POLYDIMETHYLSILOXANE CONTAINING BLOCK COPOLYMERS:

SYNTHESIS AND CHARACTERIZATION OF ALTERNATING POLY(ARYLENE ETHER PHOSPHINE OXIDE)-b-SILOXANE AND SEGMENTED NYLON 6,6 –b-SILOXANE COPOLYMERS

by

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Dissertation submitted to the Faculty of the
Virginia Polytechnic Institute and State University
In partial fulfillment of the requirements for the degree of
DOCTOR OF PHILOSOPHY
in
Chemistry

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July 2, 2001
Blacksburg, Virginia

Keywords: Polydimethylsiloxane, Polyarylene Ether, Phenyl Phosphine Oxide, Polyamide, Nylon 6,6, Block Copolymer, Fire Resistance, Optical Materials, Nanoparticles

POLY(DIMETHYLSILOXANE) CONTAINING BLOCK COPOLYMERS: SYNTHESIS AND CHARACTERIZATION OF ALTERNATING POLY(ARYLENE ETHER PHOSPHINE OXIDE)-B-SILOXANE AND SEGMENTED NYLON 6,6-B-SILOXANE COPOLYMERS

W. David Polk

(ABSTRACT)

Two novel classes of siloxane containing, organic-inorganic block copolymers were prepared using different synthetic approaches. The first copolymers were alternating poly(arylene ether phosphine oxide)-poly(dimethylsiloxane) systems, prepared via oligomeric silylamine-hydroxyl reactions. Secondly, segmented nylon 6,6-poly(dimethylsiloxane) block copolymers were synthesized via a non-aqueous adaptation of the “nylon 6,6 salt” hydrolytic polyamidization, using bis(aminopropyl) dimethylsiloxane oligomer as a co-reactant.

Three series of “perfectly” alternating block copolymers were produced from well characterized hydroxyl-terminated poly(arylene ether phosphine oxide) and dimethylamine-terminated poly(dimethylsiloxane) oligomers, in order to investigate both block length and chemical composition effects. Copolymerization in chlorobenzene resulted in high molecular weight materials capable of forming optically clear, nanophase separated films, which displayed unusual morphologies and good mechanical strength. Thermal gravimetric analysis showed high thermo-oxidative stability and increasing char yield with increasing siloxane content. Additional thermal and mechanical investigations provided evidence of selective phase mixing, particularly at shorter block lengths. Surface analysis showed an enrichment of the siloxane blocks at the air-polymer interface in comparison to the bulk state. This behavior increased in proportion to the length of the parent siloxane oligomers. Evaluation of selected optical properties, e.g., refractive indices, revealed linear trends resulting in values of compositionally weighted averages.

Conversely, a series of nylon 6,6-siloxane copolymers were produced from the polycondensation of preformed propylamine-terminated poly(dimethylsiloxane)s, solid nylon 6,6 salt and a corresponding amount of adipic acid to afford siloxane-amide semi-crystalline copolymers with siloxane content ranging from 10 to ~45 wt%. The characterization of high molecular weight and covalent siloxane-amide linkages was hindered by insolubility. For example, crystallinity of the nylon 6,6 precluded the use of common solution techniques, while the susceptibility of the siloxane blocks towards ionic redistribution prevented the use of strongly acidic solvents. However, development of a novel analytical technique using solid state ^{13}C NMR and liquid–solid extraction provided evidence for the presence of covalent bonding between the dissimilar oligomer chains. Thermal gravimetric analysis of resultant copolymers revealed an increase in char yield with increasing siloxane content, a preliminary indicator of increased fire resistance, which was supported by subsequent qualitative Bunsen burner observations. Differential scanning calorimetry showed retention of the polyamide crystalline melt with levels of siloxane incorporation of up to 45 weight %.

In conclusion, two novel classes of polydimethylsiloxane containing block copolymers have been successfully synthesized, despite the complications created as a result of the polar/non-polar interactions developed between a semi-inorganic polydimethylsiloxane and the hydrocarbon based polyarylene ethers and nylon 6,6.

Acknowledgements

First and foremost, I would like to thank my advisor, Dr. James E. McGrath, for all of his support and guidance throughout my education at Virginia Tech. Words cannot express how much I have gained his wisdom, as well as from the many learning opportunities he afforded me during my tenure. Additionally, I would like to thank my graduate committee, Dr. Judy S. Riffle, Dr. Alan R. Schultz, Dr. John G. Dillard and Dr. Paul A. Deck, and all of the faculty with whom I have interacted, for without their insight, patience, and helpful suggestions that have shaped my development as a scientist, this thesis would not have been possible. Likewise, I must express a great deal of gratitude to Dr. Kay Turner, Dr. Jerry Adduci, and the Chemistry Faculty of the Rochester Institute of Technology. Their collective vision, which saw potential in a sophomore, gave me my first taste of research, instilled in me the desire to truly understand reactions atomistically instead of simply performing them.

I am indebted to many colleagues dispersed throughout the Virginia Tech Polymer Community -- each for multiple reasons. Those who gave the greatest direct assistance in the acquisition of data for this dissertation include Matt O'Sickey, Dave Godshall, Emmet O'Brien, Tom Glass, Steve McCartney and Dr. Y.S. Kim. Also, many thanks are owed to my former fellow graduate students and post-docs of the McGrath group, from whom I have learned so much. In particular, I am grateful to Dr. M. Sankarapandian, Dr. H. Shobha, Dr. Feng Wang, and Dr. Sue Mecham, who helped refine my synthesis techniques; and my fellow labmates, Dr. Jeff Mecham, Mike Hickner, and William Harrison, whose camaraderie and advice provided inspiration when obstacles arose.

Much appreciation is due to the secretaries, Millie Ryan, Esther Brann, Joyce Moyer, Angie Flynn, and Laurie Good; the McGrath Group would simply not function without them.

However, my deepest gratitude must to go to my parents, for encouraging my curiosity, instilling a thirst for knowledge, and infusing in me the perseverance that has enabled me to attain all that I have accomplished.

Table of Contents

List of Figures

List of Schemes

List of Tables

1 Introduction

The research described in this thesis is an exploration of the benefits of block copolymerization via the incorporation of three materials; poly(arylene ether phenylphosphine oxide) **1**, poly(dimethylsiloxane) **2**, and polyhexamethylene adipamide (nylon 6,6) **3**. These three materials have little in common. In fact, they are so different from one another that they do not even share the same physical form at room temperature. The first is a transparent, completely amorphous glassy solid, the second is an oily liquid, and the third is a semi-crystalline polymer capable of high degrees of crystallinity. Thus, some justification of how these three vastly differing materials can be the basis for a systematic scientific study is warranted.

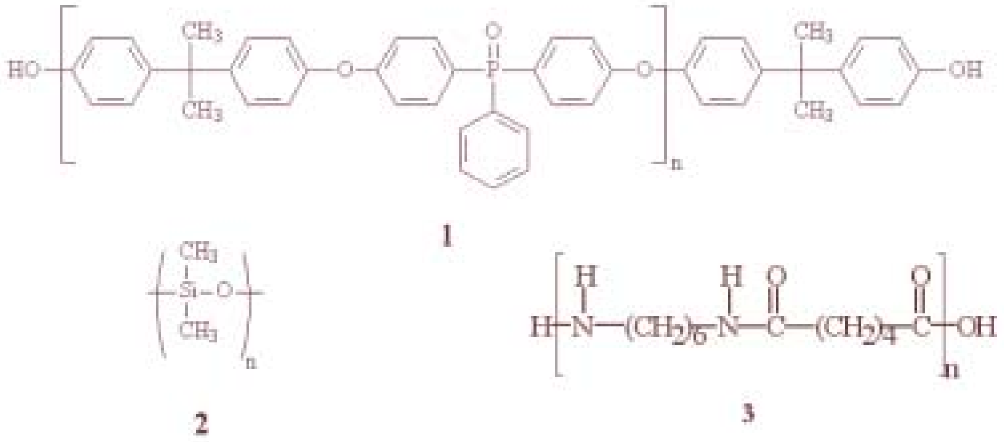

Figure 1.1: Chemical Structures of Base Homopolymers Utilized in this Thesis

The unifying theme of this work involves the incorporation of a non-polar, reactive polydimethylsiloxane oligomer into a polar matrix. Both poly(arylene ether phosphine oxide)s and nylon 6,6 are capable of high levels of polar interactions, specifically hydrogen bonding, while polydimethylsiloxanes are non-polar, hydrophobic liquids. The copolymers utilized in this research effort may have been selected for different reasons, but the challenges presented by their synthesis and characterization are similar.

Alternating block copolymers of poly(arylene ether phosphine oxide) and poly(dimethylsiloxane) were synthesized by exploiting a well-known silylamine – hydroxyl reaction. Preformed telechelic oligomers served as the building blocks for copolymers that combine the advantageous optical properties and other assets of both parent homopolymers. For example, it was necessary to explore the possibility of synergistic effects due to nanophase separation. It was hypothesized that these polyarylene ether / siloxane copolymers would complement polycarbonates for use as high refractive index lens materials. Additionally, the high glass transition temperature of the poly(arylene ether) block, combined with the flexibility of the poly(dimethylsiloxane) block, suggested their potential application as coatings or as thermoplastic elastomers. Furthermore, the ability of the phosphine oxide moiety to disperse nanoparticles of silica was also investigated. In particular, determining the preferential association of the silica with the hydrogen bonding phosphine oxide moiety and/or the structurally and electronically similar siloxane segments was briefly addressed.

A series of three polyarylene ether / siloxane copolymers varying in block length and chemical composition were synthesized. They were shown to be of high molecular weight and capable of forming optically clear, mechanically robust films from solution. Additionally, the copolymer samples displayed nanophase separation to varying degrees, which was dependent upon composition and molecular weight of the chain segments. The optical properties (e.g. refractive index and Abbe number) were found to be compositionally dependent averages of the parent materials. Further characterization of the nanophase separated copolymers did indicate potential application as optically clear thermoplastic elastomers and/or coatings, which could be used to uniformly disperse silica nanoparticles, thus affording novel nanocomposites.

Poly(dimethylsiloxane)-nylon 6,6 segmented copolymers were synthesized in an attempt to impart fire retardance and hydrophobicity to nylon 6,6 while retaining most of its semi-crystalline morphology, which accounts for many of the advantageous physical properties associated with nylon 6,6. The diamine/diacid AA/BB monomers were copolymerized with a bis-(propylpolydimethylsiloxane) oligomer to afford randomly segmented copolymers. Copolymerization was attempted by several processes, including aqueous high-pressure hydrolysis, ambient pressure ester-aminolysis in the melt, and high-pressure melt polycondensation. The latter proved to be the most successful synthetic approach.

Copolymers ranging from 10-50 nominal weight % siloxane were synthesized, producing samples with siloxane incorporations of up to 45 weight %. Characterization of the semi-crystalline amide / siloxane copolymers was more challenging than anticipated. The desired crystallinity of the polyamide portions precluded the use of most classical solution methods of analysis, while the susceptibility of the siloxane segments toward ionic redistribution reactions under strongly acidic conditions was problematic. Derivatization of the polyamide component by trifluoroacetylation was not successful.

Nonetheless, the use of solid-state NMR, combined with an extraction procedure, provided indirect verification that chemical bonding between the polyamide and the siloxane segments had occurred. Further characterization of the copolymers by thermal gravimetric analysis (TGA) in air showed an increase in char yield as the siloxane content was increased--a preliminary indicator of improved fire resistance, which was later supported by qualitative bench-top combustion experiments. Additionally, differential scanning calorimetry (DSC) analysis verified that copolymers containing up to 45 weight % siloxane oligomers still demonstrated a crystalline melting point. This observation provides evidence that some of the attractive characteristics of the nylon were maintained in the novel siloxane containing copolymers.

Thus, the synthesis and characterization of all of the copolymers produced in this thesis emphasized the obvious divergence of the non-polar polydimethylsiloxane and the polar hard blocks, which in turn generated challenging issues of solubility and compatibility. Both issues were successfully addressed by the approaches described in this thesis.

2 Literature Review

2.1 Block Copolymers

2.1.1 Classes of Hybrid Materials and Copolymers: A Brief Review

Hybrid materials are of great interest to the field of materials science The ability to combine two or more dissimilar polymers in order to enhance the physical or mechanical properties of the resulting materials is a common goal. Traditional approaches to this objective include physical blending, random or statistical copolymerization, graft or comb copolymerization, and block copolymerization. Each of these approaches has its own inherent advantages and disadvantages.

2.1.1.1 Physical Blends

Physical blending is defined as the simple mechanical mixing of two or more polymers, either in the melt or in solution.[1] At first glance, this approach would seem to be ideal for preparing hybrids, as blending is considered a simple and economical procedure that is commonly used to produce new products from existing materials.[2] However, in polymer science the effectiveness of blending is dependent upon the degree of compatibility of the polymers involved.[3] At least three general types of materials can result from blending, depending on the mutual solubility and semi-crystallinity of the constituents.

Miscible blends are defined as blends where the constituent polymers have the thermodynamic potential to be mixed at the molecular level, leading to interactions between dissimilar chains. This interaction can be verified by the observation of a single, compositionally dependent, glass transition. Miscible blends occur spontaneously when the overall energy of mixing (ΔG_{mix}) is negative, as defined by the Gibbs-Helmholtz free energy equation (Equation 1).

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[1] Paul, D. R.; Newman, S., Eds. *Polymer Blends*; Academic Press: New York, 1979; Vol. I-II.

[2] Noshay, A.; McGrath, J. E. *Block Copolymers-Overview and Survey*; Academic Press: New York, 1977.

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{1}$$

In the Gibbs-Helmholtz equation, ΔH_{mix} is the enthalpy of mixing and ΔS_{mix} is the entropy of mixing, while T is the temperature of the blend. Using the Flory-Huggins equation,[4] Scott[5] was able to further correlate enthalpy and entropy as a function of the polymer components and their properties. (Equation 2)

$$\Delta H_{mix} = \chi * V(\Phi_1 * \Phi_2) \text{ and } \Delta S_{mix} = \frac{-RV}{V_r}\left(\frac{\Phi_1 \ln \Phi_1}{X_1} + \frac{\Phi_2 \ln \Phi_2}{X_2}\right) \tag{2}$$

In Equation 2, χ is a measure of the polymer-polymer interaction energy, V is the volume of the system, Φ_i is the volume fraction of polymer *i*, R is the gas constant, T is the temperature of blending, V_r is the reference volume of the monomers and X_i is the degree of polymerization.

Examination of Equation 2 reveals that the entropy of mixing is highly dependent on the molecular weight of the blended polymers, while the enthalpy is much more dependent on the level of interaction between the polymer types. Additionally, Scott showed that as molecular weight increases to the level commonly found in commercially useful materials, ΔS approached zero (0). Therefore, polymer blends of commercial importance are primarily influenced by the rate of enthalpy. However, for polymers with weak interactions (as χ approaches 1), e.g., as observed in most polymer pairs, the enthalpy of mixing can be further reduced according to Equation 3.

$$\Delta H_{mix} = V(\delta_1 + \delta_2)^2 \Phi_1 \Phi_2 \tag{3}$$

In Equation 3, δ_i is the polymer's solubility parameter (an estimation of its ability to be dissolved in a range of solvents), derived from the square root of the cohesive energy density, pioneered by Hildebrand[6]. Thus, most early work with polymer blends concentrated on matching the solubility parameters of the component polymers. Unfortunately, the theoretical maximum difference in solubility for a 50:50 polymer blend is only 0.1 $(\text{cal/cm}^3)^{1/2}$. This narrow margin is much smaller than the standard error

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[3] Olabisi, O.; Robeson, L. M.; Shaw, M. *Polymer-Polymer Miscibility*; Academic Press: New York, 1979.

[4] Flory, P. J. *Principles of Polymer Chemistry*; Cornell: Ithaca, NY, 1953.

[5] Scott, R. L. *J. Chem. Phys.* **1949**, *17*, 279.

[6] Hildebrand, J. H.; Scott, R. L. *The Solubility of Non-electrolytes*; 3rd ed.; Reinhold Publishing Corp.: New York, 1950.

among methods used to determine solubility parameters.[7] The ability to predict miscibility of polymer pairs with strong interactions, such as donor-acceptor and hydrogen bonding, which can increase miscibility by creating an exothermic reaction upon mixing ($\Delta H < 0$), have been attempted for many years with varying degrees of success.

Most amorphous polymer blends are highly incompatible[1] and display a highly positive enthalpy of mixing, ΔH_{mix}. When such blends are attempted, macroscopically phase-separated aggregates form that generate high surface energy borders between domains, resulting in a lack of cohesiveness and poor physical strength.[8] Additionally, the desired transparency normally exhibited by an amorphous material is often lost upon blending, since the phase-domains present in incompatible blends are generally larger than the wavelengths of visible light. Unless the refractive indices of the blended polymers are relatively similar, they will scatter light and generate opacity.[9] When the refractive indices are similar, the compositionally weighted average of the two materials will be the value for the new material.[10] Blends involving semi-crystalline polymers are even more complex mixtures. Upon cooling, the crystallization process will either exclude the other polymer type and/or disrupt the crystalline lattice so significantly that the advantages of crystallinity are minimized.[2]

The formation of miscible blends is dependent on several factors, including molecular structure, average chain length, tacticity of the polymers, as well as the temperature of mixing and the blending method. If the blended polymers are miscible, ($\Delta G_{mix} < 0$) and thus compatible, the resulting material will display an amalgamation of properties, which are predictable using the same techniques as those used for random or statistical copolymers.

Polymer blends account for a significant percentage of polymer production in the U.S. Most commercial blends are produced either to reduce costs, to aid in processing, or

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[7] Paul, D. R.; Barlow, J. W. In *Multiphase Polymers; Advances in Chemistry Series no.176*; Cooper, S. L., Estes, G. M., Eds.; American Chemical Society: Washington, D.C., 1979.

[1] Paul, D. R.; Newman, S., Eds. *Polymer Blends*; Academic Press: New York, 1979; Vol. I-II.

[8] Hellmann, G. P. In *Block Copolymers*; Calleja, F. J. B., Roslaniec, Z., Eds.; Marcel-Dekker, Inc.: New York, 2000.

[9] Rosen, S. L. *Polym. Eng. Sci.* **1967**, *7*, 115.

[10] Conaghan, J.; Rosen, S. L. *Polym. Eng. Sci.* **1972**, *12*, 134.

[2] Noshay, A.; McGrath, J. E. *Block Copolymers-Overview and Survey*; Academic Press: New York, 1977.

to improve a variety of specific properties. For example, polycarbonates have been blended with polybutylene terephthalates to increase chemical resistance and to aid in processing, while polyphenylene oxides are bended with polystyrenes to improve toughness and increase glass transition temperatures.[11]

2.1.1.2 Random / Statistical Copolymers

Random or statistical copolymerization is common and often a more successful means of achieving useful hybrid materials. Most commercially important random/statistical copolymers are derived from vinyl monomers and are prepared via free radical or ionic addition reactions[12], but condensation type statistical copolymerizations are also possible.

In the synthesis of random/statistical copolymers, the desired monomers are often simultaneously introduced at the onset of the reaction. They are then copolymerized under conditions whereby both repeat units may become uniformly incorporated into short sequences along the backbone. The order of monomer incorporation is difficult to control, which may be the result of simple statistical probability, depending on resonance and polarity considerations.[13] The probability of repeat units occurring in long sequences is relatively small since the radical lifetime is somewhat short.[14] Any sequential runs of a specific repeat unit will likely exist in lengths that are not sufficient to cause any aggregation into a phase-separated structure, and the resulting product will be a single-phase system. These copolymers exhibit many physical properties (modulus, thermal behavior, chemical resistance, etc.) that are a weighted average, with respect to copolymer composition, of those of the homopolymers.[15] (See Figure 2.1-1)

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[11] Paul, D. R.; Bucknall, C. B. *Polymer Blends*; Wiley: New York, 1999.

[12] Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel-Dekker, Inc.: New York, 1996.

[13] Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization*; Pergamon Press: New York, 1995.

[14] Odian, G. *Principles of Polymerization*; 3rd ed.; Wiley Interscience: New York, 1991.

[15] Deanin, R. D.; Deanin, A. A.; Sjoblom, T. In *Advances in Polymer Blends, Grafts and Blocks*; Sperling, L. H., Ed.; Plenum Press: New York, 1974, Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel-Dekker, Inc.: New York, 1996.

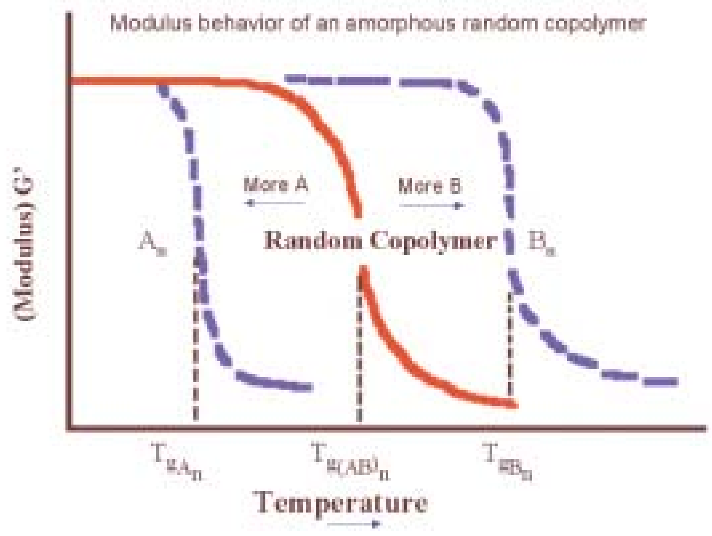

Figure 2.1-1: Effect of Composition on Modulus/Temperature Behavior of a Random Copolymer[16]

The ability to produce single-phase materials with controlled properties is the major benefit of random/statistical copolymerization. However, the precise sequences along the backbone are often impossible to determine and reproduce. Common examples of random/statistical copolymers include ethylene-vinyl acetate copolymers (EVA), used in food packaging, hose and tubing, and wire insulation, and styrene-acrylonitrile copolymers, used in various household appliances, packaging, and electronics.[14]

Frequently, the differences in reactivity of various monomer types must be taken into account and process modifications (e.g., continuous feed of faster reacting monomers, batch vs. multi-stage processes, etc.) must be developed to achieve a successful product. If the reactions with the second monomer type are preferred over homo-polymerization, an alternating structure will occur. This type of copolymer is relatively rare and usually involves a second monomer that is sterically, electronically or thermodynamically unable to homo-propagate. Such an example is the free radical copolymerization of styrene and maleic anhydride.[17,18] Maleic anhydride shows a low propensity for homo-propagation via radical processes, but it will copolymerize in an

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[16] McGrath, J. E. In *ACS Short Course on The Principles of Polymerization*: Blacksburg VA, 2000.
[14] Odian, G. *Principles of Polymerization*; 3rd ed.; Wiley Interscience: New York, 1991.
[17] Baldwin, M. G. *J. Polym. Sci* **1965**, *A3*, 703.

alternating manner. The properties of an alternating copolymer will be some combination of those of the constituent homopolymers. If the reactivities of the monomers are in opposition (reaction with like monomers is preferential to reaction with other species) then, in principle, a blocky structure will result. However, if the lifetime of the active site is short, as with most free radical processes, then a homopolymer will be produced, due to frequent radical-radical coupling or disproportionation.[2]

2.1.1.3 Graft Copolymers

Graft or comb copolymers may combine certain benefits of physical blending and random copolymerization. A graft copolymer can be considered as a chemically linked set of homopolymers. The backbone of a parent polymer A, is then attached to (or grafted with) segments of B. A representative structure of a graft copolymer is shown in Figure 2.1-2. Most graft copolymers are formed by the reaction of a parent polymer, containing reactive sites, with a second type of monomer and initiator. However, formation of homopolymer B is often unavoidable, and not all of A will accept the same number and lengths of grafts. This situation leads to a combination of blended and copolymerized materials. Homopolymer contamination and the non-uniformity of graft segment lengths all contribute to the molecular definition of graft copolymers.[19]

Two of the most common commercially available graft copolymers are derived from polystyrene. Rubber-toughened, high impact polystyrene (HIPS) is produced by the free radical addition polymerization of styrene in the presence of an unsaturated rubber, usually high 1,4- type poly(butadiene), which becomes partially grafted to the growing styrene chains.[20,21] Similarly, acrylonitrile-butadiene-styrene (ABS) is the result of the statistical azeotropic copolymerization of styrene and acrylonitrile in the presence of a rubber, again normally poly(butadiene), which has a T_g of –80°C or lower.[22]

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[18] Chiang, T. C.; Graillat, C.; Guillot, J.; Pharm, Q. T.; Guyot, A. *J. Polym. Sci. Polym. Chem. Ed.* **1977**, *15*, 2961.

[2] Noshay, A.; McGrath, J. E. *Block Copolymers-Overview and Survey*; Academic Press: New York, 1977.

[19] Allport, D. C.; W.H.Janes, Eds. *Block Copolymers*; John Wiely & Sons: New York, 1973.

[20] Brydon, A.; Burnett, G. M.; Cameron, G. C. *J. Polym. Sci. Polym. Chem. Ed.* **1973**, *11*, 3255.

[21] Ludwico, W. A.; Rosen, S. L. *J. Appl. Polym. Sci.* **1975**, *19*, 757.

[22] Basdekis, C. H. *ABS Plastics*; Reinhold: New York, 1964.

Figure 2.1-2: Types of Copolymers[16]

2.1.1.4 Block Copolymers

Block copolymers are defined as materials with a linear arrangement of blocks or long sequences of one repeat unit (A), chemically bound at one or both ends to long sequences of another unit (B).[23] These arrangements can vary from the simple A-B diblock, containing only two segments, to the triblock A-B-A, up to the multi-block or segmented copolymer $(\text{-A-B-})_n$, as illustrated in Figure 2.1-3.

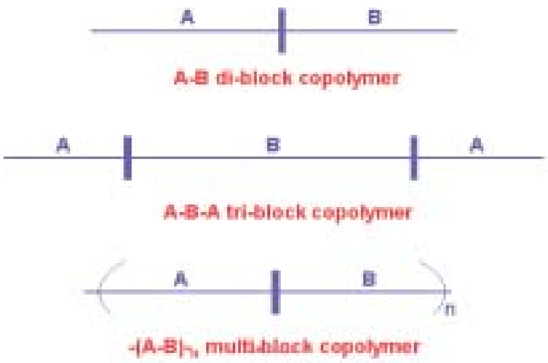

Figure 2.1-3: Linear Block Copolymer Architectures[16]

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[16] McGrath, J. E. In *ACS Short Course on The Principles of Polymerization*: Blacksburg VA, 2000.
[23] IUPAC In *Source-Based Nomenclatures for Copolymers*; Oxford Press: Oxford, UK, 1983.
[16] McGrath, J. E. In *ACS Short Course on The Principles of Polymerization*: Blacksburg VA, 2000.

The manner in which the blocks interact and associate with like segments can result in a wide variety of morphologies. The physical properties of block copolymers tend to reflect the dual nature of the copolymer and may display either a compromise of the parent material properties (phase mixed) or two separate sets of properties (phase separated), which are characteristic of the parent materials.[15]

One basic difference between block copolymers and graft copolymers is the amount and type of inter-segment linkages. Block copolymers have a few well-defined inter-segmental linkages for a given molecular weight and composition. In contrast, graft copolymer linkages are displayed more randomly. The availability of reactive sites and steric hindrance plays a much larger role in the uniformity of a graft copolymer.[2]

Block and/or graft copolymerization has several advantages over blends and random copolymerization. One major benefit over blends is the covalent bonding that exists between the dissimilar segments. This bonding prevents selective extraction or "leaching" of the chemically dissimilar components. Additionally, the covalently bonded segments can act as "compatiblizers" for blends of the parent polymers.[1] The fact that they are covalently bonded ensures that there will be a region of interpenetrating chains between the interfaces. Not only does this enhance the structural integrity, it can also act as a mechanism for transferring load between the dissimilar regions.

The remainder of this section will concentrate on block copolymers; their synthesis, characterization, and the effects of phase separation on a macroscopic versus micro- or nanoscopic scale.

2.1.2 Synthesis of Block Copolymers

Well-defined structures of block copolymers require more stringent reaction conditions and greater knowledge of reactive pathways than homopolymerization.[24] Nevertheless, block copolymers have been prepared by a variety of methods, including living ionic addition, step-growth, and even mediated free radical processes.[25,26]

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[15] Deanin, R. D.; Deanin, A. A.; Sjoblom, T. In *Advances in Polymer Blends, Grafts and Blocks*; Sperling, L. H., Ed.; Plenum Press: New York, 1974.

[2] Noshay, A.; McGrath, J. E. *Block Copolymers-Overview and Survey*; Academic Press: New York, 1977.

[1] Paul, D. R.; Newman, S., Eds. *Polymer Blends*; Academic Press: New York, 1979; Vol. I-II.

[24] Jerome, R.; Henrioulle-Granville, M.; Robin, J. J. *Prog. Polym. Sci.* **1991**, *16*, 837.

[25] Piirma, I.; Chau, L. H. *J. Appl. Polym. Sci.* **1979**, *24*, 2051.

2.1.2.1 Chain-Growth (Addition) Copolymerizations

2.1.2.1.1 *Reactivity Ratios*

High conversion copolymers synthesized by addition polymerizations can be quite different in their composition than the feed ratio of monomers. The active monomer sites have different polarities and resonance stabilization characteristics and thus different relative reactivities.[27] This feature leads to the concept of reactivity ratios, which help predict the composition of the resultant copolymer. In a relatively simple view of copolymerization, known as a first–order Markov or terminal model of copolymerization,[14] each active monomer type (M_1*, M_2*), at the end of a growing chain, has a known reactivity towards both monomers involved (M_1, and M_2). Using the following rate equations,

$$\sim\sim\sim M_1^* + M_1 \xrightarrow{k_{11}} M_1^*$$

$$\sim\sim\sim M_1^* + M_2 \xrightarrow{k_{12}} M_2^*$$

$$\sim\sim\sim M_2^* + M_1 \xrightarrow{k_{21}} M_1^*$$

$$\sim\sim\sim M_2^* + M_2 \xrightarrow{k_{22}} M_2^*$$

a ratio of the tendency to homopolymerize versus copolymerize can be determined for a pair of monomers. These values are known as reactivity ratios.[28]

$$r_1 = \frac{k_{11}}{k_{12}} \qquad \text{and} \qquad r_2 = \frac{k_{22}}{k_{21}}$$

The reactivity ratios, as defined above, can be used to anticipate the composition and connectivity of a copolymer at low conversions. Several specific correlations between reactivity ratios and the copolymers generated have been recognized. For example, if the r values are between 0 and 1, then short sequence, random/statistical copolymerization is usually possible. If the r values are much greater than one (1), then

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[26] Priddy, D. B. *Adv. Polym. Sci.* **1999**.
[27] Staudinger, H.; Scheiders, J. *Ann. Chim.* **1939**, *541*, 151.
[14] Odian, G. *Principles of Polymerization*; 3rd ed.; Wiley Interscience: New York, 1991.

the composition is likely a mixture of homopolymers and a block copolymer can likely be synthesized. If both r_1 and r_2 are equal to zero (0), then the copolymer will proceed with alternate addition of monomer types.

Addition polymerizations can be used to produce block copolymers in two different modes. If both of the reactivity ratios are greater than 1, the addition of B to B is preferable to the addition of B to A and vice versa, and block copolymers can be generated. The restricted crossover of the activated species from one monomer to the other leads to long sequences of like-monomer addition. However, this approach is not ideal, as there is no mechanism to control the size of the segments. Furthermore, though monomer crossover is restricted, it is not eliminated. This may lead to the development of mixed regions along the chain.[25]

2.1.2.1.2 *Sequential Addition of Monomers*

The second approach for addition block copolymerizations utilizes the sequential addition of monomers to living polymerization systems. First described in anionic systems by Szwarc,[29] this approach has become a standard method for the synthesis of block copolymers. In practice, during polymerization all of monomer A is consumed (Equation 4).

$$A^* + A + A \rightarrow A_n^* \tag{4}$$

Next, monomer B is added while the live end-groups still exist. The copolymer is then allowed to grow until all of monomer B is consumed (Equation 5).

$$A_n^* + B + B + B \rightarrow A_nB_n^* \tag{5}$$

At this point the reaction may be quenched to form a di-block copolymer, or more A may be added to build another A block (Equation 6).

$$A_nB_n^* + A + A + A \rightarrow A_nB_nA_n^* \tag{6}$$

This method allows the synthesis of long block lengths; the size of the segments is only regulated by the number of active sites relative to the amount of monomer added.

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[28] Stevens, M. P. *Polymer Chemistry: An Introduction*; 2nd ed.; Oxford University Press: New York, 1990.
[25] Piirma, I.; Chau, L. H. *J. Appl. Polym. Sci.* **1979**, *24*, 2051.

Sequential addition has mainly been used in non-terminated reactions to produce di- and tri-block copolymers of controlled molecular weight with narrow distributions. This procedure can be repeated until the desired structure, composition, and block lengths are achieved. Most commercial block copolymers derived from living polymerization of vinyl or diene monomers (styrene, butadiene, isoprene, etc.) are produced via sequential addition.[12]

The sequential addition of a monomer to a living system facilitates much greater control over the size, polydispersity and sequence of the copolymers blocks. Nonetheless, sequential addition does have disadvantages. The reagents involved must be virtually free of impurities, and multi-block copolymers cannot be efficiently produced. Each addition of new monomer increases the probability of premature termination and thus chain defects. Moreover, the process of multiple additions is generally inordinately laborious, requiring constant monitoring to ensure that each aliquot was fully reacted before the next addition. For these reasons, multi-block copolymers (e.g., >3 sequences) are most commonly prepared via step-growth procedures.

2.1.2.2 Step-Growth (Condensation) Block Copolymers

In the case of step-growth or condensation reactions, the production of block copolymers is best facilitated by either sequential addition, previously discussed, or by reacting preformed oligomers possessing mutually reactive endgroups.

2.1.2.2.1 *Preformed Reactive Oligomers*

The major advantage of using preformed oligomers is that the oligomers can normally be well characterized before copolymerization. This allows one to know exactly what the number average molecular weight and polydispersity of the resultant blocks will be. Block copolymers of this type could serve as the basis for the formation of “perfectly

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[29] Szwarc, M. *Nature* **1956**, *178*, 1168.

[12] Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel-Dekker, Inc.: New York, 1996.

alternating block copolymers".[2] The reasoning behind this definition is that each telechelic oligomer acts as a macro-monomer and can only react with a second oligomer containing a compatible endgroup. Consequently, if two well-characterized oligomers are reacted in the proper molar ratio to form a high molecular weight copolymer, the architecture of the copolymer is forced to be alternating in regular or "perfect" (but statistical) segmental lengths. This level of molecular control is important for the development of correlations between a copolymer's properties, its segment size and composition.

One significant drawback of the preformed oligomer route is that the oligomers used are generally limited to 1,000-25,000 g/mol in molecular weight.[24] At higher molecular weights, the concentration of reactive endgroups decreases significantly, which limits the probability for effective collisions (reactions), amplifies the effects of impurities, and makes most chemical techniques inefficient. In some extreme cases, especially where the degree of solvation of one or both of the oligomers is not ideal, the reactive endgroups may become inaccessible, or even incompatible.[30]

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[2] Noshay, A.; McGrath, J. E. *Block Copolymers-Overview and Survey*; Academic Press: New York, 1977.
[24] Jerome, R.; Henrioulle-Granville, M.; Robin, J. J. *Prog. Polym. Sci.* **1991**, *16*, 837.
[30] Legge, N. R.; Holden, G.; Schroeder, H. E., Eds. *Thermoplastic Elastomers: A Comprehensive Review*, 1987.

2.1.2.2.2 *Interfacial Copolymerization*

Interfacial copolymerization can be described as the reaction of two functionalized oligomers that have been selectively dissolved in immiscible solvents. The endgroups are selected so that they migrate to the interface of the solutions. At the interface, the reactive endgroups collect until they are concentrated enough to react and form the copolymer. The molecular weight, as well as the bulk yield of the polymer, can be increased by mechanical agitation or by removing the newly formed polymeric material from the interface, thereby creating a new reactive interface.[25]

It is important to note that these methods of synthesis are not, in principle, mutually exclusive. For example, one approach may be to form the block oligomers via chain or addition polymerization, and then condense those oligomers to form the copolymer, or vice versa.

2.1.3 Major Characteristics of Block Copolymers

Most of the physical and chemical properties of a block copolymer are dependent upon its composition and morphology. The composition is the weight or volume fraction of a particular block relative to the weight or volume of the total material. Copolymer composition dictates the degree of similarity to the parent homopolymers. The overall solid state morphology of a copolymer is defined by the way the blocks associate or dissociate with each other and can be observed as either phase mixing or separation. The extent of phase separation dictates the manner in which the similarity to the parent homopolymers is observed.

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[25] Piirma, I.; Chau, L. H. *J. Appl. Polym. Sci.* **1979**, *24*, 2051.

2.1.3.1 Block Copolymer Morphologies

2.1.3.1.1 *Miscible vs. Immiscible Copolymer Segments*

Recalling the concepts presented earlier in this review with regard to miscible and immiscible polymer blends, it is easy to extend these models to block copolymers. The Gibbs-Helmholtz free energy equation will remain the basis for the thermodynamics presented, as will the definitions of miscibility and immiscibility. That is, a copolymer will display single phase behavior with a negative ΔG_{mix} or a phase separated system where, ΔG_{mix} is positive according to the equations below (Equations 7-9).

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \tag{7}$$

$$\Delta H_{mix} = \chi * V(\Phi_1 * \Phi_2) = V(\delta_1 + \delta_2)^2 \Phi_1 \Phi_2 \tag{8}$$

and

$$\Delta S_{mix} = \frac{-RV}{V_r}\left(\frac{\Phi_1 \ln \Phi_1}{X_1} + \frac{\Phi_2 \ln \Phi_2}{X_2}\right) \tag{9}$$

In Equations 7-9, χ is a measure of the polymer-polymer interaction energy, δ_i is the solubility parameter for polymer i, V is the volume of the system, Φ_i is the volume fraction of polymer *i*, R is the gas constant, T is the temperature of blending, V_r is the reference volume of the monomers and X_i is the degree of polymerization.

The chemical nature and sequence length of the two segments in block copolymers are obviously important factors. In the case of similar segments (similar δ), a miscible, single–phase morphology is most likely to occur, even with longer segment lengths.[15,30] Copolymers with single-phase morphologies tend to display properties that deviate from those of the parent homopolymers in a linear predictable manner. The amount of change can be expected to be a compositionally weighted average of the values of the homopolymers. In this respect, single-phase copolymer systems have characteristics much like those displayed by random/statistical copolymers.[14]

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[15] Deanin, R. D.; Deanin, A. A.; Sjoblom, T. In *Advances in Polymer Blends, Grafts and Blocks*; Sperling, L. H., Ed.; Plenum Press: New York, 1974.

[30] Legge, N. R.; Holden, G.; Schroeder, H. E., Eds. *Thermoplastic Elastomers: A Comprehensive Review*, 1987.

[14] Odian, G. *Principles of Polymerization*; 3rd ed.; Wiley Interscience: New York, 1991.

However, if the segments are dissimilar (different δ), yet bound together, a wide variety of bulk and surface properties (different than those of the homopolymers) can be observed. These variances are the result of a combination of traits of the segments involved. The factors that will be discussed include segment lengths, (long vs. short) semi-crystallinity (amorphous vs. crystalline nature), and modulus (hard vs. soft segments).

2.1.3.1.2 *Effects of Segment Length on Phase Separation*

The size of the block segments is a factor that must be considered before other aspects of phase separation can be addressed. If the segmental units are below some critical length, then a phase-mixed morphology will be present. Since the entropy of mixing is highly dependent on the molecular weight of the blended polymers, shorter chains (or blocks) will increase the enthalpy term (high ΔS leads to -ΔG), thereby enhancing polymer solubility. Additionally, the blocks will not be long enough to preferably associate, thus the material will display properties that are a blend of the parent homopolymers. However, there will be some critical block length where the entropy term will become too small to overcome differences in solubility (positive ΔH) and like segments will tend to associate with each other at the exclusion of dissimilar segments.[31]

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[31] Allport, D. C.; W.H.Janes, Eds. *Block Copolymers*; John Wiely & Sons: New York, 1973.

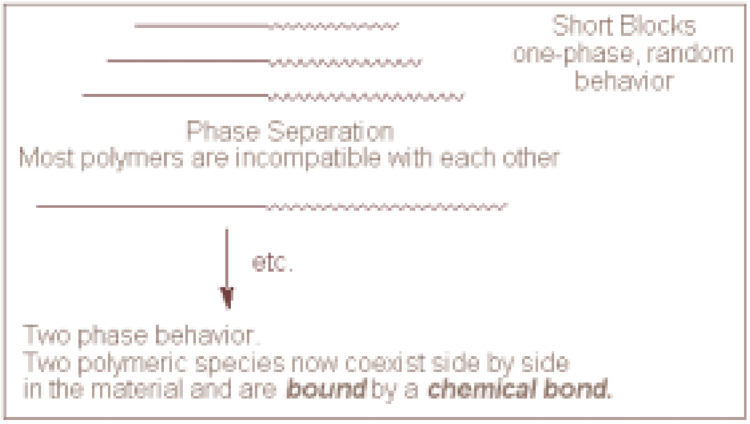

Figure 2.1-4: Illustration of Critical Block Length[16]

This selective association causes a phase-separated or two-phase morphology. It is important to note that the minimal block lengths for phase separation are not universal, but rather are a function of the chemical nature of the blocks and will vary from system to system.

2.1.3.1.3 *Theoretical Basis for Micro- or Nanoscopic Phase Separation*

Thermodynamically, the phenomenon of microdomain formation is the result of a variety of factors. The repulsive interactions between dissimilar chain segments, which cause the initial segregation, increase the size of the domains as the segmental length grows. These interactions also dictate the shape of the domain in order to minimize the interfacial surface area,[25,32] while losses of entropy in both conformational freedom and the restriction of A-B linkages to the interfacial region promote the formation of several smaller domains. Kinetically, the formation of microphases has been correlated to the diffusivity of the block copolymer in the ordered and disordered states as scaled to temperature.[33] In the case of immiscible blocks (significantly different solubility parameters, δ) the chain segments will migrate to maximize the distance between dissimilar copolymer components. Given that the segments are covalently bonded, such

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[16] McGrath, J. E. In *ACS Short Course on The Principles of Polymerization*: Blacksburg VA, 2000.

[25] Piirma, I.; Chau, L. H. *J. Appl. Polym. Sci.* **1979**, *24*, 2051.

[32] Meier, D. J. In *Polym. Blends. Mixtures*; Michigan Mol. Inst.: Midland, MI, 1985; Vol. 89, pp 173-194.

[33] Hashimoto, T.; Tsukahara, Y.; Kawai, H. *J. Polym. Sci. Polym. Lett. Ed.* **1980**, *18*, 585.

migration is obviously limited. Thus, like segments will aggregate and form as large a domain as the molecular weight of the segments will allow.[2]

2.1.3.2 Structure –Property Relationships of Block Copolymers

If a phase-separated morphology is present, certain copolymer properties may be predicted.[34] For example, an amorphous di-block A-B copolymer that shows phase separation will have two observable glass transition temperatures, corresponding to the characteristic transitions for both homopolymer A and homopolymer B. Between the two transitions one expects a plateau region. The value observed during the plateau will be dependent upon the composition of the copolymer. The width of the plateau region will remain relatively constant while composition will vary relative height. This is in contrast to the behavior of a random or single-phase copolymer, where composition determines the location of the transition, while the magnitude remains constant. (See Figure 2.1-5)

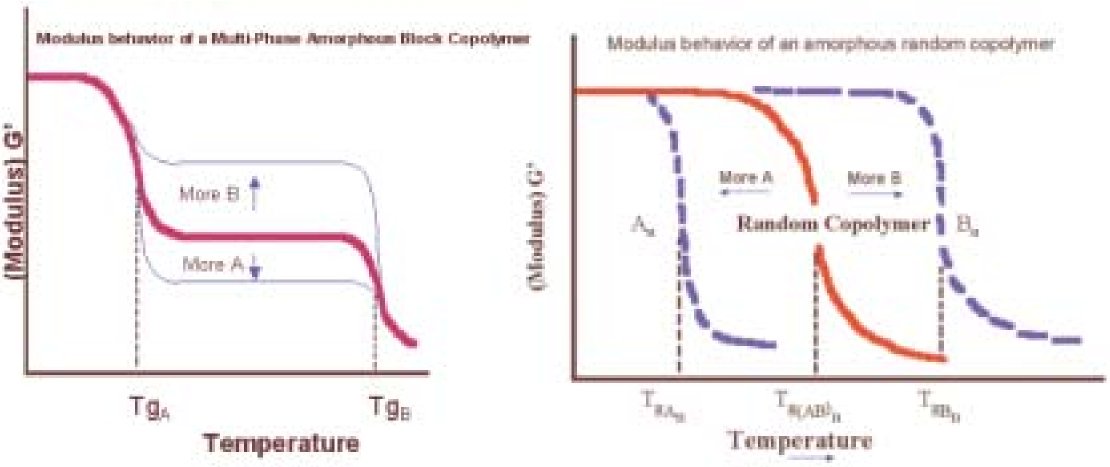

Figure 2.1-5: Multi-phase vs. Random Copolymers- Effect of Composition on Modulus-Temperature Behavior[16]

Generally, one expects the extent of phase separation to be a function of segment size.[34] The closer the segment lengths are to their critical length, the more complicated the

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[2] Noshay, A.; McGrath, J. E. *Block Copolymers-Overview and Survey*; Academic Press: New York, 1977.

[34] Folkes, M. J., Ed. *Processing, Structure and Properties of Block Copolymers*; Elsevier Applied Science: New York, 1985.

[16] McGrath, J. E. In *ACS Short Course on The Principles of Polymerization*: Blacksburg VA, 2000.

[34] Folkes, M. J., Ed. *Processing, Structure and Properties of Block Copolymers*; Elsevier Applied Science: New York, 1985.

phase behavior becomes. For example, if dissimilar segments cannot effectively become isolated from each other, it may lead to broad interfacial regions and phase mixing. A broadening of transitions can be identified as an observable effect of phase mixing. At lower segregation levels, the plateau region becomes shorter. However, for longer blocks the areas of association (domains) increase and the interfaces can become more defined, which can also be attributed to more extensive chain entanglements.

Amorphous, particularly nonpolar A-B-A tri-block copolymers above their critical block length develop a somewhat predictable morphology as a function of the overall composition.[2,35,36] As shown in Figure 2.1-6, as the composition changes from mostly A to mostly B, the observed morphologies progress from spheres of A, to rods or cylinders, to lamellar structures, followed by a matrix inversion and regression to spheres of B. Of course, as the architecture of a copolymer becomes more complex, so do the morphological variations, as do the factors that control their formation, which expand beyond basic geometric considerations.

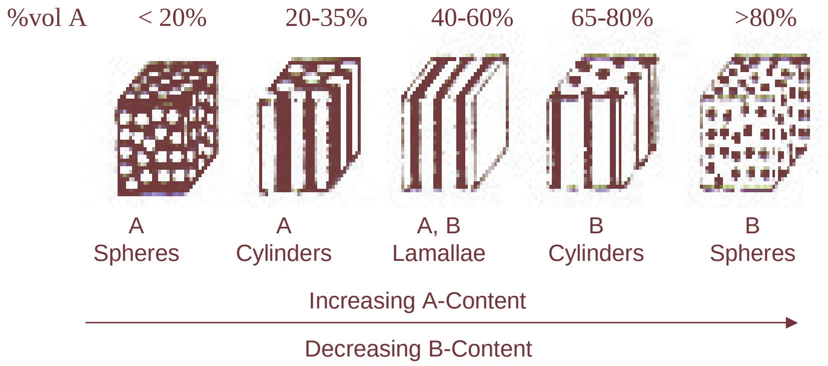

Figure 2.1-6: Influence of Composition on the Morphology of an A-B-A Block Copolymer[15,36]

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[2] Noshay, A.; McGrath, J. E. *Block Copolymers-Overview and Survey*; Academic Press: New York, 1977.

[35] Meier, D. J. *MMI Press Symposium Series, Vol. 3: Block Copolymers: Science and Technology*; Harwood Acad. Publ.: Chur, Switz, 1983.

[36] Molau, G. E., Ed. *Colloidal and Morphological Behavior of Block and Graft Copolymers*; Plenum Press: New York, 1971.

[15] McGrath, J. E. In *ACS Short Course on The Principles of Polymerization*: Blacksburg VA, 2000.

[36] Molau, G. E., Ed. *Colloidal and Morphological Behavior of Block and Graft Copolymers*; Plenum Press: New York, 1971.

Thus far, all of the situations discussed in detail have utilized amorphous materials. This is necessary for a basic understanding of phase separation before extending these concepts to a study of crystallizable segments. The fact that a copolymer segment is able to crystallize implies preferential association via phase separation. However, crystallization is not complete; some amorphous content is always present in the chain, which leads to the concept of semi-crystallinity.[14] The amorphous content provides the connectivity between ordered regions such as lamella or spherulites. The most commonly studied copolymers with crystallizable regions are those containing amorphous segments. These materials can be divided into one of two groups:[25]

1) Di-and tri- block materials, exhibiting semi-crystalline regions, with fixed periodicity, such as, styrene-caprolactone or styrene-ethylene oxide copolymers, and

2) Multi-block copolymers that lack rigorous periodicity of the ordered regions, including segmented polyurethanes and polyesters.

The ability of the crystalline regions to assemble, either from the melt, glass or from solution, can be impeded by the presence of the amorphous segments. An amorphous segment can become trapped if it is tethered to a segment already in the forming lattice. This can result in various defects in the crystalline lattice, which lowers or even eliminates the macroscopic observance of crystallinity.

2.1.3.3 Thermoplastic Elastomers

Block copolymers with crystallizable segments are most commonly used as thermoplastic elastomers, which were first identified around 1960.[37] They display many of the physical properties of chemically cross-linked rubbers, while retaining the advantage of thermoplastic processing. A thermoplastic elastomer can be a block copolymer of either tri– or multi-block architecture with chemically dissimilar segments. One fraction (the A block) is "hard" at room temperature, while the remainder (the B block) is "soft". The hard segment can be either a semi-crystalline or amorphous glass.

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[14] Odian, G. *Principles of Polymerization*; 3rd ed.; Wiley Interscience: New York, 1991.

[25] Piirma, I.; Chau, L. H. *J. Appl. Polym. Sci.* **1979**, *24*, 2051.

[37] Holden, G. In *Encylopedia of Polymer Science and Engineering*; John Wiley & Sons: New York, 1986; Vol. 5, pp 416-430.

The key to their elastomeric properties is the fact that the hard segments can form domains from the melt or solution, generating "physical crosslinks" (Figure 2.1-7). These immobile domains act as anchor points for the flexible chains, thereby limiting the soft segments' ability to flow and act as reinforcing fillers. Upon application of a load, the covalent bonding between hard domains preserves the material's connectivity. In addition, mechanical energy may be dissipated by the limited mobility of the soft segments.

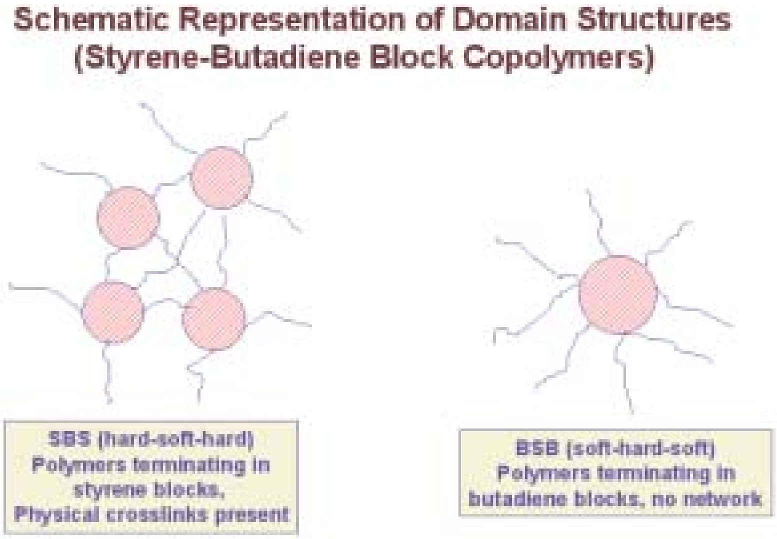

Figure 2.1-7: Representation of Physical Crosslinks

The major advantage of a thermoplastic elastomer (TPE) over a conventional thermoset network is that there is no need for additional cure chemistry to form the rubbery material. Thus the TPE can be processed with conventional thermoplastic equipment. Also, since the transition upon cooling from a melt to the reinforced rubbery substance is fast and reversible, waste material and production errors can be reworked or recycled. However, their thermoplastic nature also limits the number of suitable use environments. TPEs are more susceptible to deformation without recovery at high temperatures and often have reduced chemical resistance compared to chemically crosslinked systems. Additionally, di-block and soft-hard-soft tri-block copolymers are unable to form the required physical cross-links. In order for a continuous network to form, both ends of the flexible segments must be immobilized by a hard segment. Otherwise, the soft segment is free to rotate and slip past other chains, resulting in deformation and minimal reinforcement or recovery, which results in relatively weak materials. (See Figure 2.1-8)

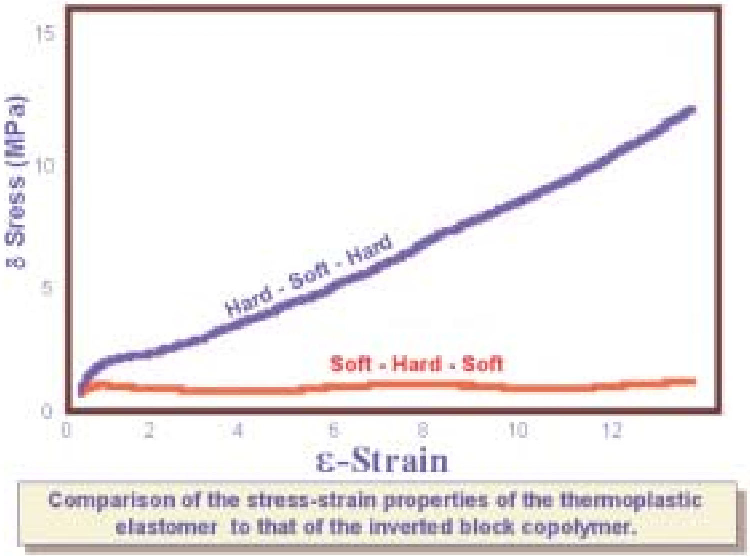

Figure 2.1-8: Thermoplastic Elastomer Properties as a Function of Block Sequence[16,38]

In summary, there are many approaches to the development of hybrid materials, each with its own strengths and weaknesses. Block copolymerization is a useful and viable approach to coalesce the advantageous properties of two dissimilar polymers. Additionally, when significant control over the synthesis of a block copolymer is utilized, the morphology of the resultant materials can be predicted.

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[16] McGrath, J. E. In *ACS Short Course on The Principles of Polymerization*: Blacksburg VA, 2000.
[38] Mohajer, Y.; Wilkes, G. L.; Wang, I. C.; McGrath, J. E. In *ACS Symposium Series, #193, Elastomers and Rubber Elasticity*; Mark, J. E., Lal, J., Eds.; American Chemical Society: New York, 1982.

2.2 Poly(arylene ether)s and Poly(arylene ether phosphine oxide)s

2.2.1 General Structure and Characteristics

The class of polymers known as poly(arylene ether)s includes a wide variety of chemical structures, some of which have been successfully commercialized.[39,40] A generic structure is shown in Figure 2.2-1, where Ar represents a number of possible aromatic structures, Y is normally a carbonyl, sulfone, or phenyl phosphine oxide moiety, and Z can be an endgroup to provide functionality and/or molecular weight control.

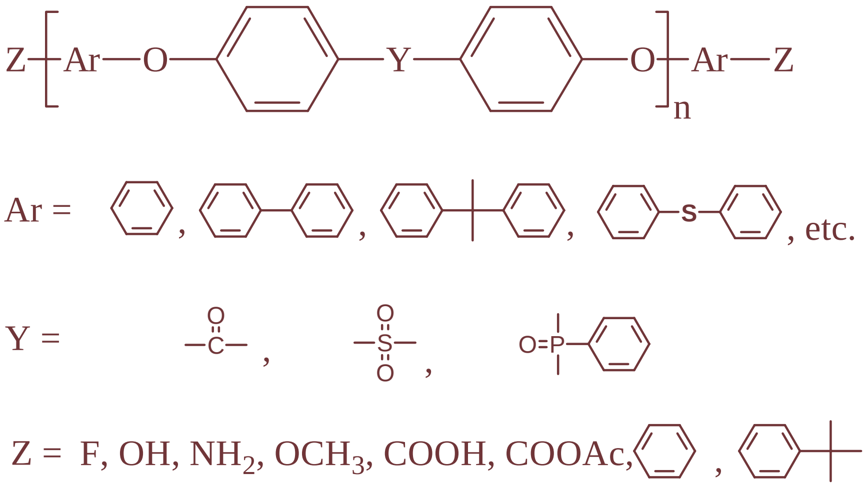

Figure 2.2-1: General Structure of a Poly(arylene ether)[16]

The unifying characteristic of all poly(arylene ether)s is the presence of an ether-linkage between two phenyl rings. The flexibility and utility of this characteristic bond affords materials with a wide range of properties. An aliphatic C-O-C ether bond has a slightly higher bond-energy than that of a C-C bond (84.0 compared to 83.1 kcal/mol).[41]

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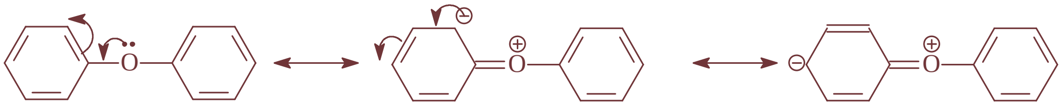
[39] Cotter, R. J., Ed. *Engineering Plastics: Handbook of Polyarylethers*; Gordon and Breach Publishers: Basel, Switzerland, 1995.

[40] Cagett, D. C. In *Encyclopedia of Polymer Science and Technology*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; John Wiley & Sons: New York, 1986; Vol. 6.

[16] McGrath, J. E. In *ACS Short Course on The Principles of Polymerization*: Blacksburg VA, 2000.

[41] Eaborn, C. *Organosilicon Compounds*; Butterworth Scientific Publications: London, UK, 1960.

However, aryl ether linkages are further stabilized through resonance, as shown for diphenyl ether in Scheme 2.2-1.[42]



Scheme 2.2-1: Resonance Stabilization of an Aryl Ether Bond[42]

Additionally, when compared to C-C bonds, the aryl C-O-C bond offers less resistance to rotation (15.1 and 11.3 kJ/mol, respectively) lower excluded volume, and decreased van der Waals interactions.[43] This combination of properties allows polymer backbones containing the aryl ether bond to be highly thermally stable, yet flexible.

