

SYNTHESIS, KINETICS AND SUPERCRITICAL FLUID
FRACTIONATION STUDIES OF FUNCTIONAL ORGANOSILOXANES AND
THEIR INCORPORATION INTO SEGMENTED COPOLYMERS

by

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(ABSTRACT)

The synthesis of organosiloxanes via equilibration processes is fairly well known, but relatively little is known about the detailed kinetics and mechanisms involved, particularly in the presence of functional endblockers. A major focus of the present study was to investigate aspects of the kinetics of siloxane equilibration polymerizations in the presence of 1,3-bis(3-aminopropyl)tetramethyldisiloxane. Catalysts studied included the commonly used potassium siloxanolate catalyst, as well as the analogous tetramethylammonium and tetrabutylphosphonium siloxanolate catalysts. The reactions of the quaternary ammonium and phosphonium systems were limited to about 80°C due to the known transient nature of those species at elevated temperatures. The rates of disappearance of the cyclic tetramer D₄ and aminopropyl disiloxane were monitored through the use of HPLC and GC techniques. The results indicated that the ammonium and phosphonium catalysts were much more efficient

at early incorporation of the aminopropyl disiloxane into the oligomer. By contrast, studies using the potassium siloxanolate catalyst were less effective, even at much higher temperatures such as 160°C. The explanations for this behavior may be related to the higher degree of dissociation and possibly enhanced solubility of the ammonium and phosphonium systems relative to the more studied potassium system. The significance of these results with respect to functional siloxane systems has not been previously appreciated.

Kinetic results indicated that the apparent rates are proportional to the square root of the catalyst concentration, in agreement with earlier studies on the potassium catalyst in nonfunctional siloxane systems. The reaction order with the bulky tetrabutylphosphonium catalyst was slightly higher, again indicating a more dissociated active siloxanolate species. Despite the rate differences, the same equilibrium number average molecular weight was obtained, regardless of catalyst concentration. The effect of catalyst is manifested mainly in the rate at which equilibrium is reached.

Supercritical fluid fractionation studies of the functional siloxanes were demonstrated to be quite feasible. Relatively narrow molecular weight distribution fractions were obtained when compared with polysiloxane standards synthesized via the organolithium initiated polymerization of the cyclic trimer. Excellent agreement was realized

between the molecular weight values determined by titration of the amine endgroups and those calculated by GPC.

Additional aspects of this study included the preparation of alkyl-substituted polyarylesters and polyformals, and modification of these materials with polydimethylsiloxanes. Tough transparent films were readily solution cast from these materials, which may have potential use as permselective gas separation membranes. Due to the intentionally short segment lengths, evidence of significant amounts of phase mixing was observed by DSC and TEM.

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Chapter I

INTRODUCTION

The importance and utility of multiphase copolymer systems has been well documented in the literature, with emphasis on their unique combination of properties and their potential material applications. Organosiloxane block polymers are a particularly interesting type of multiphase copolymer system due to the unusual characteristics of polysiloxanes, such as their thermal and UV stability, low glass transition temperature, high gas permeability and low surface energy characteristics.

Organosiloxane block copolymers are often prepared by step-growth or condensation polymerization of preformed difunctional siloxane oligomers with other difunctional monomers or oligomers. The linear, functionally terminated polysiloxane oligomers are generally prepared by the anionic or cationic ring-opening polymerization of cyclic siloxanes in the presence of a functional disiloxane or endblocker. Despite the importance and synthetic utility of these siloxane equilibration reactions, relatively little has been reported with respect to the detailed kinetics and mechanisms involved, especially in the presence of functional endblockers. A major objective of this research was to investigate various aspects of siloxane equilibration

reactions in an attempt to establish the most efficient reaction conditions for the preparation of well-defined difunctional siloxane oligomers.

The synthesis and equilibration reaction kinetics involved in the preparation of aminopropyl terminated polysiloxanes were studied most extensively due to the utility of the amino terminated species as a component of a large number of segmented copolymers such as imides, amides and ureas. The rate of disappearance of the starting materials was followed as one approach to determine the effect of catalyst type and concentration on the rate of the ring opening polymerization. Kinetic results were obtained on the potassium siloxanolate catalyzed system, as well as on the analogous tetramethylammonium and tetrabutyl phosphonium siloxanolate catalyzed systems.

Due to the random nature of the equilibration processes, the resulting siloxane oligomers generally possess a Gaussian molecular weight distribution. In addition, a ring-chain equilibrium exists, resulting in the presence of a certain amount of low molecular weight cyclics at the end of the reaction. A second objective of this research was to explore the usefulness of supercritical fluid fractionation techniques for the preparation of well-defined aminopropyl functional polysiloxanes of narrow polydispersity. The ability to isolate narrow molecular weight distribution fractions of these oligomers was

interesting from a fundamental viewpoint, since incorporation of these narrow MWD fractions into segmented copolymers would allow the determination of the effect of the polydispersity of the individual blocks on the properties of the resulting copolymer systems. Studies of the mechanical and morphological properties of such systems would result in a better understanding of the structure-property relationships in multiphase copolymer systems.

A final objective of the research involved the synthesis and characterization of a series of siloxane-modified polyarylesters and polyformals. The block copolymers contained alkyl substituents along the backbone, which suggests a potential application of these materials as permselective gas separation membranes. Solution polymerization techniques were used to prepare these perfectly alternating block copolymers, formed by the reaction of a phenolic terminated polyarylester or polyformal with a dimethylamine terminated polysiloxane.

Chapter II

LITERATURE REVIEW

A. POLYORGANOSILOXANES

1. Introduction

Polyorganosiloxanes are an important and widely studied class of semi-inorganic polymers. Early research on silicon chemistry dates to the 19th century with the isolation of silicon metal and later preparation of halogeno- and hydro-silanes [1,2]. The organic chemistry of silicon has existed since 1863 when Friedel and Crafts prepared tetraethylsilane. In 1904 Kipping prepared several R-Si-X compounds from tetrachlorosilane through the newly discovered Grignard reaction. Kipping's interest and research in organosilicon chemistry spanned several decades, from 1900 to 1940, for which he is generally recognized as the father of classical organosilicon chemistry. Most of Kipping's work focused on the aryl- and ethyl-substituted chlorosilanes. Hydrolysis of these materials led to silanol compounds which underwent intermolecular condensation to form -Si-O-Si- ring or chain compounds which have become known as polysiloxanes [3].

Industrial interest in organosilicon polymers began in the early 1930s at the Corning Glass Company as well as at the General Electric Company. The Russian scientist Andrianov and his associates began research in this area at

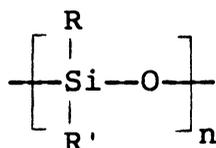
the same time. The discovery by Rochow of a direct process (rather than a Grignard process) for the preparation of organochlorosilanes was an important step towards the scale-up and commercialization of polysiloxanes [4,5]. The unique and versatile nature of silicones led to their use in a wide variety of applications. Some of their characteristic properties include a low glass transition temperature, excellent thermal and oxidative stability, high gas permeability and a low surface energy.

The physical properties of organosilicon compounds can be readily interpreted in terms of structural bond concepts [6]. The review of the literature which follows will summarize this approach to understanding the properties of polyorganosiloxanes, and will relate these properties to the range of applications in which silicones have been effectively utilized. The literature review will also include a summary of synthetic approaches for the preparation of siloxane monomers and oligomers, followed by a discussion of synthetic and kinetic aspects of siloxane equilibration reactions, especially those pertaining directly to this research. More detailed discussions on the synthesis, properties, and applications of polyorganosiloxanes can be found in a number of excellent books [6-11] and reviews [1,12-13]. Research efforts in all areas of organosilicon chemistry are continuing at a rapid pace in attempt to advance the scientific understanding of these

unique materials so that maximum advantage may be taken of their unusual array of properties.

2. Properties of Polyorganosiloxanes

The polyorganosiloxane backbone may be represented as:



where R and R' can be alkyl, haloalkyl, vinyl or phenyl groups. The methyl silicones (R,R' = CH₃) tend to dominate commercially but property enhancement can be achieved by incorporation of other substituents. The siloxane unit represented above is referred to as difunctional, as determined by the number of free valences on the oxygen. Indeed, polysiloxanes can be assembled from four types of structural units as described in Table 1 [7]. It follows that the molecular structure can vary to include linear, branched, and cross-linked topologies.

Polysiloxanes exhibit a large degree of freedom of motion due to the free rotation about the Si-O and Si-C axes, especially with small substituents such as methyl. The Si-O-Si bond angle has been the subject of much study, and has been found to vary within wide limits between compounds, and as a function of the measurement technique for the same compound [1]. The reported value of the Si-O-Si bond angle in oligomeric polydimethylsiloxanes is around 140°, while the C-Si-C bond angle is around 111° [13]. The

Table 1
Structural Units of the Polyorganosiloxanes [7]

| Structural Formula | Composition | Functionality | Symbol |
|---|----------------|-----------------|----------------|
| R_3Si-O- | $R_3SiO_{1/2}$ | monofunctional | M |
| $\begin{array}{c} R \\ \\ -O-Si-O- \\ \\ R \end{array}$ | $R_2SiO_2/2$ | difunctional | D |
| $\begin{array}{c} R \\ \\ -O-Si-O- \\ \\ O \\ \end{array}$ | $RSiO_3/2$ | trifunctional | T |
| $\begin{array}{c} \\ O \\ \\ -O-Si-O- \\ \\ O \\ \end{array}$ | $SiO_4/2$ | tetrafunctional | Q ^a |

^a The symbol "Q" is derived from "quadri-functional" rather than "tetrafunctional" to distinguish it from T for "trifunctional".

rotational barriers of the bonds in polysiloxanes are considerably lower than those in corresponding hydrocarbons, as shown in Table 2 [13]. The net freedom of motion leads to greater intermolecular distances and lower intermolecular forces. This, in turn, translates into lower glass transition temperatures ($T_g = -123^\circ\text{C}$), as well as lower viscosity, cohesive-energy density and surface tension values. Other properties exhibited by polysiloxanes which are consistent with weak intermolecular forces include a high compressibility, a low dielectric constant and a low temperature coefficient of viscosity.

The Si-O bond in tetravalent silicon compounds consists of σ bonding of the hybridized s and p electrons of the silicon atom with the p electrons of the oxygen, and an additional π interaction between the unshared p electrons of oxygen and the unfilled 3d orbitals of silicon. In contrast to the p orbitals, not all of the 3d orbitals have the same shape and relative orientation in space. Therefore, the 3d orbitals of silicon can form the π bond with any spatial orientation of the oxygen, and the large degree of mobility around the siloxane bond does not contradict the existence of $p_\pi-d_\pi$ bonding between oxygen and silicon [6]. Evidence for this type of bonding is found in the high strength of the Si-O bond (106 kcal/mole) relative to the C-O bond strength (86 kcal/mole) [14], as well as in the decrease of the observed Si-O bond length (1.64 Å) relative to the

Table 2
Silicon and Carbon Bond Rotational Barriers [13]

| Bond | Energy (kJ/mole) |
|--------------------|------------------|
| Si-O | < 0.8 |
| C-O | 11.3 |
| Si-CH ₃ | 6.7 |
| C-CH ₃ | 15.1 |

calculated value (1.83 Å) based on the additivity of the atomic radii (1.17 Å for silicon and 0.66 Å for oxygen) [8]. The high thermal and oxidative stability exhibited by polysiloxanes can be readily understood based on the high strength of the Si-O bond.

Specifically, polydimethylsiloxane homopolymers are typically stable up to 350-400°C in the absence of air, or 200°C in the presence of air. The decomposition in the absence of air is due to redistribution of the siloxane bonds, with formation of cyclic siloxanes of lower molecular weight. In the presence of air, oxidation of the C-H bonds occurs with weakening of the Si-C bonds, and ultimately, crosslinking Si-O-Si bonds form between chains [8].

The substantial thermal stability of siloxanes is also due in part to the ionic character of the siloxane bond. The Si-O bond is estimated to be ~50% ionic on the basis of Pauling's electronegativity, with silicon being the positive member. Noll [7] points out that this extensively quoted value was later revised by Hannay [15], as well as by Pauling himself [16], to an approximate polarity closer to 40%. Though quite resistant to homolytic cleavage, the ionic nature of the siloxane bond renders it quite susceptible to attack by polar reagents such as acids and bases. Indeed, this heterolytic cleavage is used to an advantage in the preparation of oligomeric polysiloxanes, as will be addressed in detail later. The Si-C bond is only

slightly ionic (~12%) and methyl groups on silicon are fairly resistant to heterolytic cleavage. The presence of strongly electronegative substituents on carbon (e.g., CH₂Cl, CCl₃, CF₃, CN) increases the Si-C bond polarity and consequently the ease with which it is attacked by bases. The polarity of the Si-C bond is also increased by aromatic substituents, rendering it more susceptible to attack by hydrogen acids [1].

The relatively mild temperature dependence of many physical properties of polyorganosiloxanes, such as viscosity, can be explained not only by weak intermolecular forces, but also by a helical structure for linear polymer molecules. The ability of the siloxane molecule to twist into spirals of possibly six to seven siloxane units, with many such coils along the chain, has been explained in terms of dipole interactions [6,17], as well as stereochemical considerations due to the large radius of the silicon atom and the large Si-O-Si bond angles [18]. The alkyl substituents on the silicon atoms project outward from the helical structure and contribute to the nonpolar and hydrophobic nature of polysiloxanes. The molecules straighten out as the temperature is raised, resulting in greater intermolecular interaction, which normally would lead to an increase in viscosity. In the case of polysiloxanes, the increased molecular entanglements partially compensate for the increased molecular agitation normally accompanying a

temperature rise, resulting in a relatively small net variation in the viscosity of silicones with temperature.

An additional interesting property of polysiloxanes is their surface activity, which is largely attributable to the tendency of the methyl groups to orient to the air or vacuum surface. Surface tensions range from 15 dyn/cm for hexamethyldisiloxane to around 22 dyn/cm for higher molecular weight silicone oils [7]. As a result of its low surface energy, the siloxane component of a phase separated copolymer or polymer blend generally tends to migrate to the air-polymer interface and provide a siloxane-rich surface. This characteristic feature of siloxanes is important in applications requiring enhanced biocompatibility [19-22] (due to their physiological inertness), lubricating properties, or resistance to atomic oxygen [23-27].

It was mentioned above that the properties of siloxanes can be modified by incorporation of substituents other than methyl groups on the silicon. The effect of several common substituents will be considered below.

The introduction of longer chain alkyl groups on the silicon generally produces a material with improved lubricity and increased compatibility with organic compounds [11]. These improvements, however, are at the expense of reduced thermal and oxidative stability, due to the lower stability of the C-C bonds, as well as increased surface tension and poorer release performance.

Phenyl substituents are commonly incorporated into silicone technical products due to the improved thermal and oxidative stability of these materials relative to polydimethylsiloxanes. In addition to the inherent stability of the aromatic ring, the phenyl group brings about a strengthening of the siloxane bond by increasing $d_{\pi-p\pi}$ contributions [7].

The low temperature flexibility may also be improved by the presence of small amounts of diphenyl substituents along the chain due to a disruption of the symmetry and crystallization of the methyl sequences. It should be noted, however, that the presence of too many phenyl groups results in crystallization of long phenyl sequences. Other effects of phenyl substitution include an increase in the glass transition temperature and the viscosity, due to the restricted mobility of the bulky phenyl groups, as well as an increase in the solubility parameter due to enhanced intermolecular interactions. The solubility parameters of dimethyl, methyl-phenyl and diphenyl substituted siloxanes are 7.5, 9.0 and 9.5 $(\text{cal}/\text{cm}^3)^{1/2}$, respectively [13,28]. The miscibility of polysiloxanes with polar organic polymers increases with increasing solubility parameter.

The solubility parameter of siloxanes can also be increased by introducing polar moieties in the form of trifluoropropylmethyl or cyanoalkyl groups along the backbone. These substituents provide excellent resistance

to degradation in hydrocarbon fuels, oils and hydraulic fluids, but may result in somewhat lower thermal and oxidative stabilities [29]. An increase in the glass transition temperature and the viscosity is again observed as a result of substitution of these groups in place of methyl groups.

Methylvinyl groups may be also be introduced into the chain to impart reactivity to the molecule in the form of sites for crosslinking. The resulting silicone elastomers are generally reinforced by the incorporation of fillers such as silicas or various pigment-grade oxides [1].

This broad overview of the structural and physical properties of polyorganosiloxanes clearly demonstrates their unique and versatile nature. In the next section, these characteristic properties will be related to the broad range of silicone applications.

3. Applications of Polyorganosiloxanes

Initial interest in silicones was aimed at developing high temperature varnishes and resins for use in electrical insulation. Such applications were successful due to the excellent thermal and oxidative stability of siloxanes. A variety of product types and application areas have arisen since that time [1,7,11-14,19,30] due to the unique combination of properties exhibited by polysiloxanes, as outlined in the previous section. A list of many of these products and application areas has been compiled and is

presented in Table 3 [12]. The application areas have been listed separately for silicone fluids, silicone resins, room-temperature vulcanized materials and heat-cured silicone elastomers, but some overlap does occur as is evident from the table.

The silicone fluids are linear, relatively low molecular weight materials (~25,000 g/mole or less) which exhibit very low mechanical strength at room temperature. They are widely used as light-duty lubricants, dielectric fluids, hydraulic fluids, antifoaming agents and release agents. In medical and surgical applications, silicone fluids are used for antibiotic storage and for treating wound dressings to prevent them from adhering to tissue [12]. These applications rely on the excellent resistance of silicones to thermal and oxidative degradation, as well as on their physiological inertness and their low surface tension.

Silicone resins are highly cross-linked systems which are usually cured through the formation of siloxane linkages by condensation of silanols in the presence of trifunctional or tetrafunctional components. Most silicone resins are, again, relatively weak, but their high resistivity and low dielectric loss, along with their environmental stability, has led to their use as impregnating varnishes for high temperature insulation of electrical coils and glass cloth. They are also used as laminating resins for electronic

Table 3

General Silicone Product Types and Application Areas [12]

Fluid Applications

| | |
|-------------------|-------------------------------------|
| plastic additives | greases |
| hydraulic fluids | coagulants |
| vibration damping | particle and fiber treatments |
| release agents | cosmetic & health-product additives |
| antifoamers | heat-transfer media |
| dielectric media | polishes |
| water repellency | lubricants |
| surfactants | |

Resin Applications

| | |
|---------------------|------------------------------|
| varnishes | electrical insulation |
| paints | pressure-sensitive adhesives |
| molding compounds | laminates |
| protective coatings | release coatings |
| encapsulants | adhesives |
| junction coatings | |

RTV Rubber Applications

| | |
|--------------------|-----------------------|
| sealants | encapsulants |
| adhesives | electrical insulation |
| conformal coatings | glazing |
| gaskets | medical implants |
| foams | surgical aids |
| molding parts | mold making |

Heat-Cured Rubber Applications

| | |
|-------------------|--------------------------------|
| tubing and hoses | auto-ignition cable |
| belting | extruding |
| medical implants | wire-cable insulation |
| surgical aids | laminates |
| penetration seals | fuel-resistant rubber parts |
| fabric coating | electrically conducting rubber |
| molded parts | embossing-calendering rollers |
| foams | |

circuit mounting boards, and as components in pressure-sensitive adhesives and in molding compounds.

Silicone elastomers are cross-linked materials which are generally reinforced with fillers to increase their mechanical strength. They may also contain other additives, such as antioxidants, to obtain specific properties. Different silicone elastomers are conveniently distinguished by their cure-system chemistries and can be categorized by the temperature conditions required for a proper cure [12].

Room-temperature-vulcanized (RTV) silicone elastomers are based on polymers of intermediate molecular weights (10,000 to 100,000 g/mole) [31], with catalysts being used to ensure controlled curing of these one- or two-component systems. One-component RTV silicone rubbers are mostly used in adhesive and sealant applications, where the cure reactions are triggered by exposure to atmospheric moisture. The higher strength two-component systems are more diverse and employ one of several different curing systems [12]. Two-component RTV silicone rubbers are extensively used in encapsulating and molding applications, but are also utilized as protective coatings and electrical insulation.

Heat-cured rubbers are based on high molecular weight polymers (300,000 to 1,000,000 g/mole) that are gums [31]. The ingredients, i.e., gums, fillers, and additives, are mixed in dough mixers or Banbury mills and are stable in the absence of heat. Curing is usually brought about by heating

the reinforced polymer with a free-radical generator such as benzoyl peroxide. Applications where heat curing is an option include liquid injection molding and coating operations for the production of wire, cable and fabric coatings, as well as molded parts.

New applications for silicones are constantly being sought as new technologies are developed. For example, in the field of electronics, silicone photoresists and silicone-containing liquid crystals are current areas of research. Further developments in silicone applications are also expected in the fields of biotechnology and life science, especially in the continuing development of biocompatible materials and drug delivery systems [32].

4. Synthesis of Polyorganosiloxanes

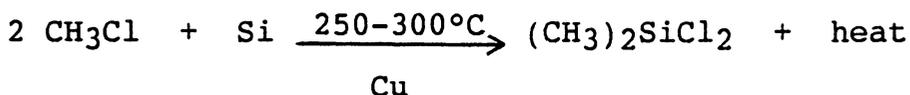
The commercial synthesis of silicone fluids and elastomers is largely based on either (1) the hydrolysis and condensation of organohalosilanes, or (2) the acid- or base-catalyzed ring opening polymerization of cyclic siloxane monomers, often in the presence of monofunctional components to control the molecular weight of the products. In the latter approach, the cyclosiloxane monomers are themselves produced by the hydrolysis of chlorosilanes. The synthetic approaches utilized in this research include the base-catalyzed equilibration of the cyclic siloxane tetramer, D₄, in the presence of amine-functional endblockers, as well as the anionic polymerization of the cyclic siloxane trimer,

D₃, using organolithium initiators. The discussion below will review the synthesis of organochlorosilane monomers, cyclic siloxane monomers, and the aminopropyl disiloxane endblocker. This will be followed by a discussion on the synthesis of siloxane oligomers by living anionic polymerization techniques and by equilibration processes.

a) Monomer Synthesis

* Organochlorosilanes

The "direct process" discovered by Rochow [4,5] has become the industry standard for the preparation of methylchlorosilanes and phenylchlorosilanes. The process involves the exothermic reaction of an organic halide, such as methyl chloride or chlorobenzene, with metallic silicon in the presence of a copper catalyst. The general reaction scheme for the preparation of dimethyldichlorosilane is shown below:

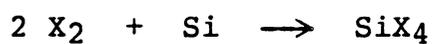
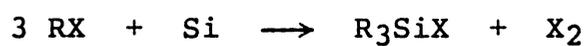
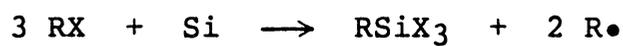


In actuality, a mixture of methylchlorosilanes is obtained due to the occurrence of other processes as depicted in Scheme I [7]. The various silanes are readily separated by fractional distillation, and yields of dimethyldichlorosilane in excess of 80% have been reported [1].

A similar procedure is followed for the preparation of diphenyldichlorosilane, where chlorobenzene is reacted at 550°C in the presence of a silver catalyst, with yields

Scheme I

Reactions Involved in the Direct Process



Generally, X = Cl and R = CH₃ or 

closer to 50% due to steric effects. The composition of the crude product can be modified by varying the reaction conditions, such as choice of catalyst, reaction temperature, and the use of diluent gases [7].

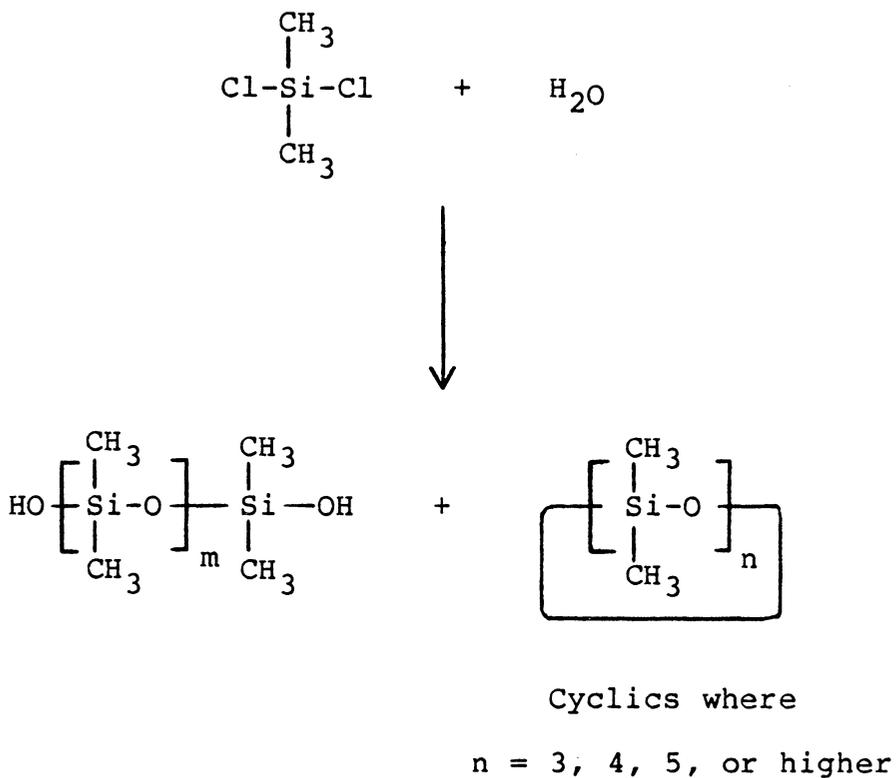
Free radical mechanisms were initially proposed for the direct process [33]. More recently, quite different explanations have been proposed involving mainly chemisorption, polarization, and charge transfer phenomena [1,7].

* Cyclic Siloxanes

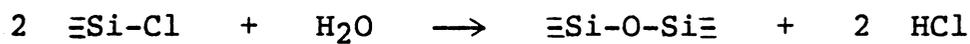
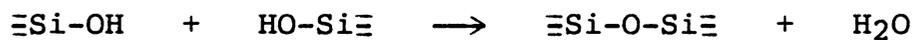
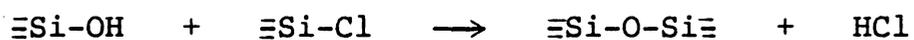
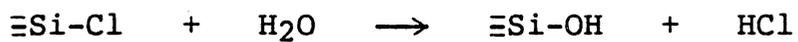
Cyclic siloxane monomers are generally prepared by the controlled hydrolysis of organochlorosilanes. The reaction product of the hydrolysis consists of a mixture of linear diols and cyclic structures, as shown in Scheme II for the hydrolysis of dimethyldichlorosilane. The various chemical reactions involved are further depicted in Scheme III. By varying the reaction conditions, the ratio of cyclic to linear species can be controlled [7]. A high proportion of the desired cyclics (~90%) is obtained by carrying out the hydrolysis in the presence of a water-insoluble, nonpolar solvent. This is due to the tendency of the organohalosilanes and the polyorganosiloxanes to solubilize in the organic phase, resulting in a reduction of the concentration of chlorosilanes in the aqueous phase. As a result of this dilution, the tendency to intramolecular condensation predominates over intermolecular condensation, and cyclic products are formed preferentially.

Scheme II

Hydrolysis of Dimethyldichlorosilane



Scheme III
Reactions Involved in the Hydrolysis
of Organohalosilanes



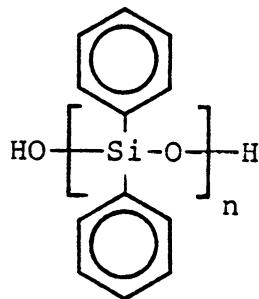
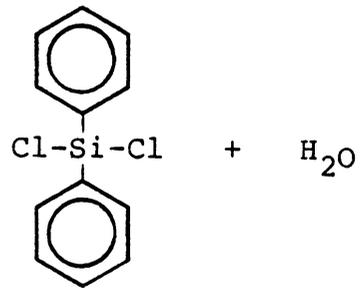
The cyclic diphenyl tetramer, D₄" is synthesized by a similar process. The reaction scheme for the hydrolysis of diphenyldichlorosilane is illustrated in Scheme IV.

* 1,3-Bis(3-aminopropyl)tetramethyldisiloxane

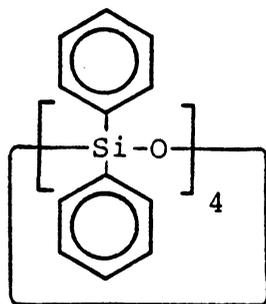
The preparation of controlled molecular weight functional polysiloxane oligomers by equilibration reaction techniques requires the presence of a functional endblocker, which serves as an effective chain transfer agent. A synthetic route for preparation of the 1,3-bis(3-aminopropyl)tetramethyldisiloxane endblocker utilized extensively in this research was pointed out some time ago by Saam and Speier [34]. Their synthetic method, using a protecting group on allylamine [35] to allow a clean hydrosilylation with tetramethyldisiloxane before conversion to the free amine, is presented in Scheme V. A similar synthetic approach using an allylamine with both hydrogens protected is presented in Scheme VI [36], where the protected allylamine undergoes hydrosilylation with dimethylchlorosilane to produce a chlorosilane intermediate. The chlorosilane is then hydrolyzed and condensed, with simultaneous hydrolysis of the labile silicon-nitrogen bond to regenerate the primary amine functionality, producing the desired aminopropylidisiloxane. Finally, a recent U.S. Patent [37] describes a third approach for the preparation of 1,3-bis(3-aminopropyl)tetramethyldisiloxane and similar bis(aminoalkyl)disiloxanes.

Scheme IV

Hydrolysis of Diphenyldichlorosilane



Base

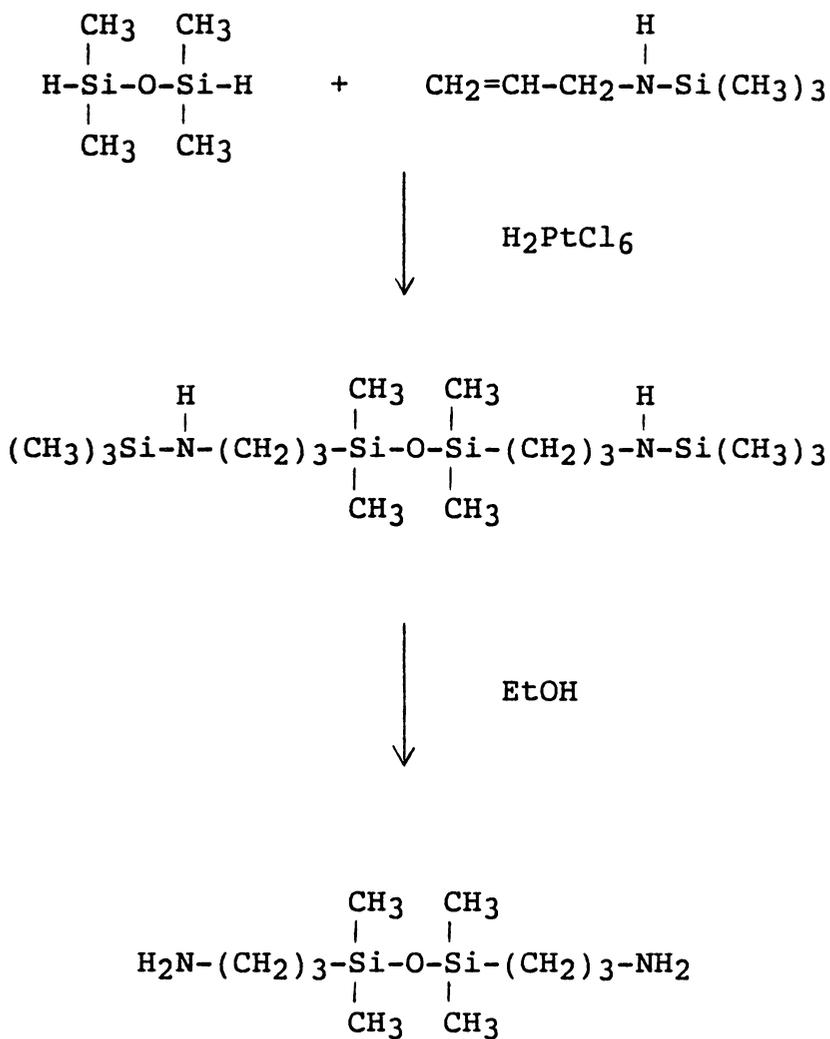


D_4 "

Scheme V

Synthesis of

1,3-Bis(3-Aminopropyl)Tetramethyldisiloxane [34]

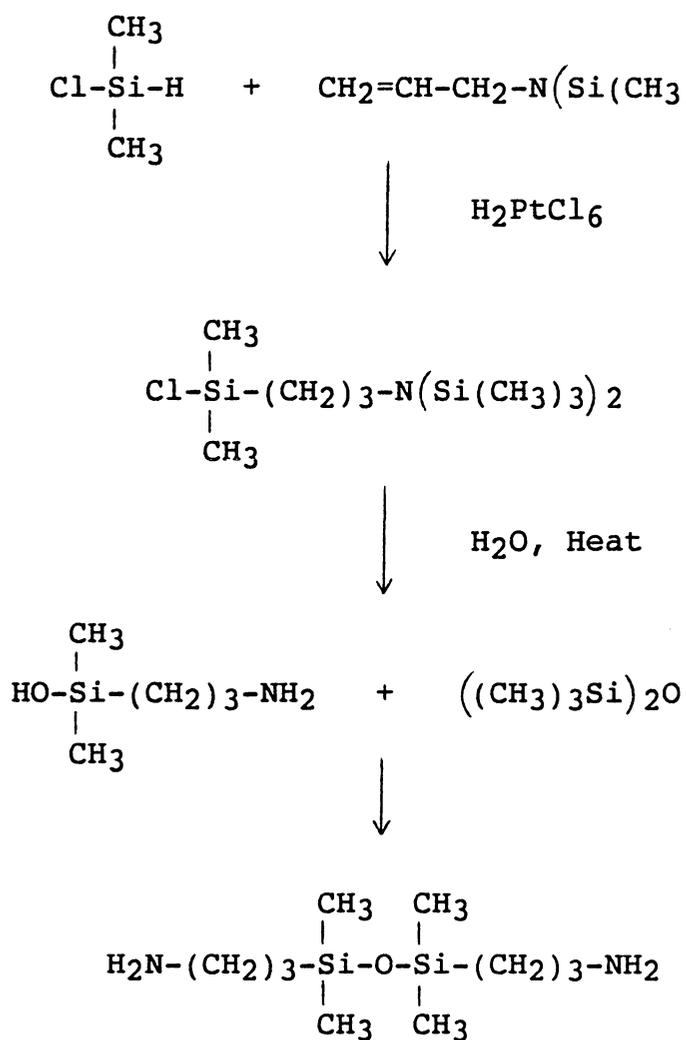


1,3-Bis(3-Aminopropyl)tetramethyldisiloxane

Scheme VI

Synthesis of

1,3-Bis(3-Aminopropyl)Tetramethyldisiloxane [36]



1,3-Bis(3-Aminopropyl)tetramethyldisiloxane

b) Synthesis of Siloxane Oligomers

* Living Anionic Polymerization

Organolithium compounds have been shown to be quite effective as initiators for the anionic polymerization of a variety of nonpolar monomers, mainly as a result of their ability to produce systems which lack spontaneous termination reactions [38-40]. The non-terminating nature of these systems allows the preparation of polymers of narrow molecular weight distributions and predictable molecular weights, and permits controlled termination reactions where the formation of chains with functional endgroups is possible. Early work on the use of organolithium compounds for the polymerization of hexamethylcyclotrisiloxane (D₃) was carried out by Bostick [41] and Lee [42], with reported yields of polysiloxanes with quite narrow molecular weight distributions. The ring-strain present in the cyclic trimer makes it a much more reactive species than the cyclic tetramer, so that it is possible, under the proper conditions, to almost completely preclude siloxane redistribution processes other than the desired ring-opening chain propagation reaction. Specifically, it was reported [42] that the use of sufficiently weak bases in hydrocarbon solvents could exploit the selective polymerization potential of strained systems such as D₃. In fact, detectable polymerization of D₃ in the presence of butyllithium does not occur except in the presence of a Lewis

base promoter such as dimethylsulfoxide or tetrahydrofuran.

Frye [43] and Fessler [44] have studied the reactivity of organolithiums with siloxanes and the subsequent reactivities of the siloxanates in solvating and unsolvating media. It was found [43] that the reaction of equimolar amounts of n-butyllithium (BuLi) with hexamethylcyclotrisiloxane proceeded rapidly and exothermically in hydrocarbon media to yield BuMe₂SiOLi and unreacted D₃, as shown below:



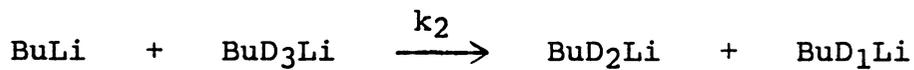
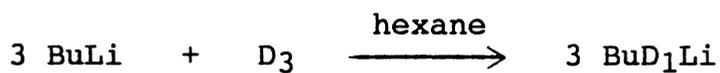
Analogous results were obtained in the much slower reaction of BuLi with D₄. This suggests that the cyclosiloxane undergoes a ring-opening alkylation in a rate-determining step, followed by a very fast series of alkylations on the resulting linear siloxanates [43] (see Scheme VII).

The presumed intermediates in Scheme VII were trapped by adding BuLi to a mixture of D₃ with Me₃SiCl. The presence of ether was necessary for reaction of the lithium siloxanates with Me₃SiCl, but essentially the same product distribution was obtained regardless of whether ether was present during or added subsequently to the BuLi addition. Other organolithium reagents were found to react similarly with D₃.

The anionic polymerization of D₃ in the presence of a variety of organolithium initiators continues to be the subject of much study as workers attempt to clarify the

Scheme VII

Alkylation Reactions of BuLi on D₃
and the Resulting Linear Siloxanates [43]



$$k_1 \ll k_2 \text{ or } k_3$$

kinetics and mechanisms of the process. The polymerization has been shown to be first order with respect to D_3 in a number of studies [45-47], and the area requiring clarification is on the nature of the active propagating species. Fractional orders with respect to initiator have been reported, often changing as a function of initiator concentration, which provides evidence for the presence of aggregates and a change in the degree of aggregation as a function of the concentration of siloxanolate end groups [46]. The use of cryptates is one approach which has been explored in attempt to suppress the formation of aggregates and aid in elucidation of the kinetics of propagation in the anionic polymerization of D_3 [47].

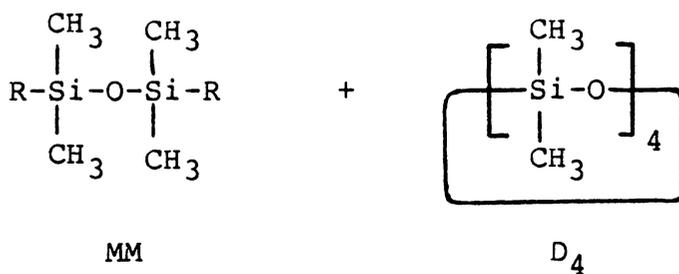
* Acid- and Base-Catalyzed Equilibration Reactions

Octamethylcyclotetrasiloxane (D_4) readily undergoes acid- or base-catalyzed ring opening for the preparation of linear polysiloxanes. The molecular weight and functionality of the resulting oligomers may be controlled by the addition of specified amounts of a linear disiloxane or endblocker [7,13,48,49]. This equilibration reaction is an important commercial process, and was widely studied in this research. A general reaction scheme for the polymerization of D_4 in the presence of an endblocker (MM) is shown in Scheme VIII.

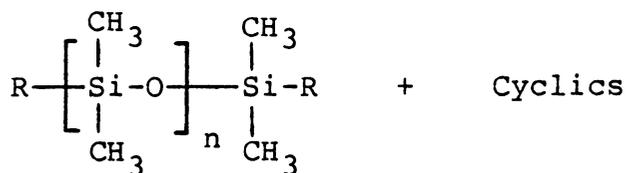
The equilibration reaction proceeds by a series of interchange or redistribution processes, resulting in a

Scheme VIII

Synthesis of Endblocked Polydimethylsiloxane



Catalyst
Heat

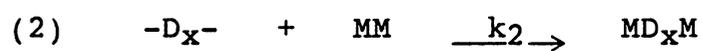
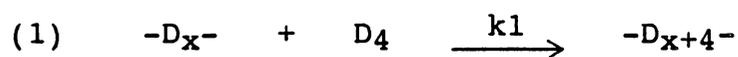


mixture of linear and cyclic species at thermodynamic equilibrium. The various redistribution processes are depicted in Scheme IX [49]. The first two reactions listed cause an increase in the number average molecular weight of the system, while reactions 3 and 4 affect only the higher moment molecular weight averages and are responsible for the attainment of the final equilibrium [49,50]. The relative rates of the various processes depend on the type of catalyst which is used, as will be discussed below. Interestingly, the polymerization of the cyclic tetramer is believed to be entropically driven, with essentially no enthalpy of polymerization. The positive ΔS may be explained by the high degree of flexibility of the linear polydimethylsiloxane chain [51].

The theory of equilibrium molecular weight distributions in linear polycondensation systems, including the equilibrium concentration of cyclics, was described by Jacobson and Stockmayer [52] some years ago. They showed that the amount of rings increased with dilution, and that beyond a critical dilution it was sometimes possible to obtain 100 percent yield of rings. Brown and Slusarczuk [53] were able to experimentally verify the Jacobson-Stockmayer cyclization theory for large rings, using GPC to measure the concentrations of macrocyclic dimethylsiloxanes (D₁₅ to D₂₀₀) in equilibrium with linear polydimethylsiloxane (PDMS). The Jacobson-Stockmayer theory was

Scheme IX

Redistribution Processes Occurring During A
Siloxane Equilibration [49]



subsequently revised by Flory and Semlyen [54] in order to account for the formation of small unstrained rings (D₄ and D₅) in large excess of predictions. The correction considers the relative orientation of the terminal bonds of a short chain when these bonds are forced into close proximity. In this situation, proximity of the termini would be conducive to ring formation [54], rather than uncorrelated as predicted by theory. This would explain the increased concentration of cyclic tetramer. A number of other studies have been reported since that time dealing with dilution and solvent effects, as well as the effect of siloxane chain conformation, on cyclization equilibrium constants [50,55-58].

The previously described ionic character of the siloxane bond allows the equilibration reaction to proceed under the influence of either acid or base catalysis. The choice of catalyst is dictated based on the nature of the endgroups on the endblocker and the types of substituents present on the silicon [59]. An acidic catalyst is chosen when the functional endgroups are susceptible to attack by base, and a basic catalyst is chosen when the endgroups are sensitive to acid.

A great deal of information has been published relating to the kinetic and mechanistic features of the cationic (or acid-catalyzed) polymerization of cyclosiloxanes [49,60-70]. Despite the extensive studies, explanations concerning the

observed behavior are still conjectural [68]. The subject will be dealt with only briefly below, since the focus of this research involved the anionic ring opening of cyclosiloxanes.

Various acidic catalysts have been studied, including sulfuric, trifluoroacetic, and trifluoromethanesulfonic (triflic) acids [60-62], as well as Lewis acids such as $\text{SnCl}_4/\text{H}_2\text{O}$ [63]. The observed order of reactivity for the acid-catalyzed polymerization of dimethylsiloxanes is [49]:



These results indicate that the susceptibility of the siloxane bond to attack by acids is directly correlated with the basicity of the siloxane oxygen atom [60]. Indeed, as a result of the increased reactivity of the more basic end-blocker (MM) relative to D_4 , the reaction does not proceed through a viscosity maximum. Siloxane oxygens are generally less basic than ether oxygens due to electron back-donation from the oxygen lone pair electrons to the d orbital of the adjacent silicon atoms [64]. The greater reactivity of D_3 may be attributed largely to the inherent strain in the cyclic trimer (~15 kJ/mole), but may also be due to less effective back-donation as a result of bond-angle distortions, leading to greater basicity in D_3 than in unstrained rings [50].

Studies on the polymerization of D_3 and D_4 initiated by triflic acid in methylene chloride solution have revealed

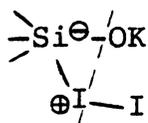
that both systems exhibit an initial first order dependence on the monomer concentration, and a higher order (2.7 to 3) in initial triflic acid concentration [68]. Significant differences are observed, however, in the overall rates of D₃ and D₄ polymerization, as well as in the role of added water and triflic esters in the respective systems. The nature and concentration of the active species in cationic siloxane polymerizations is unclear, but various activated complexes have been suggested including acid-siloxane, acid-water, and acid-silanol associated species [66]. Descriptions of the possible initiation and propagation processes, as well as viable structures of the activated species, have been described in detail elsewhere [65-68] and will not be presented here. Postulated reaction intermediates include primary [66] or tertiary [69] oxonium ions and silicenium ions [70], though no evidence has been presented for the actual existence of the silicenium ion [51].

The polymerization of cyclosiloxanes under the influence of basic catalysts has also been studied for some time though, again, relatively little is known about the detailed kinetics and mechanisms involved, especially in the presence of functional endblockers. A major focus of this research concerned the preparation of difunctional polysiloxane oligomers by the base-catalyzed polymerization of cyclosiloxanes. This subject will be addressed in some detail in the next section.

5. Kinetics and Mechanisms of Base-Catalyzed Equilibration Reactions

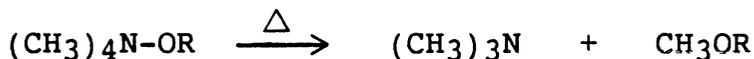
A large number of bases have been described as catalysts for the ring-opening polymerization of cyclic siloxanes [6,7,50,71]. Some of the most effective and widely used alkaline catalysts are hydroxides, phenolates and siloxanates of the alkali metals, as well as quaternary ammonium and phosphonium bases and their siloxanates.

The alkali metal hydroxides (such as KOH) and their siloxanates will endure much higher reaction temperatures (>140°C) than the quaternary bases, but they must be completely removed or deactivated to prevent depolymerization or degradation in the final siloxane product. Studies on the thermal stability of polysiloxanes [72-74] have shown that the addition of reagents capable of forming stable complexes with the active centers can suppress the depolymerization process and produce polymers with improved thermal and oxidative stability. Substances imparting various degrees of stabilizing effects include carbon dioxide, benzoic acid, metal oxides, iodine, and aluminum hydroxide. The CO₂-stabilized complex is ineffective above 150°C since it splits into its original components and frees active centers. The iodine-stabilized complex, on the other hand, imparts considerable stability since it decomposes



into KOI which undergoes disproportionation into KI and KIO₃ [75], both of which are inert towards depolymerization and oxidative degradation of the polysiloxane [74].

An alternative approach for the synthesis of thermally stable polysiloxanes is the use of thermally labile catalysts [76-78]. The quaternary ammonium and phosphonium bases are termed "transient" due to their thermal decomposition behavior above 130°C, eliminating the need for tedious washing or neutralization of the polymer. Tetramethylammonium hydroxide (TMAH) or its siloxanolate decompose to yield methanol or methoxysiloxane and trimethylamine, which will not catalyze siloxane equilibration reactions:



where R = H or (-Si(CH₃)₂O-)_n. An unattractive feature of the TMAH catalyst is the residual amine odor which is very difficult to remove completely.

The phosphonium bases decompose thermally in a different manner, producing phosphine oxides and hydrocarbons [77]:



These decomposition products are again ineffective as catalysts for siloxanes. Tetrabutylphosphonium hydroxide or its siloxanolate is preferred, due to its superior thermal stability and decomposition behavior relative to tetramethyl- and tetraethylphosphonium hydroxides [77].

Early kinetic studies on the base-catalyzed ring

opening polymerizations revealed that the order of reactivity of low molecular weight compounds toward the previously described bases is [49]:

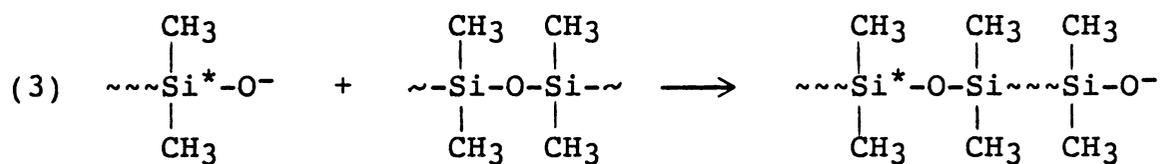
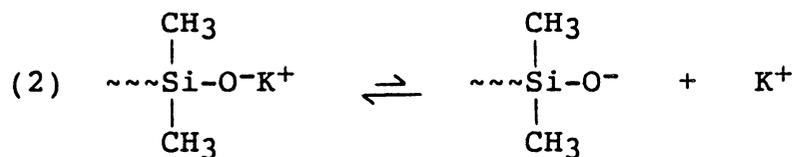
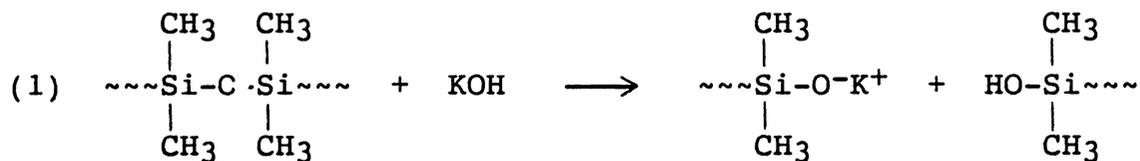


The greater reactivity of D units has been attributed to electron withdrawal from silicon by two adjacent oxygens rather than one [79]. This agrees with the mechanism postulated by Hurd et.al. [80], involving attack of the basic catalyst at the silicon atom. As a result of the observed reactivity order, the reaction mixture passes through a transient molecular weight (and viscosity) maximum, decreasing only after the less reactive endblocker equilibrates into the reaction mixture and begins to control the molecular weight [48,49].

