

**SYNTHESIS AND CHARACTERIZATION OF
CYCLOALIPHATIC AND AROMATIC
POLYESTER/POLY(DIMETHYLSILOXANE) SEGMENTED
COPOLYMERS**

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COPOLYMERS

by

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(ABSTRACT)

Linear thermoplastic polyesters are commonly used in high volume applications such as food containers, films and textile fibers. The physical and mechanical properties of these materials are well documented and are a function of chemical structure and morphology (e.g. semi-crystalline, amorphous, etc.). Polyesters, as are many organic polymers, are quite flammable.

Polydimethylsiloxane homopolymer exhibits low mechanical strength and, even at high molecular weight, exists as a viscous fluid rubbery gum due to its low glass transition temperature of approximately -123°C . However, one of the many attractive properties of this polymer is its relatively low flammability and if properly designed, organic "sand-like" silicates are produced in oxidizing atmospheres at elevated temperatures (e.g. $500\text{-}700^{\circ}\text{C}$).

This thesis discusses the synthesis and characterization of novel, high molecular weight cycloaliphatic and aromatic polyester/ poly(dimethylsiloxane) segmented copolymers. The cycloaliphatic copolymers were synthesized via a melt process using a high *trans* content 1,4 dimethylcyclohexanedicarboxylate, and 1,4 butanediol or cyclohexanedimethanol, while the partially aromatic systems were synthesized using dimethyl terephthalate and butanediol. Primary and secondary aminopropyl terminated poly(dimethylsiloxane) oligomers of controlled molecular weight were endcapped with excess diester to form an amide linked diester terminated oligomer. The latter was then incorporated into the copolymer via melt transesterification to afford a multiphase segmented

copolymer. Selected compositions showed enhanced ductility and hydrophobic surface modification.

The polysiloxane segment was efficiently incorporated into the copolymers and was unaffected by the transesterification catalyst under typical reaction conditions.

The homopolymers and copolymers were characterized by solution, thermal, and mechanical, and surface techniques. The segmented copolymers were demonstrated to be microphase separated as determined by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and transmission electron microscopy. The surface of the copolymers was enriched with the polysiloxane segment as evidenced by contact angle analysis.

Thermal gravimetric analysis of the segmented copolymers containing identical amounts of PDMS, but varying in the primary or secondary nature of their amide linkages, exhibited quantitatively identical char yields and weight loss behavior. The segmented copolymers exhibited char yields in air superior to those of their respective homopolymers.

Additionally, aromatic poly(tetramethyleneoxide) (PTMO) based polyether/polyester segmented copolymers were modified with poly(dimethylsiloxane). DMA revealed an apparent shift (higher T_g) of the PTMO segment reflecting an increase in phase mixing with the “hard” polyester segment, possibly induced by the hydrophobic PDMS phase.

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SYNTHESIS AND CHARACTERIZATION OF CYCLOALIPHATIC AND AROMATIC POLYESTER/POLYSILOXANE SEGMENTED COPOLYMERS

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Chapter I

INTRODUCTION

Multiphase copolymers are of great importance and much has been written in the literature concerning these materials. Covalent bonding of two different polymeric blocks displaying very different properties allows for specific tailoring of the ultimate performance of the two-phase system.

Poly(dimethylsiloxane) containing copolymers have been extensively studied and described frequently in the literature.^{1,2} Incorporation of poly(dimethylsiloxane) into a wide variety of homopolymers to form block or segmented copolymers is made possible due to the many organo-reactive endgroups that can be placed onto the siloxane segment. These can include carboxyl, hydroxyl, amino, epoxy, as well as others.

Polyorganosiloxanes exhibit many important and interesting properties. Although possessing a very low glass transition temperature, these polymers are able to maintain thermal stability over a wide temperature range in both inert and oxidizing environments. Furthermore, these materials are resistant to UV radiation, ozone and atomic oxygen and are known to form a silicate char under oxidizing conditions at temperatures of 500-700°C. Low surface tension, low surface energy, physiological inertness, and high gas permeability are only a few of the many other interesting properties that these materials exhibit. These physical properties are relatively unaffected by temperature.

Polyesters are produced in high volume that exceeds 30 billion pounds a year worldwide.³ Polyesters receive extensive use as fibers for textiles, coatings, and as a material for packaging of food and beverages. The vast majority of these engineering polyesters are based on aromatic starting materials, whereas the cycloaliphatic derivatives are used principally as outdoor coatings and housings due to their increased UV resistance over their aromatic counterparts due to their lack of unsaturated sites. As with many organic polymers, polyesters are flammable, and

especially in the case of textiles for young children, a flame retardant is added to combat this.

Melt transesterification is a major commercial route to the synthesis of polyesters. This solventless route involves high temperatures with relatively long reaction times that involve reduced pressures in the final step. Catalysts (*e.g.* titanium alkoxide) are required to decrease reaction times.

The major goal of this research was to use traditional melt polymerization techniques to form segmented polyester copolymers from a preformed aminoalkyl-terminated poly(dimethylsiloxane) oligomer. The hypothesis was that by forming a segmented siloxane-containing copolymer, the heat release rate would be decreased and the flammability of the copolymer would be much less than that of the polyester homopolymer. Both cycloaliphatic and aromatic polyesters were investigated since the cycloaliphatic systems providing solubility in common solvents which allowed for solution based characterization. Furthermore, the dimethyl 1,4-cyclohexanedicarboxylate based monomers have the added advantage of relatively low polarity as compared to their aromatic counterparts. Poly(dimethylsiloxane) is a very nonpolar polymer and it was hoped that by using a low polarity cycloaliphatic polyester monomer, miscibility could be maintained throughout the melt reaction. This would afford a well defined high molecular weight segmented copolymer that was soluble and allow for molecular weight and other solution characterization methodologies. Melt polymerization methods were used to generate aromatic segmented copolymers that had a high enough degree of crystallinity to be solvent resistant.

A series of cycloaliphatic and aromatic polyesters were produced with varying compositions. Thus, the weight percent of poly(dimethylsiloxane) was varied with respect to the polyester segment; either butanediol or cyclohexanedimethanol was used as the diol to afford several differing copolymer compositions. Generally, the aminopropyl-endcapped poly(dimethylsiloxane) was endcapped with diester monomer to form the amide-linked ester-terminated oligomer, prior to addition of the diol to the reaction vessel which allowed formation of the polyester *in-situ*. This

generated a polyester segment whose length was a function of composition, but which was nevertheless statistically related to the siloxane segment in length and composition.

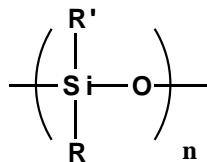
Chapter II

LITERATURE REVIEW

A. POLYORGANOSILOXANES

1. Introduction

, Polyorganosiloxanes have received the most attention of all the semi-organic polymers. They first achieved commercial significance as specialty materials in the 1940's. However, silicon chemistry has a long history dating as far back as the 19th century as illustrated by the preparation of chloro- and hydrosilanes.^{4,5} Some of the earliest publications date back to 1863-1880 with the synthesis of tetraethylsilane by Friedel and Crafts and later by Ladenburg⁶. They showed that organosilicon compounds could be synthesised by heating dialkylzincs with silicon tetrachloride to about 160°C. Later research by Pape showed that these compounds could also be formed by reaction of trichlorosilane with dipropylzinc. In 1885, Polis synthesized aromatic derivatives via the Wurtz-Fittig reaction.⁷ In 1904, Kipping utilized the Grignard reaction to synthesize R-Si-X compounds from tetrachlorosilane. These compounds could be hydrolyzed to silanol compounds which underwent self-condensation to form -Si-O-Si- cyclic or chain compounds.⁸ The cyclic monomers could then undergo polymerization or redistribution reactions in the presence of a strong acid or basic catalyst. Interestingly, Kipping overlooked the polymeric by-products and chose to investigate the monomeric crystalline compounds.^{7,9} The new polymers were first named silicoketones or silicones as an analogy to ketones because the structural unit (R₂SiO) appeared to correspond to that of organic ketones (R₂CO).² Structural studies elucidated the true structure as,



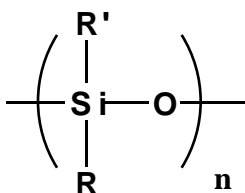
disproving the analogy.¹⁰ The terms siloxanes or polysiloxanes are most common in today's usage.

All of the above methods for siloxane synthesis required the preparation of an organometallic compound followed by a reaction with a covalent compound of silicon in a solvent or an excess of a reagent. The silicon halide must be prepared from silicon, and extra steps are required if an ester used.¹¹ Monomer synthesized in this manner afforded low yields and polysiloxanes did not reach early commercialization. It remained for Rochow (General Electric Company) to develop a direct process for the synthesis of organosiloxanes by the catalytic reaction of elemental silicon with alkyl chlorides, that scale-up was possible.^{11,12} At nearly the same time, Hyde (Corning Glass Works), and later Andrianov, made similar discoveries.⁷ Since that time, poly(dimethylsiloxane) and related derivatives were developed which broadened the application range of these new materials. The growth relates to many interesting properties including a low glass transition temperature, excellent thermal and oxidative stability, low surface energy, high gas permeability, and stability to UV radiation. The incorporation of polysiloxanes into a large number of copolymers is also possible since a large variety of functional groups can be placed on the end of the polysiloxane chain, including epoxy, amine, hydroxyl, carboxyl, and vinyl, etc.

The literature review will focus on the unique properties of polyorganosiloxanes and how these are applicable to industrial systems. The synthesis and nomenclature of polyorganosiloxanes will also be discussed. More detailed information on these issues can be found in a number of excellent books^{7,9,13-17} and review articles.^{1,2,5,10,18,19}

2. Properties of Polyorganosiloxanes

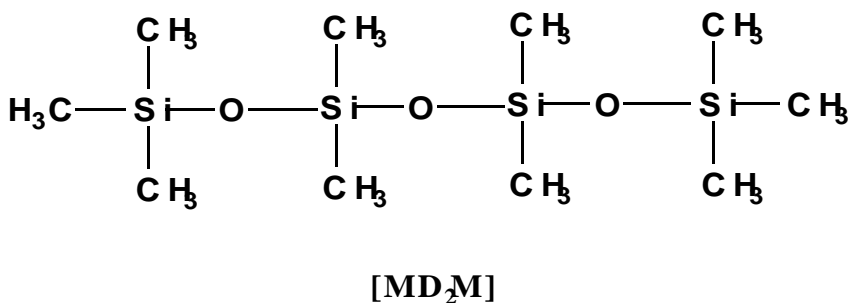
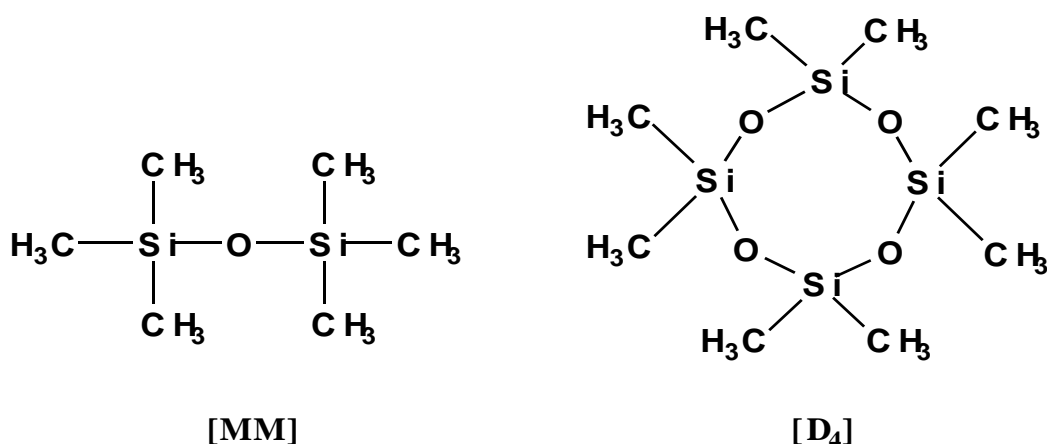
The polyorganosiloxane repeat unit consists of alternating silicon-oxygen atoms in which two monovalent organic radicals are attached to each silicon atom and can be written as



in which R and R' may be alkyl, haloalkyl, vinyl, hydrogen or phenyl substituents. Poly(dimethylsiloxane), where R=R'=CH₃, is of the greatest commercial importance, although other important substituents include phenyl, 1,1,1-trifluoropropyl, hydrogen and vinyl groups.²

Silicon has very interesting properties, including the fact that the conceptual Si=O double bond is unstable, unlike the ketone C=O double bond. Its tendency to form single Si-O-Si bonds can produce linear or cyclic polymers, unlike C=O double bonds.⁷ The Si-O bonds in tetravalent silicon compounds consist of σ bonding of the hybridized s and p electrons of the silicon atom with the p electrons of the oxygen, and an additional π interaction between the unshared p electrons of oxygen and the unfilled 3d orbitals of silicon, resulting in a partial double bond character. Unlike the p orbitals, not all of the 3d orbitals have the same shape and relative orientation in space. Therefore, the 3d orbitals of the silicon can form the π bond with any spatial orientation of the oxygen, and the large degree of mobility around the siloxane bond does not contradict the existence of $p_{\pi} - d_{\pi}$ bonding between oxygen and silicon.¹³

The silicon in polyorganosiloxanes can be combined with one, two, or three organic groups with oxygen taking up the remaining valences. If Si(CH₃)₄ is considered as a reference, then by substituting a methyl group with -O-R, one can assemble polysiloxanes from four types of structural units, as described in Table 2.1.⁷ As a result, these materials form linear, branched, and cross-linked topologies. The symbols M, D, T, and Q are used to represent Mono, Di, Tri, and Quaternary (tetra) functional siloxane monomers and polymers. Use of this common nomenclature has been applied even complex molecules. Examples of how this terminology is used are provided below:



Additionally, there is a well-established terminology to identify various siloxane structures, depending on the type of substituent attached to the silicon atom. They are D, which represents the dimethyl substituted structure, $(\text{CH}_3)_2\text{SiO}$; D', which represents the methyl-phenyl, $(\text{C}_6\text{H}_5)\text{CH}_3\text{SiO}$; D'' for diphenyl, $(\text{C}_6\text{H}_5)_2\text{SiO}$; and F, 1,1,1-trifluoropropyl, for $(\text{CF}_3\text{CH}_2\text{CH}_2)\text{CH}_3\text{SiO}$. This type of nomenclature is used widely, particularly in the patent literature.

Polysiloxanes are extremely flexible molecules due to the free rotation about the Si-O and Si-C bonds, and poly(dimethylsiloxane) exhibited the most flexibility. The Si-O-Si bond angle has been shown to vary greatly between compounds, and varies as a function of measurement technique within the same compounds.⁵ A generally accepted value for the Si-O-Si bond angle in poly(dimethylsiloxane) is 143° ²⁰ and the C-Si-C bond angle is 111° .¹⁰ The highly flexible nature of the polysiloxane chain is due to exceptionally low rotational barriers of the bonds compared to their corresponding hydrocarbon substitution.²¹ This freedom of

Table 2.1: Structural Units of Polyorganosiloxanes⁷

| <u>Structural Formula</u> | <u>Composition</u> | <u>Functionality</u> | <u>Symbol</u> |
|---|------------------------------|----------------------|---------------|
| $\text{R}_3\text{Si}-\text{O}-$ | $\text{R}_3\text{SiO}_{1/2}$ | monofunctional | M |
| $\begin{array}{c} \text{R} \\ \\ \text{---O---Si---O---} \\ \\ \text{R} \end{array}$ | $\text{R}_2\text{SiO}_{2/2}$ | difunctional | D |
| $\begin{array}{c} \text{R} \\ \\ \text{---O---Si---O---} \\ \\ \text{O} \\ \end{array}$ | $\text{RSiO}_{3/2}$ | trifunctional | T |
| $\begin{array}{c} \text{O} \\ \\ \text{---O---Si---O---} \\ \\ \text{O} \\ \end{array}$ | $\text{SiO}_{4/2}$ | quadrafunctional | Q* |

* The symbol “Q” is used to denote “quadrafunctional” instead of “tetrafunctional”, where T is used to denote “trifunctional”.

motion results in greater intermolecular distances and lower intermolecular forces, resulting in an extremely low glass transition temperature of -123°C and a large molar volume of $75.5\text{ cm}^3/\text{mole}$.²² It also results in low surface tension and low viscosity. Weak intermolecular forces also explain the low dielectric constant and low temperature coefficient of viscosity.²¹ Poly(dimethylsiloxane)s are also transparent to visible and UV light, very resistant to ozone and corona discharge^{7,13} and stable against atomic oxygen²³ and oxygen plasma.²⁴ Moreover, these properties are virtually unaffected by temperature. Other important properties include high gas permeability, hydrophobicity, and chemical and physiological inertness.⁷

The Si-O bond is one of the most thermally stable bonds formed by silicon with a bond dissociation energy of 110 kcal/mole as compared with 85.5 kcal/mole for C-O, 82.6 kcal/mole for C-C, and 76 kcal/mole for Si-C bonds.⁹ This thermal stability is partially due to the high bond strength. In addition, the Si-O bond length (1.64 \AA)^{2,10,13}, which is significantly less than the value calculated from additivity of atomic radii (1.17 \AA for silicon and 0.66 \AA for oxygen yields a theoretical value of 1.83 \AA).⁹ This supports the theory of $p_{\pi} - d_{\pi}$ bonding between silicon and oxygen as previously described. The high strength exhibited by the Si-O bond accounts for the high thermal and oxidative stability of these materials and is a result of the partial ionic character of the Si-O bond.

Early studies indicated that the Si-O bond was approximately 50% ionic in character as calculated from Pauling's electronegativity, using silicon as the positive member.⁷ Later, Hannay²⁵ and Pauling²⁶ revised this value to approximately 40% ionic character. These materials are resistant to homolytic cleavage. However, due to the ionic nature of the bond, they are very susceptible to attack by polar compounds, such as strong acids or bases. While this is a disadvantage in the final polymers, this weakness is exploited in their synthesis. The cleavage by acids and bases is in contrast to the Si-C bond (in the pendant or end groups attached to the Si-O backbone) which has an ionic character of approximately 12% (for Si-CH₃ bond). The Si-pendant group bond is therefore not generally attacked by ionic reagents, and

remains intact during polymerization. If the pendant group is strongly electronegative however (i.e. CH_2Cl , CF_3 , CN), the Si-C bond becomes more polar and can be cleaved by bases. Aromatic pendant groups cause the Si-C bond to be more susceptible to acid attack.⁵

The thermal stability of poly(dimethylsiloxane) homopolymer is considered to be in the range of 350-400°C in an inert atmosphere and 400°C in the presence of air. The large difference in stability is due to the different degradation mechanisms that occur in the presence and absence of an oxidizing environment. In the absence of air, the degradation occurs due to redistribution of the siloxane bonds resulting in the formation of low molecular weight cyclics. In the presence of air, oxidation of the C-H bonds occurs at high temperature, which weakens the Si-C bonds, and causes intermolecular cross-linking and other degradative processes.⁹

As previously mentioned, certain physical properties of polysiloxanes, unlike other polymers, are virtually unaffected by temperature. This is especially true in the case of poly(dimethylsiloxane), possibly due to weak intermolecular forces. Polymers whose properties are a result of strong intermolecular forces, e.g. hydrogen bonding, maintain those properties until a temperature is gradually reached which disrupts these forces. As soon as the polymer absorbs sufficient energy to overcome intermolecular forces, the properties of the material change, usually with unwanted results. Polyorganosiloxanes, with their low intermolecular forces, do not undergo a large intermolecular disruption at somewhat elevated temperatures, and, hence, are not very temperature dependent.

In addition to weak intermolecular forces, another point helps to explain the mild temperature dependency of polysiloxanes. The linear polymers are helical in structure and it takes approximately six or seven siloxane units to form one 360° rotation of the spiral. This has been explained due to weak dipole interactions^{5,20}, and also as a result of stereochemistry.²⁷ Due to the large radius of the silicon atom and the large Si-O-Si bond angle, the alkyl substituents on the silicon atom project outward from the helix. This largely contributes to the non-polar and hydrophobic nature of the polyorganosiloxanes. As the temperature increases, the helix uncoils,

resulting in an increase of intermolecular interactions, which would normally translate into an increase in viscosity. In the present systems, however, the increase in molecular entanglements compensates for the increased molecular movement which occurs as the temperature is increased. As a result, the viscosity of polysiloxanes is only slightly affected by temperature.

Polysiloxanes have a uniquely high viscosity index. This can be explained by comparisons with a polymer in which the silicon is replaced with carbon. One observes in a space model that is fairly rigid and cannot coil because of the small size of the carbon atom as compared to the silicon. Therefore, the high viscosity index of polysiloxanes (compared to ether or hydrocarbon analogs) is due to the large size of the silicon atom. This permits a freedom of rotation not found in hydrocarbons or molecules which contain only carbon, hydrogen, or oxygen.²⁷

Surface activity is another property unique to polyorganosiloxanes. The helical form of the poly(dimethylsiloxane) chain results in the alkyl group facing outward from the helix, and consequently, the methyl groups have a tendency to orient toward the air or vacuum surface. This results in surface tensions of 15 dyn/cm (for hexamethyldisiloxane) to 22 dyn/cm (for higher molecular weight silicone oils).⁷ As a result of its extraordinarily low surface energy, the siloxane component of a phase separated siloxane-containing copolymer or polymer blend migrates to the air/polymer interface, resulting in a siloxane rich surface. The extent of migration is dependent on whether the phase separated material is a blend or copolymer. A copolymer, in which the polysiloxane segments are covalently bonded to the bulk material would permit less movement and hence less migration. Additionally, within a series of copolymers, the molecular weight of the siloxane oligomer would also be a factor because the middle of a lower molecular weight segment would be more restricted in motion than the middle of a much longer segment, resulting in less net migration in the lower molecular weight siloxane containing copolymer. These features of siloxane copolymers have been tailored and exploited in a large number of applications which require physiological inertness and atomic oxygen resistance^{23,28,29} as well as many others.

As was mentioned previously, poly(dimethylsiloxane) is the most important of the commercial polyorganosiloxanes. However, replacing the pendant methyl groups with various substituents is possible. When this occurs, many properties are usually affected, the extent of which is dependent on the type of substituent. In this manner, the properties of a polysiloxane can be tailored to meet specific needs simply by changing the substituent attached to the silicon atom. This is not difficult, and it is what has made polyorganosiloxanes attractive and versatile. A few of the more important examples are discussed below.

Replacing the methyl groups with longer chain alkyl groups results in better lubricating properties and better compatibility with organic compounds.³⁰ Since C-C bonds are not as thermally or oxidatively stable as C-Si bonds, pendant alkyl chains decrease thermal performance. Additionally, surface tension increases and release performance decreases.

Replacing methyl groups with phenyl substituents improves the thermal and oxidative stability when compared to poly(dimethylsiloxane). This occurs because of the inherent stability of the phenyl ring and also because the phenyl group strengthens the siloxane bond by increasing d_{π} - p_{π} contribution.⁷

Adding a small percentage of diphenyl or phenyl-methyl substituents to poly(dimethylsiloxane) disrupts the symmetry, and hence low temperature crystallizability of the methyl sequences. The net result is better flexibility at low temperatures. High concentrations of phenyl groups (e.g. >50 mole%), however, result in crystallization of phenyl sequences. Poly(diphenylsiloxane) has a much higher glass transition temperature and viscosity than PDMS, due to the limited mobility of the bulky phenyl groups. This polymer also has a higher solubility parameter due to enhanced intermolecular interactions. The solubility parameters of dimethyl, methyl-phenyl, and diphenyl substituted siloxanes are 7.5, 9.0, and 9.5 (cal/cm³)^{0.5} respectively.^{21,31} As expected, the miscibility of polyorganosiloxanes with organic polymers increases with increasing solubility parameter. By increasing the polarity of the pendant substituents, one can also increase the solubility parameter making the siloxane more miscible with organic polymers. This can be

achieved by using substituents such as trifluoropropylmethyl. However, due to the polar and aliphatic nature of the substituent, the thermal and oxidative stability is sacrificed.³² The presence of these substituents also results in an increase in glass transition temperature as well as viscosity. By substituting a methyl substituent with a methylvinyl group, a cross-linking site is introduced. The resulting siloxane elastomers are then reinforced using fillers such as fume silicas.

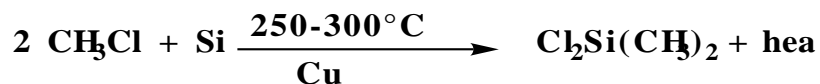
Another important modification of polysiloxanes involves the incorporation of a functional group, either along the backbone, or particularly at the chain end. A functional terminal unit allows the polysiloxane to become a reactive intermediate, and thus be incorporated into a wide range of siloxane-organic copolymers. This discussion has attempted to demonstrate the great versatility of polyorganosiloxanes and has been intended to provide an understanding of hybrid siloxane-organic copolymers are of great interest

4. Synthesis of Polyorganosiloxanes

Polyorganosiloxanes are synthesized commercially by the hydrolysis and subsequent condensation of organohalosilanes or by the acid- or base- catalyzed ring opening polymerization of cyclic siloxane monomers. Molecular weight is controlled by introducing a monofunctional component or chain transfer agent. Other methods of synthesizing polysiloxanes include the living “promoted” anionic polymerization of hexamethylcyclotrisiloxane (D₃) employing an alkyl lithium as the initiator. The following discussion will include the synthesis of monomers and polymers as well as a comparison of the living anionic and equilibration processes.

a) Monomer Synthesis

The first step in the synthesis of the monomers involves the “direct process” first discovered by Rochow^{11,12} variations of which are now used throughout the industry worldwide. This step is the preparation of methylchlorosilanes or phenylchlorosilanes. The process involves the exothermic reaction of an organic halide (i.e. methylchloride) with elementary silicon in the presence of a copper catalyst. The reaction scheme for the preparation of dimethyldichlorosilane is shown below:



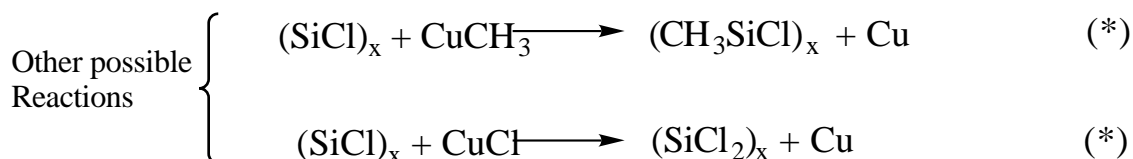
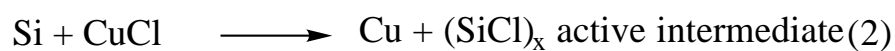
Dimethyldichlorosilane is not the only product. In fact, as expected, a mixture of substituted silanes results. The side reactions which occur are described elsewhere.¹¹ The desired product is isolated via fractional distillation, in yields greater than 80%.⁵ The mechanism for this reaction is quite complicated, but it is believed that heterogeneous reactions involving the halide, silicon, and catalyst (if present) take place at the silicon surface to produce the various organosilicon halides. The course of the primary reaction is dependent on temperature, time of contact with the silicon, the type of catalyst used, and the manner in which the catalyst associates with the silicon.¹¹ If the temperature is kept as low as possible the major product is R_2SiX_2 . As the temperature is increased, the rate of reaction also increases, but the chance of pyrolysis of free radicals also increases and mixtures of products becomes richer in halogen and lower in organic groups.¹¹

The role of the catalyst in this synthesis is equally obscure. Hurd and Rochow³³ postulated that the mechanism involves the initial formation of activated silicon nuclei which are then subject to alkylation or further halogenation. The chief function of the metal catalyst is believed to make the halogen of the organic halide readily available for reaction with (and activation of) the silicon and, secondarily, to make the organic group more labile by transporting and effectively prolonging the life of free radicals in the form of metal alkyls. The mechanism proposed by Hurd and Rochow³³ reveals that the catalyst accelerates the over-all reaction rate to such an extent that the reaction can be carried out at a lower temperature than would be required in the absence of catalyst. This results in a faster reaction rate with less pyrolysis and a higher percent yield. In the absence of catalyst, the initial activity is poor and declines rapidly, producing as major products methyltrichlorosilane and silicon tetrachloride.

