

Polydimethylsiloxane Modification of Segmented Thermoplastic Polyurethanes and Polyureas

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(Abstract)

This thesis addresses the systematic modification of poly(tetramethylene oxide) (PTMO), polyether based segmented thermoplastic polyurethane with a secondary aminoalkyl functional polydimethylsiloxane (PDMS), which was intended to improve the fire resistance of polyurethane systems. The PDMS oligomer was successfully incorporated into the polyurethane backbone *via* one step solution polymerization. The effect of PDMS content on thermal stability, morphology, surface composition, mechanical properties, and fire resistance of polyurethane was investigated. These polymers displayed a complex two phase morphology and composition-dependant mechanical properties. The PDMS segment microphase separated from other polyurethane segments and varying microphase separation morphologies were observed with differing PDMS content. Spherical dispersed complex phases and co-continuous phases occurred when the PDMS content was 15wt% and 55wt%, respectively. Similar thermal stability was observed for both the polyurethane control and the PDMS modified polyurethanes, but the later displayed increased char yield in air with increased PDMS concentration. Quantitative measurements of the fire resistance of the modified polyurethanes by cone calorimetry showed that the peak heat release rate of the 15wt% siloxane modified samples dropped 67wt%, compared with the polyurethane control. However, the peak heat release rate did not further change with increasing siloxane content. Excellent mechanical properties, in terms of tensile strength and elongation, were found for the modified polyurethane with 15wt% of PDMS. Higher PDMS levels did reduce tensile strength, probably because of the reduction in strain crystallizing

PTMO content. The PDMS modification, which resulted in improved fire resistance and excellent mechanical properties, is attributed to the low surface energy of the PDMS segment that tended to migrate to the surface of the polymer. It could be oxidized into a partially silicate-like material upon heating in air.

In addition, the syntheses of primary and secondary aminoalkyl functional PDMS based segmented polyureas are described herein. Two-phase morphology was observed for all the polyurea samples, even when the hard segment concentration was as low as 6wt%. All these polyureas formed clear transparent films that exhibited good mechanical properties even with very high PDMS content, up to 94wt%. They also demonstrated similar thermal stability, independent of the PDMS end group. However, the nature of the end group, i.e. primary or secondary aminoalkyl, had a dramatic effect on mechanical and morphological properties of these PDMS based polyureas, which was interpreted in terms of the level of hydrogen bonding.

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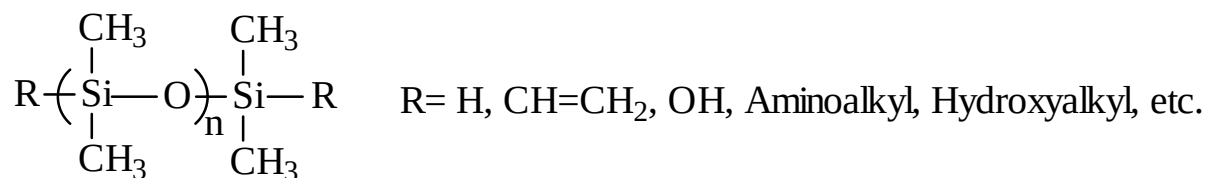
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Chapter 1 Introduction

Thermoplastic polyurethanes are a versatile group of multi-phase segmented polymers that have excellent mechanical and elastic properties, good hardness, high abrasion and chemical resistance. However, poor fire resistance restricts some of their applications. The increasing demands for fire resistant systems have stimulated the development of new materials. For example, halogen containing fire retardant polyurethanes developed some years ago, have severe drawbacks, such as the release of HX and other corrosive gases when burned. Recently, interest in halogen free fire retardant polyurethanes has begun to focus on siloxane based copolymer systems, which display significantly reduced heat release characteristics.

Polydimethylsiloxane (PDMS) such as 1, have found many applications due to their unique properties, which arise mainly from the nature of the siloxane bond (Si-O).



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These properties include extremely low glass transition temperature (-123 °C), low surface energy, high permeability to gases, good insulating properties, and very good thermal stability. Moreover, many physical properties remain relatively unchanged over a wide range of temperature. However, the mechanical properties of PDMS are usually very poor at room temperature, unless reinforced with silica and vulcanized. In order to develop useful properties, very high molecular weights are required. Even for chemically crosslinked and reinforced PDMS, the tensile strength is still relatively low, compared to other elastomer.

A promising way to improve the fire resistance of polyurethanes without significantly sacrificing the mechanical properties is to utilize PDMS as a reactive co-soft segment to make block or segmented copolymers. This approach has been used previously and several segmented siloxane-urethane copolymers have been made. These

copolymers were prepared by the reaction of hydroxy alkyl or primary amino alkyl terminated siloxane oligomers with diisocyanates and diols. They generally behave as thermoplastic elastomers and their ultimate properties depend on the nature of the hard segments and composition. However, the mechanical properties of these copolymers are usually very poor, compared to conventional polyurethanes. This may be related to the fact that high molecular weight copolymers are relatively hard to synthesize. Due to the large difference in solubility parameter between the non-polar PDMS and the highly polar urethane segment, undesirable macroscopic phase separation may often be encountered during the polymerization. Therefore, the solvent selection for the synthesis is very critical.

This research focused on improving the fire resistance of polyether based polyurethane without significantly sacrificing its excellent mechanical properties. This was approached by incorporating secondary aminoisobutyl terminated PDMS into the polyurethane backbone via solution polymerization using PDMS and/or polytetramethylene oxide (PTMO) as soft segment, and 4,4'-methylene diphenyl diisocyanate (MDI) and 1,4-butanediol as a chain extender. Structural, thermal, morphological, surface, and mechanical characterization of the products are presented and cone calorimetry results are reported.

The second part of this thesis focused on the synthesis of polyureas derived from primary aminopropyl and secondary aminoisobutyl terminated PDMS. Polyureas made from aminoalkyl functional PDMS are elastomeric and show two-phase morphology. However, they also show drastically different physical properties depending on their structure. The polyureas made from primary aminopropyl terminated PDMS are strong elastomers, even when they contain a large percentage of PDMS, e.g., up to 94wt%. The polyureas made from secondary aminopropyl terminated PDMS are much weaker than their primary analogue. These differences are attributed to the extent of hydrogen bonding in the polyureas.

Chapter 2 Literature Review

The major research areas involved in this dissertation will be reviewed in this chapter. These areas include segmented thermoplastic polyurethane, siloxane containing copolymers, and fire resistant polymeric materials.

2.1. Segmented Thermoplastic Polyurethanes

2.1.1 History and Development of Polyurethanes

The invention of polyurethanes was made by Otto Bayer and coworkers at I. G. Farbenindustrie, Germany in 1937.[1-5] This discovery was Germany's competitive response to Carothers' work on polyamides, or nylons, at E. I. du Pont. The successful development of high molecular weight polyamides at E. I. du Pont stimulated Bayer to investigate similar materials that were not covered by Du Pont's patents. The initial work was to react an aliphatic isocyanate with a diamine to form polyureas that were infusible, but very hydrophilic. Further research on this subject demonstrated that when an aliphatic isocyanate reacted with a glycol, a new material with interesting properties for production of plastics and fibers could be made. Du Pont and ICI soon recognized the desirable elastic properties of polyurethanes. The industrial scale production of polyurethane started in 1940.[6-8] But subsequent market growth of these materials was seriously impacted by World War II.

The polyurethane elastomers that were first developed consisted of three components:

- a. Polyester and polyether based macrodiols (eg. M_n of 1-2000g/mole)
- b. Chain extender such as low molecular weight diol or diamine
- c. A bulky diisocyanate, i.e. naphthalene-1,5-diisocyanate (NDI)

The polyurethane elastomers made from these components were not thermoplastic elastomers in the true sense, since their melting points were higher than the decomposition temperature of the urethane linkages. It was not until 1952, when polyisocyanate, especially toluene diisocyanate (TDI), became commercially available, that noticeable improvements in polyurethane elastomers and foams began to be seen. In 1958, Schollenberger of BFGoodrich introduced a new “virtually crosslinked”

thermoplastic polyurethane elastomer.[9] At approximately the same time, du Pont announced a Spandex fiber called Lycra, which is a polyurethane based on PTMO, 4,4'-diphenylmethane diisocyanate (MDI) and ethylene diamine. By the early 1960s, BFGoodrich produced Estane, Mobay marketed Texin, and Upjohn marketed Pellethane in the United States. Bayer and Elastgran marketed Desmopan and Elastollan, respectively, in Europe.

In addition to elastomers, polyurethanes can also be produced as foams (rigid and flexible), adhesives, binders, coatings, and paints. Because of their unique properties, polyurethanes have found a wide variety of applications in the automotive, furniture, construction, and footwear industries, as seating, exterior panels, structural foam, furniture, housing for electric equipment, shoe and boot soles, and refrigerator insulation.

In 1990, the world production of plastics exceeded 100 million tons. Following the high volume production of thermoplastics such as polyethylene (PE), polyvinylchloride (PVC), polypropylene (PP), and polystyrene (PS), polyurethanes rank 5th with over 5% of the world's total plastics production.[12]

2.1.2 Polyurethane elastomers

Polyurethane elastomers are an important member of the thermoplastic elastomer family.[11] Although the consumption of polyurethane elastomers is lower than that of polyurethane foam, they are used for a variety of unique applications that are inappropriate for other polymers. Their advantageous properties include high hardness for a given modulus, high abrasion and chemical resistance, excellent mechanical and elastic properties, and blood and tissue compatibility. Generally, polyurethane block copolymers are comprised of a low glass transition or low melting "soft" segment and a rigid "hard" segment, which often has a glassy T_g , or crystalline melting point well above room temperature. The soft segment is typically a polyester-, or polyether- diol, with a molecular weight between 500 to 5000, though in practice, molecular weights of 1000 and 2000 are primarily used. The hard segment normally includes the connection of a diisocyanate (aromatic or aliphatic) and a low-molecular-weight diol or diamine, which is the chain extender. The combination of this soft polyol segment and hard segment forms an $(AB)_n$ type block copolymer. By varying the structure, molecular weight of the

segments, and the ratio of the soft to the hard segments, a broad range of physical properties can be obtained. The materials can be hard and brittle, soft and tacky, or anywhere in between.

Polyurethane elastomers usually exhibit a two-phase microstructure, which arises from the chemical incompatibility between the soft and the hard segments. The hard, rigid segment segregates into a glassy or semicrystalline domain, and the polyol soft segments form amorphous or rubbery matrices in which the hard segments are dispersed at varying content levels. The hard domain in this two-phase microstructure can act as a physical crosslinking point and reinforcing filler, while soft segment behaves as a soft matrix. This microphase separation results in superior physical and mechanical properties, such as high modulus and high reversible deformation. The degree of phase separation or domain formation not only depends on the weight ratio of the hard to the soft segment, but also on the type of chain extender, the type and molecular weight of the soft segment, the hydrogen bond formation between the urethane linkages, the manufacturing process, and reaction conditions.[10-14] This phase segregation behavior of polyurethanes has been well established by a variety of characterization techniques, including electron microscopy, small angle X-ray scattering, infrared dichroism, dynamic mechanical analysis, and differential scanning calorimetry.[15-18]

2.1.3 Isocyanate chemistry

2.1.3.1 Primary reactions

The chemistry involved in the synthesis of a polyurethane elastomer is centered around the isocyanate reactions. The high reactivity of isocyanate toward nucleophilic reagents is mainly due to the pronounced positive character of the C-atom in the cumulative double bond sequence consisting of nitrogen, carbon and oxygen, especially in aromatic systems. The electronic structure of the isocyanate group can be represented by several resonance structures, which are illustrated in Figure 2.1.



Figure 2.1 Resonance structures of the isocyanate group

From the resonance structures, the positive charge at the C-atom becomes obvious. On the other hand, the negative charge can be delocalized onto the oxygen atom, nitrogen atom, and the R group, if R is an aromatic group. This explains why an aromatic isocyanate has a distinctly higher reactivity over an aliphatic isocyanate. Furthermore, the substituents on the aromatic ring can also influence the positive character of the NCO group: an electron withdrawing group in the para or ortho position increases reactivity, while an electron donating group reduces reactivity.

The most important reaction of isocyanate is the formation of a carbamic acid derivative through the insertion of an acidic H-atom from the nucleophilic reactant to the C=N. This is illustrated in Figure 2.2. This nucleophilic reaction is strongly influenced by the catalyst: e.g., acid compounds (mineral acid, acid halide, etc.) slow the reaction, whereas basic compounds (tertiary amines) and metal compounds (Sn, Zn, Fe salts) accelerate the reaction.[21-23]

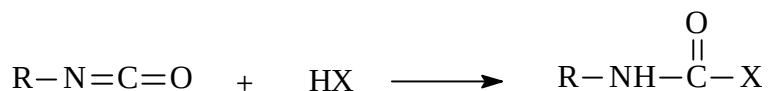


Figure 2.2 Formation of carbamic acid derivative

When the nucleophilic reactants are OH containing compounds, carbamic acid ester, or urethane, is formed. The reactivity of the hydroxy group decreases in the order of primary hydroxy, secondary hydroxy, and phenol, which is very unstable. The addition reaction is an equilibrium reaction and the isocyanate group can be regenerated at elevated temperatures, as shown in Figure 2.3.[1,21]

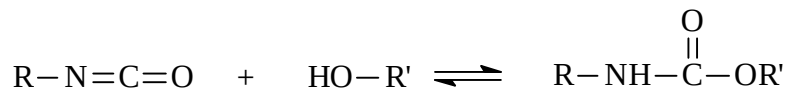


Figure 2.3 Urethane linkage formation

If the nucleophilic reactant is an amine-containing compound, the reaction between the nucleophilic reactant and the isocyanate will be much more vigorous. As a result, a urea linkage is formed as shown in Figure 2.4.[21,24]

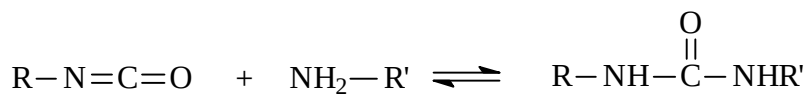


Figure 2.4 Urea linkage formation

The reaction between isocyanate and water is a special case of an alcohol/isocyanate reaction. In this reaction, the primary product is the carbamic acid, which is not stable and will decompose to the corresponding amine and carbon dioxide. The amine formed will then react immediately with the isocyanate group in the system and forms a urea.[21,25] This reaction is very important for the formation of polyurethane foam, since the carbon dioxide acts as a blowing agent. However, this reaction can also create problems in the storage of isocyanate. Moreover, to obtain a high molecular weight linear thermoplastic polyurethane, it is essential to completely exclude water from the reaction system, as illustrated in Figure 2.5.

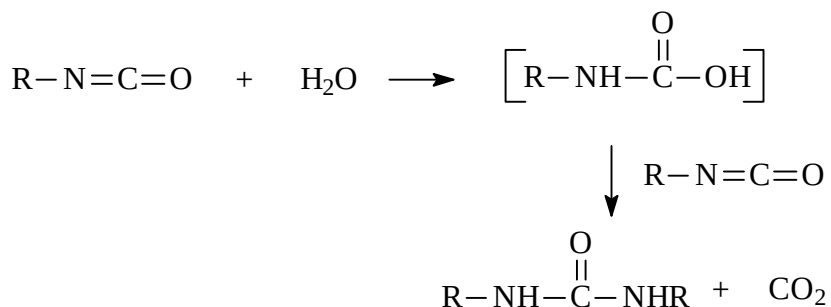


Figure 2.5 Reaction between water and isocyanate

2.1.3.2 Secondary reactions

The urethane and urea formed from the previous reactions still contain active hydrogen. Even though the reactivity of these compounds is lower than the starting reactants, alcohol and amine, they are still capable of a nucleophilic attack at the isocyanate under more rigorous reaction conditions, which results in an allophanate and a biuret. Allophanates are usually formed between 120°C and 150°C and biurets are formed between 100°C and 150°C.[19,20,26] Due to their low thermal stability, allophanates and biurets will dissociate into starting components above 150°C, as shown in Figure 2.6.

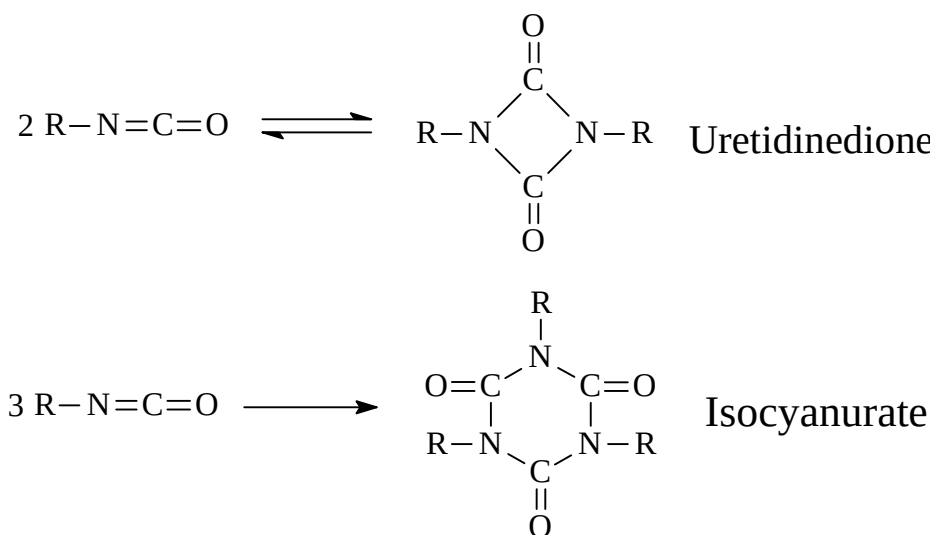


Figure 2.7 Dimerization and trimerization of isocyanate

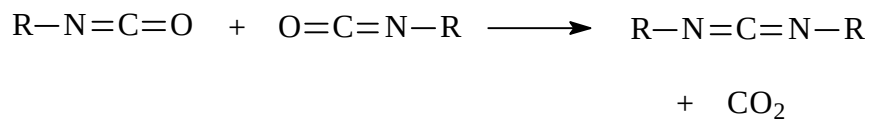


Figure 2.8 Formation of carbodiimide

The carbodiimides formed in this condensation reaction can further react reversibly with an isocyanate group to form a uretoneimine. [34] Figure 2.9

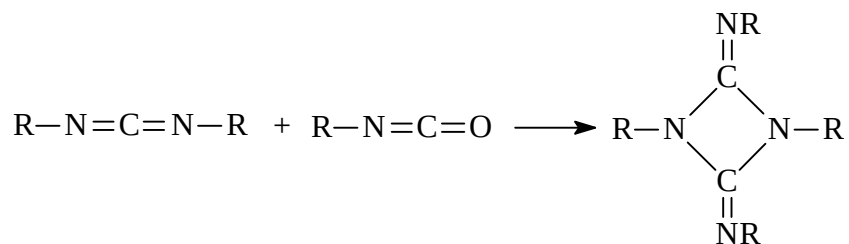


Figure 2.9 Formation of uretoneimine

2.1.4 Segmented polyurethane elastomer synthesis

2.1.4.1 Building blocks for segmented polyurethane elastomers

A urethane group is formed by the reaction between an alcohol and an isocyanate group. Thus, polyurethanes result from the reaction between an alcohol with two or more hydroxy groups (diol or polyol) and an isocyanate containing two or more isocyanate groups (diisocyanate or polyisocyanate). The most widely used diisocyanates are shown in Table 2.1.

The isocyanate building blocks in segmented polyurethane elastomers can be either aromatic or aliphatic. The aromatic isocyanates are more reactive than aliphatic isocyanates, which can only be utilized if their reactivities match the specific polymer reaction and special properties desired in the final product. For example, polyurethane coatings made from aliphatic isocyanates are light stable [35-38], while coatings made from an aromatic isocyanate will undergo photo-degradation.[39-41] Furthermore, the reactivity of an isocyanate group can vary dramatically even for the same class of isocyanate. The structure, substituents, and steric effect can all influence reactivity. For example, in 2,4-toluene diisocyanate, the isocyanate group para to the methyl group is 25 times more reactive than the other NCO group at the ortho position.[12] Moreover, the reactivity of the second NCO group can change as a result of the initial reaction.

Two of the most important aromatic isocyanates are TDI and MDI. TDI consists of a mixture of the 2,4- and 2,6-toluene diisocyanate isomers. The commercially available TDI is a mixture of these two isomers with various ratios, although the pure 2,4- compound is also available commercially. TDI can be synthesized in a variety of ways, but is primarily produced by the phosgenation of the corresponding diamine, as shown in Figure 2.10.[42,43] This synthetic route often starts with toluene via nitration, hydrogenation, and phosgenation to generate the diisocyanate. The nitration process leads to a mixture of ortho-, meta-, para-nitrotoluene isomers and the mixture can be separated by several distillation steps.[12]

Table 2.1 Diisocyanate building blocks for polyurethanes

Diisocyanates	Structure
4,4'-methylenediphenyl diisocyanate (MDI)	
2,4-, 2,6-toluene diisocyanate (TDI)	
1,5-Naphthalene diisocyanate (NDI)	
1,6-hexamethylene (HDI)	$\text{OCN}-(\text{CH}_2)_6-\text{NCO}$
4,4'-dicyclohexylmethane diisocyanate (H ₁₂ MDI)	
3-isocyanatomethyl-3,5,5-trimethylcyclohexyl isocyanate (isophorone diisocyanate IPDI)	
para-phenylene diisocyanate	
cyclohexyl diisocyanate	
2,2,4-trimethyl-1,6-hexamethylene diisocyanate (TMDI)	
3,3'-tolidene-4,4'-diisocyanate	
3,3'-dimethyl-diphenylmethane-4,4'-diisocyanate	

The starting materials for MDI are aniline and formaldehyde, which are reacted using hydrochloric acid as a catalyst, followed by phosgenation of the corresponding diamine as shown in Figure 2.11.

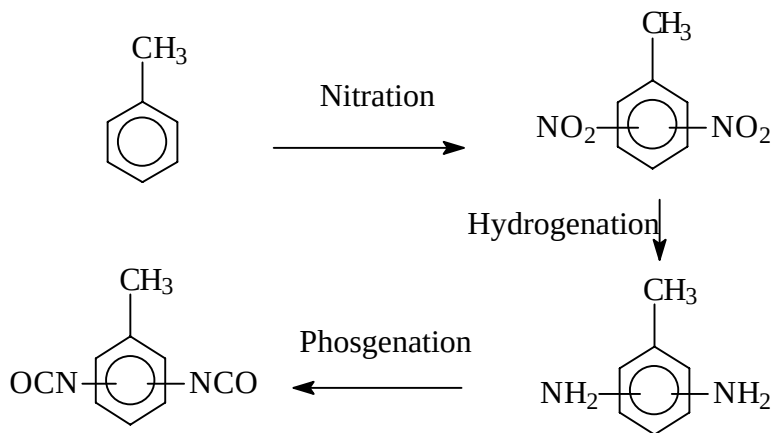


Figure 2.10 Synthesis of toluene diisocyanates

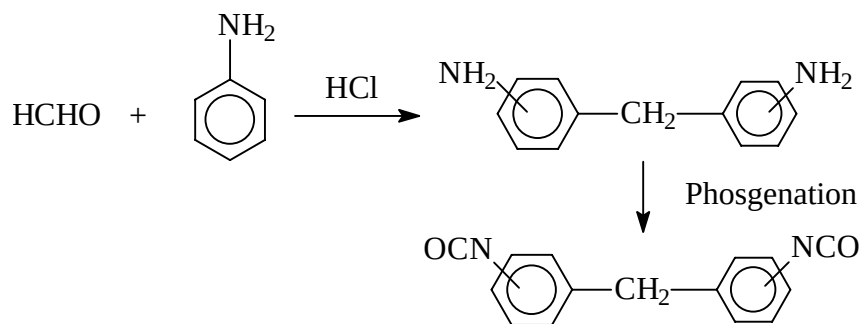


Figure 2.11 Synthesis of diphenylmethane diisocyanates

Aliphatic isocyanates can also be made from the corresponding aliphatic diamines via the phosgenation process. Cyclic aliphatic diamines are, in many cases, available through ring hydrogenation of the corresponding aromatic amines, such as the hydrogenation of diamino diphenyl methane (MDA) to give diamino dicyclohexyl methane. The most important aliphatic isocyanates are 1,6-hexamethylene diisocyanate (HDI), 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl-cyclohexane (IPDI) and 4,4'-diisocyanato dicyclohexylmethane (H_{12} MDI). These aliphatic isocyanates, or their modified forms, are widely used in the coatings industry.[44]

The soft segments used in polyurethane elastomers are dihydroxy terminated long chain macroglycols with a molecular weight between 500 to 5000. They include

polyethers, polyesters, polydienes or polyolefins, and polydimethylsiloxanes. The chemical structures for these macroglycols are listed in Table 2.2. Polyurethane elastomers have traditionally been made from polyether or polyester soft segments. Polyester-based urethanes have relatively good material properties, but they are susceptible to hydrolytic cleavage of the ester linkage. On the other hand, polyether based urethanes have relatively high resistance to hydrolytic chain scission. Polyethylene oxide (PEO) based urethanes exhibit poor water resistance due to the hydrophilic nature of the ethylene oxide. Polypropylene oxide (PPO) has been also been widely used because of its low cost and reasonable hydrolytic stability, although the mechanical properties of urethanes made from polypropylene oxide are not as good as those made from PTMO or polyester.[87]

Among the polyether based polyurethane elastomers, the one made from the soft segment polytetramethyleneoxide (PTMO) exhibits the best mechanical properties which are comparable to those of polyester polyurethanes. In addition, these polyurethanes show outstanding hydrolytic stability, good low temperature flexibility, good thermal stability, high fungus resistance, and excellent abrasion resistance. The PTMOs are usually produced by the cationic polymerization of tetrahydrofuran.[302]

When the application requires good environmental stability, a polydiene based soft segment is a good candidate. Hydrogenated polybutadiene and polyisobutylene based polyurethanes often show excellent resistance to photo degradation, thermal degradation, and hydrolysis.[55,64] However, the physical properties of these polyurethanes are poor compared to those of conventional polyurethanes. Furthermore, the synthesis of these materials is complicated, which can increase the cost. However, introducing of polydimethylsiloxane (PDMS) as a soft segment results in a polyurethane with improved low-temperature properties, since the glass transition temperature (T_g) of PDMS is around -123°C . Nonetheless, the physical properties of these urethanes are still not as good as those of conventional polyurethanes at room temperature.[77]

Table 2.2 Chemical structure of typical polyol soft segments

Polyol	Abbreviation	Chemical Structure	Reference
Polyethylene oxide	PEO	$\text{HO}-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	45
Polypropylene oxide	PPO	$\text{HO}-(\text{CH}_2\underset{\text{CH}_3}{\text{CH}}\text{CH}_2\text{O})_n\text{H}$	46-48
Polytetramethylene oxide	PTMO	$\text{HO}-(\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_n\text{H}$	49-54
Polyisobutylene	PIB	$\text{HO}-(\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{C}}}-\text{CH}_2)_n\text{OH}$	55-58
1,4-Polybutadiene diol	PBD	$\text{HO}-(\text{CH}_2\text{CH}=\text{CH}-\text{CH}_2)_n\text{OH}$	59-64
Polyethylene adipate	PEA	$\text{HO}-(\text{CH}_2)_2\left[\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_2\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-(\text{CH}_2)_2\right]_n\text{OH}$	65,66
Polytetramethylene adipate	PTMA	$\text{HO}-(\text{CH}_2)_4\left[\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_4\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-(\text{CH}_2)_4\right]_n\text{OH}$	67,68
Polycaprolactone	PCL	$\text{HO}-\left[(\text{CH}_2)_5\overset{\text{O}}{\parallel}{\text{C}}-\text{O}\right]_n(\text{CH}_2)_5\text{OH}$	69-71
Polydimethylsiloxane	PDMS	$\text{HO}-(\text{CH}_2)_4\left(\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{Si}}}-\text{O}\right)_n\underset{\text{CH}_3}{\overset{\text{CH}_3}{\text{Si}}}-(\text{CH}_2)_4\text{OH}$	72-76

In addition to polyol and diisocyanate, low molecular weight diol and diamine chain extenders play a very important role in polyurethanes as well. Without a chain extender, a polyurethane formed by directly reacting diisocyanate and polyol generally has very poor physical properties and often does not exhibit microphase separation. Thus, the introduction of a chain extender can increase the hard segment length to permit hard-segment segregation, which results in excellent mechanical properties, such as an increase in the modulus and an increase in the hard-segment glass transition temperature (T_g) of the polymer. By modifying the ratio between the polyol and chain extender, polyurethanes can change from a hard, brittle thermoplastic to a rubbery elastomer,

simply as a result of to the variation of the hard segment concentration in the block copolymer. Hard segment concentration is defined as the ratio of the mass of the non-polyol components to the total mass of the polymer.[13]

Polyurethane chain extenders can be categorized into two classes: aromatic diol and diamine, and the corresponding aliphatic diol and diamine. In general, polyurethanes chain extended with an aliphatic diol or diamine produce a softer material than do their aromatic chain extended counterparts.[78] Also, diamine chain extenders are much more reactive than diol chain extenders and give properties superior to those of similar polymers prepared with the equivalent diol chain extender. This is because the hard segment (urea linkage) has a higher density of hydrogen bonding, which results in a higher T_g and higher thermal stability. However, for the same reason, polyurethane ureas made from diamine chain extenders tend to be less soluble in common solvents and are thus more difficult to melt process. In addition, due to electron delocalization, the aromatic chain extenders have less reactivity than aliphatic chain extenders, which could be favorable in reactions that need to be highly controlled. Common chain extenders for polyurethane synthesis are shown in Table 2.3.

