, the quantity of 2 does not enter into the calculation; it serves as a reminder that the endcapper is monofunctional. Then, to synthesize the 10,000 g/mol phenyl-terminated poly(arylene ether sulfone) analog, one calculates exactly as above:

$$DP \approx 10,000 \text{ g/mol} / 442.515 \text{ g/mol} \quad \text{[Equation 14]}$$

$$= 22.598.$$

$$X_n = 2DP = (2)(22.598) = 45.196 \quad \text{[Equation 6].}$$

$$r = [X_{n-1}] / [X_{n+1}] = [44.196] / [46.196] \quad \text{[Equation 13]}$$

$$= 0.9567 = \text{bisphenol A/dichlorodiphenyl sulfone.}$$

Because phenol is the endcapper, dichlorodiphenyl sulfone is again needed in excess over the bisphenol A. Now, one must use Equation 15 to calculate how much phenol is necessary to synthesize the appropriate molecular weight:

$$2A' = [(1 \text{ mol}) - (0.9567)(0.9567 \text{ mol})] / 0.9567$$

$$= 0.0811 \text{ mol phenol needed.}$$

These calculations conclude that for each one mole of dichlorodiphenyl sulfone, 0.9567 mole of bisphenol A and 0.0811 mole phenol are needed to synthesize a 10,000 g/mol phenyl-terminated poly(arylene ether sulfone).

The Carothers equation has led to the other very useful forms of that equation that allow for easy and fairly reproducible molecular weight control of most polymer systems. This method was used extensively in this research to prepare amine-terminated engineering

thermoplastics of oligomeric molecular weights, which were involved in post-polymerizations to yield perfectly alternating segmented copolymers. In addition, this method of control was applied to one copolymer system in order to prepare an unreactive phenyl-terminated perfectly alternating segmented copolymer for GPC analysis.

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Experimental

A. Reagents and Purification Procedures

Table 10 details structures and formulae of all compounds listed.

1. *5,5'-(1,1,3,3-tetramethyl-1,3-disiloxanediyl)-bis-norbornane-2,3-dicarboxylic acid anhydride*

a. Reagent grade toluene (J. T. Baker or Fisher) was cooled to approximately 10°C. It was washed with concentrated sulfuric acid (Fisher) to remove thiophene impurities. The temperature of this mixture of liquids was not allowed above 30°C so that sulfonation of toluene could not occur. The toluene layer was separated from the acid and then washed once with a 5% sodium bicarbonate (Fisher) aqueous solution and twice with deionized water. The toluene was dried over magnesium sulfate (Fisher), then decanted and dried over calcium hydride (Fisher). It was finally distilled from the calcium hydride under nitrogen and stored under nitrogen pressure in a round bottom flask stoppered with a copper wire-secured rubber septum. Removal of the purified toluene for later use was via syringe.

b. Isopropanol (J. T. Baker or Fisher) was distilled and stored in a desiccator in a small vial with a tight fitting lid sealed with Parafilm.

c. Hexachloroplatinic acid ($\text{H}_2\text{PtCl}_6 \cdot x\text{H}_2\text{O}$) was used as received from Aldrich. The remainder of the catalyst was stored in a plastic bottle with a Parafilm wrapped screw cap in a desiccator.

d. 5-Norbornene-2,3-dicarboxylic acid anhydride, or Norbornene anhydride (Kodak Chemicals) was either recrystallized from chloroform (Fisher), azeotroped with toluene prior to reaction, or used as received. It was determined that these

three purification procedures gave similar results.

e. **1,1,3,3-Tetramethyldisiloxane** (Petrarch Systems, Inc., presently Huls Corp.) was dried over and distilled from calcium hydride. It was then stored under nitrogen pressure in a round bottom flask with a copper wire-secured rubber septum. Removal of disiloxane was via a syringe.

2. *Anhydride-Terminated Poly(dimethylsiloxane)s*

a. **Octamethylcyclotetrasiloxane (D4)** was obtained from Petrarch Systems, Inc. (Huls Corp.). The D4 was dried over calcium hydride and vacuum distilled using a water aspirator. It was stored in a desiccator in a round bottom flask stoppered with a wire-secured rubber septum.

b. **Trifluoromethanesulfonic acid** (Kodak Chemicals), or **triflic acid**, was used as received. It was stored in the original amber colored screw capped bottle in a larger glass bottle containing a desiccant. The catalyst was then stored in a freezer.

c. **5,5'-(1,1,3,3-tetramethyl-1,3-disiloxanediyl)-bis-norbornane-2,3-dicarboxylic acid anhydride (NADSX)** was purified as described in the synthesis of the compound.

d. **Calcium oxide** (catalyst quenching agent) was used as received from J. T. Baker.

e. **Toluene** (J. T. Baker or Fisher), a diluent, was used directly without further purification.

3. *Amine-Terminated Engineering Thermoplastics*

a. **1-Methyl-2-pyrrolidinone (NMP)** purchased from Fisher was a purified grade. It was dried over and vacuum distilled from calcium hydride. The NMP was stored

in a round bottom flask stoppered with a wire-secured rubber septum under nitrogen pressure. Removal of the solvent was via syringe.

b. Reagent grade toluene (J.T. Baker or Fisher) was used directly from the bottle without further purification.

c. Technical grade *ortho*-dichlorobenzene (Fisher), *o*-dichlorobenzene, was purified by vacuum distillation from calcium hydride utilizing a water aspirator. It was stored under positive nitrogen pressure in a round bottom flask with a wire-secured rubber septum. Removal of this solvent was via syringe.

d. Reagent grade glacial acetic acid was used as received from Fisher.

e. High purity bis(4-fluorobenzoyl)benzene (BFBB) was generously donated by BASF. It was used without further purification.

f. 4,4'-Dichlorodiphenyl sulfone (DCDPS) was supplied by Amoco Chemical Company. It was recrystallized from toluene with charcoal at approximately 60 w/v percent solids concentration. The solution was stirred for several hours while refluxing, then cooled slightly. Celite was added to the solution and stirred for 30 minutes. A glass funnel with fluted filter paper was placed over the opening of a separate Erlenmeyer flask in which a small volume of toluene was refluxing. The DCDPS/toluene solution was filtered through the hot funnel (to prevent crystallization within the funnel) to yield a colorless DCDPS/toluene solution free of Celite and charcoal. The solution volume was reduced and DCDPS precipitated upon cooling. The crystals were collected, washed with cold toluene, and dried in a vacuum oven at 60°C for 12 hours.

g. 2,2'-bis(4-hydroxyphenyl)propane, or Bis A, was provided by Dow Chemical Company. It was recrystallized from a 25 w/v percent solids concentration toluene solution that was refluxing for several hours and precipitated when cooled to room temperature. The crystals were collected, washed very briefly with cold toluene, then dried

in a vacuum oven for 12 hours at 60°C.

h. **Biphenol (BP)**, purchased from Aldrich as 97%, was recrystallized from deoxygenated acetone. Dry house nitrogen was vigorously bubbled through refluxing acetone in a large Erlenmeyer flask. The acetone was saturated with BP to yield a concentrated solution. A nitrogen adapter was fitted over the the mouth of the flask so that the solution cooled under an inert atmosphere. BP crystals precipitated from the acetone upon cooling slowly to room temperature. The crystals were collected by filtration, crushed with a mortar and pestle, and finally dried under vacuum at 60°C for 12 hours.

i. **Bis(4-fluorophenyl)phenyl phosphine oxide, BFPPPO**, was synthesized and purified by a modification of known Grignard techniques published by Hirose, *et al.* [15]. This modification, which provides a method to prepare polymer grade BFPPPO, is referred to Smith, *et al.* [18]. Only the purification will be discussed here. The crude BFPPPO (wet from water washings) was dissolved in toluene with charcoal and refluxed for several hours to azeotropically distill off the water. The solution was then filtered through Celite, and the toluene was stripped using reduced pressure. The still crude crystalline monomer was vacuum distilled at 160°C to 170°C on a short path distillation apparatus. The purified BFPPPO was recrystallized from toluene, dried in a vacuum oven at 70°C for 12 hours, and stored in a screw-capped amber glass jar.

j. **Meta-aminophenol (*m*-AP)** was purchased from Aldrich. The *m*-AP was sublimed at 130°C under full vacuum provided by a mechanical pump. The purified crystals were stored in a tightly screw-capped amber colored glass jar until needed.

k. Occidental Chemical Corp. donated polymer grade **4,4'-oxydiphthalic anhydride (ODPA)** which was used without further purification.

l. Polymer grade **4,4'-[1,4-phenylene-bis(1-methyl ethylidene)] bisaniline** (donated by Air Products and Chemicals, Inc.), or **Bis P**, was used without

further purification.

m. **Potassium carbonate** (Fisher), K_2CO_3 , was crushed with a mortar and pestle and dried in a vacuum oven at 120°C for at least 12 hours.

n. Certified grade **tetrahydrofuran** (J. T. Baker or Fisher), **THF**, was used directly from the bottle without further purification.

4. *Perfectly Alternating Engineering Thermoplastic-Poly(dimethylsiloxane) Segmented Copolymers*

a. **Ortho-dichlorobenzene** was purified as stated under the previously discussed section on *Reagents for Amine-Terminated Engineering Thermoplastics*.

b. **2-Hydroxypyridine (2-OHpy)** was obtained from Aldrich as 97% purity. This colored material was recrystallized from absolute ethanol with charcoal. The solution was filtered through a bed of Celite in a medium pore fritted glass funnel. The solution volume was reduced until crystals precipitated at room temperature. The 2-OHpy was dried in a vacuum oven at room temperature for 16 hours. This catalyst was then stored in a plastic bottle with a screw cap in a desiccator.

c. **Amine-terminated engineering thermoplastic oligomers** were coagulated into a methanol (75 v %) and water (25 v %) mixture and dried under vacuum at 120°C. **Anhydride-terminated poly(dimethylsiloxane) oligomers** were stripped of cyclic impurities at 150°C under vacuum.

c. As a diluent, **chloroform** or **methylene chloride** (J. T. Baker or Fisher) was used directly from the bottle.

Table 10. Reagents and Chemical Information.

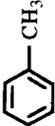
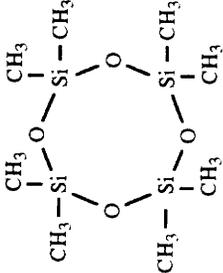
Reagents	Structure/Formula	Mol. Wt.	Purification Information
Toluene		92.14 g/mol	Wash with H ₂ SO ₄ , distill at 110°C from CaH ₂ .
Isopropanol	$\begin{array}{c} \text{H} \\ \\ \text{CH}_3 - \text{C} - \text{OH} \\ \\ \text{CH}_3 \end{array}$	60.10 g/mol	Distill under N ₂ .
Hexachloroplatinic Acid	H ₂ PtCl ₆	409.82 g/mol	Use as received. Store in a desiccator.
5-Norbornene-2,3-dicarboxylic Acid Anhydride		164.16 g/mol	Use as received.
1,1,3,3-Tetramethyl-disiloxane	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{H} - \text{Si} - \text{O} - \text{Si} - \text{H} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	134.33 g/mol	Distill at 70°C from CaH ₂ .
D ₄		296.62 g/mol	Vacuum distill from CaH ₂ using water aspirator. B.P. = 176°C

Table 10. Continued.

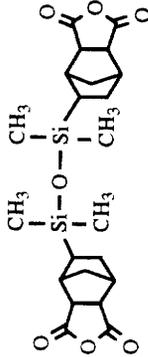
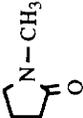
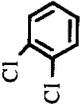
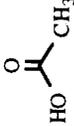
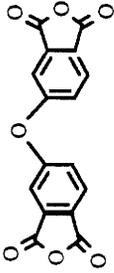
Reagents	Structure/Formula	Mol. Wt.	Purification Information
Triflic Acid	$\text{CF}_3\text{SO}_3\text{H}$	150.08 g/mol	Use as received. Store in dessicator.
NADSX		462.65 g/mol	Solidify with ether. Store in dessicator.
Calcium Oxide	CaO	56.07 g/mol	Use as received.
NMP		99.13 g/mol	Vacuum distill from CaH_2 .
ODCB		147.00 g/mol	Vacuum distill from CaH_2 .
Glacial Acetic Acid		60.05 g/mol	Use as received.
ODPA		310.23 g/mol	Use as received; polymer-grade.

Table 10. Continued.

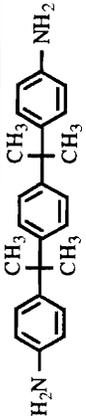
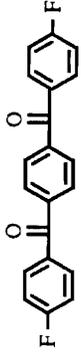
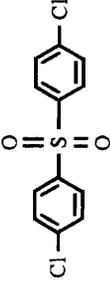
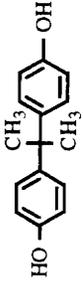
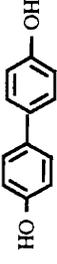
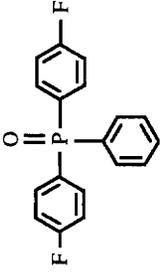
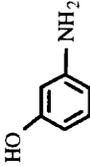
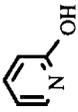
Reagents	Structure/Formula	Mol. Wt.	Purification Information
Bis P		344.50 g/mol	Use as received; polymer grade.
BFBB		322.23 g/mol	Use as received; polymer grade.
DCDPS		228.27 g/mol	Recrystallize from toluene with charcoal.
Bis A		228.27 g/mol	Recrystallize from toluene.
BP		186.21 g/mol	Recrystallize from deoxygenated acetone.
BFPPO		314.27 g/mol	Vacuum distill at 160°C.

Table 10. Continued.

Reagents	Structure/Formula	Mol. Wt.	Purification Information
<i>m</i> -AP		109.13 g/mol	Vacuum sublime.
Potassium Carbonate	K_2CO_3	130.21 g/mol	Crush, vacuum dry. Stored in desiccator.
THF		72.11 g/mol	Used as received.
2-OHpy		95.10 g/mol	Recrystallize from absolute ethanol with charcoal. Store in desiccator.
Chloroform	$CHCl_3$	119.38 g/mol	Use as received.
Methylene Chloride	CH_2Cl_2	84.93 g/mol	Use as received.

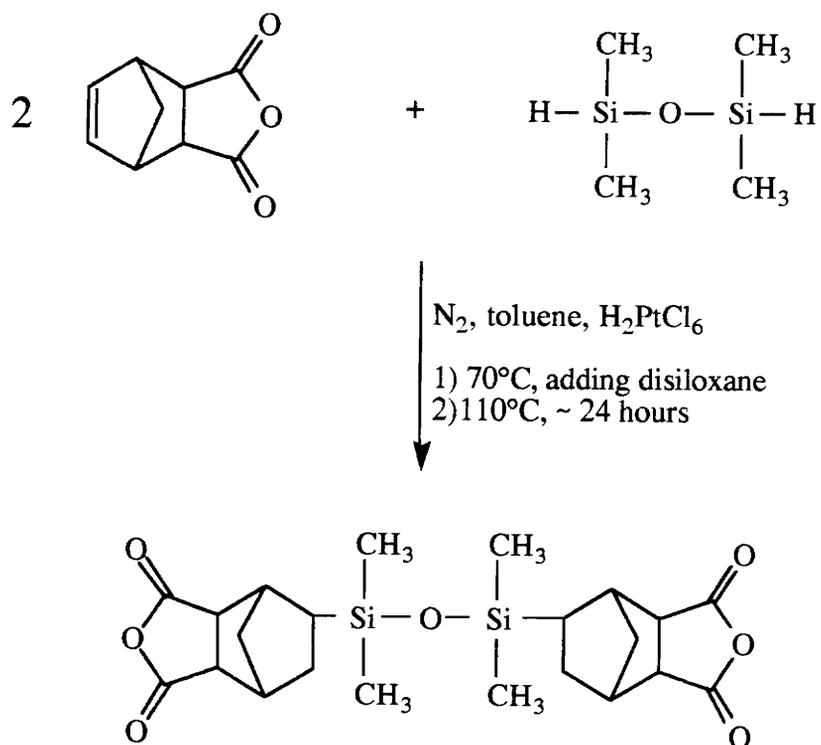
B. Dimer, Oligomer and Perfectly Alternating Segmented Copolymer Syntheses

1. Synthesis of 5,5'-(1,1,3,3-tetramethyl-1,3-disiloxanediyl)-bis-norbornane-2,3-dicarboxylic acid anhydride (denoted NADSX from hereon)

Two hydrosilylation procedures were attempted for the synthesis of NADSX. However, only one gave satisfactory results. The successful procedure will be discussed here, while only a few comments will be made in the *Results and Discussion* regarding the less successful method. The synthesis [56] is schematically represented in Scheme 23.

Prior to running the NADSX reaction, a catalyst solution was prepared in the following manner. It was normally prepared about 24 hours in advance. Hexachloroplatinic acid, a hydrosilylation catalyst, was weighed into a clean and dry sample vial and then capped with a rubber septum secured with copper wire. The sample vial was then purged with dry house nitrogen by using inlet and outlet needles for about five minutes. The needles were removed and a few drops of isopropanol was added via syringe to dissolve the platinum compound. Toluene was then added to make a dilute solution. The vial was placed in a cool, dark area (in a bench drawer away from the oven) to stand until the next day.

A 100-ml, three-neck round bottom flask containing a Teflon-coated magnetic stirring bar was fitted with a condenser and calcium sulfate filled drying tube, pressure equilibrating addition funnel stoppered with a rubber septum, and nitrogen inlet/thermometer adapter at each opening (see Figure 6). All male joints were wrapped in Teflon tape. The apparatus was flamed dry with a Bunsen burner under a rapid nitrogen purge. After the glassware was cool, crushed norbornene anhydride weighed onto a Teflon-coated aluminum sheet was quickly added to the flask. Toluene was used to rinse the remaining norbornene



Scheme 23. Synthesis of NADSX via hydrosilylation of norbornene anhydride.

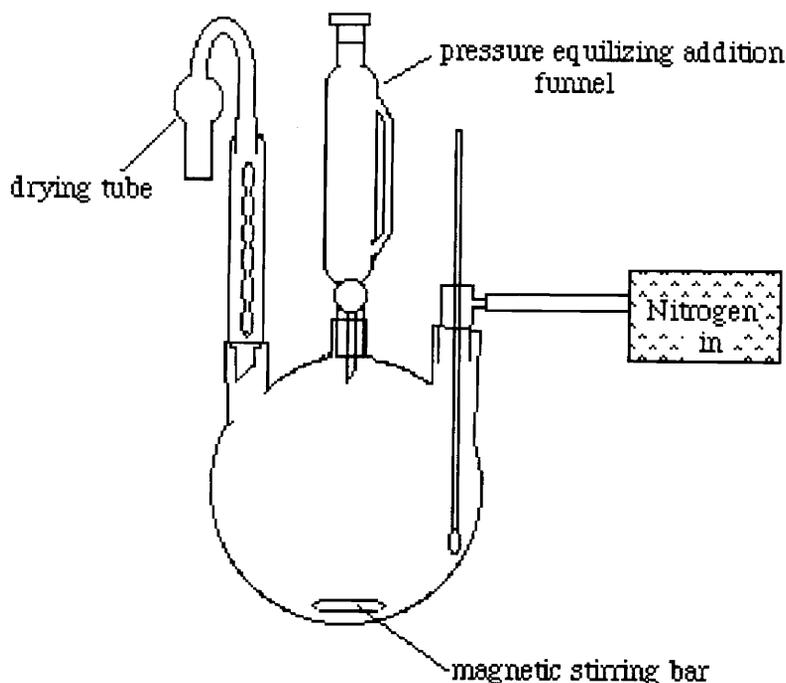


Figure 6. Reaction apparatus for preparation of NADSX.

anhydride into the flask. The previously prepared catalyst solution was added to the flask. More toluene was added to the reaction vessel to yield around 50 percent solids content. The joints were sealed with Teflon tape so that the hot toluene would not escape. This solution was immediately stirred and heated to 70°C to 80°C with a silicone oil bath while under a slow nitrogen flow. 1,1,3,3-Tetramethyldisiloxane was transferred to the closed addition funnel through the use of a syringe. It was added dropwise to induce a gentle reflux at about 85°C to 95°C. This exotherm is indicative of a successful hydrosilylation. Upon addition of the disiloxane the clear colorless solution changed to various shades of yellow. As all of the disiloxane was added, the resulting reaction mixture remained transparent, but was deep yellow to brown in color. After complete addition, the reaction temperature was increased to about 110°C to produce a toluene reflux. Due to the sensitivity

of the catalyst, the reaction temperature was not allowed to exceed 115°C. This reaction was run overnight (at least 24 hours).

The following day, the reaction was slowly cooled to approximately 40°C. Charcoal was then added to adsorb the catalyst and stirred until the solution reached room temperature. The solution was then filtered through a bed of Celite within a porcelain Büchner funnel. The Celite was rinsed with toluene. The resulting pale yellow to colorless transparent solution was poured into a single-neck round bottom flask, and the toluene was removed by vacuum stripping on a Rotovap. Anhydrous diethyl ether was added to the oily product so that it would solidify. The flask was then stoppered with a rubber septum and left undisturbed overnight. The solidified NADSX, a pale tan to white powder, was scraped from the walls of the flask and agitated in the ether just prior to filtration. The ether filtrate was reserved to collect the remaining NADSX that did not initially solidify. The collected NADSX was dried under vacuum at room temperature, and the ether filtrate was again allowed to stand overnight in the closed flask, whereafter a second batch of NADSX was removed and dried. Finally, the filtrate was disposed of after recovery of a small third batch of product. The three collections of dried powder were combined and stored in one glass jar in a desiccator.

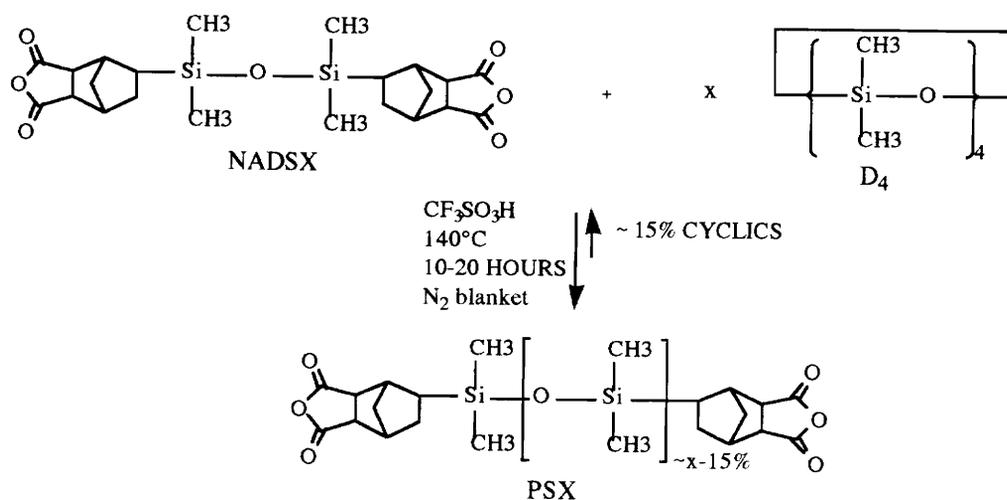
A typical reaction consisted of 14.8430 g (0.0904 mol) of norbornene anhydride and 6.0729 g (0.0452 mol, 8 ml) of 1,1,3,3-tetramethyldisiloxane, which was converted to a volume quantity for convenience. This represents a molar ratio of exactly two to one. Based on the molar amount of carbon-carbon double bond in the norbornene anhydride, 0.0205 g (0.000043 mol, 4.7×10^{-4} mol catalyst/mol C=C) of hexachloroplatinic acid was dissolved in less than one ml of isopropanol and about one ml of toluene. Usually the amount used ranged from 5×10^{-5} to 5×10^{-4} mole catalyst per mole carbon-carbon double bond. Final yields were approximately 60 percent, due to the loss of product during

filtration and transfers. Product confirmation was carried out by titration, melting temperature, ^1H NMR and ^{29}Si NMR.

Initially, a 2.1-to-1 molar ratio of norbornene anhydride to 1,1,3,3-tetramethyl-disiloxane was used in order to completely "endcap" the disiloxane. This procedure was not followed in later reactions due the extended purification needed to remove the excess norbornene anhydride. It was also determined that an exact two-to-one ratio effectively yielded complete hydrosilylation. This aspect will be more fully covered in the *Results and Discussion* chapter.

2. Synthesis of Anhydride-Terminated Poly(dimethylsiloxane) Oligomers (denoted PSX from hereon)

The procedure given here is a cationic ring-opening equilibration polymerization [57]. The cyclic siloxane tetramer D_4 is opened to give a linear species which is then endcapped with the "monofunctional" NADSX via essentially a chain transfer process. The reaction is shown in Scheme 24. A 250-ml, three-neck round bottom flask was fitted with the



Scheme 24. Synthesis of anhydride-terminated poly(dimethylsiloxane) oligomer via cationic ring-opening equilibration reaction.

following: a nitrogen inlet and thermometer adapter, an overhead mechanical stirrer, and a calcium sulfate filled drying tube. All male joints were wrapped with Teflon tape. With a rapid nitrogen purge, the glassware was flamed dry using a Bunsen burner. After the vessel was cool, the nitrogen inlet was modified so that there was an inert atmospheric blanket rather than a purge; the drying tube was replaced with a rubber septum. All joints were wrapped with Teflon tape to prevent loss of triflic acid catalyst and D₄ monomer. An illustration of the final reaction set-up is shown in Figure 7.

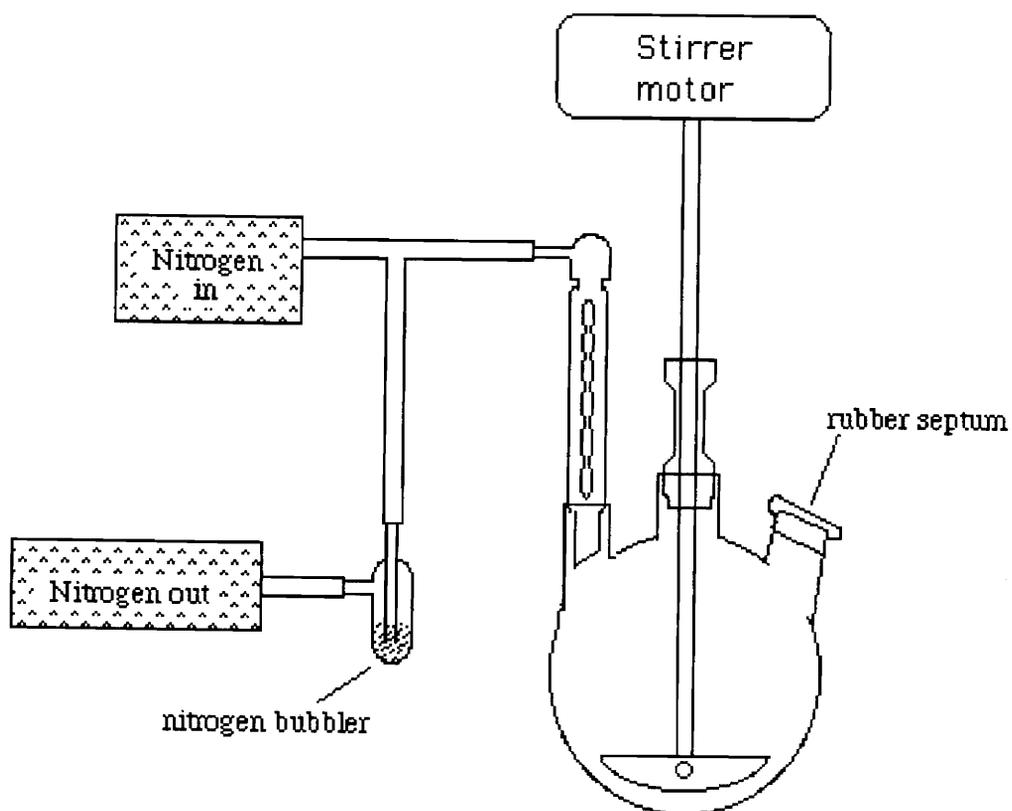


Figure 7. Reaction apparatus for preparation of PSX

The previously prepared and characterized NAD₄SiX₃ was weighed onto Teflon-coated aluminum pans and transferred into the reaction flask. The D₄ was transferred from its storage flask into the reaction vessel using a flamed and cooled syringe with volumetric markings. The heterogeneous mixture was stirred and heated to approximately 130°C to 140°C. At this point, the triflic acid was measured into a microsyringe and charged into the flask through the septum. Immediately, the acidic vapor could be seen, and after approximately five minutes it was noticed that the mixture was becoming both viscous and apparently homogeneous. Homogeneity was not achieved at reaction temperatures lower than 125°C. The equilibration reaction was maintained stirring at 130°C to 140°C for at least 10 hours. The oil bath was then removed, and the resulting clear anhydride-terminated PSX oligomer was slowly cooled to room temperature. Finely powdered calcium oxide was added to quench the catalyst, and the mixture was stirred for an additional 10 or more hours. Reaction times (both ring-opening and quenching) were not less than 10 hours, but greater lengths of time were often used for convenience. For higher molecular weight PSX, a small amount of toluene was added at the quenching stage to reduce the viscosity (to ensure even dispersion of the quenching agent).

Following the quenching stage, enough toluene was added to the PSX slurry for ease of filtration of the solution through a medium pore fritted glass funnel. The filtered siloxane solution was then poured into a single-neck round bottom flask, and the toluene was removed under reduced pressure and elevated temperature. The oily PSX oligomer was further purified by vacuum stripping off cyclic siloxanes that form in the equilibration reaction. This was done by using a mechanical pump attached to a heated Kugelrohr, a short path distillation unit. The pure PSX oligomer was then stored in a small glass jar in a desiccator.

Depending on the oligomer molecular weight desired, the D₄-to-PSX ratio changed.

Assuming that the polymerization does not involve an equilibrium, an expected molecular weight of 1500g/mole would employ a ratio of 3.50 moles of D₄ to 1 mole of NAD SX.

This is explained by the following calculation:

$$1500 \text{ g/mol PSX} - 462.65 \text{ g/mol from NAD SX endgroup} = 1037.35 \text{ g/mol}$$

$$1037.35 \text{ g/mol PSX} / 74.15 \text{ g/mol for dimethylsiloxane repeat unit} = 13.98$$

$$14 \text{ dimethylsiloxane repeat units are needed: } 14/4 \text{ (siloxane repeat units/D}_4 \text{ mol)}$$

$$14/4 = 3.50 \text{ mol D}_4 \text{ needed per mol NAD SX (endgroup).}$$

Scaled down appropriately, this reaction used 6.88 g (0.0149 mol) of NAD SX and 16.35 g (0.0558 mol, 17.3 ml) of D₄. Also used were 20 μl (0.00023 mol, 0.034 g, 0.0015 w %) of triflic acid and 0.51 g (0.0091 mol) of calcium oxide, an adequate excess. But because this polymerization is an equilibration reaction between cyclic and linear siloxanes, one must expect a molecular weight reduced by about 10 to 15 percent (85 w % linear polymer, 15 w % cyclics). Knowing this, one may chose to increase the amount of D₄ by 15 percent, as was done in most of the PSX syntheses in this research. Recovered yields were about 70 percent. Molecular weight was confirmed by titration and, in some cases, ¹H NMR.

3. *Synthesis of Amine-Terminated Engineering Thermoplastic Oligomers*

a. Amine-Terminated Poly(Arylene Ether)s: Poly(Ether Sulfone), Poly(Ether Ketone Ketone) and Poly(Ether Phosphine Oxide) (denoted from hereon as PES, PEKK and PEPO, respectively)

Poly(arylene ether)s, a class of engineering thermoplastics, vary in many ways as can be noted by their names, and hence their functional groups. While this research has involved the synthesis of three similar oligomers, only one will be discussed here in detail. Table 11 shows the monomers used to prepare the corresponding poly(arylene ether)

Table 11. Poly(arylene ether) engineering thermoplastics utilized in this research.

Activated Dihalide	Bisphenol	Polymer Structure (repeat unit)	Acronym
			PES
			PEKK
			PEPO

oligomers. Because these reactive oligomers must have a controlled molecular weight, a sample calculation is provided. The Carothers equations applied were explained previously in the *Background* chapter. The polycondensation reaction is one of nucleophilic aromatic substitution involving an activated dihalide and a bisphenol anion, along with a "monofunctional" endcapper that provides both molecular weight control and telechelic endgroups for future reactivity.

