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Synthesis and properties of diarylsiloxane and (aryl/methyl)siloxane polymers

Lee, Michael Kang-Jen, Ph.D.
Case Western Reserve University, 1994
SYNTHESIS AND PROPERTIES OF DIARYLSILOXANE AND 
(ARYL/METHYL)SILOXANE POLYMERS

by

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Submitted in partial fulfillment of the requirements 
for the degree of Doctor of Philosophy

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GRADUATE STUDIES

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Polydiarylsiloxanes are highly crystalline, high melting polymers with excellent high temperature properties. As a consequence of the rigid polymer backbone, the polydiarylsiloxanes show crystal → liquid crystal transitions, and both nematic and possibly smectic states have been observed by optical microscopy. The polymers of greatest interest in this investigation have been those containing phenyl and p-tolyl substituents on the siloxane backbone. We have prepared a series of polymers with various combinations of these substituents, as well as the end members of the series, polydiphenylsiloxane and polydi(p-tolyl)siloxane. The polymers are prepared with controlled molecular weights and distribution by ring-opening anionic polymerization of the cyclic trimers in solution.

The crystal → liquid crystal transition temperatures $T_{lc}$ for polydiphenylsiloxane and polydi(p-tolyl)siloxane are very high (265°C and 300°C, respectively) and the polymers are only soluble in a few solvents at temperatures above 150°C. However, the liquid crystal transition temperatures are reduced for the mixed poly(phenyl/p-tolyl)siloxanes and the polymers become soluble at lower temperatures. In contrast to the retention of the crystalline and liquid crystalline character of the mixed diarylsiloxanes, the replacement of a single phenyl group by a methyl group in the repeat hexaphenyl triad sequence of polydiphenylsiloxane is sufficient to destroy both the crystalline and liquid crystalline character of the polymer.
The solution properties of three different types of poly(phenyl/p-tolyl)siloxanes have been investigated in order to characterize the chain stiffness properties. The Mark-Houwink-Sakurada exponents, "a", for these polymers are between 0.75 and 0.86. The values of these exponents are below the values expected for a rigid chain (a > 1.0) but are at the upper end or above the values expected for a flexible random coil polymer in a good solvent. The values indicated that the configuration of these polymers in solution is most likely that of a random coil, but with a relatively large persistence length. The shear viscosity of a solution of the mixed poly(phenyl/p-tolyl)siloxane polymers increases monotonically with increasing polymer concentration. This behavior indicates that these polymers do not behave as rigid-rods in solution.

In addition to the phenyl and p-tolyl siloxane polymers, other diarylsiloxane polymers have been synthesized and characterized. The crystal → liquid crystal transition temperatures are dependent upon the nature of the substituents and are in the order di(anisole) > di(p-tolyl) > di(phenyl) > di(4-propylphenyl) and di(p-tolyl) > di(m-tolyl). Polydi(anisole)siloxane and polydi(4-propylphenyl)siloxane are soluble only at high temperatures, but polydi(m-tolyl)siloxane is soluble in toluene and chloroform at room temperature. The 10% weight loss temperatures (by TGA) of the various diaryl polymers are generally between 460 to 510 °C, but polydi(anisole)siloxane shows a lower value, with DSC measurements showing degradation beginning at 425 °C. The preparation of hexa(o-tolyl)cyclotrisiloxane and polydi(o-tolyl)siloxane...
were not successful due to the extreme steric hindrance of the o-tolyl groups on the siloxane backbone.
DEDICATION

To my wife, Debbie and our two daughters, Grace and Gloria
ACKNOWLEDGMENTS

I wish to express my sincere appreciation for the guidance and advice provided by Dr. Dale Meier throughout the course of this work, and also to Dr. Alexander Jamieson since his help made this work possible.

Thanks also go to Dr. Gary Burns from, Dow Corning Corporation, and Drs. Ned Gvozdic and John Saam, from Michigan Molecular Institute (MMI) for their many helpful suggestions. I would also like to thank Kevin Battjes, Ann Jurek, Linda Myers, and Mike Rozniak of MMI for their assistance with the experimental portion of this work. That gratitude is extended to all the faculty and administration of both MMI and the Department of Macromolecular Science at Case Western Reserve University for strongly supporting this program during the past few years.

Finally, I am deeply indebted to my wife, Debbie, for her encouragement and patience.
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CHAPTER 1

DEFINITIONS AND GENERAL BACKGROUND
1.1 BACKGROUND

In the last twenty years, a new and interesting class of polymers has been developed which has received a great deal of attention from both industry and academia. These materials are called liquid crystalline polymers. The liquid crystalline behavior of small molecules has been known since 1888 when Reinitzer (1) observed that cholesteryl benzoate melted to form a turbid melt which would clear at a higher temperature. The term "liquid crystal" was first used by Lehmann (2) in 1890 to describe these materials. The liquid crystalline states may be obtained from a crystalline state by introduction of positional or orientational degrees of freedom. This means that liquid crystalline materials have the properties of both the liquid (disordered and isotropic) and of the solid crystal (three dimensionally ordered). Structurally, the liquid crystalline phase is intermediate between a crystal and a liquid, and is also referred to as a mesomorphic structure or a mesophase ("mesos" meaning "intermediate", and "morphe" meaning "form") (3). The liquid crystalline states are truly thermodynamic phases; reversible phase transitions occur between the crystalline state and the liquid crystalline states, and between the liquid crystalline states and the isotropic fluid state.

There are two major classifications of liquid crystals, thermotropic (4) and lyotropic (5). The thermotropic liquid crystals are molecules which display a liquid crystalline state with variation in temperature. The lyotropic liquid crystals are prepared by mixing two or more components
together and result when their relative concentrations are varied. Usually, the lyotropic liquid crystalline states are obtained through dissolution of strongly ordered crystals in suitable solvents. Three basic structures have been identified for thermotropic liquid crystals (as shown in Figure 1.1): nematic (meaning "thread"), smectic (meaning "soap-like") and cholesteric (6). In the nematic structure, molecules are aligned parallel to one another either in a longitude or latitude direction. When viewed through a polarized microscope, one sees a thread-like Schlieren pattern, as shown in Figure 1.2 (7). The smectic liquid crystals have molecules aligned parallel to one another in both longitudinal and latitudinal directions. When viewed through a polarized microscope, one sees a focal-conic or a fan-shaped pattern, as shown in Figure 1.3 (8). The cholesteric structure is a special form of the nematic structure. Molecules are brought together in each layer as in the nematic form, but each layer rotates or twists a certain degree from its neighboring layer. When viewed through a polarized microscope, one sees oily streaks and striated patterns as shown in Figure 1.3 (9). It is possible for a liquid crystal to have more than one thermotropic mesophase. A smectic phase is more stable than a nematic phase and there are distinct phase transition temperatures corresponding to each liquid crystalline state. The stability order is as follows:

solid crystal > smectic > nematic > isotropic liquid

The smectic liquid crystalline phase can be further separated into smectic-A, smectic-B etc.
The first reference to a polymeric mesophase was in 1937 by Bawden and Pirie (10). It was until 1970's that the first commercially important synthetic lyotropic liquid crystalline polymers such as poly(p-phenylene terephalamide) (Kevlar®) were prepared by DuPont, and first thermotropic liquid crystalline polymers were reported by Roviello and Sirigu (11). The unique physical and chemical properties of liquid crystalline polymers make them attractive to both science and technology, and have led to a large number of research papers and to commercial applications. Although most of the literature concerning polymers with mesophases uses the term "liquid crystalline polymers", it should be mentioned that Wunderlich (12) has divided the mesophases into three types: liquid crystals, plastic crystals, and condis crystals. According to his definition, the "liquid crystals" are materials having orientational order but lose positional order. The "plastic crystals" are a group of materials with a mesophase which shows orientational disorder but positional order. The "conformationally disordered crystals" (condis crystals) are materials having conformational change without losing positional or orientational order. However, the definition and nomenclature seem ambiguous and confusing, and probably has appeared too late to be generally accepted. Nowadays, most people just simply use the term "liquid crystalline polymers" for polymers with mesomorphic states.

The original molecular theories that predict the relationship between the liquid crystalline state and the aspect ratio of the rod-like molecules were by Onsager (13) and Flory (14). In general, the liquid
crystalline state is a consequence of molecular shape anisotropy, such as is found in rigid-rod shape molecules or relatively stiff chain segments with a high axial ratio (usually greater than 3). The rigid unit responsible for the liquid crystalline behavior is referred to as the mesogen. The compositions for liquid crystalline polymers are mesogenic units with or without spacers present. The mesogenic units usually have the appearance of an ellipsoid, but flat and disk shapes have also been observed to lead to a liquid crystalline state. The mesogenic groups usually have ester (15), azo or azoxy (16), trans-vinylene or trans-stilbene (17), and imino (18) type linkages. Liquid crystalline states result from intermolecular repulsions and are not dependent on intermolecular associations. Rod-like molecules can only be arranged randomly in solution or melt up to a limited number of molecules, and a liquid crystalline state may form when the number exceeds this critical number.

Liquid crystalline polymers can be classified into two types: main-chain and side-chain liquid crystalline polymers (Figure 1.4). In the side-chain liquid crystalline polymers, the mesogenic units are linked to a polymer backbone as pendant side-chains, with or without a flexible spacer. Those polymers that contain a flexible spacer, linking the main chain to the pendant mesogenic group, often show a greater ability to form a mesophase than polymers lacking a spacer, when other factors are kept constant. The spacer serves to dissociate the disorder of the main chain from the greater order of the mesogenic groups and to decouple the motions of the mesogenic moiety from those of the polymer backbone. In
the main-chain liquid crystalline polymers, the mesogenic groups form the backbone of the molecular chains. Flexible spacers have also been extensively used to separate mesogenic groups placed in the main-chain from each other and the backbone flexibility achieved by this approach has the effect of markedly improving solubility and lowering transition temperatures, in contrast to those of the rigid-rod polymers of comparable composition. The flexible spacers for both main-chain and side-chain liquid crystalline polymers usually are polymethylene (19), poly(ethylene oxide) (20) or polysiloxane (21) type spacers. The differences between types of spacers in liquid crystalline polymers has been studied by Lenz (22). He indicated that the range of mesophase stability and melting temperature was greater for a polymer with a polymethylene spacer than that with a polysiloxane spacer. Liquid crystalline polymers with poly(ethylene oxide) spacers were shown to have transition temperatures similar to those for polymers with polymethylene spacers of the same length, but the mesophase formed could be quite different. Liquid crystalline polymers with polysiloxane spacers and mesogenic units identical to those present in polymers with polymethylene spacers, showed different mesophase structure in addition to much lower transition temperatures.

The most common type of silicone containing liquid crystals are the side-chain liquid crystalline polymers where the mesogenic groups are attached to a polydimethylsiloxane backbone. These materials are synthesized by the hydrosilation of vinyl terminated mesogenic compounds with (methyl/hydrogen)siloxane and dimethylsiloxane
copolymers, as shown in Figure 1.5. The reactions are usually performed in solvent with hydrogen hexachloroplatinate (IV) hydrate (H₂PtCl₆·H₂O) catalyst present. A wide range of polymers with different mesogenic side groups have been synthesized and characterized. Polydimethylsiloxane (PDMS) is known to have very low glass transition temperature (about -124 °C). Polysiloxane backbones show favorable qualities for liquid crystalline polymers because their high flexibility decreases the degree of coupling between the backbone and the mesogen and reduces the effective chain packing and the interchain forces. One consequence of this is a decrease in the transition temperatures and a significant improvement of the solubility, in contrast to rigid rod polymers of comparable composition. Many of these siloxane containing polymers showed liquid crystallinity at room temperature (21, 23). The use of polysiloxane as spacers, instead of backbones in main-chain liquid crystalline polymers, has also been investigated. The spacers increase the flexibility of the polymer, decrease the degree of coupling between the backbone and the mesogen and substantially lower the melting and clearing temperatures of the polymers. A typical synthetic method to prepare main-chain liquid crystalline polymers containing siloxane units is by hydrosilation, as shown in Figure 1.6. Polymers with a wide range of different mesogenic backbone units and dimethylsiloxane block lengths have been prepared. The effect of these variations on the thermal behavior of liquid crystalline phenomenon was investigated (21-22, 24). There was an indication that the widths of liquid crystalline phases depend on the type of the
mesogenic units, but were not strongly influenced by the dimethylsiloxane spacers.

A different variety of liquid crystalline polymers are the polyorganosiloxanes (25) and polyphosphazenes (26). Both are liquid crystalline polymers and are distinctly different from the traditional mesogenic types of liquid crystalline polymers. This is responsible for the great interest in studying them. It is important to mention that all symmetric polydiaklysiloxanes are liquid crystalline polymers except polydimethylsiloxane (PDMS). The mesospheric state of polydiethylsiloxane and polydipropylsiloxane was first observed by Lee (27) and confirmed later by others (28). The majority of the polymers which show liquid crystalline behavior contain the traditional mesogenic groups either in the main chain or in the side chains, but these polydiaklysiloxanes form a liquid crystalline state in spite of being flexible linear polymers and with no traditional mesogenic groups in either the main or side chain. The melting points of these polymers increase as the alkyl group becomes more bulky. For a given liquid crystalline polydiaklysiloxane, the phase range (the temperature range between liquid crystalline and isotropic transition temperature) increases with increasing molecular weight (25). Boileau (28) indicated a strong molecular weight dependence of the melting temperature while the liquid crystal transitions depended little on molecular weight. However, some organic liquid crystalline polymers do show molecular weight dependence of the liquid crystal transition temperature (T_{lc}). Our diarylsiloxane polymers
show strong relationships between molecular weight and $T_{lc}$ as is discussed in Chapter 2 in this dissertation.

The physical characteristics of liquid crystalline polymers have been determined by optical microscopy (19, 29), X-ray diffraction (30), thermal analysis (31), rheology (32) and NMR methods (33). Optical microscopy is the most commonly used method for characterizing liquid crystals. Optical properties of liquid crystals are rather distinctive, and the textures of liquid crystals, as observed under cross-polarized light, can be used to identify the class of liquid crystalline order. The test methods and the means of identification have been described and summarized by Hartshorne (34) and by Demus and Richter (35). Both low molecular weight liquid crystals and high molecular weight liquid crystalline polymers show similar colorful textures when observed under polarized microscopy. However, due to differences in relaxation response, viscosity, light transmissions and thermal stability, identification of structure type for liquid crystalline polymers is much more difficult than for a low molecular weight liquid crystalline materials.