Grubb and Osthoff [81] determined that (in the presence of hexamethyldisiloxane) the equilibration reaction shows a first order dependence in D_4 concentration and a square root dependence in potassium catalyst concentration. Their technique was to monitor the vapor pressure of the reaction mixture and compare that with the vapor pressure over mixtures of polymer and known amounts of D_4 . They also demonstrated [81] that the rate is approximately the same whether potassium hydroxide or its siloxanolate is used as the catalyst. As a result of their findings, the following mechanism was proposed for the base-catalyzed polymerization of cyclo-siloxanes (see Scheme IX), described below in terms of the

Scheme X

Mechanism for the Base-Catalyzed Polymerization
of Cyclosiloxanes [81]



(ring or chain
siloxane)

more commonly used potassium hydroxide.

The potassium hydroxide is believed to react essentially quantitatively with siloxane bonds to form potassium siloxanolate groups. Alternatively, the siloxanolate may be prepared separately prior to the equilibration reaction, and added in that form. The potassium siloxanolate is assumed to partially ionize according to some equilibrium constant, forming siloxanolate anions which are the active polymerization species. The rate-determining step is then attack of the siloxanolate anion on the electropositive silicon atom of the cyclic or linear siloxanes.

In general, this mechanism is supported by the observed order of reactivity among the alkali metal hydroxides, which increases in the order [71,80,82]:



Indeed, the fastest polymerization rates are observed in the presence of cesium hydroxide, which would be expected to be the most ionic in nature. Increased ionization of the siloxanolate should yield a higher concentration of active species. While Grubb and Osthoff [81] assumed a single associated ion-pair, Chojnowski and coworkers [83-86] have stressed the importance of ion-pair aggregation in the interpretation of the kinetics of the anionic polymerization of siloxanes. The reactivity order of the alkali metal hydroxides can then be rationalized on the basis of a decreasing tendency toward ionic aggregation with increased

size of the counter ions. Various structures of aggregates have been suggested (see Scheme X), including complexed species involving interaction of the siloxane chain with an alkali metal counterion of polysiloxanates which may or may not be a part of aggregates [85].

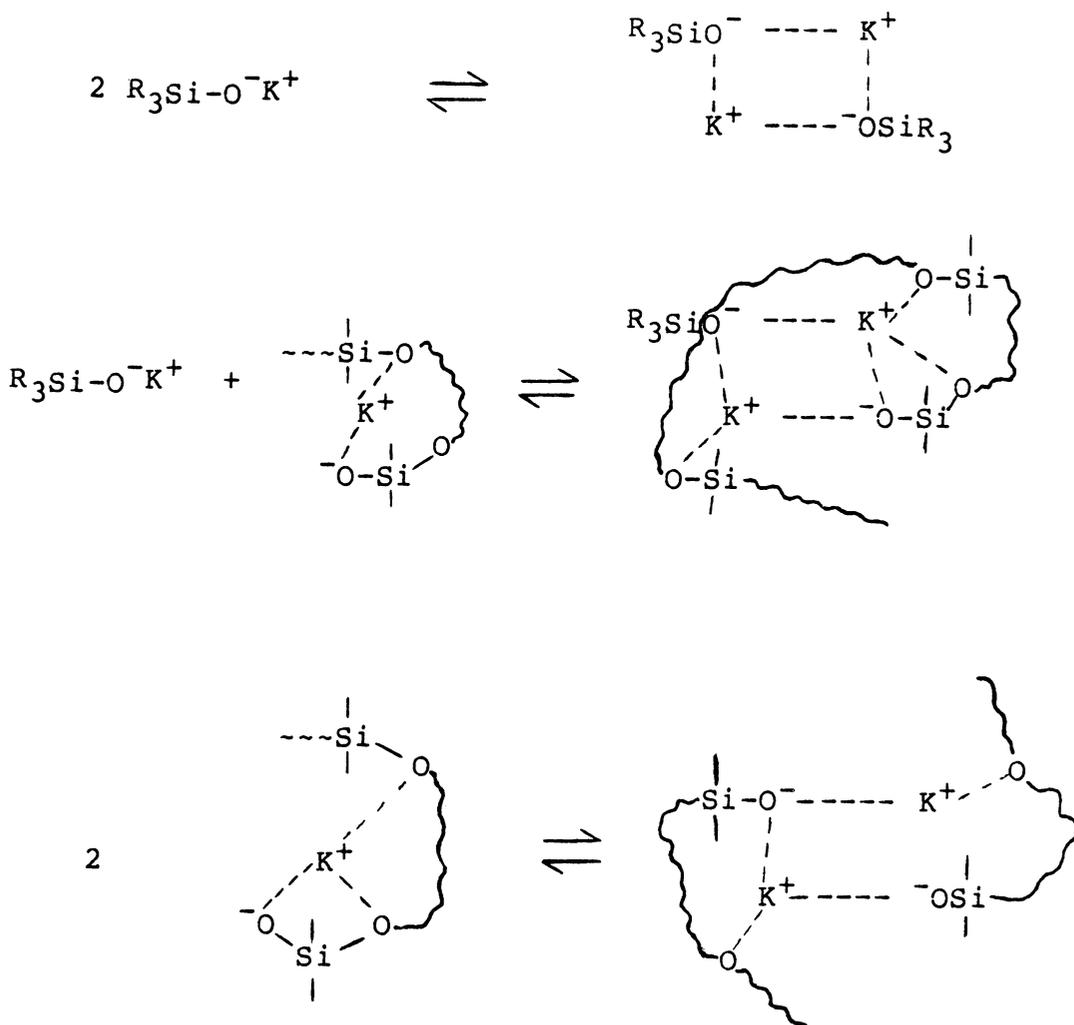
The ionic effect has also been confirmed by kinetic studies in media of different dielectric constant [87,88]. As the polarity of the polymerization medium was increased, the rate of polymerization also increased, but the other parameters of the system, i.e., equilibrium concentration of cyclics, molecular weight, etc., were not significantly affected [79]. Cooper and Elliott [89] reported similar rate enhancements by the addition of significantly smaller amounts of organosulfur derivatives, such as dimethylsulfoxide. The large accelerating effect in this case was attributed to selective solvation of the cation by the sulfoxide, thereby promoting ionization of the metal siloxanolate. Other additives which have been found to be effective in promoting base-catalyzed siloxane rearrangements include trialkyl phosphine oxides, phosphoric triamides, and trialkyl phosphates [90]. The promoter is thought to transform the intimate ion pair into a solvent separated ion pair, increasing the concentration of active centers which are available for attack on siloxane chains:



There is a need for continued examination and study of

Scheme XI

Proposed Structures of Aggregates of Active Centers
in the Siloxane Polymer [85]



siloxane equilibration reactions in order to determine the exact nature of the active polymerization species, and the effect of various reaction parameters on the ability to prepare well-defined difunctional siloxane oligomers. A number of these areas were explored in the present study, and the results are presented in Chapter IV (Results and Discussion).

B. SUPERCRITICAL FLUID FRACTIONATION OF POLYMERS

A great deal of attention has focused recently on the use of supercritical fluids in a variety of chemical processes. A number of excellent reviews are available detailing the development of supercritical fluid (SCF) technology and the diverse areas in which this technology has found application [91-96]. One of the more commonly known commercial SCF extraction processes is the decaffeination of coffee. Studies which have been reported in the area of polymer processing include 1) high-pressure polyethylene polymerization/fractionation, 2) extraction of low molecular weight oligomers from polymers, 3) supercritical fluid chromatographic analysis of polymers, 4) polymer fractionation, and 5) polymer-organic solvent phase separation [91]. The focus of this research was to explore the usefulness of supercritical fluids in the fractionation of aminopropyl terminated polysiloxane oligomers. The literature review which follows will discuss some of the

distinctive features of supercritical fluids, followed by a summary of the previous studies which have been reported in the area of polymer fractionation. The reader interested in a more comprehensive review on polymer fractionation studies using SCFs is referred to the excellent book by McHugh and Krukonis [91].

1. Characteristic Features of Supercritical Fluids

A supercritical fluid is a substance that has been heated above and compressed beyond its critical temperature (T_C) and pressure (P_C). The SCF region for a pure component is shown in the phase diagram in Figure 1. The usefulness of SCFs is largely related to their variable solvating power. In the supercritical region, small changes in temperature and/or pressure result in significant changes in the density and, therefore, the solvating power of the supercritical fluid. The region of greatest interest is near the critical point, $0.9 < T_R < 1.2$ and $1.0 < P_R < 3.0$, where T_R and P_R are reduced temperature and pressure, respectively ($T_R = T/T_C$; $P_R = P/P_C$). In these temperature and pressure ranges, the reduced density (ρ_R) of the solvent can change from a value of about 0.1 to about 2.5 (see Figure 2) [91]. As the density increases (and becomes more liquid-like), the intermolecular mean distance decreases and the specific interactions between solvent and solute increase [93]. A number of methods have been proposed [94,97-99] for calculating the solubility parameter of a

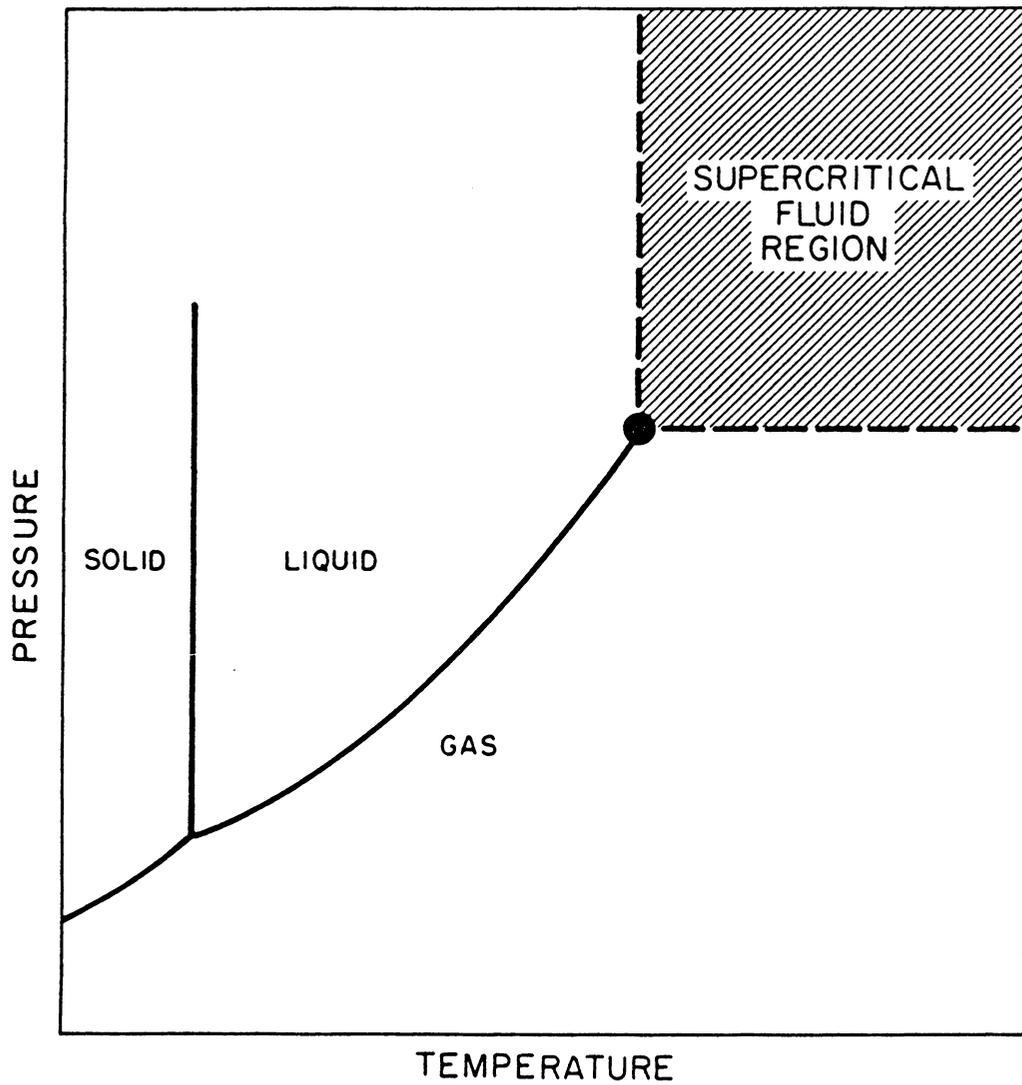


Figure 1: Pressure-Temperature Diagram for a Pure Component [91].

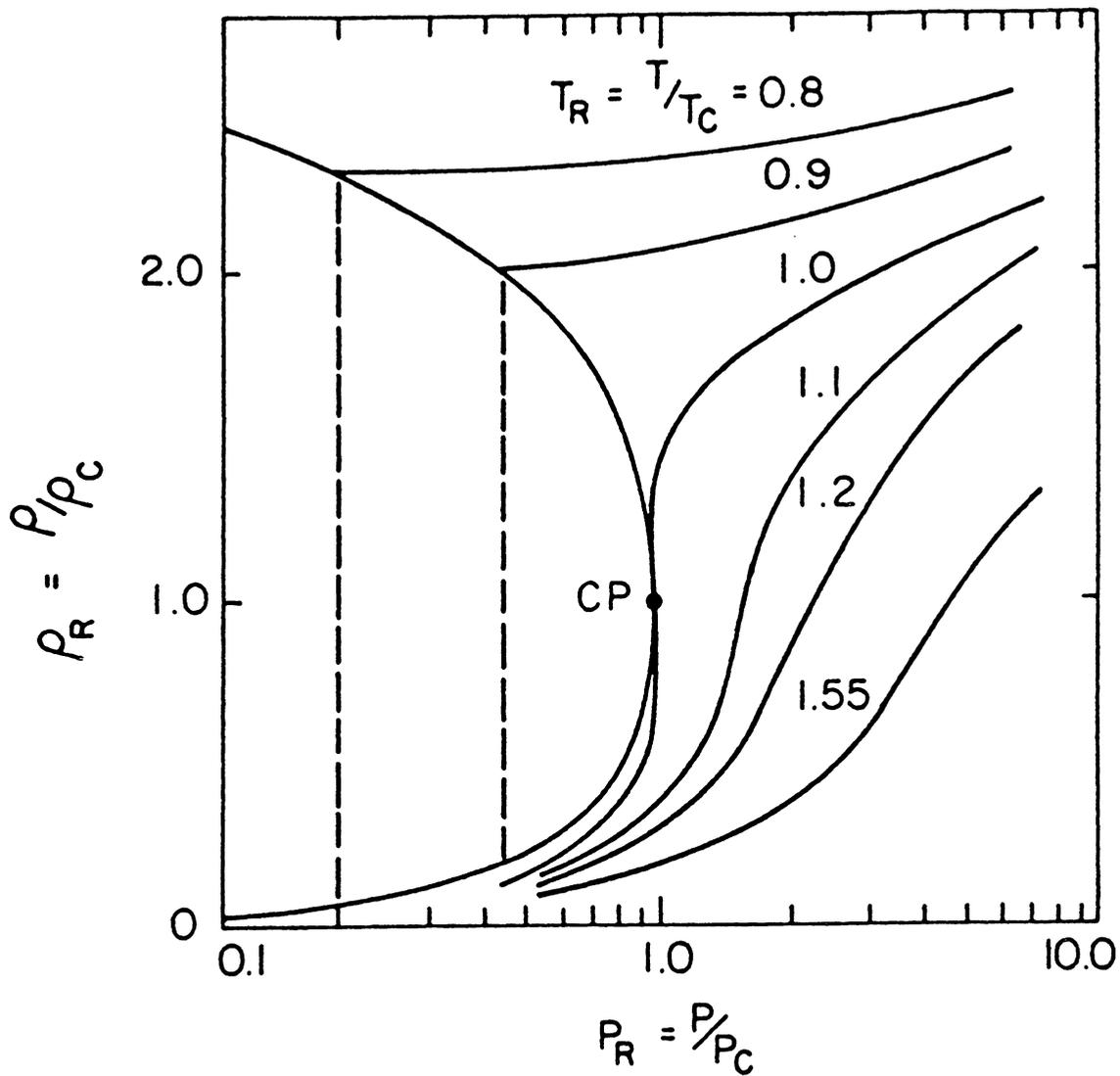


Figure 2: Variation of the Reduced Density (ρ_R) of a Pure Component in the Vicinity of its Critical Point [91].

supercritical fluid in an attempt to describe the solvent power of compressed gases as a function of pressure. (Alternative equations have also been described for calculating solubility parameters for polymers, where the Hildebrand equation generally does not apply due to the inability of polymers to vaporize without decomposing [94].) Regardless of how the solubility is described, the ability to use both temperature and pressure to regulate the density of the supercritical solvent is an attractive feature of SCF processes. A favorable result of this capability is enhanced control over the solvating power for various solute-solvent combinations.

In addition to their unique solvent characteristics, supercritical fluids possess a number of other properties which contribute to their effectiveness. In general, SCFs exhibit properties intermediate between those of a liquid and those of a gas. The density of a SCF more closely resembles that of a liquid, while its transport properties and compressibility are like that of a gas (see Table 4) [93]. The higher diffusivities and lower viscosities of SCF solvents allow them to penetrate substrates and approach equilibrium faster than normal liquids. SCF solvents also avoid problems with wetting due to their zero surface tension characteristics.

Finally, supercritical solvents are attractive from a practical point of view. Increased concern about the effect

Table 4
 Properties Typical of
 Gas, Liquid, and Supercritical Fluid [93]

| Phase | Property | | |
|--------|---------------------------------|--|--------------------------|
| | Density (g/cm ³) | Diffusion Coefficient (cm ³ /s) | Viscosity (cp) |
| Gas | (0.6-2.0) x 10 ⁻³ | 0.1-0.4 | (1-3) x 10 ⁻² |
| SCF | 0.2-0.9 | (0.2-0.7) x 10 ⁻³ | (1-9) x 10 ⁻² |
| Liquid | 0.6-1.6 | (0.2-2.0) x 10 ⁻⁵ | 0.2-3.0 |

of chemicals on the environment makes SCFs appealing since the most commonly used supercritical solvent, CO₂, is non-toxic and non-flammable. In addition, the SCF solvent can be easily removed or recycled after the extraction process to regenerate the pure material [100].

2. Polymer Fractionation with Supercritical Fluids

The first commercial-scale use of SCFs to fractionate polymers dates to the 1940s with the high pressure polymerization/fractionation of polyethylene. Several patents were issued [101-104] describing the process which involves the compression of ethylene to 40,000 psia (276 MPa) at an operating temperature of 250°C. A free radical initiator is added, resulting in the formation of polyethylene. The fractionation of the polymer according to molecular weight occurs downstream of the reactor with an isothermal lowering of the reaction pressure. As the pressure is reduced, the solvating power of supercritical ethylene decreases and the polymer precipitates from solution. The pressure reduction is carried out in stages, and fractions are collected at each stage [91].

Aside from the polyethylene operation described above, there has been relatively little reported on the use of SCFs to fractionate polymers on an industrial scale. In pilot plant (or industrial scale) polymer fractionation, however, a multiple step, sequential pressure reduction system would again be employed. A schematic of a continuous fraction-

ation system with several extraction/separation vessels is shown in Figure 3 [91]. The polymer is fed into the primary contacting vessel, as is the supercritical extractant which dissolves all or part of the polymer, depending on the operating parameters chosen for the primary vessel. (The system depicted in Figure 3 indicates that a high molecular weight fraction was allowed to remain in the primary vessel for later removal.) The extract phase containing dissolved polymer leaves the first vessel and is expanded to a lower pressure, which causes the highest molecular weight oligomers in solution to precipitate. The remaining solubilized oligomers are precipitated in a series of pressure reductions, until the lowest molecular weight material is no longer soluble. The solute-free gas is then recompressed and recycled. The number of fractions obtained is determined by the number of pressure reduction stages, while the polydispersity of each fraction is related to the pressure reduction ratio per stage [91].

The broad potential of SCF technology in the area of polymer fractionation has been realized largely as a result of successful laboratory scale separations on a variety of polymer systems. One such system is a perfluoroalkylpolyether fractionated by Krukonis [91] using supercritical carbon dioxide at 80°C. The fluoroether is used as a computer disc lubricant and as a seal fluid for computer disc drives. Both of these applications rely on the

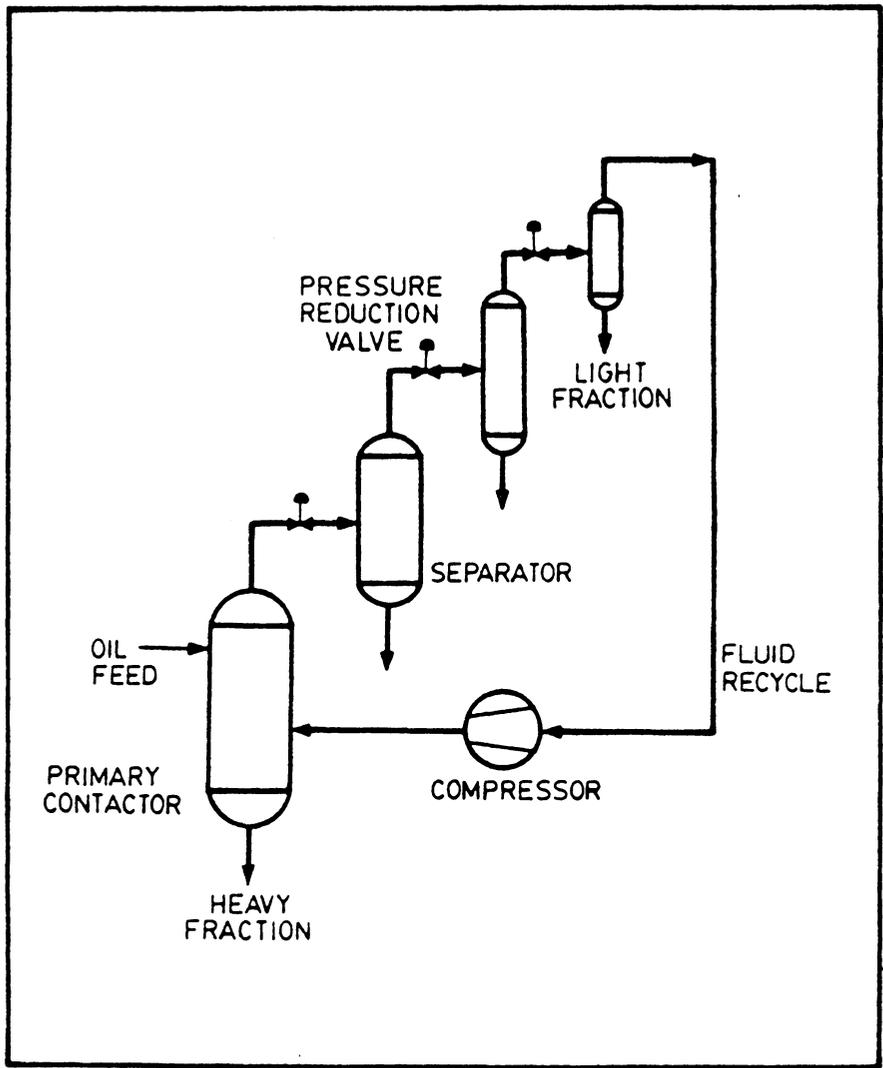


Figure 3: Flow Diagram of a Continuous Supercritical Fluid Fractionation Process [91].

viscosity and lubricating properties of the polymer for successful operation. Data was presented [91] where fractionation of the parent polymer (viscosity ~2000 cps) into five equal fractions resulted in materials with room temperature viscosities ranging from 800 cps to 9000 cps. The fractions were collected over a pressure range from 1200 psia (8.3 MPa) to 4000 psia (27.6 MPa). Viscosity analysis of the materials showed that SCF fractionation techniques provide a practical approach for obtaining polymers with carefully controlled properties.

Additional studies reported include the fractionation of a high molecular weight polydimethylsiloxane [91] and controlled molecular weight carboxypropyl terminated polydimethylsiloxanes [105]. The fractionations were carried out using supercritical carbon dioxide, and each produced a series of siloxanes with narrower molecular weight distributions than those of the parent materials from which they were derived. The fractions were obtained at constant temperatures (generally ~80°C) over a pressure range from ~1600 psia (11.0 MPa) to ~6500 psia (44.8 MPa). These conditions were sufficient for dissolving even the 100,000 g/mole fraction of the ~42,000 g/mole parent polydimethylsiloxane. Subsequent fractionation studies on poly(methylphenyl)siloxane required the use of supercritical ethylene at 80°C and 8500 psia (58.6 MPa) to dissolve the ~5000 g/mole fraction of the 2100 g/mole parent oligomer [91].

Thus, replacement of one of the methyl groups on the silicon with a phenyl group was observed to lower the solubility in CO₂ substantially. The various fractionated polysiloxanes (with narrower polydispersities and the absence of low molecular weight species) were expected to provide advantageous properties in areas such as electronics applications or in liquid crystalline copolymers.

Supercritical fluids have also been shown to be effective in fractionating various styrene/acrylic resins which are used in high-solids coatings applications [106]. Characterization data on the fractions provided detailed knowledge of the effects of molecular weight and molecular weight distribution on glass transition temperatures and viscosities. This data is particularly important for resins that are used as polymeric binders in high-solids paints and coatings where increases in coating viscosities can adversely affect the application properties [94].

The gel permeation chromatograms (GPCs) of these styrene/acrylic resins were performed using ultraviolet (UV) and refractive index (RI) detectors in series. The RI trace was considered a function of the overall concentration of polymer eluting from the column at a given time, and the UV detector was set at 254 nm for the detection of styrene. Since the ratio of UV to RI responses represents the concentration of chromophore in a given sample, and since the polymer had been separated into increasingly higher

molecular weight fractions, it was possible to characterize the copolymers in terms of their chemical composition as a function of molecular weight [106]. The results indicated a decrease in the styrene level at higher molecular weights. This was attributed to the formation of unstable Diels-Alder adducts from styrene monomer, where the adducts may ultimately appear as endgroups in the polymer since they undergo decomposition to form free radicals capable of initiating polymerization. The low molecular weight oligomers, with a higher percentage of mass occupied by end groups, in turn exhibit the highest proportion of styrenic endgroups. Additional peaks observed in the low molecular weight fractions were attributed to the presence of dimeric side products formed during the high-temperature free radical polymerization process.

A major focus of another recently reported study [107] involves the use of SCF fractionation techniques in elucidation of the chemical composition distribution (CCD) of poly(methyl methacrylate)-g-poly(dimethylsiloxane) copolymers. The graft copolymers had been prepared by both anionic and free radical copolymerization techniques. The samples were fractionated using supercritical chlorodifluoromethane, then characterized for molecular weight, MWD and composition by GPC, membrane osmometry, and NMR analysis techniques. The chemical composition distribution was readily observed by plotting cumulative weight fraction

of copolymer versus composition. Results of these plots indicate that the CCD is substantially more uniform for the anionically prepared copolymer than for the free radically prepared analogue. This result was anticipated based on inherent differences in the two copolymerization mechanisms. The study has also been extended to include the analysis of the same graft copolymer prepared using group transfer polymerization techniques [108].

It should be noted that interesting applications involving supercritical fluid processing of polymers are not limited to purification and fractionation procedures. Petersen, et. al. [109] have described the rapid expansion of supercritical fluid polymer solutions (RESFS) as a useful process for the formation of uniform thin films, powders and fibers. In order to realize the full potential of SCF technology as it applies to polymer systems, considerable effort has been underway to gain an understanding of the solubility and phase behavior of polymer solutions in supercritical solvents. Pertinent studies include the determination of pressure-temperature phase diagrams for various polymer-solvent combinations [110-112], as well as the development of lattice models based on statistical mechanics that reproduce the solubility data for various polymer-solvent combinations, i.e., determination of the dependence of oligomer partition coefficients on chain length, pressure and temperature [113,114].

Additional classes of polymers which have been fractionated into narrower molecular weight distribution fractions using supercritical fluids include polysilanes, useful as photoresist materials, polyisobutylene-succinic anhydride copolymers, useful as surfactants in engine lubricants, and polycarbosilanes, useful as precursors to silicon carbide ceramic materials [91,109]. As was the case in the previous examples, the fractions obtained in these separation studies generally exhibited more desirable properties for their respective end-use applications than those displayed by the parent polymeric materials. The results of all of these studies indicate that polymers processed by SCF fractionation procedures often have much more precisely controlled physical and chemical properties than are attainable using conventional processing techniques. This generally leads to materials with improved performance capabilities.

C. POLYARYLESTERS

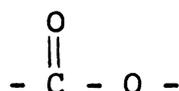
1. Introduction

Polyesters have been of considerable interest to polymer chemists since the early work of Carothers who laid the foundations of step-growth polymerizations [115]. The resulting concepts led to Carothers' discovery of nylon-6,6 in 1935 and the development of poly(ethylene terephthalate) (PET) by Whinfield and Dickson in 1941 [116]. A variety of

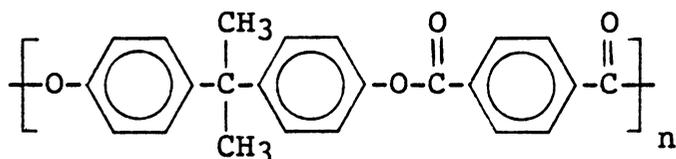
polyester structures can be prepared which offer a wide range of properties and uses. The discussion below will deal primarily with polyarylesters since they are pertinent to this research. More detailed discussions on polyesters can be found in a number of books and reviews [117-120].

2. Properties and Applications

Polyesters are characterized by the presence of carboxylate ester groups in the polymer backbone:

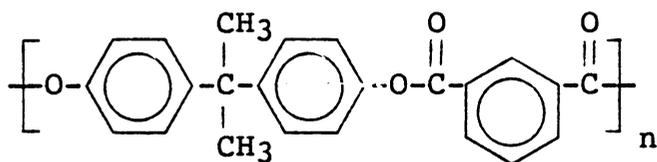


The properties of polyesters are determined by the structure, symmetry, polarity and segmental mobility of their repeating units [119]. In general, the presence of predominately cyclic components in the backbone leads to polyesters with higher glass transition temperatures and, if crystalline, higher melting temperatures. This effect is due to restricted chain motion in the ring relative to an acyclic component of similar length. The effect of symmetry was studied by Conix [121] and Eareckson [122], who independently synthesized a series of aromatic polyesters. They showed that a highly crystalline polyester may be prepared from bisphenol-A and terephthaloyl chloride:



However, the polyester synthesized from bisphenol-A and

isophthaloyl chloride may be either crystalline or amorphous depending on the solvent casting conditions:



In the range from 10:90 to 90:10 isophthaloyl chloride to terephthaloyl chloride, a completely amorphous polyarylester was obtained. The ability to crystallize, and the glass transition temperature, is also affected by the presence of bulky substituents on the aromatic rings [123].

Desirable properties of polyester fibers include their high melting and glass temperatures, UV and thermal stability, resistance to moisture, and high modulus. Variations in molecular weight, orientation and crystallinity allow the properties of polyesters to be tailored for their particular end uses. Polyester fibers are used in apparel, curtains, upholstery, and fiberfill, as well as for industrial applications such as tire cords and filter fabrics [119].

Polyester films are also widely used in applications such as bases for magnetic, video, and computer tapes, and packaging. The excellent barrier properties of PET has led to its use for injection blow molding to form bottles for carbonated beverages [124].

The UV stability of even highly aromatic polyesters is a result of the photo-Fries rearrangement which is shown in

Scheme XII. The newly formed ortho-hydroxybenzophenone structure is believed to remain on the surface of the film where it protects the bulk of the sample [125-127]. Aromatic polyesters with substituents in the ortho position are unable to undergo the Fries rearrangement.

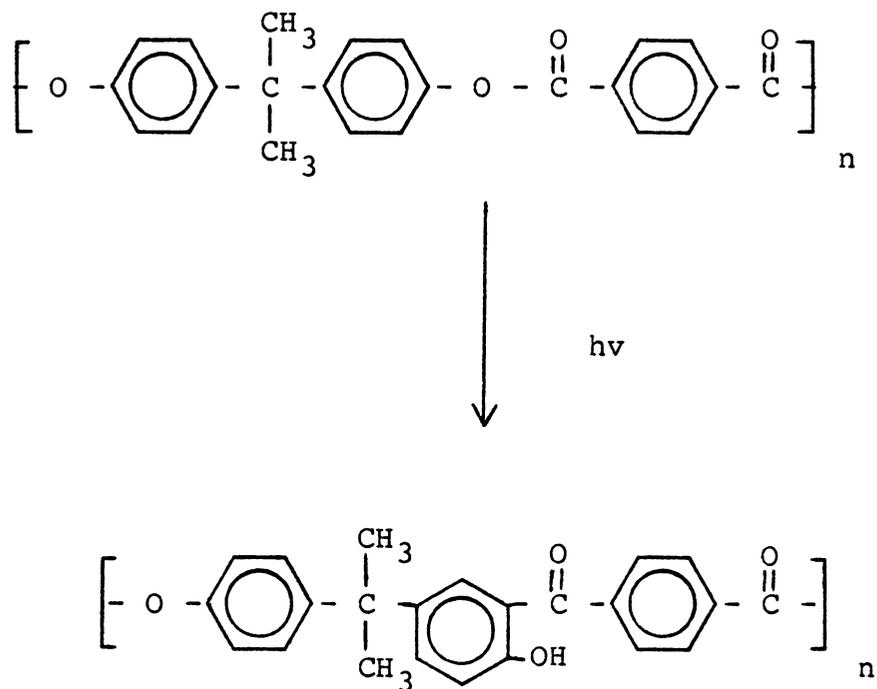
3. Synthesis

A number of synthetic approaches are available for the preparation of polyarylestere [117,120,128]. These include direct esterification, transesterification (ester interchange), and the reaction of alcohols with diacid chlorides. The general reactions involved in these three methods are illustrated in Scheme XIII. Each of the reactions involves nucleophilic addition to the carbonyl group, which is facilitated by the polar nature of the carbon-oxygen bond and the ability of the carbonyl oxygen to assume a formal negative charge. A general mechanism may be written as shown in Scheme XIV. Each step is reversible, except in the case of the diacid chloride where the reaction by-product (HCl) is less nucleophilic than alcohol and is generally removed as the reaction proceeds.

Direct esterification and transesterification are relatively slow equilibrium processes. Catalysts are often employed to increase the rate of reaction. Acidic catalysts used include protonic acids, Lewis acids, and titanium alkoxides. The acidic catalysts coordinate with the carbonyl oxygen, rendering the carbonyl carbon more

Scheme XII

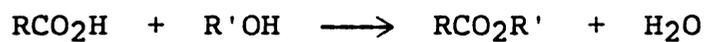
The Photo-Fries Rearrangement of Polyarylesters



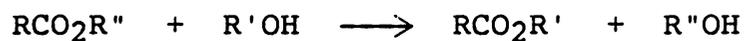
Scheme XIII

General Reactions Involved in Ester Formation

Direct Esterification



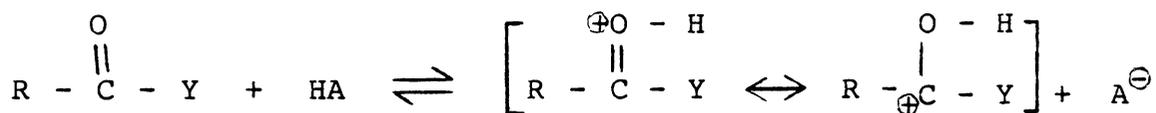
Transesterification



Reaction of Alcohols with Acid Chlorides



susceptible to nucleophilic attack:



Weakly basic catalysts are also employed for the ester-interchange polymerizations, where their role is to convert the reacting hydroxyl group to the corresponding alkoxide or phenoxide anion, which is the effective intermediate for the reactions involved in the interchange process.

a) Direct Esterification

The simplest method of polyester synthesis involves the reaction of a diol with a dicarboxylic acid or the self-condensation of a hydroxycarboxylic acid. The by-product of direct esterification reactions is water. Since these are equilibrium processes, the progress of the reaction is determined by the efficiency with which water is removed from the reaction mixture. Reaction temperatures around 150°C are generally employed, with a later stage at higher temperatures (>200°C). Care must be taken to avoid thermal degradation during the several hours of reaction time required to reach the desired molecular weight [119].

The requirement for a stoichiometric equivalence of functional groups to achieve high conversions is often difficult to obtain in the reaction of a dicarboxylic acid with a diol. The latter is often quite volatile, and losses may occur. This problem is avoided by employing an excess of the diol (about 10-20 mole %) in the initial condensation

stage.

b) Transesterification

The transesterification approach for the preparation of polyarylesters involves the reaction of a dialkyl (usually dimethyl) ester with an excess of diol in an ester exchange process liberating an alcohol (such as methanol) and forming a bis(hydroxyalkyl)ester. In a second stage, the ester is subjected to polycondensation by alcoholysis, forming the polyester and liberating a molecule of diol for each step of chain growth. The general reaction is shown in Scheme XV. The first stage is carried out at 150-200°C until the evolution of methanol is complete. The process is then continued at 230°-285°C under reduced pressures to drive the reaction to completion [119]. The use of excess diol, which is removed from the reaction mixture in the second stage, avoids the problem of trying to get 1:1 stoichiometry.

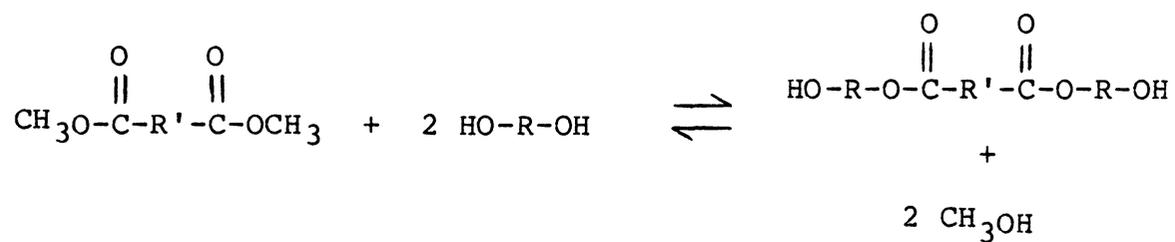
c) Acylation

Another approach for preparing polyarylesters is the reaction of a diacid chloride with a bisphenol monomer. The reaction can be done in the melt or in a high boiling inert solvent, with HCL being evolved [129-132]. A more versatile method is the Schotten-Baumann reaction which employs a base such as pyridine to catalyze the reaction and act as an acid acceptor for the HCl produced [120,133-135]. The latter reactions can be run at ambient temperatures.

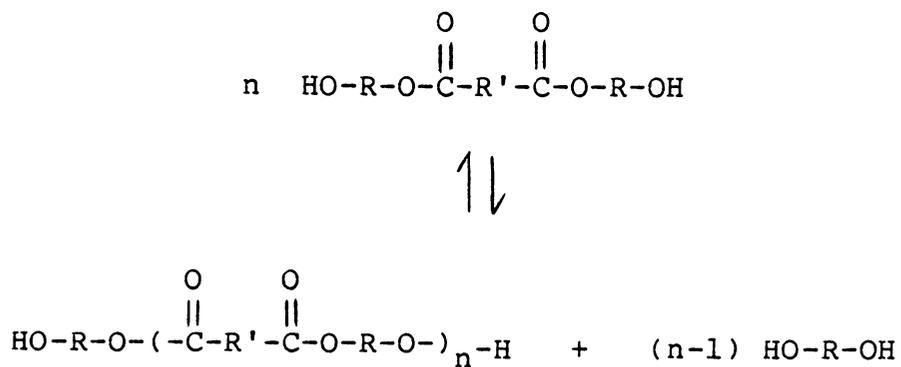
Alternatively, the acylation route may be conducted via

Scheme XV
Transesterification Reactions

(1) Ester Exchange



(2) Alcoholysis



an interfacial polycondensation [120], in which a solution of the diacid chloride in an organic solvent is rapidly agitated with an aqueous alkali solution of the bisphenol. The polymer forms immediately at the interface, and either precipitates or remains soluble in the organic solvent. A phase-transfer catalyst such as a tetraalkylammonium halide is usually added.

Interfacial methods do not depend upon exact stoichiometry to achieve high molecular weight since the reaction is diffusion-controlled. The solution polycondensation methods, however, require high purity starting materials and carefully controlled stoichiometry. A controlled stoichiometric imbalance (Carothers equation) is often employed to obtain a desired molecular weight oligomer with functional endgroups. The well-defined difunctional oligomers are then used in subsequent copolymerization reactions.

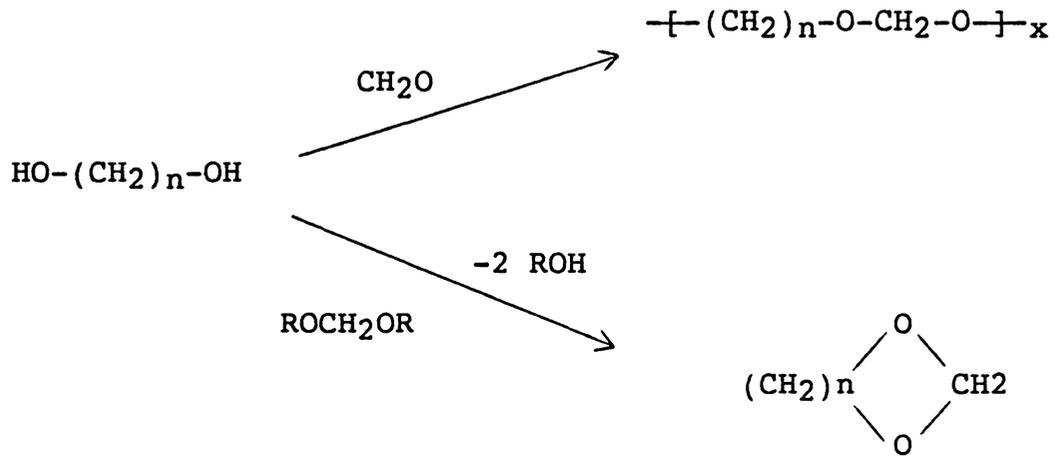
D. AROMATIC POLYFORMALS

1. Introduction

The synthesis of aliphatic polyformals involves the reaction of an aliphatic diol with formaldehyde or dialkyl formals as shown in Scheme XVI [136,137]. Unfortunately, when the diol contains 2, 3 or 4 carbon atoms, formation of the cyclic formal is favored (see Scheme XVI) [138,139]. Musser and Jackson [140] have described the preparation of low molecular weight aliphatic polyformals based on tetra-

Scheme XVI

Synthesis of Aliphatic Polyformals [137]



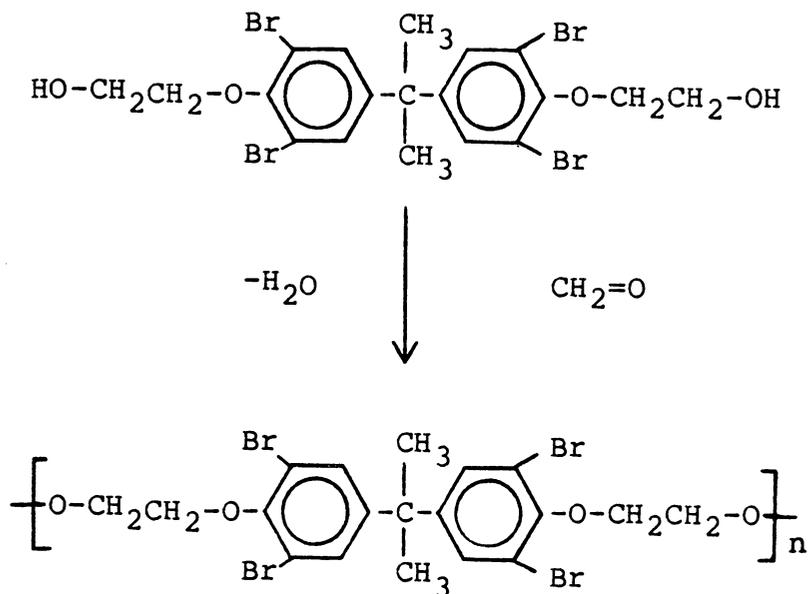
Cyclic Formals

bromobisphenol-A diethanol. The reaction is shown in Scheme XVII [140]. The materials were reported to be useful as flame retardant additives in polyester fibers.

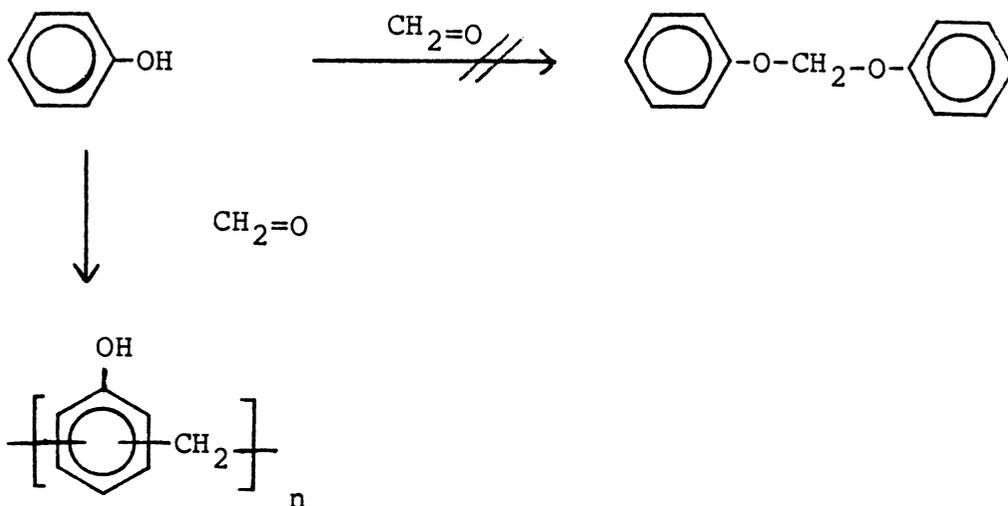
Aromatic polyformals cannot be synthesized by similar routes due to the predominance of C-alkylation of the phenol, resulting in the well known phenol-formaldehyde resins (see Scheme XVIII) [137]. Barclay was the first to report an alternate route [141] for the preparation of aromatic polyformals in 1962 when he reacted the disodium salt of bisphenol-A with bromochloromethane in DMSO. A variety of new aromatic polyformals and copolyformals have been prepared since that time based on similar chemistry. Despite these efforts, very little has been reported in the literature regarding the properties of these new materials, other than their wide range of glass transition temperatures [137]. Aromatic polyformals which are of commercial interest are not known at this time. However, a number of patents have described such materials which may be of interest for optical devices [142] or which have good processability (molding) and compatibility with styrene and vinyl chloride copolymers [143]. Aromatic cyclic polyformals have also been described as useful plasticizers for polymers in wire coating formulations [144]. The following section contains a brief review of the synthetic routes which have been utilized in the preparation of aromatic polyformals, and the various structures which have been reported.

Scheme XVII

Preparation of Aliphatic Polyformals Based On
Tetrabromobisphenol-A [137]



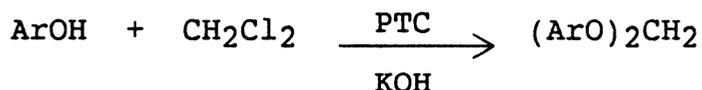
Scheme XVIII
C-Alkylation in the
Preparation of Aromatic Polyformals [137]



2. Synthesis

The synthesis of low molecular weight polyformals based on bisphenol-A was first reported by Barclay [141]. The hydroxyl terminated oligomers were isolated and further reacted with phosgene to form high molecular weight formal carbonate copolymers, as depicted in Scheme XIX. Matzner, Noshay and McGrath have also reported the use of hydroxyl terminated aromatic linear formals to form organosiloxane block copolymers [145].

In 1974, McKillop and coworkers [146] reported the formation of di-p-t-butylphenoxymethane from the attempted alkylation of p-t-butylphenol with benzyl chloride and a catalytic amount of a phase transfer catalyst (PTC) in methylene chloride. Dehmlow and Schmidt [147] also found that methylene chloride would react with phenols or alcohols in the presence of solid KOH and a phase transfer catalyst to yield formals, as shown below:

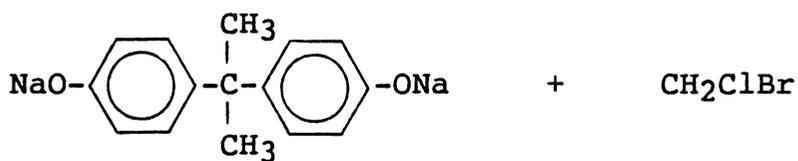


As a result of these efforts, Hay and coworkers [148] investigated the reaction of bisphenols and methylene halides under phase transfer catalyzed conditions in an attempt to prepare aromatic polyformals which would be of sufficient molecular weight to allow for an evaluation of their properties.