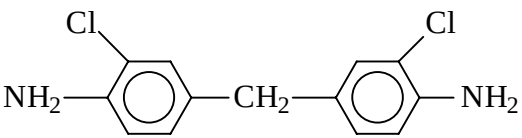
2.1.4.2 Synthetic methods for segmented polyurethane elastomers

The various methods for producing segmented polyurethane elastomers can be differentiated according to the medium of preparation (bulk, solution, water) and the addition sequence of the reactants (one-step process, prepolymer process). In some cases, catalysts are added to accelerate the polyaddition reaction. [12]

Bulk polymerization, either one-step or two-step, has been the main industrial process for polyurethane production, because of its environmentally friendly solvent-free synthesis. On the other hand, solution polymerization has largely been used for the laboratory or experimental synthesis of polyurethanes. As expected, different synthetic processes have an effect on both rate and yield. For example, in some type of polyurethane bulk synthesis, the incompatibility between the reactants induces polymerization to form a heterogeneous system or the system becomes heterogeneous at a relatively early stage of the reaction. Therefore, the composition of the final product is controlled by the diffusion rate of the reactants from one phase to the other, as well as by

the reaction rate between different functional groups.[79,80] However, in the solution process, the problem of heterogeneity can be alleviated by the choice of solvent since incompatible reactants can be dissolved by the same solvent, thus helping to bring them into one phase. Common solvents used in urethane synthesis are dipolar aprotic solvents including N, N'-dimethylacetamide (DMAc) and dimethylformamide (DMF).

Table 2.3 Polyurethane chain extenders and their structure

Chain Extender	Structure
1,4-Butandiol	$\text{HO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{OH}$
1,6-Hexanediol	$\text{HO}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-\text{OH}$
Ethylene glycol	$\text{HO}-\text{CH}_2\text{CH}_2-\text{OH}$
Ethylene diamine	$\text{NH}_2-\text{CH}_2\text{CH}_2-\text{NH}_2$
4,4'-Methylene bis(2-chloroaniline)	

Solution polymerization can also be a one-step or two-step process. In one step synthesis, the reaction is carried out by simultaneously mixing a polyol, a diisocyanate, and a chain extender together in the reaction solvent and heating the solution above 80 °C. In some cases, catalysts are applied to accelerate the reaction.

However, the more common route of making polyurethane is via the two-step synthesis, or prepolymer, route. This process is illustrated in Figure 2.12. In this method, the first step is to react the polyol with excess diisocyanate to form a diisocyanate terminated intermediate oligomer, i.e. a prepolymer, with a molecular weight of 1000 to 5000, depending upon the polyol's molecular weight and the ratio between these two reactants. The prepolymer that is formed is normally a viscous liquid,

or a low-melting-point solid, which is easily stored. The second step is to convert this prepolymer to the final high molecular weight polyurethane by further reaction with a diol or diamine chain extender. This step is usually referred to as chain-extension. [14]

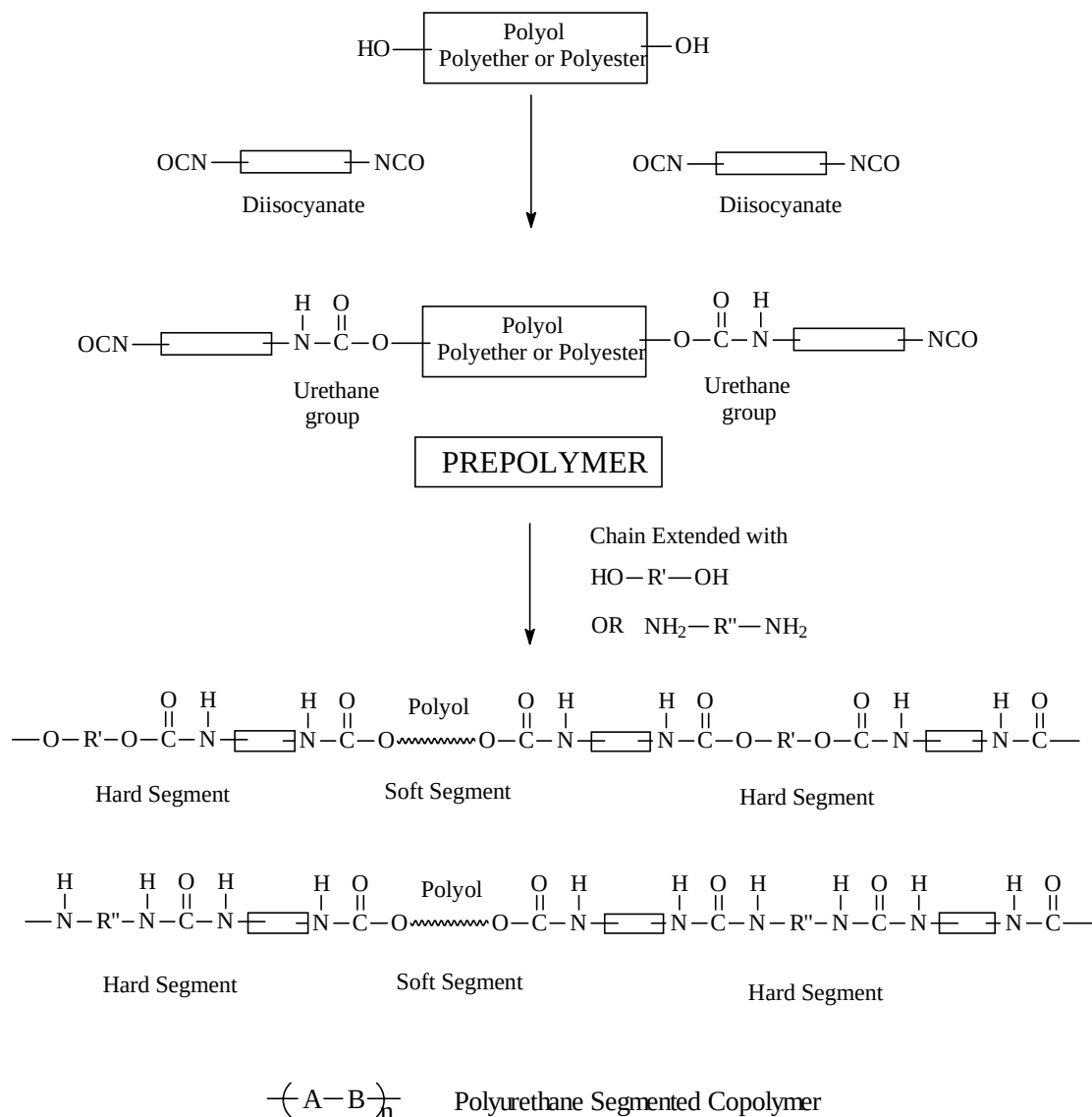


Figure 2.12 Two-step prepolymer technique for the synthesis of polyurethane and polyurethaneurea

A polyurethane structure made by the two-step method tends to be more regular than the corresponding polyurethane made by the one-step method. This is because the two-step method caps the polyol with diisocyanate and then connects these oligomers with chain extenders. Therefore, the polymer chain has a more regular hard-soft-hard

sequence than seen in the random distribution of hard segments in the one-step process, therefore, the hard segment size distribution is narrower than in the one-step method. This structural regularity may impart better mechanical properties to the polyurethane since the hard segments more easily aggregate or crystallize to form physical crosslink points.[88]

2.1.5 Structure-Property relationships of segmented polyurethane elastomers

2.1.5.1 Morphology

It is evident that the morphology of a multiphase system plays an important role in determining the final properties of the polymers. By controlled variation of the morphology, the desired properties can be obtained for a material. Hence, a profound knowledge of morphology is essential to understanding structure-property relationships. Unfortunately, the morphology of segmented polyurethanes is very complicated, not only because of their two-phase structure, but also because of other physical phenomena such as crystallization and hydrogen bonding in both segments. Nevertheless, this area has attracted wide interest among many researchers who have tried to elucidate the detailed micro- and superstructure using a variety of techniques.[11]

From a thermodynamic point of view, the incompatibility between the polar hard segment and less polar soft segment in the polyurethane causes the heat of mixing to be positive and drives the two segments to phase separate. The degree of phase segregation between the hard and soft segments depends on molecular weight and the interaction of hard segments with each other and with the soft segments. For example, phase segregation is more pronounced in polybutadiene urethanes than in polyether urethanes, and is least evident in polyester urethanes. Moreover, the interaction between the hard segments depends on the symmetry of the diisocyanate and on the selection of the chain extender (diol or diamine). A diisocyanate and a chain extender having a more symmetrical structure will enhance the formation of organized structures, and thus, more complete phase segregation. A urea-containing hard segment formed from low molecular weight diamine chain extender has a much more pronounced phase separation than urethane- containing hard segments because of the higher polarity of the urea hard segment. This also accounts for the fact that very short urea hard segments can still

segregate from the soft phase. Typical hard segments have a molecular length of only about 25-100 Å.[12]

The morphology of segmented polyurethanes can be studied at three different structural levels according to their size. The smallest structural level is the molecular structure such as crystal structure, block sequence and sequence distribution, which can be investigated by NMR and IR spectroscopy. The second level of structure is domain structure, which has the dimension of 50-1000 Å. A complete description of sample morphology at this level consists of the determination of the phase volume fraction, size, shape, orientation, connectivity, and interfacial thickness as a function of segment content and sample history.[13] This structural level can be directly probed by electron microscopy, or more quantitatively by small angle X-ray scattering. The third level of morphology is spherulitic texture and when size considerations are in the micron range. This type of morphology can be investigated using small angle light scattering, electron microscopy and polarized light microscopy. These methods can be complemented by thermal analysis methods such as differential scanning calorimetry and dynamic mechanical analysis to render additional, if somewhat less direct, information on the domain structure.

The first direct evidence for the formation of a two-phase structure was obtained from the SAXS studies by Bonart and Clough.[89,18] However, detailed information could not be derived from the single peak in their SAXS profiles without some ambiguity, since the polyurethane had a disordered two-phase morphology. The two-phase microstructure was first observed by Koutsky and Cooper using transmission electron microscopy on polyether and polyester urethane.[90] They found that the sizes of hard domains were from 30 to 100 Å for both the polyester and polyether urethanes, although this observation has been disputed. The later TEM and SAXS works carried out by Thomas et al., Chen-Tsai et al., and Serrano et al. on the morphology of PBD/TDI/BD based polyurethanes with varying hard segment concentration (HSC) also elucidated the two-phase morphology.[91-93] However, it cannot be assumed on the basis of the obtained evidence that complete phase separation occurred. In fact, there was evidence that appreciable hydrogen bonding existed between the hard and soft segments, which implied incomplete phase separation. A TEM micrograph of a polyurethane based on

PTMO ($M_n=2000$)/MDI/BD is shown in Figure 2.13. A schematic representation of the domain and chain formation for the segment outlined in the TEM and the cylinder model of the hard segment are provided in Figure 2.14. From the TEM micrograph, the two-phase structure is clearly demonstrated.[12,94]

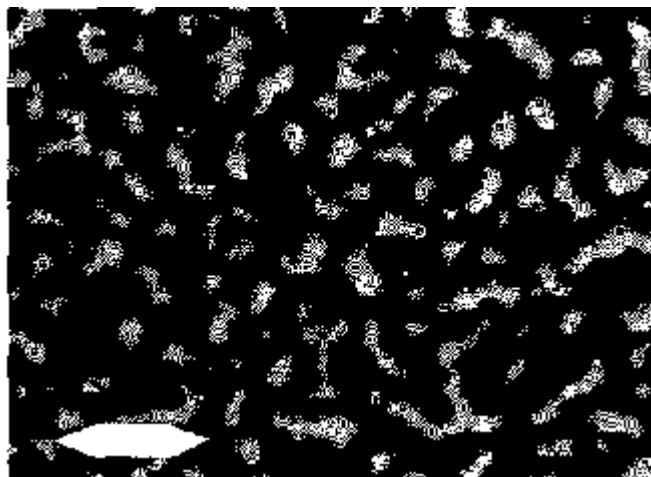


Figure 2.13 Transmission-Electron-Micrograph (TEM) of a segmented polyurethane elastomer film. Shown is the element specific (nitrogen) picture (ESI) of the film having thickness 200 Å cast from DMF solution (0.2 wt%) without special contrast. The cylinder shaped hard domains are represented by the white areas. The scale, arrow on the picture corresponds to 200 Å.[12]

Li and coworkers used high voltage electron microscopy (HVEM), high resolution scanning electron microscopy (SEM), and SAXS to study the morphology of polybutadiene/BD/MDI based polyurethanes having variable HSC.[95] The results are summarized in Table 2.4. A rod-like or lamellar structure was observed for polyurethane with hard segment concentration of 42%-67%. However, when the hard segment was less than 31wt%, the hard segment phase was dispersed in the matrix of soft segments in the form of either short cylinders or spheroids.

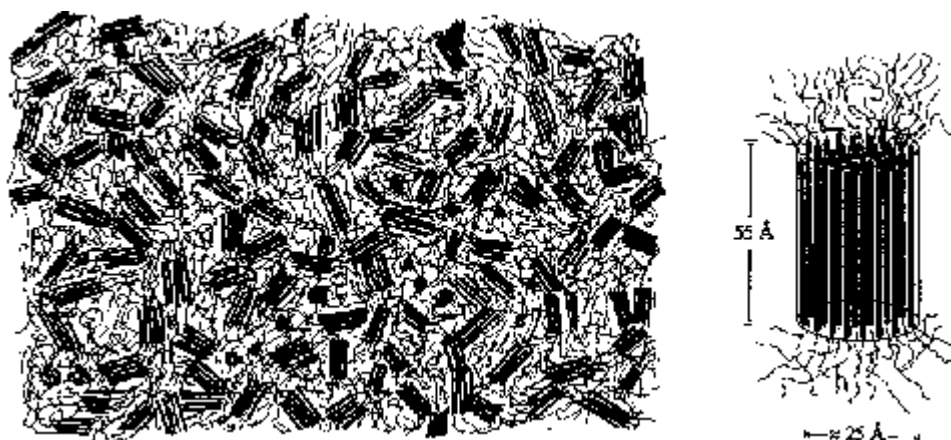


Figure 2.14 Schematic representation of the domain and chain formation for the segment outlined in the TEM and the cylinder model of the hard domains

Table 2.4 The effect of HSC (hard segment concentration) on polyurethane morphology and microdomain spacing measured by SAXS and HVEM [95]

HSC, %	V_h	Morphology	L, nm	d_i	d_{is}
31	0.27	Short cylinders	10.6	9.5	
42	0.35	Lamellar/rod-like	12.2	11	
49	0.43	lamellar	12.9	12	
58	0.51	Lamellar/rod-like	12.7	13	13
62	0.55	Lamellar/rod-like	14.1	14	14
67	0.67	Lamellar/rod-like	16.8	14	14
75	0.68	Cylindrical/plate-like	27.1	31	24

V_h : volume fraction, L: long spacing from SAXS curve, d_i : microdomain spacing from HVEM micrographs on the thin film, d_{is} : microdomain spacing from HVEM micrographs on thin sections.

Another model of domain structure in a segmented polyurethane, proposed by Estes, is illustrated in Figure 2.15.[96] In this model, it was assumed that phase separation

was not complete because some hard segments were dispersed in the rubbery matrix. The shaded areas are the hard domains. Both phases were represented as being continuous and interpenetrating, which requires a sufficient amount of hard segment concentration.

Although there are other models proposed by Bonart, Wilkes, and Blackswell, based on X-ray diffraction results for different polyurethane systems, the exact nature of microphase structure of polyurethanes has yet to be elucidated.[89,97-99, 303]

Crystallization of hard and soft segments provides additional information on the behavior of polyurethanes. The crystalline form of the hard segments depends on their structure, as well as on the crystallization conditions.[13] For example, effect of the chain extender length on the structure of MDI/diol hard segments showed that 1,4-butane diol and longer diol chain extenders produced structures whose properties depended on whether the diol had an even or odd number of methylene groups. A polyurethane chain extended with "even" diols adopts the lowest energy fully extended conformation that allows hydrogen bonding and, therefore, higher crystalline order. This explains why elastomers based on 1,4-butanediol and higher diols with their hard segment conformation generally possess better properties. Hard segments based on these chain extenders can crystallize more easily, thus helping phase separation.[12]

Large supermolecular structures, in the form of spherulites, were often found to be associated with crystallization of the polyether segment. Spherulites were observed in PCI/MDI/BD,[100,101] PTMO/MDI/BD,[102,103] PEO/HMDI/paraphenyldiame systems,[104] and other segmented thermoplastic elastomers.[105-107]



Figure 2.15 Representation of domain structure in segmented copolymer [96]

2.5.1.2 Structure-Property relationship of segmented polyurethane elastomers

The primary structure of a segmented polyurethane includes chemical composition, type, molecular weight and distribution of hard and soft segments, block length distribution (distribution of segment size), and degree of branching or crosslinking. These primary structures determine the secondary structure, such as three-dimensional chain orientations (i.e. three-dimensional organized proximity zone), crystallinity, and consequently, the morphology of the polyurethanes. Both primary and secondary structures contribute to the final properties of the polyurethanes.[12]

The primary structure can be well controlled by synthetic conditions. For example, varying the ratio of the soft and hard segments can control the composition. The type of soft and hard segment can be chosen from array of compounds listed in Table 1-3 and molecular weights can be varied. Moreover, a new monomer could also be synthesized for a specialized purpose. The distribution of segment size is also closely related to the synthetic method. The two-step prepolymer method affords a more regular structure than the one-step route, although not perfect. The ideal primary structure of a segment polyurethane is provided in Figure 2.16, which is a perfect alternating block copolymer. However, under practical conditions, the structure of the soft segment, as well as the urethane reaction, follows a statistical Flory distribution. Therefore, the hard segment formed is not perfectly alternating and the block length may vary as shown in Figure 2.17.[12]

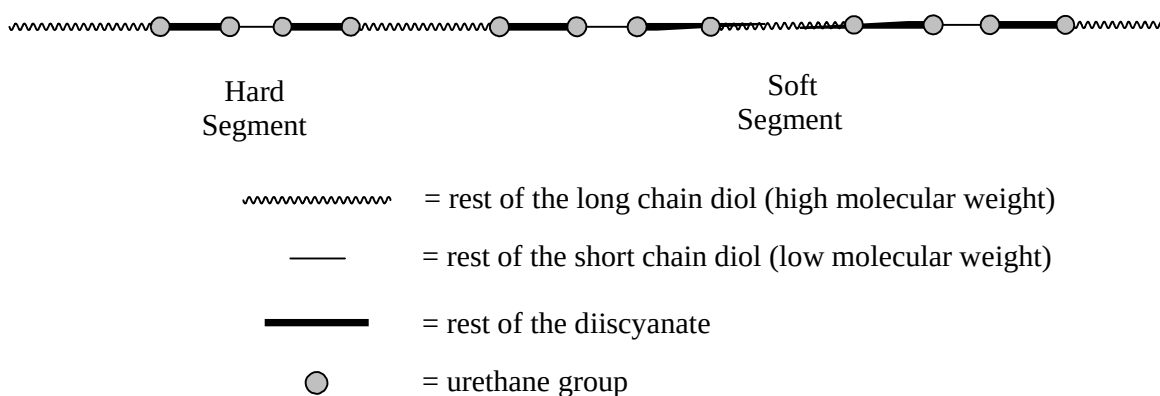


Figure 2.16 The ideal structure of a segmented polyurethane

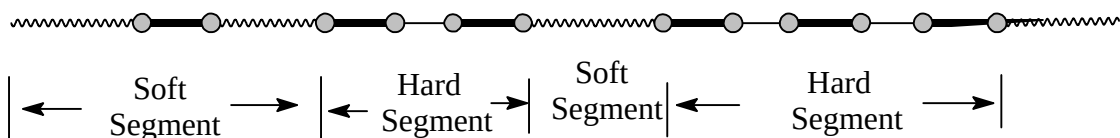


Figure 2.17 The realistic structure of a segmented polyurethane

The branching and crosslinking can also be attributed to the synthetic strategy. For example, the branching and crosslinking structures formed during the synthesis of linear segmented polyurethanes are caused by the side reaction of isocyanate and urethane or urea linkage, which has been described previously.

Several excellent papers have been published dealing with structure-property relationship.[108-119] The property differences caused by structure variations can be classified as polyol effect, chain extender effect and diisocyanate effect.

Effect of polyol type and molecular weight

The mobility of the polyol results in low-temperature properties and the variation in ultimate stress values in the segmented polyurethane. Therefore, it is obvious that features related to the mobility of the polyols such as T_g , T_m , and the ability to crystallize under deformation, will certainly impact mechanical properties. It also has been reported that stress induced crystallization can improve tear resistance and tensile strength, while at the same time diminishing recovery characteristics.[97,119-120] Polyol mobility depends to a large extent on the type and the molecular weight of the polyol. To prepare products with typical rubber elasticity, an average molecular weight of between 1000 and 4000 (which corresponds to a chain length of 180 and 300 Å) is desirable.[12]

Higher molecular weight polyols afford materials with better tensile properties but with an increased tendency to cold-harden, which is a phenomenon caused by gradual crystallization of the flexible blocks during storage. This can be avoided by incorporating copolyester to provide structure irregularity.[87] In general, the primary consequences of increasing the molecular weight of the soft block for a given overall molar ratio of polyol block to hard block (diisocyanate plus chain extender) are, a decrease in modulus and an increase in elongation at break, as illustrated in Table 2.5, and a reduction in T_g of the soft block.

Table 2.5 Molecular weight influence on the physical properties of polyethylene adipate-based elastomer (with naphthalene diisocyanate)

Molecular Weight of Poly(ethylene adipate)	Tensile Strength (MPa)	Elongation at break (%)	Hardness	300% Modulus (MPa)
4500	38	770	60	5
3500	35	750	65	7
2500	34	700	70	10
2000	32	700	80	11
1000	31	450	83	15

Polyethers usually have a lower T_g and a weaker interchain force than polyesters, thus generally render the corresponding polyurethanes with reduced mechanical properties. This is often attributed to the stronger hydrogen bonding between the NH and the ester carbonyl group, rather than urethane NH-ether oxygen bond. Among polyethers, Poly(tetramethylene glycol) based polyurethane has the best physical properties, which reflect the regularity of its chain structure and its ability to crystallize upon extension. On the other hand, the atactic side chain methyl group in poly(propylene glycol) prevents crystallization, resulting in weaker mechanical properties as shown in Table 2.6.[122]

Table 2.6 Effect of polyol structure on the properties of some thermoplastic polyurethanes

Polyol/ Molecular Weight	DSV*	Shore Hardness	Tensile Strength (psi)	Elongation (%)	300 % modulus (psi)	T_2 (°C)
Poly(ethylene adipate)glycol/980	0.824	86(A)	7400	655	900	136
Poly(tetramethylene adipate)glycol/989	0.904	88(A)	7800	530	1300	160
Poly(hexamethylene adipate)glycol/986	1.058	82(A)	8600	560	1200	147
Poly(1,4-cyclohexyldimethylene adipate) glycol/1190	0.697	60(D)	5600	355	4800	142
Poly(tetramethylene glycol)/974	0.935	90(A)	5300	725	1000	130
Poly(propylene glycol)/1005	0.874	76(A)	4200	800	640	146

* DSV= dilution solution viscosity, Components: MDI/Macroglycol/1,4-butandiol=2/1/1;
DSV= dilute solution viscosity; T_2 = Processing Temperature

Effect of Chain Extender

The effect of a chain extender on material properties depends on the type of chain extender used. When diamine is used as chain extender, Better physical properties usually result than if a diol were used, due to stronger interchain interaction from the urea linkage.