The number and type of applications for liquid crystalline polymers now appears to be limited only by one's imagination. They have been used in highly specialized applications, particular in the following market areas (36): consumer and appliances, construction industry, chemical environment, electronics, aerospace and transportation, and telecommunications. They are used as: temperature sensors, storage
devices, electronic displays, toys and decorative materials, switching
devices, separation tower packings and high strength materials (37). The
largest market for liquid crystalline polymers is for fibers, principally
poly(p-phenylene terephalamide) (38). These fibers are high strength, low
density, chemical resistance, nonabrasiveness and exhibit dimensional
and thermal stability. Applications of these fibers include products such as:
bullet-proof vests, gloves, rope and thread, radial tires, brake linings,
gasket and packing, clutch facings, conveyer belts and boats (39). World-
wide production of liquid crystalline fibers is estimated to be worth about 1
billion dollars.

Siloxane polymers have several unique properties such as good
thermal and oxidative stability, low temperature flexibility, high
permeability, low surface energy, high biocompatibility, good insulation
and low toxicity (40). The most common and widely used siloxane
polymers are based principally on polydimethylsiloxane (PDMS). It is a
fluid or gum at room temperature, depending on the molecular weight.
The viscosity of PDMS fluid changes very little with temperature and is
widely used as vacuum pump oil, hydraulic fluid and lubrication oil in
different instruments. The principle method for preparing a high
molecular weight PDMS polymer in the research laboratory is by ring
opening anionic polymerization of cyclosiloxanes. It has been shown that,
under certain conditions, hexamethylcyclotrisiloxane (D3) polymerizes to
give linear polymers of negligible cyclosiloxane contents and with narrow
molecular weight distributions. The reaction conditions include a suitable
initiator, such as a butyllithium with D3 in a hydrocarbon solvent and with a promoter present. The promoters are materials such as tetrahydrofuran, diglyme, dimethoxyethane, and dimethylsulfoxide (41). A catalyst such as potassium hydroxide (KOH) is not suitable for making narrow molecular weight distribution PDMS since it not only opens the D3 ring, but also causes the polymer chain to reshuffle and establish ring-chain equilibrium. At equilibrium, the polydimethylsiloxane system will consist of about 80% polymer and 20% low molecular weight oligomers and cyclics. The effect of the type of silicone substituents on the concentrations of cyclosiloxanes at equilibrium was examined by Sigwalt (42). The weight fraction of polymer from a siloxane equilibrium polymerization is inversely proportional to the bulkiness of the substituents. For example, the weight fraction of cyclosiloxanes for PDMS polymerization is about 20%, compared to about 12% for

\[
\left( \text{Si} \right) \left( \text{O} \right)_n \left( \text{Si} \right) \left( \text{O} \right) \left( \text{H} \right)
\]

and about 80% for

\[
\left( \text{Si} \right) \left( \text{O} \right)_n \left( \text{Si} \right) \left( \text{O} \right) \left( \text{CH}_2\text{CH}_2\text{CH}_3 \right)
\]

The estimated cyclics in the equilibrium polymerization of polydiphenylsiloxane is greater than 90%.
Although PDMS networks (elastomers) are widely used, a PDMS network has poor mechanical properties unless a reinforcing agent, such as silica, is present (43). An alternative way to improve the mechanical strength properties of PDMS is via block copolymer molecular architecture (44). If microphase separation occurs in the block copolymer in which the second block component forms rigid or crystalline domains, the resulting domains will serve as the required reinforcing agent for the elastomeric PDMS chains and excellent mechanical properties are possible. A wide variety of homopolymers and copolymers have been prepared by ring-opening polymerization of the corresponding cyclic trimers including various types of siloxane copolymers that contain diphenylsiloxane (P) (45). These polymer types include di- and tri-block copolymers with diphenylsiloxane as one block component and dimethylsiloxane (M) or (methyl/phenyl)siloxane (P/M) as the second component. The choice of these components was based on several factors: a desire that the copolymer can be based wholly on siloxane components; polydiphenylsiloxane (PDPS) is a thermally stable, highly crystalline solid with a liquid crystalline state and a very high melting (clearing) temperature. Block copolymers of controlled molecular weight and architecture can be prepared by anionic polymerization of hexaphenylcyclotrisiloxane and D₃ by using lithium-based anionic polymerization techniques, as first described by Bostic (46). Polymers of controlled molecular weights and molecular architecture can be prepared by these techniques since, when properly used, lithium-based initiators do not randomize the sequence distributions of resulting copolymers. Using these techniques, a variety of
block copolymers of the di-block (P-M), triblock (P-M-P) and star-block, (P-M)ₙ₋ₓ types (where x represents the common junction of n-arms of a star-block polymer) have been prepared and characterized (45, 47) (Figures 1.7 and 1.8). With appropriate block compositions, the tri- and star-block copolymers are highly elastic, with strength properties among the highest ever reported for a siloxane elastomer. In contrast, P-M di-block copolymers are grease-like materials.

Random and statistical copolymers (48) are also interesting since they demonstrate, in a striking way, the influence that subtle differences in molecular architecture can have on physical properties. The term "statistical copolymer" is used here to designate that the copolymer is "random" but the randomness is of triad siloxane units of a given type. Although the difference between lengths of one unit as compared with three units would appear to be minor, the differences in the physical properties of the two types of "random" copolymers are very large. With molar ratios near 1:1 and with molecular weights of ~10⁵, the statistical copolymer is an elastic solid with appreciable mechanical properties, whereas the random copolymer is a sticky gum.

The goal of this study has been to synthesize and characterize various polydiarylsiloxanes and poly(aryl/methyl)siloxane polymers of controlled structure and molecular weight with a view of establishing further information concerning the structure/property relationships for these types of polymers. A further goal has been to obtain siloxane
polymers with lower transition and solution temperatures than for polydiphenylsiloxane, so that the liquid crystalline states and the solution properties could be more easily characterized. In the future, these polymers may be used to incorporate with the PDMS to construct the block copolymers which will be high-temperature stable, liquid crystalline thermoplastic elastomers soluble at room temperature. We have synthesized and characterized a series of diaryl and (aryl/methyl) cyclic trimers and prepared polymers with controlled molecular weight and distribution by the ring-open anionic polymerization of corresponding cyclic trimers. The polymers that we have investigated include o-, m- and p-isomers of polyditolylsiloxanes, various "mixed" poly(phenyl/p-tolyl)siloxanes, various mixed poly(phenyl/methyl)siloxanes, polydi(4-propylphenyl)siloxane and polydi(anisole)siloxane. The polymerization yields, molecular weights, sequence distribution, thermal transitions, solution and rheological properties and thermal stability will be described.

This thesis consists of five chapters. Chapter 1 covers the definitions and general background of the organic and silicone liquid crystalline polymers. Previous research work in our laboratory is also briefly discussed. Chapter 2 will cover the synthesis and characterization of a number of cyclic trimer monomers and resulting polymers, with an emphasis on their thermal properties. Chapter 3 will focus on solution and rheological properties. Chapter 4 will emphasize the effect of different aryl substituents on the thermal properties of polydiarylsiloxanes. Finally, all the results will be summarized in last Chapter 5.
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Figure 1.1. Three Basic Structures for Thermotropic Liquid Crystalline Polymers

- Cholesteric
- Smectic
- Nematic
- Isotropic
Figure 1.2  A typical nematic thread-like Schlieren pattern by optical microscopy.
From Ref. 7
a: low molecular weight oligomer
b: high molecular weight polymer
Smectic fan-shaped texture with focal conics

Cholesteric texture

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Figure 1.5: Silicong Containing Side Chain Liquid Crystal Polyimide Prepared by 

Hydroxylation Reaction

CH$_3$CH$_2$CH$_3$

Hydroxylation

CH$_3$CH$_2$CH$_3$

CH$_3$CH$_2$CH$_3$

CH$_3$CH$_2$CH$_3$

CH$_3$CH$_2$CH$_3$

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CH$_3$CH$_2$CH$_3$

CH$_3$CH$_2$CH$_3$

CH$_3$CH$_2$CH$_3$

CH$_3$CH$_2$CH$_3$

CH$_3$CH$_2$CH$_3$
Hydrostilation Reaction

Figure 1.6 Siliccone Containing Main Chain Liquid Crystalline Polymer Prepared by

\[ \text{(Mesogenic Unit)} \]

\[ \text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2 + \text{CH}_3\text{C}_\text{H}(\text{OSi})_x\text{CH}_3 \]

\[ \rightarrow \text{Hydrostilation} \]
Figure 1.7: Synthesis of P-M diblock copolymers. 
P: diphenylsiloxane; M: dimethylsiloxane 
From Ref. 48.
Figure 1.8: Synthesis of P-M-P triblock copolymers. P: diphenylsiloxane; M: dimethylsiloxane
From Ref. 48.
CHAPTER 2

SYNTHESIS AND PROPERTIES OF DIARYLSILOXANE AND
(ARYL/METHYL)SILOXANE POLYMERS: THERMAL PROPERTIES
2.1 INTRODUCTION

To date, it is only polydimethylsiloxane, poly(methyl/trifluoropropyl)siloxane and poly(methyl/phenyl)siloxane out of the many possible types of siloxane polymers that have become widely used. These polymers have excellent thermal, chemical and environmental stability, as well as excellent biocompatibility properties. As a result, they are widely used in numerous industrial and consumer applications (1-2). Only limited attention has been paid to other siloxane polymers, although it is recognized that these too can have unique and perhaps desirable properties. For example, it has been established that the symmetrically substituted polydialkylsiloxanes such as polydiethylsiloxane or polydipropylsiloxane are liquid crystal-forming polymers (3-6), despite the absence of traditional mesogenic groups. The polydiarylsiloxanes such as polydiphenylsiloxane also show liquid crystalline properties (7). Because of the relatively bulky phenyl groups and resulting steric interactions, the chains of polydiphenylsiloxane are rigid, in contrast to the highly flexible chains of siloxane polymers with the smaller methyl substituent group. As a consequence of chain rigidity, polydiphenylsiloxane is a highly crystalline polymer with a transition to the liquid crystalline state $T_{lc}$ near 265 °C, and a clearing temperature $T_m$ (to the isotropic melt) above 500 °C (7-9). Relatively few publications have dealt with the characterization and physical properties of polydiarylsiloxanes since the synthesis and the very high melting and solution temperatures have presented experimental difficulties (10-13).
The goal of this study has been to synthesize and characterize various polydiarylsiloxanes of controlled structure and molecular weight with a view of establishing structure/property relationships for this class of polymers. A further goal has been to obtain polymers with lower transition and solution temperatures than for polydiphenylsiloxane, so that the liquid crystalline states and the solution properties could be more easily characterized. Ring-opening anionic polymerization of the cyclic trimers are used to obtain polymers with well-defined compositions and molecular weights. This chapter will cover the synthesis and characterization of a number of cyclic trimer monomers and resulting polymers, with an emphasis on their thermal properties. Chapter 3 will focus on solution and rheological properties.

2.2 EXPERIMENTAL

2.2.1 MATERIALS

4-Bromotoluene (Aldrich), silicon tetrachloride (Aldrich), 1,3-dichlorotetramethyldisiloxane (Hüls), dimethyldichlorosilane (Aldrich), methylphenyldichlorosilane (Aldrich), phenyltrichlorosilane (Dow Corning), diphenyldichlorosilane (Dow Corning), hexaphenylcyclotrisiloxane (Dow Corning) and sec-butylithium (Aldrich) were used without further purification. Diphenyl ether (Aldrich) was used as the solvent for the anionic polymerizations and was purified by vacuum distillation, passed through activated alumina and then distilled again over calcium hydride. Tetrahydrofuran (Fisher) was refluxed with lithium aluminum hydride and
distilled prior to use. Magnesium turnings (Aldrich) were dried at 100°C under vacuum to remove any trace of water.

2.2.2 SYNTHESIS OF THE CYCLIC TRIMER MONOMERS

The general procedures used to prepare the cyclotrisiloxanes of this investigation was by cyclization of the corresponding dichlorosilanes with ZnO (14) or by reacting the dichlorosilanes with the pyridine complex of tetraphenyldisiloxanediol (15-16). The diaryldichlorosilanes were prepared by the Grignard reaction between silicone tetrachloride and arylmagnesium bromide, or between phenyltrichlorosilane with arylmagnesium bromide (17-18). The preparation procedures are outlined in Figures 2.1 to 2.3 and are described in the following section.

Di(p-tolyldichlorosilane and (phenyl/p-tolyldichlorosilane:

4-Bromotoluene (180g, 1.05 mole) was dissolved in 300 ml of ethyl ether and slowly added to Mg turnings (24.3g, 1 mole) in 200 ml of ethyl ether. The Grignard reaction gradually initiated under refluxing conditions and after completion of the 4-bromotoluene addition (1 hour), the reaction was allowed to continue for 1 to 2 hours until the Mg was nearly completely consumed. SiCl₄ (82g, 0.48 mole) or PhSiCl₃ (190g, 0.90 mole) in 200 ml of ether was added at a rapid dropwise rate with vigorous stirring at room temperature. The desired di(p-tolyldichlorosilane or (phenyl/p-tolyldichlorosilane were obtained from the reaction mixture by fractional distillation under vacuum
(-165 °C/1 mmHg for di(p-tolyl) dichlorosilane and -135 °C/0.5 mmHg for (phenyl/p-tolyl)dichlorosilane after the MgBrCl was filtered off. The yields were typically between 60 to 80%.

**Pyridine complex of 1,1,3,3-tetraphenyl disiloxanediol-1,3:**

The pyridine complex of 1,1,3,3-tetraphenyl disiloxanediol-1,3 was prepared by the technique described in reference 15. Diphenyl dichlorosilane (1.0 mole) in 200 ml acetone was slowly added over a one hour period to a flask containing 800 ml of 1/1 acetone/water mixture at room temperature. After stirring for an additional 15 minutes, the acetone layer with the desired diol was separated from the water layer and the acetone then removed by evaporation. The crude diol product was dissolved in 400 ml of ether and the tetraphenyl disiloxediol-pyridine complex was precipitated by the addition of 150 ml of pyridine. This gave about a 80% yield of the complex, which was then purified by crystallization from methanol solution.