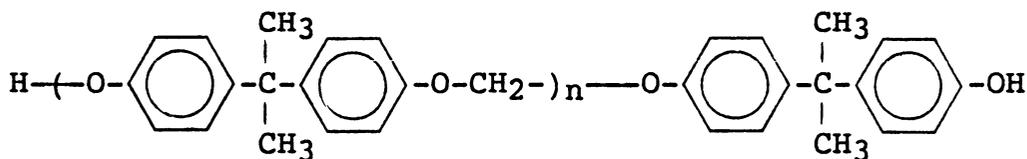
The polyformals were synthesized in refluxing methylene

Scheme XIX

Synthesis of Aromatic Polyformals and
Formal-Carbonate Copolymers Based On Bisphenol-A [141]

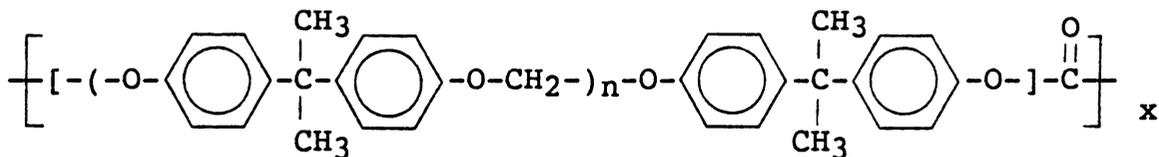


DMSO
55-60°C, 21 hr
150°C, 3 hr



Hydroxyl Terminated Polyformal

NaOH
COCl₂



Polyformal-Polycarbonate Copolymer

chloride and in a mixed chlorobenzene/methylene chloride solvent system. The polymers obtained had intrinsic viscosities greater than 0.54 dl/g, but GPC analysis revealed the presence of a large amount of low molecular weight material (40-50%). Further examination by reverse phase liquid chromatography resolved this low molecular weight material into a series of cyclic oligomers, as shown in Figure 4 [148]. The structures were confirmed by a combination of preparative liquid-liquid chromatography and mass spectrometry. The high cyclic content was attributed to the low solubility of the bisphenol-A anion in the system, which results in high dilution conditions for the reaction. A cyclic content between 7-11% (before isolation of the polymer) was found to be attainable by using tetrabutylammonium bromide (PTC) in a 1:1 mole ratio with bisphenol-A. Alternatively, the cyclic content was lowered to a similar level by increasing the solubility of the anion through the use of a dipolar aprotic solvent such as N-methylpyrrolidone (NMP) as a cosolvent with methylene chloride in the absence of a phase transfer catalyst. Substitution of methylene bromide or chlorobromomethane for methylene chloride did not result in a reduction in the amount of cyclics formed.

A number of aromatic polyformals based on other bisphenols were also prepared, although they were not extensively characterized. Some of the bisphenols utilized and

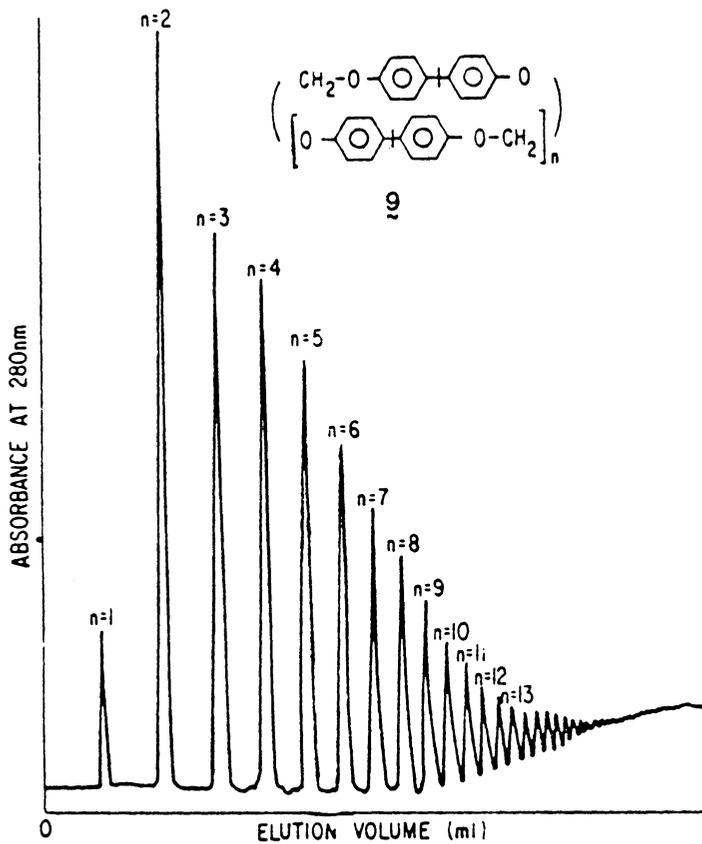


Figure 4: Gradient Elution Liquid Chromatogram of Low MW Cyclic Formals [148].

the glass transition temperatures of the resulting polyformals are listed in Table 5 [137]. The introduction of two or more ring substituents was generally found to increase the glass transition temperature, especially in the case of tetramethylbisphenol-A, which exhibits a T_g more than 50°C above that of the unsubstituted polymer [148]. In some cases, the T_g for the corresponding polycarbonate is also given.

Copolyformals based on bisphenol-A and other bisphenols were also prepared using the NMP/CH₂Cl₂ system in attempt to raise the T_g of the resulting polymer relative to the homopolymer based on bisphenol-A. The various combinations are listed in Table 6 [137]. The only characterization data available was the intrinsic viscosity values and the glass transition temperatures which are listed in the table. Block copolymers of poly(phenylene oxides) and polyformals based on bisphenol-A and tetramethylbisphenol-A have also recently been reported [149], again using NMP/CH₂Cl₂ as the polymerization solvent.

E. BLOCK COPOLYMERS

1. Introduction

The need for polymers which possess particular combinations of properties not attainable with simple homopolymers has led to the increasing development of various copolymer systems [150,151]. The copolymers may take the

Table 5
Aromatic Polyformals [137]

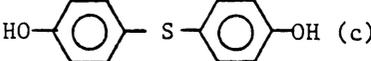
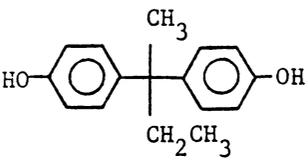
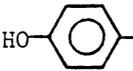
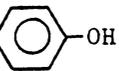
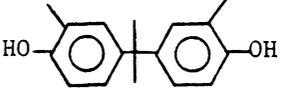
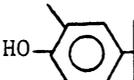
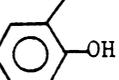
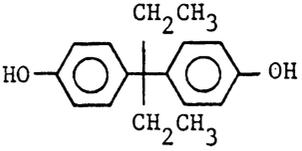
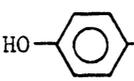
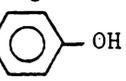
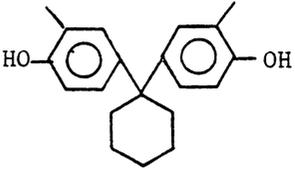
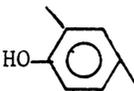
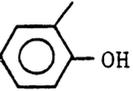
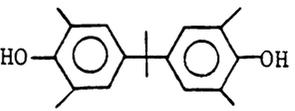
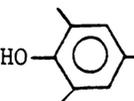
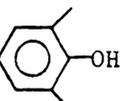
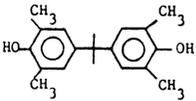
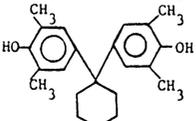
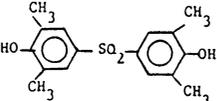
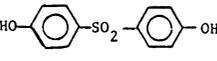
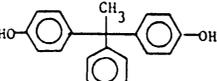
| Bisphenol | T_g °C (T_m °C) Polyformal | T_g °C Polycarbonate |
|--|------------------------------------|---------------------------|
|  HO—  —OH | (b) 41 (200) | |
|  HO—  —S—  —OH | (c) 63 (164) | |
|  HO—  —C(CH ₃)(H)—  —OH | 87 | 134 |
|  HO—  —C(CH ₃)(H)—  —OH | 90 | |
|  HO—  —C(CH ₂ CH ₃) ₂ —  —OH | 95 | |
|  HO—  —  —  —OH | 105 | |
|  HO—  —C(CH ₃)(H)—  —OH | 121 | 203 |

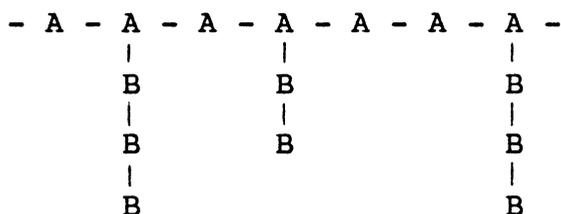
Table 6
Copolyformals With Bisphenol-A [137]

| Bisphenol | Mole Ratio of BPA/Bisphenol | | [η] (dl/g) | T _g °C |
|---|-----------------------------|---------------------|-------------------|-------------------|
| | Initial | ¹³ C-NMR | | |
|  | 75/25 | 71/29 | 0.58 | 102 |
| | 50/50 | 47/53 | 0.50 | 110 |
| | 25/75 | 31/69 | 0.62 | 122 |
|  | 75/25 | 75/25 | 0.32 | 106 |
| | 50/50 | 51/49 | 0.59 | 124 |
| | 25/75 | 35/65 | 0.58 | 133 |
|  | 75/25 | 80/20 | 0.42 | 114 |
| | 50/50 | 53/47 | 0.52 | 135 |
| | 25/75 | 30/70 | 0.25 | 152 |
|  | 80/20 | 81/19 | 0.52 | 106 |
| | 65/35 | 68/32 | 0.37 | 119 |
| | 40/60 | 39/61 | 0.26 | 138 |
|  | 50/50 | 56/44 | 0.37 | 114 |

form of either random, alternating, graft or block copolymers. Polymer blends, which would be economically more attractive, do not generally provide the desired "hybridization" of properties attainable in chemically-linked copolymers since physical blends of polymers are very rarely truly compatible [151]. The lack of interfacial adhesion between the separate phases in highly incompatible blends usually results in materials with very poor mechanical properties [152].

Random copolymers are the most versatile and economical type of copolymer, and they are readily synthesized by a variety of free radical and ionic addition techniques. The backbone consists of a statistical distribution of monomer units, dependent on the composition of the comonomer feed and the monomer reactivity ratios. Alternating copolymers are less common due to difficulties involved in their synthesis [51]. The random and alternating copolymers exhibit properties which represent a weighted average of the individual homopolymer properties.

Graft copolymers can be thought of as chemically linked homopolymers which display properties characteristic of each of the components, rather than a weighted average of their properties [151,153,154]. The general structure of graft copolymers may be represented as shown below:



Free radical, anionic and cationic mechanisms have been utilized for the preparation of graft copolymers by polymerization of a monomer in the presence of a previously synthesized reactive oligomer.

Block copolymers are comprised of two or more polymeric segments of different chemical composition which are connected end-to-end [155,156]. The possible structures include A-B, A-B-A, $-[A-B]_n-$ and radial block copolymers, as depicted in Figure 5. The extra synthetic efforts required for the preparation of block copolymers lead to well-defined structures with novel, desirable properties. The covalent bond between dissimilar segments restricts the extent to which the phases can separate, so that the two-phase morphology is generally exhibited on a micro-scale rather than a macro-scale. Block copolymers with highly compatible segments exhibit a single-phase morphology. Excellent control over the molecular architecture is possible in block systems, which leads to materials with interesting thermal and mechanical properties. The effect of block architecture on various properties will be considered briefly below.

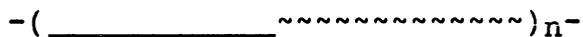
A-B Block Copolymer



A-B-A Block Copolymer



-[A-B]_n- Block Copolymer



Radial Block Copolymer

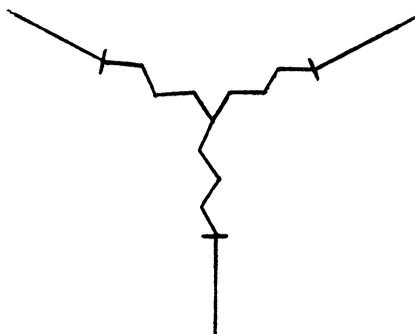


Figure 5: Block Copolymer Architectures.

2. Properties and Applications

a) Morphology

The extent to which microphase separation occurs in block copolymer systems depends upon the compositional dissimilarity, molecular weight, and crystallizability of the segments [151]. Single-phase morphology is observed when the segments are compatible due to chemical similarity and/or short length. Two-phase systems are produced when a fairly large solubility parameter difference exists between the two segments and/or the blocks are of sufficient length. The ability of either of the segments to crystallize is a driving force for phase separation.

In the case of $-[A-B]_n-$ block copolymers, complete microphase separation becomes more difficult, and varying degrees of partial microphase separation becomes more prevalent [157]. The domain size and shape takes on various forms as a result of different degrees of phase mixing and variations in fabrication conditions [158,159]. All of these factors affect the macroscopic bulk properties of the material.

b) Thermal Properties

The existence of a single T_g intermediate to that of the two homopolymers indicates a single phase amorphous block copolymer, as observed in random copolymer systems. In two-phase systems, two distinct glass transition temperatures are observed, as with physical blends. The modulus-

temperature behavior of single-phase versus two-phase block and graft copolymers is contrasted in Figure 6 [160].

c) Mechanical Properties

Block copolymers are generally comprised of a hard segment (T_g above room temperature) and a soft segment (T_g below room temperature). The toughness of an inherently brittle material can be improved by incorporation of minor amounts of a soft segment. Thermoplastic elastomers, on the other hand, are comprised of a major proportion of soft segment and a minor proportion of hard segment. The soft block provides flexibility and elastomeric character, while the hard block provides physical cross-links which improve the strength and recovery characteristics in the elastomer.

d) Applications

Commercially available block copolymers can be categorized as either elastomers, toughened thermoplastic resins, or surfactants. The elastomers are styrene-diene copolymers or their hydrogenated derivatives, ester-ether block copolymers, or urethane-ester block copolymers. Elastomeric materials are used in application areas such as automotive, electrical and electronic, sealants, adhesives, and footwear.

Toughened thermoplastic resins such as an amorphous radial styrene-butadiene block copolymer are useful in transparent packaging applications since they are tough and optically clear. Block copolymer surfactants include poly-

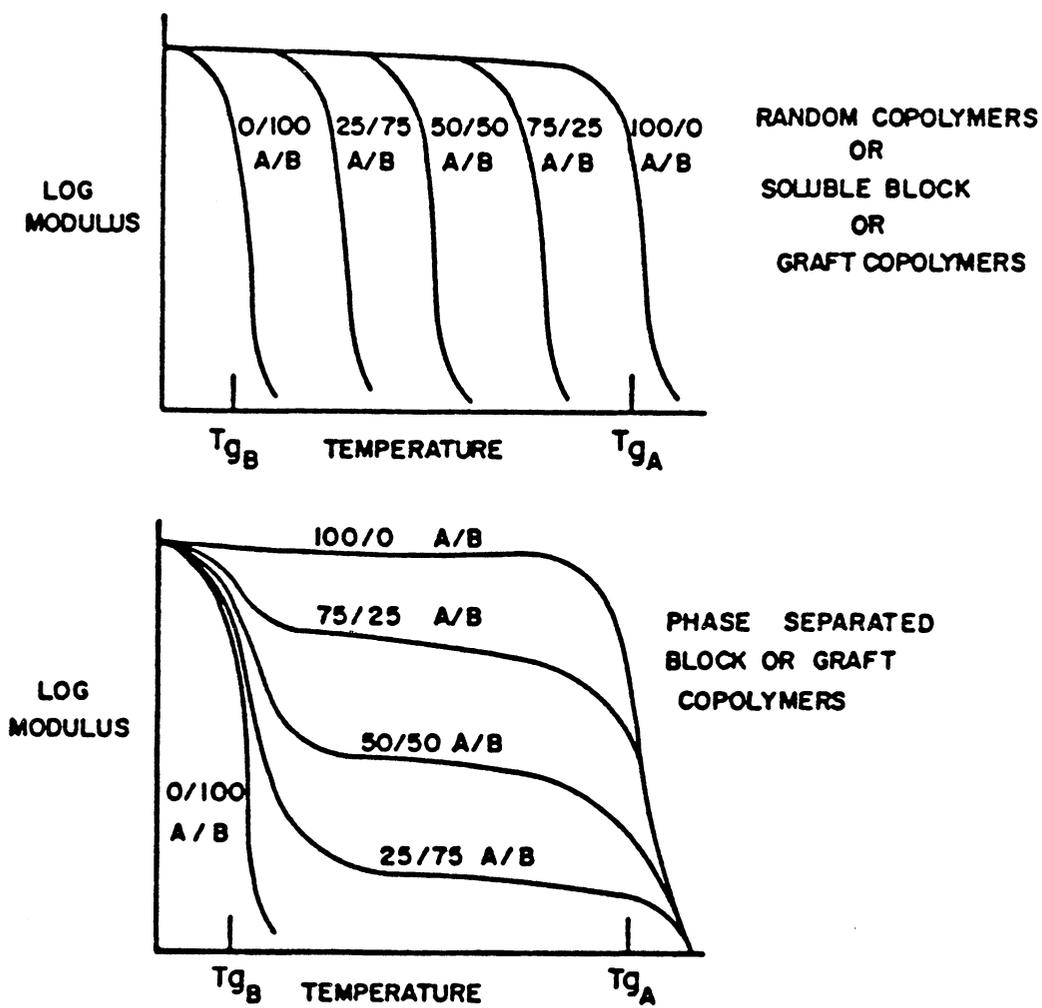


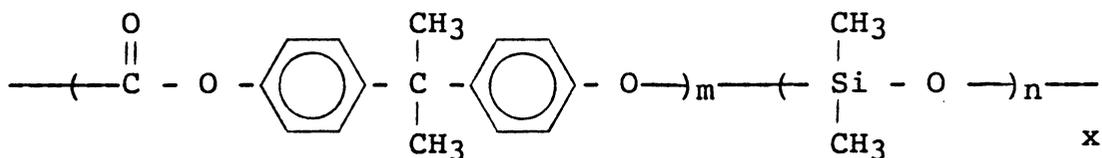
Figure 6: Modulus-Temperature Behavior of Single-Phase and Two-Phase Block and Graft Copolymers [160].

propylene oxide-co-polyethylene oxide A-B and A-B-A block copolymers and silicone-alkylene oxide copolymers.

3. Synthesis of Siloxane-Containing Block Copolymers

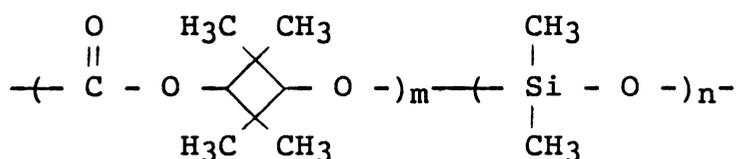
Block copolymers are commonly prepared via living addition polymerization techniques and step-growth condensation techniques. The synthetic approach utilized is dictated by the architecture desired in the resulting copolymer. Detailed discussions on the synthesis of block copolymers can be found in a number of excellent books [150,151,154,156]. The synthesis of siloxane-ester and siloxane-formal block copolymers will be considered briefly below.

The polyester blocks which have been combined with siloxanes include bisphenol-A carbonate, tetramethyl cyclobutylene carbonate, and arylene (or alkylene) phthalates. The bisphenol-A carbonate-dimethylsiloxane block copolymers were first synthesized by Vaughn [161] by the phosgenation of bisphenol-A and a dichloro-terminated dimethylsiloxane in the presence of pyridine. More controlled block sequences are attainable by the interaction of preformed chlorine-terminated siloxane oligomers and hydroxyl-terminated bisphenol-A carbonate oligomers in the presence of a tertiary amine [162,163] or the condensation reaction of bis(dimethylamine)-terminated dimethylsiloxane oligomers with dihydroxyl-terminated polycarbonate oligomers [164,165]. The structure of these copolymers is shown below:



High molecular weight polymers with varying siloxane contents were readily obtained. The materials generally exhibited microphase separation due to the large difference in solubility parameter between the carbonate and siloxane phases [166]. The mechanical properties of the copolymers range from rigid to elastomeric as the siloxane content is increased. The materials have also been reported to have useful electrical and permeability properties [167,168].

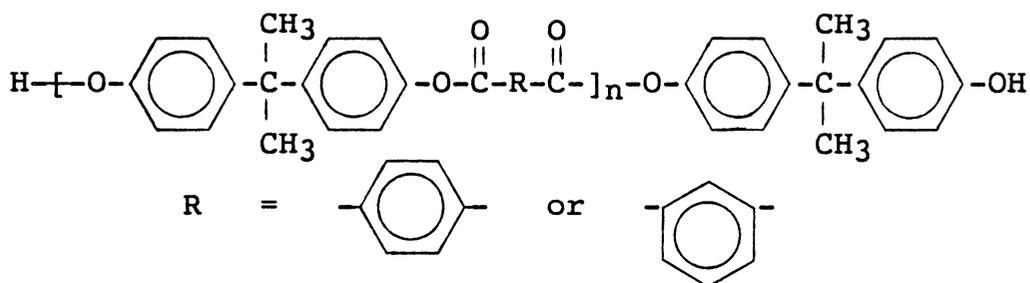
Tetramethyl cyclobutylene carbonate-dimethylsiloxane block copolymers were synthesized by the condensation of preformed well-characterized carbonate oligomers with bis(dimethylamine)-terminated polysiloxane oligomers, as described by Matzner, et al. [169,170].



The reaction rate is slower for the aliphatic, sterically hindered hydroxyl endgroups than for the phenolic endgroups in the bisphenol-A polycarbonate. The mechanical properties again varied with siloxane content, and the copolymers showed excellent processability and good thermal, hydrolytic, and ultraviolet stability.

Block copolymers containing siloxane segments and aryl

or alkyl phthalate segments were also reported by Matzner, et al. [169-173]. Well-defined hydroxyl-terminated oligomers were reacted with bis(dimethylamine)-terminated dimethylsiloxane oligomers. The ester block consisted of either bisphenol-A isophthalate (terephthalate) or hexamethylene terephthalate:



The block copolymers prepared from the bisphenol-A phthalate oligomers displayed good mechanical properties, while the more flexible hexamethylene terephthalate-siloxane block copolymers displayed poorer mechanical properties.

Polyformal-polysiloxane block copolymers have been reported by Matzner, et al. [145], using a similar synthetic technique to that described above for the polyesters. The formal-siloxanes were reported to exhibit good melt processibility, but fairly low modulus values.

Chapter III

EXPERIMENTAL

A. REAGENTS AND PURIFICATION PROCEDURES

1. Siloxane Starting Materials

Hexamethylcyclotrisiloxane (D₃) obtained from Petrarch Systems, Inc. was purified by stirring a known amount of the molten monomer and calcium hydride (CaH₂) in a pre-weighed flask for 24 hours, followed by vacuum sublimation into a calibrated flask cooled by an isopropanol/dry ice bath. The sublimed crystals were then dissolved and diluted to a known volume with highly purified cyclohexane. The original flask/CaH₂ was again weighed after sublimation in order to determine by difference the exact amount of monomer which had been sublimed and subsequently diluted. This solution (generally 45 weight percent D₃ in cyclohexane) was transferred under nitrogen via a double-ended needle (cannula) to a clean dry bottle containing a small amount of calcium hydride. The bottle had been fitted with a rubber septum secured in place with a copper wire. This solution could be stored under nitrogen pressure until needed for polymerization reactions.

Octamethylcyclotetrasiloxane (D₄) and octaphenylcyclotetrasiloxane (D₄") were generously supplied by the General Electric Company. The D₄ was dried over calcium

hydride and vacuum distilled before use, while the D₄" was recrystallized from toluene. Decamethylcyclopentasiloxane (D₅) obtained from Petrarch Systems, Inc. for chromatographic calibration procedures was used as received. 1,3-Bis(3-aminopropyl)tetramethyldisiloxane (referred to as aminopropyl disiloxane), also purchased from Petrarch Systems, Inc., was vacuum distilled from calcium hydride prior to use. The purity of the siloxane starting materials was checked by capillary gas chromatography (GC) using the procedure described later in this chapter. GC analysis of the disiloxane produces two peaks with almost identical retention times due to the presence of 1-2 % of 1,3-bis-(2-aminopropyl)tetramethyldisiloxane. The reactivity of this minor component should be similar to that of the 1,3-bis(3-aminopropyl)tetramethyldisiloxane.

Additional silicon-containing materials employed include phenyldimethylchlorosilane and a low molecular weight dimethylamine terminated polydimethylsiloxane oligomer (~600 g/mole). These materials were used as received from Petrarch Systems, Inc..

2. Monomers

High purity bisphenol-A and tetramethylbisphenol-A were obtained from Dow Chemical Company and generally could be used without further purification. However, if necessary, the bisphenol-A was recrystallized from toluene, while the tetramethylbisphenol-A crystallized nicely from methanol/H₂O

(75/25).

Reagent grade terephthaloyl chloride and isophthaloyl chloride were purchased from Eastman Kodak Company and required recrystallization to remove hydrolyzed acidic impurities. The general recrystallization procedure followed for all of the above monomers is described below. The impure monomer was dissolved with stirring in the refluxing recrystallization solvent. The hot solution was then filtered through hot fluted filter paper and allowed to cool slowly. In the case of the acid chlorides the solution was refluxed and filtered a second time to ensure removal of the insoluble terephthalic and isophthalic acid impurities. The filtered solutions were allowed to cool slowly at room temperature, then for several hours in the refrigerator. The pure crystalline monomer was isolated by filtration, dried under vacuum and stored in a desiccator until use.

3. General Reagents and Catalysts

Potassium hydroxide (KOH), tetramethylammonium hydroxide (TMAH·5H₂O) and tetrabutylphosphonium bromide (TBPBr) used in the preparation of the siloxanolate catalysts were obtained from Aldrich and used as received. Tetrabutylphosphonium hydroxide (TBPOH) was available from RSA Corporation as a 40 weight % aqueous solution. High purity sodium bicarbonate (NaHCO₃), calcium hydride (CaH₂) and tetradecane (C₁₄) were also obtained from Aldrich and used as received. Sec-butyl lithium, available from Lithium

Corporation as a 1.35 M solution in cyclohexane, was distilled on a high vacuum line at 65°C and 10^{-6} torr. Distillation was necessary to remove any alkoxide impurities which might be present due to hydrolysis of the sec-butyl lithium. The freshly distilled sec-butyl lithium was diluted to ~0.28 M with highly purified cyclohexane. The exact molarity was determined by titration with 0.100 N HCl.

4. Solvents

Fisher Certified Grade solvents used for potentiometric titrations and solution polymerizations were dried by distilling from calcium hydride. High performance liquid chromatography (HPLC) grade solvents used in the chromatographic analyses were also purchased from Fisher Scientific.

B. OLIGOMER AND POLYMER SYNTHESIS

1. Siloxanolate Catalysts

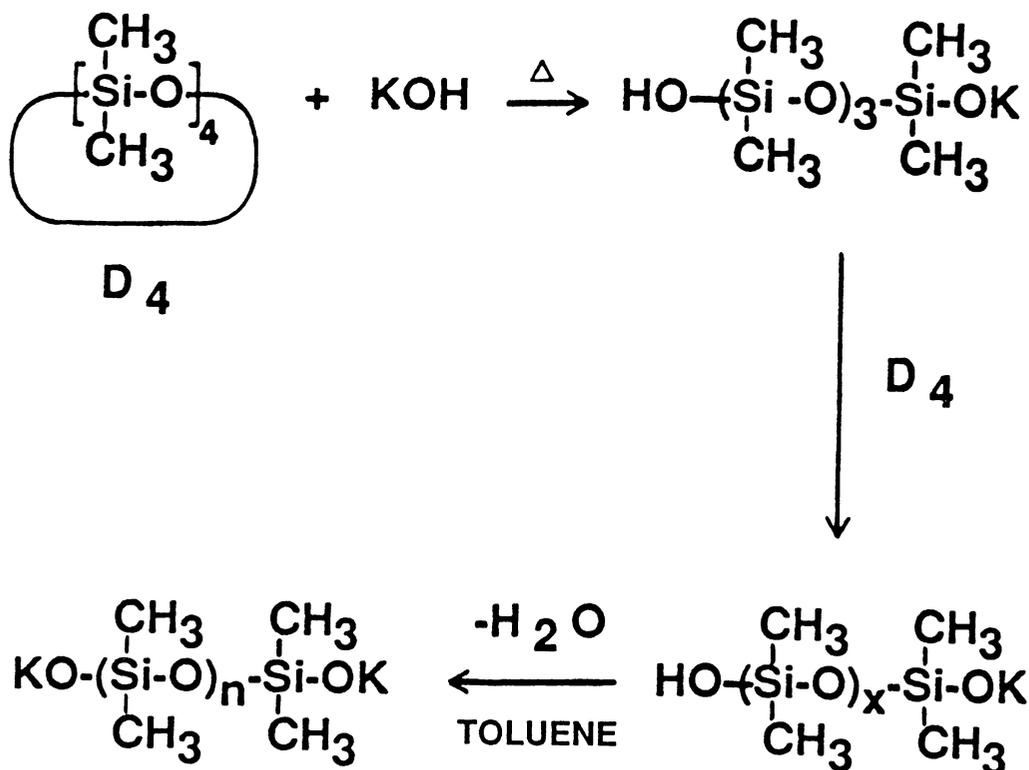
Several approaches were investigated in attempt to prepare a homogeneous, moisture-free siloxanolate catalyst with a known concentration of active endgroups, as required for a valid kinetic study. The development of the techniques which were finally employed is described in Chapter IV (RESULTS AND DISCUSSION). Provided below are the details of the synthetic routes utilized for the preparation of a) potassium siloxanolate catalyst, b) tetrabutylphosphonium siloxanolate catalyst and c) tetramethylammonium siloxanolate catalyst.

a) Potassium Siloxanolate Catalyst

The potassium siloxanolate catalyst used to investigate the equilibration reaction kinetics of D₄ in the presence of 1,3-bis(3-aminopropyl)1,1,3,3-tetramethyldisiloxane was prepared in solution according to the following procedure, also depicted in Scheme XX. Finely crushed potassium hydroxide, D₄ and toluene were weighed into a flask equipped with an overhead stirrer and an attached Dean Stark trap with condenser. Argon was bubbled through the solution from below the level of the liquid to promote the elimination of water via a toluene azeotrope as the reaction proceeded. A schematic of the apparatus used to prepare all of the siloxanolate catalysts is shown in Figure 7. In a typical reaction, 35.00g (0.1180 mole) of D₄, 2.20g (0.039 mole) of KOH and 35 ml of toluene were charged to the flask and heated in a 120°C silicone oil bath under a rapid stream of argon. This represents a D₄:KOH molar ratio of 3:1 and approximately 50% wt./vol. solution. Though initially the potassium hydroxide was not soluble, the reaction mixture became homogeneous and gradually more viscous as the potassium hydroxide reacted with the D₄, and as the toluene/water azeotrope was eliminated. After 24 hours, the potassium siloxanolate catalyst was clear and fairly viscous. At that point the catalyst was dissolved in dry toluene (~35% wt./vol.) to prepare a "stock" solution of the catalyst with a low enough viscosity such that it could be

Scheme XX

Synthesis of Potassium Siloxanolate Catalyst



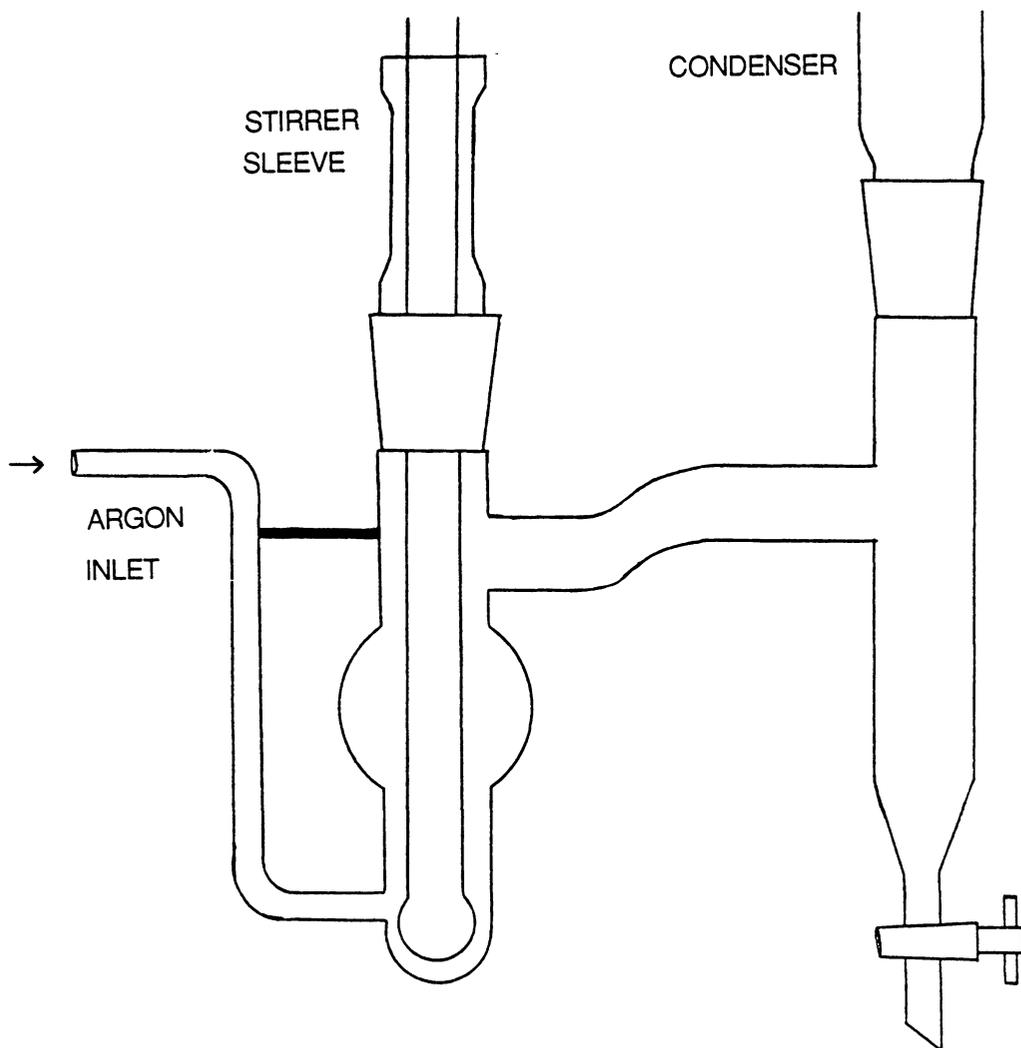


Figure 7: Apparatus Used in the Preparation of Siloxanolate Catalyst.

easily transferred using a syringe. The catalyst solution was stored in a desiccator until needed for a siloxane equilibration reaction.

b) Tetrabutylphosphonium Siloxanolate Catalyst

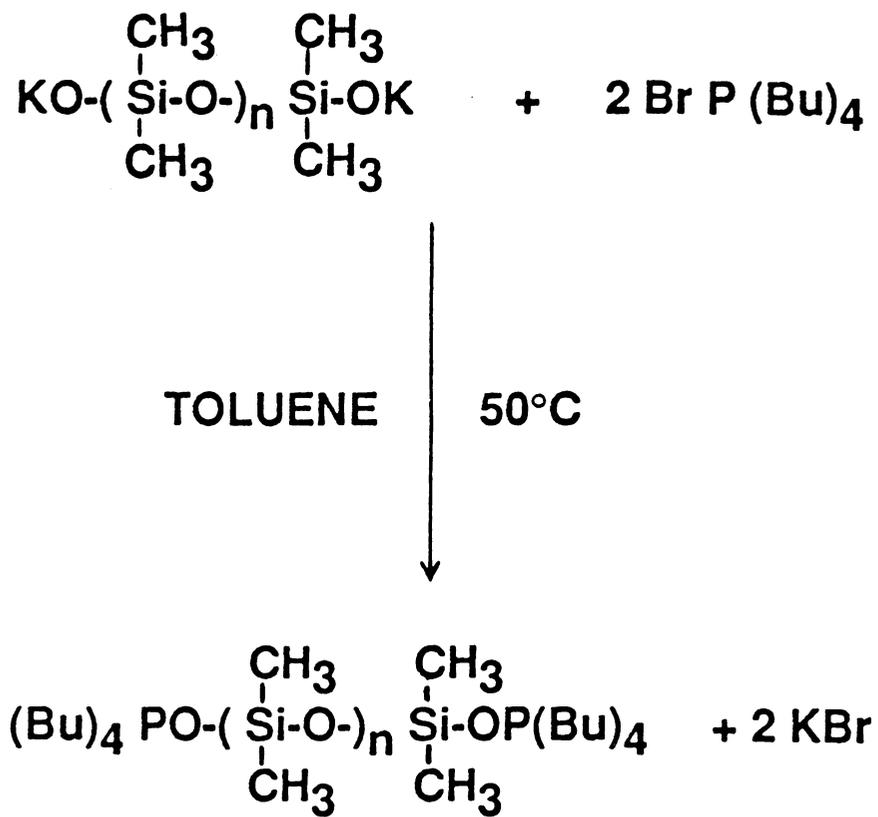
The tetrabutylphosphonium siloxanolate catalyst was prepared from the stock solution of potassium siloxanolate catalyst described above. The solution was titrated with 0.100 N HCl to determine the number of moles of base per gram of catalyst solution. Separately, a 35% wt./vol. solution of tetrabutylphosphonium bromide (TBPBr) in toluene was prepared containing enough TBPBr to completely convert the potassium siloxanolate catalyst to tetrabutylphosphonium siloxanolate catalyst as outlined in Scheme XXI. Upon mixing the two clear solutions at 50°C, the potassium bromide which formed as a result of cation exchange was observed to immediately precipitate out of solution. The newly formed tetrabutylphosphonium siloxanolate catalyst was decanted into vials and stored in a desiccator until needed.

c) Tetramethylammonium Siloxanolate Catalyst

The procedure used for preparation of the tetramethylammonium siloxanolate is similar to that described for preparation of the potassium siloxanolate catalyst. Typically, 23.73g (0.0800 mole) D₄ and 1.45g (0.008 mole) tetramethylammonium hydroxide pentahydrate (TMAH·5H₂O) were weighed into the apparatus illustrated in Figure 7. The reaction temperature in this case was held near 80°C, since

Scheme XXI

Synthesis of Tetrabutylphosphonium Siloxanolate Catalyst



slow decomposition of the catalyst begins above 90°C, and complete decomposition occurs rapidly above 130°C. A toluene azeotrope was not possible due to this limitation on reaction temperature, but generally 5 to 10 ml of toluene was added after the D₄ and TMAH·5H₂O had been heated to 80°C. After 24 hours, 1-2 ml of toluene was observed in the Dean Stark trap along with a drop of H₂O, indicating that some solvent loss had occurred at 80°C due to the rapid argon flow. The tetramethylammonium siloxanolate catalyst, a fairly viscous, translucent liquid, was transferred to vials and stored in a desiccator until use.

2. Amine Terminated Polysiloxane Oligomers

The amine terminated difunctional polydimethylsiloxane oligomers were synthesized in bulk by reacting D₄ and an amine functional endblocker in the presence of one of the siloxanolate catalysts just described. The molecular weight of the resulting oligomers, which are formed by a series of redistribution reactions, was controlled by the mole ratio of tetramer to endblocker. Sample calculations for the preparation of controlled molecular weight polydimethylsiloxane oligomers are presented in Appendix A. The procedure outlined below describes the apparatus and techniques employed for carrying out equilibration reactions which involved the removal of samples with time for the purpose of studying equilibration reaction kinetics.

Immediately prior to starting an equilibration reaction,

the siloxanolate catalyst was removed from the desiccator and titrated with 0.100 N HCl to determine the number of moles of siloxanolate present per gram of catalyst solution. The average result of three titrations was used to determine the amount of catalyst solution required for the desired catalyst level in any given equilibration reaction.

The reaction was carried out in a three-necked round bottom flask which had been thoroughly cleaned and dried overnight at 120°C in a convection oven. The flask, which contained a magnetic stir bar, was removed from the oven and fitted with rubber septa during cooling. Two of the three septa were then removed, and the D₄ and disiloxane were weighed directly into the flask in the proper amounts. The remaining two necks of the flask were fitted with a reflux condenser and an argon inlet. In addition, a thermocouple connected to a temperature controller was inserted into the reaction mixture through the rubber septum in order to allow the reaction temperature inside the flask to be monitored at all times. The oil bath temperature, and therefore the reaction temperature, was controlled by a forced-air cooled copper coil operating inside the oil bath, while the oil bath was heating on a hot plate with magnetic stirrer. Once the reaction temperature had stabilized at the desired value, the proper amount of siloxanolate catalyst (as calculated using the titration results) was added via a syringe through the rubber septum. The time of addition of

catalyst was considered $t=0$. The exact amount of catalyst added was noted by weighing the syringe before and after catalyst addition. Samples were subsequently removed via syringe at various reaction times and quenched in a dry ice/isopropanol bath to prevent further equilibration. The samples were stored in a refrigerator for later chromatographic analysis. The samples were found to be stable for long periods of time, but in most cases were analyzed within 24 hours.

It was desirable to terminate the equilibration reaction after 24 to 48 hours for analysis and isolation of the resulting siloxane oligomer. The transient tetramethylammonium and tetrabutylphosphonium siloxanolate catalysts were readily decomposed by heating for 30 minutes above 145°C. On the other hand, the potassium siloxanolate catalyst required neutralization of the catalyst with acetic acid, followed by washing with water and drying. The oligomer was analyzed to determine the amount of cyclics remaining at equilibrium. The cyclics were then removed by vacuum distillation at 100°C and 300 millitorr. The siloxane oligomer was characterized by a number of methods as outlined later in this chapter under Characterization of Oligomers and Polymers.

A similar procedure was followed for the preparation of aminopropyl and/or silylamine terminated polysiloxane oligomers for subsequent supercritical fluid fractionation

or for incorporation into block copolymers. An obvious deviation in these cases, however, is that samples were not removed during the course of the equilibration reaction. In addition, knowledge and control of the exact catalyst concentration and reaction temperature was somewhat less critical than was necessary for the kinetic studies.

Poly(dimethyl-co-diphenyl)siloxanes were prepared by charging the required amount of D₄" into the flask at the same time as the D₄ and the disiloxane. These mixtures were initially heterogeneous, but became clear and homogeneous as the D₄" was incorporated into the polysiloxane oligomer.

3. Phenolic Terminated Polyarylester Oligomers

Controlled molecular weight phenolic terminated polyarylesters were prepared for incorporation into siloxane-containing block copolymers. The polyarylesters were based on tetramethylbisphenol-A (TMBA) and a 50:50 mixture of terephthaloyl chloride and isophthaloyl chloride. Triethylamine was added to act as both an acid acceptor and a catalyst. Molecular weight control was achieved through the use of a stoichiometric imbalance of starting materials as determined by the Carothers equation [51]. Sample calculations for a 10,000 g/mole polyarylester are presented in Appendix B.

The reactor consisted of a four-necked round bottom flask equipped with an overhead mechanical stirrer, condenser, inert gas inlet, addition funnel and thermometer.

The tetramethylbisphenol-A monomer (30.00g, 0.1055 mole) and triethylamine (32.3 ml, 0.232 mole) were charged to the reaction flask with 450 ml methylene chloride. The system was continuously stirred and purged with inert gas. A solution of terephthaloyl chloride (10.269g, 0.0506 mole) and isophthaloyl chloride (10.269g, 0.0506 mole) in 50 ml methylene chloride was placed in an addition funnel and added dropwise to the reaction mixture over a period of one hour. A slight exotherm was observed, and the solution became increasingly viscous. The reaction was allowed to continue for 3 hours after complete addition of the acid chlorides. The polymer solution was then filtered to remove the triethylamine-hydrogen chloride salt formed during the reaction. The filtered solution was extracted with a 10% aqueous sodium bicarbonate solution to remove the last traces of the salt. The polymer was precipitated in excess methanol, filtered, and dried under vacuum with a 75 percent yield of a white powder-like solid.

4. Polyformals

Solution polymerization techniques were used to prepare high molecular weight polyformals, as well as controlled molecular weight phenolic terminated polyformals, based on tetramethylbisphenol-A and bisphenol-A. Sample calculations for preparing a 10,000 g/mole polyformal with a 70:30 molar ratio of tetramethylbisphenol-A (TMBA) to bisphenol-A are shown in Appendix C.

The reactor was a 500 ml, four-necked round bottom flask equipped with a mechanical stirrer, Dean Stark trap with condenser, thermometer, inert gas inlet and addition funnel as shown in Figure 8. In a typical reaction to produce a 10,000 g/mole phenolic terminated polyformal, 19.901g (0.0700 mole) TMBA and 6.845g (0.0300 mole) bisphenol-A were charged to the flask and dissolved in 100 ml freshly distilled dimethylsulfoxide (DMSO). This corresponds to approximately 30% solids for the reaction. The bisphenate of the monomers was formed by the slow addition of 17.20g of a 46.5 wt.% aqueous sodium hydroxide solution. Formation of the phenate resulted in a slight exotherm, as well as a noticeable color change in the reaction mixture. The phenate species produced a clear dark amber solution, which turned to a clear olive green upon the addition of 80 ml of toluene. The temperature was raised to ~120°C in order to allow dehydration of the system via a toluene/water azeotrope. Once the system had been dehydrated, the reaction was cooled to 80°C for dropwise addition of 8.26g (0.097 mole) of methylene chloride in 10 ml DMSO. An exotherm was again observed (generally 10 to 15°C) and the solution became turbid due to the formation of sodium chloride salt as the reaction proceeded. After 3 hours, the whitish-green reaction mixture was cooled and the polymer could be observed as a viscous gel on the bottom of the reactor due to its limited solubility in DMSO. The

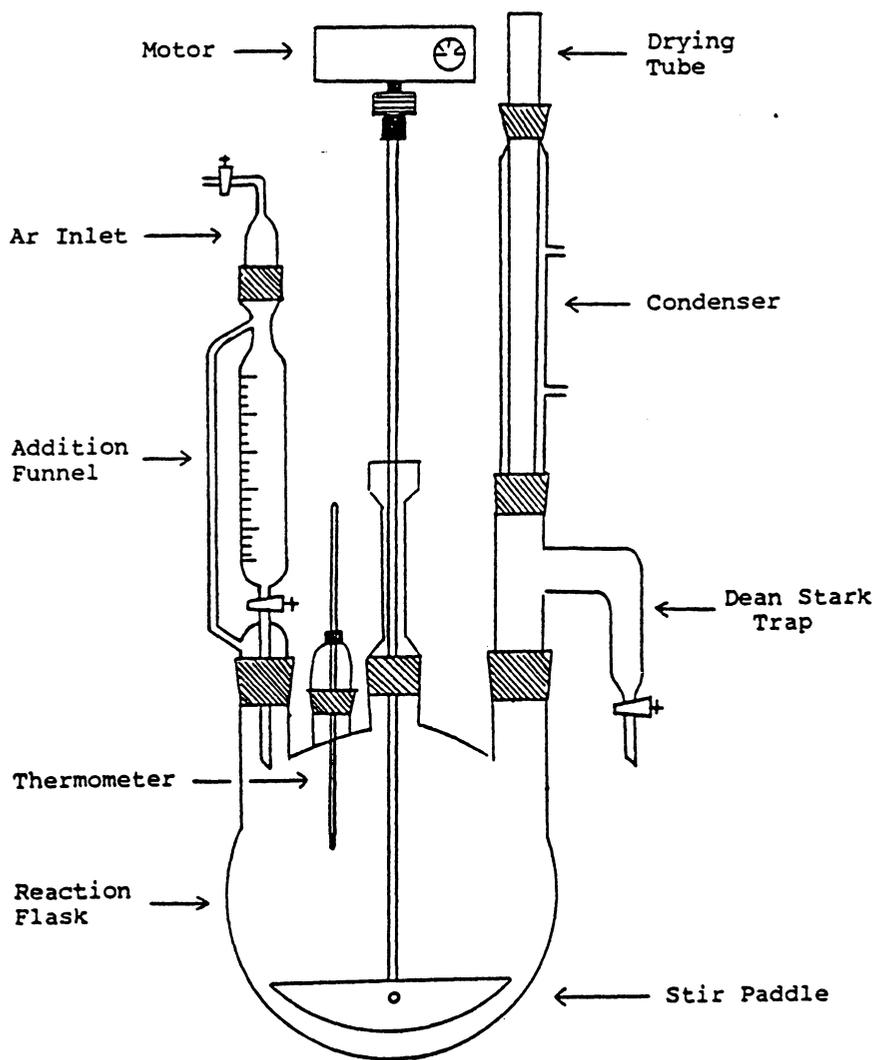


Figure 8: Apparatus Used in the Preparation of Polyformals.

mixture was diluted with methylene chloride which slowly dissolved the polymer. The solution was neutralized with oxalic acid in DMSO, resulting in more salt formation and a color change (to white) at the equivalence point. The solution was filtered through a Buchner funnel, producing an amber-gold solution which was not perfectly clear due to residual salt contamination. The polymer was coagulated in methanol and isolated by filtration to produce a fine tannish powder. Fairly low yields were obtained (~50%) due to the large amount of mechanical loss during the work-up procedure, as well as possible loss of conversion due to the limited solubility of the polymer in the reaction solvent. However, higher yields (~80%) were obtained when stoichiometric amounts of reactants were used to prepare high molecular weight polyformals.