While copper is the best catalyst for the preparation of alkylsilicon halides, diphenyldichlorosilane is reportedly synthesized by reacting chlorobenzene with metallic silicon at 550°C in the presence of a silver catalyst. Yields are approximately 50% possibly due to steric effects. By varying the reaction conditions, such as temperature and catalyst, the composition of the crude product can be modified.^{7,11}

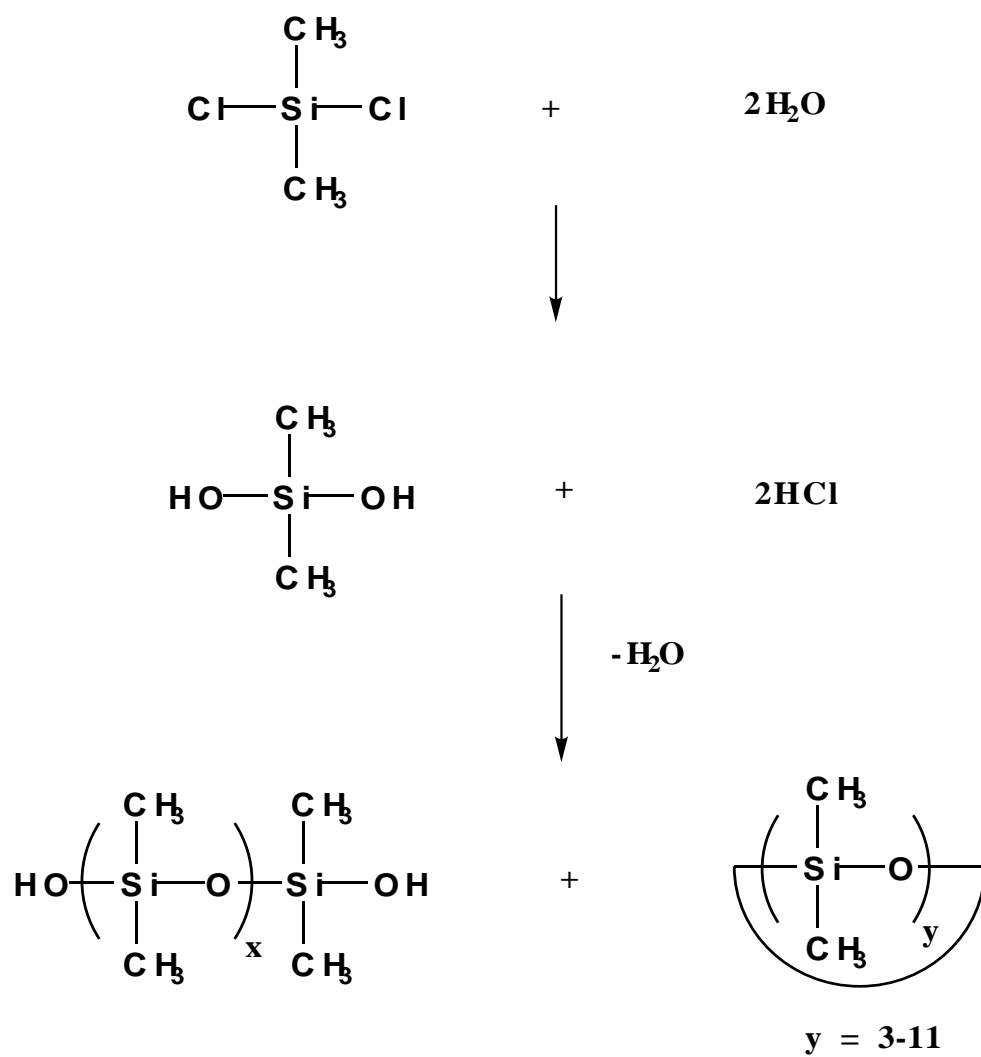
While early researchers believed that the direct process proceeded via free radical mechanisms³³, more recent suggestions involve chemisorption, polarization and charge transfer phenomena.^{5,7}

The organochlorosilanes just described undergo hydrolysis followed by self-condensation to produce a mixture of linear diols and cyclics of various sizes. The hydrolysis and subsequent condensation reactions of dimethyldichlorosilane are shown in Scheme 2.2. The ratio of cyclic to linear products can be controlled somewhat by varying the reaction conditions.⁷ Conducting the hydrolysis in the presence of a water-insoluble, non-polar solvent, produces the desired cyclics in as high as 90% yield. This is because the non-polar, organic solvent solubilizes the organohalosilanes and the polyorganosilanes, which lowers their concentration in the aqueous phase. Therefore, intramolecular condensation predominates over intermolecular condensation, and cyclics are preferentially formed.



The reaction continues to form SiCl_4

Scheme 2.2: Mechanism of the Synthesis of Methylchlorosilanes³³



$M_n \approx 1-3000$ g/mole

Scheme 2.3: Hydrolysis and Condensation of Dimethyldichlorosilane²
 The cyclic diphenyl tetramer, D4'', is synthesized by a similar process.¹⁷

The preparation of controlled molecular weight functional polysiloxane oligomers by equilibration processes often requires the use of a functional endblocker, which acts as a chain transfer agent. Functionally terminated siloxane oligomers can be classified into two groups. The first group consists of oligomers in which the functional unit is bonded directly to the silicon (Si-X). The second group consists of oligomers in which the functional group is attached to an alkyl or aromatic group which is then bonded to the silicon (Si-R-X).² The Si-X type of functionality is used in silicone rubber technology, and was the first example of functionally terminated siloxanes. The literature contains many discussions regarding these types of materials.^{7,14,17,31} Important functionalities in this group include chloro, hydroxyl, methoxy, ethoxy, hydrogen, amine, dimethyl amine, and vinyl. The Si-X functionality is much more reactive toward nucleophilic reagents compared to their C-X counterparts. This is due to the difference in electronegativities of silicon (1.8) and carbon (2.5)⁹. The Si-X bond is much more polar than the C-X bond. Therefore, the silicon halides are much more reactive toward nucleophilic reagents than halocarbons.² These materials are used in RTV silicone rubber and adhesives.^{2,7,34}

Upon incorporation of Si-X functionalities into copolymers, an Si-O-C link is formed, which is susceptible to hydrolysis.^{1,35} Although the Si-O-C link is not as susceptible to hydrolysis in polymers as it is in small molecules, it is still often undesirable and it becomes necessary to replace this with another, more stable linkage. The Si-R-X functional oligomers eliminate this problem. Also, by choosing the appropriate R group, the miscibility of the siloxane oligomer and organic monomers can be enhanced,² increasing the ease of copolymerization. These carbofunctional siloxanes have a longer shelf-life since they do not undergo hydrolysis. α,ω -Organofunctionally terminated disiloxanes are the key starting materials in the preparation of functionally terminated siloxane oligomers via equilibration reactions. Some functional groups include hydroxyl, 1° and 2° amino, carboxyl, epoxy, halogen and others.²

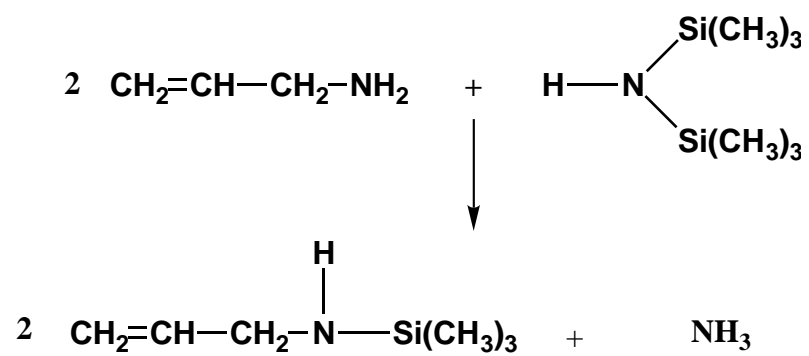
Aliphatic primary and secondary amine terminated poly(dimethylsiloxane) oligomers were used in this research. The synthesis of 1,3-bis(3-aminopropyl)tetramethyldisiloxane (primary aminoalkyl disiloxane) is discussed here. One synthetic route for the preparation of this material was reported by Saam and Speier.³⁶, while further work in this area has been conducted by our research group more recently. Their method involves hydrosilation and is shown in Scheme 2.4. It involves the protection of the alkyl-protected amine³⁷ to allow a clean hydrosilation with tetramethyldisiloxane before conversion to a free amine. The coupling step involves addition of the Si-H bond to the CH₂=CH double bond. Here, silicon can add to either the CH₂ or CH carbon. Steric considerations suggest that the major attack would be on the CH₂ carbon. and indeed this is the case (abnormal addition). The product does contain a small amount of the isopropyl moiety, however. This results in a decrease in the thermal and oxidative stability of this endblocker. The mechanism of hydrosilation reactions is not very clear, but it is known that catalyst type and concentration, structure of the olefinic compound, reaction temperature, and solvent all play key roles.³⁸

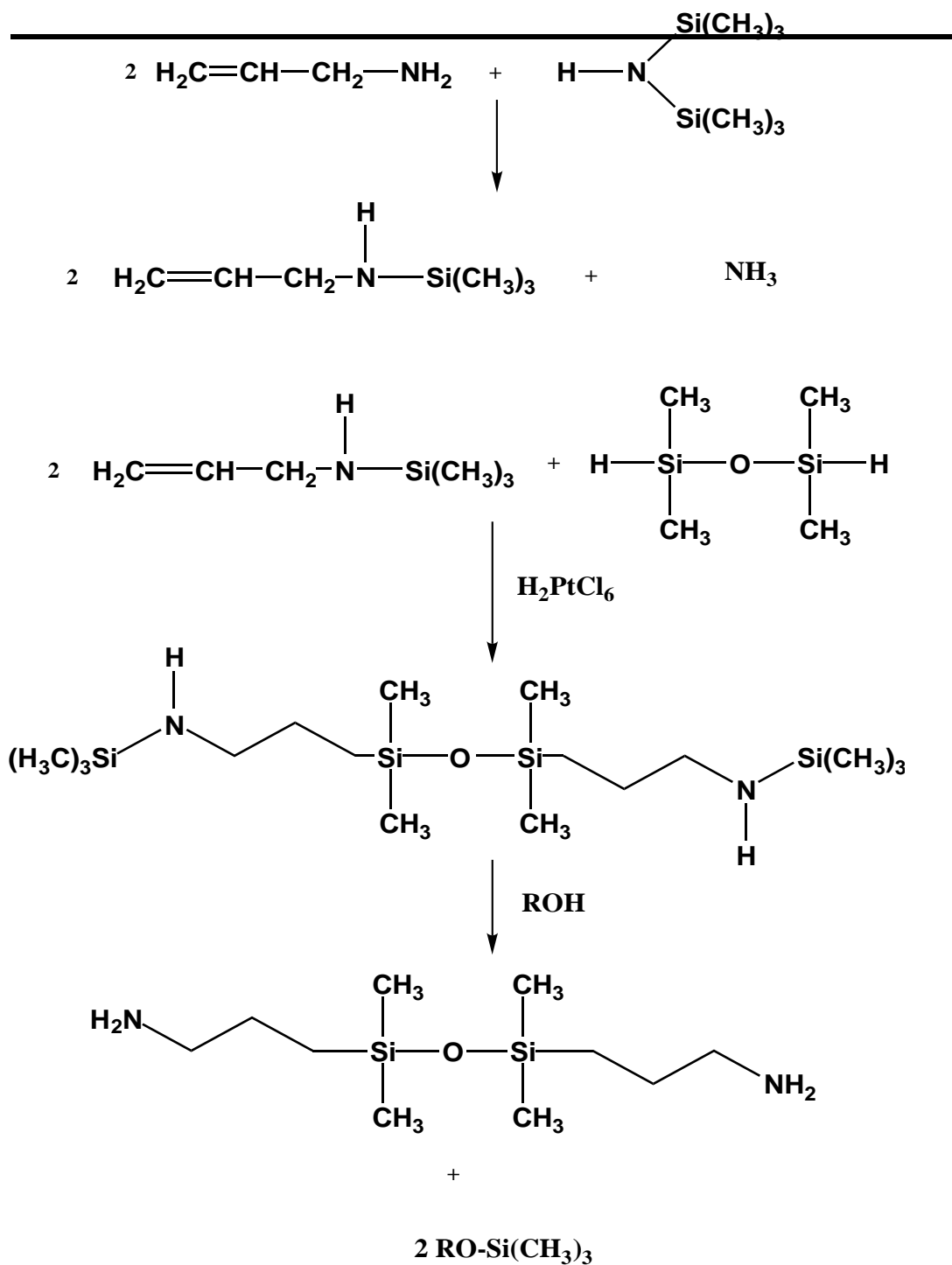
b) Synthesis of Polysiloxane Oligomers

As previously described, polysiloxane oligomers can be synthesized via various routes. They include living anionic polymerization, acid-catalyzed equilibration and base-catalyzed equilibration. In this research, base-catalyzed equilibration was used to generate primary and secondary aminoalkyl terminated poly(dimethylsiloxanes). The discussion will focus on anionic and base catalyzed synthetic methods.

i) Living Anionic Polymerization of Polyorganosiloxanes

Early work on the use of organolithium compounds as initiators for the polymerization of hexamethylcyclotrisiloxane (D₃) was reported by Bostick³⁹ and Lee.⁴⁰ The resulting polysiloxanes are reported to have





1,3-Bis(3-aminopropyl)tetramethyldisiloxane

Scheme 2.4: Synthesis of 1,3-Bis(3-aminopropyl)tetramethyldisiloxane³⁵

controlled molecular weights and narrow molecular weight distributions, in accordance with living polymerization.⁴¹ It is possible to polymerize D₃ in this fashion due to its high ring-strain. D₄ can also be polymerized by this method, but narrow molecular weight distributions and controlled molecular weights are not possible. Unlike D₄, D₃ is planar⁴², its Si-O-Si bond angle is 136° its O-Si-O bond angle is 104°²⁰, abnormally low, compared to the non-planar, unstrained D₄ molecule. This ring strain in D₃ results in an exothermic ΔH which permits exclusion of redistribution processes and ring-forming side reactions other than the desired ring-opening chain propagation process. Specifically, it was reported³³ that the use of sufficiently weak- bases in hydrocarbon solvents would result in the selective polymerization of strained systems such as D₃. In this case, polymerization of D₃ does not proceed except in the presence of a “moderate” Lewis base promoter such as tetrahydrofuran. It is possible to terminate these reactions to introduce a reactive end group into the polymer chains. This is an excellent method for the preparation of macromonomers.⁴³ The literature contains many excellent references regarding the living anionic polymerization of cyclosiloxanes.⁴⁴⁻⁵⁰

ii) Equilibration Polymerization of Polyorganosiloxanes

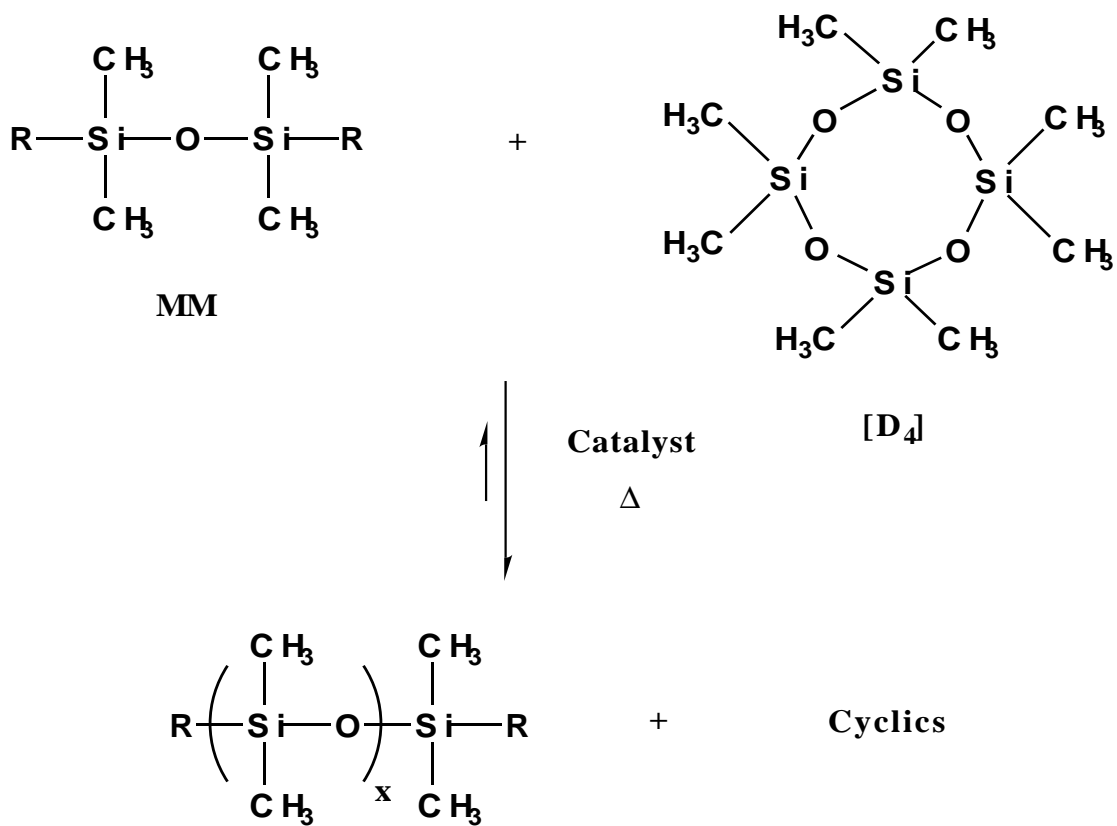
There are two general methods used for the equilibration polymerization of polyorganosiloxanes. They are catalysts with acids⁵¹⁻⁵⁴ or with strong bases.⁵⁵ The molecular weight and functionality of the resulting oligomers can be controlled by the addition of specified amounts of linear disiloxane endblocker.^{7,21,51,56} This equilibration reaction is an important commercial process. The general scheme for the polymerization of D₄ in the presence of an endblocker (MM) is shown in Scheme 2.5.

Equilibration (or redistribution) of siloxanes is the process where Si-O bonds in a mixture of siloxanes (both cyclic and linear) are continuously broken and reformed, in the presence of a catalyst, until the system reaches its thermodynamically most stable equilibrium state. Because of the random nature of the equilibration process, the molecular weight distribution of the linear species is Gaussian at thermodynamic equilibrium. At equilibrium, the reaction mixture consists of linear

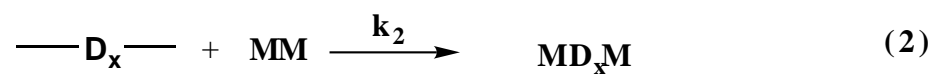
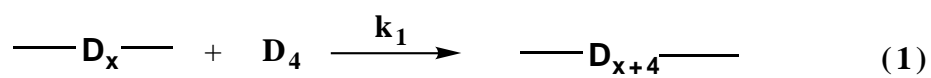
polymers and about 10- 15 weight percent cyclics. The equilibrium concentration of cyclic species increases as a function of molecular weight of the linear chains. The distribution of the rings decreases as ring size increases. The equilibrium weight fraction of rings increases with the polarity of the alkyl substituent bonded to the silicon.⁵⁷ In addition, the equilibrium concentration of small, unstrained rings increases with the size of the substituent.⁵⁸



and the equilibrium concentration for larger cyclics decreases with increase in substituent size. This can be explained using steric arguments. Small rings can adopt many conformations which would keep the molecule free from steric, or strained, interactions. The larger the substituent, the less amount of strain-free conformations become available to the cyclic, so more linear chains are formed.⁵⁸ By increasing the pressure of the reaction, the equilibrium concentration of cyclics decreases. A more detailed review of equilibration reactions of cyclosiloxanes has been published by Wright.⁵⁹ The redistribution reactions are shown in Scheme 2.6⁵⁶. Reactions (1) and (2) result in an increase in the number average molecular weight of the system, while reactions (3) and (4) affect only the higher moment molecular weight averages and are responsible for the attainment of the final equilibrium.^{56,59} The position of equilibrium is independent of the type of catalyst and is instead determined by the nature of the substituents on the silicon atom, temperature, and extent of dilution (bulk vs. solution polymerization).^{2,13,60} The type of catalyst, however, affects the path by which final equilibrium is reached. Equilibrium concentrations of cyclics increase with increasing size and polarity of the substituent on the silicon atom. The change in enthalpy of the ring opening of D_4 is approximately zero, and the process is believed to be entropically driven. The positive change in entropy can be explained by the high degree of flexibility of the linear poly(dimethylsiloxane) chain.⁶¹



Scheme 2.5: Synthesis of an Endblocked Poly(dimethylsiloxane)⁶²



Scheme 2.6: Redistribution Processes Occurring During Siloxane Equilibration⁵⁶

The theory of equilibrium molecular weight distribution in linear polycondensation systems, including the equilibration of cyclics, was first described by Jacobson and Stockmayer.⁶⁰ They showed that the percent of rings increased with dilution and that a critical dilution existed above which it was possible to obtain a 100% yield of rings. Brown and Slusarczuk⁶³ experimentally verified this theory for large rings, using GPC to measure the concentrations of macrocyclic dimethylsiloxanes (D_{15} to D_{200}) in equilibrium with linear poly(dimethylsiloxane). This theory was revised by Flory and Semlyen in order to account for the formation of small unstrained rings (D_4 and D_5) which were present in large excess of predictions. They took into account the relative orientation of the terminal bonds of a short chain when these bonds are forced into close proximity. Here, the proximity of the termini would be conducive to ring formation, rather than uncorrelated as predicted by theory. This consideration accounts for high concentrations of the cyclic tetramer. Other studies concerning dilution, solvent effects, and siloxane chain conformation on cyclization equilibrium constants have been reported.⁶⁴⁻⁶⁶

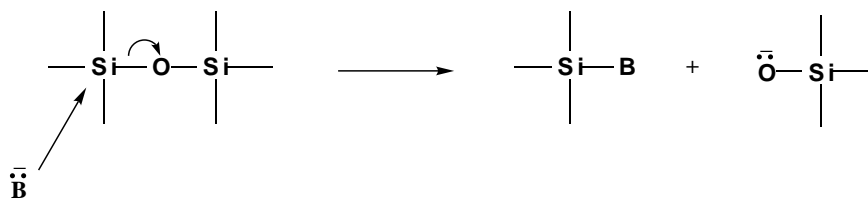
As previously described, the nature of the Si-O bond is partially ionic, and this permits the synthesis to proceed in the presence of either an acid or basic catalyst. The choice of catalyst is dependent on the nature of the endgroups on the endblocker and the types of substituents present on the silicon.⁵⁷ An acid catalyst is required when the functional groups are susceptible to attack by base, and a basic catalyst is required when the functional groups are susceptible to attack by acid.

Many studies have been presented regarding the acid catalyzed polymerization of cyclosiloxanes.⁶⁷⁻⁷⁶ This method will be discussed only briefly, since the polysiloxanes in this research were synthesized using a basic catalyst.

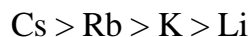
Base-Catalyzed Polymerization of Polyorganosiloxanes

The base-catalyzed ring opening-polymerization of cyclosiloxanes has been extensively studied.^{7,13,77-79} It has been well established that the active agent is the oxygen atom, or ionic form derived from it, which acts as an electron donor to silicon (which has a partial positive charge associated with it) in the siloxane linkage

exchange mechanism. This proceeds by the attack of a base on a silicon atom with displacement of a siloxanyl bond.^{80,81} The mechanism is shown below:⁵⁶



The most widely used basic catalysts are hydroxides, phenolates and siloxanates of the alkali metals and quaternary ammonium and phosphonium bases and their siloxanates. The activity of the alkali metal hydroxides and siloxanates decrease in the following order:²



This trend indicates a decrease in tendency for ionic aggregation with a corresponding increase in the nucleophilicity of the silanolate terminal. The activity of the tetramethylammonium and tetrabutylphosphonium siloxanates are close to the cesium siloxanates.⁸¹ Rates of the various processes depend on the catalyst type, concentration, temperature, and nature of the substituent attached to the silicon atom. Electron acceptor substituents increase the effective positive charge on the silicon atom, facilitating nucleophilic attack by base.

The alkali metal hydroxides (such as KOH) and their siloxanates can withstand higher reaction temperatures (>140°C) than the quaternary bases, but then must be completely removed or deactivated to prevent depolymerization or degradation in the final polymer product, should it be exposed to higher temperatures.

Instead of using a catalyst which requires neutralization or deactivation of the final product, thermally labile catalysts can be utilized.⁸²⁻⁸⁴ These are the quaternary ammonium and phosphonium bases which are termed "transient" due to their thermal instability. They decompose rapidly above 130°C and the products of the decomposition are of neutral pH, and are either volatile or thermally and oxidatively stable. Here, the need for tedious washing or exact neutralization of the polymer is eliminated. For example, tetramethylammonium hydroxide or its

siloxanolate decomposes to methanol or methoxysilane and trimethylamine, which will not catalyze siloxane equilibration reactions. Therefore, no danger exists for degradation of the polysiloxane due to residual catalyst at high temperatures. A disadvantage of this catalyst is the residual amine odor which is almost impossible to completely remove.

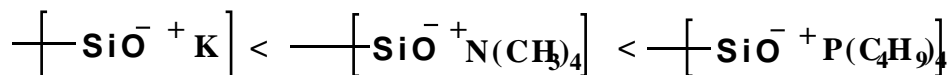
The phosphonium bases thermally decompose to form phosphine oxides and hydrocarbons.⁸³ These decomposition products are also ineffective towards decomposition or redistribution of the final polymers.

Early kinetic studies on the base-catalyzed ring opening polymerization of cyclosiloxanes determined that the order of reactivity towards the basic catalysts discussed is:⁵⁶



The greater reactivity of the D dominated compounds is due to electron withdrawal from silicon by two adjacent oxygens rather than one (as is the case for MM)⁸⁵, resulting in an increased partial positive charge on the silicon atom. This agrees with the mechanism proposed by Hurd, et al.⁸¹, which involves the attack of the basic catalyst at the silicon atom. Because the cyclic monomer is much more reactive than the functional endblocker, during the course of the reaction, the molecular weight builds up rapidly, resulting in a viscosity maximum (in Scheme 2.6, $k_1 \gg k_i$). As the less reactive endblocker is then incorporated during the equilibration process, the molecular weight, and hence viscosity, decreases.^{51,56}

The various siloxanolate catalysts incorporate D_4 and the aminopropyldisiloxane endblocker at different relative rates, although in each case, D_4 is incorporated faster. The rate of the incorporation by the catalyst of D_4 and endblocker increases in the following order:⁶²



Although all three incorporate D_4 efficiently, a large difference exists in the rate of incorporation of the disiloxane. This order of reactivity follows the order of increasing dissociation of the ion pair. The more dissociated the species, the higher

the concentration of active catalyst. In addition to ion dissociation, the more organic tetramethylammonium and tetrabutylphosphonium catalysts would be more soluble than the potassium ion. This would also result in a higher concentration of active catalyst and therefore, a faster rate of polymerization.