1,1,3,3,5-penta(phenyl)-5-(p-tolyl) cyclotrisiloxane:

(Phenyl/p-tolyl)dichlorosilane (26.7g, 0.1 mole) in 90 ml of benzene was slowly added to a flask containing 54.2g (0.11 mole) of tetraphenyl disiloxanediol-pyridine complex, 11.9g (0.15 mole) of pyridine and 110 ml of benzene at room temperature. After the last addition of the dichlorosilane (45 minutes), the solution mixture was stirred for 60 minutes, then 100 ml more of benzene was added and the system stirred for a further
10 minutes. The solution was then washed three times with 200 ml of water, followed by removal of the benzene by evaporation. The resulting white powder was washed twice with 200 ml of methanol. The yield of the cyclic trimers was about 80%.

1,1,3,3-tetra(phenyl)-5,5-di(p-toly1)cyclotrisiloxane:

Di(p-toly1)dichlorosilane (28.1g, 0.1 mole) in 110 ml of benzene was slowly added to a flask containing 54.2g (0.11 mole) of tetraphenyldisiloxanediol-pyridine complex, 11.9g (0.15 mole) of pyridine and 200 ml of benzene at room temperature. After the last addition of the dichlorosilane (30 minutes), the solution mixture was stirred for 60 minutes, then 100 ml more of benzene was added and the system stirred for a further 10 minutes. The solution was then washed four times with 150 ml of water, followed by removal of the benzene by evaporation. The resulting white powder was washed twice with 200 ml of methanol. The yield of the cyclic trimers was about 60%.

1,3,5-tri(phenyl)-1,3,5-tri(p-toly1)cyclotrisiloxane:

(Phenyl/p-toly1)dichlorosilane (187g, 0.7 mole) in 350 ml ethylacetate was slowly added with vigorous stirring to a suspension of ZnO (86g, 1.06 mole) in 500 ml of ethyl acetate at room temperature. After the last addition of the dichlorosilane (1 hour), the solution mixture was stirred for 16 more hours at room temperature. The resulting ZnCl2 and the excess ZnO were filtered off and the solution was washed four times with 200 ml of water. Solvent was
removed by evaporation to yield a mixture consisting mainly of cyclic trimers and other cyclic oligomers. The cyclic trimers were separated by recrystallization from a toluene solution, with about a 40% yield.

Hexa(p-tolyl)cyclotrisiloxane:

Di(p-tolyl)dichlorosilane (157g, 0.56 mole) in 150 ml methylacetate was slowly added with vigorous stirring to a suspension of ZnO (63g, 0.77 mole) in 350 ml of methyacetate at room temperature. After the last addition of the dichlorosilane (1 hour), the solution mixture was stirred for 1 more hour at room temperature. The resulting ZnCl₂ and the excess ZnO were filtered off and the solution was washed four times with 200 ml of water. Solvent was removed by evaporation to yield a mixture consisting mainly of cyclic trimers and other cyclic oligomers. The cyclic trimers were separated by recrystallization from a toluene solution, with about a 40% yield.

1,1,3,3,5-penta(phenyl)-5-(methyl)cyclotrisiloxane:

(Methyl/phenyl)dichlorosilane (15.3g, 0.09 mole) in 100 ml of benzene was slowly added (90 minutes) to a flask containing 49.3g (0.1 mole) of pyridine-tetraphenyldisiloxanediol complex, 15.8g (0.2 mole) of pyridine and 200 ml of benzene at room temperature. The reaction was allowed to continue for an additional 60 minutes. After washing three time with 200 ml of water, the benzene was removed by evaporation. The resulting white powder was
washed twice with 100 ml of methanol and dried, with a resulting yield of trimers about 70%.

1,1,3,3-tetra(phenyl)-5,5-di(methyl)cyclotrisiloxane:

Dimethyldichlorosilane (6.5g, 0.05 mole) in 60 ml of benzene was slowly added (40 minutes) to a flask containing 29.6g (0.06 mole) of pyridine-tetraphenyldisiloxanediol complex, 10.3g (0.13 mole) of pyridine and 110 ml of benzene at room temperature. The reaction was allowed to continue for an additional 60 minutes. After washing three times with 100 ml of water, the benzene was removed by evaporation. The resulting white powder was washed twice with 100 ml of methanol and dried, with a resulting yield of trimers of between 50 %.

1,1-di(phenyl)-3,3,5,5-tetra(methyl)cyclosiloxane

1,3-dichlorotetramethyldisiloxane (34.6g, 0.17 mole) in 200 ml of benzene was slowly added over one hour to a reaction flask containing 43.3g (0.2 mole) of diphenylsilanediol, 31.6g (0.4 mole) of pyridine and 200 ml of benzene at room temperature. After the last addition of the dichlorosilane, the solution mixture was stirred for 16 more hours at room temperature. After washing the mixture three times with 200 ml of water, the benzene was removed by evaporation. The cyclic trimers were separated from the mixture by recrystallization from a hexane solution, with an overall yield of about 65%.
The properties of the cyclic trimers having phenyl and methyl groups and those having phenyl and p-tolyl groups are listed in Tables 2.1 to 2.2, respectively. The H and Si-29 NMR spectra of some of the cyclic trimers are listed in Tables 2.1 to 2.4 and shown in Figures 2.4 to 2.18. The data in Table 2.1 illustrate that the replacement of phenyl groups by methyl groups in hexaphenylcyclotrisiloxane dramatically reduces the melting temperature $T_m$. In contrast, the data in Table 2.2 show that the substitution of phenyl by p-tolyl groups has only a minor effect on the melting points until all of the phenyl groups are completely replaced by p-tolyl groups. Then the melting temperature is substantially increased, from 190°C for hexaphenylcyclotrisiloxane to 260°C for hexa(p-tolyl)cyclotrisiloxane. The different effects produced by substituting methyl or p-tolyl groups is, of course, related to their substantially different molecular volumes and the concomitant steric effects.

2.2.3 POLYMER SYNTHESIS:

The polymerization of cyclosiloxanes with bulky substituents by conventional basic catalysts is difficult, yields are low and the sequential distributions of a copolymer is randomized. However, Bostick (19), Lee(20) and our earlier work (7) showed that ring-opening polymerization of the cyclic trimers could be initiated by lithium alkyls and silanolates, and copolymers could be prepared in high yield without appreciable randomization of copolymer sequence distributions. We also showed (21) that lithium initiators could be used to prepare polydiphenylsiloxane with
controlled molecular weights and narrow distributions by polymerization of the cyclic trimer in a solution in diphenyl ether at high temperatures (150 - 190°C). By polymerization in a homogeneous solution, we avoided the problems associated with the earlier bulk polymerizations, where major problems occurred in the control and the product uniformity because of very high viscosities and attendant inability to properly mix components (7). The polymers for this investigation have been prepared by the lithium-initiated, ring-opening polymerization of the cyclic trimers in solution.

Sec-butyl lithium was used as the polymerization initiator with tetrahydrofuran used as the promoter (THF, 3.5 to 7.0% by volume). The polymerization reactions were conducted in a purified nitrogen atmosphere to exclude air and moisture, and at temperatures of 170 or 190 °C for a 90 minute period. The polymerizations require control of a number of variables, e.g., polymerization time, temperature, promoter concentration, etc. Table 2.5 shows the effect of the polymerization variables on the yield of polydi(p-tolyl)siloxane. The polymerization reactions were terminated with a stoichiometric excess of diphenylmethylchlorosilane. Polydiphenylsiloxane and polydi(p-tolyl)siloxane were recovered by precipitation in toluene, followed by filtration and repeated washing with toluene to remove the remaining cyclic and initiator impurities. The other polymers were recovered by precipitation with methanol and purified by fractional precipitation with a toluene/methanol mixture. The necessity to exhaustively purify the polymers from initiator residues will be discussed in a later section. Polymers were dried in a vacuum oven at 100 °C for 16 hours.
2.2.4 CHARACTERIZATION:

Molecular weights by gel permeation chromatography (GPC) were obtained using chloroform solutions at 40°C, and the reported molecular weights are based on polystyrene standards. Differential Scanning Calorimetry (DSC) data were obtained using a Dupont 910 Thermal Analyzer at a heating rate of 10 °C per minute and with a nitrogen flow rate of 40 ml/min. The glass temperatures are reported as the onset temperatures of the transition, while the crystal and liquid crystal transition temperatures are reported as peak temperatures. Thermogravimetric analysis was performed on a DuPont 951 TGA at a heating rate 10 °C per minute with nitrogen flow rate of 50 ml/minute. ¹³C and ²⁹Si NMR spectra were obtained using a Bruker 360 MHz spectrometer. A Leitz optical microscope (Dialux-Pol SB) with a Mettler FP2 hot stage was used for optical microscopy. The hot stage allowed examination of samples to 300°C.

2.3 RESULTS AND DISCUSSION

The structure of each cyclic trimer was confirmed by H and ²⁹Si NMR. The cyclic trimer 1,3,5-tri(phenyl)/1,3,5-tri(p-tolyl)cyclotrisiloxane is probably a mixtures of cis and trans isomers, but the differences between them are so small that we were unable to distinguish the separate species by NMR or DSC techniques. Both ²⁹Si and ¹³C NMR spectra show the presence of only one species and only one sharp melting point is observed by DSC. The fact that the separate species cannot be resolved is not too surprising. Similar results
are found for the cis and trans isomers of 1,3,5-trimethyl-1,3,5-
triphenylcyclotrisiloxane, for which only minor differences in melting points
and NMR spectra were found, in spite of very large difference in the size of
phenyl and methyl groups (22).

The data in Tables 2.6 and 2.7 show that the polymers prepared here were
of reasonably high molecular weight polymers (GPC data also indicated
narrow molecular weight distributions) and with yields between 50 and 80%. In
contrast, Zhdanov, et al (11) reported a maximum yield of only 39% in the
synthesis of some similar type polymers using a basic potassium initiator and
an extremely strong promoter (18-crown-6 crown ether). In addition, it is
likely that the strongly basic initiator used “scrambled” or randomized the
sequence distribution of the resulting polymers, in contrast to the retention of
the triad sequence distributions of the cyclic trimers when lithium initiators
are used (19).

The sequence distributions of the polymers prepared here were
determined by $^{29}$Si NMR (23). Such data show that the polymerization of the
cyclic trimers was predominately head-to-tail, e.g., the polymer prepared
from the cyclic trimer $\text{P-P-P*}$, with “P” representing a
diphenylsiloxane group and “P*” a phenyl/p-tolysiloxane or di(p-
tolyl)siloxane group, retained the same -P-P-P*-P-P-P*- sequence
distribution in the polymer with only a minor amount of the head-to-head
sequence -P-P-P*-P*-P-P-present. These data also indicate that a negligible
degree of randomization (“scrambling”) of the individual siloxane units
ocurred in the p-tolyl-substituted series, but did occur to a somewhat larger
degree in the methyl-substituted series, as indicated by noticeable (but weak)
secondary peaks in the NMR spectra (not shown). The chemical shifts of the
$^{29}$Si NMR spectra are listed in Tables 2.6 to 2.7 and $^{29}$Si as well as H-NMR
spectra of the p-tolyl-substituted series are shown in Figures 2.19 to 2.24.

Polydiphenylsiloxane is soluble in few solvents and then only at high
temperatures. The replacement of phenyl group in the molecule of
polydiphenylsiloxane by p-tolyl or methyl groups improves the solubility,
except when all the phenyl groups are substituted by p-tolyl, when again the
polymer becomes soluble only at very high temperatures. The mixed
phenyl/p-tolyl polymers are soluble in common solvents like chloroform,
toluene and THF at room temperature or upon slight heating (13), even
though the polymers are highly crystalline and have transition temperatures
$T_{lc}$ above 150°C.

In contrast to the crystalline and liquid crystalline character of the mixed
phenyl/p-tolyl polymers, the substitution of even one of the six phenyl
groups of the repeat triad in polydiphenylsiloxane by a methyl group
destroys the crystalline and liquid crystalline character. The polymers having
either one, two or four phenyl group(s) (P) in the repeat diphenyl triad
substituted by a methyl group(s) (M), -P$_2$-P$_2$-(P/M)-, -P$_2$-P$_2$-M$_2$-, or -P$_2$-
M$_2$-M$_2$- are totally amorphous materials with Tg's at 14, -1 and -48 °C,
respectively (Figures 2.25 to 2.27). This series of methyl-substituted polymers
(together with the properties of the end members of the series,
polydimethylsiloxane and polydiphenylsiloxane) shows that the effect of methyl-substitution on the glass transition temperatures is a monotonic function of the degree of methyl substitution, as shown in Figure 2.28. It should be noted that the literature value (24) for the glass transition temperature of poly(phenyl/methyl)siloxane with 50 mole% symmetric substitution is -86°C (187K) and does not fall on this curve. However, a sample of this polymer prepared by Y. Tarshiani at MMI (unpublished work) shows a glass transition of -22°C (251K) which does fall nicely on the curve. We suspect that the low literature value was the result of using a low molecular weight oligomeric sample.

The high temperature thermal behavior (DSC) of polydiphenylsiloxane is shown in Figure 2.29, which shows the DSC behavior of a polymer as prepared (lower trace) and a polymer which has been exhaustively purified to remove residual (lithium) impurities (upper trace). Both DSC traces show the crystal-liquid crystal transitions near 265°C, but the thermal behavior at high temperatures is quite different. The sample as recovered from the polymerization medium and purified in the normal manner by washing several times with toluene shows a complex group of endothermic transitions in the 450-480°C range, which we attribute to decomposition reactions. In contrast, the upper trace of Fig. 2.29 shows that decomposition in that temperature range is completely eliminated when the polymer is purified (by repeated solution and precipitation) to reduce the residual lithium content to below 1 ppm. The polymer now shows a reproducible sharp transition at approximately 540°C, which we attribute to the clearing temperature $T_m$.
(melting to the isotropic liquid). The high temperature DSC behavior for two other polydiarylsiloxanes are shown in Figures 2.30 to 2.31. Because of the importance of the residual lithium content on the high temperature properties, all of the polymer samples used to obtain DSC and TGA data had residual lithium concentrations below 1.5 ppm. As shown in Tables 2.8 and 2.9, the various diarylsiloxane polymers examined here are thermally stable polymers, with TGA 10% weight loss temperatures ranging from 455 to 515 °C (Figures 2.32 to 2.39). It might be noted that the DSC data for polydiphenylsiloxane show that the polymer is apparently stable to at least 540°C (with a sharp (melting) transition at this temperature), while TGA shows a 10% weight loss at a lower temperature (511°C). The differences are probably related to the different test conditions, i.e., in the DSC test the sample was in a sealed pan, whereas in the TGA test the sample was exposed to a flowing stream of nitrogen.