5. Perfectly Alternating Siloxane-Containing Block Copolymers

Perfectly alternating polyarylester-polysiloxane block copolymers and polyformal-polysiloxane block copolymers were synthesized via the silylamine-hydroxyl condensation reaction demonstrated by previous workers [172-174]. The experimental procedure was identical for both copolymer systems, and will be described below for a block copolymer formed by reacting an 8500 g/mole phenolic terminated polyarylester with a 1960 g/mole silylamine terminated polydimethylsiloxane.

The reactor consisted of a one liter, four-necked round bottom flask equipped with a mechanical stirrer, inert gas inlet, addition funnel, thermometer and inverse Dean Stark trap with condenser. The difunctional polyarylester (20.00g, 0.0023 mole) of known number average molecular weight was placed in the reaction flask with 320 ml distilled chlorobenzene. With stirring and inert gas flow, the temperature was raised to chlorobenzene reflux (132°C). The system was dehydrated by removal of approximately 80 ml of solvent through the trap. An inverse trap was required due to the greater density of chlorobenzene relative to the density of water. Dehydration was necessary before addition of the moisture sensitive silylamine terminated polysiloxane oligomer to ensure that one to one stoichiometry with the phenolic endgroups was maintained. The polysiloxane oligomer (4.62g, 0.0023 mole) was added dropwise from an addition funnel over a period of 1 to 2 hours. Evolution of dimethylamine was detected by pH paper at the top of the condenser immediately upon addition of the polysiloxane oligomer. The solution viscosity was observed to increase as the reaction proceeded. The reaction was allowed to continue until the basic by-product was no longer detected, usually overnight. The reaction mixture was then allowed to cool, and the polymer was precipitated in excess methanol/isopropanol. The fibrous white product was isolated by filtration, and dried in a vacuum oven at 80°C

overnight. The recovered yield was 95 percent.

6. Preparation of Polysiloxane Standards for GPC

Anionic "living" polymerization of hexamethylcyclotri-siloxane (D₃) initiated by secondary-butyl lithium produced polydimethylsiloxane oligomers of narrow polydispersity. The molecular weight of the oligomers was controlled by the number of grams of monomer charged relative to the number of moles of initiator. Sample calculations for preparing a 10,000 g/mole polydimethylsiloxane oligomer are shown in Appendix D.

The reactions were carried out in one-necked round bottom flasks which had been thoroughly cleaned, then dried in a 120°C oven overnight. Immediately prior to use, the flasks, which contained Teflon-coated magnetic stir bars, were removed from the oven and quickly fitted with a rubber septum fastened onto the flask with a copper wire. The flasks were flamed and allowed to cool under a nitrogen purge, followed by pressurization with approximately 6 to 8 psi of nitrogen.

A calibrated glass syringe purged with nitrogen was used to add the desired amount of the D₃/cyclohexane solution to the pressurized flask. This was followed by addition of the proper amount of sec-butyl lithium solution to initiate the polymerization. (The monomer and initiator solutions referred to here were described in detail previously under REAGENTS AND PURIFICATION PROCEDURES.)

After approximately 15 minutes, purified tetrahydrofuran was syringed into the flask (~10% by volume) to promote propagation of the siloxane chain. The tetrahydrofuran (THF) had been distilled from a mixture of sodium metal and benzophenone in attempt to remove trace impurities which might otherwise terminate the "living" anionic polymerization. The procedure followed for purification of the THF is described in detail by Long [175].

The reaction was allowed to continue at room temperature for 24 to 48 hours, with the longer reaction times being necessary for achieving target molecular weights greater than 10,000 g/mole. Solution viscosities were observed to increase as the reaction proceeded. Termination was accomplished by addition of a 10 mole percent excess of phenyldimethylchlorosilane. Almost immediately, the white LiCl salt produced by the termination reaction was observed to precipitate out of solution. The mixture was stirred for one hour to ensure complete termination. The polydimethylsiloxane was then isolated by adding the solution to a 10 times excess of rapidly stirring methanol in a beaker. The mixture was stirred for 15 minutes in order to allow the LiCl salts, cyclohexane and excess chlorosilane to dissolve in the methanol. The oily dispersion of polydimethylsiloxane in the methanol was then allowed to settle, and the methanol layer was decanted as much as possible without losing any oligomer. The remaining siloxane/methanol was

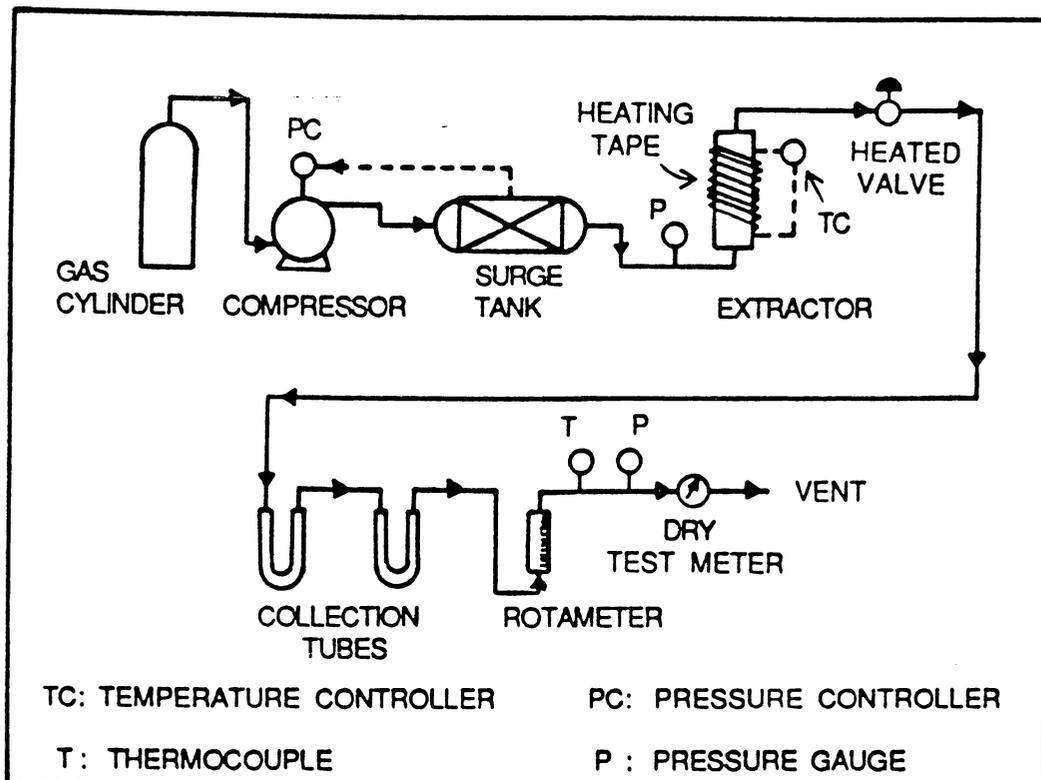
transferred to a separatory funnel and extracted twice with methanol. The oligomer was then transferred to a clean glass sample jar and dried under vacuum at 60°C until clear.

C. SUPERCRITICAL FLUID FRACTIONATION TECHNIQUES

Supercritical fluid fractionation of the aminopropyl terminated polysiloxane oligomers was carried out at Phasex Corporation by Dr. Val Krukonis and Paula Gallagher. A schematic of the experimental apparatus utilized for the fractionation procedure is shown in Figure 9 [105]. A general description of the procedure is outlined below.

Typically 30-50 grams of the siloxane oligomer to be fractionated was charged to the stainless steel extractor, which was then connected to a high pressure system (see Figure 9). The polysiloxane sample generally possessed a fairly broad molecular weight distribution due to the equilibration reaction techniques used to prepare the difunctional oligomer. Supercritical ethane was chosen as the solvent for fractionating the oligomer into narrow molecular weight distribution fractions. Once the extractor was on line with the high pressure supply of ethane, the system was brought to approximately 800 psi (5.5 MPa) and 80°C. The temperature was held constant throughout the entire process, about 50°C above the critical temperature of ethane.

The initial operating conditions dissolved only the low



Supercritical Solvent : Ethane
Pressure Profiling : 800 psi to 4000 psi
Temperature : 80°C

Figure 9: Experimental Apparatus and Conditions for Supercritical Fluid Fractionations [105].

molecular weight cyclics such as D₄ and D₅, allowing them to be removed from the extractor and isolated in the glass U-shaped collection tubes shown in Figure 9. The pressure in the extractor was then increased slightly so that the next higher molecular weight fraction of the siloxane could be solubilized in the supercritical ethane and carried out of the extractor. Once out of the extractor, the solution was expanded to ambient pressure, causing the siloxane to precipitate in a clean U-tube where it was isolated as Fraction 2. The tubes were generally immersed in a dry ice/isopropanol bath so that the sample could be trapped while the ethane was vented through meters which measured the flow rate and flow volume as it left the system. Subsequent fractions were collected in a similar manner.

Implementation of this pressure profiling technique from approximately 800 psi to 4000 psi (5.5 MPa to 27.6 MPa) allowed collection of a series of fractions with increasingly higher molecular weights due to the increased solubility of the oligomer at higher pressures of ethane. The size of the pressure increments was varied according to the molecular weight and composition of the parent oligomer. Precise control of the experimental parameters allowed collection of samples of the desired size and polydispersity. The material balance between polymer charged and polymer collected was 95%.

D. CHARACTERIZATION OF OLIGOMERS AND POLYMERS

1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a useful aid in elucidation of the chemical structure of oligomers and polymers. The spectra were recorded using a Nicolet MX-1 Fourier Transform Infrared Spectrometer that had been upgraded to a 10-DX Instrument (resolution = 2.0 cm^{-1}). Viscous liquid samples such as the polysiloxane oligomers were prepared for FTIR analysis by placing a drop of sample between two KBr salt plates. Spectra of film-forming samples were obtained by casting a dilute solution of the polymer in chloroform onto a salt plate and allowing the solvent to evaporate. The rate of evaporation was enhanced by heating the sample at low heat in a vacuum oven for 20 minutes. The samples were typically scanned at room temperature from 4000 cm^{-1} to 600 cm^{-1} with background subtraction for each analysis.

2. Nuclear Magnetic Resonance Spectroscopy (NMR)

Structural and compositional analysis of monomers, oligomers and polymers was carried out using NMR spectroscopy. Proton (^1H) NMR spectra were collected using a Bruker model WP-270 SY 270 MHz spectrometer on 10% (wt./vol.) solutions of sample in deuterated chloroform. Though tetramethylsilane (TMS) is commonly employed as a chemical shift reference, it could not be utilized in the analysis of siloxane-containing samples due to overlapping peaks. In these cases, either methylene chloride (at 5.37

ppm from TMS) or the CHCl_3 impurity (at 7.24ppm) was used as the reference.

The composition of the block copolymers was determined using the proton NMR spectra. In the case of the TMBA polyarylester-polysiloxane block copolymers, the integration of either the isopropylidene peak (at 1.7 ppm) or of the substituted methyl groups (at 2.2 ppm) due to the polyarylester backbone was compared to the integration of the silicon-methyl peak (at 0.1 ppm) due to the polysiloxane backbone. This allowed calculation of the weight percent siloxane which had been incorporated into the block copolymer. Indeed, integration of peaks due to the polyformal backbone relative to peaks produced by the siloxane backbone in polyformal-polysiloxane block copolymers provides similar information. In addition, one can obtain molecular weight information by proton NMR when analyzing oligomers of sufficiently low molecular weight (~10,000 g/mole or less) provided the structure of the chain end(s) is significantly different from that of the backbone. Integration of the peak due to the chain end(s) was compared to the integration of peaks due the repeating unit of the polymer chain to determine the number average molecular weight of the oligomer.

Similar compositional and molecular weight information was obtained through the use of ^{13}C NMR and quantitative ^{29}Si NMR. The ^{13}C spectra were obtained using a Bruker NR-

80 spectrometer operating at 20 MHz and employing an inverse-gated proton decoupling program. The polymer solutions were approximately 10% solids in deuterated chloroform.

The ^{29}Si spectra were collected on a Bruker WP-200 SY spectrometer operating at 39.75 MHz. An inverse-gated decoupling program was again employed on samples dissolved in deuterated chloroform (~15% solids) and containing a small amount (0.02M) of $\text{Cr}(\text{AcAc})_3$ to enhance relaxation times. The number of scans required depended on the signal-to-noise ratio in the sample. Accurate quantitation of the ^{29}Si NMR data was possible only to ~5000 g/mole under these operating conditions due to the poor signal-to-noise ratio obtained for the silicon peaks due to the chain ends. Increased sample concentrations, as well as collection of an increased number of scans per sample, would improve the accuracy of the results to a limited extent.

3. Potentiometric Titrations

In order to determine the number average molecular weights of functional oligomers or the concentration of siloxanolate species present in the siloxanolate catalyst solutions, potentiometric titrations were carried out using a Fisher Automatic Titrator II. A standard glass-body combination electrode was used with a Ag/AgCl reference.

The amine functional siloxane oligomers and the siloxanolate catalysts were titrated with 0.100N HCl in

isopropanol, with an isopropanol/tetrahydrofuran mixture as the titration solvent. The phenolic terminated polyarylester and polyformal oligomers were dissolved in freshly distilled tetrahydrofuran or dimethylacetamide and titrated with 0.10N tetramethylammonium hydroxide (TMAH) in methanol. The exact normality of the TMAH titrant was determined by standardization with potassium hydrogen phthalate.

The general titration procedure was to dissolve a known amount of the sample in a beaker with 100 ml of solvent. The sample size was chosen such that the endpoint would be observed at approximately 1 ml. The electrode and the titrant delivery tip were then lowered into the stirring solution, and the titration was conducted in the automatic endpoint seeking (AEP) mode. The potential of the solution (mV) was noted at the endpoint, and the total volume of titrant consumed was stored in memory by the computer. A blank titration was then conducted by titrating the exact volume of pure solvent up to the endpoint potential previously recorded. This blank volume was also recorded by the computer and subtracted from the total sample volume in calculating the number average molecular weight according to the following equation:

$$\bar{M}_n = \text{g/mole} = \frac{W \times N}{C \times (V - V_B)}$$

where W is the sample weight in grams, N is the number of

endgroups per molecule, C is the titrant concentration in moles/ml, and V and V_B are the titrant volumes (in ml) consumed for the sample and the solvent blank, respectively.

4. High Performance Liquid Chromatography (HPLC)

Quantitative analysis of the siloxane equilibration samples for determination of the D_4 and D_5 content was accomplished by reversed phase high performance liquid chromatography using a Varian 5500 liquid chromatograph.

The separations were carried out on a DuPont Zorbax ODS (C_{18}) analytical column (4.6 mm x 25 cm) with an 83:17 mixture of acetonitrile:acetone as the mobile phase. The flow rate was 0.8 ml/minute. A Rheodyne injector valve operating on compressed air was employed, with a 10 microliter sample loop for reproducible injection volumes. Samples were prepared in one ml volumetric flasks with ethyl acetate as the solvent and a concentration range of 0.5 to 2.0% weight/volume. Detection was provided by a Wilmad infrared detector set at 12.45 microns to monitor the Si- CH_3 vibration.

A Varian Vista 402 data station simplified the calibration and analysis processes. The external standard method was employed for obtaining quantitative results. Initially, standards containing known amounts of D_4 and D_5 were analyzed to calculate a calibration factor (CF) for each component (i) where

$$CF(i) = \frac{[\text{Amount}(i) \text{ in Known }]}{[\text{Area}(i) \text{ in Known }]}$$

The unknown samples were then analyzed to determine the weight percent of D₄ or D₅ (denoted i) in the sample according to the following formula:

$$\text{Result (weight\% i)} = \frac{[(\text{Area}(i) \text{ in Unknown}) \times CF(i) \times 100]}{\text{Divisor}}$$

The divisor in the above equation represents the total sample weight dissolved for the analysis run, and the multiplier of 100 converts the result to a weight percent. Reproducibilities were on the order of 1-5%. These formulae are valid only when identical sample volumes are injected for the known and unknown. This was accomplished via the sample loop described above.

5. Capillary Gas Chromatography (GC)

The disiloxane content of the polysiloxane equilibration samples was quantified through capillary gas chromatography using a Varian Vista 6000 gas chromatograph. The D₄ and D₅ content could also be determined by this technique. An 11 m fused silica column was employed, with an 0.2 mm internal diameter and a dimethylsiloxane stationary phase. The carrier gas was helium at a flow rate of 1.7 ml/minute at 80°C. The injector was used in the split mode at 275°C with a split ratio of 100:1. A flame ionization detector was used at 310°C. Sample solution concentrations in ethyl acetate ranged from 0.5 to 3%

wt./vol., and the injected sample volume was 1 microliter. The temperature programming was as follows: from 100°C to 150°C at 5°C/minute, then 150°C to 225°C at 30°C/minute.

Quantification of the data was carried out using a Varian Vista 402 data station and calibration procedures employing an internal standard of tetradecane (C₁₄) [176]. The internal standard method is dictated here because of the use of the split injector which does not deliver reproducible sample sizes onto the column with each injection. Baseline shift due to the temperature programming was stored in memory and subtracted during sample runs.

A calibration standard was prepared which contained known amounts of all the peaks of interest (in this case disiloxane, D₄ and D₅) plus an internal standard (C₁₄). This lead to the calculation of relative response factors (RRF) for each component (i) relative to the internal standard peak:

$$\text{RRF}(i) = \frac{(\text{Amount}(i) \text{ in Known}) \times (\text{Area Int. Std.})}{(\text{Area}(i) \text{ in Known}) \times (\text{Amount Int. Std.})}$$

When an unknown sample is run, the ratio of areas for the component of interest and the internal standard multiplied by the RRF and the amount of internal standard in the unknown will give the amount of the component of interest in the unknown sample. This amount can be expressed in terms of the weight% of the component of interest by introducing the divisor term (which represents the total sample weight

dissolved for the run) and a multiplier of 100. The final equation is as follows:

Result (weight% i) =

$$\frac{[(\text{Area}(i) \text{ in Unknown}) \times \text{RRF}(i) \times (\text{Amt. Int. Std.})] \times 100}{[(\text{Area Int. Std.}) \times \text{Divisor}]}$$

6. Gel Permeation Chromatography (GPC)

Molecular weights and molecular weight distributions of polymers and oligomers were commonly characterized by gel permeation chromatography. The experiments were carried out on either of two instruments routinely operating in our laboratories.

A variable temperature Waters 590 GPC was employed, operating at 30°C and equipped with a 500, 10³, 10⁴ and 10⁵ angstrom Waters ultrastyrigel column set. A Waters 490 programmable, multiwavelength UV-visible detector set at 218 nm was utilized with uninhibited HPLC grade tetrahydrofuran as the elution solvent at a flow rate of 1.0 ml/minute.

Polystyrene standards purchased from Polymer Laboratories, Inc. were used to prepare a GPC calibration curve which was fitted with linear and cubic equations. Polysiloxane standards prepared as described earlier in this chapter were also employed to prepare a calibration curve for characterization of the polysiloxane GPC samples.

A second GPC which was utilized was a Varian VISTA 5500 liquid chromatograph operating at 30°C and equipped with a 100, 500 and 1000 angstrom Waters ultrastyrigel column set

and a Waters R401 differential refractive index detector. HPLC grade toluene was used as the elution solvent at a flow rate of 1.0 ml/minute.

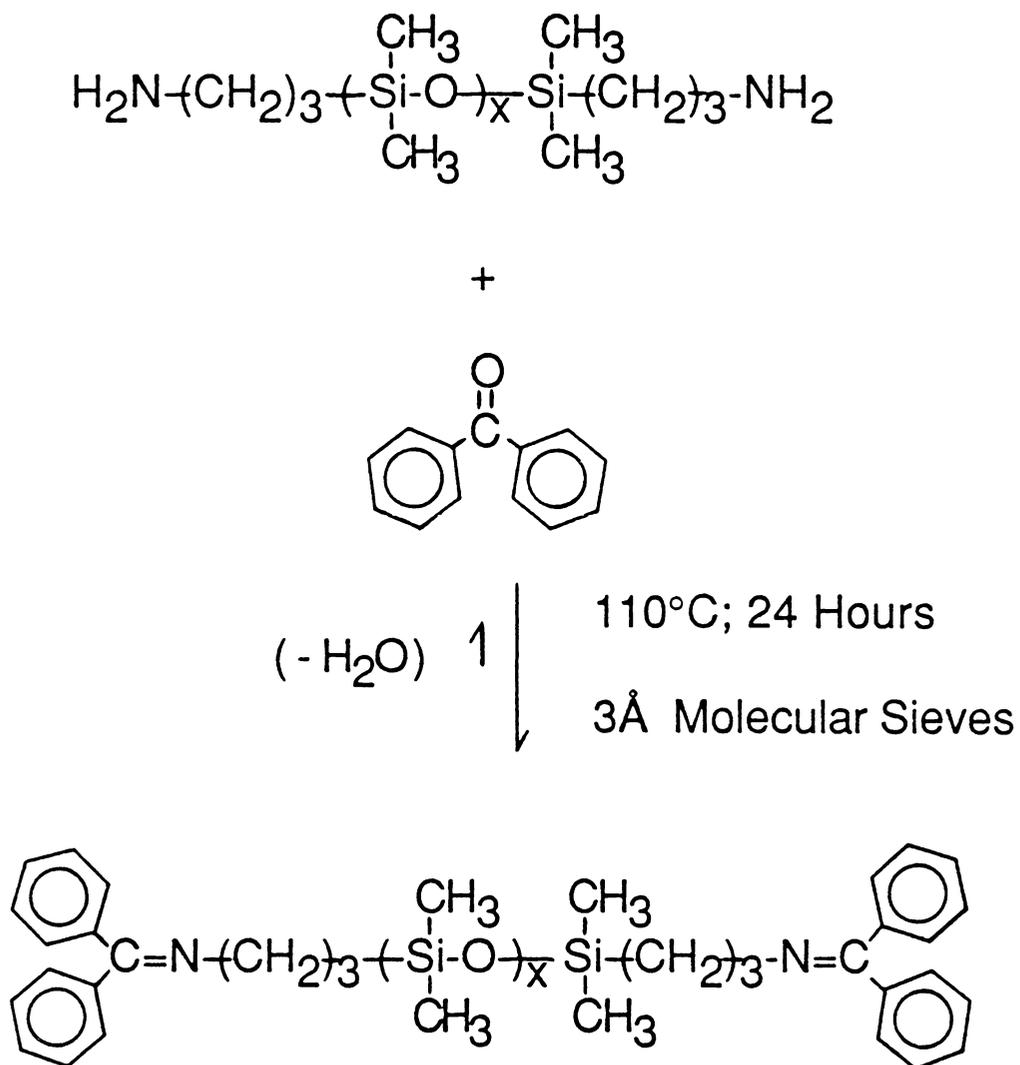
Gel permeation chromatographic analysis was not possible directly on the primary amine terminated polysiloxane oligomers because of their tendency to adsorb on the GPC columns rather than to elute. The following procedure was followed to derivatize the amine endgroups with benzophenone, forming an imine functionality and thereby allowing GPC analysis of the oligomers (Scheme XXII). The titrated molecular weights of the individual samples were used to determine the amount of benzophenone required to completely derivatize the amine functionalities. A 10 mole percent excess of the benzophenone was used to help drive the reaction to completion. The reaction was carried out in bulk at 100°C by heating the siloxane oligomer and benzophenone for 24 hours in the presence of 3A molecular sieves. The derivatized samples were then titrated with 0.100N HCl to ensure that complete derivatization had taken place before the GPC analysis was conducted.

7. Intrinsic Viscosity

Intrinsic viscosity measurements, $[\eta]$, on the oligomers and polymers synthesized were obtained using a Cannon-Ubbelohde glass capillary viscometer. The measurements were made at 25°C in chloroform. Four concentrations between 0.5

Scheme XXII

Derivatization of Amine-Terminated Polysiloxanes for GPC



IMINE-TERMINATED POLYSILOXANE

and 2 wt.% were used to determine $[\eta]$.

8. Ultraviolet (UV) - Visible Spectroscopy

Number average molecular weights of the polysiloxane GPC standards were determined by UV-visible spectroscopy utilizing a Perkin-Elmer Model 552 spectrophotometer. The molecular weights of the polysiloxane samples were quantified by measuring the absorbance of the phenyl rings on the terminated polysiloxane chains, and relating this absorbance to the concentration through the use of the Beer-Lambert law,

$$A = Ebc$$

where A is the absorbance, E is the molar absorptivity (in l/mole cm), b is the cell pathlength (in cm), and c is the concentration of UV-absorbing solute (in moles/liter). The quartz cell utilized had a pathlength of 1.0 cm. Since the molar absorptivity, E, cannot be determined if the molecular weight of the substance being studied is not known, 1,3-diphenyltetramethyldisiloxane was chosen as a standard. The value of E was then determined experimentally by preparing solutions of the standard of known concentrations and then measuring A for each of these solutions at the absorbance maximum of 211 nm. The solvent chosen was cyclohexane. A plot of absorbance versus concentration for the standard solutions produces a linear calibration curve with slope E. The value of the slope was divided in half, since the phenyl group in the polysiloxane GPC standards was located at only

one end of the chain, producing a value of E of 10,500 l/mol cm.

The unknown samples were then characterized by measuring the absorbance of solutions of the samples of known concentration (in g/l), again at 211 nm. The absorbance measurements and the calibration curve allowed one to solve for the concentration of phenyl rings present in moles/l. Assuming 100% functionality of the polymer, and assuming that E is the same for the disiloxane standard and the polysiloxane sample, one can then calculate the number average molecular weight of the unknown sample in g/mole.

One note that will be added here is that a comparison of the functional molecular weight determined by UV spectroscopy with the number average molecular weight determined by osmometry revealed that the functionality was greater than 90%.

9. Vapor Phase Osmometry (VPO)

Vapor phase osmometry was useful for evaluating number average molecular weights of oligomers having molecular weights less than 25,000 g/mole. A Wescan Model 233 Molecular Weight Apparatus was utilized at 63°C with HPLC grade toluene as the solvent. The detection limit under these conditions is 5×10^{-5} mole/l. A multiple standard calibration procedure proved most useful. The standards included sucrose octaacetate, squalene and a number of narrow molecular weight distribution polymeric standards.

Solution concentrations for the calibration standards and the unknown samples ranged from 0.7 g/l to 7.0 g/l.

10. Light Scattering Measurements

Absolute weight average molecular weights of the polysiloxane GPC standards were kindly determined by Mia Siochi through the use of static light scattering measurements. Several solution concentrations, ranging from 2.0 to 7.0 mg/ml (depending on the molecular weight), were prepared by dissolving the polysiloxane samples in HPLC grade toluene at room temperature. The solutions were used for dn/dc measurements as well as for light scattering measurements. The dn/dc data was collected using a Chromatix KMX-16 laser differential refractometer operating at 633 nm and at 27°C.

The solutions described above were filtered through an 0.5 micron Millipore filter before light scattering measurements were made on a Chromatix KMX-6 LALLS photometer operating at 633 nm and 27°C. The experiment was conducted at a 6-7° forward scattering angle. The data was processed by plotting Kc/R_{θ} versus concentration. The intercept of the graph is the inverse of the absolute weight average molecular weight of the sample.

11. Differential Scanning Calorimetry (DSC)

Glass transition temperatures as well as crystallization and melting temperatures of the oligomers and polymers were determined using a Perkin-Elmer Model

DSC-2. Sample sizes were generally greater than 10 mg, and the heating rate was 10°C/minute. Subambient as well as ambient measurements were made, with the glass transition temperature taken as the midpoint of the transition.

12. Transmission Electron Microscopy (TEM)

The bulk morphology of the siloxane-containing block copolymers was investigated by transmission electron microscopy using a Philips 420T scanning transmission electron microscope operating in the TEM mode. Due to the large difference in electron density between the siloxane and the ester blocks in the copolymers, staining of the samples was not necessary. Samples for TEM were prepared by casting dilute solutions of the polymers (approximately 5% in chloroform) onto distilled water, and then transferring the thin film onto a nickel TEM grid and allowing it to dry.

Chapter IV
RESULTS AND DISCUSSION

A. PREPARATION AND CHARACTERIZATION OF SILOXANOLATE CATALYSTS

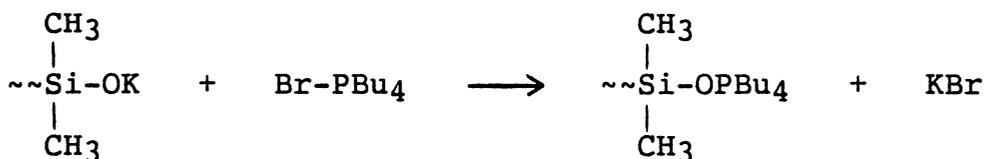
The initial step for this study on the kinetics of base-catalyzed siloxane equilibration reactions involved the preparation of a number of well-defined siloxanolate catalysts. The catalysts were prepared separately, prior to the equilibration reactions, so that a homogeneous, moisture-free system with a known concentration of active centers might be obtained. The catalysts studied included potassium siloxanolate, tetramethylammonium siloxanolate, and tetrabutylphosphonium siloxanolate catalysts. Although the hydroxide salts of these bases are effective as catalysts for siloxane equilibrations, the solid hydroxides of both potassium and tetramethylammonium are known to be quite hygroscopic and generally contain significant amounts of water. Tetrabutylphosphonium hydroxide (TBPH), on the other hand, is available only as an aqueous solution, and decomposes during attempts to concentrate the solutions above ~40% solids [77]. Since the presence of water can complicate the kinetics of the equilibration process [6], it is evident that steps were required to dehydrate the catalysts so that useful kinetic data could be obtained.

The approach utilized in this study was to prepare the siloxanates of the bases by reacting the hydroxides with D₄. Another point of consideration was the fact that the hydroxide salts of the previously mentioned catalysts are not readily soluble in siloxane media, while preparation of their siloxanates yields a catalyst which is homogeneous from the start of the equilibration reaction.

Initial attempts to prepare the siloxanates of the respective hydroxides were carried out in bulk, but often resulted in solutions which were opaque, and generally too viscous to readily handle via a syringe. The use of an azeotroping solvent, such as toluene or hexanes, generally allowed the preparation of clear solutions of catalyst, and some solvent was allowed to remain in the catalyst in attempt to dilute the catalyst solutions. This lowered the viscosity of the catalyst so that it could be readily added to the equilibration reactions via syringe at the start of each kinetic run. The concentration of residual solvent was very low and would not significantly influence ring-chain equilibria.

Detailed synthetic procedures for preparation of the siloxanolate catalysts were described in Chapter III, and will not be repeated here. A comment will be made, however, on the obvious differences in the synthetic approaches utilized for preparation of the respective catalyst systems. In the case of the relatively thermally stable potassium

siloxanolate catalyst, a toluene azeotrope was readily employed to ensure the removal of nearly all of the water initially present in the base, as well as any formed during the reaction. On the other hand, the transient nature of the quaternary ammonium and phosphonium catalysts prohibited the use of such elevated temperatures. Therefore, the removal of moisture was expected to be less efficient with these systems. This problem was avoided in the case of the phosphonium catalyst by exchanging the potassium cation of the previously dehydrated potassium siloxanolate catalyst with tetrabutylphosphonium bromide, as shown in the equation below:



Potassium bromide salt was observed to immediately precipitate out of solution. This allowed the preparation of tetrabutylphosphonium siloxanolate catalyst without employment of the thermally labile aqueous solution of tetrabutylphosphonium hydroxide. Attempts to prepare the ammonium catalyst by similar cation exchange techniques were unsuccessful due to the lack of a mutual solvent for the potassium catalyst and tetramethylammonium bromide. The use of a solvent such as n-hexanes, which forms a lower boiling azeotrope with water, is another alternative which was utilized in the case of the ammonium catalyst.

The catalyst solutions were characterized by potentiometric titration of the siloxanolate groups with alcoholic HCl. The acid generally titrated two endpoints, the first of which was attributed to the siloxanolate, and the second peak was attributed to the carbonate species. A representative titration curve is shown in Figure 10. Previous workers [49] have also reported the presence of two endpoints for the titration of tetramethylammonium hydroxide (TMAH) with HCl, using phenolphthalein and methyl orange as indicators. They identified the peaks as hydroxide and carbonate components, since it is known that TMAH readily absorbs carbon dioxide from the air. The identity of the second peak in the present study was confirmed by passing carbon dioxide gas through a solution of the catalyst, resulting in the immediate disappearance of the siloxanolate endpoint with simultaneous growth of the carbonate endpoint. It was thus possible to determine the percentages of both the siloxanolate species and carbonate species present in the catalyst solutions, though the carbonate species was assumed to have no catalytic effect on the siloxane equilibration reactions.

The use of an ion exchange technique was also explored [172] in an attempt to reverse the carbonate formation by exchange of the carbonate species in a solution of the potassium or tetramethylammonium hydroxide with a hydroxide resin (Amberlite[®] IRA-400(OH)). The hydroxide content of

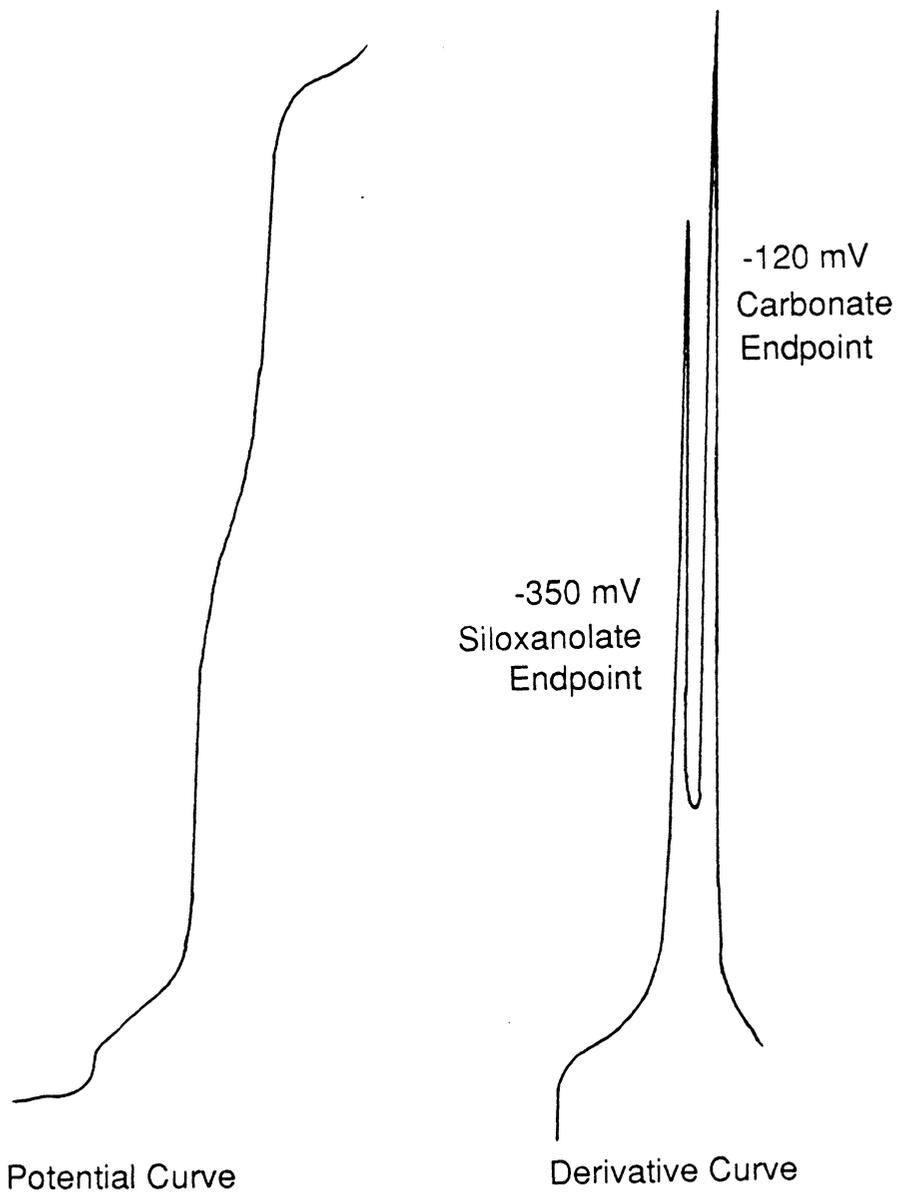


Figure 10: Representative Titration Curve for the Titration of Siloxanolate Catalysts.

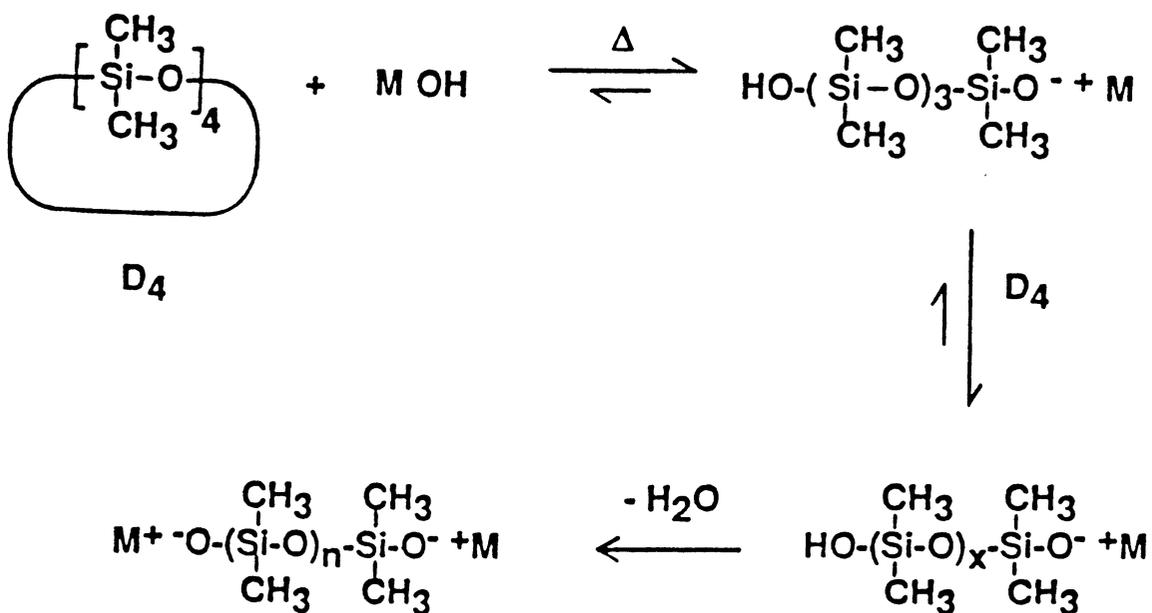
the solutions did increase at the expense of the carbonate species after passing through the exchange column, but the solutions absorbed carbon dioxide quite readily and it was not possible to isolate the pure hydroxides. The catalysts generally contained ~80 % hydroxide (or siloxanolate) and ~20 % carbonate species.

The siloxanolate catalysts were further characterized by proton NMR, where the absence of a peak for a silanol proton confirmed the assumption that the catalysts are generally difunctional. Though initially the catalyst is probably monofunctional, with only one siloxanolate per chain, it is expected that any silanol groups present would condense during the course of the catalyst preparation, liberating water and producing difunctional chains of higher molecular weight (see Scheme XXIII).

Finally, the thermal stability of the transient catalysts was investigated to ensure that the concentration of active species remained constant during the early part of the equilibration reactions, where most of the kinetic data was obtained. Solutions of the catalyst were heated under the conditions of a typical equilibration reaction, and samples were removed and titrated as a function of time. Though the tetramethylammonium siloxanolate catalyst was found to be significantly more stable than the tetrabutylphosphonium siloxanolate catalyst (as had been reported earlier [77,78]), both catalysts were observed to maintain

Scheme XXIII

Preparation of Siloxanolate Catalyst



WHERE $\text{M}^+ = \text{K}^+$ OR $(\text{CH}_3)_4\text{N}^+$ OR $(\text{C}_4\text{H}_9)_4\text{P}^+$

an essentially constant concentration of active centers at 80°C for well over the time interval required for this study. At 145°C, however, both catalysts had completely decomposed in less than five minutes, which produces a thermally and hydrolytically stable polysiloxane due to the absence of active centers. Investigation of the room temperature storage stability of the phosphonium catalyst showed a loss of approximately 15% of the active centers after three weeks of storage in a desiccator, although frequent removal was required in order to use the catalyst.

B. EQUILIBRATION REACTION KINETICS

This study investigated the effect of various reaction parameters on the synthesis and equilibration reaction kinetics in the preparation of well-defined difunctional siloxane oligomers. As pointed out in the introduction, the aminopropyl terminated species was studied most extensively, since it is readily incorporated into a variety of copolymer systems. A principal area of interest was the effect of catalyst type and concentration on the rate at which aminopropyl terminated polysiloxane oligomers of well-defined end groups and controlled molecular weight are formed. The catalysts studied include the previously described potassium siloxanolate catalyst, as well as the analogous tetramethylammonium and tetrabutylphosphonium siloxanolate catalysts. Previous workers in this area have focused on

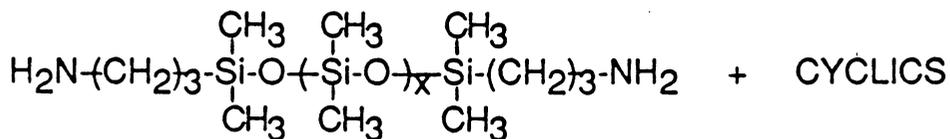
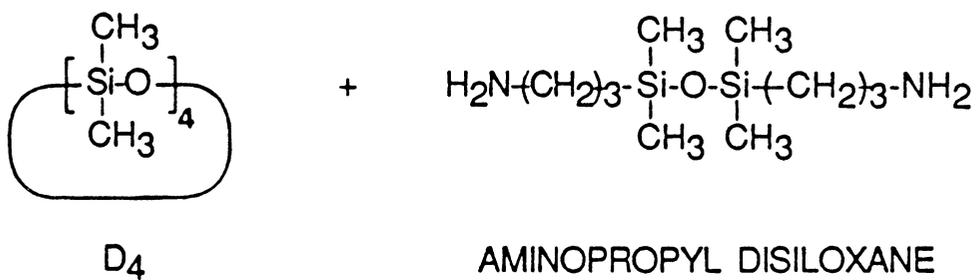
the reaction kinetics either in the absence of an endblocker [81], or in the presence of a nonfunctional endblocker such as hexamethyldisiloxane [49].

The reaction scheme for the preparation of aminopropyl terminated difunctional oligomers is illustrated in Scheme XXIV. The reaction proceeds by the anionic equilibration of the cyclic siloxane tetramer, D_4 , in the presence of 1,3-bis(3-aminopropyl)tetramethyldisiloxane. The equilibration process begins immediately upon addition of the siloxanolate catalyst, and samples were removed as a function of time for the purpose of the kinetic study. A number of experimental approaches were utilized to follow the disappearance of the starting materials, and subsequently, to determine the equilibrium concentration of cyclics and the molecular weight of the resulting difunctional oligomer. These characterization techniques have been described in detail in Chapter III. It should be pointed out that formation of the oligomeric species could not be readily followed by gel permeation chromatography, due to the tendency of the amino-terminated materials to adsorb on the GPC columns rather than to elute. A derivatization method was employed in the analysis of the final oligomer, however, so that the molecular weight distribution of the polysiloxane could be determined.

The first set of kinetic data to be presented in Figure 11 shows the disappearance of D_4 as a function of time for the commonly used potassium siloxanolate catalyst system.

Scheme XXIV

Synthesis of Aminopropyl Terminated Polydimethylsiloxanes



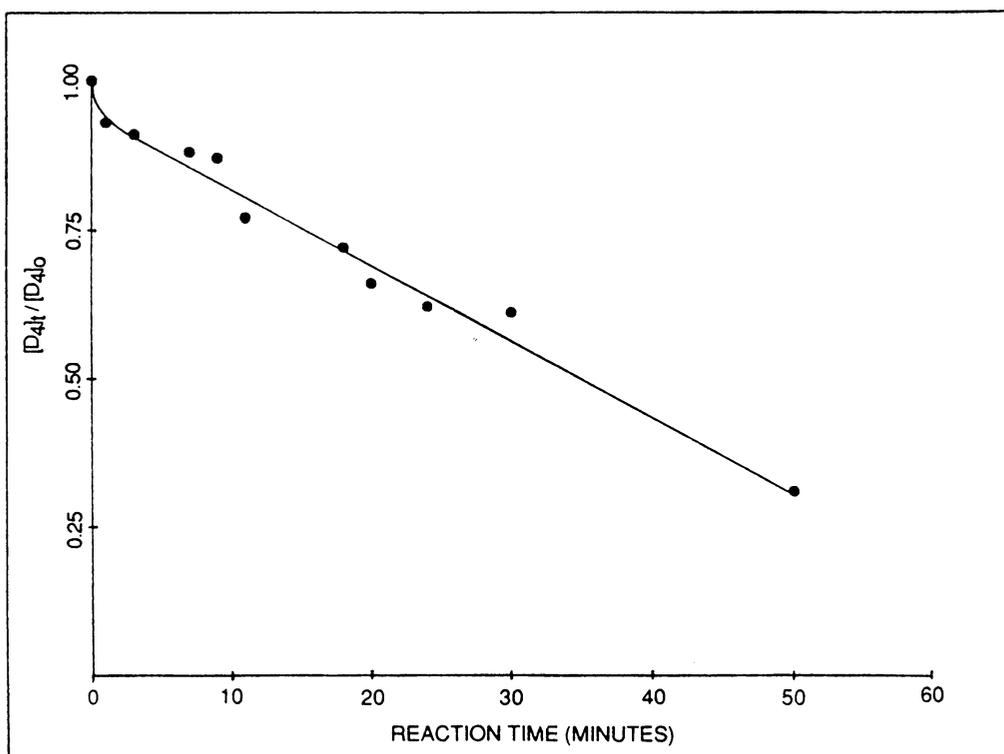


Figure 11: Disappearance of D_4 at 80°C for a Targeted $1500 \bar{M}_n$ Oligomer with 0.21 Mole % Potassium Siloxanolate Catalyst.

The reaction temperature was held constant at 80°C, and the targeted molecular weight was 1500 g/mole. Several catalyst concentrations were studied, including 0.087, 0.13 and 0.21 mole percent potassium siloxanolate catalyst, based on the total moles of starting material. An increase in the catalyst concentration logically produced an increase in the rate of reaction of D₄, but even at 0.21 mole % potassium siloxanolate catalyst, significant amounts of D₄ remained after one hour reaction time at 80°C. As the reactions were allowed to proceed, the level of D₄ continued to decrease until the equilibrium concentration of D₄ had been attained.

In addition to the ability of the catalyst to react rapidly with the cyclic tetramer, incorporation of the aminopropyl disiloxane was critical for the preparation of difunctional oligomers of controlled molecular weight. Samples were removed as a function of time and analyzed for their disiloxane content in order to determine the efficiency of the catalysts in this respect. For the previously described series of catalyst concentrations at 80°C and a targeted molecular weight of 1500 g/mole, it was observed that the disiloxane endblocker was not readily incorporated into the polysiloxane oligomer. For example, an initial disiloxane content of ~16.5 weight percent is required to produce the 1500 g/mole oligomer with D₄. After 24 hours reaction time at 80°C and a catalyst level of 0.21 mole % potassium siloxanolate, only 33% of the initially charged

disiloxane had been incorporated into the oligomer. After 40 hours, the aminopropyl disiloxane level had decreased to 6.3 weight percent (62% incorporated). Based on this value, a number average molecular weight of 2270 g/mole would be predicted. Titration of the bulk reaction mixture indicated a number average molecular weight of 1400 g/mole, which was as expected. The catalyst was neutralized at this point, and the oligomer was vacuum stripped to remove any low molecular weight nonfunctional cyclics and the unreacted disiloxane. The molecular weight of the vacuum stripped oligomer, as determined by titration of the amine endgroups, was 2140 g/mole. Indeed, the lack of efficient incorporation of the disiloxane endblocker had produced an oligomer with a higher molecular weight than was desired. The lack of molecular weight control in this system was more evident at the lower catalyst levels studied, where a catalyst concentration of 0.087 mole percent potassium siloxanolate produced a 4200 g/mole oligomer after 24 hours reaction time. This value is almost three times the desired molecular weight.