Schollenberger has investigated the effect of different diols on polyurethane properties. One polyol that was employed was poly(tetramethylene adipate)glycol ($M_n=1000$) with MDI as diisocyanate. A constant mole ratio of (1:2:1) of polyol to diisocyanate to diol was used. The results provided in Table 2.7, show that the mechanical properties resulting from this study were all excellent. However, the aliphatic glycol containing aromatic structure demonstrated the highest modulus and hardness.[122]

Table 2.7 Effect of glycol structure on the properties of some thermoplastic polyurethanes

Glycol	Hardness (Shore A)	Tensile Strength (psi)	Elongation (%)	300 % Modulus (psi)
Ethylene Glycol	80	6500	500	1000
Trimethylene glycol	80	5900	575	1200
Tetramethylene Glycol	88	7800	530	1300
Hexamethylene Glycol	87	5700	580	1100
1,4-Bis(-hydroxy-ethoxy) benzene	93	3700	550	1900

Components: MDI/Poly(tetramethylene adipate) glycol/Glycol =2/1/1

Effect of Diisocyanate

The structure of the diisocyanats has a profound effect on high temperature properties, which is illustrated in Table 2.8.[87]

Table 2.8. Effect of diisocyanate on polyurethane elastomer properties

Diisocyanate	Tensile Strength (MPa)	Elongation at Break (%)	300 % Modulus (MPa)
1,5-Naphthalene diisocyanate	29	500	21
1,4-Phenylene diisocyanate	44	600	16
2,4 - and 2,6-Toluene diisocyanate (isomers)	31	600	3
4,4'-diphenylmethane diisocyanate	54	600	11
3,3'-dimethyl-4,4'-diphenylmethane diisocyanate	36	500	4
4,4'-Diphenyl propane-[2,2]-diisocyanate	24	700	2
3,3'-Dimethyl -4,4'--biphenyl diisocyanate	27	400	16

Components: Poly(ethylene adipate)/diisocyanate/1,4-butanediol=1/3/2

The polyol employed was poly(ethylene adipate) with a molecular weight of 2000. A constant mole ratio of (1:3:2) of polyol to diisocyanate to 1,4-butanediol was used. Factors such as high symmetry and rigidity in the p-phenylene diisocyanate lead to high modulus and excellent tensile strength. Reducing the bulkiness of the diisocyanate from naphthalene to 1,4-phenylene results in a drop in modulus. Moreover, the effect of the methyl group is remarkable and results in a large drop in modulus. This is shown in comparison of 4,4'-diphenylmethane diisocyanate and 3,3'-dimethyl-4,4'-diphenylmethane diisocyanate, on the one hand, and the 2,4-toluene diisocyanate and 1,4-phenylene diisocyanate on the other. This is due to the fact that the methyl substituent can seriously disrupt the symmetry and crystallizability of the diisocyanates. Nevertheless, the symmetry of MDI is sufficient to allow the preparation of a semicrystalline hard block, which is reflected by its excellent tensile strength.

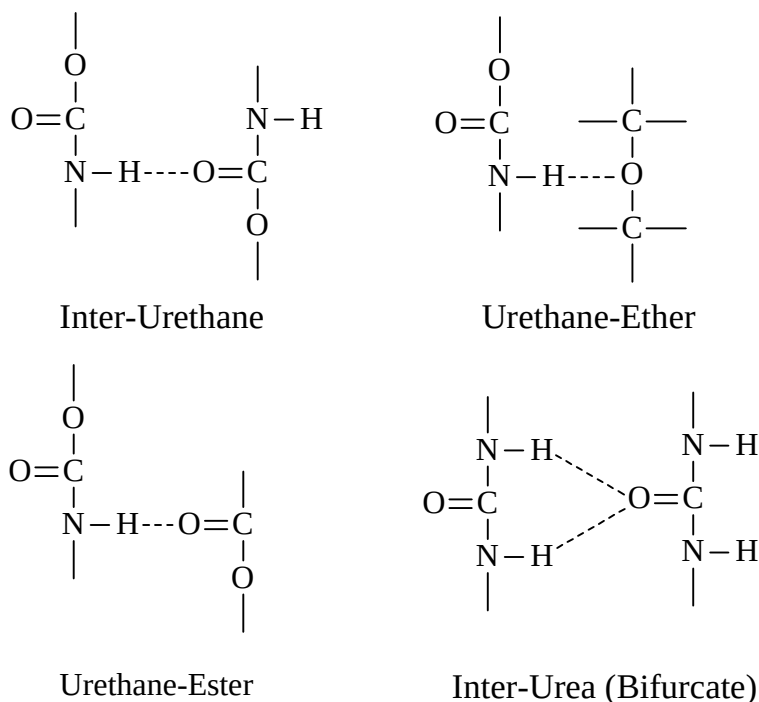
Aliphatic, e.g. hexamethylene diisocyanate, or cycloaliphatic diisocyanates, e.g. hydrogenated MDI, can offer better light stability over the aromatic isocyanate. They also show increased phase separation behavior over the corresponding aromatic diisocyanates. When the properties of H₁₂MDI elastomers were compared with those of the analogous MDI series, the aliphatic diisocyanate based elastomers generally had superior mechanical properties. However, since H₁₂MDI is usually employed as a mixture of isomers, the derived polyurethanes do not possess as high a use temperature as those do from MDI. Another important feature of the aliphatic diisocyanates is

transparency, which also arises from the presence of geometric isomers in these diisocyanates. H₁₂ MDI and IPDI are now well established as being preferred for the production of transparent weatherable polyurethane elastomers.[87]

2.1.5.3 Hydrogen Bonding

The hydrogen bond is the strongest secondary chemical bond with a strength estimated to about 20-50 kJ/mol.[121] Polyurethanes are extensively hydrogen bonded, which involves the N-H group as proton donor and the urethane carbonyl, the ester carbonyl (in polyester urethane), or the ether oxygen (in polyetherurethanes) as proton acceptor. The hydrogen bonding interaction in polyurethanes and polyurethaneureas is illustrated in Scheme 2.1.[67,125-127] Hydrogen bonding in polyurethanes can be readily detected and studied by IR spectroscopy. The hydrogen bonded and free N-H, urethane carbonyl C=O, urea carbonyl C=O are the peaks of interest.[68,96,128-135]

However, a basic concern of hydrogen bonding in polyurethanes is related to its role in phase separation. If hydrogen bonds could be formed between the two phases, quantitatively it could be assumed that a higher degree of phase mixing should be expected. On the other hand, if hydrogen bonds are formed only within the hard segment, they may enhance crystallization and thus, phase separation. The extent of hydrogen bonding, or the hydrogen-bonding index (the ration of bonded to free urethane carbonyl group), can be affected by structure, composition of the polyurethane as well as temperature. A polyether urethane has fewer hydrogen bondings, about 40% of the carbonyl in polyether urethane are hydrogen bonded, than polyester urethane with same hard segment content. Increasing the hard segment content will increase hydrogen-bonding index. At room temperature, approximately 90% of the N-H groups in the hard segment of a typical polyurethane are hydrogen bonded.[126] However, hydrogen bonding will start to dissociate as the temperature increases and this process can be accelerated by the glass transition of the hard segments. However, a measurable amount of hydrogen bonding (35-40%) remained at temperatures as high as 200°C.[127]



Scheme 2.1 Hydrogen Bonding interaction in polyurethanes and polyurethaneureas

The effect of hydrogen bonding on the mechanical properties of a polyurethane is frequently used to explain various anomalies or improved properties. However, it is difficult to isolate this effect from the effects of chemical and physical structure. Some studies have concluded that molecular mobility is not controlled by hydrogen bonding. Instead it is believed that a rapid increase in molecular mobility accompanying glass transition allows the hydrogen bonding to dissociate.[126,134,137] Therefore, hydrogen bonding does not necessarily enhance mechanical properties, although there is insufficient published data that quantitatively demonstrates the effect of hydrogen bonding on mechanical properties. A clear effect of hydrogen bonding could be observed only if mechanical tests are carried out on polyurethanes of analogous structure with and without hydrogen bonding. Nevertheless, if it does play a role, it is probably also affected by the number of hydrogen bonds in a segment, as well as by the number of interphase bonds.

2.1.5.4 Surface Properties of Segmented Polyurethane

Among a large number of polymers that have been used in biomedical applications, polyurethanes have been found to be very appealing because of their

versatile physical and chemical properties that can be readily tailored by synthesis and other modifications. As one of an increasing number of the biomaterials, their surface properties are very important in developing medical devices and diagnostic products. These properties include surface tension, surface composition, surface morphology, hydrophilicity, and surface electrical properties, to name a few.[14] To analyze the surface, a variety of physical techniques are available as illustrated in Table 2.9.[138]

Table 2.9 Selected Surface Analysis Methods

Acronym	Method
ESCA (or XPS)	Electron Spectroscopy for Chemical Analysis (X-Ray Photoelectron Spectroscopy)
AES (or SAM)	Augur Electron Spectroscopy (Scanning Auger Microprobe)
SIMS	Secondary Ion Mass Spectroscopy
ISS	Ion Scattering Spectroscopy
LEED	Low-Energy Electron Diffraction
STM	Scanning Tunneling Microscopy
AFM	Atomic Force Microscopy
ATR-IR	Attenuated Total Reflectance-Infrared
	Contact Angle Methods

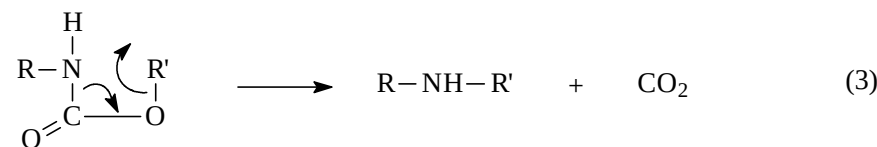
Contact angle measurement is one of the methods used to obtain information about the top few angstroms of the solid surface. Surface tension of a polyurethane can be deduced from the Owens-Wend equation by measuring the contact angle of two different liquids, whose surface tensions are known, on a polyurethane surface. Electron spectroscopy for chemical analysis (ESCA), also known as X-ray photoelectron spectroscopy (XPS), is perhaps the most widely used surface spectroscopy. It is used to characterize chemical structure and elemental analysis of a solid surface. Atomic Force Microscopy (AFM) has recently been developed as a method for characterizing solid surfaces, with the tip tapping the surface of the sample, the surface image can be collected.

Many investigators have extensively studied surface properties of segmented polyurethanes. Due to microphase separation between the hard and soft segments, segmented polyurethanes exhibit unique bulk and surface properties. Slight changes in synthetic methods, chemical composition, and process conditions can lead to variations in

2.1.6 Thermal and Photo-Degradation of Polyurethane

Thermal Degradation of Polyurethanes

The thermal degradation mechanism of polyurethane is very complicated. It has been suggested that polyurethanes break down by a combination of three independent pathways: (1) dissociation to the original polyol and isocyanate; (2) formation of a primary amine, an alkene, and a carbon dioxide in a concerted reaction involving a six-membered cyclic transition state; (3) formation of a secondary amine and carbon dioxide through a four-membered ring transition state, as shown in Scheme 2.2.[143-147]



31

This equation (1) which begins to be significant at 150-160°C, was believed to be the predominant mechanism and the resulting primary degradation products, e.g. diisocyanate and diol, have been identified through FTIR. These primary degradation products can give secondary decomposition products, such as carbondiimides, and this is shown in Figure 2.18.[147-150]

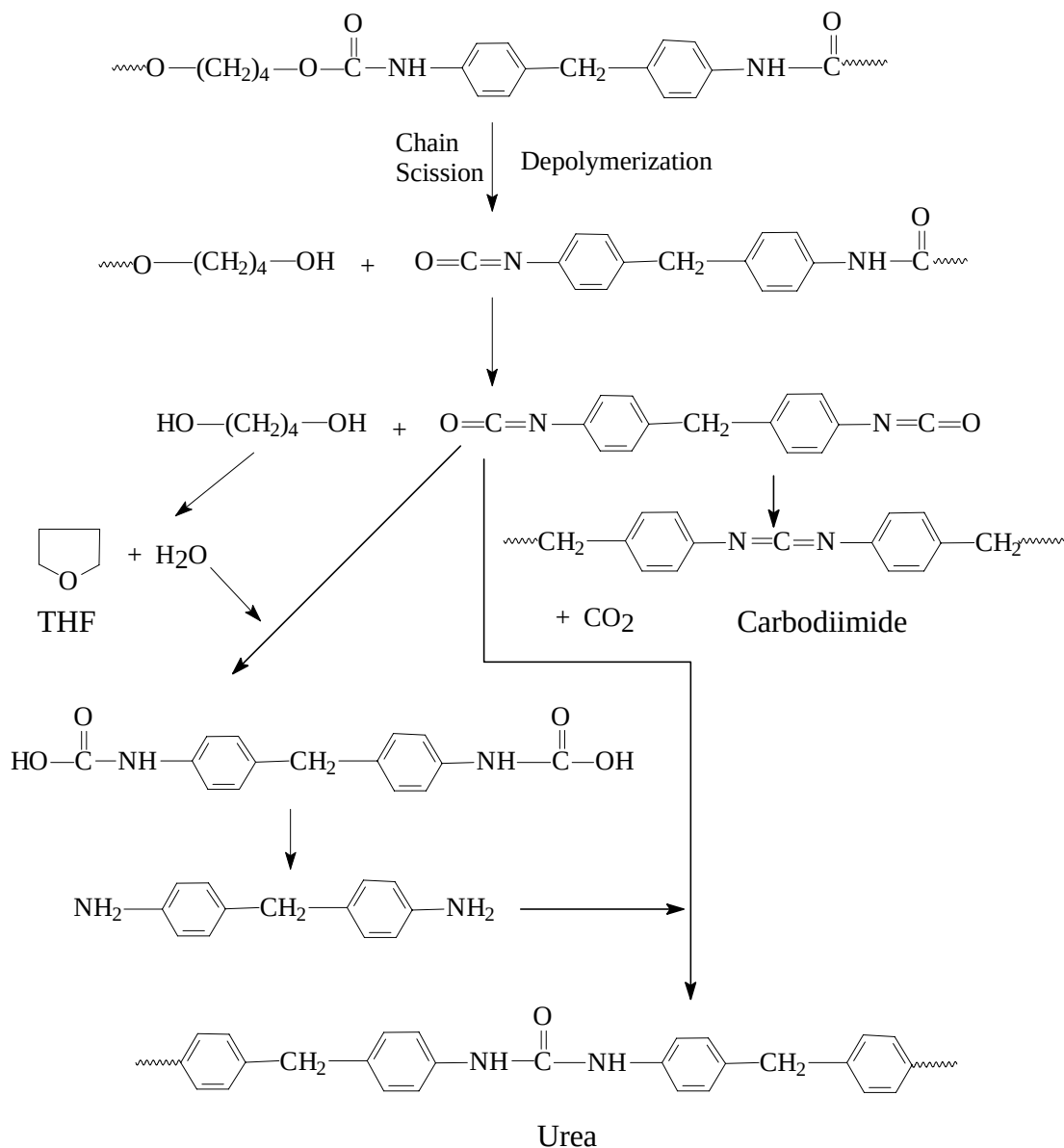
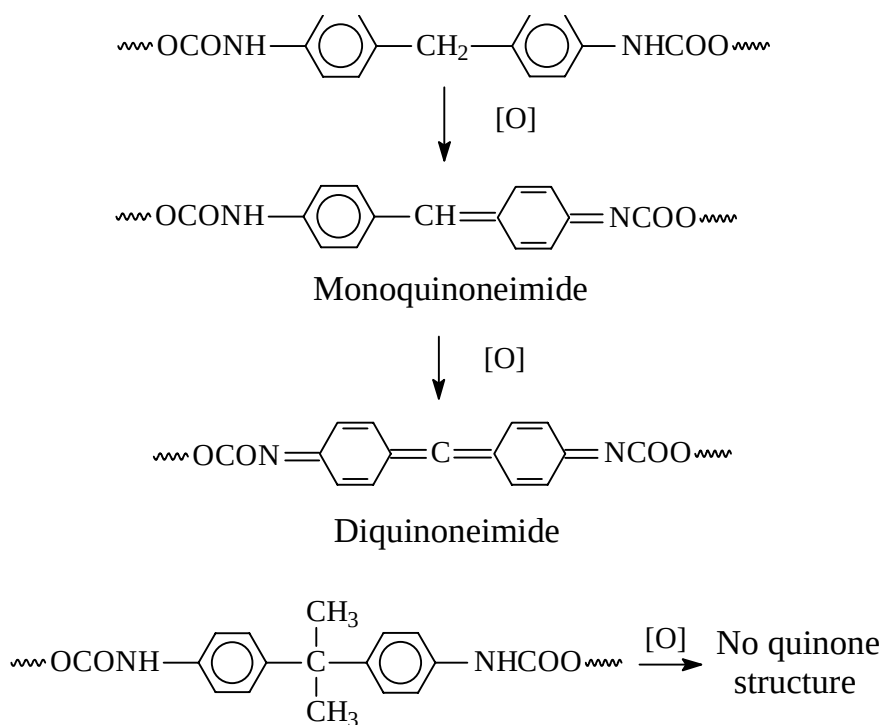


Figure 2.18 Thermal degradation mechanisms of polyurethanes

Photo-degradation and Stabilization of polyurethane

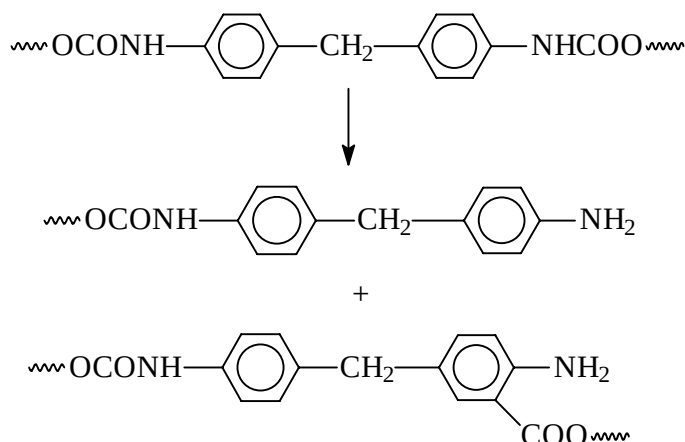
All organic polymers are prone to photo-degradation, although the rate of degradation varies tremendously with the structure of the polymer. Aromatic urethanes have long been noted for their light instability. Initial studies on the photo-degradation of polyurethanes in 1960's focused on commercially available polyurethanes derived from aromatic diisocyanates, such as MDI and TDI, which turned yellow on storage or in actual application.[20,37,41,151] Evidence has been presented that discoloration and mechanical property loss can be related to the ultraviolet-initiated auto-oxidation of the urethane linkage to quinone imide structures. However, polyurethanes derived from diisocyanates that are structurally incapable of forming such quinone species, even though they are aromatic, were able to retain excellent physical properties after accelerated aging as shown in Scheme 2.3.[37]



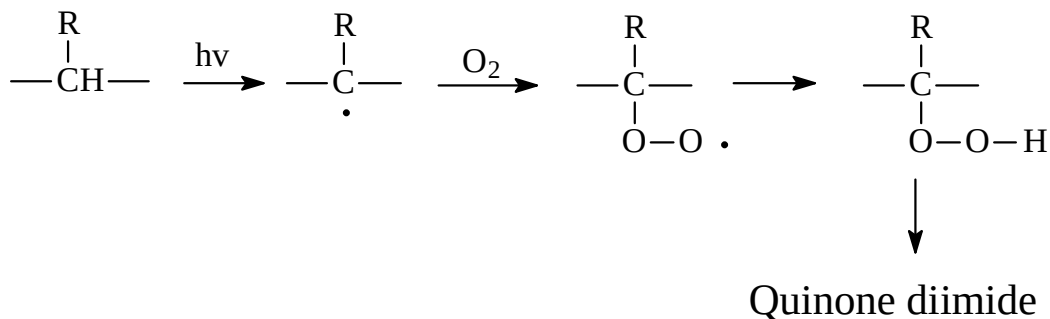
Scheme 2.3 Photo-degradation of urethane linkage

Besides the auto-oxidation degradation mechanism, it has been postulated that aromatic polyurethanes can undergo photo-Fries degradation, as shown in Scheme

2.4.[151-153] Both mechanisms have been related to the wavelength of light. The degradation was believed to occur through a photo-Fries type reaction when a shorter wavelength (<340 nm) is applied.[152-154] The auto-oxidation mechanism was observed at a longer wavelength, involving the formation of primary hydroperoxides, which consequently give a quinone imide as illustrated in Scheme 2.5.[155] This photo-degradation can be prevented by using UV stabilizer such as inorganic pigments, e.g. Fe₂O₃, Cr₂O₃, Pb₃O₄, ZnO, and organic pigments.[156,157]



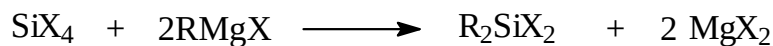
Scheme 2.4 Photo-Fries degradation mechanism



Scheme 2.5 Hydroperoxide formation in hydrocarbon moieties of the polyurethane

2.2 Siloxane containing copolymers

Since their commercial introduction in the 1940s, polyorganosiloxanes, which are also known as "silicones" or "silicone elastomers", have been recognized as an important class of specialty polymers containing an inorganic backbone.[158,159] Pioneering work on polyorganosiloxanes dates back to the studies of Friedel, Crafts, and Ladenberg in 1863.[160-162] However, Kipping, at the University of Nottingham, was the first to systematically investigate organosilicon compounds. He was also the first to find an industrially feasible method, shown in Figure 2.19, to make organohalogenosilanes.[163] Kipping is also credited with the realization that the hydrolysis of dimethyldichlorosilane does not yield the acetone analog, silicone, but rather polymeric compounds of an oil nature, i.e. polydimethylsiloxane.

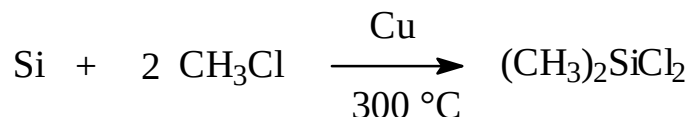


R= organic radical, e.g. —CH_3 , $\text{—C}_2\text{H}_5$

X= Cl, Br

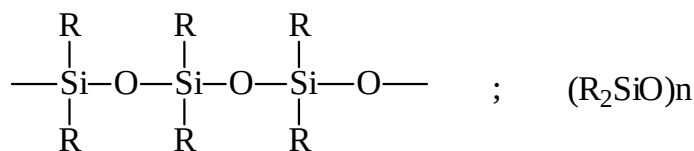
Figure 2.19 Grignard synthesis of organohalogenosilanes

However, the importance of organosiloxanes was not fully realized until the discovery of direct synthesis by Rochow and Müller in the early 1940s, which allowed the economical manufacture of organochlorosilanes from the reaction of an elemental silicon and an alkyl chloride as illustrated in Scheme 2.6.[164,165]



Scheme 2.6 Rochow synthesis of dimethyldichlorosilane

Controlled hydrolysis of these organohalogenosilanes then led to the way to the preparation of polyorganosiloxanes and cyclic siloxane monomers. These structures are provided in Scheme 2.7. The most common silicon substituents include methyl, phenyl, 1,1,1-trifluoropropyl, hydrogen, and vinyl groups. The common cyclic monomers are D₃ and D₄, which are cyclic dimethylsiloxanes with n=3 and 4, respectively.[166-168]



Scheme 2.7 Structure of polyorganosiloxanes and cyclic siloxane monomers

The Si-O bonds within a polyorganosiloxane have an "organic-inorganic" nature and substantial ionic character (40-50%), which is demonstrated by a much smaller bond length than the sum of atomic radii. Among all the polyorganosiloxanes, polydimethylsiloxanes have received the most attentions due to their unique properties, such as extremely low glass transition temperature (-123 °C); very low surface energies (20-21 dynes/cm); hydrophobicity; good thermal and oxidative stability; high gas permeability; excellent atomic oxygen resistance; biocompatibility, low dielectric constant, and low solubility parameter.[166-168]

When the methyl groups on silicon atoms are replaced by phenyl groups, either in the form of methylphenylsiloxane or diphenylsiloxane, the glass transition temperature of the siloxane will increase, as well as the thermal and the oxidative stability, and organic solubility characteristics. Trifluoropropyl substitution provides improved solvent and oil resistance. In addition, some fluorinated substituents can increase thermal stability and the low temperature properties of the copolymers.[169-171]

Despite of their advantageous properties, polydimethylsiloxanes require extremely high molecular weights to develop useful mechanical properties. Generally, PDMS must be chemically crosslinked and reinforced with finely divided high surface silica to develop useful elastic modulus and tensile strength. However, these crosslinked and reinforced siloxane elastomers experienced process difficulties.[168,172]

An alternative way to improve the mechanical properties of a weak, rubbery polymer is to synthesize a block [AB or BA] or a segmented [(AB)_n] copolymer that contains a soft, rubbery component and a glassy or crystalline hard segment. These systems usually show two phase morphologies where the hard segment domains serve as physical crosslinks and/or reinforcing fillers for the soft phase. More importantly, these

copolymers form a reversible elastomeric system that can be fabricated either from melt or from solution.[11] In fact, a variety of block or segmented copolymers containing PDMS soft segments and various thermoplastics as the hard segment have been synthesized, using reactive functionally terminated siloxane oligomers

2.2.1 Reactive Functionally Terminated Siloxane Oligomers

The main factors determining the reactivity of reactive functionally terminated siloxane oligomers toward other reactants are the type and nature of the functional end groups. According to their structure and reactivity, these oligomers can be divided into two classes. The first class consists of oligomers with (Si-X) structure and the other with (Si-R-X) structure, where X and R represent the reactive functional groups and short hydrocarbon chain, respectively.

Siloxane oligomers with a functional group directly bonded to the terminal silicon atoms (Si-X) generally have much higher reactivity toward the nucleophilic reagent than the analogues with (C-X) functionality, which is attributed to the significant difference between the electronegativities of the silicon (1.8) and carbon (2.5) atoms.[173] Due to their high reactivity, these oligomers are widely used in the RTV (Room Temperature Vulcanization) silicone rubber and in adhesive formulation.[168,174] Despite the high reactivity of the Si-X terminated siloxane oligomer, they usually lead to the formation of the Si-O-C linkage upon reacting with nucleophilic reagents. Obviously, these ionic linkages can result in the hydrolytic instability of the copolymer, depending on the condition. This can be a major drawback in various applications, especially in the presence of moisture or water.