To synthesize a 5000 g/mol aromatic amine-terminated poly(arylene ether sulfone), Bis A and DCDPS were used as the difunctional bisphenol and activated dihalide A-A and B-B monomers, and *m*-AP was the "monofunctional" endcapper. The molecular weight of the repeat unit, 442.514 g/mol, can be obtained from the representation in Table 11. Thus

$$DP \approx 5000 \text{ g/mol} / 442.514 \text{ g/mol} = 11.299$$

$$X_n = 2DP = 2(11.299) = 22.598$$

$$r = (X_n - 1) / (X_n + 1) = 21.598 / 23.598 = 0.91525 = N_A / N_B.$$

Therefore, a ratio of 0.91525 mole Bis A to 1 mole DCDPS is needed. (It may be obvious that endgroup molecular weights are not considered in these calculations for simplicity,

thus resulting in a slightly higher final oligomer molecular weight than desired.) At this point, it is acceptable to choose the amount of DCDPS to be used (based on the overall quantity of polymer needed). Thus, to synthesize approximately 35 g of amine-terminated poly(arylene ether sulfone), 22.9732 g (0.080 mol) of DCDPS was used. From this, it was calculated that 16.7155 g (0.0732 mol) of Bis A was needed. In order to determine how much *m*-AP was required, the following equation was used:

$$2NA' = [(NB - rNA) / r] = \{[0.080 - (0.91525)(0.0732)] / 0.91525\}$$

$$= 0.01419 \text{ mole } m\text{-AP needed.}$$

Therefore, 1.5483 g (0.01419 mol) of *m*-AP was utilized. Also, potassium carbonate was added as the weak base to produce the reaction phenolate of the Bis A at elevated temperatures. A 15 weight percent excess of K₂CO₃ was incorporated into the reaction flask. It was calculated from

$$(0.08 \text{ mol K}_2\text{CO}_3)(138.21 \text{ g/mol K}_2\text{CO}_3) = 11.06 \text{ g} + (11.06 \text{ g})(15\%)$$

$$= 12.72 \text{ g K}_2\text{CO}_3 \text{ needed.}$$

The amide solvent, NMP, is usually charged to yield a 15 w/v percent solids concentration.

This can be calculated readily by

$$39.6887 \text{ g monomers} / 0.15 = 265 \text{ ml NMP needed.}$$

For removal of water (by azeotropic distillation) formed in the polycondensation, 133 ml of unpurified toluene was included, which was one-half of the NMP volume.

The reaction apparatus was set-up as shown in Figure 8 and the reaction is shown in Scheme 25. A 250-ml, four-neck round bottom flask was fitted with a nitrogen inlet/thermometer adapter, an overhead mechanical stirrer, a Dean-Stark trap with a condenser and drying tube and a glass stopper. All male joints were wrapped in Teflon tape prior to assembly. With a rapid purge of nitrogen, the glassware was flamed dry. When the vessel was cool, the Dean-Stark trap was prefilled with unpurified toluene, and the joints

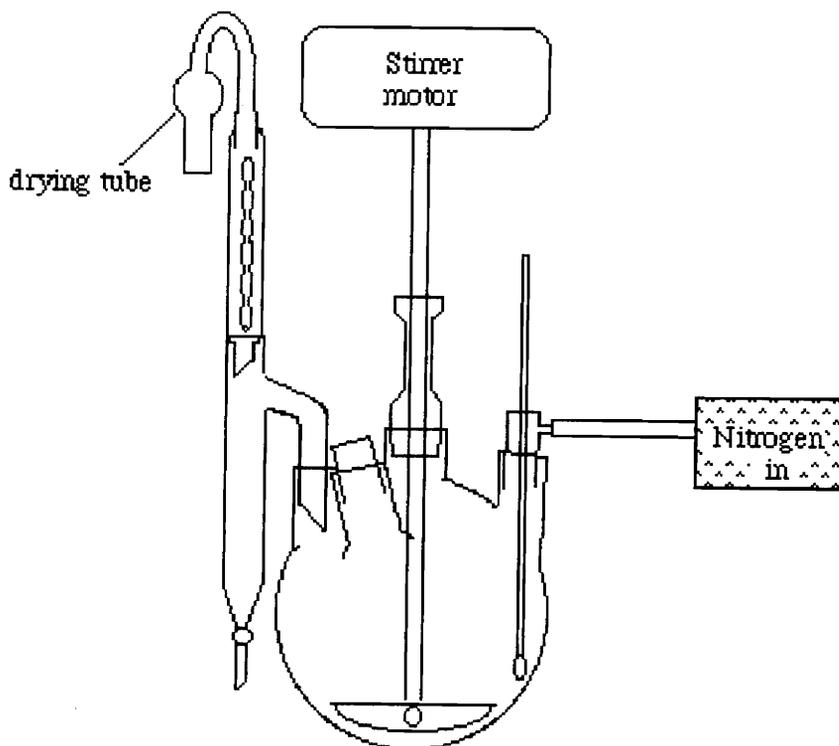
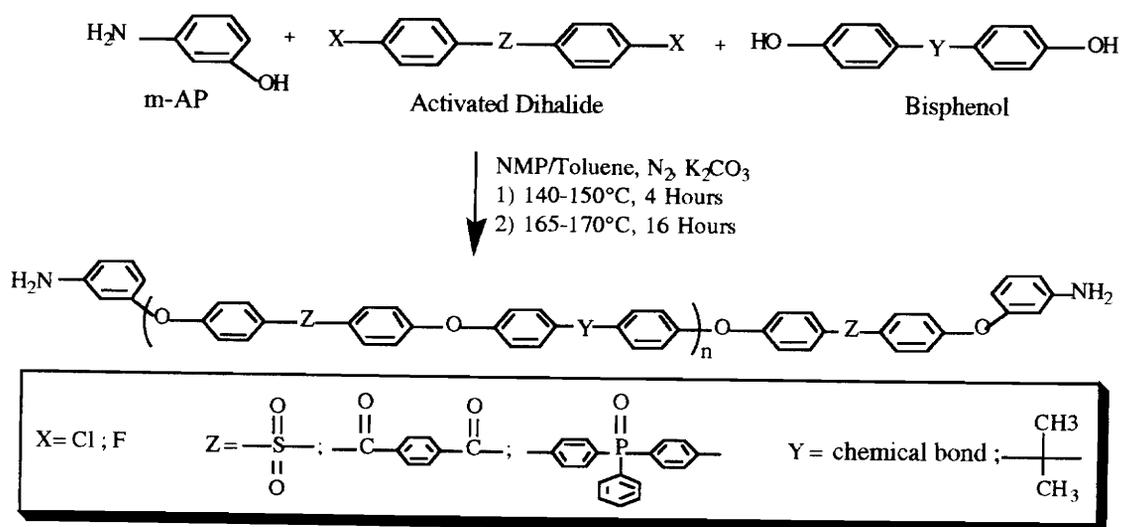


Figure 8. Reaction apparatus for preparation of poly(arylene ether)s.



Scheme 25. Synthesis of amine-terminated poly(arylene ether) engineering thermoplastic oligomer.

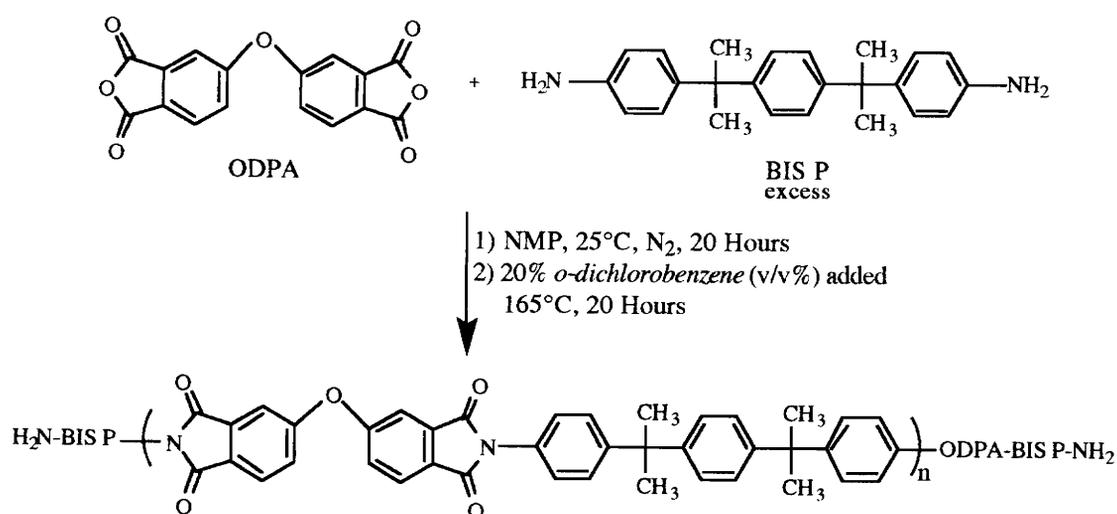
were sealed with Teflon tape. All of the reagents were weighed out as calculated and then added to the flask in no particular order. Untransferred chemicals were washed with NMP into the flask from the weighing pans and funnels. The remaining solvents were then added to the dry ingredients. Under a slow nitrogen flow, the stirring heterogeneous solution was heated to 145°C for at least four hours, to form the phenolate and distill the water by-product. The water was easily noticed in the Dean-Stark trap since it was insoluble and of higher density than the toluene. Additionally, the solution turned from colorless or yellow to a dark green hue (indicating phenolate formation). At this point, enough toluene was released from the trap to promote an increase in reaction temperature to 165°C. This temperature was maintained for 16 hours, until the green solution changed to brown.

The slightly viscous opaque solution was then cooled to room temperature and diluted with unpurified THF. It was filtered through a porcelain Büchner funnel to remove the salts and excess base. The brown polymer solution was then poured into a separatory funnel, and the solution was added to a rapidly stirring blender filled with a mixture of methanol (75 v %) and water (25 v %), the total volume being equal to 10 times the volume of the polymer/THF solution. The coagulated amine-terminated PES (~90 % yield) was air dried for several hours, then dried under vacuum in an oven at 100°C for 24 hours. Further purification was carried out by dissolving the dried oligomer in enough THF to yield a 15 percent solids content and reprecipitating the PES. Again, the powdery polymer (~80 % yield) was dried and was stored in a glass jar. Endgroup titration, DSC and intrinsic viscosity measurements were used to characterize the product.

b. Amine-Terminated Polyimide Oligomer (denoted PI from hereon)

The PI oligomer was prepared by a different polycondensation method. The reaction described here is appropriately known as an imidization and is usually run in two steps; the first is the formation of poly(amic acid), and the latter is cyclodehydration to the polyimide.

This second step can be done either neat in a heated vacuum oven or in solution as was done in this research. The latter allows for better structural control. The monomers chosen were ODPA, a dianhydride, and Bis P, a diamine. By using an excess of the diamine and offsetting the stoichiometry, a molecular weight controlled amine-terminated polyimide with a Bis P-ODPA repeat unit (molecular weight = 618.687 g/mol) was synthesized. The reaction is depicted in Scheme 26, where the proposed oligomer molecular weight was 5000 g/mol.



Scheme 26. Synthesis of amine-terminated polyimide engineering thermoplastic oligomer.

A 500-ml, four-neck round bottom flask was fitted with a nitrogen inlet/thermometer adapter, an overhead mechanical stirrer, an inverse Dean-Stark trap with condenser and drying tube, and a glass stopper. All male joints were wrapped with Teflon tape. An illustration of the glassware is shown in Figure 9. The apparatus was flame dried while a quick nitrogen purge was applied. After the glassware was cool, the trap was prefilled with dry *o*-dichlorobenzene, and the monomers were weighed out according to the

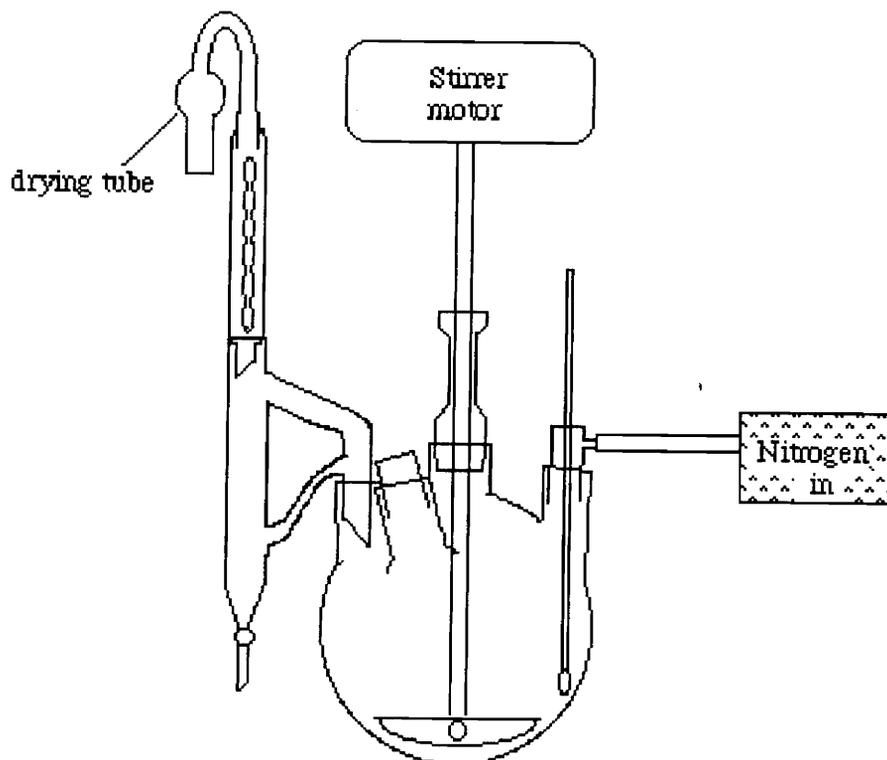


Figure 9. Reaction apparatus for the preparation of amine-terminated polyimide.

Carothers equations and calculations below:

$$DP = 5000 \text{ g/mol} / 618.687 \text{ g/mol} = 8.0816$$

$$X_n = 2DP = 2(8.0816) = 16.16326$$

$$r = (X_n - 1) / (X_n + 1) = 15.16326 / 17.16326 = 0.8835 = N_A/N_B.$$

Thus, the required molar ratio of ODPA to Bis P is 0.8835 mole to 1 mole. These were converted into the necessary weight equivalents; 15.0430 g (0.04849 mol) of ODPA and 18.9088 g (0.05489 mol) of Bis P were added to the reaction flask. The weighing pans and funnel were washed with some of the 170 ml of NMP needed for the reaction. The remaining solvent was then added to the vessel. The solution was stirred under a slow

nitrogen purge for 20 hours at room temperature. Within the first few hours of stirring, the heterogeneous yellow solution became homogeneous and slightly viscous. This was an indication of poly(amic acid) formation.

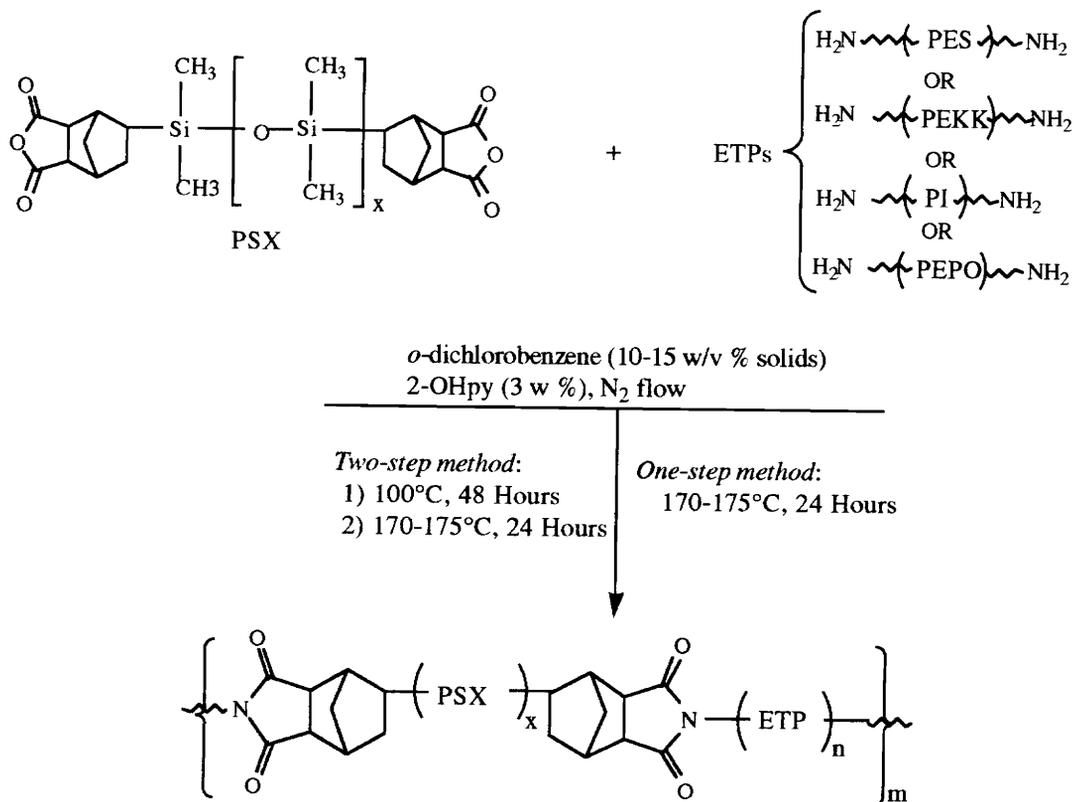
Next, 42 ml of *o*-dichlorobenzene was added to azeotropically remove water to be formed in the cyclodehydration involved in the imide formation. This value represents 20 volume percent of the original 170 ml of NMP used, and can be calculated by

$$(170 \text{ ml NMP})(0.20) / 0.80 = 42.5 \text{ ml.}$$

To hinder evaporation of *o*-dichlorobenzene, the joints were sealed with Teflon tape. The solution was immediately heated to 165°C, and the nitrogen flow was increased slightly. After approximately 2 hours at 165°C, water was seen distilling into the trap. Because of its density (compared to *o*-dichlorobenzene), the water droplets floated at the top of the trap, and hence the utilization of an inverse trap. This temperature was maintained for a total of 20 hours. After this time, the viscous solution was slowly cooled to room temperature. As the solution began cooling, the PI precipitated from the reaction medium. The yellow slurry was poured into a rapidly stirring blender filled with methanol. The coagulated PI powder was filtered and air dried for three days. It was then dried in a vacuum oven at 120°C for an additional 48 hours. The pale yellow amine-terminated PI oligomer (~85 % yield) was stored in a glass jar. It was characterized by endgroup titration, DSC, and intrinsic viscosity.

4. Synthesis of Perfectly Alternating Engineering Thermoplastic-Poly(dimethylsiloxane) Segmented Copolymers

While both poly(arylene ether) and polyimide engineering thermoplastics were employed, all segmented copolymers involved in this research utilized the imidization reaction as a coupling step. Scheme 27 shows the overall reaction for the four α,ω -diamino



Scheme 27. Synthesis of perfectly alternating segmented copolymers via two- and one-step solution imidization techniques.

oligomers studied.

Several variations of the typical solution imidization were attempted. Among these variables were: solvents, solids content, time, temperature, and catalyst. Most of the segmented copolymers produced were of uncontrolled molecular weight, so a one-to-one molar ratio of anhydride-terminated PSX and amine-terminated engineering thermoplastic was employed. Note that a single solvent, *o*-dichlorobenzene, was employed. Two similar synthetic methods were used, which are described below.

a. *Two-step Solution Imidization*

This method [39] involves the initial synthesis of the poly(amic acid) precursor. A 250-ml, four-neck round bottom flask was fitted with a nitrogen inlet/ thermometer adapter, an overhead mechanical stirrer, an inverse Dean-Stark trap with a condenser and drying tube, and a pressure equalizing addition funnel stoppered with a rubber septum. All male joints were wrapped with Teflon tape. This reaction set-up is shown in Figure 9 under PI synthesis of this chapter. The clean glassware was flamed dry with a Bunsen burner while purged with a rapid nitrogen flow. After the apparatus was cool, the trap was filled with dry *o*-dichlorobenzene, and a transformer-controlled 12-inch long strip of heating tape was wrapped around the trap to ensure azeotropic removal of water. Also, all joints were wrapped with Teflon tape so that loss of *o*-dichlorobenzene would be minimal. Calculations for a typical reaction are given below. For the synthesis of approximately 10 g of a PEKK-PSX perfectly alternating segmented copolymer of uncontrolled molecular weight:

$$3.1036 \text{ g PSX} / 2060 \text{ g/mol (by titration)} = 0.001505 \text{ mol PSX}$$

and therefore, 0.001505 mol PEKK needed

$$(0.001505 \text{ mol PEKK})(5416 \text{ g/mol PEKK})(\text{by titration}) = 8.1356 \text{ g PEKK needed}$$

$$(11.2392 \text{ g total solids})(0.03) = 0.34 \text{ g 2-OHpy for 3 \% catalyst needed}$$

$$11.2392 \text{ g total solids} / 0.15 = 75 \text{ ml } o\text{-dichlorobenzene needed for 15\% solids.}$$

The anhydride-terminated PSX was weighed via 3-ml syringe. The filled syringe was weighed, then emptied into the closed addition funnel and reweighed. The amount of PSX transferred was the basis for the amounts used, as shown above in the calculations. Approximately one-third of the total *o*-dichlorobenzene needed was added to the PSX in the addition funnel. The amine-terminated PEKK was weighed out and transferred through a funnel to the flask along with the 2-OHpy. The funnel was then rinsed with the remaining

o-dichlorobenzene. Because both reactants were soluble in *o*-dichlorobenzene, NMP was not needed to carry out this imidization. The amine solution was then heated to 100°C and stirred under a slow flow of nitrogen. When the amine dissolved, the PSX solution was added dropwise to prevent macrophase separation (due to incompatibility). The final clear amber solution was allowed to react for 24 hours to form the poly(amic acid).

After 24 hours, the solution temperature was increased to 165°C to 170°C to cyclize the prepolymer. The heating tape was then utilized, and this second step was run for 24 hours. Upon the completion of this time period, the clear, viscous solution was slowly cooled to room temperature. Chloroform was added to dilute the solution to the original 15 % solids content. The clear amber solution was poured into a separatory funnel and added to a rapidly stirring blender filled with methanol (50 v %) and isopropanol (50 v %). The tan colored, very fibrous product (~99 % yield) was filtered and washed with methanol. It was air and vacuum dried at 120°C for 24 hours. The 5400 g/mol PEKK-2000 g/mol PSX copolymer (denoted PEKK5400-PSX2000 in *Results and Discussion*) was characterized by a number of methods as covered in the *Results and Discussion* chapter.

b. One-step Solution Imidization

This procedure [75] is simply a modified imidization reaction that has eliminated the formation of the poly(amic acid) prepolymer. Since the fully imidized copolymer is soluble, the extra poly(amic acid) step was no longer necessary. Also, all reactants are added initially. It will be shown in the *Results and Discussion* that molecular weights comparable to the *two-step* method were achieved.

The reaction apparatus was identical to that used in the preparation of the amine-terminated PI (refer to Figure 9). Again, the trap was prefilled with *o*-dichlorobenzene and wrapped with heating tape. The joints were sealed with Teflon tape to prevent solvent loss. All calculations are identical to the ones given under the *two-step*

copolymer procedure.

First, a silicone oil bath was preheated to 200°C. Then, the PSX was weighed as described previously. The PSX was discharged into the clean, dry and cooled reaction vessel. The proper amount of amine needed was calculated (1:1 molar ratio) and weighed out. The appropriate amount of 2-OHpy (3 w %) was added to the PSX in the flask. One-half of the total *o*-dichlorobenzene needed was added to the flask, and the contents were stirred under a slow nitrogen flow. The amine oligomer was then added to the flask through a glass funnel which was subsequently rinsed with the remaining *o*-dichlorobenzene. The oil bath was raised to the reaction vessel to quickly heat the solution to 170°C to 175°C. The heating tape was again utilized at this point. The amber solution became homogeneous within 10 minutes and remained so throughout the 24 to 48 hours of the cyclization reaction.

The viscous copolymer solution remained homogeneous as it was cooled slowly to room temperature. It was diluted with chloroform, poured into a separatory funnel and drizzled into a rapidly stirring blender filled with methanol (50 v %) and isopropanol (50 v %). The coagulated copolymer (~99 % yield) was filtered, washed with methanol, air dried and vacuum dried in an oven at 120°C for 24 hours. The copolymer was characterized by a variety of methods, the results of which will be discussed later.

C. Characterization of Dimer, Oligomers and Copolymers

1. Nuclear Magnetic Resonance Spectroscopy (NMR)

a. ^1H NMR

A Varian 400 MHz instrument was used to obtain quantitative integrated spectra. All compounds were dissolved in deuterated chloroform, which also served as the shift reference. Tetramethylsilane was not utilized because its signal coincided with that of the siloxane-containing materials. ^1H NMR was used to confirm the production of NADSX, as well as molecular weight data about some of the PSX. A PSX molecular weight was determined by the ratio of a peak resulting from the anhydride endgroups to the methyl protons on the siloxane repeat unit (~0 ppm). The comparison to the methyl protons of the siloxanes was repeated for each of the remaining peaks caused by the anhydride endgroups. The average was taken to be the PSX molecular weight, and this value was used to complement the titrated value. ^1H NMR was also used to confirm synthesis of the poly(arylene ether)s. The Bis A methyl protons (1.7 ppm) and the aromatic protons (7-8 ppm) were observed. This was used only as qualitative information since the chloroform peak (7.24 ppm) could not be resolved from the aromatic protons. ^1H NMR was initially used on the copolymers to provide information about PSX incorporation. By the ratio of Bis A methyl protons to siloxane methyl protons, an assumed quantitative PSX incorporation could be calculated. However, as discussed in detail later, it was determined that micelles formed in even very dilute solutions, and therefore, amounts lower than the actual PSX incorporated were observed.

b. ^{29}Si NMR

A Varian 400 MHz instrument was used to obtain quantitative integrated spectra of the dimer from a 25 w/v % NADSX solution in chloroform. A single peak at ~7 ppm was

observed. When the spectrum was greatly expanded about that peak, two sharp peaks were seen. The difference between the peaks was 0.05 ppm. It was concluded that the doublet was due to endo-exo isomerism of the hydrosilylation reaction, and for all practical purposes, the NADSX was deemed pure.

c. Solid State ^{13}C NMR

A Bruker MSL 300 MHz instrument was used to obtain integrated spectra of some perfectly alternating copolymers. This was utilized to determine percent siloxane incorporation (versus percent siloxane charged). Because solution ^1H NMR gave erroneous results (mentioned earlier), this was the only in-house characterization method that could be used. The sample preparation consisted of evenly packing approximately 0.5 g of dry copolymer fibers into a plastic rotor. Adamantane was used as the chemical shift reference. Magic Angle Spinning of 57.4° was used to obtain fairly sharp peaks. Cross polarization was not applied so that the spectra could be integrated for quantitation. Other parameters used included a spinning speed of 4000 Hz, a 90° pulse of $4.5\ \mu\text{sec}$, a 5.0 msec contact time, and an acquisition time of 150.0 msec. The carbon atoms of interest are indicated in Figure 10.

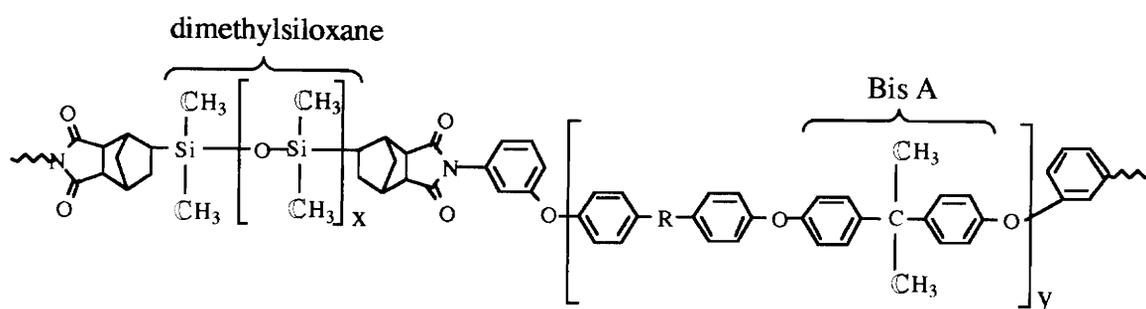


Figure 10. Generic structure of perfectly alternating ETP-PSX segmented copolymer indicating carbon atoms of interest for solid state ^{13}C NMR spectra.

From the ratio of Bis A methyl carbons to siloxane methyl carbons, PSX incorporation was determined by

Bis A units = ($\langle M_n \rangle$ amine oligomer) - (endgroup weight) / RU molecular weight, where $\langle M_n \rangle$ was the averaged titrated value of the amine-terminated oligomer, endgroup weight was the molecular weight of the endgroups, and RU molecular weight was that of the repeat unit of the amine-terminated oligomer. The theoretical number of methyl carbons from Bis A was found by

$$\text{Theo. \# Bis A methyl C} = (\text{\# Bis A units} + 1 \text{ Bis A from endgroup})(2).$$

The same was done for the PSX segment:

dimethylsiloxane units = ($\langle M_n \rangle$ PSX) - (NADSX) / dimethylsiloxane molecular wt., where $\langle M_n \rangle$ of the PSX oligomer was again obtained through titration, NADSX was the molecular weight of the NADSX dimer (which cleaves to form the endgroups), and dimethylsiloxane molecular weight was 74.15 g/mol. The theoretical number of PSX methyl carbons was likewise

$$\text{Theo. \# PSX methyl C} = (\text{\# dimethylsiloxane units} + 1 \text{ from endgroup})(2).$$

The integrated values for the PSX methyl peak at 0 ppm and the Bis A methyl peak at ~32 ppm were applied to the following calculation:

$$\begin{aligned} & [(\text{Theo. \# PSX methyl C} / \text{Theo. \# Bis A methyl C}) / (\text{NMR PSX} / \text{NMR Bis A})] 100\% \\ & = \text{mol \% PSX incorporated, based on 100 mol \% charged (for uncontrolled MW)}. \end{aligned}$$

Similarly, the weight percent PSX incorporated could be determined by multiplying the last equation by the theoretical weight percent charged, rather than 100. For example, if the molecular weight of the PSX segment is 1500 g/mol, and the engineering thermoplastic molecular weight is 5000 g/mol, one copolymer repeat unit is 6500 g/mol, and therefore,

$$[(1500 \text{ g/mol}) / (6500 \text{ g/mol})] 100\% = 23 \text{ wt \% from PSX.}$$

Then,

$$\left[\frac{\text{Theo. \# PSX methyl C}}{\text{Theo. \# Bis A methyl C}} \right] / \left(\frac{\text{NMR PSX}}{\text{NMR Bis A}} \right) \times 23\% \\ = w \% \text{ PSX incorporated, based on } 23 w \% \text{ charged (for uncontrolled MW).}$$

This characterization method was applied only to copolymers containing Bis A or Bis P in the repeat unit. All spectra and instrument information was provided by Analytical Services at VPI & SU.