B. POLYESTERS

1. Introduction

Polyesters are one of the most versatile synthetic polymers. They are widely used commercially as fibers, plastics, and coatings.⁸⁶⁻⁸⁸ They are heterochain macromolecules that possess carboxylate ester groups as integral components of their polymer backbones. They differ from other ester-containing polymers (such as polyacrylates and cellulose esters) in that the ester functionality is part of the backbone and not a pendant group.

Polyesters have received a great deal of attention since the early work of Carothers, who initiated study on many step-growth polymerizations.⁸⁹ His work involved A-B ω -hydroxy-acids, the polymerization of certain lactones, and the esterification of A-A linear diols with B-B terminal aliphatic dicarboxylic acids. The resulting polymers were of low molecular weight (8,000-10,000 g/mol) hard, crystalline solids, and susceptible to conversion from the molten (or dissolved) state to filaments which could be stretched below their melting point with an ultimate increase in strength. Carothers worked with aliphatic straight-chain polyesters, which were soluble in organic liquids, low melting and had poor resistance to hydrolysis, polyesters were not used as textile fibers.⁸⁷ The extension of these concepts later led to the discovery of nylon-6,6 in 1935 and Whinfield and Dickson's development of poly(ethylene terephthalate) (PET) in 1941.⁹⁰ A partially aromatic organic structure was necessary to increase T_m above 250°C.

A large number of polyester structures have found use in industry today which display a wide variety of properties and applications. The synthesis of all polyesters will also be discussed in this section. More detailed discussion can be found in a number of excellent books and reviews.^{3,86,88}

2. Properties and Applications of Aliphatic and Cycloaliphatic Polyesters

The properties of polyesters in general, as in many polymers, are determined by the geometry, symmetry, polarity, and segmental mobility of the chain structures. Their intermolecular reactions are relatively weak and their properties are therefore more sensitive to molecular geometry than more polar materials such as polyamides, and hence, have a wider use range.³

Aliphatic and cycloaliphatic polyesters are substantially resistant to oxidation by air or ozone under normal conditions, but are degraded rapidly by ammonia, hydrazine, warm alkali solutions and primary or secondary amines, which cleave the ester linkage forming hydroxyl groups and the salt or amide derivatives of the carboxyl functionality. Cycloaliphatic based polyesters contain two tertiary protons per repeat unit, which adds to the molecule's thermal instability. These materials are light stable and hydrophobic in nature and this provides extra resistance to chemical attack by aqueous based reagents. Hydrolysis can occur at elevated temperatures or by steam.^{3,46}

The melting points of linear aliphatic polyesters increase with increased methylene/carboxylate ester group ratio in the repeat unit. In addition, polyesters with an even number of methylene groups are consistently higher melting than those containing an odd number of methylene groups.⁹¹ These materials are capable of forming fibers at degrees of polymerization of about 40. Aliphatic polyesters do not absorb in the visible or normal-range UV spectral regions, but they do absorb in the infrared.

The properties of ring containing polyesters are dependent on the conformation, symmetry and structure of the cyclic unit. Typically, a ring-containing polyester composed of predominately cyclic component (whether it be aromatic, alicyclic, or heterocyclic), then the polyester, if it contains semi-crystalline regions, will have a melting temperature considerably higher than those of the acyclic polyesters. This trend is also reflected in the glass transition temperature, which is also higher for both amorphous and semi-crystalline materials. This is a result of the

higher restriction of chain motion in the ring as compared to the acyclic counterparts.³

With the introduction of a cycloaliphatic moiety into the unit, the ratio of cis to trans isomers becomes an important factor and can greatly affect the ultimate polymer properties. Polyesters with a high trans content are usually semi-crystalline, while those with a high cis content are amorphous, or have a much lower T_m . For example, poly(1,4 cyclohexanedimethylene propylene dicarboxylate) containing the all trans isomer has a melting temperature of 50°C, while the all cis derivative is amorphous. Poly(1,4-cyclohexanedimethylene butylene dicarboxylate) synthesized from the all trans isomer has a melting temperature of 124°C while the cis derivative has a T_m of 55°C.³

Aliphatic or cycloaliphatic polyesters are used in applications which require UV resistance since the aromatic polyesters absorb strongly in the UV region resulting in chain scission and subsequent degradation. Because of their combination of low melting points, solubility, and limited hydrolytic stability, most acyclic polyesters are not used as structural materials. Their low glass transition temperatures enable them to be used as plasticizers and as components in polyurethanes.

Some alicyclic containing polyesters are used commercially as fibers. For example, poly(cyclohexane-1,4-dimethylterephthalate) containing about 70% of the alicyclic rings in the trans configuration was commercially introduced in 1955 as Kodel® by the Eastman Kodak Company.⁸⁶ In fact, most aliphatic polyesters are utilized as one part of a copolyester block copolymer or blend, and these applications will be discussed in greater detail in a later section. More extensive discussions of the properties and applications of linear acyclic polyesters are found in various books and reviews.^{3,86-88}

3. Synthesis of Polyesters

Polyesters have traditionally been categorized as step or condensation polymers (along with polyamides, polyureas, and others) because of the loss of water or other small molecule with each step of chain growth to distinguish them from

addition polymers. However, polyesterification, involves several equilibration steps, which markedly distinguishes them from both classes of polymers. The products of polyester synthesis from difunctional monomers are linear species as well as cyclics.

A number of synthetic approaches exist for the preparation of polyesters.^{86-88,91} These include direct esterification, transesterification (ester interchange), and the reaction of alcohols with diacid chlorides. The general reaction of each of the three methods is illustrated in Scheme 2.7. Each method involves nucleophilic addition to the carbonyl group, which is facilitated by the polar nature of the carbon-oxygen bond and the ability of the carbonyl oxygen to assume a formal negative charge. Each step of the nucleophilic addition is reversible, except in the case of the reaction involving the diacid chloride. Here, the by-product (HCl) is less nucleophilic than the alcohol and is typically removed as the reaction proceeds.

Direct esterification and transesterification are slow equilibrium processes. Catalysts are generally required to increase the rate of reaction. Both acidic and basic catalysts can be used. Acidic catalysts include protonic acids, Lewis acids, and titanium alkoxides. These acidic catalysts coordinate with the carbonyl oxygen, rendering the carbonyl carbon more susceptible to nucleophilic attack. A general scheme is shown below:

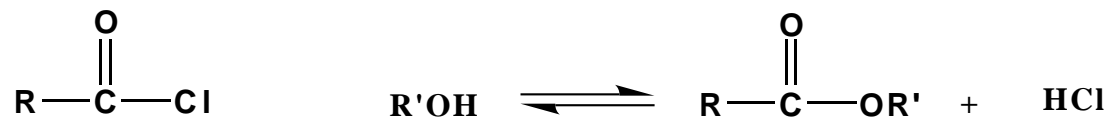
Direct Esterification



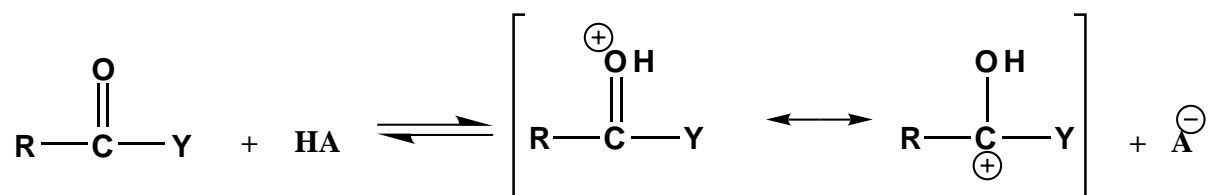
Transesterification



Reaction of Alcohols with Acid Chlorides



Scheme 2.8: General Procedures for the Synthesis of Polyesters



Weakly basic catalysts convert the reacting hydroxyl group to the corresponding (and more nucleophilic) alkoxide anion, which is then a more effective intermediate for the interchange process. The three types of polyester synthesis are discussed in greater detail below, along with the much less common addition polymerization of cyclic esters.

a) Direct Esterification

Direct esterification is the reaction of a diol with a dicarboxylic acid (or cyclic anhydride) or the self-condensation of a hydroxycarboxylic acid as shown in Scheme 2.9. The by-product of direct esterification is water. Direct esterification is a slow process. The carboxylic acid functional group provides protons to catalyze the reaction, but since the concentration of carboxylic acid groups decreases as conversion increases, it is often necessary to employ an additional catalyst. These catalysts include protonic acids or Lewis acids, titanium alkoxides, and dialkyl-tin(IV) oxides. Because this is an equilibrium process, water must be effectively removed in order to push the equilibrium toward high molecular weight polymer. To achieve this, high temperatures are required. Therefore, a reaction temperature must be chosen which strikes a balance between what is required for the reaction to proceed as a homogeneous melt, and that which minimizes the risk of thermal degradation over the required reaction time. The side reactions which can occur include readily decarboxylated acids or isomerizable cis-substituted reactants which may be transformed either partly or wholly to trans.

Achieving stoichiometric equivalence for the A-A / B-B systems is difficult since the diol is usually quite volatile. Therefore, the diol is charged in excess with respect to the diester in the initial stage.

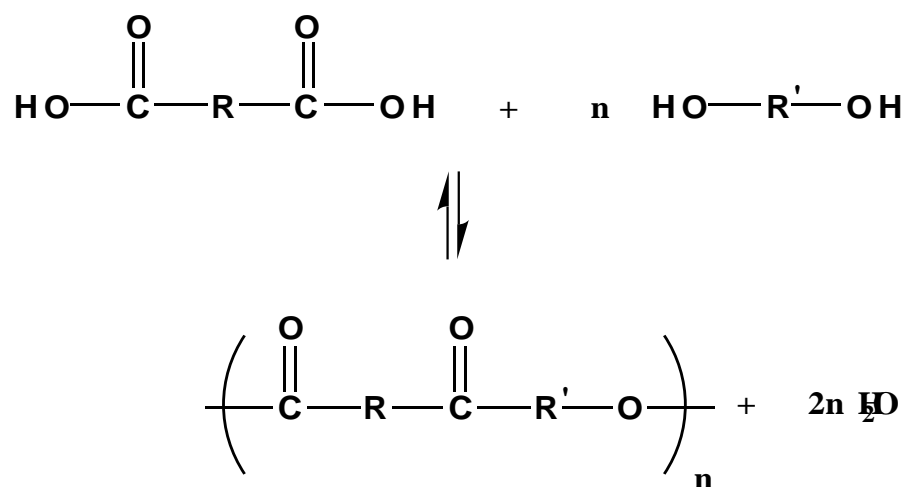
b) Transesterification

Transesterification (also known as ester exchange or ester interchange) involves a two-stage reaction of a dialkyl (i.e. dimethyl) ester (instead of a dicarboxylic acid) with a diol in an ester interchange process and is generally carried out in the presence of a proton donating or weakly basic catalyst. Such catalysts include the carbonates, alkanoates, hydrides, or alkoxides of sodium, lithium, zinc, calcium, magnesium, and bimetallic alkoxides such as $\text{NaHTi}(\text{OC}_4\text{H}_9)_6$, $\text{MgTi}(\text{OC}_4\text{H}_9)_6$, and $\text{CaTi}(\text{OC}_4\text{H}_9)_6$. The by-product is an alcohol (i.e. methanol). This procedure is widely applicable for the formation of homo- and copolyesters of aliphatic or alicyclic diols with aliphatic, alicyclic, aromatic, or heterocyclic dicarboxylic acids.

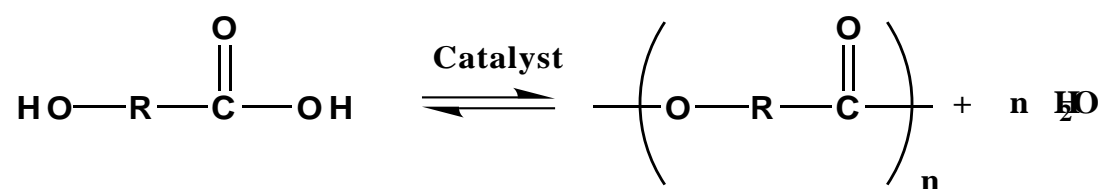
At the end of the first stage of the reaction, the major product is a bis(hydroxyalkyl) ester and/or an oligomer thereof. In the second stage, the ester is subjected to polycondensation by alcoholysis, forming the high molecular weight polyester. In this stage the by-product is the diol for each step of chain growth. The general reaction is illustrated in Scheme 2.10. The first stage is usually carried out at 150-200°C until the evolution of the alcohol is complete. The second stage is usually carried out at 220-290°C under reduced pressure in order to facilitate complete removal of the diol. The choice of the temperature of the second stage of melt polymerizations is governed by the requirement that the polymer remain a homogeneous melt. It must, therefore, be at least 20°C above the highest melting temperature of the final product. Since each stage is an equilibrium process and therefore reversible, the equilibrium can be forced to favor polymerization by continuous removal of the alcohol and diol by-products. As in direct esterification, 1:1 stoichiometry is extremely difficult to insure due to the volatility of the diol as well as the tendency of many of the diesters to sublime. The diol is charged in a 50 percent excess (by moles) with respect to the diester. This helps insure 1/1 stoichiometry in the end, but it also serves to drive the first stage of the reaction to completion at a faster rate.

Another procedure, which avoids the high temperatures and long melt reaction times, involves interrupting the polymerization at an intermediate stage and

Diol Reaction with Dicarboxylic Acid

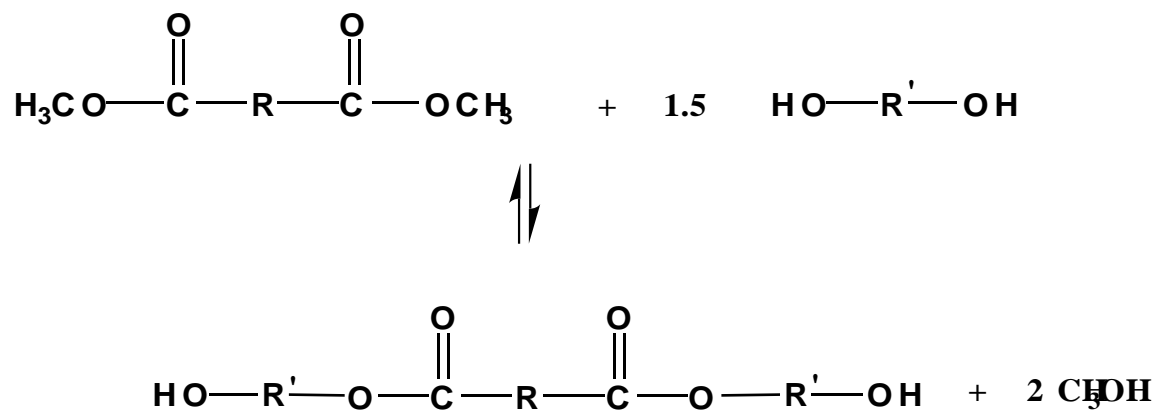


Self-Condensation of a Hydroxyacid

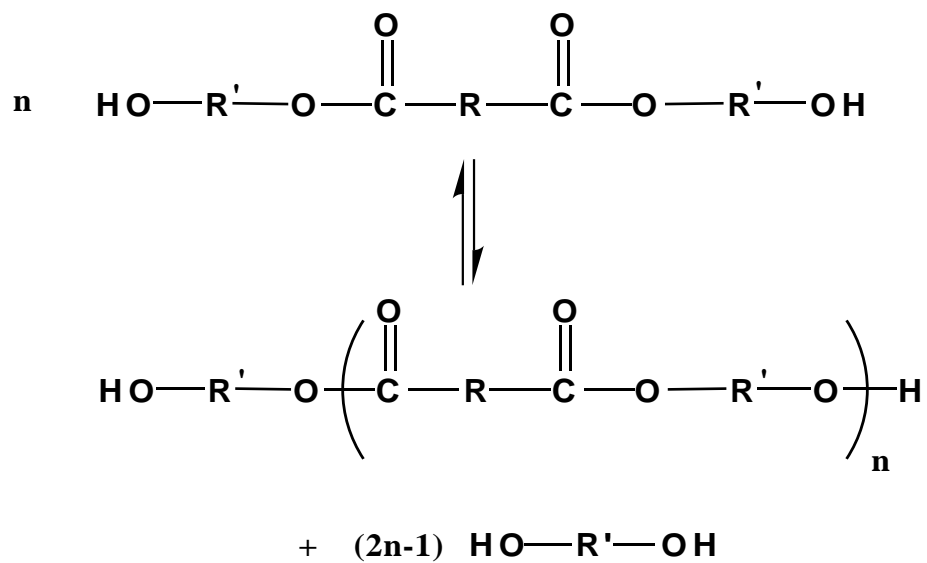


Scheme 2.9: Direct Esterification Reactions

Stage 1: Ester Exchange



Stage 2: Alcoholysis



Scheme 2.10: Transesterification

allowing the product to solidify. The material is then pulverized and heated either under vacuum or in a stream of inert gas at a temperature which is above the T_g but about 10-20°C below the T_m where the chains have some mobility and the catalyst is active, but where the polymer is thermally stable. This method of solid state polymerization often results in molecular weights much higher than those achieved by melt processes.³

c) Acylation

A third approach for the synthesis of polyesters is the reaction of a diacyl chloride with a dihydroxy compound to generate a polymer. This reaction can be performed in the melt as well as in a high boiling, inert solvent. HCl is the by-product of the reaction.⁹²⁻⁹⁴ Typically, the reaction proceeds rapidly and no catalyst is required. Another method, however, is the Schotten-Baumann reaction in which a base such as pyridine is used to catalyze the reaction and act as an acid acceptor of the HCl produced.⁹⁵⁻⁹⁷ This reaction can then be performed at ambient temperatures.

The alternative route to acylation is an interfacial polycondensation reaction. Here, two solutions are first formed: one consisting of the diacid chloride in an organic solvent and the other consisting of the diol (such as a bisphenol) in an aqueous alkali solution. The two solutions are rapidly agitated. The polymer forms immediately at the interface and either precipitates or remains soluble in the organic phase. A phase transfer catalyst such as a tetraalkylammonium halide is usually added.

Interfacial polymerizations do not precisely require 1:1 stoichiometry in the bulk because 1:1 stoichiometry is favored at the interface. These types of reactions are diffusion controlled. The solution or melt polycondensation methods, however, require high purity starting materials.

3. Properties and Applications of Aromatic Polyesters

Introduction

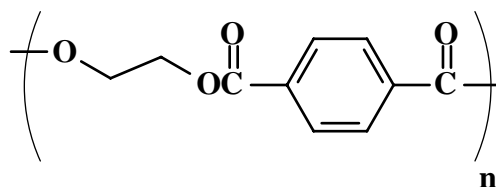
Aromatic polyesters (or polyarylestes) have a wide variety of commercial uses. Much of the early work was directed towards textile fiber applications after

the introduction of poly(ethylene terephthalate). Within the series of increasing methylene groups, poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) have been studied the most extensively. The first three members of the poly(methylene terephthalate) series (alkane group = ethane, propane, butane) have remarkably different properties than the remainders in the series. They melt above 220°C. The higher members of the series have melting temperatures below 160°C.⁹⁸

The two most important types of polyesters are based on PET and PBT, which between them have over 95% of the thermoplastic market for thermal injection moldable parts. When textiles are considered, only polyesters based on ethylene glycol, 1,3-propanediol and 1,4 butanediol are suitable due to their higher melting temperatures and solubility temperatures. This discussion will focus on PET and PBT. For more detailed information, many excellent books and reviews have been written on other materials such as unsaturated polyesters.⁹⁹⁻¹⁰⁴

i) Poly(ethylene terephthalate)

PET is a step or condensation based homopolymer based on terephthalic acid or dimethylterephthalate and ethylene glycol and has the repeat unit:



Unmodified PET plastics have been known for many years, but many molded parts were unsatisfactory due to an extremely low rate of crystallization.¹⁰⁴

The melting point of commercial PET usually falls in the range of 255-265°. Because of this slow crystallization rate, PET is best suited for applications where crystallinity can be enhanced by mechanical orientation, like soft-drink bottles, biaxially oriented blown films, fibers, etc. The glass transition temperature of PET varies depending on the polymer purity, degree of crystallinity, and method of

determination.¹⁰⁴ PET with a weight average molecular weight (M_w) of 35-40000 g/mole is suitable for oriented films and textile fibers, however M_w of about 80,000 g/mole is necessary for the higher impact strength needed for injection molded parts.¹⁰⁵

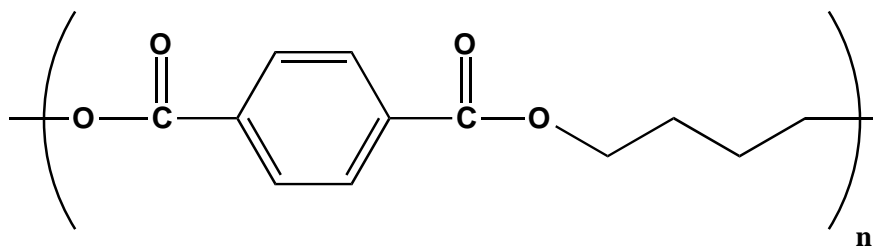
PET and PBT have good resistance to water, weak acids and bases, ketones, alcohols, glycols, ethers, aliphatic hydrocarbons and chlorinated hydrocarbons at room temperature. Strong bases rapidly degrade these materials at any temperature or aqueous bases above 50°C. This instability is exploited in the recycling of PET soft drink bottles by degrading them back to starting materials.

PET is synthesized via melt polymerization. Unlike many other poly(alkylene terephthalate)s, synthesis of PET requires a two component catalyst system in order to generate high molecular weight material.¹⁰⁶ One example of such a catalyst system utilizes zinc-acetate and antimony-trioxide. These two catalyst systems are in contrast to the single catalyst systems which previously used lead acetate.^{3,86,104}

At high temperatures and long time periods, such as those used in the synthesis of PET, thermal degradation can occur. Although many reaction schemes have been proposed, there has been little hard evidence that exists to favor one over another. It is generally accepted that PET degrades with random chain scission at the ester linkages. The methylene group is believed to be the principal point of chain weakness. The degradation of PET involves β -scission which leads to carboxyl and vinyl ester groups which can then react via an acetal ester intermediate forming carboxylic anhydride linkages plus acetaldehyde. Further reactions include polymerization of some vinyl ester groups to species which themselves suffer thermal scission and condensation of some acetaldehyde to polyene.^{3,107} Moisture causes rapid hydrolytic degradation at melting temperatures and can also be enhanced at lower temperatures in an oxidizing atmosphere. The mechanism of PET thermal degradation has been the subject of several studies.¹⁰⁸⁻¹¹²

ii) Poly(butylene terephthalate)

PBT is a step growth or condensation homopolymer based on 1,4-butanediol and dimethyl terephthalate and has the repeat unit:



PBT is one of the faster crystallizing polymers and, unlike PET, does not require nucleating agents or orientation to induce crystallization. Its melting point is 230°C, depending on sample preparation and annealing time. PBT resins contain fewer impurities than PET since the side reactions of the polymerization (tetrahydrofuran and butadiene) are volatile. Its glass transition temperature varies widely with crystallinity and the choice of measurement method. T_g 's range from 30-50°C, but have been reported as low as 20°C.¹¹³

Due to its high crystallization rate, PBT is often used in injection molding applications, where the high rates of crystallization allows short processing cycles.

PBT exhibits good electrical insulation properties which are virtually independent of temperature and humidity.¹⁰⁴ In general these materials do not exhibit good weather resistance without the aid of stabilizers. Polymer degradation is the result of UV exposure, especially in the presence of heat, moisture, oxygen, or atmospheric pollutants. The degradation is manifested as a loss in impact strength.¹¹⁴ PBT, like PET, is synthesized via melt polymerization methods and is also susceptible to β -scission after long reaction times at high temperatures. In this case, the degradation products are tetrahydrofuran and a carboxyl endgroup, which leads to carboxyl functionalities and 1,3-butadiene.

PBT has a large number of applications which include electronics, automotive, housewares, lighting, power tools, sporting goods, and plumbing. Specific applications include computer housings and automobile bumpers.

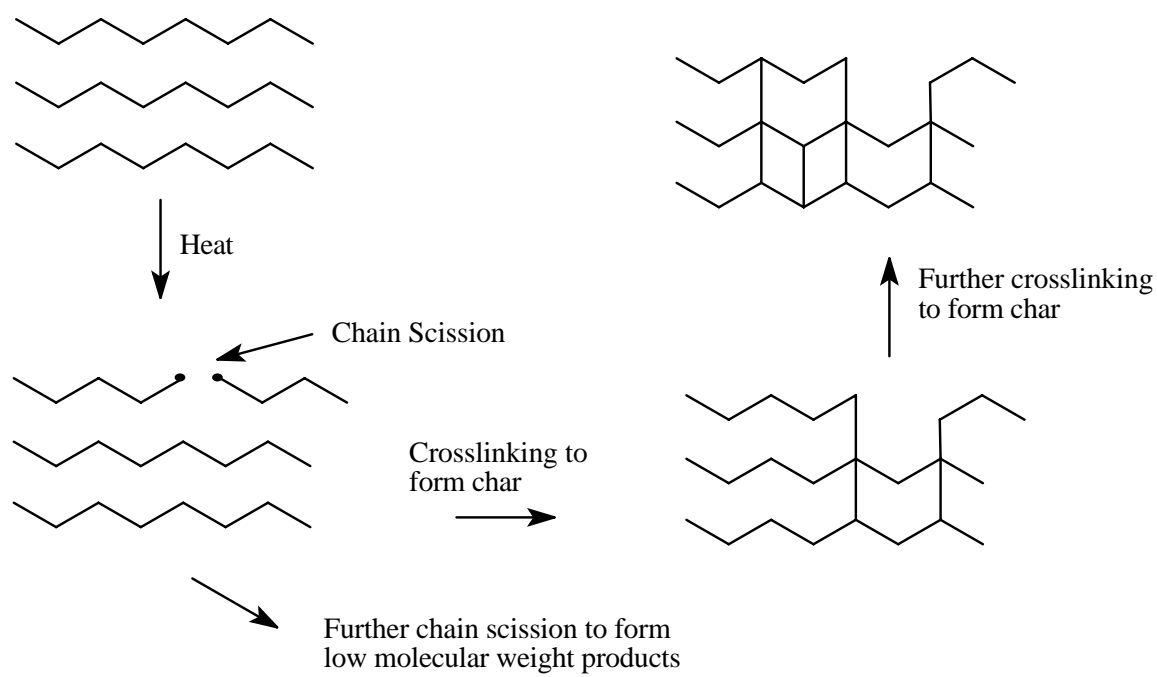
C. FLAME RESISTANCE IN POLYMERIC MATERIALS

1. Modification of Polymers to Improve Flame Resistance

Organic polymers are one of the most versatile and widely utilized class of materials used today. They are used in many applications ranging from adhesives, aircraft interiors, and electronic components and automobile parts.¹¹⁵ However, except for a limited number of so called inherently flame resistant polymers such as polytetrafluoroethylene (Teflon), polyvinyl chloride, etc. thermoplastics are generally rather flammable. Increasing the flame resistance of polymers can be achieved by using one of two different techniques. The first involves the physical blending of flame retardant additives such as Sb_2O_3 in combination with brominated aromatics¹¹⁶⁻¹²² or various phosphates with the polymer. The second approach involves the incorporation of flame retardant structures into a polymeric backbone.¹²³⁻¹²⁷ Flame retardant additives used in synthetic polymers include organic halogen and organic phosphorus compounds.¹¹⁸ A flame retardant additive interferes with one or more of the steps of the combustion cycle, which can include heating of the polymeric material, its subsequent degradation and the further combustion of volatiles that may be evolved from the material.^{119,120,122,128}

A flame retardant additive can function at one or more of these three steps. It is preferable that the additive function at more than one of these steps. Inhibition of combustion at step I is caused by formation of a glass-like coating on the surface of the material upon exposure to heat, which should preferably have low thermal conductivity. The additive can also degrade endothermically, and absorb energy from the polymer.^{118-120,122,128,129} During the ignition stage these flame retardant additives can also cause deactivation of highly reactive radical propagating species that result from chain scission during the combustion process¹³⁰ as is illustrated above in Scheme 2.11.¹²⁹

The flame retardant additive behaves in a similar manner in the second stage by reacting with radicals during the combustion of volatiles to quench the



Scheme 2.11: A mechanism for char formation

propagating nature of the fire.