The potassium siloxanolate catalyst was also studied for the preparation of a 10,000 g/mole aminopropyl functional oligomer at 80°C. The initial disiloxane content in this case is ~2.5 weight percent. The disappearance of D₄ and disiloxane as a function of time were again followed using HPLC and capillary gas chromatography. The results

are presented in Table 7. It is evident from the table that incorporation of the aminopropyl disiloxane is again the limiting step in achieving controlled molecular weight oligomers. Even when the initial disiloxane content is low, as is the case for preparation of higher molecular weight oligomers, only 36% of the dimer had been incorporated after 48 hours reaction time. After 60 hours, the number average molecular weight of the reaction mixture was titrated as 8610 g/mole. The catalyst was then neutralized, and the oligomer was washed and vacuum stripped to remove the low molecular weight materials. Confirmation of the absence of cyclics and aminopropyl disiloxane after vacuum stripping was obtained by gas chromatography. The GC chromatogram of the material before and after vacuum stripping is shown in Figure 12. The titrated molecular weight of the vacuum stripped sample was 21,500 g/mole. This corresponds to incorporation of 46% of the initial aminopropyl disiloxane after 60 hours of reaction time at 80°C. At this point it was clear that the potassium siloxanolate catalyst did not readily incorporate the aminopropyl disiloxane at 80°C and moderate catalyst concentrations. Similar kinetic studies were then conducted at 160°C to determine whether or not increased catalytic efficiency could be achieved by taking advantage of the superior thermal stability of the potassium siloxanolate catalyst.

The disappearance of D₄ as a function of catalyst

Table 7
 Disappearance of D₄ and Aminopropyl Disiloxane
 as a Function of Time^(a)

| Reaction Time (Hours) | Weight % D ₄ | Weight % Disiloxane | % Disiloxane Incorporated |
|-----------------------|-------------------------|---------------------|---------------------------|
| 0 | 97 | 2.5 | 0 |
| 12 | 7 | 2.1 | 16 |
| 24 | 6 | 1.8 | 28 |
| 48 | 6 | 1.6 | 36 |
| 60 | 6 | 1.4 | 46 |

(a) Theoretical $\bar{M}_n = 10,000$ g/mole;
 80°C ; 0.12 mole % Potassium Siloxanolate Catalyst

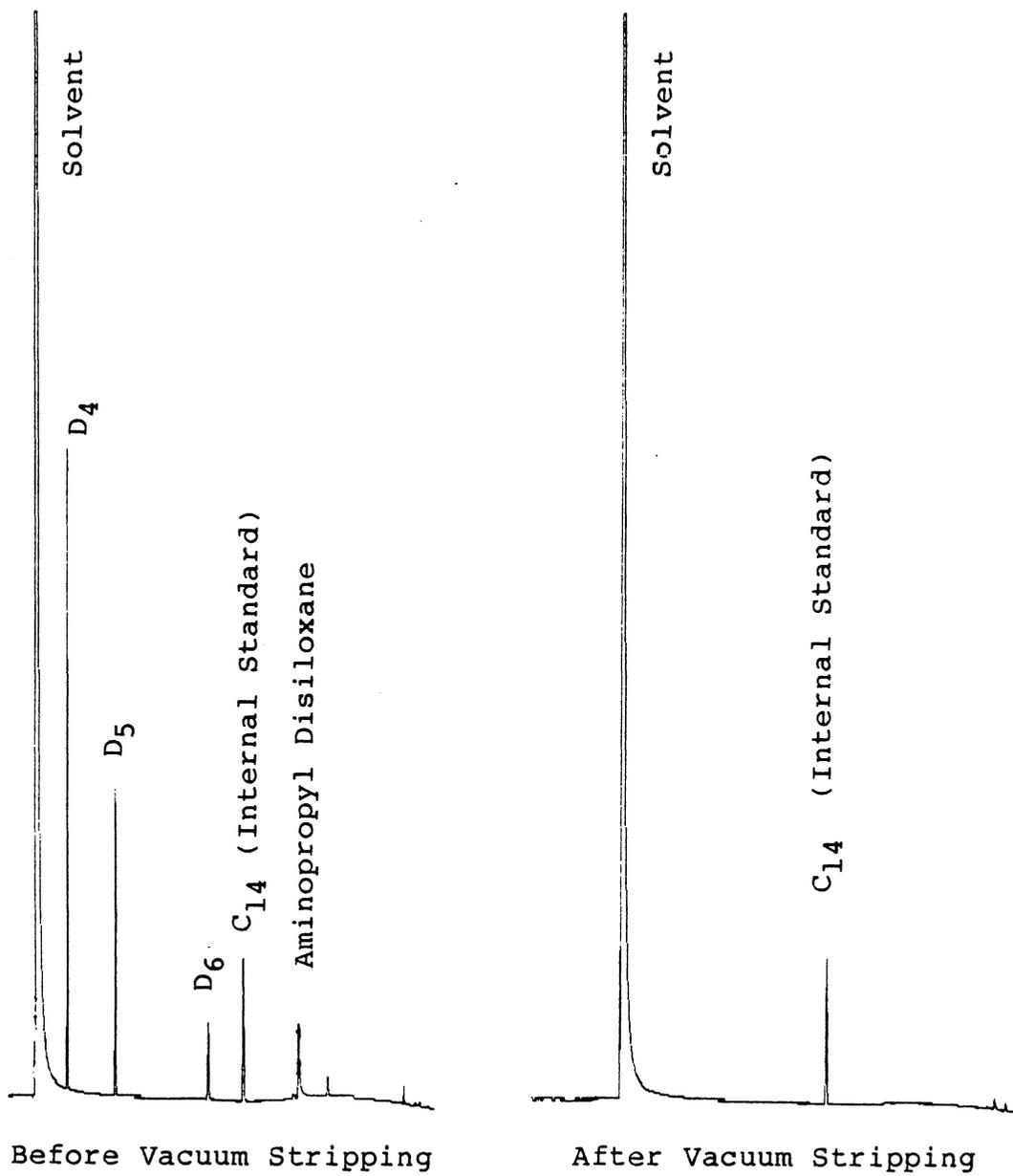


Figure 12: GC Chromatogram of an Aminopropyl Terminated Polysiloxane Oligomer Before and After Vacuum Stripping.

concentration for a targeted 1500 g/mole oligomer at 160°C is shown in Figure 13. The rate of disappearance of D₄ was markedly faster under these conditions than was observed at 80°C, but incorporation of the aminopropyl disiloxane did not appear to improve significantly (see Figure 14). This slower rate of incorporation of the aminopropyl disiloxane relative to D₄ was expected to some degree based on electronegativity differences, since the silicon atoms in the cyclics are more electropositive than the silicon atoms in the disiloxane. It was not expected, however, that such large amounts of disiloxane would remain unreacted after the previously described lengthy reaction times in the presence of the potassium catalyst. Alternative catalyst systems were subsequently focused upon for the preparation of well-defined, difunctional amine-terminated polysiloxanes.

The second system studied was the tetramethylammonium siloxanolate-catalyzed equilibration process. The reaction temperature in this case was held at 80°C to avoid decomposition of the active siloxanolate endgroups. The effect of catalyst concentration on the disappearance of D₄ is shown in Figure 15. The reaction of D₄ proceeds fairly rapidly in the range of catalyst concentrations studied, and the amount of D₄ remaining after only 20 minutes is very close to the equilibrium value. The disappearance of aminopropyl disiloxane for the same reactions is shown in Figure 16. Incorporation of the disiloxane is again much slower than

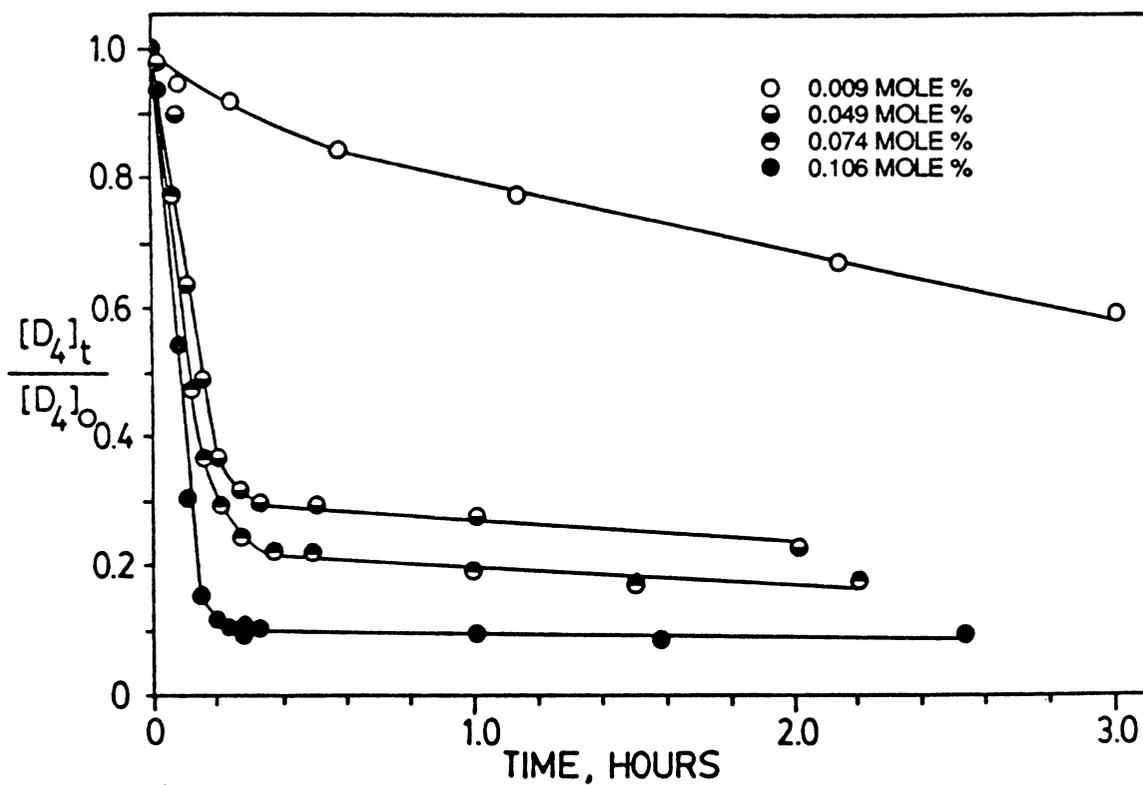


Figure 13: Effect of Catalyst Concentration on the Disappearance of D₄; 1500 \bar{M}_n ; 160°C; Potassium Siloxanolate Catalyst.

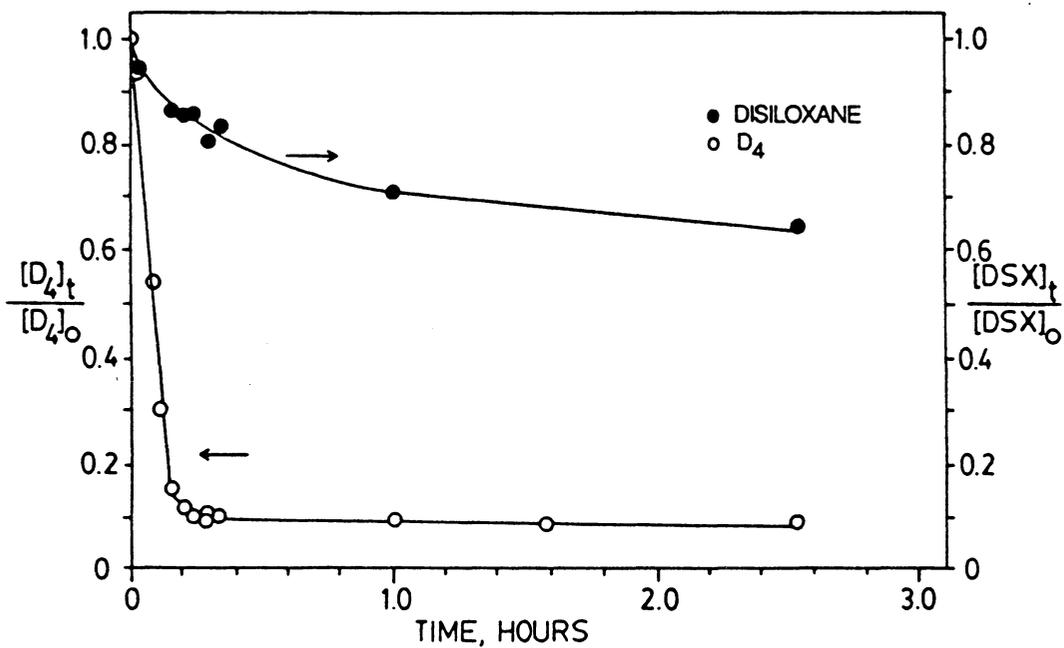


Figure 14: Disappearance of D_4 and Disiloxane at 160°C for a Targeted $1500 \bar{M}_n$ Oligomer with 0.11 Mole % Potassium Siloxanolate Catalyst.

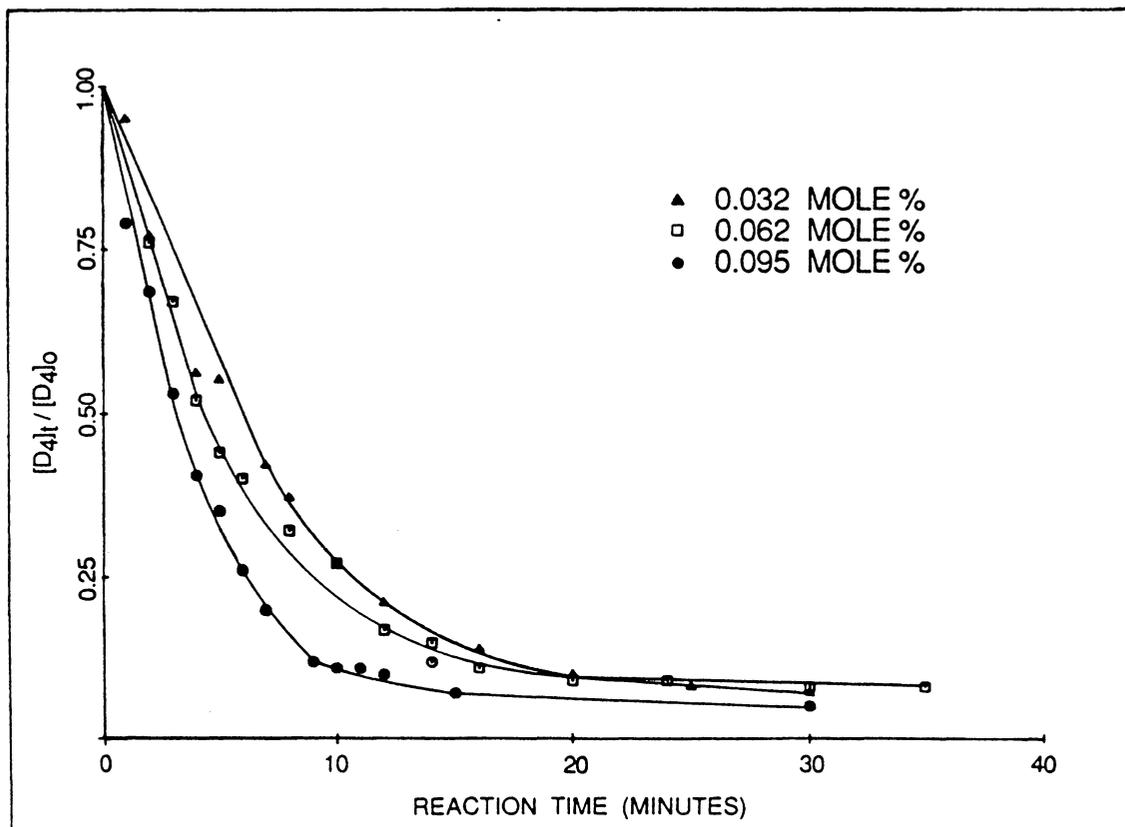


Figure 15: Effect of Catalyst Concentration on the Disappearance of D₄; 1500 \bar{M}_n ; 80°C; Tetramethyl-Ammonium Siloxanolate Catalyst.

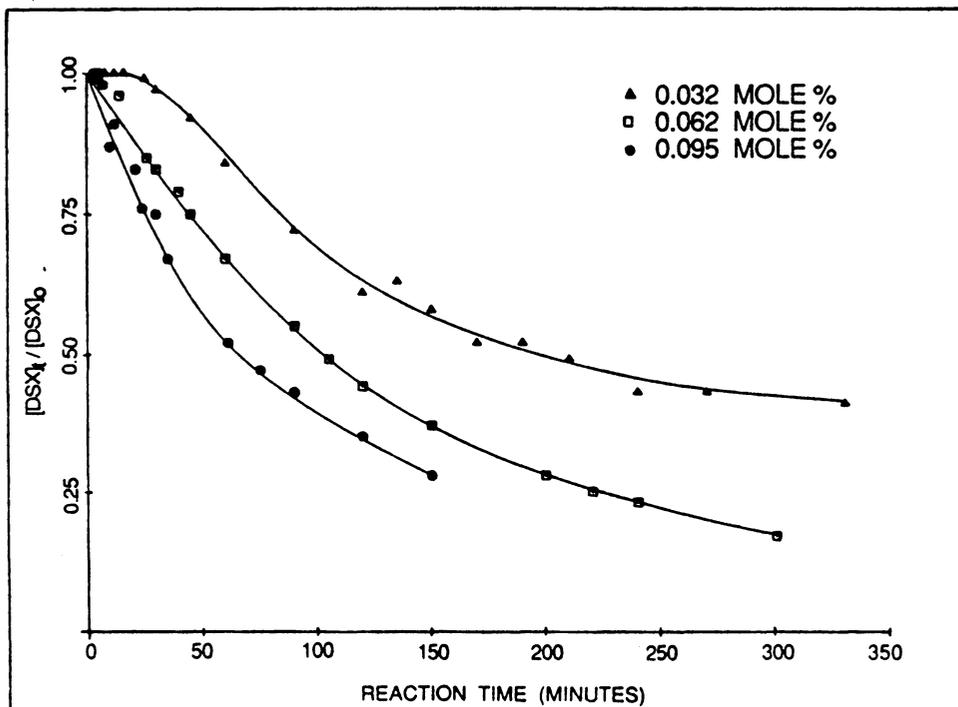


Figure 16: Effect of Catalyst Concentration on the Disappearance of Aminopropyl Disiloxane; 1500 M_n ; 80°C; Tetramethylammonium Siloxanolate Catalyst.

incorporation of D₄, but it is readily observed that the ammonium catalyst reacts with the disiloxane much more efficiently than was observed for the potassium siloxanolate catalyst.

After 24 hours of reaction time, the catalyst in these systems was decomposed by heating the reaction mixtures above 145°C for 30 minutes. The oligomers were then analyzed to determine the equilibrium concentration of cyclics, followed by vacuum stripping to remove these low molecular weight materials. The number average molecular weights of the resulting oligomers were determined by titration of the amine endgroups with HCl. The data are presented in Table 8. It can be seen that controlled molecular weight oligomers were readily obtained in 24 hours at catalyst levels greater than 0.03 mole percent tetramethylammonium siloxanolate.

The final catalyst system investigated in this study was tetrabutylphosphonium siloxanolate. The reaction temperature was again held at 80°C due to the transient nature of the catalyst. The disappearance curves for D₄ and aminopropyl disiloxane are shown in Figures 17 and 18, respectively. The disappearance of D₄ in the presence of the phosphonium catalyst was again quite rapid at 80°C, and the equilibrium level was reached in a reasonable amount of time. In addition, the disappearance of aminopropyl disiloxane was extremely fast relative to the previously

Table 8

Molecular Weight Control in Equilibration Polymerization:
 Influence of Tetramethylammonium Siloxanolate
 Catalyst Concentration(a)

| Mole % Siloxanolate | Titrated \bar{M}_n (g/mole) |
|---------------------|-------------------------------|
| 0.032 | 1910 |
| 0.055 | 1400 |
| 0.062 | 1540 |
| 0.095 | 1490 |

(a) Theoretical $\bar{M}_n = 1500$ g/mole ; 80°C;
 Reaction Time = 24 Hours

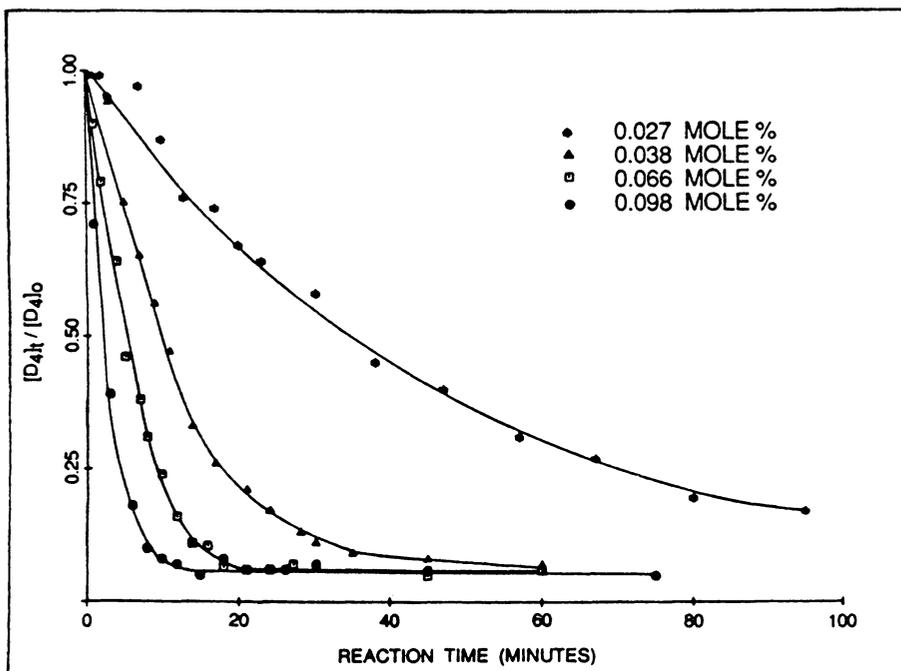


Figure 17: Effect of Catalyst Concentration on the Disappearance of D₄; 1500 \bar{M}_n ; 80°C; Tetrabutyl-Phosphonium Siloxanolate Catalyst.

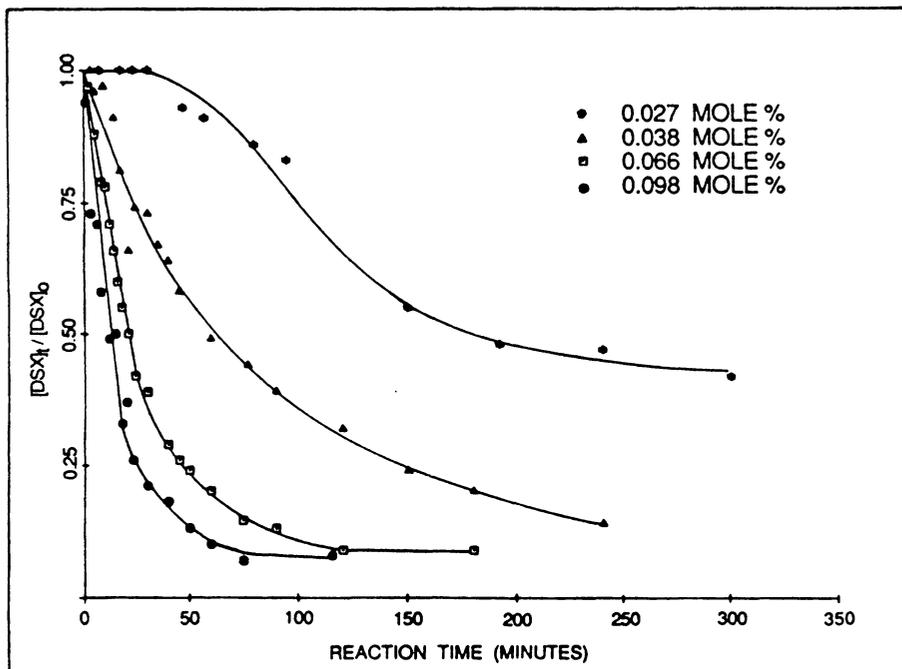


Figure 18: Effect of Catalyst Concentration on the Disappearance of Aminopropyl Disiloxane; 1500 M_n ; 80°C; Tetrabutylphosphonium Siloxanolate Catalyst.

studied catalyst systems. At catalyst concentrations greater than 0.06 mole%, the disiloxane content was very close to its equilibrium concentration in less than two hours at 80°C. Although thermodynamic equilibrium had probably been reached sooner in this system, the reactions were again allowed to proceed for 24 hours, at which time the reaction temperature was increased above 145°C for 30 minutes to decompose the catalyst. The molecular weight data for the vacuum stripped oligomers is shown in Table 9. The excellent molecular weight control achieved in the presence of the phosphonium catalyst was again a good indication of its efficiency.

The concentration of catalyst in all three systems studied ranged from 0.03 to 0.20 mole percent siloxanolate, based on the total moles of starting materials. At these catalyst levels, the D₄ was observed to react fairly comparably for the ammonium and phosphonium catalysts (see Figures 19 and 20), while the potassium siloxanolate catalyst incorporated the D₄ more slowly, even at much higher reaction temperatures. It should be pointed out here that as a result of the method of addition of the catalyst, and due to its fairly viscous nature (even as a ~35 weight % solution in toluene), it was not possible to achieve exactly the same catalyst concentration from one system to another for comparison. The rate differences were sufficient, however, so that a comparison of different catalyst levels

Table 9

Molecular Weight Control in Equilibration Polymerization:
 Influence of Tetrabutylphosphonium Siloxanolate
 Catalyst Concentration^(a)

| Mole % Siloxanolate | Titrated \bar{M}_n (g/mole) |
|---------------------|-------------------------------|
| 0.027 | 1360 |
| 0.038 | 1480 |
| 0.098 | 1420 |

(a) Theoretical $\bar{M}_n = 1500$ g/mole ; 80°C;
 Reaction Time = 24 Hours

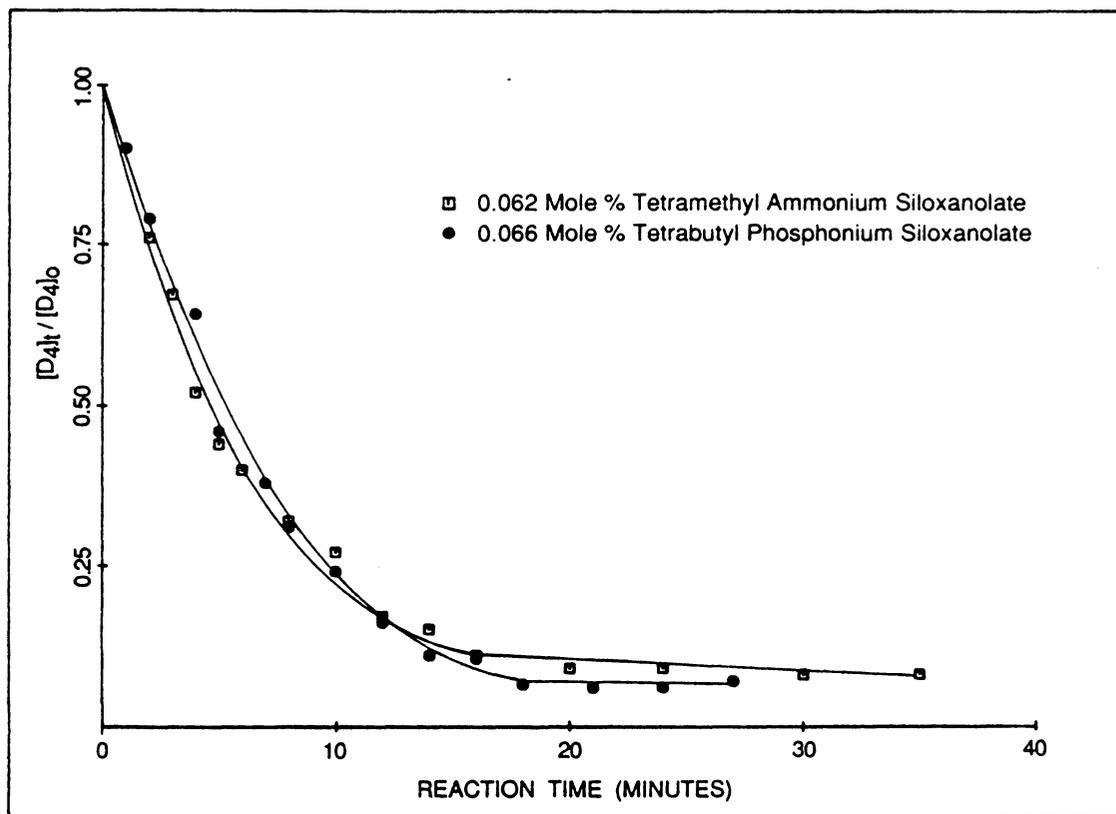


Figure 19: Effect of Catalyst on the Rate of Reaction of D₄; 1500 \bar{M}_n ; 80°C.

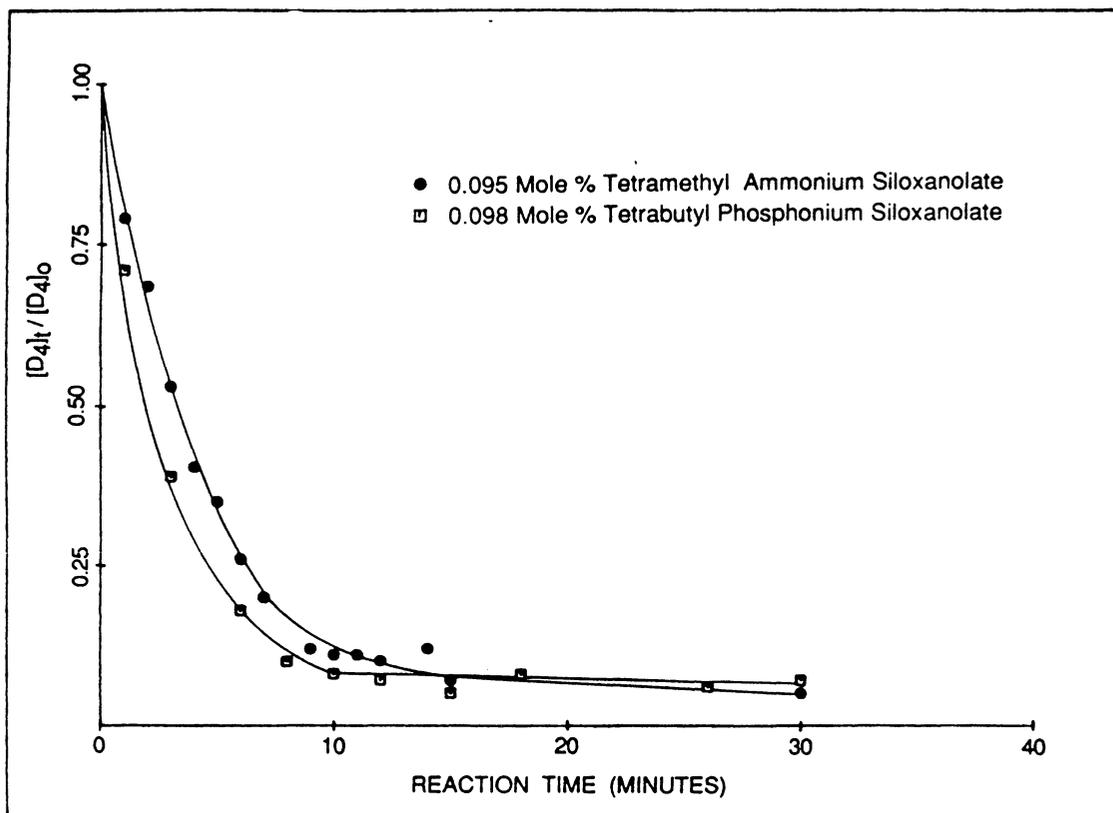


Figure 20: Effect of Catalyst on the Rate of Reaction of D₄; 1500 \bar{M}_n ; 80°C.

for different siloxanolate systems was nevertheless useful for examining the efficiency of the respective systems. For example, the disappearance of D_4 is compared in Figure 21 for reactions conducted in the presence of 0.13 mole % potassium siloxanolate catalyst and 0.066 mole % phosphonium siloxanolate catalyst. At almost twice the catalyst level, the disappearance of D_4 was still much slower in the presence of the potassium siloxanolate catalyst. The ammonium and phosphonium catalysts are compared in Figure 22. Conflicting results have been reported in the past regarding the efficiency of the tetrabutylphosphonium siloxanolate catalyst relative to the tetramethylammonium siloxanolate catalyst for incorporation of D_4 in nonfunctional siloxane systems [6]. In the presence of aminopropyl disiloxane, however, the rate of incorporation of D_4 was observed to be fairly comparable for the ammonium and phosphonium catalysts (Figure 19 and 20). In spite of the much slower D_4 reaction rate in the presence of potassium catalyst, all three systems were found to be effective in reducing the D_4 concentration to the same equilibrium level in a reasonable amount of time.

The major differences in catalyst efficiency between these three siloxanolate systems were in their rates of incorporation of aminopropyl disiloxane. This area has not been examined in detail in the past, and the results presented in the previous tables and figures provide valuable

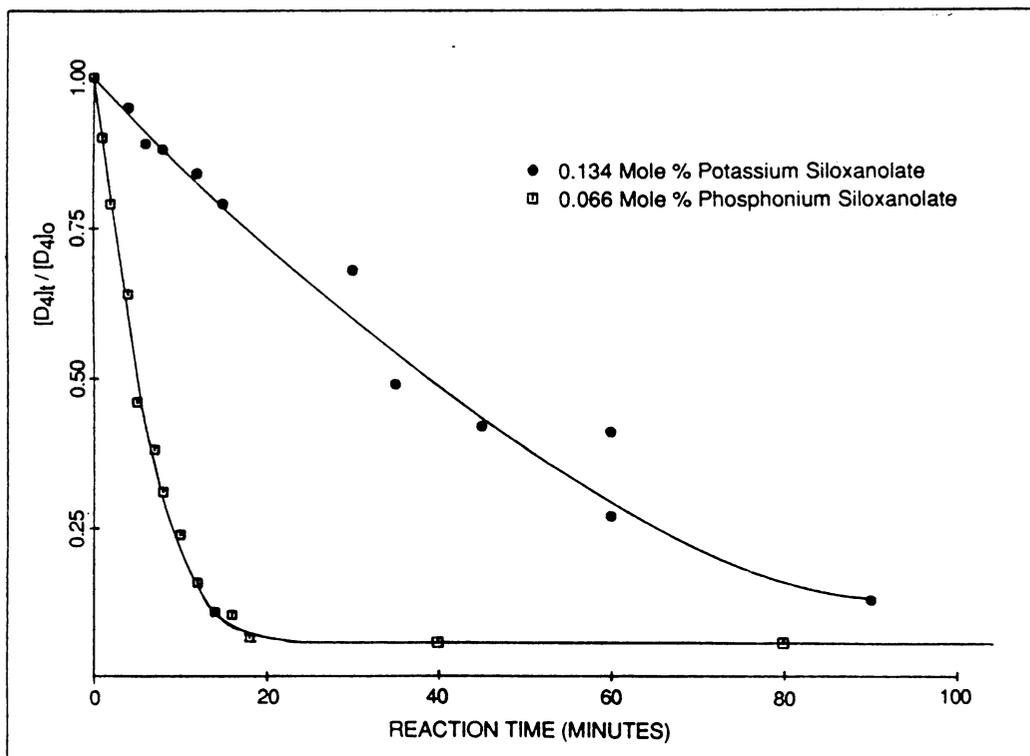


Figure 21: Effect of Catalyst on the Rate of Reaction of D₄; 1500 \bar{M}_n ; 80°C.

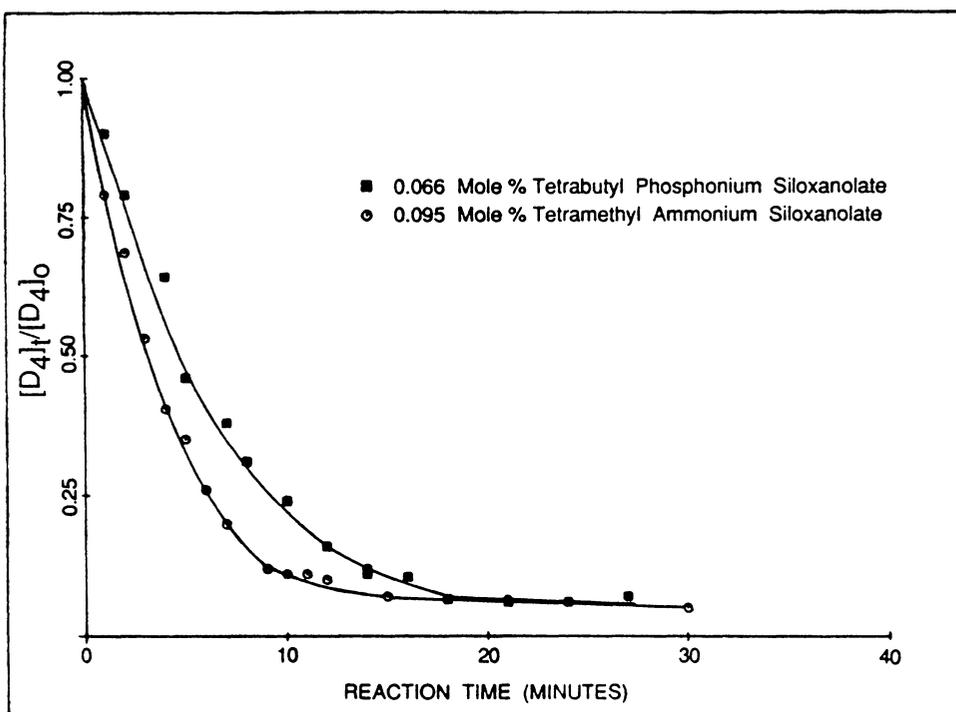


Figure 22: Effect of Catalyst on the Rate of Reaction of D₄; 1500 M_n; 80°C.

information on the effectiveness of the various catalyst systems for the preparation of aminopropyl functional oligomers. It is evident from the data presented above that the tetramethylammonium catalyst reacts with the disiloxane more slowly than was observed in the case of the tetrabutylphosphonium catalyst. The disappearance of aminopropyl disiloxane in the presence of similar concentrations of ammonium and phosphonium catalyst is further compared in Figures 23 through 25. The rate difference is clearly observed in Figure 25, where the aminopropyl disiloxane disappears faster in the presence of 0.066 mole % phosphonium siloxanolate catalyst than in the presence of 0.095 mole % ammonium siloxanolate catalyst. Similarly, while the D_4 concentration decreased faster in the presence of 0.062 mole % ammonium catalyst than in the presence of 0.038 mole % phosphonium catalyst (see Figure 26), the disiloxane disappeared faster in the presence of the lower concentration of phosphonium catalyst (see Figure 27). It must be emphasized, however, that both the ammonium and phosphonium catalysts were significantly more efficient than the potassium siloxanolate catalyst in the rate of incorporation of disiloxane. Since incorporation of the disiloxane is necessary for the preparation of controlled molecular weight oligomers, it was not surprising that the titrated molecular weights of the oligomers prepared with the potassium catalyst were significantly higher than was targeted.

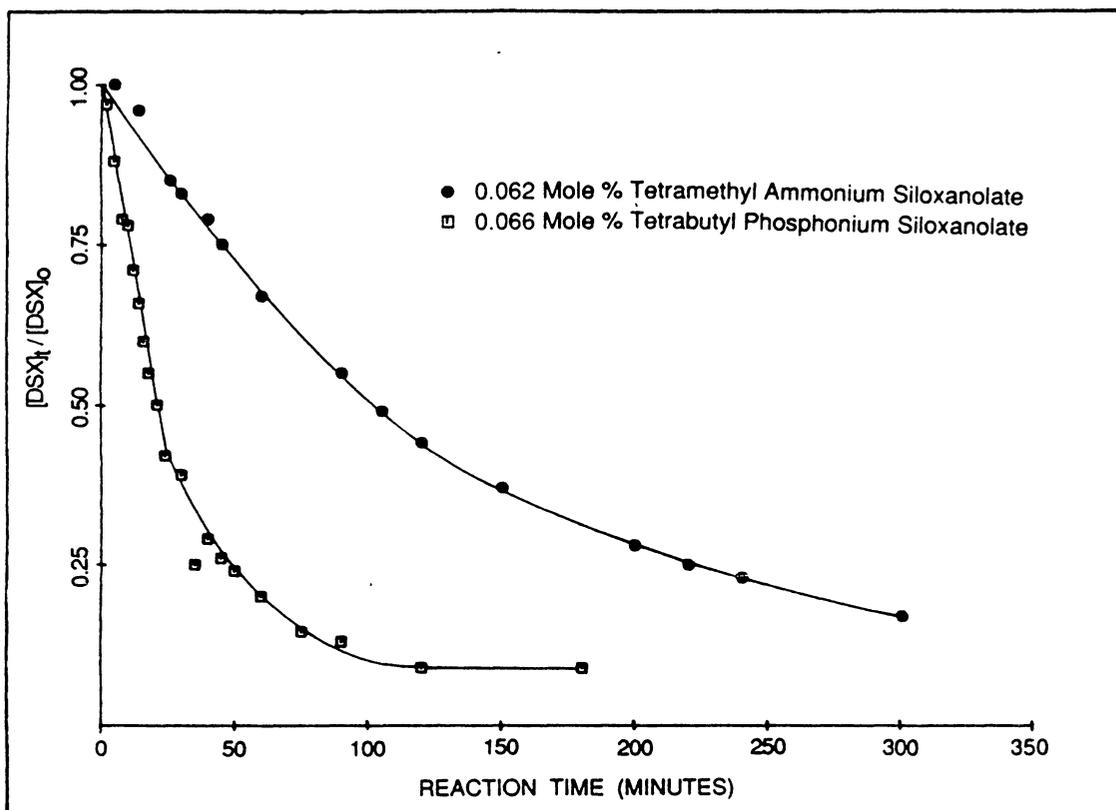


Figure 23: Effect of Catalyst on the Rate of Reaction of Aminopropyl Disiloxane; 1500 \bar{M}_n ; 80°C.

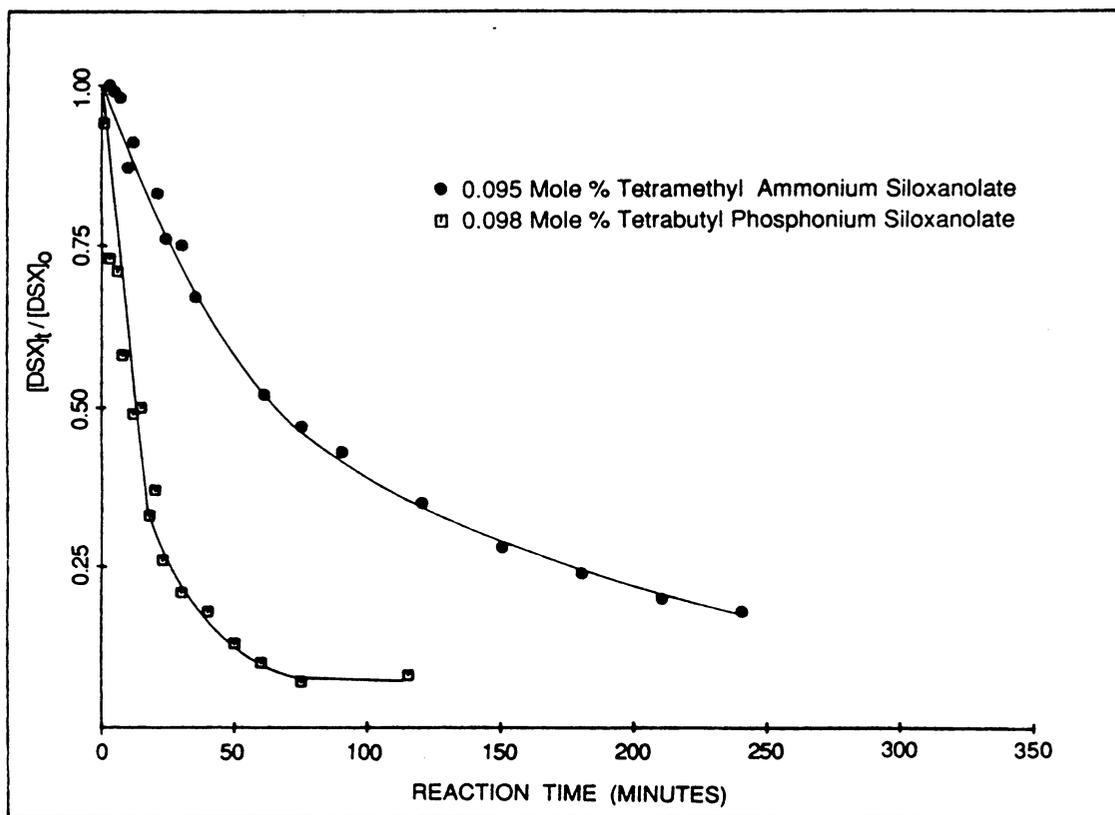


Figure 24: Effect of Catalyst on the Rate of Reaction of Aminopropyl Disiloxane; 1500 \bar{M}_n ; 80°C.

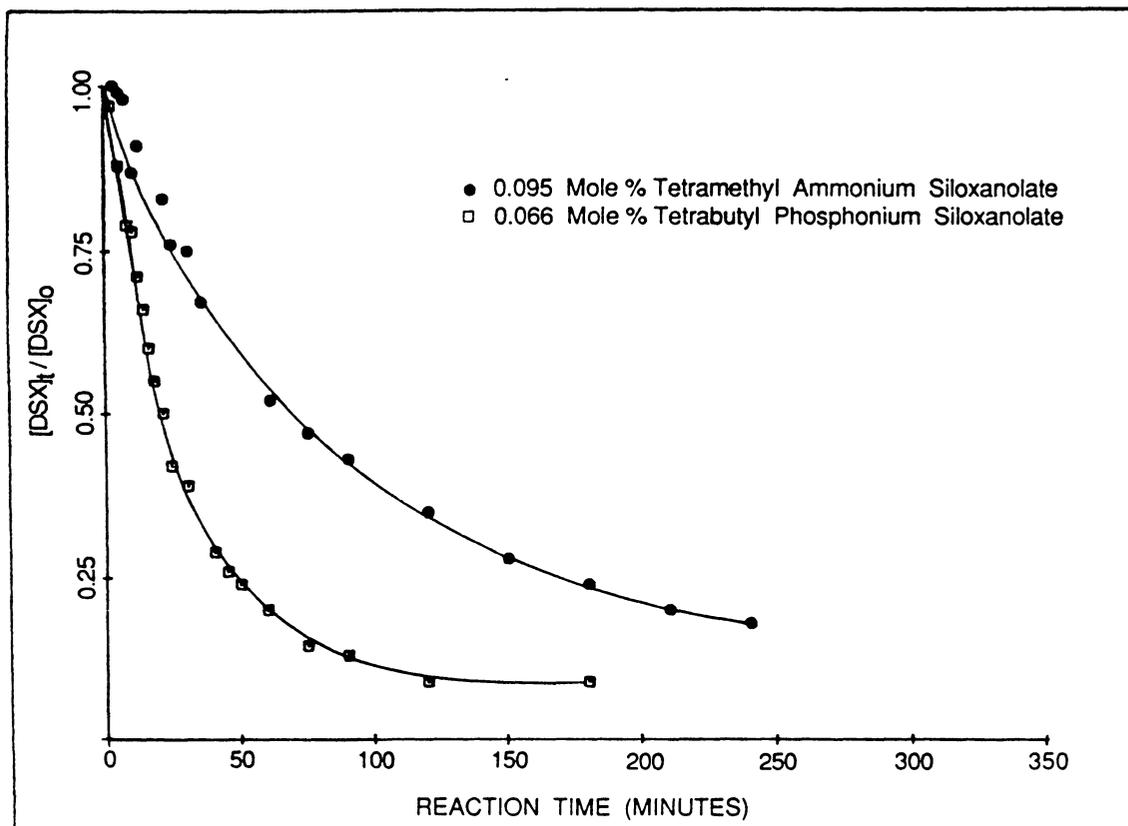


Figure 25: Effect of Catalyst on the Rate of Reaction of Aminopropyl Disiloxane; 1500 \bar{M}_n ; 80°C.