2. *Potentiometric Endgroup Titration*

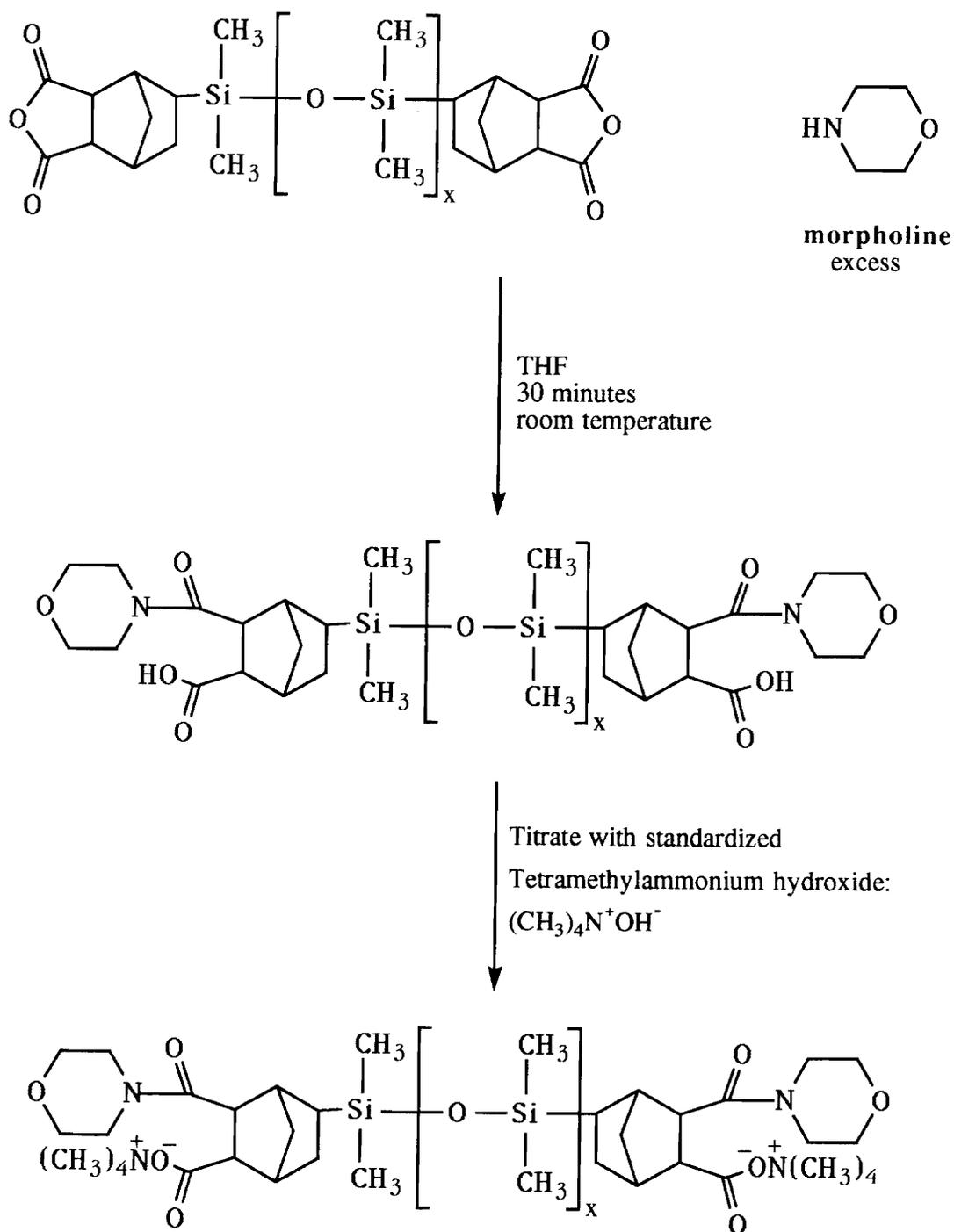
Using a MCI GT-05 Automatic Titrator (COSA Instruments Corp.), anhydride and amine endgroups could be readily titrated. The sample amounts were chosen such that three to six ml of titrant (standardized with potassium hydrogen phthalate) would be needed. The sample was accurately weighed into a 100-ml glass beaker. Then 60 to 80 ml of the appropriate solvents were added to dissolve the sample. When it was visually noted that the sample was dissolved, the functional endgroups were titrated. A minimum of three samples were titrated for each product.

a. *Dianhydrides*

Using a method developed in our labs, the NADSX and PSX anhydride moieties could be indirectly titrated. The anhydride ring was opened with morpholine to yield an amic acid. The resulting carboxylic acid function was then titrated with standardized methanolic tetramethylammonium hydroxide (Kodak Chemicals), or TMAH. From a program stored in the autotitrator, the corresponding molecular weight was calculated. Scheme 28 details the chemistry behind this reaction. The following is a typical titration calculation for NADSX:

$$0.025 \text{ M standardized TMAH} = 0.025 \text{ mol/L,}$$

and therefore, 0.0001 mol/4 ml to be used



Scheme 28. Chemistry of the indirect anhydride endgroup titration method.

0.0001 mol anhydride needed to react with 0.0001 mol 0.025 M TMAH
 $(462.65 \text{ g/mol NADSX})(0.0001 \text{ mol}) / 2 \text{ endgroups} = 0.02313 \text{ g needed.}$

Three NADSX samples were accurately weighed into three 100-ml glass beakers with a Teflon-coated magnetic stirring bar in each. Approximately 60 ml of THF was added directly from the bottle. To these solutions, one ml of a 3.2 v/v % morpholine/THF solution was added via syringe. This amount was based on the calculations below:

0.0001 mol morpholine needed to react with 0.0001 mol anhydride
 3.67 mol % excess morpholine = 0.000367 mol morpholine
 $(0.000367 \text{ mol})(87.1212 \text{ g/mol}) = 0.0319 \text{ g for 1 ml}$
 density = 1.0 g/ml, therefore, 3.19 ml / 100 ml THF.

The excess was arbitrarily chosen for ease of measuring. The morpholine-containing solutions were then stirred at room temperature for 15 to 30 minutes so that the ring-opening to the amic acid occurred. The three colorless solutions were titrated with TMAH, and the number average molecular weight was automatically calculated using the equation below:

$$M_n = [(1000 \text{ ml/L})(\text{sample size in g})(2)] / [(0.025 \text{ M TMAH})(\text{ml titrant used})],$$

where the factor of 2 in the numerator indicates that the compound is difunctional. The three values were averaged to give the final molecular weight. This procedure was successfully used to obtain molecular weights for all anhydride-terminated PSX oligomers synthesized.

b. Diamines

The amine-terminated engineering thermoplastics were titrated with a 0.025 M standardized hydrobromic acid (HBr) solution in glacial acetic acid. Both 48% HBr and glacial acetic acid were obtained from Fisher. Again, it was presumed that 4 ml of titrant would be used. Three samples were accurately weighed into separate 100-ml beakers

according to the calculations:

0.025 M HBr (standardized with KHP) = 0.025 mol/L; 0.0001 mol/4 ml HBr

0.0001 mol amine needed to react with 0.0001 mol 0.025 M HBr.

For a theoretical 5000 g/mol amine-terminated oligomer,

$[(5000 \text{ g/mol})(0.0001 \text{ mol})] / 2 \text{ endgroups} = 0.25 \text{ g needed.}$

Approximately 50 ml of chloroform or methylene chloride was added to the beakers. The solutions were stirred until the sample was dissolved. The PI and PEPO oligomers required a little heat, while the PES and PEKK readily went into solution. Twenty ml of glacial acetic acid was added to the three beakers. The solutions were stirred at room temperature for an additional minute, then titrated. The number average molecular weight was calculated, and the average of the three values was recorded as the oligomer $\langle M_n \rangle$.

3. *Dimer Melting Temperature*

The NADSX melting range was observed using a Lab Devices Mel-Temp II. The sample was transferred to a capillary tube with one end opened to the atmosphere. The wide range was due to the various stereoisomers that formed in the hydrosilylation reaction.

4. *Intrinsic Viscosity* ($[\eta]$)

A Cannon® Ubbelohde viscometer was used to indirectly measure relative changes in molecular weights of the amine-terminated oligomers and copolymers. All samples were prepared in chloroform and tested at 25°C. Four concentration-dependent measurements were performed on each sample. The flow times (between the upper and lower fiducial marks on the viscometer) of the pure chloroform (t_0) and the sample solutions (t) -- four concentrations per sample -- were measured. The chloroform viscosity is denoted as η_0 ,

and the sample solution viscosity is represented by η . The following relations allow for the determination of the specific viscosity, η_{sp} :

$$t / t_0 = \eta / \eta_0$$

$$(\eta / \eta_0) - 1 = \eta_{sp}$$

By calculating both

$$(\eta_{sp})(1 / \text{concentration of solution}), \text{ and}$$

$$[\ln (\eta / \eta_0)](1 / \text{concentration of solution}),$$

plotting both sets of points against the concentration of the solution, and extrapolating both lines to zero concentration, a graphical estimation of the sample's intrinsic viscosity was obtained. Actually, flow data was recorded, and through the aid of a computer program, intrinsic viscosities were calculated rather than plotted.

5. *Fourier Transform Infrared Spectroscopy (FTIR)*

A Nicolet MX-1 spectrophotometer was used to obtain information regarding functional group presence or absence. The monitored peaks included the disappearance of the Si-H band at $\sim 2060 \text{ cm}^{-1}$ in the hydrosilylation reaction of NADSX; the appearance of the imide C=O band at $\sim 1723 \text{ cm}^{-1}$ and the subsistence of the Si-O and Si-CH₃ bands at $\sim 800 \text{ cm}^{-1}$ and 1080 cm^{-1} , respectively, in the copolymers. Also noted were the N-H band at $\sim 3200 \text{ cm}^{-1}$ in the engineering thermoplastics, and the disappearance of that peak upon copolymerization.

The NADSX sample was prepared by grinding less than 0.5 g with IR grade KBr (Fisher) in a mortar and pestle. The powdered mixture was then pressed into a thin, translucent film in a metal die. The PSX oligomers were prepared by sandwiching a drop of neat product between two KBr plates. Thin films of the amine oligomers were cast from concentrated solutions in chloroform onto a KBr plate. The solvent was allowed to

evaporate before spectra were taken. Copolymers in *o*-dichlorobenzene were taken directly from the reaction flask and pipetted dropwise onto a KBr plate. A film was made by evenly spreading the drop on the plate and removing excess with a Kimwipe. *Ortho*-dichlorobenzene did not interfere with the peaks under investigation. FTIR was not used for kinetic studies of the hydrosilylation or copolymerization, but rather as a qualitative tool to confirm the presence of functional groups.

6. *Differential Scanning Calorimetry (DSC)*

A DuPont 912 instrument was used for high temperature analysis, while a Perkin-Elmer DSC 7 was used for subambient work. This two step characterization was necessary in order to record upper and lower glass transition temperatures of the microphase separated copolymers. Generally, the DuPont 912 was employed to scan temperatures from 50°C to 250°C. The Perkin-Elmer DSC 7 covered the temperature range from -150°C to 25°C. The expected upper T_g's due to the engineering thermoplastic segments varied from ~120°C to 200°C. The lower T_g due to the PSX segment was expected to be -123°C, regardless of segment length. The sample preparation was the same as described under TGA analysis. Two scans were carried out in air for each sample, with T_g values determined from the second scan. The sample was quench cooled with liquid nitrogen between the two scans. Temperature ramping was 10°C per minute for each scan. Samples analyzed on the Perkin-Elmer followed the same parameters, but quench cooling with liquid nitrogen between scans was performed in the presence of helium gas to prevent condensation.

DSC was initially used as sole proof of the T_g's observed. However, it was determined that a more sensitive means of characterization was necessary in order to obtain reliable results (see DMTA).

7. *Thermogravimetric Analysis (TGA)*

A DuPont 951 instrument was used to determine char yields (silicates) of the copolymer in order to give a rough estimate of PSX incorporation. Scans were run at 10°C per minute with a nitrogen flow rate of 10 ml per minute from 50°C to 700°C. Samples were prepared by solution casting thin films into aluminum weighing pans from a concentrated copolymer solution in chloroform (~10 w/v %). The solution was filtered through a plug of glass wool in a disposable pipet directly into the pan, then allowed to air dry for at least one hour and finally dried in a vacuum oven at 60°C to 80°C for several hours. The desired amount of film was then cut off using scissors, weighed, and analyzed.

8. *Dynamic Mechanical Thermal Analysis (DMTA)*

The sample was prepared by hydraulically pressing between Teflon sheets and ferrotype plates approximately 10 g of copolymer fibers. Sustaining high pressure at 150°C for approximately three minutes resulted in a translucent brown disk ~1 mm thick. From this, a rectangular-shaped specimen measuring 1 cm by 3 cm was cut with scissors. The sample was analyzed in nitrogen from -150°C to 150°C (1°C per minute) at a frequency of 1 Hz.

9. *Transmission Electron Microscopy (TEM)*

Thin solution-cast films were prepared from chloroform with approximately 15 to 20 w/v percent solids concentration. The viscous copolymer solution were filtered through glass wool plugs within disposable glass pipets directly into aluminum weighing pans. The filled pans were covered very loosely with tissue paper and left undisturbed overnight to allow for evaporation of chloroform. The following day, the filled pans were transferred to a vacuum oven and heated to 90°C for 24 hours under reduced pressure to remove trace

amounts of solvent. Finally, the translucent 0.1 mm to 0.2 mm-thick films were given to Mr. Steve McCartney for TEM sample preparation and measurement. This involved cooling the sample in liquid nitrogen to slightly above the PSX segment T_g and slicing an extremely thin layer from a cross-sectioned portion of the film using a cold (-90°C) glass or diamond knife, a method called *cryo-ultramicrotoming*. The prepared specimen was then trimmed to approximately 0.1 mm by 0.1 mm and placed in the sample holder which was cooled to -100°C . (A more detailed procedure can be found in York's thesis [79].) Parameters used on the Philips EM-420 Scanning Transmission Electron Microscope included transmission mode operation at 100 kV. Micrograph negatives were photographically shot at magnifications of 105,000 and 230,000. Positive 8x10-inch photographic enlargements were prepared resulting in modified magnifications of 278,000 and 608,000, respectively.

10. Small Angle X-ray Scattering (SAXS)

Solution-cast thin films were prepared identically to those for TEM analysis. A Philips PW1729 x-ray generator was operated at 40 kW and 20 mA. The camera was used in the slit configuration, with a slit width of $100\mu\text{m}$. Intensities were calibrated using Lupolen. All data obtained for measurement of interdomain spacing was smeared.

11. Solubility

All block copolymers, as well as their homopolymer components, were tested for solubility in a wide variety of common organic solvents. The dried sample was weighed into a small glass sample vial with a snap-on lid. A solvent was pipetted into the vial to achieve a solids concentration of approximately three to five w/v percent. The solution was either stirred with a magnetic stirrer or vigorously shaken until homogeneous. If the

polymer did not appear to dissolve within 10 minutes, a small amount of heat was applied. A homogeneous solution, with or without heat, was marked as soluble (\checkmark). A solution in which the polymer was dissolved, yet the solution was cloudy, was marked marginally soluble (m). And, a polymer that was not affected by the solvent and/or heating was marked insoluble (X).

12. Mechanical Properties

Using an Instron Corporation Series IX Automated Materials Testing System v4.03e, a tensile test with extensometer was performed for one perfectly alternating segmented copolymer that was synthesized. Sample preparation consisted of cutting three dogbone-shaped specimens from a compression-molded thick film (used remainder from DMTA sample disk). All samples were approximately 0.032 inch thick (0.8 mm) and 0.125 inch wide at the position of testing. Parameters included a sample rate of 3.64 pts/sec, crosshead speed of 0.250 in/min and full scale load range of 200 lbs. A plot of load versus displacement was obtained, and Young's modulus, percent strain and percent stress were calculated.

13. Elemental Analysis

Elemental analysis was performed on several of the copolymers in order to obtain silicon content, and therefore to confirm complete incorporation of the PSX charged. All atoms theoretically present were evaluated. This characterization was used in accordance with solid state ^{13}C NMR. All analyses were carried out by Galbraith Laboratories, P.O. Box 51610, Knoxville, TN 37950.

14. Gel Permeation Chromatography (GPC, also known as Size Exclusion Chromatography)

A phenyl-endcapped perfectly alternating segmented copolymer was accomplished through the incorporation of phthalic anhydride. Controlled to 40,000 g/mol, the copolymer was prepared with unreactive endgroups so that GPC analysis could be carried out without absorbance of reactive aromatic amine groups onto the column substrate.

Approximately 2.1 mg of copolymer fibers were dissolved in 1 ml NMP with LiBr (5 g/L). The sample was run on a Nicolet instrument using polystyrene standards and a universal calibration curve so absolute molecular weight results were achievable. At a flow rate of 1ml/min and chart speed of 1cm/min, the elution volumes of standards and the copolymer were recorded. The GPC chromatogram of the copolymer was obtained using UV, refractive index and viscosity detectors. With the aid of a computer program, the $\langle M_n \rangle$, $\langle M_w \rangle$ and $\langle M_z \rangle$ were calculated.

Results and Discussion

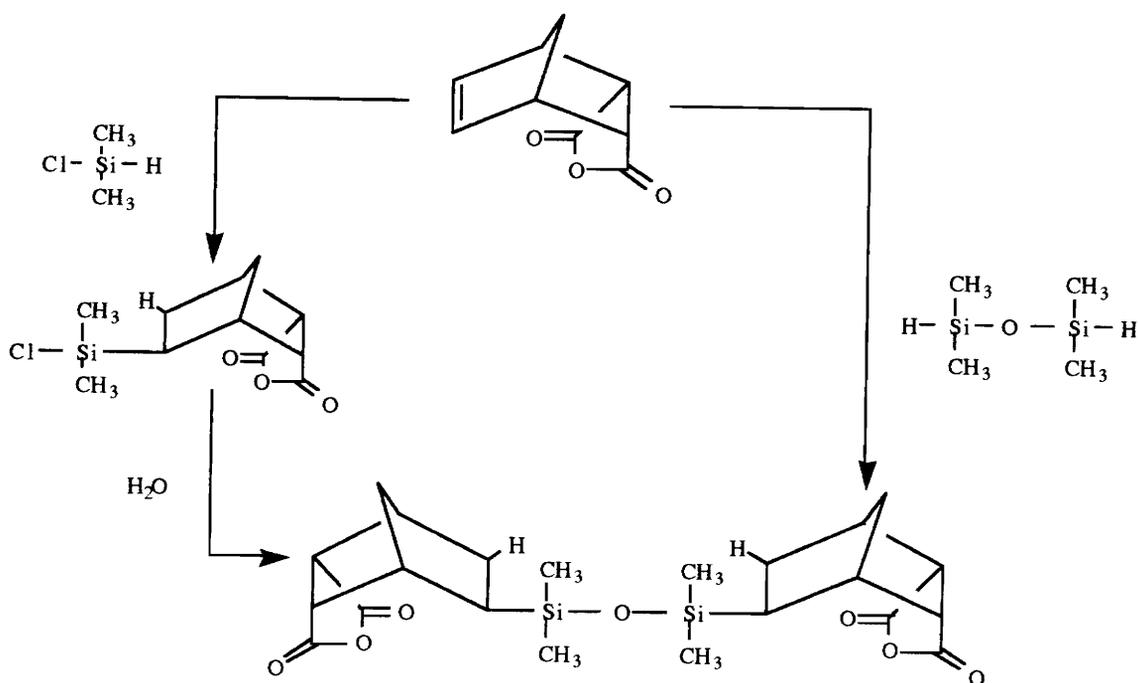
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Results and Discussion

A. Synthesis and Characterization of NADSX

Patent literature [56,58] briefly described two routes for the synthesis of 5,5'-(1,1,3,3-tetramethyl-1,3-disiloxanediyl)-bis-norbornane-2,3-dicarboxylic acid anhydride, or NADSX. One involved hydrosilylation of 1,1,3,3-tetramethyldisiloxane with norbornene anhydride [56]. The other involved hydrosilylation of dimethylchlorosilane with norbornene anhydride, then hydrolysis to yield the coupled disiloxane [58]. A comparison of these reactions is shown in Scheme 29. After trying both methods, the former route was preferentially chosen because the reaction yields were greater, and the extra hydrolysis step was eliminated. The chronological development of optimum reaction



Scheme 29. Two routes to prepare NADSX [56,58].

conditions will include both approaches.

1. *Initial Attempted Syntheses of NAD SX*

Initially, reactions were run as close as possible to those stated in the patent [56]. The following is a description from that patent. In the presence of a platinum catalyst, a slight excess of norbornene anhydride was added to a reaction vessel along with 1,1,3,3-tetramethyldisiloxane to yield a 2.1-to-1 molar ratio of anhydride to siloxane. Dry chlorobenzene was added until a 100 w/v percent solids content was achieved. The solution was stirred for four hours at 70°C to 80°C and then 100°C to 110°C overnight. After cooling, charcoal was added and the solution was stirred for an additional 30 minutes. Finally, the solution was filtered, stripped of solvent under vacuum and heat, and addition of dry diethyl ether resulted in the solidification of the product, NAD SX.

Although it was not stated in the patent, it was assumed that the reaction was to be carried out under an inert, dry atmosphere. The appropriate apparatus (see *Experimental*, Figure 6), was assembled and dried as described previously. 10.08 g (0.061 mol) norbornene anhydride and 3.9 g (5.2 ml, 0.290 mol) disiloxane were added to the reaction vessel along with 10 ml dry chlorobenzene. The catalyst (0.0013 g), hexachloroplatinic acid, was added to the solution. Because the amount was not specified in the patent, the amount chosen ($\sim 5 \times 10^{-5}$ mol catalyst/mol double bond) was based on previous hydrosilylation work in our labs [80]. At this point, neither the norbornene anhydride nor the catalyst dissolved in the chlorobenzene. Once the initial reaction temperature of 73°C was reached, the solution became homogeneous and yellow-green in color. During this four hour period, tiny black flakes were noticed in the solution. It was assumed to be degraded catalyst. After four hours at 73°C, the reaction temperature was increased to approximately 100°C for 18 hours. It was then cooled to room temperature and unexpectedly, a solid precipitated. The solution was heated to 35°C at which temperature the solid redissolved. Charcoal was added to adsorb the catalyst, and after 30 minutes of

stirring at 35°C, the solution was quickly filtered through a bed of Celite. The solid immediately precipitated.

A small portion of the wet white solid was smeared onto a KBr plate for FTIR analysis. The sharp band at approximately 2120 cm^{-1} indicated that the Si-H bond of the 1,1,3,3-tetramethyldisiloxane was still present. A comparison of absorbance spectrum of the neat disiloxane and the supposed synthesized NADSX indicated that the Si-H band intensities were practically the same. Thus, it was concluded that the reaction did not occur. Additionally, the vinylic protons of the norbornene anhydride, which show a chemical shift of 6.3 ppm, were still present after the entire reaction time.

The reaction was attempted in tetrahydrofuran, THF. Although the catalyst was not soluble in THF, the addition of a few drops of isopropyl alcohol (IPA) allowed for solvation. Prior to running the reaction, the catalyst was weighed into a sample vial and dissolved in a minimum amount of IPA (~0.5 ml). THF was then added and the catalyst solution was set aside. The glassware was modified slightly so that a 10 ml pressure equilibrating addition funnel could be attached. Again utilizing a clean, dried, and N_2 -flushed reaction vessel with a magnetic stirring bar, 6.566 g (0.040 mol) norbornene anhydride was transferred to the flask. Nine ml THF was added, and the mixture was stirred at room temperature for about 10 minutes. With an oil bath, the THF solution was heated to approximately 45°C. The catalyst solution was then poured into the reaction flask and stirred another minute. Next, 2.955 g (3.9 ml, 0.022 mol) disiloxane was transferred to the addition funnel via a syringe. Then, one-tenth of the disiloxane was introduced into the reaction vessel. Because hydrosilylation reactions typically experience exotherms, some temperature increase in the reaction solution was expected. However, there was no indication of such an exotherm. At 15 minute intervals, small quantities of disiloxane were added until all disiloxane was incorporated into the reaction flask. After each addition, a

FTIR spectrum was taken. Because the Si-H band at 2120 cm^{-1} never disappeared --as it should have-- the reaction was allowed to continue overnight. After 18 hours at 45°C , the reaction was dismantled. FTIR showed no indication of NADSX production.

2. *A Different Approach to NADSX Synthesis*

The synthetic approach was then changed. Following a different patent [58] from G. E., the objective was to first hydrosilylate the norbornene anhydride with dimethylchlorosilane, then hydrolyze that product to the dianhydridedisiloxane via coupling. THF was again used as the solvent. The platinum catalyst was dissolved in THF with a few drops of IPA. Similar to the procedure above, the anhydride was dissolved in THF, and the disiloxane was incrementally added to the vessel from an addition funnel. FTIR and ^1H NMR spectra indicated that very little reaction occurred. The hydrolysis (coupling) step was not carried out because the initial hydrosilylation did not occur to an appreciable extent.

3. *Modified Synthesis of NADSX*

At this point, it was felt that an increase in reaction temperatures may alleviate problems experienced with the first procedure. To utilize higher temperatures than THF would allow, the reaction medium was changed to toluene, and temperatures were increased to around 80°C . The catalyst still needed to be dissolved first in IPA, then toluene since it was soluble in only IPA. Both routes were attempted in toluene several times, but FTIR and ^1H NMR spectra continually proved that very little product was formed. Reaction conditions were optimized through help from Dr. Martin Weber (currently of BASF in Germany) while he was a post-doctoral researcher in our labs. It was found that thiophene impurities in the toluene were poisoning the catalyst. Since drying over calcium

hydride and distillation did not remove these impurities, a method in a purification handbook [81] was followed. This procedure was previously discussed in the *Purification of Reagents* section of the *Experimental* chapter. This purification method proved to be very effective in removal of the trace amounts of thiophene impurities. Dr. Weber also felt that the hexachloroplatinic acid was most effective after standing at room temperature several hours prior to addition to the reaction solution. With the freshly purified and distilled toluene, the first method of hydrosilylation reaction [56] was retried. Calculating 5×10^{-4} mol catalyst / mol norbornene anhydride, 0.0205 g (0.00005 mol) platinum acid was weighed into a sample vial and dissolved in 0.5 ml IPA and 1 ml toluene. This solution was tightly capped and set aside in a dark bench drawer for 24 hours.

The following day, the reaction was run in a clean, dried flask under a N_2 atmosphere. The anhydride (14.8430 g, 0.0904 mol) and catalyst were quickly transferred to the reaction flask with 21 ml purified toluene. After the solution had equilibrated to the reaction temperature of about $80^\circ C$, the disiloxane (6.011 g, 0.044 mol) was added dropwise from the addition funnel. Immediately, a noticeable $28^\circ C$ exotherm was coincident with gentle boiling of the toluene. Upon complete addition of all disiloxane into the reaction flask, the solution ceased refluxing. The reaction temperature was raised to approximately $110^\circ C$, and the solution was stirred at this temperature for 24 hours, then slowly cooled to room temperature and stirred overnight.

The following day, charcoal was added to adsorb the catalyst and stirred with the reaction solution for 30 minutes at room temperature. Finally, the solution was filtered through a bed of Celite in a Büchner funnel. The Celite was washed well with unpurified toluene to extract all product. Toluene was stripped from the resulting colorless solution under reduced pressure and elevated temperatures ($90^\circ C$) with a Rotovap, leaving the crude product as a very viscous off-white oil. Short-path vacuum distillation was used to remove

any unreacted anhydride (the five percent excess that was initially added), mono-reacted disiloxane, and trace amounts of toluene. This distillation apparatus, called a Kugelrohr (Aldrich), employed a mechanical vacuum pump to create pressures near 1 atm and high temperatures (150°C) to remove the impurities. Left in the original flask was the brown, oily NADSX. However, this procedure was rather time consuming, often requiring more than eight hours. When the oily NADSX had cooled to room temperature, dry diethyl ether was added to the stoppered round bottom flask. Diethyl ether solidified the brown oil to a waxy tan powder that adhered to the flask walls. The NADSX was scraped from the walls with a metal spatula and collected onto filter paper, dried in a vacuum oven at room temperature, then stored capped in a desiccator.

FTIR analysis indicated that the Si-H band at 2120 cm^{-1} was no longer present (see Figure 11), which verified that hydrosilylation was successful. Before distillation in the Kugelrohr, the excess amount of unreacted norbornene anhydride remained as indicated by the vinylic protons at 6.3 ppm in ^1H NMR spectra. After distillation, spectra proved that the Kugelrohr effectively purified the NADSX, as no vinylic protons (due to either unreacted anhydride or mono-reacted anhydride) were seen in ^1H NMR spectra.

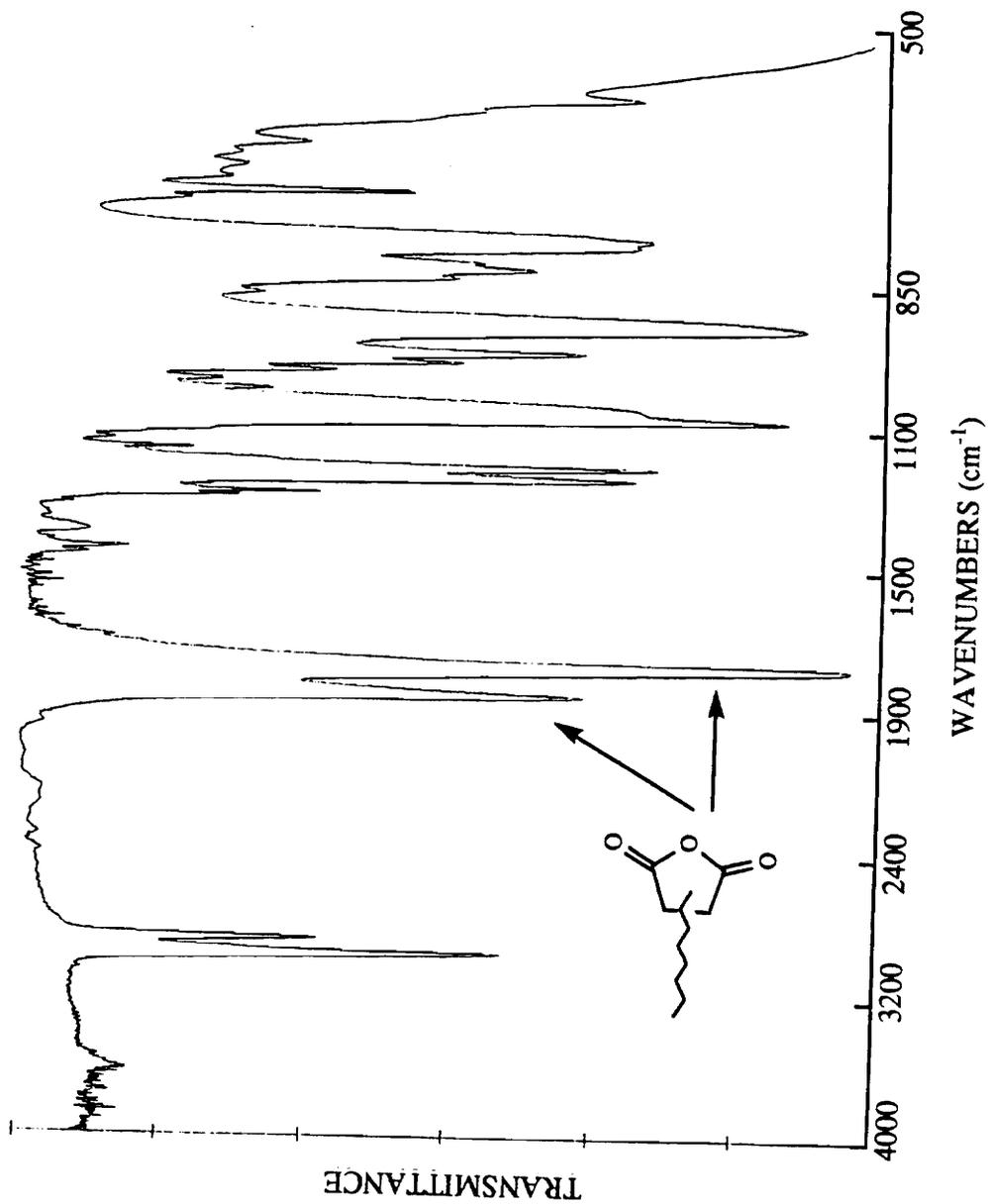


Figure 11. FTIR spectrum of NADSX prepared via hydrosilylation reaction.

Additionally, ^1H NMR confirmed product identification. Initially spectra could not be fully understood, but after realization that three possible stereoisomers (shown in Figure 13) were present, assignments of these peaks could be made (see Figure 12). Product yields were quantitative, and recovered yields were approximately 70 percent.