The effectiveness of the halogen depends on many factors, including the halogen used, the polymeric structure and the concentration of halogen. The effectiveness of the halogen follows the order $\text{Br} > \text{Cl} > \text{F}$ and generally large amounts of halogen (between 15-30 wt. %) are required.^{116,119,131} Those halogens bonded to aliphatic carbons are better flame retardants than aromatic halogens.¹¹⁹ This is probably due to that fact that aliphatic halogens degrade at a lower temperature via a radical mechanism than aromatic halogens. However, there are problems with physically blended flame retardant additives including compatibility issues, the additive leaching out over time, and the fact that the decomposition temperature of the fire retardant needs to be appropriate for a specific polymeric material. An example of these issues are provided by Clough, who¹³¹ studied the aging effects of ethylene-propylene rubber (EPR) containing various amounts of halogen-hydrocarbon additives combined with Sb_2O_3 and discovered a significant loss of both the halogen additive and the Sb_2O_3 due to aging.

In order to avoid this problem with aging, one may add halogens bonded to the backbone of thermoplastics. This is particularly true for and epoxies.^{122,132} Halogen incorporation resulted in an increased char yield and higher limiting oxygen index which is one of the often used measurement methodologies.¹²² Commercially, tetrabromobisphenol-A or its diglycidylether ("FR-4) is often used to cure epoxies for use in printed circuit boards and other applications where fire resistance is needed.¹³²

The disadvantage with halogen based flame retardants is that upon combustion toxic gases of the form HX are emitted. Phosphorus or nitrogen containing additives, and others, are being investigated as a possible way to overcome this problem.^{117,118,124,128}

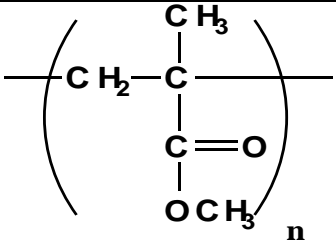
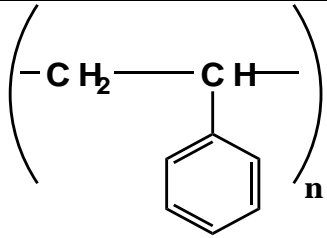
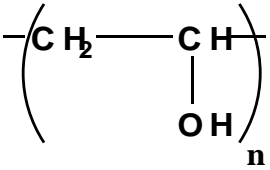
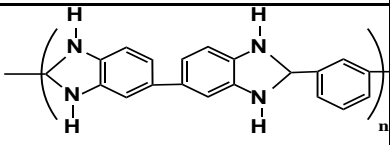
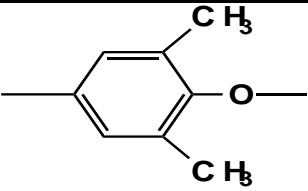
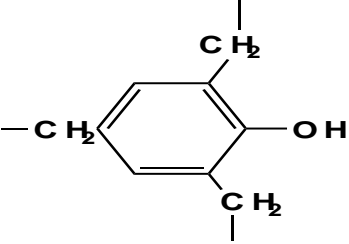
Another area of interest is the mechanism of char formation and how to induce high char yields in polymers in order to make them more flame resistant. Scheme 2.11 illustrates a proposed mechanism for char formation.¹²⁹ In this mechanism, a

polymer is thermally decomposed via chain scission. After the initial decomposition step, the polymer may either undergo further decomposition or react with another polymer chain to form a crosslinked network. If the polymer undergoes further decomposition it may form small molecular weight volatile byproducts that do not form char and, may in fact, enhance the combustion process. However, if after initial decomposition the polymer radical reacts with another polymer chain the polymer may form a crosslinked char. This mechanism would help to explain why the char of many highly aromatic polymers contain graphitic structures on the surface. These char forming condensed phase reactions are important in fire resistant polymers such as poly 2,6-dimethyl-1,4-phenylene oxide (PPO) and phenolic resins. Fenimore and Martin¹³³ illustrated that the high limiting oxygen index of PPO was due to its ability to form char residue upon heating. Table 2.2 illustrates the effect of aromatic ring upon char formation in non-halogenated polymers. It is evident from this data that as the char yield increases so does the limiting oxygen index, which is discussed in the next section. Siloxane containing polymers also exhibit char formation.

Polyorganosiloxanes have long been known to have good thermal stability over a wide temperature range. It has been shown that the siloxane bond is the only bond involved in the depolymerization process. In the presence of oxygen, degradation involving all bonds is observed.¹⁹

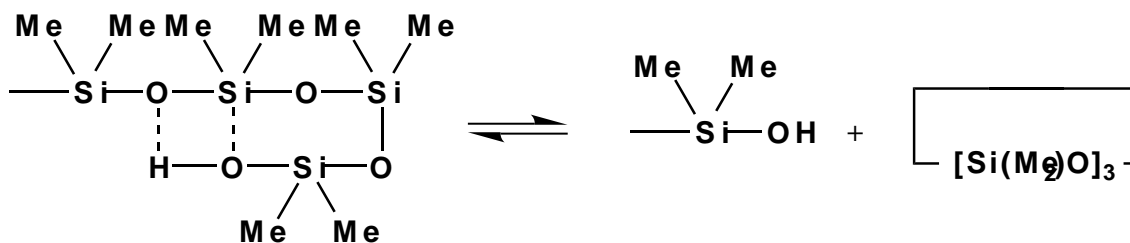
Numerous data indicates that a thermal degradation of poly(dimethylsiloxane) under vacuum causes a depolymerization that yields cyclic oligomers.¹³⁴⁻¹³⁷ The cyclic trimer, hexamethylcyclotrisiloxane (D_3) is reported to be the most abundant product, with lesser amounts of D_4 , D_5 , D_6 , and higher cyclics. Thomas and Kendrick

Table 2.2: Effect of Aromatic Rings on the oxygen index and char yield of non-halogenated polymers 120

| Polymer | Structure | Oxygen Index | Char Yield |
|---------------------------|--|--------------|------------|
| Poly(methyl methacrylate) |  $\left(\text{CH}_2 - \underset{\begin{array}{c} \text{C} \\ \\ \text{C}=\text{O} \\ \\ \text{OCH}_3 \end{array}}{\text{C}} \right)_n$ | 17 | 0 |
| Poly(styrene) |  $\left(\text{CH}_2 - \underset{\text{C}_6\text{H}_5}{\text{CH}} \right)_n$ | 18 | 0 |
| Poly(vinyl alcohol) |  $\left(\text{CH}_2 - \underset{\text{OH}}{\text{CH}} \right)_n$ | 22 | 0 |
| Poly(benzimidazole) |  | ----- | 58 |
| Poly(phenyleneoxide) |  | 28 | 40 |
| Phenolic Resin |  | 35 | 60 |

investigated depolymerization products of a trimethylsilyl terminated linear PDMS and accounted for the low depolymerization energy (177 kJ/mol), as determined by thermal gravimetric analysis, compared to the energy of the siloxane bond (451 kJ/mol).¹³⁸ They hypothesized a cyclic four-membered transition state which was accompanied by a rearrangement of siloxane bonds. Further study of substituent effects on other siloxane polymers supported this hypothesis, which is now widely used to explain the results of the depolymerization of a variety of polysiloxanes.

Variation of endgroups on PDMS can effect thermal behavior. It has been demonstrated that hydroxyl terminated PDMS is less thermally stable than the analogous polymers with trimethylsilyl endgroups.^{135,139,140} The depolymerization mechanism is presumed to proceed via the initial reaction of hydroxyl groups as shown below:



Poly(dimethylsiloxane) Depolymerization Mechanism¹⁹

However, the volatile products are the same for both polymers: cyclic oligomers. In both cases neither hydrogen nor methane was detected, which supports Si-O cleavage as the primary bond that is broken.

Weight loss behavior differs greatly when results from analyses in nitrogen and air atmospheres are compared. Thermal gravimetric analyses (TGA) of trimethylsilyl terminated PDMS in nitrogen show initial weight loss at 350°C with complete weight loss by approximately 600°C.¹³⁷ When a TGA experiment was conducted on the same material in air, initial weight loss was observed at 250°C and analysis after heating to 600°C showed a char yield of 62 percent of the original sample. Differential scanning calorimetry (in air) of this polymer revealed an

exothermal process occurring at about 250°C which achieved a maximum rate at about 325°C. This has been attributed to oxidative crosslinking via the methyl substituent groups and has been previously reported.^{141,142}

The ability of poly(dimethylsiloxane) to form a char under exposure to an oxygen-containing atmosphere has been exploited previously to increase the fire resistance of thermoplastic copolymers. Kambour was able to increase the fire resistance of bisphenol-A (BPA) polycarbonate above that of poly(2,6 dimethylphenyleneoxide) by synthesis of an 18 weight percent PDMS-co-BPA polycarbonate and that had a 30 weight percent char yield in air.¹⁴³ They cited the protective insulating silica layer formed by the char, caused by oxidation, as the main reason for enhanced fire resistance. Other studies on bisphenol fluorenone polycarbonates copolymerized with PDMS showed similar improvements.¹⁴⁴ In this case the limiting oxygen index (LOI) was close to 51, which approaches that of graphite which has an LOI of 58.

2. Methods for Testing Flammability

The combustion of polymeric materials is a complex process which includes environment, ignition, flame growth, fire retardants, and "burn out" to name a few. A single flammability test is thus only a partial indicator of how the material may behave in a "real" fire. Many tests have been developed to characterize each aspect of a materials combustion behavior. The research areas of combustion include; ease of ignition, flame spread, ease of extinction, smoke obscuration, smoke toxicity and heat release rate.^{122,129,145}

Ease of ignition may be measured by subjecting a specimen to an ignition source for a specified amount of time.^{122,129} The ignition source may be at a specific temperature or heat flux. If the material ignites it fails the test. The angle to which the sample is exposed to the ignition source and the heat flux of the source are the two main variables in this test. Another situation that may occur for materials that have low melting or softening points, is that the surface melt may flow away

from the ignition source.¹²⁹ If the softening temperature is below the ignition temperature the material may simply flow away from the ignition source and avoid ignition. If a material can withstand exposure to a heat source without ignition the fire will not occur and combustion is prevented; thus ease of ignition is extremely important. However, this resistance to ignition generally coincides with an increase in emission of smoke and toxic gases such as carbon monoxide.¹²⁹ This is to be expected since many flame retardants work by inhibiting the combustion process resulting in partially burned or combusted products.

The characteristic of the flame after ignition is also important, including how fast the flame spreads. This is especially important in materials that may cover a wall or the interiors of aircraft.^{122,129} In general, if a material ignites easily then its flame will spread rapidly. This is easy to understand if one views the propagating flame front as an advancing ignition. There are many analyses to characterize how a flame spreads. They consist of igniting a specimen with a specific orientation to the product exhaust (i.e. product exhaust carried into specimen flames) and analyzing visually how the flame spreads over the surface of the test specimen. Flame spread depends upon ignition temperature, orientation, thermal properties of the polymer, and flame heat flux.¹²⁹ The orientation of the sample is an extremely important variable in a flame spreading experiment. For example, a flame will spread up to an order of magnitude faster up a vertically oriented sample ignited at the bottom than it will with the same sample ignited at the top. This is because the heat is transferred more efficiently ahead of the burning zone if the flame propagation is in an upwards direction.¹²⁹ The heat release rate is another factor in characterizing the flammability of polymeric materials. It is currently regarded by many as the most important variable in fire resistance. Although most deaths in a fire occur due to inhalation of toxic gases, the heat release rate is considered by many to be the best predictor of a fire hazard.¹⁴⁵ Heat release rate is usually analyzed utilizing cone calorimetry. The cone calorimeter applies a specific heat flux to a sample and measures the ignitability, heat release rate, and toxic gases emitted.¹⁴⁵ The

ignitability is measured by determining how long a sample can withstand exposure to a specific heat flux before ignition occurs. After ignition, the heat release rate is measured as a function of time using an oxygen compensation method which involves calculating the heat release rate from the amount of oxygen consumed by the polymer during combustion.¹⁴⁵ From the heat release rate, it is also possible to monitor the heat release behavior through the combustion cycle from ignition to burn out.

Another important issue in determining the flammability of a material is how quickly a material quickly extinguishes after ignition. This is generally analyzed by determining a materials limiting oxygen index.¹²² The limiting oxygen index (LOI) is the minimum percentage of oxygen in an oxygen/nitrogen environment that is required to sustain combustion.¹⁴⁶ Thus, if a material has a high LOI it is considered easier to extinguish than a material with a low LOI. A material is considered flammable if its LOI is <0.27 .¹⁴⁶

In addition to how a material behaves thermally when exposed to heat, it is also important to determine the amount of smoke that is emitted upon combustion. Obviously, in a fire it is desirable to have as little smoke as possible. Smoke can cause loss of visibility, loss of breath and panic among people trapped in a fire. The structure-property relationships between polymer materials and smoke generation are not well understood. It appears to be extremely dependent upon the conditions of combustion.¹²⁹

Chapter III

EXPERIMENTAL

A. PURIFICATION OF STARTING MATERIALS

1. Polysiloxane Starting Materials

An oligomeric ($M_n = 1230$ g/mol) secondary aminopropyl terminated poly(dimethylsiloxane) (PDMS) was graciously provided by Dr. Gary Burns of Dow Corning.¹⁴⁷ The material was stripped under high vacuum at approximately 150 °C for approximately 4 hours, to remove residual cyclics. The purified PDMS was stored at room temperature under nitrogen to avoid contamination with water. A Gel Permeation Chromatography experiment was conducted to which confirmed a number average molecular weight was approximately 1300 g/mole. Proton, ^{13}C and ^{29}Si -NMR also agreed with the value.

An oligomeric ($M_n = 1200$ g/mol) primary aminopropyl terminated poly(dimethylsiloxane) (PDMS) was graciously provided by Shin-Etsu Corporation. Gel permeation chromatography, Proton, ^{13}C and ^{29}Si -NMR values for the molecular weight of the oligomer agreed.

2. Polyester Starting Materials

The diester monomers were generously provided by Dr. Tim Long of Eastman Chemical. 1,4-Dimethylcyclohexanedicarboxylate was received in monomer grade purity as a 98+% *cis/trans* mixture of isomers and was dried overnight under vacuum at room temperature prior to use. The isomeric ratio was confirmed by solution ^1H NMR spectroscopy. Dimethylterephthalate was received in monomer grade purity and was dried overnight under vacuum at room temperature prior to use. 1,4-Butanediol was purchased from Aldrich Chemical Company at 99+% purity, dried over molecular sieves overnight, and distilled under reduced pressure. 1,4-Cyclohexanedimethanol was purchased from Aldrich Chemical Company as a mixture of *cis/trans* isomers at a purity of 99+%. Titanium isopropoxide was purchased from Aldrich Chemical Company at 99.999% purity. This material was

then diluted in freshly distilled 1,4-butanediol to a concentration of 0.0032 g/mL. The solution was stored under nitrogen pressure until needed for polymerization.

B. OLIGOMER AND COPOLYMER SYNTHESIS

1. Poly(butylene cyclohexanedicarboxylate)

Poly(butylene cyclohexanedicarboxylate) was synthesized using melt polymerization methods. 1,4-Dimethylcyclohexanedicarboxylate and 1,4-butanediol were charged in a 1:1.5 molar ratio to a 250mL one neck round bottom flask equipped with a special overhead stir shaft adapter that allowed for nitrogen entrance and exit shown in figure 3.1. The stir shaft adapter, complete with a 24/40 male joint that connected to the round bottom flask and 18/9 knuckle joint for the stir shaft, was fabricated in the Department of Chemistry Glass Shop. The adapter was also connected to a distillation arm to collect methanol and excess butanediol that evolved during the reaction. The nitrogen inlet line could be closed and vacuum applied to the condensing arm as needed. The reaction pot was immersed in a salt bath composed of 53 wt. % potassium nitrate, 40 wt.% sodium nitrate, and 7 wt. % sodium nitrite, whose melting point was approximately 150 °C and was stable higher than 350°C. The bath allowed for easy observation of the flask contents as the reaction progressed. After addition of monomers, the flask was purged with nitrogen for 3 minutes and the vacuum was then applied for another 3 minutes. These steps were repeated 3 times to remove any trace amounts of water remaining in the monomers. At this point, a slow nitrogen flow was started and the salt bath, preheated to 200 °C, was raised and stirring was commenced. After the monomers had melted, the titanium isopropoxide catalyst was added through the separated ball joint with a long needled syringe at a concentration based on the total moles of monomers. Reaction was allowed to proceed with slow nitrogen flow at 200 °C for two hours. It was then raised to 220 °C for another 2 hours under slow nitrogen flow. The temperature was further increased to 250 °C for one-half hour while under nitrogen purge. The pressure within the reaction flask was then decreased to

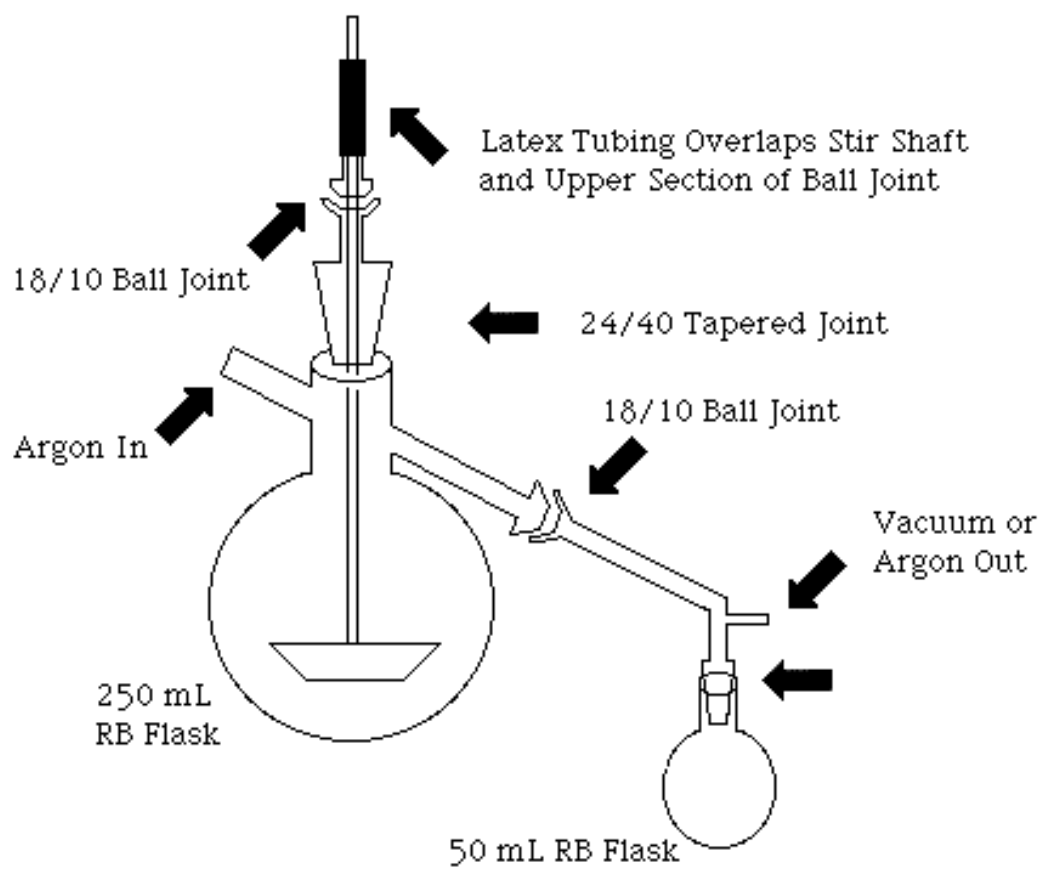


Figure 3.1: Melt Polymerization Reactor

approximately 10 mTorr for 10 minutes. This was accomplished by balancing the nitrogen flow against the vacuum to attain the desired reduced pressure, so as to avoid bumping of the reaction contents. The final step was to achieve high vacuum conditions by crimping off the nitrogen inlet line while maintaining 250 °C. It should be mentioned that this final temperature is determined by the boiling point of the excess diol under vacuum conditions. This was the point at which the reaction viscosity increased rapidly. A special apparatus was built by the author to allow control of the depth of the stir paddle within the flask while maintaining the vertical position of the flask in the hood. This allowed the reaction contents to remain in contact with the walls of the flask and avoided the possibility of the high polymer from “climbing” the stir shaft and cooling down due to lack of heat transfer by conduction from the flask surface. After approximately 2 hours at 250 °C and high vacuum, the reaction was stopped. The bath was lowered from the flask and its contents allowed to cool until the stir shaft could no longer be moved manually. At this point, the bath was raised and a small torque applied to the stir shaft with the overhead motor. As soon as the polymer broke free of the surface of the flask, the stir shaft was raised to “pull” the polymer away from the flask. By pulling the polymer away from the flask, formation of a 15 weight percent solution in chloroform could be greatly hastened by stirring the polymer in the solvent. After dissolution, the polymer was precipitated in methanol and dried at 100°C under vacuum.

2. Poly(cyclohexanedimethanol cyclohexanedicarboxylate)

Poly(cyclohexanedimethanol cyclohexanedicarboxylate) was synthesized in a manner virtually identical to poly(butylene cyclohexanedicarboxylate) detailed in section 3.B.1. The major difference in the synthetic approach was the final temperature. Excess 1,4-cyclohexanedimethanol was removed in the final step of the reaction at 280 °C under high vacuum. All other conditions, including time, temperature, vacuum, catalyst concentration, removal, and precipitation of product remained the same.

3. Poly(butylene terephthalate)

Poly(butylene terephthalate) was synthesized in a manner very similar to poly(butylene cyclohexanedicarboxylate) detailed in section 3.B.1. Time, temperature and catalyst concentrations remained the same; however, workup conditions had to be changed. The resulting polymer was insoluble in both hot chloroform and n-methyl pyrrolidone. Unfortunately, the only way to remove the polymer was to first “pull” it off the glass and then rupture the round bottom flask with a hammer. The polymer was then cut off the stir paddle using pruning shears.

4. Effect of Catalyst on Poly(dimethylsiloxane)

It was necessary to determine whether the titanate catalyst was causing any degradation or redistribution of the poly(dimethylsiloxane) oligomer under reaction conditions at catalytic concentrations. The model reaction was conducted in a 2 neck 100mL round bottom flask charged with ester terminated PDMS. The flask was heated to 200 °C and 100ppm of titanium isopropoxide was added and allowed to stir under a nitrogen purge for 2 hours. The temperature was then increased to 250 °C and the reaction was continued for another 2 hours. The PDMS was then submitted for GPC analysis and molecular weight and polydispersity index were compared to the PDMS starting material.

5. Poly(butylene cyclohexanedicarboxylate) / Poly(dimethylsiloxane) Segmented Copolymers a. Endcapping of Poly(dimethylsiloxane)

The secondary aminopropyl terminated poly(dimethylsiloxane) oligomer was reacted with a 5 fold excess of 1,4-dimethylcyclohexanedicarboxylate to yield an ester terminated poly(dimethylsiloxane) with an amide link at each end. It was hypothesized that the amide link would be stable during the transesterification reaction.

The endcapping reaction was conducted in a one neck flask equipped with a condensing arm, a temperature controlled oil bath set to 150 °C, a magnetic stirbar, and nitrogen flow that was bubbled through the hot solution. As the reaction progressed, the methanol evolved was removed from the pot. Depending on the

volume charged to the flask, the actual amount of time needed for the reaction to go to completion was on the order of 6 to 8 hours. This was easily monitored by infrared spectroscopy and was assumed to be complete with the disappearance of the amine stretch at approximately 3500 cm^{-1} . The product was then stripped of the excess 1,4-dimethylcyclohexanedicarboxylate under high vacuum at 150°C .

b. Poly(butylene cyclohexanedicarboxylate) /
Poly(dimethylsiloxane) Segmented Copolymers

A series of copolymers containing 5-30 weight percent polydimethylsiloxane were prepared. The methods used to synthesize these materials were very similar to those used to make the previously mentioned homopolymers (sections 3.B.1-3). The materials were charged to the 250 mL round bottom flask and allowed to react under the same time and temperature conditions used to make the homopolymers. Once again, the final temperature reached was 250°C and determined by the boiling point of the diol under high vacuum; however, it was found that in order to reach high conversions, an additional aliquot of titanium catalyst was needed. Half the volume of the initial aliquot was added prior to taking the reaction to reduced pressure. The entire series of poly(butylene cyclohexanedicarboxylate) / poly(dimethylsiloxane) segmented copolymers was soluble in chloroform. The solutions were then precipitated into a 50/50 mixture of methanol/isopropanol to remove any unreacted poly(dimethylsiloxane). This allowed for correct experimental determination of the weight percent of poly(dimethylsiloxane) incorporated into the copolymer in later ^1H NMR studies.

6. Poly(cyclohexanedimethanol cyclohexanedicarboxylate) /
Poly(dimethylsiloxane) Segmented Copolymers

a. Endcapping of Poly(dimethylsiloxane)

The PDMS oligomer was endcapped with dimethylcyclohexanedicarboxylate as previously detailed in section 3.B.5a.

b. Poly(cyclohexanedimethanol cyclohexanedicarboxylate)

Poly(dimethylsiloxane) Segmented Copolymers

A series of copolymers containing 3-30 weight percent polydimethylsiloxane were prepared. The methods used to synthesize these materials were very similar to those used to make the previously mentioned homopolymers (sections 3.B.1-3). The materials were charged to the 250 mL round bottom flask and allowed to react under the same time and temperature conditions used to make the homopolymers. The final temperature reached was 280 °C and determined by the boiling point of the cyclohexanedimethanol under high vacuum. An additional aliquot of titanium catalyst was needed to reach high conversions. Half the volume of the initial aliquot was added prior to taking the reaction to reduced pressure. The entire series of poly(cyclohexanedimethanol cyclohexanedicarboxylate) / poly(dimethylsiloxane) segmented copolymers was soluble in chloroform. The solutions were then precipitated into a 50/50 mixture of methanol/isopropanol to remove any unreacted poly(dimethylsiloxane). This allowed for correct experimental determination of the weight percent of poly(dimethylsiloxane) incorporated into the copolymer in later ¹H NMR studies.

7. Poly(butylene terephthalate)/Poly(dimethylsiloxane)

Segmented Copolymers

a. Endcapping of Poly(dimethylsiloxane)

The secondary aminopropyl terminated poly(dimethylsiloxane) oligomer was reacted with a 2.2 molar excess of dimethylterephthalate to yield an ester terminated poly(dimethylsiloxane) with an amide link at each end. It was hypothesized that the amide link would be stable during the transesterification reaction.