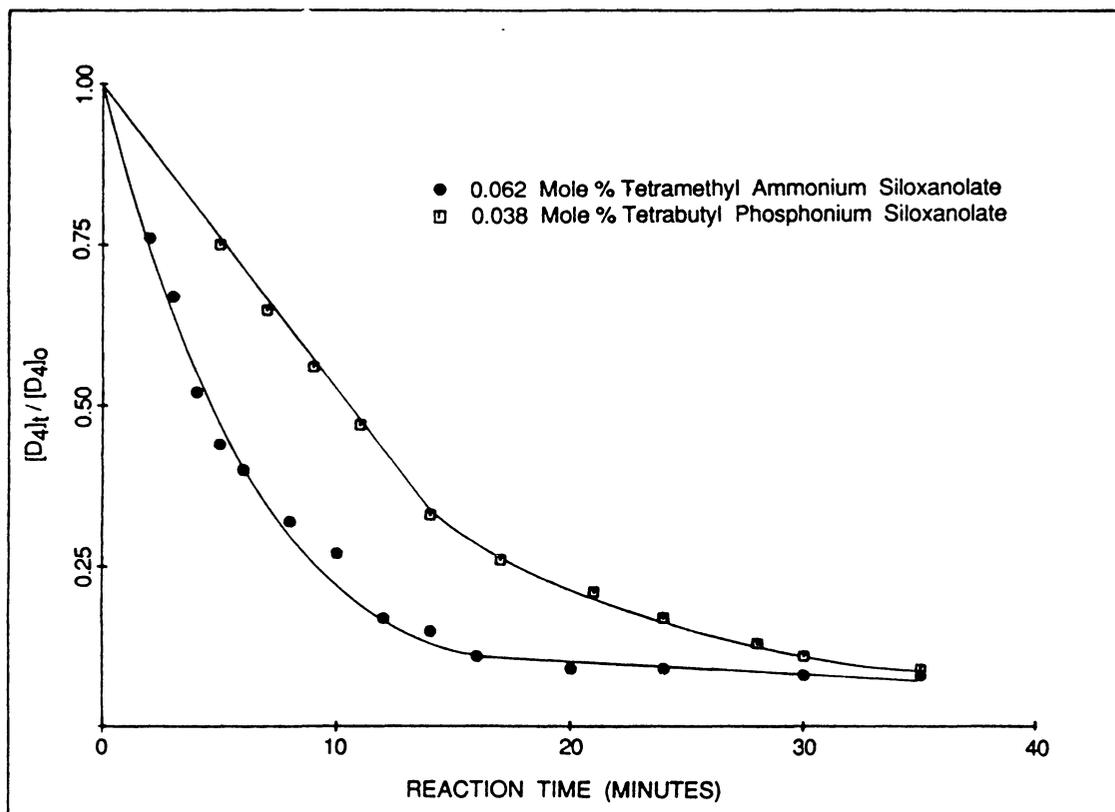


Figure 26: Effect of Catalyst on the Rate of Reaction of D₄; 1500 \bar{M}_n ; 80°C.

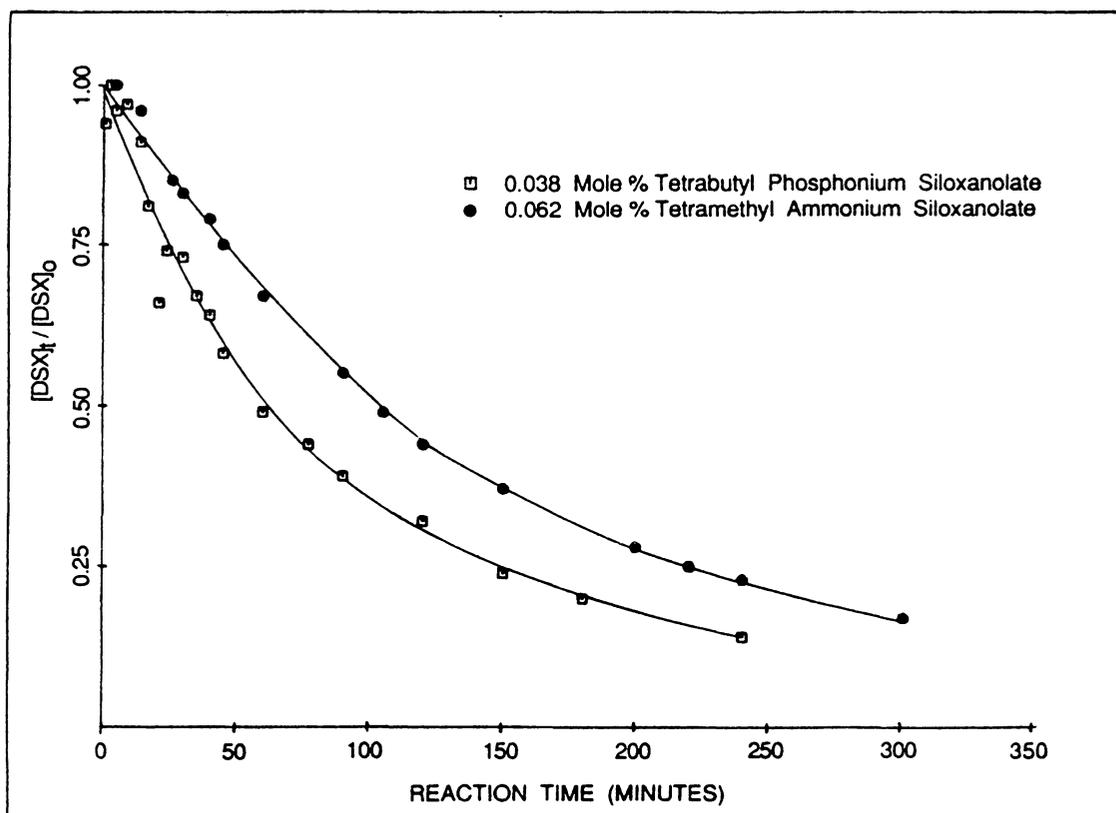


Figure 27: Effect of Catalyst on the Rate of Reaction of Aminopropyl Disiloxane; 1500 \bar{M}_n ; 80°C.

An important feature of these equilibration reactions is that the equilibrium number average degree of polymerization, \bar{X}_n , is dependent on the molar ratio of M to D units, and is not a function of the concentration or the type of catalyst which is employed. Indeed, in all of the systems studied, the equilibrium concentration of D₄ was consistently ~4 to 5 weight percent of the final reaction mixture, and the D₅ content was ~3 weight percent of the final reaction mixture. Further evidence of the attainment of the same equilibrium mixture is found in the similarity of the gel permeation chromatograms of theoretically 1500 g/mole oligomers produced by three different concentrations of phosphonium catalyst (see Figure 28). The effect of the catalyst and catalyst concentration is manifested mainly in the rate at which equilibrium is reached.

The initial reaction rate data for D₄ was further analyzed to determine the reaction orders for the disappearance of D₄ with respect to the siloxanolate catalysts in the presence of the aminopropyl functional endblocker. The disappearance rate of D₄ can be expressed as

$$-d[D_4]/dt = k[D_4]_0^x [R_3Si-O^-M^+]^y [DSX]^z$$

where $[D_4]$ and $[D_4]_0$ are the concentrations of D₄ at time t and $t=0$, $[R_3Si-O^-M^+]$ is the concentration of siloxanolate catalyst, $[DSX]$ is the concentration of aminopropyl disiloxane, k is the apparent or "global" rate constant, and x , y , and z are the reaction orders with respect to D₄,

VARIAN 5500 HPLC
SOLVENT: Toluene; 30°C
RI Detector
Ultrastyrigel Column Set:
100, 500 and 1000 Å

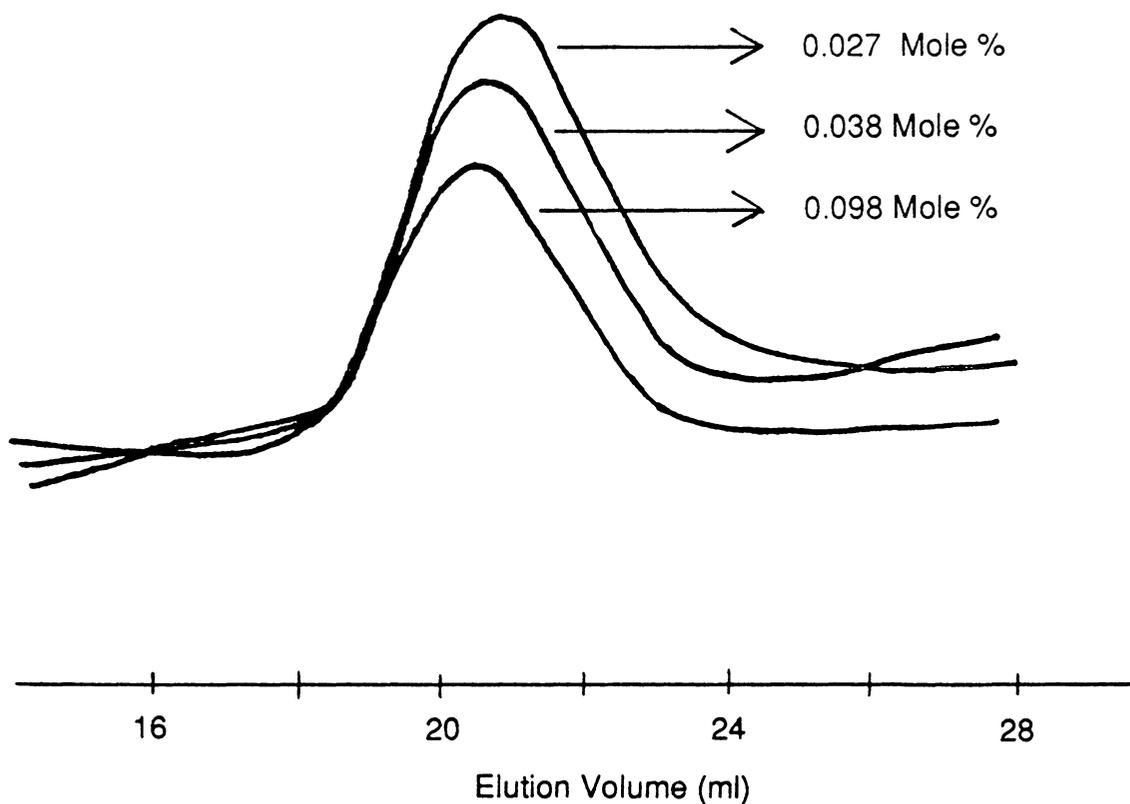


Figure 28: Gel Permeation Chromatograms of Theoretically 1500 \bar{M}_n Oligomers Produced by Three Different Concentrations of Tetrabutylphosphonium Siloxanolate Catalyst.

siloxanolate catalyst, and disiloxane, respectively. This equation can be converted into a linear form by taking the logarithm of both sides and combining constant terms. It can then be rewritten as

$$\log [-d[D_4]/dt] = \log K + y \log [R_3Si-O^-M^+]$$

where K contains k , $[D_4]_0^x$ and $[DSX]^z$. A plot of the left hand side of this equation versus $\log [R_3Si-O^-M^+]$ will give a straight line with slope y and intercept $\log K$.

The initial rate of disappearance of D_4 for the various systems was determined from a plot of the amount of D_4 which had reacted as a function of time. The slope of this plot is the initial rate of reaction of D_4 , which increases with increasing catalyst concentration as shown in Figure 29 for the tetrabutylphosphonium siloxanolate catalyzed system. The log of the rate was then plotted versus the log of the catalyst concentration and the slope of the resulting straight line is the reaction order for the disappearance of D_4 with respect to siloxanolate catalyst. The reaction order observed in the case of the phosphonium catalyst was 1.8, as shown in Figure 30. This value was unexpectedly high based on the square root dependence which had been observed by Grubb and Osthoff [81] for the disappearance of D_4 in the presence of potassium siloxanolate catalyst for nonfunctional siloxane systems. Indeed, a first order dependence could more readily have been explained by assuming that the siloxanolate is more dissociated when the

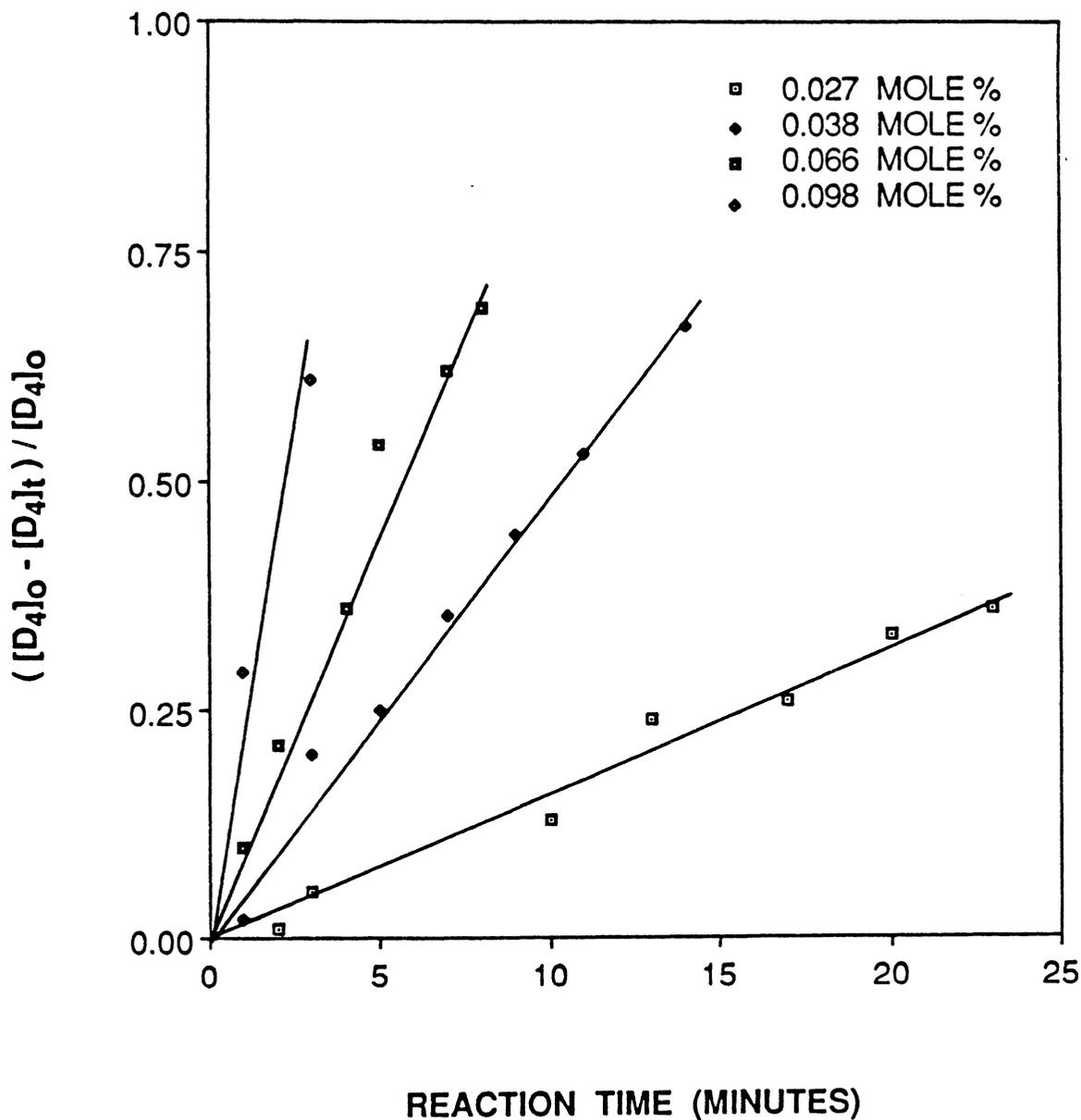


Figure 29: Initial Disappearance of D_4 as a Function of Catalyst Concentration; $1500 \bar{M}_n$; 80°C ; Tetra-Butylphosphonium Siloxanolate Catalyst.

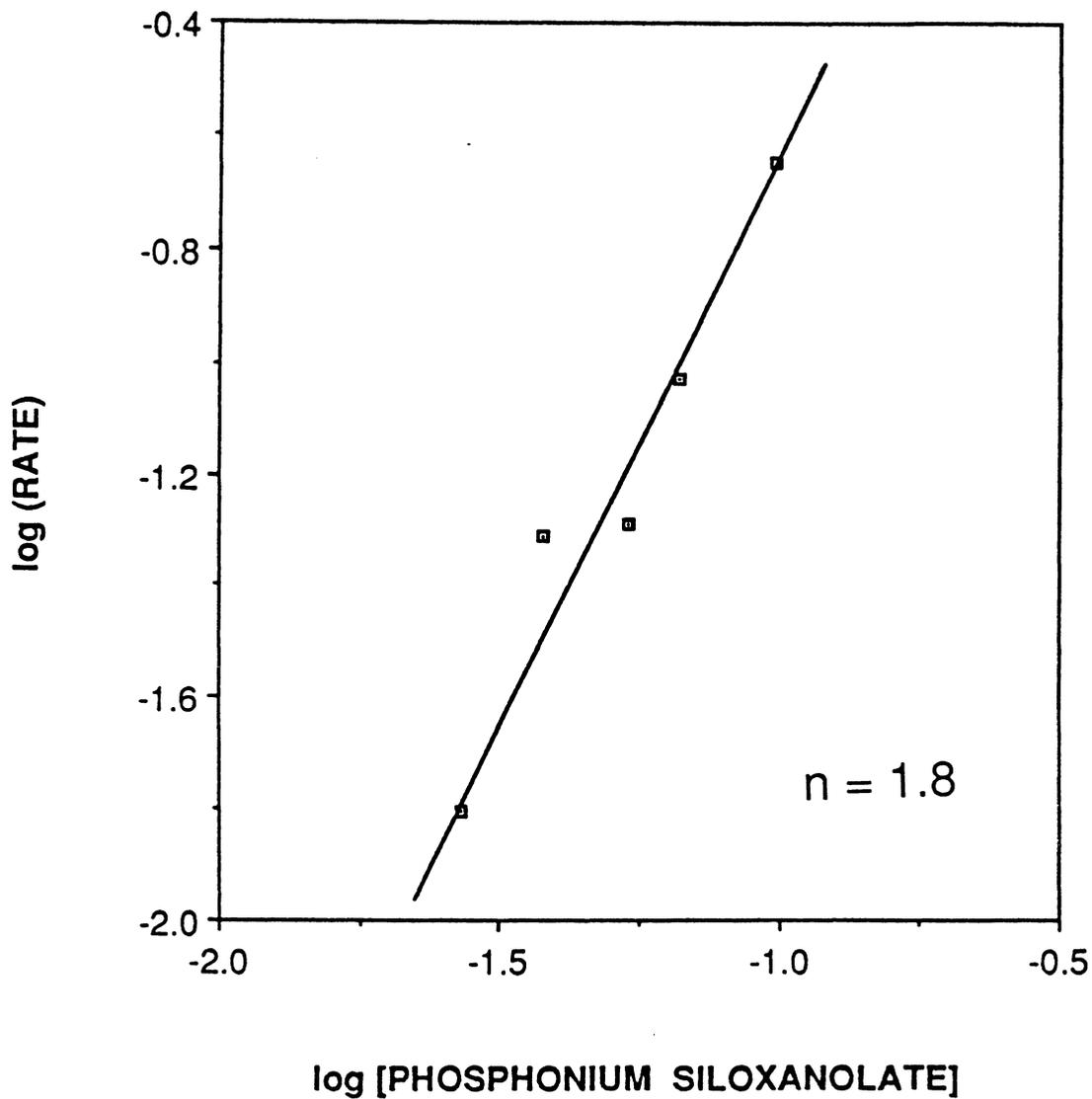


Figure 30: Log-log Plot for the Initial Rate of Reaction of D_4 as a Function of Catalyst Concentration; $1500 \bar{M}_n$; 80°C ; Tetrabutylphosphonium Siloxanolate Catalyst.

bulky tetrabutyl group is the counterion.

The data for the disappearance of D_4 in the presence of several concentrations of tetramethylammonium siloxanolate catalyst was also analyzed, and the log-log plot is shown in Figure 31. In this case the reaction order was found to be equal to 0.5, indicating a square root dependence on the tetramethylammonium siloxanolate catalyst concentration.

Finally, analysis of the data on the potassium siloxanolate catalyst for the disappearance of D_4 in the presence of aminopropyl disiloxane also revealed a square root dependence on catalyst concentration. The reaction orders for all three catalyst systems were determined at 80°C for a targeted 1500 g/mole oligomer. Results on the potassium catalyst system which were obtained at 160°C indicated a reaction order slightly greater than one-half ($n = 0.6$) for the disappearance of D_4 with respect to catalyst. The log-log plots for all of these systems are compared in Figure 32.

The greater dependence on catalyst concentration in the case of the phosphonium catalyst is evident from the steep slope of its rate curve (Figure 32) relative to the curves for the other catalysts studied. The differences in reaction orders cannot be readily interpreted, since the much higher dependence on catalyst concentration in the case of the phosphonium catalyst would imply that a different reaction mechanism is responsible for incorporation of D_4 in the

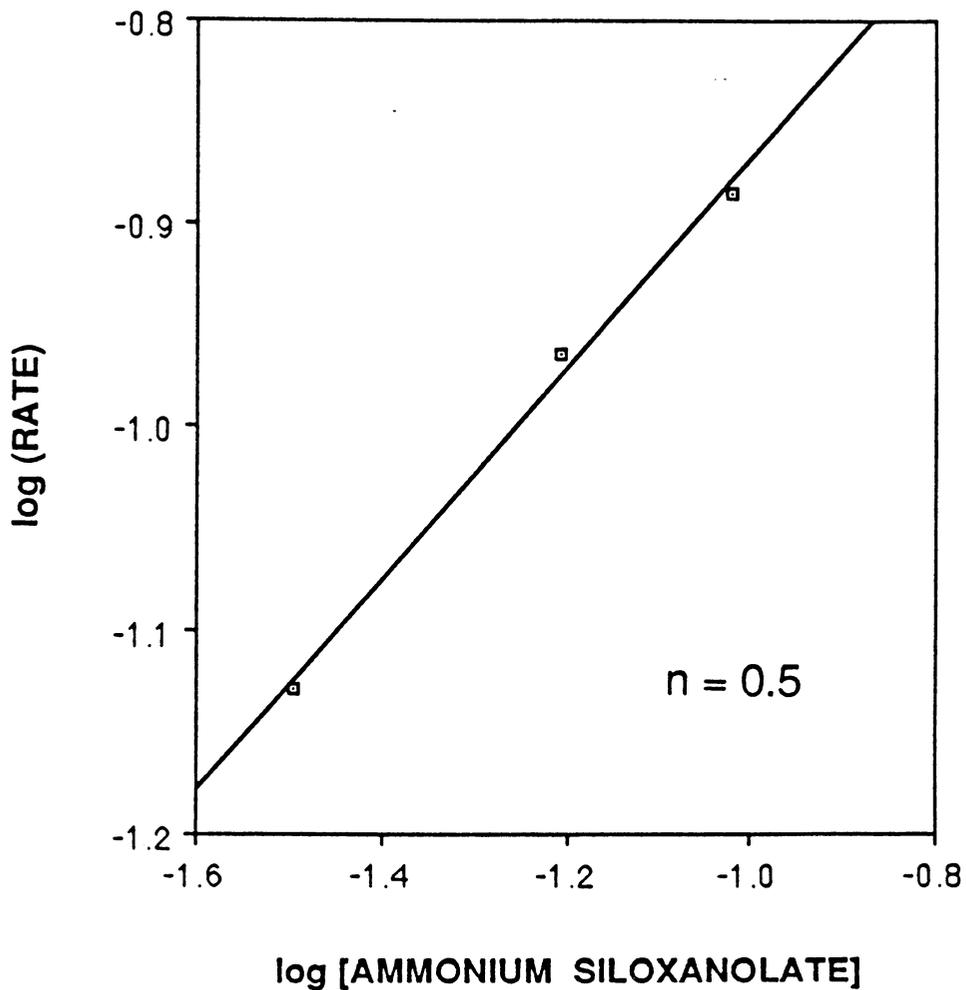


Figure 31: Log-log Plot for the Initial Rate of Reaction of D_4 as a Function of Catalyst Concentration; $1500 \bar{M}_n$; 80°C ; Tetramethylammonium Siloxanolate Catalyst.

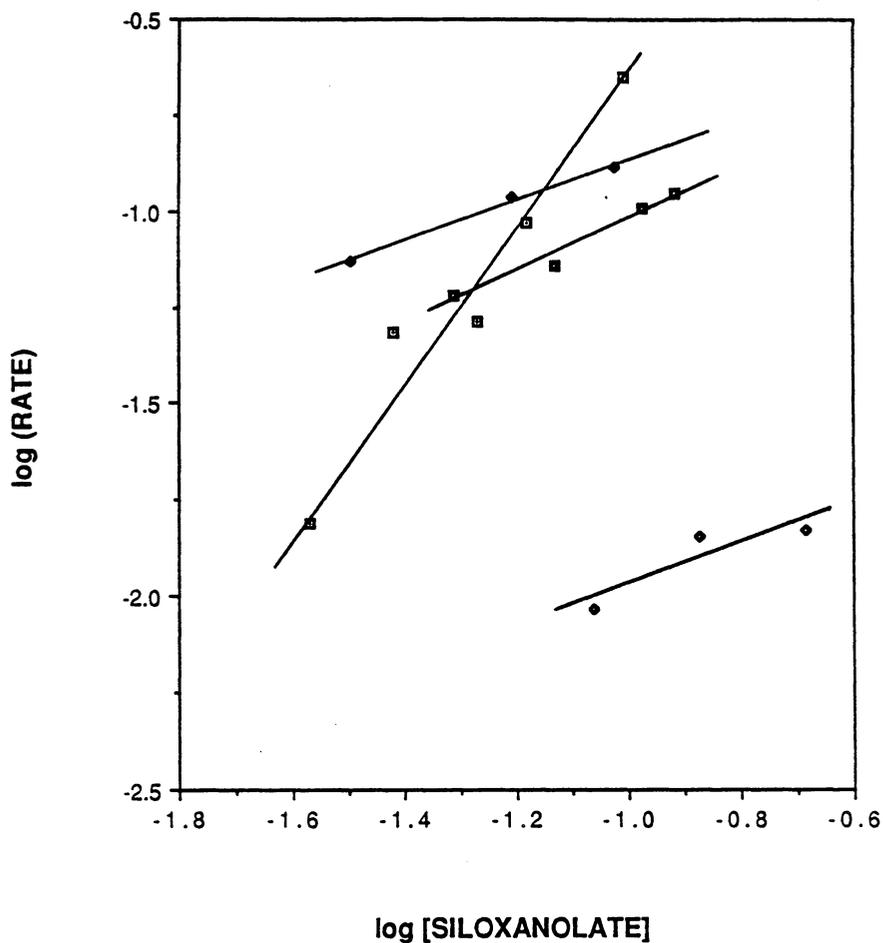


Figure 32: A Comparison of the Log-Log Plots as a Function of Catalyst for the Initial Rate of Reaction of D₄.

presence of that particular catalyst. It was discussed in the literature review that minor amounts of phosphine oxides are quite effective in promoting base-catalyzed siloxane rearrangements [90]. Since a decomposition product of the transient phosphonium catalyst is a phosphine oxide, it is certainly feasible that the presence of minor amounts of decomposition products from the catalyst are effectively promoting the equilibration reaction. This could at least partially account for the dramatic reaction rate increase observed in the case of the phosphonium catalyst. Another factor which may be influencing the reaction kinetics is the presence of catalytic amounts of water, due to the difficulty encountered in quantitatively removing moisture from the aminopropyl disiloxane starting material. The one-half order dependencies observed in the presence of the other two catalysts studied are consistent with the mechanism proposed for nonfunctional systems [81], where a partially dissociated siloxanolate ion is thought to be the active species. The reaction orders for the disappearance of aminopropyl disiloxane with respect to siloxanolate catalyst were not readily determined due to an apparent induction period prior to incorporation of the disiloxane. The length of the induction period varied as a function of the catalyst and catalyst concentration, and was generally observed to be related to the amount of D₄ remaining in the system relative to the amount of disiloxane.

While the reaction order for the disappearance of D₄ with respect to the phosphonium catalyst concentration is somewhat difficult to explain, the actual order of reactivity of the various catalysts can be more readily interpreted. Specifically, the rates of incorporation of both D₄ and aminopropyl disiloxane were observed to increase as the bulkiness of the siloxanolate counterion increased. It is expected that the presence of a bulky counterion would decrease the tendency for aggregate formation, and at the same time favor the existence of a less associated siloxanolate ion pair. The siloxanolate anion should then be more available for attack on silicon-oxygen bonds in the cyclic, linear or disiloxane species. While these tendencies have been studied in the past for the disappearance of D₄, the significance of the results with respect to functional siloxane systems has not been previously appreciated.

In addition to the expected greater availability of the siloxanolate anions in the presence of bulkier counterions, the faster rate of incorporation of disiloxane with these materials might be attributed to a greater solubility of the siloxanolate species in the siloxane media. Specifically, the more organic nature of the alkyl-containing tetramethylammonium and tetrabutylphosphonium cations may lead to a greater solubility of these species with the aminopropyl segments than in the case of the potassium cation. In any event, as a result of the minimal incorporation of the

aminopropyl disiloxane in the presence of the potassium siloxanolate catalyst, even at elevated catalyst concentrations and reaction temperatures, the potassium catalyst does not appear to be a viable alternative for efficient preparation of controlled molecular weight difunctional aminopropyl terminated polysiloxane oligomers. On the other hand, the tetramethylammonium siloxanolate catalyst and tetrabutylphosphonium siloxanolate catalysts were very effective at incorporating both the D₄ and the disiloxane within reasonable reaction times and temperatures, with the phosphonium catalyst being the most efficient of the catalyst systems studied.

C. SUPERCRITICAL FLUID FRACTIONATION STUDIES ON AMINOPROPYL TERMINATED POLYSILOXANES

The versatility offered by aminopropyl terminated polysiloxane oligomers for incorporation of siloxane components into various block and segmented copolymer systems was elaborated upon earlier. The difunctional nature of these materials is a distinct advantage, but the Gaussian molecular weight distributions produced by equilibration processes may limit the range of fundamental properties which may be examined in the resulting materials. Indeed, the properties of a siloxane-containing block copolymer are highly dependent on the nature of the difunctional precursors, as well as on the degree of microphase

separation of the respective blocks in these segmented copolymer systems [151,156].

Supercritical fluid fractionation techniques have been explored in attempt to separate the aminopropyl terminated oligomers into fractions of narrow polydispersity. The fractionation process was completed at Phasex Corporation (360 Merrimack Street, Lawrence, MA 01843). The fractions were then completely characterized in terms of their structure, molecular weight, molecular weight distribution, and functionality. The results of these fractionation studies will be presented below.

The amine functional oligomers were synthesized as described previously using ~0.06 mole% tetramethylammonium siloxanolate catalyst at 80°C. The reactions were generally allowed to proceed for 48 hours to ensure that thermodynamic equilibrium had been reached. The catalyst was then decomposed by heating at elevated temperatures, and the bulk reaction mixture was fractionated using the pressure profiling technique described in Chapter III. Supercritical ethane was employed at 80°C. This is ~50° above the critical temperature of ethane ($T_c = 32.2^\circ\text{C}$). Supercritical carbon dioxide is often preferred for economic and environmental reasons, but its use was prohibited here due to the deleterious side reaction which occurs between carbon dioxide and aliphatic amines.

The first set of fractionation data to be presented is

for a 4200 g/mole aminopropyl terminated oligomer. The sample was separated into eight fractions of increasing molecular weight due to the enhanced solvating ability of the supercritical ethane with increased pressure. As expected, the first two fractions contained nonfunctional low molecular weight cyclics. The content of these fractions was determined by HPLC and GC, and the absence of functionality was confirmed by titration and the lack of amine absorptions by FT-IR. The infrared spectrum of the combined sample of fractions 1 and 2 is shown in Figure 33. The absence of cyclics in the higher fractions was confirmed via the same techniques, and the number average molecular weights were determined by titration of the amine endgroups with alcoholic HCl. An infrared spectrum typical of the higher fractions is shown in Figure 34.

It was mentioned previously that the presence of the amine functionality caused the oligomers to adsorb on the GPC columns, so a derivatization method was developed [173] to convert the primary amine to an imine functionality, thereby allowing GPC analysis of the oligomers. The derivatization reactions were carried out in bulk at 80°C in the presence of excess benzophenone, as depicted in Scheme XXII of Chapter III (EXPERIMENTAL). The characterization results on the 4200 g/mole sample are summarized in Table 10. The GPC traces on the parent oligomer and its fractions are reproduced in Figure 35. The fractions are of narrower

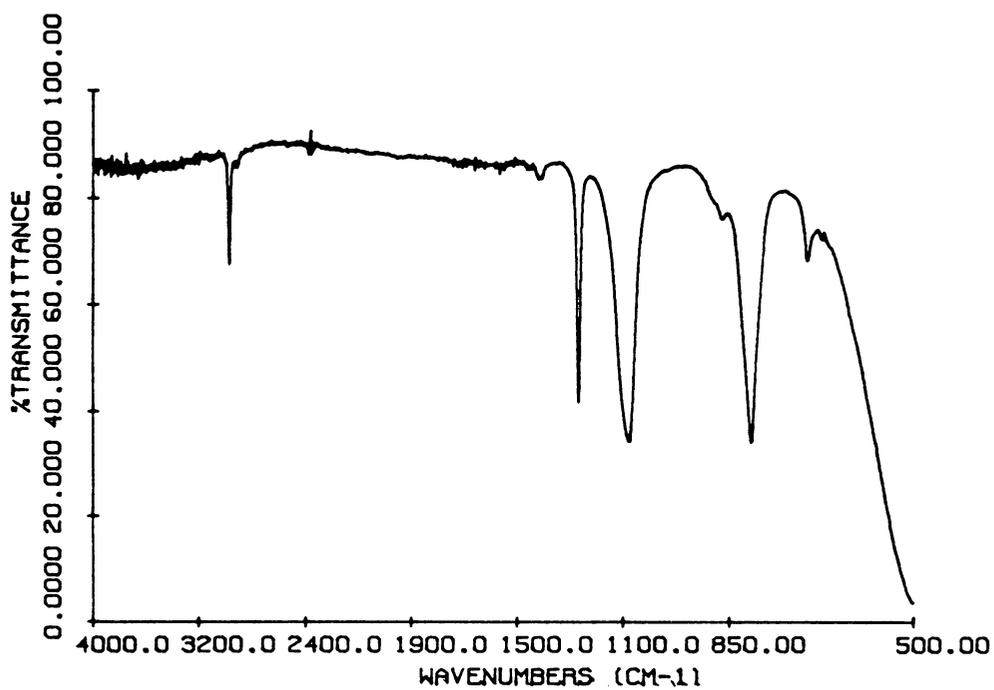


Figure 33: FTIR Spectrum of Fractions 1 and 2 Containing Nonfunctional Cyclic Siloxanes.

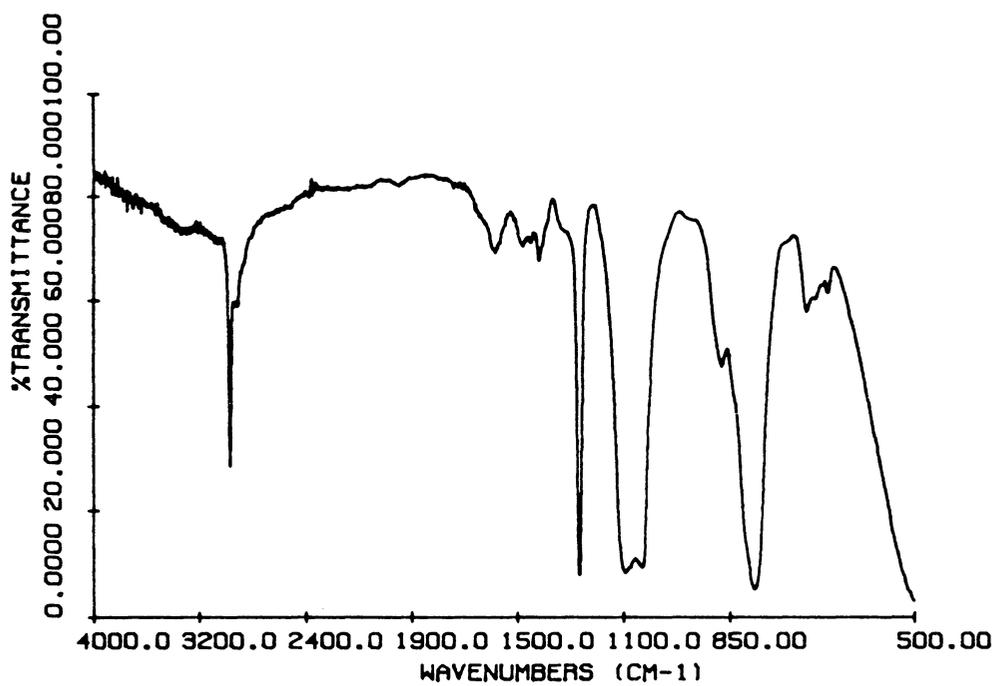


Figure 34: FTIR Spectrum of Higher Fractions Containing Aminopropyl Terminated Polydimethylsiloxanes.

Table 10
 Fractionation of Aminopropyl Terminated
 Polydimethylsiloxane:
 Solvent: Supercritical Ethane

| Fraction | Titrated \bar{M}_n (g/mole) | Weight % D ₄ | Weight % D ₅ | \bar{M}_w/\bar{M}_n (a) |
|----------|----------------------------------|----------------------------|----------------------------|---------------------------|
| Control | 4200 | 4.5 | 4.2 | 2.14 |
| 1 | --(b) | | | -- |
| 2 | --(b) | 41 | 45 | -- |
| 3 | 1460 | 0 | 5 | 1.30 |
| 4 | 2820 | 0 | 0 | 1.25 |
| 5 | 4920 | 0 | 0 | 1.26 |
| 6 | 6600 | 0 | 0 | 1.33 |
| 7 | 9550 | 0 | 0 | 1.36 |
| 8 | 15,550 | 0 | 0 | 1.71 |

(a) Based on Polystyrene Standards.

(b) Contains Only Nonfunctional Cyclic Species.

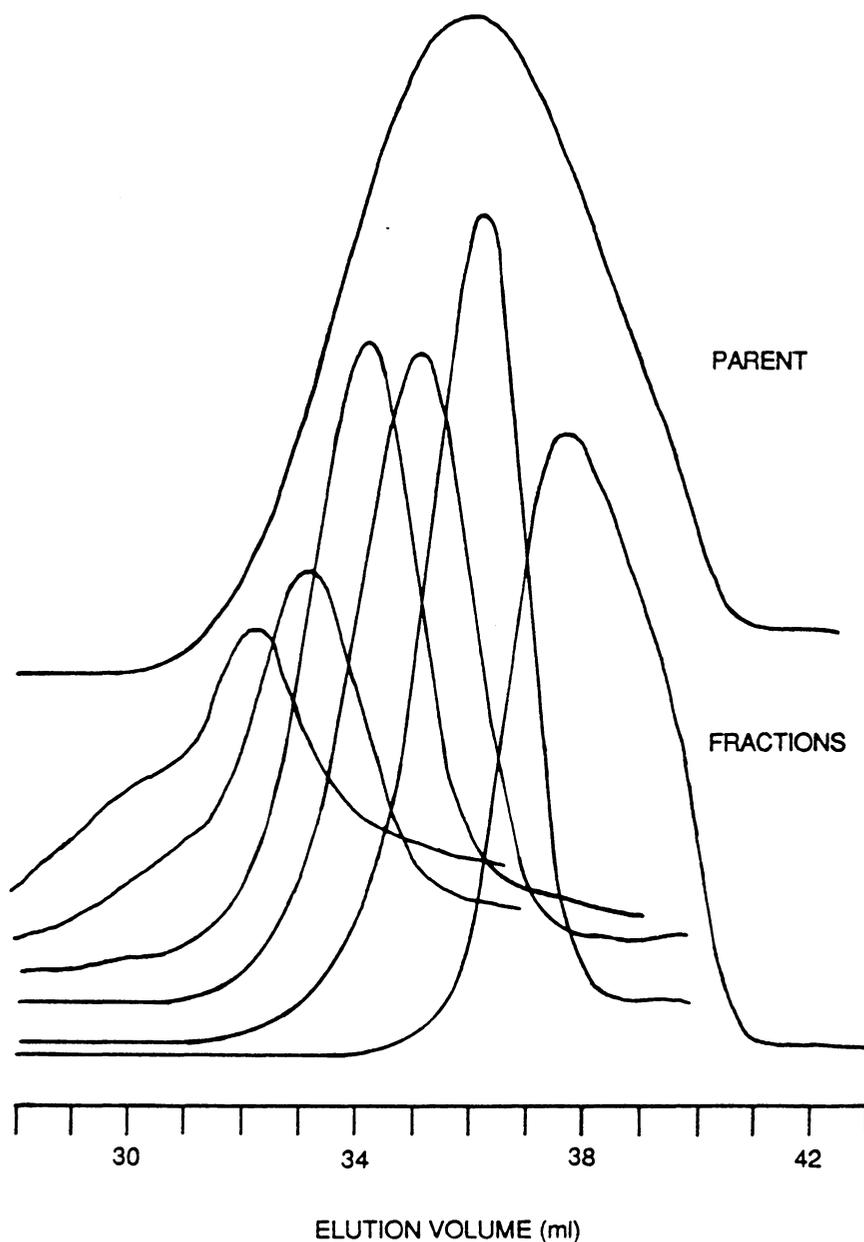


Figure 35: GPC Chromatograms of Aminopropyl Terminated Polydimethylsiloxane and Its Fractions.

molecular weight distribution than the parent oligomer, though the experimental parameters in the fractionation process had not been optimized for precise control over the characteristics of the samples. Also, the polydispersities reported in Table 4 were determined with respect to polystyrene standards which have a different hydrodynamic volume than polysiloxanes and therefore are not a true indication of the molecular weight distributions of the samples.

Since narrow molecular weight distribution polysiloxane standards are not commercially available, a series of standards was prepared via "living" anionic polymerization techniques, and subsequently characterized for use. It was anticipated that the availability of polysiloxane standards would allow subsequent fractionated samples to be characterized more completely. Before proceeding with results on the supercritical fluid fractionation of functional siloxane oligomers, the synthesis and characterization of the polysiloxane standards for GPC will be described.

Anionic polymerization of hexamethylcyclotrisiloxane (D₃) initiated by secondary-butyl lithium and terminated with phenyldimethylchlorosilane produced polydimethylsiloxane oligomers of narrow polydispersity. The standards ranged in molecular weight from 1700 g/mole to 21,000 g/mole. The molecular weight was controlled by the ratio of the number of grams of monomer to the number of moles of initiator (see Appendix D). The reaction scheme for the

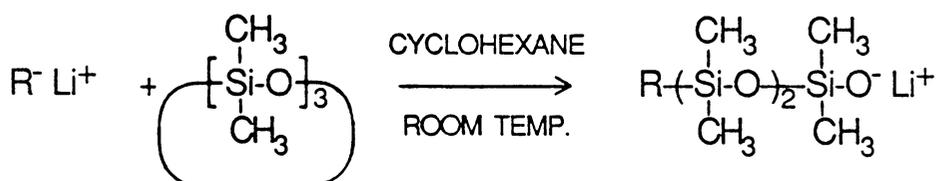
synthesis is shown in Scheme XXV. The promoting solvent was tetrahydrofuran and was added ~15 minutes after the initiator. After 24 to 48 hours, the reactions were terminated with phenyldimethylchlorosilane. The longer reaction times were necessary to achieve high conversions in the preparation of the higher molecular weight standards. The oligomers were isolated as described in Chapter III (EXPERIMENTAL). The phenyl-containing terminating reagent had been specifically chosen so that a UV detector might be utilized in the GPC analysis. The fractions separated via the supercritical fluid fractionation process would also contain phenyl groups on the ends of the chains after derivatization with benzophenone.

The standards were characterized by a number of techniques so that the molecular weight of the samples could be precisely determined. Number average molecular weights were determined by vapor phase osmometry and UV-visible spectroscopy, as well as by quantitative ^{29}Si NMR for the lower molecular weight samples. The ^{29}Si NMR spectrum for the theoretically 1620 g/mole standard is shown in Figure 36. The ratio of the integration for the silicon peak due the terminating reagent over that due to the silicon next to the initiator allows determination of the percentage of chains which were terminated with the phenyldimethylchlorosilane. The results indicated that the efficiency of termination is generally around 90%. The molecular weight

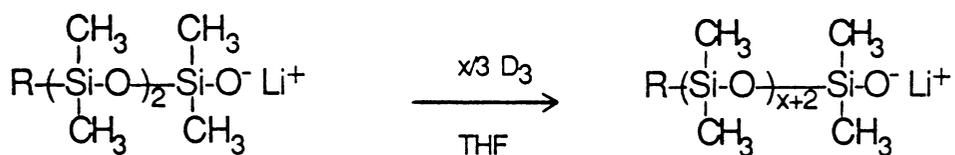
Scheme XXV

Preparation of Polydimethylsiloxane Standards for GPC

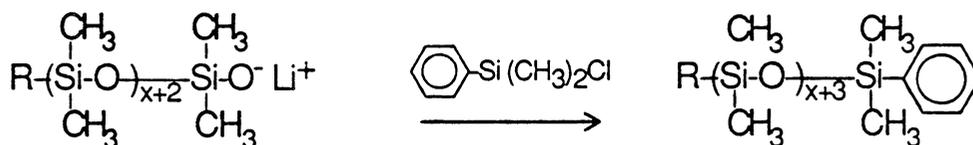
INITIATION



PROPAGATION



TERMINATION



where R = sec-Butyl

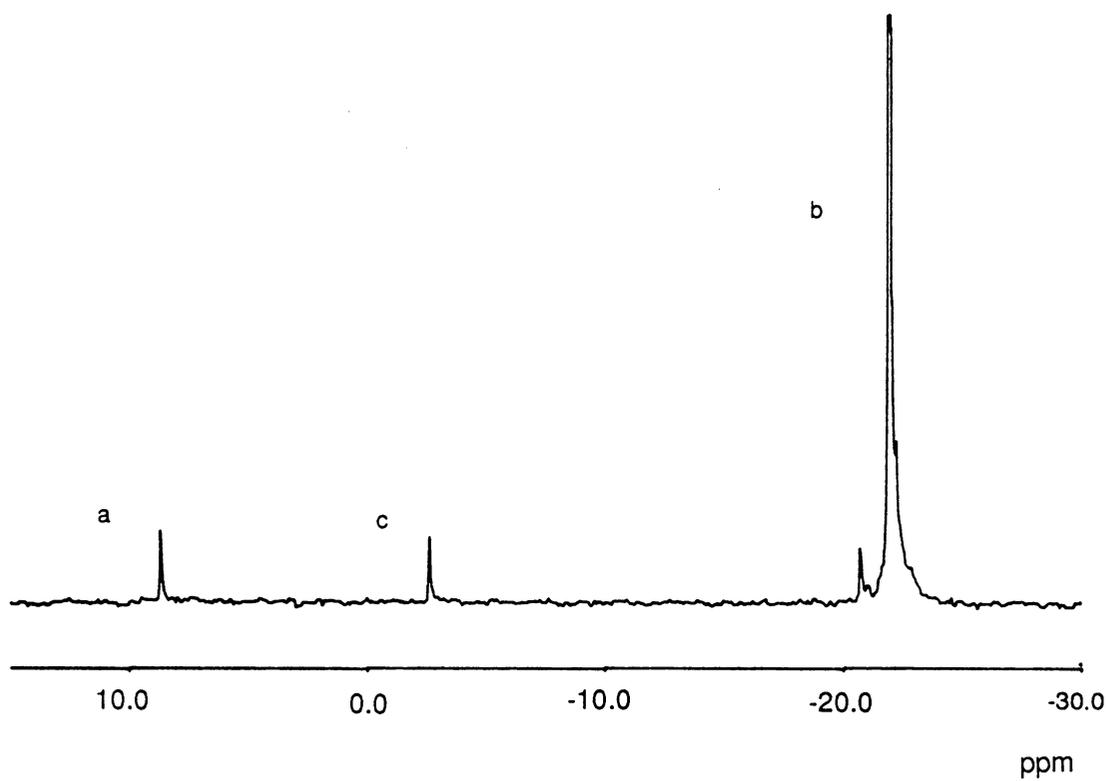
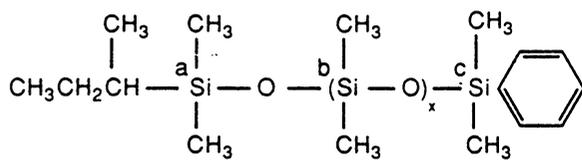


Figure 36: ^{29}Si NMR Spectrum of a Theoretically 1620 \bar{M}_n Polydimethylsiloxane GPC Standard.

of the sample was also determined by the ratio of the area due to the silicon backbone relative to that due to the silicon next to the initiator.

Absolute weight average molecular weights of a number of the standards were determined through the use of static light scattering measurements, as described in Chapter III. Average dn/dc , \bar{M}_w , and A_2 values for several of the samples are shown in Table 11. A typical plot of Kc/R_θ versus concentration for the determination of \bar{M}_w is shown in Figure 37. Correlation coefficients for all the plots were greater than 0.99. The molecular weight data obtained using all of the previously described techniques is summarized in Table 12. The GPC calibration curve based on these polydimethylsiloxane standards is shown in Figure 38. These standards were subsequently utilized to characterize the polysiloxane fractions obtained by supercritical fluid fractionation of aminopropyl terminated oligomers.