At this point, a potentiometric titration method was developed to analyze the anhydride termini of the NADSX. Discussed in detail in the *Characterization* section of the *Experimental* chapter (see Scheme 28), this method reproducibly confirmed the functionality and molecular weight of the dianhydride-disiloxane. The NADSX was accurately weighed into a beaker containing a magnetic stirring bar and dissolved in THF. An aliquot of morpholine solution was added to the NADSX and allowed to stir at room temperature for 15 to 30 minutes. Morpholine attacked and opened the anhydride moieties to form the corresponding amic acid. The acid group was then titrated with a standardized tetramethylammonium hydroxide/methanol solution. Table 12 lists titration results from several batches of NADSX. Generally, three samples were titrated, and the resulting molecular weight data obtained from the MCI Automatic Titrator were rounded-off to the nearest 1/100, then averaged. Molecular weights of all three samples were usually within two percent of each other. The averaged value was usually within five percent of the theoretical molecular weight of 462.65 g/mol. From this, it was concluded that this reaction method provided reproducible results and that the product was difunctional.

Table 12. Potentiometric endgroup titration results for several batches of NADSX.

Batch / Sample	Molecular Weight Results	Average	% Diff.*
A Sample 1 Sample 2 Sample 3	450 g/mol 470 g/mol 460 g/mol	460 g/mol	0.6 %
B Sample 1 Sample 2 Sample 3	450 g/mol 440 g/mol 450 g/mol	450 g/mol	2.7 %
C Sample 1 Sample 2 Sample 3	470 g/mol 470 g/mol 470 g/mol	470 g/mol	1.6 %

* % Diff = percent difference from the theoretical molecular weight of NADSX, 462.65 g/mol, and was calculated by:

$$| [\text{theoretical value} - \text{titrated average value}] / \text{theoretical} | \times 100\%$$

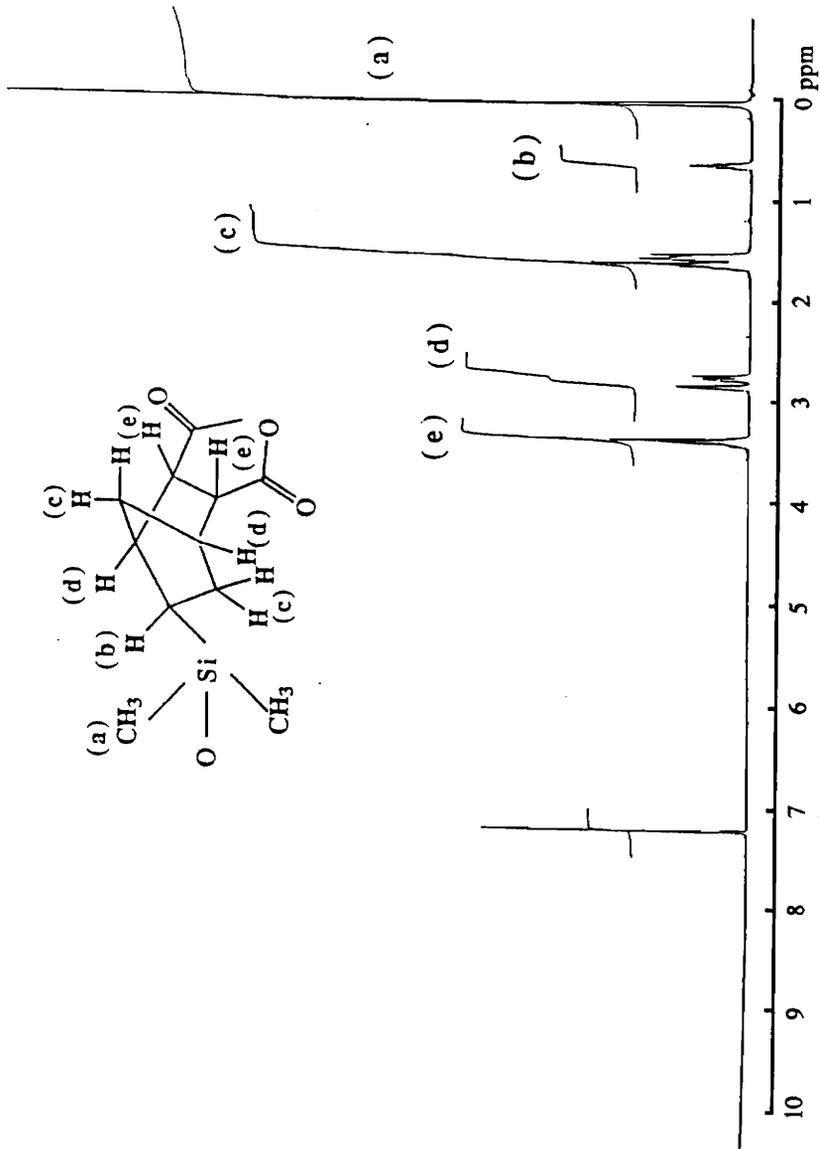


Figure 12. ^1H NMR spectrum of NADSX prepared via hydrosilylation.

4. *Optimized NADSX Procedure*

Although the reaction conditions for the synthesis of the dianhydridedisiloxane worked well, the procedure was modified one last time. The method described here was the optimized procedure that was detailed in the *Experimental* chapter. Because removal of the excess norbornene anhydride required lengthy distillation times, no excess was utilized in later hydrosilylation reactions. Thus, an exact 2-to-1 molar ratio of norbornene anhydride to 1,1,3,3-tetramethyldisiloxane was employed. Reaction conditions were not changed, but distillations on the Kugelrohr were reduced to approximately three hours at 150°C for removal of trace toluene. Recovered yields, after all purifications, were approximately 70 percent.

Both FTIR and ^1H NMR spectra gave positive results that NADSX was quantitatively synthesized. Potentiometric endgroup titration indicated that difunctionality was achieved, and molecular weight was again within five percent of the expected value. ^{29}Si NMR spectra, when greatly expanded, showed the presence of stereoisomers which appeared as two singlets with only 0.05 ppm difference (see Figure 13 for ^{29}Si NMR spectrum and structures of the isomers). Two conclusions can be made about this. First, all three isomers formed (see Figure 13), but two resonate in the same chemical shift region. Or second, only two stereoisomers were produced; and in most probability, those occurred by exo-exo and exo-endo silicone additions across the unsaturated carbons.

The melting range of NADSX was visually observed at 128-145°C on the Mel-Temp II instrument and was in exact agreement with the patent literature. The broad range was an indication of the three stereoisomers that were formed. Since the commercial process for preparing norbornene anhydride is a Diels-Alder reaction that yields greater than 99 percent of the endo-isomer, it was expected that the major product was the exo-exo addition of both silicon atoms at each susceptible carbon [82]. It was thought that the

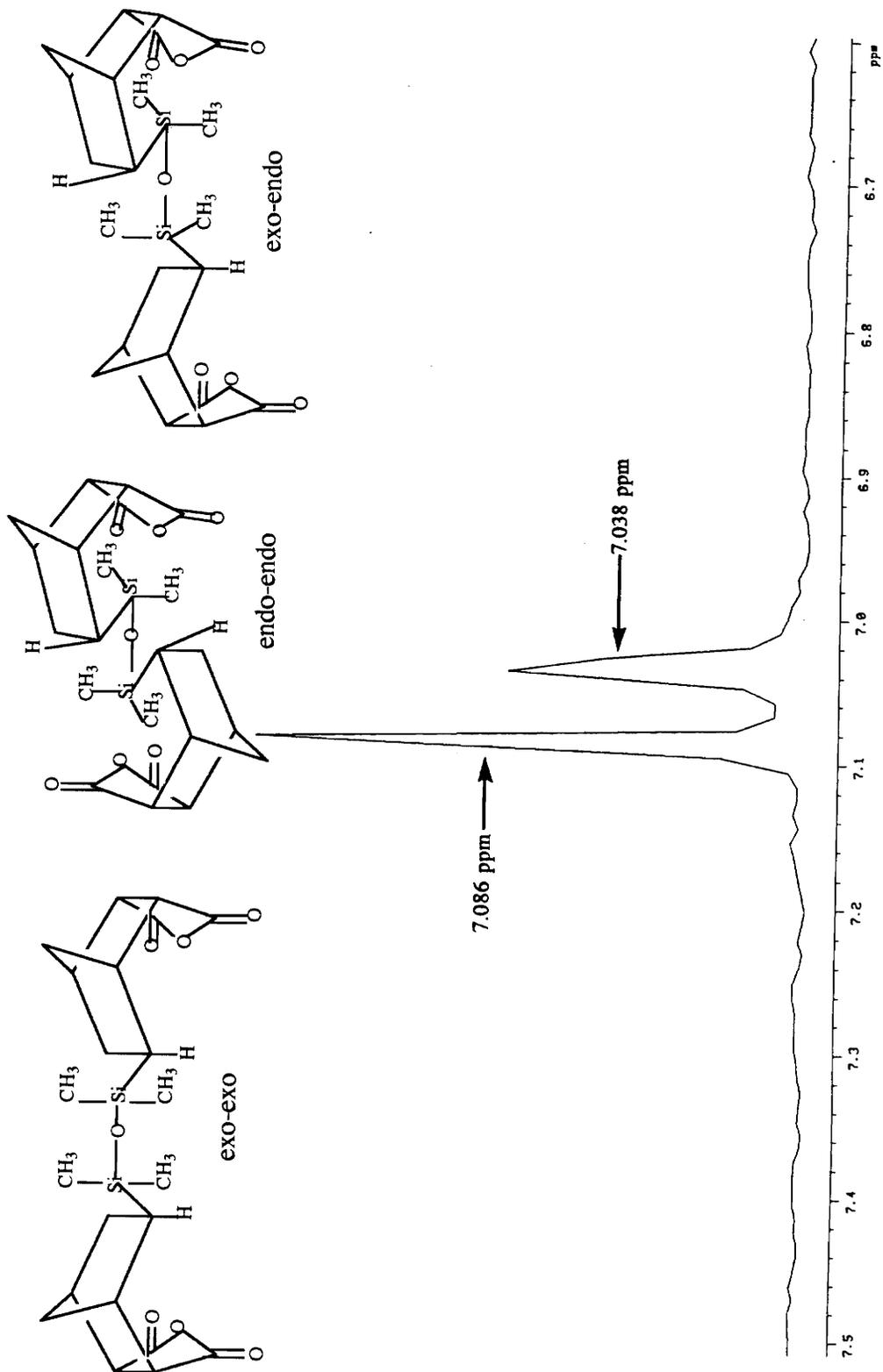


Figure 13. Expanded ^{29}Si NMR spectrum of NADSiX indicating stereoisomers.

exo-endo and endo-endo addition of silicon atoms would be minor products due to steric hindrance by the anhydride ring endo to the norbornene adduct.

5. Attempted Synthesis of Exo-Norbornene Anhydride

As a related aside, synthesis of exo-norbornene anhydride was attempted. Based on literature from workers at G. E. [82], reported hydrosilylation reactions of the exo-isomer of norbornene anhydride could be carried out in a little as 30 minutes. However, exo-norbornene anhydride was not commercially available and had to be prepared from the endo-isomer. Thus, the original German procedure reported by Alder [83] (referenced by G. E.) was followed in order to prepare the exo-anhydride. Two attempts at this five-step method, which involved brominating the double bond, breaking the anhydride ring, reforming the ring in the exo position and re-creating the double bond, failed to yield any product. It was also concluded that the amount of time needed to succeed at this multistep approach, as well as the time required for the method itself, exceeded the three day limit and simply could not be justified. Furthermore, optimization of reaction conditions for the hydrosilylation of the endo-anhydride afforded complete reaction and purification within two days as stated in the optimized procedure.

B. Synthesis and Characterization of Anhydride-Terminated PSX Oligomers

Due to the acidic nature of the NADSX endcapping species, the anhydride-terminated PSX oligomers were synthesized via an acid-catalyzed route. Acid-catalyzed ring-opening equilibrations of PSX have been well documented, but the mechanism has not yet been

confirmed. Many chemists suggest that it is a cationic pathway, and therefore, this route is often referred to as a cationic ring-opening equilibration. A discussion of this mechanism is in the *Background* chapter. Utilizing triflic acid (trifluoromethanesulfonic acid), a strong protic acid, D₄ can be polymerized easily. In the presence of an acidic endcapper, such as NADSX, molecular weight and telechellicity can be controlled.

Patented work from G. E. [57, 58] disclosed two similar cationic polymerization methods for the preparation of anhydride-terminated PSX. While both polymerizations utilized triflic acid as the ring-opening catalyst, quenching the catalyst was accomplished by two different reagents. Buese [57] used magnesium oxide which was then filtered off in a separate step. Hallgren and Brezniak [58] employed hexamethyldisilazane so that the volatile quenching byproducts could be removed along with the cyclic siloxanes in one distillation. Elimination of the filtration step made Hallgren and Brezniak's approach alluring, and therefore this latter method was followed for the early efforts.

1. Attempt at Synthesis of an Anhydride-Terminated PSX using Hexamethyldisilazane as the Quenching Agent

Initial polymerizations of anhydride-terminated PSX were run under similar conditions to those reported by Hallgren and Brezniak. Using the ratio of triflic acid to D₄ stated in the patent [58], appropriate quantities of reactants were calculated. For a desired molecular weight of 3400 g/mol (40 dimethylsiloxane repeat units), 7.60 g (0.0164 mol) NADSX and 48.72 g (51 ml, 0.164 mol) D₄ were measured. The original apparatus consisted of a magnetic stirring bar within a 2-neck round bottom flask fitted with a nitrogen inlet/thermometer adapter and drying tube. The weighed NADSX was transferred to the flask along with the D₄. As the heterogeneous solution was being heated to 125°C (G. E. reported 160°C) under the slow N₂ purge, 0.0984 g (58 μl, 0.00066 mol) triflic

acid was added to the reaction solution via microsyringe. The heterogeneous solution became homogeneous and dark brown in color after approximately 30 minutes of stirring. After 20 hours of reaction time, the viscous burgundy liquid was slowly cooled to room temperature and 300 μ l hexamethyldisilazane (0.00143 mol) was added to quench the triflic acid catalyst as per the patented procedure. The suggested 2-to-1 ratio of base to acid was employed. After stirring for 45 minutes, the PSX oligomer was diluted with THF and filtered through glass wool in a paper filter. The resulting clear golden colored liquid was stirred with charcoal to decolorize, however, the golden color was not removed. Stripping of the THF, cyclic siloxanes and quenching byproducts was carried out on the Rotovap and Kugelrohr, sequentially. The final anhydride-terminated PSX was very viscous, slightly hazy and caramel colored. Analysis by ^1H NMR indicated that the molecular weight was about 2700 g/mol. Potentiometric endgroup titration of three morpholine-reacted samples gave an averaged molecular weight of 3300 g/mol.

After discussions with Prof. McGrath and Dr. Weber, it was suspected that as the hexamethyldisilazane quenched the triflic acid, the ammonia byproduct would react with the anhydride endgroups, thus resulting in the corresponding imide endgroups. FTIR analysis, shown in Figure 14, proved through the imide carbonyl band at 1723 cm^{-1} that some imidization had occurred during the high temperature stripping. The anhydride carbonyl stretches present in the spectrum at 1785 cm^{-1} and 1860 cm^{-1} indicated that some anhydride endgroups were still intact. Despite the adverse quenching/stripping reaction, FTIR also implied that polymerization was successful. The strong, broad bands at 1060 cm^{-1} and 800 cm^{-1} were evidence of many Si-O-Si and $\text{CH}_3\text{-Si-O}$ bonds.

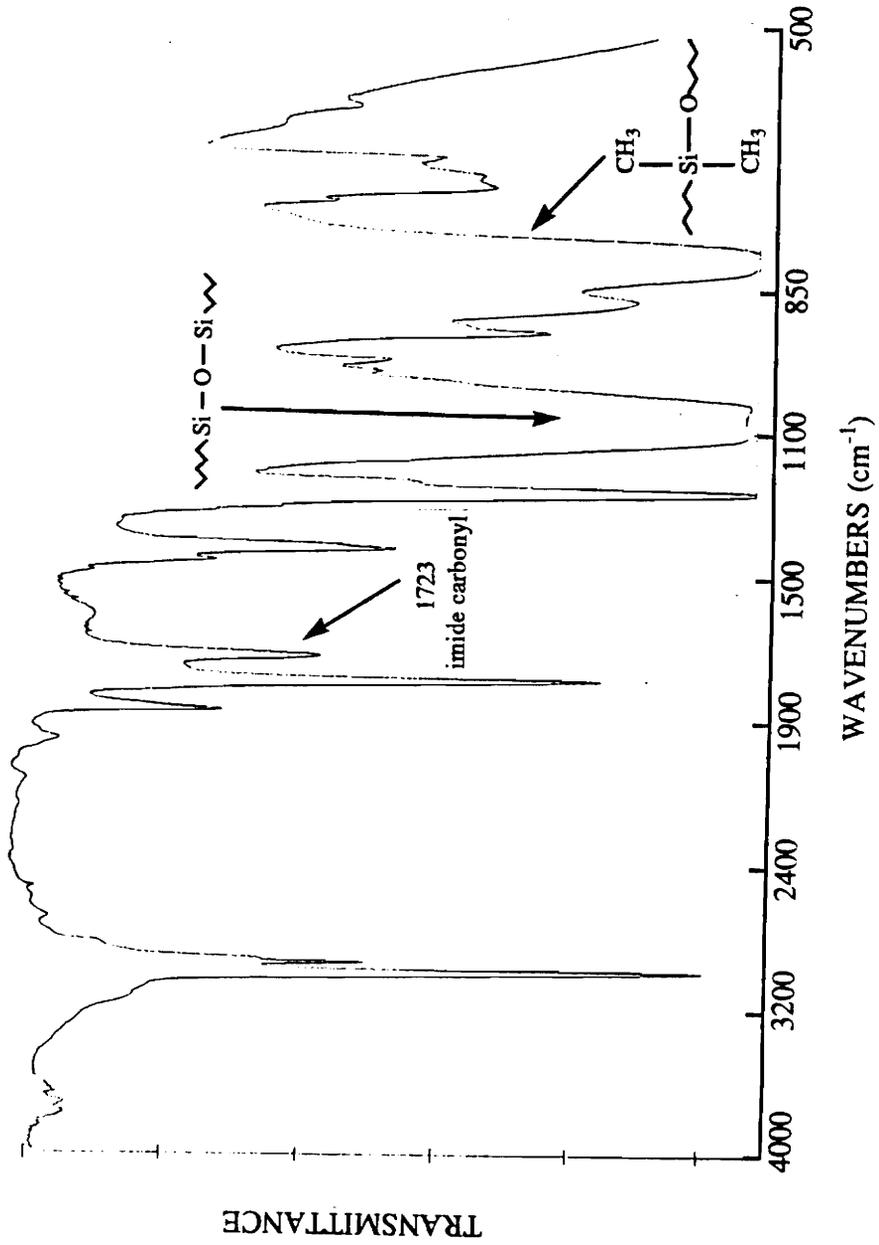


Figure 14. FTIR spectrum of partially imidized anhydride-terminated PSX quenched with hexamethyldisilazane.

2. Synthesis of an Anhydride-Terminated PSX using Calcium Oxide as the Quenching Agent

Due to imidization of the anhydride moieties, a milder quenching agent, calcium oxide, was used instead. Buese [57] utilized extreme reaction temperatures of 200°C to 400°C. Through help from Dr. Weber, reaction conditions were modified to temperatures of around 150°C to 160°C for five to 10 hours. Initial GPC results by Dr. Weber indicated this reaction was complete within 30 minutes. The beginning of the reaction was marked as the point when the heterogeneous mixture of liquid D₄ and solid NADSX became clear and homogeneous. This usually required several hours (five to 10 hours), and it was not until this homogeneity was achieved that the 30 minute period was marked.

For the first polymerization that was run using calcium oxide, identical apparatus to that described above was used. To prepare a 2000 g/mol PSX oligomer, 1.000 g (0.00216 mol) NADSX and 4.1984 g (4.4 ml, 0.01416 mol) D₄ were measured. This molecular weight value was based on 15 percent cyclics expected to form during the equilibration. Thus, 15 weight percent excess of D₄ was added along with the amount needed. If the reaction was not an equilibration, the expected molecular weight would be approximately 2300 g/mol ($2000 + 0.15(2000) = 2300$). Both reactants were charged to the reaction vessel and heated to 150°C to 160°C with an oil bath. Meanwhile, 8 μl (0.0136 g, 0.00009 mol) triflic acid was added to the solution, and a slow N₂ purge was applied to the system. Polymerization was allowed to take place for 20 hours for time convenience. It was noted, however, that the solution became homogeneous within two or three hours at these elevated temperatures. After 20 hours, the solution was slowly cooled to room temperature, at which time 0.2 g (0.003 mol) calcium oxide was added. Based on the amount that Buese reported in the patent, roughly 25 fold excess metal oxide to triflic acid was employed. The quenching agent was stirred into the viscous telechelic PSX for an additional 20 hours,

again chosen for convenience. Finally, the oxide was filtered off, and the oligomer was stripped of cyclics in the Kugelrohr. The resulting hazy, off-white viscous liquid was characterized using FTIR and potentiometric endgroup titration. FTIR analysis (see Figure 15) indicated that the anhydride ring was intact as evidenced by the sharp bands at approximately 1785 cm^{-1} and 1860 cm^{-1} . Strong, broad bands at 1060 cm^{-1} and 800 cm^{-1} confirmed that a large quantity of Si-O-Si and $\text{CH}_3\text{-Si-O}$ bonds were present. However, quantitative results were not attainable from FTIR analysis. Therefore, potentiometric endgroup titration was employed to indirectly give a measure of the number of dimethylsiloxane repeat units incorporated. Table 13 lists the titration values for three samples of this anhydride-terminated PSX analyzed. The average of the three samples was 2060 g/mol. Thus, 12 percent (of 2000) cyclics formed during the equilibration. The percent cyclics were calculated as follows:

$$\text{Desired or theoretical molecular weight} = 2000\text{ g/mol,}$$

$$\text{Averaged titrated molecular weight} = 2060\text{ g/mol,}$$

$$(2300\text{ g/mol}) - x = 2060\text{ g/mol}$$

$$x = 240\text{ g/mol}$$

$$(2000\text{ g/mol})(y\%) = 240$$

$$y = 12\%, \text{ thus } 12\% \text{ cyclics formed during equilibration.}$$

The cyclics produced fell within the estimated 10 to 15 percent expected.

Table 13. Potentiometric endgroup titration results for anhydride-terminated PSX of desired molecular weight = 2000 g/mol.*

Sample	Molecular Weight Results*	Average	% Cyclics
1	2060 g/mol	2060 g/mol	12 %
2	2100 g/mol		
3	2040 g/mol		

* See *Experimental* for explanation of titration method and equation used to obtain molecular weight results.

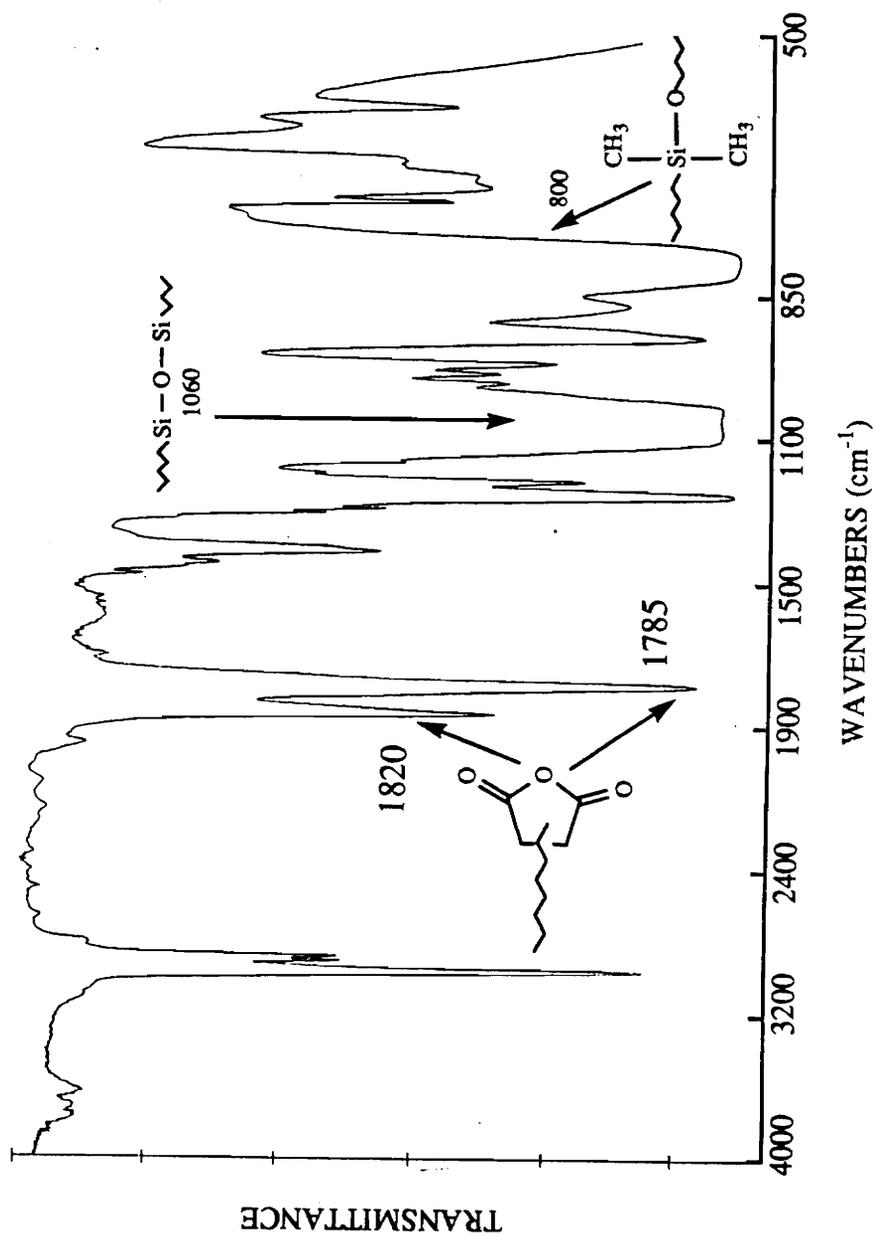


Figure 15. FTIR spectrum of anhydride-terminated PSX oligomer quenched with calcium oxide.

Various molecular weights of anhydride-terminated PSX were prepared using the same synthetic procedure described for the 2000 g/mol PSX. Appropriate changes were made in reactant quantities to prepared desired molecular weights of 1350 g/mol, 3500 g/mol, 5000 g/mol, 7500 g/mol and 10,000 g/mol. Total reaction times varied from 24 to 48 hours and chosen only for convenience. Triflic acid was measured to be roughly 0.2 weight percent based on combined weight of reactants used. Calcium oxide was employed as the quenching agent in at least a 10 fold (weight) excess based on the triflic acid quantity. Table 14 provides specifics for the individual PSX equilibrations.

Table 14. Reaction specifics used for several anhydride-terminated PSX equilibrations.

Desired Molecular Weight	Weight percent excess D4 [§]	Triflic acid concentration [‡]	CaO used [#]	Reaction time allotted
1350 g/mol	10 %	0.15 %	25	40 hrs.
2000 g/mol	15 %	0.20 %	24	43 hrs.
3500 g/mol	10 %	0.19 %	25	40 hrs.
5000 g/mol	15 %	0.18 %	24	72 hrs.
7500 g/mol *	4 %	0.20 %	25	40 hrs.
10,000 g/mol	11 %	0.80 %	10	42 hrs.

* 7500 g/mol was desired molecular weight, but this was not properly calculated for.

§ Weight percent excess was based on desired molecular weight. See text for further explanation.

‡ Triflic acid concentration was calculated as weight percent based on total weight of reactants.

Amount of CaO used to quench triflic acid was 24, 25 or 10 times the weight of triflic acid used.

Visually, the five viscous siloxane oligomers ranged from colorless to faintly yellow in color and slightly hazy in clarity. Upon setting undisturbed for several weeks, the viscous polymers usually cleared up with a small amount of white precipitate settled at the bottom of the storage vials. Most probably this was an unreactive calcium byproduct resulting from the quenching stage that could not be retained within the sintered glass funnel. It did not interfere with or show up in any analyses undertaken.

Potentiometric endgroup titration was used to analyze these four PSX for molecular

weights. Table 15 lists the desired, or theoretical, and titrated values (averaged) for these telechelic oligomers. By calculating the amount of formed cyclics from the titrated molecular weights, one can deduce that the higher molecular weight equilibrations resulted in larger portions of cyclics, and in some cases exceeded the expected 15 percent. Literature [42] has alluded to the fact that as the ratio of endcapper to D₄ increases, the amount of cyclics decreases. Thus, this trend was also observed here.

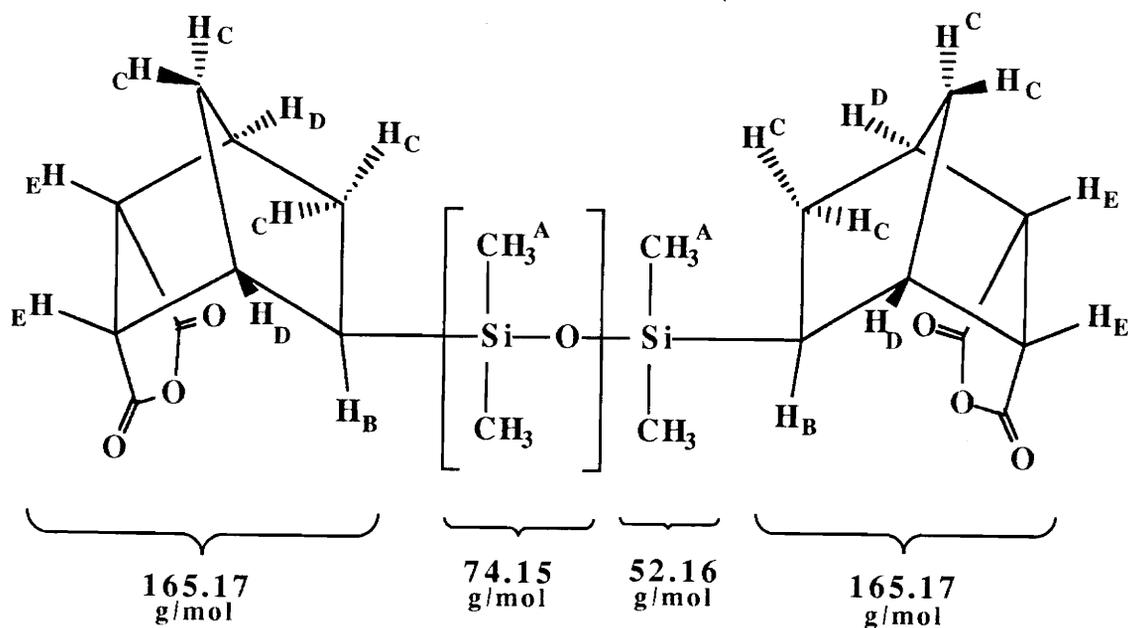
Table 15. Molecular weight data for anhydride-terminated PSX oligomers.

Desired Molecular Weight	Titrated Molecular Weight*	% Cyclics [§]
1350 g/mol	1400 g/mol	9 %
2000 g/mol	2100 g/mol	12 %
3500 g/mol	3300 g/mol	16 %
5000 g/mol	4900 g/mol	17 %
7500 g/mol	6400 g/mol	18 %
10,000 g/mol	9100 g/mol	19 %

* Titrated molecular weight was rounded-off average of three samples

§ Percent cyclics was based on desired molecular weight. See text for a detailed explanation.

The siloxane oligomers were also qualitatively characterized by FTIR and ¹H NMR to verify the production of anhydride endgroups and dimethylsiloxane repeat units. Similar to the 2000 g/mol PSX, several bands in the FTIR spectra were sought. Specifically, these were the anhydride carbonyl stretches at 1785 cm⁻¹ and 1860 cm⁻¹, the Si-O-Si bonds at 1060 cm⁻¹ and the CH₃-Si-O bonds at 800 cm⁻¹. In all PSX oligomers, these characteristic bands were present in the spectra. In addition to potentiometric anhydride endgroup titration, an estimated molecular weight was abstracted from ¹H NMR spectra for the 1500 g/mol (theoretical) α,ω -dianhydride PSX. By ratioing the methyl protons from the dimethylsiloxane repeat unit (0 ppm) to protons from the norbornane anhydride endgroups, molecular weight was calculated in the following manner:



Step 1. Subtract anhydride endgroups and calculate the number of dimethylsiloxane repeat units.

$$(\text{integral of A protons} / \text{integral of B protons})(\text{actual number of B protons}) = X$$

$X =$ number of A protons per actual number of B protons in PSX chain

$$X - 6 \text{ A protons from endgroup (as drawn above)} = Y$$

$Y =$ actual number of A protons from all repeat units of PSX

$$Y / 6 \text{ A protons} = \text{number of repeat units in PSX chain}$$

$$(\text{number of repeat units})(74.15 \text{ g/mol [repeat unit molecular weight]}) = Z$$

$Z =$ molecular weight contribution from repeat units.