The endcapping reaction was conducted in a one neck flask equipped with a condensing arm, a temperature controlled oil bath set to 175 °C, a magnetic stirbar, and nitrogen flow that was bubbled through the hot solution. As the reaction progressed, the methanol evolved was removed from the pot. Depending on the volume charged to the flask, the actual amount of time needed for the reaction to go to completion was on the order of 6 to 8 hours. This was easily monitored by

infrared spectroscopy and was assumed to be complete with the disappearance of the amine stretch at approximately 3500 cm⁻¹.

b. Poly(butylene terephthalate)/Poly(dimethylsiloxane)

Segmented Copolymers: 2° Aminoalkylterminated-Poly(dimethylsiloxane)

A series of copolymers containing 5-30 weight percent polydimethylsiloxane were prepared. The methods used to synthesize these materials were very similar to those used to make the previously mentioned homopolymers (sections 3.B.1-3). The materials were charged to the 250 mL round bottom flask and allowed to react under the same time and temperature conditions used to make the homopolymers. The final temperature reached was 250 °C and determined by the boiling point of the butanediol under high vacuum. An additional aliquot of titanium catalyst was needed in order to reach high conversions. Half the volume of the initial aliquot was added prior to taking the reaction to reduced pressure. The entire series of poly(butylene terephthalate) / poly(dimethylsiloxane) was insoluble in both hot chloroform and hot n-methyl pyrrolidone. The polymer was “pulled” (as detailed in 3.B.1) from the glass surface and the reaction flask ruptured in order to remove the material.

c. . Poly(butylene terephthalate)/Poly(dimethylsiloxane)

Segmented Copolymers: 1°Aminoalkylterminated-Poly(dimethylsiloxane)

A series of copolymers containing 10-30 weight percent polydimethylsiloxane were prepared using a 1° aminoalkylterminated poly(dimethylsiloxane) with a M_n of approximately 1200 g/mol which was provided by the Shin-Etsu corporation. The methods used to synthesize these materials were very similar to those used to make the previously mentioned homopolymers (sections 3.B.7a).

8. Poly(butylene terephthalate) / Poly(dimethylsiloxane)

/Poly(tetramethyleneoxide) Segmented Copolymer

a. Endcapping of Poly(dimethylsiloxane)

The secondary aminopropyl terminated poly(dimethylsiloxane) oligomer was endcapped as previously detailed in section 3.B.7a

b. Poly(butylene terephthalate) / Poly(dimethylsiloxane)
/ Poly(tetramethyleneoxide) Segmented Copolymers

Synthesis of a 30 weight percent soft segment copolymer was achieved using a reaction procedure previously detailed in section 3.B.7b. In this case the soft segment was comprised of 10 weight percent poly(dimethylsiloxane) and 20 weight percent poly(tetramethyleneoxide). The poly(tetramethyleneoxide) portion of the soft segment possessed an M_n of approximately 1000 g/mol and was provided by the BASF corporation. The reaction yielded a light tan polymer that was insoluble in chloroform and hot n-methylpyrrolidone.

C. CHARACTERIZATION OF OLIGOMERS AND POLYMERS

1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR can be very useful when used to determine the molecular structure of the material. The spectra were obtained using a Nicolet Impact 400 Fourier Transform Infrared Spectrometer (resolution=1.0 cm^{-1}) coupled to a Gateway 66Mhz Personal Computer which was used for data output and analysis. Liquid samples, such as poly(dimethylsiloxane), were prepared by placing a drop of the material between two KBr salt plates. Film forming samples were prepared by casting a thin film from a dilute solution of chloroform. A background spectra was obtained before the sample spectra was collected. The software included with the FTIR automatically subtracted the background spectra from the sample spectra. Sample spectra were collected at room temperature from 4000 cm^{-1} to 600 cm^{-1} .

2. Nuclear Magnetic Resonance Spectroscopy (NMR)

a) Solution Proton (^1H) NMR

Solution ^1H NMR was used for compositional and structural analysis of polymers and oligomers. Proton NMR spectra were obtained using a Varian Unity 400, 400Mhz spectrometer on 5-10% (wt./vol.) solutions of sample in deuterated chloroform. No tetramethylsilane (TMS) was used in the deuterated chloroform sample solvent due to the potential overlap with the methyl protons in the siloxane oligomer. The chloroform reference peak at 7.24ppm was to ensure accuracy of peak assignments.

b) ²⁹Si Solution NMR

Solution ²⁹Si NMR was used for compositional and structural analysis of the poly(dimethylsiloxane) oligomer. ²⁹Si NMR spectra were obtained using a Varian Unity 400, 400Mhz spectrometer on 5-10% (wt./vol.) solutions of sample in deuterated chloroform.

3. Intrinsic Viscosity

Intrinsic Viscosity measurements [η]₀ on the homopolymers and copolymers were made using a Cannon-Ubbelohde glass capillary viscometer. All measurements were taken at 25 °C in chloroform. Four concentrations between 0.5 and 2 weight percent, with 3 replicate runs per concentration, were used to determine the intrinsic viscosity of the samples.

4. Gel Permeation Chromatography

The molecular weight and molecular weight distributions for the polysiloxane oligomer, polyester homopolymers, and copolymers were determined using gel permeation chromatography. The instrument used was a Waters GPC equipped with inline Viscotek refractive index and Viscosity detectors. This allowed for universal calibration and absolute molecular weight numbers as well as determination of the Mark-Houwink constants for the samples analyzed.¹⁴⁸ All samples were run in HPLC grade chloroform as the mobile phase at 30 °C with a flow rate of 1.0mL/minute. The columns used were μ Styragel-HT with a pore size of 10⁴ and 10³ Angstroms.

5. Compression Molding

Compression molded films of a controlled thickness were created using a SmartPress. The sample was sandwiched between two pieces of 3mm thick aluminum plate and was centered in a mold of desired thickness. A silicone based release agent (Miller-Stephenson TFE-based Release Agent and Dry Lubricant #MS-122N-CO2) was used to facilitate sample removal. The samples were heated 20°C above their T_m and hydraulic pressure was alternately applied and released to insure

that all trapped air was allowed to escape to negate void formation. These films were then utilized for various thermal and mechanical analyses.

6. Differential Scanning Calorimetry

Melting temperatures and the crystallization temperatures of the polyester homopolymer and the polyester segment of the copolymers were determined by differential scanning calorimetry using a Perkin-Elmer Series 7 Instrument. Sample sizes were in the range of 5-10mg. Each sample was analyzed by heating from 30 °C-250°C at a heating rate of 10 °C/minute. The sample was held at 250 °C for three minutes and cooled at a rate of 10 °C/minute and held at 30 °C for three minutes. The sample was then heated from 30 °C to 250 °C at a heating rate of 10 °C/ minute. Melting temperatures were taken from the second heat, ensuring that all samples had the same thermal history. The crystallization temperatures were reported from the cooling curve. The transitions were taken as the minimum of the crystallization peak and the maximum of the melting peak.

7. Thermal Gravimetric Analysis

Weight loss versus temperature was determined by thermal gravimetric analysis using a Perkin-Elmer Series 7 Instrument in an oxidizing (air) environment. The analysis was conducted using 7-10mg of sample and heating from 30-700°C at a heating rate of 10 °C/minute. Data was collected and analyzed by the computer which plotted the data as weight percent (y) against temperature(x). The 5 percent weight loss values were recorded and the corresponding temperatures used to avoid degradation during differential scanning calorimetry (DSC) experiments.

8. Dynamic Mechanical Analysis

Dynamic mechanical analyses of the homopolymers and copolymers was conducted using a Perkin-Elmer Series 7e Instrument in an air environment. Compression molded samples with a thickness of approximately 0.5mm were used to generate data via the extension mode provided with the instrument. The samples were heated from 140-200°C at a rate of 5°C per minute and a frequency of 1Hz using strain control (one of several methods available within the Perkin-Elmer software). The amount of strain control varied with the copolymer composition, but

was in the range of 0.2-0.5%. Both modulus and tan delta values vs. temperature could be obtained from these measurements

9. Transmission Electron Microscopy

Transmission electron micrographs were generously provided Mr. Steve McCartney from compression molded samples which were subsequently microtomed to the desired thickness. This later step proved difficult due to the low T_g of the poly(dimethylsiloxane) segment and may help to explain the unusual “smearing” of the soft segments in the hard segment matrix.

10. Elemental Analysis

Elemental analysis of the homopolymers and copolymers was obtained from Galbraith Labs. Relative percentages of carbon, hydrogen, oxygen, and silicon were obtained.

Chapter IV

RESULTS AND DISCUSSION

A. POLY(BUTYLENE CYCLOHEXANEDICARBOXYLATE)

The ^1H NMR of the 98+% *cis* isomeric mixture of dimethyl 1,4-cyclohexane dicarboxylate (DMCD) is shown in figure 4.1. The *cis* and *trans* peaks appear at 2.42 and 2.22 ppm respectively and are clearly resolvable. The comparison of the areas under the peaks by integration allowed for quantification of the isomeric ratio. Previous results in this research group²⁰ have shown no significant *cis/trans* isomerism occurs at the conditions used for the melt polymerization of the DMCD with butanediol.

Synthesis of poly(butylene cyclohexanedicarboxylate) (PBCD) 98+% *cis* DMCD is described in Chapter III. The reaction is depicted in Scheme 4.1. It is assumed that the resulting polymer is hydroxyl terminated since an excess of diol is used during the polymerization. Due to side reactions that can result in chain scission during the formation of polyesters in the melt, some carbonyl endgroups (ester, acid) can result. The strong carbonyl absorbance at $1730\text{-}1740\text{ cm}^{-1}$ is apparent as well as the broad absorbance due to the C-O bond centered between 1100 and 1200 cm^{-1} . The aliphatic C-H stretch occurs at 2920 cm^{-1} and the $-\text{CH}_2$ absorption appears at 1440 cm^{-1} .

The polyester homopolymer was characterized by GPC. A representative chromatogram is shown in figure 4.3. The homopolymer was dissolved in chloroform and run against polystyrene standards using a Waters Chromatograph equipped with a refractive index and a Viscotek[®] viscosity detector which allowed for universal calibration. The molecular weight distribution as judged by M_w/M_n is very near 2 which is characteristic of equilibration and step-growth polymerization.

Poly(butylene cyclohexanedicarboxylate) synthesized from DMCD high in *cis* content is generally low in crystallinity. The amorphous material is soluble in many common solvents.

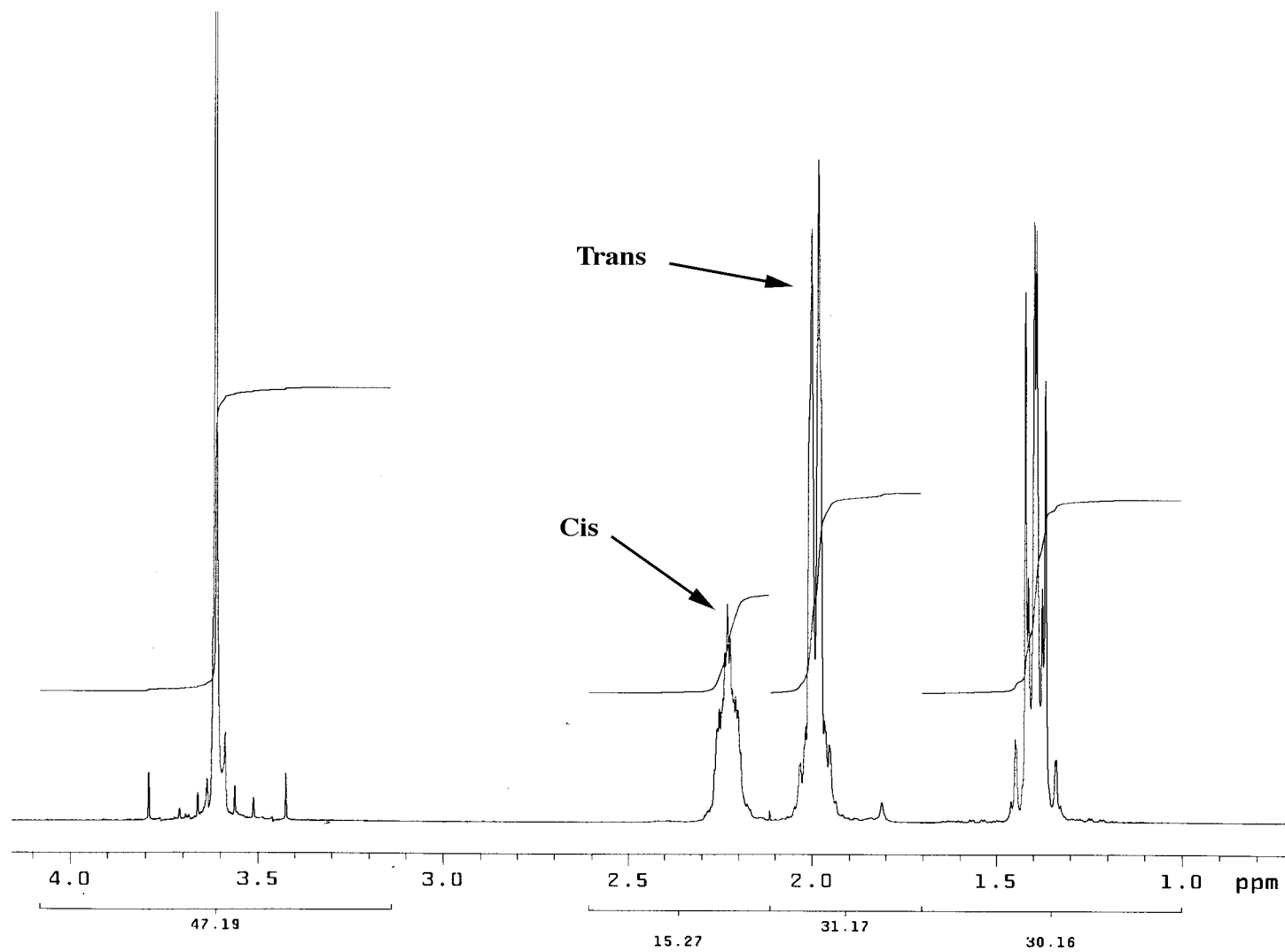


Figure 4.1: ^1H NMR of 90% trans 1,4 dimethylcyclohexanedicarboxylate

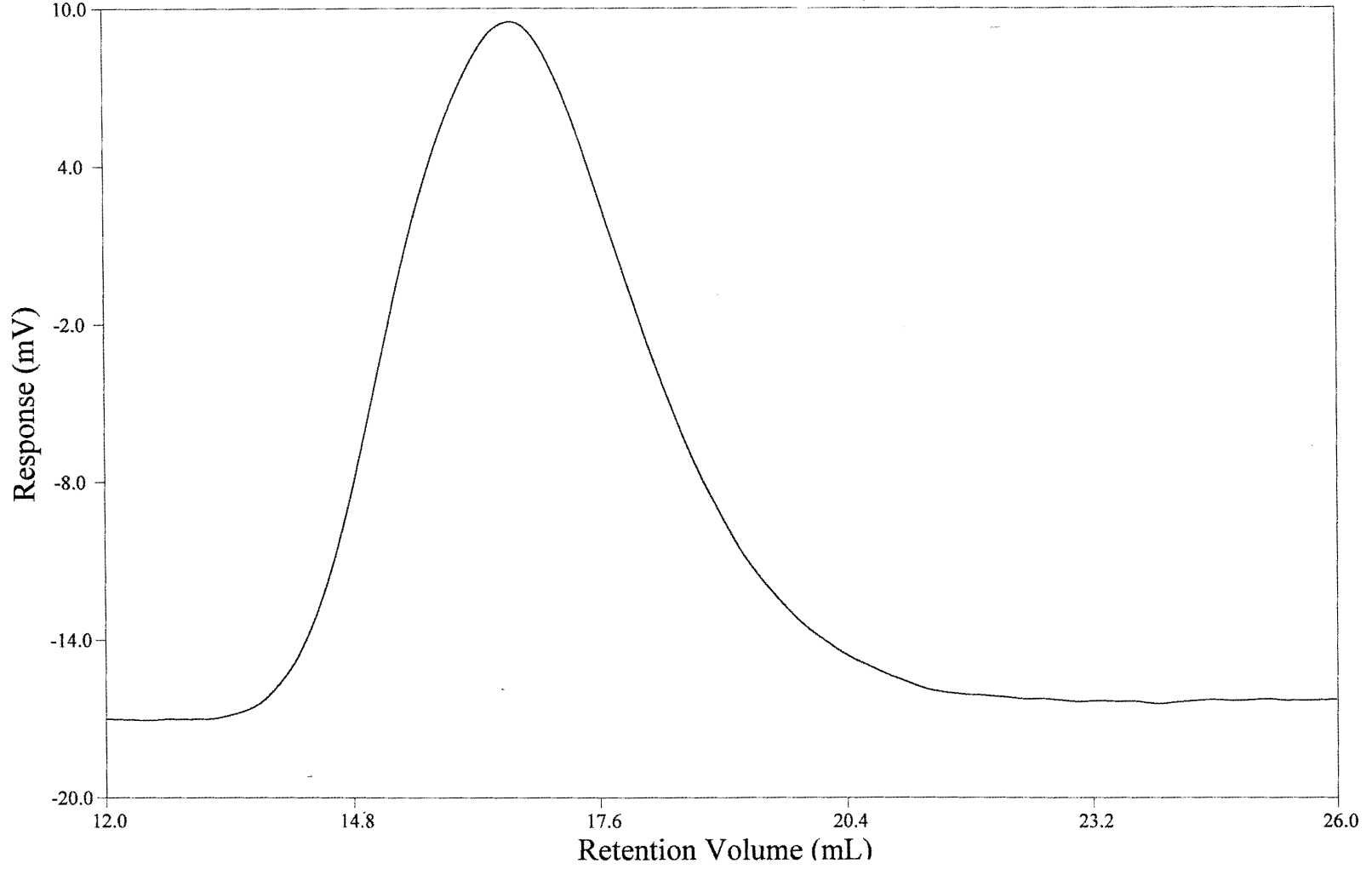
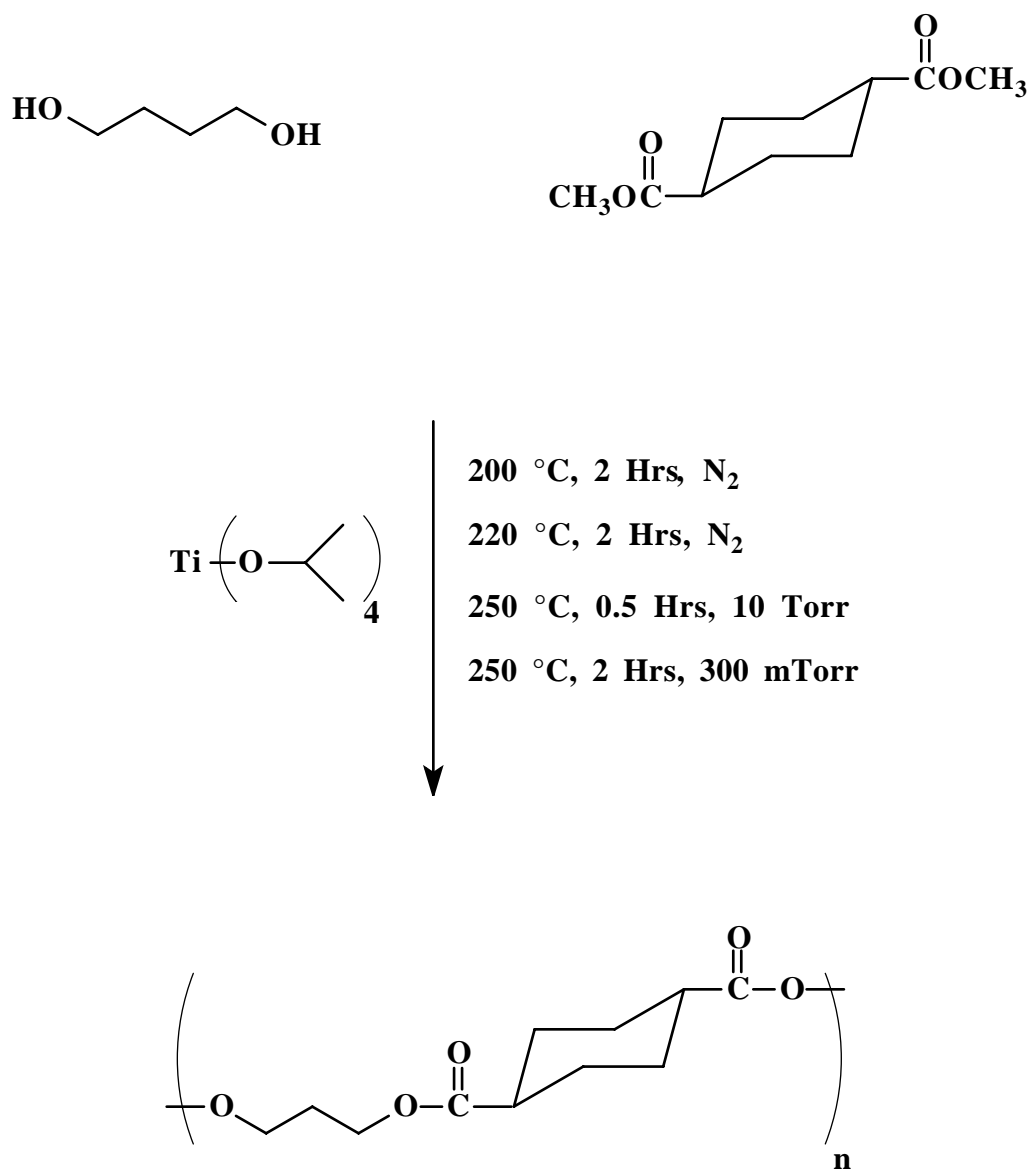


Figure 4.3: Gel Permeation Chromatogram of Poly(butylencyclohexanedicarboxylate)



Scheme 4.1: Synthesis of poly(butylene cyclohexanedicarboxylate)

B. POLY(CYCLOHEXANEDIMETHANOL CYCLOHEXANEDICARBOXYLATE)

1,4 Cyclohexane dimethanol was purchased from Aldrich Chemical Company as a mixture of *cis* and *trans* isomers. This diol, along with DMCD, was polymerized using melt polymerization techniques discussed in Chapter III. The reaction scheme for the synthesis of poly(cyclohexanedimethanol cyclohexanedicarboxylate) (PCDCD) is shown in scheme 4.2. A representative GPC chromatogram is shown in figure 4.4. The molecular weight distribution is near 2 and the M_n is approximately 25,000 g/mole. GPC data was obtained from a sample dissolved in chloroform. A representative DSC thermogram (figure 4.5) shows the occurrence of the semi-crystalline phase in the mostly amorphous material. The melt endotherm occurs near 180°C. It should be noted that this material can be quenched from a melt compression mold to form a clear transparent film; however, when a film of the polymer is cast from a dilute solution of chloroform, the film was opaque (white).

C. POLY(BUTYLENE TEREPHTHALATE)

Poly(butylene terephthalate) was polymerized using melt polymerization techniques discussed in Chapter III. The reaction scheme for the synthesis of poly(butylene terephthalate) (PBT) homopolymer is shown in scheme 4.3. GPC data was not obtained due to the insolubility of the semi-crystalline material. PBT is known to be a semi-crystalline polymer with a melting point (T_m) of approximately 230°C and a T_g of about 40°C. A representative DSC thermogram (figure 4.6) confirms that the T_m occurs at about 230°C. The DSC experiment must be initiated at sub-ambient conditions to confirm the existence of the T_g at near room temperature, but this was not attempted for this polymer.

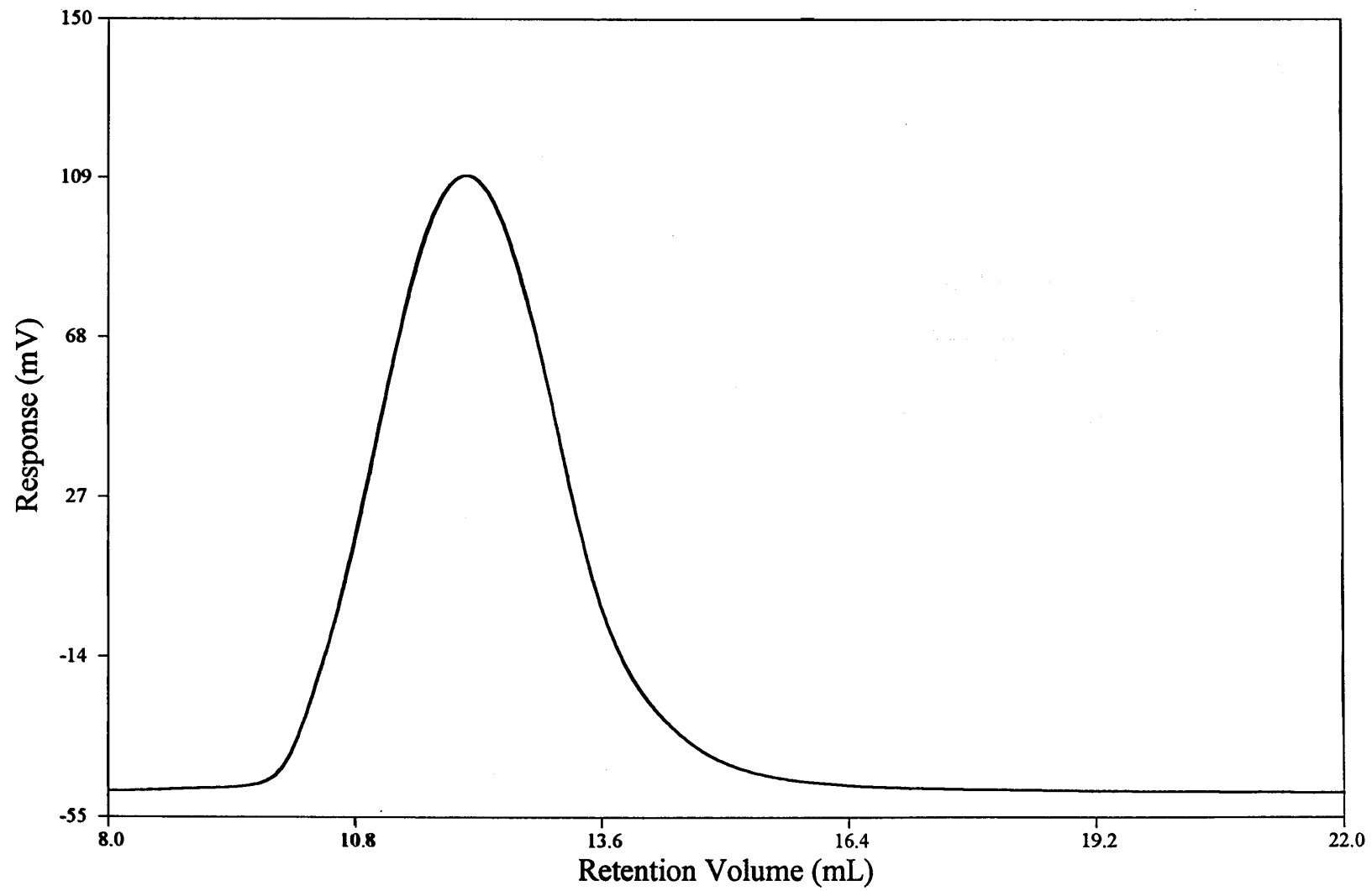


Figure 4.4: Gel Permeation Chromatogram of poly(cyclohexanedimethanolcyclohexanedicarboxylate)

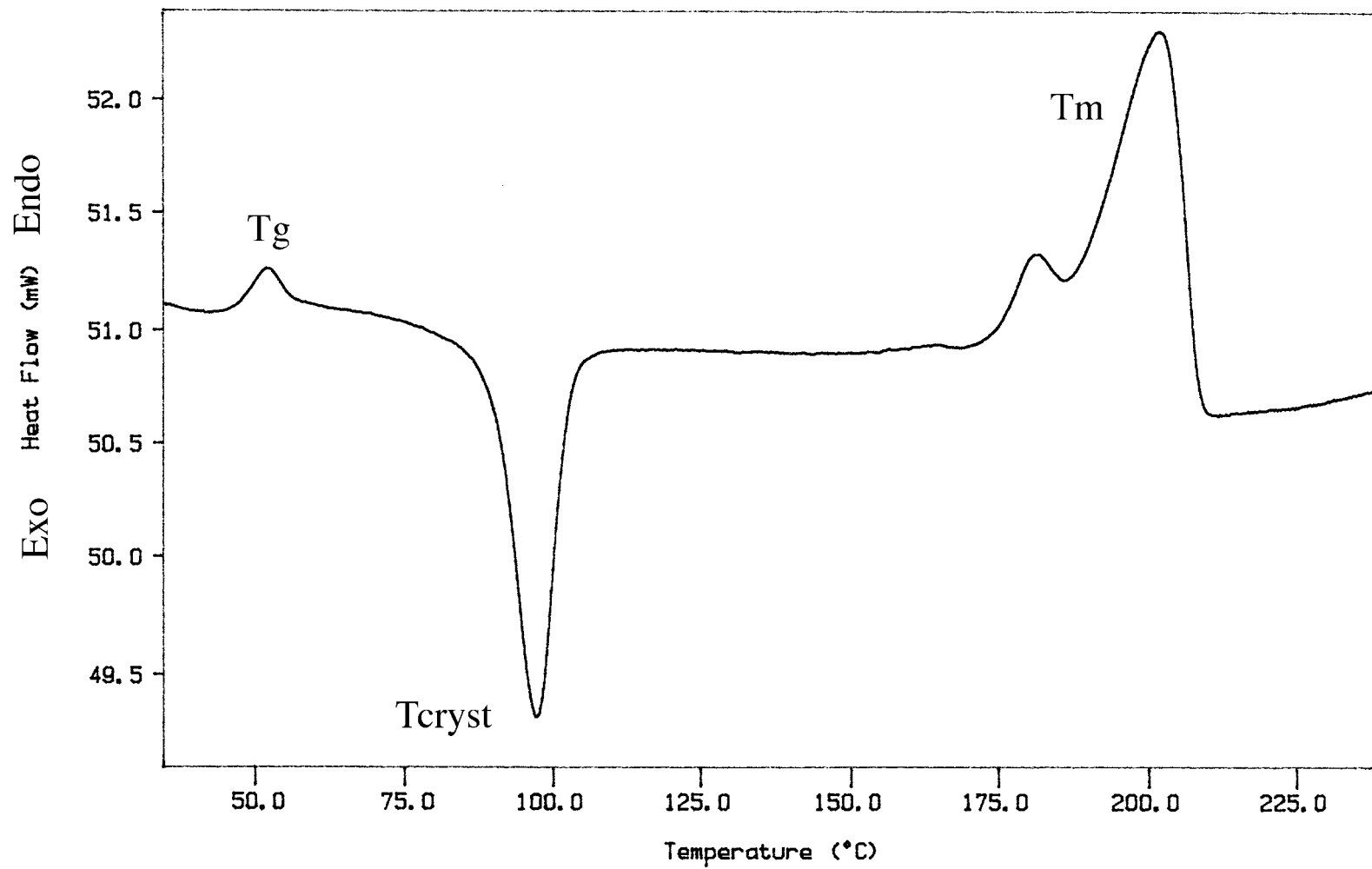


Figure 4.5: DSC thermogram of PCDCD homopolymer. Experiment was conducted in nitrogen at a heating rate of 10°C/min.