The ability to dissipate energy via chain rotation is thought to be a key reason for the observed toughness and impact resistance characteristic of poly(arylene ether)s. Most poly(arylene ether)s display secondary modulus loss transitions. In their analysis of data from torsional pendulum studies, Robeson et al.[44] attributed these secondary transitions to the segmental motion of the arylene ether bond. This conclusion was later supported by deuterium NMR investigations of the β–relaxations in poly(arylene ether sulfone)s by Dumais and co-workers.[45] In this study the authors concluded that the primary mode of the segmental motion was the 180 degree flipping of the phenyl rings.

It is important to note that the relative ease of rotation of the aryl ether bond does not imply that poly(arylene ether)s should possess low glass transition or semi-crystalline melting temperatures. In fact, the highly aromatic nature of poly(arylene ether)s increases the T_g or T_m relative to their aliphatic counterparts.

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[42] Patai, S. *The Chemistry of the Ether Linkage*; Interscience: London, UK, 1967.

[43] Stark, F. O.; Falender, J. R.; Wright, A. P. *Comprehensive Organometallic Chemistry*; Pergamon Press: New York, 1982; Vol. 2.

[44] Robeson, L. M.; Farnham, A. G.; McGrath, J. E. In *Molecular Basis of Transitions and Relaxations*; Boyer, R. F., Meier, D. J., Eds.; Gordon: New York, 1978; pp 405-425.

[45] Dumais, J. J.; Cholli, A. L.; Jelinski, L. W.; Hedrick, J. L.; McGrath, J. E. *Macromolecules* **1986**, *19*, 1884.

2.2.2 Commercialized Examples

Poly(arylene ether)s are widely used as engineering thermoplastics. The ability to display high thermal transitions (or melting points) and stability, fracture and impact toughness, and excellent resistance to oxidation and hydrolysis; coupled with a wide variety usable monomers and synthetic chemistries, have resulted in many commercialized poly(arylene ether)s.[14,39,40] Some of the most successful materials possess sulfone or ketone linkages. Products including bisphenol-A based polysulfones (Udel®, Radel® BP-Amoco), poly(ether sulfone)s (Victrex®- ICI), poly(arylene ether ether ketone)(*PEEK*, Victrex® PEEK- ICI), poly(arylene ether ketone) (*PEK*, Stilan®-Raychem Corp.), and poly(arylene ether ketone ether ketone ketone) (*PEKEKK*, Ultrapek®- BASF) are all examples of commercialized poly(arylene ether)s, some of which are no longer currently available. Figure 2.2.2

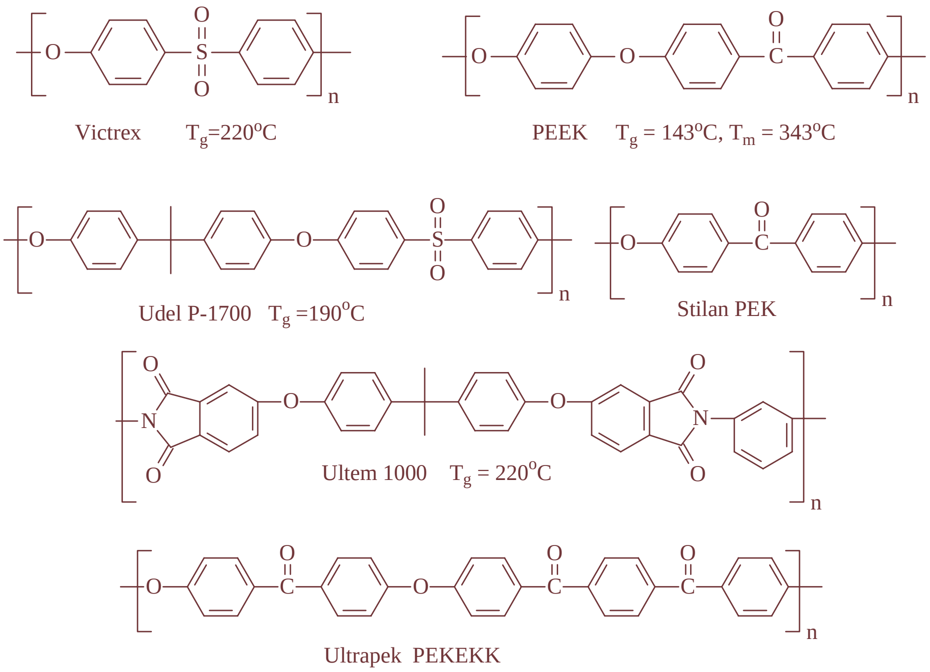

Figure 2.2-2: Examples of Commercialized Poly(arylene ether)s

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[14] Odian, G. *Principles of Polymerization*; 3rd ed.; Wiley Interscience: New York, 1991.

[39] Cotter, R. J., Ed. *Engineering Plastics: Handbook of Polyarylethers*; Gordon and Breach Publishers: Basel, Switzerland, 1995.

[40] Cagett, D. C. In *Encyclopedia of Polymer Science and Technology*; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; John Wiley & Sons: New York, 1986; Vol. 6.

The nature of the complementary chemical links along the polyarylene ether backbone can lead to both amorphous and semi-crystalline morphologies. Those with ketone bridges or wholly aromatic reactants may be semi-crystalline, while sulfone- and phosphine oxide-containing arylene ethers are mostly amorphous as a result of non-coplanar geometries.[14] Since the phosphine oxide oligomers used in this investigation are amorphous, the reactive conditions and discussions that follow will concentrate on amorphous examples.

2.2.3 Synthetic Approaches and Mechanisms for Poly(arylene ether)s

Poly(arylene ether)s can be synthesized to high molecular weights by an array of synthetic routes. These include electrophilic aromatic substitution,[46,47] nucleophilic aromatic substitution,[48] silyl-ether displacement,[49] ring opening of arylene ether cyclics and macro cyclics,[50,51] and metal mediated coupling reactions.[52] Although the synthetic routes for producing poly(arylene ether)s vary, the majority (including the oligomers used in this research effort) are produced via nucleophilic aromatic substitution.

In the following sections, the synthetic routes to poly(arylene ether)s will be discussed using polysulfone as an example. This seems appropriate, since the electronic effects and molecular symmetries of the sulfones, both in halide and phenolic compounds, are similar to those of aryl phosphine oxide. The actual synthesis of the phosphine oxide oligomers will be discussed at length in Chapters 3.3 and 3.4, which are the polyarylene ether phosphine oxide experimental and results sections, respectively. Ketones containing polyarylene ethers can be produced using similar techniques. However, the reaction conditions and intermediates will be different, as the carbonyl linkages are both less electron-withdrawing and more planar. Additionally, the semi-

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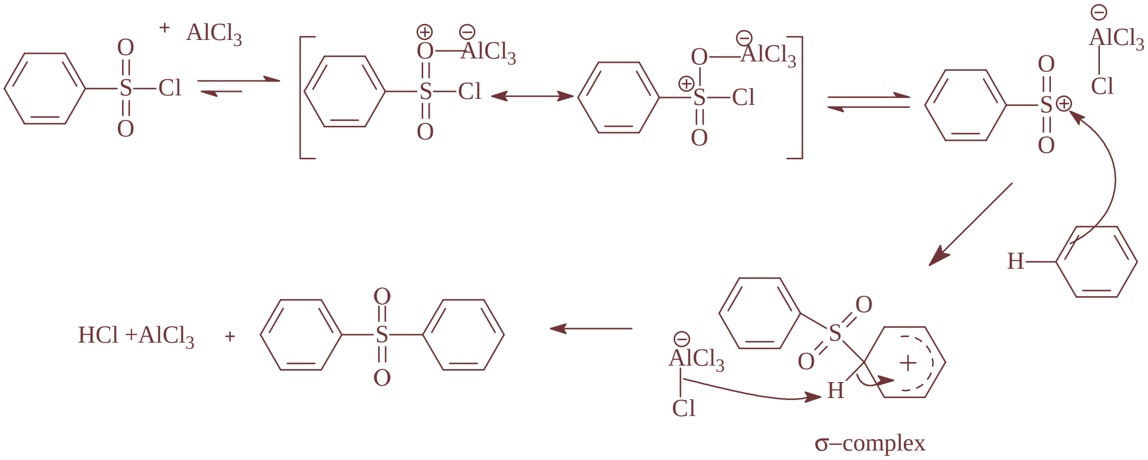
[14] Odian, G. *Principles of Polymerization*; 3rd ed.; Wiley Interscience: New York, 1991.
[46] Attwood, T. E.; Newton, A. B.; Rose, J. B. *Br. Polym. J.* **1972**, *4*, 391.
[47] Chang, I. Y. *Sci. Adv. Matl. Proc. Eng. Ser.* **1988**, *33*, 194.
[48] Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F.; Merriam, C. L. *J. Polym. Sci. Polym. Chem. Ed.* **1967**, *5*, 2375.
[49] Kricheldorf, H. R.; Delius, U.; Tonnes, K. U. *New Polym. Mater.* **1988**, *1*, 127.
[50] Colquhoun, H. M.; Dudman, C. C.; Thinass, M.; O'Mahoney, C. A.; Williams, D. J. *J. Chem. Soc. Chem. Comm.* **1990**, *3*, 336.
[51] Xie, D.; Gibson, H. W. *Macromol. Chem.* **1996**, *197*, 2133.
[52] Ueda, M.; Ito, T. *Polymer* **1991**, *23*, 297.

crystalline nature of some of the ketone containing poly(arylene ether)s raises solubility issues, which affect both synthetic routes and means of characterization, not experienced in amorphous analogs. Thus, their synthesis will not be addressed in this review.

2.2.3.1 Electrophilic Aromatic Substitution.

Generation of poly(arylene ether sulfone)s, or any poly(arylene ether), involves the addition of a linking group to one or more compounds containing a preformed aromatic ether bond. Friedel-Crafts catalysis has been a widely accepted pathway for the electrophilic production of poly(arylene ether)s. First, a Lewis acid is used to generate the electrophile followed by the formation of a σ-complex and subsequent rearomatization via proton loss[53]. This mechanism is detailed in Scheme 2.2-2 using benzenesulfonyl chloride and benzene to illustrate the mechanism of the linkage formation.



Scheme 2.2-2: Electrophilic Aromatic Substitution – Friedel-Crafts Chemistry[54]

In the above reaction, the electrophile is generated by the removal of a halide from the sulfone by a Lewis acid. Suitable Lewis acids are those common to Friedel-Crafts chemistry such as $AlCl_3$, $FeCl_3$, $SbCl_5$, $AlBr_3$, BF_3, etc.[54] Similarly, carbonyl compounds can be used in Friedel-Crafts chemistry to form poly(arylene ether)s. However, the use of acid chlorides, such as terephthaloyl or isophthaloyl chloride, limits

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[53] Olah, G. A. In *Friedel-Crafts Chemistry*; Wiley Interscience: New York, 1973; p 488.

[54] Carey, F. A.; Sundburg, R. J. In *Advanced Organic Chemistry: Part A: Structure and Mechanisms*; 3rd ed.; Plenum Press: New York, 1993; p 570.

the use of typical catalysts to $AlCl_3$ and strong acids solutions such as polyphosphoric acid, HF/BF_3, and CF_3SO_3H.[55]

Sulfonylation and similar Friedel-Crafts reactions are facilitated by the presence of electron-donating groups on the aryl ring. The mechanism requires that the ring have sufficient electron density to attack the electrophile. Additionally, resonance from the donating group concentrates the electron density on the *ortho*- and *para*- positions. Therefore, these two positions often become the preferred sites for electrophilic substitution, with the *para*- being slightly favored due to steric considerations.

The formation of polymeric arylene ethers via electrophilic aromatic substitution can proceed through two general routes, either the condensation of AA-BB type monomers or self-condensing AB type monomers.[56,57] Both approaches to the Friedel-Crafts type polymerization have their strengths and weaknesses.

In the case of AA-BB condensation, there is generally little difference between the aromatic hydrogens to be replaced. Since a reaction conversion of > 99% is needed to achieve high or controlled molecular weights, it is understandable that the barriers dictating *ortho*- *meta*- or *para*- hydrogen activation can be easily overcome by the conditions required for quantitative reactions. Disubstitution, attachment to differing ring-positions, and even reactions with the catalyst can lead to irregularities in the chain structure. It has been observed that when high amounts of catalyst are used, the quantities of HCl isolated, after completion, are in excess of the theoretical.[56] This is most likely due to the attack of metal halides on aromatic nuclei, a known reaction of $AlCl_3$ and $FeCl_3$ under anhydrous conditions.[58] To minimize the likelihood of possible side reactions, routes using smaller amounts of catalyst (0.1-4 wt%) both in bulk and in solution have been explored.[57]

Bulk polysulfonylation was initially attempted via melt polymerization. The resulting low molecular weight material was then ground and sintered at high temperature (150-350°C) under nitrogen to achieve high molecular weight. During the final stage of

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[55] March, J. In *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*; 4th ed.; John Wiley &Sons: New York, 1992; p 539.

[56] Cohen, S. M.; Young, R. H. *J. Polym. Sci. Polym. Chem. Ed.* **1966**, *4*, 722.

[57] Cudby, M. E. A.; Feasey, R. G.; Gaskin, S.; Jones, M. E. B.; Rose, J. B. *J. Polym. Sci., Chem. Ed.* **1969**, *22*, 747.

[58] Thomas, C. A. In *Anhydrous Aluminum Chloride in Organic Chemistry*; Reinhold: New York, 1961; p 648.

[57] Cudby, M. E. A.; Feasey, R. G.; Gaskin, S.; Jones, M. E. B.; Rose, J. B. *J. Polym. Sci., Chem. Ed.* **1969**, *22*, 747.

the reaction, a vacuum was applied to aid in the elimination of HCl from the product. Unfortunately, sulfonyl chlorides tend to undergo thermal decomposition above 250°C. The resultant radicals proceeded to crosslink the polysulfones chains, creating insoluble, unprocessible materials.[59]

In contrast, polysulfonation via solution processes using a lower catalyst concentration afforded soluble high molecular weight polymers.[60] Using $FeCl_3$ (1-5 mol%) as the catalyst, low temperatures (120-140°C), and solvents like nitrobenzene, dimethylsulfone, or chlorinated biphenyls, the polysulfones produced still had one unresolved issue; namely, the metal hydride catalyst needed to be selectively removed from solution. Any catalyst remaining in the isolated product would have detrimental effects on the ultimate properties and stability of the polysulfone. This requirement became the “Achilles’ heel” for the commercial synthesis of poly(arylene ether)s by electrophilic aromatic substitution.

The AB self-condensation of monosulfonyl chlorides does have some advantages over AA-BB condensates. One of the best features of a self-condensing monomer is that it allows for guaranteed 1:1 stoichiometry. There is no mode of preferential loss of monomer. Any reactive group lost in transfer automatically takes one of its complementary reactive sites with it, correcting for any physical error. However, the sulfonyl group deactivates its attached aryl rings by withdrawing electrons. Therefore, high temperature is required for high conversion. This eliminates most volatile, low boiling solvents as they will distill off, and it reintroduces a means for crosslinking side reactions to occur.

In summary, poly(arylene ether)s can be produced through the use of electrophilic aromatic substitution. Nonetheless, the reaction conditions required to do so are complex and can lead to a variety of side reactions.

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[59] Bain, P. J.; Blackman, E. J.; Cummings, W.; Hughes, S. A.; Lynch, E. R.; McCall, E. B.; Roberts, R. J. *Proc. Chem. Soc.* **1962**, 86.

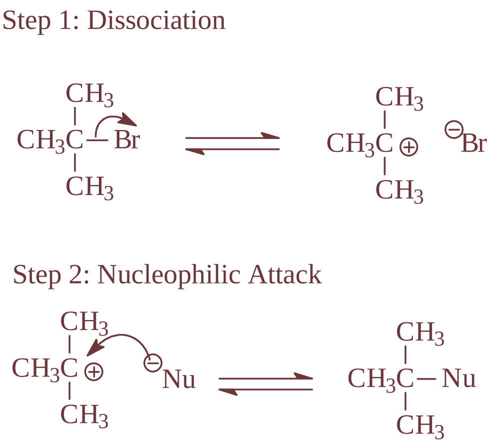
[60] Cudby, M. E. A.; Feasey, R. G.; Jennings, B. E.; Jones, M. E. B.; Rose, J. B. *Polymer* **1965**, *6*, 589.

2.2.3.2 Nucleophilic Aromatic Substitution.

Since Johnson *et al.*,[61] first produced high molecular weight poly(ether sulfone)s by nucleophilic aromatic substitution, this pathway has become the most studied and well developed method to produce poly(arylene ether)s. Additions by a nucleophilic processes are generally thought to proceed through one of four canonical mechanisms (S_N1, S_N2, S_NAr, and $S_{RN}1$.[62] In this section, general characteristics each mechanism will be briefly described followed by a discussion of its applicability to aromatic substitution.

2.2.3.2.1 *S_N1 and S_N2 Mechanisms*

The first mechanism is the S_N1 pathway, shown in Scheme 2.2-3. In the S_N1 mechanism, the halide substituent must completely dissociate from the aromatic ring before substitution occurs.[63] This reaction is a two-step process in which the intermediate carbocation can react by multiple paths. Impurities from carbocation rearrangement and racemization of stereochemistry (from a mixture of front and back-side attack of the nucleophile) are often encountered. Additionally, since the dissociation of the leaving group is the rate-determining step, unimolecular kinetics are observed.



Scheme 2.2-3: The S_N1 Mechanism[64]

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

[62] March, J. In *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*; 4th ed.; John Wiley &Sons: New York, 1992; p 641.

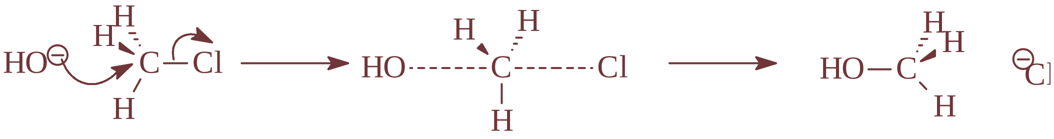
[63] Volhardt, K. P. C. *Organic Chemistry*; W.H. Freeman and Company: New York, 1987. 235-244

[64] Volhardt, K. P. C. *Organic Chemistry*; W.H. Freeman and Company: New York, 1987. 236

In reference to aromatic substitution, it has been argued that the reaction rates can be influenced, depending on ring position, by the chemical nature of existing aryl substituents.[55,65,66] If an inductively electron donating group is located *meta*- to the leaving group, it may stabilize the intermediate aryl cation. If the activating group is located at the *ortho*- or *para*- positions, both inductive and resonance stabilization are possible. Any stabilization of the aryl cation increases the reaction rates as it lowers the energy of the transition state.

However, the applicability of the S_N1 reaction scheme to aryl substitution is limited.[67] Aryl cations are extremely unstable, even less stable than primary carbocations. Furthermore, the geometry of a proposed S_N1 intermediate, when examined closely, refutes any resonance stabilization arguments. In order to be formed from a halide bond, the sp^2 orbital must be localized, and thus perpendicular to the plane of the π-orbitals of the aromatic ring. This situation would allow minimal stabilization via resonance. Although the electron density on the carbon can be increased, the empty sp^2 orbital cannot directly accept electrons via resonance. Thus any so-called resonance stabilization is more of an extended inductive stabilization rather than resonance.

The S_N2 mechanism involves the simultaneous cleavage and formation of carbon bonds, shown in Scheme 2.2-4. S_N2 reactions are one-step, concerted reactions in which the transition state resembles a trigonal bipyramidal geometry with a pentacoordinate carbon.[68]



Scheme 2.2-4: The S_N2 mechanism[68]

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[55] March, J. In *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*; 4th ed.; John Wiley &Sons: New York, 1992; p 641.
[65] Rinehart, K. L., Ed. *Aromatic Substitution Reactions*; Prentice-Hall Inc.: Englewood, NJ, 1968.
[66] Lewis, E. S.; Miller, E. B. *J. Am. Chem. Soc.* **1975**, *97*, 791.
[67] Carey, F. A.; Sundburg, R. J. In *Advanced Organic Chemistry: Part A: Structure and Mechanisms*; 3rd ed.; Plenum Press: New York, 1993; pp 579-587.
[68] Volhardt, K. P. C. *Organic Chemistry*; W.H. Freeman and Company: New York, 1987. 196

The general S_N2 mechanism, also called the direct displacement mechanism, is characterized by an inversion of stereochemistry (as the nucleophile attacks exclusively from the backside) and bimolecular kinetics. Since the product is formed as the leaving group departs, the rate of reaction is dependent upon the concentrations of both species.

Unfortunately, the utility of this mechanism to describe nucleophilic substitution on aryl rings is not possible.[67] The conditions surrounding aromaticity demand that the back lobe of an sp^2 hybridized orbital used to form any radial bond points directly to the center of the ring. The geometry of the remainder of the aryl ring restricts access to the reactive lobe, such that no backside attack is possible. This physical blockade of the reaction site effectively halts all consideration of the S_N2 mechanism for aryl substitution.

2.2.3.2.2 *Aryne and S_NAr mechanisms*

There are two universally accepted nucleophilic aromatic substitution mechanisms.[55,65,67,69] In both cases a two-stage reaction occurs, one being the addition of the nucleophile and the other the elimination of the leaving group. The classical addition-elimination "S_NAr" mechanism is the most prevalent and commonly encountered explanation, while the elimination-addition "aryne" mechanism is a more unusual rationalization.

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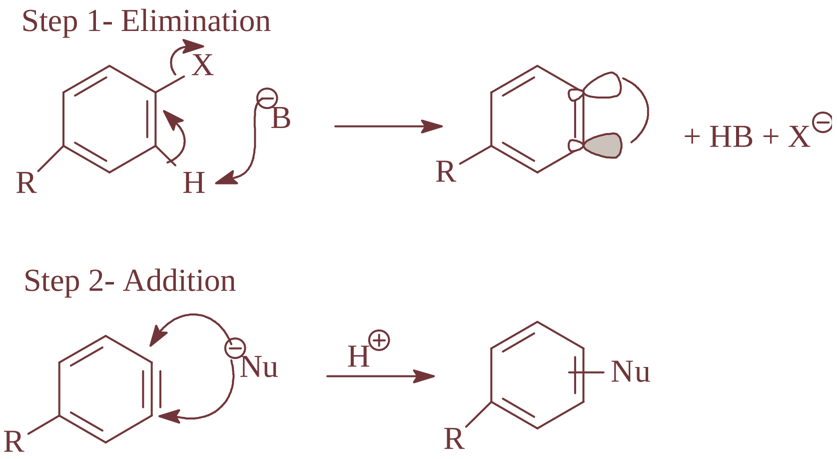
[67] Carey, F. A.; Sundburg, R. J. In *Advanced Organic Chemistry: Part A: Structure and Mechanisms*; 3rd ed.; Plenum Press: New York, 1993; pp 579-587.

[55] March, J. In *Advanced Organic Chemistry: Reactions, Mechanisms, and Structure*; 4th ed.; John Wiley &Sons: New York, 1992; p 641.

[65] Rinehart, K. L., Ed. *Aromatic Substitution Reactions*; Prentice-Hall Inc.: Englewood, NJ, 1968.

[69] Miller, J. *Aromatic Nucleophilic Substitution*; Elsevier: New York, 1968.

2.2.3.2.2.1 “Aryne” Elimination-Addition Mechanism



Scheme 2.2-5: “Aryne” Elimination – Addition Mechanism[70]

In the “aryne” elimination-addition mechanism (Scheme 2.2-5), a strong base is used to abstract a proton, *ortho*- to the halide group, from a non-activated aryl halide ring.[70] The addition of electron density to the ring system induces the departure of the leaving group. The “unbonded” neighboring sp^2 orbitals then share electrons left by the proton abstraction to form a weak bond in the plane of the ring.[71] The overall bond character of the “triple” bond is stronger and shorter than that of a typical C=C, but weaker and longer than a typical C≡C.[72] The aryne (also known as dehydrobenzene and benzyne)[73] formed, with all of its electron density, is quite susceptible to nucleophilic attack and will react to regain its aromaticity. However, this reaction path is not selective and the nucleophile can attack either end of the “triple” bond. A mixture of regioisomeric products is characteristic of this mechanism,[74,75] as is the fact that more polarizable substituents and different leaving groups accelerate the reaction.[76]

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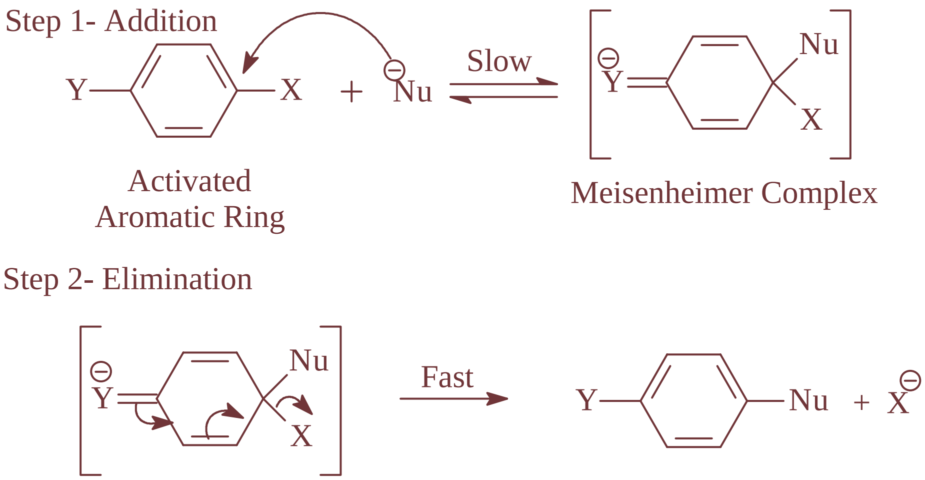
[70] Volhardt, K. P. C. *Organic Chemistry*; W.H. Freeman and Company: New York, 1987.
[71] Hoffman, R. W.; Inamura, A.; Hehre, W. J. *J. Am. Chem. Soc.* **1968**, *90*, 1499.
[72] Laing, J. W.; Berry, R. S. *J. Am. Chem. Soc.* **1976**, *98*, 660.
[73] Hoffman, R. W. *Dehydrobenzene and Cycloalkynes*; Academic Press: New York, 1967.
[74] Roberts, J. D.; Semenow, D. A.; Simmons, H. E.; Carlsmith, L. A. *J. Am. Chem. Soc.* **1956**, *78*, 601.
[75] Friedman, L.; Longullo, F. M. *J. Org. Chem.* **1968**, *34*, 3595.
[76] Huisgen, R.; Sauer, J. *Angew. Chem.* **1960**, *72*, 91.

2.2.3.2.2.2 S_NAr – Addition-Elimination Mechanism

The addition-elimination pathway to nucleophilic substitution is called the S_NAr mechanism. This mechanism involves the addition of a nucleophile to the same carbon to which the halide leaving group is bonded. The overall S_NAR mechanism is illustrated in Scheme 2.2-6.



Y = Electron withdrawing group,
X = Halogen - Leaving group,   Nu = Nucleophile

Scheme 2.2-6: The S_NAr Mechanism

The addition of the nucleophile is normally the rate-determining step, as the aromaticity of the activated ring is disturbed. The resonance-stabilized intermediate is called a Meisenheimer complex,[77] and the reaction is completed by the elimination of the halide anion and a restoration of aromaticity. The unusual ipso addition of the nucleophile without the displacement of the leaving group (forming the Meisenheimer complex) is thought to be attributed to the use of a vacant carbon π*-orbital to form the new nucleophile carbon bond.[69] This proposed pathway is supported by the isolation of some Meisenheimer complexes, as salts.[78,79]

The reactivity of an aromatic species toward nucleophilic aromatic substitution is a result of several factors. Electron withdrawing groups, such as nitro, sulfonyl, carbonyl,

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[77] Meisenheimer, A. *J. Leibligs. Ann. Chem.* **1902**, *323*, 205.
[69] Miller, J. *Aromatic Nucleophilic Substitution*; Elsevier: New York, 1968.
[78] Buncel, E.; Norris, A. R.; Russell, K. E. *Q. Rev. Chem. Soc.* **1968**, *22*, 123.
[79] Strauss, M. J. *Chem. Rev.* **1970**, *70*, 667.

and phosphine oxides, located either *ortho*- or *para*- to the leaving group can activate the aryl halide by stabilizing the Meisenheimer complex via resonance, and thus accelerate substitution. Conversely, electron-donating groups like amines and methoxy groups hinder substitution by increasing the stability of the starting material.

The nature of the leaving group also influences the reaction; surprisingly the standard scaling with bond strength (stronger bond, slower reaction) is not observed. Instead, the polarizability of the C-X bond becomes a greater factor than the strength of the bond.[69] This is reasonable since the rate-determining step is the addition of the nucleophile. Thus, the greater the partial positive charge on carbon becomes, the more attractive it is to the nucleophile, which results in faster formation of the intermediate and a more facile overall reaction. Since the slow step involves the addition of the nucleophile, the identity of the nucleophile is key to the rate of reaction. Additionally, the expected scaling, (stronger nucleophile, faster addition) with nucleophilic strength applies.[80]

In order to form the Meisenheimer complex, the nucleophile must first be generated. For the synthesis of polyarylene ethers this is most commonly achieved through the reaction of a base with an aromatic bisphenol. The selection of the required base and its relative strength is not trivial. If a strong base such as aqueous sodium hydroxide (NaOH) is used to generate the bisphenate, then an exact stoichiometric amount (relative to the bisphenol) must be used. Any excess base may cause hydrolysis of the dihalide. This would disrupt the stoichiometric balance of the bisphenate and the activated dihalide (by generating additional phenate groups from the dihalide), resulting in lower molecular weight material.[81]

In contrast, if a weaker base such as sodium or potassium carbonate (Na_2CO_3 or K_2CO_3) is used, many of the side reactions may be minimized.[82] Generally, carbonates are much weaker bases compared to hydroxides. Additionally, it has been shown that K_2CO_3 only reacts rapidly with bisphenols at elevated temperatures and is rather

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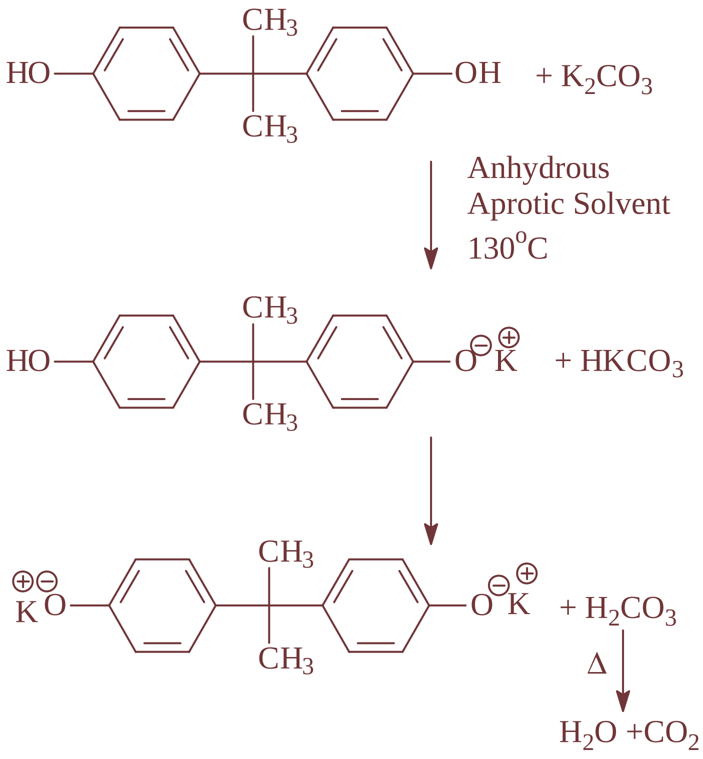
[69] Miller, J. *Aromatic Nucleophilic Substitution*; Elsevier: New York, 1968.

[80] Bunnett, J. F.; Zahler, R. E. *Chem. Rev.* **1951**, *49*, 273.

[81] Johnson, R. N.; Farnham, A. G. *J. Polym. Sci., Part A-1* **1967**, *5*, 2399.

[82] Clendinning, R. A.; Farnham, A. G.; Zutty, N. L.; Priest, D. C. In *847 963*; Union Carbide Corp.: Canadian Patent, 1970.

unreactive towards activated dihalides.[83,84] Therefore, an excess of weak base (up to ~50 %) can be used to ensure formation of the bisphenates without the disturbance of the phenate-halide stoichiometric balance. In using K_2CO_3 to form the bisphenates, water and carbon dioxide are also formed, as shown in Scheme 2.2-7.



Scheme 2.2-7: Generation of Bisphenates by K_2CO_3 (Weak Base Method)[85]

The formation of water during decomposition is an important reason that the step polymerization is performed in two stages.[83] The first is a lower temperature stage (~130°C) where the bisphenate and water are formed. Next, the water is removed and the temperature is increased (165-190°C) to facilitate the formation of a high molecular weight polymer. Other Lewis bases, like fluoride salts (e.g., KF) for example, can be used to catalyze nucleophilic substitution, but the reaction temperatures needed to achieve high molecular weight materials are more extreme (220-280°C).[86,87]

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[83] Viswanathan, R.; Johnson, B. C.; McGrath, J. E. *Polymer* **1984**, *25*, 1927.

[84] Viswanathan, R. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, Va, 1981.

[85] Hedrick, J. L.; Mohanty, D. K.; Johnson, B. C.; Viswanathan, R.; Hinkley, J. A.; McGrath, J. E. *J. Polym. Sci. Polym. Chem. Ed.* **1986**, *23*, 287.

[83] Viswanathan, R.; Johnson, B. C.; McGrath, J. E. *Polymer* **1984**, *25*, 1927.

[86] Ando, T.; Yamawaki, J.; Kawate, T. *Chem. Lett.* **1979**, *45*.

The success or failure of a nucleophilic aromatic substitution reaction often hinges on the use of a proper solvent. Generally, dipolar aprotic solvents such as DMSO, NMP, DMAc, DMF, CHP, diphenyl sulfone or crown ethers are used. These solvents must be compatible with the otherwise highly insoluble polar bisphenates, co-monomers and resultant polymers. However, a co-solvent or non-solvent is often added to azeotrope water, as its removal is key to the formation of high molecular weight polymers. If there is no mechanism to remove water formed by the decomposition of the requisite base, then the water may compete as a nucleophile and react with the activated aryl halide. Either way, the result is a disruption of stoichiometry, which will result in lower molecular weight materials.[88]

2.2.3.2.3 *Additional Nucleophilic Aromatic Substitution Processes*

2.2.3.2.3.1 Silyl-displacement

Most nucleophilic aromatic substitutions for the formation of polyarylene ethers are carried out in solution. Nonetheless, Kricheldorf et al.[49] demonstrated that polyarylene ethers could be formed from the melt using a reaction of bis(trimethylsilyl ether)s of bisphenols and bis(4-fluorophenyl)sulfone (Scheme 2.2-8).

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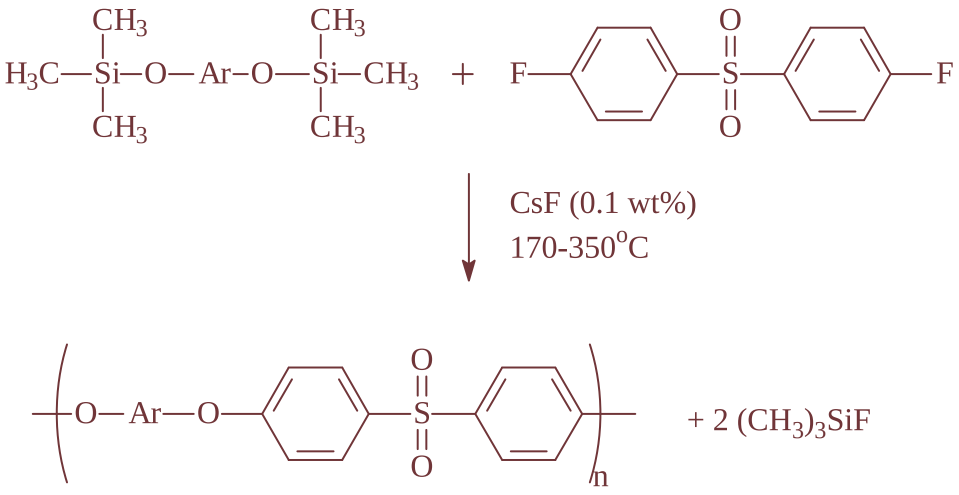
[87] Ando, T.; Yamawaki, J.; Kawate, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 2504.
[88] Hedrick, J. L. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, Va, 1985.
[49] Kricheldorf, H. R.; Delius, U.; Tonnes, K. U. *New Polym. Mater.* **1988**, *1*, 127.



Scheme 2.2-8: Silyl-displacement Reaction[49]

In this case, the desilylation is facilitated by the use of a catalytic amount of fluoride salt, which had previously been shown in small molecule chemistry by Corey and Snider[89] and refined by Fieser in 1982.[90] Unfortunately, the reaction of silylated bisphenols is not applicable to all aromatic dihalides; indeed only the difluoro-compounds are applicable since salts of other halides (KCl, CsCl, KBr, etc.) are not able to initiate the desilylation reaction.[91] Very recently, McGrath and coworkers successfully extended this approach to afford a bisphenol A based poly(arylene ether phosphine oxide) by melt polymerization.[92]

2.2.3.2.3.2 $S_{RN}1$ - A Radical Side Reaction

As previously mentioned, aryl fluorides form high molecular weight polymers more readily than aryl chlorides via nucleophilic substitution. Longer reaction times and higher temperatures should allow researchers to overcome the difference in reactivities. Unfortunately, often when the aryl halide is activated by a carbonyl group, only low molecular weight oligomers are produced. This observation can be explained by a possible competing "$S_{RN}1$" radical mechanism resulting in the reductive elimination of

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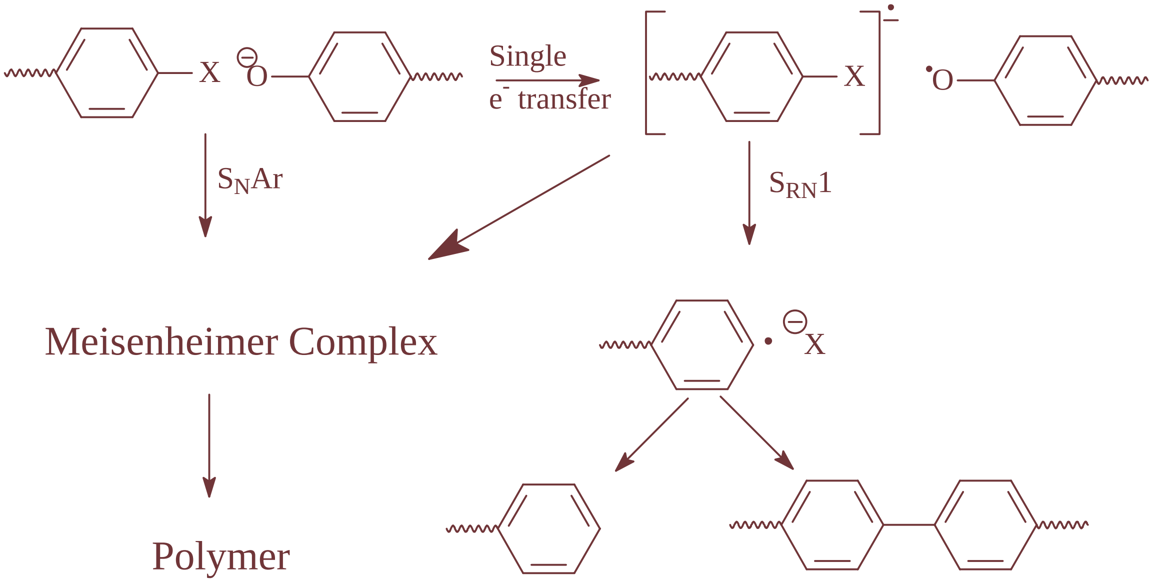
[89] Corey, E. J.; Snider, B. B. *J. Am. Chem. Soc.* **1972**, *94*, 2549.
[90] Fieser, M. *Reagents for Organic Synthesis*; Wiley: New York, 1982; Vol. 10.
[91] Kricheldorf, H. R.; Jahnke, P. *Makromol. Chem.* **1990**, *191*, 2027.
[92] McGrath, J. E.; Mecham, S. J.; Hickner, M. A.; Sankarapandian, M.; Greico, L. M. *SAMPE* **1999**, *16*.

chlorine. Percec and Clough[93,94] first postulated that the elimination of chlorine would result in an endcapping of the polymer chain with a non-reactive phenyl ring, terminating the chain end.



Scheme 2.2-9: An $S_{RN}1$ Side Reaction, Producing a “Dead” Chain End[93]

As shown in Scheme 2.2-9, a radical anion is generated from the activated aryl halide via single electron transfer (SET) from the bisphenate. Then the radical anion can either form an ether linkage by recombination with a phenoxy radical or it may dissociate into an aryl radical and the halogen anion. The aryl radical then reacts with a nucleophile to produce a new radical anion, which then transfers its electron to an arylhalide, thereby completing the catalytic cycle. As with most radical processes, termination can occur with the abstraction of a hydrogen, resulting in a non-reactive phenyl ring. This proposed pathway was confirmed by Mohanty et al. in 1993.[95] They were able to achieve high molecular weights using 4,4’-dichlorobenzophenone, which is otherwise well known to have low reactivity, by employing a radical scavenger. Other ways to avoid this side reaction are by careful selection of solvents that do not favor SET, and by the use of more reactive nucleophiles.

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[93] Percec, V.; Wang, J. H.; Clough, R. S. *Makromol. Chem., Macromol. Symp* **1992**, *54/55*, 272.
[94] Percec, V.; Clough, R. S. *Macromolecules* **1994**, *24*, 1535.
[95] Mani, R. S.; Zimmerman, B.; Bhatnagar, A.; Mohanty, D. K. *Polymer* **1993**, *34*, 171.

2.2.3.2.3.3 Metal Mediated Coupling Reactions

Aromatic ethers have long been known to result from the reaction of phenols and aromatic halides in the presence of a catalytic amount of copper (the Ullman reaction).[96] This reaction was first extended to the formation of polymeric materials by Farnham and coworkers[97] and further refined by Farnham, Robeson, Burgoyne and McGrath.[44,98,99,100] The reaction proceeds though the formation of a phenolic salt which reacts with the halide, much like an S_NAr reaction. However, the copper catalyst enables the use of non-activated aromatic halides. As a result, poly(arylene ether)s not possible to synthesize via conventional nucleophilic routes may be obtained. It is interesting to note that the ease of halogen displacement, though the copper mediated reaction, is the opposite of that observed under classical substitution conditions. The larger, less electronegative halides (I, Br, and Cl) with weaker aryl-halogen bonds, react much faster than fluorine. Ullman reactions are typically conducted in inert solvents like benzophenone at elevated temperatures, while the typical copper catalyst is a cuprous chloride/pyridine complex. High molecular weight materials have been achieved using bisphenols and dibromoarylenes; however, poor reproducibility, the need for expensive brominated monomers, and the laborious selective removal of soluble copper salts have limited its wide scale commercialization to unusually high performance applications.[99]

The use of metal mediated synthesis for polyarylene ethers is not limited to the formation of the aryl ether linkage. Nickel can be used to facilitate an aromatic carbon-carbon bond from aryl halides.[101] Using this technique, biphenol units can be incorporated into the structure of a polyarylene ether without encountering the limited solubility of bisphenates. In fact, nickel-mediated coupling allows the use of both activated and non-

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[96] Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; 2nd ed.; Wiley-Interscience: New York, 1994.

[97] Johnson, R. N.; Farnham, A. G. In *US Patent 3 332 909*: US, 1967.

[44] Robeson, L. M.; Farnham, A. G.; McGrath, J. E. In *Molecular Basis of Transitions and Relaxations*; Boyer, R. F., Meier, D. J., Eds.; Gordon: New York, 1978; pp 405-425.

[98] Jurek, M. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, Va, 1987.

[99] Robeson, L. M.; Burgoyne, W. In *US Patent 5,658,994*; Air Products, Inc., 1997.

[100] Jurek, M.; McGrath, J. E. *Polymer Preprints* **1987**, *28(1)*, 180.

[99] Robeson, L. M.; Burgoyne, W. In *US Patent 5,658,994*; Air Products, Inc., 1997.

[101] Colon, I.; Kwiatokowski, G. T. *J. Polym. Sci. Polym., Polm. Chem.* **1991**, *28*, 367.

activated dihalides under mild reaction conditions. Using a zero-valent nickel complex, like nickel-tetratriphenylphosphine, reactions can be conducted in aprotic solvents at relatively low temperatures (60-80°C).[102] Other examples of nickel catalyzed coupling reactions include the synthesis of poly(4-4'diphenylphenylphosphine oxide) by Ghassemi and McGrath using a mixture of $NiCl_2$, bipyrridine, zinc powder and triphenylphosphine in an inert atmosphere.[103] Also, DeSimone et al.[104] have explored the polymerization of the Schiff base of 4,4'-dichlorobenzophenone. Nickel is not the only metal than has been used to form poly(arylene ether)s, and additional coupling reactions have mimicked the Scholl reaction $FeCl_3$[105] to form poly(ether sulfone)s and poly(ether ketone)s and the Suzuki reaction (palladium tetratriphenylphosphine) to yield poly(arylene ether ketone)s.[106]

2.2.4 Phosphine and Phosphine Oxide Containing Organic Polymers

Perhaps the first reported synthesis of a polymeric material containing phosphorus was in 1897, when Stocks introduced polyphosphazine, a so-called "inorganic rubber".[107] Though developed in the late 19th century, the commercial potential of this class of polymers was underdeveloped until the 1960s. More recently, a wide range of phosphorus containing organic polymers has been investigated, resulting in a wide range of properties for uses in fire retardants, aerospace, maritime applications, and oil discovery.[108] As a class of materials, phosphorus containing organic polymers display certain common traits. They are known to be highly fire retardant, show increased adhesion to metals, and increased polarity when compared to their non-phosphorus containing analogs. Synthetically, many condensation- and addition-polymerization routes can be used to produce phosphorus containing organic polymers. Of particular interest are the polyphosphazines,[109] polyphosphonites,[110] polyphosphonates,[108,111,112,113]

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[102] Colon, I.; Marcesca, L. M.; Kwiatokowski, G. T. In *US. Patent 4,263,466*; Anoco: US, 1999.
[103] Ghassemi, H.; McGrath, J. E. *Polymer* **1997**, *38*, 3139.
[104] Phillips, R. W.; Sheares, V. V.; Samulski, E. T.; DeSimone, J. M. *Macromolecules* **1994**, *27*, 2354.
[105] Percec, V.; Wang, J. H.; Oishi, Y. J. *J. Polym. Sci. Polym. Chem. Ed.* **1991**, *29*, 949.
[106] Rehahn, M.; Schluter, A. D.; Wegner, G. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 535.
[107] Stocks, H. N. *Am. Chem. J.* **1897**, *19*, 782.
[108] Millich, F.; Lambing, L. L. *J. Polym. Sci., Polym. Chem.* **1980**, *18*, 2155.
[109] Allcock, H. R. In *ACS Symposium Series No. 360*; ACS: Washington, D.C., 1988.
[110] Steininger, E.; Sander, M. *Kunststoffe* **1964**, *54*, 507.
[108] Millich, F.; Lambing, L. L. *J. Polym. Sci., Polym. Chem.* **1980**, *18*, 2155.

poly(styrene phosphonate diethyl ester),[114] poly(4-vinylbenzene phosphonic acid diethyl ester),[115] and phosphine oxide containing polymers. The successful incorporation of phosphine oxide moieties has been reported for polyimides,[116],[117] polyamides,[118] epoxy resins,[119] polycarbonates,[120] polyurethanes,[121] and poly(arylene ether)s.[122,123,124]

Initial explorations of polymeric phosphonate and phosphine oxide containing materials have generally yielded hydrolytically unstable products due to the utilization of P-O-C bonds along the backbone. Some P-O-C bonds are notoriously susceptible to hydrolysis. In fact they are so unstable that hydrolysis can be initiated with atmospheric moisture.[125,126] The desire to increase the stability of phosphorus containing polymers led to the development of triaryl- and diphenylmethyl- phosphine oxide monomers.[123] These new monomers incorporated stable C-P-C bonds and were found not only to increase stability but also to impart fire retardance, disruption of crystallinity, binding sites for hydrogen bonding, and reactive sites for further reactions when incorporated into the backbone of a polymer. The very nature of a phosphine oxide bond accounts for most of these qualities. The polarizability of the P=O bond justifies the observed increase in a polymer's ability to hydrogen bond and complex with salts. Additionally, the oxides may be easily reduced to phosphines, further increasing the potential for complexation through the available lone pairs.[127,128] Aryl phosphine oxides are normally non-coplanar in

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[111] Kim, K. S. *J. Appl. Polym. Sci.* **1983**, *28*, 1119.

[112] Shobha, H. K.; Johnson, H.; Sankarapandian, M.; Rangarajan, P.; McGrath, J. E. *46th International SAMPE Symposium,* **2001**.

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[114] Cabasso, I.; Jagur-Gradzinski, J.; Vofsi, D. *J. Appl. Polym. Sci.* **1974**, *18*, 2137.

[115] Hartmann, H.; Hipler, U.-C.; Carlsohn, H. *Acta. Polym.* **1980**, *31*, 700.

[116] Varma, I. K.; Roa, B. S. *J. Appl. Polym. Sci.* **1983**, *28*, 2805.

[117] Tan, B.; Tchatchoua, C. N.; Dong, L.; McGrath, J. E. *Polym. Advan. Technol.* **1998**, *9*.

[118] Wan, I. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, VA, 1995.

[119] Senear, A. E.; Valient, W.; Wirth, J. *J. Org. Chem.* **1960**, *25*, 2001.

[120] Knauss, D. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, VA, 1995.

[121] Ji, Q.; Muggli, M. W.; Wang, F.; Ward, T. C.; Burns, G. W.; Sorathia, U.; McGrath, J. E. *Polym. Prepr.* **1997**, *213*, 120.

[122] Riley, D. J.; Gungor, S. A.; Srinivasan, S.; Sankarapandian, M.; Tchatchoua, C. N.; Muggli, M. W.; Ward, T. C.; McGrath, J. E.; Kashiwagi, T. *Poly. Eng. Sci.* **1997**, *37*, 1501.

[123] Hashimoto, S.; Furukawa, I.; Ueyama, K. *J. Macromol. Sci. Chem.* **1977**, *A11*, 2167.

[124] Smith, C. D.; Grubbs, H.; Webster, H. F.; Gungor, S. A.; Wightman, J. P.; McGrath, J. E. *High Perform. Polym.* **1991**, *4*, 211.

[125] Tchatchoua, C. N. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, Va, 1999.

[126] Maiti, S.; Banerjee, S.; Palit *Prog. Polym, Sci.* **1993**, *18*, 227.

[123] Hashimoto, S.; Furukawa, I.; Ueyama, K. *J. Macromol. Sci. Chem.* **1977**, *A11*, 2167.

[127] Bonaplata, E. In *M.S. Thesis*; Virginia Polytechnic Institute and State University: Blacksburg, VA, 1994.

[128] Bonaplata, E.; Ding, H.; Hanson, B. E.; McGrath, J. E. *Polymer* **1995**, *36*, 3035.

structure (See Figure 2.2-3) and provide “kinks” along the polymer backbone, hindering the chain’s ability to properly align for crystallization. This often results in an amorphous morphology where otherwise one would expect crystallinity to be observed.

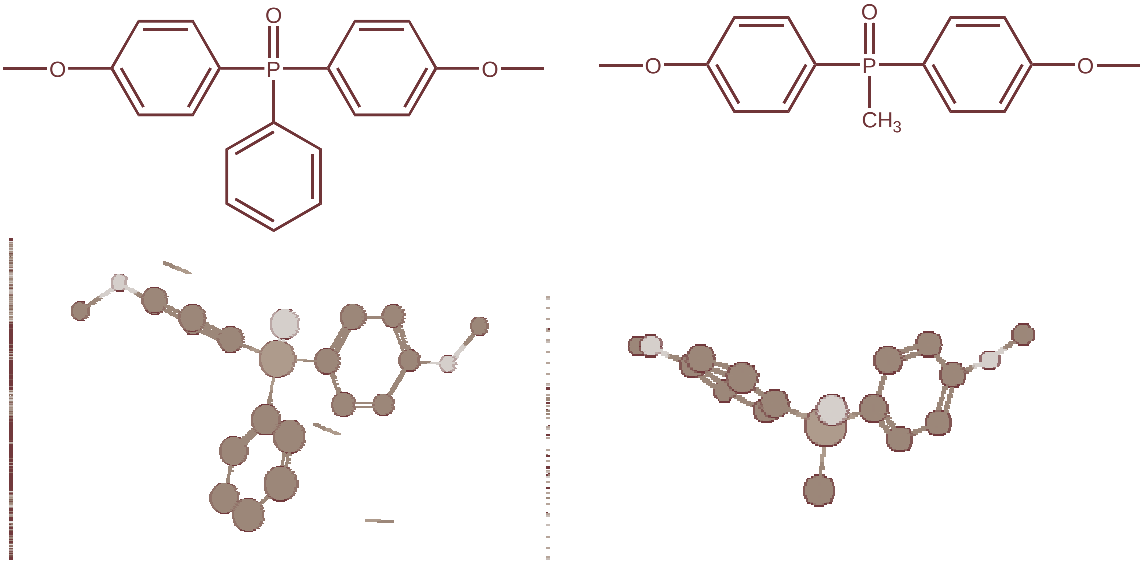

Figure 2.2-3: 3D model of Aryl Phosphine Oxide Monomers
(shown with methoxy endcaps- model from Chem3D Pro)

The incorporation of a triaryl-phosphine oxide group in a poly(arylene ether) was first reported in 1977. Hashimoto et al.[123] were able to produce low molecular weight oligomers from bis(4-chloropheny)phenylphosphine oxide and bisphenols in aprotic polar solvents using sodium hydroxide as the base. As described previously in the discussion of the S_NAr mechanism, the use of such a strong base introduces competing reactions, which reduces molecular weight. Later, Hergenrother et al.[129] and Smith et al.[124] prepared high molecular weight PEPOs using bis(4-fluorophenyl)phenyl phosphine oxide and a weaker base (K_2CO_3). Priddy[130] and later Riley et al.[122,131] extended this work and many structural units, such as carbonyl, sulfonyl, etc. were successfully incorporated into the polymer backbone. These polymers were found to be thermally stable, amorphous with high T_gs, and demonstrated very high decomposition temperatures. Thermogravimetric analysis showed high char yield both in nitrogen and in air, indicating potential application as fire retardant materials, which was later confirmed by cone calorimetry.[131] It should also be noted that the new polymer was totally amorphous, optically clear, and colorless. In addition, the poly(arylene ether phosphine oxide) displayed a much higher refractive index (n=1.68) than polycarbonate (n=1.58), suggesting their potential application as optical materials.

Recently, McGrath and coworkers successfully synthesized a bisphenol A based PEPO by melt polymerization[92] via a silyl ether displacement, similar to the synthesis of polysulfone by Kricheldorf et al.[49] This approach does not require the removal of catalyst and avoids using a solvent. Moreover, the resulting polymer can be directly melt processed. Additional studies by McGrath and Wang showed the ability to uniformly disperse nanoparticles of silica and metal salts via hydrogen bonding or complexation

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[123] Hashimoto, S.; Furukawa, I.; Ueyama, K. *J. Macromol. Sci. Chem.* **1977**, *A11*, 2167.
[129] Hergenrother, P. M.; Jensen, B. J.; Havens, S. J. *Polymer* **1988**, *29*, 356.
[124] Smith, C. D.; Grubbs, H.; Webster, H. F.; Gungor, S. A.; Wightman, J. P.; McGrath, J. E. *High Perform. Polym.* **1991**, *4*, 211.
[130] Priddy, D. B. In *Ph. D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, VA, 1994.
[122] Riley, D. J.; Gungor, S. A.; Srinivasan, S.; Sankarapandian, M.; Tchatchoua, C. N.; Muggli, M. W.; Ward, T. C.; McGrath, J. E.; Kashiwagi, T. *Poly. Eng. Sci.* **1997**, *37*, 1501.
[131] Riley, D. J. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, Va, 1997.
[92] McGrath, J. E.; Mecham, S. J.; Hickner, M. A.; Sankarapandian, M.; Greico, L. M. *SAMPE* **1999**, *16*.
[49] Kricheldorf, H. R.; Delius, U.; Tonnes, K. U. *New Polym. Mater.* **1988**, *1*, 127.

with phosphine oxide containing poly(arylene ether)s.[132]

Furthermore, phosphine oxide containing polymers can be chemically modified by reducing the phosphonyl group to phosphine using phenylsilane.[133] The phosphine group can be further reacted with halo-compounds to generate phosphonium salts.[134] This kind of polyelectrolyte has also been employed to prepare nonlinear optical (NLO) materials.[131]

To summarize, although many other routes have been explored, the most effective and efficient way to produce poly(arylene ether)s is via nucleophilic aromatic substitution. This substitution reaction proceeds through the S_NAr mechanism. The incorporation of phosphine oxide moieties into the backbone of polymers, increases fire retardance, solubility and the amorphous content of a polymer, and introduces the ability to hydrogen bond or complex with metal salts. Moreover, the phosphine oxide group provides a site for further reactions via reduction to phosphines.

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[132] Wang, S. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, Va, 2000.
[133] Ghassemi, H.; McGrath, J. E. *Polymer* **1997**, *38*, 3139.
[134] Ghassemi, H.; Riley, D. J.; Curtis, M.; Bonaplata, E.; McGrath, J. E. *Appl. Organomet. Chem.* **1998**, *12*, 781.
[131] Riley, D. J. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, Va, 1997.

2.2.5 Overview of Selected Optical Properties of Polymers

Poly(arylene ether phosphine oxide)s are amorphous transparent polymers with a glass transition temperature (T_g) near 200°C or even higher[124,122]. They have high refractive index values ~1.648, and therefore have been considered for use as a possible optical lens materials. To put these considerations in a clearer frame of reference, a brief overview of the utilization of polymers as optical materials will be presented.

The refractive index (n) is the most well known parameter used to evaluate optical materials. It is used to describe the ratio of the speed of light through a given material and the speed of light in a vacuum (c_o= 3.00x10^8 m/s) as follows. $n = \frac{c_o}{c}$. As a beam of light passes from one medium to another of greater density (air to lens), the velocity of the light is reduced and the path is bent towards the normal of the surface.[135] The larger the value of the refractive index, the more a beam of light is bent. If the surface is curved, as in the case with convex lenses, then light can be concentrated at a distance proportional to the curvature and refractive index of the material (the focal length). The refractive indices (and Abbe numbers, defined later) of several polymers and inorganic glasses are given in Table 2.2-1.

Material	Refractive Index n	Density g/m3	Abbe #
polydimethylsiloxane	1.404	975	40.4
poly(methyl methacryate)	1.491	1190	57.2
allyl diglycol carbonate (thermoset)	1.499	1320	57.8
polyacrylontirile	1.518	1170	n/a
silicate crown glass	1.525	2530	58.6
poly(acrylonitrile-co-styrene)	1.571	1070	35.3
bisphenol-A polycarbonate	1.586	1200	30.3
polystyrene	1.59	1100	30.9
polyarylene ether phosphine oxide	1.648	n/a	24.5

Table 2.2-1: Optical Properties of Common Polymers and Glass[136]

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[124] Smith, C. D.; Grubbs, H.; Webster, H. F.; Gungor, S. A.; Wightman, J. P.; McGrath, J. E. *High Perform. Polym.* **1991**, *4*, 211.