Step 2. Add molecular weight contribution from endgroups.

$$Z + 382.50 \text{ g/mol [endgroup molecular weight]} = \text{PSX molecular weight.}$$

Step 3. Repeat Steps 1 and 2 using the remaining endgroup protons, C,D and E, and then take the average of the results to obtain $\langle M_n \rangle$ by ^1H NMR.

For example, Figure 16 shows an integrated ^1H NMR spectrum of the 1500 g/mol (theoretical) anhydride-terminated PSX. Using the integration values obtained by the instrument, molecular weight calculations were carried out as follows:

Step 1. $A/B = 90 / 2.14 = 42.056$ A protons per single B proton,
 since there are 2 B protons (1 at either end), the ratio becomes
 $A/B = 84.112$ A protons / 2 B protons
 $84.112 - 6$ A protons from endgroup = 78.112 repeat unit protons
 $78.112 / 6$ A protons = 13.0187 repeat units
 $(13.0187)(74.15 \text{ g/mol molecular weight of repeat unit}) = 965.337 \text{ g/mol}$
 $965.337 \text{ g/mol} = \text{molecular weight contribution from repeat units}$

Step 2. $965.336 \text{ g/mol} + 52.16 \text{ g/mol} + 2(165.17 \text{ g/mol}) = 1347.84 \text{ g/mol}$
 $1347.84 \text{ g/mol} = \text{PSX molecular weight based on } A/B.$

Step 3. Repeat for remaining peaks, then take average.

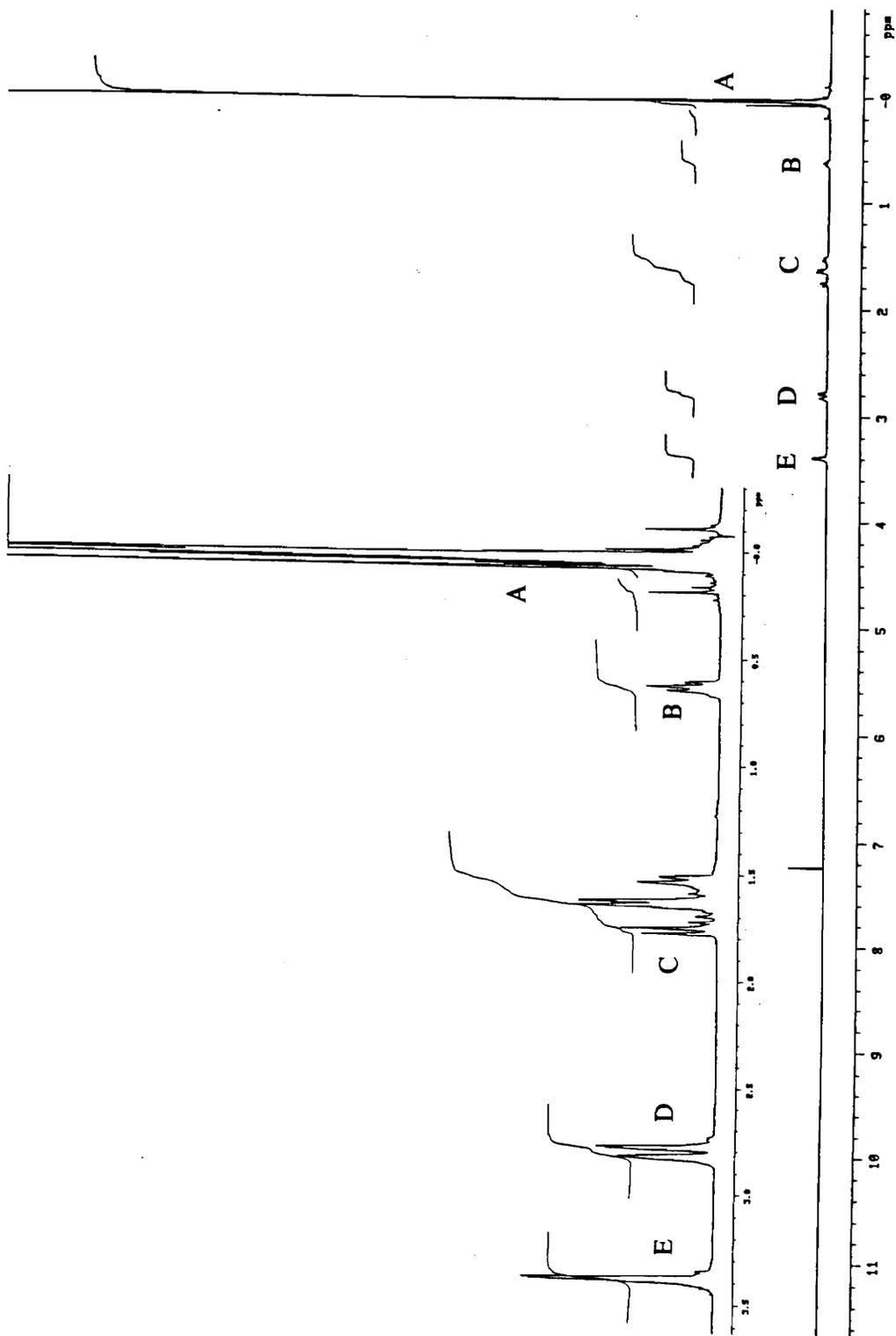


Figure 16. ^1H NMR spectrum of 1500 g/mol (theoretical; titrated = 1389 g/mol) anhydride-terminated PSX.

Calculated ^1H NMR results are compared with potentiometric titration values for the same anhydride-terminated PSX in Tables 16a and 16b. Within experimental error, these two methods of characterization gave complimentary conclusions of approximately 1400 g/mol. As expected, roughly nine percent cyclics were formed during the equilibration based on the desired molecular weight. It is clear that as the molecular weight of the PSX increases, the dimethylsiloxane protons increase greatly, and integration of the few endgroup protons can become difficult. For this reason, ^1H NMR was not used to detail molecular weights for the anhydride-terminated PSX greater than 1500 g/mol, but rather was used as a qualitative identification tool.

Tables 16a and 16b. Comparison of molecular weights obtained through ^1H NMR and Potentiometric Endgroup Titration

a. ^1H NMR results.

Peak Ratio	Values from Spectrum; Calculated	Molecular Weight Obtained*	^1H NMR AVERAGE*
A/B	$90/2.14 = 42.056$	1400 g/mol	1400 g/mol
A/C	$90/9.45 = 9.524$	1300 g/mol	
A/D	$90/4.25 = 21.177$	1400 g/mol	
A/E	$90/4.12 = 21.845$	1400 g/mol	

b. Potentiometric Titration results.

Sample	Molecular Weight Obtained*	Titration AVERAGE
1	1400 g/mol	1400 g/mol
2	1400 g/mol	
3	1400 g/mol	

*All values listed were rounded to incorporate an approximate experimental error.

C. Synthesis and Characterization of Amine-Terminated Poly(Arylene Ether) Oligomers

The poly (arylene ether)s synthesized for this research included a poly(arylene ether ketone ketone) (PEKK), a poly (arylene ether sulfone) (PES) and a poly (arylene ether phosphine oxide) (PEPO). Utilizing procedural methods developed in our labs [9, 10], these nucleophilic aromatic substitution reactions were easily tailored to accomplish desired molecular weights and reactive endgroups. Specifically, all oligomers had theoretical molecular weights of 5000 g/mol with α,ω -diamine functionality.

Based on successful laboratory work in our labs, reactions were carried out under established conditions. Using a form of the Carothers equation, the desired molecular weight was used to calculate exact amounts of necessary ingredients. An extensive discussion on achieving molecular weight control can be found in the *Background*. While bisphenol and dihalide monomers varied depending on the type of poly(arylene ether) desired, all products utilized *meta*-aminophenol for amine endgroup functionality. Table 17 is a reminder of the bisphenols and dihalides utilized in each case.

Table 17. Poly(arylene ether) engineering thermoplastics utilized in this research.

Activated Dihalide	Bisphenol	Polymer Structure (repeat unit)	Acronym
			PES
			PEKK
			PEPO

Each reaction was run in the same manner. The appropriate glassware (see Figure 8 of *Experimental*) was assembled and flamed dry with a Bunsen burner while rapidly being purged with nitrogen. After the apparatus was cool, the *meta*-aminophenol ("monofunctional" endcapper), bisphenol, activated dihalide and potassium carbonate (with 15 weight percent excess) were accurately weighed into teflon-coated aluminum pans. All reactants were transferred to the flask, and dry NMP was used to wash the pans. An additional amount of NMP was added so that the mixture contained 15 w/v percent solids. Unpurified toluene was also added in the amount of one-half the total NMP volume. This was added to act as an azeotrope to remove water that formed during phenate formation. Because the toluene was used for this purpose, the final solids concentration remained at 15 w/v percent.

The reaction mixture was stirred with by overhead unit and heated with an oil bath to 145°C. Upon heating, the bisphenol and activated dihalide dissolved in the NMP. It was maintained at this temperature for approximately four hours to ensure complete phenate formation as indicated by azeotropic distillation of water and toluene. Additionally, phenate formation was followed by the color of the reaction solution. Prior to phenate formation, the solution was slightly yellow-green and clear with white solid potassium carbonate. As the phenate formed, the solution turned darker green. When the water/toluene mixture cooled in the Dean-Stark trap, the more dense aqueous layer separated and settled in the bottom of the trap. A slow increase in reaction temperature was accomplished by draining the liquids from the trap.

After all toluene was removed, the temperature was increased to 170°C and maintained overnight (at least 16 hours). After this time, the solution was very dark green (almost black) and opaque. A fine white powder --a potassium halide salt-- was also visually apparent. The oil bath was removed, and the solution was allowed to slowly cool

to room temperature. As the solution cooled, the viscosity was noticeably greater than the initial viscosity. This qualitatively indicated that the reaction was successful.

In order to aid in filtering off the potassium salt, the solution was diluted with unpurified THF to reduce the viscosity. The white powder was collected in a Büchner funnel, and the brown polymer solution was transferred to a separatory funnel. A few drops of glacial acetic acid were added to the cooled polymer solution, which resulted in a color change from dark green to dark brown. The acetic acid was added to revert any unreacted phenate to bisphenol and to neutralize any (excess) potassium carbonate that may have been dissolved in the polymer solution.

A high-speed blender with metal blades was filled with 400 ml methanol and 400 ml distilled water. The polymer solution was slowly added to the rapidly stirring alcohol mixture through the separatory funnel. The poly(arylene ether) coagulated as a powder which was then collected in a sintered glass funnel and washed several times with methanol and water. After air drying in the funnel overnight, the powdery poly(arylene ether) was transferred to a glass bottle and vacuum dried at 120°C overnight. A second precipitation was carried out by dissolving the dried oligomer in enough unpurified THF to yield 15 to 20 w/v percent solids content and coagulating in a 1:1 methanol-to-water solution in a rapidly stirring blender. Air drying and vacuum drying was repeated, and the "polymer grade" amine-terminated oligomer was stored in the capped glass bottle.

All three poly(arylene ether)s were prepared identically. During the reactions, visual clues were also identical (i. e., all solutions were dark green at some point, dark brown after addition of acid, and slightly viscous). Because all poly(arylene ether)s were the same theoretical molecular weight, they were equally powdery in appearance. Differences were found only in the final polymer color: PEKK was slightly yellow, PES was white, and PEPO was off-white.

Monomers were chosen primarily for their availability. Bisphenol A, dichlorodiphenyl sulfone and bis(4-fluoro)benzoyl benzene were readily available (as donated monomers) in high purity. Therefore, bisphenol A and dichlorodiphenyl sulfone were used to prepare the PES; bisphenol A and bis(4-fluoro)benzoyl benzene were used to synthesize the PEKK. A relatively new monomer, bis(4-fluorophenyl)phenyl phosphine oxide was prepared by a colleague, Mr. Carrington Smith, in high purity. Bisphenol A was not used in the preparation of the PEPO oligomer due to the difficulty in precipitating the oligomeric product. To avoid those problems, biphenol (also readily available) was used as the bisphenol. The more rigid ring system of biphenol provided a workable powdery product.

Potentiometric endgroup titration was used to confirm amine telechellicity, as well as provide experimental molecular weight data. To prepare an oligomer for titration, three samples were accurately weighed into beakers and dissolved in 40 ml chloroform or methylene chloride followed by 20 ml glacial acetic acid. The solutions were titrated with standardized HBr in glacial acetic acid, and the three values were averaged to obtain the number-average molecular weight, $\langle M_n \rangle$. The PEKK had a titrated $\langle M_n \rangle$ of 5400 g/mol, the PES had a titrated $\langle M_n \rangle$ of 5700 g/mol and the PEPO had a titrated $\langle M_n \rangle$ of 6500 g/mol. Past research with this type of reaction has always shown molecular weights above theoretical. This can be explained by the fact that endgroup molecular weight is not factored into the equation for calculation of DP (see Equation 14 in *Background* chapter). The PEKK and PES were both considered very close to the theoretical, while the PEPO was slightly higher than expected, but not excessive.

In addition to using titration to detect amine functionality, FTIR spectra of each polymer displayed two bands at approximately 3500 cm^{-1} indicating the amine termini. An example spectrum is shown in Figure 17.

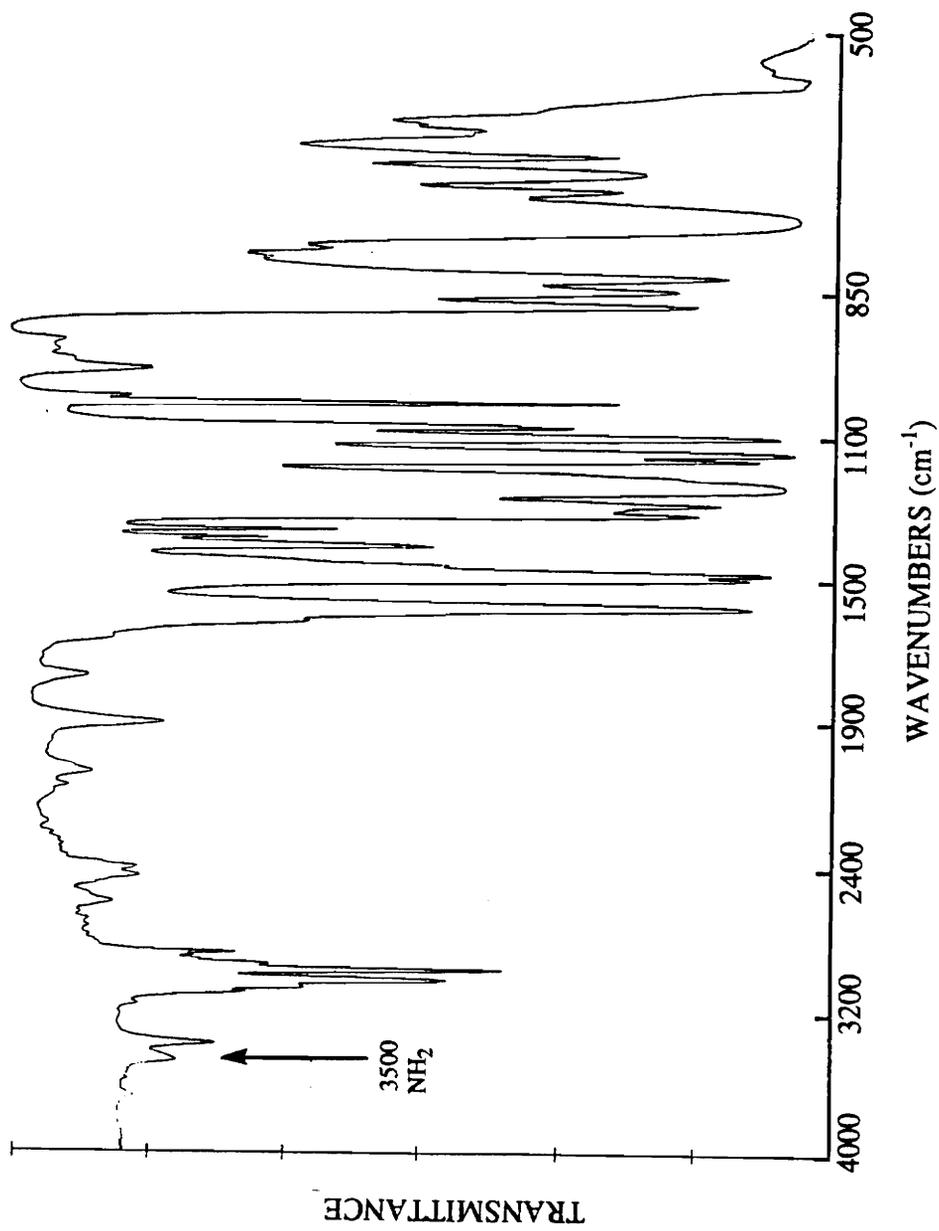


Figure 17. FTIR spectrum of amine-terminated poly(arylene ether sulfone) (PES5700).

Differential scanning calorimetry (DSC) was used to obtain Tgs of these amorphous poly(arylene ether) oligomers. Because the fine powder was difficult to weigh into an aluminum DSC pan, samples were prepared by compressing a moderate amount of powder in a metal IR press and making a thin disk of polymer and then carefully expelling it from the press. Table 18 lists measured thermal data. As it was mentioned earlier, the Tg is dependent on the molecular weight as well as the chemical composition. Intrinsic viscosity (IV) was employed as a qualitative measure of molecular weight for later comparison with copolymer intrinsic viscosities. Table 18 also lists these IV measurements.

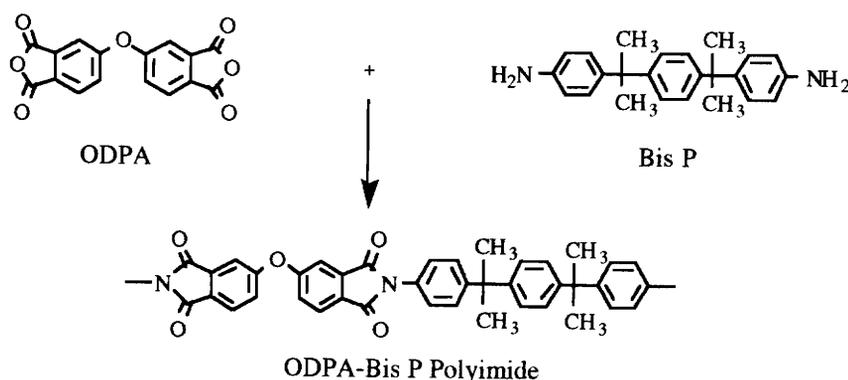
Table 18. Properties of poly(arylene ether)s synthesized.

Poly(arylene ether)	$\langle M_n \rangle$ (titration average)	Tg (°C)	$[\eta]_{\text{CHCl}_3}^{25^\circ\text{C}}$
PEKK	5400 g/mol	144	0.245 dL/g
PES	5700 g/mol	165	0.162 dL/g
PEPO	6500 g/mol	206	0.228 dL/g

$[\eta]_{\text{CHCl}_3}^{25^\circ\text{C}}$ = intrinsic viscosity run in chloroform at 25°C

D. Synthesis and Characterization of Amine-Terminated Polyimide Oligomer

Conditions for the solution imidization of a poly(amic acid) to the corresponding polyimide have been fairly well established within our research group [62, 63]. The first step of this two-step process involves formation of the soluble poly(amic acid) pre-polymer at room temperature. The second step cyclizes the amic acid moieties to the thermally stable polyimide and requires temperatures above 150°C. Utilization of monomers that provide some degree of solubility allows for solution imidization techniques. Chosen for this work was one of the more soluble (and traditional) polyimide systems prepared from bisaniline P (Bis P) and oxydiphthalic anhydride (ODPA) (see Scheme 30). Its soluble nature is limited to amide solvents and some chlorinated solvents above room temperature. An additionally important factor in solubility is molecular weight. At 5000 g/mol, it was presumed that the BisP-ODPA polyimide would be soluble enough to dissolve in warmed chloroform so that molecular weight characterization by endgroup titration would be possible.



Scheme 30. Basic reaction scheme of ODPA-Bis P Polyimide.

Therefore, keeping with the theoretical molecular weights of 5000 g/mol like the poly(arylene ether)s, the necessary amounts of each monomer were calculated from a form of the Carothers equation. As in the poly(arylene ether) cases, amine endgroups were also needed for the polyimide for post-polymerization. Because Bis P is an aromatic diamine, amine functionality for the polymer was achieved through an added calculated excess of this monomer.

The glassware was very similar to that used for the poly(arylene ether)s, except that an inverse Dean-Stark trap replaced the Dean-Stark trap (see Figure 9 of *Experimental*). After the flame-dried apparatus was cool, 15.0430 g (0.0485 mol) ODPA and 18.9088 g (0.0549 mol) Bis P were weighed into teflon-coated aluminum pans. The polymer grade monomers were transferred to the reaction flask, and the pans were washed with dry NMP until the solids content was approximately 15 w/v percent (170 ml NMP). The colorless mixture was stirred at room temperature for 20 hours, during which time the solution became homogeneous and yellow in color. Within the first few minutes of this 20 hour period, the monomers began reacting to form the poly(amic acid) as indicated by the solvation of monomers and slight (visual) viscosity increase. Based on past research with poly(amic acid) formation, eight hours would have been sufficient; however, the 20-hour allotment was most convenient.

Next, 20 v/v percent (42 ml) dry *o*-dichlorobenzene was added to the yellow poly(amic acid) solution which was then heated 165°C with an oil bath. Nitrogen was increased slightly to induce distillation of the water/*o*-dichlorobenzene azeotrope. As the liquids distilled into the inverse Dean-Stark trap, the less dense water droplets floated on the heavier organic phase. The distilled liquids were drained from the trap and fresh, dry *o*-dichlorobenzene was added to the reaction vessel. Cyclodehydration of the poly(amic acid) was allowed to continue for 20 hours at 165°C, followed by cooling of the polyimide

solution.

As the reaction cooled, the polyimide precipitated from the NMP/*o*-dichlorobenzene media resulting in a dull yellow slurry. Although the polyimide had already precipitated, it was treated as a solution to be coagulated. Thus, this slurry was cast into a rapidly stirring blender filled with 400 ml methanol and 400 ml distilled water. The dull yellow powdery polyimide was collected in a sintered glass filter and washed with methanol and water. It was air dried overnight, and vacuum dried at 120°C for 48 hours.

The 5000 g/mol (theoretical) ODPA-Bis P amine-terminated polyimide was characterized by potentiometric endgroup titration, DSC and IV. Three samples of polyimide were accurately weighed into individual glass beakers. Approximately 50 ml of unpurified chloroform was added to each. With vigorous stirring by magnetic stirring bars and lightly applied heat (~ 50°C), the polyimide went into solution. Twenty ml of glacial acetic acid was added to the warm polyimide solution and stirred for an additional minute. Titrating with standardized HBr in glacial acetic acid, amine difunctionality was confirmed and molecular weight data was calculated. Well within the expected range, $\langle M_n \rangle$ was found to be 5500 g/mol.

A DSC sample was prepared as described above for the poly(arylene ether)s, and the ODPA-Bis P polyimide displayed a T_g of 225°C. This value was perhaps slightly lower than expected, when compared to ODPA-Bis P polyimides of 40,000 g/mol. However, no previous T_g results were available on such an oligomeric polyimide for direct comparison.

Intrinsic viscosity was measured for future molecular weight comparison between the homopolyimide and polyimide-PSX copolymers. The measured IV value of 0.223 dL/g was expected for the 5500 g/mol size.

Table 19 recapitulates characterization data for each α,ω -diamino oligomer.

Table 19. Properties of four amine-terminated oligomers synthesized.

ETP	$\langle M_n \rangle$ (titrated)	T _g (°C)	$[\eta]_{\text{CHCl}_3}^{25^\circ\text{C}}$
PI	5500 g/mol	225	0.233 dL/g
PEKK	5400 g/mol	144	0.245 dL/g
PES	5700 g/mol	165	0.162 dL/g
PEPO	6500 g/mol	206	0.228 dL/g

E. Synthesis and Characterization of Perfectly Alternating ETP-PSX Segmented Copolymers

Anhydride and amine reactions suggest imide bond formation. From the synthesis of anhydride-terminated PSX and amine-terminated ETP, the ultimate goal of this research was to prepare perfectly alternating segmented copolymers comprised of imide-linked thermoplastic and siloxane segments. Ideally and presumed, established solution imidization techniques were to be employed as the copolymerization method. However, many failed attempts proved otherwise. As for the NADSX, a progressive account of the developments that led to elucidation of the copolymerization method will be discussed.

1. Attempted Chain Extension of NADSX with Amine-Terminated PEK

This rough model polymerization was run in order to ensure difunctionality of both the dianhydride and diamine, as well as to prove that two thermodynamically incompatible species could be copolymerized through solution imidization techniques. Molecular weight

control was not exercised. Thus, a 1:1 molar ratio of NADSX to amine-terminated poly(arylene ether ketone) (3290 g/mol and thus denoted PEK₃₂₉₀, prepared by Dr. Jeffrey Hedrick, currently at IBM, New York) was calculated. (At that time, the amine-terminated PEKK₅₄₀₀ (a major component in the later experiments of this research) was not yet prepared, and the PEK₃₂₉₀ was the only available amine-terminated homopolymer.)

Using flame-dried glassware as shown in Figure 8 in the *Experimental* chapter, 0.8548 g (0.00185 mol) NADSX was weighed into a teflon-coated pan and transferred to the reaction vessel along with 5 ml dry NMP. Next, 6.0786 g (0.00185 mol) PEK₃₂₉₀ was added to the flask from a teflon-coated pan washed with 43 ml NMP so that the solids content was 15 w/v percent. This solution was stirred under nitrogen for 22 hours at room temperature. The final solution was clear and orange-brown in color. Unexpectedly, it was not viscous as a high molecular weight poly(amic acid) solution should have been.

Regardless, the prepolymer solution was prepared for cyclodehydration by adding 12 ml dry *o*-dichlorobenzene. Also, the inverse Dean-Stark trap was prefilled with dry *o*-dichlorobenzene. An oil bath was used to heat the poly(amic acid) solution to 165°C and maintained at this temperature for 48 hours. However, no water byproduct was noticed in the trap throughout this lengthy cyclodehydration period.

The burgundy-brown polymer solution was cooled and worked-up by precipitation into a rapidly stirring blender filled with 600 ml methanol and 200 ml distilled water (75%:25% alcohol:water). The powdery off-white product was collected in a sintered glass funnel, air dried for several hours, then vacuum dried at 110°C for 48 hours.

A distinct peak at ~1723 cm⁻¹ was observed in the FTIR spectrum (see Figure 18) of the product and thought to be generated by the imide carbonyl moiety. Moreover, the amine band at ~3500 cm⁻¹ was absent. FTIR analysis was promising enough to encourage further characterization by DSC and IV.

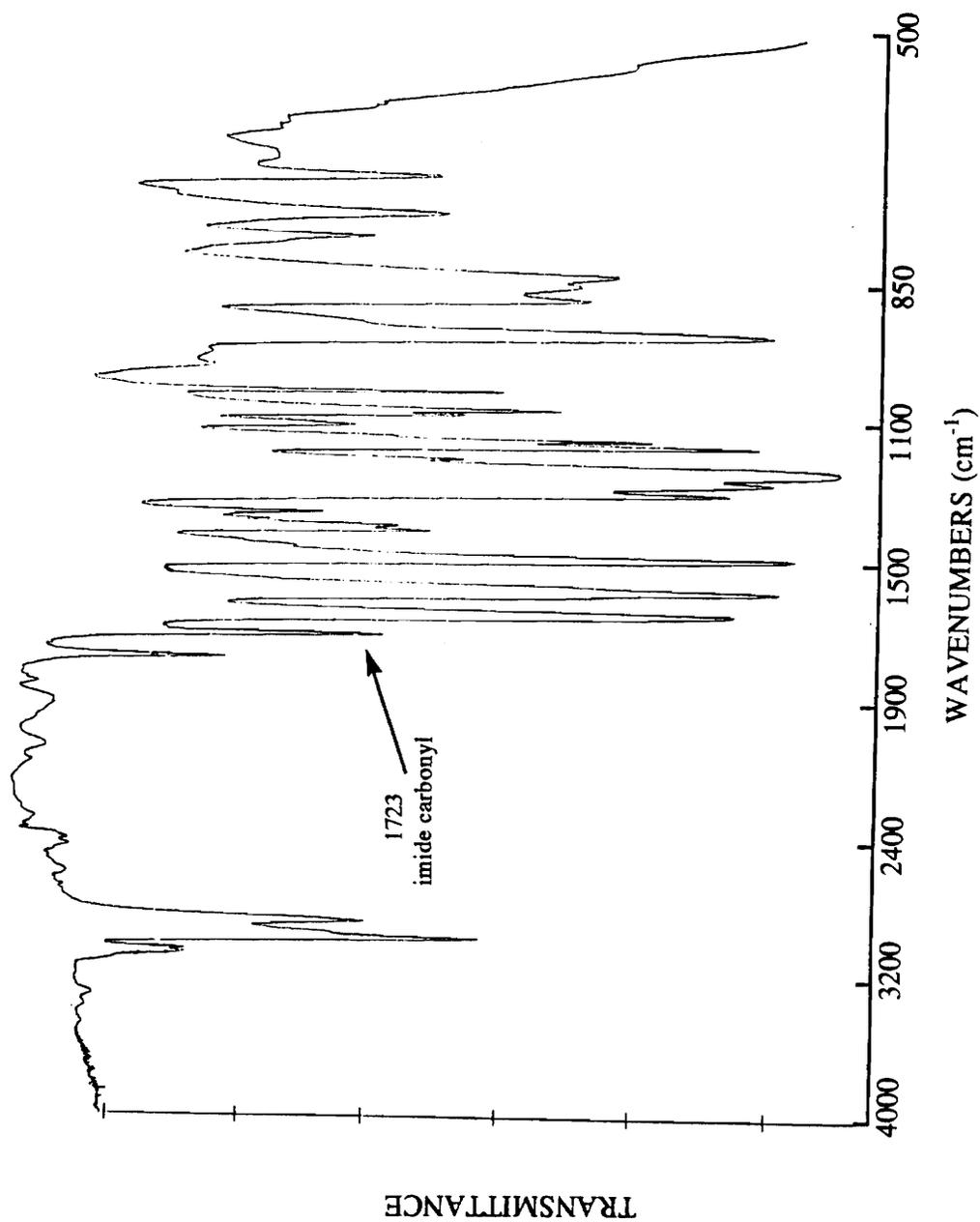


Figure 18. FTIR spectrum of NADSX-PEK₃₂₉₀ copolymer.

DSC results (Figure 19) showed very little change in T_g from the homo-PEK₃₂₉₀ to the assumed PEK₃₂₉₀-NADSX copolyimide. An 8°C change from 125°C for the homo-PEK₃₂₉₀ to 134°C for the PEK₃₂₉₀-NADSX copolyimide evidenced that the product was not appreciably formed. Visually, the powdery quality justifies that very low molecular weight copolyimide was prepared. Furthermore, IV measurements also showed no appreciable increase from the homo-PEK₃₂₉₀ to the copolyimide. The value of 0.165 dL/g, only 0.025 dL/g difference from the IV of the homo-PEK₃₂₉₀ (IV = 0.14 dL/g), verified that no appreciable amount of high molecular weight PEK₃₂₉₀-NADSX copolyimide was prepared.

Because it was not obvious where the problems existed, a chain extension of the PEK₃₂₉₀ with a small polymer-grade dianhydride, benzophenonetetracarboxylic dihydride (BTDA), was successfully carried out. This indicated that perhaps the obstacle was either the imidization technique or the NADSX itself. Good titration results for the NADSX provided information that influenced the idea that the NADSX was not at fault. However, having exhausted the PEK₃₂₉₀ supply, reactions could not be repeated. A 10 g sample of 5700 g/mol amine-terminated PEKK was provided by colleague Mr. Paul Wood, and the chain extension was retried with this poly(arylene ether).