The polydiarylsiloxanes examined in this study show glass transition temperatures between 40° and 50°C, but these transitions can only be observed by DSC on the first heating cycle. If the polymers are recovered from the polymerization procedures without heating above their liquid crystal transition temperature, they remain partially amorphous and a glass transition temperature can be detected. However, when heated above the Tlc transition, further crystallization occurs and the amorphous content becomes so low that the transition cannot be observed in the DSC. Figures 2.40 to 2.44 show this effect for polydiarylsiloxanes, in which the Tg transitions for all
these polymers apparent near 50°C on the first heating cycle, but not on the second heating.

The \( T_{lc} \) transitions of this series of polymers pass through a minimum as phenyl groups are replaced by p-tolyl groups, with the end member of the series, polydiphenylsiloxane and polydi(p-tolyl)siloxane, having the highest values (approximately 265°C and 300°C, respectively). The clearing temperatures \( T_m \) also follow the same pattern, decreasing at first with increasing numbers of p-tolyl groups, and then rising with additional units. The \( T_{lc} \) transition temperatures also increase with increasing molecular weight (Figure 2.45) up to a molecular weight of about 55,000 (DP ~ 250), as shown in Figure 2.46 for poly(phenyl/p-tolyl)siloxane. The liquid crystal transition temperatures of the poly(diarylsiloxane)s appears much more sensitive to molecular weight than for other liquid crystal-forming polymers, where the liquid crystal and clearing temperatures generally level off at DP's above 100 (25). The average temperature difference between the liquid crystal transition temperature \( T_{lc} \) and the clearing temperature \( T_m \) for these polymers averages about 285°C, and is much larger than the values found for other types of liquid crystalline polymers (26). Thermal transition data are summarized in Tables 2.10 and 2.11.

The liquid crystalline state of these polymers was observed visually by cross-polarized optical microscopy at 10 to 40°C above their \( T_{lc} \) transition temperatures. However, in order to allow high-magnification photography, the samples were quenched to room temperature, as has been described in
other work (27). By visual observation, the liquid crystalline character was not changed by quenching. Figure 2.47 shows the threaded Schlieren pattern (27) typical of the nematic state which was found for all of the diarylsiloxane polymers except polydi(p-tolyl)siloxane. Figure 2.48 shows evidence of a possible smectic pattern (28) for polydi(p-tolyl)siloxane (the differences in the nematic and smectic textures are much more obvious when observed in color). However, the observation of the smectic structure made with the optical microscopy is as odds with the X-ray results of Ober (29). He found that polydi(p-tolyl)siloxane appeared to also form a nematic liquid crystalline state.

2.4 CONCLUSIONS

We have shown that a variety of polydiaryl/siloxane and poly(aryl/alkyl)siloxane polymers with controlled sequential distribution, molecular weight and distribution can be prepared by the lithium-initiated, ring-opening anionic polymerization of the cyclic trimers in solution. The polymers having phenyl and p-tolyl substituents are of great interest since they have a liquid crystalline state as a consequence of steric interactions which leads to chain rigidity. The liquid crystalline state of the polymers is nematic except for polydi(p-tolyl)siloxane which appears to be smectic by optical microscopy. In contrast to polydiphenylsiloxane and poly(p-tolyl)siloxane which become soluble (in solvents such as diphenyl ether) only at very high temperatures, the mixed poly(phenyl/p-tolyl)siloxanes are soluble in common solvents like tetrahydrofuran and chloroform at room
temperature. We find this somewhat surprising since these polymers are highly crystalline and have liquid crystal transitions above 140°C.

The glass transition temperatures of the diarylsiloxane polymers are near 40°C, but the transitions are only detectable if the polymers have not been heated above the liquid crystal transition temperatures. If heated above their transition temperatures and then cooled, the polymers become so highly crystalline that Tg is no longer detectable by DSC. The liquid crystalline temperature span for these polymers is very large, i.e., the difference between the liquid crystal and the clearing temperatures is about 285°C.

In contrast to the crystalline and liquid crystalline character of polymers with phenyl and p-tolyl substituents, the replacement of a single phenyl group by a methyl group in the repeat triad of diphenyl units is sufficient to destroy both the crystalline and liquid crystalline character of the polymer. This difference in the behavior of the phenyl/p-tolyl systems and the phenyl/methyl systems is attributed to the different molecular volumes of methyl and the p-tolyl substituents and the concomitant differences in the steric interactions on the polymer chain.
2.5 REFERENCES


| Figure 2.1 | Synthesis of cyclotrisiloxanes containing diphenyl and di(p-tolyl) substituents. |
| Figure 2.2 | Synthesis of cyclotrisiloxanes containing diphenyl and phenyl/p-tolyl substituents. |
| Figure 2.3 | Synthesis of cyclotrisiloxanes containing diphenyl and dimethyl or phenyl/methyl substituents. |
| Figure 2.4 | $^{29}$Si NMR spectrum of hexaphenylcyclotrisiloxane. |
| Figure 2.5 | $^{29}$Si NMR spectrum of cyclotrisiloxane PPP' where P is diphenylsiloxane and P' is (phenyl/p-tolyl)siloxane. |
| Figure 2.6 | $^{29}$Si NMR spectrum of cyclotrisiloxane PPP'' where P is diphenylsiloxane and P'' is di(p-tolyl)siloxane. |
| Figure 2.7 | $^{29}$Si NMR spectrum of cyclotrisiloxane P'P'P' where P is (phenyl/p-tolyl)siloxane. |
| Figure 2.8 | $^{29}$Si NMR spectrum of cyclotrisiloxane PP(P/M) where P is diphenylsiloxane and (P/M) is (phenyl/methyl)siloxane. |
| Figure 2.9 | $^{29}$Si NMR spectrum of cyclotrisiloxane PPM where P is diphenylsiloxane and M is dimethylsiloxane. |
| Figure 2.10 | $^{29}$Si NMR spectrum of cyclotrisiloxane PMM where P is diphenylsiloxane and M is dimethylsiloxane. |
| Figure 2.11 | H-NMR spectrum of hexaphenylcyclotrisiloxane. |
| Figure 2.12 | H-NMR spectrum of cyclotrisiloxane PPP' where P is diphenylsiloxane and P' is (phenyl/p-tolyl)siloxane. |
| Figure 2.13 | H-NMR spectrum of cyclotrisiloxane PPP'' where P is diphenylsiloxane and P'' is di(p-tolyl)siloxane. |
| Figure 2.14 | H-NMR spectrum of cyclotrisiloxane P'P'P' where P' is (phenyl/p-tolyl)siloxane. |
| Figure 2.15 | H-NMR spectrum of hexa(p-tolyl)cyclotrisiloxane. |
Figure 2.16  H-NMR spectrum of cyclotrisiloxane PP(P/M) where P is diphenylsiloxane and (P/M) is (Phenyl/methyl) siloxane.

Figure 2.17  H-NMR spectrum of cyclotrisiloxane PPM where P is diphenylsiloxane and M is dimethylsiloxane.

Figure 2.18  H-NMR spectrum of cyclotrisiloxane PMM where P is diphenylsiloxane and M is dimethylsiloxane.

Figure 2.19  $^{29}$Si NMR spectrum of polymer PPP' where P is diphenylsiloxane and P' is (phenyl/p-toly)l siloxane.

Figure 2.20  $^{29}$Si NMR spectrum of polymer PPP" where P is diphenylsiloxane and P" is di(p-toly)l siloxane.

Figure 2.21  $^{29}$Si NMR spectrum of polymer P'P'P' where P' is (phenyl/p-toly)l siloxane.

Figure 2.22  H-NMR spectrum of polymer PPP' where P is diphenylsiloxane and P' is (phenyl/p-toly)l siloxane.

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   ■ Samples prepared in this investigation
   ▲ Literature value (28)

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-3.5, 23ppm
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140°C
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Samples prepared in this investigation

Value (28) ▼

Melting Groups, mole %

Glass Transition Temperature vs. Melting Substitution

T^G/K
Figure 2.29  High-temperature DSC behavior of as-prepared and of purified polydiethyleneoxide.

Temperature, °C

Heat flow →

as prepared

after extensive purification (IU > 1 ppm)
Figure 2.30 **High Temperature DSC Behavior of Partially Polymerized PP**

- **(phenyl)triphenylsiloxane**

Where P is diphenylsiloxane and P' is (phenyl)$_3$Si.
where \( P \) is diphenylsiloxyene and \( P' \) is diphenyl(toly)siloxyene.

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490°C
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Temperature °C

Heat flow
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Figure 2.43

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Figure 2.4.5

DSC heats of polymer PPh with different molecular weight
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---

Temperature (°C)

DSC Heat Flow (mW)
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Temperature

10ойловіді

Sample quenched from 300°C to room

Optical micrograph (900x) of "smectic" texture of polypeptide

Figure 2.48
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<th>( \Delta H_m ) J/gm</th>
<th>(^{29}\text{Si NMR chemical shift} ) ppm</th>
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Table 2.1 Thermal behavior and \(^{29}\text{Si NMR chemical shifts of cyclotrisiloxanes containing phenyl and methyl substituents.} \)
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<th>Cyclic trimer</th>
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<th>$^{29}$Si NMR chemical shift ppm</th>
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Table 2.2 Thermal behavior and $^{29}$Si NMR chemical shifts of cyclotrisiloxanes containing phenyl and p-tolyl substituents.
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<td>Methyl</td>
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<td>(b)</td>
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Table 2.3 H-NMR chemical shifts of cyclotrisiloxanes containing phenyl and methyl substituents
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<th>Chemical shift (ppm)</th>
<th>Ratio of H(phenyl)/H(alkyl)</th>
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Table 2.4  H-NMR chemical shifts of cyclotrisiloxanes containing phenyl and p-tolyl substituents.
Table 2.5  Polymerization yield and the liquid crystal transition temperature of polydi(p-tolyl)siloxane as a function of polymerization variables. THF promoter levels: “high” ~ 7 vol. %, “low” ~ 3.5 vol. %.
<table>
<thead>
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<th>Polymer Repeat Unit</th>
<th>Mol. Wt</th>
<th>Yield (%)</th>
<th>Solubility</th>
<th>Chemical shift ($^{29}$Si NMR, ppm)</th>
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<tbody>
<tr>
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<td>50</td>
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<td>-32.68 (v) -33.28 (vw) -46.42 (vw) -46.91 -47.24 (vw)</td>
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<tr>
<td>Ph−Si−O−Si−O−Ph</td>
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<td>83</td>
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<tr>
<td>Ph−Si−O−Si−O−Me</td>
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<td>30</td>
<td>Yes</td>
<td>-19.27 (vw) -20.47 -21.67 (w) -47.60 (vw) -48.37</td>
</tr>
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</table>

Table 2.6 Polymerization yields, molecular weights, solubility and $^{29}$Si NMR chemical shifts of siloxane polymers having phenyl and methyl substituents.

"w" = weak, "vw" = very weak.
<table>
<thead>
<tr>
<th>Polymer Repeat Unit</th>
<th>Mol. Wt.</th>
<th>Yield (%)</th>
<th>Solubility CHCl₃, R.T.</th>
<th>Chemical shift ($^{29}$Si NMR)</th>
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Table 2.7 Polymerization yields, molecular weights, solubility and $^{29}$Si NMR chemical shifts of siloxane polymers having phenyl and p-tolyl substituents.
<table>
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<th>Polymer Repeat Unit</th>
<th>TGA temp. °C 10% weight loss</th>
<th>Residual lithium content (ppm)</th>
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<td>Ph</td>
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<td>Ph</td>
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<td>Ph</td>
<td>454</td>
<td>&lt; 1.5</td>
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<tr>
<td>Ph</td>
<td>469</td>
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<tr>
<td>p-Tol</td>
<td>516</td>
<td>&lt; 1</td>
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Table 2.8 Thermal gravimetric (TGA) behavior of siloxane polymers having phenyl and p-tolyl substituents.
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<th>Polymer repeat unit</th>
<th>TGA, temp. at 10% weight loss, °C</th>
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Table 2.9  Thermal gravimetric (TGA) behavior of siloxane polymers having phenyl and methyl substituents.
<table>
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<tr>
<th>Polymer repeat unit</th>
<th>$T_g$ (°C)</th>
<th>$T_{le}$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$T_m - T_{le}$ (°C)</th>
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<td>460</td>
<td>275</td>
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<td>Ph(\text{Si-O-Si-}\text{O-Si-}\text{O-}\text{p-Tol})</td>
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<td>140</td>
<td>430</td>
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<td>50</td>
<td>160</td>
<td>450</td>
<td>300</td>
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<tr>
<td>p-Tol(\text{Si-O-Si-}\text{O-Si-}\text{O-}\text{p-Tol})</td>
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<td>300</td>
<td>480</td>
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Table 2.10 Thermal transitions of siloxane polymers having phenyl and p-tolyl substituents.
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<th>$T_{lc} \degree C$</th>
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Table 2.11 Thermal transitions of siloxane polymers having phenyl and methyl substituents.
CHAPTER 3

SYNTHESIS AND PROPERTIES OF DIARYLSILOXANE AND (ARYL/METHYL)SILOXANE POLYMERS: SOLUTION AND RHEOLOGICAL PROPERTIES
3.1 INTRODUCTION

Liquid crystalline polymers are currently receiving a great deal of attention as a result of their excellent strength and high temperature properties. The polymers of greatest interest have been the polyarylesters (1) and polyaramids (2). The solution and rheological properties of these main chain liquid crystalline polymers have been the subject of a number of investigations (3-9), but there are many questions yet unanswered concerning their solution behavior. Most polymers of these types are produced by condensation reactions which limit the molecular weight range available and also give a broad molecular weight distribution. Even more important, such liquid crystalline polymers dissolve in only a few (usually noxious) solvents such as concentrated sulfuric or phosphoric acids and makes the characterization of their molecular and solution properties difficult. Additional complications also arise from polyelectrolyte effects from protonation of the polymers when dissolved in strong acids (5,7).