The next sample which was fractionated was a 1900 g/mole oligomer, as determined by titration of the amine endgroups in the vacuum stripped oligomer. This particular sample was fractionated into 18 fractions, and the molecular weight data is presented in Table 13. While the initial fractions (1 through 3) were fairly broad due to an anomaly in the fractionation process, fractions 4 through 18 were of increasing higher molecular weight and extremely narrow molecular weight distributions. The molecular weight

Table 11
Data From Static Light Scattering Measurements
on Polysiloxane Standards(a)

| Standard # | dn/dc | \bar{M}_w (g/mole) | A_2 (mole cm ³ /g ²) |
|---------------|---------|-------------------------|--|
| 3 | -0.0872 | 10,400 | 8.16 x 10 ⁻⁴ |
| 4 | -0.0875 | 17,160 | 8.59 x 10 ⁻⁴ |
| 5 | -0.0879 | 26,700 | 6.51 x 10 ⁻⁴ |

(a) Chromatix KMX-6 LALLS Photometer
633 nm; 6-7° Forward Scattering Angle
Solvent: Toluene; 27°C

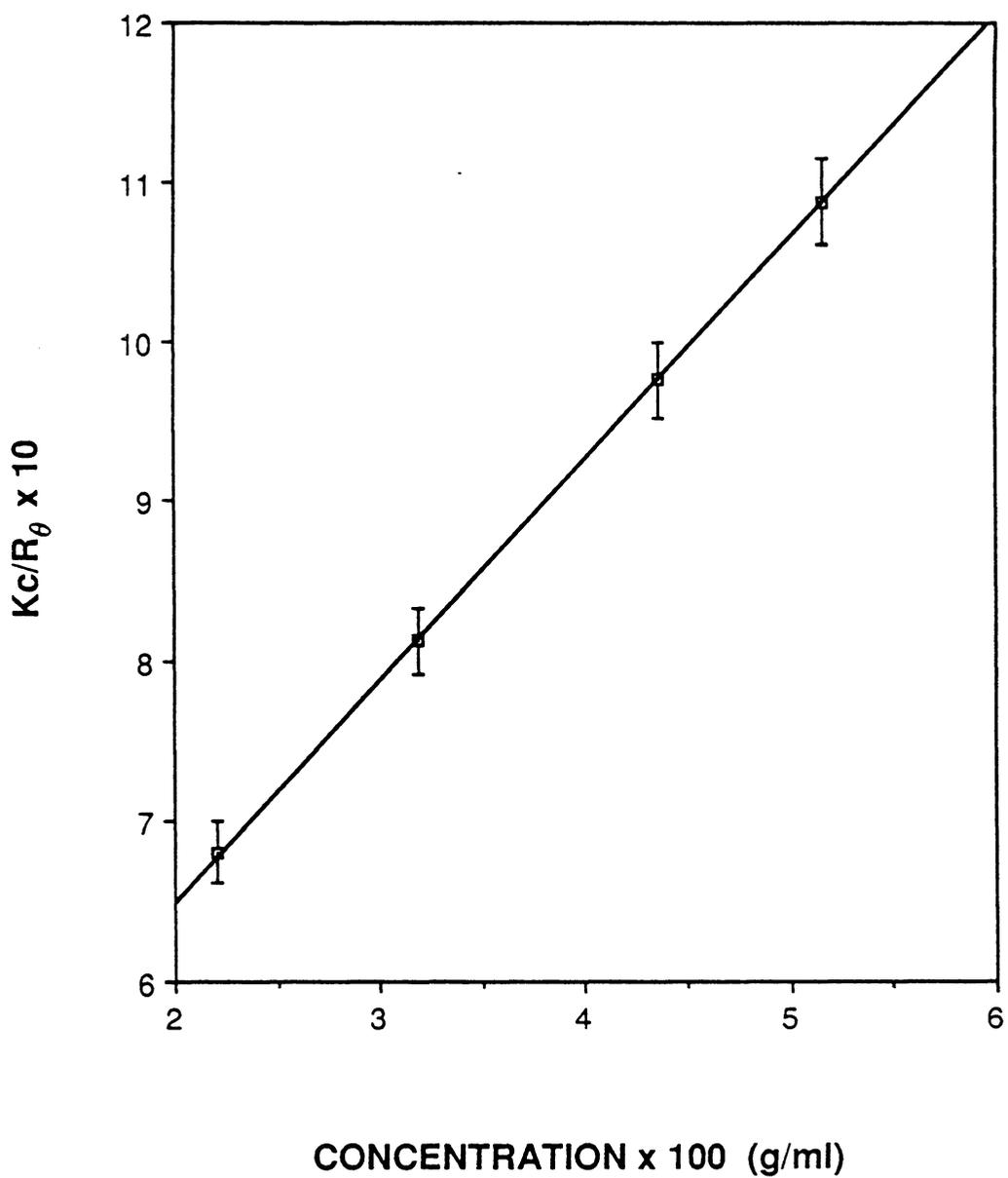


Figure 37: Typical Plot of Kc/R_{θ} versus Concentration for the Determination of \bar{M}_w by LALLS.

Table 12
Molecular Weight Data on
Polydimethylsiloxane Standards for GPC

| Standard # | \bar{M}_n by VPO | \bar{M}_n by UV - Vis | \bar{M}_n by ^{29}Si NMR | \bar{M}_w by LALLS |
|------------|--------------------|-------------------------|-------------------------------------|----------------------|
| 1 | 1715 | 1710 | 1850 | NA |
| 2 | 3970 | 4100 | NA | NA |
| 3 | 9275 | 8070 | NA | 10,400 |
| 4 | 13,870 | 12,360 | NA | 17,160 |
| 5 | NA | 21,000 | NA | 26,700 |

NA = Not Available

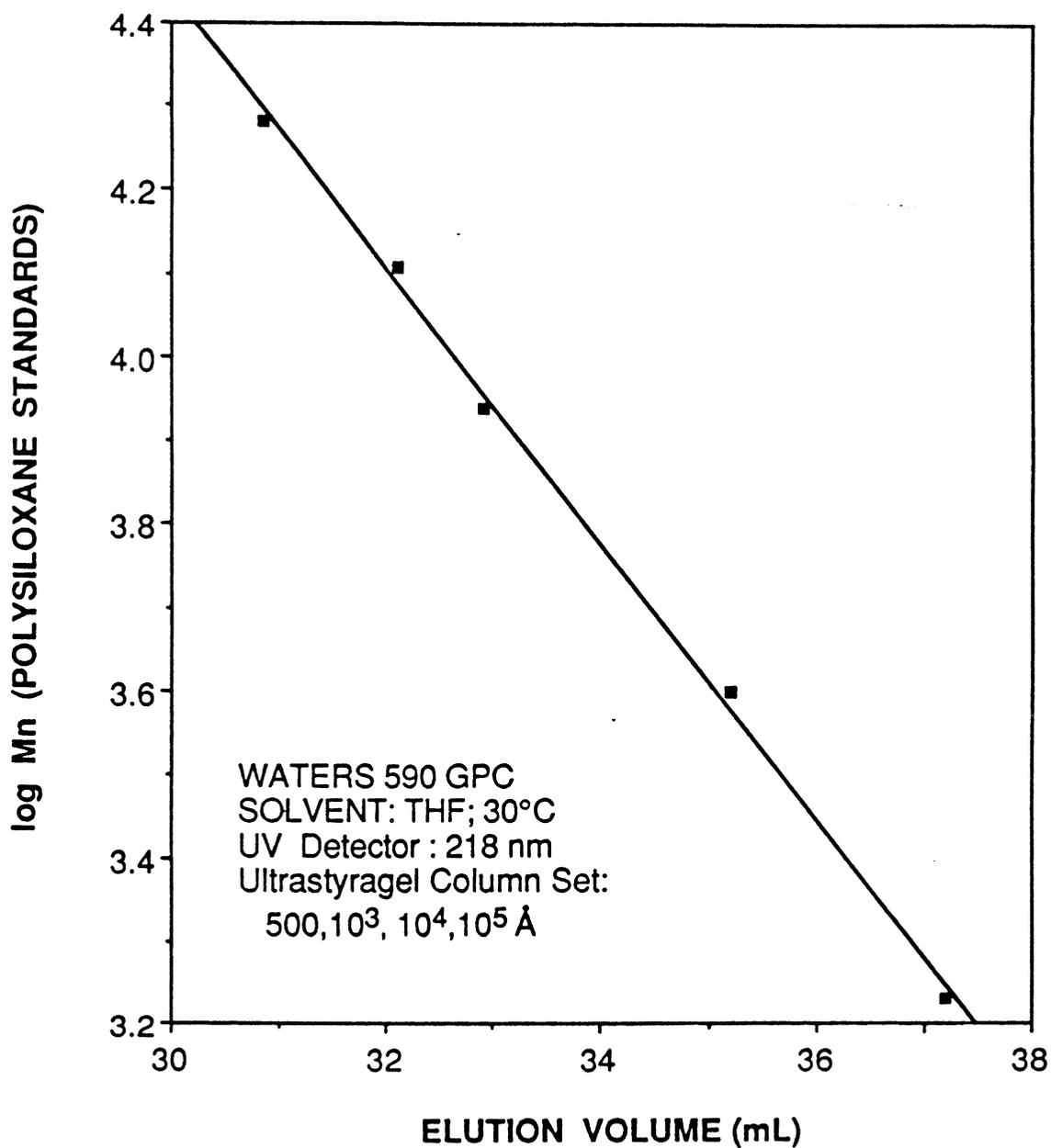


Figure 38: GPC Calibration Curve Constructed from Phenyl-Terminated Polydimethylsiloxane Standards.

Table 13
 Fractionation of Aminopropyl Terminated
 Polydimethylsiloxane

| FRACTION | TITRATED \bar{M}_n | GPC RESULTS* | |
|----------|-------------------------|-----------------------|-------------|
| | | \bar{M}_w/\bar{M}_n | \bar{M}_n |
| Control | 1900 | 1.58 | 1400 |
| 1 | 1700 | -- | --- |
| 2 | 1300 | -- | --- |
| 3 | 1000 | 1.33 | 500 |
| 4 | 840 | 1.13 | 700 |
| 5 | 1050 | 1.22 | 600 |
| 6 | 1300 | 1.14 | 1000 |
| 7 | 1550 | 1.12 | 1300 |
| 8 | 1800 | 1.12 | 1700 |
| 9 | 1900 | 1.13 | 1800 |
| 10 | 2300 | 1.06 | 2100 |
| 11 | 2550 | 1.12 | 2600 |
| 12 | 2900 | 1.12 | 2900 |
| 13 | 3250 | 1.15 | 3500 |
| 14 | 3900 | 1.12 | 4000 |
| 15 | 4450 | 1.10 | 4600 |
| 16 | 5100 | 1.09 | 5300 |
| 17 | 5900 | 1.18 | 6700 |
| 18 | --- | -- | --- |

* Based on polysiloxane standards.

distributions reported in Table 13 were calculated with respect to polysiloxane standards. Indeed, excellent agreement was realized between the molecular weight values determined by titration of the amine endgroups and those calculated by GPC. The GPC traces for the parent oligomer and several of the fractions derived from it are reproduced in Figure 39. The efficiency of this technique at producing difunctional fractions of narrow polydispersity is readily observed from Table 13 and Figure 39. The difunctional nature of the fractions was confirmed by comparing the number average molecular weight determined by titration of the amine endgroups with the value obtained by VPO analysis for several samples. The results are presented in Table 14. The excellent agreement of the molecular weight values confirms the difunctionality of the materials before and after the fractionation process.

Polysiloxanes are readily fractionated by supercritical fluid extraction techniques due to their excellent solubility characteristics. Indeed, polydimethylsiloxanes up to 100,000 g/mole have been solubilized by supercritical fluids [91]. In the present study on amine terminated polysiloxanes, similar results were observed. However, the desired molecular weight of difunctional precursors for segmented copolymer systems is generally less than 20,000 g/mole. The next set of fractionation results are on a 7500 g/mole parent oligomer which was separated into 11 fractions

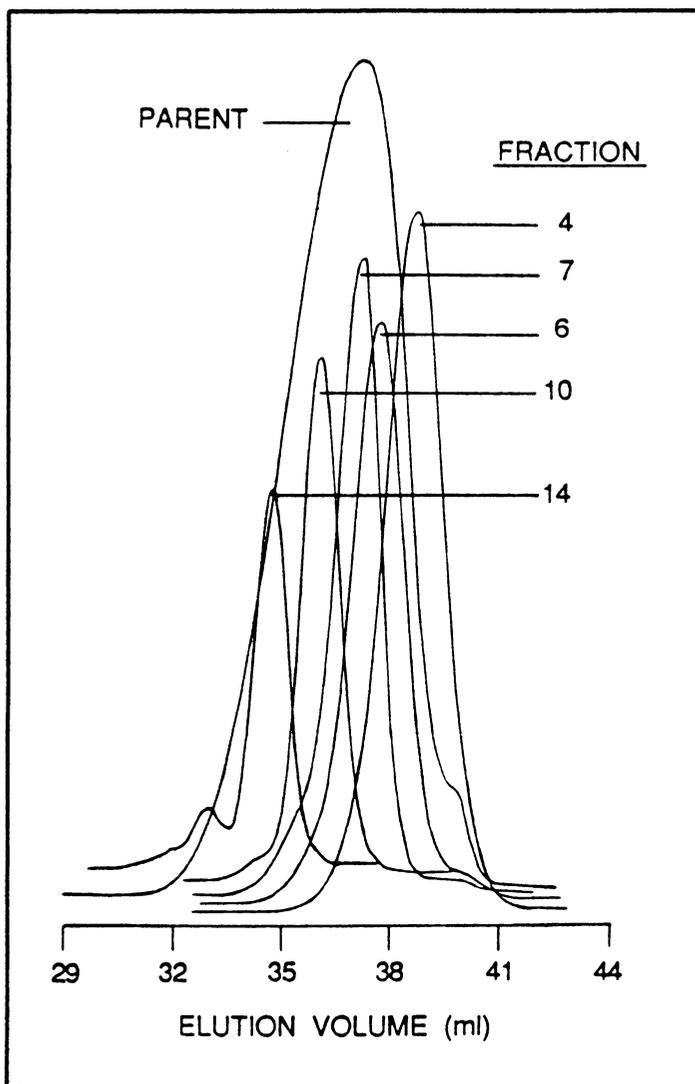


Figure 39: GPC Chromatograms of Aminopropyl Terminated Polydimethylsiloxane and Its Fractions.

Table 14

Molecular Weight Characterization
of Fractionated Aminopropyl Terminated Polydimethylsiloxane

| FRACTION | TITRATED \bar{M}_n | \bar{M}_n BY VPO [*] |
|----------|-------------------------|------------------------------------|
| Control | 1900 | 1710 |
| 4 | 850 | 760 |
| 6 | 1300 | 1330 |
| 7 | 1550 | 1520 |
| 10 | 2300 | 2420 |
| 14 | 3900 | 3970 |

*

Vapor Phase Osmometry : Toluene ; 63°C

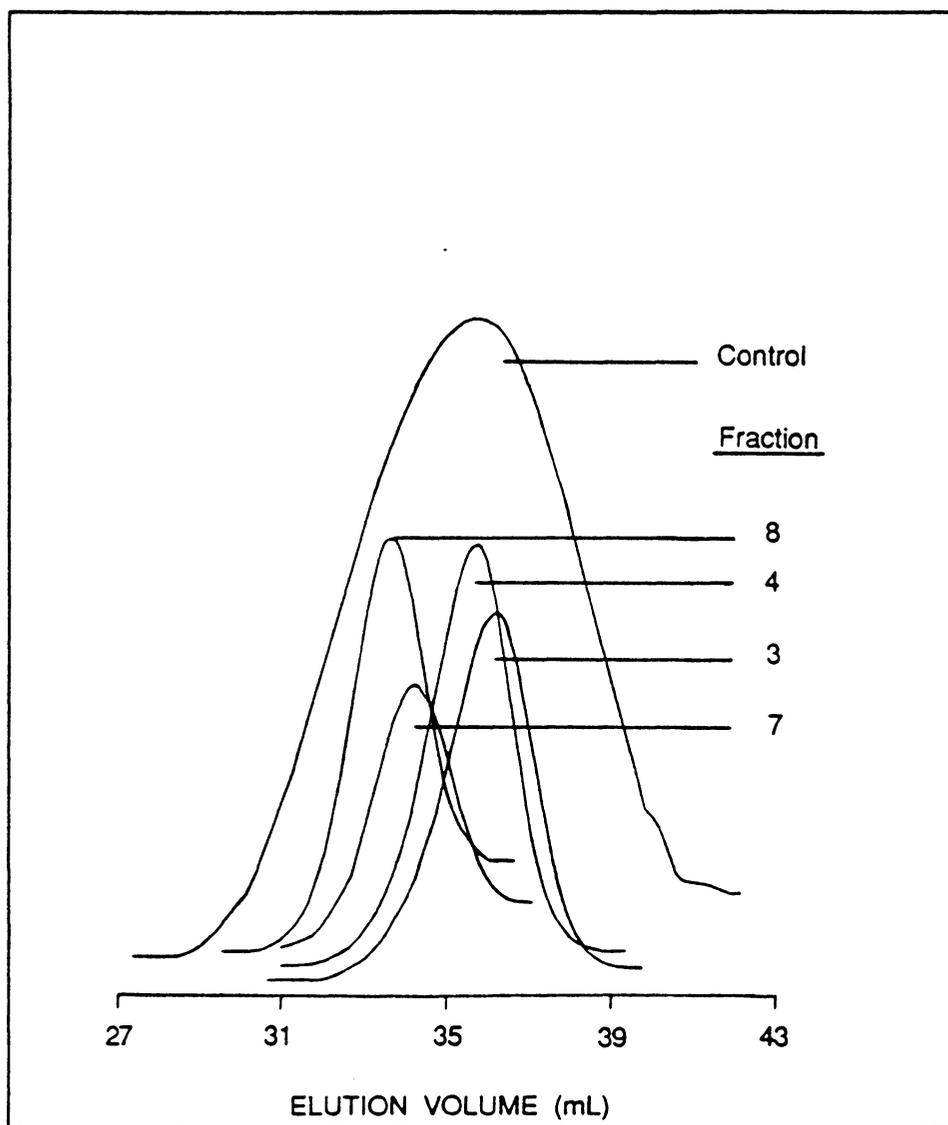
ranging in molecular weight from 2400 g/mole to 17,700 g/mole (see Table 15). This sample had been vacuum stripped prior to the fractionation process, so early fractions containing nonfunctional cyclics were not obtained. The molecular weight distributions of these fractionated materials are again significantly lower than the polydispersity of the parent oligomer. The GPC traces of the parent oligomer and several fractions are reproduced in Figure 40. The broad polydispersity of the parent oligomer caused major portions of several of the GPC traces to be out of the range of the calibration curve based on polysiloxane standards, so molecular weight values based on GPC calculations are not reported. Polydispersities were calculated based on polystyrene standards as well, and values closer to 1.20 were obtained where the polysiloxane standards had indicated polydispersities near 1.12. It is difficult to prepare standards under 1500 g/mole by anionic polymerization techniques since they generally are broader than the higher molecular weight standards. Certainly, low molecular weight standards could be prepared, then fractionated themselves and fully characterized for use at the low molecular weight end of the GPC calibration curve. There is also a need to prepare polysiloxane standards to extend the calibration curve at the high molecular weight end.

An alternative approach is to prepare a GPC calibration curve from the fractionated samples as shown in Figure 41.

Table 15
 Fractionation of Aminopropyl Terminated
 Polydimethylsiloxane

| FRACTION | TITRATED \bar{M}_n | \bar{M}_w/\bar{M}_n BY GPC* |
|----------|-------------------------|----------------------------------|
| CONTROL | 7500 | 1.82 |
| 1 | 2400 | --- |
| 2 | 2800 | 1.25 |
| 3 | 4560 | 1.18 |
| 4 | 6800 | 1.17 |
| 5 | 7000 | 1.13 |
| 6 | 6950 | 1.12 |
| 7 | 8650 | 1.12 |
| 8 | 12840 | 1.11 |
| 9 | 13600 | 1.08 |
| 10 | 14100 | — |
| 11 | 17700 | — |

*
 Based on polysiloxane standards.



* Based on polysiloxane standards.

Figure 40: GPC Chromatograms of Aminopropyl Terminated Polydimethylsiloxane and Its Fractions.

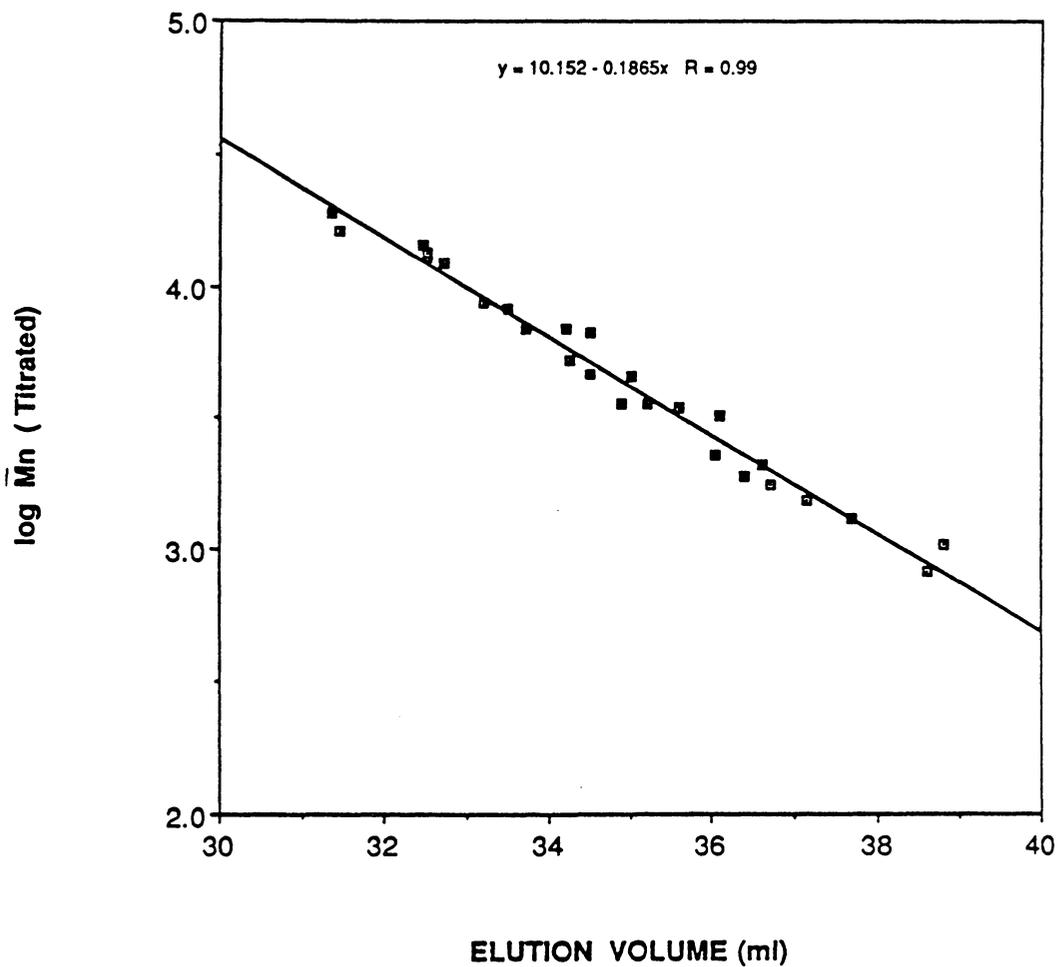


Figure 41: GPC Calibration Curve Constructed from Fractionated Aminopropyl Terminated Polydimethylsiloxanes.

The log of the titrated molecular weights were plotted versus the respective elution volumes for a number of fractions. As expected, the points fall on a straight line with a correlation coefficient of 0.987.

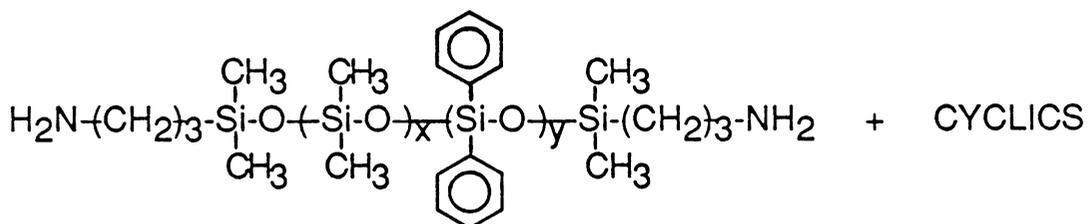
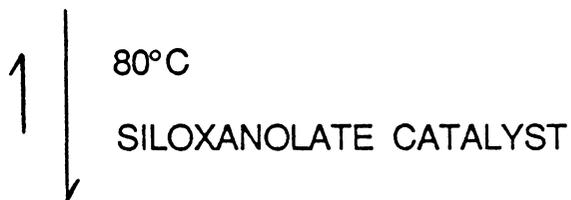
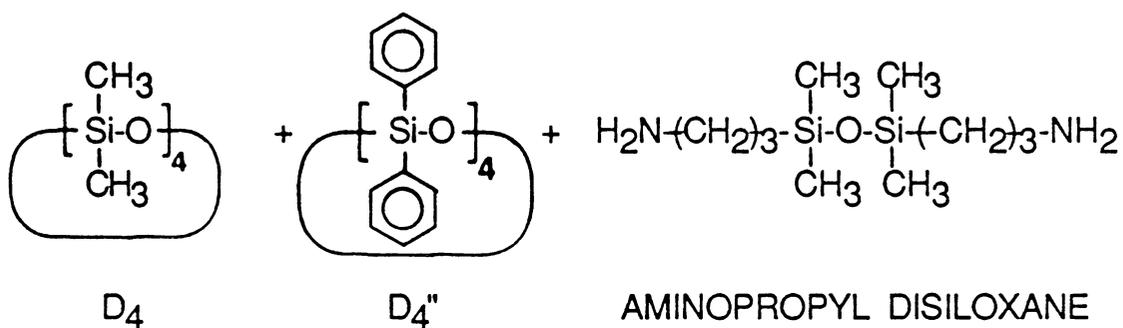
Poly(dimethyl)-co-(diphenyl)siloxanes are also of interest as precursors for siloxane-containing copolymer systems. The co-oligomers are useful for a number of reasons, including the enhanced miscibility of phenyl-containing siloxanes with many organic polymers. Efforts are underway to extend the supercritical fluid fractionation process to diphenyl-containing amine functional polysiloxane systems. Results of the initial studies on the poly-(dimethyl)-co-(diphenyl)siloxanes will be described below.

The synthetic scheme for preparation of poly(dimethyl)-co-(diphenyl)siloxanes is shown in Scheme XXVI. In addition to trace amounts of D_4 and D_4'' , the cyclics remaining in the co-oligomers at equilibrium contain mixed amounts of dimethyl and diphenyl substituents on the silicon atoms. The D_4'' and mixed cyclics are difficult to remove from the functional oligomers by conventional separation techniques due to their very high boiling points. It was hoped that supercritical fluid fractionation techniques would allow for efficient removal of these cyclics.

Feasibility tests for the removal of phenyl-containing cyclics and fractionation of the functional co-oligomers were conducted with supercritical ethane. Somewhat higher

Scheme XXVI

Synthesis of Aminopropyl Terminated
Poly(Dimethyl-Co-Diphenyl)Siloxanes



pressures were required in this case, due to the lower solubility of these materials relative to the all-methyl materials. Unfortunately, cyclics which contained significant amounts of phenyl substituents were of similar solubility to the mixed oligomers, and the cyclics smeared into all of the attempted fractions obtained using supercritical ethane as the solvent. The concurrent effect of two variables, namely molecular weight and composition, in the fractionation of co-oligomers was found to complicate the separation process dramatically.

The second approach tested involved the use of supercritical carbon dioxide, which was mentioned previously to undergo a reaction with the amine-functional siloxanes. It was thought that the amines could be reacted with carbon dioxide to form a carbamic acid species which had been shown to be less soluble, at least in the case of the aminopropyl disiloxane. It was hoped that the mixed cyclics could then be selectively removed from the converted oligomer with supercritical carbon dioxide, followed by conversion of the carbamic acid species back to the free amine by flushing the system with ethane at elevated temperatures. Subsequent fractionation of the linear species, generally considered to possess a random distribution of diphenyl substituents, would be conducted with supercritical ethane.

The above procedure was carried out on aminopropyl disiloxane as a model reaction for studying the reversi-

bility of the carbon dioxide-amine reaction. The clear liquid disiloxane was reacted with supercritical CO₂ to form a clean white powder, assumed to be the carbamic acid species. The powder was insoluble in many solvents which readily dissolve the amine-functional disiloxane, and obvious structural changes were evident by FT-IR analysis. The FT-IR spectrum of aminopropyl disiloxane (Figure 42) clearly shows absorptions at 3371 cm⁻¹ and 3296 cm⁻¹ which can be attributed to the primary amine doublet. The primary amine bands have disappeared in the infrared spectrum of the disiloxane-carbon dioxide reaction product (Figure 43), and new absorptions become apparent at 3275 cm⁻¹, 1640 cm⁻¹, and 965 cm⁻¹. These new absorbances are characteristic of a carbamic acid or a 2° amide species. The white precipitate was converted back to the aminopropyl disiloxane by flushing the system with ethane at elevated temperatures. It was observed that the powder was transformed into a cloudy, white gel, then a clear liquid containing some white precipitate, and finally back to a clear liquid. The clear liquid had the same characteristic FT-IR bands as aminopropyl disiloxane, indicating that the reaction was indeed reversible. The titrated molecular weight of the final liquid (249 g/mole) was in excellent agreement with the theoretical value (248.5 g/mole). Upon successful completion of this test, the fractionation of a phenyl-containing polysiloxane oligomer was attempted via the same procedure.

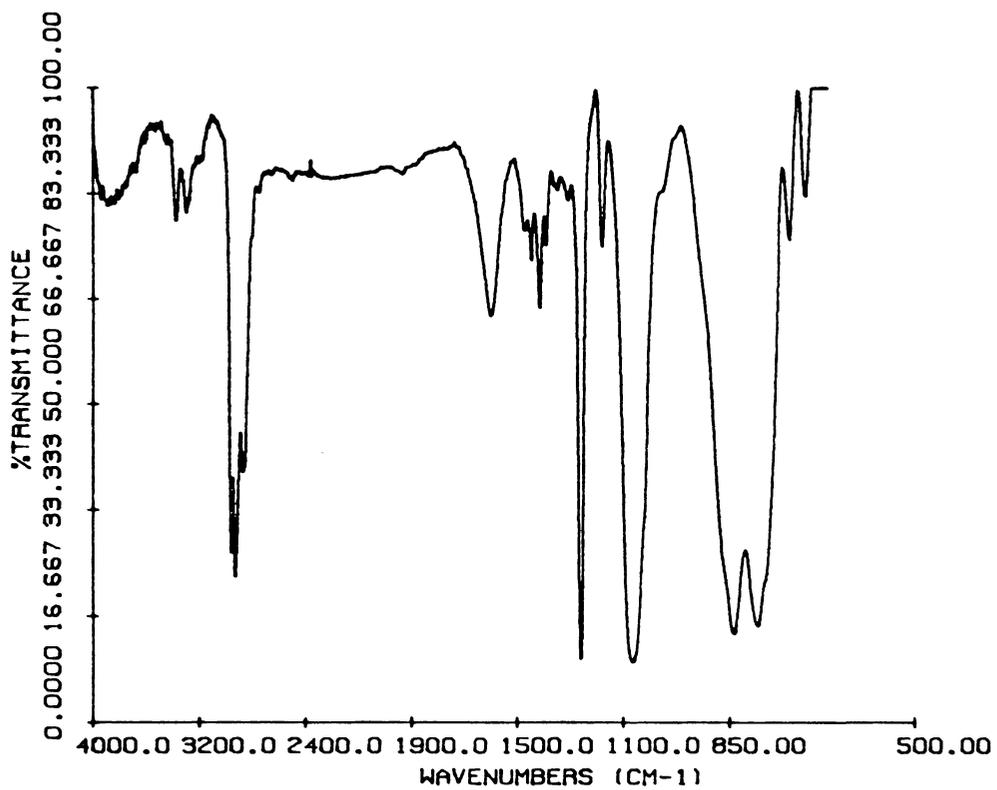


Figure 42: FTIR Spectrum of Aminopropyl Disiloxane.

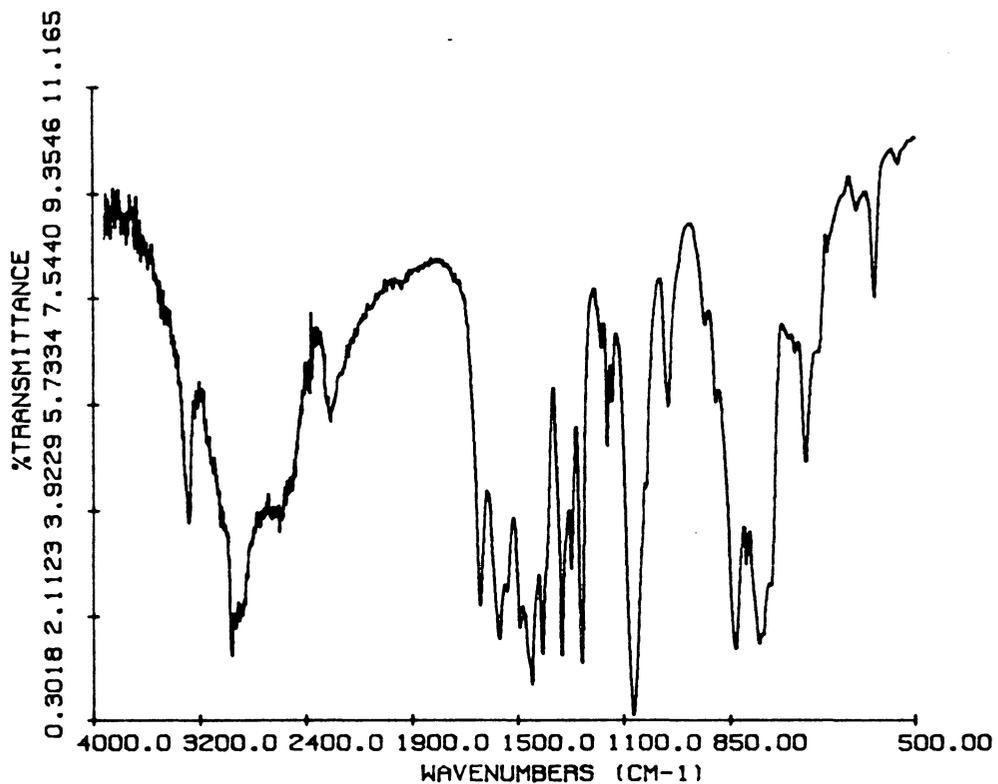


Figure 43: FTIR Spectrum of the Aminopropyl Disiloxane-Carbon Dioxide Reaction Product.

A 5,600 g/mole aminopropyl terminated polysiloxane oligomer containing 25 weight percent diphenyl substituents was reacted with carbon dioxide within the extraction vessel of the fractionation apparatus (see Figure 9, Chapter III). Initial fractions were removed using supercritical carbon dioxide at pressures of up to 6000 psi, followed by introduction of a steady stream of supercritical ethane to favor conversion of the endgroups back to amines. The sample was then fractionated into a few fractions which could be analyzed to determine if the cyclics had been selectively removed with carbon dioxide, and if the amine-carbon dioxide reaction had been completely reversed. Reaction of the oligomer with carbon dioxide again caused the liquid polysiloxane to become a viscous gel with white precipitate. Extraction of this material with carbon dioxide did appear to selectively remove the phenyl-containing cyclics from the higher molecular weight oligomer, and the cyclics were not present in the higher fractions by HPLC or GPC. The reversion back to the amine was less successful in the case of the higher molecular weight oligomer, and a thorough study is needed to determine whether or not the oligomers stop at the carbamic acid species, or if they further react to form urea linkages which are not reversible. Early results indicate that the outcome is dependent upon such factors as the temperature and the partial pressure of CO₂ which is present. The method does appear promising as an

approach for removing high boiling phenyl-containing siloxane cyclics from poly(dimethyl)-co-(diphenyl)siloxane oligomers. Alternative methods presently employed include the use of white film evaporators or selective fractionation with liquid solvents. If the carbon dioxide-amine route does not prove useful, fractionation with other supercritical solvents having different solvating characteristics may be a viable alternative.

The utility of supercritical fluid extraction techniques in the fractionation of polysiloxanes has been demonstrated in the data presented here. The polydispersity values for the fractions are comparable to those generally attainable only by anionic polymerization techniques, where difunctionality is often difficult to obtain. It is anticipated that the ability to isolate these well-defined fractions will lead to important fundamental studies on structure-property relationships in multiphase copolymer systems.

D. PREPARATION OF ALKYL-SUBSTITUTED HOMOPOLYMERS AND SILOXANE-CONTAINING BLOCK COPOLYMERS

1. Research Introduction

A final objective of this research involved the synthesis and characterization of a series of siloxane-modified polyarylestere and polyformals. The materials were based on tetramethylbisphenol-A monomer, with the intent of

preparing materials which might be potentially useful as permselective gas separation membranes. A number of reviews [179-182] have emphasized the importance of the chemical nature of the polymer, and thus segmental motion and packing, on the effectiveness of a material as a permselective membrane. In particular, the introduction of bulky structures onto the polymer backbone has been shown to produce relatively high flux, high selectivity materials [183]. The bulky substituents generally resist compact packing of segments, so that intersegmental separations in the rigid bulky polymers may be large enough to permit the penetration of molecules below a certain critical size. The results presented below describe the synthesis and characterization of polyarylesters and polyformals based on tetramethylbisphenol-A, and the modification of these materials with small amounts of polysiloxanes to improve the ductility of the otherwise brittle materials. The actual evaluation of these materials as permselective gas separation membranes was not attempted in the present study.

2. Polyarylester-Polysiloxane Copolymers

a) Phenolic-Terminated Polyarylester Oligomers

Controlled molecular weight phenolic terminated polyarylesters were prepared via a solution technique as shown in Scheme XXVII. A calculated excess of tetramethylbisphenol-A (TMBA) was used with equimolar amounts of

terephthaloyl and isophthaloyl chlorides (see Appendix B). An excess of the bisphenol monomer provides molecular weight control and hydroxyl functionality. The mixture of acid chlorides was used to ensure that the resulting polyesters would be amorphous [121,122]. Triethylamine was added to serve as an acid acceptor and as a catalyst.

Structure analysis was determined by FTIR and proton NMR as shown in Figures 44 and 45, respectively. The observed FTIR bands and their assignments are listed in Table 16. The strong ester band is evident, but the hydroxyl band is generally small since the -OH groups are found only on the ends of the polymer chains.

The observed proton NMR peak positions and splitting patterns are listed in Table 17 for the TMBA polyarylesters. For phenolic-terminated oligomers under ~10,000 g/mole, the NMR spectra may be enlarged around 4.5 ppm to observe the peak due to the -OH endgroups. Integration of this peak relative to peaks due to the repeating unit of the polyester allows calculation of the molecular weight of the oligomer.

The molecular weight of the phenolic terminated oligomer was also determined by titration with an 0.10 N solution of methanolic tetramethylammonium hydroxide. The titrant was standardized with potassium hydrogen phthalate prior to use. The titration solvent was tetrahydrofuran. The importance of using freshly distilled solvents in these nonaqueous titrations has been reported previously [184],

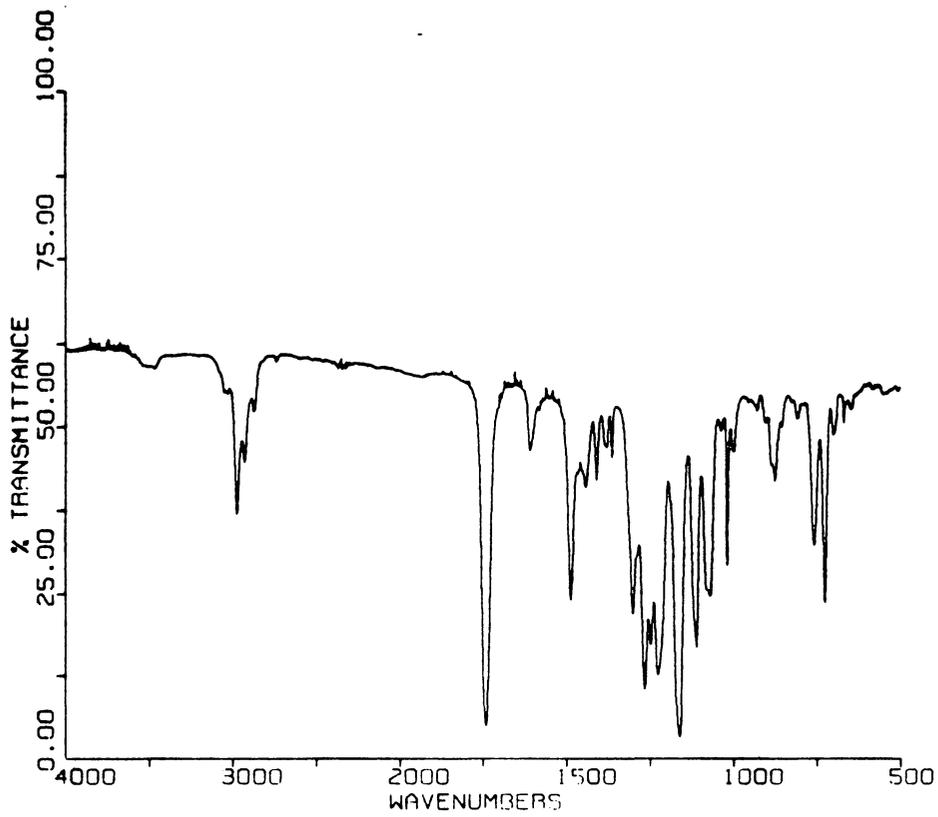


Figure 44: FTIR Spectrum of a Hydroxyl Terminated Tetramethylbisphenol-A Polyarylester Oligomer.

Table 16

FTIR Band Assignments For Hydroxyl-Terminated
Tetramethylbisphenol-A Polyarylesters

| Frequency (cm ⁻¹) | Assignment |
|-------------------------------|------------------------|
| 3500 | O-H stretch |
| 3050-2900 | C-H stretch |
| 1750-1735 | Ester carbonyl stretch |
| 1600-1585 | C-C stretch, aromatic |
| 1400-1200 | O-O |
| 1270-1170 | Strong ester bands |
| 1150 | C-O |
| 825-700 | Substituted aromatics |

Table 17
 Proton NMR Peak Positions and Assignments for
 Hydroxyl-Terminated Polyarylester Oligomers

| Peak (ppm) | Assignment |
|---------------|--|
| 1.7, singlet | Isopropylidene hydrogens derived from tetramethylbisphenol-A |
| 2.2, singlet | Methyl hydrogens on tetramethylbisphenol-A |
| 7.0, singlet | Aromatic hydrogens derived from tetramethylbisphenol-A |
| 7.6, triplet | Aromatic hydrogen derived from isophthaloyl chloride |
| 8.35, singlet | Aromatic hydrogens derived from terephthaloyl chloride |
| 8.5, doublet | Aromatic hydrogens derived from isophthaloyl chloride |
| 9.1, singlet | Aromatic hydrogen derived from isophthaloyl chloride |

since the presence of water leads to large solvent blanks and broad endpoints.

The thermal properties of the materials were evaluated using differential scanning calorimetry (DSC). The highly aromatic character of the polymer, as well as the presence of bulky substituent groups, led to the observance of relatively high glass transition temperatures. A typical DSC trace for a polyarylester oligomer is shown in Figure 46.

b) Silylamine-Terminated Polysiloxane Oligomers

Silylamine-terminated oligomers were prepared via an equilibration process similar to the procedure described previously for the preparation of aminopropyl-terminated polysiloxanes. In this case, however, the silylamine end-blocker which provides the molecular weight control and the functionality is not a disiloxane, but rather a low molecular weight oligomer itself. The proper amounts of endblocker and D₄ were charged to the reaction flask in the presence of the tetramethylammonium siloxanolate catalyst and heated at 80°C for 48 hours (see Scheme XXVIII). The catalyst was then decomposed at elevated temperatures, and the oligomer was vacuum stripped to remove low molecular weight cyclics. The Si-N bond in these polysiloxanes is extremely susceptible to hydrolysis, and extra caution was required to prevent loss of the silylamine endgroups.

Structure analysis was readily performed using FTIR. A typical FTIR spectrum of a silylamine-terminated poly-

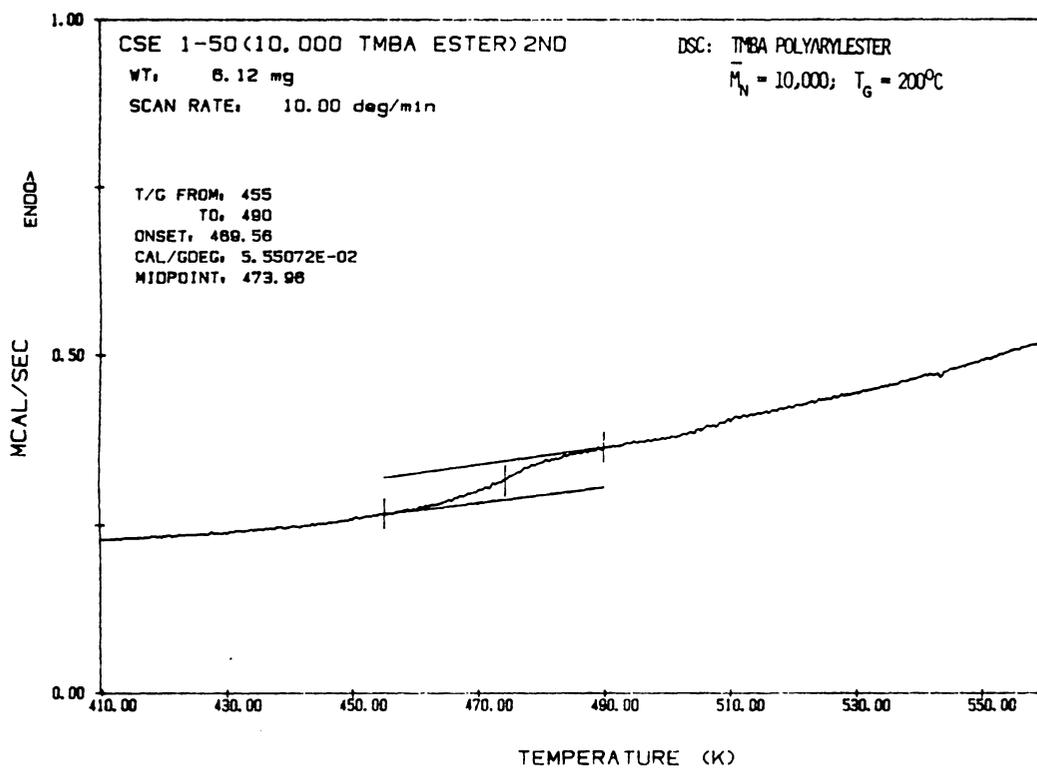
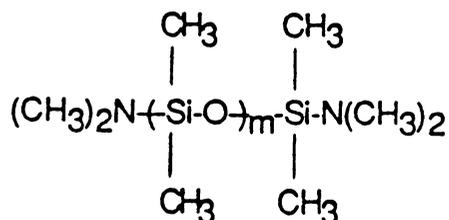


Figure 46: DSC Trace of a 10,000 \bar{M}_N Tetramethylbisphenol-A Polyarylester Oligomer.

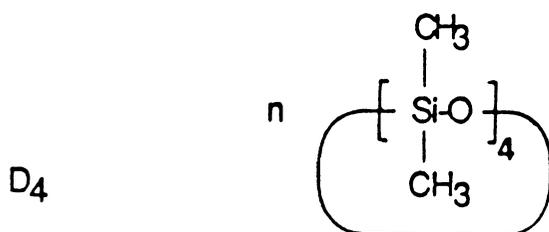
Scheme XXVIII

Synthesis of Silylamine Terminated Polysiloxane Oligomers

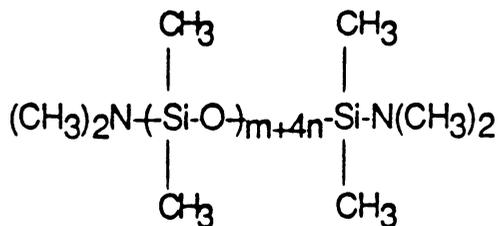


SILYLAMINE TERMINATED SILOXANE ENDBLOCKER

+



ARGON
TMAH "N" CATALYST
80°C FOR 45 HOURS
150°C FOR 3 HOURS



dimethylsiloxane oligomer is shown in Figure 47, and the corresponding bands are identified in Table 18. Number average molecular weights of the oligomers were determined by potentiometric titration with alcoholic HCl.

c) Perfectly Alternating Polyester-Polysiloxane
Block Copolymers

Noshay and coworkers [169,170] have demonstrated the utility of the reaction of various hydroxyl-terminated oligomers with silylamine-terminated polydimethylsiloxanes to form perfectly alternating $-(A-B)_n-$ block copolymers. The functional oligomers are well characterized since they are prepared separately. It follows that the resulting copolymer structures are also well-defined, since the organic and siloxane blocks can react with each other but not with themselves.

The morphology of these block copolymers is dependent upon the molecular weight of the individual blocks [185]. Although the two phases have very different solubility parameters, a single-phase system is usually obtained below the critical block molecular weight (\bar{M}_n) of about 2000 to 5000 g/mole. The properties of these materials are characteristic of random copolymers. Above this level, a two-phase morphology is obtained, resulting in materials which display properties characteristic of both homopolymers.