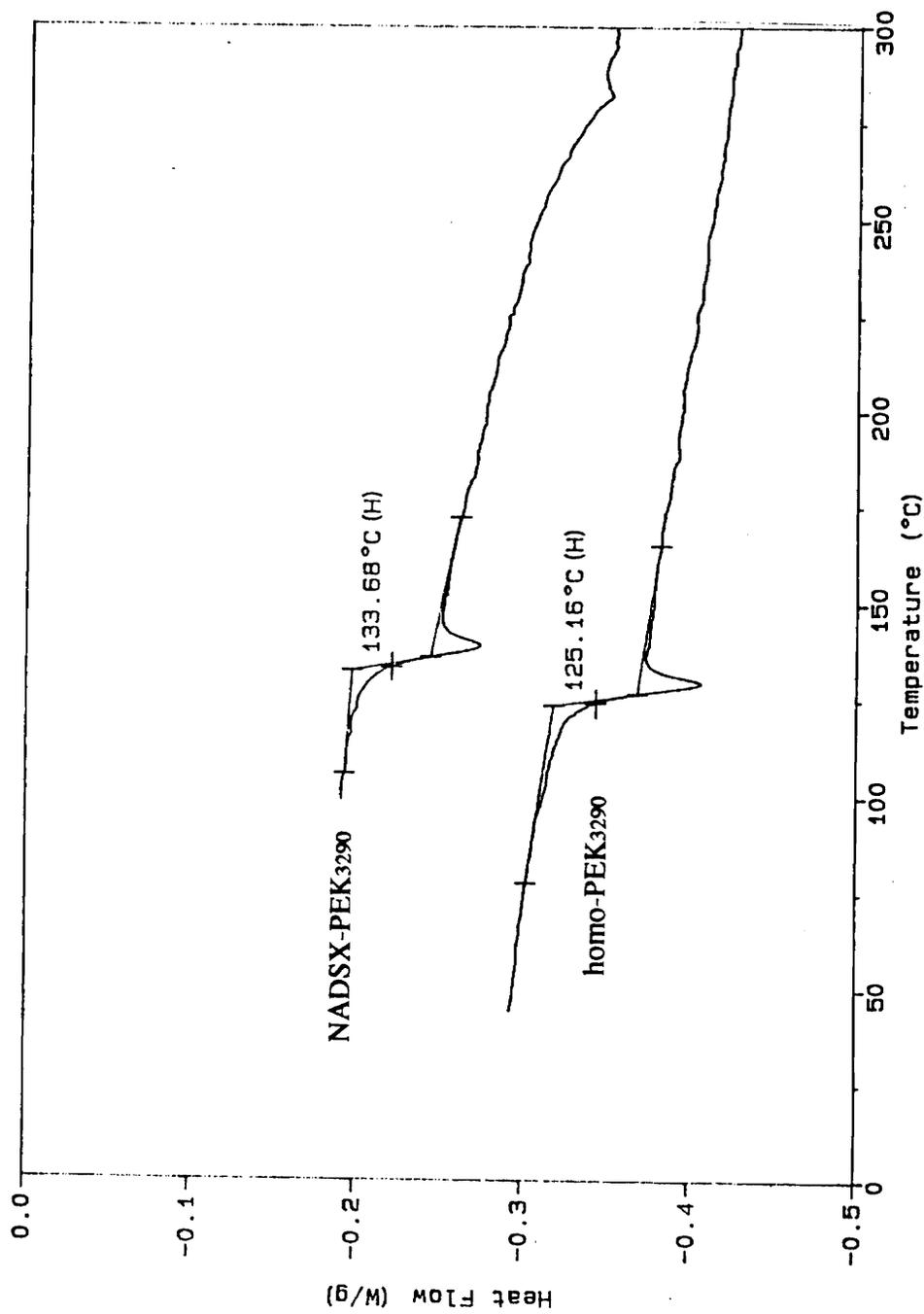


Figure 19. DSC thermograms of homo-PEK₃₂₉₀ and NADSX-PEK₃₂₉₀ copolymer.

2. Chain Extension of NADSX with Amine-Terminated PEKK₅₇₀₀

Using identical apparatus, another chain extension of the NADSX was run with a newly available 5700 g/mol amine-terminated PEKK (denoted PEKK₅₇₀₀). Based on previous solution imidizations in our labs involving siloxanes, the procedure was modified to include THF. Although in the first chain extension attempt NADSX was solvated by NMP, this amide solvent is not a solvent for polysiloxanes. Therefore, THF was used to insure solvation of the NADSX. Additionally, THF was a good solvent for the PEKK₅₇₀₀.

Again exercising no molecular weight control, 0.3246 g (0.000702 mol) NADSX and 4.000 g (0.000702 mol) PEKK₅₇₀₀ were charged to the reaction vessel with 44 ml dry NMP and 13 ml dry THF resulting in eight w/v percent solids concentration. This dilution level was not predetermined.

The mixture was stirred under nitrogen at room temperature overnight (approximately 16 hours), followed by the addition of 15 ml (20 v/v percent) of dry *o*-dichlorobenzene. The inverse Dean-Stark trap was prefilled with *o*-dichlorobenzene, and the clear orange-brown poly(amic acid) solution was heated to 165°C for 48 hours. As before, no water byproduct was detected in the trap during this period.

Next, the copolyimide solution was cooled and coagulated in a rapidly stirring blender filled with 650 ml methanol and 150 ml distilled water (80%:20% alcohol:water). The fibrous, pale yellow product was collected in a sintered glass funnel, washed with methanol, air dried for several hours and finally vacuum dried at 100°C overnight. The PEKK₅₇₀₀-NADSX copolyimide was redissolved in chloroform and reprecipitated a second time, again yielding fibrous, pale yellow product.

The copolyimide was characterized by IV only. Having almost doubled the IV of the homo-PEKK₅₇₀₀ (IV = 0.269 dL/g), the PEKK₅₇₀₀-NADSX IV was 0.51 dL/g. Gel permeation chromatography (GPC) was considered as a molecular weight characterization

method, however was inapplicable due to the reactive amine endgroups theoretically present. Past experience in our labs has shown that there is an affinity between the GPC column and amine endgroups, resulting in adherence of the polymer to the column. Since few reaction conditions were changed, it was assumed that the addition of THF in the first step was necessary for high molecular weight achievement.

3. Attempted Synthesis of Perfectly Alternating PEKK₅₇₀₀-PSX₂₆₀₀ Segmented Copolymer

Success with the chain extension confirmed that the NADSX was efficient and prompted copolymerization of the amine-terminated PEKK₅₇₀₀ and nadic anhydride-terminated PSX. Using the PEKK₅₇₀₀ and a 2600 g/mol PSX (denoted PSX₂₆₀₀), 1:1 molar amounts were calculated. In a teflon-coated aluminum pan, 4.000 g (0.000702 mol) PEKK₅₇₀₀ was weighed and transferred to the reaction flask with 28 ml dry NMP. A plastic syringe was used to weigh and transfer to the flask 1.8200 g (0.000700 mol) of the viscous PSX₂₆₀₀ oligomer. Eighteen ml of dry THF was added to the stirring mixture, but because the solution seemed to contain much undissolved PEKK₅₇₀₀ even after vigorously stirring, the solution was heated to approximately 45°C with an oil bath. After 12 hours of stirring under nitrogen at 45°C, the solution remained cloudy and yellow. Ten ml of dry *o*-dichlorobenzene was added to the solution, and the temperature was raised to 165°C and maintained for 24 hours. During this time, the viscous yellow solution turned dark brown indicating degradation of the NMP, yet never lost its hazy appearance.

The brown copolymer solution was cooled and transferred to a separatory funnel from which it was slowly added to a rapidly stirring blender filled with methanol. The tan, powdery product was collected in a Büchner funnel, washed with methanol, air dried and finally vacuum dried at 100°C overnight.

The dried product was separated into thirds so that one-third was extracted with hexanes, one-third was stirred with isopropanol and the remaining one-third was left "unwashed." The washing was employed to remove any unreacted PSX₂₆₀₀ oligomer if any was not already washed into the initial methanol precipitation. This was done so that percent siloxane incorporation could be calculated.

DSC scans of each third were run. Data suggested that no PSX₂₆₀₀ remained in any case since all three gave T_g values at 150°C to 151°C. An IV of 0.378 dL/g (homo-PEKK₅₇₀₀ IV = 0.269 dL/g) demonstrated that the powdery copolymer was fairly low molecular weight.

Discussions with colleagues and Prof. McGrath established that due to the cloudy nature of the solution throughout the entire two-step solution imidization process, mutual availability of endgroups was not achieved. The incompatibility of the two polymer systems was so great that despite the addition of THF, both oligomers could not be solvated in the presence of each other. It was then considered that perhaps NMP should not be used in future reactions since PSX oligomers were not soluble in amide solvents. Because both oligomers were soluble in *o*-dichlorobenzene, the next approach replaced NMP with 100 percent *o*-dichlorobenzene.

4. Attempted Synthesis of Perfectly Alternating PEKK₅₇₀₀-PSX₂₆₀₀ Segmented Copolymer via Modified Techniques

Preparation of perfectly alternating PSX-containing copolymers produced through the silylamine-phenol reaction (Noshay, *et al.* [66]) employed slow addition of the PSX oligomer to allow for compatibilization of the two systems. By initially introducing a small amount of PSX relative to the PES, the system was not overwhelmed with gross incompatibility. Given enough time to react, the small amount of copolymer that formed

(evidenced by trimethylamine vapor) acted as a compatibilizer for the remaining PSX to be incorporated. This was the basis for the method used in this second copolymerization attempt.

Thus, for preparation of an uncontrolled molecular weight PEKK₅₇₀₀-PSX₂₆₀₀ copolymer, 2.08 g (0.000365 mol) PEKK₅₇₀₀ was added to the reaction vessel along with 25 ml dry *o*-dichlorobenzene. The mixture, stirred under nitrogen at room temperature, became homogeneous within 10 minutes. Weighed into and transferred from a plastic syringe, 0.9399 g (0.000362 mol) PSX₂₆₀₀ was charged to a pressure equalizing addition funnel and dissolved in 10 ml each of dry *o*-dichlorobenzene and THF. Over a 30 minute period, approximately 10 ml of the PSX solution was added dropwise into the clear amber colored PEKK₅₇₀₀ solution. At this point, the reaction solution started to become cloudy. The PSX₂₆₀₀ addition was halted, and the reaction solution was stirred for three hours. As it was noticed that the solution was becoming increasingly turbid, a small amount of heat (~60°C) was applied to the solution for eight hours. Since no changes were achieved, an additional 5 ml of *o*-dichlorobenzene was added to reduce the solids content and heating continued overnight.

The following day, the solution temperature was increased to 100°C at which temperature the cloudiness disappeared and the remaining PSX₂₆₀₀ solution was added dropwise. After 22 hours of sustained optical clarity at 100°C, the temperature was raised to 165°C and held for 48 hours for cyclodehydration of the poly(amic acid).

Next, the copolymer solution was cooled and added from a separatory funnel to a rapidly stirring blender filled with 650 ml methanol and 150 ml isopropanol (80%:20% methanol:isopropanol). The pale yellow product was isolated, washed with isopropanol, air dried and vacuum dried overnight at 100°C.

FTIR analysis did not reveal an imide carbonyl band at 1723 cm⁻¹. Comparison of

the PEKK₅₇₀₀-PSX₂₆₀₀ IV of 0.298 dL/g to the homo-PEKK₅₇₀₀ IV of 0.269 dL/g confirmed that no copolymer was produced.

Having depleted the supply of PEKK₅₇₀₀, the copolymerization was retried with an 11,700 g/mol amine-terminated PEKK (denoted PEKK₁₁₇₀₀) that was also obtained from Mr. Wood. Similar negative results were obtained for three attempts with a 3900 g/mol PSX (denoted PSX₃₉₀₀), noted by nearly identical IV measurements for the homo-PEKK₁₁₇₀₀ and the presumed PEKK₁₁₇₀₀-PSX₃₉₀₀ copolymers.

Reverting to smaller thermoplastic segments, a large batch of 5400 g/mol amine-terminated PEKK (denoted PEKK₅₄₀₀) was kindly prepared and made available for this research by colleague Mr. Gregory Lyle. The use of a smaller segment size, such as 5000 g/mol, would possibly reduce the macrophase separation that was occurring during the copolymerization. Segment sizes lower than this would perhaps defeat the ETP characteristics that were desired.

5. Successful Synthesis of Perfectly Alternating PEKK₅₄₀₀-PSX Segmented Copolymer

In 1990, two chemists at G. E. described the synthesis of polyimides prepared from NADSX and *meta*-phenylene diamine [59]. Using 2-hydroxypyridine as a condensation catalyst and slightly modified solution imidization reaction conditions, a high molecular weight NADSX-containing polyimide was prepared.

Applying those conditions to oligomeric "macromonomers", a reaction was performed utilizing the PEKK₅₄₀₀ and a 2000 g/mol PSX (denoted PSX₂₀₀₀). (The actual average titrated <Mn> values of 5416 g/mol and 2060 g/mol were used for calculations, however.) As per their directions, three w/w percent 2-hydroxypyridine (2-OHpy) was incorporated into the reaction scheme. Unfortunately, the chemists offered neither an

explanation regarding the catalytic involvement nor a justification for the amount employed. Using the appropriate glassware (Figure 8 of *Experimental*) and calculations for a 1:1 molar ratio of PEKK₅₄₀₀ to PSX₂₀₀₀, 3.1036 g (0.00150 mol) PSX₂₀₀₀ was transferred from the plastic syringe into the pressure equilizing addition funnel and dissolved in approximately 20 ml dry *o*-dichlorobenzene. Although the NADSX was added initially, precautions were taken against macrophase separation. Thus, the PSX₂₀₀₀ was to be added incrementally to the reaction mixture. Next, 8.1367 g (0.00150 mol) PEKK₅₄₀₀ was weighed and charged to the reaction flask with 0.34 g (0.00357 mol) 2-OHpy, 3 w/w percent based on the total amount of both oligomers. The inverse Dean-Stark trap was prefilled with dry *o*-dichlorobenzene. For 15 w/v percent solids content, 60 ml dry *o*-dichlorobenzene was added to the solid mixture which was then immediately stirred under nitrogen and heated to 100°C. According to the G. E. chemists, the poly(amic acid) would form when the solution was heated to 100°C and then precipitate within two hours. The solution would then require an increased temperature of 180°C which should be maintained for 18 hours.

When the PEKK₅₄₀₀ and 2-OHpy were dissolved in the hot *o*-dichlorobenzene, the PSX₂₀₀₀ solution was added in a continuous dropwise fashion over a one hour period. During this time and the following two hours, the poly(amic acid) never precipitated. To ensure poly(amic acid) formation, the reaction solution was stirred for a total of three days, during which time the poly(amic acid) remained in solution and the solution retained its clarity. Then, the temperature was raised to 175°C and held for 24 hours for cyclodehydration of the poly(amic acid). Water byproduct was not detected in the trap during this 24 hour reflux period. However, a marked viscosity increase was observed within 10 hours.

Finally, the copolymer solution was cooled and diluted with roughly 15 ml unpurified

chloroform to reduce the viscosity. It was transferred to a separatory funnel from which it was slowly added in a steady stream to a rapidly stirring blender filled with methanol. The very fibrous, tan PEKK₅₄₀₀-PSX₂₀₀₀ copolymer was collected in a sintered glass funnel, washed with methanol, air dried and vacuum dried at 100°C overnight. Contrary to G. E.'s work-up, the polymer was not washed with 2 N HCl to rid the product of 2-OHpy. Because the catalyst was soluble in methanol, it was assumed that several washings with the alcohol would efficiently remove the 2-OHpy as well as any unreacted PSX₂₀₀₀.

Initial characterization included DSC, IV, film-forming ability, solubility and ¹H NMR. The copolymer upper T_g of 134°C corresponding to the PEKK₅₄₀₀ segment was observed as a weak transition (see Figure 20) determined on the DuPont 912 DSC instrument. Compared to the homo-PEKK₅₄₀₀ T_g of 144°C, this slight depression indicated a very small amount of siloxane phase mixing into the poly(arylene ether). There were no presumptions made about how greatly the upper T_g would be effected, so the 10°C difference was accepted. Sub-ambient T_g for the PSX₂₀₀₀ segment was not accessible on this instrument, however. (This copolymer was later analyzed on the Perkin-Elmer DSC 7 for sub-ambient T_g. Details will be discussed later.)

Intrinsic viscosity measurements proved that the noted visual viscosity increase was indeed great. Having more than doubled the homo-PEKK₅₄₀₀ IV of 0.245 dL/g, the apparently high molecular weight PEKK₅₄₀₀-PSX₂₀₀₀ copolymer IV was 0.723 dL/g.

The ability to form fibers and a very strong solution cast film also qualitatively proved high molecular weight achievement. The first solution-cast films of this polymer were prepared from *o*-dichlorobenzene, but resulted in hazy, caramel-colored films. Chloroform-cast thin films were much more clear with borderline transparent-translucent clarity. Films could be cast from both chlorinated solvents as well as NMP, DMAc and THF since the

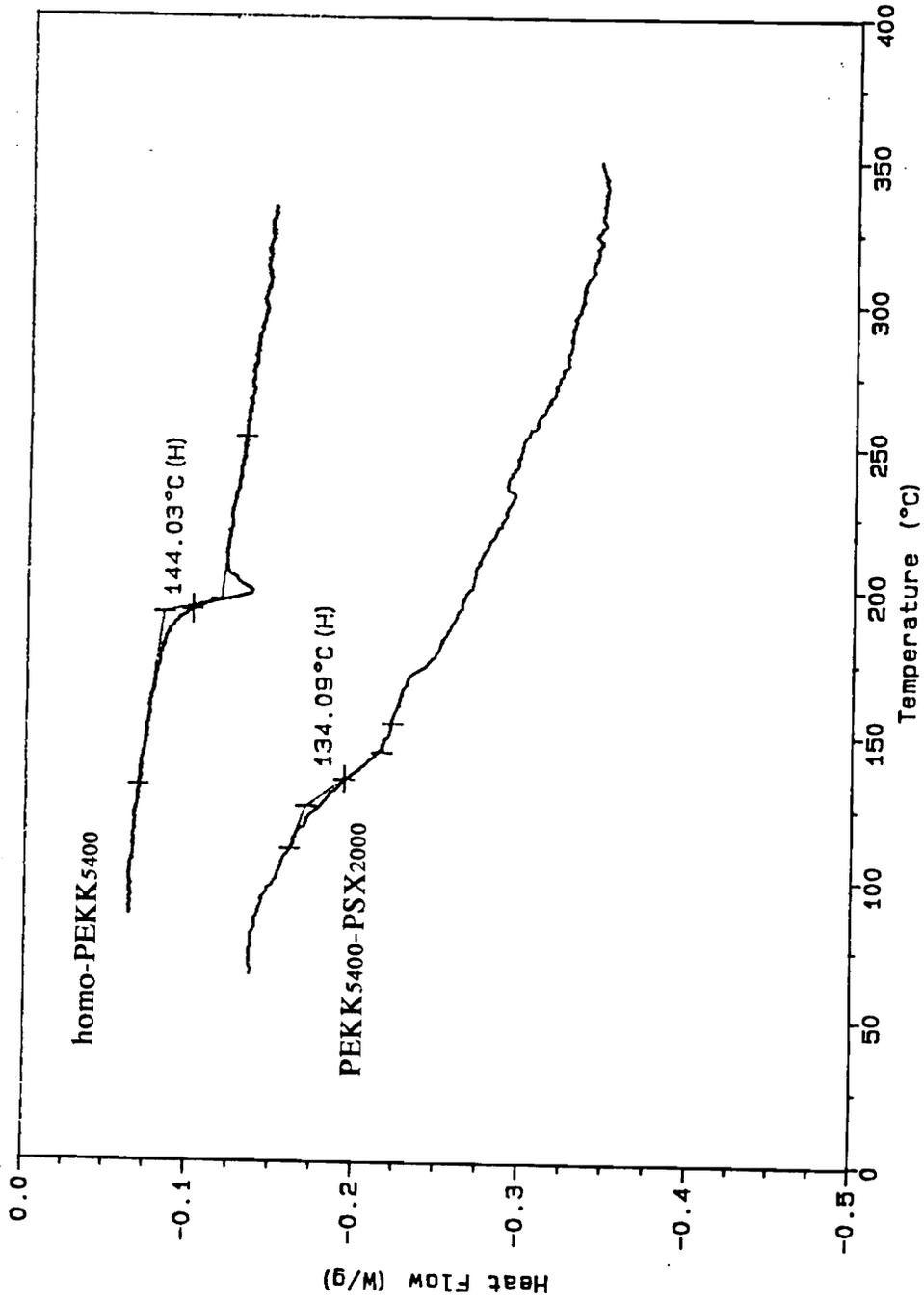


Figure 20. DSC thermogram of perfectly alternating PEKK₅₄₀₀-PSX₂₀₀₀ segmented copolymer.

copolymer was readily soluble in all five organic solvents at room temperature.

^1H NMR was initially used to quantitatively define the percent siloxane incorporated in the copolymer. A sample was dissolved in deuterated chloroform (CDCl_3) without TMS, and a spectrum was run using CDCl_3 as the chemical shift reference. TMS methyl protons, which resonate at 0 ppm, would have interfered with the methyl protons of the PSX2000 segment repeat units, which resonate at roughly 0 ppm, causing erroneous results. From the integrated spectrum, the ratio of dimethylsiloxane protons of the PSX2000 repeat unit (0 ppm) to bisphenol A methyl protons of the PEKK5400 (1.7 ppm) repeat unit could be calculated. This value, obtained from the ^1H NMR spectrum shown in Figure 21, was considered the "actual" ratio. Then, the "theoretical" ratio was taken to be the total number of dimethylsiloxane protons from the PSX2000 segments weighed out for the reaction to the total number of bisphenol A methyl protons from the PEKK5400 segments weighed out for the reaction. Therefore, the "theoretical" ratio expressed 100 mole percent incorporation of siloxane. The actual mole percent siloxane incorporated was then

$$\begin{aligned} &(\text{"actual" ratio} / \text{"theoretical" ratio}) \times 100\% = \\ &(0.5801 / .78) \times 100\% = 74 \text{ mole percent.} \end{aligned}$$

This value, 74 mole percent, implies that 26 mole percent of the 100 mole percent PSX2000 charged to the flask was not reacted into the copolymer. In terms of weight percent, the copolymer theoretically consisted of 72.5 weight percent PEKK5400 and 27.5 weight percent PSX2000. Converting from mole percent, ^1H NMR found the copolymer to contain only 20 weight percent PSX2000. This fact was very puzzling since visually the copolymer had very high molecular weight. Such a large stoichiometric upset, a ratio of 1 mole PEKK5400 to 0.74 mole PSX2000, would have resulted in low molecular weight copolymer. The discrepancy, as described later to be due to micelle formation, was set aside while copolymerizations were continued with other poly(arylene ether)s.

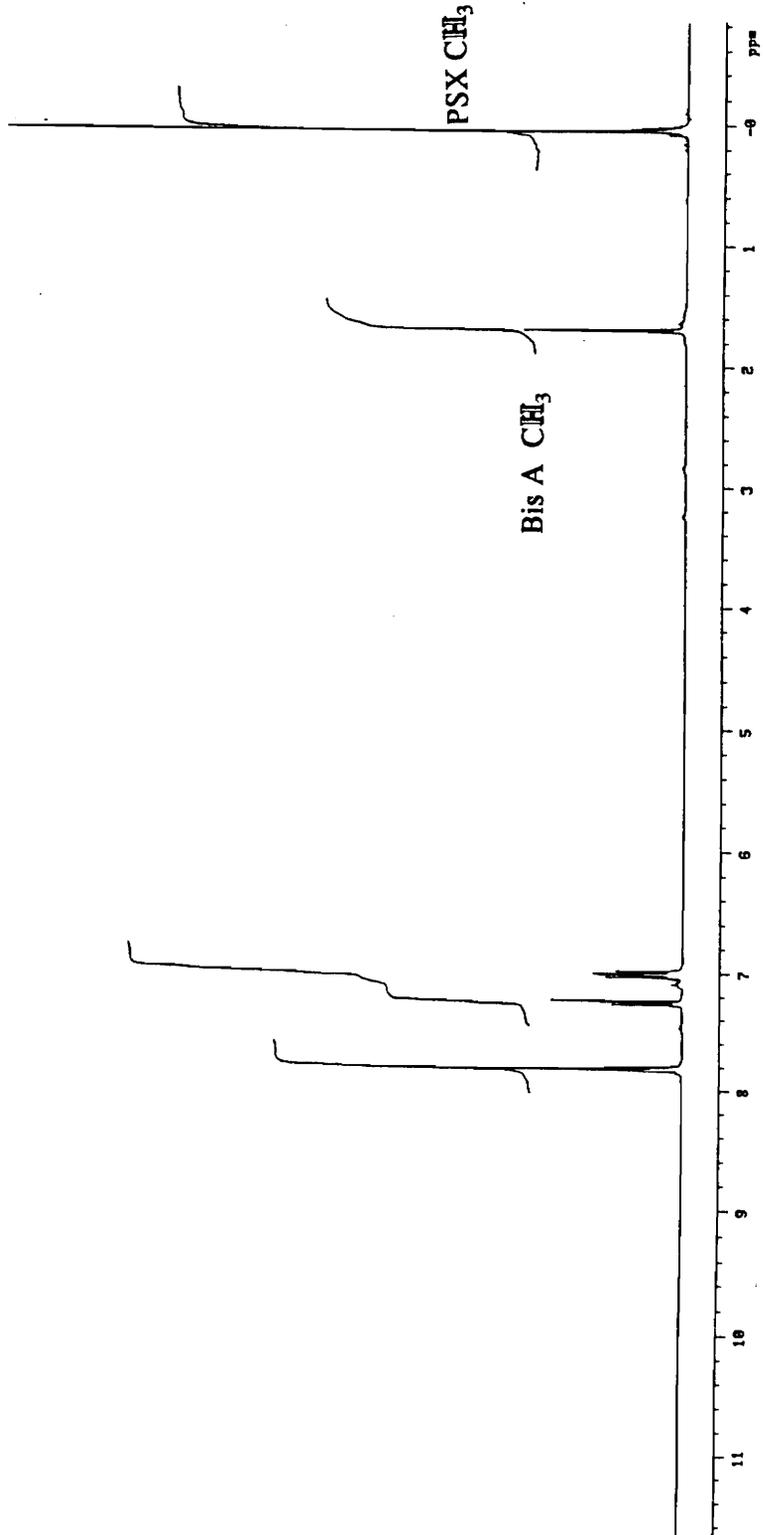


Figure 21. ^1H NMR spectrum of perfectly alternating PEK₅₄₀₀-PSX₂₀₀₀ segmented copolymer.

6. *Synthesis of Perfectly Alternating PES₅₇₀₀-PSX₂₀₀₀ Segmented Copolymer*

A copolymerization was run employing a 5700 g/mol PES (denoted PES₅₇₀₀) and the PSX₂₀₀₀. (Actual averaged titrated $\langle M_n \rangle$ values of 5760 g/mol and 2060 g/mol were used for calculations, however.) Reaction conditions were comparable to those stated above for the successful PEKK₅₄₀₀-PSX₂₀₀₀ solution imidization. Thus, 3.1570 g (0.00153 mol) PSX₂₀₀₀ in 20 ml *o*-dichlorobenzene was incrementally introduced into the reaction solution of 8.8300 g (0.00153 mol) PES₅₇₀₀, 0.36 g (0.00379 mol) 2-OHpy and 60 ml dry *o*-dichlorobenzene. After three days at 100°C, the poly(amic acid) solution temperature was raised to 175°C for 24 hours. The viscous copolymer solution was cooled, diluted with chloroform and coagulated into methanol exactly as described above. The very fibrous, nearly white PES₅₇₀₀-PSX₂₀₀₀ copolymer was isolated and dried methodically.

Initial characterization included DSC, IV, film-forming ability, solubility and ¹H NMR. Similar to the PEKK₅₄₀₀-PSX₂₀₀₀ copolymer, a small amount of phase mixing was observed in the upper T_g depression from 165°C for the homo-PES₅₇₀₀ to 141°C for the PES₅₇₀₀-PSX₂₀₀₀ copolymer. Intrinsic viscosity measurements obtained showed that the copolymer IV of 0.581 dL/g were nearly four times greater than the homo-PES₅₇₀₀ IV of 0.162 dL/g, qualitatively confirming that high molecular weight was achieved. Soluble in *o*-dichlorobenzene, chloroform, NMP, DMAc, and THF, strong solution-cast films could be easily prepared with translucent to transparent clarity of nearly colorless quality.

Similar puzzling results to those of the PEKK₅₄₀₀-PSX₂₀₀₀ were obtained for the ¹H NMR spectrum shown in Figure 24. Calculations determined that only 77 molar percent PSX₂₀₀₀, or 20 of 26 weight percent charged, was incorporated into the copolymer. Again, this matter was set aside until after a perfectly alternating PI-PSX copolymer could be synthesized.

7. Several Attempts at Synthesis of Perfectly Alternating PI₅₅₀₀-PSX₂₀₀₀ Segmented Copolymer

a. Initial Attempt: "gelled" product

The first attempt at making a PI-PSX copolymer from a 5500 g/mol PI (average titrated $\langle M_n \rangle$ of 5496 g/mol, denoted PI₅₅₀₀) and the PSX₂₀₀₀ was not completely unsuccessful. From calculations for 1:1 stoichiometry, 2.7249 g (0.00132 mol) PSX₂₀₀₀ was charged to the pressure equalizing addition funnel with 15 ml dry *o*-dichlorobenzene, and 7.2532 g (0.00132 mol) PI₅₅₀₀ and 0.31 g (0.0033 mol) 2-OHpy were added to the reaction flask with 51 ml dry *o*-dichlorobenzene. The solution was vigorously stirred and heated to 100°C, but the PI₅₅₀₀ oligomer did not dissolve. Twenty ml dry NMP was added to the solution, reducing the solids concentration to 12 w/v percent. Yet, the amine-terminated polyimide still was not solvated.

Regardless, the siloxane solution was slowly added dropwise. When, after all the PSX₂₀₀₀ was charged to the reaction mixture the solution was still heterogeneous, the temperature was increased to 135°C. The reaction solution became clear and deep yellow, so the temperature was maintained for poly(amic acid) formation for 30 hours.

Afterwards, the temperature was raised to 165°C to 170°C for 20 additional hours for cyclodehydration to the copolymer. During that period, most of the solvent was lost due to excessive nitrogen flow, resulting in a very dark brown viscous product adhered to the walls of the flask. The flask was cooled, and chloroform was added to dissolve any possible copolymer produced. The small amount of dark viscous product that was dissolved was coagulated into methanol in a rapidly stirring blender. The end product was fibrous and tan in color. The fibers were isolated, washed and dried as usual. Presumably the PI₅₅₀₀-PSX₂₀₀₀ copolymer desired, the dried fibers were very brittle. The remaining product that did not dissolve was assumed to be a crosslinked polyimide (and perhaps

siloxane-containing) network since it was insoluble in all common organic solvents even at elevated temperatures.

The fibers were characterized by DSC, IV, film-forming ability, solubility and ^1H NMR. The T_g of the copolymer was determined to be 195°C by DSC (see Figure 25). Comparing this to the homo-PI5500 T_g of 225°C , one conclusion is that phase mixing of the PSX2000 into the PI5500 segments was fairly high causing the upper T_g of the copolymer to experience a 30°C depression. The IV obtained for this copolymer was also rather significant, as it was measured to be 1.91 dL/g in chloroform (homo-PI5500 IV = 0.23 dL/g). The copolymer was easily solvated by room temperature *o*-dichlorobenzene, NMP and chloroform from which a tough, brown translucent film was cast.