[122] Riley, D. J.; Gungor, S. A.; Srinivasan, S.; Sankarapandian, M.; Tchatchoua, C. N.; Muggli, M. W.; Ward, T. C.; McGrath, J. E.; Kashiwagi, T. *Poly. Eng. Sci.* **1997**, *37*, 1501.

[135] Meeten, G. H. In *Optical Properties of Polymers*; Meeten, G. H., Ed.; Elsevier Science: New York, 1986.

[136] Mills, N. J. In *Encyclopedia of Polymer Science and Engineering*: New York, 1991; Vol. 10, pp 493-540.

It is important to note that since the refractive index measures differences in velocity on the scale of 1.00x10^7 meters per second, a variance of 0.01 is noticeable by the eye, while a variance of 0.1 is remarkable.[137] To give an example of the scale of these changes, imagine being given a pair of transparent plates of even thickness. One is common borosilicate crown glass (n~1.52)[136] and the other is the transparent plastic polymethyl methacrylate, commonly known by the ICI trade name Plexiglass™ (n~1.49).[136] If these plates were placed on a piece of paper with a solid line drawn on it, this line would appear to break, if viewed at any angle other that 90° to the surfaces.

The refractive index varies for each wavelength of light such that the longer the wavelength, the greater the velocity, the less it refracts. Thus, if a material has a high refractive index, the longer wavelength waves will refract less, causing a splitting of the incident beam of light. As illustrated in Figure 2.2-4. This effect is known as the chromatic dispersion or, as sometimes called, the “rainbow effect”.

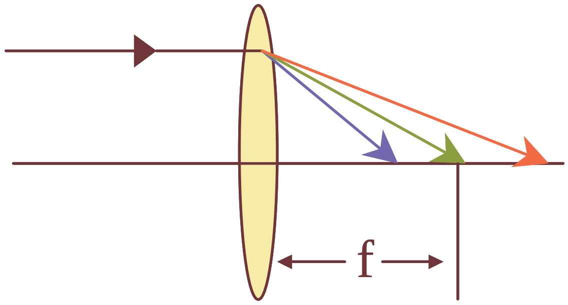

Figure 2.2-4: Illustration of Chromatic Dispersion, the Splitting of Light Due to Differences in Refraction at Given Wavelengths.

This effect is quantified by a value called the Abbe number (v). The Abbe number is a practical quantification of the cohesiveness of visible light transmitted through a material. Experimentally, the actual number is derived by measuring the refractive index of a material at three different wavelengths (461, 589, and 656 nm) and applying those values as shown in Equation 10.[138]

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[137] Carruth, G.; Ehrlich, E., Eds. *The Student Handbook*; Southwestern: New York, 1984; Vol. 2.

[136] Mills, N. J. In *Encyclopedia of Polymer Science and Engineering*: New York, 1991; Vol. 10, pp 493-540.

[138] Keyes, D. In *CRC Handbook of Laser Science and Technology*; CRC Press: New York, 1995; Vol. IV, pp 85-90.

$$\upsilon = \frac{\eta_{589} - 1}{\eta_{481} - \eta_{656}} \tag{10}$$

Higher Abbe numbers indicate a more cohesive beam of light, and thus a clearer image can be delivered to the focal point of the lens. Unfortunately, it has often been observed that the greater the refractive index, the lower the Abbe number becomes. This trend can also be seen upon examination of Table 2.2-1. The classic trade-off of these two competing properties is the main obstacle for researchers of optical materials for lens applications. Ideally, one would want a material with both a high refractive index and Abbe number, which would produce sharp images with minimal distortions.

The human eye has been estimated to have an Abbe value between 43 and 45.[139] As a result, the eye is unable to discern any difference in image quality between two materials with Abbe values greater than 45. At this point the eye itself becomes the limiting factor.

Thermoplastics have many inherent advantages when compared to inorganic glasses. Given a choice of borosilicate or polycarbonate sunglasses, from experience, most people realize that the polycarbonate lenses will have better impact resistance and weigh much less than the silicate lenses. This is due to the fact that for a given focal length, the weight of a lens is proportional to the density of a material divided by its refractive index. In general, these thermoplastics are approximately half as dense as silicate glasses. This results in a lens of comparable refractive index, but about half as thick as traditional counterparts.[136]

Another advantage of thermoplastics is that they are generally melt processible and can be injection molded. This allows the rapid production of finished products without extensive grinding and polishing. Additionally, mounting tabs or slots can be molded into the lenses with relative ease. Thermoplastics also tend be more impact resistant, as they can yield before failure. This flexibility results in less brittle fragmentation and safer conditions for the wearer.[136]

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[139] Okoroafor, M. O., PPG Industries, Inc; Non-Proprietary Internal Document.

[136] Mills, N. J. In *Encyclopedia of Polymer Science and Engineering*: New York, 1991; Vol. 10, pp 493-540.

Unfortunately these advantages do not come without a price. Optical thermoplastics are notorious for their low abrasion resistance, thus eliminating polymeric optical materials as candidates for many applications. Luckily, the application of hard-coats can alleviate some of the susceptibility to scratches, but their inherent low yield stress remains a deterrent. The benefits of relatively low processing temperatures are often offset by two effects. During injection molding, outer layers and thinner parts tend to cool faster and have lower densities than that thicker ones. Therefore, a double convex lens will cool the fastest at the edges while the middle may still be molten. The variances between the skin and the core of a molded lens will often yield a gradient in the refractive index that may be unacceptable for a given application. The second effect of "low" processing temperatures is that it leads to low heat tolerances. Even organic polymers with extremely high glass transition temperatures (up to 260°C) pale in comparison to the heat stability of silicate glasses (> 500°C).[136] Furthermore, most thermoplastic materials undergo 0.7% shrinkage,[140] in the direction of injection, upon cooling. This will affect the ability to produce lenses with a constant radius of curvature. Since a lens has a variable thickness, the physical amount of shrinkage will vary along the curve. This effect can be corrected if the relative amount of shrinkage experienced is known. However, this brings up another potential problem of polymeric optical materials. The thermal variation of the refractive index is much higher than that of silicate glasses. Thus they cannot be trusted to maintain constant image formation over wide temperature ranges (>100°C).

Additionally, to be useful, polymeric optical materials must display little or no absorbance of light from ~380–1000 nm. Unfortunately, most polymeric materials begin to show absorbance from 380-450 nm, as thermal degradation occurs. This can cause a yellowing of the plastic lenses if they are held in the melt for too long. For some applications this can be circumvented by the addition of a blue toner to brighten the resulting product to "water clear". Not only does the blue tint make a product look more clear, if any yellowing does occur, the product will have a slight green color instead of appearing degraded.[138]

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[140] *Handbook of Plastics Optics*; 2nd ed.; U.S. Precision Lenses, Inc.: Cincinnati, Oh, 1983.

[138] Keyes, D. In *CRC Handbook of Laser Science and Technology*; CRC Press: New York, 1995; Vol. IV, pp 85-90.

Typically, new lens technology is focused along one of two different approaches. One is to develop new base materials, which have higher refractive indices and Abbe numbers than current materials. The other involves the production of high refractive thin films, which can be used as coatings for a standard base lens. In this case the power of the lens is determined by varying the thickness of the coating, while the high Abbe base material maintains the cohesive quality of the image. Additionally, silicate glasses are often tuned with metal oxides to achieve the proper index and Abbe numbers.[136] However, most optical plastics are not miscible with the metal oxides, other polymers, and common optical additives to the degree that their incorporation can cause opacity.

Most of the current optical polymers in the open literature are homopolymers, although studies have been conducted on random or statistical copolymers. A typical result of such a study reveals a Fox-like compositional effect on both refractive index and Abbe number.[141] However, the effect of block copolymerization has apparently not been thoroughly explored. This is not surprising since most block copolymers show some form of macroscopic phase segregation or are copolymers based on possibly semi-crystalline, opaque homopolymers. Any heterogeneity exhibiting phase domains on the order of the wavelengths of light will scatter the light and cause opacity. Conversely, if the domain sizes can be limited to below the wavelengths of visible light, (<1000 Å) one expects that a transparent product could be produced.[141] This leads one to wonder how this nanophase separation would affect the optical properties of the resultant material. Indeed, such speculation provided the incentive for the research described in this dissertation.

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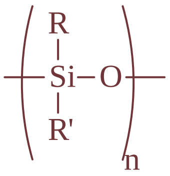
[136] Mills, N. J. In *Encyclopedia of Polymer Science and Engineering*: New York, 1991; Vol. 10, pp 493-540.
[141] Rosen, S. L. *Polym. Eng. Sci.* **1967**, *7*, 115.

2.3 Polydimethylsiloxanes and Siloxane Containing Copolymers

2.3.1 Historical Development and Nomenclature

Polysiloxanes are one of the most unique materials available today. As a class of polymers, polydimethylsiloxanes display an unusually wide range of properties. They can be viscous yet lubricating as liquids, while an apparently solid form can be either rigid or elastomeric. In almost all cases they are highly thermally and oxidatively stable, display a high degree of chemical inertness, show high UV resistance, have low surface energies, have good dielectric strength (making them good insulators), and have attractive physical properties over a wide range of temperatures.[142,143] Siloxanes can be either linear, branched or crosslinked to varying degrees, according to different synthetic routes and/or the use of specialty end or side groups. This diversity of architectures and side groups, as well as their property profiles, helps to explain the wide variety of siloxane materials available today.

Polysiloxanes are macromolecules composed of repeating silicon–oxygen bonds (Si-O-) along the backbone.[144] The silicon atom will generally have two carbon based pendant groups (R) to complete its octet. (Figure 2.3-1) The methyl group is the most important pendant group encountered in industry. Larger groups are less economically and thermodynamically favorable for the formation of high molecular weight polymeric products, although trifluoropropyl, vinyl and phenyl groups are widely employed.



$$-\!\left(\overset{\displaystyle R}{\underset{\displaystyle R'}{\overset{|}{\underset{|}{\mathrm{Si}}}}}-\mathrm{O}\right)_{n}\!-$$

Figure 2.3-1: Siloxane Repeat Unit

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[142] Divornic, P. R.; Lenz, R. W. *Macromolecules* **1992**, *25*, 3769.
[143] Yilgor, I.; McGrath, J. E. In *Adv. Polym. Sci*; Springer-Verlag: New York, 1988; Vol. 86, pp 1-86.
[144] Voronkov, M. G.; Milileshevich, V. P.; Yuzhelevich, Y. A. *The Siloxane Bond*; Consultants Bureau: New York, 1978.

In a discussion of polysiloxanes, the related terminology can be more confusing than for many other polymeric systems. The differences in spelling between terms like silicon, silicone, silica, and siloxane may be subtle, but their meanings are diverse. Silicon is an element; it is a semi-metal used in the production of microelectronic circuits. Silica is a mineral, a naturally occurring silicon-oxygen compound, and the most common source of pure silicon.[145] (See Scheme 2.3-1)

$$\mathrm{SiO_2 + 2\,C} \xrightarrow[3000^{o}\mathrm{C}]{\Delta} \mathrm{Si + 2\,CO}$$

Scheme 2.3-1: Isolation of Silicon from Silica[145]

Silicone is a commercial term applied to polymers and elastomers with silicon-oxygen main chains. However, “the term silicone has no place in scientific nomenclature”.[146] The more scientifically sound terms for a silicon-oxygen based polymers, polysiloxane and siloxane, with the appropriate designations (e.g. dimethyl- etc.) will be used in this review.

The term silicone was coined in the early 1900s by Richard Kippling,[147] and was intended to classify a category of compounds with disubstituted silicon oxygen double bonds ($R_2Si{=}O$), analogous to ketones ($R_2C{=}O$). Kippling theorized that silicone-diols ($R_2Si(OH)_2$) could be dehydrated much like hydrocarbon diols, nevertheless the product isolated was constantly identified to be the higher molecular weight Si-O-Si compounds.[146] Consequently, the materials he isolated were called silicones even though its meaning had inadvertently been changed. Silicone came to represent any number of complex silicon-oxygen polymeric products, many of which were structurally indefinable.[146] This misnomer has persisted to this day. While most polymer chemists and material scientists prefer the more accurate term, polysiloxane, the term silicone continues to persist.

The industrial development of polysiloxanes, such as polydimethylsiloxane, was

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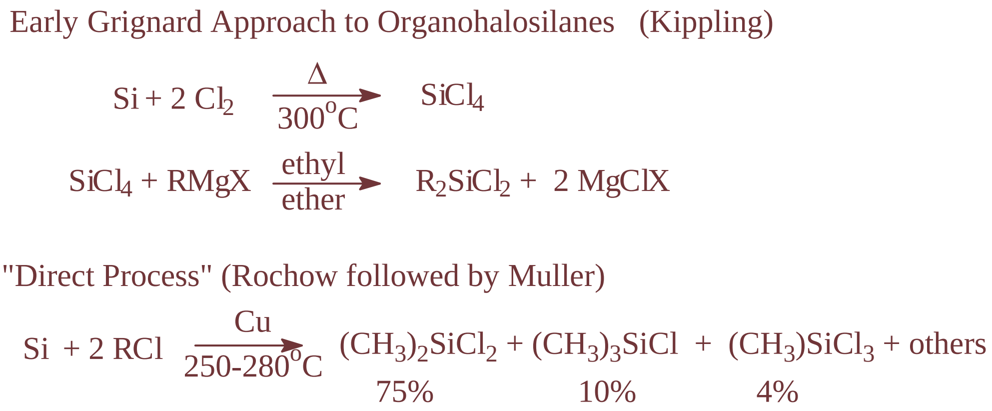
[145] McQuarrie, D. A.; Rock, P. A. *Descriptive Inorganic Chemistry*; W.H. Freeman and Company: New York, 1985.
[146] Hardman, B.; Torkelson, A. In *Encyclopedia of Polymer Science and Engineering*: New York, 1991; Vol. 15.
[147] Kippling, F. S.; Loyd, L. L. *J. Chem. Soc.* **1901**, *79*, 449.

delayed until the 1930s.[148] This lag in development occurred for two reasons. First, Kippling focused on the characterization of the smaller molecules and failed to see the significance of his polymers and polymerization as a whole.[149] Second, the monomers could not be conveniently synthesized on a commercial scale. However, during the 1930s there was a push by several laboratories in the US (Hyde at Corning Glass, Patonode and Rochow at General Electric), Germany (Muller at VEB Silikonchemie) and the former Soviet Republic (Dologov and Andrianov) to independently produce organosilicon monomers and polymers. The race to receive the first patent in the development of commercial organosilicon polymers went to Andrianov in 1939.[150] However, Rochow,[151] followed closely (nine months later) by Muller,[152] made the more significant breakthrough by developing the so-called "direct process" for the economical production of organochlorosilanes used in polysiloxane synthesis.



Early Grignard Approach to Organohalosilanes (Kippling)

$$Si + 2\,Cl_2 \xrightarrow[300^{o}C]{\Delta} SiCl_4$$

$$SiCl_4 + RMgX \xrightarrow[ether]{ethyl} R_2SiCl_2 + 2\,MgClX$$

"Direct Process" (Rochow followed by Muller)

$$Si + 2\,RCl \xrightarrow[250\text{-}280^{o}C]{Cu} \underset{75\%}{(CH_3)_2SiCl_2} + \underset{10\%}{(CH_3)_3SiCl} + \underset{4\%}{(CH_3)SiCl_3} + \text{others}$$

Scheme 2.3-2: Production of Polysiloxane Precursors[153]

The "direct process", a methylchloride/silica gas – solid reaction, yields ~ 75-90% dialkyldichlorosilane, which is isolatable by distillation.[154] The remaining trialkylchlorosilanes and alkyltrichlorides can then be treated with heat and catalysts, such as aluminum chloride, to afford the more useful dialkyldichlorosilanes via a

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[148] McGregor, R. R. *Silicones*; McGraw-Hill: New York, 1954.
[149] Kippling, F. S. In *Proc. Royal Soc. Ser. A*: London, UK, 1937; Vol. 159, p 139.
[150] Andrianov, K. A. In *Russ. Patent 55,889*, 1939.
[151] Rochow, E. G. In *US. Patent 2,380,995*; General Electric Co., 1941.
[152] Muller, R. In *East German Patent 5,348*, 1942.
[153] Voorhove, R. J. H. *Organohalosilanes: Precursors to Silicons*; Elsevier: New York, 1967.
[154] Rochow, E. G. *Chemistry of Silicones*; Wiley: New York, 1951.

"redistribution" reaction.[155]

With the advent of the "direct process," the building blocks for polysiloxanes could be produced from elemental silicon and alkyl chlorides. The controlled hydrolysis of the resultant organochlorosilanes would then afford linear oligomers and cyclic siloxane monomers. These cyclic species could in turn be polymerized by either base or acid- catalyzed ring-opening reactions (a detailed mechanistic discussion is presented in section 2.3.3).

Commercial development of polysiloxanes occurred during World War II, when the need increased for a new breed of materials that could be suitable for a wide range of applications. Polysiloxanes were used for waterproofing and sealant greases, as well as instrument damping liquids and thermoset engine gaskets. After the conclusion of the war, production rapidly expanded into civilian arenas. Currently, siloxanes can be found in rubbers, caulkings, sealants, varnishes, paints, water repellants, diving equipment, adhesives, encapsulants and even medical devices such as replacement heart valves.[14]

Terminology and nomenclature of polysiloxanes is somewhat complicated by the predominance of a shorthand jargon within the industry. However, this shorthand is easily explained. The terminology is dependent on the number and type of subtituents attached to a silicon atom.[156] If a core silicon has a hydrolyzable moiety other than an alkyl group, then it is said to be substituted. A monosubstituted silicon is symbolized by an M, disubstituted by a D, trisubstituted by a T, and tetrasubstituted by a Q (quaternary). The methyl group is the most common side group encountered in polysiloxane chemistry. Thus a dimethyldichlorosilane, and in turn a dimethylsiloxane unit, will be designated D, while any non-methyl substituent is designated by adding a prime (') to the letter of its substitution level. For example, D' could mean either ethylmethylsiloxane or methylphenylsiloxane, while D" could be diphenylsiloxane; the determining factor is the context in which the character is used. Subscripts such as D_n signify that there is a sequence of siloxane bonds equal to the number n. If a subscripted letter stands alone, this signifies a cyclic species, while a subscripted letter enclosed in two or more other

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[155] Stevens, M. P. *Polymer Chemistry: An Introduction*; 2nd ed.; Oxford University Press: New York, 1990.
[14] Odian, G. *Principles of Polymerization*; 3rd ed.; Wiley Interscience: New York, 1991.

letters designates a linear moiety. For further examples see Figure 2.3-2.

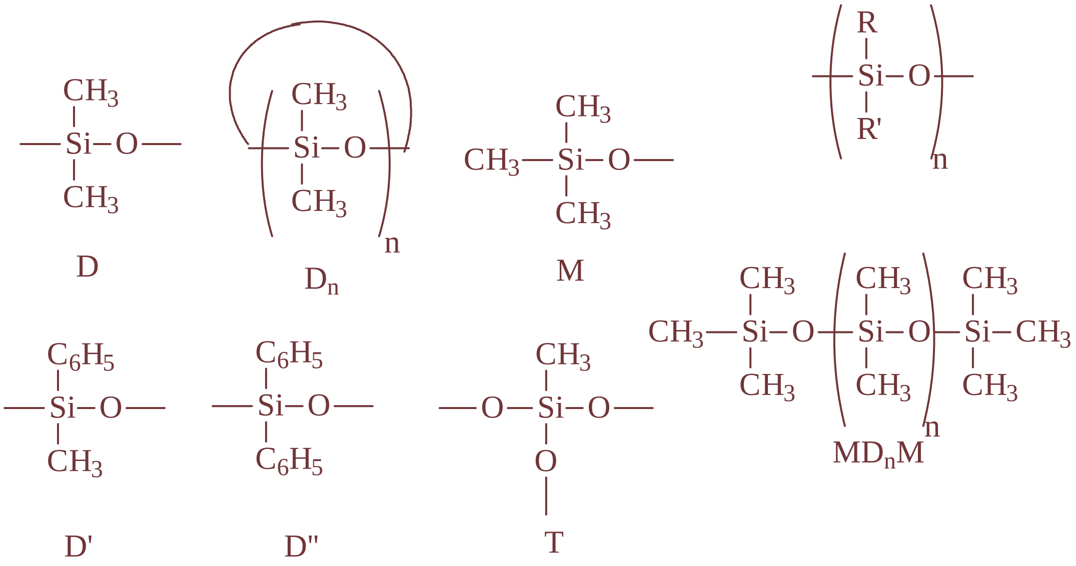

Figure 2.3-2- Common Examples of the MDTQ Shorthand for Siloxanes[146]

This MDTQ nomenclature is actually quite useful when commonly discussing six and eight member cyclic starting materials of different types. In fact, it is more common to see or hear D_4, methyltetramer, or even tetramer than the proper IUPAC nomenclature for octamethylcyclotetrasiloxane.[157]

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[156] Meals, R. N.; Lewis, F. M. *Silicones*; Rienhold Publishing Co.: New York, 1959.
[146] Hardman, B.; Torkelson, A. In *Encyclopedia of Polymer Science and Engineering*: New York, 1991; Vol. 15.
[157] *Chem. Eng. News* **1952**, *30*, 4517.

2.3.2 General Features of Siloxanes

In the following discussions of polysiloxanes, polydimethylsiloxane will be used as a representative for all of the various R groups that may be attached to the silicon. This is reasonable since polydimethylsiloxane (PDMS) is the most commonly utilized siloxane in industry today. The effects of the inclusion of various pendant groups will be discussed after the generic properties have been explored.

2.3.2.1 Unusual Bonding Characteristics of Siloxanes

Polydimethylsiloxanes have been shown to be able to withstand short term exposure to severe conditions > 400°C (in inert atmospheres) and extended exposures at 200°C (in air) without any significant changes in their properties.[158] The strong Si-O bond itself aids the thermal and oxidative stability of siloxanes. The bond energy of a Si-O bond (~107 kcal) is more than 20 kcal higher than that of C-C bonds (83 kcal) and C-O bonds (85 kcal).[41] Therefore the amount of thermal energy needed to break the polysiloxane backbone, under neutral pH conditions, is much greater than that of most polymeric materials. This high bond strength is a consequence of the type of bonding which occurs between silicon and oxygen. In addition to the "normal" σ bonding between silicon and the sp^3 hybrid orbitals of oxygen, silicon has available 3d orbitals. These orbitals are able to participate in π bonding with other atoms. In Si-O bonding, the unshared π electrons of oxygen can occupy with the silicon 3d orbitals. This $p\pi$–$d\pi$ bonding lends a partial double-bond character, which helps to account for the greater bond strength.[144] Additional support for this unusual $p\pi$–$d\pi$ pseudo-double bonding is the shortening of the expected Si-O bond length. An arithmetic summation of the atomic radii of silicon (1.17 Å) and oxygen (0.66 Å) indicates a bond length of 1.83 Å, yet the accepted literature value is a substantially shorter, 1.63 Å.[159]

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[158] Liebhasfsky, H. A. *Silicones under the Monogram*; John Wiley & Sons, Inc.: New York, 1978.
[41] Eaborn, C. *Organosilicon Compounds*; Butterworth Scientific Publications: London, UK, 1960.
[144] Voronkov, M. G.; Milileshevich, V. P.; Yuzhelevich, Y. A. *The Siloxane Bond*; Consultants Bureau: New York, 1978.
[159] Barry, A. J.; Beck, H. N.; Stone, F. G. A.; Graham, W. A. G., Eds. *Inorganic Polymers*; Academic Press, Inc.: New York, 1962.

One would think that the π-like bonding of the Si-O bond would limit the mobility of the bonded atoms. However, the energetic rotational barrier about the Si-O bond is substantially lower (<0.8 kJ/mol) than that of most carbon bonds (C-C =15.1, C-O = 11.3 kJ/mol).[160] This is at least partially due to the highly ionic nature of the Si-O bond, which has been estimated to be up to 40-50% ionic.[144] Silicon's highly electropositive nature (1.7 on Pauling's electronegativity scale) coupled with oxygen's high electronegativity (~3.5) make such estimations believable.[161] However, a lower rotational barrier is not exclusive to the Si-O bond. The Si-C bonds also show greater rotatibility (6.7 kJ/mol) when compared to carbon counterparts (15.1 kJ/mol).[160] Again this can be attributed to a partial ionic character (~12 % for Si-C) of the covalent bonds.[146]

Another major contributing factor to the ease of rotation is the large bond angles of the siloxane backbone. Commonly accepted bond angles evident in polysiloxanes are Si-O-Si ~144° and O-Si-O ~ 110°, while the C-Si-C bond angle is 111°.[144] These wide angles reduce the likelihood of a restriction of rotation by steric interactions, thus allowing lower barrier energies. With a low barrier to rotation about both bonds along the chain axis and of the pendant R-Si groups, the siloxane chain flexes and undergoes segmental motion easily. This is reflected on a macroscopic level by the observance of extremely low glass transition temperatures (ca. –123°C for polydimethylsiloxane)[144,162]. Additionally, the large interchain distances and molar volume ~ 75.5 cm^3/mol[163] (which leads to high permeability) of siloxanes, as well as low intermolecular forces,[164] are often ascribed to the ease of bond rotations and wide bond angles.

A secondary result of the unusual bond angles encountered in polysiloxanes, is

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[160] Stark, F. O.; Falender, J. R.; Wright, A. P. *Comprehensive Organometallic Chemistry*; Pergamon Press: New York, 1982; Vol. 2.

[144] Voronkov, M. G.; Milileshevich, V. P.; Yuzhelevich, Y. A. *The Siloxane Bond*; Consultants Bureau: New York, 1978.

[161] Pauling, L. *The Nature Of the Chemical Bond*; University Press: Ithica, NY, 1940.

[160] Stark, F. O.; Falender, J. R.; Wright, A. P. *Comprehensive Organometallic Chemistry*; Pergamon Press: New York, 1982; Vol. 2.

[146] Hardman, B.; Torkelson, A. In *Encyclopedia of Polymer Science and Engineering*: New York, 1991; Vol. 15.

[144] Voronkov, M. G.; Milileshevich, V. P.; Yuzhelevich, Y. A. *The Siloxane Bond*; Consultants Bureau: New York, 1978.

[162] Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1968.

[163] Hurd, C. B. *J. Amer. Chem. Soc.* **1946**, *68*, 364.

[164] Rochow, E. G.; LeClair, H. G. *J. Inorg. Nucl. Chem.* **1955**, 92.

the observance of a helical structure with six or seven siloxane units needed to complete each turn. This twisting of the siloxane backbone can be explained by an intramolecular dipole-dipole interaction. The Si-O bond is highly ionic, creating a large dipole with the silicon atom bearing the positive charge. Due to the large interchain distances that result from the ease of rotation, an intramolecular assistance is the only way to account for the consistency of the dipole moment as molecular weight increases.[165] The highly polar Si-O bonds form the core, while the non-polar alkyl substituents are projected towards the outer surface. This structural effect can be shown using the successive -Si-O-Si-O-Si-O- bonds in an energetically minimize short polydimethylsiloxane chain. (Figure 2.3-3)

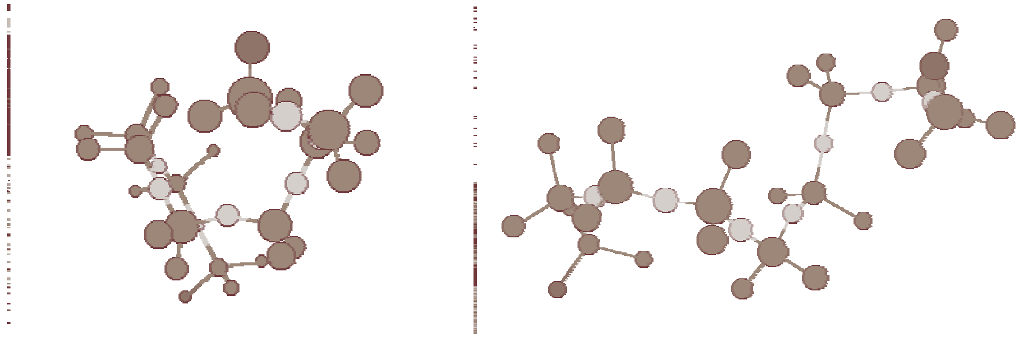

Figure 2.3-3: Helical Structure of a Siloxane Chain

(model from Chem3D Pro)

The helical structure affords the polysiloxanes a non-polar shield encasing the partially polar Si-O core. This results in the odd combination of surface and solution properties consistent with non-polar moieties (hydrophobicity, low surface energies, solubility in non-polar solvents), while the ionic core remains susceptible to ionic attacks (both acidic and basic).[160]

2.3.2.2 Major Substituents Other Than Methyl Groups

The use of different substituents along the siloxane chain has been investigated for many years. There are many commercially available cyclic siloxanes with pendant

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[165] Brandt, P. J. A. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, VA, 1986.
[160] Stark, F. O.; Falender, J. R.; Wright, A. P. *Comprehensive Organometallic Chemistry*; Pergamon Press: New York,

groups other than methyl. Still, most siloxane monomers will have at least one methyl group on each silicon atom. Another important class of commercial siloxanes is the room temperature vulcanizing systems (RTVs). Because their functionality is attached directly to the siloxane chain, these materials are often grouped with possible pendant moieties. However, in this review, terminally functionalized siloxane chains (including RTVs) are addressed separately. (See Section 2.3.4)

Groups such as diphenyl, methyl phenyl, methyl vinyl, methyl hydrido, trifluoropropyl, and cyanopropyl have been incorporated into siloxane chains. Although these cyclic "monomers" can be homopolymerized, they are more often copolymerized with dimethylsiloxane in small amounts (5-10 wt %). This is often done to modify or tailor a specific property of PDMS to a specific need.[166] The elimination of low temperature crystallizations is an example. Therefore, using polydimethylsiloxane as a base, this section will explore the effects of incorporating different pendant groups on a siloxane chain. All references to any increase or decrease in a given characteristic are relative to polydimethylsiloxane

<u>Alkyl Substituents</u>- When increasing lengths of alkyl chains are attached to the silicon, the siloxane fluid will become more like a hydrocarbon. The non-polar outer sheath will increase in size and have fewer gaps. This effect is apparent on a macroscopic scale with an increase in the solubility and greater miscibility with other organic compounds and polymers. Additionally, the T_g of siloxane copolymers are effected by both the length of the side chain and the composition of the copolymer. In fact, a polydiethylsiloxane homopolymer has been found to have a T_g of –143°C, 20°C lower than a pure PDMS.[167] However, a decrease in thermo-oxidative stability has been observed as the proportion of C-C bonds is increased.[168] "Monomers" for such copolymers can be prepared by hydrosilation with 1-alkenes.

<u>Phenyl Substituents-</u> The aromatic nature of the phenyl group causes a decrease in the pπ-dπ interactions. The reduced interactions, coupled with the inherent thermo-

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1982; Vol. 2.

[166] Yilgor, I.; McGrath, J. E. In *Adv. Polym. Sci*; Springer-Verlag: New York, 1988; Vol. 86, pp 1-86.

[167] Ward, W. J.; Ritzer, A.; Carroll, K. M.; Flock, J. W. In *US. Patent 4,500,724*; General Electric Co.: US., 1985.

[168] Frye, C. L.; Klosowski, J. M. *J. Amer. Chem. Soc.* **1971**, *93*, 4599.

oxidative stability of the aryl ring, increases the overall stability of the chains. The bulky aryl rings also require more energy to rotate increasing the T_g. Furthermore, the incorporation of a small amount of diphenylsiloxane increases the low temperature flexibility of siloxane materials as its bulkiness disrupts the symmetry and crystallization of dimethylsiloxane sequences at low temperatures. It has been stated that the incorporation of too many diphenyl groups (>10-15%) can induce increased low temperature crystallinity as π-π stacking begins to occur.[169] However, Brandt was able to produce 50:50 dimethyl-diphenyl siloxane copolymers, up to 10,000 g/mol, which displayed no evidence of low temperature crystallinity, yet showed a single glass transition of approximately –75°C.[160,170]

Fluorinated Substituents- Fluorinated groups such as trifluoropropyl groups become incorporated in an asymmetric or random stereochemistry. Two or more methylene units are needed to connect the fluorinated group to the cyclic trimers and tetramers in order to produce good hydrolytic stability. These materials are often used in aerospace applications because of their excellent resistance to swelling and degradation at elevated temperatures in hydrocarbon rich environments. Unfortunately, they are also quite expensive.[171]

Cyanopropyl Substituents- Like many other substituents, the cyano groups helps to disrupt the low temperature crystallization of PDMS and to increase its low temperature flexibility. Additionally, increases in oil and solvent resistance can be observed. The incorporation of the cyano moiety also provides a reactive site for grafting or crosslinking. Unfortunately, the addition of the propyl chain decreases the thermal and perhaps also hydrolytic stability.[172]

These are just some examples of wide variety of pendant side groups that have been explored. Further information on possible pendant groups can be found in the

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[169] Arkles, B. C.; Petersen, W. R., Eds. *Silicon Compounds Register and Review*; Petriarch Systems, Inc.: Bristol, PA, 1984.

[160] Brandt, P. J. A. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, VA, 1986.

[170] Brandt, P. J. A.; Elsbernd, C. S.; York, G.; Patel, N. M.; McGrath, J. E. *Polymer (London)* **1990**, *31*, 180.

[171] Pierce, O. R.; Kim, Y. K. *J. Elastoplast.* **1971**, *3*, 83.

[172] Warrick, E.; Pierce, O. R.; Polmanteer, K.; Saam, J. C. *Rubber Chem. Technol.* **1979**, *52*, 437.

literature.[169]

2.3.3 Synthetic Approaches and Reaction Mechanisms for Polysiloxanes

The synthesis of high molecular weight polysiloxanes is usually achieved through the ring-opening polymerization of cyclic trimers or tetramers. It is important to briefly review the concept of a "ceiling temperature."[146] In most ring opening polymerizations, the ultimate driving force is the relief of ring strain. By opening the ring to form linear species, strained bond angles are allowed to revert to their more natural values, creating a net loss in enthalpy ($\Delta H < 0$). However, the change in enthalpy is only one component of the overall free energy of a reaction. Reviewing the Gibbs-Helmholtz free energy equation (Equation 11), in order for a reaction to occur spontaneously the total free energy associated with it must be negative.

$$\Delta G = \Delta H - T\Delta S \tag{11}$$

The creation of one large molecule from several small molecules occurs only with a loss of entropy ($\Delta S < 0$). Above some "ceiling temperature" (T_c), the $-T\Delta S$ term will be both positive and greater than the loss of enthalpy. Above this temperature polymerization is no longer possible.[14]

To polymerize the cyclic siloxane precursors, they must first be generated. Polydimethylsiloxane will serve as an example for the description of the mechanisms. Some of the reaction conditions may need to be altered if a different pendant group is involved, but the basic principles are usually applicable. The dichlorodimethylsilanes generated in the "direct process"[151] described earlier can be hydrolyzed with a controlled amount of water into unstable silanols that rapidly condense to form both cyclic and linear polydimethylsiloxanes.[155] (Scheme 2.3-3)

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[169] Arkles, B. C.; Petersen, W. R., Eds. *Silicon Compounds Register and Review*; Petriarch Systems, Inc.: Bristol, PA, 1984.

[146] Hardman, B.; Torkelson, A. In *Encyclopedia of Polymer Science and Engineering*: New York, 1991; Vol. 15.

[14] Odian, G. *Principles of Polymerization*; 3rd ed.; Wiley Interscience: New York, 1991.

[151] Rochow, E. G. In *US. Patent 2,380,995*; General Electric Co., 1941.

[155] Stevens, M. P. *Polymer Chemistry: An Introduction*; 2nd ed.; Oxford University Press: New York, 1990.

Scheme 2.3-3: Synthesis of Cyclic and Linear Siloxane Precursors via Condensation Reactions

When an excess of water is added to dimethyldichlorosilane, the hydrogen chloride produced dissolves in the excess water while a light, colorless, siloxane oil condenses to form a two-phase system. Due to the Si-O bond angles, this oil contains mostly cyclic species with a small portion being low molecular weight (1,000-3,000 g/mol) linear chains. The largest distillable fraction collected is D_4, the cyclic tetramer, with decreasing amounts observable as the ring size increases. Only a small amount of D_3, the cyclic trimer, is isolated.[146]

As a general method, the hydrolysis of dichlorosilanes to prepare polydimethylsiloxanes is not a viable approach. The formation of cyclics is unavoidable and the linear species generated are limited to low molecular weights. In order to achieve high molecular weight linear chains, one must initiate a ring-opening polymerization of either the distilled cyclic trimer or tetramer.[173]

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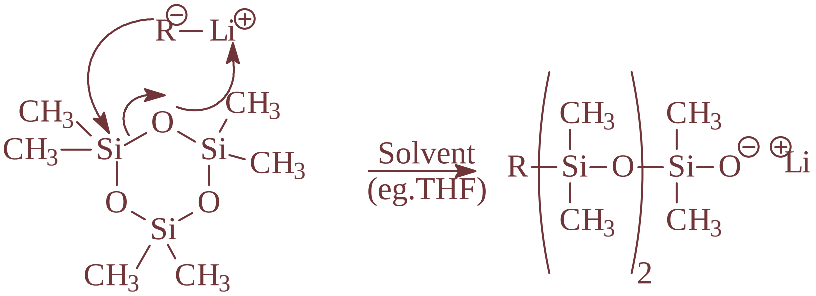
[146] Hardman, B.; Torkelson, A. In *Encyclopedia of Polymer Science and Engineering*: New York, 1991; Vol. 15.

[173] Gomes, A. D.; Cavalcanti, T. D. R. D. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 2671.

2.3.3.1 “Living” Anionic Ring Opening Polymerization of Hexamethylcyclotrisiloxane (D_3)

The ring opening polymerization of cyclic siloxanes has been successfully demonstrated with a variety of ionic techniques. The “living” anionic ring-opening of D_3 is the most easily understood siloxane ring-opening polymerization. D_3 (a low melting solid) is a planar six-membered ring with Si-O-Si bond angles that are slightly compressed in comparison to linear siloxanes (136° vs. 141°).[144] The compacted siloxane bond angles of D_3 result in a slightly strained ring. Although this ring strain is minimal (~3.5 kcal/mol),[146] it is large enough to facilitate ring opening to essentially quantitative conversion under carefully optimized conditions.



Scheme 2.3-4: Initiation of the Anionic “Living” Polymerization of D_3

The “living” ring-opening polymerization of D_3 can be initiated by the addition of an organolithium species at room temperature.[174] Using a non-polar solvent (benzene or cyclohexane) the cyclic siloxane is subjected to nucleophilic attack by the highly polar C-Li bond. The partially negative carbon attacks the partially positive silicon (Scheme 2.3.-4). This breaks the slightly strained Si-O bond, opening the ring producing a siloxanolate anion.

Propagation occurs as the newly generated siloxanolate attacks a neighboring ring. However the rate of propagation can be greatly enhanced by the inclusion of an

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[144] Voronkov, M. G.; Milileshevich, V. P.; Yuzhelevich, Y. A. *The Siloxane Bond*; Consultants Bureau: New York, 1978.
[146] Hardman, B.; Torkelson, A. In *Encyclopedia of Polymer Science and Engineering*: New York, 1991; Vol. 15.
[174] Bostick, E. E. In *Ring-Opening Polymerization*; Frisch, K. C., Reegen, S. L., Eds.; Marcel-Dekker: New York, 1969.

aprotic polar solvent.[166] The polar solvent will complex with the lithium counter ion to "loosen" the ionic pair, in effect activating the siloxanolate. This effect is so advantageous that the anionic polymerizations of D_3 are now often performed in pure tetrahydrofuran (THF) or THF/cyclohexane mixtures.[175,176] The cyclic "monomer" will continue to become incorporated into the growing siloxane chain until either the all of the D_3 is consumed, or a means to terminate the reaction is introduced. This results in a linear plot of molecular weight vs. conversion time, (Figure 2.3-4) allowing excellent molecular weight control and relatively narrow molecular weight distributions ($M_w/M_n \sim 1.1$).[177,178]

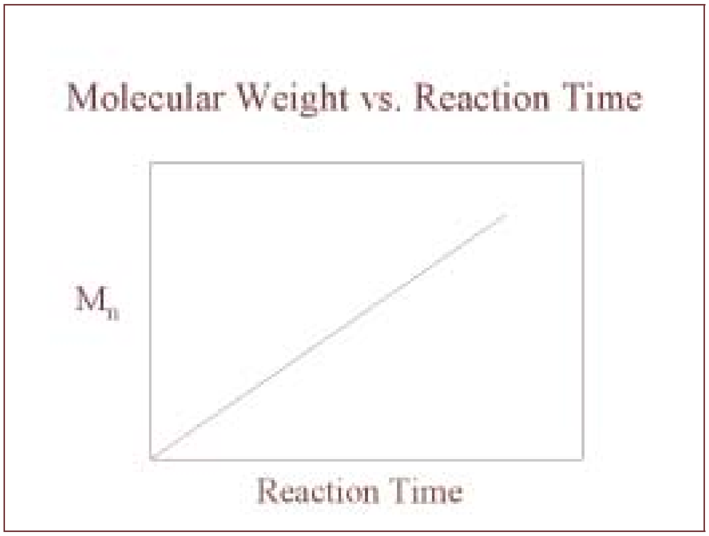

Figure 2.3-4: Plot of Molecular Weight as a Function of Reaction Time for "Living" D_3 Systems[12]

Termination can be facilitated by the addition of aprotic solvent or the introduction of an endcapping reagent (a monofunctional electrophile).[179] The use of specific endcapping reagents to yield siloxane chains with functional end groups has

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[166] Yilgor, I.; McGrath, J. E. In *Adv. Polym. Sci*; Springer-Verlag: New York, 1988; Vol. 86, pp 1-86.

[175] Smith, S. D. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, VA, 1987.

[176] Smith, S. D.; DeSimone, J. M.; Huang, H.; York, G.; Dwight, D. W.; Wilkes, G. L.; McGrath, J. E. *Macromolecules* **1992**, *25*, 2575.

[177] Bostick, E. E. In *Ring-Opening Polymerization*; Frisch, K. C., Reegen, S. L., Eds.; Marcel-Dekker: New York, 1969.

[178] Lee, C. L.; Johannson, O. K. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 729.

[12] Hsieh, H. L.; Quirk, R. P. *Anionic Polymerization: Principles and Practical Applications*; Marcel-Dekker, Inc.: New York, 1996.

received considerable of attention. This aspect will be explored in greater detail during the discussion of siloxane containing materials.

The "living" anionic polymerization of D_3 is not the most commercially viable method currently in use. Since the majority of the cyclic siloxanes produced by the "direct" process are the tetramer (D_4), it is logical that the ionic ring opening of D_4 is the most commonly encountered polymerization route.

2.3.3.2 Ionic "Redistribution" Polymerizations of Octamethylcyclosiloxane (D_4)

Octamethylcyclosiloxane or D_4 can be converted into linear polymers chains by both anionic and cationic approaches.[162] These ionic reactions are termed "equilibrium" or "redistribution" reactions since they progress through the constant breaking and reforming of cyclic and linear Si-O bonds.[166] (See Scheme 2.3-5) This dynamic process proceeds until a thermodynamic equilibrium between the cyclics and chains is reached. Upon equilibration, the reaction mixture contains mainly linear chains with a small portion of cyclics (~10-15%) ranging in size from D_4 up to D_{400}.[180] In most commercially available siloxanes produced by redistribution, there is a significant content (2-3%) of non-volatile cyclics such as D_{12}.[181]

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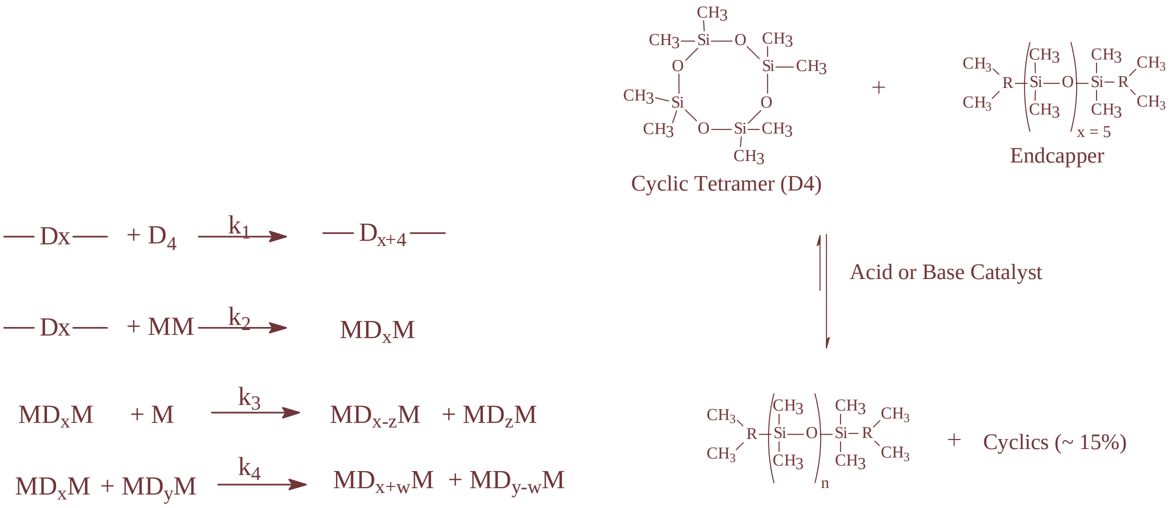
[179] Rempp, P. F.; Franta, E. *Adv. Polym. Sci.* **1984**, *58*, 1.

[162] Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1968.

[166] Yilgor, I.; McGrath, J. E. In *Adv. Polym. Sci*; Springer-Verlag: New York, 1988; Vol. 86, pp 1-86.

[180] Riffle, J. S. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, VA, 1980.

[181] Hardman, B.; Torkelson, A. In *Kirk-Othmer Encyclopedia of Chemical Technology*; 3rd ed.; Grayson, M., Ed.; Consultants Bureau: New York, 1982.



$$—D_x— + D_4 \xrightarrow{k_1} —D_{x+4}—$$

$$—D_x— + MM \xrightarrow{k_2} MD_xM$$

$$MD_xM + M \xrightarrow{k_3} MD_{x-z}M + MD_zM$$

$$MD_xM + MD_yM \xrightarrow{k_4} MD_{x+w}M + MD_{y-w}M$$

Scheme 2.3-5: Redistribution Process of Equilibrium Reactions of D_4[182]

The theory of an equilibrium process for the formation of siloxanes was first proposed by Jacobson and Stockmayer[183] and was later verified experimentally by Brown and Slusarczuk[184] Utilizing a GPC, Brown and Slusarczuk were able to quantify the concentrations of macrocyclics (D_{15} and larger) in equilibrium with linear siloxanes. Flory and Semlyen[185] further refined the equilibrium theory to explain the formation of smaller unstrained cyclics (D_4 and D_5) in larger proportions than predicted.

The base-catalyzed systems result in an anionic mechanism and will be discussed first because of its similarity to the “living” D_3 system and the fact that this method is utilized in this research. Conversely, acid catalyzed systems are cationic in nature, less studied, and consequently not well understood. Most redistribution reactions are normally conducted with control over molecular weight and functionality in mind. Therefore, the reaction is normally pursued with some type of endcapping reagent (either a monofunctional silane or a siloxane dimer) involved.

Under normal redistribution conditions (both acidic and basic), the Si-O bonds can be cleaved rather easily while the Si-C, and other less polar bonds (C-C, C-O) remain stable. [166] This disparity allows for the consecutive breaking and reforming of the Si-O

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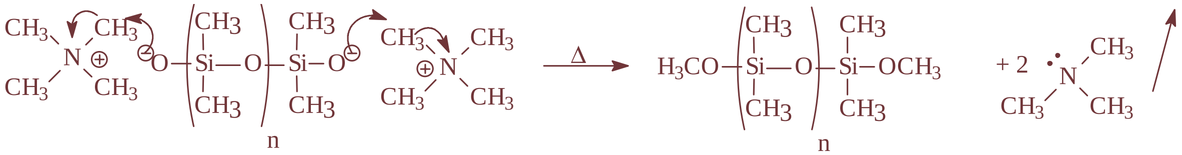
[182] Kantor, S. W.; Grubb, W. T.; Osthoff, R. C. *J. Amer. Chem. Soc.* **1954**, *76*, 5190.
[183] Jacobson, H.; Stockmayer, W. H. *J. Phys. Chem.* **1950**, *18*, 1600.
[184] Brown, J. F. J.; Slusarczuk, G. M. J. *J. Amer. Chem. Soc.* **1965**, *88*, 3209.
[185] Flory, P. J.; Semylen, J. A. *J. Amer. Chem. Soc.* **1966**, *88*, 3209.
[166] Yilgor, I.; McGrath, J. E. In *Adv. Polym. Sci*; Springer-Verlag: New York, 1988; Vol. 86, pp 1-86.

bonds necessary for the build up of molecular weight, while the component bonds that convey functionality in the endcapping reagents persist. Meanwhile, the main factor in determining which reaction system to use is the nature of the end groups or side chains desired. The initiator and the active chain ends during propagation should be selected so that there are no interfering side reactions with the endcapping reagent. Therefore, in general, acidic endcapping reagents require acidic catalysis, while basic endcapping reagents utilize base catalyzed reactions.[186]

2.3.3.2.1 *Base Catalyzed Anionic "Equilibrium" Polymerizations*

A variety of bases have been used to facilitate the anionic production of siloxanes from D_4. The most commonly encountered are alkali metal hydroxides (e.g. KOH), quaternary ammonium hydroxides (R_4NOH), phosphonium bases, and siloxanolates ($Si\text{-}O^{-}\ {}^{+}M$) derived from these bases.[41,144,162] Initiator concentrations are typically 10^{-2} -10^{-4} mole percent depending on their activity and reaction conditions.[166] Quaternary ammonium siloxanolates are convenient because they are completely soluble and display "transient" catalyst properties. "Transient" catalysis refers to species that are catalytically active at reaction temperatures (25–100 °C) but can be easily removed as they decompose into inert chains and gaseous products at higher temperatures (>115 °C).[187] The controllable evolution of trimethyl amine means there is no need to extract out any remaining catalyst prior to the distillation of residual cyclics. (Scheme 2.3-6)



Scheme 2.3-6: Thermal Degradation of a "Transient" Siloxanolate Catalyst

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[186] McGrath, J. E.; Riffle, J. S.; Bantia, A. K.; Yilgor, I.; Wilkes, G. L. *ACS Symposium Series 212* **1983**.
[41] Eaborn, C. *Organosilicon Compounds*; Butterworth Scientific Publications: London, UK, 1960.
[144] Voronkov, M. G.; Milileshevich, V. P.; Yuzhelevich, Y. A. *The Siloxane Bond*; Consultants Bureau: New York, 1978.
[162] Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1968.
[166] Yilgor, I.; McGrath, J. E. In *Adv. Polym. Sci*; Springer-Verlag: New York, 1988; Vol. 86, pp 1-86.
[187] Gilbert, A. K.; Kantor, S. W. *J. Polym. Sci.* **1959**, *40*, 35.

The equilibrium process manifests itself during propagation. There is a significant amount of competition between the propagation of linear chains and a “backbiting” reaction that causes the reformation of cyclic siloxanes. The reactivities under basic conditions of Si-O bonds by type has been shown to be as follows.[146]

$D_3 > D_4 > D_5$ ~ Linear Chains > Endcapping reagents.

Since the cyclic tetramer is the most stable siloxane ring and it closely preserves the established bonding angles of the linkages. Therefore, ring strain is not present in the polymerization of D_4, and the change in enthalpy for polymerization is close to zero. However, the slight difference in entropy between D_4 and the linear chains ($\Delta S = 6.7$ J/mol K)[178] drives the equilibrium toward the formation of mostly linear polymers. Additionally, the order of reactivity shows that the endcapping reagents are less reactive to the anionic groups when compared to D_4. This results in a need to decrease the concentration of cyclics before significant endcapping reagent incorporation, thus affording high molecular weight species before complete equilibration.[165]

The incorporation of the cyclics into linear chains can easily be observed as an increase in the viscosity of the reaction solution. Conversely, any depolymerization or cyclic reformation will result in a decrease in viscosity. Since the viscosity of the reaction solution is proportional to the molecular weight of the polymer formed, a plot of viscosity vs. reaction time can be used to assess the manner in which the reaction proceeds (See Figure 2.3-5). The rate of the increase in viscosity and thus molecular weight has been found to scale with the square root of the catalyst concentration.[162]

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[146] Hardman, B.; Torkelson, A. In *Encyclopedia of Polymer Science and Engineering*: New York, 1991; Vol. 15.
[178] Lee, C. L.; Johannson, O. K. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 729.
[165] Brandt, P. J. A. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, VA, 1986.
[162] Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1968.

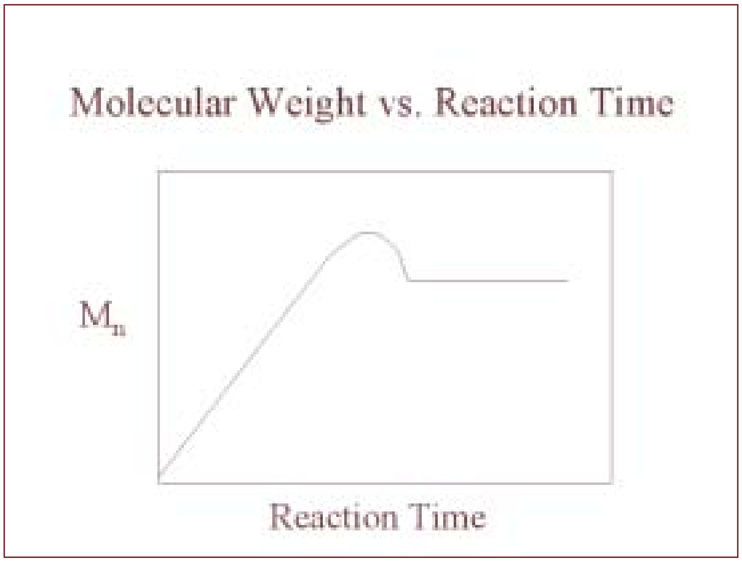

Figure 2.3-5: Molecular Weight as a Function of Reaction Time for Redistribution Reactions.[188]

Examination of a typical viscosity profile shows that, as the reaction proceeds, a quick build-up of viscosity is followed by a small decrease before equilibrium is achieved. Assuming that all changes in viscosity are the direct reflection of the average molecular weight of the growing polymers, it is evident that build up of linear chains peaks before equilibrium is reached. The molecular weight of the polymer at the peak of viscosity will be inversely proportional to the amount of initiator used to activate the chain ends. This feature allows for the production of controlled high molecular weight polymers. Alternately, the molecular weight and functionality of a polysiloxane can be predetermined by adding a known amount of the endcapping reagent at the beginning of the reaction. During polymerization, the active chain ends will attack the Si-O bond of the dimer and facilitate incorporation of the chain terminating endcapping reagent. The molecular weight will continue to grow until equilibrium as the active chain ends can “ring open” a preexisting chain and insert themselves in the manner of a combination termination reaction.[182]

The exact ratio of cyclics to polymer depends on many factors, including the type of substituents on the silicon atoms, the temperature of equilibration, and the

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[188] McGrath, J. E., Ed. *Ring Opening Polymerization; ACS Symposium Series 285*; ACS: Washington D.C., 1985.
[182] Kantor, S. W.; Grubb, W. T.; Osthoff, R. C. *J. Amer. Chem. Soc.* **1954**, *76*, 5190.

concentration of starting cyclics. The amount of cyclics present increases with the size and polarity of the substituents. In bulk polymerizations, the order of increasing cyclic content as a function of R groups is as follows.[189]

$$-CH_2CH_2CF_3 > -C_6H_5 > -CH_2CH_2CH_3 > -CH_2CH_3 > -CH_3$$

Larger and more electron withdrawing groups not only activate the siloxane bonds to nucleophilic attack, but they also sterically favor a conformation that can facilitate intrachain "backbiting".[190]

The dilution of the "monomeric" D_4, by the use of an inert solvent such as toluene or cyclohexane, increases the amount of cyclics remaining at equilibrium. In fact, if diluted past a certain concentration, polymerization is no longer possible.[183]

2.3.3.2.2 *Acid Catalyzed Cationic "Equilibrium" Polymerizations*

The cationic polymerization of D_4 is more complicated and, despite significant investigation,[191,192,193] less fully understood than anionic processes. Various Bronsted and Lewis acids have been shown to initiate polymerization, but supported sulfuric acid and its derivatives (alkyl and aryl sulfonic acids as well as triflic acid) have afforded the most success.[162,194] To facilitate post polymerization removals, these acids are commonly anchored to supports such as clays or polystyrene beads.[166]

Cationic polymerization is initiated by the acidic attack on the partially negative oxygen of the polarized Si-O bond to form either an oxonium ion or a silicenium cation.[14] The propagation is the cause of the most ambiguity. Propagation is proposed to proceed in analogous manner as in the anionic case with the oxonium containing cyclic as the

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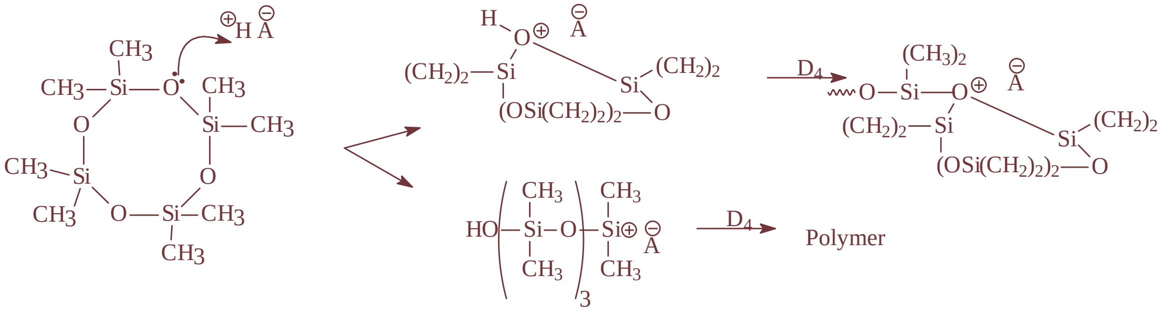
[189] Wright, P. V.; Semylen, J. A. *Polymer* **1969**, *11*, 462.
[190] Beevers, M. S.; Semylen, J. A. *Polymer* **1971**, *12*, 373.
[183] Jacobson, H.; Stockmayer, W. H. *J. Phys. Chem.* **1950**, *18*, 1600.
[191] Ishizuka, S.; Aihara, T. *J. Chem. Soc. Jpn.* **1959**, *59*, 1198.
[192] Gruber, V. N.; Mukhina, L. S. *Vysokomol. Soedin.* **1959**, *2*, 1194.
[193] Andrianov, K. A.; Iakushkina, S. E. *Polym. Sci. USSR* **1960**, *1*, 221.
[162] Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1968.
[194] Rochow, E. G. *Silicon and Silicones*; Springer-Verlag: Berlin, 1987.
[166] Yilgor, I.; McGrath, J. E. In *Adv. Polym. Sci*; Springer-Verlag: New York, 1988; Vol. 86, pp 1-86.
[14] Odian, G. *Principles of Polymerization*; 3rd ed.; Wiley Interscience: New York, 1991.

active chain end. (Scheme 2.3-7.) However, the observed and complicated reaction kinetics indicates that there are additional factors involved.[195,196]



Scheme 2.3-7: Acid Catalyzed Equilibrium Reaction[155]

In either case, the use of sulfonic acids introduces additional issues. First, sulfonic acids facilitate chain transfer, limiting molecular weight. Second, the sulfate and sulfonate anions created tend to associate closely with the active site of the chain. In fact, this ion pairing is so tight that the sulfates often become incorporates into the polymer backbone.[144]

The resulting sulfone bridges are highly susceptible to hydrolysis. Any hydrolytic degradation encountered will decrease the viscosity and thus reduce the molecular weight of the siloxane produced. Interestingly, any silanol (Si-OH) or Si-O-SO_3H groups generated by hydrolysis will react to reform the unstable sulfonate linkage.[144] As in the anionic polymerizations, endcapping reagents can be used to control functionality and molecular weight of the siloxanes produced. Cationic siloxane polymerization is particularly useful to prepare methyl hydride siloxane oligomers, which are important precursors for addition cured PDMS networks and nonionic surfactants.