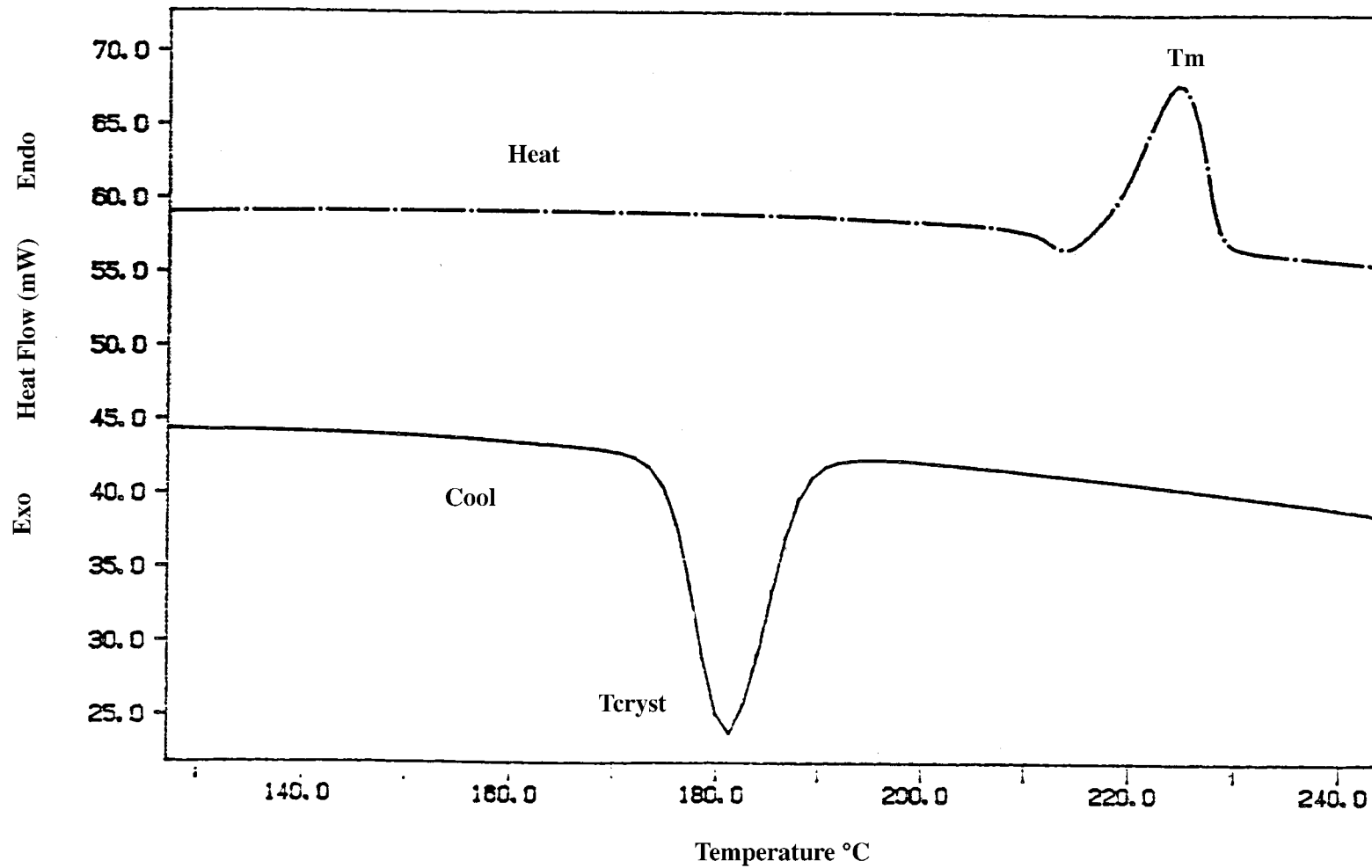
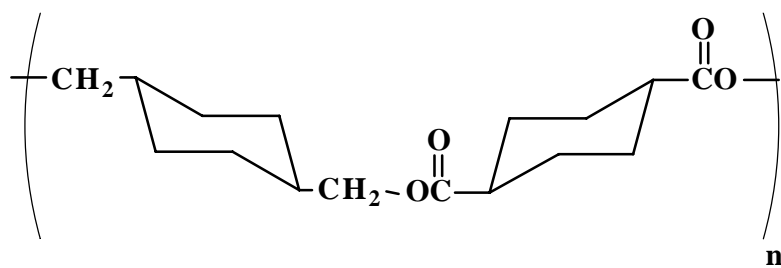
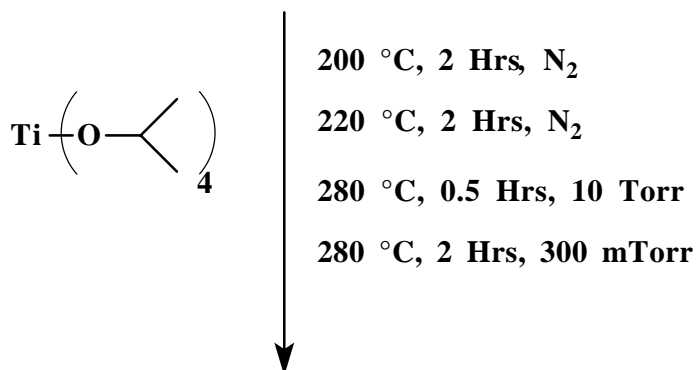
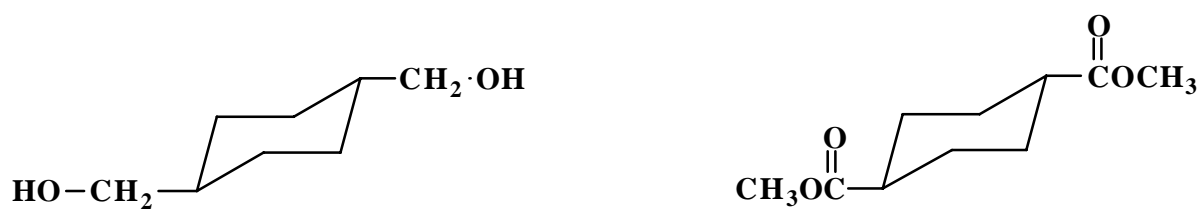
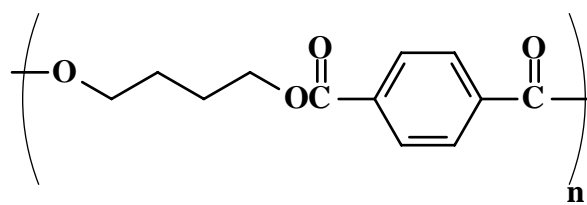
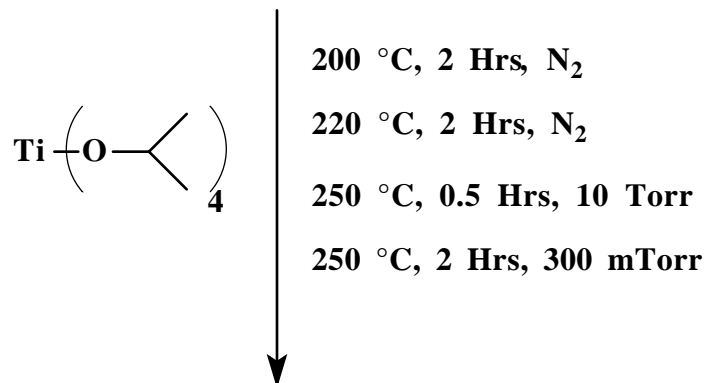


Figure 4.6: DSC thermogram of PBT homopolymer. Experiment was conducted in nitrogen at a heating rate of 10°C/min.



Scheme 4.2: Synthesis of poly(cyclohexanedimethanol cyclohexanedicarboxylate)



Scheme 4.3: Synthesis of poly(butylene terephthalate)

D. SYNTHESIS OF POLYESTER/POLYDIMETHYLSILOXANE SEGMENTED COPOLYMERS

1. Research Introduction

An objective of this research was to synthesize a series of polyester/polydimethylsiloxane segmented copolymers that could be fabricated by melt processing. If block or segmented copolymers are highly incompatible, they can become unprocessable due to the resulting phase-separation. The microphase separation can become so stable that the viscosity increases dramatically, making the copolymer difficult or impossible to melt process.¹

The first polymers synthesized utilized the cycloaliphatic polyester segment due to the non-polar nature of the dimethyl cyclohexane dicarboxylate monomer. It was hoped that this would help the polyester remain miscible with the polysiloxane during polymerization as well as during later melt processing. In this research, the polysiloxane segment was preformed and was incorporated into the polyester during the melt transesterification reaction, in the presence of a titanium isopropoxide catalyst. Later experiments showed that the aromatic dimethyl terephthalate was also capable of polymerization to high molecular weight during the melt transesterification reaction.

The copolymers were synthesized from the PDMS and polyester starting materials (monomers) instead of reacting two homopolymers with reactive endgroups. It was hoped this would help to decrease the possibility of phase separation as well as increasing the chance of miscibility throughout the melt transesterification reaction. Since there is no solvent to solubilize the endgroups, the miscibility of the reactants controls the efficiency of the coupling. Poly(dimethylsiloxane) is a very non-polar material because of its helical structure, which forces all of the methyl groups to the outside of the helix, as discussed earlier. This helps to explain why poly(dimethylsiloxane) is immiscible with most organic polymers. The monomeric polyester starting materials, in contrast, were expected to be more miscible with the poly(dimethylsiloxane) soft segment. The resulting

segmented copolymer was expected to be melt processable; something that is not easily attainable for many copolymers containing poly(dimethylsiloxane).

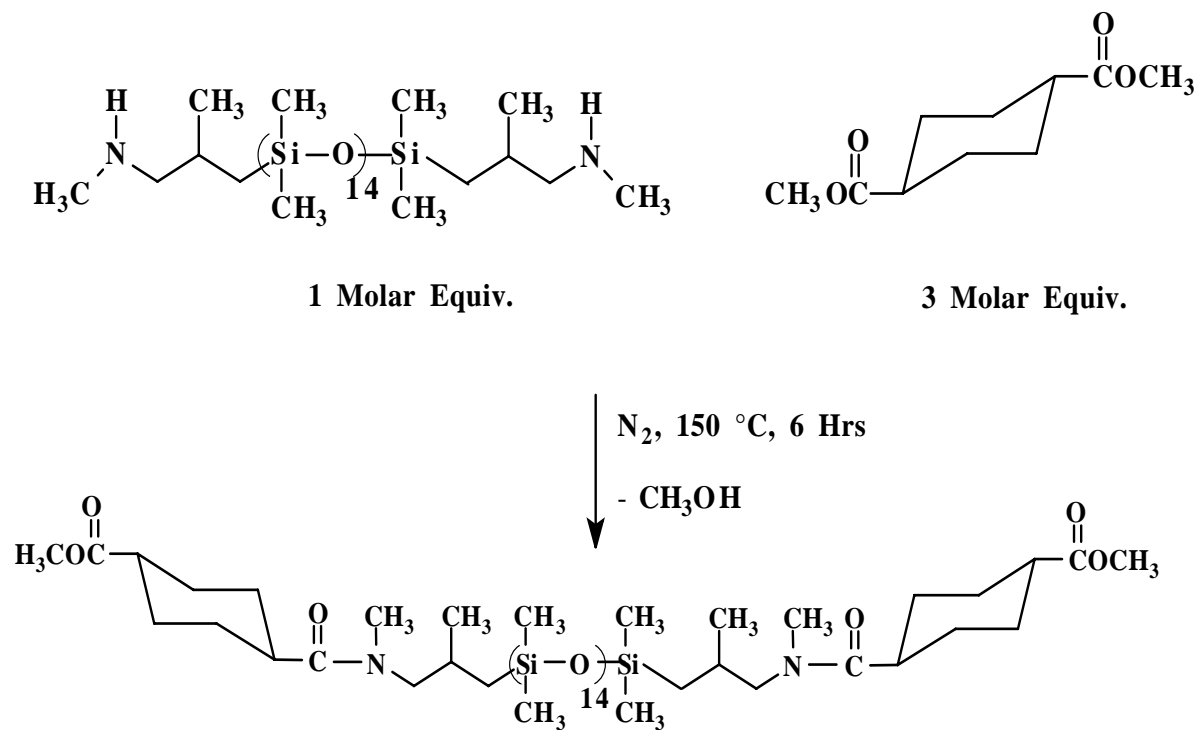
Due to the UV stability of both segments and the hydrophobicity of the poly(dimethylsiloxane) segment, these materials would be potentially useful in outdoor applications. Because poly(dimethylsiloxane) is itself a weatherable, light stable material, the properties of the two segments should be complementary; however, the actual testing of weatherability of these was not attempted in this thesis.

2. Effect of Titanate Catalyst on Poly(dimethylsiloxane)

The poly(dimethylsiloxane) (PDMS) oligomer was reacted with the titanate catalyst as described in Chapter III. The polysiloxane was characterized by GPC before and after exposure to the titanate catalyst. The two chromatograms are shown in figure 4.7. The amino alkyl terminated poly(dimethylsiloxane) was first derivatized with benzophenone before introduction to the GPC column to minimize association. There was no change in the elution volume, peak shape, or size. These data indicate that no significant redistribution or degradation of the poly(dimethylsiloxane) occurs in the presence of the titanate catalyst under these reaction conditions, confirming earlier studies.^{149,150}

3. Endcapping of Poly(dimethylsiloxane)

The synthesis for the endcapping of the 2° amine terminated PDMS to an ester terminated PDMS is illustrated in scheme 4.4. The PDMS oligomer was reacted with a five fold excess of dimethyl 1,4-cyclohexane dicarboxylate (DMCD). The reactants were charged to a 2-neck round bottom flask that was continuously purged with nitrogen to remove the methanol evolved as the reaction progressed. The PDMS was allowed to react for approximately six hours at 150 °C. After the reaction reached completion, the excess DMCD was removed via reduced pressure distillation. This step was conducted due to the crystallization of the DMCD from the PDMS oligomer, resulting in a two phase heterogeneous material. Distillation resulted in a clear, homogeneous material. The ester terminated PDMS was characterized by GPC to ensure that chain extension had not occurred.



Scheme 4.4: Synthesis of ester terminated PDMS

A GPC curve of the amine terminated PDMS is also shown for comparison. There is no significant change in the size, shape, and elution volume, taking into account the that different endgroups are present in each case.. Complete functionalization to the diester was verified via infrared spectroscopy (figure 4.9). The absence of the amine stretch (N-H, 3300 cm^{-1}) was further indication of complete functionalization. Further characterization by ^1H NMR showed the absence of the amine peak at 1.2ppm. This set of data indicates that the conversion of the amine terminated PDMS to an ester terminated PDMS is quantitative and that, as was expected, no chain extension occurred.

4. Poly(butylene cyclohexanedicarboxylate) / Poly(dimethylsiloxane) Segmented Copolymers

The synthesis of poly(butylene cyclohexanedicarboxylate)/poly(dimethylsiloxane) segmented copolymers is illustrated in scheme 4.5. All copolymers were synthesized using the 98+% *cis* isomer of DMCD. The copolymers were synthesized from PDMS oligomers and polyester monomers to ensure the miscibility of the reacting functional groups. Unlike the polyester homopolymers, a second aliquot of catalyst was added to ensure a high molecular weight product. Previous research^{149,150} indicated that the catalyst may partially deactivated by complexation with the PDMS oligomer.

During the copolymerization reaction, a number of important observations were noted. In the early stages of the reaction, with PDMS oligomer, diester and diol monomers present, the reactants formed a clear colorless homogeneous mixture above the melting point of the *cis* DMCD. As the temperature was increased, and throughout the ester interchange process, the material remained clear, light tan, and homogeneous. As vacuum was applied, after the addition of the second aliquot of catalyst, the material changed to an opaque tan and viscosity increased dramatically. This may be an indication of phase separation of the two segments. Care was taken to ensure that the viscous material remained in contact with the flask, as it had a tendency to “climb” the stir shaft. Upon cooling, the whole series of poly(butylene cyclohexanedicarboxylate) / poly(dimethylsiloxane) (3, 10, 20, and 30 wt %)

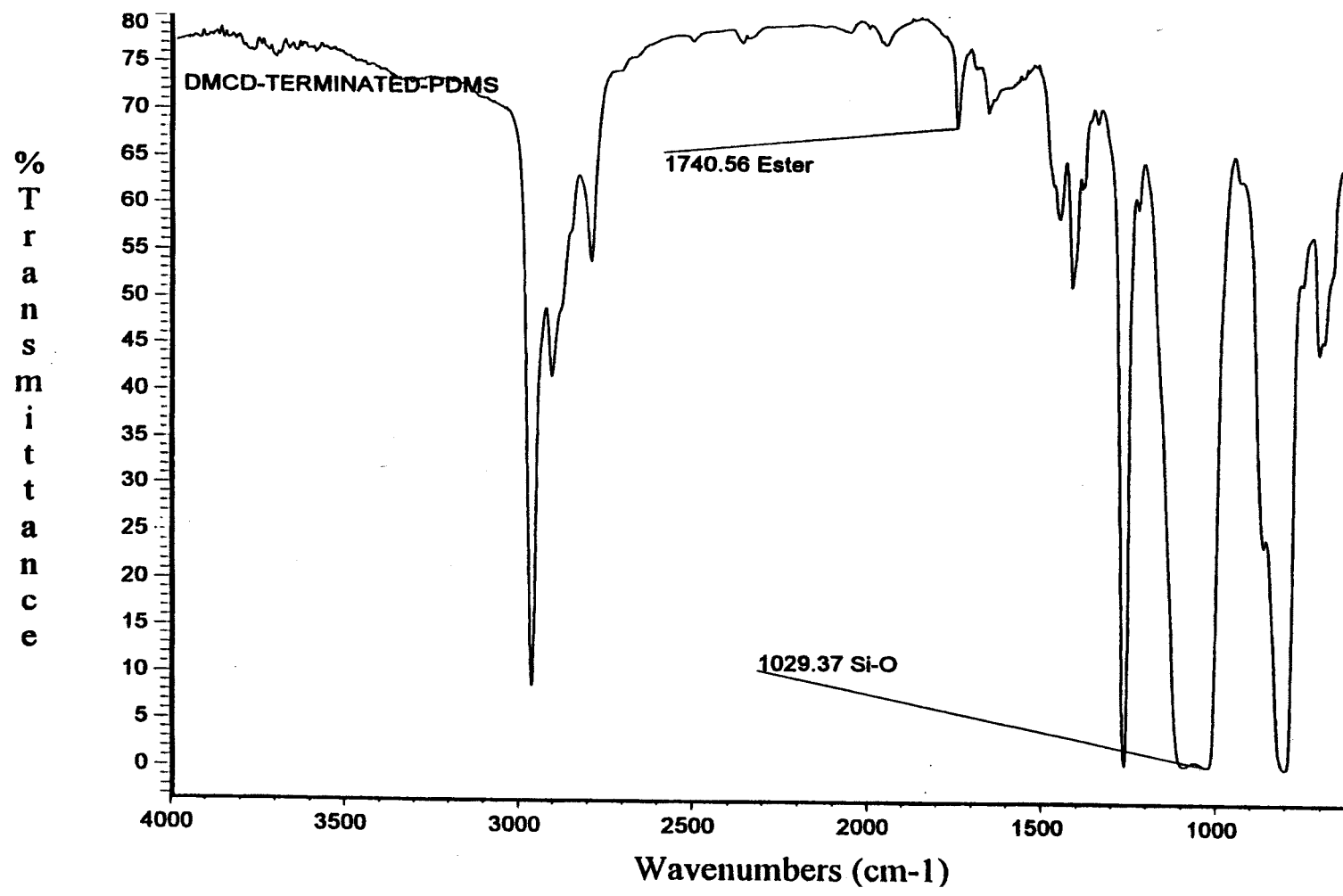
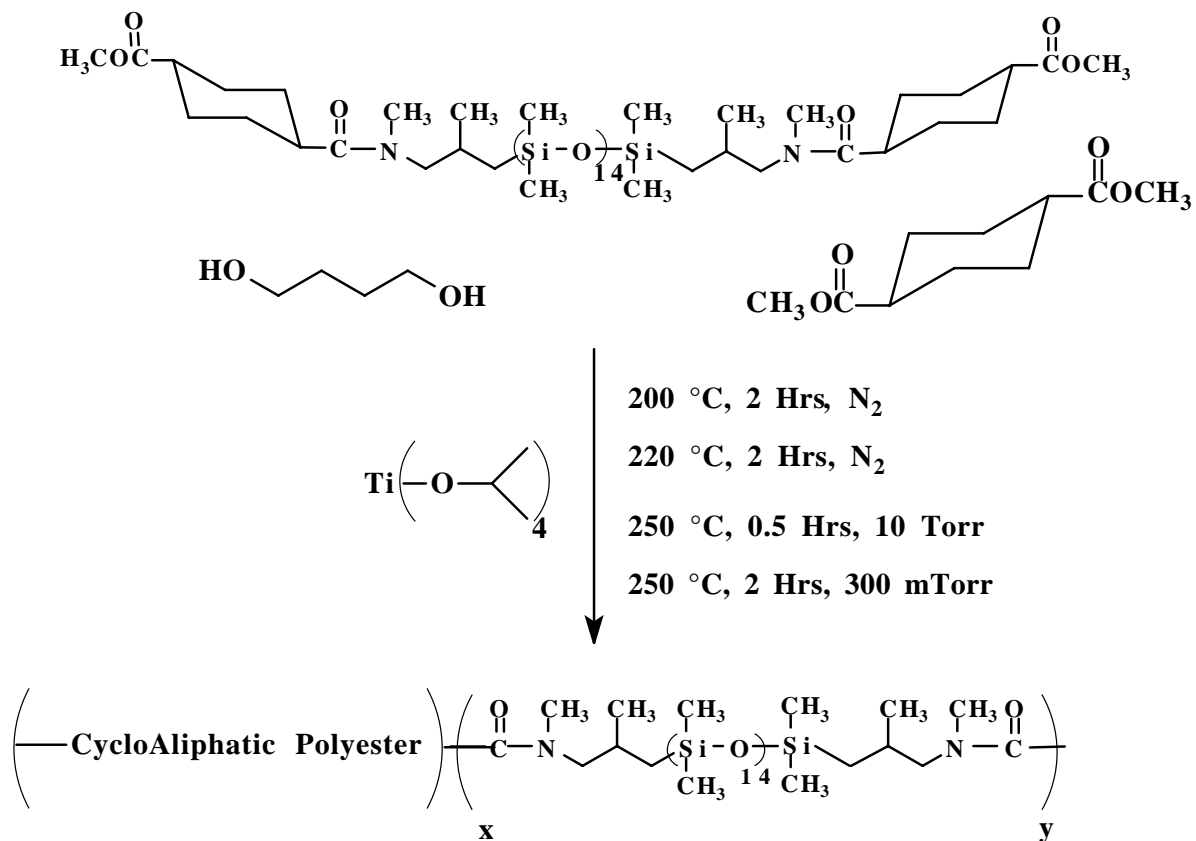


Figure 4.9: Infrared spectra of 1,4 dimethylcyclohexanedicarboxylate-terminated PDMS



Scheme 4.5: Synthesis of poly(butylene cyclohexanedicarboxylate) / poly(dimethylsiloxane) segmented copolymers

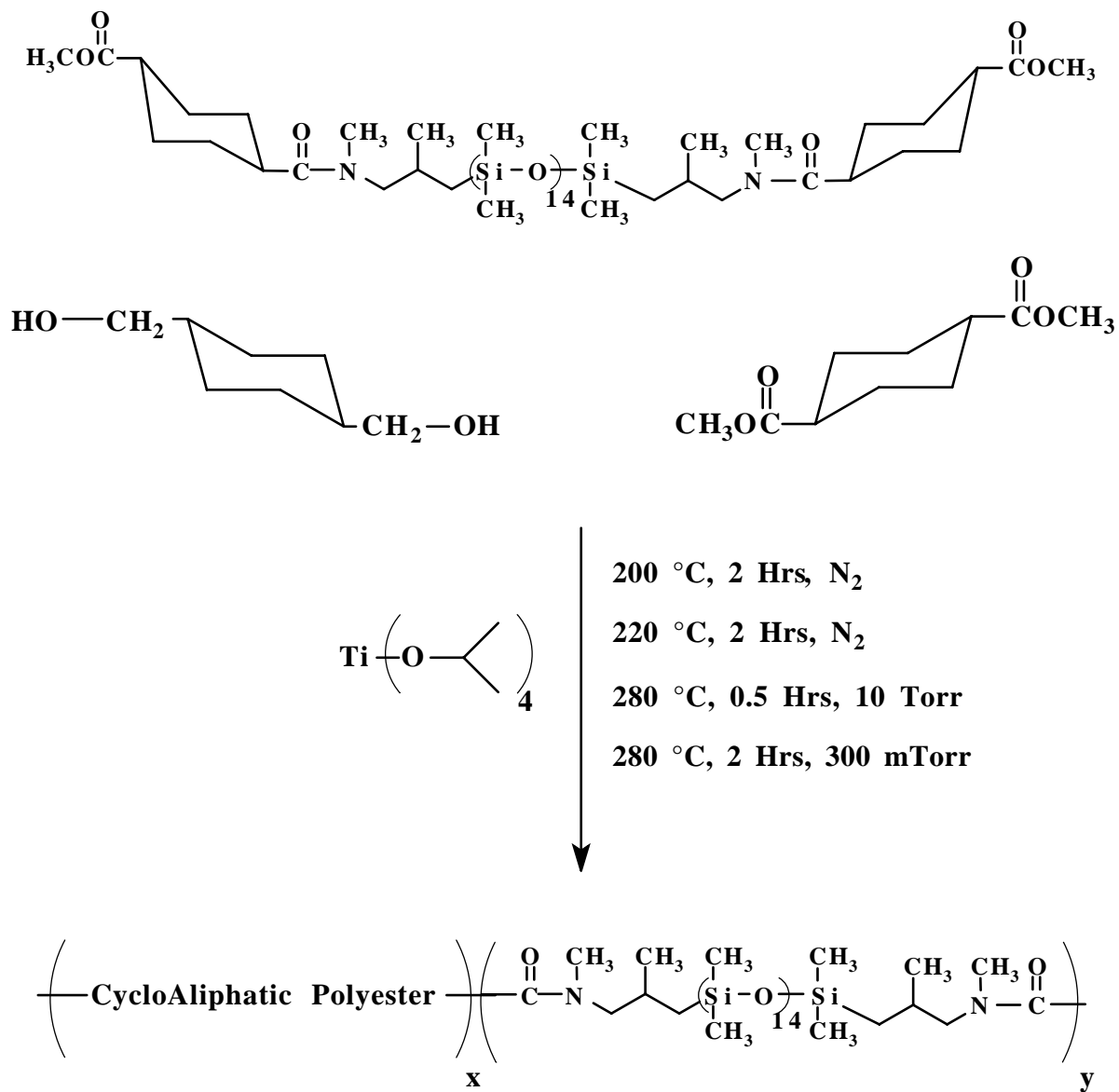
copolymers were opaque due to their semi-crystalline nature. Attempts to polymerize a 50 weight percent PDMS copolymer failed, due to phase separation in the early stages of the reaction. A 60 weight percent PDMS copolymer was also attempted, with similar results of phase separation in the early stages of the reaction. A 70 weight percent PDMS copolymer was successfully synthesized, but the resulting copolymer was a very viscous “grease” at room temperature with little mechanical integrity, probably suggesting low molecular weight.