Again similar to all other ^1H NMR copolymer spectra, only 81 mole percent PSX2000, or 22 of the 27 weight percent charged, was incorporated in the copolymer by ^1H NMR results. Because the copolymerization was not well controlled, the reaction was repeated.

b. Second gelled product

Depletion of the PSX2000 supply caused the use of a 1400 g/mol PSX (averaged titrated $\langle M_n \rangle$ was 1389 g/mol , denoted PSX2000) in the second attempt. Rather than slowly adding the PSX1400 solution to the PI5500 and 2-OHpy in the reaction flask, 1.5000 g (0.00108 mol) PSX1400, 5.9352 g (0.00108 mol) PI5500, 0.23 g (0.0024 mol) 2-OHpy and 50 ml *o*-dichlorobenzene were added to the flask concurrently. The reaction was heated to 135°C , and within two hours, the solution became homogeneous and red-brown in color. This solution was maintained stirring under nitrogen at 135°C for 24 hours. Then, the reaction temperature was increased to 165°C to 170°C for an additional 24 hours to cyclodehydrate the poly(amic acid). Unfortunately, the overhead mechanical stirrer stopped

during the 24 hour period when the reaction was unattended causing a second "gellation." Once again, the red-brown product adhered to the walls of the flask. The flask was cooled, and chloroform was added to dissolve any uncrosslinked copolymer product. Approximately three-fourths of the original volume of reactants was solvated and isolated as routinized.

The very fibrous, off-white copolymer was characterized by IV. Not quite as high as the first product (IV = 1.91 dL/g), the second copolymer IV was 1.073 dL/g. Because the reaction was not well-controlled, characterization was not taken further, and a third copolymerization was run.

c. Third attempt: minimal "gelation" occurred

The final attempt at synthesizing a PI5500-PSX1400 copolymer was carried out under identical conditions. Each reactant, 2.1398 g (0.00154 mol) PSX1400, 8.4677 g (0.00154 mol) PI5500, 0.30 g (0.0032 mol) 2-OHpy and 71 ml *o*-dichlorobenzene, was added to the flask initially. The reaction was run as described for the second attempt. Despite proper stirring and controlled nitrogen flow, a slight "gel" was again found at the end of the 24 hour cyclodehydration period. The viscous copolymer solution was transferred to a separatory funnel and precipitated into methanol to yield off-white fibers. The jelly-like semi-solid remaining in the flask was not a true crosslinked, or gelled, network since it dissolved in NMP at 70°C within a 16 hour period. Precipitation of this product yielded a powdery tan solid.

Both the copolymer fibers and powdery solid were characterized by IV. Following a decreasing trend, the IV of the PI5500-PSX1400 copolymer was 0.813 dL/g. Being nearly four times the value of the homo-PI5500 of 0.23 dL/g, high molecular weight was obviously still accomplished. Soluble in THF, chlorinated solvents and amide solvents, tough nearly transparent, solution-cast films were prepared from chloroform. Apparently,

the copolymer possessed great adhesive quality. This was noted in the difficulty separating the dried copolymer film from the aluminum substrate onto which it was cast. Analysis of the powder gave an IV of 0.362 dL/g. While the exact composition of the powder was not confirmed, it was presumed to be low molecular weight copolymer that simply adhered to the flask walls.

8. One-step Solution Imidization: Synthesis of Perfectly Alternating PEKK₅₄₀₀-PSX₄₉₀₀ Segmented Copolymer

By eliminating the initial "poly(amic acid) formation" step at 100°C to 135°C, several copolymerizations were carried out in one cyclodehydration step at 170°C to 175°C. Because the final polymer was to be soluble--a main advantage of siloxane incorporation -- it was assumed that the soluble prepolymer (important in traditional imidizations) was not essential.

Based on other work published by G. E. [75], the imidization involving PES₅₇₀₀ and PSX₁₄₀₀ oligomers was run for only seven hours at 170°C to 175°C in *o*-dichlorobenzene. After seven hours, the solution was cooled and coagulated in a 1:1 volume mixture of methanol and isopropanol within a rapidly stirring blender. The powdery precipitate indicated that low molecular weight product was attained. Intrinsic viscosity for the PES₅₇₀₀-PSX₁₄₀₀ copolymer was 0.314 dL/g (homo-PES₅₅₀₀ IV = 0.162).

Retrying this reaction for a longer period of time with the PEKK₅₄₀₀ and a 4900 g/mol (average titrated $\langle M_n \rangle$ was 4880 g/mol., denoted PSX₄₉₀₀) PSX, a high molecular weight PEKK₅₄₀₀-PSX₄₉₀₀ copolymer was synthesized. All reactants, 2.8256 g (0.000579 mol) PSX₄₉₀₀, 3.1361 g (0.000579 mol) PEKK₅₄₀₀, 0.18 g (0.0019 mol) 2-OHpy and 40 ml dry *o*-dichlorobenzene, were charged to the flask at one time. The solution was immediately stirred under nitrogen and heated to 170°C to 175°C and

maintained for 24 hours.

Next, the solution was cooled and transferred to a separatory funnel from which it was added to methanol and isopropanol (1:1 mixture) in a rapidly stirring blender. The coagulated fibrous and dull yellow copolymer was dried as usual.

The PEKK₅₄₀₀-PSX₄₉₀₀ copolymer was characterized by DSC, IV, solubility and film-forming ability. From DSC, there was obtained a very weak signal at 122°C indicating an upper T_g due to the PEKK₅₄₀₀ segment (see Figure 22). Generally, the smaller the segment lengths, the greater the chance of phase mixing. As it was noted for the PEKK₅₄₀₀-PSX₂₀₀₀, the upper T_g was 126°C, a depression of 18°C from the homo-PEKK₅₄₀₀ of 144°C. Expected to be higher than 126°C, the 122°C T_g of this PEKK₅₄₀₀-PSX₄₉₀₀ copolymer indicated, perhaps, that slightly more phase mixing occurred. A sub-ambient DSC scan was run, but was concluded to be too insensitive to observe the PSX₄₉₀₀ T_g expected to be around -123°C.

Intrinsic viscosity data indicated that this apparently high molecular weight PEKK₅₄₀₀-PSX₄₉₀₀ copolymer yielded an IV of 0.687 dL/g. This decrease, compared to other copolymer IVs, was regarded as a result of the longer PSX segment length used. It, however, cannot be concluded whether or not the molecular weight was as high as the other copolymers. Because reactive amine endgroups were still present for all of these uncontrolled molecular weight copolymers, GPC could not be employed to determine molecular weight.

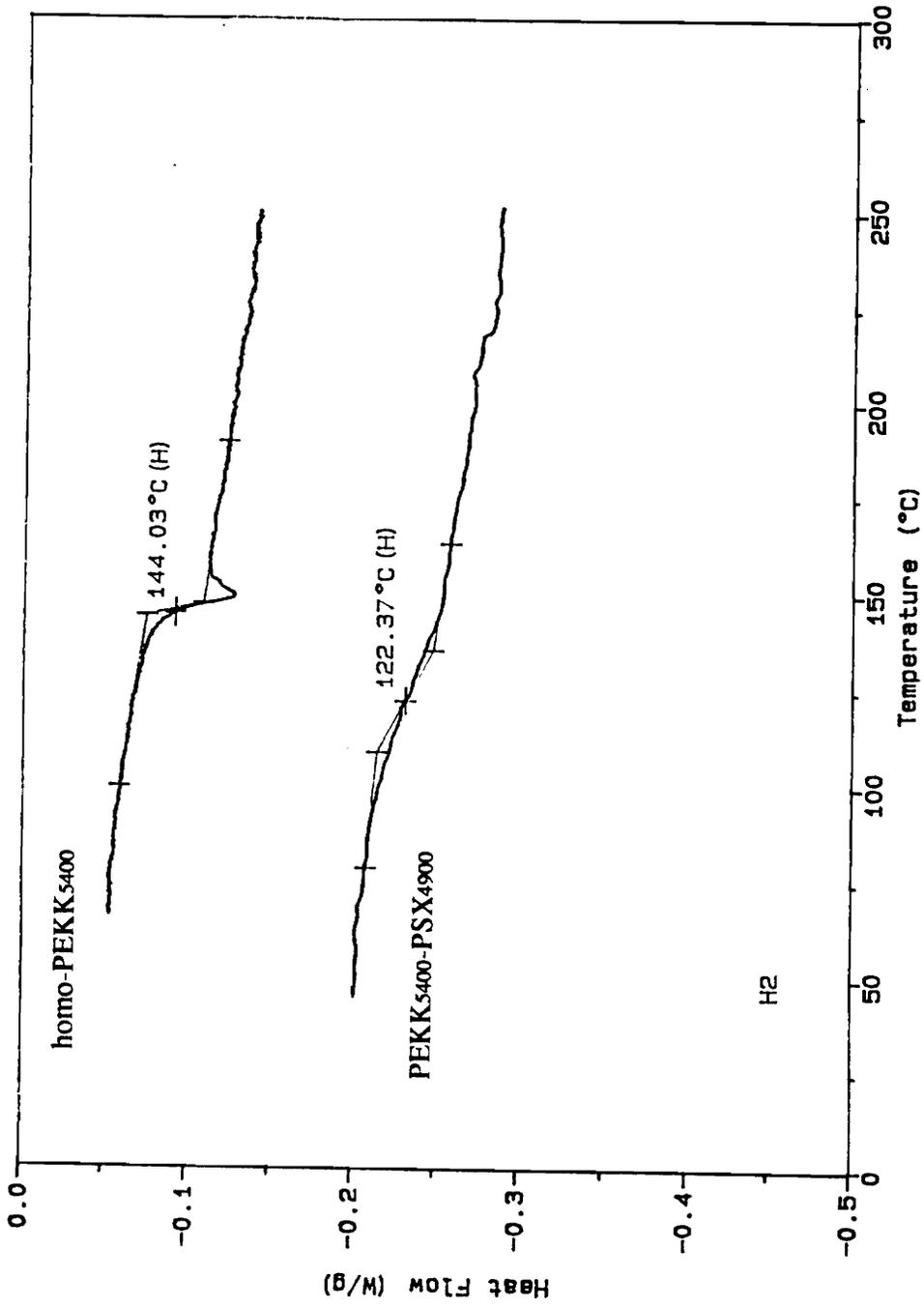


Figure 22. DSC thermograms of homo-PEKK₅₄₀₀ and perfectly alternating PEKK₅₄₀₀-PSX₄₉₀₀ segmented copolymer.

PEKK₅₄₀₀-PSX₄₉₀₀ copolymer was soluble in THF, chlorinated and amide solvents like the previous copolymers. Additionally, it was soluble in room temperature toluene for approximately 30 minutes, after which time it seemed aggregates of micelles formed, and the solution appeared as an opalescent gelled semi-solid. A transparent yellow film was solution-cast from chloroform, which to the touch felt waxy and very pliable (did not hold a crease). Upon stretching, the PEKK₅₄₀₀-PSX₄₉₀₀ film was distorted and did not possess noticeably elastic behavior.

9. Other One-step Syntheses

Using the same one-step method described above, several other perfectly alternating ETP-PSX copolymers were prepared. These were PI₅₅₀₀-PSX₄₉₀₀, PI₅₅₀₀-PSX₆₄₀₀, PI₅₅₀₀-PSX₉₁₀₀, PEKK₅₄₀₀-PSX₆₄₀₀, PEKK₅₄₀₀-PSX₉₁₀₀ and PEPO₆₅₀₀-PSX₃₂₀₀ copolymers. All reactions were run at 170°C to 175°C under nitrogen for 24 to 48 hours. Calculated from the total amount of monomers used, approximately three weight percent 2-OHpy was employed in each situation. *Ortho*-dichlorobenzene quantity varied such that 10 to 15 weight percent solids concentration was achieved, where PI-containing reactions seemed to be less likely to gel with lower solids content. Intrinsic viscosity, solubility and film-forming characterization results for each are listed in Table 20.

As the PSX segment length was increased, a trend in decreasing IV was noticed. Again, it was not clear as to whether or not the copolymer molecular weights were comparably as high as earlier copolymers. But, it was presumed that there was increased mobility in the polymer chain due to the long PSX segments causing lowered IV values.

Table 20. Characteristics of several perfectly alternating segmented copolymers.

Copolymer	$[\eta]_{\text{CHCl}_3}^{25^\circ\text{C}}$	Solubility			Film
		Amide	Chloro.	Toluene	
PI5500-PSX4900	0.482 dL/g	✓	✓	m	Tough, clear
PI5500-PSX6400	0.414 dL/g	✓	✓	m	Tough, clear
PI5500-PSX9100	0.237 dL/g	✓	✓	m	Weak, clear
PEKK5400-PSX6400	0.452 dL/g	✓	✓	m	Tough, clear
PEKK5400-PSX9100	0.434 dL/g	✓	✓	m	Weak, clear
PEPO6500-PSX3200	0.393 dL/g	✓	✓	X	Tough, clear

amide = NMP and DMAc Chloro. = *ortho*-dichlorobenzene and chloroform
 ✓ = soluble m = soluble for 30 minutes X = insoluble

All six copolymers were soluble in the five test solvents. Additionally, like the PEKK5400-PSX4900, copolymers containing PSX segments of 4900 g/mol and greater were initially soluble in room temperature toluene. The appearance of a gelled semi-solid after 30 minutes seemed to be aggregated micelles. Solution-cast films of varying apparent toughnesses were prepared from chloroform. All were transparent, pliable (did not hold a crease) and waxy to the touch, except for PEPO6500-PSX3200, which was transparent, creaseable and tough.

DSC data implied that neither the DuPont nor the Perkin-Elmer instruments were sensitive enough to detect upper and lower T_g values for any copolymers except PEKK5400-PSX9100. This was possibly attributed to the high siloxane content of the sample. Two scans run from -150°C to -50°C, quenched with liquid nitrogen in between, yielded at soft segment T_g at -122°C and broad crystallization temperature at -79°C (see Figure 23), both within expected temperatures [86]. Ideally, Dynamic Mechanical Thermal Analysis (DMTA) would have been sensitive enough to detect both upper and lower T_gs

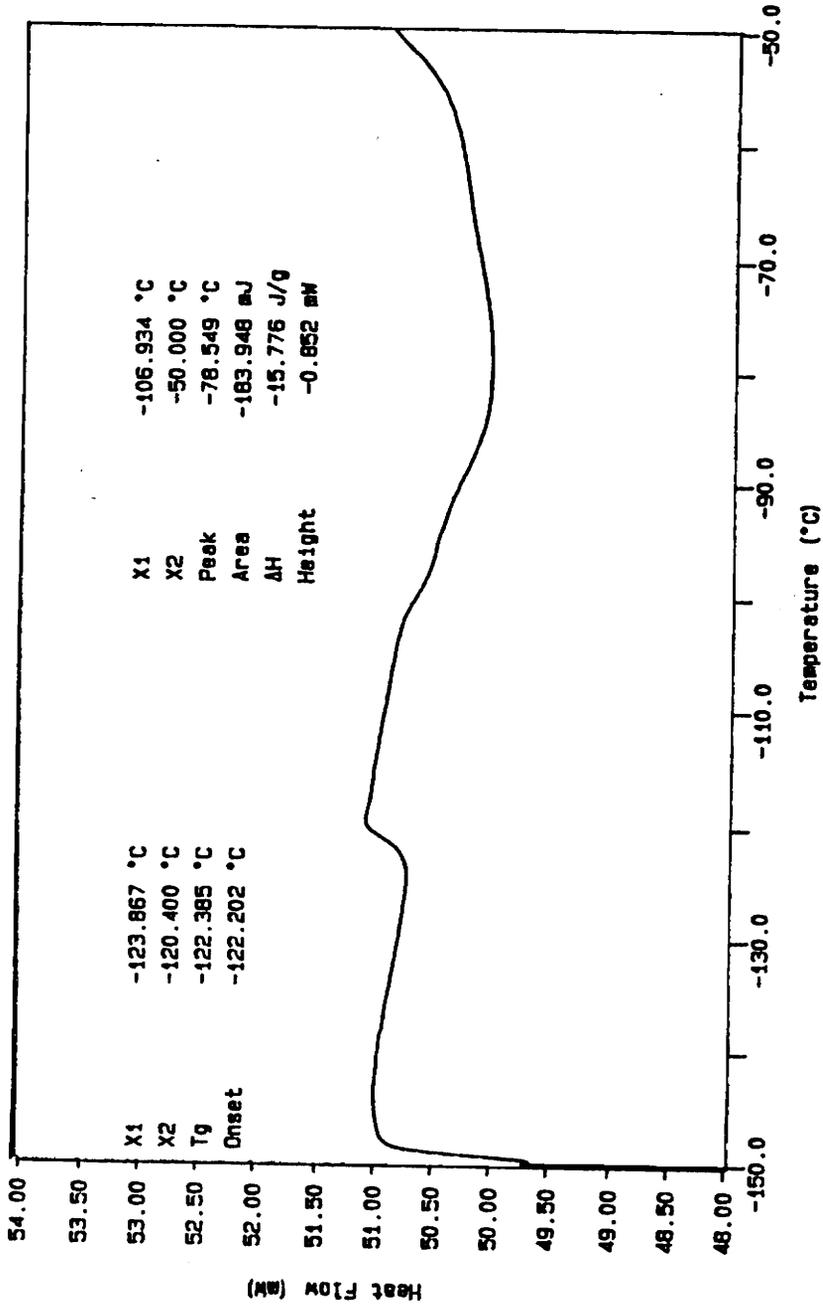


Figure 23. Sub-ambient DSC analysis for PEKK5400-PSX9100.

for the remaining copolymers. However, sample quantity was limited and inadequate for DMTA specimen preparation (see *Experimental* chapter for details) except for PEKK₅₄₀₀-PSX₂₀₀₀, as discussed later.

10. Synthesis of Perfectly Alternating PEKK₅₄₀₀-PSX₄₉₀₀ Segmented Copolymer of Controlled Molecular Weight

Through the use of phthalic anhydride as an endcapper, a PEKK₅₄₀₀-PSX₄₉₀₀ copolymer was controlled to 40,000 g/mol overall molecular weight. Utilizing a form of the Carothers equation, amounts of the three "monomers" -- anhydride, dianhydride and diamine -- were calculated as described in the *Background* chapter:

$$40,000 \text{ g/mol} / 10,259.96 \text{ g/mol per copolymer repeat unit} = 3.8986507$$

$$DP = 3.8986507$$

$$X_n = 2DP = 7.7973014$$

$$r = (X_n - 1) / (X_n + 1) = 6.7973124 / 8.7973014 = 0.7726576$$

arbitrarily chose to use 0.000995 mol (5.3895 g) PEKK₅₄₀₀, therefore
 $(0.000995)(0.7726576) = 0.0007688 \text{ mol}$ (3.1517 g) PSX₄₉₀₀ needed, and
 $\{[0.000995] - [(0.7726576)(0.0007688)]\} / 0.7726576 = 0.000519 \text{ mol}$

therefore, need 0.000519 mol (0.0769 g) phthalic anhydride.

Consequently, 5.3895 g (0.000995 mol) PEKK₅₄₀₀, 3.7518 g (0.000769 mol) PSX₄₉₀₀, 0.0782 g (0.000528 mol) phthalic anhydride and 0.2758 g (0.0029 mol, 3 w/w %) 2-OHpy were measured and transferred to the reaction vessel simultaneously. For 10 w/v percent solids, 91 ml dry *o*-dichlorobenzene was added to the flask. The mixture was immediately heated to 170°C and stirred under nitrogen for 48 hours, after which time the homogeneous solution was cooled, coagulated into methanol and dried as usual.

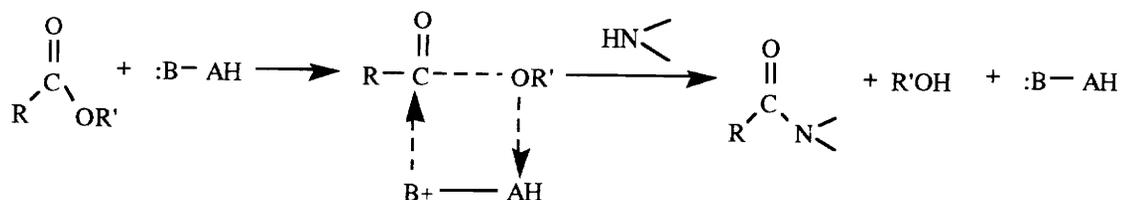
The fibers of deep yellow copolymer were analyzed by DSC, IV and GPC. Results

obtained by the DuPont showed a broad T_g at 139°C. Intrinsic viscosity was measured to be 0.329 dL/g for the controlled molecular weight copolymer. The uncontrolled perfectly alternating PEKK₅₄₀₀-PSX₄₉₀₀ segmented copolymer had an IV of 0.687 dL/g, approximately twice as high, indicating that (apparently) molecular weight to some extent was controlled by the inclusion of phthalic anhydride as a monofunctional endcapper. GPC was unsuccessful in obtaining molecular weight data for the copolymer. Both absolute measurements (via viscosity and universal calibration curve) and measurements against polystyrene standards were attempted, yielding fairly consistent <M_n> values of 12,600 g/mol and 12,200 g/mol, respectively. However, this corresponds to a DP of approximately 1.2. Because a fibrous, film-formable product was obtained, it was unlikely that even absolute GPC analysis is reliable. The hard and soft thermodynamically incompatible units of perfectly alternating segmented copolymers (such as PEKK-PSX) retain homopolymer hydrodynamic volumes, but GPC instrumentation cannot reliably accommodate these systems. Therefore, only qualitative conclusions can be abstracted from thermal and viscosity analyses as mentioned above.

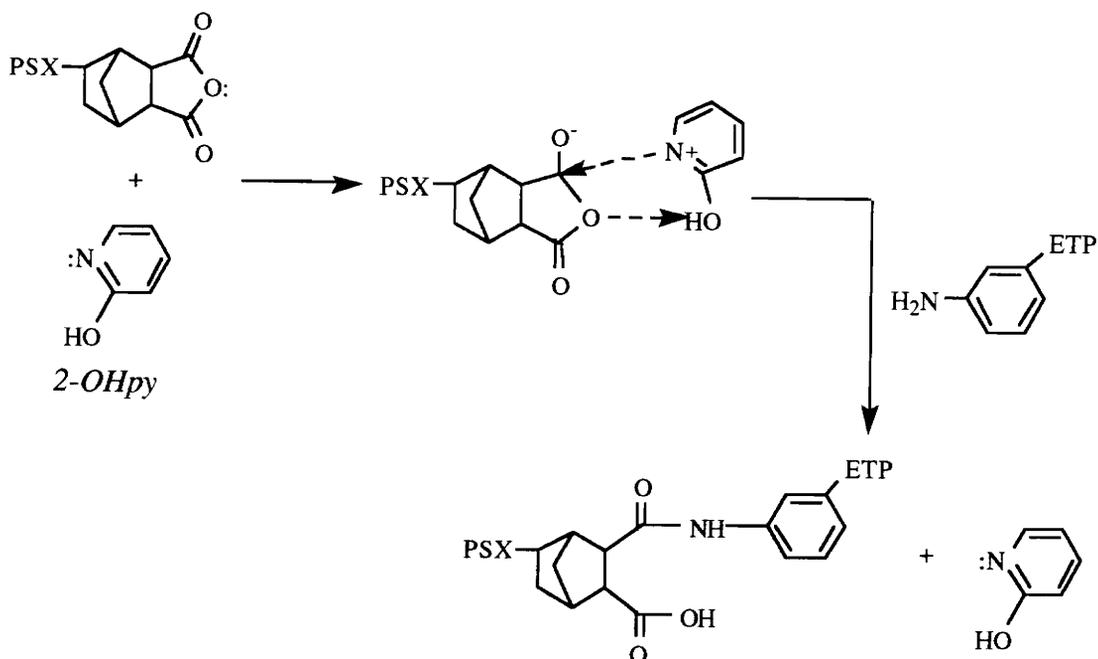
11. Suggested Mechanistic Pathway for Catalyst Action

Several early attempts at copolymerizations proved unsuccessful when 2-OHpy, a known condensation catalyst, was not employed. Following the reaction conditions stated in a paper published by Keohan and Hallgren of G. E. [59], three weight percent 2-OHpy was needed in order to form the poly(amic acid) prepolymer in the copolymerization-by-imidization reaction (see Scheme 27 of *Experimental* chapter). Scarcely published literature shows that the mechanistic pathway has not been confirmed, but a single proposal has been published without dispute [84]. Formation of amides and peptides by aminolysis of an ester were noted to be accelerated when in the presence of a

bifunctional catalyst possessing both a mildly acidic and a mildly basic moiety. Mutual accessibility of those groups possibly allowed for a cyclic transition state and concerted displacement, as suggested in Scheme 31 and Scheme 32 for the polyimide-type copolymerization.



Scheme 31. Suggested mechanistic pathway showing bifunctional catalyst action.



Scheme 32. Proposed mechanism of copolymerization involving 2-OHpy catalyst.

Although literature has not been published regarding the proof of this mechanism, a 1988 review article [85] stated that such catalysts have been commonly used for the preparation of carboxylic esters and amides by means of activation of the carboxylic acids, thus

supporting this route.

Generally observed during these copolymerizations was quick compatibility between the hard and soft segments. For reactions lacking the catalyst, the slightest addition of PSX solution to diamine solution resulted in an almost immediate precipitation of amine oligomer, even at elevated temperatures ($>140^{\circ}\text{C}$). When the catalyst was used, the full amount of both oligomers could be introduced to the reaction flask, and a homogeneous solution was readily achievable.

Because extensive studies were not undertaken on the catalyst, a basic conclusion is that the complex formed acted as a compatibilizing agent in the first step of solution imidization. Several trial reactions were run using the catalyst in typical room temperature poly(amic acid) reactions. In all cases, however, the diamine oligomer precipitated. Copolymerizations did not stay homogeneous until the the reaction solution was heated to approximately 100°C or more. Assuming that some cyclodehydration must occur at these temperatures, molecular weight data for pure poly(amic acid) could not be determined.

Later copolymerizations were run at the final cyclodehydrating temperature of 170°C during the entire course of the reaction. Although this was considered a one-step approach, in actuality it was the two-step method in which poly(amic acid) formation was immediately followed by imide formation. Because the catalyst was necessary and because the catalyst did not act in the cyclodehydrating step, the reaction must first go through a poly(amic acid) stage. Additionally, because the final copolymer was soluble in the reaction medium, imidization was possible at modest temperatures reducing chances of isoimide formation.

12. Understanding the Siloxane Incorporation Discrepancy as Determined by ¹H NMR Results for PEKK5400-PSX2000, PES5700-PSX2000 and PI5500-PSX1400 Copolymers

It was assumed that each of these perfectly alternating copolymers was very surface active. By continuously diluting a ¹H NMR sample from 10 weight percent to 0.125 weight percent copolymer in CDCl₃, calculations for siloxane content showed a decreasing content trend with lower concentrations, thus proving that micelles were forming. Therefore, due to micelle formation, solution ¹H NMR could not be accurately used to calculate percent PSX segment incorporation. Two solutions to this problem were used to yield very appealing positive results. Elemental silicone analysis and solid state ¹³C NMR (see *Experimental* chapter for details on sample preparation and calculations) determined that 100 mole percent of the PSX charged to the flask was successfully incorporated into the copolymer in each case. Results of each method can be seen in Tables 21 and 22, along with the solid state ¹³C NMR spectra of PEKK5400-PSX2000 and PI5500-PSX1400 copolymers in Figures 24 and 25, respectively.

Table 21. Mole percent siloxane incorporation determined by various methods.

Copolymer	¹ H NMR *	¹³ C NMR [‡]	Si Elemental Analysis	C Elemental Analysis
PEKK5400-PSX2000	74 %	100 %	96 %	100 %
PES5700-PSX2000	74	--	93	100
PI5500-PSX1400	81	100	91	100

* CDCl₃ solution

[‡] solid state

Table 22. Elemental analysis and theoretical atomic contents of three perfectly alternating segmented copolymers.

Copolymer : method	% C	% H	% N	% S	% Si	
PEKK ₅₄₀₀ -PSX ₂₀₀₀	Theoretical	69.92	5.83	0.46	---	8.91
	Elemental Analysis	70.36	5.84	0.42	---	8.51
PES ₅₇₀₀ -PSX ₂₀₀₀	Theoretical	63.74	5.71	0.44	5.38	8.51
	Elemental Analysis	63.82	5.82	0.35	5.43	7.89
PI ₅₅₀₀ -PSX ₁₄₀₀	Theoretical	70.68	5.59	3.91	---	5.97
	Elemental Analysis	70.63	5.71	3.67	---	5.41

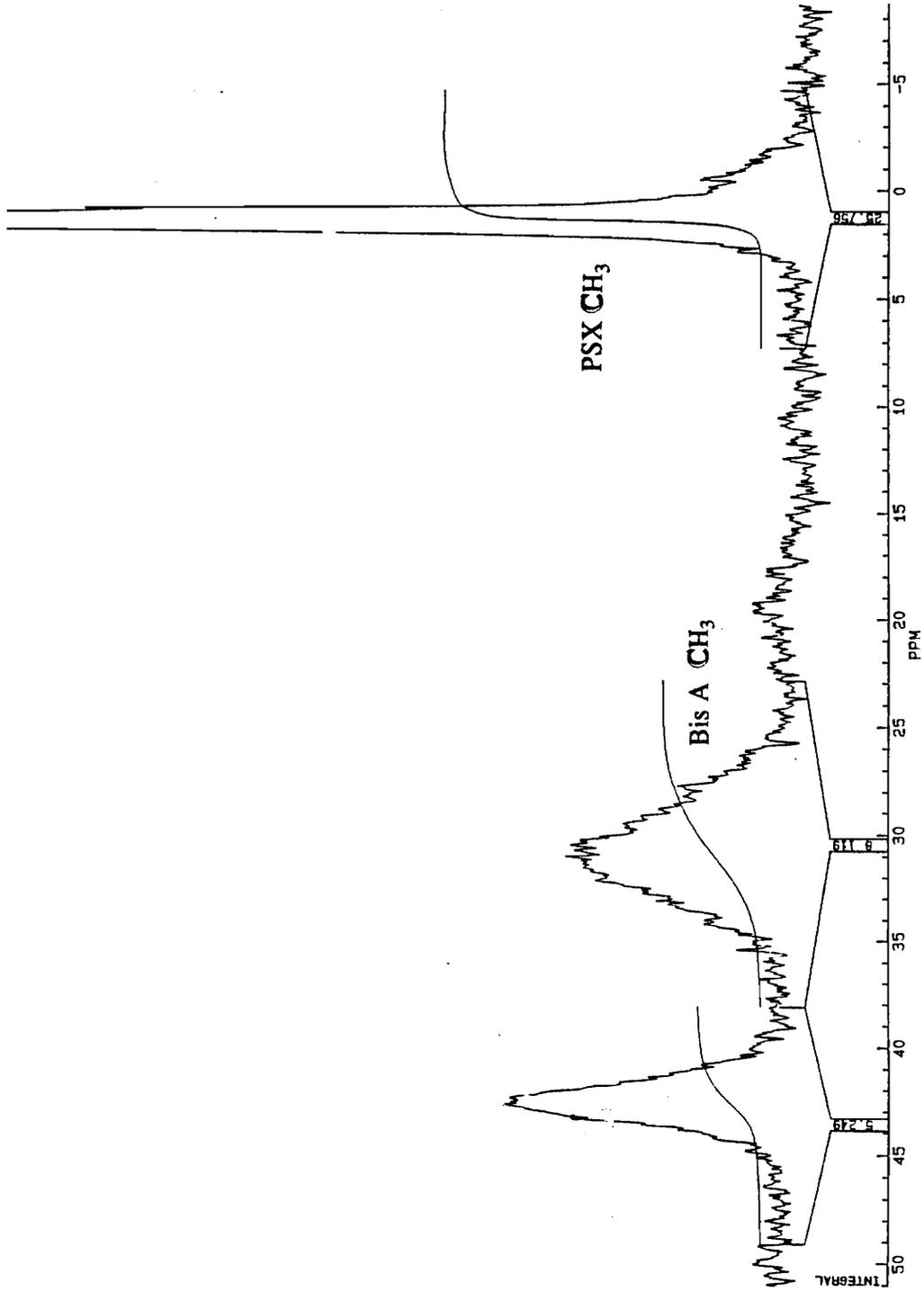


Figure 24. Solid state ^{13}C NMR spectrum of perfectly alternating PEKK5400-PSX2000 segmented copolymer

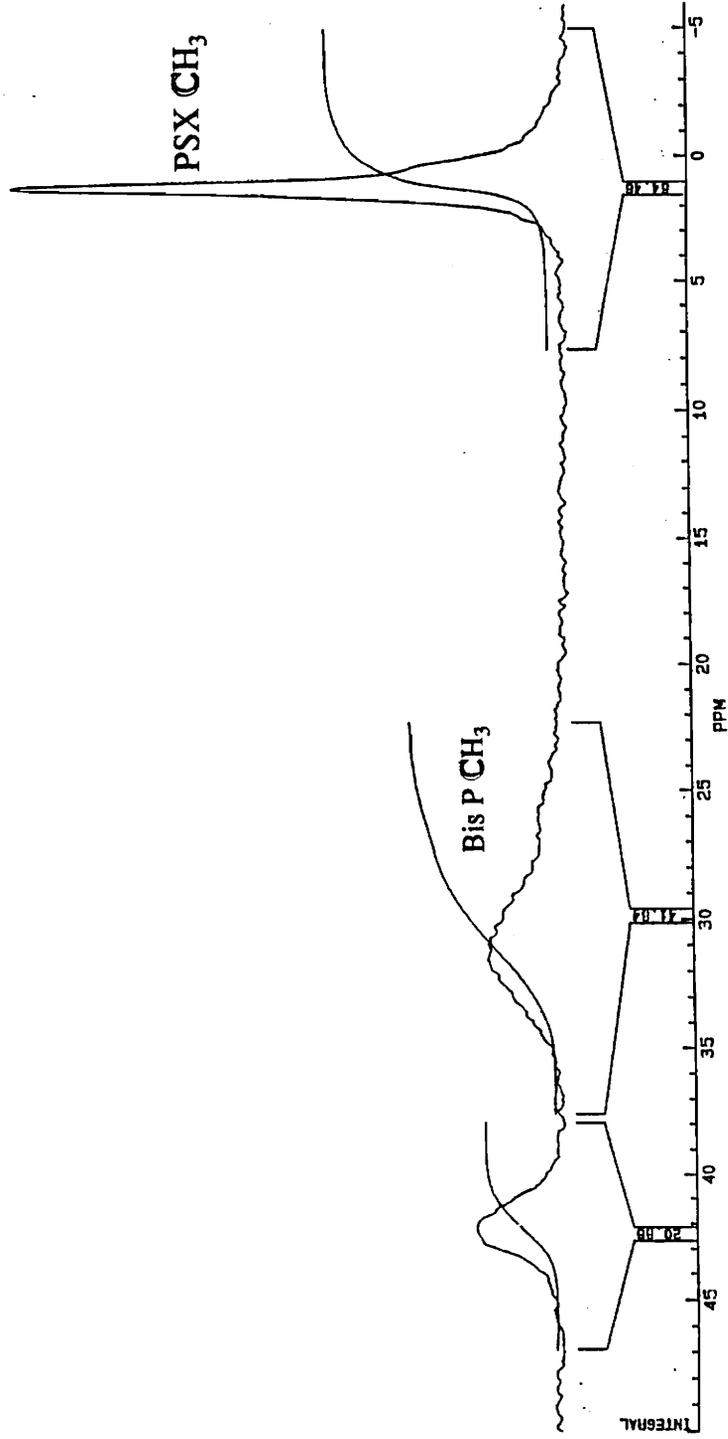


Figure 25. Solid state ^{13}C NMR spectrum of perfectly alternating PI500-PSX1400 segmented copolymer

13. Determination of Upper and Lower Tgs of PEKK5400-PSX2000 Through Dynamic Mechanical Thermal Analysis (DMTA)

PEKK5400-PSX2000 was kindly analyzed by Mr. George Dallas for upper and lower Tg values with a Polymer Laboratories DMTA. An adequate amount of this copolymer was synthesized making DMTA possible. The sample was prepared by hydraulically pressing between teflon sheets and ferrotype plates approximately 10 g of copolymer fibers. Sustaining high pressure at 150°C for approximately 3 minutes resulted in a translucent brown disk 1 mm thick. From this, a rectangular-shaped specimen measuring 1 cm wide by 3 cm long was cut with scissors.