Another class of polymers which have been shown to have liquid crystalline states are certain polydialkylsiloxanes, e.g., polydiethylsiloxane (10) and polydiarylsiloxanes such as polydiphenylsiloxane (11). These siloxane polymers have a great advantage over the conventional liquid crystalline polymers produced by condensation reactions in that they can be obtained with any desired molecular weight and with a narrow molecular weight distribution using anionic polymerization techniques.
In addition, certain of the polydiarylsiloxanes which have a liquid crystalline state are quite soluble in common solvents at room temperature.

The published work on the properties of the polydialkylsiloxanes and polydiarylsiloxanes which have a liquid-crystalline state in bulk has focused on the thermal behavior of the various crystal transitions. Solution and related chain stiffness properties of the liquid crystalline dialkylsiloxanes have only been reported for polydipropylsiloxane (12). In this chapter, we report on the solution properties of various diarylsiloxanes which have a liquid-crystalline state, and include the solution properties as a function of molecular weight (determination of the Mark-Houwink-Sakurada parameters) and the rheological behavior as a function of concentration.

In Chapter 2, we described some of the thermal properties of various polydiarylsiloxanes with phenyl and p-tolyl substituents. These polymers are highly crystalline and, depending on composition, melt to a liquid crystalline state at temperature from 150 to 300°C. Melting to the isotropic liquid state occurs at temperatures near or above 500°C. The polymers which have been of greatest interest for this investigation are those which contain both phenyl and p-tolyl substituents on the siloxane backbone. By combining these substituents, the liquid crystalline transition temperatures are reduced, and, more importantly, the polymers become soluble in common solvents at room temperature. In contrast, the
polymers which contain only phenyl substituents (polydiphenylsiloxane) or only p-tolyl substituents (poly(di-p-tolyl)siloxane) are soluble in few solvents and then only at temperatures above 150°C - with concomitant difficulties in the characterization of the solution properties. We have investigated the solution properties of three varieties of polydiarylsiloxanes which have mixed phenyl and p-tolyl substituents on the siloxane backbone. They are:

\[
\begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{p-Tol} \\
\text{Si} \\
\text{O} \\
\text{Si} \\
\text{O} \\
\text{Si} \\
\text{O} \\
\text{Si} \\
\text{O} \\
\end{array}
\]  
(designated as PPP')

\[
\begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{p-Tol} \\
\text{Si} \\
\text{O} \\
\text{Si} \\
\text{O} \\
\text{Si} \\
\text{O} \\
\text{Si} \\
\text{O} \\
\end{array}
\]  
(PPP’’)

\[
\begin{array}{c}
\text{Ph} \\
\text{Ph} \\
\text{Ph} \\
\text{p-Tol} \\
\text{p-Tol} \\
\text{p-Tol} \\
\text{Si} \\
\text{O} \\
\text{Si} \\
\text{O} \\
\text{Si} \\
\text{O} \\
\text{Si} \\
\text{O} \\
\end{array}
\]  
(P'P’P’’)

where P represents a diphenylsiloxane group, P' represents a phenyl/(p-tolyl)siloxane group and P'' represents a di(p-tolyl)siloxane group in the repeat triads of these polymers. Note that these triad sequences repeat
exactly along the polymer chains - "scrambling" or randomization of the individual siloxane units does not occur with the polymerization method used to prepare these polymers (11).

3.2 EXPERIMENTAL

3.2.1 Polymer Synthesis

The mixed poly(phenyl/p-toly)siloxanes with different molecular weights have been prepared by the lithium-initiated, ring-opening polymerization of the cyclic trimers in diphenyl ether solution. The detailed procedure was described in the preceding chapter (11). The polymerization reactions were done at 160°C under a purified nitrogen atmosphere, using sec-butyl lithium as the polymerization initiator and dimethylsulfoxide (DMSO) or tetrahydrofuran (THF) as the promoter. The polymers were recovered by precipitation with methanol and purified from residual cyclics by fractional precipitation using a toluene/methanol mixture. Polymers were dried in a vacuum oven at 100°C for 16 hours.

3.2.2 Molecular Weights

The molecular weights of polymers were obtained by using gel permeation chromatography (GPC) in toluene or chloroform solution at 40°C. The reported molecular weight are based on polystyrene standards, but corrected to "absolute" molecular weights using the "Universal
Calibration” (13) relationship, i.e., by the relationship \([\text{M.W.}]_\text{Si} [\eta]_\text{Si} = [\text{M.W.}]_\text{ps} [\eta]_\text{ps}\) at equal elution (hydrodynamic) volumes.

3.2.3 Solubilities

The solubilities of the polymers in various solvents were determined by mixing 1% of the polymer with solvents, and observing the solubility after three days at 25°C or one day at 40°C. Solvents with solubility parameter ranged from 7.4 (heptane) to 11.9 (acetonitrile) were used.

3.2.4 Intrinsic Viscosities

Ubbelohde viscometers (Cannon Instruments Co.) were used for viscosity measurements. Intrinsic viscosities at 25°C were determined by extrapolation of reduced viscosities and inherent viscosities obtained at four or five different concentrations to a common intercept at zero concentration. The drop times were sufficiently long (>100 seconds) that kinetic energy corrections were not necessary.

3.2.5 Viscosities of Concentrated Solutions

Viscosities as a function of concentration of the P'P'P' polymer in toluene at 25°C were determined using a Carri Med CLS-100 Controlled-
Stress Rheometer, using cone-plate geometry with a 60 mm cone and 1° cone angle.

3.3 RESULTS AND DISCUSSION

The solubility of various polydiarylsiloxanes in a variety of solvents is shown in Tables 3.1 to 3.2. Polydiphenylsiloxane (PPP) and polydi(p-tolyl)siloxane (PP'PP"") are not soluble in any known solvent at room temperature, while the three "mixed" poly(phenyl/p-tolyl)siloxanes (PPP', PPP" and PP'PP') are soluble at or near room temperature in many solvents. The polymers PPP" and PP'PP' are soluble at 25°C in solvents with solubility parameters ranging from 8.6 to 9.7, while the polymer PPP' with only one p-tolyl group is soluble at 40°C in solvents with solubility parameters ranged from 9.3 to 9.7 (this polymer remains in solution in these solvents when cooled to 25°C).

Intrinsic viscosities were obtained by extrapolation of the relative solution viscosity data to zero concentration, using both the Huggin's equation (14)

\[ \eta_{sp}/c = [\eta] + k[\eta]^2c \]

and the Kraemer's equation (15)

\[ (\ln \eta)_{sp}/c = [\eta] + k'[\eta]^2c \]
where \( \eta_r = \eta / \eta_0 \), \( \eta_{sp} = \eta_{r-1} \) and \( k \) and \( k' \) are the Huggins and Kraemer constants, respectively, \( (k - k')c = 0.5 \). The extrapolations of \( \eta_{sp}/c \) (reduced viscosity) and \( (\ln \eta_r)/c \) (inherent viscosity) versus \( c \) for polymer PPP' with different molecular weights are shown in Figure 3.1 to 3.6, for polymers PPP" are shown in Figures 3.7 to 3.12 and for polymers P'P'P' are shown in Figures 3.13 to 3.17. Most of the data extrapolate to the same intercept at \( c = 0 \), with the difference in slopes having almost the theoretical value of 0.5. The plots of \( \eta_{sp}/c \) versus concentration for each polymer with different molecular weights are combined together as shown in Figures 3.18 to 3.20. The plot is linearly dependent on concentration.

Tables 3.3 to 3.5 give the intrinsic viscosities as a function of molecular weight for the three mixed poly(phenyl/p-tolyl)siloxanes examined here, and log-log plots of these data are shown in Figures 3.21 to 3.23. The parameters "\( a \)" and "\( K \)" of the Mark-Houwink-Sakurada equation \( [\eta] = KM^a \) obtained from these Figures are summarized in Table 3.6 and listed below:

PPP' \[ [\eta] = 4.94 \times 10^{-5} M_w^{0.75} \text{ in chloroform} \]

PPP" \[ [\eta] = 9.84 \times 10^{-5} M_w^{0.71} \text{ in toluene} \]

PPP" \[ [\eta] = 3.19 \times 10^{-5} M_w^{0.81} \text{ in toluene (neglecting lowest molecular weight)} \]

P'P'P' \[ [\eta] = 1.72 \times 10^{-5} M_w^{0.86} \text{ in toluene} \]

with \( [\eta] \) in units of dl/g.
As indicated, if the lowest molecular weight sample \( (M=8400) \) of the PPP" series is neglected, the Mark-Houwink-Sakurada exponent increases to 0.81 from 0.71. A justification for neglecting that very low molecular weight \( (DP \sim 70) \) sample is given by the data of Bianchi, et al. (16), who have shown that the exponent of all linear polymer systems tends towards lower values (towards 0.5) as molecular weights are reduced.

It is of interest to note that the coefficients reported for polydimethylsiloxane (a very flexible chain) in toluene at 25°C have ranged from 0.5 (16) to 0.84 (17), with intermediate values of 0.59 (18), 0.62 (19), 0.66 (20) and 0.72 (21). Values reported for other siloxane polymers are 0.58 for polydipropylsiloxane (12) and 0.78 for poly(methyl/phenyl)siloxane (23), both also in toluene at 25°C. It is obvious from the values of these exponents that they do not correlate with the tendency to form a liquid crystalline state in the bulk, since polydipropylsiloxane \( (a = 0.58) \) does have a liquid crystalline state (22), while poly(methyl/phenyl)siloxane \( (a = 0.78) \) does not (23). Of course, the value of the exponent is also a function of the quality of the solvent and this will be affected by the polymer composition, so the comparison is only completely valid for solution of similar thermodynamic quality, i.e., theta solutions. With regard to the tendency to form a liquid crystalline state in bulk, we have shown (11) for siloxane polymers having phenyl and methyl substituents that the presence of a single methyl group in the repeat triads is sufficient to completely eliminate both the crystalline and liquid crystalline states, i.e., the polymer with the repeat
hexaphenylsiloxane triad is highly crystalline and liquid crystalline, while the polymer with the repeat pentaphenyl/methyl triad is neither crystalline nor liquid crystalline.

The Mark-Houwink-Sakurada exponents found here for the polydiarylsiloxanes are somewhat higher than those found for other siloxane polymers, most probably a consequence of the enhanced bulkiness of the diaryl substituents and resulting enhanced steric interactions along the siloxane chain. However, the values are much lower than those expected for rigid rod polymer (a > 1.0). The values of the exponents are at the upper end of values expected for random coil polymers, and probably indicate that the polymers behave as random coil polymers in solution, but with a relative large persistence length.

The shear viscosity of the P'P'F' polymer increases monotonically with increasing polymer concentration, as shown in Figure 3.24. There is no indication of a transition to a liquid crystalline (anisotropic) state above a critical concentration as has been observed with rigid chain polymers such as the aramids in sulfuric acid solution (8-9). This fact, together with the Mark-Houwink-Sakurada exponent being lower than expected for a rigid rod, again indicates that the poly(phenyl/p-tolyl)siloxanes do not behave as typical rigid rod polymers in solution, although they do have liquid-crystalline states in bulk.
3.4 CONCLUSIONS

The solution properties of three types of polydiarylsiloxanes having both phenyl and p-tolyl substituents on the siloxane backbone have been evaluated in order to relate their chain stiffness properties in solution to the high temperature liquid crystalline state which is observed in bulk. These "mixed" phenyl/p-tolyl diarylsiloxanes were chosen to investigate because of experimental convenience. In contrast to the "unmixed" polydiphenyl- and polydi(p-tolyl)siloxane, they are soluble at room temperature in common solvents, whereas the unmixed polymers are soluble only at temperatures above 150°C. The diaryl polymers PPP" and P'P'P' are soluble at 25°C in solvents with solubility parameters between 8.6 and 9.7. Polymer PPP' is not soluble at 25°C, but will dissolve at 40°C in solvents with solubility parameters between 9.3 and 9.7, and will then remain in solution when cooled to 25°C. The values of Mark-Houwink-Sakurada exponent "a" are between 0.75 and 0.86. These values are below the values expected for rigid rod polymers, but at the upper end of values expected for random coil polymers in good solvents. Additional indication that these polymers do not behave as rigid rods in solution is the absence of an anisotropic state above a critical concentration, as expected from theory (24) and observed with rigid rod polymers such as the aramids (8-9).
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Figure 3.2 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and $\ln \eta_r$ (inherent viscosity) vs. concentration to obtain $[\eta]$ for sample PPP$'$ with molecular weight of 56,000.

Figure 3.3 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and $\ln \eta_r$ (inherent viscosity) vs. concentration to obtain $[\eta]$ for sample PPP$'$ with molecular weight of 105,000.

Figure 3.4 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and $\ln \eta_r$ (inherent viscosity) vs. concentration to obtain $[\eta]$ for sample PPP$'$ with molecular weight of 132,000.

Figure 3.5 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and $\ln \eta_r$ (inherent viscosity) vs. concentration to obtain $[\eta]$ for sample PPP$'$ with molecular weight of 133,000.

Figure 3.6 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and $\ln \eta_r$ (inherent viscosity) vs. concentration to obtain $[\eta]$ for sample PPP$'$ with molecular weight of 223,000.

Figure 3.7 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and $\ln \eta_r$ (inherent viscosity) vs. concentration to obtain $[\eta]$ for sample PPP$''$ with molecular weight of 8,400.

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Figure 3.16 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and $\ln \eta_r$ (inherent viscosity) vs. concentration to obtain $[\eta]$ for sample P'P'P' with molecular weight of 97,000.
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Figure 3.18 Plot of $\eta_{sp}/c$ (reduced viscosity) vs. concentration for sample PPP' with different molecular weights.

Figure 3.19 Plot of $\eta_{sp}/c$ (reduced viscosity) vs. concentration for sample PPP'' with different molecular weights.

Figure 3.20 Plot of $\eta_{sp}/c$ (reduced viscosity) vs. concentration for sample P'P'P' with different molecular weights.

Figure 3.21 Log $[\eta]$ vs. log MW for sample PPP'.

Figure 3.22 Log $[\eta]$ vs. log MW for sample PPP''. Solid line indicates best fit using all data. Dotted line indicates best fit neglecting lowest molecular weight sample.

Figure 3.23 Log $[\eta]$ vs. log MW for sample P'P'P'.

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Table 3.5  Intrinsic viscosity vs. molecular weight for sample P'P'P'.