The polymers produced in this study for the purpose of permselective membrane applications employed the silylamine-

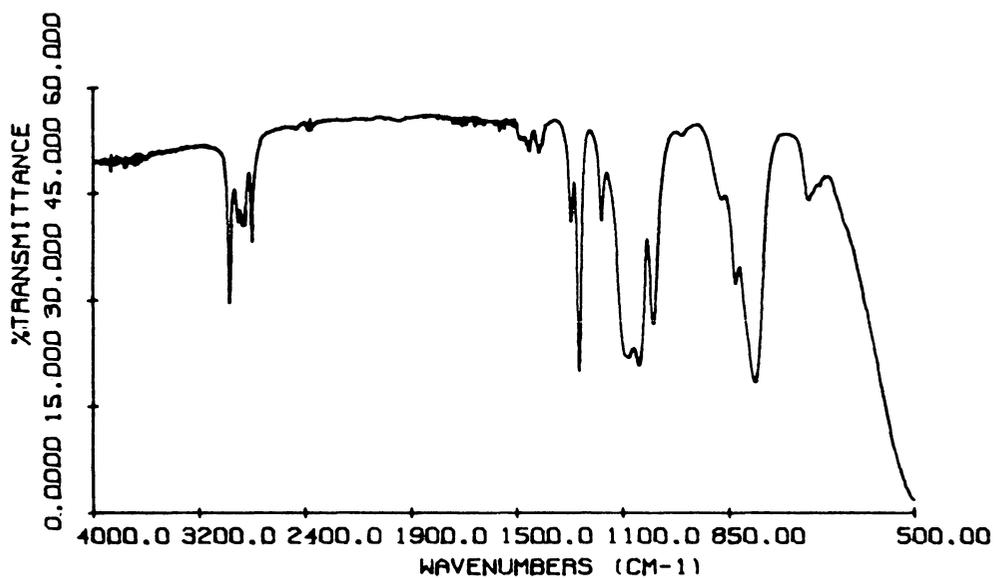


Figure 47: FTIR Spectrum of a Silylamine Terminated Polydimethylsiloxane Oligomer.

Table 18
Polydimethylsiloxane FTIR Band Assignments

| Frequency (cm ⁻¹) | Assignment |
|-------------------------------|--|
| 3050-2900 | C-H stretch of CH ₃ |
| 1260 | Si(CH ₃) ₂ O symmetric deformation |
| 1100-1000 | Si-O-Si stretch vibration |
| 800 | Si(CH ₃) ₂ stretch ; CH ₃ rock |
| 715 | Si(CH ₃) ₂ O stretch |

hydroxyl condensation reaction. The molecular weight of the individual blocks was purposely kept low, so that a single-phase morphology might be obtained. The presence of the siloxane was generally to improve the ductility of the materials, without the formation of siloxane domains which might complicate the permeability behavior. Polysiloxanes are known to be extremely permeable to a number of gases, and the presence of siloxane domains might lead to a loss of selectivity.

The reaction scheme for the preparation of TMBA polyarylester-polysiloxane copolymers is shown in Scheme XXIX. The evolution of dimethylamine as the reaction proceeded was detected with litmus paper at the top of the condenser, and its absence was an indication that the reaction had gone to completion. The amine by-product was observed immediately upon addition of the polysiloxane, and generally continued to evolve for up to 24 hours.

Structure analysis of the siloxane-ester block copolymers was accomplished by FTIR and proton NMR. Typical spectra are shown in Figures 48 and 49, respectively. The copolymer FTIR spectrum contains bands observed previously in the spectra of the siloxane (Figure 47) and ester (Figure 46) oligomers, with the exception of any bands due to end-groups. The copolymer bands are listed in Table 19.

The proton MNR peak assignments and splitting patterns of a typical siloxane-ester copolymer are listed in Table

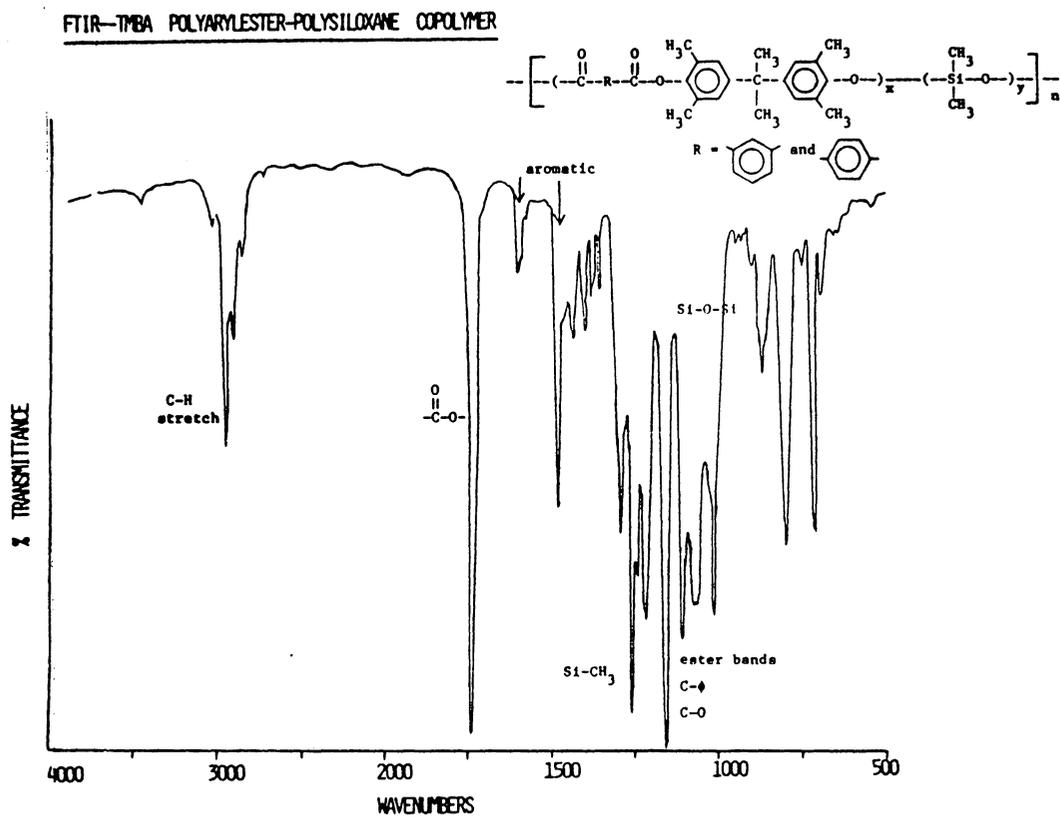


Figure 48: FTIR Spectrum of a Polyarylester-Polysiloxane Block Copolymer.

¹H NMR TMBA POLYARYLESTER-POLYSILOXANE COPOLYMER

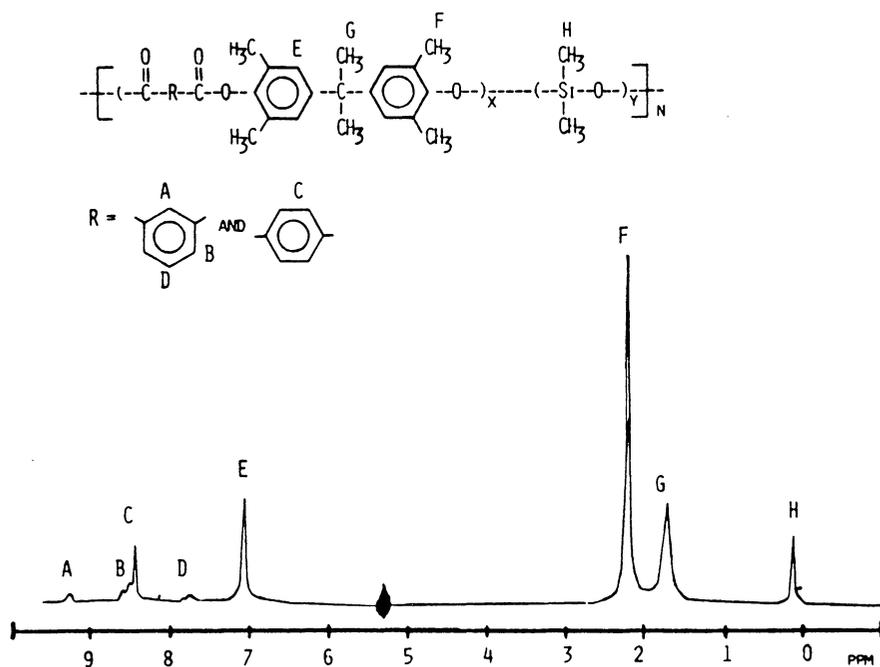


Figure 49: Proton NMR Spectrum of a Polyarylester-Polysiloxane Block Copolymer.

Table 19

FTIR Band Assignments for a Perfectly Alternating
Polyarylester-Polysiloxane Block Copolymer

| Frequency (cm ⁻¹) | Assignment |
|-------------------------------|--|
| 3050 | C-H stretch, aromatic |
| 2950 | C-H stretch, aliphatic |
| 1750-1735 | Ester carbonyl stretch |
| 1600, 1500 | C-C stretch, aromatic |
| 1400-1200 | O-O ester band |
| 1300 | Si-CH ₃ symmetric deformation |
| 1100-1000 | Si-O-Si stretch vibration |
| 850-775 | Si-CH ₃ |

20. In addition to structure confirmation, proton NMR was useful for determination of the amount of siloxane which had been incorporated into the block copolymer. The integration ratio of the $\text{Si}(\text{CH}_3)_2\text{O}$ peak at 0.1 ppm to either the isopropylidene peak at 1.7 ppm or the TMBA methyl peak at 2.2 ppm allows the weight percent siloxane to be calculated.

Characterization results on a series of perfectly alternating polyester-polysiloxane copolymers is shown in Table 21. The intrinsic viscosity values were determined in CHCl_3 at 25°C, and are typical of polymers of fairly high molecular weight. The polymers were all readily cast into tough, transparent films, which was also an indication that the materials were of sufficient molecular weight to be useful. The weight percent polysiloxane values reported in Table 21 were determined by proton NMR, and generally reflect an essentially quantitative incorporation of the polysiloxane oligomer which had been charged to the reaction flask.

Glass transition temperatures for the functional polyester and polysiloxane oligomers are reported in Table 21 as well, along with the observed transitions in the resulting copolymers. The substantial lowering of the upper glass transition temperature in the copolymer relative to the T_g of the ester oligomer is an indication that a large degree of mixing of the siloxane phase into the ester phase has occurred. This result was expected since the molecular

Table 20

Proton NMR Peak Assignments for Perfectly
Alternating Polyester-Polysiloxane Block Copolymers

| Peak (ppm) | Assignment |
|---------------|--|
| 0.1, singlet | Dimethylsilicon hydrogens |
| 1.7, singlet | Isopropylidene hydrogens derived from bisphenol-A |
| 2.2, singlet | Methyl hydrogens on tetramethyl-bisphenol-A |
| 7.0, singlet | Aromatic hydrogens derived from tetramethylbisphenol-A |
| 7.65, triplet | Aromatic hydrogens derived from isophthaloyl chloride |
| 8.4, singlet | Aromatic hydrogens derived from terephthaloyl chloride |
| 8.5, doublet | Aromatic hydrogens derived from isophthaloyl chloride |
| 9.2, singlet | Aromatic hydrogens derived from isophthaloyl chloride |

Table 21

Characterization Results on Perfectly Alternating
Tetramethylbisphenol-A Polyarylester-Polysiloxane
Block Copolymers

| Sample | [η] ²⁵ CHCl ₃ | Weight % Siloxane | Tg Oligomers | | Tg Copolymers by DSC | |
|--------|---|----------------------|--------------|-------|-------------------------|------|
| | | | Sx | Ester | Low | High |
| 1 | 0.46 | 3 | -136 | 209 | -109 | 203 |
| 2 | 0.51 | 9 | -130 | 200 | -102 | 186 |
| 3 | 0.48 | 15 | -130 | 200 | ----- | 188 |
| 4 | 0.40 | 18 | -127 | 200 | -112 | 141 |

- Molecular weight of ester block ~10,000 \bar{M}_n

weight of the polysiloxane blocks range from several hundred to 2000 g/mole, and the ester block is approximately 10,000 g/mole. The lower glass transition temperatures reported for the copolymers were very weak and broad, but appeared to be slightly higher than the T_g of the polysiloxane oligomer, indicating that some ester had mixed into the siloxane phase as well.

Transmission electron microscopy (TEM) is often used to study the bulk morphology of two-phase systems. The TMBA polyarylester-polysiloxane block copolymers were cast from dilute solution onto nickel TEM grids for observation of the microphase separation. Staining of one of the phases was not necessary since there is a large enough electron density difference between the siloxane and ester phases. Representative TEM micrographs are shown in Figures 50 and 51. There was no evidence of a separate siloxane phase by TEM, even at 175,000X magnification. This supports the DSC data which indicated a high degree of phase mixing. If a separate siloxane phase were present at these compositions, it would be expected to be a dispersed spherical phase, and its detection may be limited by the TEM optics.

3. Polyformal Homopolymers and Polyformal-Polysiloxane Copolymers

Initial efforts to prepare a polyformal based solely on tetramethylbisphenol-A and methylene chloride as monomers were unsuccessful due to the tendency towards crystalliza-



Figure 50: TEM Micrograph of a Polyester (10K)-Polysiloxane (1K) Block Copolymer; Magnification 175,000X.

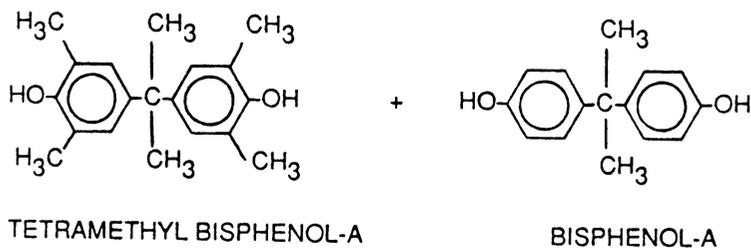


Figure 51: TEM Micrograph of a Polyester (10K)-Polysiloxane (2K) Block Copolymer; Magnification 175,000X.

tion which prevented the reaction from going to completion. Polyformals based on bisphenol-A monomer had been reported earlier [142], and were repeated here as a control. Since the bisphenol-A control experiments proceeded readily and remained soluble throughout the reaction, experiments were then conducted using increasing amounts of this monomer along with the tetramethylbisphenol-A (TMBA), until at a molar ratio of 70:30 TMBA:bisphenol-A a successful polymerization was achieved. Incorporation of 30 mole % of bisphenol-A was sufficient to break up the symmetry and keep the polymer from crystallizing out of solution.

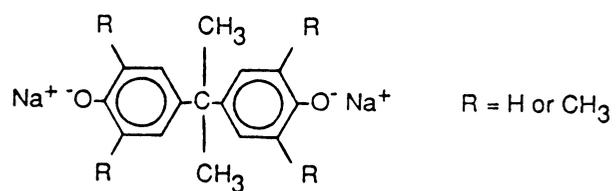
The synthetic route for the preparation of polyformals is illustrated in Scheme XXX. The bisphenol monomers were dissolved in dimethylsulfoxide (DMSO), and converted to the phenate by the addition of a stoichiometric amount of sodium hydroxide. Toluene was added as an azeotroping agent. Once the system had been dehydrated, the reaction temperature was lowered for the addition of the methylene chloride monomer. The low boiling methylene chloride was dissolved in DMSO prior to dropwise addition to prevent loss of the monomer. The reaction between the bisphenates and the methylene chloride was extremely rapid, so that controlled molecular weight phenolic-terminated oligomers could be prepared, as well as high molecular weight polyformals which would not be modified with polysiloxanes. The more flexible nature of the polyformal backbone relative to the rigid polyarylester

Scheme XXX
Synthesis of
Tetramethylbisphenol-A-co-Bisphenol-A Polyformals



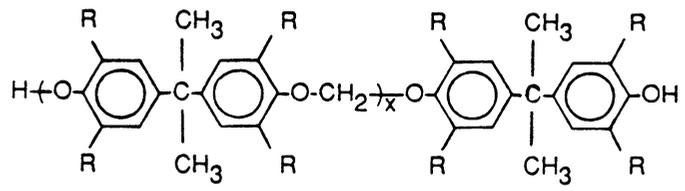
↓

NaOH
 DMSO
 TOLUENE AZEOTROPE
 ~120°C



↓

COOL TO 75°C.
 ADD CH₂Cl₂/DMSO DROPSWISE.
 HEAT TO 120°C FOR 2 HOURS.



HYDROXYL-TERMINATED TETRAMETHYLBISPHENOL-A -
 CO -BISPHENOL-A POLYFORMAL

backbone allowed films to be cast from a solution of the high molecular weight homopolymers, as well as from a solution of the siloxane-modified material.

Structure analysis of the polyformals was determined by FTIR and ^{13}C NMR. The FTIR spectrum for a 70:30 TMBA:bisphenol-A polyformal is shown in Figure 52. The large band at 1050 cm^{-1} confirms the presence of the $-\text{O}-\text{CH}_2-\text{O}-$ linkage in the polyformal.

The presence of both the TMBA and bisphenol-A monomers in the polyformal backbone were readily detected by NMR, and three peaks were observed for the polyformal linkage by proton NMR, indicating that the formal linkage had formed readily between two TMBA monomers, two bisphenol-A monomers, and between one TMBA monomer and one bisphenol-A monomer. The ^{13}C NMR spectra of a polyformal based on 100% bisphenol-A is shown in Figure 53. This spectrum was useful for identifying the peaks in the ^{13}C spectrum of a 70:30 TMBA:bisphenol-A polyformal, as shown in Figure 54.

The molecular weight of the phenolic terminated polyformals was determined by titration with 0.10 M tetramethylammonium hydroxide. The solvent was freshly distilled dimethylacetamide.

Silylamine-terminated polysiloxanes were prepared and characterized as described previously for the polyarylester-polysiloxane block copolymers. The polyformal-polysiloxane block copolymers were also prepared by a similar procedure

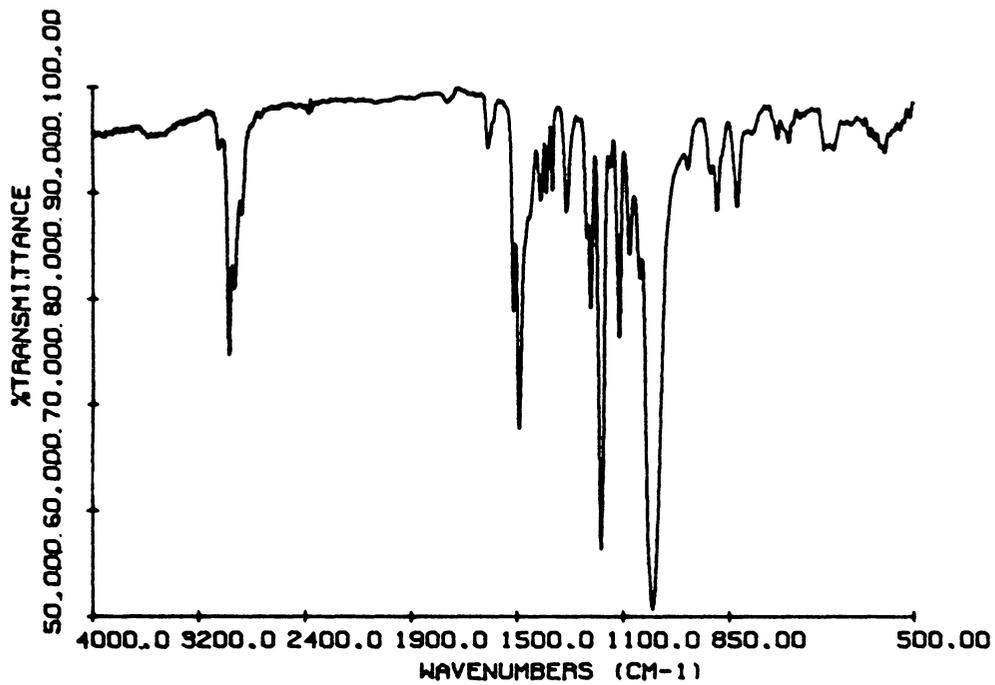


Figure 52: FTIR Spectrum of a 70:30 Tetramethylbisphenol-A: Bisphenol-A Polyformal.

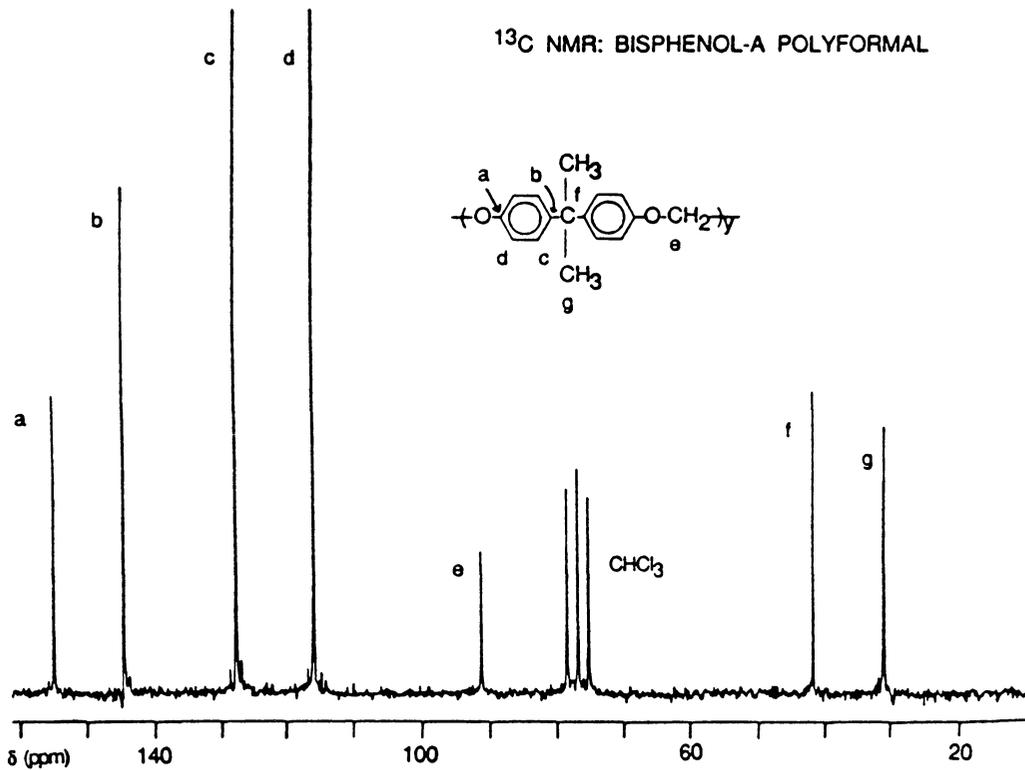


Figure 53: ^{13}C NMR Spectrum of a Bisphenol-A Polyformal.

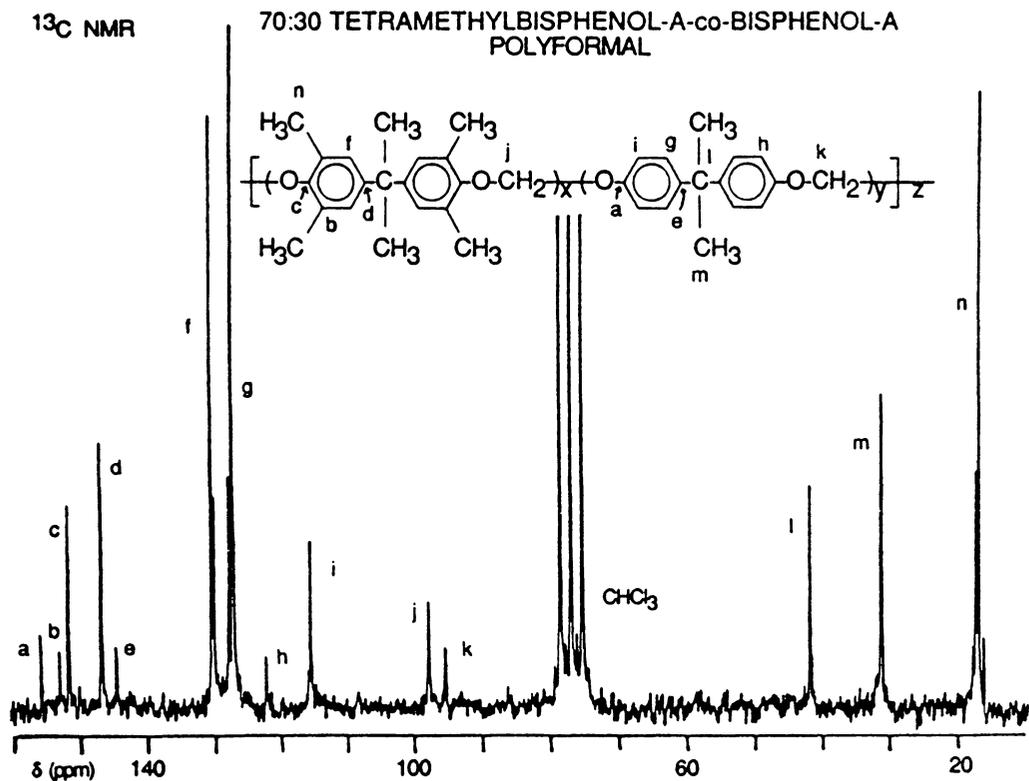


Figure 54: ¹³C NMR Spectrum of a 70:30 Tetramethylbisphenol-A:Bisphenol-A Polyformal.

to the one described previously for the preparation of polyester-polysiloxane block copolymers, as shown in Scheme XXXI. The evolution of dimethylamine was again useful for following the progress of the reaction.

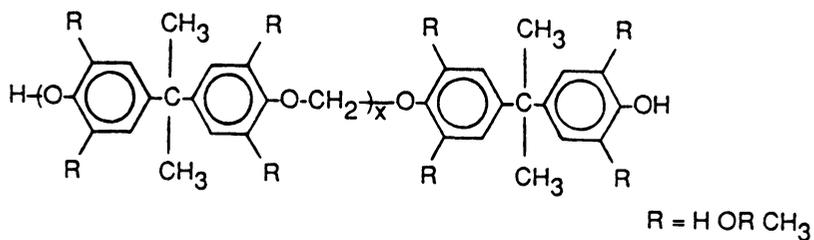
FTIR and proton NMR were used to confirm the structure of the resulting copolymers. The FTIR spectrum of a typical polyformal-polysiloxane copolymer is shown in Figure 55. The spectrum of the copolymer is a combination of the spectra of the polyformal and polysiloxane oligomers used in its preparation.

Proton NMR was used for structure analysis as well as for the determination of the percent siloxane incorporated into the block copolymer. This was done using the integration ratio of the peaks due to the silicon methyl groups relative to any of the peaks due to the repeating unit of the polyformal block. A comparison of the results obtained using the separate ratios generally gave approximately the same siloxane content.

Characterization results on the polyformals and polyformal-polysiloxane block copolymers are shown in Table 22. Intrinsic viscosity values for the high molecular weight polyformals based on 100% bisphenol-A and 70:30 TMBA:bisphenol-A are indicative of high molecular weight materials. The intrinsic viscosity value for the 8000 g/mole is quite low, but increases dramatically upon incorporation of this functional oligomer into a perfectly

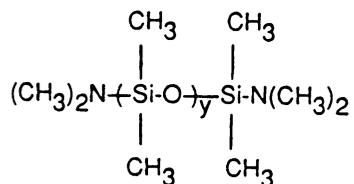
Scheme XXXI

Synthesis of Polyformal-Polysiloxane Block Copolymers



HYDROXYL-TERMINATED TETRAMETHYLBISPHENOL-A -
CO-BISPHENOL-A POLYFORMAL

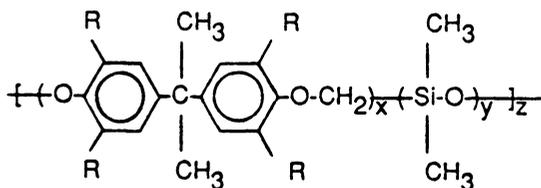
+



AMINE TERMINATED POLYSILOXANE OLIGOMER



CHLOROBENZENE
REFLUX ~130°C
ARGON



POLYFORMAL-POLYSILOXANE BLOCK COPOLYMER

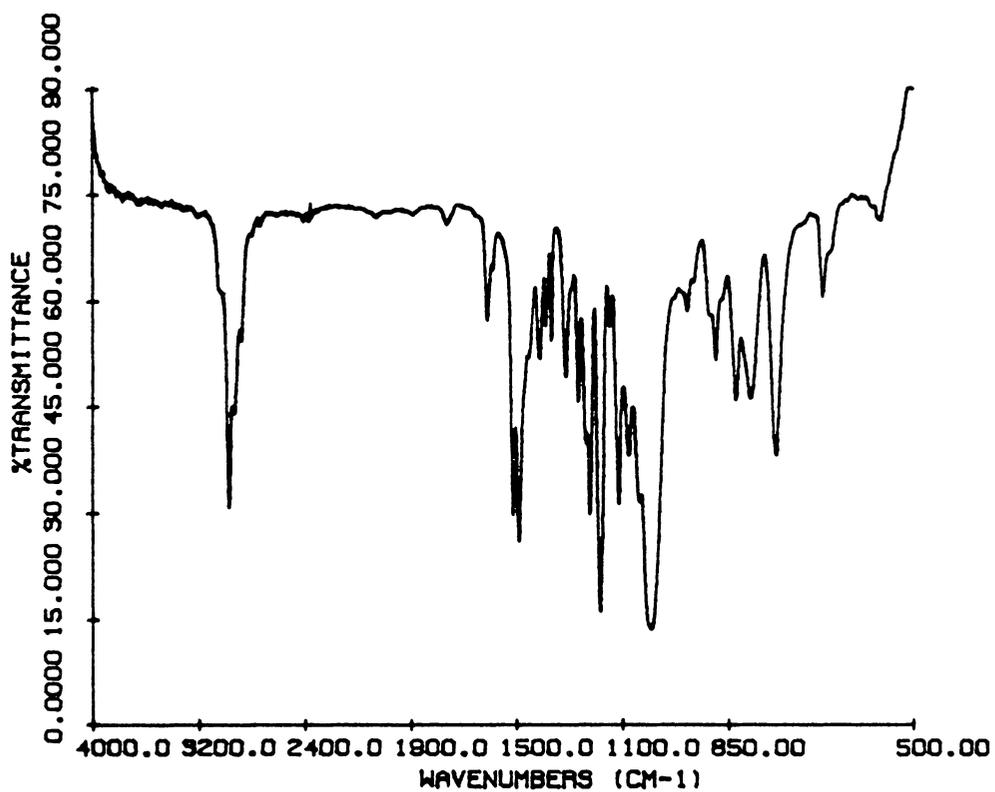


Figure 55: FTIR Spectrum of a Polyformal-Polysiloxane Block Copolymer.

Table 22

Characterization Results on Aromatic Polyformals and
 Perfectly Alternating Polyformal-Polysiloxane
 Block Copolymers

| SAMPLE | $[\eta]_{\text{CHCl}_3}$ 25°C | T_g (°C) | GPC RESULTS | |
|---|----------------------------------|------------------------|------------------------|-----------------------|
| | | | \bar{M}_n (PS STDS.) | \bar{M}_w/\bar{M}_n |
| 100% BISPHENOL-A POLYFORMAL | 1.28 | 88 | 210K | 1.78 |
| 70:30 TMBA:BIS-A POLYFORMAL | 1.10 | 113 | 190K | 2.21 |
| 8000 \bar{M}_n POLYFORMAL 70:30 TMBA:BIS-A | 0.12 | 108 | 14.5K | 1.76 |
| POLYFORMAL- POLYSILOXANE BLOCK COPOLYMER (6.5 WT.% PSX) | 1.38 | upper-97 lower-weak | 151K | 1.8 |

alternating block copolymer.

The glass transition temperature of the polyformal based mostly on TMBA is higher than the T_g of the material based on bisphenol-A due to the lower mobility which results from the presence of the bulky methyl groups on the aromatic rings. As expected, the T_g of the 8000 \bar{M}_n oligomer which contains 70 mole % TMBA is slightly lower than the T_g of the 70:30 TMBA:bisphenol-A high molecular weight polyformal. The glass transition temperature is depressed even further in the siloxane-containing block copolymer, indicating that some of the siloxane phase had mixed into the polyformal phase. Again this was expected based on the low molecular weight of the individual blocks in this copolymer. The low temperature transition was too weak to observe this sample.

GPC was used as a qualitative check on the nature of the molecular weight and molecular weight distribution. The polymers were characterized with respect to polystyrene standards. The values in Table 22 do not represent actual molecular weights or molecular weight distributions due to the lack of suitable GPC standards for these new polymer and copolymer systems [186].

In general, the polymers displayed broad, unimodal distributions of molecular weight typical of step-growth polymers. The functional oligomers eluted at higher elution volumes than the siloxane-containing copolymers, indicating that they were of lower molecular weight than the corre-

sponding block copolymers. Another important observation made from the GPC traces was the presence of significant amounts of low molecular weight material eluting with the polyformal homopolymer based on bisphenol-A. The oligomer had been precipitated twice in methanol to remove unreacted starting materials, and the peaks were not due to monomer. It had been reported in the literature [137] that the polyformals based on bisphenol-A form significant amounts of low molecular weight linear and cyclic species. Indeed, the presence of these impurities was readily observed by GPC. It was immediately noted, however, that the polyformals based mostly on tetramethylbisphenol-A did not show the presence of similar impurities by GPC analysis. The oligomers were subsequently analyzed by HPLC for improved sensitivity in characterizing these low molecular weight materials. The results of the HPLC analyses are shown in Figure 56. The HPLC conditions used were those which had been reported [141] for analysis of bisphenol-A based polyformals. The HPLC results again showed the presence of the low molecular weight cyclics and linear species in the bisphenol-A based system, but the low molecular weight materials were not observed in the polyformal based mostly on tetramethylbisphenol-A. It is feasible that the presence of the methyl groups on the phenyl rings in TMBA are effectively hindering the formation of significant amounts of cyclics in this system. Certainly this would be

REVERSE PHASE C₁₈ COLUMN
UV DETECTOR; 254 nm
20 μl SAMPLE LOOP; 1% SOLUTIONS
1 HOUR SOLVENT GRADIENT: THF 60–100%
H₂O 40–0%

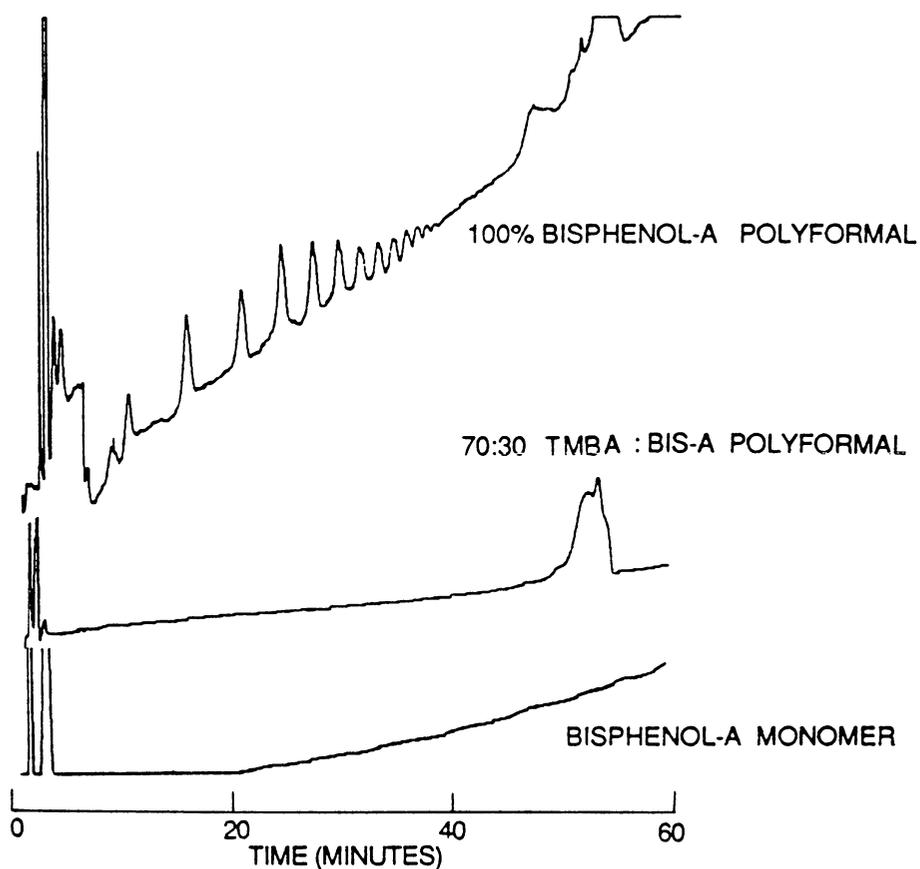


Figure 56: HPLC Analysis of Low Molecular Weight Cyclic and Linear Species in Polyformals.

advantageous since the presence of low molecular weight species can greatly affect the properties of polymeric materials.

4. Summary

Polyarylesters and polyformals based on tetramethylbisphenol-A were successfully prepared and subsequently modified with polysiloxanes. The materials formed clear tough films when cast from solution as a result of the siloxane modification. The polyarylesters are otherwise quite brittle and do not readily form materials with any structural integrity. Thermal characterization studies and TEM microscopy studies indicate that a great deal of phase mixing exists in the block copolymers, which was expected based on the short block lengths of the dissimilar segments. The alkyl substituted copolymers were prepared as potentially interesting permselective gas separation membranes, based on previously established concepts on material selection for permselective membrane materials.

Chapter V

CONCLUSIONS

The synthesis and equilibration reaction kinetics involved in the preparation of perfectly difunctional aminopropyl terminated polysiloxanes has been investigated. HPLC and GC techniques were utilized to monitor the disappearance of the cyclic tetramer and disiloxane. The catalyst systems studied included the thermally stable potassium siloxanolate catalyst, as well as the thermally labile tetramethylammonium siloxanolate and tetrabutylphosphonium siloxanolate catalyst systems.

In the catalyst concentration range studied, the D₄ was observed to react at fairly comparable rates in the presence of the ammonium and phosphonium catalysts, while the potassium siloxanolate catalyst incorporated the D₄ more slowly, even at much higher temperatures. Significant differences in catalyst efficiency were also observed with respect to the rate of incorporation of the aminopropyl disiloxane. Results of these studies indicated that the tetrabutylphosphonium siloxanolate catalyst was more efficient at incorporating the aminopropyl disiloxane than the tetramethylammonium siloxanolate catalyst. However, both of these quaternary catalysts readily produced controlled molecular weight difunctional materials at

reasonable catalyst concentrations and reaction temperatures. The potassium siloxanolate catalyst, on the other hand, incorporated only a minimal amount of disiloxane and generally produced oligomers with significantly higher molecular weights than were targeted.

Further analysis of the reaction rate data revealed a higher reaction order for the disappearance of D_4 with respect to phosphonium siloxanolate catalyst concentration than the square root order which was observed in the case of the ammonium and potassium siloxanolate catalysts. A square root order had also been reported in the literature for the potassium siloxanolate catalyst in nonfunctional systems. The higher reaction order and greater catalytic efficiency of the phosphonium siloxanolate catalyst may be related to a higher degree of dissociation and possibly enhanced solubility of the catalyst in the bulk reaction media. In all of the catalyst systems studied, the equilibrium number average degree of polymerization, \bar{X}_n , was independent of the catalyst concentration, and influenced only by the molar ratio of cyclic tetramer to disiloxane. As anticipated, the effect of catalyst and catalyst concentration is manifested mainly in the rate at which equilibrium is reached. While a number of these trends have been studied in the past with regard to the disappearance of D_4 , the significance of the results with respect to functional siloxane systems has not been previously appreciated.

In addition to the kinetic studies on functional polysiloxane oligomers, supercritical fluid fractionation techniques were explored for the separation of aminopropyl terminated polysiloxanes into narrow molecular weight distribution fractions. It was anticipated that the ability to fractionate these versatile materials would lead to a number of fundamental studies on structure-property relationships in multiphase copolymer systems.

Fractionation of the amine-functional materials with supercritical ethane successfully produced a number of fractions with narrow molecular weight distributions. The fractions were compared to polydimethylsiloxane standards synthesized via the organolithium initiated polymerization of the cyclic trimer. Excellent agreement was realized between the molecular weight values determined by titration of the amine endgroups and those calculated by GPC. The difunctional nature of the fractionated oligomers was confirmed by comparing the titrated molecular weights with the values obtained by VPO analysis. Again, excellent agreement found. The results of the fractionation studies have indicated that supercritical fluid fractionation techniques are quite feasible for the isolation of functional polysiloxanes of narrow polydispersity.

Finally, a series of tetramethylbisphenol-A polyarylesters and polyformals were prepared and subsequently modified with polysiloxanes. The synthetic approaches were

quite successful at producing materials which readily formed tough ductile films. The deliberate use of short block lengths successfully produced materials with a large degree of phase mixing between the hard and soft components, as indicated by DSC and TEM results.

Chapter VI

SUGGESTED FUTURE STUDIES

The kinetic aspects of siloxane equilibration reactions in the presence of functional endblockers are still relatively unclear. The results reported in this study have led to more questions on the nature of the active species in these reactions, and the factors affecting the relative rates of incorporation of the cyclic tetramer and the disiloxane. Useful additional studies might include an investigation of the equilibration reaction kinetics employing the various siloxanolate catalysts in the presence of hexamethyldisiloxane. Such a study would determine if the observed catalyst efficiencies and reaction orders are affected by the presence of the fairly polar aminopropyl disiloxane, or merely a function of the cation. A comparison of the ammonium and phosphonium catalysts with the same counterion would also be useful in this regard (such as tetrabutylammonium siloxanolate versus tetrabutylphosphonium siloxanolate). Unfortunately, the increased tendencies of tetramethylphosphonium siloxanolate and tetrabutylammonium siloxanolate towards degradation may present a problem.

Other future studies of interest which were referred to in the text include an extension of the supercritical fluid

fractionation studies to phenyl-containing polysiloxane systems and an investigation of the gas permselectivity of the polyarylester-polysiloxane and polyformal-polysiloxane block copolymers.

Appendix A

Sample Calculations for the Preparation of Functional Siloxane Oligomers

The number average molecular weight, \bar{M}_n , of the difunctional polysiloxane oligomers was controlled by the mole ratio of tetramer to endblocker. Sample calculations for the preparation of an aminopropyl terminated polydimethylsiloxane (PDMS) oligomer are presented below.

Let: \bar{M}_n (Olig) = Target \bar{M}_n for the resulting oligomer
 \bar{M}_n (DSX) = Molecular weight of the disiloxane (or endblocker)

The remainder of the PDMS backbone (BB) must be due to the incorporation of cyclic tetramer, D₄. Thus,

$$\bar{M}_n (\text{BB}) = \bar{M}_n (\text{Olig}) - \bar{M}_n (\text{DSX})$$

The number of grams of D₄ needed for a given amount of disiloxane is then determined by

$$\text{grams D}_4 = \bar{M}_n (\text{BB}) \times \frac{\text{grams disiloxane}}{\bar{M}_n (\text{DSX})}$$

Specifically, for a 5000 g/mole aminopropyl terminated PDMS:

$$\bar{M}_n (\text{Olig}) = 5000 \text{ g/mole}$$

$$\bar{M}_n (\text{DSX}) = 248.5 \text{ g/mole}$$

$$\bar{M}_n (\text{BB}) = 5000 - 248.5 = 4751.5 \text{ g/mole}$$

If one chooses to start with 3.00 grams of disiloxane, then

$$\text{grams D}_4 = 4751.5 \text{ g/mole} \times \frac{3.00 \text{g DSX}}{248.5 \text{ g/mole}} = 57.36 \text{g}$$

Appendix B

Sample Calculations for the Preparation of Phenolic Terminated Polyarylester Oligomers

Molecular weight control of the phenolic terminated polyarylester oligomers was achieved through the use of a stoichiometric imbalance of the starting bifunctional monomers [1]. Sample calculations for a 10,000 g/mole polyarylester are presented below.

Let: \bar{M}_n (Olig) = Target \bar{M}_n for the resulting oligomer
 \bar{M}_n (RU) = Molecular weight of the repeating unit
in the oligomer
 \bar{X}_n = Number average degree of polymerization
DP = Average number of repeat units per
molecule
r = Stoichiometric imbalance of functional
groups

It follows that $DP = \frac{\bar{M}_n \text{ (Olig)}}{\bar{M}_n \text{ (RU)}}$

For the polymerization of A-A + B-B bifunctional monomers,

$$\bar{X}_n = 2 \times DP$$

One can then calculate the desired stoichiometric imbalance, r, which is always less than one, according to

$$r = \frac{\bar{X}_n - 1}{\bar{X}_n + 1}$$

Specifically, for a 10,000 g/mole phenolic terminated tetramethyl bisphenol-A (TMBA) polyarylester, the TMBA monomer would be used in slight excess with respect to the acid chlorides, as calculated below:

$$\begin{aligned} \bar{M}_n \text{ (Olig)} &= 10,000 \text{ g/mole} \\ \bar{M}_n \text{ (RU)} &= 414 \text{ g/mole} \\ \\ \text{DP} &= \frac{10,000 \text{ g/mole}}{414 \text{ g/mole}} = 24.1546 \\ \\ \bar{X}_n &= 2 \times 24.1546 = 48.3092 \\ \\ r &= \frac{(48.3092 - 1)}{(48.3092 + 1)} = 0.9594 \end{aligned}$$

If one chooses to use 30.00g (0.1055 mole) TMBA, then

($r \times 0.1055$ mole TMBA) = 0.1012 mole acid chloride would be required. This corresponds to 0.0506 mole (10.269g) each of terephthaloyl and isophthaloyl chloride.

Two moles of the acid acceptor, triethylamine (TEA), are required for each mole of TMBA. In addition, a 10 mole percent excess was utilized:

$$(2 \times 0.1055 \times 1.1) = 0.2321 \text{ mole TEA}$$

This was converted to volume units using the formula weight and the density of TEA:

$$(0.2321 \text{ mole TEA}) (101 \text{ g/mole TEA}) (1 \text{ ml}/0.726 \text{g TEA}) = 32.3 \text{ ml triethylamine}$$

Appendix C

Sample Calculations for the Preparation of Phenolic Terminated Polyformals

Controlled molecular weight phenolic terminated polyformals were prepared by using a stoichiometric imbalance of functional groups as calculated using the equations outlined in Appendix B. Since a 70:30 ratio of tetramethyl bisphenol-A (TMBA) to bisphenol-A monomer was charged to the reaction flask, the average molecular weight of the repeat unit was determined by assuming that the two monomers were also incorporated in a 70:30 ratio. The bisphenol monomers were used in slight excess with respect to the methylene chloride (CH_2Cl_2) as shown below:

$$\bar{M}_n (\text{Olig}) = 10,000 \text{ g/mole}$$

$$\bar{M}_n (\text{RU}) = (240 \times 0.3) + (296 \times 0.7) = 279.2 \text{ g/mole}$$

$$\text{DP} = \frac{10,000 \text{ g/mole}}{279.2 \text{ g/mole}} = 35.8166$$

$$\bar{X}_n = 2 \times 35.8166 = 71.6332$$

$$r = \frac{(71.6332 - 1)}{(71.6332 + 1)} = 0.9725$$

If one chooses to use 0.070 mole (19.901g) of TMBA and 0.030 mole (6.845g) of bisphenol-A, then

$$(r \times 0.100 \text{ mole bisphenol}) = 0.0972 \text{ mole } \text{CH}_2\text{Cl}_2$$

would be required. This corresponds to 8.26g of methylene chloride.

Before the addition of the methylene chloride monomer, the bisphenate of both the TMBA and bisphenol-A monomers was formed by the addition of two moles of NaOH for each mole of TMBA or bisphenol-A monomer. The NaOH was added as a 46.5 wt.% aqueous NaOH solution:

$(0.200 \text{ moles NaOH required}) \times (40 \text{ g NaOH/mole}) = 8.00 \text{ g NaOH}$

$8.00 \text{ g NaOH} \times (1 \text{ ml solution} / 0.465 \text{ g NaOH}) = 17.20 \text{ g solution}$

Therefore, 17.20g of the 46.5wt.% aqueous NaOH solution was added for formation of the bisphenate.

Appendix D

Sample Calculations for the Preparation of Polysiloxane Oligomers by the Anionic "Living" Polymerization of D₃

The number average degree of polymerization for a living polymer is given simply by the ratio of the concentrations of monomer and initiator [51]. The molecular weight can be controlled by the ratio of the number of grams of monomer relative to the number of moles of initiator. The calculations below are for a 10,000 g/mole oligomer initiated with an 0.28 N sec-butyl lithium solution:

$$\bar{M}_n (\text{Olig}) = \frac{(\text{grams of monomer})}{(\text{moles initiator})}$$

If one chooses to use 15.00g of monomer, then the number of moles of initiator required is given by

$$\text{moles initiator} = \frac{15.00\text{g monomer}}{10,000 \text{ g/mole}} = 0.00150 \text{ moles}$$

Since the sec-butyl lithium solution is 0.28 N, the initiator charge should be

$$0.00150 \text{ moles} \times \frac{1 \text{ liter}}{0.28 \text{ moles}} \times \frac{1000 \text{ ml}}{1 \text{ liter}} = 5.36 \text{ ml}$$

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