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[195] Chinojnowski, J.; Wilczek, L. *Makromol. Chem.* **1979**, *180*, 117.
[196] Sigwalt, P. *Polym. J.* **1987**, *19*, 567.
[155] Stevens, M. P. *Polymer Chemistry: An Introduction*; 2nd ed.; Oxford University Press: New York, 1990.
[144] Voronkov, M. G.; Milileshevich, V. P.; Yuzhelevich, Y. A. *The Siloxane Bond*; Consultants Bureau: New York, 1978.

2.3.4 Organofunctional Siloxane Oligomers and the Synthesis of Siloxane Containing Copolymers

The incorporation of polydimethylsiloxane into the backbone of organic polymers has been investigated since the 1950s.[197] The first block and graft copolymers containing siloxanes were polysiloxane-poly(alkylene oxide) systems used as stabilizers in the production of flexible polyurethane foams.[166] Since then, siloxane surfactants and emulsifiers have become widely accepted and utilized by industry today.[146] The advent of living polymerizations brought about the development of well-defined dimethylsiloxane-diphenylsiloxane type copolymers as well as vinyl-siloxane copolymers. These types of di, tri and multi-block copolymers have been reviewed in the past by Juliano,[198] and by Plumb and Atherton.[197] However, the most complete reviews of siloxane containing polymers can be found in either Noshay and McGrath's book on block copolymers,[2] or the review of siloxane-containing copolymers by Yilgor and McGrath.[166]

In recent years, interest in the incorporation of siloxanes into the backbone of organic polymers has risen as the interest in multi-phase materials has increased. The low solubility parameter, in combination with the low surface energy of siloxanes, often afford phase-separated materials when incorporated into homopolymers.[166] Most siloxane containing copolymers are produced through the condensation preformed organofunctional siloxane oligomers reacted with either preformed organic oligomers or monomers with mutually reactive groups. Exclusive copolymerization of preformed oligomers, as previously discussed in the block copolymer section of this review (Section 2.1.2.2.1), yield alternating block copolymers, while competition of reactive oligomers and monomers with the same functionality result in random block copolymers.

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[197] Plumb, J. B.; Atherton, J. H. In *Block Copolymers*; Allport, D. C., Janes, W. H., Eds.; Halsted Press: New York, 1972.

[166] Yilgor, I.; McGrath, J. E. In *Adv. Polym. Sci*; Springer-Verlag: New York, 1988; Vol. 86, pp 1-86.

[146] Hardman, B.; Torkelson, A. In *Encyclopedia of Polymer Science and Engineering*: New York, 1991; Vol. 15.

[198] Juliano, P. C. In *New Silicone Elastoplastics*; General Electric: Schenectady, NY, 1974.

[197] Plumb, J. B.; Atherton, J. H. In *Block Copolymers*; Allport, D. C., Janes, W. H., Eds.; Halsted Press: New York, 1972.

[2] Noshay, A.; McGrath, J. E. *Block Copolymers-Overview and Survey*; Academic Press: New York, 1977.

[166] Yilgor, I.; McGrath, J. E. In *Adv. Polym. Sci*; Springer-Verlag: New York, 1988; Vol. 86, pp 1-86.

The synthesis of these functional oligomers is most commonly achieved by redistribution reactions of D_4 with the appropriate $\alpha-\omega$ functionalized disiloxane as the endcapping reagent for control of molecular weight.[199] For the purpose of this discussion, the manner in which the organofunctional groups are anchored to the siloxane chain will be divided into two categories. Those with the functional group (G) bound directly to a silicon atom, (Si-G) and those with carbofunctional groups (Si-R-G).

The most common Si-G groups have been hydroxyl, amine, epoxy, carboxyl, acetoxy and methoxy groups.[167,200] The most recognizable of the Si-G reactive oligomers are the room temperature vulcanization or RTV silicone rubbers and adhesives (where G = acetoxy or methoxy). The Si-G bonds are more polar than their carbon analogs and are in turn much more reactive to nucleophilic attack. The increase in reactivity is often attributed to the difference in the electronegativity of silicon (1.8) and carbon (2.5).[161] This allows crosslinking and copolymerization reactions to occur under rather mild conditions. Si-G type oligomers have been reacted with many polymer backbones such as polyesters, polyimides, polysulfones, polycarbonates, linear epoxies, polyarylethers and others.[201] However, these copolymerization reactions generally result in Si-O-C linkages. In small molecules the Si-O-C bond is notoriously susceptible to hydrolytic cleavage. However, in siloxane oligomers and their resultant copolymers, the hydrolytic stability is markedly increased. Bisphenol A based polysulfone-siloxanes have been prepared, which show 80% retention of reduced viscosity (a reflection of molecular weight) after immersion in boiling water for 2 weeks.[202] The link may even be stable under ordinary conditions for ten or more years.[166] The remarkable stability was attributed to several factors. First, the hydrophobic nature and steric bulk of the siloxane chains may have shielded the "unstable" linkage. Second, the low concentration of the Si-O-C links

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[199] Elsbernd, C. S.; Spinu, M.; Krukonis, V. J.; Gallagher, P. M.; Mohanty, D. K.; McGrath, J. E. In *Silicon-Based Polymer Science: A Comprehensive Review*; Zeigler, J. M., Fearon, F. W. G., Eds.; American Chemical Society, 1990; pp 145-164.

[167] Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1968.

[200] Noshay, A.; Matzner, M.; Merriam, C. N. In *U.S. 3,539,657*; Union Carbide Corp., 1970.

[161] Pauling, L. *The Nature Of the Chemical Bond*; University Press: Ithica, NY, 1940.

[201] Yilgor, I.; McGrath, J. E. In *Adv. Polym. Sci*; Springer-Verlag: New York, 1988; Vol. 86, pp 1-86.Specifically Table 13, p.30

[202] Noshay, A.; Matzner, M. *Angew. Makrmol. Chem.* **1974**, *37*, 215.

[166] Yilgor, I.; McGrath, J. E. In *Adv. Polym. Sci*; Springer-Verlag: New York, 1988; Vol. 86, pp 1-86.

relative to remainder of the copolymer backbone would reduce the effect of any hydrolytic cleavage. And third, the two-phase morphology of the copolymers may have in some way stabilized the linkages.[202]

The belief that Si-O-C bonds will not be hydrolytically stable is ingrained in organic chemistry since the Si-O-C bond is commonly used as a "protective group" to preserve hydroxyl functionality and is well known to be easily cleaved with the addition of water.[203] However, the desire to avoid such arguments over stability in a polymer vs. small molecules, led to the development of Si-R-G carbofunctional oligomers. The addition of some alkyl based spacer between the silicon and the functional group eliminates many hydrolytic concerns. The questionable Si-O-C bond is replaced by a stable Si-C bond. In effect this removes the weak link in the chain and causes the polymer to be more hydrolytically robust. One major advantage that Si-R-G type oligomers have over Si-G types is that they do not readily undergo hydrolysis, so they are able to have longer shelf lives.[166]

Carbofunctional endgroups also allow for increased miscibility in reaction mixtures. As the length of the hydrocarbon spacer increases, so does its miscibility in organic media. This factor increases as the oligomer reacts and the copolymer chain becomes more hydrocarbon-like. On a macroscopic scale, the growing copolymer chains become in situ compatiblizers for unreacted siloxane chains. Commonly encountered Si-R-G, groups are hydroxyls, amines, carboxyls, alkyl halides, and epoxies.[166] These groups have been coupled with functional oligomers and monomers of most commercially available polymers.

Copolymerization of siloxanes with organic polymers is one method of further enhancing their many advantageous qualities. Siloxanes have a low T_g, which makes then the ideal soft segment for many thermoplastic elastomers. Furthermore, by controlling the amount and block size of the siloxane introduced to the copolymer backbone, the modulus at a given use temperature may be predicted before synthesis. Additionally, the low surface energy of siloxanes and their low compatibility with most organic polymers

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[202] Noshay, A.; Matzner, M. *Angew. Makrmol. Chem.* **1974**, *37*, 215.
[203] Pierce, A. E. *Silylation of Organic Compounds*; Pierce Chem. Co.: Rockford, MD, 1968.

result in a tendency for the siloxane chains to migrate to the air-polymer interface.[204] This siloxane enrichment brings hydrophobicity and a chemically bound lubricity to the surface. Moreover, the siloxane-enriched surface will display intumescence or silicate char formation upon combustion.[205] This factor will be addressed later in Section 2.4.5 of this dissertation.

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[166] Yilgor, I.; McGrath, J. E. In *Adv. Polym. Sci*; Springer-Verlag: New York, 1988; Vol. 86, pp 1-86.

[204] Dwight, D.; McGrath, J. E.; Lawson, G.; Patel, N.; York, G. In *Multiphase Macromolecular Systems*; Culbertson, B. M., Ed.; Plenum Press: New York, 1989; pp 265-288.

[205] Nelson, G. L., Ed. *Fire and Polymers II; ACS Symposium Series. No 599*; American Chemical Society: Washington D.C., 1995.

2.4 Nylon 6,6 and Related Polyamides

2.4.1 General Structure, Nomenclature, and Commercial Applications

By definition, polyamides are polymers in which an amide group (-NH-CO-) provides the linkage between repeat units.[206] Since their discovery by Carothers et al. in the early 1930s, polyamides have been one of the most successful polymeric materials. Patented and marketed by DuPont[207] under the trade name Nylon, polyamides were the first synthetic polymer materials to be used both as fibers and an engineering thermoplastics. In fact, the marketing of nylon was so successful that the whole class of aliphatic polyamides is often referred to by the DuPont trade name. Nylons are extremely versatile materials and have been utilized in numerous commercial products ranging from carpet fibers, ropes, and parachutes to gears, casings, and even spatulas.[208]

Although most of the initial investigations for the utility of nylons were performed with poly(nonanoamide) (nylon-9)[206], over 98% of the current polyamide market is held by just two polymers.[209] These two materials, poly(ε–caprolactam) and poly(hexamethylene adipamide), are often referred to as Nylon 6 and Nylon 6,6, respectively. As was previously discussed with regard to siloxanes, a nylon-related shorthand jargon has also emerged – although in a more straightforward manner. The common nomenclature system for nylons uses the number of backbone carbons in the monomer units to identify the polymers.[206] If a polymer is produced from a self-condensing monomer, such as a cyclic lactam or amino acid, a singular number is sufficient (e.g. Nylon 6). Polymers derived from AA BB type condensations require two numbers separated by comma (e.g. Nylon 6,6). The first value corresponds to the number of carbons in the diamine, while the second reflects the length of the diacid or diacid

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[206] Zimmerman, J. In *Encyclopedia of Polymer Science and Engineering*; 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley-Interscience: New York, 1987; Vol. 11, pp 315-353.

[207] DuPont Patent

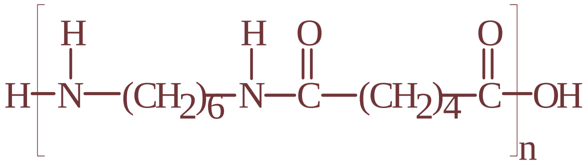
[208] Kohan, M. I. *Nylon Plastics*; Wiley-Interscience: New York, 1973.

[206] Zimmerman, J. In *Encyclopedia of Polymer Science and Engineering*; 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley-Interscience: New York, 1987; Vol. 11, pp 315-353.

[209] Subbulakshmi, M. S.; Kasturiya, N.; Hansraj; Bajaj, P.; Ararwal, A. K. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **2000**, *C40*, 85.

[206] Zimmerman, J. In *Encyclopedia of Polymer Science and Engineering*; 2nd ed.; Mark, H. F., Bikales, N. M.,

derivative utilized in the synthesis. In the cases of aromatic nylons derived from isophthalic and terephthalic acids, an I or a T is substituted for the second digit.[206]



$$H\left[\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n OH$$

Figure 2.4-1: Poly(hexamethylene adipamide) or Nylon 6,6

2.4.2 General Properties of Nylon 6,6

Poly(hexamethylene adipamide) or nylon 6,6 (Figure 2.4-1) is the polyamide produced in the highest volume.[206] The actual synthetic routes to this and other polyamides will be discussed in a later section. Nylon 6,6 is a highly crystalline, chemically resistant material, with good mechanical strength. The high degree of crystallinity is primarily due to the spacing of the amide bonds along the backbone. This spacing allows the carbonyl oxygens and the hydrogens of the amide linkages to almost perfectly align themselves for hydrogen bonding.[208] (See Figure 2.4-2.) The strong interactions between chain segments result in a tightly packed crystalline lattice. In fact, nylon 6,6 has been reported to be up to ~50% crystalline.[14] Additionally, this high degree of crystallinity is thought to be responsible for the unexpectedly low solubility of nylon 6,6.[208] Only strong acids, such as, phenols, formic acid, fluorinated alcohols, and mineral acids are able to solvate nylon 6,6 at room temperature.[210] It is theorized that a highly acidic nature is needed to disrupt the hydrogen bonding of the polymer chains before the sample can dissolve into solution.[206]

Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley-Interscience: New York, 1987; Vol. 11, pp 315-353.

[206] Zimmerman, J. In *Encyclopedia of Polymer Science and Engineering*; 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley-Interscience: New York, 1987; Vol. 11, pp 315-353.

[208] Kohan, M. I. *Nylon Plastics*; Wiley-Interscience: New York, 1973.

[14] Odian, G. *Principles of Polymerization*; 3rd ed.; Wiley Interscience: New York, 1991.

[208] Kohan, M. I. *Nylon Plastics*; Wiley-Interscience: New York, 1973.

[210] Putscher, R. E. In *Kirk-Encyclopedia of Chemical Technology*; Wiley: New York, 1978; Vol. 18, p 328.

[206] Zimmerman, J. In *Encyclopedia of Polymer Science and Engineering*; 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley-Interscience: New York, 1987; Vol. 11, pp 315-353.

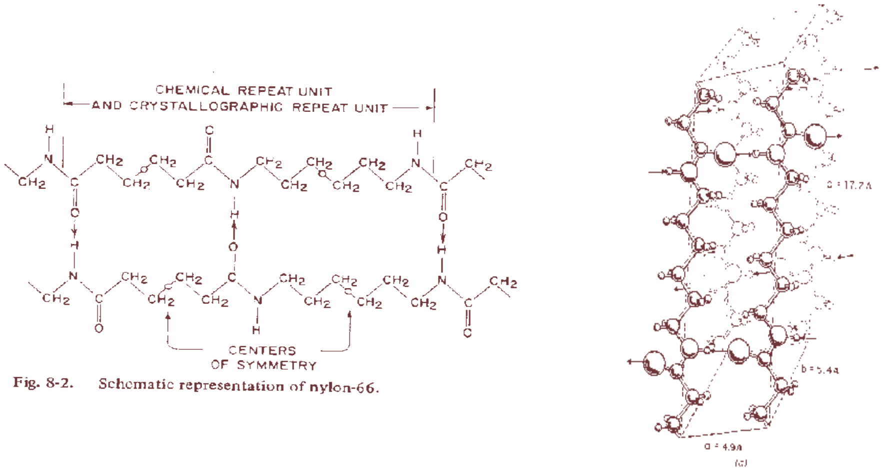


Fig. 8-2. Schematic representation of nylon-66.

Figure 2.4-2: Crystalline Lattice Resulting From Hydrogen Bonding in Nylon 6,6 [208]

Unfortunately, nylon 6,6 does have its drawbacks. For example, it burns rather easily and melts while burning.[211] Moreover, the pyrolysis of nylon 6,6 results in the formation of hydrogen cyanide (HCN).[212] This combustion product is quite toxic; thus a means to either limit or eliminate its evolution, by reducing the flammability of nylon 6,6, would be well received.

In addition, the extent of inter-chain hydrogen bonding, which is responsible for many of the advantageous properties, allows moisture to greatly affect mechanical properties.[213] Water can hydrogen bond with the amide linkages and act as a plasticizer, reducing the observed T_g. Water sorption experiments have show that nylon 6,6 will absorb ~ 8-9% water at 100% relative humidity and retain up to ~ 7% water when annealed.[214] The influence of water as a plasticizer is so pronounced that the environment in which a nylon component is to be used can affect how the component is designed.[208]

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[208] Kohan, M. I. *Nylon Plastics*; Wiley-Interscience: New York, 1973.

[211] Subbulakshmi, M. S.; Kasturiya, N.; Hansraj; Bajaj, P.; Ararwal, A. K. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **2000**, *C40*, 85.

[212] Jellinek, H. H. G.; Das, A. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 2715.

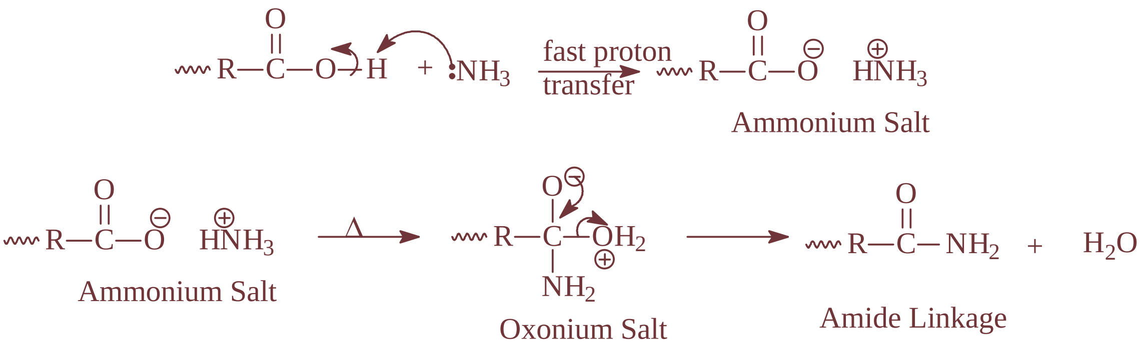
[213] Ellis, T. S. *J. Appl. Polym. Sci.* **1988**, *36*, 451.

[214] Starkweather, H., Jr. *J. Appl. Polym. Sci.* **1959**, *2*, 129.

[208] Kohan, M. I. *Nylon Plastics*; Wiley-Interscience: New York, 1973.

2.4.3 Synthetic Approaches and Mechanism for Polyamides

Polyamides are produced through the formation of amide linkages. The most common components used to form the amide linkage are dicarboxylic acids and diamines.[215] The reaction proceeds through an addition-elimination process with the creation of water in the manner shown in Scheme 2.4-1.[216]



Scheme 2.4-1: Formation of the Amide Linkage[216]

When exposed to carboxylic acids, amines undergo fast proton exchange to form an ammonium salt. Upon heating this salt formation is reversed, creating an oxonium salt that degrades to form the more thermodynamically favored amide bond.[217] It should be noted that while amide interchange reactions are possible, they are not as common as in polyesters. Consequently, amide interchange will not be discussed in this review.

Although polyamides have produced by various methods, the most common procedures are via high-pressure hydrolytic melt methods.[218] These processes have been refined for most industrially important polyamides, including those derived from cyclic lactams and amino acids.[208,219] Additionally, the conversion of dimethyl esters and amines to polyamides via ester aminolysis has been utilized especially for diacids of limited thermal stability.[220] The ionic ring-opening of cyclic lactams, both via cationic and

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[215] Stevens, M. P. *Polymer Chemistry: An Introduction*; 2nd ed.; Oxford University Press: New York, 1990.
[216] Volhardt, K. P. C. *Organic Chemistry*; W.H. Freeman and Company: New York, 1987.
[217] Carey, F. A.; Sundburg, R. J. In *Advanced Organic Chemistry: Part A: Structure and Mechanisms*; 3rd ed.; Plenum Press: New York, 1993.
[218] Odian, G. *Principles of Polymerization*; 3rd ed.; Wiley Interscience: New York, 1991.
[208] Kohan, M. I. *Nylon Plastics*; Wiley-Interscience: New York, 1973.
[219] McGrath, J. E., Ed. *Ring Opening Polymerization; ACS Symposium Series 285*; ACS: Washington, D.C., 1985; Vol. 286.
[220] Chang, H. J.; Vogel, O. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 311.

anionic routes, has also been explored, but will not be discussed in this review. Further insight to the ring-opening of lactams can be found in Frisch and Reegen's book on ring opening polymerization.[221]

2.4.3.1 Hydrolytic Polyamidization of Hexamethylene Diamine and Adipic Acid

Industrially, nylon 6,6 can be produced either by batch or continuous processes.[206] The requisite 1:1 stoichiometry is commonly preserved through the use of a "nylon salt," which can be prepared in either an isolatable form or an aqueous solution. The isolatable crystals are prepared by separately dissolving adipic acid and hexamethylene diamine in methanol, followed by the subsequent mixing of the two solutions at ~50°C.[222] Mixing results in a fast proton exchange, yielding the insoluble salt via crystallization. Any error in stoichiometry is automatically corrected for due to the fact that an excess of either starting material, as well as most impurities present, will remain in the methanol solution.[206] If further purification is deemed necessary, the salt may be recrystallized from a water/alcohol solution. For reference, the accepted melting point of the pure nylon 6,6 salt is 195°C.[206] Industrially, polymerization is pursued using a concentrated aqueous solution (~50-80% solids).[218] This solution can be prepared from the isolated nylon salt or by directly dissolving the monomers in water. In this case, the 1:1 stoichiometry can be ensured by adjusting the pH of the salt solution (1:1 stoichiometry correlates to a pH of 7.6).[223,224]

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[221] Frisch, K. C.; Reegen, S. L., Eds. *Ring Opening Polymerization*; Dekker: New York, 1969.

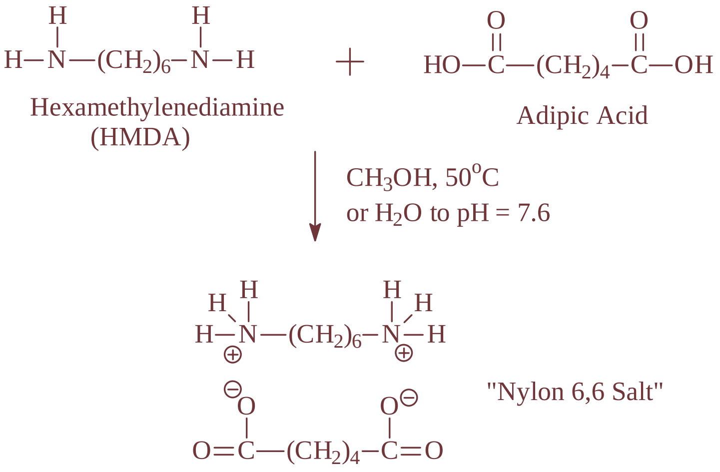
[206] Zimmerman, J. In *Encyclopedia of Polymer Science and Engineering*; 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley-Interscience: New York, 1987; Vol. 11, pp 315-353.

[222] Jacobs, D. B.; Zimmerman, J. In *Polymerization Processes*; Schildknecht, C. E., Skeist, I., Eds.; Wiley & Sons: New York, 1977.

[218] Odian, G. *Principles of Polymerization*; 3rd ed.; Wiley Interscience: New York, 1991.

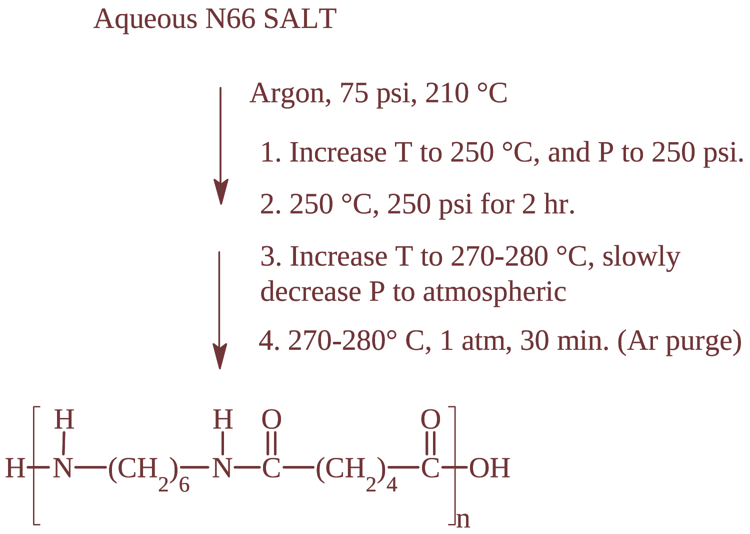
[223] Gaymans, R. J.; Sikkema, D. J. *Comprehensive Polymer Science* **1989**, *5*, 357.

[224] Peebles Jr., L. H.; Huffman, W. H. *J. Polym. Sci., Part A.* **1971**, *9*, 1807.



Scheme 2.4-2: Synthesis of Nylon 6,6 Salt[206]

Although nylon 6,6 can be polymerized by both batch and continuous processes, the batch process is the easiest to duplicate on a laboratory scale and thus is the system emulated in this research. Batch polyamidization[218] (Scheme 2.4-3) is accomplished by first purging the vessel with an inert gas, followed by slowly heating the aqueous salt to approximately 250°C.



Scheme 2.4-3: Industrial Batch Process for the Hydrolytic Polymerization of Nylon 6.6[222]

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[206] Zimmerman, J. In *Encyclopedia of Polymer Science and Engineering*; 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley-Interscience: New York, 1987; Vol. 11, pp 315-353.

[218] Odian, G. *Principles of Polymerization*; 3rd ed.; Wiley Interscience: New York, 1991.

[222] Jacobs, D. B.; Zimmerman, J. In *Polymerization Processes*; Schildknecht, C. E., Skeist, I., Eds.; Wiley & Sons: New York, 1977.

The nitrogen or argon purge ensures the exclusion of oxygen minimizing the risk of oxidation, while the elevated temperature converts the water to steam and prevents the subsequent crystallization of the nylon salt.[208] The pressure within the reaction vessel can be maintained at ~ 250 psi (~1.7 MPa) by the occasional venting of excess steam. High pressure is needed both to keep the volatile diamine from evaporating (once the temperature is high enough to dissociate the salt) and to keep water in the system, maintaining a molten state while below the product's melting point.[222,223] However, too much water limits the molecular weight. Conversion to high molecular weight can be facilitated by slowly increasing the temperature to 270-280°C, while reducing the pressure to one atmosphere over 1-1.5 hours. This reduces the water content and allows the formation of high molecular weight material.[225] The polymer can be further increased in molecular weight by employing an inert gas purge, application of a vacuum, or subsequent solid-state polymerizations.[226]

2.4.3.2 Additional Routes of Polyamidization

The hydrolysis of polyamides derived from longer chain diacids (n6,10 ; n6,12) are more difficult to produce using aqueous solutions, due to the fact that their salts are often only marginally soluble in water. In these cases, the formation of the aqueous slurry is often avoided and polymerization proceeds utilizing the solid salt and a catalytic amount of water.[208] It should be noted that this fact is not mentioned in most discussions of polyamides since they tend to focus on the more polar and industrially important nylon 6,6, and nylon 6.

Cyclolactams can be polymerized via hydrolytic ring opening polymerizations.[219] The main difference from the salt reactions is that only a catalytic amount of water (5-10% water) is needed to induce ring-opening to the amino acid followed by both salt

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[208] Kohan, M. I. *Nylon Plastics*; Wiley-Interscience: New York, 1973.

[222] Jacobs, D. B.; Zimmerman, J. In *Polymerization Processes*; Schildknecht, C. E., Skeist, I., Eds.; Wiley & Sons: New York, 1977.

[223] Gaymans, R. J.; Sikkema, D. J. *Comprehensive Polymer Science* **1989**, *5*, 357.

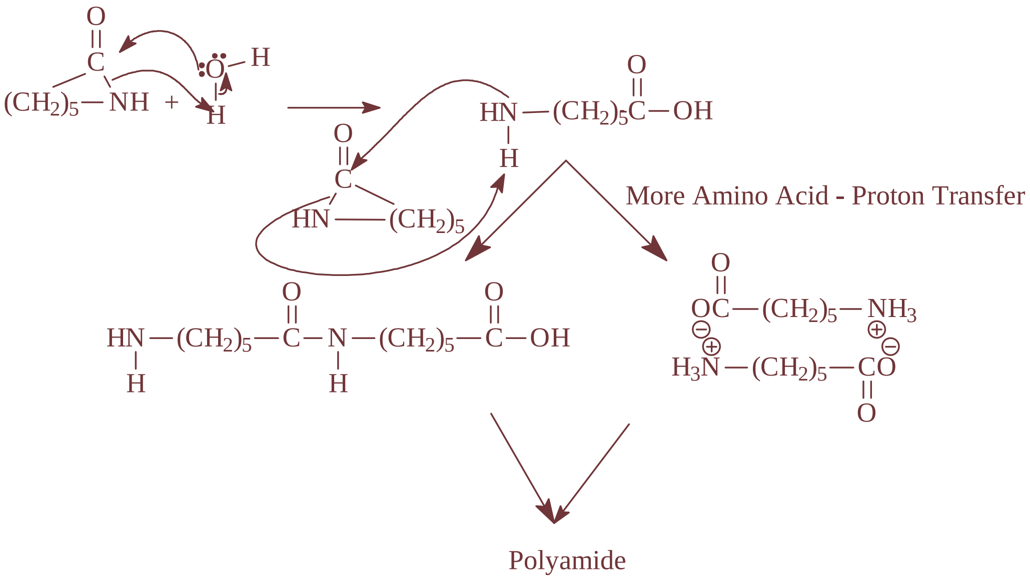
[225] Wan, I.-Y. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, VA, 1994.

[226] Wiloth, F. In *US. Patent 3,031,433*, 1962.

[208] Kohan, M. I. *Nylon Plastics*; Wiley-Interscience: New York, 1973.

[219] McGrath, J. E., Ed. *Ring Opening Polymerization; ACS Symposium Series 285*; ACS: Washington, D.C., 1985; Vol. 286.

formation and the opening of neighboring rings.[215] (Scheme 2.4-4)



Scheme 2.4-4: Reaction Pathways of the Hydrolytic Ring-Opening Polymerization of Caprolatam[215]

Ester aminolysis, although a less common route to polyamidization, (Scheme 2.4-5), has been studied both in solution and in the bulk state.[227] The development of this reaction was motivated by the desire to eliminate the need for the high pressure hydrolysis reactions. The key factor hindering the reduction of pressure is the inability of the dimethyl ester to readily form a stable nylon salt. With ester aminolysis, the strong association of the monomers experienced in the salt is avoided, thus the reactions can begin at lower reaction temperatures (just above the melting temperatures of the reactant). The ester aminolysis route is generally used for diacids with lower thermal stabilities and more nonpolar monomers, because solubility in water is not a factor.[215]

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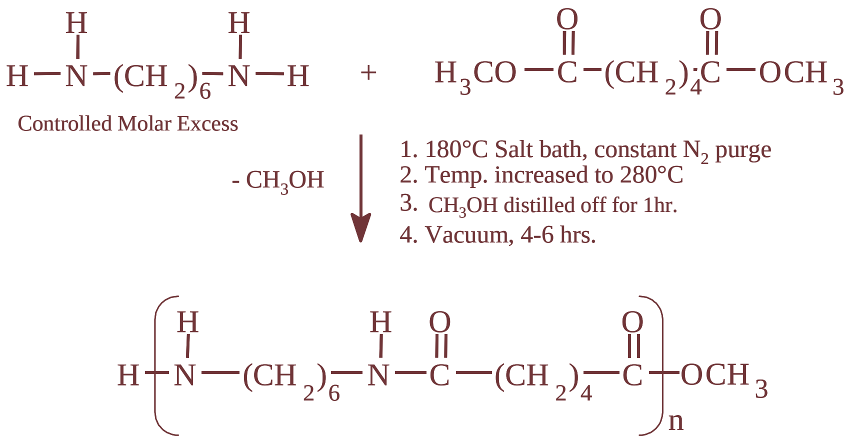
[215] Stevens, M. P. *Polymer Chemistry: An Introduction*; 2nd ed.; Oxford University Press: New York, 1990.
[227] Jouffret, F.; Madec, P.-J. *J. Polym. Sci., Part A.* **1996**, *34*, 2363.



Scheme 2.4-5: Ester Aminolysis Route for Nylon 6,6

2.4.4 Characterization Concerns in the Analysis of Polyamides

The high crystallinity of polyamides, although a key component of most of their advantageous properties, also makes the analysis of polyamides difficult by most conventional methods. The lack of solubility in common NMR solvents creates the need for either expensive specialty deuterated strong acids, or the use of solid-state NMR. Infrared analysis cannot be relied upon, since the high crystallinity causes too much scattering.

Estimating molecular weight can be a particularly daunting task. Although intrinsic viscosity is relatively easy to do with strongly acidic solvents, most laboratories are not equipped to use m-cresol or sulfuric acid as a solvent for Gel Permeation Chromatography (GPC). Endgroup analysis is also difficult because it must be performed in either m-cresol or benzyl alcohol at elevated temperatures.[206] The general limitation of analytical methods for polyamides has lead to the development of a rather elegant method, by Schutenburg and Shultz,[228] to enable the use of common GPC solvents. A N-trifluoroacetylation reaction can be used to disrupt the hydrogen bonding of the amide linkages, as illustrated in Scheme 2.4-6.

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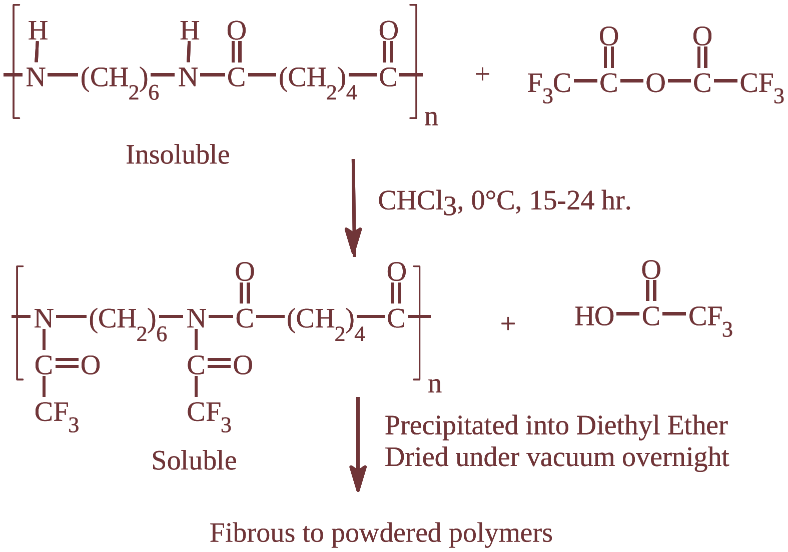
[206] Zimmerman, J. In *Encyclopedia of Polymer Science and Engineering*; 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley-Interscience: New York, 1987; Vol. 11, pp 315-353.

[228] Schuttenburg, H.; Schultz, R. C. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 777.



Scheme 2.4-6: Derivatization of Nylon 6,6 for GPC Analysis[228]

Using trifluoroacetic anhydride, acetylation occurs on the nitrogen of the amide bond, eliminating a proton. This proton subsequently adds to the trifluorocarboxylate yielding trifluoroacetic acid.[229] The dispersed nylon particles become soluble in the reaction solution as the sites for hydrogen bonding are removed. Thus, the reaction is complete when particles of nylon can no longer be observed. The derivatized nylon can then be precipitated into diethyl ether, dried and prepared for analysis in a number of common GPC solvents. However, the true elegance of this method only becomes apparent upon the regeneration of the nylon to its original composition with no significant degradation, simply with the addition of water.[229]

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[229] Jacobi, E.; Schuttenburg, H.; Schultz, R. C. *Makromol. Chem. Rapid Commun.* **1980**, *1*, 397.

2.4.5 Flame Resistance in Polymeric Materials

Organic polymeric materials have become the basis for some of the most common and versatile products around the world today. Polymers are utilized in applications ranging from adhesives, to aerospace materials, to electronic components.[230] However, with the exception of a few “inherently” flame resistant polymers (polytetrafluoroethylene, polyvinyl chloride, etc.), most thermoplastics are not highly flame retardant. Although organic materials suitable for fabrication of products cannot be made completely non-combustible[231], improving the fire retardance of polymeric materials is a common and highly desirable goal for many researchers. In fact, as early as 1993, 50-60% of the polymeric materials produced were required to show some degree of fire retardance.[231] Before exploring the methods commonly used to improve fire retardance, it is important to understand some flammability fundamentals and the processes of polymer combustion.

First, flammability is not a scientific term in the sense that there is no single intrinsic property that can be measured to quantify the extent of flammability. Rather flammability is the summation of a variety of intrinsic properties (ease of ignition, rate of flame spread, etc.). Moreover, combustion behavior is not an inherent property of the material but instead a reflection of the material’s structure and several external factors, such as heat of ignition, shape of the sample, ventilation, pressure, temperature, etc.[231]

There are many conditions under which combustion occurs in fires. Additionally, there are many causes for a material’s flammability within each of these circumstances. Therefore, one fire model cannot be fully inclusive. However, the inability to determine a simple root cause for a property, such as flammability or combustion behavior, does not mean that it cannot be quantified. Scientists worldwide have developed over 800 separate tests to determine the flame retardance of polymeric materials.[232] Some of the most accepted test for flame retardant materials are the limiting oxygen index (LOI), char yield

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[230] Hergenrother, P. M. *Angew. Chem. Int. Ed. Engl.* **1990**, *29*.

[231] Camino, G.; Luda, M. P.; Costa, L. *Journal De Phisique IV* **1993**, *3*, 1539.

and cone calorimetry.

The limiting oxygen index (LOI) (ASTM-D-2683) has been defined as the minimum percentage of oxygen in a oxygen-nitrogen atmosphere in which a material will ignite and sustain for 3 minutes the candle-like burning of a vertical specimen.[233] Typically, a material with an LOI greater than 27 is considered to be flame retardant.[215] This test has become the most useful and reproducible procedure for small scale testing. Char yield is perhaps the most accessible method for most polymer chemists. The values can be acquired from dynamic thermogravimetric analysis (TGA) of the polymer, where the material is simply heated in a balance at a given heating rate (normally 10°C/min.) and the relative amount of residual char at a given temperature is recorded. The greater the char yield, the more likely a material is to be classified as flame retardant. In fact, the char yield of many polymers has been correlated to the LOI by Van Krevelen, in a linear relationship, as given by Equation 12.[234]

$$\text{LOI} * 100 = 17.5 + 0.4*(\text{Char Yield @ } 900\ ^{\circ}\text{C}) \tag{12}$$

However, a real fire does not have an enriched oxygen atmosphere as is present during an LOI test. Thus, in order to more accurately reproduce actual burning under controlled conditions, a novel technique called cone calorimetry (ASTM E1354) was developed. With cone calorimetry, an apparatus (shown in Figure 2.4.-3) comprised of an electrical heater in the form of a truncated cone is capable of generating a heat fluxes up to 100 kW/m^2. This enables the pyrolysis of polymeric materials to be examined at atmospheric conditions. Additionally, the cone calorimeter is equipped with a variety of detection devices that allow the simultaneous analysis of smoke production and composition, weight loss, heat release rates, and other properties. The ability to more accurately simulate burning conditions, coupled with the simultaneous analysis of the combustion products, is making cone calorimetry an increasingly popular technique.

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[232] Becker, W. *Polym. Deg. and Stab.* **1990**, *30*, 141.
[233] Fenimore, C. P.; Martin, F. J. *Mod. Plast.* **1966**, *44*, 141.
[215] Stevens, M. P. *Polymer Chemistry: An Introduction*; 2nd ed.; Oxford University Press: New York, 1990.
[234] van Krevelen, D. W. *Polymer* **1975**, *16*, 615.

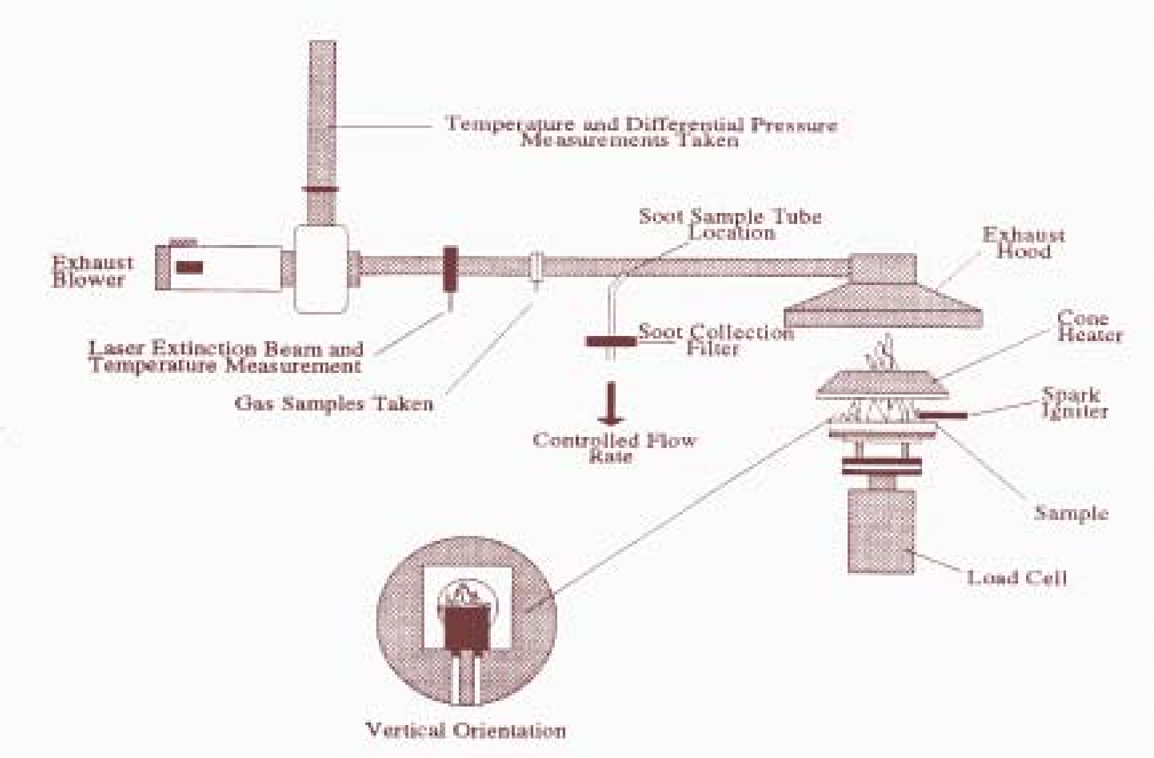

Figure 2.4.-3: Schematic of a Cone Calorimeter[235]

The behavior of a polymeric material under combustion is a complicated process involving a series of four interdependent steps.[234,236] These steps can be best represented as a cycle as illustrated in Figure 2.4-4.

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[235] Nelson, G. L., Ed. *Fire and Polymers Il;ACS Symposium Series No 599*; American Chemical Society: Washington D.C., 1995.
[236] Aseeva, R. M.; Zaikov, G. E. *Adv. Polym. Sci.* **1985**, *70*, 171.

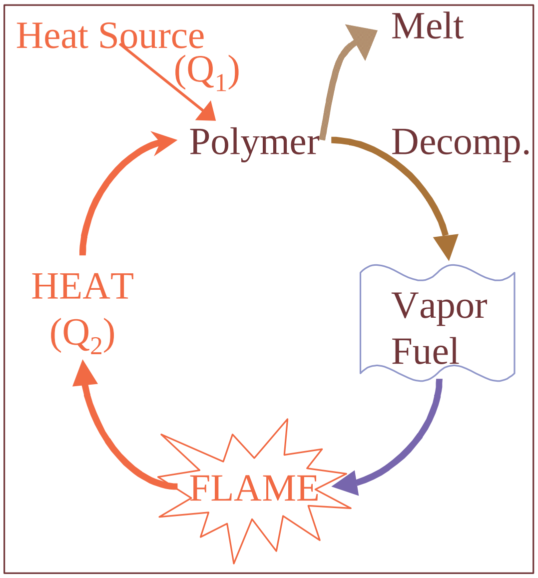

Figure 2.4-4: Combustion Cycle of Polymeric Materials[234,236]

First, heat is applied to the polymer from some source; the application of heat (Q_1) then leads to a combination of degradation and/or melting. Q_1 must be greater than the weakest bonds of those encountered along the polymer backbone to initiate thermal decomposition. This decomposition breaks covalent bonds through a radical mechanism known as chain scission, generating either volatile hydrocarbons that form vaporous fuel or a highly cross-linked char, while melting allows the polymer to flow (often further complicating the reaction). Once the vaporous fuel has been produced, it ignites to form the visible flame, which can be sustained as long as the concentration of gaseous fuel is maintained and oxygen is readily available. Examination of this process reveals that the polymeric material is not actually the source of the flame, but rather a relatively large reservoir of fuel. The burning vaporous fuel releases more heat (Q_2), which is transferred to the polymer. If Q_2 is greater than the weakest bond strength, it will then initiate the further decomposition of the polymer, yielding more fuel for the fire, thus completing the combustion cycle.[237] An ideally fire retardant system will have a large heat of ignition (Q_1) and a small heat of combustion (Q_2).[234]

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[237] Ebdon, J. R.; Jones, M. S. In *Polymeric Materials Encyclopedia*; Salamon, Ed.; CRC Press: New York, 1996; p 2397.

[234] van Krevelen, D. W. *Polymer* **1975**, *16*, 615.

Efforts to limit the flammability of polymeric materials must disrupt the cycle of combustion at one or more of its stages. Commonly, imparting fire resistance to a polymeric material is attempted by either the utilization of small molecules as flame retardant additives (such as Sb_2O_3, aromatic bromides, and phosphates),[238] or the incorporation of flame retardant moieties (like organic halogens, phosphorus, or polydimethylsiloxanes) directly into the polymer backbone.[239,240,241,242]

The use of additives, which are generally physically blended into the polymer matrix, provides a relatively cheap and facile way to impart fire retardance to a material. Additives and fire retardant moieties commonly disrupt the combustion cycle in one or more of the following three modes. First, they may degrade to form a carbonaceous, silicate, or glass-like char on the surface of the polymer thereby insulating the polymer from the heat source. Second, they could degrade in an endothermic manner, effectively reducing the overall heat of combustion. Third, the additive might act as a radical scavenger, limiting the chain scission reactions and in turn the production of vaporous fuel, or they could react with atmospheric oxygen making it unavailable for the oxidation of the flammable gases.[243]

One of the most common strategies to add fire retardance to a polymeric material is to introduce halogenated organics to the polymers, either as additives or attached to the polymer structure. The effectiveness of the halogen depends on many factors including the reactivity of the halogen towards radicals, the nature of its hydrocarbon support, and its concentration. Generally, the larger the halogen, the greater its reactivity, so bromine is more effective than chlorine, which is more effective than fluorine. Additionally, aliphatic halides are better flame retardants than aromatic halides. This trend is most likely due to the fact that aliphatic halides are more susceptible to homolytic cleavage

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[238] Kuryla, W. C.; Papa, A. J. *Flame Retardancy of Polymeric Materials*; Marcel-Dekker: New York, 1978; Vol. 4.

[239] Nelson, G. L., Ed. *Fire and Polymers II; ACS Symposium Series. No 599*; American Chemical Society: Washington D.C., 1995.

[240] Maiti, S.; Bannerjee, S.; Palit, S. K. *Prog. Polym. Sci.* **1993**, *18*, 227.

[241] Hashimoto, S.; Furukawa, I.; Kondo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 2356.

[242] March, J. *Advanced Organic Chemistry*; McGraw-Hill, Inc.: New York, 1977.

[243] Subbulakshmi, M. S.; Kasturiya, N.; Hansraj; Bajaj, P.; Ararwal, A. K. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **2000**, *C40*, 85.

than aromatics and thus become active at lower temperatures.[244] However, to show significant improvement in flame retardance, large concentrations of halogens are needed (15-30 wt%). The use of organohalogens as additives leads to certain inescapable problems. Leaching, or the exclusion of the additive from the polymer matrix, will occur with aging or upon exposure to solvents. This leaching effect upon aging has been documented by Clough[245] who found significant loss of both Sb_2O_3 and organohalogens in his study of flame retardant ethylene-propylene rubbers. One way to avoid the problem of leaching is to covalently bond the halogen to the polymer backbone. This method has been proven to be relatively easy in the cases of polyolefins[234] and epoxies,[246,247] thereby increasing char yield and the LOI. Yet upon combustion, these materials release halogen acids (HX) as gases, creating a highly toxic environment.[131] Other additives, specifically phosphorus and nitrogen containing compounds, have been investigated as alternatives to halogenated species.

The incorporation of triarylphosphine oxide moieties and polydimethylsiloxane into the backbone of various polymeric materials has been investigated by the McGrath research group and others for approximately 20 years.[248] These investigations have shown that the inclusion of triarylphosphine oxides and siloxanes in organic polymers increases the fire retardance of the homopolymers, most likely through the production of foamed inorganic chars (a process known as intumescence) which may insulate the polymer from the heat released during combustion. Although, briefly addressed by Wescott's study of polyimide-siloxane block copolymers,[249] the possible synergistic effect of including both species into one polymer has never been fully explored.

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[244] Wang, S. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, Va, 2000.
[245] Clough, R. L. *J. Appl. Polym. Sci.* **1983**, *34*, 767.
[234] van Krevelen, D. W. *Polymer* **1975**, *16*, 615.
[246] Nelson, G. L., Ed. *Fire and Polymers Il;ACS Symposium Series No 599*; American Chemical Society: Washington D.C., 1995.
[247] Yang, C.; Lee, T. *J. Appl. Polym. Sci.* **1987**, *34*, 2733.
[131] Riley, D. J. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, Va, 1997.
[248] Dr. McGrath and his students have published 4 patents, 193 refereed papers and reviews, 16 Ph.D. Dissertations, and 7 M.S. Theses on novel polydimethylsiloxane and/or phosphine oxide containing materials from 1980 up to the publication of this document, with many ongoing projects in development.
[249] Wescott, J. M. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, VA, 1993.

3 Perfectly Alternating Segmented Poly(arylene ether phosphine oxide)-b-Poly(dimethylsiloxane) Copolymers

3.1 Introduction

3.1.1 Motivations for Copolymerization

Both poly(arylene ether phosphine oxide)s (PEPO) and poly(dimethylsiloxane)s (PDMS) have been proven to be useful materials in their own right. Poly(arylene ether phosphine oxide)s are well known to be highly thermally stable, totally amorphous, optically clear, and colorless materials with high T_gs. In addition, poly(arylene ether phosphine oxide)s convey a much higher refractive index (n = 1.64) than polycarbonates (n = 1.58), suggesting their potential application as optical lenses. However, the chromatic dispersion or "rainbowing" of a coherent beam of light is greater (lower Abbe number, ν) than that encountered in polycarbonates. Although polydimethylsiloxanes have a relatively low refractive index (n = 1.40), they maintain cohesive light much better(ν = 40) than both polycarbonates (ν = 28) or poly(arylene etherphosphine oxide)s (ν = 25).[136]

One goal of this thesis was to combine the high refractive index of PEPO with the low chromatic dispersion of PDMS through the use of block copolymerization. At this point, it is convenient to review a few points stated in the overview of optical properties included in the literature review (Section 2.2.5). While it was known that both random copolymerizations and copolymers derived from materials with similar refractive indices result in products with optical properties correlating to compositionally weighted averages,[141] the effects of nanophase separation displayed by block copolymers of dissimilar chemical nature and refractive index have not been fully explored. This discrepancy can be explained by the fact that most immiscible block copolymers display macroscopic (larger then the wavelengths of visible light) phase separation and are therefore opaque materials.[19] The light is scattered in a manner analogous to a polymer

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[136] Mills, N. J. In *Encyclopedia of Polymer Science and Engineering*: New York, 1991; Vol. 10, pp 493-540.

[141] Rosen, S. L. *Polym. Eng. Sci.* **1967**, *7*, 115.

[19] Allport, D. C.; W.H. Janes, Eds. *Block Copolymers*; John Wiley & Sons: New York, 1973.

filled with particles of equal size. Prior experimentation by McGrath and co-workers indicated that optically clear siloxane-polyarylene ether block copolymers could be produced, but no formal study of the resultant optical properties has been conducted.[88] This effort is intended to partially fill this void in the comprehension of the properties of siloxane block copolymers.

A secondary motivation was to investigate the thermoplastic elastomeric properties of PEPO-PDMS copolymers. The high T_g and good mechanical strength of the PEPO segments anchor the highly flexible and energy dissipating PDMS segments to result in an optically clear coating of controlled modulus that could serve as an alternative to crosslinked silicone rubbers.

Additionally, studies by McGrath, Bonaplata, and Wang illustrate the ability to uniformly disperse nanoparticles of silica and metal salts via hydrogen bonding or complexation with phosphine oxide containing poly(arylene ether)s.[127,132] This discovery further extended the scope of the exploration of PEPO-PDMS copolymers to determine if any selective association would be present between a silica particle and the hydrogen bonding PEPO segments or the silica-like nature of the siloxane.

3.1.1 Methods of Copolymerization

Block copolymers are traditionally produced by one of two methods, sequential addition or step-wise condensation.[2] However, great care is required to avoid unknown block sizes and sequences.[250] With sequential addition, crossover from one growing chain end to another is crucial and can result in polydispersed blocks, mixed monomer regions, and/or large fractions of homopolymer. In the case of condensation copolymerizations, coupling agents are commonly used. A coupling agent is a reactive moiety that reacts similarly with both types of oligomers. However, this lack of selectivity leads to unpredictable block sequences. The only way to guarantee regular block sequences is to

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[88] Hedrick, J. L. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, Va, 1985.
[127] Bonaplata, E.; Ding, H.; Hanson, B. E.; McGrath, J. E. *Polymer* **1995**, *36*, 3035.
[132] Wang, S. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, Va, 2000.
[2] Noshay, A.; McGrath, J. E. *Block Copolymers-Overview and Survey*; Academic Press: New York, 1977.
[250] Noshay, A.; Matzner, M.; Merriam, C. N. *J. Polym. Sci., Part A* **1971**, *19(11)*, 3147.

eliminate all other reactive pathways. The direct condensation of mutually reactive oligomers is one way to eliminate defects in the sequence of the copolymer blocks.

Perfectly alternating segmented copolymers may be achieved by the condensation of pre-formed telechelic oligomers. In this approach, oligomers of the block types desired are separately prepared with different, mutually reactive endgroups. The two oligomers, A and B, are selected so the A groups cannot react with other A groups, B groups cannot react with other B groups, and neither can react with the solvent. Since A and B are mutually reactive, the only logical product of copolymerization becomes alternating blocks of A and B. Given that the oligomers are preformed, they can be isolated and well characterized. The reaction conditions are selected such that the oligomer lengths cannot change, resulting in copolymers of known segmental length. The product of this type of synthesis can be defined as a perfectly alternating block copolymer because the block lengths are both known and constant, and the block types alternate along the backbone. In this research effort, a silylamine-hydroxyl reaction, in conjunction with the reactive oligomer approach, was used to facilitate the synthesis of the block copolymers.

3.1.2 Historical Development of the Silylamine-Hydroxyl Reaction

The development of the direct condensation of oligomers was greatly enhanced by Noshay et al. in the early 1970s.[250] Their work was the first to utilize a silylamine-hydroxyl reaction for the production of regulated block copolymers.[251] In their effort to synthesize polysulfone-polydimethylsiloxane copolymers, Noshay and co-authors used hydroxyl-terminated sulfone oligomers that were dissolved in either chlorobenzene or THF, then reacted with silylamine-terminated polydimethylsiloxane oligomers. The silylamine-hydroxyl reaction was selected as it was facile and produced a gaseous condensation product. Previous work involving hydrosilation and silylchloride-hydroxyl reactions resulted in lower molecular weight materials. Additionally, the silylchloride reaction products required more purification, since the HCl released necessitated the addition of a stoichiometric amount of base, such as pyridine, to prevent acid catalyzed redistribution within the siloxane block.[250] However with the silylamine-hydroxyl

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[250] Noshay, A.; Matzner, M.; Merriam, C. N. *J. Polym. Sci., Part A* **1971**, *19(11)*, 3147.
[251] Noshay, A.; Matzner, M.; Merriam, C. N. In *U.S. 3,539,657*; Union Carbide Corp., 1970.

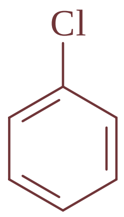
method, the oligomers could be well characterized (thus the number average block sizes were known) and the copolymers could be isolated free of contamination. These well defined block copolymers allowed studies of the effect of block size on morphology and selected physical properties to be conducted.

3.2 Experimental

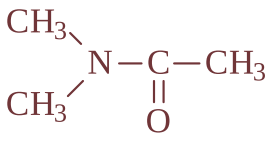
3.2.1 Solvents and Purifications

Solvents used in synthesis:

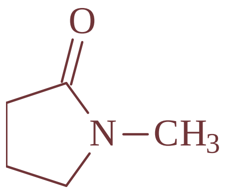
Chlorobenzene (Aldrich Chemical Company) was stirred over calcium hydride overnight followed by distillation under reduced pressure at ~ 45°C. (bp 132 °C/ 760 mmHg). The purified fraction was then stored under nitrogen in a round-bottomed flask until use.



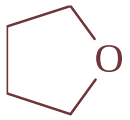
N,N-Dimethylacetamide (DMAc, Aldrich Chemical Company) was stirred over phosphorus pentoxide overnight followed by distillation under reduced pressure at ~ 60°C. (bp 165 °C/ 760 mmHg) The purified fraction was then stored under nitrogen in a round-bottomed flask until use.



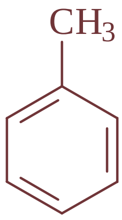
N-Methyl-2-Pyrrolidone (NMP, Aldrich Chemical Company) was stirred over phosphorus pentoxide overnight followed by distillation under reduced pressure at ~80°C (bp 205°C/ 760 mmHg) The purified fraction was then stored under nitrogen in a round-bottomed flask until use.



Tetrahydrofuran (THF, Aldrich Chemical Company) was purified by distillation from sodium. The purified fraction was then stored under nitrogen in a round-bottomed flask until use.