An upper Tg of 130°C and a lower Tg of -127°C were found upon analysis by DMTA. The upper Tg value determined by the DuPont DSC instrument was 134°C and was in good agreement with DMTA values. As it was stated earlier, the Perkin-Elmer DSC instrument was unable to detect a PSX transition for the sub-ambient scan. Regarding the actual data, shown in Figure 26, one can see that during the DMTA experiment the sample slipped in the clamps during a short period. This is marked by the vertical displacement of the baseline between 0°C and 70°C on the DMTA plot. Because it did not interfere with either Tg, the data was honored. It should also be noted that transitions were still rather broad.

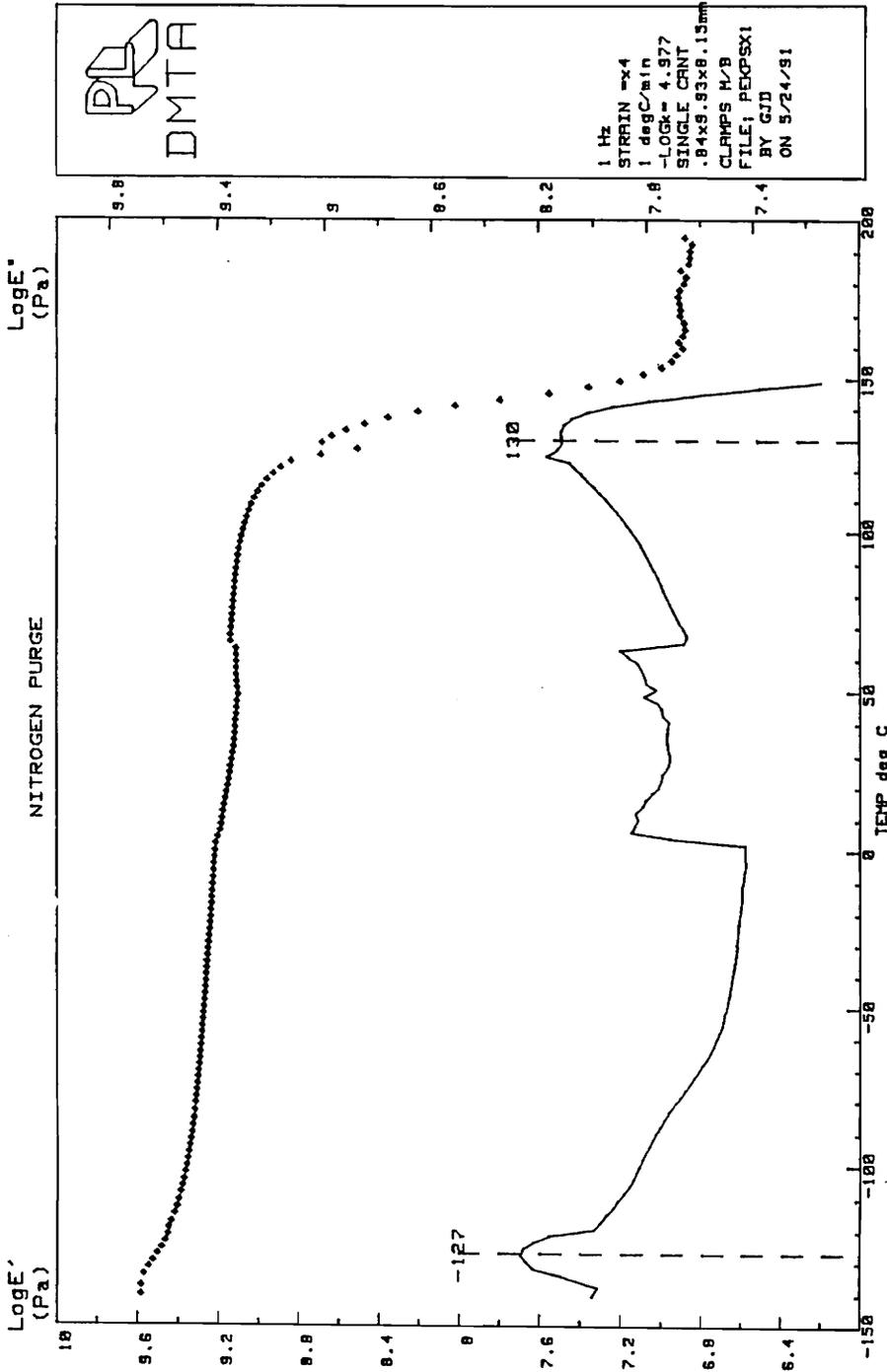


Figure 26. DMTA plot of perfectly alternating PEKK₅₄₀₀-PSX₂₀₀₀ segmented copolymer

14. Thermal Stability and Char Yield as a Function of Siloxane Segment Length in a Series of Perfectly Alternating PEKK₅₄₀₀-PSX Segmented Copolymers

Thermal stability and char yield were studied by Thermogravimetric Analysis (TGA) for three copolymers: PEKK₅₄₀₀-PSX₁₄₀₀, PEKK₅₄₀₀-PSX₄₉₀₀ and PEKK₅₄₀₀-PSX₉₁₀₀. Randomly segmented PI-PSX copolymers reported by Arnold, *et al.* [76, 78] exhibited higher thermal stabilities at lower siloxane incorporation, but lower char yields at lower siloxane incorporation. Equally so, lower thermal stabilities and higher char yields were achieved when the PSX content was increased. In this series of perfectly alternating PEKK₅₄₀₀-PSX segmented copolymers, results were exemplary. The char yield levelling was thought to be due to volatilization of small cyclic dimethylsiloxane compounds (such as D₃, D₄, D₅, *etc.*) that do not form as highly in the lower siloxane-content copolymers. The trend of thermal stabilities and char yields is provided in Table 23 and Figure 27.

Table 23. Thermal stability and char yield as a function of weight percent siloxane content for a series of perfectly alternating PEKK₅₄₀₀-PSX segmented copolymers.

Copolymer	Weight percent siloxane	5% weight loss (°C)	Char yield at 800°C
PEKK ₅₄₀₀ -PSX ₁₄₀₀	20.4 %	464	12 %
PEKK ₅₄₀₀ -PSX ₄₉₀₀	47.4 %	444	22 %
PEKK ₅₄₀₀ -PSX ₉₁₀₀	62.7 %	435	25 %

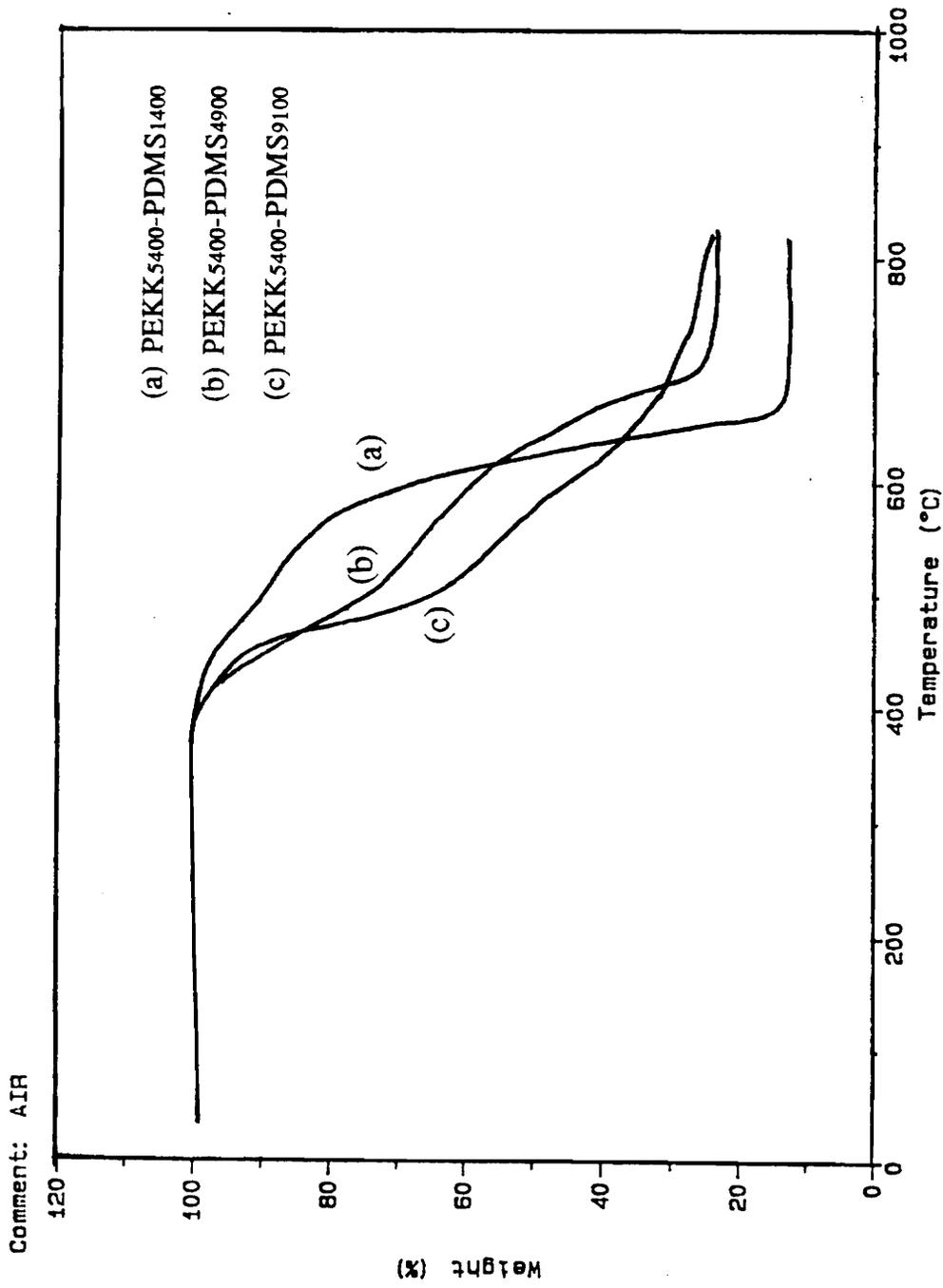


Figure 27. Thermogravimetric analysis of a series of perfectly alternating PEKK₅₄₀₀-PSX segmented copolymers with various siloxane segment lengths.

15. Mechanical Properties of PEKK₅₄₀₀-PSX₂₀₀₀ Obtained Through Stress-Strain Measurements

Using the remainder of the 1 mm thick disk of copolymer compression-molded for the DMTA specimen, three dogbone-shaped samples were cut with a metal die. Sample cutting and measurements were performed by Mr. Saikat Joardar and are discussed in the *Experimental* chapter.

Because the film was non-uniform, two of the three samples did not break in the center as expected; thus, only qualitative conclusions could be drawn. Young's Modulus measurements, however, were more reliable, as all three values were within eight percent of each other (see Table 24). For the sample that broke in the expected portion of the dogbone, strain at break was 15 percent and stress at yield was 7400 psi. Values obtained by Dr. Jim Senger for a high molecular weight homo-PEKK show break yield was 110 percent, yield stress was 10,000 psi and modulus was 350 ksi [87].

Table 24. Young's moduli of compression-molded samples of perfectly alternating PEKK₅₄₀₀-PSX₂₀₀₀ segmented copolymer.

Specimen	Young's Modulus	Average
1	310 ksi	290 ksi
2	300 ksi	
3	270 ksi	

16. Morphological Investigations by Transmission Electron Microscopy (TEM)

Solution-cast films approximately 0.1 mm thick were given to Mr. Steve McCartney for TEM sample preparation and measurement, as described in the *Experimental* chapter. Three inch - by - four inch negatives were obtained at magnifications of 105,000 and 230,000. Eight inch-by-ten inch, black-and-white photographic enlargements were made, resulting in modified magnifications of roughly 278,000 and 608,000. Microphase separation was seen in all copolymers, as evidenced by the domains visible in the actual micrographs in Figures 28 through 36. In all photographs, the dark siloxane-rich regions can be distinguished from the lighter engineering thermoplastic areas.

Comparing PEKK₅₄₀₀-PSX₂₀₀₀ (21 w % PSX), PES₅₇₀₀-PSX₂₀₀₀ (26 w % PSX) and PI₅₅₀₀-PSX₂₀₀₀ (27 w % PSX) (Figures 28-30 on the following page), the sulfone-containing copolymer was the most microphase separated while the diketone-containing copolymer was the least. This can be noted by the smaller, more spherical dark siloxane regions of the PES₅₇₀₀-PSX₂₀₀₀ when compared to the PEKK-based copolymer. From this, it can be concluded that the thermoplastic was the continuous phase, as would be expected at those weight concentrations.

Following the same trend, it was also evident that the perfectly alternating PI₅₅₀₀-PSX₄₉₀₀ (47 w % PSX) segmented copolymer was more microphase separated than the PEKK₅₄₀₀-PSX₄₉₀₀ (48 w % PSX) analog, also marked by the more spherical pale imide regions in the micrograph of PI₅₅₀₀-PSX₄₉₀₀ (Figures 31 and 32). It can be seen that phase inversion has occurred in this series since the continuous phase is the siloxane (dark).

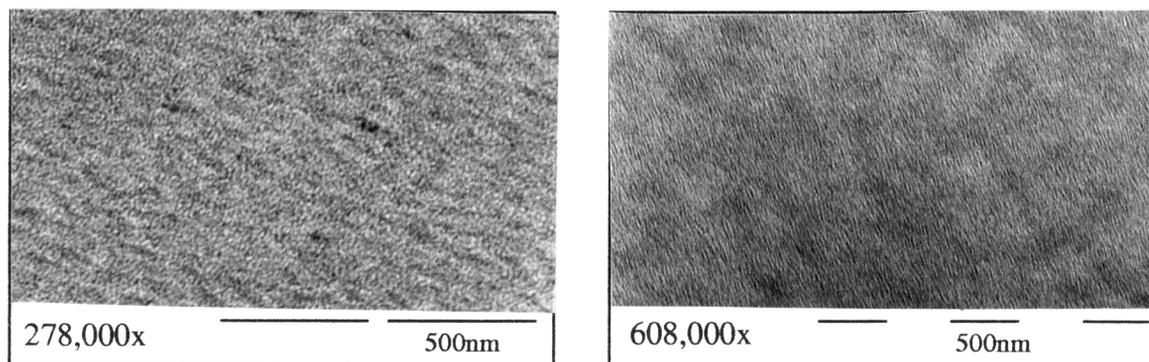


Figure 28. TEM micrographs of PEKK₅₄₀₀-PSX₂₀₀₀ at two magnifications.

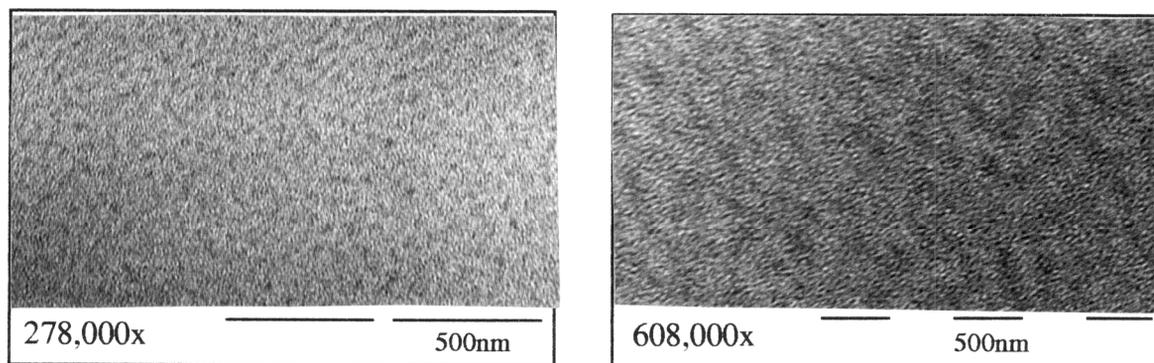


Figure 29. TEM micrographs of PES₅₇₀₀-PSX₂₀₀₀ at two magnifications.

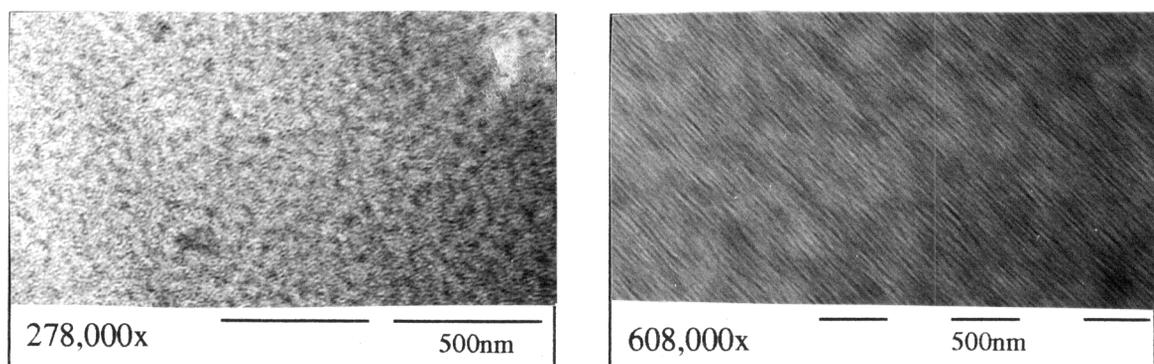


Figure 30. TEM micrographs of PI₅₅₀₀-PSX₂₀₀₀ at two magnifications.

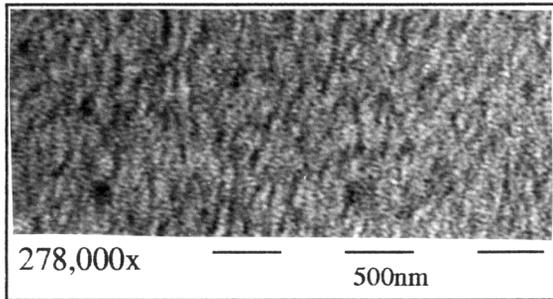


Figure 31. TEM micrograph of PEKK₅₄₀₀-PSX₄₉₀₀ at 278,000x.

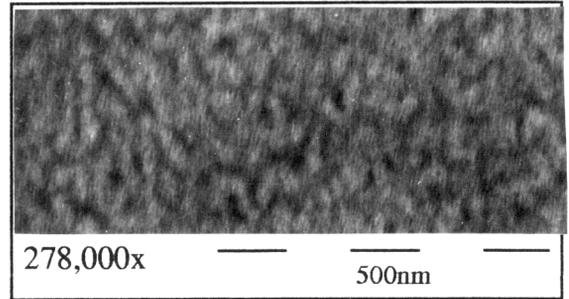


Figure 32. TEM micrograph of PI₅₅₀₀-PSX₄₉₀₀ at 278,000x.

As mentioned above, phase inversion could be observed when comparing PEKK₅₄₀₀-PSX₁₄₀₀ (21 w % PSX) with PEKK₅₄₀₀-PSX₄₉₀₀ (48 w % PSX) (Figures 33 and 34).

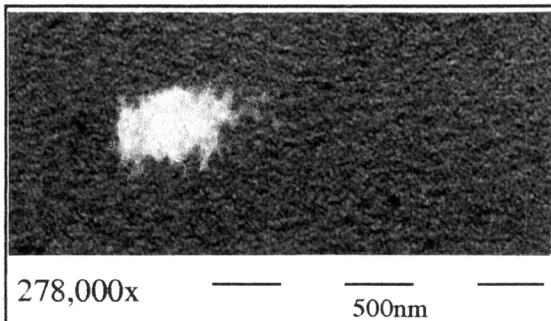


Figure 33. TEM micrograph of PEKK₅₄₀₀-PSX₁₄₀₀ at 278,000x.

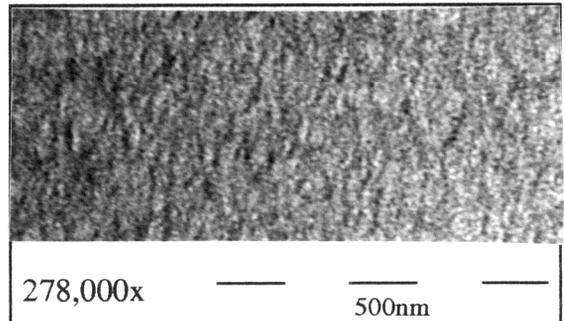


Figure 34. TEM micrograph of PEKK₅₄₀₀-PSX₄₉₀₀ at 278,000x.

Moreover, for both PEKK-containing copolymers, sphericity was difficult to perceive as the micrographs showed slightly striated regions. PEKK copolymers with longer siloxane segments --6400 g/mol and 9100 g/mol-- yielded "brain" (lamellar) morphology which indicates a higher degree of phase mixing (see Figures 35 and 36). This can account for the broad upper and lower T_g values and subsequent difficulty in obtaining such thermal data by DSC.

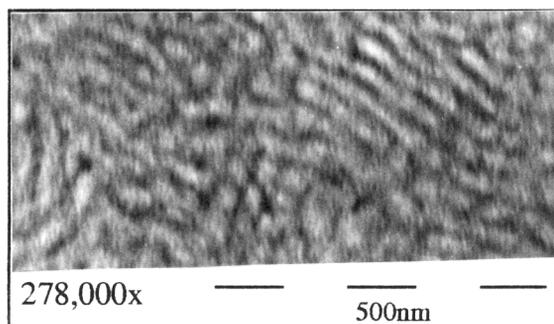


Figure 35. TEM micrograph of PEKK₅₄₀₀-PSX₆₄₀₀ at 278,000x.

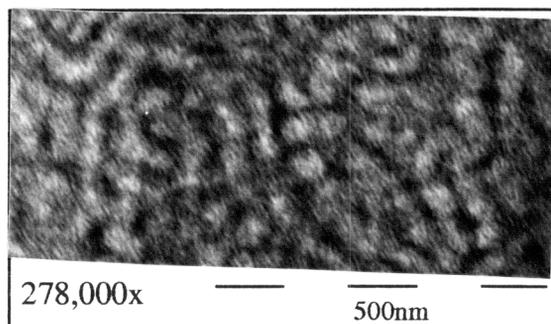


Figure 36. TEM micrograph of PEKK₅₄₀₀-PSX₉₁₀₀ at 278,000x.

Correlation could not be made between the DSC and TEM results regarding the significant reduction in upper T_g observed in the PI-, PES- and PEPO-based copolymers (see Table 25). A significant lowering should have resulted due to a large degree of phase mixing. While the micrographs did not show well-defined spheres, the degree of phase mixing implied by DSC was perhaps greater than that marked by TEM. Conversely, PEKK-based copolymers exhibited much more phase mixing (than the other copolymers) by TEM analysis, whereas hard segment glass transitions obtained by DSC showed at the most a 15°C depression. However, it should be stressed that many thermal transitions observed by DSC were very broad and weak; and since transitions were manually marked off, upper T_g values could only be roughly estimated.

Measured manually from TEM micrographs, interdomain spacings were approximately 200 Å for copolymers with siloxane segments of 4900 g/mol or shorter. These values were on the same order of magnitude as those found by Hedrick [86] for some perfectly alternating poly(arylene ether sulfone) - PSX segmented copolymers. Additionally, like Hedrick's SAXS data, good agreement with SAXS values obtained for these perfectly alternating copolymers was observed.

Table 25. Upper Tg depressions observed by DSC for all perfectly alternating segmented copolymers characterized.

Copolymer	Hard Segment Tg (°C)	Upper Tg (°C)	Tg depression (°C)
PEKK ₅₄₀₀ -PSX ₁₄₀₀	144	135	9
PEKK ₅₄₀₀ -PSX ₂₀₀₀	144	134	10
PEKK ₅₄₀₀ -PSX ₄₉₀₀	144	129	15
PEKK ₅₄₀₀ -PSX ₆₄₀₀	144	131	13
PEKK ₅₄₀₀ -PSX ₉₁₀₀	144	138	6
PI ₅₅₀₀ -PSX ₁₄₀₀	225	210	15
PI ₅₅₀₀ -PSX ₂₀₀₀	225	195	30
PI ₅₅₀₀ -PSX ₄₉₀₀	225	215	10
PI ₅₅₀₀ -PSX ₆₄₀₀	225	---	---
PI ₅₅₀₀ -PSX ₉₁₀₀	225	---	---
PES ₅₇₀₀ -PSX ₂₀₀₀	165	141	24
PEPO ₆₅₀₀ -PSX ₃₂₀₀	206	178	28

17. Small Angle X-ray Scattering (SAXS) Results for PEKK₅₄₀₀-PSX₁₄₀₀, PEKK₅₄₀₀-PSX₂₀₀₀, PI₅₅₀₀-PSX₁₄₀₀ and PI₅₅₀₀-PSX₄₉₀₀

To obtain interdomain spacings for the phases, SAXS samples were prepared from thin, chloroform-cast films and analyzed by Dr. David Rodriques, detailed in the *Experimental* chapter. Smear plots showed that interdomain spacings varied from 175 Å for the shorter siloxane segments to 274 Å for the longer siloxane segments (listed in Table 26), as observed in earlier related research [86] and in agreement with approximations obtained in TEM micrographs.

Table 26. Interdomain spacing determined by SAXS for several perfectly alternating segmented copolymers.

Copolymer	Interdomain Spacing (Å)
PEKK ₅₄₀₀ -PSX ₁₄₀₀	175
PEKK ₅₄₀₀ -PSX ₂₀₀₀	200
PEKK ₅₄₀₀ -PSX ₄₉₀₀	274
PI ₅₅₀₀ -PSX ₁₄₀₀	183
PI ₅₅₀₀ -PSX ₄₉₀₀	255

Summary

Novel perfectly alternating segmented copolymers have been synthesized from norbornane anhydride-terminated poly(dimethylsiloxane)s and various amine-terminated engineering polymers, including poly(arylene ether) and polyimide oligomers. Preparation and characterization of each homopolymer component was necessary prior to copolymerization in order to obtain a perfectly alternating architecture.

Hydrosilylation of norbornene anhydride with 1,1,3,3-tetramethyldisiloxane in a two-to-one molar ratio yielded the "monofunctional" endcapping species utilized in preparation of telechelic poly(dimethylsiloxane) oligomers. Several controlled molecular weight norbornane anhydride-terminated poly(dimethylsiloxane)s were synthesized by appropriately varying the ratio of endcapper to octamethylcyclotetrasiloxane (D4) employed in these triflic acid-catalyzed cationic ring-opening equilibrations. Both molecular weight and difunctionality were confirmed for all norbornane anhydride-containing species by an indirect potentiometric endgroup titration method developed for this the research.

Furthermore, controlled molecular weight amine-terminated engineering thermoplastic homopolymers were synthesized using one of two polymerization routes: nucleophilic aromatic substitution for poly(arylene ether)s and solution imidization for the polyimide. Hard segment molecular weights, predetermined by calculations based on the Carothers equation, were obtained by conventional titration procedures.

Linking these thermodynamically incompatible systems together with an imide group, copolymerization was accomplished through solution imidization techniques. Modification of established solution imidization procedures was necessary as component immiscibility led to macrophase separation within the reaction vessel, and thus low extent of conversion. By incorporation of a bifunctional condensation catalyst,

2-hydroxypyridine, high molecular weight copolymers were achieved; however, it was not determined exactly how the catalyst acted in these systems. In addition, a one-step method was devised in which all reactants were charged to the copolymerization vessel initially, along with a single solvent that served as both a reaction medium and dehydrating solvent.

All perfectly alternating segmented copolymers prepared demonstrated surfactant qualities, observed through solution ^1H NMR. Due to this fact, solution analysis was inappropriate for calculation of siloxane incorporation. Elemental silicon analyses and solid state ^{13}C NMR indicated that at least 91 mole percent of siloxane charged was incorporated into the final copolymers after purification, thus assessing high extents of conversion. Visually, these perfectly alternating segmented copolymers were very fibrous, therefore confirming high molecular weight achievement.

As evidenced by both DSC and TEM analyses, these copolymers exhibited microphase separation with some phase mixing. TEM micrographs showed that phase separation was greatest in the poly(arylene ether sulfone)-containing copolymer, less in the polyimide analog, and least in the poly(arylene ether ketone ketone) system. Thermal data indicated that glass transitions for both segments were observed. However, these transitions were often broad and depressed as segment sizes increased (especially noticed in the ketone-containing copolymers), revealing that phase mixing occurred to some extent. A series of poly(arylene ether ketone ketone)-poly(dimethylsiloxane) copolymers in which the siloxane segment length was varied displayed striated to lamellar morphologies in TEM micrographs.

Interdomain spacings were found to range from 175Å to 275Å by SAXS for copolymers in which siloxane segment lengths were equal to or less than that of the hard segments. Approximated values manually measured in TEM micrographs showed good agreement.

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