All of the high molecular weight copolymers were soluble in chloroform. A 15 weight percent solution was made of each copolymer. These were then precipitated into a 50:50 (v:v) percent mixture of methanol / 2-propanol to insure that any unincorporated PDMS was solubilized and removed. This allowed for correct determination of the percent PDMS present in the copolymers.

5. Poly(cyclohexanedimethanol cyclohexane dicarboxylate) / Poly(dimethylsiloxane) Segmented Copolymers

The synthesis of poly(cyclohexanedimethanol cyclohexane dicarboxylate) / poly(dimethylsiloxane) segmented copolymers is illustrated in scheme 4.6. All copolymers were synthesized using the 98+% *cis* isomer of DMCD. The copolymers were synthesized in a manner identical to the poly(butylene cyclohexanedicarboxylate) / poly(dimethylsiloxane) segmented copolymers, in respect to the reaction approach, as well as the catalyst addition.

As the copolymerization reaction progressed, a number of observations were noted. In the early stages of the reaction, as before, with PDMS oligomer, diester and diol monomers present, the reactants formed a clear colorless homogeneous mixture above the melting point of the *cis* DMCD. As the temperature was increased, and throughout the ester interchange process, the material remained clear, light tan, and homogeneous. As vacuum was applied, after the addition of the second aliquot of catalyst, the material changed to an opaque tan and viscosity increased dramatically. Again, care was taken to ensure that the viscous material remained in contact with the flask, as it had a tendency to “climb” the stir shaft. Upon cooling, the whole series of poly(cyclohexanedimethanol cyclohexane dicarboxylate) /



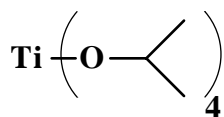
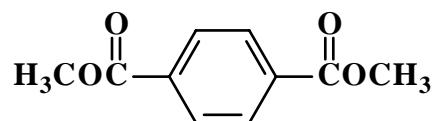
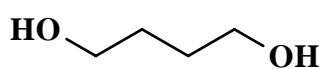
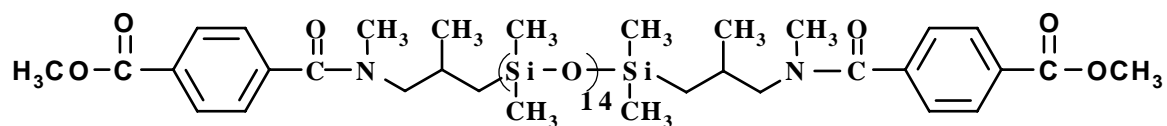
Scheme 4.6: Synthesis of poly(cyclohexanedimethanol cyclohexanedicarboxylate) / poly(dimethylsiloxane) segmented copolymers

poly(dimethylsiloxane) (5, 10, 20, and 30 wt %) copolymers were opaque due to their semi-crystalline nature. Due to the higher boiling point of cyclohexane dimethanol, the final reaction temperature under high vacuum was increased 30 °C to 280 °C compared to 250 °C for the poly(butylene cyclohexanedicarboxylate) / poly(dimethylsiloxane) copolymers. The molecular weights and intrinsic viscosities for these two aliphatic polyester copolymer series differed greatly. This is discussed in more detail in section 4.E.4. The series of poly(cyclohexanedimethanol cyclohexane dicarboxylate) / poly(dimethylsiloxane) copolymers was precipitated in a manner identical to the poly(butylene cyclohexanedicarboxylate) / poly(dimethylsiloxane) copolymers from a 15 weight percent solution of chloroform into a 50:50 (v:v) percent mixture of methanol / 2-propanol to insure that any unincorporated PDMS was solubilized and removed. This allowed for correct determination of the percent PDMS present in the copolymers.

6. Poly(butylene terephthalate) / Poly(dimethylsiloxane) Segmented Copolymers: 2° Aminoalkylterminated Poly(dimethylsiloxane)

The synthesis of poly(butylene terephthalate) / poly(dimethylsiloxane) segmented copolymers is illustrated in scheme 4.7. The 2° aminoalkylterminated poly(dimethylsiloxane) was first endcapped with dimethylterephthalate as described in section 3.B.7a. The copolymers were synthesized in a manner identical to the poly(butylene cyclohexanedicarboxylate) / poly(dimethylsiloxane) segmented copolymers, in respect to the reaction approach, as well as the catalyst addition.

As the copolymerization reaction progressed, a number of observations were noted. In the early stages of the reaction, as before, with PDMS oligomer, diester and diol monomers present, the reactants formed a clear colorless homogeneous mixture above the melting point of dimethyl terephthalate. As the temperature was increased, and throughout the ester interchange process, the material remained clear, light tan, and homogeneous. As vacuum was applied, after the addition of the second aliquot of catalyst, the material changed to an opaque tan and viscosity increased even more dramatically than the aliphatic polyester copolymers. Again, care was taken to ensure that the viscous material remained in contact with the flask, as it had a tendency to

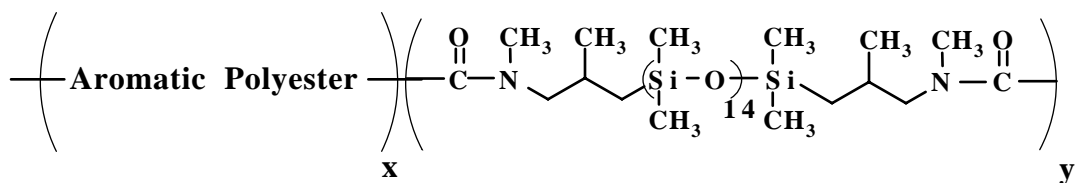


200 °C, 2 Hrs, N₂

220 °C, 2 Hrs, N₂

250 °C, 0.5 Hrs, 10 Torr

250 °C, 2 Hrs, 300 mTorr



Scheme 4.7: Synthesis of poly(butylene terephthalate) / poly(dimethylsiloxane) segmented copolymers

“climb” the stir shaft. Upon cooling, the whole series of poly(butylene terephthalate) / poly(dimethylsiloxane) (10, 20, and 30 wt %) copolymers were opaque due to their semi-crystalline nature. These copolymers were insoluble in hot chloroform and hot N-methylpyrrolidone, presumably due to a higher level of crystallinity than their aliphatic counterparts. The copolymers were removed by breaking the round bottom flask. This was done shortly after the reaction was stopped so that the material was below T_m , but was well above the T_g , which allowed the material to be cut off the stir shaft easily with pruning shears.

6. Poly(butylene terephthalate) / Poly(dimethylsiloxane) Segmented Copolymers: 1° Aminoalkylterminated Poly(dimethylsiloxane)

The 1° aminopropylterminated poly(dimethylsiloxane) was first endcapped with dimethylterephthalate as described in section 3.B.7a. The copolymers were then synthesized in a manner identical to the poly(butylene cyclohexanedicarboxylate) / poly(dimethylsiloxane) segmented copolymers, in respect to the reaction approach, as well as the catalyst addition.

This series of polymers was synthesized so that their characteristics including thermal gravimetric behavior could be compared to that of the 2° aminoalkylterminated poly(dimethylsiloxane) containing segmented copolymers. TGA analysis revealed qualitatively identical thermal behavior.

E. CHARACTERIZATION OF COPOLYMERS

1. Incorporation of PDMS into Copolymers

It was necessary to determine if all of the poly(dimethylsiloxane) charged to the reaction vessel was actually incorporated into the copolymer. As mentioned previously, all of the copolymers containing the cycloaliphatic diester, DMCD, were soluble in chloroform. This allowed the copolymers to be dissolved, after completion of the melt reaction, to form a 15 weight percent solution in chloroform. The solutions could then be precipitated into a 50:50 (v:v) mixture of methanol / 2-propanol. This would allow any unincorporated PDMS to be solubilized into the 2-propanol, while the copolymer would precipitate out of solution forming a fibrous

precipitate. The precipitate was then dried under vacuum conditions at 60 °C for at least 8 hours. Following the drying step, the various copolymers were then subjected to analysis using ^1H NMR spectroscopy. The copolymers were dissolved in deuterated chloroform and the peak areas for the methylene protons of the cyclohexanedimethanol and butanediol and were compared to the peak area of the silicon methyl protons using integration techniques (figure 4.10). The charged weight percent PDMS was compared to the experimental data obtained from the NMR experiments and it was found that the data matched well within the experimental error of the Varian Unity 400 NMR spectrometer as determined by Mr. Tom Glass. Unfortunately, due to the insolubility of the samples, the aromatic copolymers percent PDMS incorporation was not determined. A summary of the data for the cycloaliphatic copolymers can be found in table 4.1.

2. Chemical Composition

Elemental analysis was performed on both the aliphatic and aromatic polyester polyd(dimethylsiloxane) copolymers. Results from analysis generally followed the trends found from ^1H NMR experiments. In the case of the aromatic copolymers, only elemental analysis was performed; these materials were insoluble and solution NMR could not be obtained. Samples were sent to Galbraith Laboratories for elemental analyses. Although generally less expensive, Atlantic Microlab did not have the ability to characterize a Silicon content. In table 4.2, data is shown for the aliphatic copolymers. The aromatic copolymer data is shown in table 4.3.

3. Fourier Transform Infrared Spectroscopy

The FTIR spectrum of a 30 weight percent PDMS / 70 weight percent PBCD copolymer is shown in figure 4.11. The band assignments are listed in table 4.4. Both the polyester and the polysiloxane segments are represented by the ester carbonyl at 1730 cm^{-1} and the $\text{Si}(\text{CH}_3)_2$ stretch at 800 cm^{-1} , respectively.

Table 4.1: Incorporation of poly(dimethylsiloxane) into cycloaliphatic polyester copolymers. Charged weight percent PDMS is compared to experimental weight percent PDMS obtained from ¹H NMR results

| <u>Sample</u> | <u>Theoretical Weight % PDMS</u> | <u>Experimental Weight % PDMS (± 10%)</u> | <u>Diol</u> |
|---------------|--------------------------------------|---|------------------------|
| JBM-2-015 | 3 | 2 | Cyclohexane dimethanol |
| JBM-2-032 | 10 | 9 | Cyclohexane dimethanol |
| JBM-2-033 | 20 | 17 | Cyclohexane dimethanol |
| JBM-2-036 | 30 | 28 | Cyclohexane dimethanol |
| JBM-2-061 | 5 | 5 | Butanediol |
| JBM-2-060 | 10 | 9 | Butanediol |
| JBM-2-062 | 20 | 18 | Butanediol |
| JBM-2-065 | 30 | 28 | Butanediol |

Table 4.2: Theoretical and experimental values for % Si and weight % PDMS are shown for the cycloaliphatic polyester copolymers. Experimental values were obtained from ¹H NMR and elemental analysis experiments.

| <u>Sample</u> | <u>% Si (theory)</u> | <u>% Si (expt) (Elem. Anal)</u> | <u>Theo. Weight % PDMS</u> | <u>Expt. Weight % PDMS (NMR)</u> | <u>Diol</u> |
|----------------------|-----------------------------|--|-----------------------------------|---|------------------------|
| JBM-2-015 | 0.7 | 0.6 | 3 | 2 | Cyclohexane dimethanol |
| JBM-2-032 | 2.5 | 2.7 | 10 | 9 | Cyclohexane dimethanol |
| JBM-2-033 | 4.9 | 4.1 | 20 | 17 | Cyclohexane dimethanol |
| JBM-2-036 | 7.7 | 7.2 | 30 | 28 | Cyclohexane dimethanol |
| JBM-2-061 | 1.2 | 0.8 | 5 | 5 | Butanediol |
| JBM-2-060 | 2.4 | 2.0 | 10 | 9 | Butanediol |
| JBM-2-062 | 5.0 | 4.6 | 20 | 18 | Butanediol |
| JBM-2-065 | 7.4 | 7.1 | 30 | 28 | Butanediol |

Table 4.3: Theoretical and experimental values for % Si present in the PDMS / aromatic polyester copolymers by elemental analysis.

| <u>Sample</u> | <u>Theo. Weight % PDMS</u> | <u>% Si (theory)</u> | <u>% Si (expt.)</u> |
|----------------------|-----------------------------------|-----------------------------|----------------------------|
| JBM-2-70 | 10 | 2.5 | 2.1 |
| JBM-2-71 | 20 | 4.7 | 4.4 |
| JBM-2-74 | 30 | 7.4 | 7.1 |

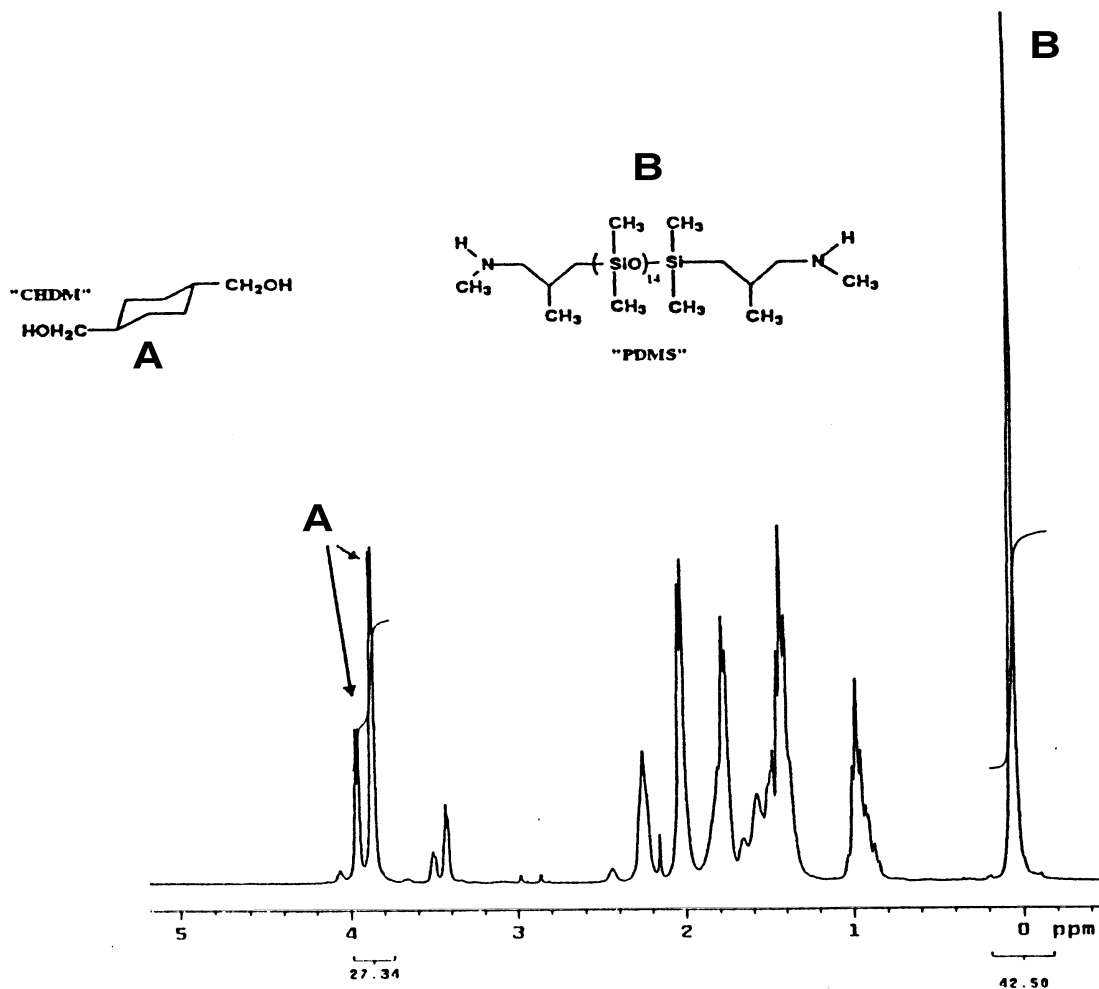


Figure 4.10: ^1H NMR of poly(cyclohexanedimethanolcyclohexanedicarboxylate)

4. Intrinsic Viscosity

Table 4.5 lists the intrinsic viscosities of the polyester homopolymers and copolymers. Once again, only the cycloaliphatic copolymer's intrinsic viscosities could be determined due to the insolubility of the aromatic homopolymer and corresponding copolymers.

A broad range of values are shown, making it difficult to draw quantitative conclusions from this data. For a homopolymer, viscosity scales with molecular weight; however, with the copolymers, this relationship may not exist. Each copolymer has a different chemical composition which changes the solution behavior and the Mark-Houwink constants are different in each case. Due to this, the intrinsic viscosities cannot be compared to each other. The Mark Houwink equation is stated below:

$$[\eta] = kM^a$$

While direct comparisons cannot be made, some observations are possible. The PDMS / PCDCD copolymers (*i.e.* cyclohexanedimethanol, cyclohexanedicarboxylate) showed a much lower intrinsic viscosity at each weight percent PDMS when compared to the PDMS / PBCD copolymers (*i.e.* butanediol, cyclohexanedimethanol). This obviously is related to their very different solution characteristics. The PDMS / PCDCD copolymers, after precipitation from chloroform, tended to be in the form of very short fibers. The PDMS / PBCD copolymers tended to be longer thicker fiber after precipitation from the same weight percent chloroform solution. The compression molded films made from the two different series of copolymers also behaved differently. The PDMS / PBCD series of copolymers produced compression molded films that were much tougher than films made from the PDMS / PCDCD series of copolymers.

5. Gel Permeation Chromatography

Recently, we have been fortunate to be able to generate absolute molecular weights for soluble homo- and copolymers due to the capabilities of our gel permeation chromatograph equipped with viscosity and refractive index detectors. As mentioned previously, only the cycloaliphatic polyester homo- and copolymers

Table 4.4: Infrared Assignments for PBCD / PDMS Copolymer

| <u>Frequency (cm⁻¹)</u> | <u>Assignment</u> |
|------------------------------------|---|
| 2960 | C-H stretch of CH ₃ |
| 2864 | Alkane stretch |
| 1730 | Ester carbonyl |
| 1456 | Methylene bend |
| 1257 | Si(CH ₃) ₂ O symmetric deformation |
| 1171 | C-O |
| 1051 | Si-O-Si stretch vibration |
| 800 | Si(CH ₃) ₂ stretch, CH ₃ rock |

Table 4.5: Intrinsic viscosities of soluble homo- and copolymers. All experiments were conducted with chloroform as solvent, at 25°C.

| <u>Polymer Type</u> | <u>PDMS Weight %</u> | <u>Intrinsic Viscosity (dL/g)</u> |
|---|----------------------|-----------------------------------|
| Poly(butylencyclohexanedicarboxylate) (PBCD) | 0 | insoluble |
| PBCD | 5 | 2.04 |
| PBCD | 10 | 1.55 |
| PBCD | 20 | 1.25 |
| PBCD | 30 | 1.46 |
| Poly(cyclohexanedimethanolcyclohexanedicarboxylate) (PCDCD) | 0 | 0.55 |
| PCDCD | 3 | 0.56 |
| PCDCD | 10 | 0.52 |
| PCDCD | 20 | 0.48 |
| PCDCD | 30 | 0.39 |

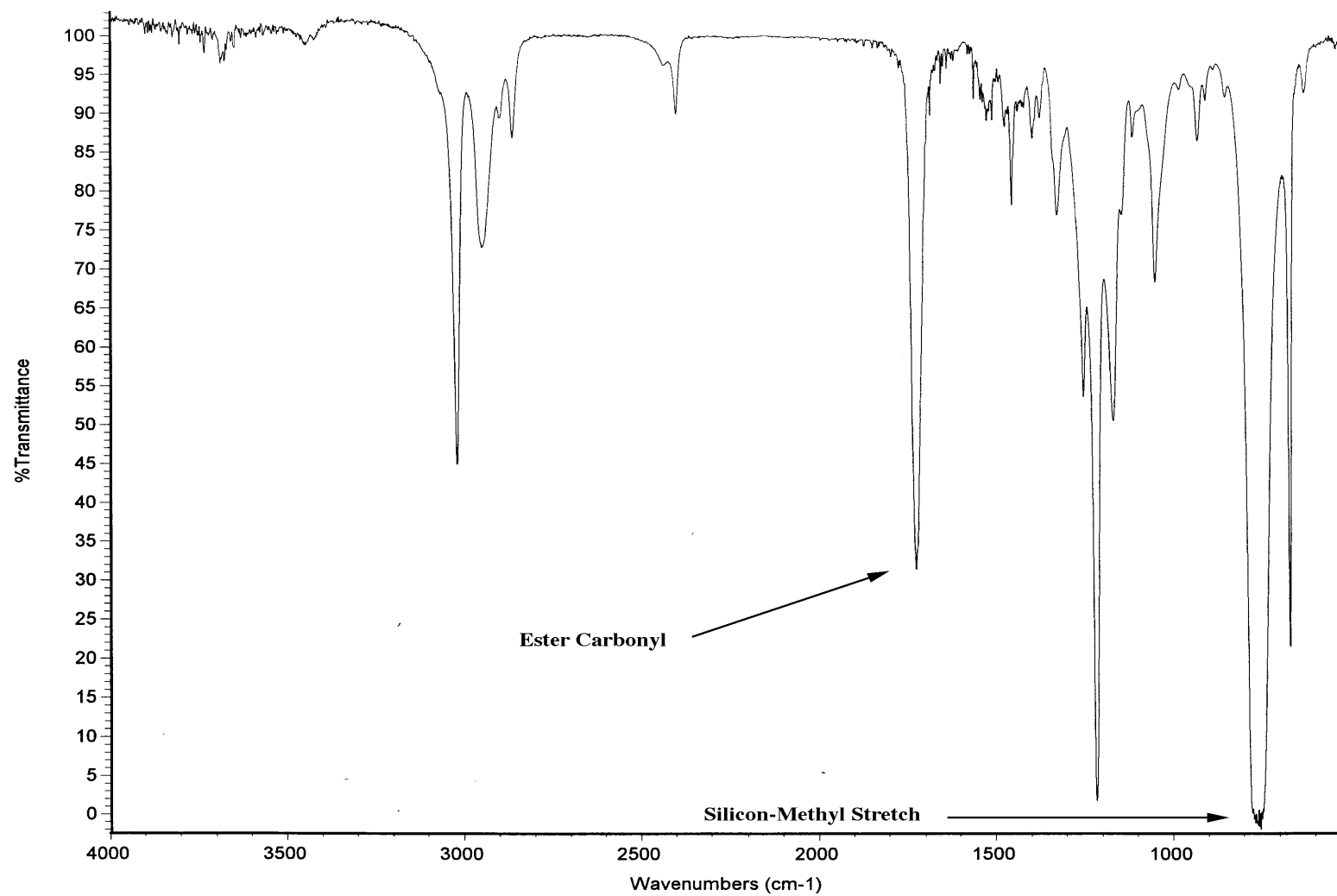


Figure 4.11: Infrared spectra of 30 weight percent PDMS/PBCD segmented copolymer

exhibited solubility and for this reason molecular weight data was not obtainable via GPC for the aromatic homopolymers and copolymers. The data for the cycloaliphatic polyester homo- and copolymers are shown in table 4.6. All data was obtained at 25°C with chloroform as solvent.

6. Thermal Analysis

Dynamic scanning calorimetry, thermal gravimetric and dynamic mechanical analyses were conducted using Perkin-Elmer instruments. All data was obtained from fresh compression molded samples.

One of the goals of this research was to decrease the heat release rate and increase the char yield of the polyesters under study by incorporation of a poly(dimethylsiloxane) segment. One method that can be used to study thermal weight loss is thermal gravimetric analysis (TGA). Both the cycloaliphatic and aromatic copolymers exhibited very similar behavior when subjected to TGA analyses. A representative example of the data for the aromatic poly(butylene terephthalate) / poly(dimethylsiloxane) copolymer series is shown in figure 4.12.

Dynamic scanning calorimetry (DSC) of all samples revealed that all polyester copolymers retained at least some degree of the crystallinity characteristic of the homopolymers from which they were derived. In the case of the aromatic copolymers, even the highest weight percent PDMS copolymers showed a percent crystallinity very near that of the homopolymer, as determined by integration of the melt endotherm to reveal ΔH of crystallization. The DSC thermograms of PBT and 30 weight percent PDMS/PBT are shown in figures 4.13a and 4.13b.