Toluene was obtained from Aldrich Chemical Company and was used as received without further purification.



General Solvents: Acetone, acetic acid, methanol, chloroform, DMAc, NMP, THF, and 2-propanol were obtained from Aldrich chemical and were used as received without further purification. House deionized water was used for precipitations and all reactions without further purification unless otherwise stated.

NMR Solvent: Deuterated chloroform ($CDCl_3$, Cambridge Isotope Laboratories) was used as received for all NMR experiments unless otherwise stated.

Drying Agents: Calcium hydride, magnesium sulfate, and phosphorus pentoxide were purchased from the Aldrich Chemical Company and stored in desiccators under nitrogen until use. Sodium metal was acquired from the same source and stored under mineral oil.

3.2.2 Commercially Available Monomers and Reagents

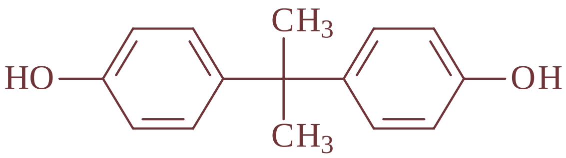
Bisphenol-A (Bis-A)

Supplier: Aristech

Molecular Formula: $C_{15}H_{16}O_2$

Molecular Weight: 228.27 g.mol

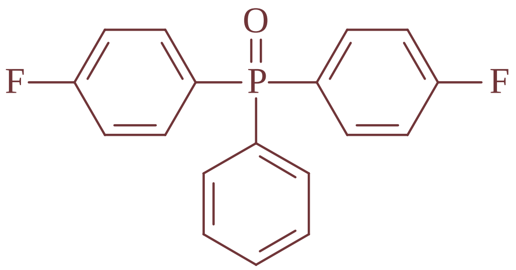
Melting Point: 156-157°C



Purification: Aristech provided monomer grade (99.9% purity) Bis-A that required no further purification beyond vacuum drying at 100°C overnight prior to use. However, if needed Bis-A may be recrystallized from toluene.

4,4’-Bis(fluorophenyl)phenylphosphine Oxide (BFPPO)

Supplier: Avecia Specialties
(formerly Zeneca)
Molecular Formula: $C_{18}H_{13}F_2OP$
Molecular Weight: 314.28 g/mol
Melting Point : 130-131°C



Purification: High purity (monomer grade) BFPPO was generously supplied by Avecia Specialties and was used after vacuum drying at 100°C overnight. Unfortunately, the availability of this monomer varies periodically; therefore its synthesis is provided below.

Synthetic Procedure:[252]

BFPPO was prepared from dichloro(phenyl)phosphine oxide using a previously published Grignard procedure.[252] 2.1 moles of 1-fluoro-4-bromobenzene was needed for every mole of dichloro(phenyl)phosphine oxide to ensure disubstitution.

For example, 12.1 g (0.5 moles) of magnesium turnings and 450 mL of freshly distilled tetrahydrofuran (THF) were added to a 1000 mL 3-neck flask fitted with a mechanical stirrer, an addition funnel, a nitrogen inlet, and a condenser. Then, 86.6 g (0.49 moles) of 1-fluoro-4-bromobenzene was added drop-wise, via addition funnel, at room temperature over the course of 1-2 hours. The mixture was stirred overnight to produce the Grignard reagent. Next 48.2 g (0.24 moles) of dichloro(phenyl)phosphine oxide was slowly added dropwise at room temperature. The reaction mixture was allowed to stir overnight producing a clear yellow solution. Aqueous sulfuric acid (10 vol%) was added until the solution was acidic. Water (180 mL) and diethyl ether (25 mL) was then added to the mixture to create a 2-phase system. The organic layer (top) was decanted. The water layer was washed well with diethyl ether (3-4 times), and all organic layers were combined. The organic layer was then dried over anhydrous magnesium sulfate,

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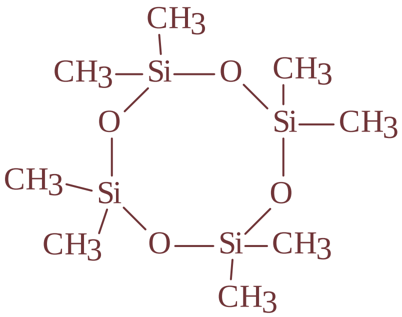
[252] Smith, C. D. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, Va, 1991.

filtered and the filtrate was evaporated to afford a light yellow solid. This material was purified by distillation using a Kuegelrohr apparatus followed by recrystallization from a 1:5 THF/cyclohexane mixture. The resulting material was monomer grade with a melting point of 130-131°C (lit. 124-126 °C) The yield of the reaction was 80-85% after purification. Elemental analysis for $C_{18}H_{13}F_2OP$: C, 68.8%; H, 4.2%; Found: C, 68.9%; H, 4.3%.

Octamethycyclotetrasiloxane (D_4)



Supplier: Dow Corning

Molecular Formula: $C_8H_{24}O_4Si_4$

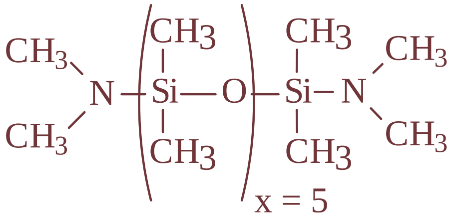
Molecular Weight: 296.6 g/mol

Density: 0.956 g/mL

Boiling Point: 120°C/ 760 mmHg

Purification: Crude octamethycyclotetrasiloxane was dried over calcium hydride then fractionally distilled under reduced pressure at ~ 45°C (bp 120°C/760 mmHg) to isolate the eight member cyclic species. The purified fraction was then stored under nitrogen in a round-bottomed flask until used.

α,ω–Bis(dimethylamino)polydimethylsiloxane (endcapping reagent)



Supplier: CK Witco

(now Crompton)

Molecular Formula: Oligomer Average x = 5

Molecular Weight Average: 516 g/mol

Purification: The endcapping reagent was characterized for both purity and molecular weight by ^{1}H NMR and potentiometric titration, then used as received.

“Catalytic” Bases: Potassium carbonate, and tetramethylammonium hydroxide penta hydrate were purchased from Mallinckrodt Chemical Company and were used as received.

Colloidal Suspension of 10-12nm Silica Particles in DMAc

Supplier:	Nissan Chemical Company (lot# 070852)
Specific Gravity:	1.077
Wt% SiO_2:	20.6

Purification: Silica particles, 10-12nm in average diameter, were dispersed in a colloidal suspension using N,N-dimethylacetamide (DMAc) as the “solvent”, by Nissan Chemical Company. The suspension was clear to the eye and was used as received.

3.2.3 Synthesis of Functional Oligomers

Synthesis of High Molecular Weight Control Poly(arylene ether phosphine oxide) (PEPO)

In order to ensure that controlled molecular weight poly(arylene ether phosphine oxide)s could be achieved, approximately 10 g of a high molecular weight (1:1 stoichiometry) control polymer was produced *via* nucleophilic aromatic substitution (S_NAR) step growth polymerization of 4,4'-bis(fluorophenyl)phenylphosphine oxide (BFPPO) with Bisphenol A. This polymer was synthesized to provide a homopolymer sample for comparison to siloxane containing block copolymers. The reaction was carried out in a three-necked 150 mL flask fitted with a mechanical stirrer, a nitrogen inlet, a thermocouple, a Dean-Stark trap, and a condenser, as illustrated in Figure 3.2-1.

Firstly, 6.26 g (0.01992 moles) of BFPPO and 4.54 g (0.01992 moles) of Bisphenol A were quantitatively transferred to the flask. Freshly distilled NMP (40 mL) was used to rinse the weighing vessels and dilute the reaction conditions to ~ 20% solids. Next, 3.30 g (0.02393 moles) of potassium carbonate (K_2CO_3) was added in ~ 20 mol% excess to ensure a quantitative reaction. Toluene was then added as an azeotroping agent (15 mL) and the reaction solution was heated to 135-140°C (reflux). The mixture was refluxed for 6 hours to completely dehydrate the system and ensure that the base had generated the phenolate anion. The reaction temperature was then raised to ~170°C by the removal of toluene. After a total of 30 hours, the solution was quite viscous and the reaction was halted. After cooling, the solution was diluted with ~ 50 mL of DMAc followed by vacuum filtration to remove most of the salts (*eg.* KF, K_2CO_3). 0.1 mL of glacial acetic acid was then added to protonate any residual phenolate anions. The polymer was isolated by precipitation into a 25/75 v/v water/methanol mixture using a Waring blender. The resulting white fibrous material was filtered and vacuum dried at ~170°C overnight, then redissolved in THF (20% solids), reprecipitated in water, and dried under the same conditions. Analysis of the high molecular weight control polymer will be discussed in Section 3.4.1.1.1.

Controlled Molecular Weight Hydroxyl-Terminated Poly(arylene ether phosphine oxide)s (PEPO)

The controlled molecular weight hydroxyl-terminated PEPO oligomers were prepared similarly to the high molecular weight control polymer, with a few alterations to facilitate controlled molecular weight and larger amounts of sample per reaction. Control over molecular weight and reactive endgroups was achieved by utilizing stoichiometric imbalances as prescribed by the Carothers equation.[253] The following is a typical reaction procedure for the preparation of approximately 30 g of a 5,000 g/mol hydroxyl-terminated oligomer. A four-necked 250 mL flask was fitted with a mechanical stirrer, a nitrogen inlet, a thermocouple, a Dean-Stark trap, and a condenser, as illustrated in Figure 3.2-1

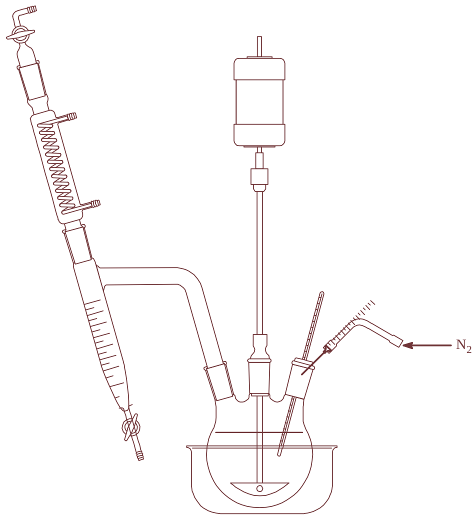


Figure 3.2-1: Glassware Assembly for the Synthesis of PEPO Oligomers

17.96 g (0.0571 moles) of BFPPO and 14.49 g (0.0635 moles) of Bisphenol A were quantitatively transferred to the flask. 150 mL of freshly distilled NMP was used to rinse the weighing vessels and dilute the reaction conditions to ~ 20% solids. Next, 10.17 g (0.0735 moles) of potassium carbonate (K_2CO_3) was added in ~15 mol% excess to facilitate a quantitative reaction. Toluene was then added as an azeotroping agent (50 mL) and the reaction solution was heated to 135-140°C (reflux). The mixture was then

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[253] Odian, G. *Principles of Polymerization*; 3rd ed.; Wiley Interscience: New York, 1991.

held at reflux for 4-6 hours. to completely dehydrate the system and ensure the base had generated the phenolate anion. Next, the reaction temperature was raised to ~170°C by the removal of toluene. During this higher temperature step, the reaction solution darkens and the KF salt byproduct precipitates, resulting in a dark brown to black solution with dispersed white particles. After 16-24 hours, the reaction was assumed to be complete ($p > 99.9\%$). After cooling, the solution was diluted with ~ 100 mL of DMAc followed by filtration to remove most of the salts and solid impurities (*e.g.*, KF, K_2CO_3). 0.5 mL of glacial acetic acid was then added to protonate any residual phenolate anions. The polymer was isolated by precipitation into a 25/75 v/v methanol/water mixture using a Waring blender. The resulting white to off-white powder was filtered and vacuum dried at ~170°C overnight before it was redissolved in chloroform (20% solids), then reprecipitated and dried under the same conditions. Analysis of the oligomers will be described in Section 3.4.1.1.2.2.

Synthesis of Dimethylamino-Terminated Polydimethylsiloxane Oligomers

Synthesis of the Siloxanolate Catalyst

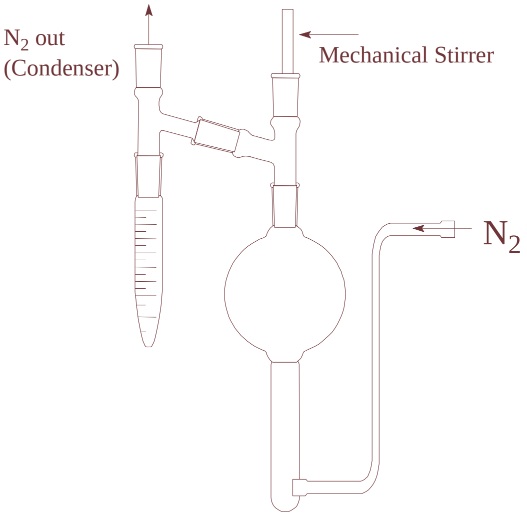

Figure 3.2-2: Glassware Assembly for Siloxanolate Catalyst Synthesis

A glass apparatus (Figure 3.2-2) was assembled and flame dried under flowing nitrogen. 0.76 g (4.22×10^{-3} moles) of tetramethylammonium hydroxide penta hydrate (TMAH) was added as a solid to the reactor. Next, 15 mL (14.4 g) of purified D_4, a siloxane cyclic, was added via syringe to prepare a 5 wt% TMAH in D_4 solution. The mixture was then stirred with nitrogen bubbling through it for 1 hour at room temperature. During this incubation period, phase separation occurred since the TMAH had some moisture associated with it. This moisture was removed upon heating by the nitrogen purge. Meanwhile, an oil bath was heated to 80°C. Once the bath had equilibrated, the reactor was lowered into it and the stirring and nitrogen purge were continued. The reaction solution quickly became opaque, but within 20 minutes the solution cleared. It is important to note that the nitrogen flow must be strong enough to transfer the water produced to the Dean-Stark trap where it can be removed, but not so rapid that it enables the distillation of the D_4. The reaction was held at 80°C with stirring and a nitrogen purge for 24 hours. A distinct increase in viscosity was noticed before removal from heat. The catalyst was allowed to cool and was sealed under a nitrogen blanket. An additional 15 mL of dry D_4 was added to dilute the slightly cloudy solution, since upon cooling it became too viscous to easily transfer via syringe. The catalyst solution was stored in the reaction vessel and used within 2-3 days of synthesis to minimize hydrolysis by atmospheric moisture.

Synthesis of Dimethylamino-Terminated Polydimethylsiloxane Oligomers

The dimethylamino-terminated polydimethylsiloxane oligomers were prepared via bulk anionic equilibrium redistribution reactions. First, a low molecular weight α,ω–bis(dimethylamino)siloxane endcapping reagent was obtained from CK Witco. Its molecular weight was confirmed by ^{1}H NMR and titration prior to use. The endcapping reagent was mixed with D_4, a cyclic siloxane tetramer, in a controlled molar ratio to attain oligomers of the desired molecular weights. With the addition of a siloxanolate catalyst, redistribution of the ring-chain populations occur until equilibrium is achieved (see Literature Review, Section 2.3.3.2). Manipulation of the ratio of endcapping reagent to cyclic “monomer” allows control over the molecular weight of the oligomer produced. For example, the procedure for the synthesis of 150 mL of a 10,000 g/mol dimethylamino-terminated oligomer is as follows.

A 250 mL round-bottomed flask was fitted securely with a septum and a magnetic stirring bar. The flask was flamed dry under dry nitrogen. After the flask had cooled, 25.91 g of α,ω–bis(dimethylamino)siloxane endcapping reagent (27 mL, 0.0172 moles) was added via syringe. Then, 124.01g (129 mL, 0.419 moles) of purified D_4 was introduced via syringe. The solution was placed in an 80°C oil bath, stirred and allowed to come to thermal equilibrium. The siloxanolate catalyst solution was added to the warm reaction solution in a concentration of 0.04 mol% relative to the amount of D_4, ($1.68x10^{-4}$moles, 1.2 mL of a 2.5 wt% TMAH catalyst solution). At this point the nitrogen purge was ceased, leaving a sealed vessel under an inert atmosphere, limiting any possible sources of moisture. A noticeable increase in viscosity was observed within minutes, but the system was allowed to equilibrate at 80°C for at least 18 hours. The nitrogen purge was then resumed after submerging the inlet needle in the reaction solution. The temperature was increased to 145°C to decompose the catalyst for 2-3 hours, until no evidence of trimethylamine in the nitrogen outlet was detected with moistened pH paper. The oligomer was allowed to cool under flowing nitrogen before the flask was fitted with a vacuum distillation head. To obtain pure functionalized oligomers the residual cyclics (15-20 wt%) from the equilibrium process were distilled at 100°C under reduced pressure for 4-5 hours. Analysis by ^1H NMR and potentiometric titration indicated M_n values of 9,900 and 10,100 g/mol. respectively.

3.2.4 Synthesis of Perfectly Alternating Poly(arylene ether phosphine oxide)-Poly(dimethylsiloxane) Block Copolymers

Perfectly alternating block copolymers were synthesized in solution, using a silylamine-hydroxyl condensation pioneered by Noshay et al.[250] The reaction was carried out in a flame-dried, 250 mL four-necked, flask fitted with a mechanical stirrer, a reverse Dean-Stark trap, a condenser, and an addition funnel with a nitrogen inlet. (Figure 3.2-3). In order to produce ~10 g of high molecular weight copolymer, 10.13 g (0.00207 moles, 5,000 g/mol) of PEPO was quantitatively transferred to the reaction vessel and dissolved in 130 mL of chlorobenzene. The solution was heated under nitrogen until the distilled solvent filled the empty trap (~30 mL) and a steady reflux rate was obtained (~ 150°C bath temp). The solution was allowed to reflux for 3-4 hours to remove any water that may have been bound to the phosphine oxide sites along the oligomer backbone. Once the system was dehydrated, the addition funnel was flame dried again to remove any surface moisture. When cool, 2.8 mL (2.68 g, 1300 g/mol, 0.00208 moles) of dimethylamine terminated polydimethylsiloxane (PDMS) was transferred to the addition funnel via syringe. Approximately half of the PDMS was added to the solution and allowed to react. As the polydimethylsiloxane oligomer reacted, dimethylamine was released as a side product, which was carried out of the system by the inert gas stream. This basic product was observable with the use of dampened pH paper held near the exhaust. Once the evolution of dimethylamine had almost ceased, the remainder of the siloxane was added slowly, allowing the evolution of dimethylamine to slow between aliquots, until a noticeable increase in viscosity was observed. This increase suggested that the point of 1:1 stoichiometry had been reached. The solution was allowed to react overnight to form high molecular weight material. Once cool, the polymer was isolated by precipitation into a ten-fold excess of methanol. The product was a white to off-white fibrous material which was filtered and vacuum dried (160°C) to a constant weight.

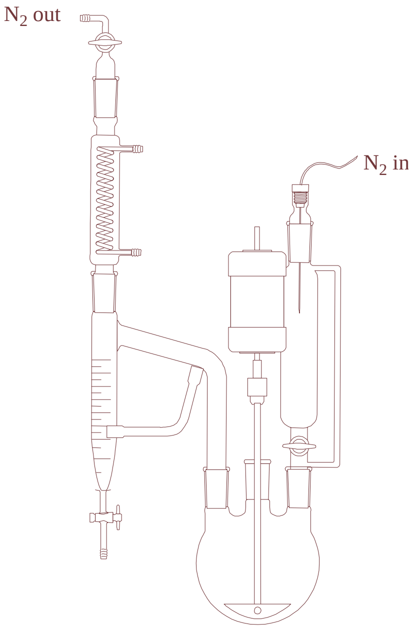

Figure 3.2-3: Glassware Assembly for the Synthesis of Copolymers.

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[250] Noshay, A.; Matzner, M.; Merriam, C. N. *J. Polym. Sci., Part A* **1971**, *19(11)*, 3147.

3.2.5 Preparation of Silica-Poly(arylene ether phosphine oxide-b-dimethylsiloxane) Nanocomposite Films

Silica nanocomposite films were prepared in an attempt to reveal any possible selective association of the silica nanoparticles when exposed to the PEPO-PDMS copolymers. It was proposed that the domain separation within the copolymer films could provide a means to elucidate, which presented a greater affinity for the particles, the complexing phosphine oxide moiety or the structurally and chemically similar siloxane units. Copolymers containing 10, 20, and 50 wt% polysiloxane were blended in DMAc with colloidal 12 nm silica particles. The copolymers were dissolved in DMAc then the requisite amount of the silica suspension, was added to allow 10% of the phosphine oxide units on the copolymer chain to associate with the silica nanoparticles (10/100 wt/wt silica/PEPO). This amount was determined using the following series of equations.[128]

wt copolymer sample * wt% PEPO(from NMR data)= wt PEPO

Wt PEPO*0.1 = wt silica needed

Wt silica needed ÷ 0.2 (wt % silica in DMAc) = wt DMAc suspension

The nanocomposite films were cast from 15 wt% solids in DMAc, solidified using an infrared lamp overnight, then dried in a vacuum oven overnight at 100°C. However, in the case of the 50/50 wt/wt PDMS/PEPO copolymer, a homogeneous DMAc solution was not attainable. The high polysiloxane content of the copolymer was not compatible with DMAc. Therefore the copolymer solution was prepared in chlorobenzene while the silica was added suspended in DMAc, as received.

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[128] Wang, S. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, Va, 2000.

3.3 Characterization Methods

3.3.1 Nuclear Magnetic Resonance (NMR) Spectroscopy

Proton (^{1}H), carbon (^{13}C), and phosphorus (^{31}P) NMR spectra were acquired in $CDCl_3$, using a Varian Unity 400 MHz instrument. No internal standard (tetramethylsilane, TMS) was used in this study. This reference material was omitted to avoid any confusion of the siloxane peak assignments. The signals from methylene groups of the polysiloxane oligomers and copolymers would have overlapped with the TMS reference peak. The NMR spectra were used to determine chemical composition and extent of reaction of monomers, oligomers and copolymers.

3.3.2 Melting Point Determinations of Monomers

The melting points of purified compounds were determined in a capillary tube with a Lab Devices Melt-Temp II. Samples were ground to a powder before measurement and the formation of a meniscus was defined as the beginning of the melt.

3.3.3 Intrinsic Viscosity

The intrinsic viscosities, $[\eta]$, of the oligomers and polymers were measured in $CHCl_3$ using a Cannon-Ubbelohde viscometer at 25°C. The intrinsic viscosity was obtained by measuring the specific viscosity, $\eta_{sp} = (\eta / \eta_0) - 1$, and the reduced viscosity, $\eta_{red} = \ln(\eta / \eta_0)$, at four dilutions and extrapolating (η_{sp} / c) and (η_{red} / c) to zero concentration.

3.3.4 Potentiometric Titration of Oligomers

The number average molecular weights (M_n) of the dimethylamino-terminated polysiloxanes and phenolic hydroxyl-terminated polyarylene ether phosphine oxide oligomers were determined by potentiometric titration of the functional endgroups using a Fisher Titrimeter II automatic titration system. A calomel electrode was used in conjunction with a standard double junction reference. The polysiloxane oligomers were dissolved in isopropanol and titrated with a 0.5 N solution of HCl in isopropanol, while polyarylene ether phosphine oxide oligomers were dissolved in freshly distilled NMP and titrated with a 0.025 N solution of tetramethylammonium hydroxide in isopropanol.

The sample size for the oligomers was chosen to give a titration volume of approximately 4 mL. This is easily accomplished by calculating the amount of oligomer, assuming the target molecular weight was achieved, needed to neutralize 4 mL of titrant. The oligomer was weighed directly into a 100 or 150 mL beaker, followed by 60-70 mL of solvent. The oligomer samples were allowed to completely dissolve using a magnetic stir-bar for agitation. Once the oligomer was completely in solution, the electrodes were lowered and the titration was begun. The titrator was operated in the automatic endpoint seeking mode. The time, volume, and final potential (mV) were observed and recorded. The electrodes were then rinsed with titrant solution, followed by water and placed in a pH 4.0 buffer for storage. Any amount of titrant consumed by the solvent was corrected for by the use of a blank titration, whereby the same volume of neat solvent was titrated to the same potential as the endpoint, and this blank volume was subtracted from the sample titration. The M_n of the oligomers was determined according to Equation 13.

$$M_n = \frac{2 * W}{N * (V - V_B)} \qquad (13)$$

In Equation 13, 2 is the number of endgroups per chain, W is the weight of the oligomer sample (g), N is the normality of the titrant (moles/mL), V is the volume of titrant needed to reach the endpoint, and V_B is the volume of the blank.

3.3.5 Gel Permeation Chromatography (GPC)

Molecular weights (M_n) as well as polydispersity indices, were obtained through the use of a Waters 150C ALC/GPC chromatograph fitted with a differential refractive index detector in series with a Viscotek Model 100 viscosity detector. Either HPLC grade N-methylpyrrolidone (NMP) containing ~ 0.02 N P_2O_5, or HPLC grade chloroform filtered through a 0.5 μm Teflon filter, served as the mobile phase. A series of three stainless steel columns (7.8 mm I.D. x 30 cm) packed with crosslinked polystyrene gel (Waters μstyragel HT, 10^2, 10^3 and 10^4 Å columns, with a mean particle diameter of 10 μm) acted as the stationary phase. Samples were prepared at known concentrations (~ 2-4 mg/mL) in the appropriate mobile phase and filtered through 0.2 μm Teflon filters prior to analysis. The injection volume was 200 μL and the flow rate was set to 1.0 mL/min. Additionally, the temperature of the system (injector, lines, columns, and detectors) was held constant (60°C for NMP and 30°C for chloroform) The use of the two detectors and careful calibration allowed for the resultant data to be taken as absolute molecular weights under the principles of universal calibration.[254]

3.3.6 Thermogravimetric Analysis (TGA)

Dynamic TGA was performed using a Perkin-Elmer TGA 7 instrument. Samples (~4-10 mg) were heated at 10°C/min with flowing air in a platinum sample pan unless otherwise noted. Only samples that had been prepared similarly were compared to each other. That is, solvent cast films were compared to other cast films and not to samples of another physical form (e.g. powdered, melt pressed). The percent weight loss was measured as a function of temperature.

3.3.7 Differential Scanning Calorimetry (DSC)

Glass transition temperatures, melting points and recystallization temperatures above 25°C were detected using a Perkin-Elmer DSC 7 instrument. Heating and cooling scans were run from 25°C to 220°C at 10 °C/min under nitrogen. Samples (4-8 mg) were sealed in crimped aluminum sample pans. The data reported is taken from the second heating scans, after annealing for 3-5 min above the maximum T_g of the samples in order to minimize any physical aging effects.

In the case of transitions below 25°C, the data was collected on a Perkin-Elmer Pyris 1 DSC. The samples were analyzed using the same specifications (heating rate, sample size, etc.) excepting, of course, the temperature range. The pyris system was used to analyze samples both from –150 to 125°C and 25 to 220°C. Data from the upper temperature region was collected to ensure accurate concurrence between the two systems.

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[254] Konas, M.; Moy, T. M.; Rogers, M. E.; Shultz, A. R.; Ward, T. C.; McGrath, J. E. *J. Polym. Sci. Polym. Phys.* **1995**, *33*, 1429.

3.3.8 Dynamic Mechanical Analysis (DMA)

Dynamic Mechanical Analysis was performed on a Seiko DMS-200 DMA in the extension mode. The frequency was 1 Hz and the heating rate was 2°C/min. The samples analyzed were from cast films and had average dimensions of 8 x 1 x 0.2 mm.

3.3.9 Stress-Strain Behavior

The stress-strain behavior was measured at room temperature using an Instron 1123 equipped with a strain gauge extensometer (Instron 2630-013). The dog bone samples (ASTM D-638 #5) were cut using a die from well-dried films having an average thickness of 0.5 mm, cast from chlorobenzene. The samples were tested at an average crosshead speed of 0.5 in/min. (ASTM D-683). Approximately 5 samples were tested for each polymer and their results were averaged.

3.3.10 Refractive Index Measurements (n)

The refractive indicies of the solution cast films were measured using a Metricon Model 2010 Prism Coupler in the bulk mode. The laser used was a low power (0.5 mW nominal) He-Ne (632.8nm) laser.

3.3.11 Abbe Number measurements

Abbe number measurements were supplied by the Johnson and Johnson Spectacle Group (formerly known as Innotech).

3.3.12 X-Ray Photoelectron Spectroscopy (XPS)

XPS analysis was performed using a Perkin-Elmer 5400 spectrometer with a MgK_{α} (1253.6 eV) achromatic X-ray source operated at 14 KeV with a total power of 300 watts. Typical operation pressures were $< 1x10^{-7}$ torr and the surface area analyzed was a 1 x 3 mm section. The spectrometer had been calibrated to the $4f_{7/2}$ photopeak of gold at 83.8eV and the $2p_{3/2}$ photopeak of copper at 932.4 eV. Additionally, all of the binding energies were referenced to the main carbon 1s photopeak at 285.0 eV.

3.3.13 Transmission Electron Microscopy (TEM)

The bulk morphology of the copolymers was directly observed using a Philips 420T Scanning Transmission Microscope. The samples were prepared from solution cast films that had been vacuum dried to a constant weight. The sections imaged were cryo-ultramicrotomed with a Reichert-Jung Ultracut E microtome equipped with a diamond knife. The resultant samples were ~ 700 Å thick. Due to the large difference in electron density between the arylene ether and siloxane phases, additional sample preparation such as staining was unnecessary.

3.3.14 Atomic Force Microscopy (AFM)

The surface morphology was obtained using a Dimension 3000 AFM from Digital Instruments operated at room temperature with micro-fabricated cantilevers operating at a force constant of approximately 40 N/m. Image analysis, was executed using the Dimension 3000 image processing software. The AFM was operated in the tapping mode. Therefore, the force applied to the surface can dramatically alter the image obtained. For this study, the ratio of amplitudes used as a feedback control was adjusted to 0.7 of the free air amplitude for all samples examined. Under these conditions the phase data obtained is sensitive to differences in the stiffness of the first several nanometers of the uppermost surface.

3.4 Results and Discussion

3.4.1 Synthesis and Characterization of Functional Oligomers

3.4.1.1 Evaluation of Monomer Purity

Bisphenol A

Bisphenol A supplied by Aristech was of monomer grade and was used with out further purification. However, prior to use the purity of the Bisphenol-A was confirmed by melting point determinations and ^{1}H NMR in DMSO-d_6. The material supplied by Aristech showed a sharp melting point at 156-157°C consistent with literature values, while the NMR analysis displayed no signs of contamination as shown below in Figure 3.4-1. The characteristic aromatic peaks at 6.65 ppm (Hc) and 6.97 ppm (Hb), the isopropylidene (H_d) peak at 1.52 ppm, and the phenolic proton (Ha) at 9.13 ppm resonated in the expected locations with proper integration ratios of 4 aromatic protons to 3 aliphatic protons to 1 phenolic proton, as predicted by the structure and reference spectra.

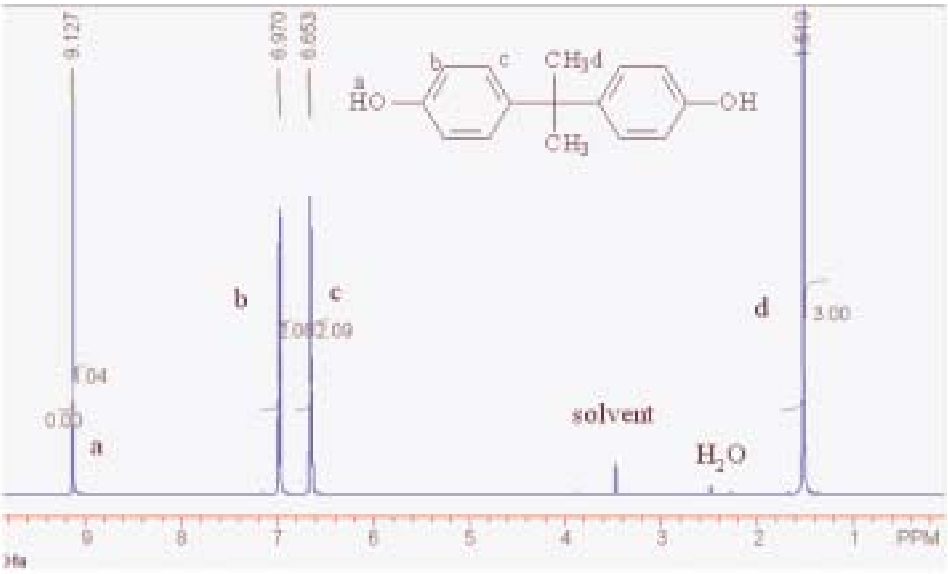

Figure 3.4-1: ^{1}H NMR of Bisphenol-A in d-DMSO

4,4'-Bis(fluorophenyl)phenylphosphine oxide (BFPPO)

BFPPO was supplied by Avecia Specialty Chemicals, however its availability varies periodically. The synthetic procedure (via Grignard chemistry) has been outlined previously in Section 3.3.1. The Grignard reaction involving *p*-bromofluorobenzene and dichloro-phenylphosphine oxide was conducted at room temperature and resulted in 80-85% yield after distillation and recrystallization from a 1:5 THF/cyclohexane mixture. The melting point of the compound was sharp at 130-131°C, while ^{1}H and ^{31}P NMR in $CDCH_3$ confirmed the structure (Figure 3.4-2). Five different aromatic protons $H_{a,b}$ (7.65 ppm), H_c (7.56 ppm), H_d (7.48 ppm), and H_e (7.16 ppm) were observed and located in accordance to structure based computer predictions. However, the protons appear with higher multiplicities than initially expected, due to possible coupling with the phosphorus as the ^{31}P isotope also has a spin of ½ and is detectable by NMR. Additionally, the phosphorus NMR shows a single signal at 28.1 ppm, with spinning side bands equidistant from the parent peak, indicative of complete disubstitution. Analyses of the materials supplied by Avecia were consistent with those of monomer produced within our labs.

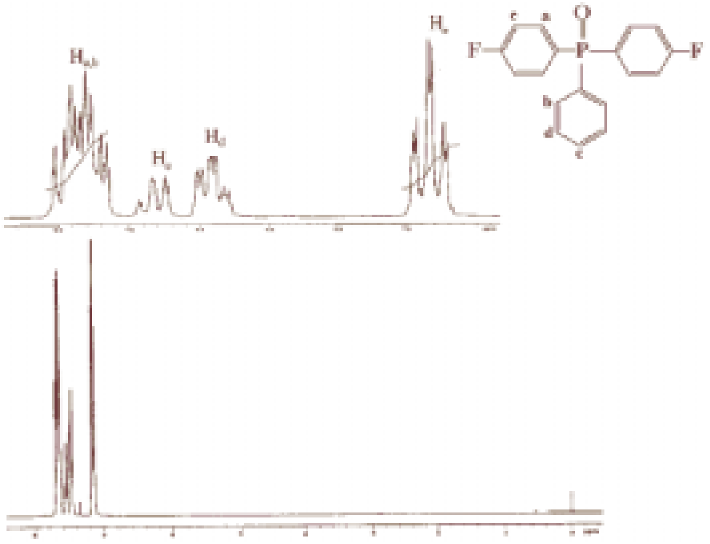

Figure 3.4-2: ^{1}H NMR of BFPPO in $CDCl_3$

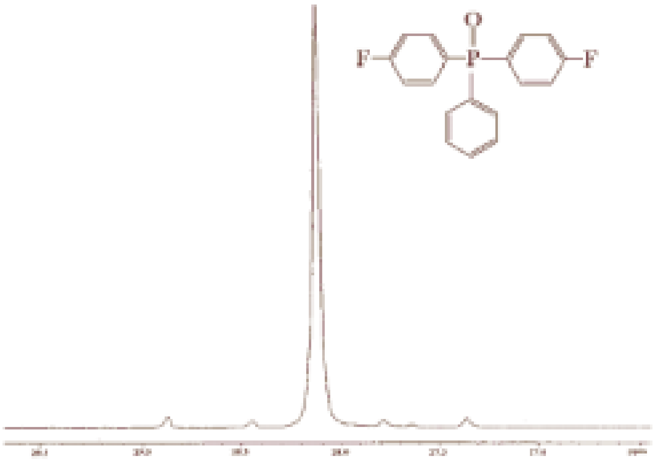

Figure 3.4-3: ^{31}P NMR of BFPPO in $CDCl_3$

Octamethylcyclotetrasiloxane (D_4)

Crude octamethylcyclotetrasiloxane was supplied by Dow Corning as a liquid. This fluid was dried over calcium hydride and fractionally distilled under reduced pressure to isolate the cyclic tetramer. The structure and purity of the collected fraction was established by ^{29}Si NMR. (Figure 3.4-4) The cyclic tetramer shows its characteristic signal at –18.4 ppm, however a small amount of D_3 (-21.3 ppm) is present even after vacuum distillation. Since the D_3 is as reactive to the redistribution reactions as D_4, this minor impurity can be assumed to be insignificant.

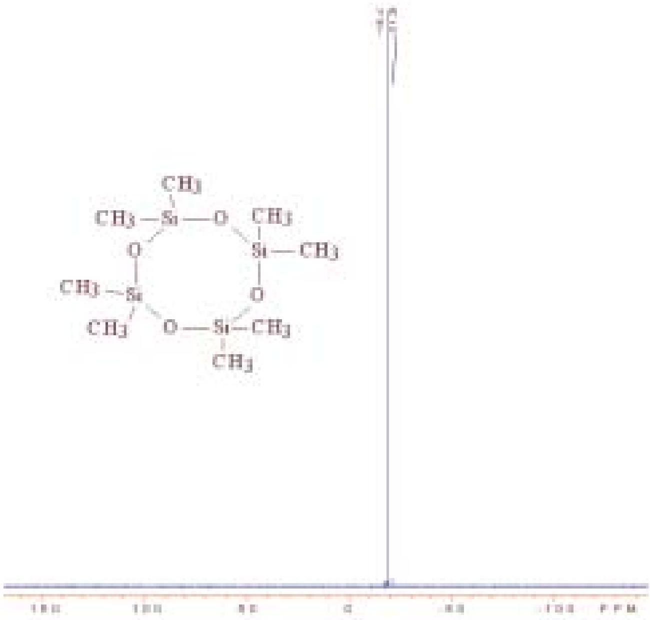

Figure 3.4-4: ^{29}Si NMR of Octamethyltetrasiloxane or D_4

α–ω- Bis(dimethylamino)polydimethylsiloxane (endcapping reagent)

A low molecular weight dimethylamine-terminated oligomer was supplied by CK Witco. Upon arrival, the oligomer was carefully transferred to a flame-dried round bottom flask sealed with a wire-tied septum and purged with nitrogen to prevent hydrolysis of the endgroups. Once properly isolated from ambient moisture, samples were taken via syringe and analyzed by ^{1}H NMR for purity and molecular weight using deuterated chloroform stored over molecular sieves. The spectra, shown in Figure 3.4.-5, displayed only two major signals; the first corresponded to the methyl groups directly bonded to the silicon at 0.07 ppm, and the second is attributable to the dimethylamino terminal functionality at 2.47 ppm. The small satellite peaks are the result of hydrolysis in the NMR tube that can occur from exposure to atmospheric moisture during sample preparation and analysis and the remainder of the spectrum is clear. The absence of extraneous peaks was compelling evidence of purity, and a ratio of the integration values of the major signals present was calculated to determine the molecular weight of the endcapping reagent. This resulted in a 2.5/1 silicon/nitrogen ratio, therefore with 2 amine endgroups on each oligomer the siloxane chain was on average 5 units long. This average number of repeat units corresponds to a molecular weight of 516 g/mol, which was then used to determine the sample size for acid-base titration and in further equilibration reactions to produce higher molecular weight oligomers.

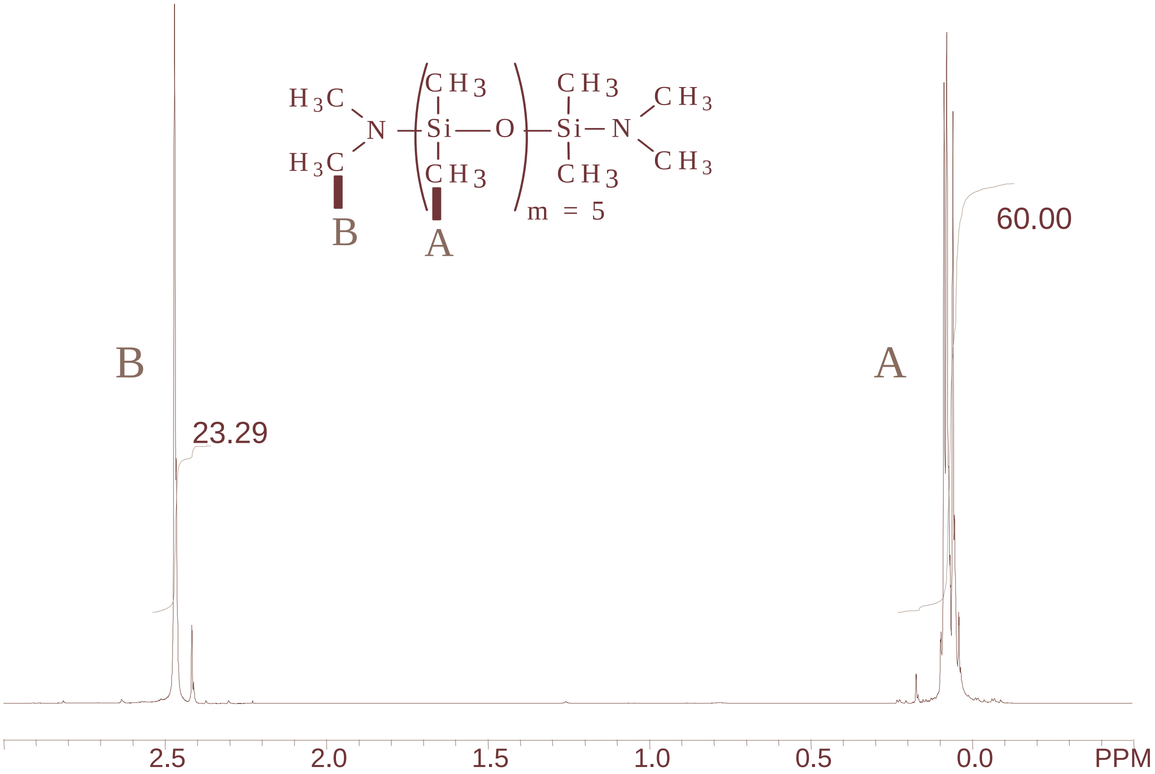

Figure 3.4.-5: ^{1}H NMR of the Dimethylamino-siloxane Endcapping Reagent

The endcapping reagent was then titrated with 0.05 N HCl in isopropyl alcohol to confirm the NMR estimation. Again, multiple analysis methods were used to determine accurate molecular weight, as well as to reduce the effect of possible error on subsequent reactions. The acid-base titration of the silylamine group resulted in the consistent observation of a sharp endpoint resulting in an equivalent weight of ~500 g/mol. A representative titration curve is illustrated in Figure 3.4-6.

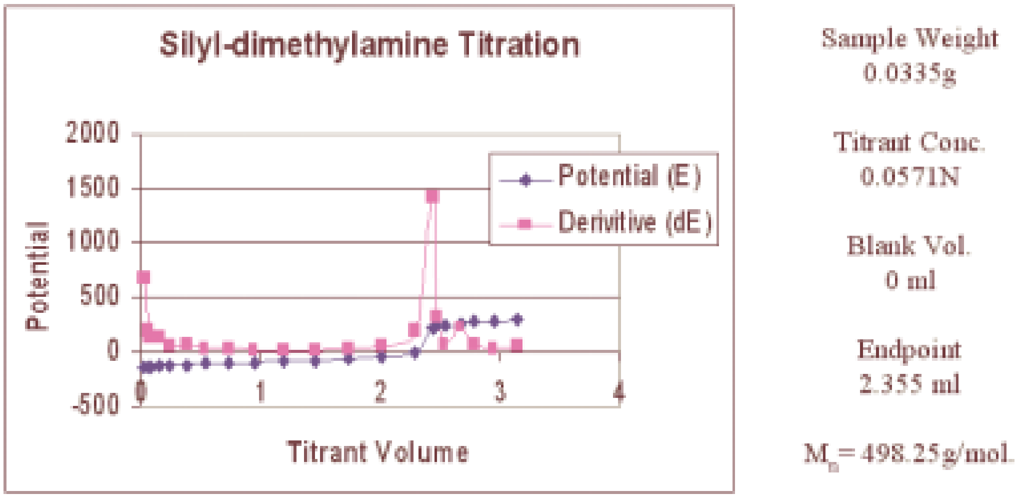

Figure 3.4.-6: Potentiometric Acid-Base Titration of the Silyl-dimethylamine Endcapping Reagent

In summary, the molecular weight estimations by NMR and acid-base titration agreed almost perfectly and yielded a value of ~500 g/mol. A molecular weight of 516 g/mol was accepted and used for all calculations for the synthesis of controlled molecular weight dimethylamine-terminated siloxane oligomers, since it is the weight of the closest whole number degree of polymerization, X_n=5.

3.4.1.2 Hydroxyl-Terminated Poly(arylene ether phosphine oxide)s

3.4.1.2.1 *Synthesis of a High Molecular Weight Poly(arylene ether phosphine oxide)*

A high molecular weight control polymer (1:1 stoichiometry) was produced to establish familiarity with nucleophilic aromatic substitution (S_NAr), and provide a material for comparison to the polysiloxane containing copolymers. The high molecular weight polymer was analyzed for molecular structure by ^1H NMR, as shown in Figure 3.4-7, and examined for molecular weight by intrinsic viscosity in $CHCl_3$, $[\eta]=0.498$, and universally calibrated GPC in NMP ,with 0.25% P_2O_5 to disrupt any hydrogen bonding between the phosphine oxide moiety and the column. The GPC trace showed a unimodal molecular weight distribution with a M_n of 42,400 g/mol and a M_w of 76,600, generating a polydispersity index of 1.8.

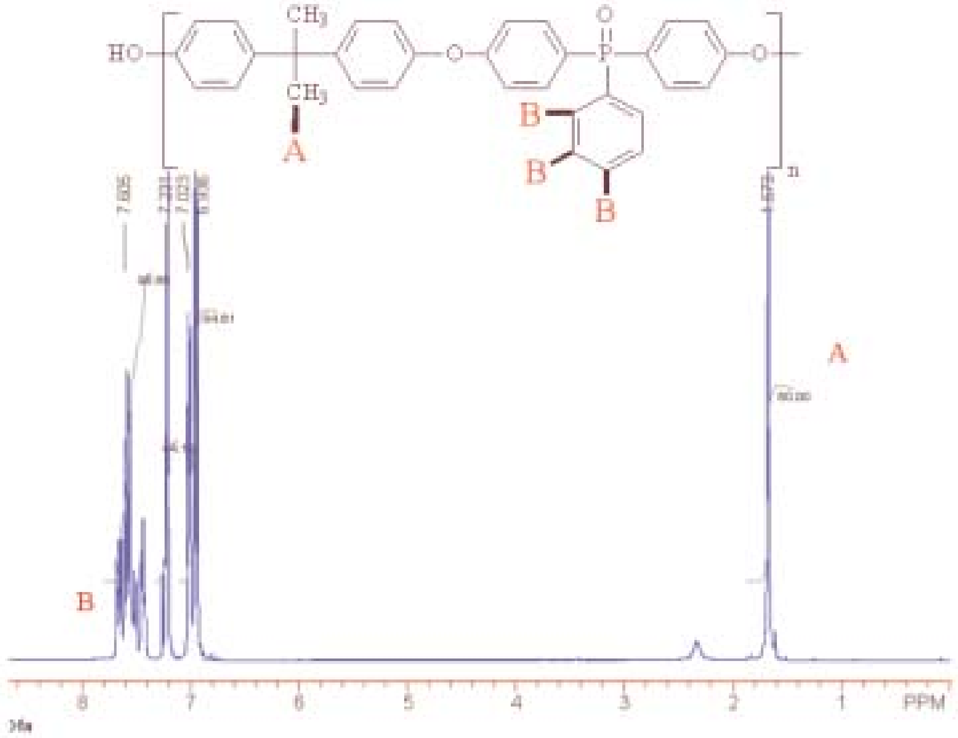

Figure 3.4-7: ^1H NMR of 1:1 Stoichiometry Bis-A-PEPO

Bisphenol A based poly(arylene ether phosphine oxide)s have been prepared previously in our laboratories[84,131] using potassium carbonate as the weak base and either NMP or DMAc as the solvent. Potassium carbonate was selected as the weak base since it had been previously shown to facilitate the substitution reaction while minimizing side reactions.[81] Additionally, the weaker bases have limited reactivity towards aryl halides at low temperatures,[84] allowing the complete generation of the bis-phenate (at ~135°C) before the temperature is increased to facilitate substitution (165-190°C). Freshly distilled NMP was used as the solvent for this reaction to keep the reaction conditions consistent with the methodology used for the controlled molecular weight oligomers. The polymeric material was precipitated into 25/75 water/methanol mixture to afford fibrous material in a yield >90%.

3.4.1.2.2 *Controlled Molecular Weight Hydroxyl-Terminated Poly(arylene ether phosphine oxide) Oligomers*

A series of relatively low molecular weight hydroxyl-terminated poly(arylene ether phosphine oxide) oligomers ranging from 2,500 – 10,000 g/mol were produced. The functionality and molecular weight were ensured by utilizing a controlled excess of bisphenol-A to provide a stoichiometric imbalance as prescribed by the Carother's equation.

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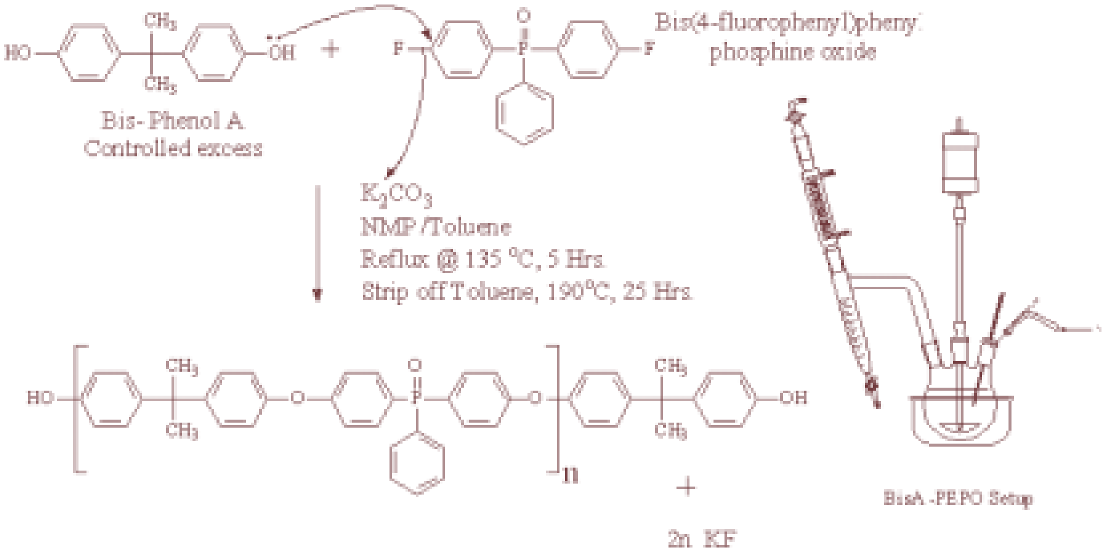
[84] Viswanathan, R. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, Va, 1981.

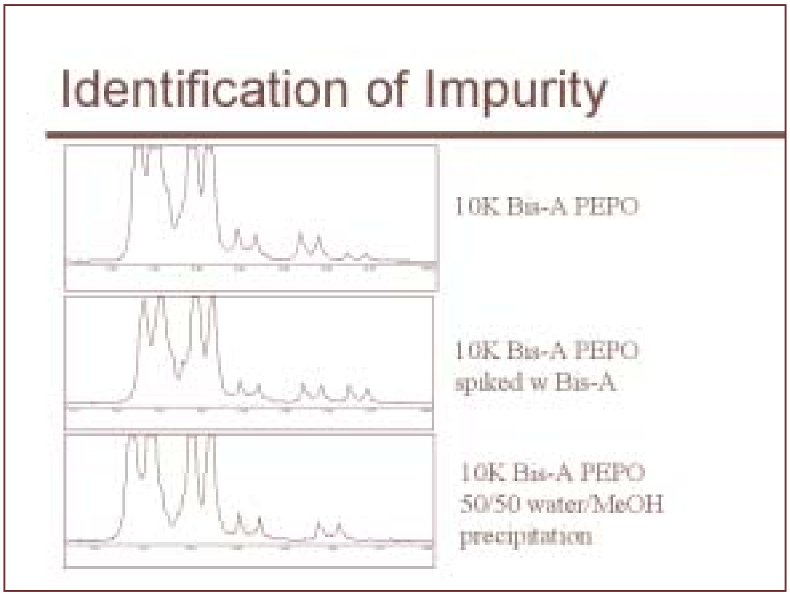
[131] Riley, D. J. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, Va, 1997.

[81] Clendinning, R. A.; Farnham, A. G.; Zutty, N. L.; Priest, D. C. In *847 963*; Union Carbide Corp.: Canadian Patent, 1970.



Scheme 3.4.-1: Synthesis of Hydroxyl-terminated PEPO Oligomers

Molecular weights targeted were 2,500, 5,000, and 10,000 g/mol. Synthesis proceeded in a manner analogous to that for the high molecular weight control polymer. However, when attempting to control the molecular weight of a polymer with a large repeat unit (mw =502 g/mol) the need for quantitative reactions is critical. ^{1}H NMR analysis of the products of polymerizations attempted at lower temperatures (155°C) revealed small unexpected peaks in the aromatic region. These unanticipated peaks were identified as unreacted bisphenol-A and eliminated in a series of NMR experiments. Purified 10,000 g/mol PEPO was spiked with ~ 0.1 mol % bisphenol-A, then the same sample was precipitated in various solvents with the goal of selectively precipitating the oligomer while any residual bisphenol-A remained in solution (see Figure 3.4.-8). The solvent system that was shown to be the most selective was a 50:50 methanol:water solution.



Identification of Impurity

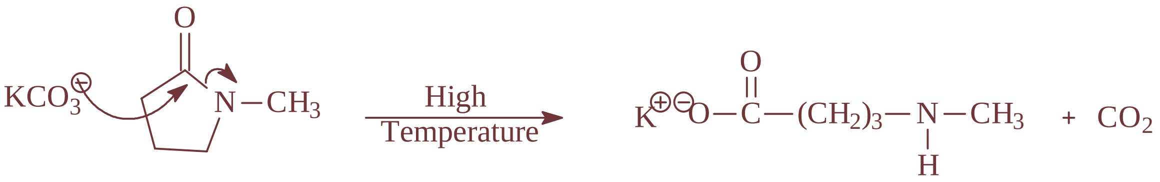
10K Bis-A PEPO

10K Bis-A PEPO spiked w Bis-A

10K Bis-A PEPO 50/50 water/MeOH precipitation

Figure 3.4.-8: Identification and Elimination of Residual Bisphenol-A Discovered in Low Temperature (155°C) PEPO Synthesis by NMR.

Therefore, increased reaction temperatures (~190°C compared to 155°C previously published) were required to facilitate quantitative conversions. This factor led to the selection of NMP as the solvent. Although NMP is known to undergo ring opening (observable as a darkening of the solvent) when exposed to high temperatures in the presence of bases (Scheme 3.4-2), and analogous decompositions are less frequent with DMAc, NMP was required to achieve the higher reaction temperatures as DMAc refluxes at 165°C.



Scheme 3.4-2: High Temperature Ring Opening Decomposition of NMP[255]

The oligomers used for copolymerization were isolated from the NMP reaction solutions. Precipitation of the oligomers was preformed using a 25/75 v/v methanol/water mixture. This mixture contains more water than the solvent mixture used for the isolation of high molecular weight PEPO in order to ensure the removal of any unreacted bisphenol A.

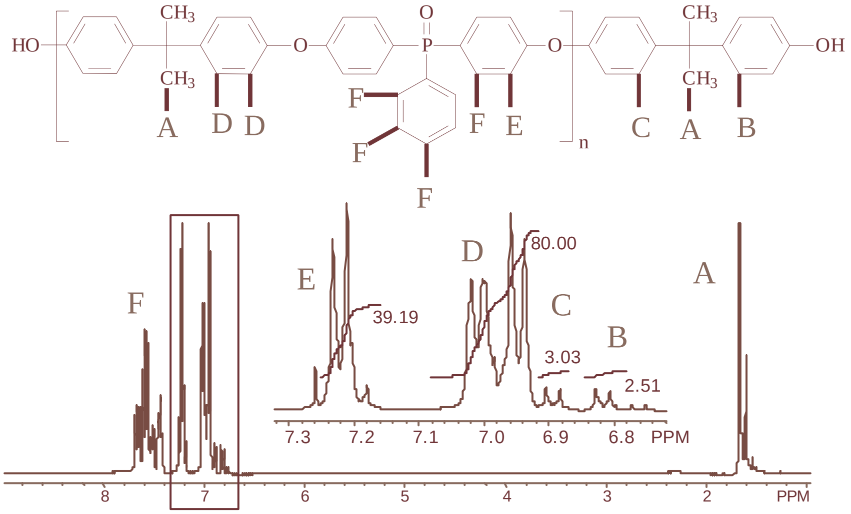


Figure 3.4-9: Representative ^{1}H NMR of a Hydroxyl-Terminated Poly(arylene ether phosphine oxide) Oligomer

Characterization of Hydroxyl-Terminated PEPO Oligomers

Structural analysis of the oligomers produced by the higher temperature reaction was performed by ^{1}H NMR. The characteristic peaks and a significant reduction in unreacted bisphenol-A is evident in Figure 3.4-9. Additionally, the M_n of the oligomers were calculated by endgroup analysis, utilizing the integration ratios of the hydrogen *ortho*- to the terminal hydroxyl group and the isopropylidene signal of the main chain as shown below. Unfortunately, this method of molecular weight estimation is slightly erroneous as the isopropylidene group is present in both the endcapping reagent and the main chain, but the signals employed (protons A and B) were the most accurately identifiable signals that could be isolated within the spectra. The phenolic proton was not directly observable as proton exchange with the NMR solvent occurred and broadened the relatively small signal to the point that it was undetectable.