On the other hand, siloxane oligomers with Si-R-X end group, α,ω -organofunctionally terminated siloxane, can prevent the formation of such linkages upon reacting with a nucleophilic reagent. In addition, the R group can also have other advantages over Si-X, such as promoting miscibility between the siloxane and other organic monomers. The morphology and overall properties of the resulting copolymer can also be influenced by the R group, depending on the hard segment and its block length.[175]

In general, linear polysiloxanes can be synthesized by both anionic and cationic polymerization of the cyclic siloxanes, using acid or base catalyst. The polymerizations are usually called "equilibration" or "redistribution" reactions. In the equilibration, Si-O bonds in a mixture of siloxanes (e.g. cyclic and linear) are continuously broken and reformed until the system reaches its thermodynamically equilibrium state. At equilibrium, the reaction mixture consists primarily of linear oligomers and, to a less extent, ($\approx 10\text{-}15\text{wt}\%$), of cyclic species. The reaction mixture composition at equilibrium depends on the nature of the substitutes on the silicon atoms, temperature, and concentration of the siloxane units in the system (i.e. bulk or solution). Equilibrium concentrations of the cyclic species increase with an increase in the size and polarity of the substituents on the silicon atoms, as well as with the addition of inert solvents such as toluene or cyclohexane.[176,177]

In a ring opening polymerization the catalyst plays a very important role. In anionic polymerization, alkali metal hydroxide, quaternary ammonium (R_4NOH), phosphonium (R_4POH) bases, and siloxanates (Si-OM^+) are the widely used catalysts. [168,173] They are usually used at a level of 10^{-2} to 10^{-4} weight percent depending on their activities and the reaction conditions. In addition to their high activities, R_4NOH and R_4POH type catalysts decompose at elevated temperatures ($110\text{-}150\text{ }^\circ\text{C}$) and produce volatile products, which make them easy to remove from the system.[178] Cationic polymerization of cyclosiloxanes is also well known, but less practiced, than anionic polymerization. The most widely used catalysts include sulfuric acid, alkyl and aryl sulfonic acid, and trifluoroacetic acid.[168,177]

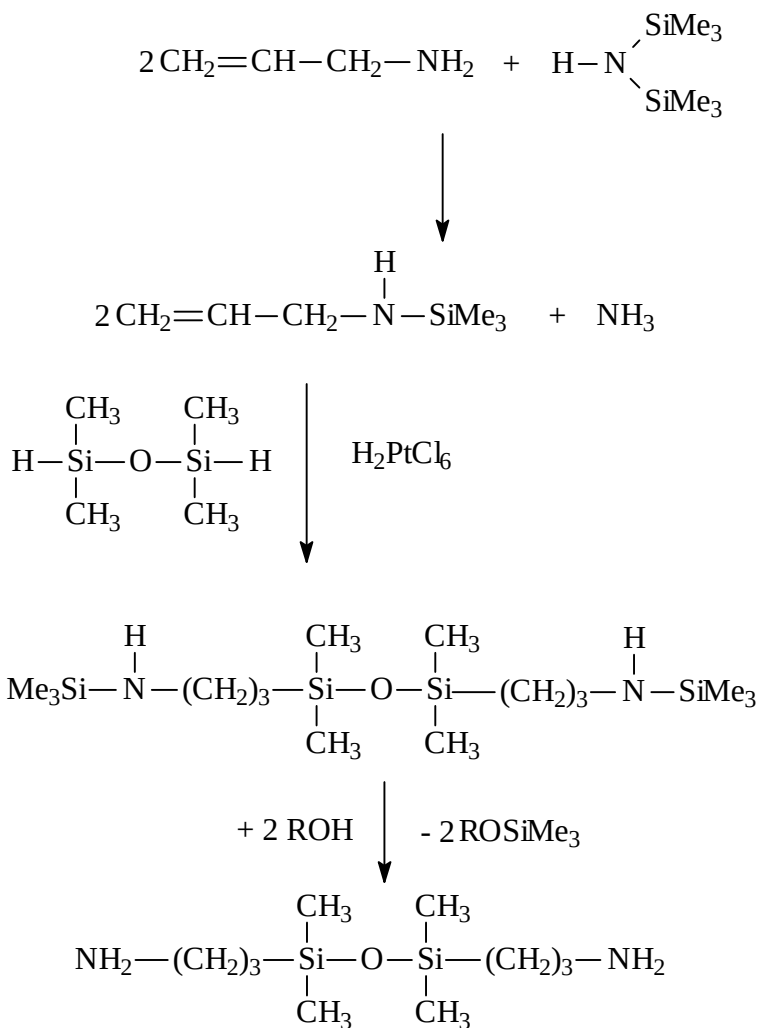
In addition to the catalysts, another key starting material in preparing reactive siloxane oligomers is α,ω -organofunctionally terminated disiloxane, which is also known as an "end-blocker". These disiloxanes play two major roles in the ring open polymerization of cyclosiloxanes. The first is that they determine the type of the end-group on the oligomer, and the second is that they control the number average molecular weight of the final siloxane oligomer, which is achieved by varying the initial ratio of the cyclic monomer to the end-blocker. A list of important α,ω -organofunctionally terminated disiloxane that are widely utilized to prepare segmented copolymer is given in Table 2.10

Table 2.10 Important α,ω -organofunctionally terminated disiloxane precursors for reactive polyorganosiloxane

$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{X}-\text{R}-\text{Si}-\text{O}-\text{Si}-\text{R}-\text{X} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	
X—R—	Reference
$\text{NH}_2-(\text{CH}_2)_3-$	179
$\text{HN} \begin{array}{c} \diagup \quad \diagdown \\ \text{ } \end{array} \text{N}-\text{CH}_2-\text{CH}_2-\text{NH}-\overset{\text{O}}{\parallel}{\text{C}}-(\text{CH}_2)_3-$	180
$\text{NH}_2-\text{C}_6\text{H}_4-\text{O}-(\text{CH}_2)_x-$ $X=1, 3, 4$	181
$\text{HO}-(\text{CH}_2)_4-$	182
$\text{HOOC}-(\text{CH}_2)_3-$	168
$\text{HOOC}-\text{C}_6\text{H}_4-$	183
$\text{H}_2\text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{ } \end{array} \text{CH}-\text{CH}_2-\text{O}-(\text{CH}_2)_3-$	184
$\text{H}_2\text{C} \begin{array}{c} \diagup \text{O} \diagdown \\ \text{ } \end{array} \text{CH}-\text{CH}_2-\text{C}_6\text{H}_5$	185
$\text{Cl}-(\text{CH}_2)_3-$	186

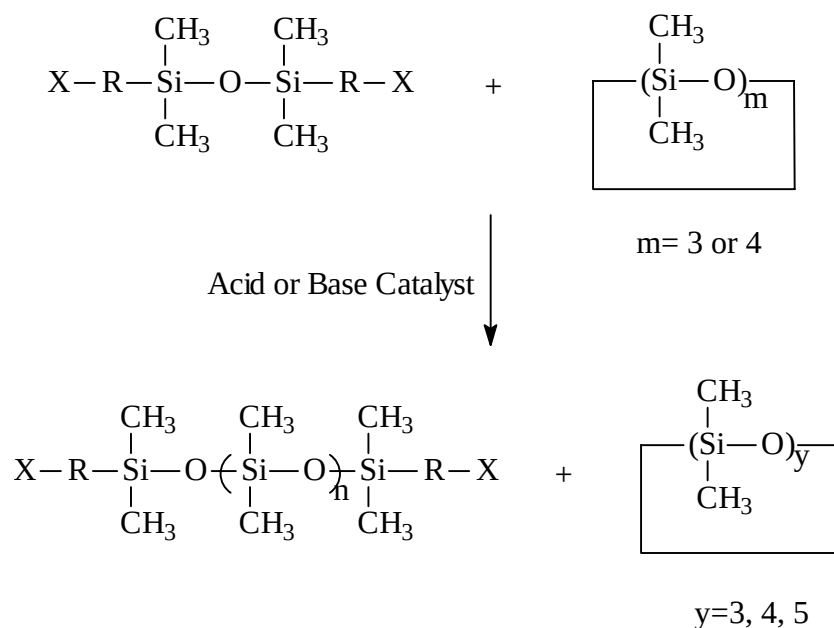
Among several methods for synthesizing reactive disiloxanes, hydrosilation has become the most popular and practical process. Hydrosilation is the term used for the addition of silicon hydrides (Si-H) to multiple bonds such as olefins (C=C) or acetylenes (C $\equiv$ C) in the presence of various catalysts. The most widely used catalyst for this reaction is chloroplatinic acid (H₂PtCl₆ • 6 H₂O), in a solution of isopropyl alcohol mixed with a polar solvent such as tetrahydrofuran. When olefinic compounds with OH, NH₂,

or NHR functionalities are used, they must be protected in order to prevent the reaction of Si-H group (or the catalyst) with these active hydrogen containing end groups. After hydrosilation, these end groups can then be regenerated by hydrolysis. As an example, the synthesis of 1,3-bis(3-aminopropyl) tetramethyldisiloxane is given in Scheme 2.8:[179]



Scheme 2.8 Synthesis of 1,3-bis(3-aminopropyl)tetramethyldisiloxane

Starting from cyclicsiloxanes and reactive end-group containing disiloxane, well defined α,ω -organofunctionally terminated siloxane oligomers can be synthesized via the equilibration reaction shown in Scheme 2.9.



Scheme 2.9 General route for the preparation of α,ω -organofunctionally terminated siloxane oligomers by equilibration reactions

2.2.2 Synthesis of Siloxane Containing Copolymer

The increasing interest in siloxane containing multiphase copolymers is mainly due to their unique combination of properties, which is directly related to their chemical structure and macromolecular architecture. For example, the first major application of siloxane containing block and graft copolymers was siloxane-poly(alkylene oxide) systems which have been used as stabilizers in the formation of flexible polyurethane foams. These types of materials are still widely used as emulsifiers or surfactants in many applications.[197] Siloxane containing multiphase copolymers have since been utilized for specialized materials, such as biomaterials, photoresists, gas separation membranes, protective coatings, and elastomers.

The synthetic approaches leading to the formation of siloxane containing copolymers can be classified according to the type and nature of the copolymerization reactions: 1. Living Anionic Polymerization; 2. Step Growth Polymerization; 3. Polymerization by Hydrosilation; 4. Ring-Opening Polymerization.

Living Anionic Polymerization

Living anionic polymerization is a very effective method for preparing AB or ABA type siloxane copolymers with controlled structure, such as dimethylsiloxane with diphenylsiloxane, styrene, methyl methacrylate, and other vinyl monomers. The preferred monomer for a siloxane segment is usually D₃ instead of D₄ because of its higher reactivity toward the anionic initiator. Typical initiators of this type of reaction include organoalkali compounds and lithium siloxanates.[11] In the initiators, lithium counterions are usually preferred to those of sodium and potassium due to their lower catalytic activity in siloxane redistribution reactions. Living anionic polymerization reactions are usually conducted in THF since it can solvate the ion-pair at the growing chain end.

Styrene-dimethylsiloxane triblock copolymers have been synthesized by anionic polymerization of styrene and D₃ or D₄ in toluene/THF, using lithium and sodium biphenyl as the initiator.[198] The use of sodium biphenyl and/or D₄ resulted in a broader molecular weight distribution in comparison with lithium and D₃. Methyl methacrylate-siloxane, p-methylstyrene-siloxane, (fluoroalkyl, methyl) siloxane-dimethylsiloxane, dimethylsiloxane-diphenylsiloxane block copolymers have also been reported in the literature.[199-202]

Step Growth Polymerization

Although living anionic polymerization can produce a siloxane containing copolymer with a well defined structure, step growth polymerization is perhaps the most versatile technique used for synthesizing siloxane containing segmented multiphase copolymers. This is mainly due to the availability of a wide variety of siloxane oligomers with different reactive end groups, which has been previously discussed. These siloxane-containing copolymers possess a variety of properties which can be tailored from either the siloxane soft segments or the plastic hard segments. The copolymer systems that have been studied are provided in Table 2.11.

Among all the reactive siloxane oligomers, the aminoalkyl-terminated oligomers have been the most versatile starting materials, having been used in siloxane-urea, siloxane-amide, siloxane-imide, and siloxane-amide-imide. Siloxane-urea copolymers

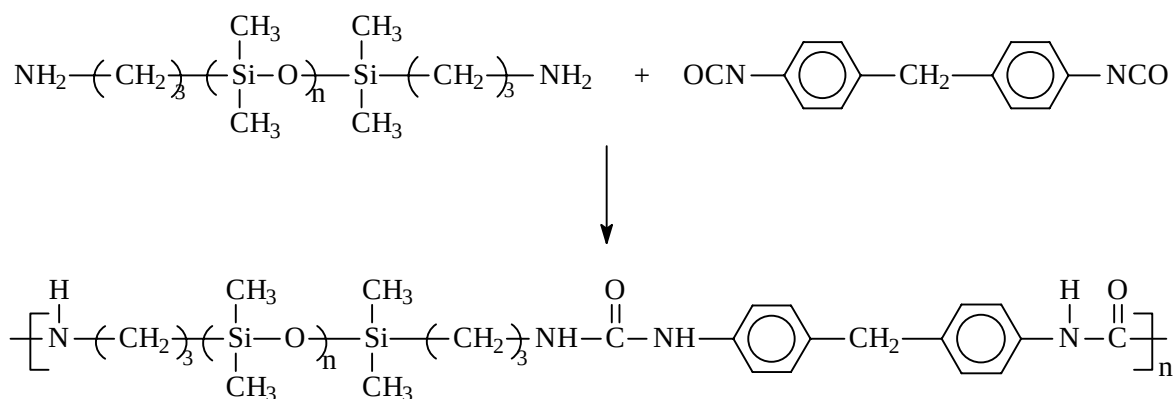
were prepared by direct reaction of aminopropyl terminated siloxane oligomers and diisocyanate in solution at room temperature as shown in Scheme 2.10.

The siloxane-based polyureas were found to have high molecular weight, according to intrinsic viscosity, and high yield. In these siloxane-based polyureas, hard segment content is determined by the molecular weight of the PDMS oligomer, since it was reacted with stoichiometric amount of MDI.[203,204]

Table 2.11 Organosiloxane containing copolymer systems

Copolymer System	Reference
Siloxane/Urea	175, 187,203-205
Siloxane/Amide	175
Siloxane/Imide	188, 189
Siloxane/Amide/Imide	190
Siloxane/Urethane	190
Siloxane/Ester	191
Siloxane/Carbonate	191,192,193
Siloxane/Sulfone	194
Siloxane/Epoxide Resin Network	184,196
Siloxane-Vinyl	195

The structure and thermal properties of the segmented copolymer have been determined by ¹H NMR, DSC, TMA, and DMA.[205] The polymer film obtained from either compression molding or solvent cast was found to be transparent and showed excellent elastomeric properties.



Scheme 2.10 Synthesis of MDI based siloxane-urea segmented copolymers

Structural variations of siloxane based polyureas were also investigated. Instead of dimethylsiloxane, an aminopropyl terminated poly(dimethyl-diphenyl) siloxane and poly(trifluoropropyl, methyl dimethyl) siloxane oligomer was used. In general, these modifications resulted in lower molecular weight copolymers, compared to the PDMS based analogues.

A critical factor in this type of reaction (which is also true for many other polymerization reactions involving siloxane and any other organic monomers) has been the proper choice of the reaction solvent. This is extremely important in obtaining a high molecular copolymer, which is essential for producing useful mechanical properties. It is well known that PDMS is very non-polar and has very low solubility parameters. Therefore, it is not soluble in polar solvents such as DMAc, DMF, and NMP, which are the conventional solvents for polyurea and polyurethane. High molecular weight polyureas were obtained when 2-ethoxyethyl ether (EEE) and THF were used as solvents. Moreover, the type of the diisocyanate also has an effect on determining the best solvent for polymerization.[203] The solvent effect on molecular weight is clearly demonstrated in Table 2.12 for the siloxane-urea copolymers, which clearly shows that EEE is a far superior solvent when compared to THF.

Table 2.12 Effect of solvents on the siloxane-urea copolymers based on MDI and aminopropyl terminated PDMS[203]

Sample No.	M _n (PDMS) (g/mole)	Reaction Solvent	Recovered Yield (wt%)	[η] (dL/g) (25 °C in THF)
1	1140	EEE	80	0.24
2	1770	EEE	86	0.57
3	3660	EEE	96	0.63
4	3660	EEE	97	0.70
5	1140	THF	86	0.13
6	1770	THF	83	0.14
7	3660	THF	94	0.40
8	3580	THF	91	0.48

Siloxane-Urethane copolymers can also be synthesized by step growth polymerization. These copolymers have received widespread attention for a long time, and was first synthesized from a silanol terminated siloxane oligomer, which was believed to be good substituent for the conventional polyols.[206] However, the resulting siloxane-urethane copolymers hydrolyzed very easily and decomposed by water and alcohols, due to the instability of the urethane bond formed between the silanol and the isocyanate. To increase hydrolytic stability, organohydroxy terminated siloxane oligomers were reacted with various diisocyanates via melt polymerization.[207] However, the molecular weight of these polymers were not sufficiently high, presumably due to the incompatibility between the siloxane and urethane segments in melt.

The synthesis of PDMS based segmented polyurethanes suffers from two major problems. The first is the thermal instability of the hydroxyalkyl (primary hydroxyl) end groups on the siloxane oligomer when polymerized. It has been shown that hydroxypropyl end groups undergo cyclization reactions when heated, which results in loss of functionality and reactivity. The second problem is that the PDMS and urethane components have very different solubility index which makes the selection of a suitable solvent difficult, similar to the siloxane-urea systems.

The preparation of segmented siloxane-urethane copolymers from MDI, hydroxybutyl terminated polydimethylsiloxane oligomers and disiloxane has been reported.[208] The polymers displayed two glass transition temperatures at -120°C and 80°C. However, the molecular weights were fairly low. Similar results were reported for siloxane-urethane copolymers based on hydroxypropyl terminated siloxane oligomers ($M_n=2000$ g/mole), MDI, and 1,4-butanediol.[209,210] Since the functionality of the starting oligomer was less than 2 and the reaction solvent was toluene (which is poor for urethane segments), low molecular weight products were obtained.

Better synthetic results, as well as a detailed characterization study of a series of segmented siloxane-urethane copolymers, were described by Cooper and co-workers.[211] In this study, a hydroxybutyl terminated PDMS oligomer ($M_n=2000$ g/mole) was used as the soft segment. The hard segments were comprised of MDI, which was chain extended with either 1,4-butanediol or N-methyldiethanolamine (MDEA). Instead of using a single solvent, the reactions were performed in a mixture of THF/DMAc (3/1v/v) via a two step method. In the first step, PDMS was end capped with an excess of MDI at 60-70°C in the presence of stannous octoate and triethylamine catalysts. The second step involved the chain extension of the resulting prepolymer with stoichiometric amount of 1,4-butanediol or MDEA. The reactions were followed by FTIR spectroscopy. The siloxane content in the copolymers varied between 61wt% to 87wt%. All polymers were soluble in THF and had overall molecular weights ranging from 50,000 to 100,000 g/mole as determined by GPC, using a polystyrene standard. The absolute molecular weight, however, was probably not as high. All polymers showed two phase morphology as demonstrated by DSC results.

More recently, Yilgör reported a two step method to synthesize high molecular weight, high strength siloxane-urethane copolymers.[212] In this study, α,ω -hydroxyhexyl terminated PDMS ($M_n=900, 2300$ g/mole) were used as the soft segment. The hard segment was consisted of HMDI, which was chain extended with 1,4-butanediol. The polymerization reactions were conducted via a two step method and the reactions were monitored by FTIR spectroscopy. The first step involved end capping the PDMS with HMDI in the presence of dibutyltin dilaurate (DBTDL). The reactions were conducted in DMF at 60°C. Prior to the chain extension, the reaction solution was

diluted with THF. The chain extender solution, 1,4-butanediol in DMF, was then added to chain extend the prepolymers. The polymerization solutions were further diluted to THF/DMF (1/1) as the viscosity of the reaction solution increased during chain extension. The resulting copolymers seemed have high molecular weight, as judged from the intrinsic viscosity of the polymers shown in Table 2.13. No molecular weight data from GPC is available. A two-phase morphology was demonstrated by the two glass transition temperatures that were detected by DSC, one at -120°C and the other around 75°C. The tensile strength of these copolymers was found to be quite high as shown in Table 2.14. In fact the higher modulus and tensile strength of these materials when compared to the control analogue, which contained PTMO ($M_n=2000$ g/mole) as the soft segment, was rather peculiar. The author attributes this phenomena to better phase separation in the PDMS based copolymer system. However, the lower modulus and tensile strength of the control samples may have been a result of their low molecular weight, even though they were synthesized under the same condition as the PDMS based copolymer.

Table 2.13 Characteristics of siloxane-urethane segmented copolymers [212]

Sample No.	PDMS Segment M_n (g/mole)	Hard Segment Content (wt%)	Yield (wt%)	$[\eta]$ 25°C in THF (dL/g)
PUS-1	900	22.6	92	0.90
PUS-2	900	38.9	93	0.72
PUS-3	900	41.0	93	0.80
PUS-4	2300	21.3	89	0.67
PUS-5	2300	29.9	90	0.73
PUS-6	2300	36.7	95	0.79
PUS-7	2300	43.3	92	0.81

Table 2.14 Comparison of the tensile properties of siloxane-urethane and polyether-urethane segmented copolymers [212]

Sample No.	Soft Seg. Type	Soft Seg. M_n (g/mole)	Hard Seg. (wt%)	Ten. Mod. (MPa)	Ult. Str. (MPa)	Elong. (%)
PSU-5	PDMS	2300	29.9	14.3	11.0	350
PSU-6	PDMS	2300	36.7	35.1	16.4	310
PSU-7	PDMS	2300	43.3	63.9	17.7	250
PUE-1	PTMO	2000	29.9	10.7	3.56	475
PUE-2	PTMO	2000	36.8	23.9	7.68	450
PUE-3	PTMO	2000	43.2	50.9	17.2	425

Polymerization by Hydrosilation

Hydrosilation reactions are one of the earlier method for synthesizing of siloxane containing block copolymers.[11] A major focus of this method has been directed toward the synthesis of siloxane-alkyleneoxide block copolymers, which have been used extensively as emulsifiers and stabilizers. This type of reaction has also been utilized to synthesize of various novel thermoplastic liquid crystalline copolymers where siloxanes have been employed as flexible spacer.[213,214]

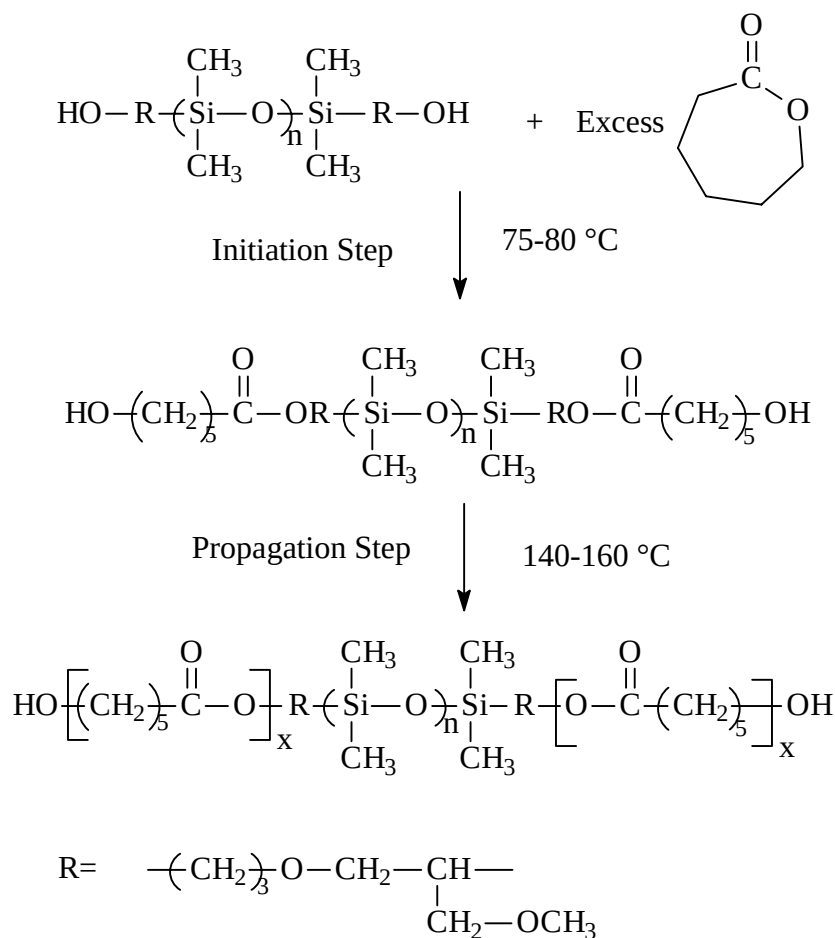
Ring-Opening Polymerization

In the last 20 years, ring-opening polymerization has received widespread attention as a versatile method to synthesize well-defined polymers and polymeric intermediates. Ring-opening polymerizations of siloxane containing AB or ABA type block copolymer using reactive end group terminated siloxane oligomers and various cyclic monomers have been reported.[215-217] During these reactions, reactive end groups of siloxane oligomers initiate the ring-open polymerization of cyclic monomers to produce block copolymers. The molecular weights of the growing segments were controlled by the ratio of the cyclic monomers to the oligomer initiators.

ABA type polycaprolactone-b-polydimethylsiloxane block copolymers have been prepared by Yilgör, Riffle and co-workers [217] via the ring opening polymerization of caprolactone, using an hydroxyalkyl terminated siloxane oligomer as the initiator and

macromonomer in the presence of stannous octoate as the catalyst.[218] The reactions were conducted either in bulk or in butyrolactone solution depending on the overall molecular weight of the final product. These polymerization reactions were completed in two steps, as shown in Scheme 2.11. The first step, i.e. the initiation step, was to end cap PDMS with caprolactone, which was performed at 70-80°C. The second step was conducted at 140-160°C for 3-4 hours. The initially immiscible reaction mixture became clear and viscous as the polymerization proceeded at 140°C. Completion of the reaction was monitored by GPC, observing the disappearance of caprolactone peak. The block length of the PDMS and caprolactone varied between 2000-20000 and 1000-10000 g/mole, respectively. The two phase morphology was clearly indicated by the glass transition temperature of siloxane at -120°C and the polycaprolactone melting point at around 60-65°C.

The interesting feature of these triblock copolymers is the presence of reactive hydroxy end groups, which can be used as reactive oligomers for the synthesis of segmented siloxane-urethane or siloxane-ester copolymers and in the siloxane modification of epoxy or phenoxy networks. Because of the terminal polycaprolactone block, these copolymers provide good solubility in polar solvents such DMF, DMAc, and NMP, which are widely used in the preparation of polyurethanes. This structural advantage is very important in terms of overcoming the biggest obstacle in the synthesis of siloxane containing segmented copolymers, problems of solubility, which in turn facilitates the formation of high molecular weight copolymers. Since the molecular weight of either block can be well controlled, a variety of triblock macromonomers with reactive end groups can be synthesized. The siloxane content in the macromonomer can also be controlled by the block length of both the PDMS and the caprolactone. This could ultimately lead to a high molecular weight siloxane-urethane with a well-defined structure.



Scheme 2.11 Reaction scheme for the preparation of polycaprolactone-b-polydimethylsiloxane triblock copolymers

The same synthetic methodology has been applied to produce BA and ABA type polyoxazoline (B)-polydimethylsiloxane (A) block copolymers. Consisting of a water-soluble polyoxazoline block and a hydrophobic PDMS block, these block copolymers display very interesting solubility characteristics and have been evaluated as non-ionic emulsifiers in various systems. These copolymers have also been used as surface modifiers because of their good miscibility with various polymers, such as PMMA, PVC, polyurethanes, nitrocellulose, etc.. By incorporating a relatively low level (0.5-3wt%) of addition, the surface of the parent system was dramatically altered.

2.2.3 Morphology and Properties of Siloxane Containing Block and Segmented Copolymers

The morphology of siloxane containing copolymers is determined by three variables: solubility parameter, block length, and segment crystallizability. The extremely non-polar nature of the PDMS structure combined with weak intermolecular interaction, leads to the formation of blends that are both thermodynamically and mechanically incompatible with virtually all other polymeric systems. The most critical variable in determining this two-phase morphology is the low solubility parameter of the PDMS ($\delta=7.3-7.5(\text{cal}/\text{cm}^3)$), compared to other polymers ($\delta=8.5-14(\text{cal}/\text{cm}^3)$). It is also due to the important fact that the influence of block length and segment crystallizability in the siloxane containing systems are not as important as in other polymeric systems. In many cases, a siloxane segment with a molecular weight as low as 500-600 g/mole (6-8 siloxane repeat units) and an organic segment having only single repeating unit is sufficient to obtain two-phase morphology.[187,205] Another important factor to be considered is that the glass transition temperature of the PDMS segment is extremely low. It should behave like a non-polar viscous liquid at room temperature, where most characterizations are conducted. Therefore, the low glass transition temperature also provides ideal condition for the formation of phase separated polymer morphology.