Table 3.6  The constants K and a of Mark-Houwink-Sakurada equation for samples PPP', PPP'' and P'P'.
Polymer: PPP' where P: diphenylsiloxane and
(M. W. = 33,000) P': (phenyl/p-tolyl)siloxane

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Figure 3.1 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and $\ln \eta_r$ (inherent viscosity) vs. concentration to obtain $[\eta]$ for sample PPP' with molecular weight of 33,000.
Polymer: PPP' where P: diphenylsiloxane and (M. W. = 56,000) P': (phenyl/p-tolyl)siloxane

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Figure 3.2 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and ln $\eta_r$ (inherent viscosity) vs. concentration to obtain $[\eta]$ for sample PPP' with molecular weight of 56,000.
Polymer: PPP' where P: diphenylsiloxane and
(M. W.= 105,000) P': (phenyl/p-tolyl)siloxane

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Figure 3.3 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and $\ln \eta_r$ (inherent viscosity) vs. concentration to obtain $[\eta]$ for sample PPP' with molecular weight of 105,000.
Polymer: PPP' where $P$: diphenylsiloxane and
(M. W. = 132,000) $P'$: (phenyl/p-tolyl) siloxane

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Figure 3.4 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and $\ln \eta_r$ (inherent viscosity) vs. concentration to obtain $[\eta]$ for sample PPP' with molecular weight of 132,000.
Polymer: PPP' where P: diphenylsiloxane and (M. W. = 133,000) P': (phenyl/p-tolyl)siloxane

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Figure 3.5 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and ln $\eta_r$ (inherent viscosity) vs. concentration to obtain $[\eta]$ for sample PPP' with molecular weight of 133,000.
Polymer: PPP' where P: diphenylsiloxane and (M. W. = 223,000) P': (phenyl/p-tolyl)siloxane

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Figure 3.6 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and $\ln \eta_r$ (inherent viscosity) vs. concentration to obtain $[\eta]$ for sample PPP' with molecular weight of 223,000.
Polymer: PPP" where P: diphenylsiloxane and (M. W.= 8,400) P": di(p-tolyl)siloxane

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Figure 3.7 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and $\ln \eta_r$ (inherent viscosity) vs. concentration to obtain $[\eta]$ for sample PPP" with molecular weight of 8,400.
Polymer: PPP" where P: diphenylsiloxane and (M. W.= 34,000) P": di(p-tolyl)siloxane

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Figure 3.8 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and $\ln \eta_r$ (inherent viscosity) vs. concentration to obtain $[\eta]$ for sample PPP" with molecular weight of 34,000.
Polymer: PPP" where P: diphenylsiloxane and (M. W.= 38,000) P": di(p-tolyl) siloxane

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<tbody>
<tr>
<td>0.615</td>
<td>0.1832</td>
<td>0.1736</td>
</tr>
<tr>
<td>1.000</td>
<td>0.1889</td>
<td>0.1731</td>
</tr>
<tr>
<td>1.599</td>
<td>0.1965</td>
<td>0.1708</td>
</tr>
<tr>
<td>2.665</td>
<td>0.2079</td>
<td>0.1654</td>
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</table>

Figure 3.9 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and ln $\eta_r$ (inherent viscosity) vs. concentration to obtain [$\eta$] for sample PPP" with molecular weight of 38,000.
Polymer: PPP" where \( P: \) diphenylsiloxane and (M. W. = 51,000) \( P": \) di(p-tolyl)siloxane

<table>
<thead>
<tr>
<th>Conc. (g/dl)</th>
<th>Red. Vis. (dl/g)</th>
<th>Inh. Vis. (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.535</td>
<td>0.2105</td>
<td>0.1994</td>
</tr>
<tr>
<td>0.870</td>
<td>0.2165</td>
<td>0.1984</td>
</tr>
<tr>
<td>1.391</td>
<td>0.2251</td>
<td>0.1958</td>
</tr>
<tr>
<td>2.319</td>
<td>0.2388</td>
<td>0.1900</td>
</tr>
</tbody>
</table>

Figure 3.10 Extrapolation of \( \eta_{\text{sp/c}} \) (reduced viscosity) and ln \( \eta_r \) (inherent viscosity) vs. concentration to obtain [\( \eta \)] for sample PPP" with molecular weight of 51,000.
Polymer: PPP" where $P$: diphenylsiloxane and
(M. W. = 55,000) $P"$: di(p-tolyl)siloxane

<table>
<thead>
<tr>
<th>Conc. (g/dl)</th>
<th>Red. Vis. (dl/g)</th>
<th>Inh. Vis. (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.474</td>
<td>0.2167</td>
<td>0.2063</td>
</tr>
<tr>
<td>0.770</td>
<td>0.2242</td>
<td>0.2068</td>
</tr>
<tr>
<td>1.231</td>
<td>0.2338</td>
<td>0.2054</td>
</tr>
<tr>
<td>2.052</td>
<td>0.2478</td>
<td>0.2003</td>
</tr>
</tbody>
</table>

Figure 3.11 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and
$\ln \eta_r$ (inherent viscosity) vs. concentration to
obtain $[\eta]$ for sample PPP" with molecular
weight of 55,000.
Polymer: PPP" where

\[ P: \text{ diphenylsiloxane and} \]
\[ (M. \ W.= \ 77,000) \]
\[ P": \text{ di(p-tolyl)siloxane} \]

<table>
<thead>
<tr>
<th>Conc. (g/dl)</th>
<th>Red. Vis.(dl/g)</th>
<th>Inh. Vis. (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.381</td>
<td>0.3366</td>
<td>0.3167</td>
</tr>
<tr>
<td>0.620</td>
<td>0.3421</td>
<td>0.3103</td>
</tr>
<tr>
<td>0.991</td>
<td>0.3566</td>
<td>0.3054</td>
</tr>
<tr>
<td>1.652</td>
<td>0.3807</td>
<td>0.2954</td>
</tr>
<tr>
<td>2.478</td>
<td>0.4234</td>
<td>0.2895</td>
</tr>
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</table>

**Figure 3.12** Extrapolation of \( \eta_{sp}/c \) (reduced viscosity) and \( \ln \eta_r \) (inherent viscosity) vs. concentration to obtain \([\eta]\) for sample PPP" with molecular weight of 77,000.
Polymer: \( P'P'P' \) where \( P' \): (phenyl/p-tolyl)siloxane (M. W.= 40,000)

<table>
<thead>
<tr>
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<th>Red. Vis. (dl/g)</th>
<th>Inh. Vis. (dl/g)</th>
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<tr>
<td>0.788</td>
<td>0.166</td>
<td>0.156</td>
</tr>
<tr>
<td>1.575</td>
<td>0.175</td>
<td>0.154</td>
</tr>
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<td>2.625</td>
<td>0.186</td>
<td>0.152</td>
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<tr>
<td>3.938</td>
<td>0.201</td>
<td>0.148</td>
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</table>

**Figure 3.13** Extrapolation of \( \eta_{sp}/c \) (reduced viscosity) and \( \ln \eta_r \) (inherent viscosity) vs. concentration to obtain \([\eta]\) for sample \( P'P'P' \) with molecular weight of 40,000.
Polymer: P'P'P' where P': (phenyl/p-tolyl)siloxane (M. W.= 62,000)

<table>
<thead>
<tr>
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<th>Red. Vis.(dl/g)</th>
<th>Inh. Vis. (dl/g)</th>
</tr>
</thead>
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<tr>
<td>0.787</td>
<td>0.221</td>
<td>0.204</td>
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<tr>
<td>1.573</td>
<td>0.239</td>
<td>0.203</td>
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<tr>
<td>2.622</td>
<td>0.260</td>
<td>0.198</td>
</tr>
<tr>
<td>3.933</td>
<td>0.286</td>
<td>0.192</td>
</tr>
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</table>

Figure 3.14 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and $\ln \eta_r$ (inherent viscosity) vs. concentration to obtain $[\eta]$ for sample P'P'P' with molecular weight of 62,000.
Polymer: P'P'P' where P': (phenyl/p-tolyl)siloxane
(M. W.= 86,000)

<table>
<thead>
<tr>
<th>Conc. (g/dl)</th>
<th>Red. Vis.(dl/g)</th>
<th>Inh. Vis. (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.618</td>
<td>0.308</td>
<td>0.282</td>
</tr>
<tr>
<td>1.236</td>
<td>0.328</td>
<td>0.276</td>
</tr>
<tr>
<td>2.059</td>
<td>0.355</td>
<td>0.266</td>
</tr>
<tr>
<td>3.089</td>
<td>0.389</td>
<td>0.255</td>
</tr>
</tbody>
</table>

Figure 3.15  Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and $\ln \eta_r$ (inherent viscosity) vs. concentration to obtain $[\eta]$ for sample P'P'P' with molecular weight of 86,000.
Polymer: P'P'P' where P': (phenyl/p-tolyl)siloxane (M. W.= 97,000)

<table>
<thead>
<tr>
<th>Conc. (g/dl)</th>
<th>Red. Vis.(dl/g)</th>
<th>Inh. Vis. (dl/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.373</td>
<td>0.339</td>
<td>0.319</td>
</tr>
<tr>
<td>0.586</td>
<td>0.345</td>
<td>0.314</td>
</tr>
<tr>
<td>0.820</td>
<td>0.356</td>
<td>0.312</td>
</tr>
<tr>
<td>1.367</td>
<td>0.376</td>
<td>0.303</td>
</tr>
<tr>
<td>2.051</td>
<td>0.402</td>
<td>0.293</td>
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</table>

Figure 3.16 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and $\ln \eta_r$ (inherent viscosity) vs. concentration to obtain [$\eta$] for sample P'P'P' with molecular weight of 97,000.
Polymer: P'P'P' where P': (phenyl/p-tolyl)siloxane (M. W. = 116,000)

<table>
<thead>
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<th>Inh. Vis. (dl/g)</th>
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<tr>
<td>0.331</td>
<td>0.409</td>
<td>0.384</td>
</tr>
<tr>
<td>0.496</td>
<td>0.421</td>
<td>0.383</td>
</tr>
<tr>
<td>0.794</td>
<td>0.442</td>
<td>0.379</td>
</tr>
<tr>
<td>1.323</td>
<td>0.474</td>
<td>0.368</td>
</tr>
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<td>1.985</td>
<td>0.507</td>
<td>0.351</td>
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</table>

Figure 3.17 Extrapolation of $\eta_{sp}/c$ (reduced viscosity) and $\ln \eta_r$ (inherent viscosity) vs. concentration to obtain $[\eta]$ for sample P'P'P' with molecular weight of 116,000.
Figure 3.18  Plot of $\eta_{sp}/c$ (reduced viscosity) vs. concentration for sample PPP with different molecular weights.
Figure 3.19  Plot of $\eta_{sp}/c$ (reduced viscosity) vs. concentration for sample PPP" with different molecular weights.
Figure 3.20 Plot of $\eta_{sp}/c$ (reduced viscosity) vs. concentration for sample P'P'P' with different molecular weights.
Figure 3.21  Log $[\eta]$ vs. log MW for sample PPP'.
Figure 3.22  Log [η] vs. log MW for sample PPP'. Solid line indicates best fit using all data. Dotted line indicates best fit neglecting lowest molecular weight sample.
Figure 3.23 Log [η] vs. log MW for sample P'P'P'.
Figure 3.24  Shear viscosity of sample P'P'P' vs. concentration in toluene.
Table 3.1: Solubilities of various derivatives in solvents

<table>
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<tr>
<th>N</th>
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<th>N</th>
<th>N</th>
<th>N</th>
<th>N</th>
<th>N</th>
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<tbody>
<tr>
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<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
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<td>N</td>
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<td>N</td>
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<table>
<thead>
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<table>
<thead>
<tr>
<th>2.0</th>
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<th>6.5</th>
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<table>
<thead>
<tr>
<th>Polymer</th>
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<tr>
<td>Polymer</td>
</tr>
<tr>
<td>------------------</td>
</tr>
</tbody>
</table>

Table 3.2: Solubilities of various diaryl siloxanes in solvents of varying solubility parameters at 40°C.
Table 3.3  Intrinsic Viscosity vs. Molecular Weight for Sample PpP:

<table>
<thead>
<tr>
<th>M&quot;/M&quot;</th>
<th>M, V, in Chlrorom</th>
<th>Polymer:</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.465</td>
<td>0.0000</td>
<td>(d/L)</td>
</tr>
<tr>
<td>0.339</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>0.328</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>0.296</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>0.285</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>0.259</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>0.196</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>0.190</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>0.164</td>
<td>0.0000</td>
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</tr>
<tr>
<td>0.161</td>
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<tr>
<td>0.159</td>
<td>0.0000</td>
<td></td>
</tr>
<tr>
<td>0.156</td>
<td>0.0000</td>
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</table>
Table 3.4: Intrinsic viscosity vs. molecular weight for sample P

<table>
<thead>
<tr>
<th>M (g/mol)</th>
<th>M&quot;W&quot; M&quot;M&quot;</th>
<th>M&quot;W&quot;</th>
<th>n</th>
<th>M&quot;W&quot;</th>
<th>M&quot;M&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>77,000</td>
<td>1.07</td>
<td>0.7</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>80,000</td>
<td>1.08</td>
<td>0.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>85,000</td>
<td>1.11</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>51,000</td>
<td>1.13</td>
<td>1.3</td>
<td></td>
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</tr>
<tr>
<td>34,000</td>
<td>1.09</td>
<td>0.9</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>38,000</td>
<td>1.13</td>
<td>1.3</td>
<td></td>
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<tr>
<td>60,000</td>
<td>1.19</td>
<td>1.9</td>
<td></td>
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<td>84,000</td>
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<td>0.4</td>
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Intrinsic Viscosity in Toluene

Polymers:

---

---
Table 3.5 Intrinsic viscosity vs. molecular weight for sample PDP.