Since the hydroxyl-terminated oligomers were to be used in further copolymerizations, their molecular weights had to be determined as accurately as possible to enable proper 1:1 stoichiometry in the subsequent reactions. The level of known error present in the NMR determination was significant enough to warrant confirmation by multiple methods. Potentiometric titration and Gel Permeation Chromatography (GPC) were then used to corroborate the molecular weight estimations

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[255] Bhatnagar, A. In *Ph. D. Dissertation*; Central Michigan University, 1995.

obtained from NMR calculations. A summation of the molecular weight estimations for the PEPO oligomers used in the preparation of perfectly alternating siloxane copolymers can be found in Table 3.4.-1

Target M_n (g/mol.)	M_n Titration (g/mol.)	M_n* GPC NMP (g/mol.)	M_n ^{1}H NMR (g/mol.)
2,500	**2,600**	**N/A**	**2,680**
5,000	**5,410**	**5,400**	**5,130**
10,000	**9,100**	**8,910**	**9,630**

*Universal Calibration, 60°C, with 0.025% P_2O_5

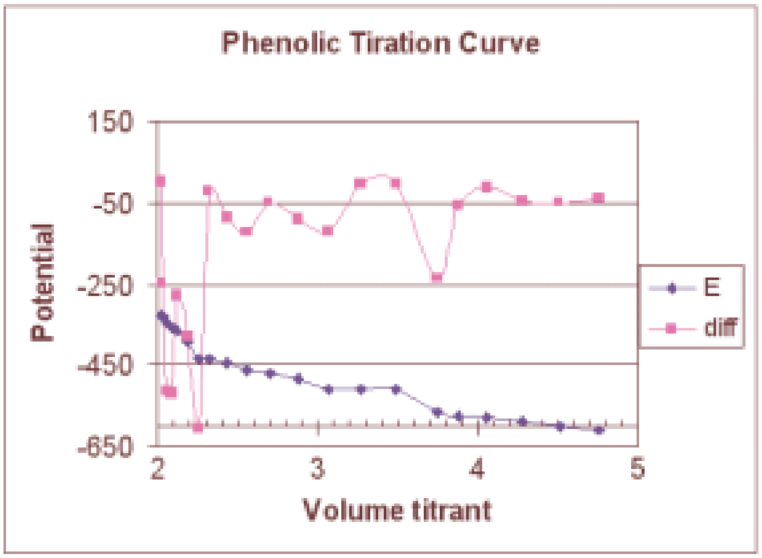
Table 3.4-1 Molecular Weight Estimations of PEPO Oligomers

The potentiometric (acid-base) titration of the phenolic end-groups was pursued in freshly distilled NMP and titrated with a 0.025 N solution of tetramethylammonium hydroxide in isopropanol. The M_n of the oligomers could then be determined as follows.

$$M_n = \frac{2 * W}{N * (V - V_B)} \tag{13}$$

In Equation 13, 2 is the number of endgroups per chain, W is the weight of the oligomer sample (g), N is the normality of the titrant (moles/mL), V is the volume of titrant needed to reach the endpoint, and V_B is the volume of the blank.

The simple titration of the phenolic endgroups proved to be more challenging than anticipated. A sharp endpoint was difficult to obtain as the acidity of the phenolic group (pKa=10) was compromised by water (pKa =15.7), the main contaminant in the sample solution, even though the titrant diluent (isopropanol) is relatively inert to the reaction conditions (pKa=30.2). This competition of the phenolic group with the solvent and residual water could easily lead to the signal becoming “swamped out” by the required blank titration volume. A typical titration curve for a calculated 10,000 g/mol PEPO yielded an M_n of 10,107 g/mol, which is shown in Figure 3.4-11.



Mass of Sample
0.4518g

Titrant Conc.
0.02514N

Blank Vol.
0.19 ml

Endpoint
3.746 ml

M_n=10,107g/mol

Figure 3.4-11: Potentiometric Acid-Base Titration of a Hydroxyl-Terminated PEPO

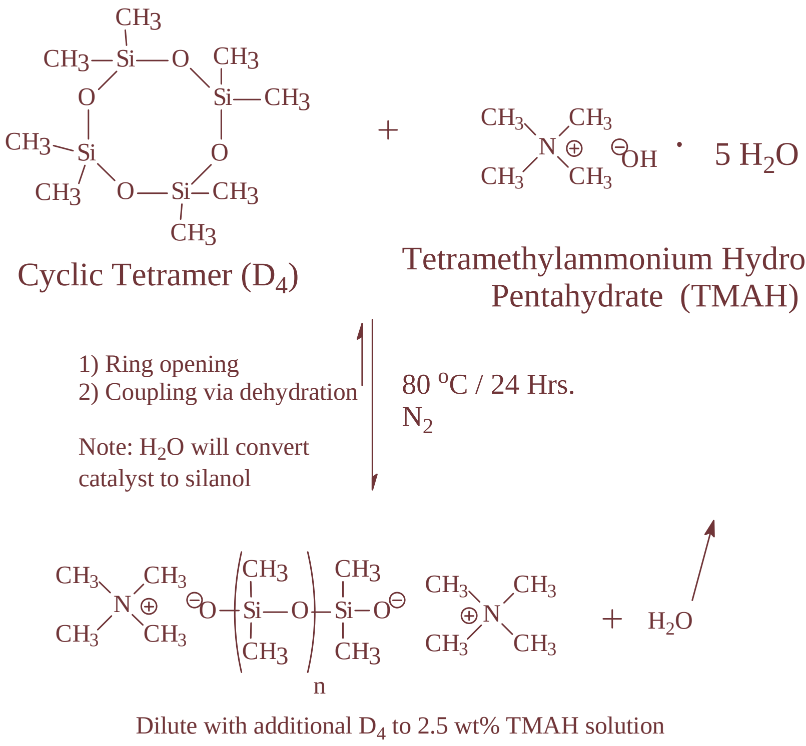
In order to further confirm the molecular weight of the oligomers, GPC in NMP + 0.025 N P_2O_5 at 60°C was employed. NMP was selected for the mobile phase as it readily solvates the oligomers. The P_2O_5 additive is often used in conjunction with NMP to disrupt any possible interactions with the column often encountered in the analysis of polymers containing dipolar moieties like phosphine oxides. Generally, GPC is thought to be too inaccurate at lower molecular weights for the characterization of oligomers. However, given the need for an accurate estimation of molecular weight, a “three-pronged attack” was employed to ensure agreement of the three fundamentally different methods (each with their own sources of error). If all yielded the same result, then that figure was accepted as the number average molecular weight of the oligomer. Furthermore, any error transferred to subsequent stoichiometry calculations would lie within the realm of standard physical error.

Examination of Table 3.4.-1 reveals good relative agreement among the three methods of molecular weight estimation, as well as with the targeted molecular weights. Thus, molecular weight control was achieved according to the Carother’s equation. The values for molecular weight assigned to the samples and employed in subsequent reactions were averages of the results of the individual methods.

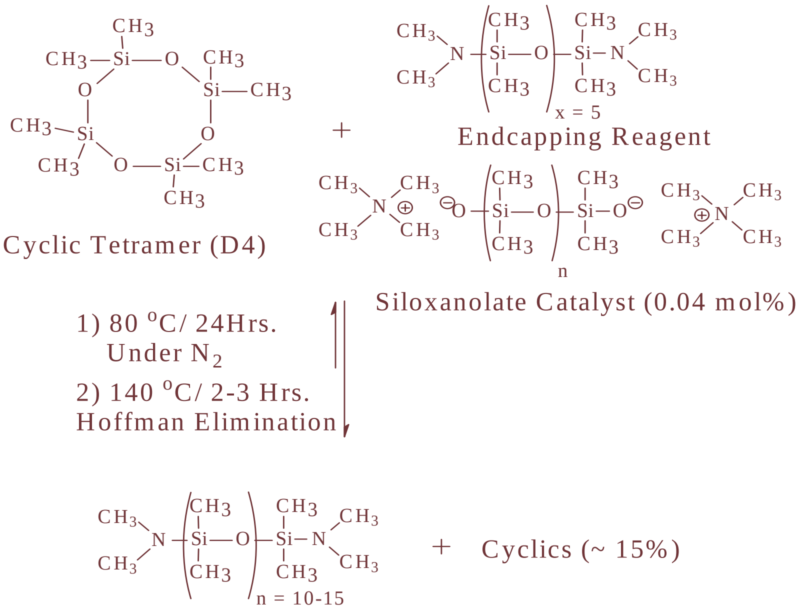
3.4.1.3 Dimethylamine-Terminated Poly(dimethylsiloxane)s

3.4.1.3.1 *Controlled Molecular Weight Dimethylamine-Terminated Poly(dimethylsiloxane) Oligomers*

The synthesis of controlled molecular weight dimethylamino-siloxanes was achieved by the anionic redistribution reaction, outlined in the literature review and detailed in Section 3.2.3. The siloxanolate catalyst was separately prepared from freshly distilled D_4 and tetramethylammonium hydroxide (Scheme 3.4-3), and used at 0.04 mol% relative to the concentration of D_4 required. Synthesis of the controlled oligomer from D_4 and the difunctional endcapping reagent is summarized in Scheme 3.4-4. The molecular weight was controlled by the ratio of endcapping reagent to D_4.



Scheme 3.4-3 : Generation of the Siloxanolate Catalyst



Scheme 3.4-4: Synthesis of Dimethylamino-polydimethylsiloxane

First, it was necessary to determine the number of moles of endcapping reagent needed to produce a given amount of a targeted molecular weight polymer. This was accomplished by assuming that for each mole of polymer chains produced, one mole of a difunctional endcapping reagent will be consumed. Therefore, the molar amount of endcapping reagent needed is the same as the molar amount of polymer to be produced, which is in turn is dictated by the amount and molecular weight of the polymer desired. A sample calculation is provided below for clarity.

In order to produce, 200g of a difunctional 5,000 g/mol dimethylamino-terminated polydimethylsiloxane, the molar amount of the oligomer desired must be determined.

$$\frac{mass\quad Polymer}{M_n Desired}=\frac{200\quad g}{5{,}000\quad g/mol}=0.04\text{ moles} = \text{moles of endcapping reagent needed}$$

The molar amount of endcapping reagent required can be expressed in grams by use of the endcapping reagents molecular weight.

0.04 Moles * 516 g/mol = 20.64 g of endcapping reagent

The amount of endcapping reagent needed is then subtracted from the overall desired mass to yield the amount of D_4 required.

$$200\text{ g} - 20.64\text{ g} = 179.36\text{ g of } D_4$$

Conversion of the D_4 to moles allows the calculation of the molar ratio of D_4/endcapping reagent.

$$\frac{179.36 \quad g}{296 \quad g/mol} = 0.6059 \text{ moles of } D_4\text{; therefore } \frac{D_4}{\text{Endcapper}} = \frac{0.6059}{0.04} = 15.14$$

Interestingly, the D_4/endcapping reagent ratio turns out to be equal to the degree of polymerization of the oligomer desired and provides a means to check the calculation. X_n for a linear polymer is defined as the molecular weight of the polymer, minus its endgroups, divided by the molecular weight of the repeat unit, or in this case the monomer,

$$X_n = \frac{M_n - endcapping \quad reagent}{D_4} = \frac{5{,}000 - 516}{296} = 15.14$$

It is important to realize that when calculating the degree of polymerization as a verification of stoichiometry, the molecular weight of the "repeat unit" and the "monomer" must be the same, otherwise the calculated values will not be consistent.

Molecular weights for the dimethylamine-terminated poly(dimethylsiloxane) oligomers targeted were 500 (neat endcapping reagent), 2,500, 5,000, and 10,000 g/mol. Structural identity and molecular weights of the resultant siloxane fluids were established by NMR after thermal decomposition of the siloxanolate catalyst and removal of the cyclics by Keugelrhor distillation. The NMR spectra were obtained in $CDCl_3$ in the manner previously described in the identification of the endcapping reagent. Acid-base titration was also performed analogously to the endcapping reagent identification. Spectra and titration data have been summarized in Table. 3.4.-2.

Target M_n (g/mol.)	**M_n Titration (g/mol.)**	**M_n ^{1}H NMR (g/mol.)**
500	500	500
1,000	1,200	1,300
5,000	6,500	7,600
10,000	9,800	9,600

Table 3.4.-2: Molecular Weight Estimations for Dimethylamine-Terminated Poly(dimethylsiloxane)s

Gel permeation chromatography was not employed as a method of molecular weight determination. If there were even trace amounts of water trapped within the column, the extremely unstable silyl-amine linkage would have undergone hydrolysis, befouling the instrument, which was not an acceptable risk. In theory, the oligomers could have been reacted with a weak acid, such as phenol, replacing the silyl-amine link with more stable Si-O-C bond, prior to analysis. However the ease of peak identification in the NMR, coupled with the sharp titration curves, as well as the level of agreement between the two methods, provided compelling verification of the estimations of molecular weight.

3.4.2 Perfectly Alternating Poly(arylene ether phosphine oxide)-Poly(dimethylsiloxane) Block Copolymers

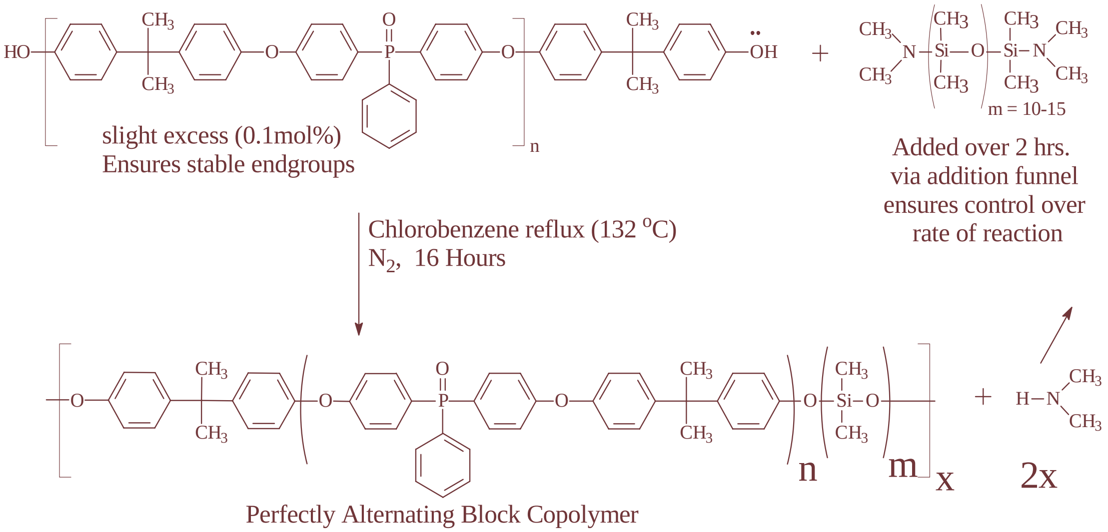
Per the following discussion, the copolymers produced are often referred to by the molecular weights of their component oligomers. For clarification, the samples are identified by the molecular weight of the poly(arylene ether phosphine oxide) (PEPO) used in the copolymers synthesis, followed by the molecular weight of the poly(dimethylsiloxane) (PDMS or siloxane) segment. For example, a 5k/1300 copolymer, corresponds to a copolymer derived from the 5,000 g/mol PEPO oligomer and the 1300 g/mol siloxane. Additionally, at times a series of copolymers containing the same PEPO component may be identified simply by the molecular weight of the PEPO segment. Generally, in these cases a trend has been observed as the siloxane block size varies, and this discussion will provide further clarification as needed. Alternately, some concepts were easier to relate as a function of weight percent siloxane incorporated. Both of these methods of sample identification for the PEPO/PDMS copolymers will be used periodically throughout the remainder of this thesis.

3.4.2.1 Synthesis, Compositional Analysis, and Molecular Weight Estimations of Poly(arylene ether phosphine oxide)-Poly(dimethylsiloxane) Block Copolymers

Synthesis

The well-known silylamine-hydroxyl reaction was employed, using telechelic oligomers, for the production of perfectly alternating $(A\text{-}B)_n$ poly(arylene ether phosphine oxide)-poly(dimethylsiloxane) block copolymers in the manner pioneered by Noshay and coworkers in the 1970’s. This reaction has been proven to be both facile and nearly quantitative, resulting in block copolymers with well-defined structures.

PEPO-PDMS copolymers were produced from the hydroxyl-terminated PEPOs and silylamine terminated PDMS, by sequential addition of oligomers.(Scheme 3.4-5)



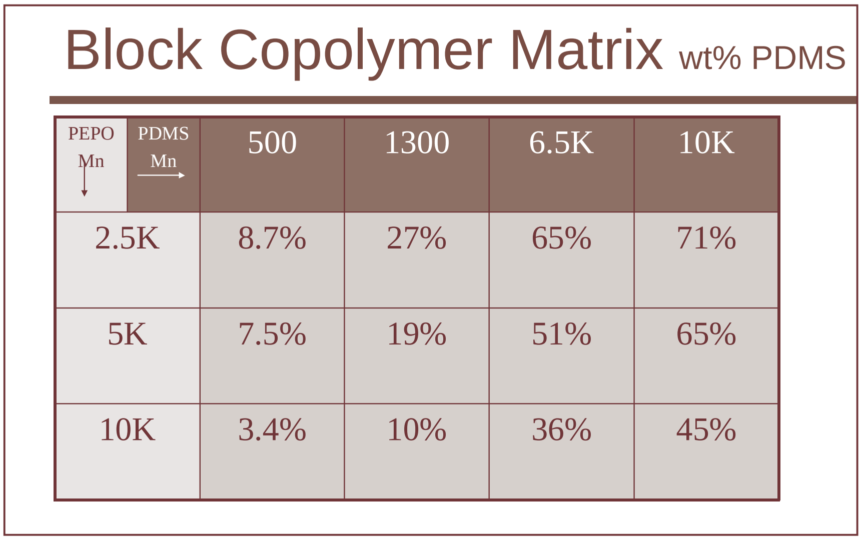
Scheme 3.4-5 : Synthesis of Perfectly Alternating PEPO/PDMS Block Copolymers

Sequential addition of the oligomers was employed for several reasons. First, oligomers containing the phosphine oxide moiety are difficult to keep fully dry. The phosphine oxide bond is so prone to hydrogen bonding that it will readily absorb water from the atmosphere. This factor becomes physically observable when the vacuum dried PEPO oligomer is dissolved in chlorobenzene. Although chlorobenzene will azeotrope water, they are immiscible. Thus, when the hydrogen bonded PEPO is dissolved in chlorobenzene, water is released from the P=O bond by solvation. The newly freed water readily forms aggregates in the nonpolar solvent, resulting in a cloudy solution. However, the concentration of bound water is small enough that it can be removed by azeotrope, as evidenced by a clearing of the oligomer solution after prolonged reflux. The full dehydration of the system prior to the addition of the silylamine functional siloxane is vital to preventing hydrolysis of the Si-N bond necessary for copolymerization. Moreover, any water associated with the PEPO oligomer adversely affects the stoichiometry calculations and the sample mass will not truly reflect the molecular mass.

The silylamine-hydroxy reaction proceeds rapidly, during which a gaseous side product, dimethylamine, is released. Therefore, it is beneficial to slowly add one reactant to the other in order to limit the amount of gas released at any given time. Otherwise the reaction would foam as the viscosity increases, resulting in inconsistent reaction conditions from point to point and possibly producing bimodal molecular weight distributions.

Finally, the slow addition of the reactive siloxane to the dehydrated PEPO oligomer allows for the correction of any errors encountered in the stoichiometric calculations, regardless of their origin. A slow approach to exact stoichiometry via small incremental additions prevents “overshooting” the ideal reaction composition while allowing some room for underestimation, as more siloxane can be added to the reaction system until the desired sharp viscosity increase is observed.

Three series of perfectly alternating poly(arylene ether phosphine oxide)-poly(dimethylsiloxane) block copolymers were produced in the compositions stated in the following matrix. As a guide, the molecular weight of the dimethylamine-terminated poly(dimethylsiloxane) oligomers comprises the top axis, while the M_n of the hydroxyl-terminated poly(arylene ether phosphine oxide) oligomers constitute the left axis, and the percentage values listed within the matrix are the weight percent siloxane present in the copolymers produced.



Block Copolymer Matrix wt% PDMS

PEPO Mn ↓ PDMS Mn →	500	1300	6.5K	10K
2.5K	8.7%	27%	65%	71%
5K	7.5%	19%	51%	65%
10K	3.4%	10%	36%	45%

Figure 3.4.-11: Matrix of copolymers produced.

<u>Compositional Analysis</u>

The PEPO-siloxane multi-block copolymers produced were isolated by precipitation into methanol, producing materials that ranged in appearance from fine powders to fibers. Structural and compositional analysis of the isolated materials was accomplished by ^{1}H NMR analysis. The overall copolymer composition can be calculated using integration ratios of the Si-CH_3 peak of the siloxane (0.075 ppm) and the isopropylidene signal (1.67 ppm) of the arylene ether segment. High molecular weight was confirmed by its film forming ability, as well as by intrinsic viscosity measurements obtained in chloroform. There values are summarized in Table 3.4.-3, along with the targeted and experimental copolymer compositions.

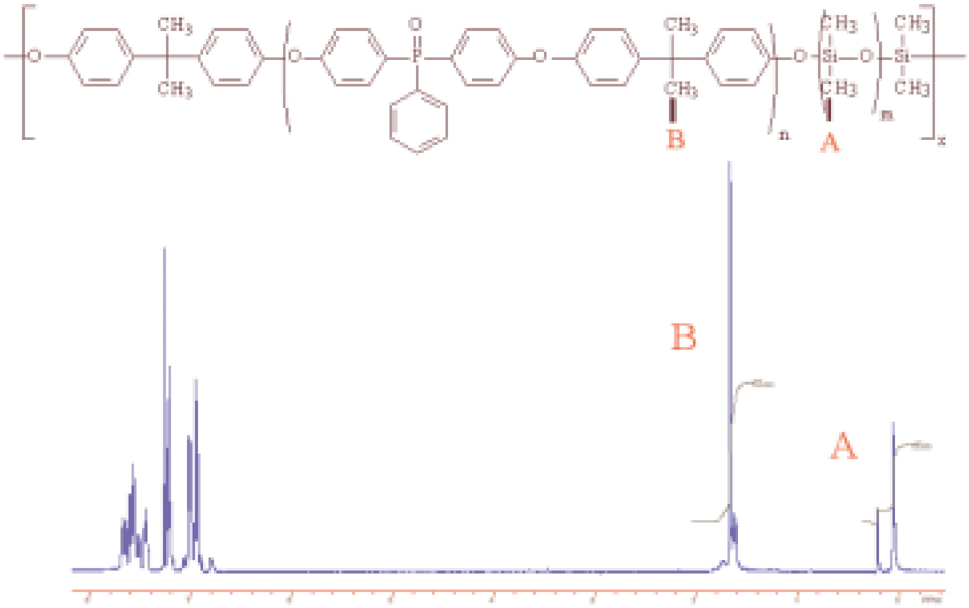
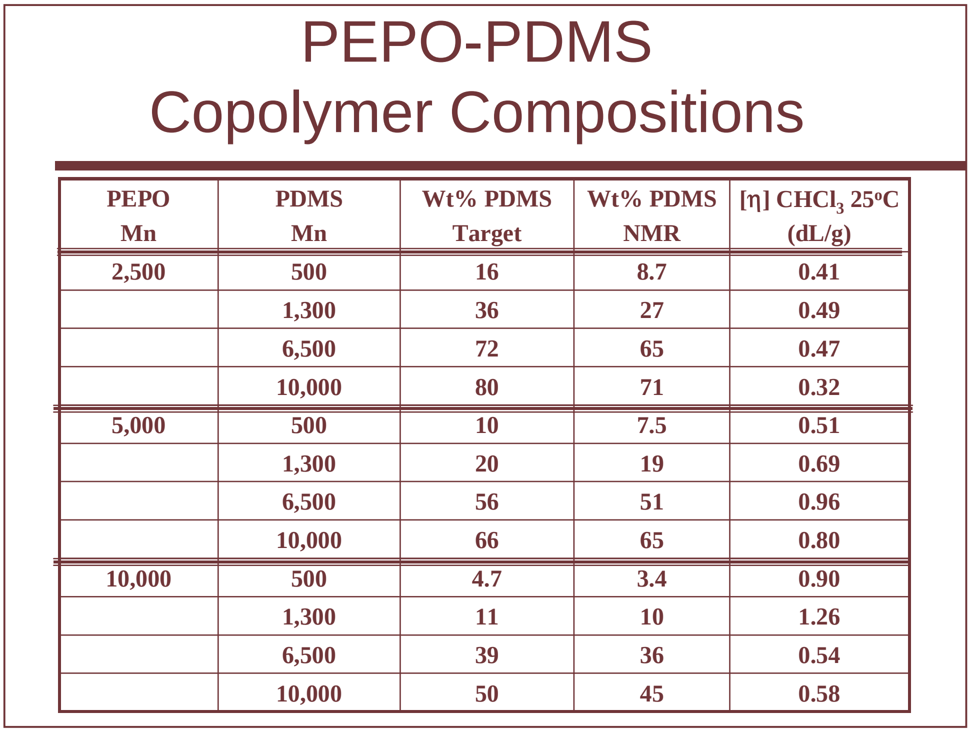


Figure 3.4-12: ^{1}H NMR of a Poly(arylene ether phosphine oxide)-b-Poly(dimethylsiloxane)copolymer



PEPO-PDMS
Copolymer Compositions

PEPO Mn	PDMS Mn	Wt% PDMS Target	Wt% PDMS NMR	[η] $CHCl_3$ 25^{o}C (dL/g)
2,500	500	16	8.7	0.41
	1,300	36	27	0.49
	6,500	72	65	0.47
	10,000	80	71	0.32
5,000	500	10	7.5	0.51
	1,300	20	19	0.69
	6,500	56	51	0.96
	10,000	66	65	0.80
10,000	500	4.7	3.4	0.90
	1,300	11	10	1.26
	6,500	39	36	0.54
	10,000	50	45	0.58

Table 3.4-3: Summation of PEPO-PDMS Copolymers Produced

Interestingly, comparison of the level of target and observed siloxane incorporation reveals a consistent deficiency of ~10% of the targeted siloxane content. The effectiveness of siloxane incorporation can best be visualized as a series of graphs depicting target siloxane level, actual incorporation, and error--except for materials with the lowest block lengths. These demonstrate even lower levels of siloxane incorporation, due to the difficulty of effectively controlling lower molecular weight systems, where Carother’s equation begins to lose applicability, and thus increasing the difficulty of attaining proper 1:1 stoichiometry.

Molecular Weight Estimations

GPC is universally used to establish molecular weight estimations of polymeric materials. This procedure is fast and accurate in most cases. However, the unique combination of phosphine oxide and siloxane bonds within the same polymer backbone raises some interesting issues, which unfortunately precluded extensive analysis of the copolymers.

Polymers containing phosphine oxides are known for their ability to hydrogen bond and readily participate in complex associations. This factor has proven to be beneficial in a wide variety of areas, such as the formation of nanocomposites and polymer blends. Unfortunately, this capability is not limited to desired complexations. Unless precautions are taken, the phosphine oxide moieties will somehow associate with the column of the GPC in a manner that is not fully understood, resulting in erroneously long retention times and thus underestimations of the molecular weights.[256] However, these associations can be disrupted with a small concentration (0.02-0.025 N) of an electrolyte (often LiCl, LiBr, or P_2O_5) in the mobile phase.[254]

Additionally, the polymer-solvent interactions of polydimethylsiloxane and polyarylene ethers are quite different, possibly influencing the hydrodynamic volume and leading to erroneous molecular weight estimations. Possible selective solubility of the copolymer segments, as well as the phosphine oxide interactions with the column, limited the selection of mobile phases.

Three mobile phases were used in an attempt to characterize high molecular weight copolymers. Initial attempts with $CHCl_3$ and THF as mobile phases resulted in retention times beyond the calibrated range, indicating that polymer-column interactions were present, rendering any molecular weight data to be qualitative at best. Analysis of copolymers in NMP with 0.02 N P_2O_5, 60°C yielded GPC data showing inconsistent intrinsic viscosity data, due to the fact that samples with high viscosities would often yield low M_n via GPC. Additionally, it was noted that although sample solutions would be homogeneous prior to injection, the eluent often appeared to be opaque, suggesting that some kind of change in solubility or fractionation occurred within the column.

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[256] Ding, Y.; Hay, A. S. *J. Polym. Sci., Part A* **1998**, *36*, 519.

[254] Konas, M.; Moy, T. M.; Rogers, M. E.; Shultz, A. R.; Ward, T. C.; McGrath, J. E. *J. Polym. Sci. Polym. Phys.* **1995**, *33*, 1429.

Sample	%PDMS	[η] $CHCl_3$	[η] GPC	M_n GPC
2.5/10	71	0.32	0.018	31,900
5/10	66	0.80	0.040	27,500
5/6.5	51	0.96	0.057	17,700
2.5/1300	26	0.49	0.068	10,000
5/1300	20	0.69	0.113	8,860
5/500	7	0.51	0.128	7,680

Table 3.4-4: Copolymer Characterization by GPC in NMP+0.02 N P_2O_5

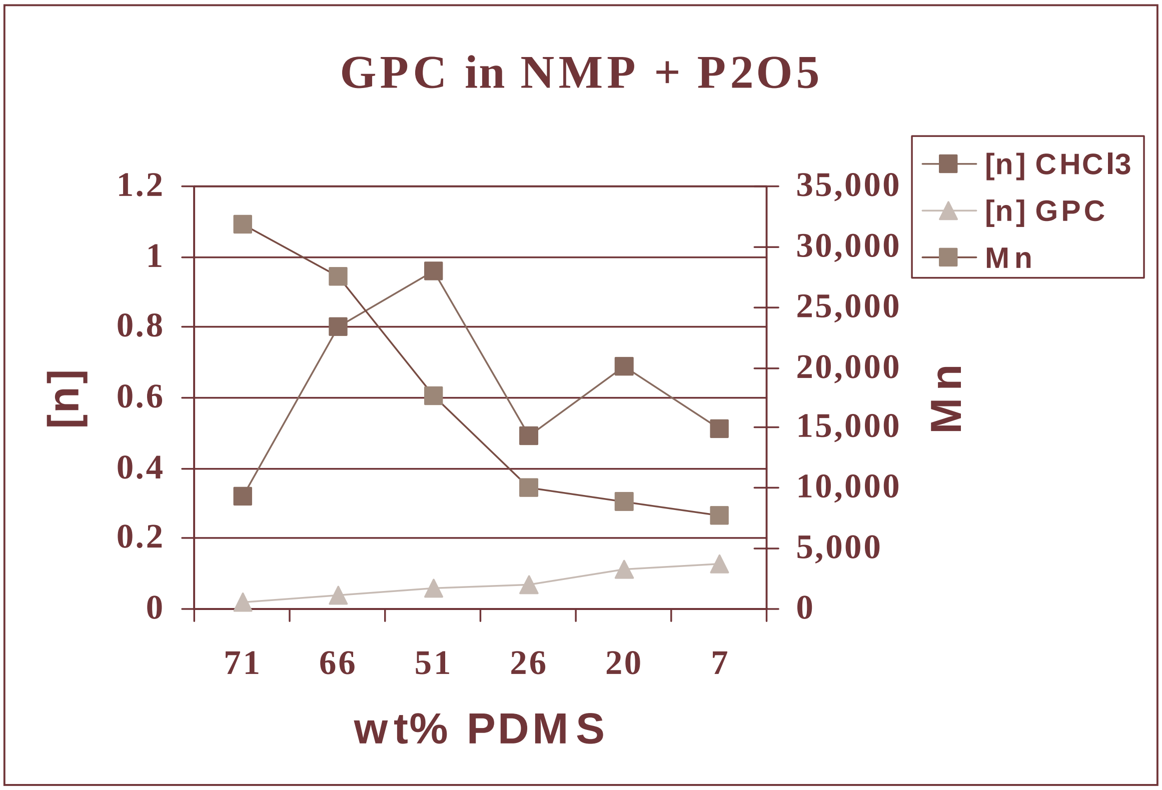

Figure 3.4-13: Graphic Representation of the Inconsistencies Encountered with GPC Analysis

P_2O_5 may have initiated redistribution of the siloxane chains or hydrolytically cleaved the Si-O-C copolymer linkages. Moreover, the NMP is simply such a poor solvent for siloxanes that the PDMS segments collapse to the point that their effect on the hydrodynamic volume is negligible when compared to the extended PEPO segments. Differentiation between these possible causes could be accomplished by adding LiBr, LiCl, or P_2O_5 to either the chloroform or THF, known solvents for both polymer types. It was thought that by avoiding the polymer-column interactions and alleviating selective solubility, the precise effect of the electrolyte could be identified. Unfortunately, this experiment required recalibration of the instruments and no convenient time could be allotted for such a task.

Another difficulty in obtaining accurate molecular weight data for block copolymers by GPC involves the dependence on the refractive index detector to indicate changes in the concentration of the polymer solution. The use of a refractive index detector assumes that the index of the copolymer solution is either greater or lesser than the solvent at all elution volumes. In the case of a block copolymer, this may not be true because the refractive index of the solvent may be influenced by that of the component oligomers. This situation could result in erroneous estimations of both the molecular weight and the distribution, since the copolymer concentration would not be accurately obtained at any given time.

Therefore, the ability to form strong self-supporting, transparent, films from chlorobenzene other solvents, displayed by all but two copolymer samples--coupled with the intrinsic viscosity results--provided verification that high molecular weight copolymers were indeed produced.

3.4.2.2 Selected Optical Properties of the Copolymers Produced

One of the initial research goals of this project was to develop an optically clear material with a higher refractive index and Abbe number than polycarbonate (n = 1.58, υ = 30.3).[136] Optically clear films were cast from 15 wt% chlorobenzene solutions onto glass plates. The films were cast in a glass enclosure with flowing nitrogen, while an infrared lamp was used to aid in the evaporation of solvent. The refractive index of the copolymers was obtained with a Metricon Model 2010 Prism Coupler by reporting the angle of complete internal reflection. The Abbe numbers of selected copolymer samples were measured by the Johnson and Johnson Spectacle Group (formerly known as Innotech). Additionally a Fox-type prediction given by the equation,

$$n_{PEPO-PDMS} = W_{PEPO} n_{PEPO} + W_{PDMS} n_{PDMS}$$

where, n_i is the refractive index of polymer i , and W_i represents the volume or weight fraction of i in the copolymer, was calculated and compared to the experimental data. The observed optical properties along with the Fox predictions are summarized in Figure 3.4.-14.

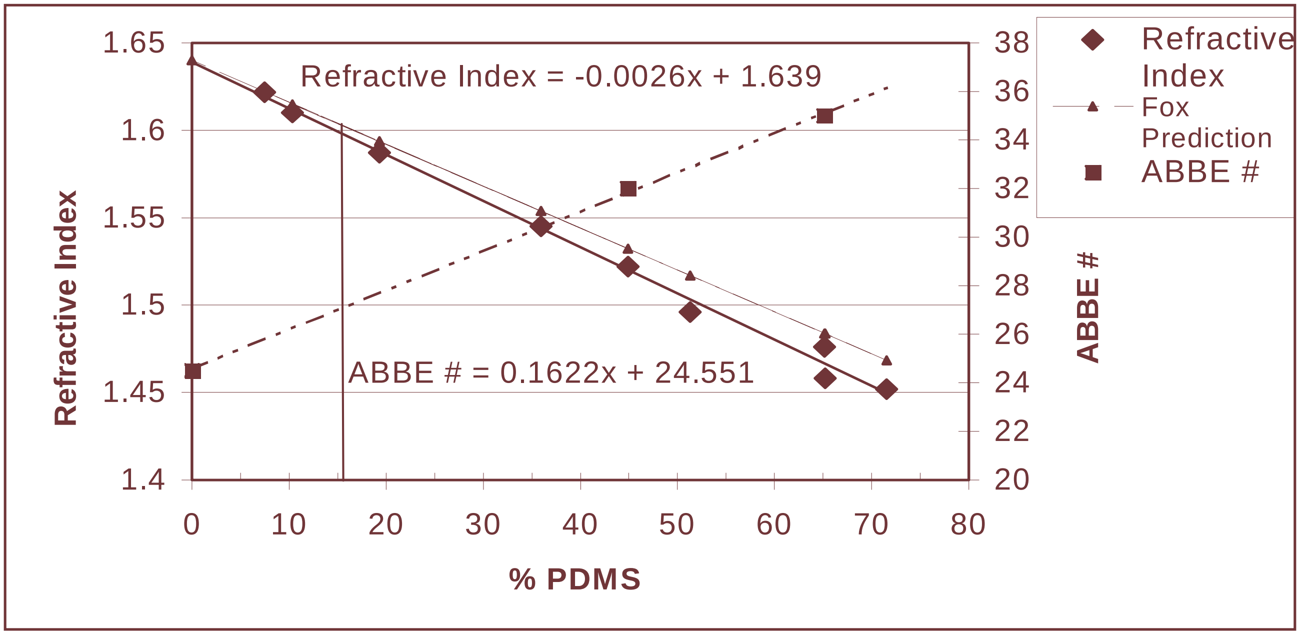

Figure 3.4-14: Correlation of Optical Properties to Copolymer Composition

Examination of the optical data gathered reveal opposing linear trends with respect to composition. It quickly becomes apparent that the desired combination of properties (refractive index >1.60 and Abbe number >30) is not attainable with this copolymer system. From the data collected, the maximum % PDMS allowable to maintain a refractive index above 1.6 is approximately 16% siloxane. Unfortunately, this level of siloxane incorporation only increases the Abbe number of the PEPO from 24 to 27, which is an improvement, but insufficient to compete with existing materials. It was hoped that the microphase separation would have a synergistic effect on the optical properties. However, from the review of the literature it was realized that this may have been an unrealistic expectation. It was known that in order for a block copolymer with components of differing refractive indices to remain optically transparent, any domains present must be smaller than the wavelengths of visible light (< 1000 Å).[141] However, it was ascertained that copolymers displaying domains this small are essentially the same as random copolymers, in the respect that the refractive index and Abbe number will be compositionally weighted averages of the values associated with the parent homopolymers. As illustrated above, the experimental results of this study support this conclusion.

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[136] Mills, N. J. In *Encyclopedia of Polymer Science and Engineering*: New York, 1991; Vol. 10, pp 493-540.
[141] Rosen, S. L. *Polym. Eng. Sci.* **1967**, *7*, 115.

3.4.2.3 Thermal Analysis of Poly(arylene ether phosphine oxide)-Poly(dimethylsiloxane) Block Copolymers.

Thermal analysis of the copolymer produced was pursued using multiple methods. Dynamic thermogravimetic analysis (TGA), was used to determine the thermo-oxidative stability of the copolymers, while dynamic differential scanning calorimetry (DSC) and dynamic thermomechanical analysis (DMA), were used to elucidate the transition temperatures and begin the exploration of the effect of block length on the extent of phase separation. However, since the DMA relies on the observation of mechanical properties as a function of temperature, the results gathered from DMA analysis will be examined during the discussion of selected mechanical properties.

Thermogravimetric Analysis

Both polyarylene ether phosphine oxides and polydimethylsiloxanes are thermally and oxidatively stable materials. Copolymers should likewise show excellent stability. TGA analysis of the copolymers was used to determine the onset of degradation; any material leaving the sample was noted by a loss in mass. This onset of degradation was defined as the temperature (at a heating rate of 10°C/min) when a sample, free of residual solvent, lost 5% of its mass by any one of several possible degradation mechanisms. The 5% weight loss temperatures of the copolymers were over 400°C and relatively constant, with the exception of two samples containing the smallest block sizes. This could be explained by the fact that the same two samples are suspected to be the lowest in molecular weight due to brittleness displayed in the resulting films cast from chlorobenzene. Additionally, the weight loss profiles reveal a direct correlation between the siloxane content and the amount of residual char (in air) at 800°C.

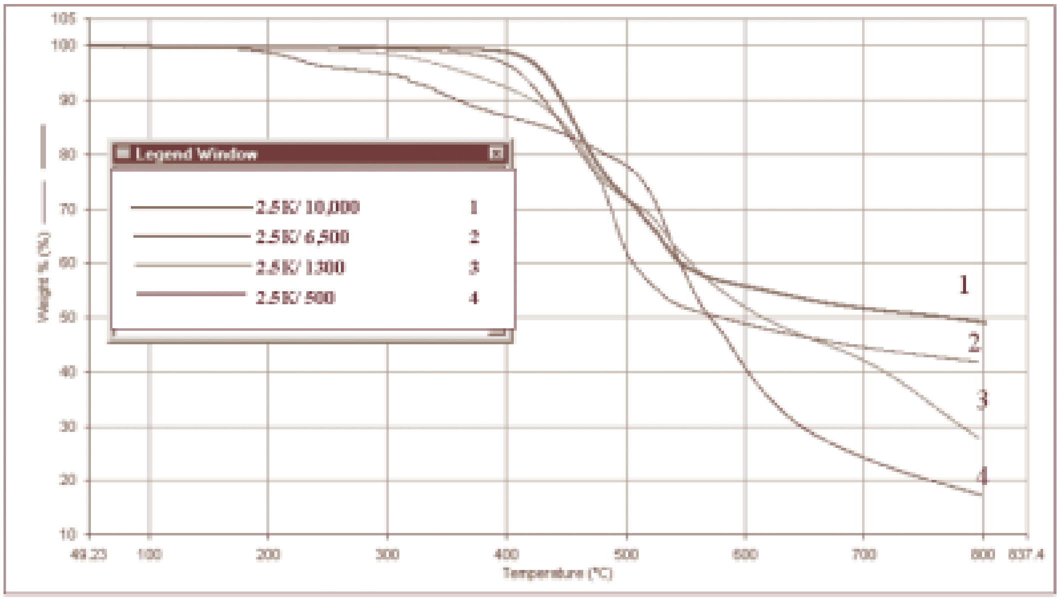

Figure 3.4-15: TGA Analysis of the 2,500 g/mol. PEPO Copolymer Series

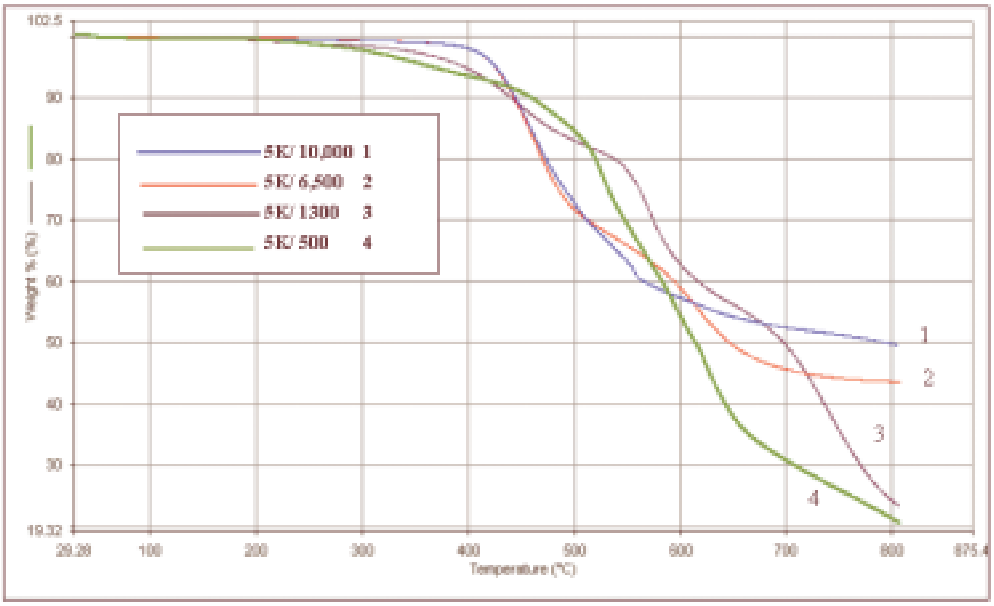

Figure 3.4-16: TGA Analysis of 5,000 g/mol PEPO Copolymer Series

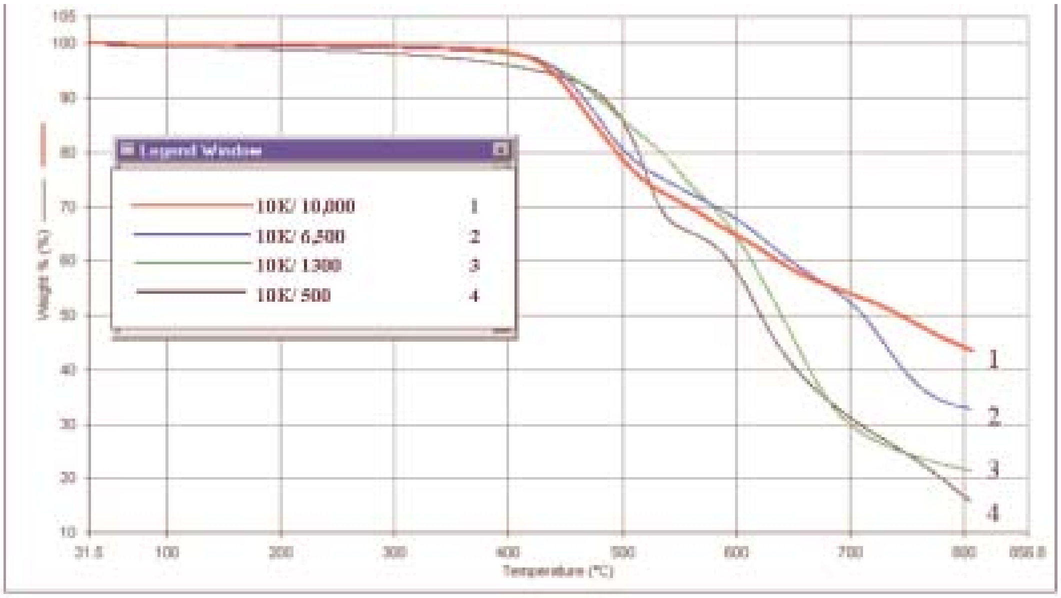

Figure 3.4-17: TGA Analysis of the 10,000 g/mol PEPO Copolymer Series

The presence of residual char can be used as a preliminary indicator of flame retardance. In fact, van Krevelen has correlated Char Yield to the Limiting Oxygen Index (a common test for fire retardance, discussed in the review of the literature - Section 2.4.5). In the following equation, Char Yield is defined as the residual mass after pyrolysis and is normally measured at 900°C.

$$LOI * 100 = 17.5 + 0.4\ (\text{Char Yield @ } 900°C)$$

However, the use of platinum sample pans in the TGA, as well as guidelines concerning frequent usage of the instrument, limited experimental observations to 800°C. Assuming that the disparity between the observed char temperature and the accepted temperature will not significantly affect the amount of char present, then the van Krevelen correlation can be applied to the TGA data providing estimations for the LOI of the copolymers. A composite of the data collected from TGA analysis in relation to PDMS content is shown in Figure 3.4-18

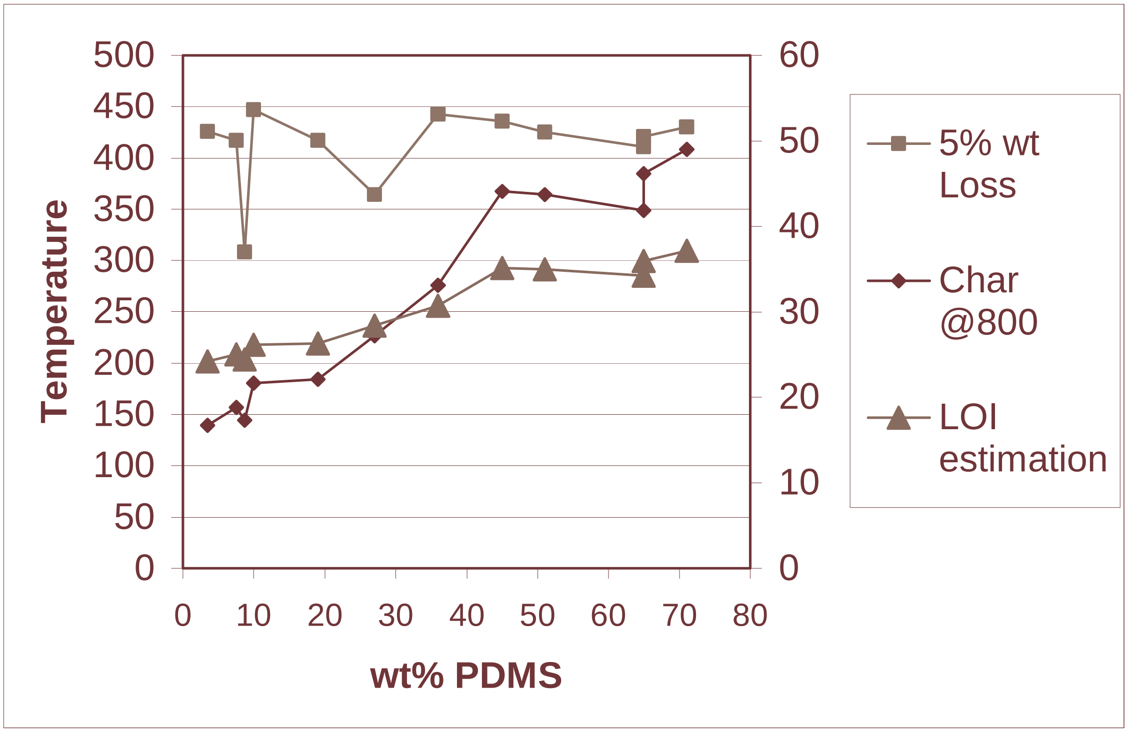

Figure 3.4-18: Compilation of the TGA Data Collected for PEPO-PDMS Copolymers

The LOI estimations reveal a significant step occurring between 36 and 45% siloxane incorporation. This step may also be indicative of when fire retardance begins to take place. Traditionally, a material with a LOI value above 27 is considered to be fire retardant. Since the data was collected at 100°C below standard conditions, the LOI estimations may be inflated and thus may require a relative value of over 30 to exhibit flame retardance. After the initial step up in LOI, the curve begins to flatten, possibly indicating that there may be a limit to the amount of fire retardance that can be gained by incorporating a siloxane component. Again these calculated results must be taken as estimations and not as concrete values indicating fire retardance.

Differential Scanning Calorimetry (DSC)

Conditions for DSC analysis depend on TGA results. Thus, any degradation, thermal or otherwise, within the instrument should be avoided to maintain the sensitivity of the DSC. It was therefore determined that, as a general rule, the maximum allowable temperature for DSC measurements should be at least 50°C below the 5% weight loss established from the TGA data. However, in this study there was no reason to go above 220°C, since all the observable transitions occurred at or below 200°C. Some difficulties in detecting transitions occurred due to limitations in sample size. Given that the samples examined ranged from 4-10 mg in mass, segments present in small weight fractions may not have significantly contributed to the heat capacity and therefore will remain undetected. Additionally, a small sample size may lead to a low signal-to-noise ratio rendering broad transitions undistinguishable from possible baseline drift.

The high temperature transitions of the PEPO segments were detected with a Perkin-Elmer DSC-7. The data is presented for series of copolymers grouped by the molecular weight of the PEPO segment, in order to better illustrate the overall trends observed, as shown in Figures 3.4-19 through 3.4-22.

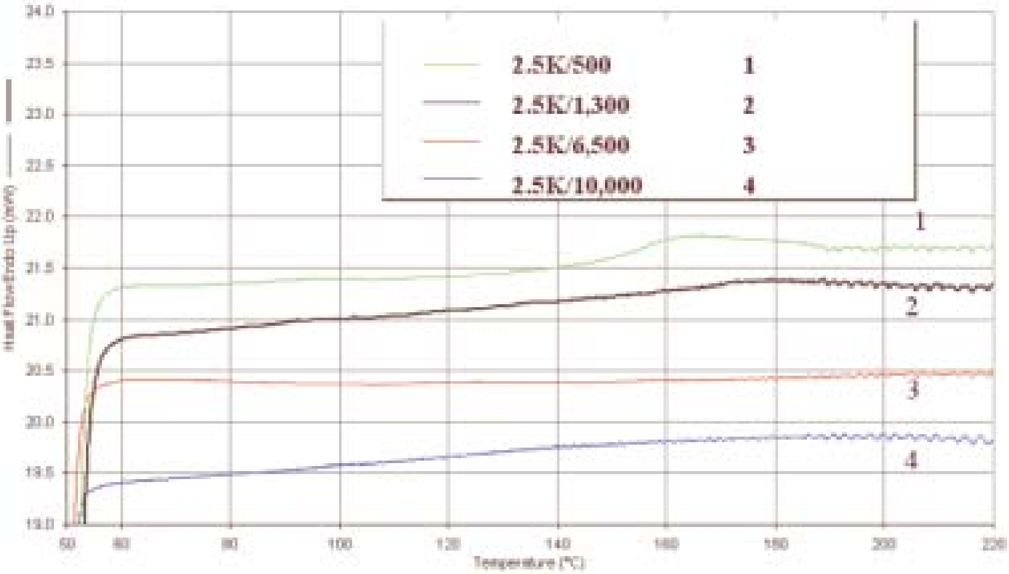

Figure 3.4-19 High Temperature DSC Analysis of the 2,500 g/mol PEPO Copolymer Series

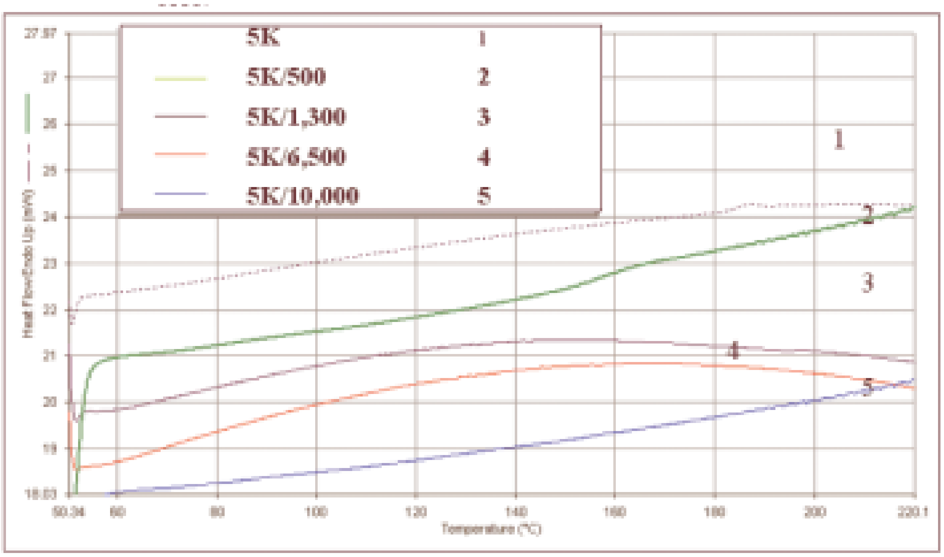

Figure 3.4-20: High Temperature DSC Analysis of the 5,000 g/mol PEPO Copolymer Series

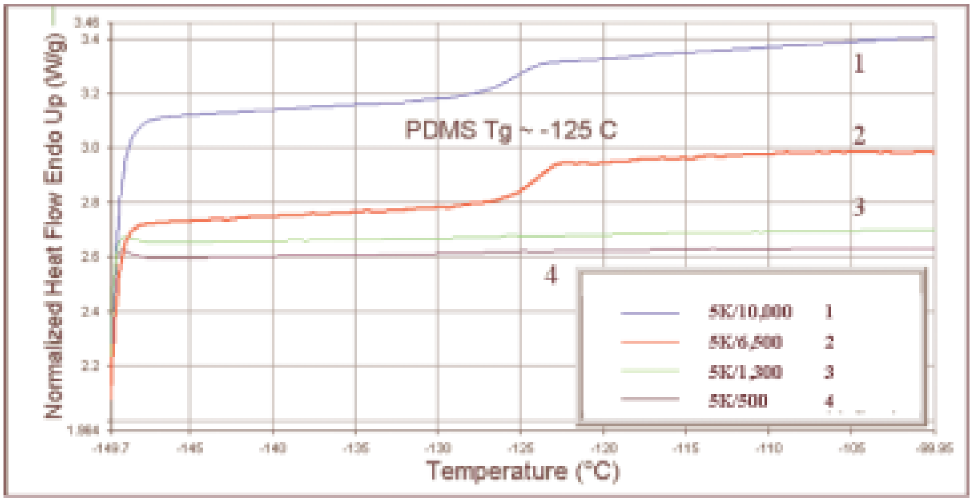

Figure 3.4-21: Low Temperature DCS Analysis of the 5,000 g/mol PEPO Copolymer Series Obtained From the Pyris 1 System

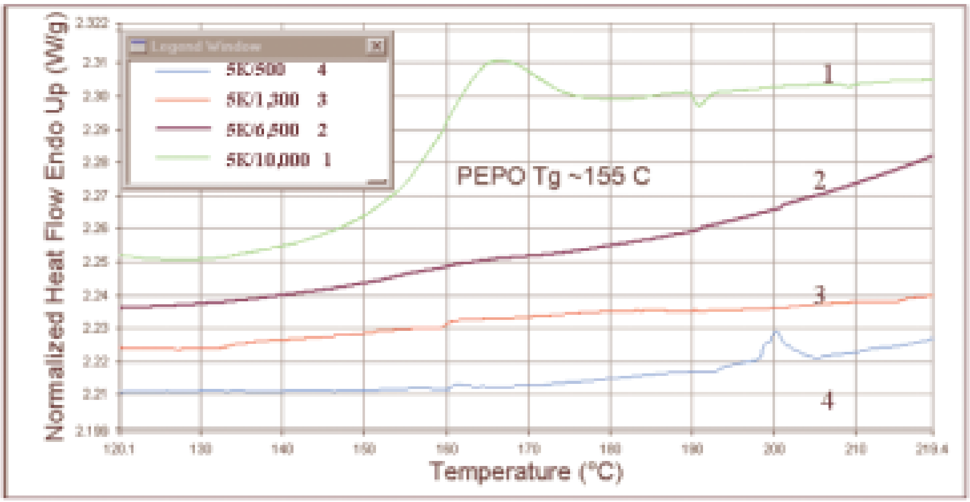

Figure 3.4-22: High Temperature DSC Analysis of the 5,000 g/mol PEPO Copolymer Series Obtained From the Pyris 1 System for Comparison.

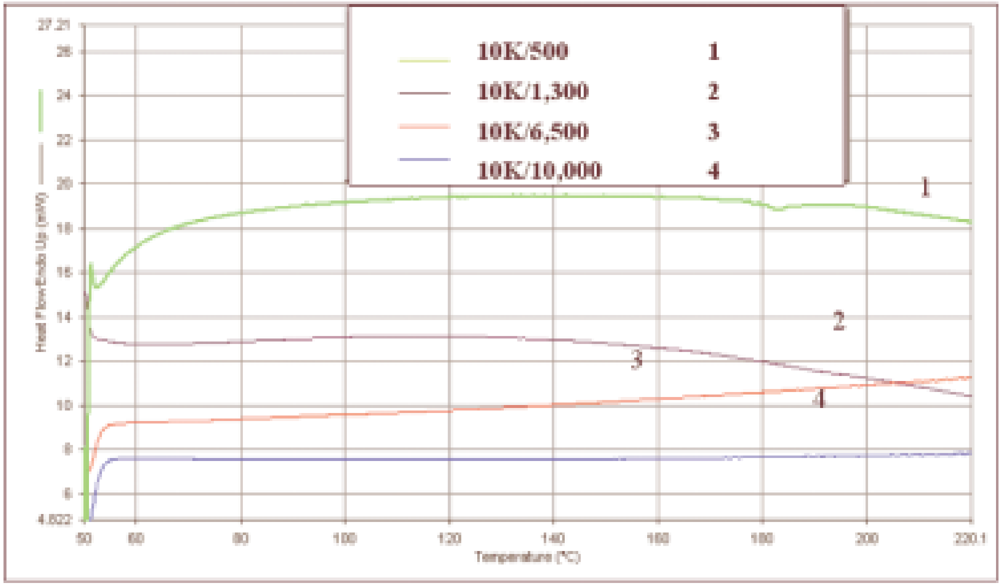

Figure 3.4-23: DSC Analysis of the 10,000 g/mol PEPO Copolymer Series.