The morphology and mechanical properties of ABA and (AB)_n type PDMS (A) - polystyrene (B) block copolymers were first reported in the early 80's.[198,199] The microphase morphology of the copolymer thin film was found to be dependant on the type of casting solvent utilized. When the cast solvent was modified from THF or methyl ethyl ketone (good solvent for polystyrene) to cyclohexane (an effective solvent for PDMS segments), the morphology of the resulting copolymer changed from a continuous glassy phase with aggregated PDMS to a PDMS matrix with small rod-like structures of polystyrene. When toluene, a mutual solvent for both segments, was used, a lamellar structure was observed. Dynamic mechanical analysis of (AB)_n type copolymer showed a sharp $\tan \delta$ peak at around -110°C and a smaller broad peak at approximately -48°C, which corresponded to the T_g and T_m of PDMS, respectively. The T_g of the polystyrene was 90°C. The morphology of the poly(p-methylstyrene)-PDMS triblock copolymers was investigated using TEM.[200] The sample displayed a PDMS spherical domain in

the poly(p-methylstyrene) matrix when the PDMS content was low (12%), and a continuous lamellar morphology for nearly equimolar composition. In both cases, the domain structure was very fine, with a domain size of 50-200 Å.

Detailed morphological studies of siloxane-urea copolymers produced by reacting aminopropyl terminated PDMS and MDI or HMDI without a chain extender was conducted by Wilkes and coworkers.[203-205] Two phase morphology and good thermoplastic elastomeric behavior, even at very low hard segment content (6wt%), were observed, which was attributed to the excellent phase separation and very strong hydrogen bonding in the urea hard segments. Dynamic mechanical analysis of the copolymers showed a PDMS T_g at around -110°C and an increase in the value of the rubbery plateau modulus when the hard segment content was increased. This indicates that the mechanical strength of these materials is directly related to the level of the urea linkages in their backbone. SAXS studies have suggested that a better than 70% degree phase separation for copolymers based on low molecular weight PDMS (M_n = 900 and 1140 g/mole), and an almost 100% degree of phase separation, was achieved when the molecular weight of the PDMS segments was high (M_n = 1770, 3660 g/mole). As a direct consequence of this, siloxane-urea copolymers showed a much smaller interfacial region compared to polyurethanes or other vinyl block copolymers such as SBS. The interdomain spacing was constant for the hard segments at 1.7 nm and increased in the soft PDMS segments from 4.0 to 6.0 nm with an increase in the siloxane's molecular weight. The resulting mechanical properties of these copolymers were directly related to hard segment content and soft segment molecular weight. It was found that these linear, segmented siloxane-urea copolymers have noticeably superior mechanical properties than conventional filled silicone rubber. They also showed very low hysteresis, which is comparable to segmented polyurethanes.

In addition to morphology and mechanical properties, surface property is another important characteristic of siloxane containing copolymers. As a consequence of their very large molar volume, very low cohesive energy density (intermolecular interaction), and high flexibility (low T_g), the PDMS has extremely low surface energy.[218] For linear polydimethylsiloxanes, the surface tension increases from 15 dynes/cm for hexamethyldisiloxane to 21-22 dynes/cm for high molecular weight PDMS. This is

much lower than for many other polymers, such as PMMA (38-40 dynes/cm), polystyrene (30-34 dynes/cm), polyurethane (35-45 dynes/cm), and nylon-6 (38-42 dynes/cm). Thus, the surface of siloxane containing copolymers, as well as their polymer blends, are significantly enriched with siloxane segments.

Surface modification of conventional polymers through the addition of a small amount of siloxane containing copolymers has received increasing attention since it was first reported by Zisman.[219] This modification method has two distinctive advantages. First, only a small amount of siloxane additive is needed (0.1-2.0wt%), which usually does not change the bulk properties of the polymer; and second, the siloxane additives can be easily compounded through solution or melt blending.

Surface morphology of siloxane containing copolymers has also been reported.[220-223] Thomas and coworkers have studied surface morphology of PS-PDMS copolymers using contact angle measurement and ESCA. In their study, the PDMS content of the copolymers was routinely kept below 20wt%, while the surface tension of the control polystyrene was 34 dynes/cm. Under these conditions, the surface tension of the copolymer with a short PDMS block (DP=3-9) showed a gradual decrease from 32 to 25 dynes/cm. When the PDMS block length increased to DP>17, however, the copolymer surface showed complete siloxane coverage with a surface tension of 22-23 dynes/cm.

Dwight et. al studied the surface properties of siloxane containing copolymers including siloxane-ester, siloxane-urea, siloxane-sulfone, and siloxane-imide.[222] An angular dependence depth profile, i.e. when the PDMS enriches gradually from bulk to surface, was observed for all systems except for the siloxane-urea copolymers, containing very high PDMS content. It was found that a siloxane molecular weight of between 6800 and 12800 was required to form a complete siloxane monolayer on the surface.

2.3 Fire Resistance in Polymeric Materials

2.3.1 Enhancement of fire resistance in polymeric materials

Polymeric materials have long been utilized in products made from wood, textile, and paper. In the past 50 years, however, polymers of rubber, plastic, and fiber, have

become increasingly versatile and even more widely used. Because of their unique properties, organic polymers are gradually replacing conventional metals and ceramic materials and find a wide range of applications in the construction, electronic, and automobile industries, to name a few.

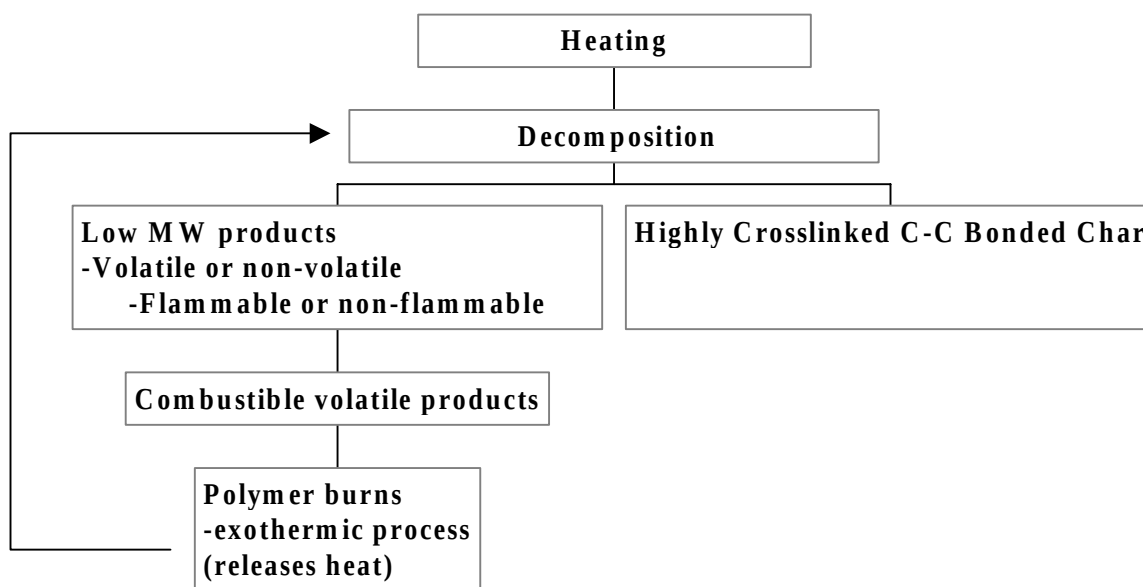
Unlike metals and ceramic materials, organic polymers, both synthetic and natural, are inherently combustible, which has been a concern since they were first utilized. In fact, an attempt to reduce the fire hazard associated with polymeric materials can be traced back to at least the fifth century BC when the Egyptians soaked timber in alum (potassium aluminum sulfate) to reduce combustability.[224-226]

When polymers are heated above a critical temperature, the combustion process begins, which takes place in a continuous cycle as represented in Scheme 2.12. The combustion cycle usually involves four stages: 1. Heating, 2. Decomposition, 3. Ignition, 4. Combustion. When a polymer is subjected to a heat source and sufficient thermal energy is provided to break the weakest bond within the polymer chain, it will begin to decompose. As the polymer degrades, two classes of products can be generated: low molecular weight products, either volatile or non-volatile, flammable or non-flammable, and highly crosslinked C-C bonded char. The volatile combustible products, or fuel, when mixed with air will ignite if the temperature is above ignition temperature. The heat generated from the flame is then transferred back to the polymer surface to further decompose the polymer and produce more fuel. [227,228,233]

It is obvious, then, that the polymer combustion cycle must be interrupted to achieve fire resistance. To accomplish this, there are at least two approaches that should be considered:

The first of these, solid phase inhibition, focuses on the modifying the polymer substrate to: (1) improve the thermal stability of the polymer which normally require more heat to decompose; (2) promote highly crosslinked char formation, which means that a concurrent decrease in the volatile product and the carbonaceous char can reduce the heat transfer from the flame and cut off diffusion of new fuel into the gas phase; and (3) generate water to cool the surface of the polymer and increase the amount of heat needed to maintain the flame.

The second approach, gas phase inhibition, focuses on quenching the flame in the gas phase. This usually involves the formation of hydrogen halides that can diffuse into the flame and stop the branching radical reactions, the so-called "poisoning effect". Polymer systems that produce carbon dioxide and water vapor can protect the material by diluting the volatile products in the gas phase.



Scheme 2.12 Polymer combustion cycle

Except for a limited number of polymers with high thermal stability, such as highly aromatic polyimides, polybenzimidazoles, and polytetrafluoroethylenes (Teflon), most polymers are not fire retardant. To improve flame resistance, fire retardant chemicals may be incorporated into the polymer, either by an "additive" or "reactive" approach. In the first method, the "additives" are mechanically blended with the polymer. Although this method is very flexible and inexpensive, the additives may be incompatible with the polymer, and consequently leach out with water and other solvents. In the second approach, fire retardant properties are structurally introduced via backbone modification or copolymerization. This route has the advantage of avoiding the fire retardant properties because they cannot migrate or be extracted. Thus the polymer is better protected since the evolution of the fire retardant structure will be simultaneous with the decomposition of the polymer. For an additives to be effective, its decomposition temperature must be carefully matched with the decomposition

temperature of the polymer and remain intact during processing. Other goals regarding the introduction of additives is that they should not have a negligible effect on the desirable physical properties of the polymer, and no interaction with other additives such as antioxidants.

2.3.2 Fire retardant additives

Some widely used fire retardant additives include inorganic hydroxides, organic halides, organic halide with antimony compounds, and organic phosphorus compounds. Comprehensive description of fire retardant additives can be found throughout the literature.[224-239] Some common fire retardants are listed in Table 2.15.

Inorganic Hydroxide

Aluminium trihydroxide and magnesium dihydroxide are the most widely used inorganic fire retardant additives. Volume-wise aluminium trihydroxide is the largest flame-retardant additive used in plastics. Their actions depend on the endothermic

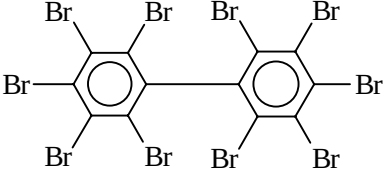
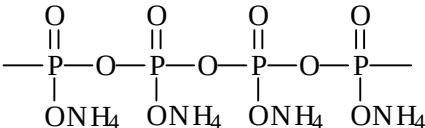
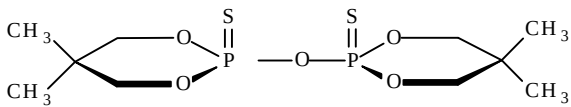
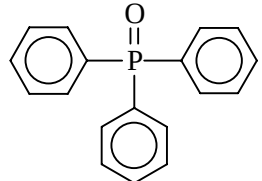


dehydration reaction that occur at 180-220°C (1) and at 325-350°C (2), with the evolution of water vapor.[241-243]

Even though the effectiveness of both these hydroxides are relatively poor, since they require 50-60% concentration to reach desired fire retardant levels, they are still very attractive because of their low cost, lack of toxic byproducts, and lower smoke emission. The fire resistant properties of these additives involve the following processes:

1. An endothermic dehydration reaction acts as a heat sink to reduce the temperature of the polymer.
2. A large amount of water vapor evolved can dilute the volatile combustible products and may also act as a barrier towards oxygen diffusion into the flame.
3. The dehydration products, metal oxides, which are deposited on the surface of the polymer can reduce the heat transfer back to the polymer. They can also catalyze other degradation products to be oxidized to carbon dioxide, which account for the smoke suppression.

Table 2.15 Common fire retardant additives

Compound	Structure	Reference
Aluminium Trioxide	Al(OH)_3	240,241
Magnesium Dihydroxide	Mg(OH)_2	242,243
Decabromodiphenyl Oxide		289,291
Chloroparaffin	—CH—CH—CH— Cl Cl Cl	237
Antimony Trioxide	Sb_2O_3	237,289
Tris(2-chloroethyl) phosphate	$(\text{Cl—CH}_2\text{CH}_2\text{O})_3\text{P=O}$	248
Ammonium Polyphosphate		243,292
Phosphine Sulfide		293
Triphenyl Phosphine oxide		228
Borax	$\text{Na}_2\text{B}_2\text{O}_7 \cdot 10 \text{H}_2\text{O}$	248

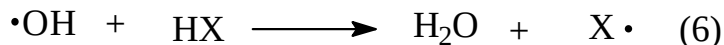
Halogen Based Fire Retardants

Organic halogen compounds are the most effective fire retardants among commercially available additives. They are often used in combination with metal compounds, especially antimony oxide. The widely accepted fire retardant mechanism for this system involves the liberation of hydrogen halide, which acts as radical scavenger in the flame. In addition to the gas phase action, some studies show that the halogen compound may also be involved in the solid phase reaction. The effectiveness of the hydrogen halide decreases in the order of $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$. Because organic iodides are thermally unstable, organic chlorides and bromides are more generally used. In addition, aliphatic halides are more effective than aromatic halides because they more readily break down to produce a halogen radical.

The free radical chain reactions that take place in hydrocarbon combustion involve many steps, two of which are particularly important. The first involves the consumption of oxygen to generate the most active chain carriers: $\text{H}\cdot$ and $\text{OH}\cdot$. The second step is the highly exothermic oxidation of carbon monoxide to carbon dioxide, performed by $\text{OH}\cdot$: (3), (4)



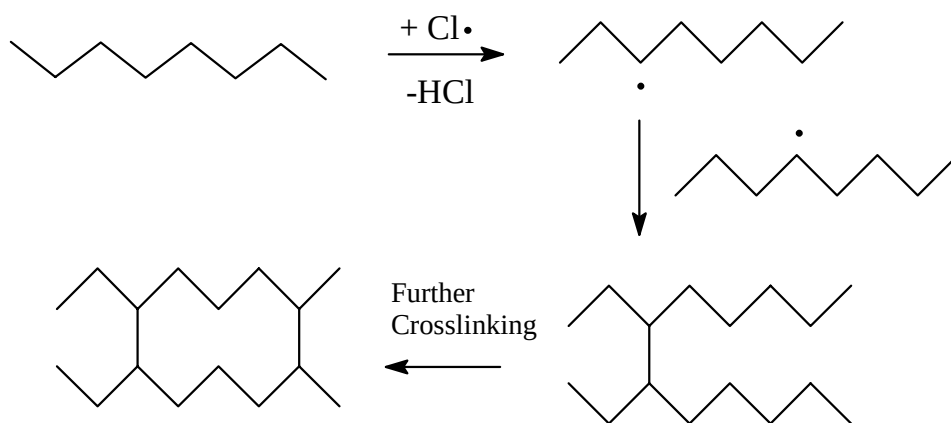
The hydrogen halide generated from the decomposition of the halogen compound can react with active $\text{H}\cdot$ and $\text{OH}\cdot$ and replace them with less active halogen radicals: (5), (6)



The halogen radicals can then further react with a hydrogen donor to regenerate the hydrogen halides: (7)



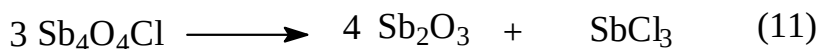
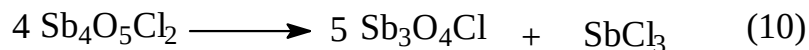
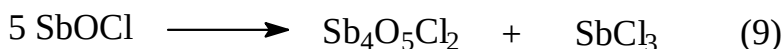
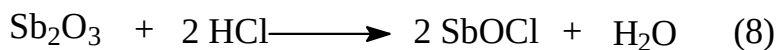
Therefore, the hydrogen halides can react catalytically and the retardation process is very efficient. Moreover, hydrogen abstraction in the last step allows the polymer solid phase to decompose to form protective char in some cases, as shown in Scheme 2.13.



Scheme 2.13 Possible mechanism for char formation in the halogen compound additive systems

Antimony Trioxide

Although antimony trioxide (Sb_2O_3) has been widely used as a fire retardant additive, it has very little activity when was used alone. Instead, antimony trioxide is generally used in combination with halogen compounds to greatly enhance their effectiveness in fire retardancy. Although the reaction between antimony trioxide and halogen compounds is not yet fully understood, this so-called "synergistic effect" is believed to result from antimony oxyhalide (SbOCl), which is produced by the reaction of antimony trioxide and hydrogen halide.(8) The antimony oxyhalide will further decompose to form antimony halide (SbCl_3) and antimony trioxide.(9-11) The antimony halide, which is volatile, will then react with active radicals and form hydrogen halide, which undergoes the reactions described previously.(12)-(14) The whole mechanism is illustrated in Scheme 2.14. Evidently, antimony halide can not be used directly because of its volatility and hydrolytic instability.

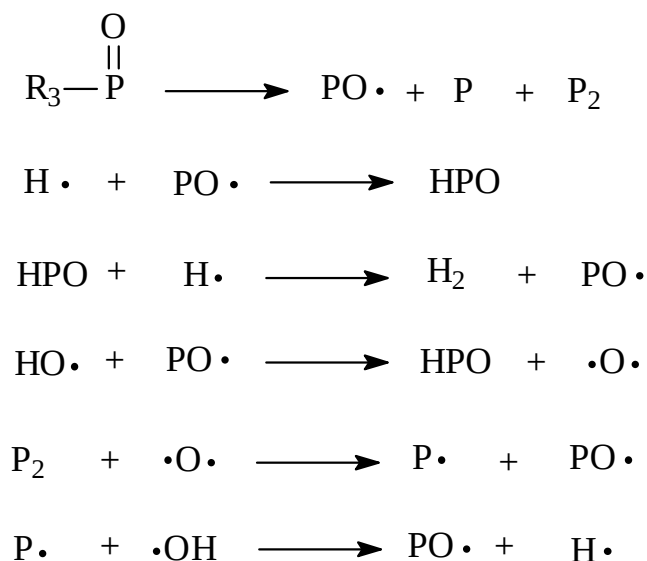


Scheme 2.14 Suggested mechanism for vapor phase inhibition of the synergistic systems

Antimony oxide particles can also catalyze radical recombination and form a protective layer to prevent the heat flow from the flame. [238-240]

Phosphorus Compounds

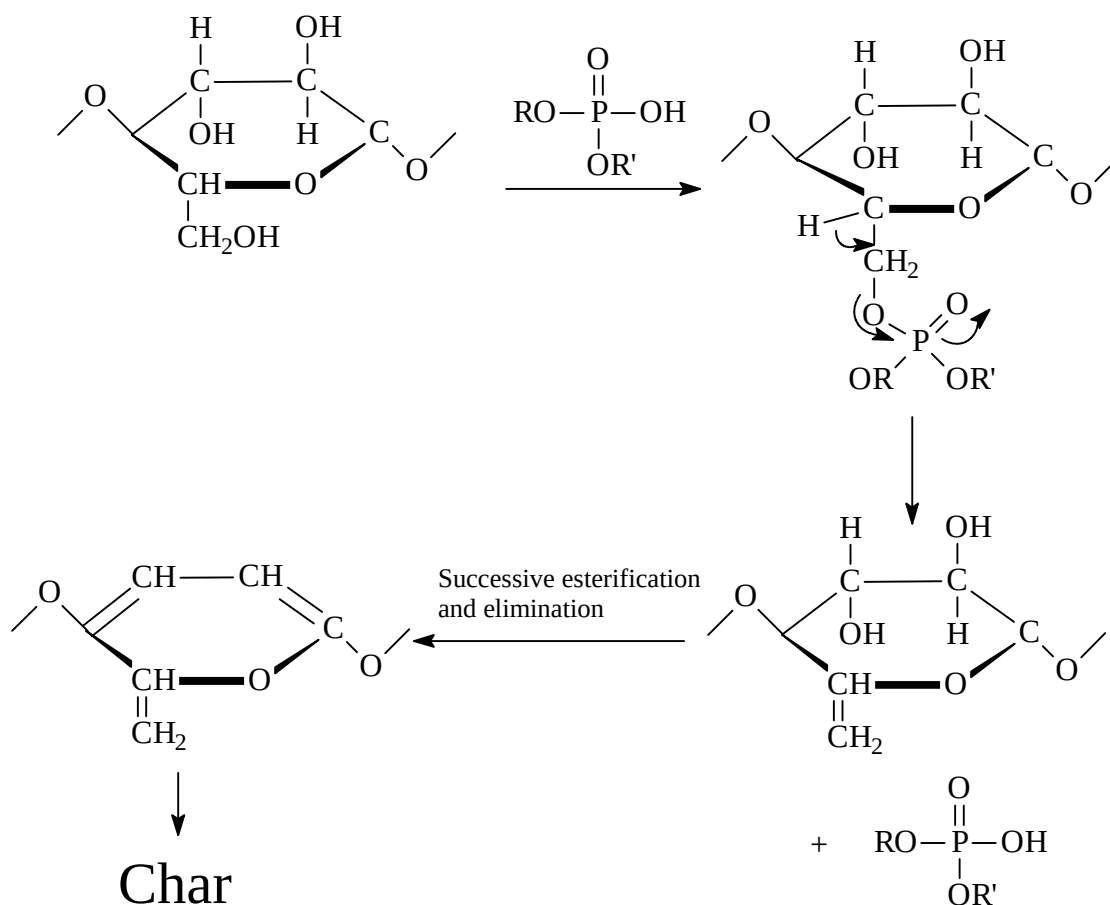
Phosphorus containing fire retardant additives can act in either a gas phase or a solid phase. Phosphorus compounds that exhibit vapor phase inhibition include trimethylphosphate, triphenylphosphate, and triphenylphosphine oxide. A suggested mechanism for the vapor phase inhibition of phosphine oxide containing additives is illustrated in Scheme 2.15. The phosphine oxide radical generated may also undergo a similar catalytic radical recombination process as suggested for antimony oxide.



Scheme 2.15 Possible vapor phase inhibition mechanism of phosphine oxide containing fire retardant

Phosphorus containing fire retardants may also act as condense phase inhibitors. An organo-phosphorus compound containing a P-O-C bond can thermally or hydrolytically decompose to phosphoric acid, which then reacts with the hydroxy group in polymer such as cellulose to form cellulose phosphate. The cellulose phosphates formed as a result of this reaction will then dehydrate to generate phosphoric acid and an unsaturated site on the polymer chain. The resulting unsaturated materials will then form crosslinked char, which can promote fire resistance in the following ways: First, the char act as an insulation layer to protect the underlying polymer from the heat and cut off the fuel supply to the flame. Second, this layer will behave as barrier preventing oxygen from reaching the condensed phase, which may cause further degradation. This condensed phase inhibition is illustrated in Scheme 2.16.

It has been shown by Inagaki et al that there is a linear correlation between the weight percent of the phosphorus and the limiting oxygen index (LOI) for cotton samples treated with phosphorus containing fire retardants.[298] The LOI is a test method to assess the fire resistance of a polymer. The higher the LOI value, the more fire resistant the material will be. This study also showed that the LOI increases linearly with the amount of phosphorus contained within the test range.



Scheme 2.16 Degradation and char formation induced by phosphoric acid

Intumescent Systems

Intumescent fire retardant additives are usually a mixture of carbon rich polyhydric compound, an acid-forming catalyst, and a gas-foaming compound.[240,244,245] Upon heating, the mixture forms a cellular foamed char, which is thermally stable and protects the underlying polymer from the flame. This layer also impedes the diffusion of the volatile fuel toward the flame and the oxygen. The carbon rich polyhydric compound supplies the char ("carbonific") and gas-foaming compound, which usually is an organic amine/amide, blows the char to a foamed structure ("spumific").

A major drawback for most intumescent additive systems is that a relatively large amount (20-30%) has to be used, compared to the halogen containing system. However, in some cases only a small amount of an acid-forming agent is needed to promote

intumescence. For example, in the polycarbonate system, only 0.2-1% of aromatic sulfonates are required because the sulfonates can catalyze the carbonaceous char formation during polymer pyrolysis.[246]

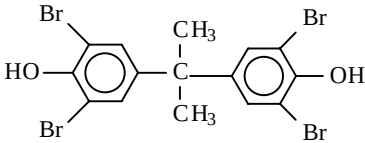
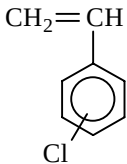
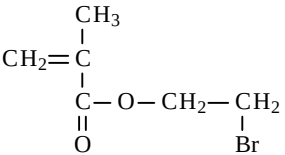
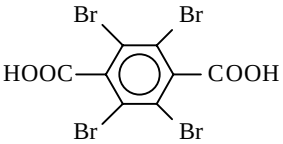
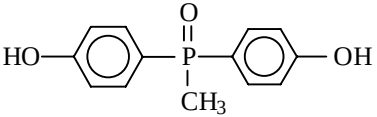
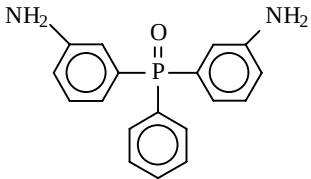
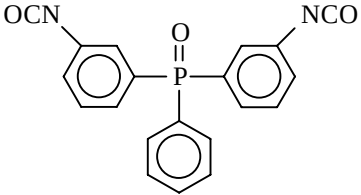
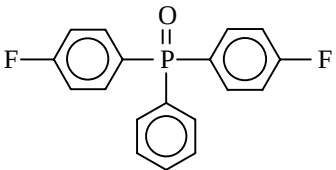
2.3.3 Reactive Fire Retardants and Modification of Polymer Structure

Reactive fire retardants usually contain a functional group, which means that they are monomers containing a fire retardant structure. These monomers can be incorporated into the polymer structure through one or more chemical reactions. Fire retardant structures usually contain either halogen or phosphorus elements and may also have hydroxy, carboxyl, amine, anhydride, or isocyanate end-groups, which can be incorporated into the polymer chain via chain reaction or step-growth reaction. Some examples of these are illustrated in Table 2.16

In addition to the reactive fire retardant approach, polymers with enhanced fire resistance can also be achieved by redesigning their chemical structure. There are three groups of polymers for which this approach is appropriate:

1. Synthesis of inorganic and heteroatom polymers that produce little or no fuel gases during decomposition.[228] This group of polymers contains phosphorus-nitrogen bonds (polyphosphazenes), silicon-nitrogen bonds (polysiloxane), and boron-containing polymers (siloxane polymers with carborane groups). However, these types of materials suffer from hydrolytic instability, especially for polymer with P-N-P, P-O-P, Si-O-Si linkage.
2. Synthesis of polymers that give off mainly incombustible gases upon heating, even though the decomposition temperature may be low.[251] These polymers include polyperfluoroalkylenetriazines, nitrosofluorocarbon elastomers, and polytetrafluoroethylene.