<table>
<thead>
<tr>
<th>Molecular Weight (M)</th>
<th>Intrinsic Viscosity in Toluene (cP)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.07</td>
<td>116.000</td>
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<tr>
<td>1.00</td>
<td>97.000</td>
</tr>
<tr>
<td>1.00</td>
<td>86.000</td>
</tr>
<tr>
<td>1.21</td>
<td>62.000</td>
</tr>
<tr>
<td>1.13</td>
<td>40.000</td>
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M wastewater polymer:

![Polymer Structure]
The constants $K$ and $a$ of Mark-Houwink-Sakurada equation for samples of $pp$ and $pp$.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>$K$ (x $10^3$)</th>
<th>$a$</th>
<th>$[\eta]$ (M&lt;sup&gt;_w&lt;/sup&gt;)</th>
<th>$\tilde{M}_n$ (g/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>0.86</td>
<td>1.72</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>0.71</td>
<td>9.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>0.75</td>
<td>4.94</td>
<td></td>
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</table>

Polymers
CHAPTER 4

SYNTHESIS AND PROPERTIES OF DIARYLSILOXANE AND (ARYL/METHYL)SILOXANE POLYMERS: NEW ARYL SUBSTITUENTS
4.1 INTRODUCTION

In the previous two chapters, we have described the thermal and solution properties of a number of diarylsiloxane polymers having phenyl or p-tolyl substituent groups. We showed that polydiphenylsiloxane and poly(p-tolyl)siloxane are highly crystalline and melt at high temperatures (265° and 300°C) to liquid crystalline states. The liquid crystalline character is still observed in the "mixed" poly(phenyl/p-tolyl)siloxanes, although the transition temperatures are lower and the solubility properties are greatly different from the "parent" polymers, polydiphenylsiloxane and poly(p-tolyl)siloxane. We also showed (1) that the replacement of one or more phenyl group(s) by methyl group(s) in the repeat triad of the polymer chain (e.g., changing the repeat triad from hexaphenyl to pentaphenyl/monomethyl) completely eliminated the crystalline and liquid crystalline character of the polymer.

In this chapter, we report on the synthesis and properties of several new diarylsiloxane polymers, with the objective of providing additional information concerning the relationship of structure to properties for this class of polymers. We shall particularly emphasize the thermal properties of these polymers.

4.2 EXPERIMENTAL

4.2.1 Materials

4-Bromoanisole (Aldrich), 1-bromo-4-propylbenzene (Aldrich), 2-chlorotoluene, 3-chlorotoluene, silicone tetrachloride (Aldrich), and sec-butyl lithium (Aldrich) were used without further purification. Diphenyl ether (DPE, Aldrich) was used as the solvent for the anionic polymerization and was purified by vacuum distillation, followed by passing through activated alumina and then distilled again over calcium hydride. Dimethylsulfoxide (DMSO, Aldrich) and hexane (Fisher) were
distilled over calcium hydride before use. Magnesium turnings (Aldrich) were dried at 100°C under vacuum to remove any trace of water.

4.2.2 Synthesis of the Cyclic Trimers

The general procedure used to prepare the cyclotrisiloxanes of this investigation was by cyclization of the corresponding dichlorosilanes with ZnO (2). The diaryldichlorosilanes were prepared by the Grignard reaction between silicone tetrachloride and the arylmagnesium bromides or chlorides (3-6). The detailed procedures are described in the following section and an example is illustrated in Figure 4.1.

Di(4-propylphenyl)dichlorosilane

1-bromo-4-propylbenzene (1 mole) was dissolved in 200 ml of ethyl ether and slowly added to Mg turnings (0.95 mole) in 400 ml of ether. The Grignard reaction gradually initiated under refluxing conditions and after completion of the 1-bromo-4-propylbenzene addition (1 hour), the reaction was allowed to continue for 1 to 2 hours until the Mg was nearly completely consumed. SiCl₄ (0.45 mole) in 150 ml of ether was added at a rapid dropwise rate with vigorous stirring at room temperature. The addition time was one hour and the reaction was continued for two hours under refluxing conditions. The desired di(4-propylphenyl)dichlorosilane was obtained from the reaction mixture by fraction distillation under vacuum (~170°C/1.5 mmHg) after the MgBrCl was filtered off. The yields was about 56%.

Di(anisole)dichlorosilane

4-bromo-anisole (1 mole) was dissolved in 150 ml of THF and slowly added to Mg turnings (0.95 mole) in 100 ml of THF. The Grignard reaction gradually initiated at room temperature and after completion of the 4-bromoanisole addition (1.5 hour), the reaction was allowed to continue for 2 hours until the Mg was nearly completely consumed. SiCl₄
(0.45 mole) in 250 ml of hexane was added at a rapid dropwise rate with vigorous stirring at room temperature. The addition time was 1 hour and the reaction was continued for 2 hours at 60°C. The desired di(anisole)dichlorosilane was obtained from the reaction mixture by fraction distillation under vacuum (~200°C/2 mmHg) after the MgBrCl was filtered off. The yield was about 40%.

Di(o-tolyl)dichlorosilane and Di(m-tolyl)dichlorosilane

2-chlorotoluene or 3-chlorotoluene (1.5 mole) was dissolved in 300 ml of THF and slowly added to Mg turnings (1.35 mole) in 100 ml of THF. The Grignard reaction was initiated by adding 5 ml of 1,2-dibromoethane or corresponding bromotoluene at 100 °C and after completion of the chlorotoluene addition (90 minutes), the reaction was allowed to continue for 2 hours until the Mg was nearly completely consumed. SiCl₄ (0.65 mole) in 100 ml of THF was added a rapid dropwise rate with vigorous stirring at room temperature. The desired di(o-tolyl) or di(m-tolyl)dichlorosilane was obtained from the reaction mixture by fractional distillation under vacuum (~140 °C/1 mmHg) after the MgCl₂ was filtered off. The yields were typically about 50%.

Hexa(4-propylphenyl)cyclotrisiloxane,
Hexa(anisole)cyclotrisiloxane, Hexa(o-tolyl)cyclotrisiloxane
and Hexa(m-tolyl)cyclotrisiloxane

Diaryldichlorosilane (0.25 mole) in 200 ml ethyl acetate was slowly added with vigorous stirring to a suspension of ZnO (0.375 mole) in 250 ml of ethyl acetate at room temperature or at 50 °C. After the last addition of the dichlorosilane (1 hour), the solution mixture was stirred for a few hours up to 24 hours at room temperature. The resulting ZnCl₂ and the excess ZnO were filtered off and the solution (added 300 ml of benzene) was washed four times with 200 ml of water. Solvents were removed by evaporation to yield a mixture consisting mainly of cyclic trimers and other cyclic oligomers. The cyclic trimers other than hexa(m-
tolyl)cyclotrisiloxane were separated by recrystallization from a toluene/methanol solution, with about a 10-30% yield. The yield for hexa(o-tolyl)cyclotrisiloxane was only about 2-3%. Hexa(m-tolyl)cyclotrisiloxane was recovered by precipitation in toluene/methanol solution, but significant amounts of the cyclic tetramer remained.

4.2.3 Polymer Synthesis

The detailed polymerization procedures are described in Chapter 2. In general, the polymers were prepared by ring-opening anionic polymerization of corresponding cyclic trimers in diphenyl ether solution at 150°C or 190°C for an one hour period. Sec-butyl lithium was used as the polymerization initiator with DMSO as the promoter (1, 7-8). An attempt was also made to obtain polydi(o-tolyl)siloxane by polymerization in bulk using KOH as the initiator, but without success. Polydi(anisole)siloxane was recovered by precipitation in toluene, followed by filtration and repeated washing with toluene to remove the remaining cyclic and initiator impurities. Polydi(n-propylphenyl)siloxane and polydi(m-tolyl)siloxane were recovered by precipitation with methanol and purified by fractional precipitation with a toluene/methanol mixture. Polymers were dried in a vacuum oven at 80-100°C for 16 hours.

4.2.4 Characterization

The molecular weights of polydi(n-propyl)siloxane and polydi(m-tolyl)siloxane which are soluble in chloroform at 40°C were obtained by gel permeation chromatography (GPC), with reported molecular weights being based on polystyrene standards. The molecular weight of polydi(anisole)siloxane was obtained from intrinsic viscosity measurements at 200°C, using a Ubbelohde Viscometer (Cannon Instruments Co.). The reported value is based on the intrinsic viscosities of polystyrene standards, also obtained at 200°C.
Differential Scanning Calorimetry (DSC) data were obtained using a DuPont 910 Thermal Analyzer at a heating rate of 10°C per minute and with a nitrogen flow rate of 40 ml/min. The glass transition temperatures are reported as the mid-point of the temperature range of the transition, while the crystal and liquid crystal transition temperatures are reported as peak temperatures.

Thermogravimetric analysis was performed on a DuPont 951 TGA at a heating rate 10°C per minute with nitrogen flow rate of 50 ml/min.

Proton and $^{29}$Si NMR spectra were obtained using a Bruker 360 MHz spectrometer.

### 4.3 RESULTS AND DISCUSSION

Thermal data for the new diaryl cyclic trimers are shown in Table 4.1. The melting points of the trimers decreases as the length of the alkyl group on the benzene ring increases, as shown by comparing the melting points of hexa(p-tolyl)cyclotrisiloxane (260 °C (1)) with that of hexa(n-propylphenyl)cyclotrisiloxane (118 °C). The melting point of the toyl trimers is also lowered significantly when the methyl group on the benzene ring is moved from the para to the ortho to the meta position. Zhdanov (9) has reported the melting point of hexa(m-tolyl)cyclotrisiloxane as 80 °C, but we did not observe a melting transition, perhaps because our sample contained a significant amounts of the cyclic tetramer. A mixture of the cyclic trimer of dimethylsiloxane (hexamethylcyclotrisiloxane, $D_3$) and the cyclic tetramer (octamethylcyclotetrasiloxane, $D_4$) is a liquid, although $D_3$ is a crystalline solid with a melting point of 65 °C. It would then not be surprising to find that a mixture of trimers and tetramers of di(m-tolyl)cyclotrisiloxane is also a liquid at room temperature.

The cyclization of di(o-tolyl)dichlorosilane was very difficult and only a trace amount of the cyclic trimers was formed. The limited yield
could arise from either steric hindrance of o-tolyl groups preventing the cyclization reaction, or from the limited solubility of di(o-tolyl)dichlorosilane in methylacetate or ethylacetate which are used as the cyclization medium.

The composition and structure of these trimers were confirmed by H and $^29$Si NMR. The chemical shifts of $^29$Si NMR are shown in Figures 4.2 to 4.5 and listed in Table 4.1, and confirm that the materials are the cyclic trimers. The peaks are located between -33 and -34 ppm, which is the region which has been identified as that for the cyclic trimers (1). The cyclic tetramers have chemical shift peaks between -42 and -43 ppm (10). The chemical shifts of the proton NMR from Table 2 confirm the composition of each trimer. The chemical shift of H from phenyl is located between 6.7 to 7.6 ppm and H from alkyl is located between 0.9 to 3.7 ppm (Figures 4.6 to 4.8). The experimental area ratio of H(phenyl) to H(alkyl) agrees quite well with the calculated values.

The yields and molecular weights of the polymers are shown in Table 4.3. All molecular weights are based on polystyrene standards, either GPC standards in CHCl$_3$ at 40°C or [η] standards at 200°C (Table 4.4 and figure 4.9). Polydi(4-propylphenyl)siloxane is a highly crystalline solid and is not soluble at or near room temperature in chloroform. However, it can be recovered from the hot polymerization medium by precipitation with cold methanol in a form which is soluble in chloroform at 40°C. This allows the molecular weight to be obtained by GPC techniques. However, if the polymer is annealed for one day at 120°C, the crystallinity increases to the extent that it is no longer soluble. Polydi(m-tolyl)siloxane is soluble in common solvents such as chloroform and toluene at room temperature. The solubility of polydi(anisole)siloxane is similar to polydi(p-tolyl)siloxane and polydiphenylsiloxane in that they are only soluble in DPE or DMSO at temperatures above 150°C.

The thermal properties of these three new polymers are summarized in Table 4.5 and the DSC curves are shown in Figures 4.10 to
4.12. The thermal behavior of polydi(anisole)siloxane is similar to polydi(p-tolyl)siloxane, with \( T_g \approx 35^\circ C \) and \( T_{lc} \approx 300^\circ C \). However, the clearing or melting temperature \( T_m \) is not observed due to polymer degradation which begins at about 425 \( ^\circ C \). Both polydi(4-propylphenyl)siloxane and polydi(m-tolyl)siloxane have glass transitions \( T_g \) below 0 \( ^\circ C \), and their crystal \( \rightarrow \) liquid crystal transitions \( T_{lc} \) are much lower than for polydi(p-tolyl)siloxane or polydiphenylsiloxane. However, their melting temperatures \( T_m \) are only slightly lower than that for polydiphenylsiloxane (500\( ^\circ C \) and 530\( ^\circ C \) vs. 541\( ^\circ C \)).

The thermal gravimetric data (TGA) are listed in Table 4.5 and TGA curves are shown in Figures 4.13 to 4.15. These data indicate that these polymers are thermally stable, with 10\% weight loss temperatures between 450-509 \( ^\circ C \). For comparison, the 10\% weight losses temperature for polydimethylsiloxane is reported as 400-440 \( ^\circ C \) (11) and that for poly(methyl/phenyl)siloxane as 450-470 \( ^\circ C \) (12). Polydi(anisole)siloxane seems to have a lower decomposition temperature than any of the diarylsiloxane polymers which we have examined.

**4.4 CONCLUSIONS**

Three new polydiarylsiloxanes with anisole, 4-propylphenyl, or m-tolyl substituents have been synthesized and characterized. The polymers were prepared by the lithium-initiated, ring-opening anionic polymerization of the cyclic trimers in solution. The structure and compositions of these cyclic trimers were confirmed by the proton and \( ^{29}\text{Si} \) NMR. The polymers are all highly crystalline and all show a transition to a liquid crystalline state at high temperatures. Polydi(m-tolyl)siloxane is soluble in common solvents such as chloroform and toluene at room temperature. Polydi(anisole)siloxane is only soluble in DPE or DMSO at temperatures greater than 150 \( ^\circ C \). Poly(4-propylphenyl)siloxane can be obtained in a soluble form by precipitation in cold methanol, but after annealing it also becomes soluble only at high temperatures. The thermal transition temperatures (\( T_g \) and \( T_{lc} \)) for polydi(anisole)siloxane is similar
to polydi(p-tolyl)siloxane and is much higher than polydi(4-propylphenyl)siloxane or polydi(m-tolyl)siloxane. The liquid crystal transition temperatures \( T_{lc} \) for the polydiaryl siloxanes which are reported here and in previous Chapter 2 follow the order: di(anisole) > di(p-tolyl) > diphenyl > di(4-propylphenyl), and also di(p-tolyl) > di(m-tolyl). The TGA 10% weight loss temperatures of the various diaryl polymers are generally between 460-510°C, but polydi(anisole)siloxane has somewhat lower value, with DSC measurements showing degradation beginning at about 425 °C.