Careful examination of the DSC traces show that the T_g of the PEPO segment can be clearly observed in those samples containing smaller PDMS segments ($\leq$ 1,300 g/mol). This may be due to limitations in sample size; with the larger PDMS blocks, the weight percentage of PEPO may be too small to detect in a 10 mg sample. However, when a T_g was observed, the transition tended to be both depressed and broadened compared to high molecular weight PEPO and the PEPO oligomers, suggesting some degree of phase mixing. However, any suggested trends based on data collected with the DSC-7 should only be considered as support for theories generated by other methods, because the magnitude of the transitions are not distinct enough to distinguish them from possible baseline drift.

The low temperature transitions of the PDMS block were detected on a Pyris 1 DSC, a more sensitive instrument with the ability to analyze samples at sub-ambient temperatures. Since time on the instrument was limited, only the series of copolymers containing the 5,000 g/mol PEPO segment were studied. The lower temperature transitions of the copolymers, attributable to the PDMS segments, were observed at –125°C and were sharp when the copolymer composition provided enough PDMS mass to be detectible. In contrast to the high temperature data gathered on the DSC-7, analysis of the higher temperature regions showed (1) a sharp transition for the sample containing the largest siloxane blocks, (2) possible phase mixing for the 6,500 g/mol blocks and (3) signals that are difficult to distinguish from baseline noise for copolymers containing the shorter segments.

3.4.2.4 Characterization of Selected Mechanical Properties of Copolymers Produced

Copolymers that formed robust films from solution were analyzed for potential as thermoplastic elastomers, with the help of members of Professor Garth Wilkes' lab. Their DMA proved to be more suitable for low temperature analysis and would allow one continuous scan from about -150 to 200°C, while similar instrumentation in the McGrath labs would have required two separate experiments for subambient and higher temperature (> 150°C) transitions. Additionally, stress-strain curves were generated using an Instron in the Wilkes lab to elucidate the tensile strength of the materials generated.

The DMA analysis was attempted on two series of copolymers containing either the 5,000 or 10,000 g/mol PEPO blocks. The analysis was limited to these two series of samples due to the nature of the analysis. DMA analysis, in the tensile mode, subjects a suspended film or molded sample of a material to an oscillatory stress. The sample is stretched and relaxed at a given rate, in this case 1 Hz, while heating at a rate of 2°C/min. DMA can be used to determine the storage modulus (E'), the loss modulus (E'') and the loss tangent ($\tan \delta = E''/E'$).

The storage modulus measures the recoverable deformation of a material caused by the application of a load. As the name implies, this component of stress can be stored as energy and recovered. The loss modulus is a measure of the energy dissipated by a material in the form of non-recoverable deformation or heat. This discrepancy is due to molecular motions reflected in the loss modulus. The loss tangent or tan δ is the ratio of the amount of energy dissipated (E'') over the maximum energy recoverable (E') from one cyclic loading. Therefore, tan δ is a measure of the amount physical damping caused by the material. This type of energy dissipation occurs only with changes in the mobility of the polymer chains, which is greatest during glass transition. This makes DMA an excellent method for determining glass transition temperature, as well as for identifying the extent of phase mixing. An observed decrease in the storage modulus (E') can be interpreted as a softening of the material, while a peak in tan δ corresponds to a maximum of damping (a glass-transition).

Self-supporting films of reasonable strength were required for analysis, since static load and oscillatory stress must be applied in order to observe variance with temperature. Two of the copolymers containing the 2,500 g/mol PEPO segment did not form large enough continuous films for use. Therefore, data and related discussions will be limited to copolymers containing the 5,000 and 10,000 g/mol PEPO oligomers. Additionally, changes in the mechanical resistance to stress are often more sensitive than heat capacity measurements used in DSC. Furthermore, in DMA analysis heating rates are generally lower, allowing better resolution. The DMA data is shown as raw data curves in Figures 3.4-24 through 3.4-27.

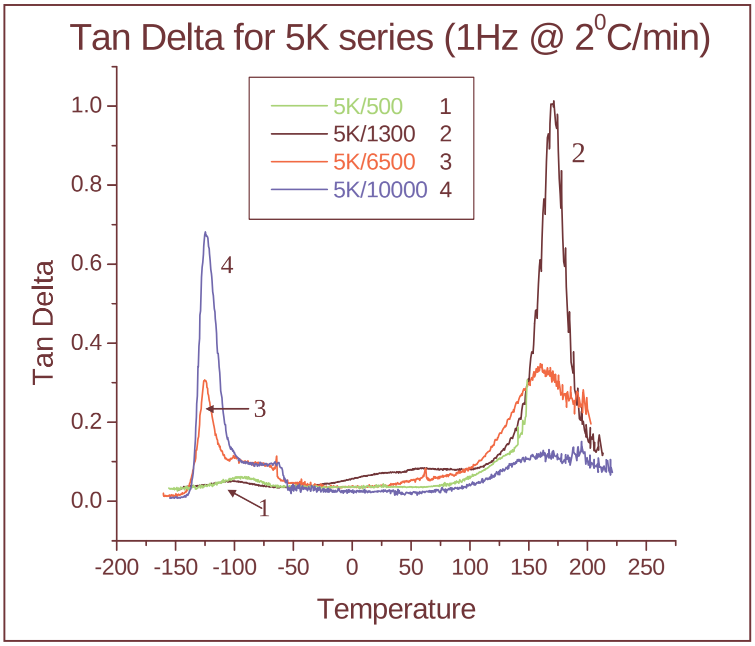

Figure 3.4-24: Storage Modulus-Temperature Behavior of the 5,000 g/mol PEPO Copolymer Series

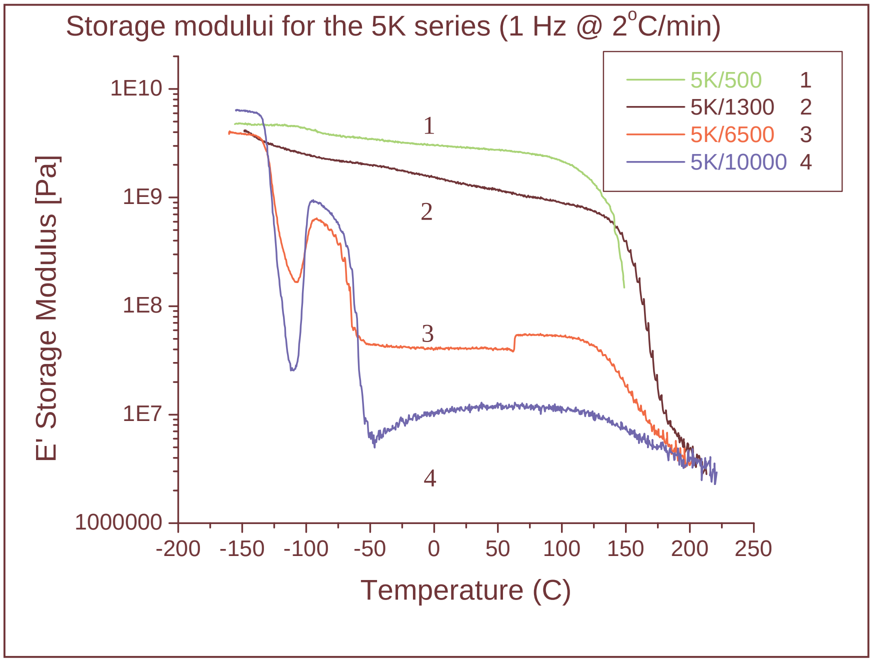

Figure3.4.-25: Effect of Temperature on the Storage Modulus of the 5,000 g/mol PEPO Copolymer Series

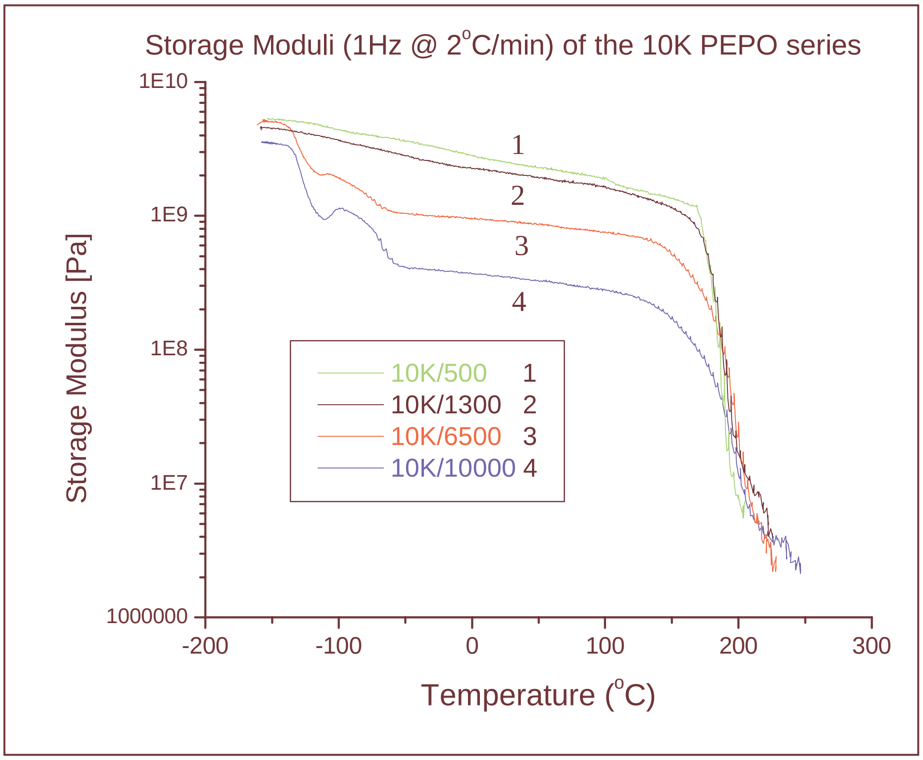

Figure 3.4-26: Storage Modulus-Temperature Behavior of the 10,000 g/mol PEPO Copolymer Series

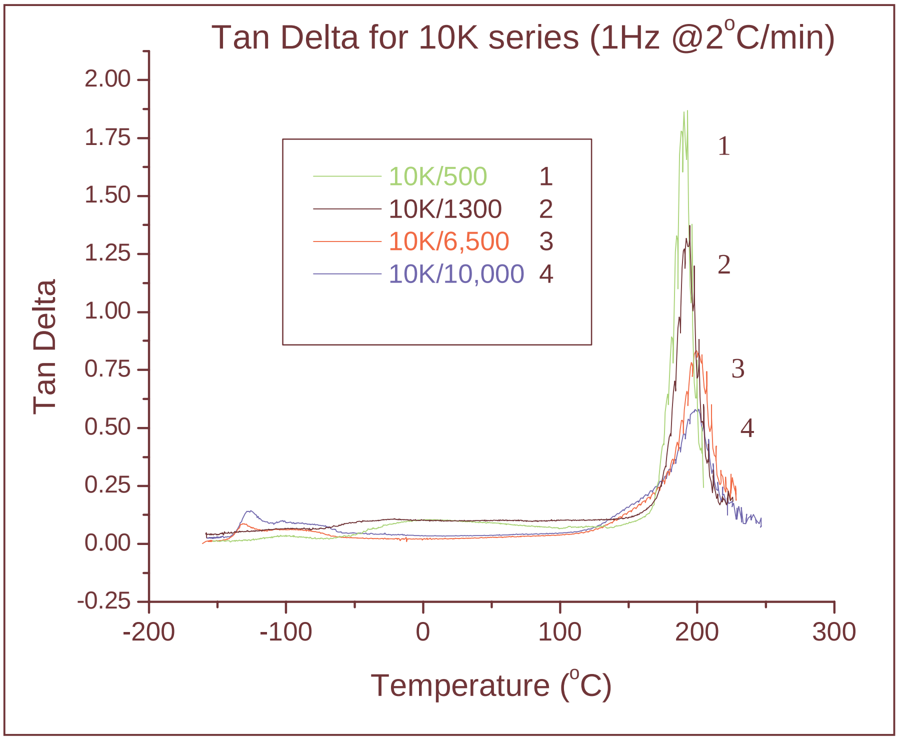

Figure 3.4-27: Effect of Temperature on the Physical Damping of the 10,000 g/mol PEPO Copolymer Series

Examination of the storage modulus-temperature behavior for the series of copolymers containing the 5,000 g/mol PEPO segments (Figures 3.4-24 and 25) show broadened low temperature transitions at elevated temperatures for the 500 and 1,300 g/mol PDMS samples (-95 and –100°C respectively), demonstrating possible phase mixing. However, higher molecular weight samples showed sharp transitions (-125°C) and even transient increases in stiffness as the temperature increased, due to cold-crystallization (-100°C) and subsequent melting (-40°C) of the siloxane segments, which is indicative of strong phase separation. With regard to the high temperature portion of the curves, one observes the opposite pattern. The more distinct transitions (near 160°C) are associated with the samples containing smaller siloxane segments, while the copolymers with longer siloxane blocks displayed broader transitions. This same pattern of transitions, low temperature signs of phase mixing for the smaller siloxane blocks, with crystallization of PDMS blocks > 5,000 g/mol was observed, while the PEPO blocks transitions showed opposite trends, i.e., sharper transitions occurring with smaller siloxane segments.

This apparent contradiction can only be rationalized once it is understood that phase mixing is not a straightforward process, whereby either A mixes into B or it does not. Rather, it is important to determine what block is the secondary phase that mixes into the matrix before the extent of mixing can be determined.

Thus, it can be said that in samples with smaller siloxane block lengths (< 5,000 g/mol), the PDMS domains can be considered contaminated with PEPO, resulting in broader elevated T_gs, while the relatively pure PEPO domains yield sharp transitions. Conversely, for the samples with large siloxane blocks, the PEPO domains are contaminated with siloxane while the relatively pure siloxane domains undergo crystallization as if the PEPO were not even present.

It is important to mention that the actual numeric values reported above are obtained from the tan δ curve, because it is more convenient to determine a peak value or the beginning of a plateau, rather than determine the mid-point of a transition.

Stress-Strain Behavior

The stress–strain behavior of two series of copolymers (5K and 10K) were observed using an Instron tensile tester. The samples tested were ~ 0.5 mm thick and cut from solution cast films using a dogbone shaped die. At this point is appropriate to note that the copolymers containing the lower molecular weight blocks (PDMS - 500 g/mol, PEPO - 2,500 g/mol.) fractured during removal from the aluminum mold, and therefore were not tested.

The data curves reported are the averages of 5 to 7 measurements on each material (with a new physical sample for each trial). Each sample was subjected to extension at a rate of 10 mm/min under ambient conditions.

The following parameters were obtained from the stress-strain profiles of the copolymers: tensile modulus from the initial slope of the curve, strain at break, and tensile stress at break. The averaged data curves are shown in Figures 3.4-28 and 29, and the numerical data is summarized in Table 3.4-5.

The lower siloxane content samples were anticipated to exhibit rubber toughening, but the observed changes in modulus and ultimate strength were not significantly improved. In the case of the higher molecular weight siloxane blocks, it becomes readily apparent that their copolymers display remarkably lower tensile moduli and deform to a greater extent (a strain of 1 corresponds to 100% extension). Additionally, one notices that as the siloxane content increases, the tensile modulus decreases. Unfortunately, the strains at break for all of the samples are too low for them to be considered as thermoplastic elastomers.

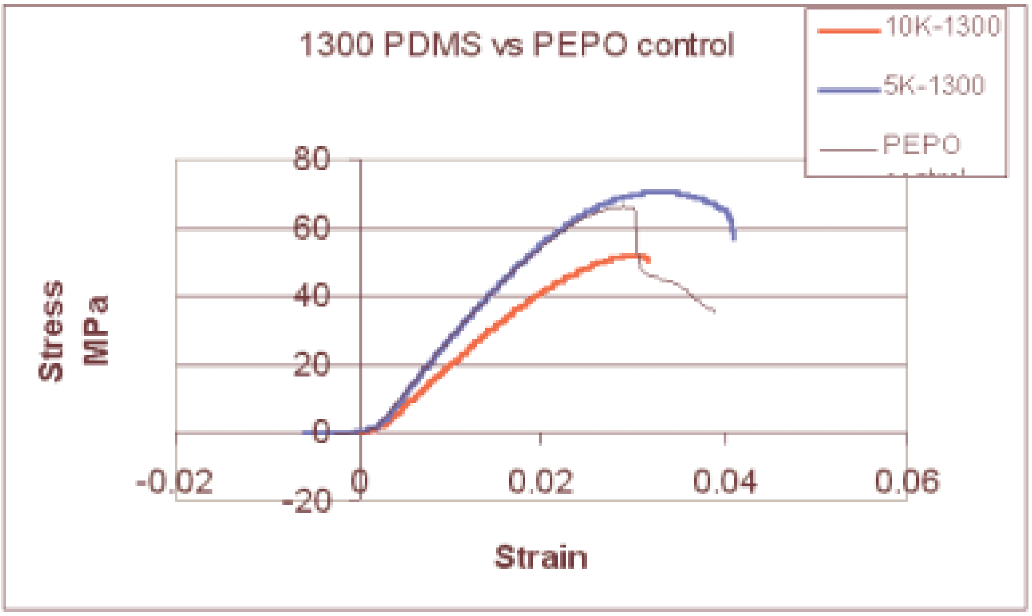

Figure 3.4-28: Stress-Strain Behavior of PEPO and Two 1,300 g/mol PDMS Copolymers

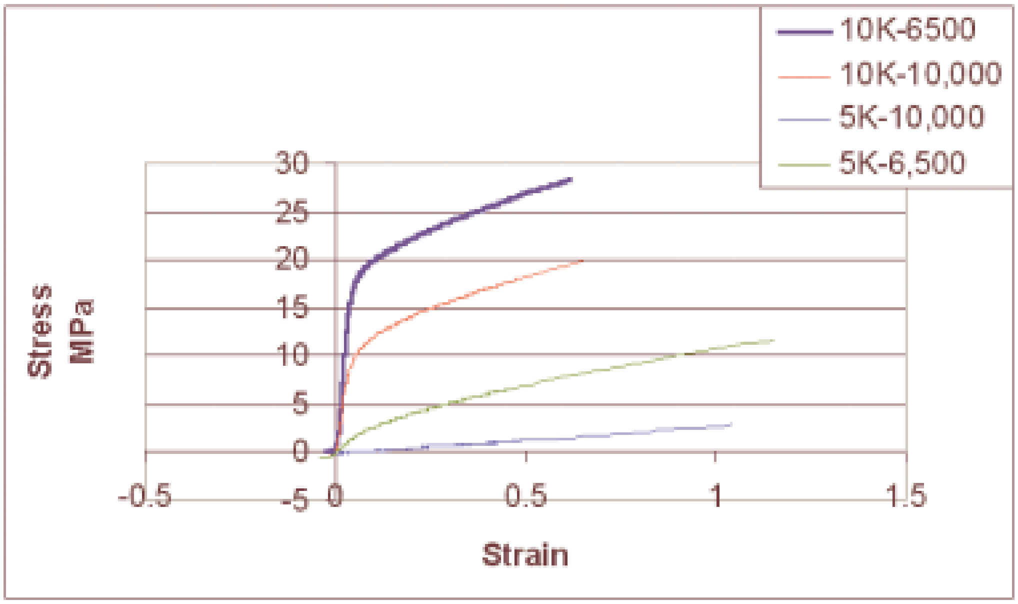

Figure 3.4-29:Stress-Strain Behavior of PEPO-PDMS Copolymers with Higher Siloxane Loading

SAMPLE	**Tensile Modulus (MPa)**	**Tensile Strength ((MPa)**	**% Elongation**
5K / 1,300	3180	70	4.1
5K / 6.500	39.0	11.7	115
5K / 10,000	2.5	2.9	107
10K / 1,300	2456	50.8	3.2
10K / 6.500	264	28.3	61
10K / 1,300	307	19.8	68

Table 3.4-5: Summation of the Stress-Strain Behavior.

3.4.2.5 Examination of Copolymer Morphology by Transmission Electron Microscope (TEM), Atomic Force Microscopy (AFM), and X-ray Photoelectron Spectroscopy (XPS)

The thermal and mechanical analysis of the copolymers showed indications of some phase mixing. Therefore, it was thought that the direct observation of the morphologies present would provide some insight into the effects of copolymer composition and block size -- both on the morphology and the physical properties previously observed. With this in mind, films cast from chlorobenzene solutions were analyzed by TEM to determine the bulk (cross-sectional) morphologies, and by AFM in the tapping mode to elucidate the morphological configuration of the air polymer-interface. Visual comparison of the images obtained from the TEM and AFM methods revealed a disparity between the bulk and surface morphologies, and possibly the effective copolymer compositions. In order to better quantify this difference, XPS was used to determine the relative atomic composition of the copolymer surfaces compared to the overall composition previously determined by NMR.

Transmission Electron Microscopy (TEM)

The bulk morphologies of selected copolymers produced were directly visualized by TEM after being cryogenically microtomed without additional sample preparation such as staining, due to the significant differential in electron density between the largely inorganic polydimethylsiloxane segments and the hydrocarbon based poly(arylene ether phosphine oxide) segments. The siloxane regions, containing more electron density, were more resistant to the transmittance of electrons and therefore appear darker in the TEM image.

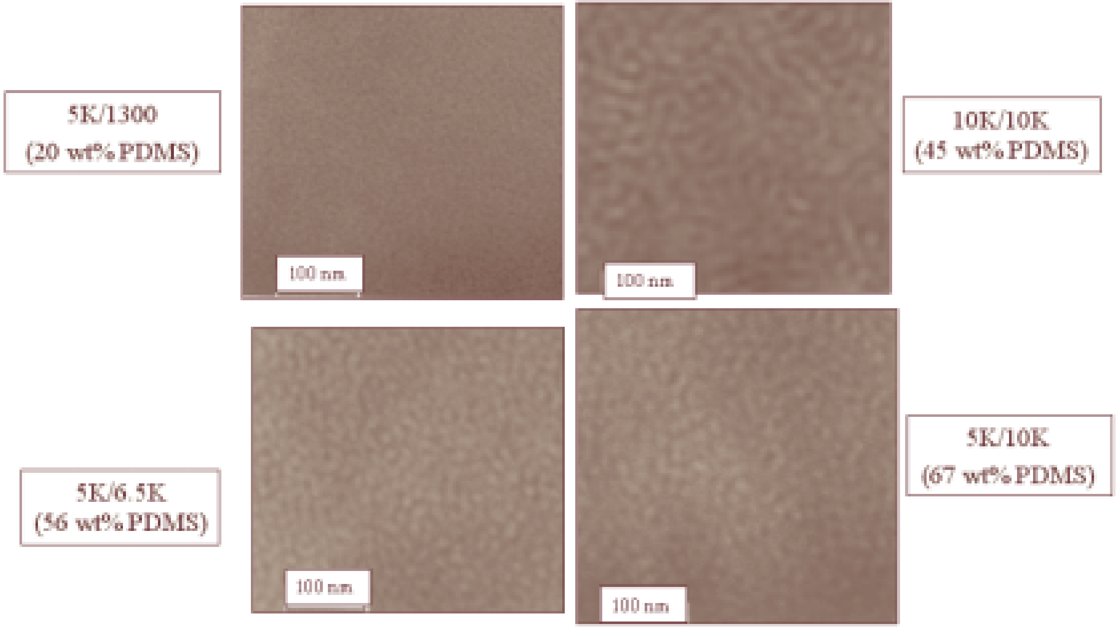

Figure 3.4-30: Representative TEMs Illustrating the Domain Size is Dictated by the Block Length of the Secondary Phase

Representative TEM micrographs are shown in Figure 3.4.-30. Examination of these images reveals several interesting points. First, all of the copolymer samples show some evidence of phase separation, even though if uniform phase mixing were present the TEM images would be relatively featureless. Yet in every sample there are clearly signs of concentrations in electron density, which can be interpreted as siloxane rich regions. This factor highlights the necessity of directly examining the morphology of a material instead of basing morphological conclusions on secondary indicators. Once the phases become small enough they may not be easily discernable by thermal or mechanical methods, while still remaining obvious via microscopy.

A second point is that there is a distinct pattern in the domain sizes present. It appears that the dominant factor in determining the domain size for the nanophase-separated materials is the length of the siloxane block. Side by side comparisons of copolymer samples with the same siloxane segment length, but significantly different PEPO block sizes, show no noticeable difference in the size of the siloxane domains. This indicates that there is a limit to the degree of phase mixing observed, dependent on the size of the secondary phase and independent of the dominant block length.

Third, as the siloxane block is lengthened and the compositions approach parity, more order and thus more defined phase separation begins to develop in the co-continuous structures. This feature can be correlated to the information provided via DMA analysis, which confirms that composition parameters dictate the manner in which the phase mixing occurs, where the compositionally dominant fraction is partially solubilized into the secondary component, leaving the dominant fraction essentially pure.

Atomic Force Microscopy (AFM)

The surface morphology was directly observed through the use of atomic force microscopy in the tapping mode. With this method, a cantilever taps on the surface of a material at a given frequency with a known force. The softer the substrate (i.e., polymer) is at a given location, it will cause a phase lag between the programmed oscillation and the position observed as the stylus deforms the material. As the material begins to stiffen, this lag becomes smaller. Thus, the differences between a siloxane segment (above its T_g) and a PEPO segment (below its T_g) should be easily observable by AFM. In the images discussed in this work, the softer segments (PDMS) are represented by the lighter portions, while stiffer portions (PEPO) will be darker.

Representative samples of the copolymers produced were analyzed by AFM. The compositions studied were selected to allow examination of a wide range of siloxane content, (7-66 wt%), and the resulting phase images can be found in Figure 3.4-31. The analysis of the copolymer surfaces resulted in images that consistently show a significant increase the siloxane domain size, in comparison to the cross-sectional morphology determined by TEM. Additionally, visual estimation of the relative area covered by the enlarged siloxane phases appears to be greater than that of the overall copolymer composition previously established by solution NMR analysis. This effective siloxane surface enrichment was not unexpected as the migration of siloxane segments to the air-polymer interface is commonly observed in the analysis of siloxane containing block copolymers.[257] However, in an attempt to quantify the extent of surface enrichment relative to the overall composition, a more definitive technique was required.

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[257] Dwight, D.; McGrath, J. E.; Lawson, G.; Patel, N.; York, G. In *Multiphase Macromolecular Systems*; Culbertson, B. M., Ed.; Plenum Press: New York, 1989; pp 265-288.

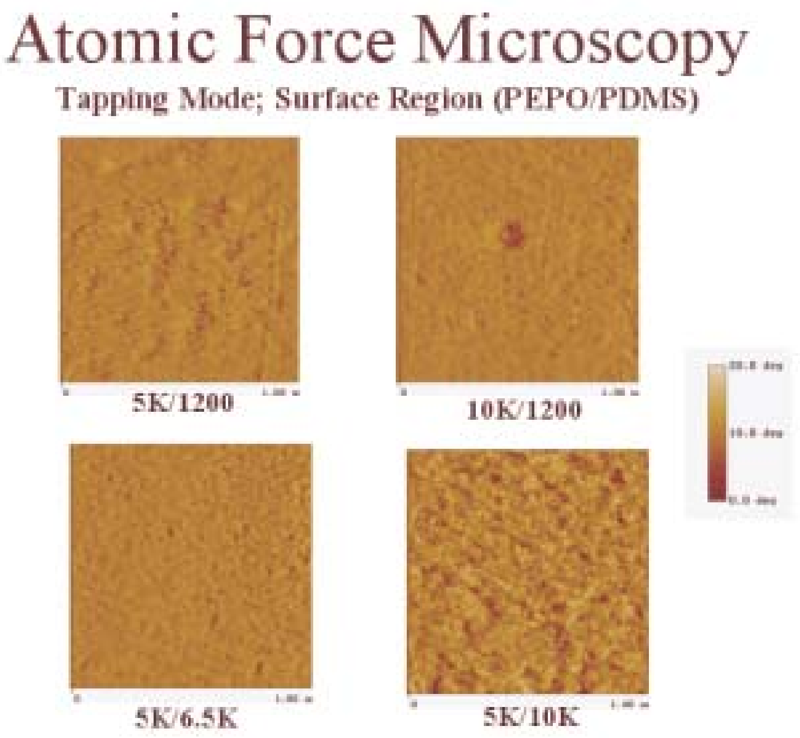

Figure 3.4-31: Representative AFM Phase Images

X-ray Photoelectron Spectroscopy (XPS)

The extent of siloxane surface enrichment present in the copolymer samples was quantified by XPS. X-ray photoelectron spectroscopy, also known as electron spectroscopy for chemical analysis (ESCA), is commonly used to determine the atomistic composition of the first 10-50 Angstroms of a material's surface. Analysis by XPS can be used to establish atomic identification, oxidation states present, and molar ratios of component atoms.[258] Additionally, XPS allows the relatively non-destructive analysis for virtually all atoms (excluding hydrogen) of the uppermost portion of almost any solid material that can withstand X-ray bombardment and exposure to vacuum.[259] Furthermore, varying the angle of observation allows the comparison of atomic concentrations at different depths.[260]

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[258] Dwight, D.; McGrath, J. E.; Wightman, J. P. *J. Appl. Polym. Sci.* **1978**, *34*, 35.

[259] Ghosh, P. K. *Introduction to Photoelectron Spectroscopy*; Wiley: New York, 1983.

[260] Fadley, S. In *Progress in Solid State Chemistry*; Somorjai, G., J., M., Eds.; Pergamon Press: Oxford, 1976.

XPS analysis is based on the measurement of the energy required to eject a core electron from the atoms of the substrate upon application of monoenergetic X-rays. This energy, known as the binding energy, is unique for each element and its oxidation state. The actual process can be summarized as follows. A substrate is exposed to incident x-ray radiation of known energy (eV). If this energy exceeds the binding energy (BE) of a core electron, the electron will be ejected from the sample with a kinetic energy (KE) equal to the difference of the binding energy consumed and the energy applied, such that

$$KE = eV - BE$$

Because the incident energy is fixed and the binding energies are known for each atom, oxidation state, and type of electron ejected (e.g., 1s, 2p, etc.), by measuring the kinetic energy of an ejected electrons, the identification and relative concentration of a given atom may be determined. XPS analysis utilizes the core electrons of the atoms to avoid any possible confusion arising from the difficulty in detection of valence electrons, with low kinetic energy, of similar oxidation states.

The copolymer samples were observed at two different angles, corresponding to the first 15 and 50 Å of the surface, in order to not only quantify the extent of siloxane enrichment, but also to gain some insight as to the overall depth of the siloxane enriched surface, before reversion to the bulk state occurs. A representative XPS scan is shown in Figure 3.4-32.

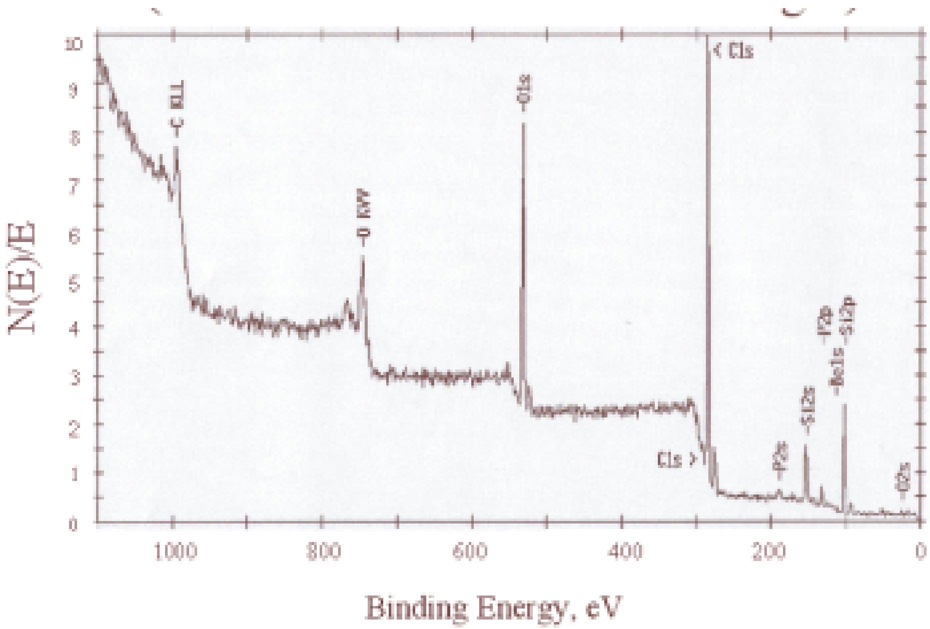


Figure 3.4-32 Characteristic XPS scan of a Poly (arylene ether phosphine oxide)-b-Poly(dimethylsiloxane) copolymer (5K/1300 sample at 90° angle of observation)

Using the sharp silicon 2p and the carbon 1s signals, a ratio of silicon to carbon could be established. The actual weight percent of siloxane present in the surface was then calculated from this compositional ratio. A summary of the XPS results and a comparison to the bulk composition are illustrated in Table 3.4-6.

Sample PEPO/PDMS	**PDMS Bulk, wt% (^{1}H NMR)**	**Surface PDMS[a], wt%**	
		15° (10 A)	**90° (50 A)**
5K/1300	**19**	**62**	**51**
10K/1300	**10**	**60**	**51**
5K/6.5K	**48**	**82**	**77**
5K/10K	**66**	**92**	**85**

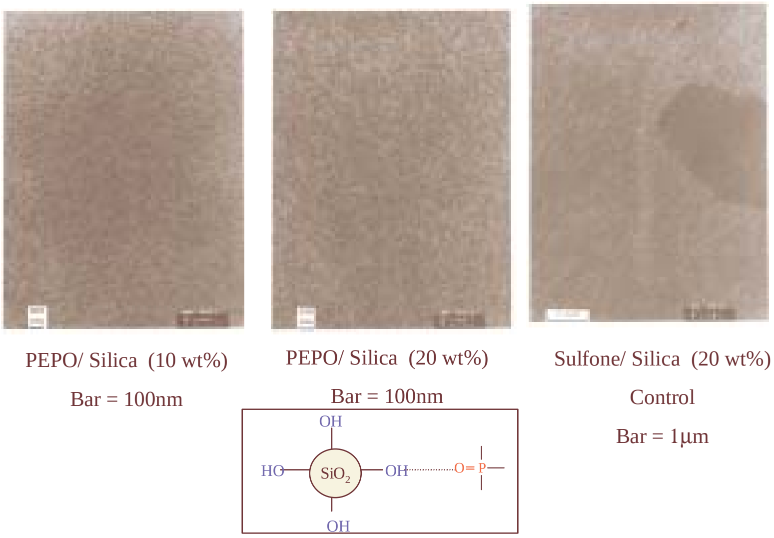
a. Calculated from XPS data: wt% = [33(Si2p/C1s)/(19.4(Si2p/C1s)+6.8)]x100

Table 3.4-6: Compilation of The XPS Surface Analysis

The XPS data shows a distinct pattern, indicating that the amount of surface enrichment is dependent on the length of the siloxane block. This observation is understandable because in order to migrate to the surface, the siloxane segment must be free to move. The segmental motion of the shorter blocks is restricted by covalent bonds to the PEPO more frequently than in the longer block lengths. Thus, the longer blocks will be more accessible to the air-polymer interface, affording greater siloxane content on the surface.

3.4.3 Preparation and Characterization of Poly(arylene ether phosphine oxide)-b-Poly(dimethylsiloxane) – Silica Nanocomposite Films

Previous experience within the McGrath research group has shown that the phosphine oxide moiety displays the ability to complex with metal salts and silica nanoparticles. Recently, Wang[128] has demonstrated this ability by solution blending poly(arylene ether phosphine oxide) and a colloidal suspension of 12 nm silica particles. Illustrated in the TEM images (Figure 3.4-33), the PEPO is able to uniformly distribute the silica particles throughout the film, while the use of an analogous polysulfone yields an agglomeration of the particles.



PEPO/ Silica (10 wt%)
Bar = 100nm

PEPO/ Silica (20 wt%)
Bar = 100nm

Sulfone/ Silica (20 wt%)
Control
Bar = 1µm

Figure 3.4-33: Demonstration of the PEPO/ silica Nanocomposites Compared to a Negative Control

In an attempt to extend this research, silica nanocomposite films were produced from the siloxane-phosphine oxide copolymers in an attempt to reveal any selective association of silica nanoparticles when simultaneously exposed to the complexing phosphine oxide moiety and the structurally and chemically similar siloxane blocks. To this end, copolymers of 10, 20, and 50 wt% siloxane were blended in solution with 12nm silica particles suspended in DMAc. The copolymers were dissolved in DMAc, then the requisite amount of the silica suspension was added to allow 10% of the phosphine oxide units on the copolymer chain to associate in a 1:1 fashion.

TEM images of the nanocomposites formed from 10 and 20 wt% siloxane copolymers (Figure 3.4-34,-35) revealed that the domain sizes of the copolymers were smaller than the particles to be dispersed, rendering visual evidence that selective association was impossible to determine. Still, copolymers maintained the ability to uniformly distribute the silica particles.

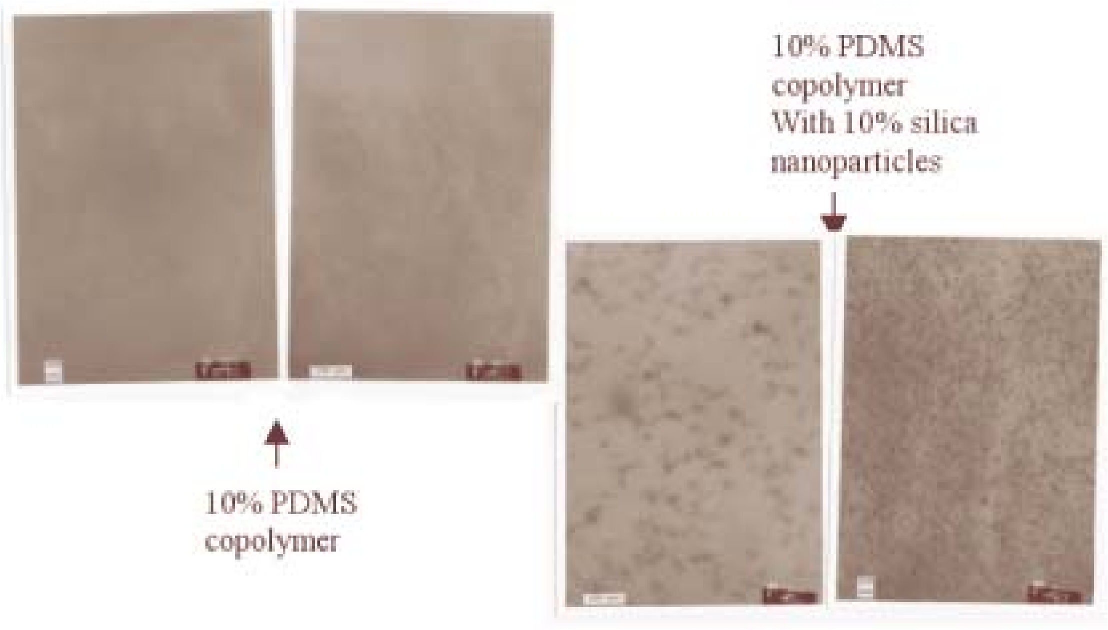


Figure 3.4-34: Comparison of 10 wt% Siloxane PEPO-PDMS –Silica Nanocomposite

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[128] Wang, S. In *Ph.D. Dissertation*; Virginia Polytechnic Institute and State University: Blacksburg, Va, 2000.

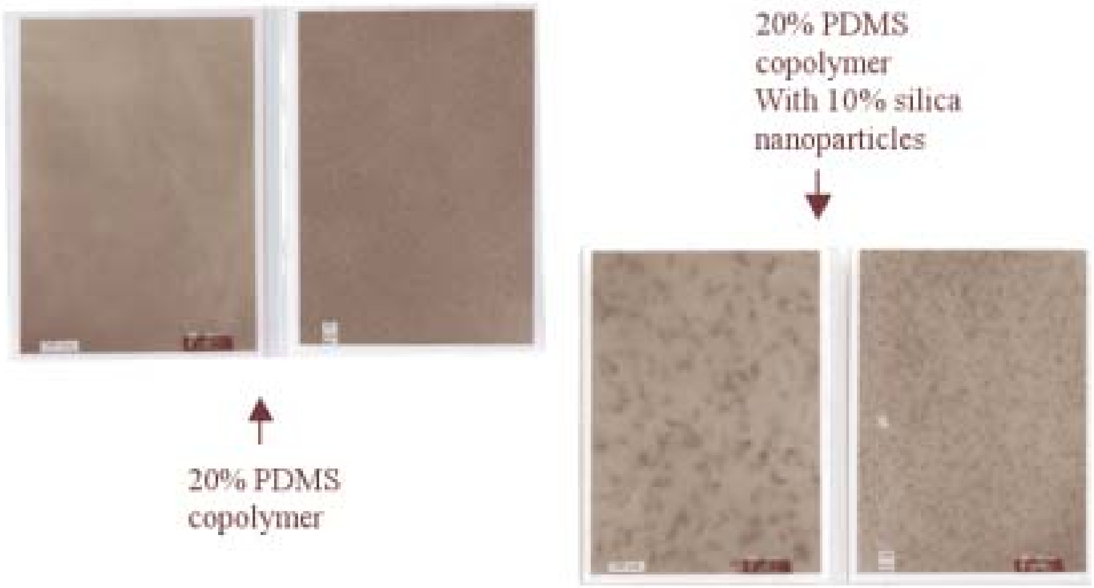

Figure 3.4-35: Comparison of 20% Siloxane PEPO-PDMS Copolymer –Silica Nanocomposite

In the case of the 50% siloxane copolymers, which showed the greatest degree of phase separation, it was hoped that the domain sizes would be large enough to observe selective association. However, a homogeneous DMAc solution was not attainable, therefore the copolymer solution was prepared in chlorobenzene, while the DMAc-silica suspension was used as received. It is believed that this may have led to the selective association of DMAc in the chlorobenzene solution, wherein the silica particles were not efficiently dispersed throughout the sample, as illustrated in Figure 3.4-36.

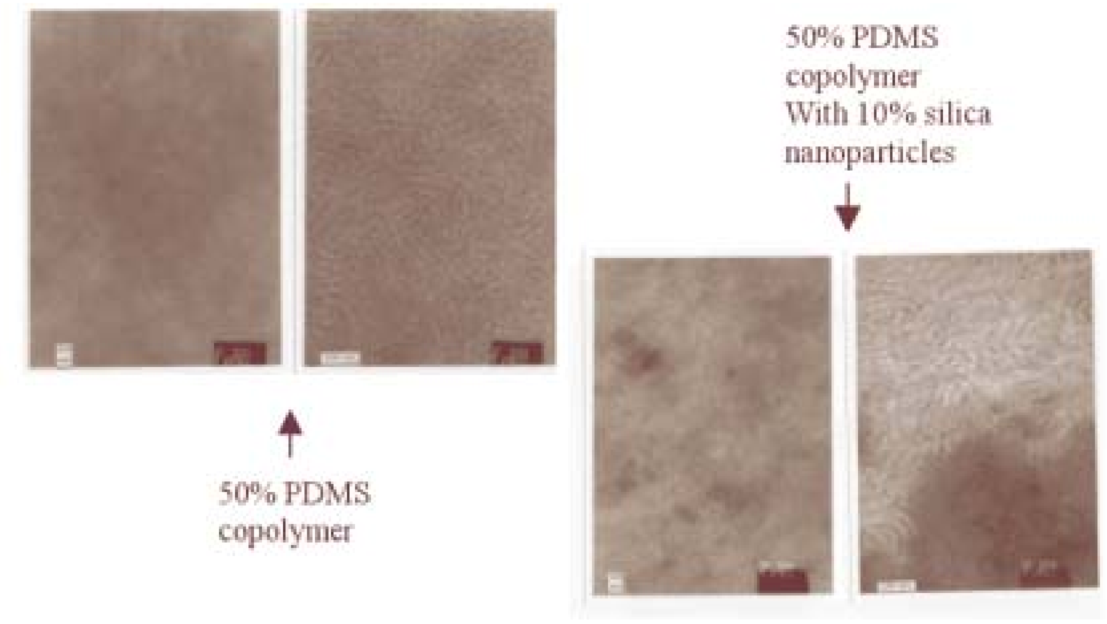

Figure 3.4-36: Comparison of 50 wt% Siloxane PEPO-PDMS-silica Nanocomposite Cast From Chlorobenzene

3.5 Conclusions

A series of three high molecular weight alternating poly(arylene ether phosphine oxide)-Poly(dimethylsiloxane) block copolymers were synthesized from preformed telechelic oligomers, via the silylamine-hydroxyl reaction. The oligomers were produced separately, using different chemistries, to afford well-controlled molecular weight materials with the appropriate functional chain ends, as verified by acid-base titration, ^{1}H NMR, and where applicable, by GPC analysis.

The hydroxyl functionality was provided by the use of a stoichiometric excess of bisphenol, as prescribed by the Carother's equation, in the nucleophilic aromatic substitution of bisphenol-A and bis(fluorophenyl)-phenylphosphine oxide to yield oligomeric poly(arylene ether phosphine oxide)s of 2,000, 5,000, and 10,000 g/mol. The silylamine oligomers of 1,300, 6,500, and 10,000 g/mol were produced using an anionic redistribution reaction employing a "transient" siloxanolate catalyst and commercially available 500 g/mol $\alpha-\omega$ dimethylamino-poly(dimethylsiloxane).

These oligomers were copolymerized to provide poly(arylene ether phosphine oxide) copolymers with varying degree of siloxane content and different component block sizes in an effort to present a variety of phase separated and possibly phase-mixed morphologies. One of the initial goals of this investigation was to develop a material with optically attractive properties that might rival those of the standards polycarbonates. Although the copolymers produced were optically clear, the desired combination of a high refractive index, coupled with a high Abbe number (low chromatic aberration), was not achieved. Despite this fact, a systematic study of block size effects on alternating block copolymer with chemically different component oligomers was an opportunity too attractive to ignore.

Therefore, a classical thermo-mechanical analysis was pursued, revealing the following trends. Thermo-oxidative char yields, and possibly fire retardance (as illustrated by an increase in the LOI estimation) of the copolymers increase as the siloxane loading increases. A significant change can be observed in the char yield and thus in the LOI calculation, between 35 and 45 wt % siloxane, possibly indicating that a minimal loading of siloxane is necessary before fire retardance can be observed.

Studies of the differential heat capacity, by DSC, showed mixed results. The sample sizes were often too small to yield reliable data when the segment to be studied was the secondary phase; any observable transitions would frequently be buried in the normal heat absorption of the dominant phase. The inability to garner reliable data from the DSC led to the use of DMA, a mechanical test, which is more sensitive to thermal transitions, since a loss in mechanical energy is reflected in a more easily measurable phase lag.

Results from the DMA analysis indicated that phase separation was apparent in each sample tested. Moreover, as a component increased in block size--and thus in overall concentration--its transition became sharper, indicating a greater extent of phase separation. However, it was also noted that phase mixing was simultaneously occurring in the secondary phases, evidenced by a constant broadening of transitions as a component became more “contaminated” with the dominant phase.

Additional mechanical analysis was used to elucidate the stress-strain behavior of the novel copolymers and evaluate their potential as thermoplastic elastomers. However, tensile testing showed no significant signs of rubber toughening with the smaller siloxane segments. And although the samples containing longer siloxane blocks did display lower tensile modulus, they failed to display adequate elongation for thermoplastic elastomeric applications.

The direct observation of the bulk morphologies by TEM support earlier conclusions of the thermal and mechanical testing that phase segregation was present in all of the copolymer samples tested. Additionally, the relatively constant domain size of the secondary phase suggests that the extent of phase mixing, though driven by the dominant phase, may be limited by the block length of the minor component. AFM analysis in the tapping mode was attempted to confirm the TEM findings, but the air-polymer surfaces tested revealed much larger siloxane domains than those evident in the bulk morphologies. The siloxane surface enrichment was quantified by XPS analysis, and a direct correlation between siloxane block length and the extent of surface enrichment was established.

An attempt to elucidate any preferential association between silica nanoparticles and the component segments of the siloxane-phosphine oxide copolymers resulted in inconclusive data, since the particles dispersed in the copolymer matrix were larger than the domain sizes present.

In summary, a series of three novel copolymers were produced, displaying a wide range of thermal and mechanical properties that are ultimately dependent on morphological effects dictated by the molecular weight of the parent oligomers.

4 Nylon 6,6 – Polydimethylsiloxane Copolymers

4.1 Introduction

4.1.1 Motivations for Copolymerization

Block copolymerization has long been seen as a route to permanently altering the physical and chemical properties of a given material.[2] By incorporating a segment of another polymer into the chemical structure of the initial polymer, a hybrid material displaying a combination of the properties of the pure polymers will result. Ideally, this material will retain most of the advantageous properties of the components, while eliminating the disadvantages. In this research, nylon 6,6 has been copolymerized with polydimethylsiloxane to enhance its fire resistance and decrease its hydrophilic nature.

Poly(hexamethylene adipamide), commonly referred to as nylon 6,6, is one of the world's most important engineering thermoplastics, with applications ranging from textile fibers to machined parts.[208] Nylon 6,6 is a tough, high melting material (T_m = 265°C) with good mechanical properties[206] due to the high degree of hydrogen bonding between amide linkages.[208] However, nylon 6,6 does have its drawbacks, as it tends to melt and drip during combustion, exacerbating an already hazardous situation.[209] In addition, the physical properties (moduli, tensile strength, etc.) are highly dependent upon the relative humidity of the surroundings.[213] The extensively hydrogen bonded nature of polyamide links result in an affinity for water. This associated water then acts as a plasticizer reducing the effective T_g of the material.

Polydimethylsiloxanes (PDMS) are known to impart fire resistance when incorporated into the backbone of polymers.[261] Improved fire retardance is achieved through the formation of a silicate-like char upon combustion in air. It is believed that

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[2] Noshay, A.; McGrath, J. E. *Block Copolymers-Overview and Survey*; Academic Press: New York, 1977.

[208] Kohan, M. I. *Nylon Plastics*; Wiley-Interscience: New York, 1973.

[206] Zimmerman, J. In *Encyclopedia of Polymer Science and Engineering*; 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Kroschwitz, J. I., Eds.; Wiley-Interscience: New York, 1987; Vol. 11, pp 315-353.

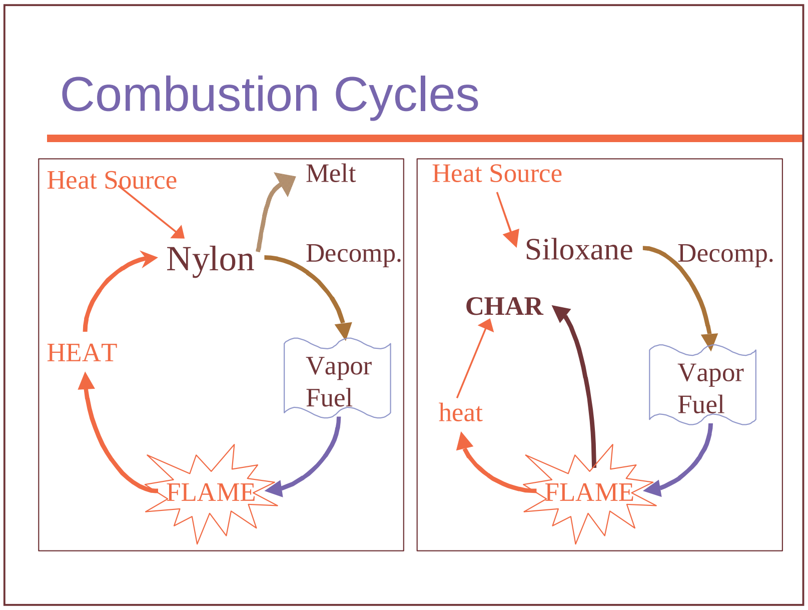
[209] Subbulakshmi, M. S.; Kasturiya, N.; Hansraj; Bajaj, P.; Ararwal, A. K. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **2000**, *C40*, 85.

[213] Ellis, T. S. *J. Appl. Polym. Sci.* **1988**, *36*, 451.

[261] Hashimoto, S.; Furukawa, I.; Kondo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 2356.

the resultant char then acts as an insulating layer to cut the fuel off from the fire.[209] In principle, this effect impairs its ability to sustain a combustion cycle, as illustrated in Figure 4.1-1. Additionally, this char layer may add a structural component to reduce drip.

Figure 4.1-1: Conceptual Representation of How Siloxanes Perform as Fire Retardants



Utilizing primary aminopropyl-terminated siloxane oligomers as co-reactants, amide bonds could be formed, covalently linking the siloxane segments to the polyamide backbone. Any added fire retardance would be a permanent non-leachable property of the new material. Secondly, non-polar PDMS segments have been shown to migrate to the air-copolymer interface when incorporated into copolymers.[257] Theoretically, this migration will create a siloxane enriched hydrophobic surface, decreasing the availability of hydrogen bonding sites to ambient moisture.

The idea of covalently bonding siloxane units to polyamides is not a novel concept. Kiyotsukuri et al.[262] produced siloxane–containing polyamides in 1987. Using their approach, a disiloxane amine monomer was polymerized with multiple diacids. However, they did not report mixed amine copolymers or the use of long chain siloxanes

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[209] Subbulakshmi, M. S.; Kasturiya, N.; Hansraj; Bajaj, P.; Ararwal, A. K. *J. Macromol. Sci. Rev. Macromol. Chem. Phys.* **2000**, *C40*, 85.

[257] Dwight, D.; McGrath, J. E.; Lawson, G.; Patel, N.; York, G. In *Multiphase Macromolecular Systems*; Culbertson, B. M., Ed.; Plenum Press: New York, 1989; pp 265-288.

[262] Kiyotsukuri, T.; Tsusumi, N.; Ayama, K. *J. Polym. Sci., Part A* **1988**, *26*, 807.

and the data disclosed concentrated solely on the amide-linked disiloxane units. Still, the research efforts described in this dissertation are believed to be novel both in methodology and resultant materials.

4.1.2 Methods of Copolymerization

The actual creation of covalent bonds between a pair of highly incompatible (Nylon hydrophilic / PDMS hydrophobic) materials proved to be a challenging synthetic endeavor. Numerous synthetic approaches were explored before a successful procedure was discovered. These approaches included mimicking the current industrial aqueous "Nylon salt" high-pressure reaction using an ambient pressure melt ester-amidolysis reaction, and a melt polymerization method combining the positive aspects of both the salt and aminolysis approaches.

Initial efforts to synthesize nylon 6,6-siloxane block copolymers involved the adaptation of the industrial polymerization of nylon by a batch process. A 1528 g/mol propylamine-terminated siloxane and the conjugate amount of adipic acid were added to the aqueous salt solution to facilitate incorporation. Unfortunately, the difference in polarity of the reaction components (water / PDMS) prevented the production of high molecular weight materials.

Ester aminolysis was the next method explored. The additional non-polar nature of the methyl ester of adipic acid, combined with its inability to form the nylon salt and the absence of water, should allow the incorporation of the siloxane oligomer. However, the polar/non-polar interactions were still a significant issue and needed to be addressed before the synthesis of siloxane-nylon copolymers could proceed. Pre-reacting or endcapping the amine-terminated siloxane with the methyl ester should effectively increase the polarity of the siloxane. Additionally, endcapping in conjunction with a slow addition of diamine would allow the mixture to slowly change in polarity, affording a miscible reaction solution and thus produce a high molecular weight material. However, a high molecular weight control polymer was not attainable since the volatile diamine sublimed out of the reaction at temperatures necessary to maintain a molten reaction mixture. The inability to produce a control polymer inspired little optimism for the production of siloxane copolymers via aminolysis and the search for another approach began anew.

Ultimately, a successful route was developed. The key to this approach was to eliminate the addition of water from the initial reaction conditions, while preserving the hydrolysis mechanism’s ability to achieve high molecular weight. The exclusion of excess water would circumvent the initial incompatibility issues experienced when a siloxane is added to an aqueous solution. However, the utilization of a pressure reactor would allow the development of high molecular weight because the diamine cannot sublime easily while under pressure. This minor modification of the industrial nylon 6,6 route may help facilitate the ultimate development of siloxane-nylons as commercial products.

4.2 Experimental

4.2.1 Commercially Available Monomers and Reagents

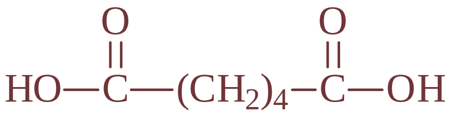
Adipic Acid

Supplier: Aldrich Chemical Company

Molecular Formula: $C_6H_{10}O_4$

Molecular Weight: 146.14 g/mol

Melting Point: 152-154°C



$\mathrm{HO-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-OH}$

Purification: The adipic acid was obtained in monomer grade (99.9% purity) that required no further purification beyond vacuum drying at 100°C overnight prior to use. However, if needed, adipic acid may be recrystallized from ethanol.

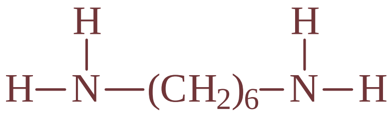
Hexamethylene Diamine (HMDA)

Supplier: Aldrich Chemical Company

Molecular Formula: $C_6H_{14}N_2$

Molecular Weight: 116.21 g/mol

Melting/Boiling Point: 42-45 / 204-205°C



$\mathrm{H-\overset{\overset{H}{|}}{N}-(CH_2)_6-\overset{\overset{H}{|}}{N}-H}$

Purification: Hexamethylene diamine was purified by distillation under reduced pressure (bp~ 135°C). The purified fraction was allowed to crystallize and was stored under nitrogen in a round-bottomed flask until use.

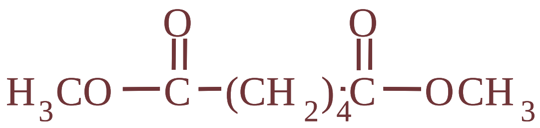
Dimethyl Adipate (dimethyl ester)

Supplier: DuPont Chemical

Molecular Formula: $C_8H_{14}N_2$

Molecular Weight: 174.20 g/mol

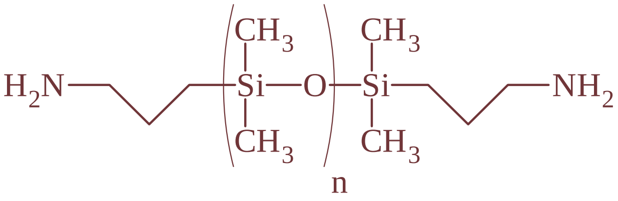
Boiling Point: 109-110°C/ 14mm



$\mathrm{H_3CO-\overset{\overset{O}{\|}}{C}-(CH_2)_4\overset{\overset{O}{\|}}{C}-OCH_3}$

Purification: Dimethyl adipate was graciously supplied by DuPont chemical and was used as received without further purification.