Table 2.16 Reactive fire retardants

Compound	Structure	Reference
Tetrabromobisphenol A		266
Chlorostyrene		248
2-Bromoethyl methacrylate		226,248
Tetrabromophthalic Acid		248
4,4'-Bis(hydroxyphenyl) methylphosphine Oxide		294,295
3,3'-Bis(aminophenyl) phenylphosphine Oxide		295,296
3,3'-Bis(isocyanophenyl) phenylphosphine Oxide		276
4,4'-Bis(fluorophenyl) phenylphosphine Oxide		295, 297

3. Synthesis of polymers consisting of aromatic and heterocyclic structures that is characterized by high ignition temperature, and form a larger quantity of carbonaceous char after decomposition. These so-called "high-performance polymers" have been available since the 1960's and include polyphenylene, polyimides, polybenzimidazoles, and polybenzoxazoles.

2.3.4 Fire retardant Polyurethanes

Like the vast majority of synthetic polymers, polyurethanes are flammable materials. The combustion of polyurethanes is primarily dependent on the thermal properties of the polymer, the supply of oxygen, the presence of impurities and formulation residue in the polymer. The yield of toxic product as a result of the combustion depends upon the decomposition conditions and primarily include isocyanate, CO, HCN, and NO_x. Although polyurethanes are used in many applications, polyurethane foams are the primary focus for fire retardant research and development. An overview of fire retardant polyurethanes can be found throughout the literature.[230,279,280]

As with other polymeric materials, the fire retardancy of a polyurethane can also be improved by the incorporation of either nonreactive additives or reactive fire retardants. The latter approach is preferable since they tend to change the physical and mechanical properties of the materials to a lesser extent.

The nonreactive additives include inorganic compounds, organic halogens, phosphorus, and nitrogen compounds. Although the inorganic reagents are more economical, their use has been limited by serious processing difficulties and their lower flame retardant efficiency, compared to organo halogen and phosphorus compounds. The most widely used inorganic additive is antimony oxide, which is generally used in the combination of with organic halides, such as polyvinyl chloride. [273,274]

In addition to inorganic additives, organic halogens [252-256,267] and phosphorus containing compounds [257-260,262-266,268-271] are the other fire retardants of commercial significance for polyurethane foams. In some of these foams, nitrogen containing compounds, such as melamine, was used as the fire retardant additive.[261,272] As mentioned previously, when organic halides decompose they

liberate hydrogen halides, which act as radical scavengers to deactivate the flame. The organic phosphorus containing additives, which include phosphates, phosphonates, and phosphites, are believed to generate a phosphoric acid upon decomposition. This phosphorus acid then promotes the formation of char to protect the polyurethane from flame and heat. Phosphorus compounds generally lower the initial decomposition temperature of a polyurethane but tend to increase char formation at higher temperatures.

The reactive fire retardants include halogenated polyols, phosphorus and halogen containing polyols, phosphorus containing polyols, and phosphorus containing isocyanate, although use of the later is quite limited.[275-278] Phosphorus containing isocyanates are usually obtained in prepolymer form by reacting an excess of isocyanate with phosphorus polyols. In general, phosphoric compounds (phosphates, phosphonates, and phosphites) are more effective than halogen containing flame-retardants.

2.3.5 Testing Methods for fire retardant polymers

In order to effectively evaluate and monitor improvement of fire resistance, it is necessary to have a quantitative method to measure the flammability of the polymer. However, flammability can not be measure by a single parameter because of the extremely complex nature of the combustion process. For example, a house fire is likely to have different characteristics than an airplane fire. Indeed, many test methods have been developed to characterize the different aspects of a material's combustion behavior. Some parameters used to describe the combustion of a polymer include ease of ignition, flame spread, ease of extinction, smoke obscuration, smoke toxicity, and heat release rate.[234,249,280]

Ease of ignition is very important for evaluating the fire resistance of a polymer because if the material can withstand exposure to a heat source without ignition, then combustion is prevented. This parameter can be measured by submitting a specimen to an ignition source for a specific amount of time. The ignition source may either be a specific temperature or heat flux and the material is considered to have failed if it ignites under those conditions. The major variables in this test are the angle to which the sample is exposed to the ignition source and the heat flux of the source. It is obvious that varying the test angles will result in different ignitability. Indeed, significant differences

in horizontal vs vertical tests are observed. During this test, materials that have low melting or softening points will melt and flow away from the ignition source. This is desirable in terms of fire resistance because if the melting or softening points of the material is lower than the ignition temperature, the material will simply flow away from the ignition source and avoid ignition. However, ignition resistance is generally accompanied by an increase in smoke emission and toxic gases, such as carbon monoxide.[280]

Once the material has ignited, the next important characteristic of the flame is how fast it spreads. This is especially important for materials that are used in construction and transportation applications. Different test methods have been developed for this purpose.[281-283] For example, the test method FAR 25.853, developed by US Department of Transportation Federal Aviation Administration (FAA), is extensively utilized in the global aircraft industry. In this test, the specimen is oriented vertically, horizontally, or at a 45 degree angle and exposed to a specified Bunsen burner ignition source. Test criteria consist of burn distance, the occurrence of dripping behavior, and whether the material continue to burn once the ignition source is removed. In general, if a material ignites easily, then its flame will spread rapidly. This can be easily understood if one considers the flame propagation front as an advancing ignition. Flame spread depends on ignition temperature, orientation, thermal properties of the polymer, and flame heat flux. The orientation of the sample is an extremely important variable in the flame spreading test. For example, a flame will spread up to one order of magnitude faster up a vertically orientated sample ignited at the bottom than has that same sample been ignited at the top. This is because the heat is transferred more efficiently ahead of the burning zone if flame propagation proceeds in an upward direction.[281]

Heat release rate is another factor that characterizes the flammability of a polymeric material. Many experts in this area currently regard it as the most important variable in flammability testing. Even though most fire deaths are primarily due to inhalation of toxic gases, the heat release rate is still the best predictor of fire hazard. [284] Heat release rate is currently measured by cone calorimetry, which is based on the oxygen consumption principle. In this method, the cone calorimeter applies a specific heat flux, which can be varied from 0 to 100 kW/m², to a horizontally or vertically

orientated specimen and measures the ignitability, heat release rate, and toxic gases emitted. Ignitability is measured by the period of time that a sample can withstand exposure to a specific heat flux before ignition occurs. Once the specimen has ignited, the heat release rate is measured as a function of time using the oxygen compensation method. In other words, the heat released is measured by the amount of oxygen consumed from the air stream. This is based on for each Joule of combustion heat generated, there is a fixed number of oxygen molecules that are removed from the exhaust stream. However, in practice, instead of counting oxygen molecules, the test measures flow rate and levels of oxygen concentration.[285] From the heat release rate, the combustion process of a material can be carefully monitored from start to finish.

Another important and well-established test method for evaluating flammability is the Limiting Oxygen Index (LOI) Test. In this test, a bar specimen is placed vertically in an up-stream atmosphere of oxygen and nitrogen and is ignited at the top. The composition of the atmosphere is measured at the point at which self-sustained combustion occurs after ignition, and the LOI is calculated by the mole fraction of oxygen in the mixture:

$$LOI = \frac{[O_2]}{[O_2] + [N_2]} \times 100$$

The advantage of the LOI method is its reproducibility and ranking of materials by a large number scale. This allows one to study the effect of chemical structure on the combustion behavior of a material. For example, a material with $LOI > 21$, which is the mole fraction of oxygen in air, should not sustain combustion. However, because actual fire conditions are likely to be different from test fire conditions, a material is normally considered as flammable if the LOI is smaller than 26.[286] Some typical LOI values are presented in Table 2.17.

Table 2.17 Limiting oxygen index values of polymeric materials

Material	Limiting Oxygen Index	Reference:
Cotton	16-17	285
Polyethylene	17	285
Polypropylene	17	285
Polystyrene	18	285
Poly(ethylene terephthalate)	21	285
Polycarbonate	23-25	285
Nylon 6,6	23	285
Wool	25-26	285
Polysulfone	30	285
Phenol-formaldehyde resin	35	285
Poly(vinyl chloride) rigid	45-49	285
Poly(vinylidene chloride)	60	285
Polytetrafluoroethylene	95	285

It is clear from this table that chlorine-containing polymers are far less flammable than other polymers. For example, polytetrafluoroethylene requires almost pure oxygen to burn. Clearly, an effective fire retardant compound must increase the LOI of the polymer. This can be verified if the LOI increases as the concentration of the fire retardant compounds increased. It has been proposed by Van Krevelen that there is a linear correlation between percent oxygen index OI and percent char yield Y for halogen free polymers without additives:[286]

$$\text{OI} = 0.4\text{Y} + 17.5$$

For fluorinated and chlorinated polymers, Hoftyzer and Van Krevelen proposed a composition parameter CP, which can be calculated from

$$\text{CP} = \text{H/C} - 0.65(\text{F/C})^{1/3} - 1.1(\text{Cl/C})^{1/3}$$

where H/C, F/C, and Cl/C are the ratios of the number of hydrogen atoms to carbon atoms, fluorine atoms to carbon atoms, chlorine atoms to carbon atoms, respectively.[287] The oxygen index is then predicted by

$$\text{OI} = 0.6 - 0.425\text{CP}, \text{CP} \leq 1$$

$$\text{OI} = 0.175, \text{CP} \geq 1$$

These predicted values work well for polymers containing C, H, F, Cl, but not for polymers containing other heteroatoms, which form char. Nevertheless, the generalization that an increase in char yield results in an increase in the oxygen index is accurate.

In addition to the thermal behavior of a material, the risk of fire hazard is also associated with other side effect, such as dripping, evolution of smoke and toxic gases. In fact, smoke and toxic gases from combustion are greater cause death than fire itself. Like the other parameters, these side effects can not be considered as inherent properties of a material. They are very much dependant on environmental factors such as spatial arrangement and ventilation.

The smoke density of a material is usually measured by XP-2 chamber and the NBS chamber.[288,289] The measurements are based on the attenuation of a light beam due to the build up of particulate combustion products. However, other parameters associated with a real fire must be taken into consideration before conclusion can be drawn from these transmission data, particularly with regard to reduced visibility associated with actual fire condition. There have been several attempts to determine the acute toxicity of smoke by evaluation of the chemical nature of a material, as well as the analysis of the major components of combustion products.[290] However, because decomposition models do not produce a relevant smoke stream, these trials were not very successful. In addition, toxicologists are of the opinion that neither the identification of the chemical composition of the combustion products, nor the analytically measured concentrations, are sufficient to determine acute toxicity. This issue is still a vigorously debated.

Chapter 3 Experimental

3.1 Purification of Solvents

3.1.1 N,N-Dimethylacetamide

Acronym: DMAc

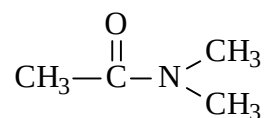
Supplier: Aldrich Chemical Company

Molecular Formula: C₄H₉NO

Molecular Weight: 87.12 g/mole

Boiling Point: 165°C/760 torr

Chemical Structure:



Purification Procedure:

DMAc was stirred over CaH₂ for 12 hours and distilled under reduced pressure at approximately 70°C. The constant boiling fraction was collected and stored in a round bottom flask with molecular sieve (4A) under nitrogen.

3.1.2 Tetrahydrofuran

Acronym: THF

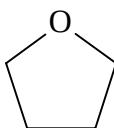
Supplier: Aldrich Chemical Company

Molecular Formula: C₄H₈O

Molecular Weight: 72.11 g/mole

Boiling Point: 67°C/760 torr

Chemical Structure:



THF was purified by distillation over sodium and benzophenone under nitrogen. The distilled solvent was collected in a round bottom flask with molecular sieves (4A) under nitrogen

3.1.3 Toluene

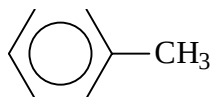
Supplier: Fisher Chemical Company

Molecular Formula: C_7H_8

Molecular Weight: 92.14g/mole

Boiling Point: 110.6°C/760 torr

Chemical Structure:



Toluene was stirred over CaH_2 for 12 hours and distilled under nitrogen. The solvent was collected in a round bottom flask with molecular sieve (4A) under nitrogen.

3.2 Synthesis and Purification of Monomer

3.2.1 Methylene diphenyl diisocyanate

Acronym: MDI

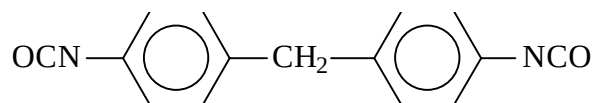
Supplier: Bayer

Molecular Formula: $C_{15}H_{14}N_2O_2$

Melting Point: 30°C/760 torr

Boiling Point: 150°C/ 0.2 torr

Chemical Structure:



Purification & Storage Procedure:

MDI was distilled at 150°C under vacuum. The monomer grade MDI was stored at 1-4°C under nitrogen for no more than 3 months. Fresh MDI was used for each reaction to avoid possible hydrolysis.

3.2.2 1,4-Butanediol

Acronym: BD

Supplier: Aldrich Chemical Company

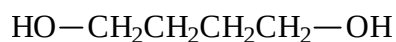
Molecular Formula: $C_4H_{10}O_2$

Molecular Weight: 90.12 g/mole

Melting Point: 16°C

Boiling Point: 230°C/ 760 torr

Chemical Structure:



BD was distilled under vacuum and stored in a round bottom flask.

3.2.3 Polytetramethylene oxide

Acronym: PTMO

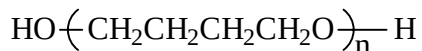
Supplier: BASF

Molecular Formula: $(C_4H_8O)_n$

Molecular Weight: 1000 g/mole

Melting Point: 27°C

Chemical Structure;



PTMO was used as received without any further purification. It can be dehydrated at 90°C under vacuum for 2 hours if necessary.

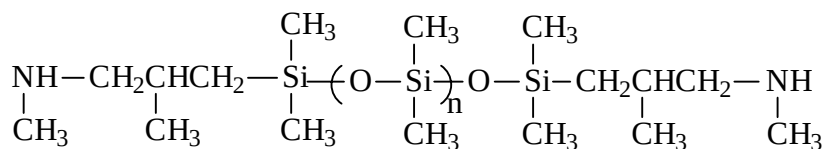
3.2.4 Secondary amino isobutyl silyl terminated polydimethylsiloxane

Acronym: PDMS

Supplier: Dow Corning Corporation

Molecular Weight: 1235, 3380 g/mole

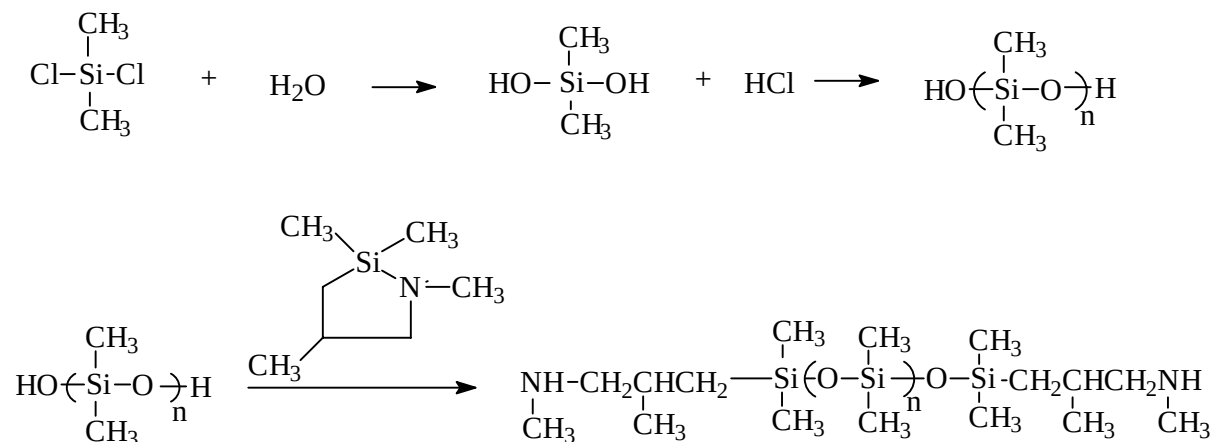
Chemical Structure:



Possible Synthetic Procedure:

The secondary diaminoalkyl terminated PDSM was supplied by Dow Corning Corporation. Although the synthetic route for obtaining such a siloxane oligomer is not precisely known, according to U.S. patents filed by Dow Corning Corporation,[304] it is postulated that this siloxane oligomer can be synthesized via the route shown in Scheme 3.1. This synthetic approach is quite different from conventional methods of making a α,ω -diaminoalkyl terminated siloxane, which is the ring opening polymerization of D_3 or D_4 in the presence of a α,ω -diaminoalkyl terminated disiloxane. The reaction starts with a conventional self-catalyzed hydrolysis condensation of dichlorodimethylsilane to give dihydroxy terminated polydimethylsiloxane oligomer. The molecular weight of this dihydroxy terminated PDMS oligomer can be precisely controlled by the reaction conditions. The siloxane oligomer obtained can further react with a silicon contained five-member ring. The ring-opening reaction affords difunctional end-capped PDMS. According to the literature, this type of ring-opening reaction can be conducted at room temperature and the yield is almost quantitative.[302,303]

The PDMS oligomers were used as received. The molecular weights of the oligomer were determined by ^1H , ^{13}C , ^{29}Si NMR and end-group titration.



Scheme 3.1 A possible route for the synthesis of secondary amino alkyl terminated polydimethylsiloxane

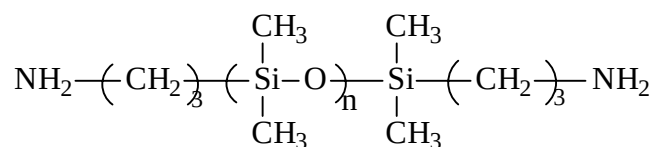
3.2.5 α,ω -Diaminopropyl terminated polydimethylsiloxane

Acronym: PDMS

Supplier: Shin-Etsu Chemical Corp.

Molecular Weight: 1528, 2897, 4229 g/mole (M_n)

Chemical Structure:



The PDMS oligomers were used as received. The molecular weights of the oligomers were determined by ^{29}Si NMR and end group titration.

3.2.6 Stannous 2-ethylhexanoate

Acronym: Stannous Octoate

Supplier: Sigma Chemical

Molecular Weight: 405 g/mole

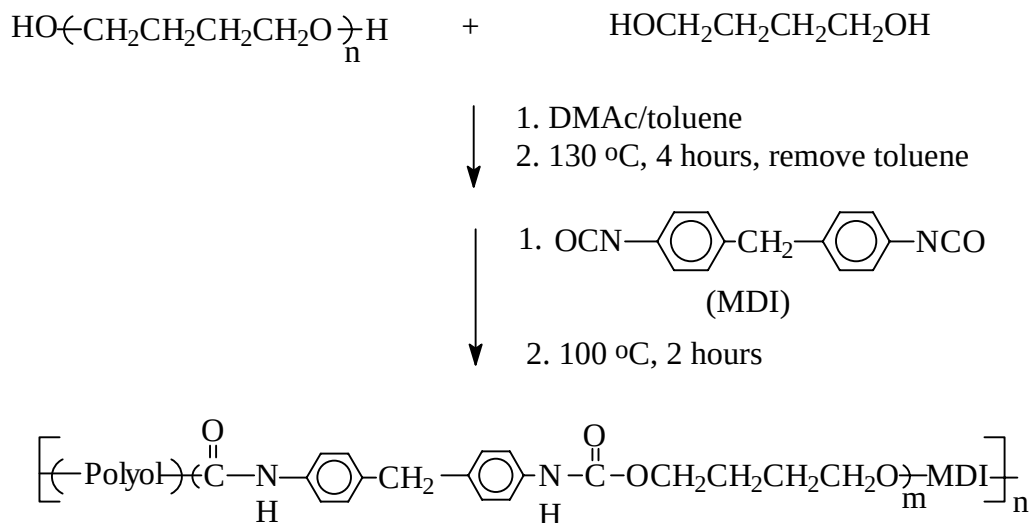
$$\begin{array}{c} \text{CH}_3\text{CH}_2 \diagdown \\ \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2 \diagup \text{HC} - \overset{\text{O}}{\parallel} \text{C} - \text{O} - \text{Sn} - \text{O} - \overset{\text{O}}{\parallel} \text{C} - \text{CH} \begin{array}{l} \diagup \text{CH}_2\text{CH}_3 \\ \diagdown \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3 \end{array} \end{array}$$

3.3.1 Synthesis of Segmented Thermoplastic Polyurethane Control

By varying the ratio of PTMO to MDI & BD, segmented thermoplastic polyurethanes with varying soft segment concentrations were synthesized. The synthesis of a segmented thermoplastic polyurethane with 63wt% soft segment concentration is used here as an example.

76

was added to dilute the reaction solution, which was then stirred for another hour after dilution. The polymer solution was coagulated into water using a Waring blender. The fibrous polymer was filtered and washed with water and methanol several times and dried in a vacuum oven at 100°C for 24 hours.



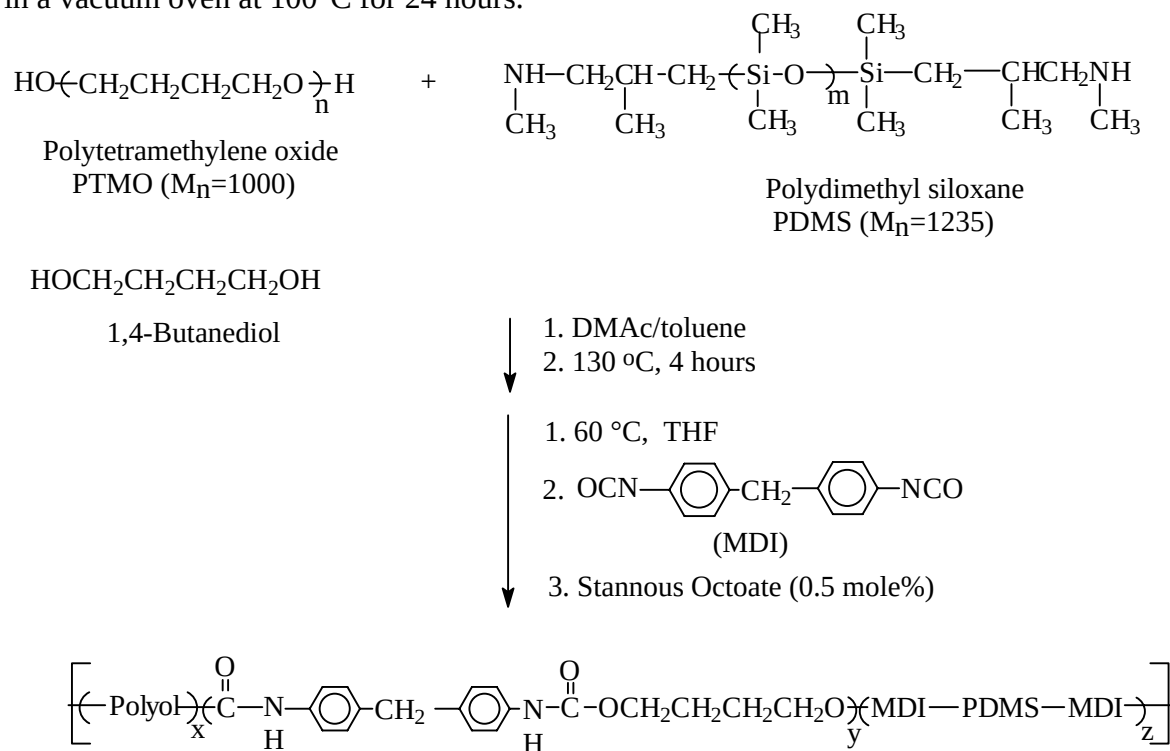
Scheme 3.2 Synthesis of segmented thermoplastic polyurethane controls

3.3.2 Synthesis of PDMS containing segmented thermoplastic polyurethanes

PDMS containing segmented thermoplastic polyurethanes were synthesized via a one step polymerization, similar to the polyurethane control. Instead of using PTMO exclusively as the soft segment, PDMS and PTMO were both used as soft segments. The siloxane concentration in the polyurethane was controlled by the ratio of PDMS to PTMO. The reaction procedure is as follows, using polyurethane with 15% PDMS as an example:

To a 250 mL 4-neck round bottom flask equipped with mechanical stirrer, nitrogen inlet and Dean-Stark trap, were added PTMO (Mn=989) (7.92 g, 0.008 mole), PDMS (Mn=1235) (2.47 g, 0.002 mole), BD (0.9012 g, 0.01 mole), DMAc (28 mL), and toluene (18 mL). The solution was heated to 130°C under reflux of toluene for 4 hours to azeotropically remove the small amount of water in the system. The toluene was then removed by distillation. After that, the solution was cooled to 40°C and freshly distilled dry THF was added to the reaction flask. MDI (5.0052g, 0.02 mole) was charged into the

flask to afford a concentration of 30% solid. Stannous octoate (1×10^{-4} mole) was added to the reaction flask after the addition of MDI. The solution was stirred at 60°C for three hours. The polymer solution was coagulated into water using a Waring blender. The fibrous polymer was filtered and washed with water and methanol several times and dried in a vacuum oven at 100°C for 24 hours.



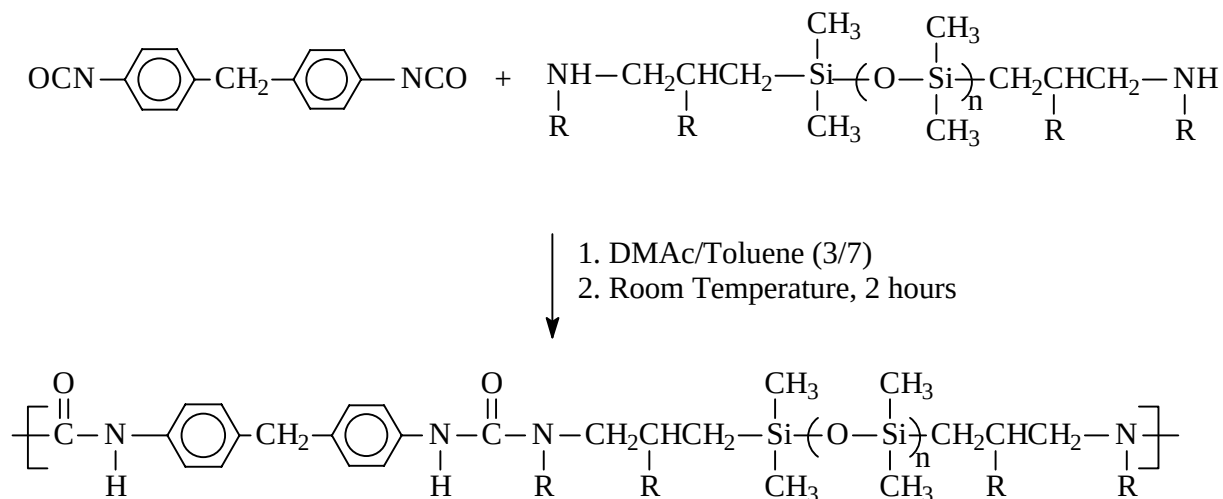
Scheme 3.3 Synthesis of PDMS containing segmented thermoplastic polyurethanes

3.3.3 Synthesis of PDMS based polyurea

PDMS based segmented thermoplastic polyureas were synthesized by the direct reaction of diamine (primary or secondary) terminated PDMS with MDI at room temperature. The siloxane concentration and hard segment concentration were controlled by varying the molecular weight of the PDMS soft segment, i.e. soft segment length. The reaction procedure is as follows, using polyurea with 86wt% PDMS as an example.