Dynamic mechanical analysis (DMA) of the aromatic polyesters and polyethers was conducted on the compression molded films by use of the extension mode provided with the instrument. In all cases, analysis was conducted at sub-ambient temperatures to reveal the low temperature transitions of the poly(dimethylsiloxane) and poly(tetramethyleneoxide) segments. DMA thermograms for PDMS/PBT series of copolymers are shown in figure 4.14. Figure 4.15 shows the DMA thermograms for the polyether control and PDMS/polyether

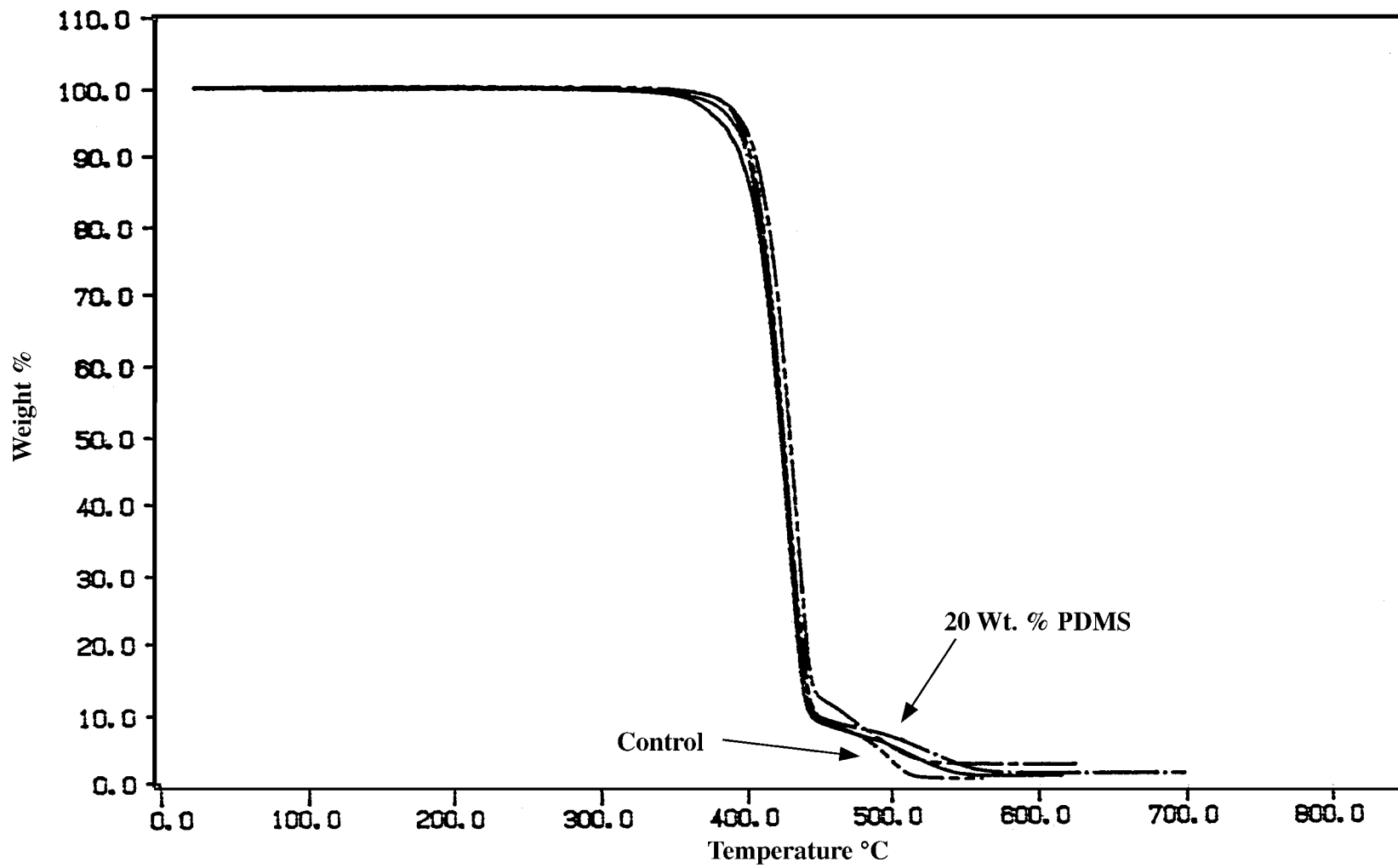


Figure 4.12: TGA of PBT homopolymer and copolymers. Experiments were conducted in air with a heating rate for 10°C/min.

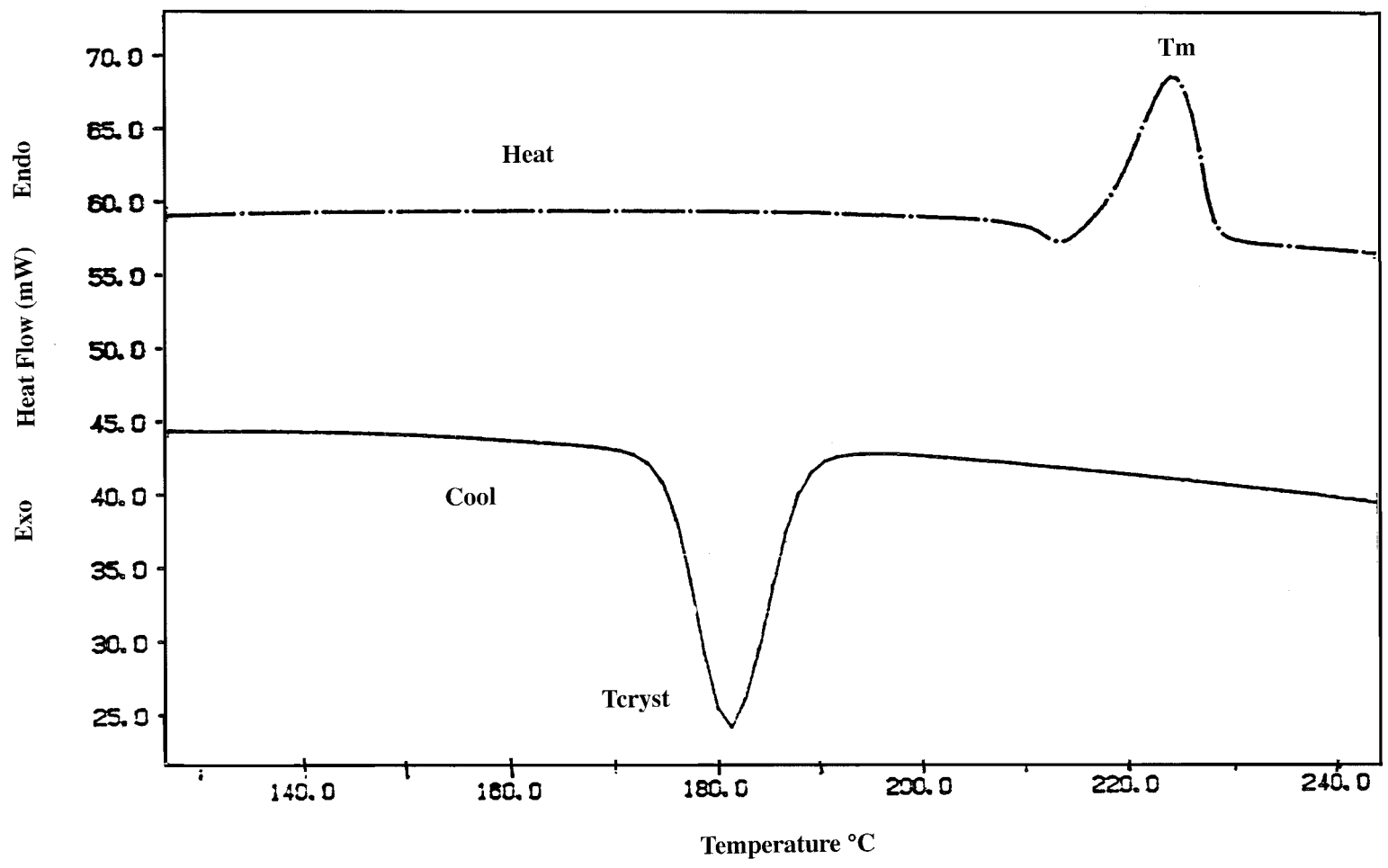


Figure 4.13a: DSC thermogram of PBT homopolymer. Experiment was conducted in air with a heating rate of 10°C/min.

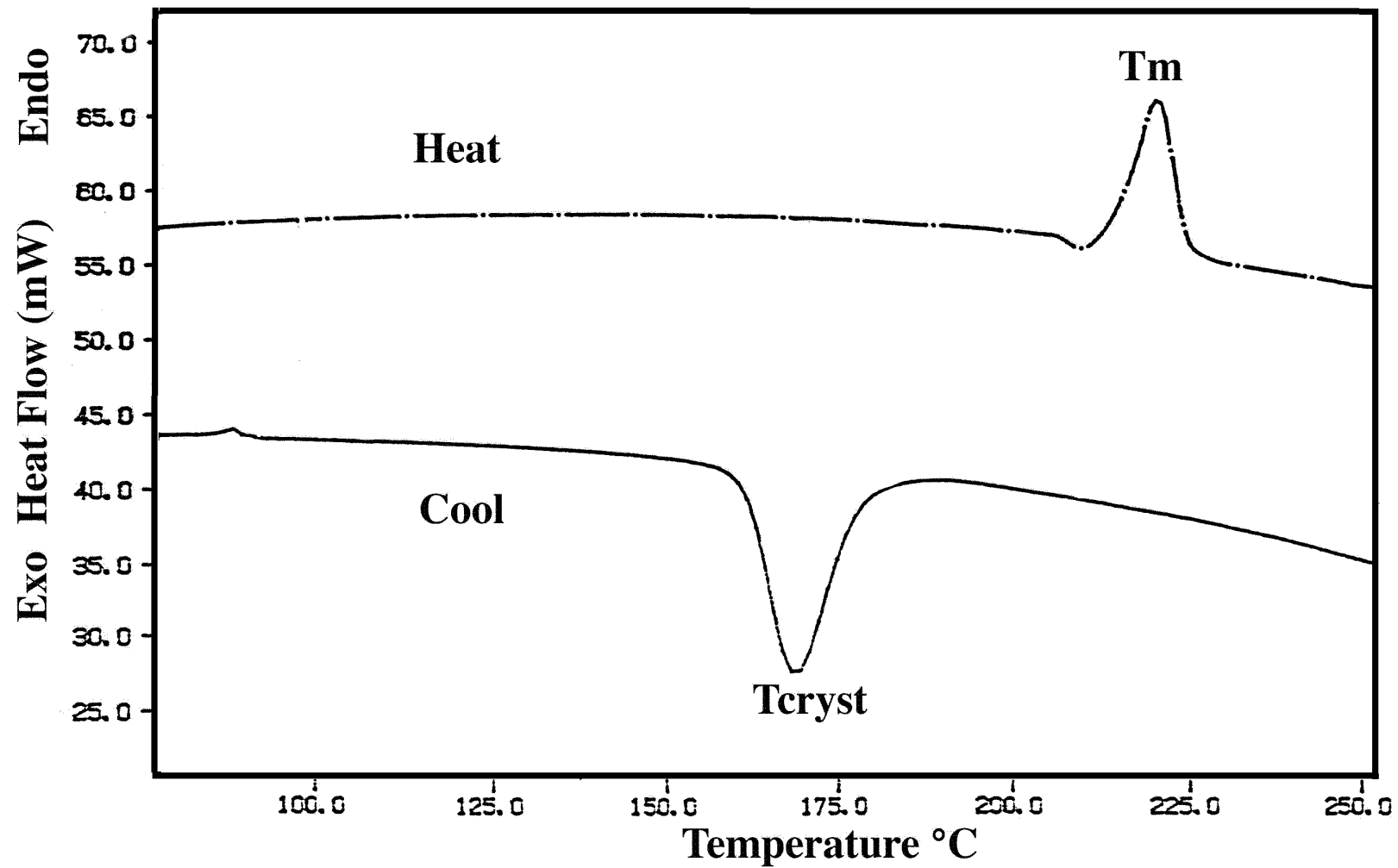


Figure 4.13b: DSC thermogram of a 30 wt. percent PDMS/PBT copolymer. Experiment was conducted nitrogen at a heating rate of 10°C/min.

copolymer. The DMA results for the PBT/PDMS copolymers revealed that increasing the amount of PDMS in the copolymer caused the T_g of the hard segment to shift to a lower value, possibly indicating an increase in phase-mixing. When the DMA results for the two polyethers are considered, the opposite trend seems to be the case. Inclusion of PDMS into the polyether increases the T_g of the hard segment, which may indicate a decrease in phase mixing.

7. Transmission Electron Microscopy

Transmission electron micrographs of the aromatic PBT/PDMS series of copolymers containing 10, 20, and 30 weight percent of soft segment are shown in figure 4.16. All samples were compression molded films that were then microtomed to generate samples for TEM analysis. Some smearing of the PDMS soft segment is apparent. It was difficult to keep the sample below the T_g of PDMS during the cutting of the films in the microtome. The micrograph shown is from a 20 weight percent PDMS/PBT segmented copolymer, in which phase separation is evident. This is consistent with the data obtained from DMA analysis. Samples from 10 and 20 weight percent PDMS/PBT copolymers revealed similar results from TEM experiments and had domain sizes consistent with the weight percent PDMS present in thesegmented copolymers.

8. Mechanical Testing

Stress strain curves of the PBT homopolymer, as well as the 10 and 20 percent PDMS segmented copolymers, were obtained from compression molded films approximately 0.5mm thick which were cut into tension bars. These samples were then put under tension at a rate of 5mm/min in a Polymer Labs Minimat instrument. The copolymers showed yield stresses similar to the homopolymer, but had a much greater elongation to break. The copolymers tended to stress-whiten upon elongation which could be an indication of cavitation and/or crazing. The results are shown in figure 4.17.

9. Contact Angle Analysis

Contact angle analyses were conducted on compression molded films of PBT and PBT/PDMS segmented copolymers containing 10, 20 and 30 weight

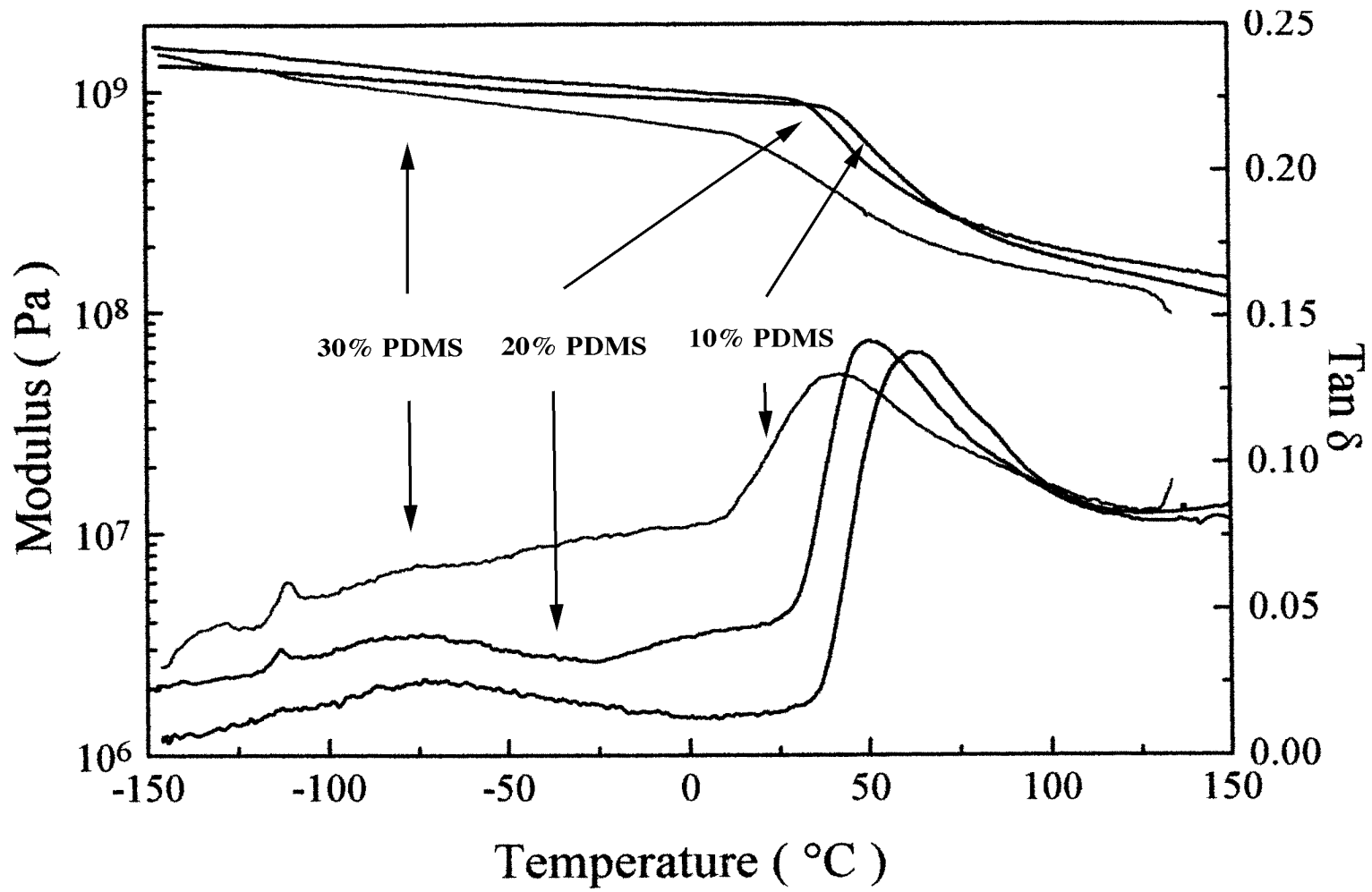


Figure 4.14: DMA of PDMS/PBT segmented copolymers

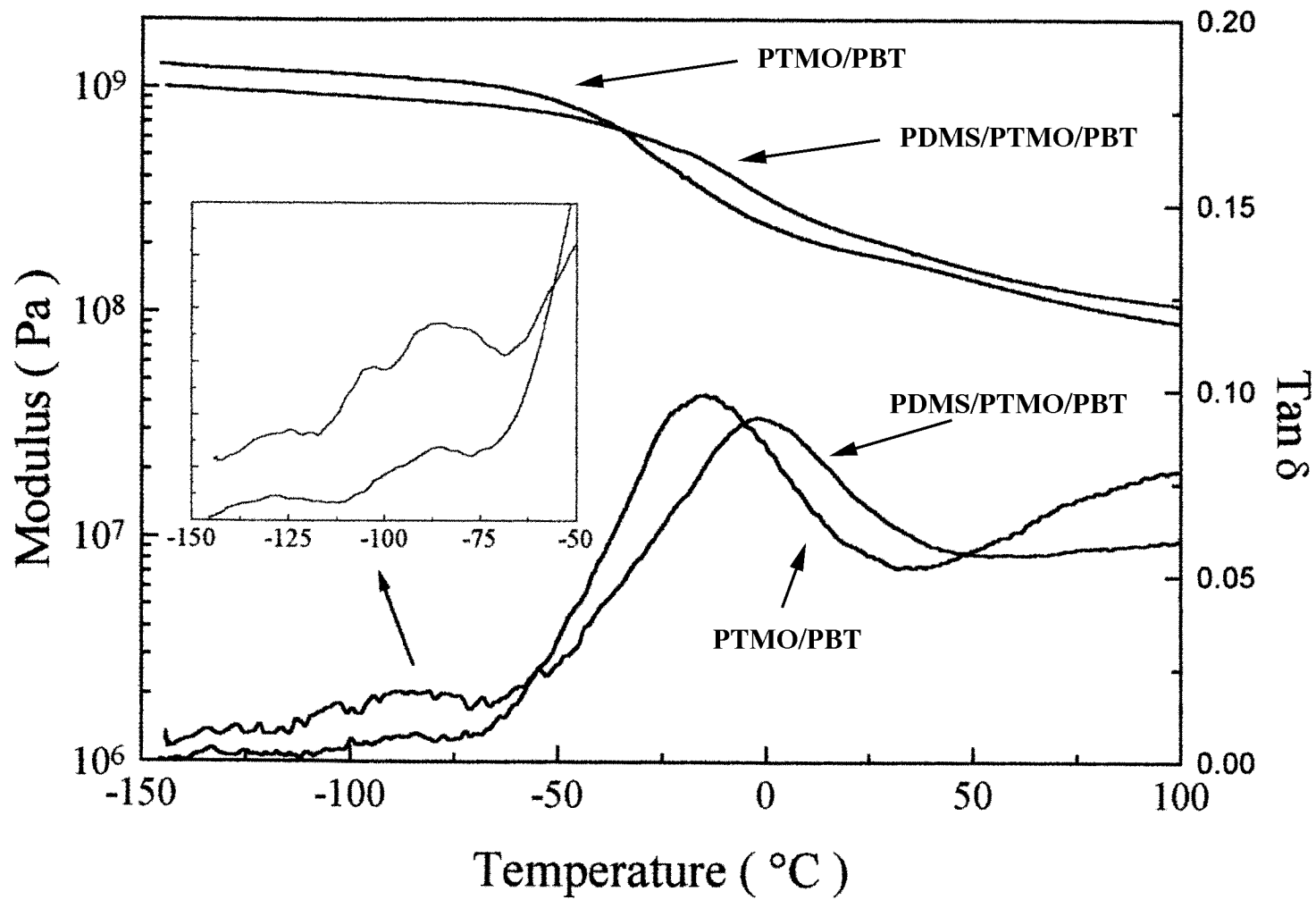


Figure 4.15: DMA of PDMS/PTMO/PBT and PTMO/PBT segmented copolymers



Figure 4.16: A transmission electron micrograph of a 20% PDMS/PBT copolymer

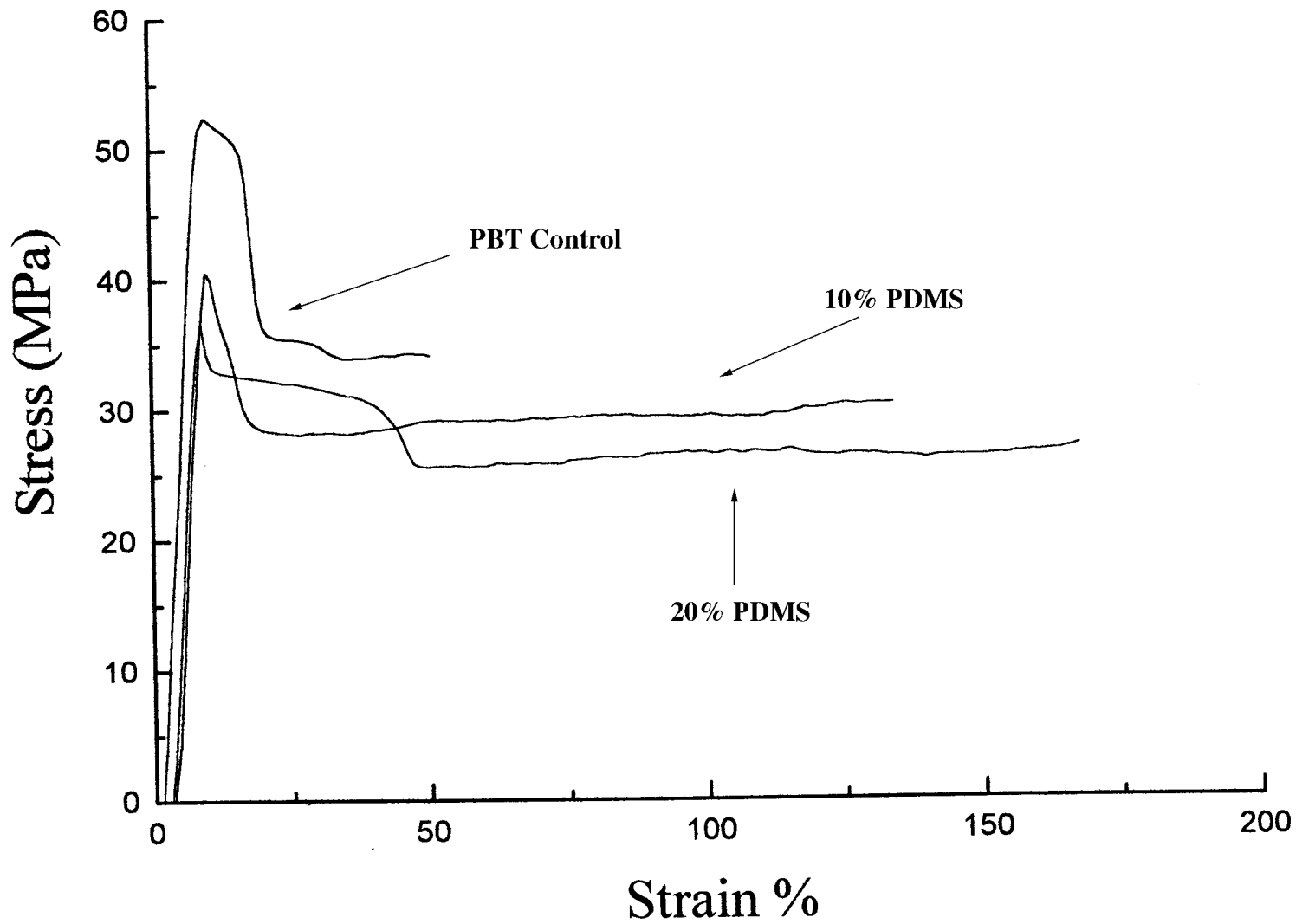


Figure 4.17: Stress-Strain Curves for PBT homopolymer and PBT/PDMS copolymer

Chapter V

CONCLUSIONS

Melt polymerizations to form polyester/poly(dimethylsiloxane) segmented copolymers with high molecular weights were successful using either 1° or 2° amino alkyl functional oligomer. In these investigations an upper limit of about 40 weight percent siloxane was observed, otherwise macrophase separation resulted and reasonable molecular weights could not be achieved. In this research, a poly(dimethylsiloxane) oligomer was chosen to minimize this phenomenon. Oligomers with smaller molecular weights may allow higher weight percent siloxane containing copolymers.

Compression molding above T_m of the well defined copolymers resulted in tough, ductile films. The ability to compression mold these materials was of importance, since many polysiloxane copolymers are difficult to process in the melt due to their macrophase separation, even when above T_m .

Multiple transitions corresponding to the polysiloxane and polyester phases were observed in both dynamic mechanical and differential scanning calorimetry experiments. This evidence supports the possibility of microphase separation. However, some phase mixing may be occurring as evidenced by melting point and glass transition temperature behavior.

Under the reaction conditions described, the titanium isopropoxide catalyst does not cause degradation or redistribution of the polysiloxane oligomer during copolymerization.

The soluble cycloaliphatic segmented copolymers allowed for removal of any unincorporated polysiloxane via precipitation techniques. Studies revealed little if any poly(dimethylsiloxane) was unincorporated using the reactions described.

The segmented polyester/polysiloxane copolymers exhibited better mechanical properties than the polyester homopolymers.

Copolymer molecular weight was heavily dependent on the ability to achieve high vacuum in the final step of the reaction sequence to allow removal

of the excess diol. This forced the reaction to completion and with carefully controlled stirring rates and high temperatures, high molecular weights could be achieved.

Chapter VI

SUGGESTED FUTURE STUDIES

Since the PBCD/PDMS segmented copolymers are expected to have improved weatherability properties over their aromatic counterparts, weatherability studies should be considered. This could be achieved via the use of a weather-o-meter which controls UV-radiation, humidity and temperature, allowing for long time periods to be condensed into a shorter time.

With the recent commercialization of 2,6-dimethylnaphthalate and its polymerization to form poly(ethylenenaphthalate), PEN, future studies should include the investigation of melt polymerization of the appropriate monomers to form PEN or PBN/PDMS segmented copolymers. These polymers should have a higher degree of crystalline content and increased barrier properties over the PBT segmented copolymers. PEN has a higher melting point than PBT or PET, so it would be imperative to choose reaction conditions in order to avoid thermal degradation of the polysiloxane segment.

Modification of segmented PTMO polyether-polybutylene terephthalate segmented copolymers may provide improved materials systems.

CHAPTER VII

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VITA

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