α,ω-Bis(aminopropyl)-poly(dimethylsiloxane)



Supplier: Shin-Etzu

Molecular Formula: Oligomer n=19

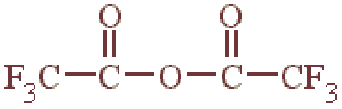
Molecular Weight: 1525 g/mol

Purification: The endcapping reagent was first characterized, for purity and molecular weight, by both ^{1}H NMR and Potentiometric Titration. Once assured of purity, the oligomer was used as received.

Composition of "Salt Bath" used for High Temperature Reactions

Potassium Nitrate:	KNO_3	53%
Sodium Nitrite:	$NaNO_2$	40%
Sodium Nitrate:	$NaNO_3$	7%
Melting Point:		~15°C

Trifluoroacetic Anhydride



Supplier: Aldrich Chemical Company

Molecular Formula: $C_4O_3F_6$

Molecular Weight: 210.03 g/mol.

Boiling Point: 39-40°C

Purification: Trifluoroacetic anhydride was obtained at 99 +% purity that required no further purification and was used as received

4.2.2 Attempted Synthesis of Nylon 6,6 – Siloxane Copolymers Via Aqueous Industrial Method

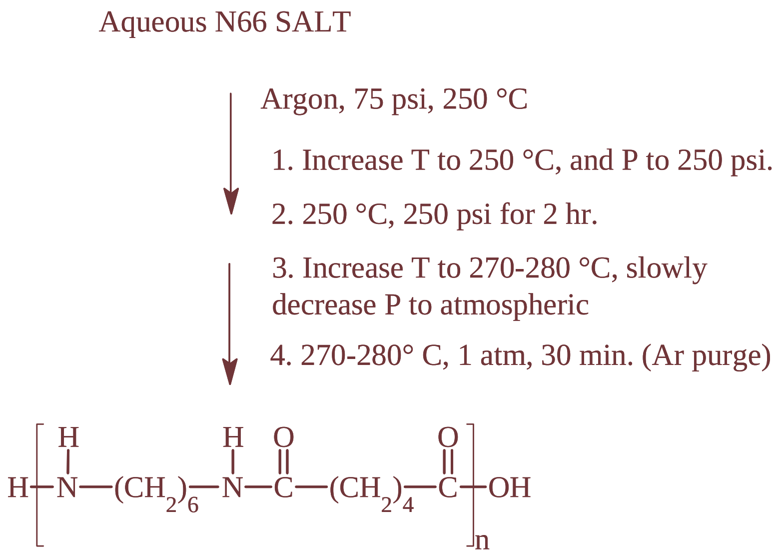
Synthesis of the "Nylon Salt":

11.6 g (0.01 mol) of vacuum distilled hexamethylene diamine (HMDA) was dissolved in 100 mL of methanol at 50°C. In a separate flask, 14.6 g (0.01 mol) of adipic acid was dissolved in 100 mL of methanol at 50°C. The two equimolar solutions were combined at the elevated temperature to form an insoluble salt. The mixture was stirred 50°C for 1hr. The solution was then cooled to room temperature and placed in a refrigerator overnight to maximize yield. The resultant salt was isolated via filtration and washed with hot (50°C) methanol. The salt was then vacuum dried overnight at 110°C. Yield at this point was 93%. The salt was then recrystallized from an ethanol/water mixture (4/1 ratio) and the final product was isolated with an overall yield of 77% and agreed well (198-199°C) with the melting point reported in literature and of an industrial reference material (202-205°C and 197-198°C, respectively).

Synthesis of Control Nylon 6,6

Initial attempts to produce nylon 6,6 – siloxane copolymers paralleled the industrial batch reaction as closely as laboratory conditions permitted. However, before copolymers could be explored, a control polymer was produced to ensure a product consistent to commercial samples could be produced.

Approximately 75 g of nylon 6,6 salt and 100 mL of water were added to a 300 mL Parr pressure reactor fitted with an anchor stirrer, a thermocouple, a pressure gauge, gas inlet and outlet valves, and a safety release disc rated for 1000 psi (Figure 4.2-1). The reactions were conducted on a 100 mL scale to insure immersion of the thermocouple. The reaction vessel was sealed, followed by a cyclic purging (75 psi to atmospheric) of argon to exclude oxygen from the reaction. The mixture was then heated to 250°C. It should be noted that it took approximately 1.5 hours to reach 250°C. This is reasonable considering the large thermal lag inherent in the thick stainless steel reaction vessel and the amount of energy required for the vaporization of water under pressure. A steam bleed was established to maintain a constant pressure of 300 psi (~17-18 atm.) The reaction was allowed to proceed at 250°C for 2 hours, venting steam when necessary. After 2 hours, the temperature was increased to 270°C, while the pressure was reduced by 50 psi every 15 minutes until atmospheric pressure was reached. The reaction continued at ambient pressure under an argon purge until the viscosity increased to a point that stirring was no longer possible.



$$H\left[\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_n OH$$

Scheme 4.2-1: Industrial Polycondensation of “Nylon 6,6 salt”

Figure 4.2-1: Parr Pressure Reactor

Trifluoroacylation of Polyamides to Enable Analysis by Gel Permeation Chromatography (GPC)

Utilizing the method of Schutenburg and Schultz,[228] polyamide samples were cryogenically ground to a powder, and subjected to derivatization reactions to enable analysis in common GPC solvents. A typical reaction is as follows.

5.0158 g of powdered nylon 6,6, supplied by DuPont was dispersed in 50 mL of dried chloroform in a 100 mL round-bottomed flask. The flask was then sealed with a wire-tied septa, purged with flowing nitrogen for 5 minutes, and submerged in an ice bath. 10 mL of trifluoroacetic anhydride was added via syringe. The mixture was allowed to react for 10 hours instead of the prescribed 6 hours, to compensate for the large initial particle size. Over the course of the reaction, the dispersed polymer particles are dissolved affording a clear, slightly yellow, homogeneous solution. The derivatized polymer was then isolated by precipitation into diethyl ether and dried at 80°C under vacuum for 2 hours.

Copolymerization Attempts

The synthesis of 5 and 10 wt% siloxane copolymers was attempted using the aqueous salt method. In order to facilitate the formation of the copolymer amide linkage, a PDMS/ adipic acid salt was formed prior to reaction. A typical reaction procedure for the production of a 5% PDMS copolymer is as follows. 3.4691 g of 1528 g/mol propylamine terminated siloxane was added to 100 mL of water. Then 0.3868 g of adipic acid was slowly added to the agitated mixture thereby forming a suspension. To this suspension, 66.15 g of nylon 6,6 salt was added and the mixture agglomerated. This swollen gel-like substance was then transferred to the Parr reactor followed by a cyclic argon purge. Copolymerization proceeded in accordance to the control polymerization profile: temperature increase to 250°C, pressure bleed to maintain 300 psi over 2 hours, followed by a slow return to ambient pressure, coupled with an increase in temperature to maintain a molten reaction mixture. Unfortunately, the materials produced were brittle and not uniform in color, indicating that although a mechanical blend may have been

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[228] Schuttenburg, H.; Schultz, R. C. *Angew. Chem. Int. Ed. Engl.* **1976**, *15*, 777.

achieved, true incorporation was not.

4.2.3 Attempted Synthesis of Nylon 6,6 – Siloxane Copolymers Via Ester Aminolysis

Attempted Synthesis of Control Nylon 6,6

13.75 g (0.079 mol) of dimethyl adipate (dimethyl ester) was placed in a glass pressure reactor assembled as shown in Figure 4.2-2. 9.26 g (0.079 mol) of hexamethylene diamine (HMDA) was then transferred to the addition funnel, while the reaction vessel was heated 160°C. This temperature was selected to ensure even heating and a consistent molten heat source as the salt bath did not melt until 150°C. The HMDA was melted with the use of a heat gun and then added drop-wise, over 20-30 minutes, to the dimethyl ester. This approach was used so that it would correlate with the copolymerizations requirement to slowly change the polarity of the mixture. Once all of the HMDA was added, an immediate methanol cloud could be observed above the reaction mixture and the nitrogen purge was increased. After ~30 minutes, crystallization began to become apparent. The bath temperature was then increased to 280°C and allowed to react for 2 hours before a partial vacuum was applied. The reaction proceeded under partial vacuum for 10 minutes before the nitrogen flow was halted allowing a full vacuum (150 mtorr) to be established. Nitrogen flow was resumed after 5 hours and the pressure was increased to atmospheric while the polymer melt was allowed to cool. The resultant product was an off-white material, apparently low in molecular weight.

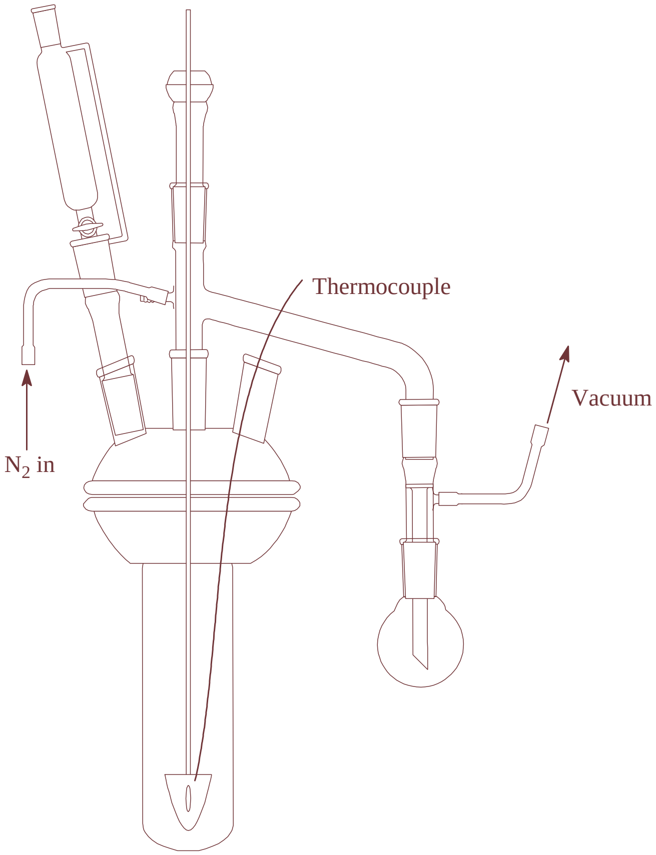


Figure 4.2-2: Glass Reactor for Ester Aminolysis Reactions

Copolymerization Attempts

Although production of a satisfactory control polyamide was not evident, the copolymerization of 5 and 10 wt% siloxane-nylon were attempted. It was thought that the viscous siloxane solution might prevent the sublimation of volatile diamine long enough for the diester and ester-capped siloxanes to react. The reaction profile to produce 60 g of a 5 wt% siloxane-nylon copolymerization is as follows.

23.33 g (0.2 mol) of HMDA was transferred to a flame-dried addition funnel, and fitted to the glassware as previously shown in Figure 4.3-2. Next 3.3 g (0.002 mol, 1528 g/mol) of PDMS and 35.2 g (0.202 mol) of DBE-6 were added to the reaction vessel and subjected to a nitrogen purge. Meanwhile a salt bath was heated to 160°C, once thermally equilibrated the reaction vessel was lowered and endcapping of the PDMS began. Almost immediately a vapor cloud was evident indicating the production of methanol via aminolysis. After 2 hours, the HMDA was introduced dropwise. Upon addition of the HMDA, a slight haziness began to appear which evolved into a two phase system. After 30 minutes, a bi-layered melt was observed and crystallization began in the lower layer assumed to be the polyamide. The reaction temperature was increased to 280°C and homogeneity was restored after 3 hours. A vacuum was applied to aid the evolution of methanol and the reaction was halted after 2.5 hours of reduced pressure. The reaction mixture was cooled to room temperature, yielding a slightly greasy, almost waxy, white to off-white material.

4.2.4 Synthesis of Nylon 6,6 – Siloxane Copolymers Via Solid Nylon Salt Reactions

Synthesis of Control Nylon 6,6 via Solid Nylon Salt Reaction

Solid nylon 6,6 salt (50.71 g) was placed in a 300 mL Parr pressure reactor, fitted with an anchor stirrer, a thermocouple, a pressure gauge, gas inlet and outlet valves, and a safety release disc rated for 1000 psi, as shown in Figure 4.2-3. The reactions were conducted on a 50 g scale to ensure the immersion of the thermocouple. The reaction vessel was sealed followed by a cyclic purging (75 psi to atmospheric) of argon to exclude oxygen from the reaction. The reaction mixture was then heated to 260°C. It should be noted that in the absence of water, 260°C was achieved in approximately 30 minutes. As the temperature increased, so did the pressure. However, the amount of steam produced by the "solid" salt reaction is much lower than in the case of an aqueous solution. With this in mind, the overall pressure of the reaction was maintained, via steam bleed, at 200 psi. The reaction was allowed to proceed at 260°C for 3 hours, venting steam when necessary. Then the temperature was increased to 270°C while the pressure was reduced by 50 psi every 15 minutes until atmospheric pressure was reached. The reaction was halted after 30 minutes at ambient pressure under an argon purge, as the viscosity had increased to the point that stirring was no longer possible.

Figure 4.2-3: A closer look at the configuration of the Parr Reactor

Polydimethylsiloxane- Adipic Acid “Homopolymerization”

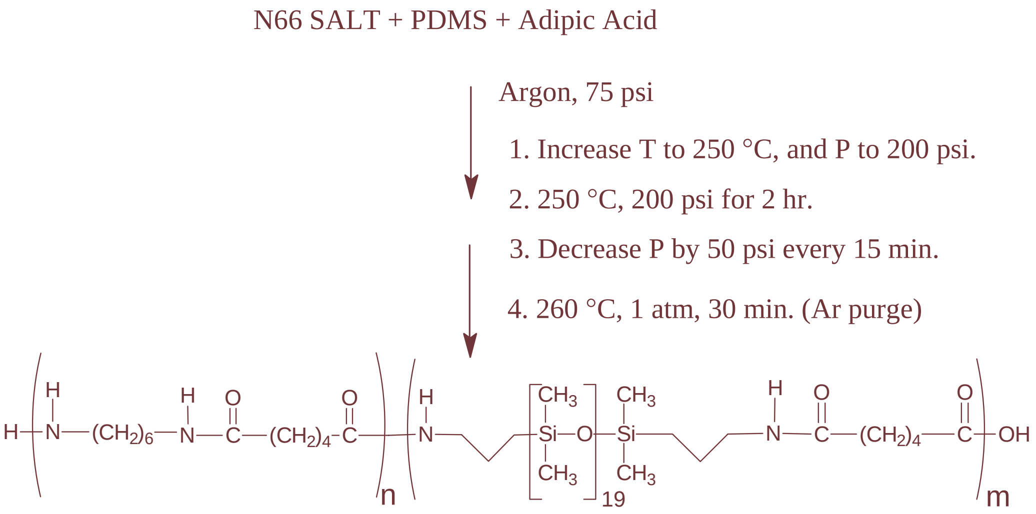
The ability to form siloxane-amide bonds under conditions similar to those of the copolymerization reactions was confirmed by the “homopolymerization” of PDMS and adipic acid.

PDMS, 3.6378 g (M_n= 1525, 0.00238 mol) and 0.3500 g (0.00239mol) of adipic acid were placed in a 20 mL vial that was sealed with a wire-tied septum. An inert gas purge was then applied using 18 gauge needles as the gas inlet and outlet. The vial was lowered into a 200°C salt bath, resulting in the immediate development of a cloud of water vapor above the reaction solution. It should be noted that the initial reaction mixture was heterogeneous; however, upon heating the solution cleared and thickened. In fact, the solution became so viscous that a sample could not be readily drawn though an 18-gauge needle. Subsequent analysis by chloroform GPC revealed an M_n of 17,500 g/mol was achieved in just 1 hour at 200°C.

Copolymerization Attempts

A series of 10-50 wt% siloxane-nylon copolymers was prepared in accordance to the procedure outlined in the solid salt synthesis of the control nylon 6,6. The only alteration was the inclusion of the siloxane and the conjugate amount of adipic acid required to facilitate incorporation.

For example, in the synthesis of a 10wt% siloxane copolymer, 50.84 g of solid nylon salt, 5.084 g (0.00333 mol) of 1524 g/mol amine-terminated siloxane and 0.487 g (0.00333 mol) of adipic acid were added to the Parr reactor. The reactor was then sealed and cyclically purged with argon. The mixture was then allowed to react as prescribed in the control polymerization (Scheme 4.2-2).



Scheme 4.2-2: Copolymerization Via Solid Nylon Salt Reaction

Extraction of Nylon Copolymers with 2-Propanol

In order to confirm the incorporation of the polydimethylsiloxane oligomers, powdered copolymer was extracted with refluxing isopropyl alcohol for 5 days to remove any non-bonded siloxane trapped in the polyamide matrix. Isopropyl alcohol (IPA) was selected for the extraction medium as it is an excellent solvent for siloxanes and the temperature of refluxing IPA is above the T_g of pure nylon 6,6 (52°C). Thus, any siloxane that is not tethered to the nylon particles should be removed by the conclusion of the experiment. Copolymer samples were analyzed by solid state NMR before and after extraction to determine the levels of siloxane incorporation.

4.3 Characterization Methods

4.3.1 Intrinsic Viscosity

The intrinsic viscosity, [η], of the oligomers and polymers synthesized were measured using a Cannon-Ubbelholdhe viscometer at 25°C in m-cresol. The intrinsic viscosity was obtained by measuring the specific viscosity, $\eta_{sp}= (\eta / \eta_0) - 1$, and the reduced viscosity, $\eta_{red} = \ln(\eta / \eta_0)$, at four dilutions and extrapolating (η_{sp} / c) and (η_{red} / c) to zero concentration.

4.3.2 Nuclear Magnetic Resonance (NMR) Spectroscopy

Solution NMR

When possible, proton (^1H) and carbon (^{13}C) NMR spectra were acquired with Varian 400 mHz instrument in $CDCl_3$ without internal standard (tetramethlysilane, TMS), which would interfere with Si-CH_3 quantitation. The NMR spectra were used to determine purity, and estimate the molecular weight of the oligomers utilized.

Solid State NMR

Polymerized samples were analyzed by solid state ^{29}Si and ^{13}C NMR on a 300 MHz Bruker MSL 300 NMR. The effective field strength was 75.74 MHz and 59.60 MHz for ^{13}C and ^{29}Si, respectively. The presence of PDMS in the copolymerized samples was determined by ^{29}Si NMR, while ^{13}C NMR was used for quantification of the amount of siloxane in each sample. This was accomplished by evaluation of the ratio of the silyl-methyl groups to the carbonyl resonance of the amide links followed by a conversion to the weight percent of PDMS present.

4.3.3 Potentiometic Titration of Oligomers

The number average molecular weight (M_n) of the aminopropyl-terminated siloxane oligomer was determined by potentiometric titration of the functional endgroups using a Fisher Titrimeter II automatic titration system. A calomel electrode was used in conjunction with a standard double junction reference. Samples of the siloxane oligomer were dissolved in isopropanol and titrated with a 0.5 N solution of HCl in isopropanol.

The sample size for the oligomer was chosen to give a titration volume of approximately 4 mL. This is easily accomplished by calculating the amount of oligomer, assuming the target molecular weight was achieved, needed to neutralize 4 mL of titrant. The oligomer was weighed directly into a 100 or 150 mL beaker, followed by 60-70 mL of solvent. Once the oligomer was completely in solution, the electrodes were lowered and the titration was begun. The titrator was operated in the automatic endpoint seeking mode (AEP) and when an endpoint was detected, the computer noted the time, volume and final potential (mV). The electrodes were then rinsed with titrant solution, followed by water and placed in a pH 4.0 buffer for storage. Any amount of titrant consumed by the solvent was corrected for by titrating the same volume of neat solvent to the same potential and subtracting this blank volume from that of the sample titration. The M_n of the oligomers could then be determined as follows.

$$M_n = \frac{2 * W}{N * (V - V_B)} \tag{13}$$

In Equation 13, 2 is the number of endgroups per chain, W is the weight of the oligomer sample (g), N is the normality of the tirtrant (moles/mL), V is the volume of titrant needed to reach the endpoint, and V_B is the volume of the blank.

4.3.4 Gel Permeation Chromatography (GPC)

Molecular weights (M_n) as well as polydispersity indices of the oligomers and the derivitized polyamides were obtained through the use of a Waters 150C ALC/GPC chromatograph fitted with parallel differential refractive index and Viscotek Model 100 viscosity detectors. HPLC grade chloroform filtered through a 0.5 μm Teflon filter served as the mobile phase. A series of three stainless steel columns (7.8 mm I.D. x 30 cm) packed with crosslinked polystyrene gel (Waters μstyragel HT, 10^2, 10^3 and 10^4 Å columns, with a mean particle diameter of 10 μm) acted as the stationary phase. Samples were prepared at known concentrations (~ 2-4 mg/mL) in the mobile phase and filtered through 0.2 μm Teflon filters prior to analysis. The injection volume was 200 μL and the flow rate was set to 1.0 mL/min. The temperature of the system (injector, lines, columns, and detectors) was held to a constant 25°C. The use of the parallel detectors and careful calibration allowed for the resultant data to be taken as absolute molecular weights under the principle of universal calibration.

4.3.5 Thermogravimetric Analysis (TGA)

Initial evaluation of thermal stability was established via dynamic TGA using a Perkin-Elmer TGA 7 instrument. Samples (~4-10 mg) were heated at 10°C/min in a flowing air environment, in a platinum sample pan, unless otherwise noted. The percent weight loss was measured as a function of temperature.

4.3.6 Bench Flame Tests

Though not quantitative, the direct observance of the behavior of the novel materials when exposed to a flame was informative. Bulk samples, roughly the same size as the control polymer and the successful copolymers, were held in forceps and ignited with a Bunsen burner till a sustained flame was apparent. The sample was then removed from the burner and observations concerning its behavior were recorded.

4.3.7 Differential Scanning Calorimetry (DSC)

Glass transition temperatures, melting points and recystallization temperatures above 25°C were detected using a Perkin-Elmer DSC 7 instrument. Scans were run from 25-300°C at 10°C/min, both heating and cooling under nitrogen. The samples (4-8 mg) were sealed in crimped aluminum sample pans for analysis. The data reported was taken from the second heating after annealing for 3-5 min above the crystalline melting point of the samples.

4.4 Results and Discussion

4.4.1 Characterization of $\alpha-\omega$- Bis(aminopropyl)-poly(dimethylsiloxane)

Evaluation of Purity and Molecular Weight

A low molecular weight propylamine-terminated oligomer was supplied by Shin-Etzu Corp. Upon arrival the oligomer was analyzed by ^{1}H NMR for purity and molecular weight using deuterated chloroform stored over molecular sieves. The spectrum, shown in Figure 4.4.-1, displayed only the expected major signals. Si-CH_3 near 0.0 ppm, CH_2s at 0.51, 1.43, and 2.66 ppm and a broadened NH_2 at 1.25 ppm the remainder of the spectrum is clear. The absence of extraneous peaks provided compelling evidence of purity, and a ratio of the integration values of the major signals present was calculated to determine the molecular weight of the oligomer. This resulted in a silicon:nitrogen ratio, consequently with 2 amine endgroups on each oligomer, the siloxane chain was, on average, 19 units long. This corresponds to a molecular weight of 1525 g/mol. This initial molecular weight was then used to determine the sample size for acid-base titration.

The endcapping reagent was then titrated with 0.05 N HCl in isopropyl alcohol to confirm the NMR estimation. Again, multiple analysis methods were used to provide as accurate a molecular weight as possible and reduce the effect of possible error on subsequent reactions. The acid-base titration of the terminal amine group resulted in the consistent observation of a sharp endpoint resulting in an equivalent weight of ~1500 g/mol. The siloxane titration was quite straightforward, similar to the titration of the dimethylamino-functional siloxanes discussed previously.

4.4.2 Attempted Synthesis of Nylon 6,6-Siloxane Copolymers Via Aqueous Industrial Method

The initial approach for the production of nylon 6,6-siloxane copolymers was to (1) parallel the current industrial approach for the synthesis of nylon 6,6, and (2) add the functional siloxane oligomer in as a co-monomer. By adding a conjugate molar amount of adipic acid it was hoped that the siloxane would "chain extend", making the oligomer more polar as the growing polar chain ends became incorporated into the nylon melt. It is important to realize that this approach was an initial investigation, and as such, many of the factors that will be discussed are largely qualitative issues.

Synthesis and Characterization of the "Nylon 6,6 Salt"

The production of the nylon salt was a facile process requiring only minutes to perform. However, to ensure the elimination of contaminants (such as trapped unassociated diacids or diamines), the salt was allowed to crystallize from solution overnight, followed by recrystallization from 4:1 ethanol/water. The resultant material showed a melting point (198-199°C) consistent with that of a commercial sample (197-198°C) and literature values (202-205°C).

Synthesis and Characterization of Control Nylon 6,6 via Aqueous Salt Technique

A high molecular control polyamide was produced from a high concentration (75% solids) aqueous salt solution in the method paralleling the industrial synthesis previously described. The polymer obtained was a relatively hard off-white to yellow semi-crystalline material, which was removed from the reactor as a solid mass. It was removed from the anchor stirrer by fracturing the sample with a hammer and chisel. Intrinsic viscosity measurements, obtained in 25°C m-cresol, indicated a high molecular weight comparable to that of an industrial control supplied by DuPont.($\eta_{\text{experimental}}$= 1.16 dL/g, η_{DuPont}= 1.12 dL/g). Derivatization by N-trifluoroacetylation produced samples soluble in chloroform and able to be analyzed by GPC. Comparisons of both GPC and intrinsic viscosity data between the material produced in our labs and the industrial control sample were favorable, indicating the successful production of Nylon 6,6. The numerical results of analysis are as follows: the experimentally produced sample showed an M_n of 49,300 g/mol with a polydispersity index (PDI) of 2.56, while the industrial sample displayed slightly lower values (M_n=31,900 g/mol, PDI= 2.3).

Copolymerization Attempts

Attempts to produce 5 and 10 wt% siloxane–nylon copolymers were only marginally success. The order of assembly of the pre-polymerization reaction was thought to be key to the formation of high molecular weight copolymers. Extending this concept of the addition of a preformed nylon salt to the siloxane-adipic acid interaction, the amine terminated siloxane was dispersed in water. The required amount of adipic acid was then added to this dispersion, at which time the formerly clear dispersion clouded to form a suspension. The exact structure of this suspension was not elucidated, but it was thought to be analogous to a “nylon salt”. It was proposed that this polar association at the ends of the siloxane chain would reside exclusively at the interphase of any siloxane domains present in the suspension. Next, the proper amount of solid nylon salt was added to the reaction mixture. The salt quickly lost its crystalline character, but the reaction mixture agglomerated into a hydrogel-like mass. This viscous, heterogeneous, mass was then introduced to the reaction bomb and was cyclically purged with argon. Polymerization was then attempted according to the procedures established for the production of high molecular weight nylon 6,6.

The resulting materials were observed to be opaque, viscous melts that yellowed upon cooling, and upon simultaneous exposure to atmospheric oxygen. Solidification yielded inhomogeneous samples with streaks of white through discolored regions. In addition, the samples obtained were significantly more brittle than the nylon homopolymer previously produced, and the brittleness observed increased as the siloxane content was increased from 5 to 10 wt%. Because the pressure reactor used was stainless steel, the conditions during the reaction could not be ascertained. Given that the reaction mixture was heterogeneous at the beginning of the reaction and showed evidence of heterogeneity in the resulting materials, there was no method to ensure the participation of all reactive groups necessary to achieve a high molecular weight copolymer.

In summary, the expectation that the association of the amine-terminated siloxane-adipic acid suspension would be able to counteract the hydrophobicity of the siloxane oligomer was dispelled by the inability to observe a homogeneous reaction solution during any stage of the polymerization. Without the observance of a miscible reaction solution or a mechanically sound end product, convincing arguments supporting incorporation of siloxane into the polymer backbone could not be proposed.

4.4.3 Attempted Synthesis of Nylon 6,6- Siloxane Copolymers Via Ester Aminolysis

A subsequent approach was to use ester aminolysis to avoid the incorporation of water in the reaction mixture. Additionally, a slow addition of the diamine to a prereacted or endcapped siloxane oligomer would allow the polarity of the reaction mixture to be increased slowly. This would hopefully allow the siloxane oligomer to gain a more polar nature as the molecular weight of the polyamide segments increased. Furthermore, since high pressure is not required for the formation of the amide linkages, the use of a glass reaction apparatus is practical, allowing direct observation of the molten reaction as it proceeds along the reaction profile and becomes a more polar mixture.

<u>Synthesis of Control Nylon 6,6</u>

Again, in order to ensure that high molecular weight copolymers may be produced, a nylon homopolymer was utilized to gain familiarity with the reaction and establish a base procedure. Thus, hexamethylene diamine was slowly added (20-30 min) to a dimethylester of an adipic acid at 160°C, in order to correlate this synthesis with the anticipated copolymerization conditions. The addition of the diamine to the hot diacid resulted in the immediate formation of a vaporous cloud (assumed to be methanol), as well as a solid substance apparently subliming from the molten oligomer (this substance was later proven to be diamine by NMR analysis). The growing homopolymer melt was clear, yellow, and slightly viscous. Approximately 30 minutes after the diamine addition was completed, crystallization became apparent, first as opacity in the flowing melt, followed by solidification. The oligomer began to flow again after the temperature was increased to 280°C, above the melting point of the expected polymer. The polymer melt was then held at this temperature, under flowing nitrogen for 2 hours before a vacuum was applied to facilitate high molecular weight formation.

Unfortunately, despite multiple attempts employing varying molar excesses of diamine, at various heating and addition rates, a homopolymer comparable to the industrial sample could not be produced. This conclusion was based on the fact that the materials produced via ester aminolysis showed intrinsic viscosities ranging from 0.54 to 0.80 dL/g, significantly lower than that of the industrial control (1.12 dL/g).

Copolymerization Attempts

Nylon copolymers containing 5 and 10 wt% siloxane were then attempted, as follows. The siloxane oligomer was prereacted at 160°C with the dimethylester for 2 hours, in order to increase the polarity prior to the addition of the diamine. During this endcapping procedure a methanol cloud was formed, and the clear, colorless solution yellowed, but remained homogeneous. However, upon addition of the diamine, more methanol was released and the solution began to haze, possibly the result the crystallization of nylon oligomers. The reaction was allowed to continue until the haziness developed into definite crystallization. The temperature was maintained at 280°C, at which point a two phase system began to develop. A brownish oily layer separated from the crystallizing solid. At the conclusion of the reaction, the isolated product was a greasy, almost waxy, white/yellow solid. The observance of phase separation during the reaction, combined with the greasy quality of the product, indicated that copolymerization did not occur.

4.4.4 Synthesis of Nylon 6,6 – Siloxane Copolymers Via Solid Nylon Salt Reactions

Utilizing the positive aspects of the two approaches explored earlier, the third and final approach to producing siloxane-nylon copolymers used pressure to keep the volatile diamine and diacid in the melt, while the absence of water and endcapping of the siloxane limited the polar/nonpolar effects on the polymerization.

Synthesis of Control Nylon 6,6

The synthesis of a control material was required to determine what effect the elimination of water would have on pressure development. Industrially, pressure is supplied by steam resulting from heating an aqueous solution to 250-180°C. With the water removed, it had to be determined if the pressure generated by applying thermal energy to a pressurized container would facilitate the formation of amide bonds. It was observed that when heating pressurized solid salts, an initial pressure of 75 psi of argon was needed to eliminate oxygen from the system. Furthermore, a temperature of 260°C was found to produce sufficient pressure to allow venting of steam generated by the formation of the amide bond. In fact, the reaction was shown to proceed with high conversions, maintaining a constant pressure of 200 psi.

The reaction was allowed to continue at 200 psi, 260°C, for 3 hours before the temperature was increased to 270°C, at which point the pressure was slowly lowered to atmospheric levels. After 30 minutes of reaction time at ambient pressure under an argon purge, the viscosity of the polymer melt had increased to the point that stirring was no longer possible. The resulting polymer sample was an off white solid mass, which was then removed from the stir shaft by fracturing the sample with a hammer and chisel. GPC analysis of derivitized samples resulted in soluble materials with an M_n of 33,900 g/mol, and a PDI of 2.76; a sample of industrial nylon 6,6 resulted in slightly lower values (M_n=31,900, PDI= 2.3).

Aminopropyl-Siloxane / Adipic Acid "homopolymerization"

Having confirmed the ability to produce polyamides comparable to industrial standards, the ready formation of the siloxane-adipic acid bond had to be established. This was accomplished by the preparation of a chain extended siloxane "homopolymer" via a 1:1 stoichiometric polymerization with adipic acid. Although the initial reaction mixture was heterogeneous, it later cleared upon heating. The reaction was to be monitored by FTIR analysis, using the conversion of the carbonyl from an acid to an amide. However, the reaction proceeded faster than anticipated; after only one hour when the first sample was to be collected, the viscosity had increased to the point that a sample could not be readily drawn through an 18 gauge needle. GPC analysis, using chloroform as a mobile phase, yielded an M_n of 17,500 g/mol. and a PDI of 1.9.

Copolymerizations

A series of copolymers was synthesized, with target siloxane content ranging from 10 to 50 wt %, at 10% intervals. The method was analogous to that of the control polyamide produced by the solid salt approach. However, in order to ensure 1:1 stoichiometry and compensate for the amine endgroups of the siloxane, a corresponding molar amount of adipic acid was added. All of the necessary reactants were introduced to the Parr bomb at the onset of the reaction. It is interesting to note that the siloxane oligomer may acts as a solvent for the adipic acid and the ionic salt. It is theorized that upon heating the siloxane oligomer reacts with the adipic acid, while the increasing polarity of the endcapped siloxane allows some of the salt to dissolve prior to reaching its melting point, thus facilitating siloxane incorporation. Since the system is under pressure, the diamine and diacid could not disrupt the stoichiometry by sublimation.

The polymers produced by this method were white/yellow to tan in color and showed evidence of fibrous draw. Additionally, it was noted that samples with higher siloxane content contained more voids, possibly indicating a foaming effect.

4.4.5 Confirmation of Copolymer Synthesis

Due to the results of the initial attempts to produce high molecular weight amid-siloxane copolymers, confirmation of high molecular weight and full siloxane incorporation became a priority.

Establishing High Molecular Weight

Perhaps the most compelling evidence for the development of high molecular weight copolymers was the large increase in melt viscosity observed as the reactions neared completion. In the copolymerizations containing less than 30 wt% siloxane, this increase in melt viscosity was significant enough to halt the stirrer motor. Additionally, the resultant polymer masses were not brittle, as had been observed in the aqueous salt reactions. Rather they were quite resilient and were often isolated from the reactor with difficulty, often using a hammer and chisel.

In an attempt to verify the observance of high melt viscosities, the intrinsic viscosities of the copolymers were measured in m-cresol. Summarized in Table 4.4-1, the intrinsic viscosities of the copolymers show that at low siloxane loadings, materials with intrinsic viscosities similar to those of industrial molecular weights were produced. However, a definite trend was observed. As the siloxane loading increases, intrinsic viscosity decreases. One reason is this trend is that as more siloxane is incorporated into the copolymers, m-cresol becomes an inferior solvent for the copolymer, creating a less extended random coil in solution. This observation was anticipated, due to the high flexibility of the siloxane chains.

SAMPLE WT % PDMS CHARGED	[η] @ 25°C IN m-CRESOL M_n VIA GPC
Industrial Control	**1.12** **31,900 g/mol**
0 %	**1.14** **49,300 g/mol**
10 %	**1.16**
20%	**0.86**
30%	**0.94**
40%	**0.60**
50 %	**0.60**

Table 4.4-1: Establishment of High Molecular Weight by Intrinsic Viscosity

Ideally, this discrepancy could be resolved by GPC. However, the derivatization reaction required to disrupt the crystalline lattice of the nylon produces trifluoroacetic acid as a byproduct. Exposure of the siloxane chain segments to such a strong acid result in the redistribution of the siloxane chain, effectively cleaving the polymer backbone. Subsequent analysis by GPC would inevitably report low molecular weight materials, reflecting the degradation of the siloxane segments.

Verification of Siloxane Incorporation

Since the establishment of high molecular weight was far from conclusive, the verification of siloxane incorporation was thought to provide some assurance that high molecular weight had, in fact, been achieved. Due to the high crystallinity of the nylon portions and the low acid resistance of the siloxane segments, most conventional solution methods of analysis were unavailable. Thus, it became imperative to discover a means of determining the amount of siloxane present in the copolymers, as well as to ensure that the siloxane was chemically bound to the nylon instead of merely physically blended in.

The copolymer sample was cooled with liquid nitrogen and placed in a grinder. Exposure to liquid nitrogen was needed to produce a powdered sample. The impact resistance imparted by the siloxane prohibited fracture of the sample at room temperature. Confirmation of the presence of siloxanes was easily established by magic angle solid state ^{29}Si NMR. Any notable features were attributed to the presence of siloxane in the samples. A representative spectrum is shown in Figure 4.4-1.The resulting spectra were surprisingly sharp even allowing estimation of the siloxane segment lengths.

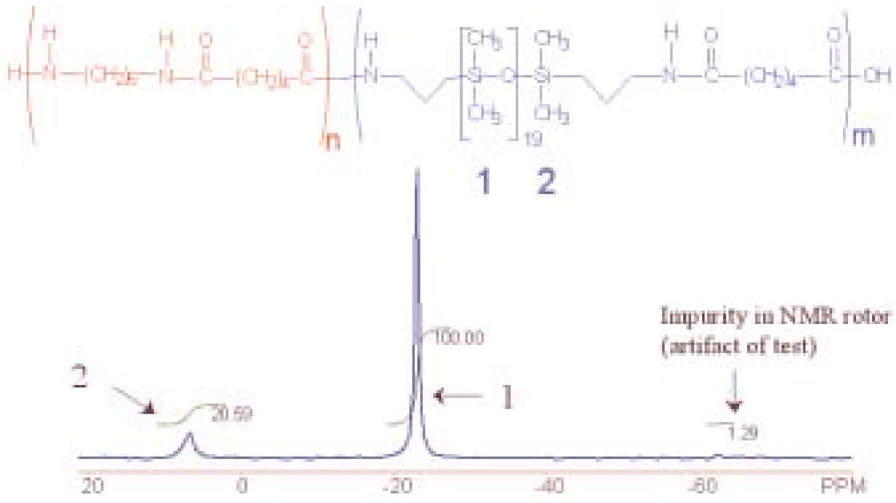


Figure 4.4-1:Representative Solid State ^{29}Si of Nylon-Siloxane Copolymer

The ground samples were then subjected to solid-state ^{13}C NMR to determine the relative concentration of siloxane present. Given that signal peaks are much wider in the solid state (Figure 4.4-2) in comparison to the solution state, an estimation of the relative weight percent of siloxane present was approaching the limits of detection for this technique.

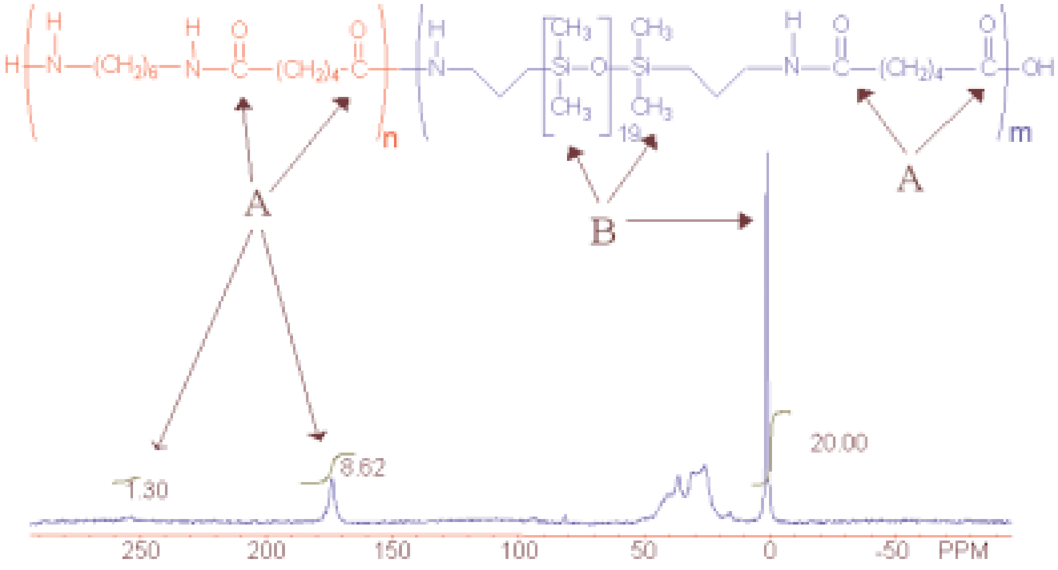


Figure 4.4-2: Representative Solid State ^{13}C NMR of Nylon –Siloxane Copolymers

The use of solid state NMR not only afforded confirmation of the presence of siloxane in the material, but even permitted an estimation of the relative amount present. However, the actual incorporation of the siloxane segments into the backbone of the nylon was still unconfirmed.

Confirmation would be achieved by the use of soxhlet extraction coupled with the solid state NMR procedure. Base spectra of ground copolymers could be collected and later compared to those of the same physical samples after exposure to refluxing isopropyl alcohol for five days. The soxhlet extractor enables the extraction volume of the solvent to be constantly exchanged, eliminating any possible saturation of the solvent. Isopropanol was selected as the extraction solvent as it is known to be a good solvent for siloxanes. Moreover, the ideal reflux temperature is 82°C, which is above the glass transition of nylon 6,6 (52°C). Therefore any siloxane present after 5 days of exposure to hot isopropanol must be chemically bound to the insoluble polyamide. Initial results could be determined by the analytic weighing of the samples before and after the extraction; if the samples showed lower weight loss than the amount of siloxane loaded into the reactor, then it was concluded that some of it must have been incorporated.

^{13}C NMR examination of the samples, both before and after isopropanol extraction as well as % weight loss are summarized on Table 4.4-2.

WT % PDMS Charged	IPA Extraction % Weight Loss	WT% PDMS Via ^{13}C NMR Before Extraction	WT% PDMS Via ^{13}C NMR After Extraction
0 %	1.98	0	0
10 %	1.16	9	9
20%	1.36	17	14
30%	3.70	28	29
40%	7.15	45	36
50 %	9.55	49	43

Table 4.4-2: Evidence of Siloxane Incorporation via Soxhlet Extraction and Solid State NMR

Additional support for verifying siloxane incorporation was observed by attempting a negative control reaction. Silicone heating oil, known to be endcapped with phenyl groups for stability, was added to a Parr reactor with the requisite amount of adipic acid and solid nylon salt. A typical reaction profile was attempted and the resulting material was initially described as “nylon 6,6 with standing siloxane fluid and a greasy film on it”. This experiment demonstrated that a physical blend was not likely under copolymerization conditions. The noted absence of visible phase separated siloxane was interpreted as an indication of incorporation.

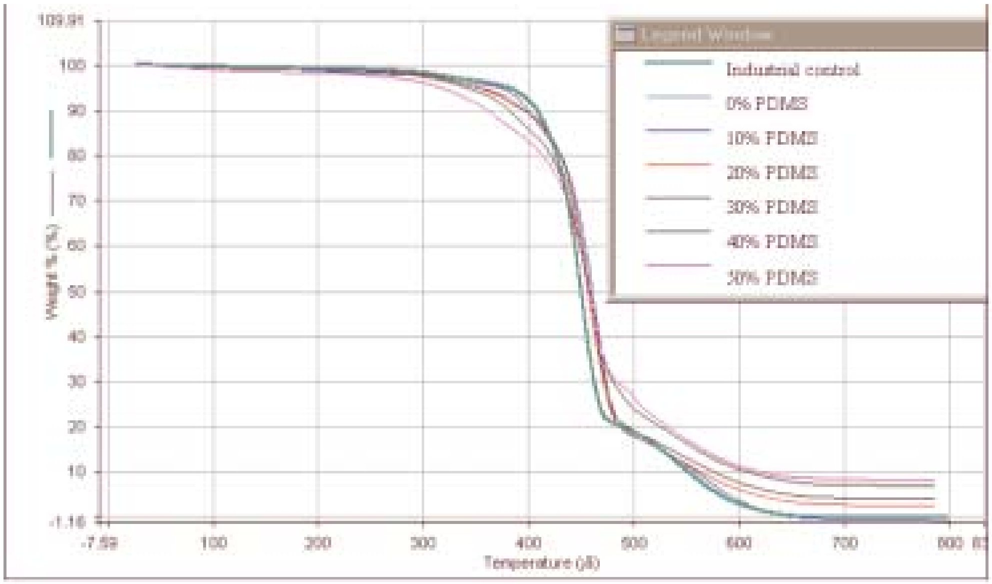


Figure 4.4-3: TGA of Nylon-Siloxane Copolymers

4.4.6 Thermal Characterization of Copolymers Produced

Themogravimetric Analysis

TGA analysis of the copolymers produced was performed at 10°C/min in air to observe possible char formation (Figure 4.4-3). Analysis of the weight loss profile revealed two distinct trends. The char yield increased as the amount of siloxane incorporated increased. However, this was offset by a linear decrease in the onset temperature of decomposition. These trends are illustrated in Figure 4.4-4. It is believed that these competing effects may hinder eventual commercialization.

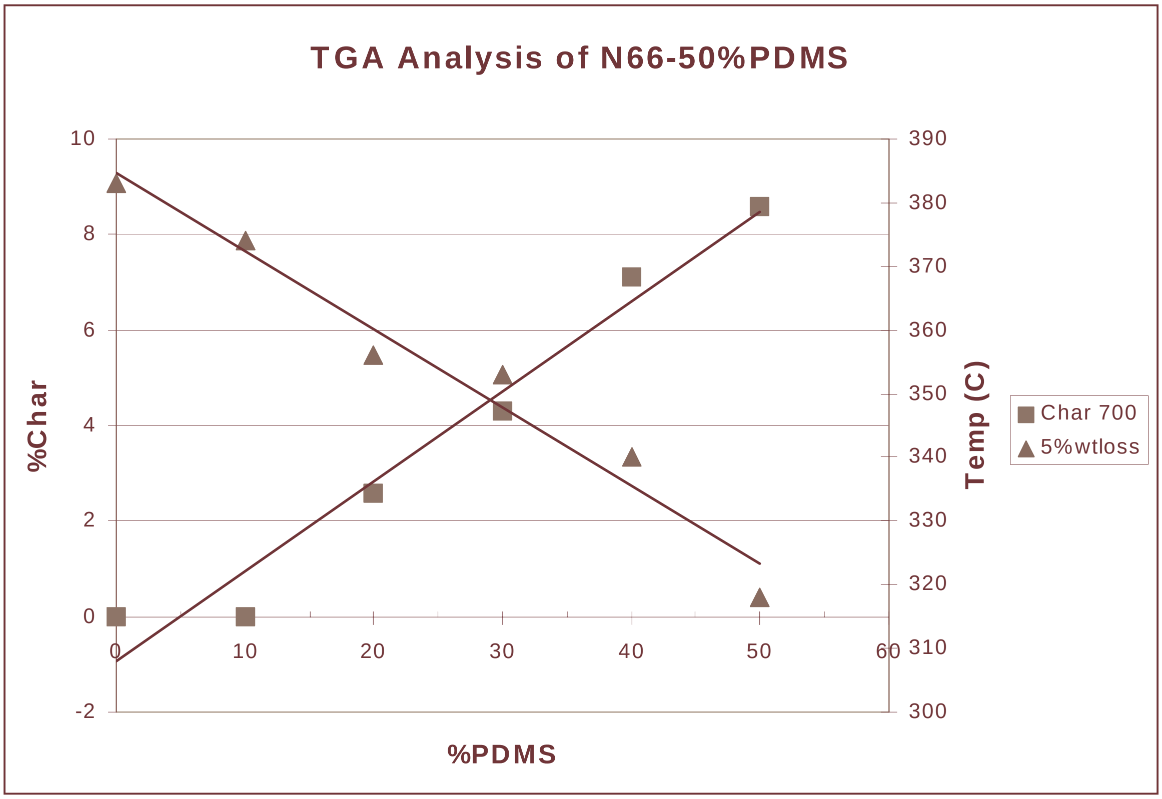


Figure 4.4-4: Graphical Representation of TGA Data

Bench Flame Tests

This test, though not quantitative, is significant as it provides insight as to how the fire resistance of copolymers might be altered by siloxane incorporation. For this test, bulk copolymer samples of approximately the same size were exposed to the blue portion of a Bunsen burner flame. The observations can be summarized as follows. The control nylon sample initially bubbled, melted and dripped, while after removal from the flame the sample slowly self-extinguished. The 10 and 20 wt % siloxane copolymers showed no sign of drip upon exposure to the flame, but combustion still occurred after removal from the flame, a char formed and extinguished the sample. However, samples containing 30-50 wt% siloxane would not sustain a flame; instead, they smoldered much like charcoal.

These observations indicate that the incorporation of siloxane may have fundamentally altered the combustion processes of the materials produced. Still, combustion under more controlled environments must be explored before indications of sustainable fire retardance are conclusively reported.

Differential Scanning Calorimetry

One of the main objectives of this research effort was to impart some of the fire retardant and hydrophobic properties of poly(dimethylsiloxane)s, without eliminating the crystallinity of nylon 6,6, which is responsible for many of its attractive qualities. High temperature DSC was used to identify the effects of the incorporation of the siloxane chains on the crystalline melting point of the nylon copolymers. Overlays of the DSC traces can be seen in Figure 4.4-5.

It appears that the hydrogen bonding ability of the nylon 6,6 unit affords a crystalline melt, even in the presence of ~ 50% of a non-polar, amorphous impurity. This crystalline melt is depressed and diminished in size and sharpness as the siloxane content increases, but it is still present. Further details, such as the exact temperature of the melting peak, as well as heat of crystallization are summarized below. However, the copolymer nominally containing 40 wt % siloxane seems to be anomalous. The data from this sample did not agree with the observed trends. This inconsistency was most likely due to a mechanical failure (pressure leak) during synthesis, which may have limited the incorporation of siloxane into the sample. Recalling the isopropanol extraction data after extraction, NMR analysis revealed that the actual amount of siloxane incorporated into this sample was between 20 and 30 %. Use of the actual amount of siloxane incorporated brought the sample back in correlation with the observed trends.

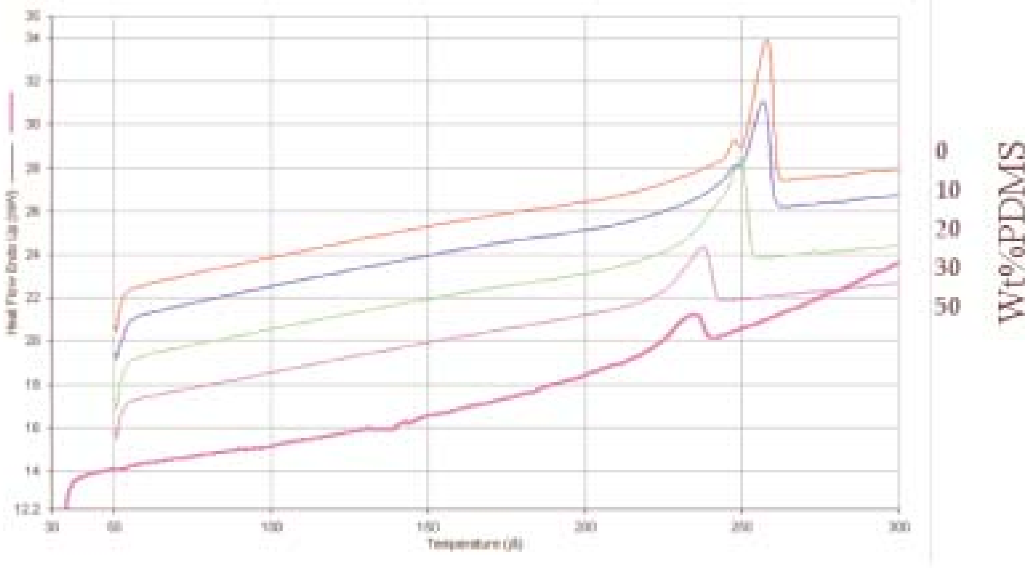


Figure 4.4-5: Effect of Siloxane Incorporation on the Crystalline Melting Point

WT % PDMS Charged	Melting Peak Temperature (°C)	Melt Range (°C)	ΔH Crystallization (J/g)
0 %	257	220 – 264	68.52
10 %	256	220 – 262	56.69
20%	249	220 – 254	47.11
30%	237	214 – 243	31.33
40%	250	226 – 257	33.92
50 %	234	220 –240	18.34

Table 4.4-3: Quantification of the effects of Siloxane Incorporation on the Crystalline Melting Point.

4.4.7 Processing Difficulties Hindering Characterization

The inability to characterize nylon-siloxane copolymers by solution techniques has been previously discussed. Unfortunately, further characterization in the solid state is also hindered by the inherent crystallinity of the nylon segments, and by the problematic behavior of the siloxane segments. Mechanical testing such as DMA and stress-strain analysis would be helpful in identifying potential applications for siloxane containing nylon copolymers. However, at this point proper samples cannot be fabricated. It appears that the temperatures required to compression mold nylon are higher than the acceptable temperatures for processing siloxane in an oxygen environment. Additionally, if oxygen were present, the nylon itself will begin to degrade. Moreover, it is uncommon to use a melt press under an inert atmosphere, as the machines are quite large and heavy. Therefore, fabrication plans are currently on hold until a means of acceptable sample preparation can be devised.

4.5 Conclusions

Several ineffective synthetic routes for the production of poly(dimethylsiloxane)-nylon 6,6 copolymers were attempted before a successful method was developed. The aqueous hydrolysis of a "nylon salt" siloxane mixture was heterogeneous from the beginning of the reaction and gave little reason to believe that miscibility occurred under pressure. Copolymers synthesized by this method were significantly more brittle than a control polyamide, and failed to show evidence of high molecular weight.

Ester aminolysis reactions proved to be the least effective route to achieving high molecular weight copolymers, as nylon homopolymers of sufficient quality could not attained. Copolymers synthesized by this route were waxy solids that possessed little mechanical strength.

Finally, propylamine-terminated poly(dimethylsiloxane) was incorporated into nylon 6,6, in compositions up to about 45 weight % siloxane, affording mechanically tough materials, indicating high molecular weight. Copolymerization proceeded through a modified hydrolysis of "nylon salt", aminopropyl-polydimethyl siloxane and a conjugate amount of adipic acid to provide the amide-siloxane linkages. The ability to produce high molecular weight control homopolymers of both nylon 6,6 and a poly(dimethylsiloxane)-adipic acid mixture under conditions similar to those experienced during copolymerization, established the ability to form the requisite nylon-siloxane amide linkage. Additionally, isopropyl alcohol extraction studies, coupled with solid-state NMR analyses, confirm the existence of covalent siloxane-nylon bonding in the copolymer samples.

DSC experiments showed the retention of a crystallizable melt with samples containing up to 45 weight % siloxane. However, the peak temperature of the transition, as well as the enthalpy of crystallization, decreased as the siloxane loading increased.

Thermal degradation studies reflected an increase in char yield with concurrent increases in siloxane content, a preliminary indication of fire retardance. This was later supported by qualitative Bunsen burner tests. Despite this fact, the crystalline nature of the polyamide segments and the chemical resistance of the siloxane block have hindered the ability to properly characterize the novel, possibly fire retardant copolymers.

5 Summary

Two novel classes of siloxane containing copolymers have been produced via differing chemistries. The first utilized the well known silylamine hydroxyl reaction of two preformed oligomers with mutually reactive endgroups to yield alternating poly(arylene ether phosphine oxide)-polydimethylsiloxane copolymers. The second adapted a commonly known industrial hydrolysis reaction resulting in segmented poly(amide)-polydimethylsiloxane copolymers. The unifying theme of this effort was the need to develop synthetic methods that overcame the polar/non-polar disparity of the partially inorganic poly(dimethylsiloxane)s and the hydrocarbon-based organic polyarylene ethers and polyamides.

Three series of “perfectly” alternating block copolymers were produced from hydroxyl-terminated poly(arylene ether phosphine oxide) oligomers with molecular weights of 2,500, 5,000, and 10,000 g/mol; and dimethylamine-terminated poly(dimethylsiloxane) oligomers of 500, 1,300, 5,000 and 10,000 g/mol. Controlled molecular weight and endgroup functionality of the oligomers was demonstrated in good agreement with theoretical expectations by ^{1}H NMR, acid-base potentiometric titration, and GPC analysis where applicable.

The arylene ether-siloxane copolymers synthesized were found to be high molecular weight materials, as demonstrated by intrinsic viscosity measurement, which could be formed into optically clear, tough, ductile films from solution. The composition of these copolymers ranged from 3-70 weight % siloxane and resulted in nanophase separated material, as illustrated by TEM analysis. The degree of phase separation was shown to fluctuate systematically from sample to sample according to thermal and mechanical analysis, depending on the bulk composition of the copolymer, with selective mixing of the dominant component into the secondary phase. However, the thermoplastic elastomeric potential of the nanophase separated materials was found to be minimal. The possibility of a synergistic effect on selected optical properties was proven to be non-existent, while an investigation of possible preferential associations of silica nanoparticles was inconclusive, due to the fact that the particles were larger than the bulk morphologies investigated. Nonetheless, examinations of the thermo-oxidative stability of the copolymers revealed an increase in char yield, and thus possibly fire retardance, as the level of siloxane incorporation was increased.

Secondly, a novel series of segmented polydimethylsiloxane-nylon 6,6 copolymers, containing up to 45 weight % siloxane, were synthesized from an ~1500 g/mol aminopropyl-terminated oligomer, adipic acid, and a nylon 6,6 salt, via a non-aqueous hydrolysis reaction. High molecular weight and chemical connectivity of the siloxane-amide copolymers was established by measuring mechanical toughness, as well as through the development of a novel analytical process combining liquid-solid extraction and solid state ^{13}C NMR. DSC analysis of the copolymers illustrated the retention of a crystalline melting point with the incorporation of up to 45 wt% siloxane. However, both melting peak temperature and extent of crystallinity were found to decrease with increasing siloxane content. Thermo-oxidative studies by TGA reflected an increase in char yield with increasing siloxane incorporation, indicating improved fire retardance. This hypothesis was supported by qualitative Bunsen burner tests.

Therefore, the production of novel siloxane containing block copolymers has been demonstrated using multiple chemistries and analytical techniques to produce high molecular weight materials. Notably, this was achieved despite the significant disparity between the polarities and other chemical features of the largely inorganic polydimethylsiloxane and the hydrocarbon based poly(arylene ether phosphine oxide)s and polyamides.

6 VITA

William David Polk, son of Dr. and Mrs. William C. Polk, was born on June 6, 1972 in Greenville, Pennsylvania. He was raised in Slippery Rock, PA, where he graduated from Slippery Rock Area High School in 1990. In the fall of that same year, David began his career in science as an undergraduate at the Rochester Institute of Technology, in Rochester, New York. In November of 1994, he graduated with a bachelor’s degree in Polymer Chemistry, and began work as an analytical polymer chemist for Xerox Corporation. After a year as a technician, David entered the polymer chemistry graduate program at Virginia Polytechnic Institute and State University, during which time he presented papers at seven national conferences. He obtained his Doctorate in 2001. His immediate plans include continued employment with PPG Industries Inc., in Monroeville, PA, as a Senior Research Chemist.