To a 250 mL 3-neck round bottom flask equipped with mechanical stirrer, nitrogen inlet, addition funnel, were added MDI (2.5026g, 0.01 mole), freshly distilled dry DMAc (26 mL), and freshly distilled dry toluene (40 mL). After the MDI was dissolved in the mixed solvents, PDMS ($M_n=1528$) (15.28 g, 0.001 mole) was dissolved

in dry toluene (23 mL) and added dropwise to the MDI solution through an addition funnel. The solution was stirred at room temperature for two hours. The polymer solution was coagulated into water/methanol (1:1) using a Waring blender. The polymer was filtered and washed with water and methanol several times and dried in a vacuum



R=H, Primary amine terminated PDMS, $M_n=1528, 2897, 4229$

R=CH₃, Secondary amine terminated PDMS, $M_n=1235, 3383$
oven at 80°C for 24 hours.

Scheme 3.4 Synthesis of PDMS based polyureas

3.4 Characterization Methods

3.4.1 Proton NMR (¹H NMR)

Proton (¹H) NMR spectra were measured on a Varian 400 MHz instrument in CDCl₃ or in DMF, depending on the solubility of the material being analyzed. All CDCl₃ spectra were referenced to tetramethylsilane (TMS) at 0 ppm.

3.4.2 Carbon NMR (¹³C NMR)

Carbon (¹³C) NMR spectra were obtained in the same manner as the proton NMR spectra, but at a frequency of 100 MHz.

3.4.3 Silicon NMR (^{29}Si NMR)

Silicon (^{29}Si) NMR spectra were obtained in the same manner as the ^1H NMR spectra, but at a frequency of 79.4 MHz. Deuterated DMF or CDCl_3 were used as solvents, depending on the situation.

3.4.4. FTIR

FTIR spectra were measured on a Nicolet Impact 400 FTIR Spectrometer using solution cast films on KBr discs. The polymer films were dried in vacuum oven at 90°C for 24 hours before FTIR measurements. The spectra data were acquired by using Omnic 2.0 software.

3.4.5 Intrinsic Viscosity

Intrinsic viscosities were measured at 25°C in a Cannon-Ubbelohde viscometer, typically using THF as the polymer solvent. When the polymer was not soluble in THF, NMP was used as solvent. Three low concentration polymer solutions were prepared and the time measured for the polymer solution (t) and the pure solvent (t_0) to pass through the viscometer were measured. Assuming $t/t_0 = \eta/\eta_0$, the specific viscosity was defined as $[\eta]_{\text{sp}} = (\eta/\eta_0) - 1$ and the reduced viscosity was defined as $\eta_{\text{red}} = \ln(\eta/\eta_0)$. Both (η_{sp}/C) and (η_{red}/C) were plotted with respect to concentration and extrapolated to zero concentration to give the intrinsic viscosity $[\eta]$.

3.4.6. Gel Permeation Chromatography

The molecular weight of the polymers was analyzed by gel permeation chromatography on a Waters 150C ALC/GPC chromatograph equipped with a differential refractometer detector and an on-line differential viscometer detector (Viscotek 150R) coupled in parallel. N-methylpyrrolidone (HPLC grade) containing 0.02M P_2O_5 filtered through 0.5 mm Teflon filter served as a mobile phase. The chromatography conditions were as follows: two stainless steel columns (7.8x300) mm packed with Waters Styragel HT 10^3 and 10^4 , mean particle diameter 10 mm, flow rate 1.0 mL/min, injection volume 200 mL, and a temperature of 60°C for both GPC and

detectors. Samples prepared at known concentrations (approx. 3mg/mL) were dissolved in the mobile phase and filtered through 0.2 mm PTFE disposable filters prior to analysis. TriSEC GPC Software V2.70e (Viscotek) was used to acquire and analyze the data. A series of narrow molecular weight distribution polystyrene standards (Polymer Laboratory) was employed to generate the universal calibration curve. Figure 3.1 is a schematic representation of the apparatus.

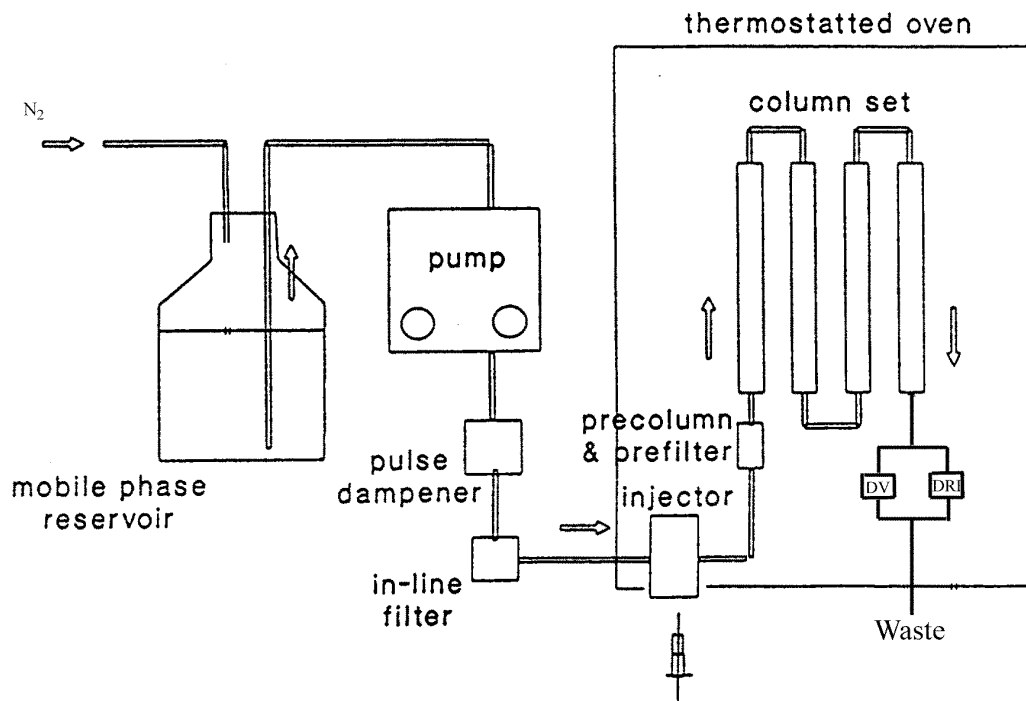


Figure 3.1 Gel permeation chromatography diagram

3.4.7 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed on a Du Pont DSC 913 or using Perkin Elmer Pyris instruments depending on the samples. The glass transition temperatures were obtained from samples that had been pressed and secured in crimped aluminum pans. Scans were run at 10°C/min and the reported T_g values were obtained from the second heat after a quench cool from the first run.

3.4.8 Dynamic Thermogravimetric Analysis

Dynamic thermogravimetric analysis (TGA) was performed on a Perkin Elmer TGA 7 instrument. The heating rate was 10°C/min in air or nitrogen. All analyses were conducted on samples in the form of solvent cast films.

3.4.9 Dynamic Mechanical Analysis

Dynamic mechanical analysis was carried out on a Perkin Elmer DMA 7e using the thin film extension mode. The frequency was 1 Hz and the heating rate was 2°C/min. The sample was a 0.2 mm thick solution cast film which was dried and aged over a week before testing.

3.4.10 Stress-Strain Behavior

Stress-Strain tests were performed in an Instron model 4204 at room temperature. Dog-bone specimens were cut from the solution cast films using DMF as solvent with a D638 Die for the mechanical testing. The film thickness ranged from 0.006-0.01 inches. The solution cast films were set at room temperature for 5 hours and at 60°C in an oven for 12 hours. The films were then dried at 100°C in vacuum oven for 24 hours. Finally, all films were left at room temperature for a week before testing. All stress-strain measurements were carried out at a strain rate of 100% per minute based on the initial sample length. Approximate 6 samples were tested and the results were averaged.

3.4.11 Transmission Electron Microscopy

All polymer samples for Transmission Electron Microscopy (TEM) analysis were solvent cast films that were prepared by the same method as the ones used in the stress-strain experiments. The films for study were cryo-ultramicrotomed at -120°C. This delicate operation had to be performed at depressed temperatures to ensure the rigidity of the siloxane phases. The microtomed samples were then carefully mounted on a 150 mesh copper TEM grid and were analyzed with Transmission Electron Microscopy at 100 kV using a Phillips 420T TEM. The microphase separation in these samples can be directly observed without selectively staining with osmium tetroxide due to the large

degree of electron density difference between the PDMS and polyurethane containing phase.

3.4.12 Electron Spectroscopy for Chemical Analysis

Electron spectroscopy for chemical analysis (ESCA), or X-ray photoelectronic spectroscopy (XPS) was performed on a Perkin-Elmer Physical Electronic Model 5400 with a hemisphere analyzer and a position sensitive detector. The spectrometer was equipped with a Mg/K α (1253.6 eV) achromatic x-ray source operated at a power of 400 watts and three take off angles: 15°, 45°, 90°, were used with the X-ray source. The spot size used was 1 mm x 3mm. Survey scans were taken in the range of 0-1100 eV. Any significant peaks in the survey scan were then subjected to narrow scans in the appropriate ranges for atomic concentration analysis. Photopeaks were curve fitted using the Apollo Version 4.0 ESCA software to obtain information on the bonding state of the elements. The binding energy of each photopeak was referenced to C 1s level from ubiquitous organic material at 285.0 eV. A pass energy of 44.75 eV was chosen for all angle-dependent acquisitions. The spectrometer was typically run at the 10⁻⁸ torr vacuum range.

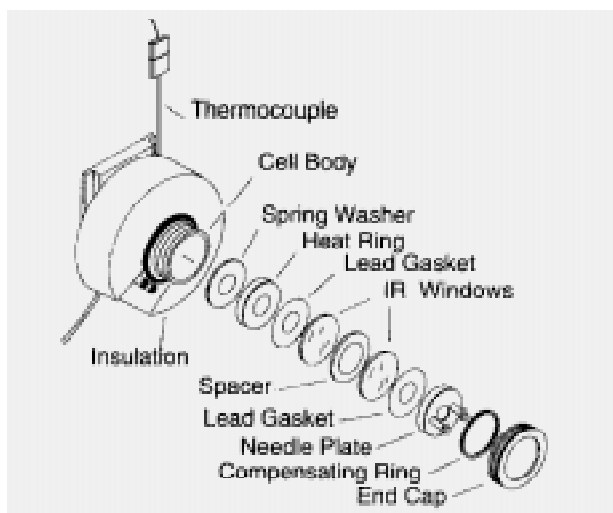
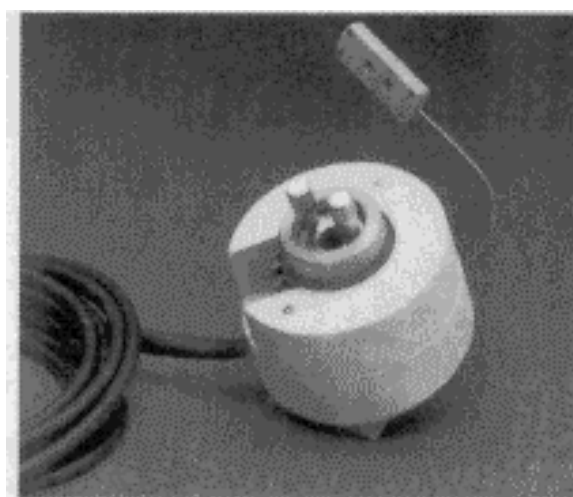
3.4.13 Contact Angle Analysis

The contact angle of water against the polymer surface was measured by the sessile drop method with a Rame-Hart 100-00 115 NRL contact angle goniometer. The measurements were conducted at room temperature using distilled water drops of five microliter in size. The water drops were carefully placed on the substrate using a microliter syringe. The polymer samples were prepared by solution cast from DMF and dried in vacuum oven before testing. The contact angles on both sides of a drop were measured. Measurements from 6-10 drops were used to obtain an average value of the contact angle.

3.4.14 High Temperature FTIR

The thermal degradation processes of the polyurethane and PDMS containing polyurethanes were monitored by high temperature FTIR. Samples, either polyurethane

or PDMS containing polyurethanes, were dissolved in DMF and cast on the KBr discs. The polymer films formed after removal of the solvent by drying at 90 °C in vacuum oven were sandwiched between two KBr discs. The KBr discs were then inserted into a heating cell that was connected to a temperature controller. The heating cell was placed on the sample holder where the IR beam can pass through. The temperature of the heating cell was varied from 25-310 °C. The cell temperature was raised by manually adjusting the temperature controller and it was allowed to equilibrate for 3 minutes after each temperature raise before the FTIR spectra were recorded. The FTIR spectra obtained at different temperatures were normalized by using the Omnic 2.0 software.



Scheme 3.5 Illustration of heating cell in the high temperature FTIR

3.4.15 End Group Titration

The molecular weights of PDMS terminated with amine (primary and secondary) end group were obtained by end group titration. The potentiometric titrations are performed on a MCI Automatic Titrator Model GT-05 which employs microprocessor control and a built-in cathode ray tube screen. The titrator automatically allows for control of the titration, detection of the inflection points and appropriate calculation of the molecular weight. The apparatus includes a standard glass electrode that functions as a detection electrode and a reference electrode that is comprised of a Ag/AgCl double junction type electrode. A movable piston effects suction of titrant from the reservoir and discharge through a microburet of 20 mL capacity. The titrant used is HCl aqueous solution. The normality of the HCl solution was standardized by standard sodium carbonate. The PDMS sample [0.1 milliequivalents (mol. wt. divided by functionality)] was dissolved in 75 ml isopropanol and stirring was maintained till ready to commence titration. The PDMS sample solution was then subjected to titration by the automatic titrator. The process was repeated 3 times and the molecular weight was calculated as the average of the three titrations.

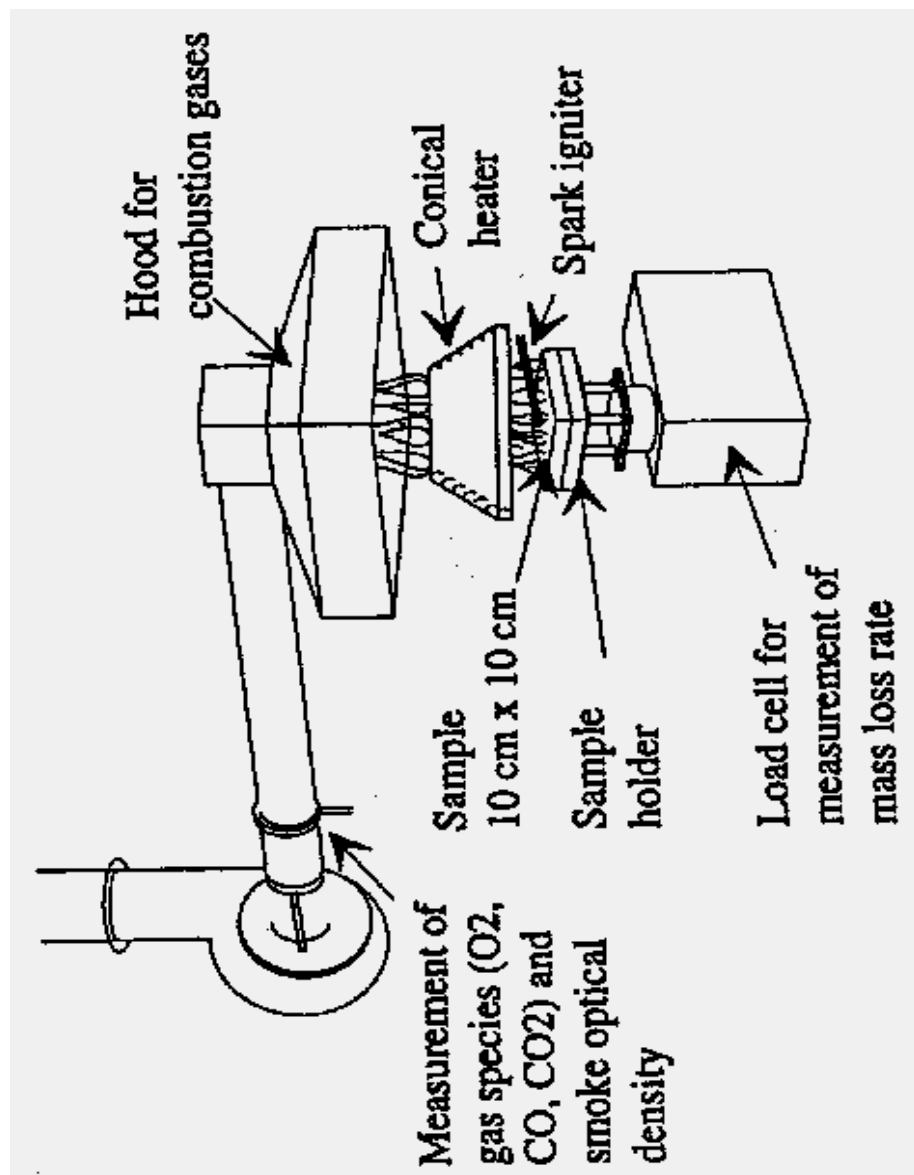
3.4.16 Cone Calorimetry[233]

Polymer samples with dimensions of 10 cm x 10 cm x 3mm were compression molded at 190°C and measured at the Naval Research Laboratory, under the supervision of Dr. U. Sorathia, where they were evaluated in air using cone calorimetry at a constant heat flux of 25 kW/m².

3.4.17 Atomic Force Microscopy

Atomic Force Microscopy (AFM) was done using a Digital Instruments Dimension 3000 and the Nanoscope IIIa controller. The tapping mode was used to obtain all the AFM micrographs. The tips used were Nanosensors TESP (tapping etched silicon probe) type single beam cantilevers with a force constant of approximately 40 N/m. The thin film samples were embedded in a commercial epoxy resin and cured at 60 °C for 12 hours. The samples were trimmed with a razor blade to expose the samples and then cryomicrotomed at -120 °C using a Reichert-Jung Ultracut-E ultramicrotome with

the FC-4D cryo-attachment. The resulting smooth surfaces were then analyzed with the AFM.



Scheme 3.6 Illustration of Cone Calorimetry test

3.4.18 Pyrolysis Study

Polymer powder samples were pyrolyzed for 5 seconds in helium at 450°C in a Pyrojector II (SGE) pyrolysis unit. The Pyrojector was attached to an on line Hewlett

Packard gas chromatograph unit connected to a VG7070E mass spectrometer. This way the polymer could be degraded at a specified temperature and the degradation products were separated via GC, prior to analysis using mass spectrometry. The condition for gas chromatography were as follows:

Carrier gas: Helium

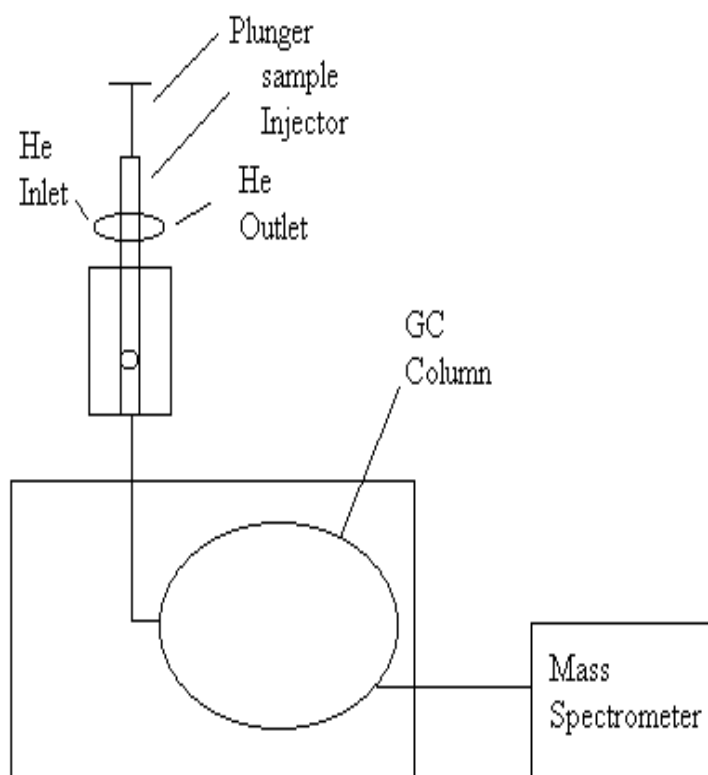
GC temperature: 25°C (1min)-150°C (rate=10°C/min)

Carrier gas pressure: 5 psi

Pressure differential between Pyrojector and column: 7 psi

Column type: 30 meter HP5 column (5% phenyl methylsilicone), 0.32 i.d.

The instrument is further illustrated in Scheme 3.7

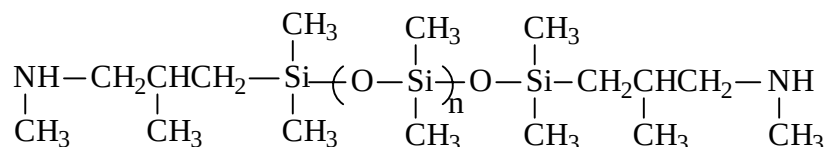


Scheme 3.7 Illustration of pyrolysis GC-MS instrumentation

Chapter 4 Results and Discussion

4.1 Monomer synthesis and characterization

4.1.1 Secondary amino isobutyl silyl terminated polydimethylsiloxane



This secondary aminoalkyl terminated polydimethylsiloxane was synthesized by end-capping a dihydroxy terminated polydimethylsiloxane with a silicon containing cyclic compound, as described in Section 3.2.4.[304.305] PDMS of two different molecular weights were investigated. The molecular structure was confirmed using ^1H , ^{13}C , and ^{29}Si NMR in CDCl_3 (Figure 4.1-Figure 4.4). In the ^1H NMR spectrum of PDMS ($M_n=1235$), the protons from the methyl and methylene groups that attached to the nitrogen (H_f) were observed at 2.4 ppm. The amine protons (H_e) were observed at 1.1 ppm. The methine proton (H_g) gave a multiplet at 1.8 ppm. The methyl protons (H_d) that attached to the methine groups were observed at 0.9 ppm. The two protons on methylene (H_b , H_c) attached to silicon gave two multiplets at 0.6 ppm and 0.4 ppm. The protons associated with the methyl group attached to silicon (H_a) showed a large up field peak at 0.1 ppm. The ^{13}C spectrum showed 6 peaks corresponding to 5 end group carbons (C_a , C_b , C_c , C_d , C_e) and the carbon of methyl group attached to silicon (C_f). The ^{29}Si NMR spectrum showed one peak at 7 ppm, which corresponds to the silicon on the end of the PDMS chain, and multiple peaks at -22 ppm, which refers to different silicon atoms in the PDMS backbone. The ^1H , ^{13}C , and ^{29}Si NMR spectra for PDMS ($M_n=3300$) were the same as that PDMS ($M_n=1235$), except that the integration ratios between the peaks were different.

The molecular structure was also confirmed by the FTIR spectra. The FTIR spectrum of PDMS ($M_n=1235$) is provided in Figure 4.5. The spectrum showed strong Si-O-Si stretching absorptions at 1023 and 1091 cm^{-1} , which are characteristic of a siloxane

backbone. In addition, the CH₃ bending and rocking peaks were observed at 1260 cm⁻¹, and 801cm⁻¹. The amine endgroup could not be detected from the spectrum, though it was quantitatively determined by endgroup titration. A complete list of FTIR structure assignments is given in Table 4.1

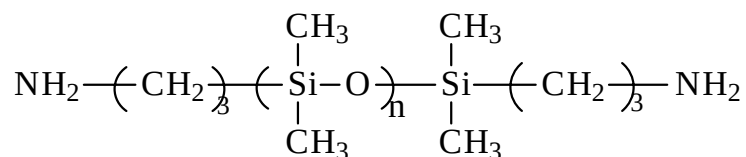
Table 4.1 Assignments of FTIR Spectrum of PTMS (M_n=1235) Soft Segment

Wavenumber (cm ⁻¹)	Assignment
2942	ν (C-H) in CH ₃
1260	δ (C-H) in Si-CH ₃
1091	ν _a (Si-O-Si) in Si-O-Si
1023	ν _s (Si-O-Si) in Si-O-Si
801	ρ (C-H) in Si-CH ₃

ν=stretching mode, ν_a =asymmetric stretching, ν_s =symmetric stretching, δ= in-plane bending or scissoring, ρ=in-plane bending or rocking

The FTIR spectrum of PDMS (M_n=3300) is provided in Figure 4.6. The number average molecular weight of the polydimethylsiloxanes was determined by end group titration of amine groups, using standardized HCl as titrant and also by NMR end group analysis.

4.1.2. α,ω-Diaminopropyl terminated polydimethylsiloxane



The primary diaminopropyl terminated polydimethylsiloxane can be synthesized by ring opening polymerization of D₄ using 1,3-bis(3-aminopropyl) tetramethyldisiloxane as end capper as discussed in section 2.3.1.[158] Three different molecular weight PDMS were prepared. The molecular structures were confirmed using ¹H, ¹³C, and ²⁹Si NMR in CDCl₃. These spectra are shown in Figure 4.7-4.14. In the ¹H NMR spectrum of PDMS (M_n=1500), the protons from the methylene groups attached to nitrogen (H_f) were

observed at 2.4 ppm. The amine protons (H_e) were observed at 1.1 ppm. The methylene protons in the middle (H_g) gave a multiplet at 1.8 ppm. The two protons on the methylenes (H_b , H_c) that are attached to silicon gave two multiplets at 0.6 ppm and 0.4 ppm. The protons associated with the methyl groups that attached to silicon (H_a) showed a large up field peak at 0.1 ppm. The ^{13}C spectrum showed 4 peaks corresponding to 3 end group carbons (C_a , C_b , C_c) and the carbon of the methyl groups attached to silicon (C_d). The ^{29}Si NMR spectrum showed one peak at 7.9 ppm, which corresponds to the silicon on the end of the PDMS chain and multiple peaks at -22 ppm which referred to different silicon atoms in the PDMS backbone. The ^1H , ^{13}C , and ^{29}Si NMR spectra for PDMS ($M_n=2800$, 4000) were the same as those for PDMS ($M_n=1235$), except that the integration ratios between the peaks are different.

The molecular structure was also confirmed by the FTIR spectra. The FTIR spectrum of PDMS ($M_n=1500$), Figure 4.15, showed a strong Si-O-Si stretching absorption at 1023 cm^{-1} , which is characteristic of a siloxane backbone. In addition, the CH_3 bending and rocking peaks were observed at 1260 cm^{-1} , and 801 cm^{-1} . The amine end group can not be detected from the spectrum, though it was quantitatively determined by end group titration. A complete list of FTIR structure assignments is given in Table 4.2

Table 4.2 Assignments of FTIR Spectrum of PTMS ($M_n=1500$) Soft Segment

Wavenumber (cm^{-1})	Assignment
2960	ν (C-H) in CH_3
1261	δ (C-H) in Si- CH_3
1098	ν_a (Si-O-Si) in Si-O-Si
1021	ν_s (Si-O-Si) in Si-O-Si
801	ρ (C-H) in Si- CH_3

ν =stretching mode, ν_a =asymmetric stretching, ν_s =symmetric stretching, δ = in-plane bending or scissoring, ρ =in-plane bending or rocking

The number average molecular weights of the polydimethylsiloxanes were determined by endgroup titration of the amine groups, using standardized HCl as titrant and also by NMR endgroup analysis. They were found to be 1528, 2897, and 4229.