The preparation of hexa(o-tolyl)cyclosiloxane by reacting the corresponding dichlorosilane with ZnO yielded only trace amounts of the trimer, and the following attempt to prepare the polymer in solution with sec-butyl lithium or in bulk with KOH was not successful. The problem is probably due to the extreme steric interaction of the o-tolyl substituents.
4.5 REFERENCES

1. Lee, M. K. and Meier, D. J., Polymer, in press.


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Figure 4.1 Synthesis of hexa(anisole)cyclotrisiloxane.

Figure 4.2 $^{29}$Si NMR spectrum of hexa(4-propylphenyl)cyclotrisiloxane.

Figure 4.3 $^{29}$Si NMR spectrum of hexa(anisole)cyclotrisiloxane.

Figure 4.4 $^{29}$Si NMR spectrum of hexa(o-tolyl)cyclotrisiloxane.

Figure 4.5 $^{29}$Si NMR spectrum of hexa(m-tolyl)cyclotrisiloxane.

Figure 4.6 H-NMR spectrum of hexa(4-propylphenyl)cyclotrisiloxane.

Figure 4.7 H-NMR spectrum of hexa(anisole)cyclotrisiloxane.

Figure 4.8 H-NMR spectrum of hexa(o-tolyl)cyclotrisiloxane.

Figure 4.9 Intrinsic viscosity of polydi(anisole)siloxane in diphenyl ether at 200°C.

Figure 4.10 DSC Transition temperatures of polydi(4-propylphenyl)siloxane.
   lower curve: crystal $\rightarrow$ liquid crystal transition temperature ($T_{lc}$).
   upper curve: crystallization temperature of $T_{lc}$.

Figure 4.11 DSC Transition temperatures of polydi(anisole)siloxane.
   lower curve: crystal $\rightarrow$ liquid crystal transition temperature ($T_{lc}$).
   upper curve: crystallization temperature of $T_{lc}$. 
Figure 4.12  DSC Transition temperatures of polydi(m-tolyl)siloxane. 
lower curve: crystal → liquid crystal transition temperature (T_{lc}).
upper curve: crystallization temperature of T_{lc}.

Figure 4.13  TGA 10% weight loss temperature of polydi(4-
propylphenyl)siloxane.

Figure 4.14  TGA 10% weight loss temperature of 
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Table 4.2  H-NMR chemical shifts of cyclotrisiloxane containing 4-propylphenyl, anisole, o-tolyl and m-tolyl substituents.

Table 4.3  Polymerization yields, molecular weights, solubility and $^{29}$Si NMR chemical shifts of siloxane polymers having 4-propylphenyl, anisole and m-tolyl substituents.

Table 4.4  Molecular weight of polydi(anisole)siloxane estimated from intrinsic viscosity at 200°C in solvent diphenyl ether.

Table 4.5  Thermal transitions and thermal gravimetric (TGA) behavior of siloxane polymers having 4-propylphenyl, anisole and m-tolyl substituents.
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Figure 4.6
H-NMR spectrum of hexa(4-propylphenyl)cyclotrisiloxane.
Figure 4.7  H-NMR spectrum of hexamethylene cyclotrisiloxane.
Figure 4.8  
H-NMR spectrum of hexadecylcycloextrin.
Figure 4.9  Intrinsic viscosity of polydi(anisole)siloxane in diphenyl ether at 200°C.
Figure 4.10 DSC transition temperatures of poly(di(4-propylphenyl)siloxane).

Upper curve: crystallization temperature of Tc.
Lower curve: crystal → liquid crystal transition temperature (Tlc).
Upper curve: crystallization temperature of Tc.
Lower curve: crystall → liquid crystall transition temperature (Tlc).

Figure 4.11 DSC Transition Temperatures of Polydisperse Siloxane.
Figure 4.12 DSC Transition temperatures of poly(di-1,4-phenylene).
Figure 4.13 TGA 10% weight loss temperature of polyl(4-Propylyphenyl)dimethoxysilane under nitrogen.

Temperature (°C)

Weight (%)
Figure 4.14
TGA 10% weight loss temperature of polydimethylsiloxane
(under nitrogen)
Figure 4.15 TGA 10% weight loss temperature of poly(dimethylsiloxane) (under nitrogen)
<table>
<thead>
<tr>
<th>Cyclic trimer</th>
<th>$T_m$ ($°C$)</th>
<th>$\Delta H_m$ (J/gm)</th>
<th>$^{29}$Si NMR chemical shift (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Chemical Structure 1" /></td>
<td>118</td>
<td>54</td>
<td>-33.28</td>
</tr>
<tr>
<td><img src="image2" alt="Chemical Structure 2" /></td>
<td>212</td>
<td>35</td>
<td>-33.10</td>
</tr>
<tr>
<td><img src="image3" alt="Chemical Structure 3" /></td>
<td>201</td>
<td>60</td>
<td>-33.61</td>
</tr>
<tr>
<td><img src="image4" alt="Chemical Structure 4" /></td>
<td>-15 * (T_g)</td>
<td>-----</td>
<td>-33.61</td>
</tr>
</tbody>
</table>

*: contains 55% of cyclic tetramers and oligomers

Table 4.1 Thermal behavior and $^{29}$Si NMR chemical shifts of cyclotrisiloxanes containing 4-propylphenyl, anisole o-tolyl and m-tolyl substituents.
<table>
<thead>
<tr>
<th>Cyclic trimer</th>
<th>Chemical shift (ppm)</th>
<th>Ratio of H(phenyl)/H(alkyl)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Phenyl</td>
<td>Methyl</td>
</tr>
<tr>
<td>![Diagram 1]</td>
<td>7.07</td>
<td>0.89</td>
</tr>
<tr>
<td>![Diagram 2]</td>
<td>7.09</td>
<td>0.91</td>
</tr>
<tr>
<td>![Diagram 3]</td>
<td>7.50</td>
<td>0.93</td>
</tr>
<tr>
<td>![Diagram 4]</td>
<td>7.52</td>
<td>1.59</td>
</tr>
<tr>
<td>![Diagram 5]</td>
<td>1.61</td>
<td>2.57</td>
</tr>
<tr>
<td>![Diagram 6]</td>
<td>6.70</td>
<td>7.38</td>
</tr>
<tr>
<td>![Diagram 7]</td>
<td>6.72</td>
<td>7.40</td>
</tr>
<tr>
<td>![Diagram 8]</td>
<td>6.81</td>
<td>7.50</td>
</tr>
<tr>
<td>![Diagram 9]</td>
<td>6.83</td>
<td>7.52</td>
</tr>
<tr>
<td>![Diagram 10]</td>
<td>6.89</td>
<td>7.18</td>
</tr>
<tr>
<td>![Diagram 11]</td>
<td>6.91</td>
<td>7.20</td>
</tr>
<tr>
<td>![Diagram 12]</td>
<td>6.93</td>
<td>7.22</td>
</tr>
<tr>
<td>![Diagram 13]</td>
<td>6.95</td>
<td>7.24</td>
</tr>
<tr>
<td>![Diagram 14]</td>
<td>6.97</td>
<td>7.50</td>
</tr>
<tr>
<td>![Diagram 15]</td>
<td>7.06</td>
<td>7.52</td>
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<td>![Diagram 16]</td>
<td>7.08</td>
<td>7.54</td>
</tr>
<tr>
<td>![Diagram 17]</td>
<td>7.16</td>
<td>7.56</td>
</tr>
<tr>
<td>![Diagram 18]</td>
<td>6.99</td>
<td>7.20</td>
</tr>
<tr>
<td>![Diagram 19]</td>
<td>7.09</td>
<td>7.26</td>
</tr>
<tr>
<td>![Diagram 20]</td>
<td>7.11</td>
<td>7.29</td>
</tr>
<tr>
<td>![Diagram 21]</td>
<td>7.13</td>
<td>7.31</td>
</tr>
<tr>
<td>![Diagram 22]</td>
<td>7.15</td>
<td>7.42</td>
</tr>
</tbody>
</table>

Table 4.2 H-NMR chemical shifts of cyclotrisiloxanes containing 4-propylphenyl, anisole, o-tolyl and m-tolyl substituents.
<table>
<thead>
<tr>
<th>Polymer structure</th>
<th>Mol. Wt.</th>
<th>Yield (%)</th>
<th>Solubility CHCl₃, R.T.</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1.png" alt="Image" /></td>
<td>21,000</td>
<td>32</td>
<td>No (after annealing)</td>
</tr>
<tr>
<td><img src="image2.png" alt="Image" /></td>
<td>44,000</td>
<td>66</td>
<td>No</td>
</tr>
<tr>
<td><img src="image3.png" alt="Image" /></td>
<td>16,000</td>
<td>10</td>
<td>Yes</td>
</tr>
</tbody>
</table>

Table 4.3 Polymerization yields, molecular weights, solubility and $^{29}$Si NMR chemical shifts of siloxane polymers having 4-propylphenyl, anisole and m-tolyl substituents.
Table 4.4: Molecular weight of poly(dimethylsiloxane) estimated from intrinsic viscosity at 200°C in solvent dioxane ether.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Molecular Weight</th>
<th>Intrinsic Viscosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.42</td>
<td>44.000</td>
<td></td>
</tr>
<tr>
<td>0.27</td>
<td>50.000</td>
<td></td>
</tr>
<tr>
<td>0.24</td>
<td>37.000</td>
<td></td>
</tr>
<tr>
<td>1.06</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a): Polystyrene standards with $M^\text{w}/M^\text{n} = 1.06$

(a): In solvent dioxane ether at 200°C
Table 4.5. Thermal transitions and thermal gravimetric (TGA) behavior of siloxane polymers having 4-propylphenyl, anisole and m-tolyl substituents.

<table>
<thead>
<tr>
<th>T&lt;sub&gt;c&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; (°C)</th>
<th>T&lt;sub&gt;g&lt;/sub&gt; (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>131</td>
<td>269</td>
<td>35</td>
<td>128</td>
<td>7</td>
</tr>
<tr>
<td>4.58</td>
<td>350</td>
<td>97</td>
<td>131</td>
<td>5</td>
</tr>
<tr>
<td>4.50</td>
<td>269 (decomposition)</td>
<td>35</td>
<td>128</td>
<td>7</td>
</tr>
<tr>
<td>5.09</td>
<td>500</td>
<td>128</td>
<td>149</td>
<td>7</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>TGA (10% Wt. Loss)</th>
<th>Polymer Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>(°C)</td>
<td></td>
</tr>
</tbody>
</table>
CHAPTER 5

SUMMARY
SUMMARY

- P-tolyl and methyl substituted polydiphenylsiloxane, polydi(4-propylphenyl)siloxane, polydi(anisole)siloxane and polydi(m-tolyl)siloxane have been prepared by ring-opening anionic polymerization of the cyclic trimers in solution.

- The molecular weight, sequence distributions, solubilities, viscosities, thermal transitions and stabilities of these polymers have been characterized by Gel permeation chromatography (GPC), Nuclear magnetic resonance (H-NMR and $^{29}$Si NMR), Viscometers, Differential scanning calorimetry (DSC) and Thermogravimetric analysis (TGA).

- The diaryl polymers show liquid crystalline behavior.

- The mixed phenyl/methyl polymers are amorphous and show no liquid crystalline behavior.

- Replacing some of phenyl by p-tolyl group(s) in the polydiphenylsiloxane reduces both $T_{lc}$ and $T_m$.

- The $T_{lc}$ of polydi(p-tolyl)siloxane and polydi(anisole)siloxane are higher (300°C) than that of polydiphenylsiloxane (265°C).

- The $T_{lc}$ of polydiarylsiloxanes follows the order: di(anisole) > di(p-tolyl) > di(phenyl) > di(4-propylphenyl) and di(p-tolyl) > di(m-tolyl).

- The p-tolyl and methyl substituted polydiphenylsiloxanes are thermally stable polymers which show a 10% wt. loss (by TGA) between 455 and 515 °C.

- Polydi(m-tolyl)siloxane and polydi(4-propylphenyl)siloxane are thermally stable polymers which show a 10% wt. loss (by TGA) between 460 and 510 °C.

- Polydi(anisole)siloxane showed a 10% wt. loss (by TGA) at a lower temperature than other diarylsiloxane polymers and the polymer begins to degrade at about 425 °C.
The mixed poly(phenyl/p-toly)l siloxanes show nematic liquid crystalline texture but polydi(p-tolyl)iloxane shows possibly smectic liquid crystalline texture.

Polydiphenylsiloxane, polydi(p-tolyl)siloxane, polydi(4-propylphenyl)siloxane and polydi(anisole)iloxane are soluble in dimethyl sulfoxide and diphenyl ether only at temperatures greater than 150 °C.

The mixed poly(phenyl/p-tolyl)siloxanes, PPP'' and P'P'P'', are soluble at 25°C in solvents with solubility parameters between 8.6 and 9.7. (where P is diphenylsiloxane, P' is (phenyl/p-tolyl)siloxane and P'' is di(p-tolyl)siloxane).

The mixed poly(phenyl/p-tolyl)siloxane, PPP', is soluble at 40 °C in solvents with solubility parameters between 9.3 to 9.7. The polymer remains in solution in these solvents when cooled to 25°C. (where P is diphenylsiloxane and P' is (phenyl/p-tolyl)siloxane).

The solubility of polydi(m-tolyl)siloxane is similar to polymers PPP'' and P'P'P''. (where p is diphenylsiloxane, P' is (phenyl/p-tolyl)siloxane and P'' is di(p-tolyl)siloxane).

The values of Mark-Houwink-Sakurada exponent "a" for the mixed poly(phenyl/p-tolyl)siloxanes are between 0.75 and 0.86.

The shear viscosity of the mixed poly(phenyl/p-tolyl)siloxane, P'P'P'', increases monotonically with increasing polymer concentration and does not show a critical concentration to an anisotropic state. (where P' is (phenyl/p-tolyl)siloxane).

The mixed poly(phenyl/p-tolyl)siloxanes do not behave as typical rigid rod polymers in solution.

Hexa(o-tolyl)cyclotrisiloxane could not be prepared by Takiguchi's method of reacting the corresponding dichlorosilane with Zinc Oxide (ZnO).

The extreme steric hindrance of the o-tolyl groups of hexa(o-tolyl)cyclotrisiloxane prevents the lithium catalyzed ring-opening polymerization.
APPENDIX

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