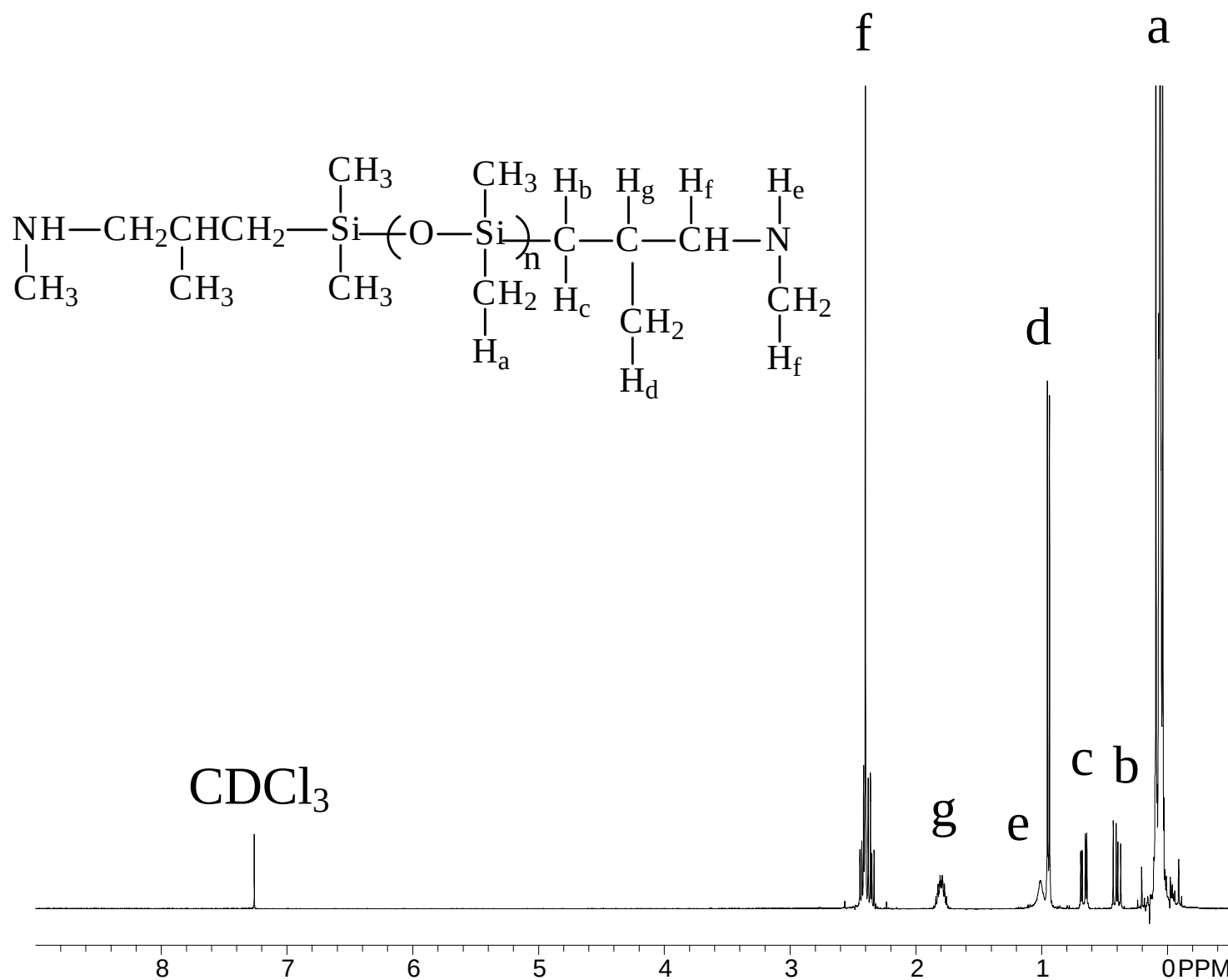


Figure 4.1 ^1H NMR spectrum of secondary aminoalkyl terminated PDMS($M_n=1235$)

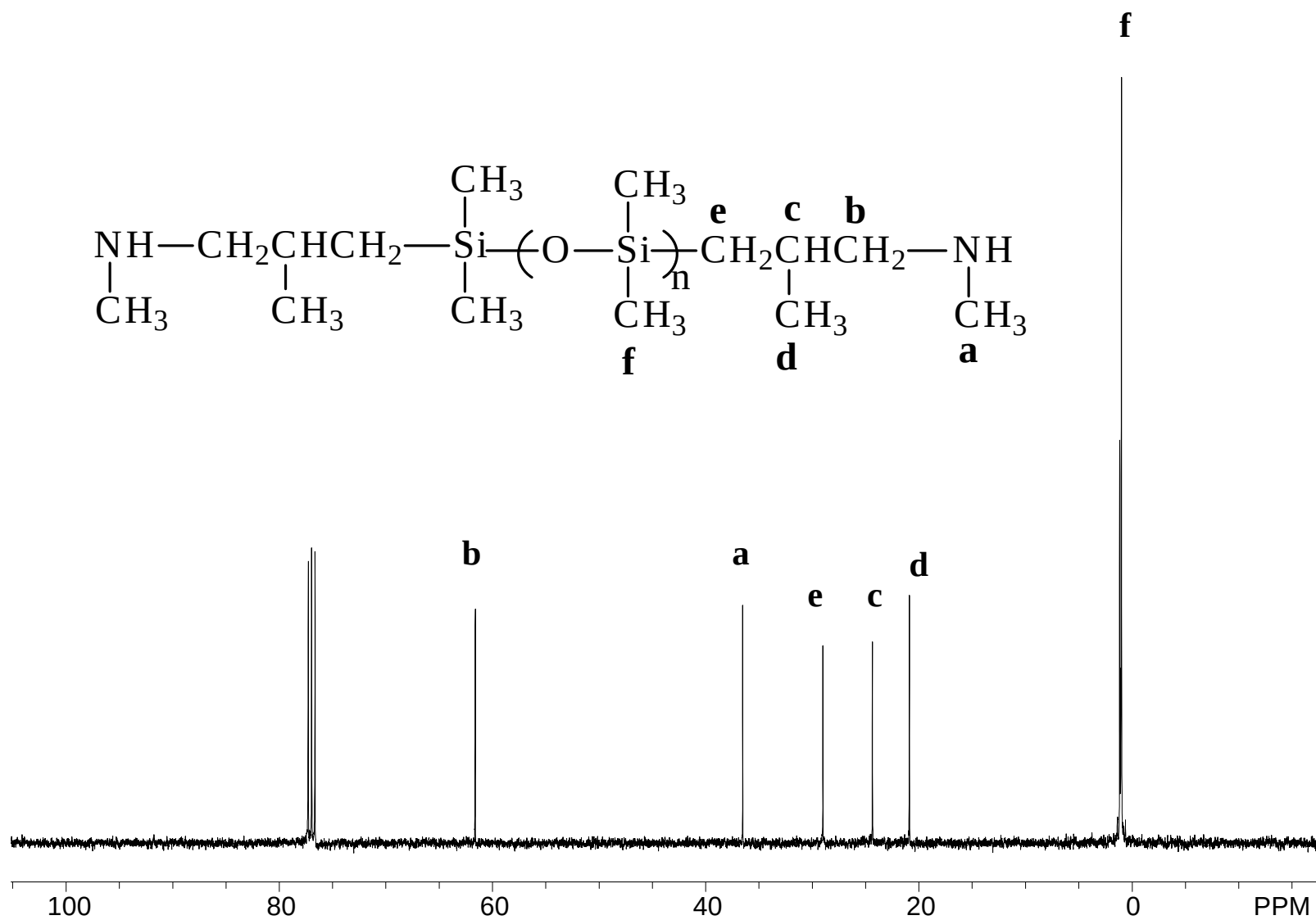


Figure 4.2 ^{13}C NMR spectrum of secondary aminoalkyl terminated PDMS ($M_n=1235$)

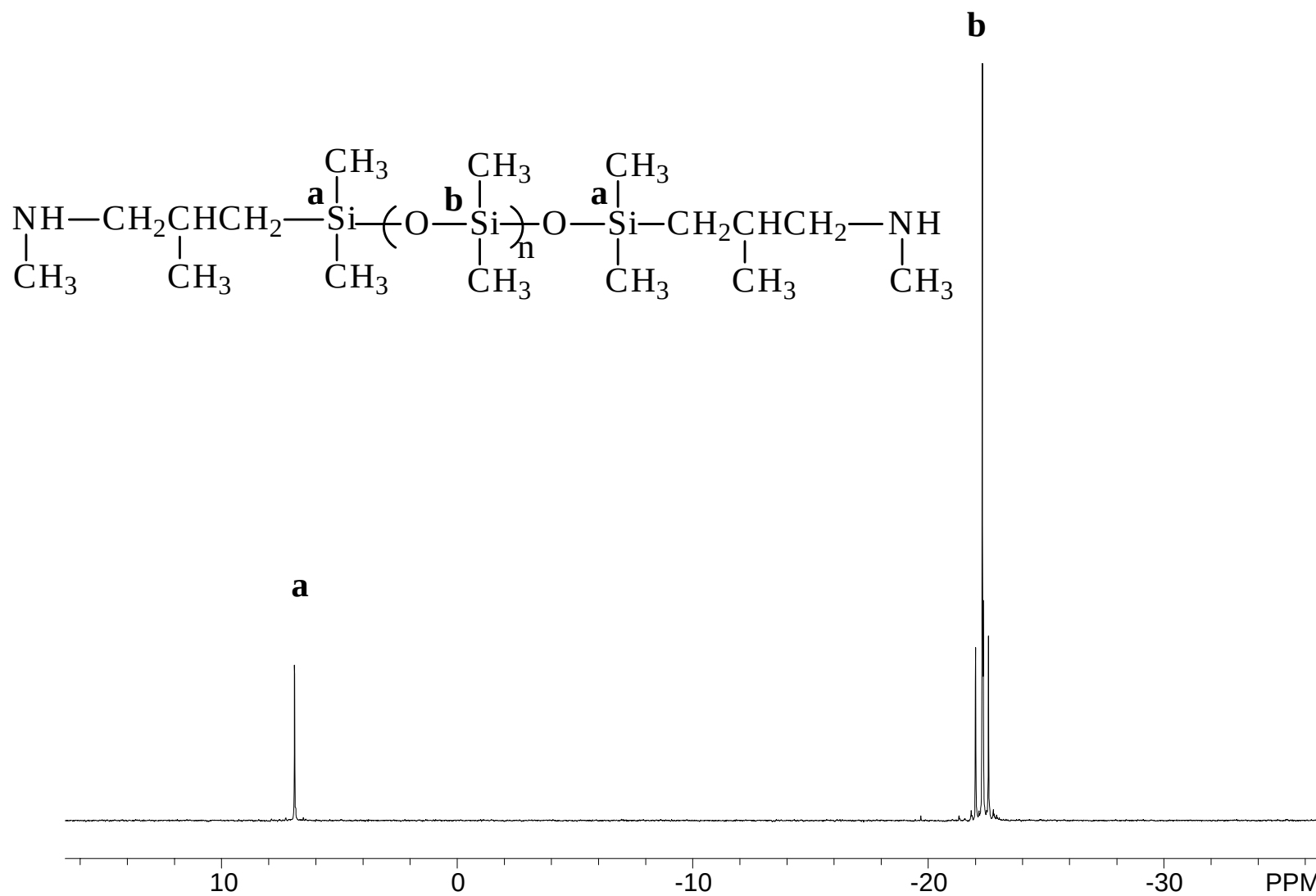


Figure 4.3 ^{29}Si NMR spectrum of secondary aminoalkyl terminated PDMS ($M_n=1235$)

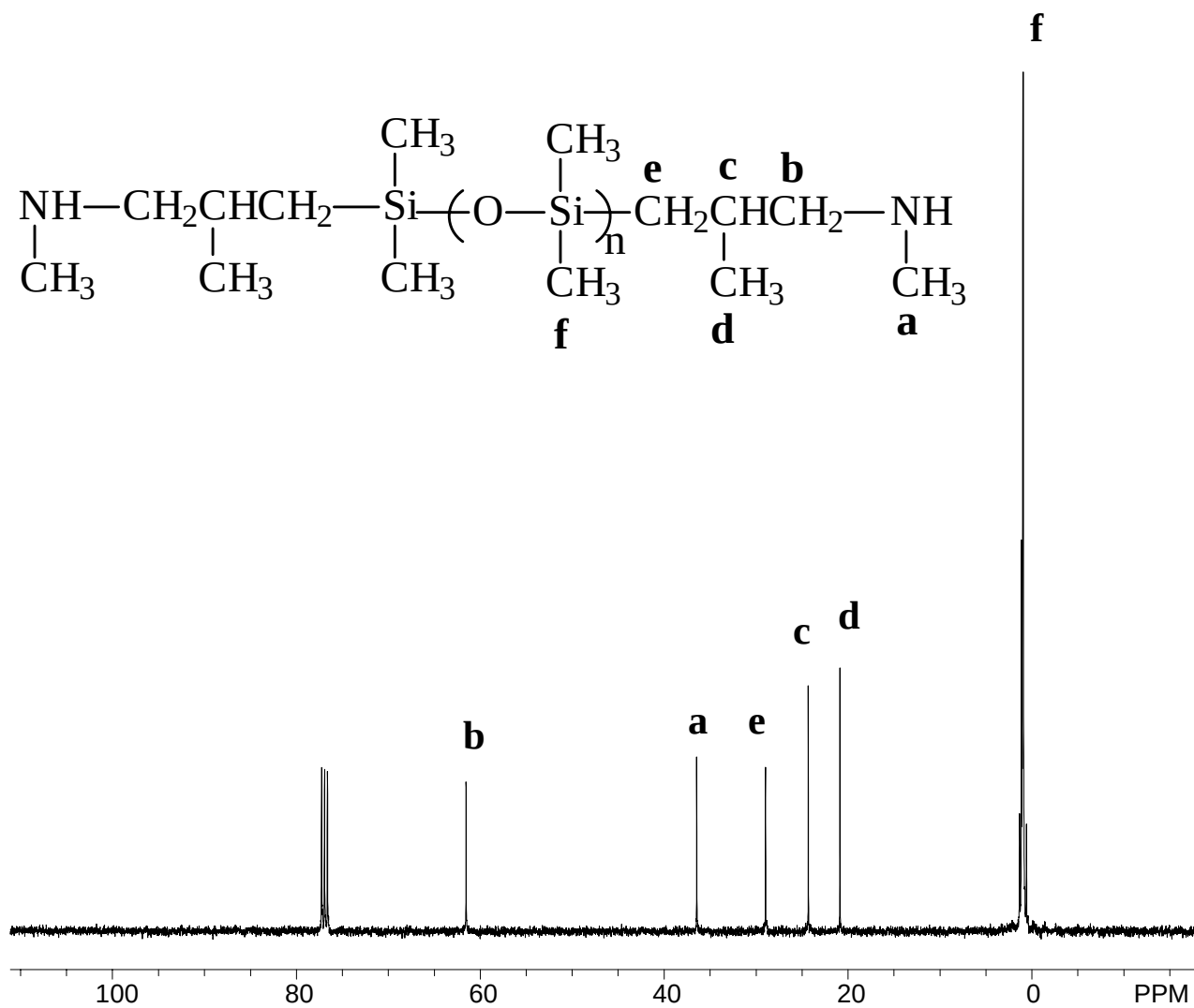


Figure 4.4 ¹³C NMR spectrum of secondary aminoalkyl terminated PDMS (M_n=3300)

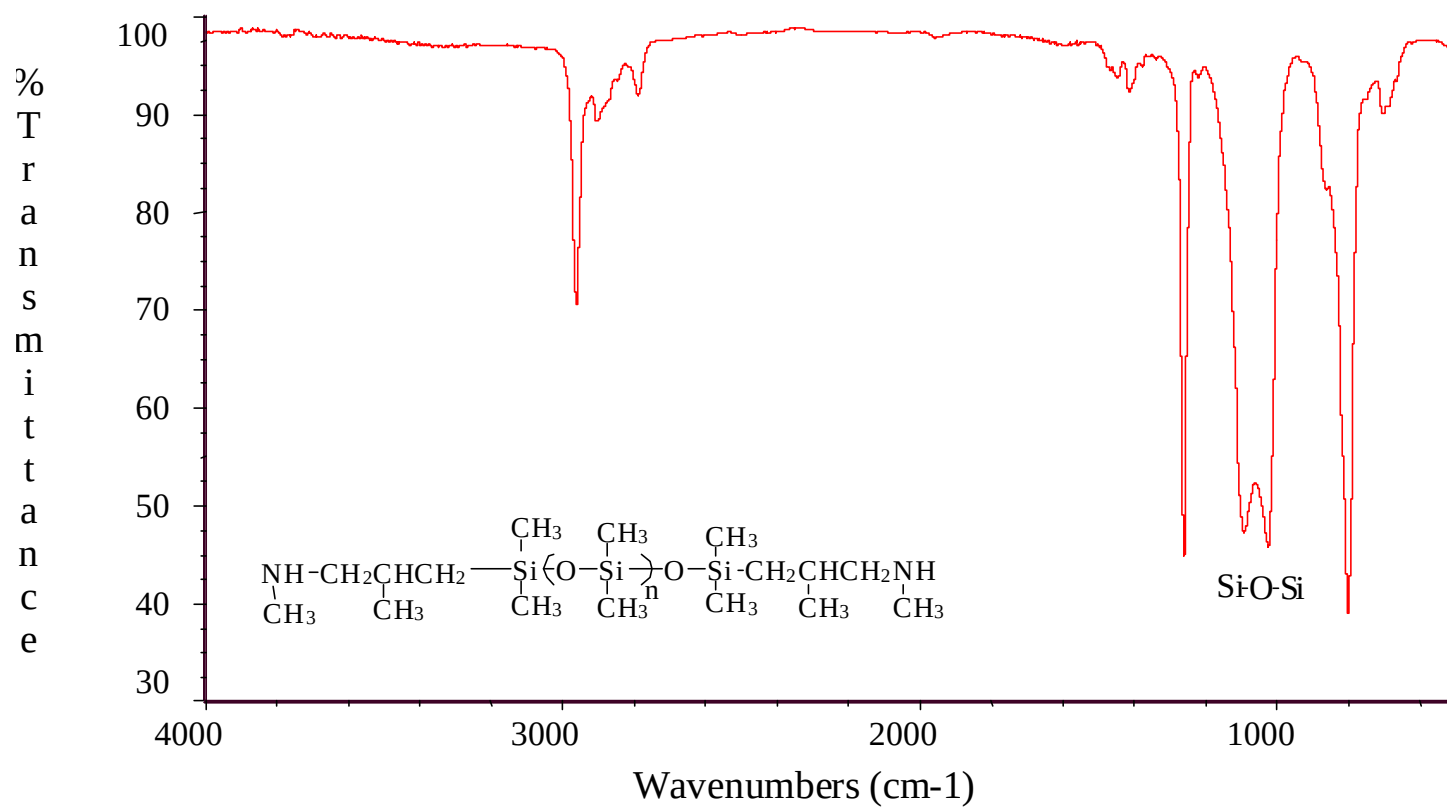


Figure 4.5 FTIR spectrum of secondary amino isobutyl silyl terminated polydimethylsiloxane ($M_n=1235$)

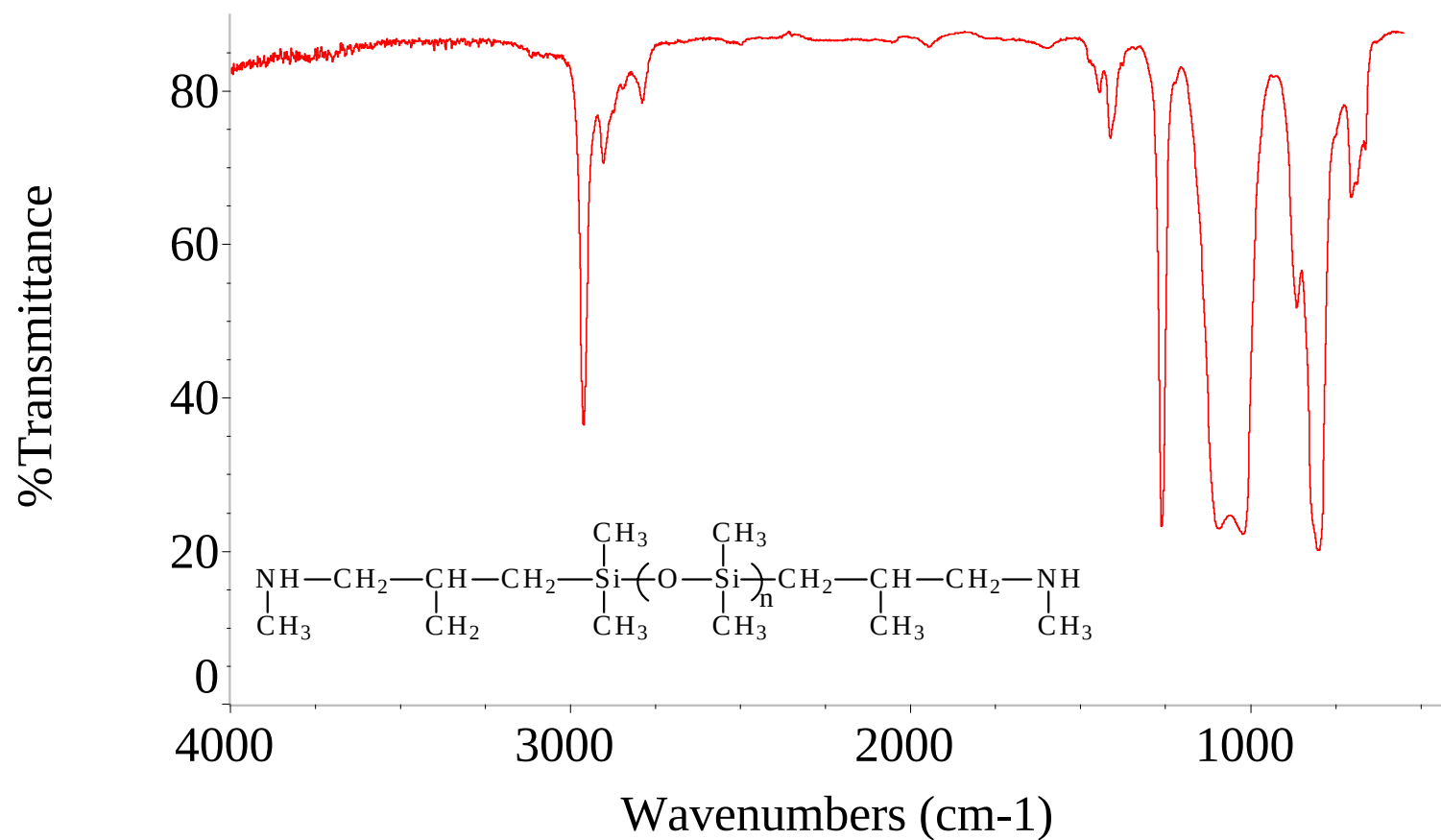


Figure 4.6 FTIR spectrum of secondary amino isobutyl silyl terminated polydimethylsiloxane ($M_n=3300$)

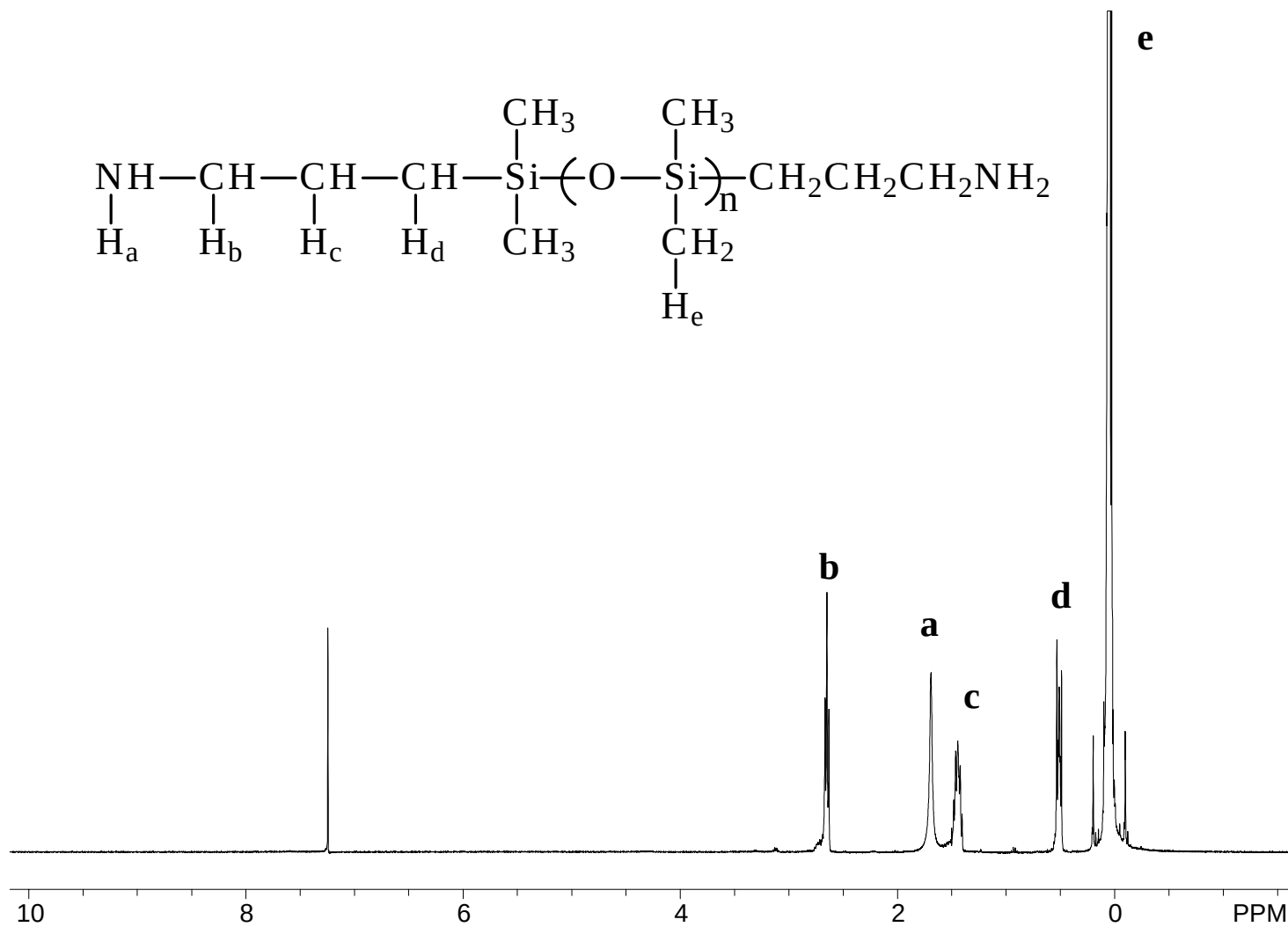


Figure 4.7 ^1H NMR spectrum of primary aminoalkyl terminated PDMS ($M_n=1528$)

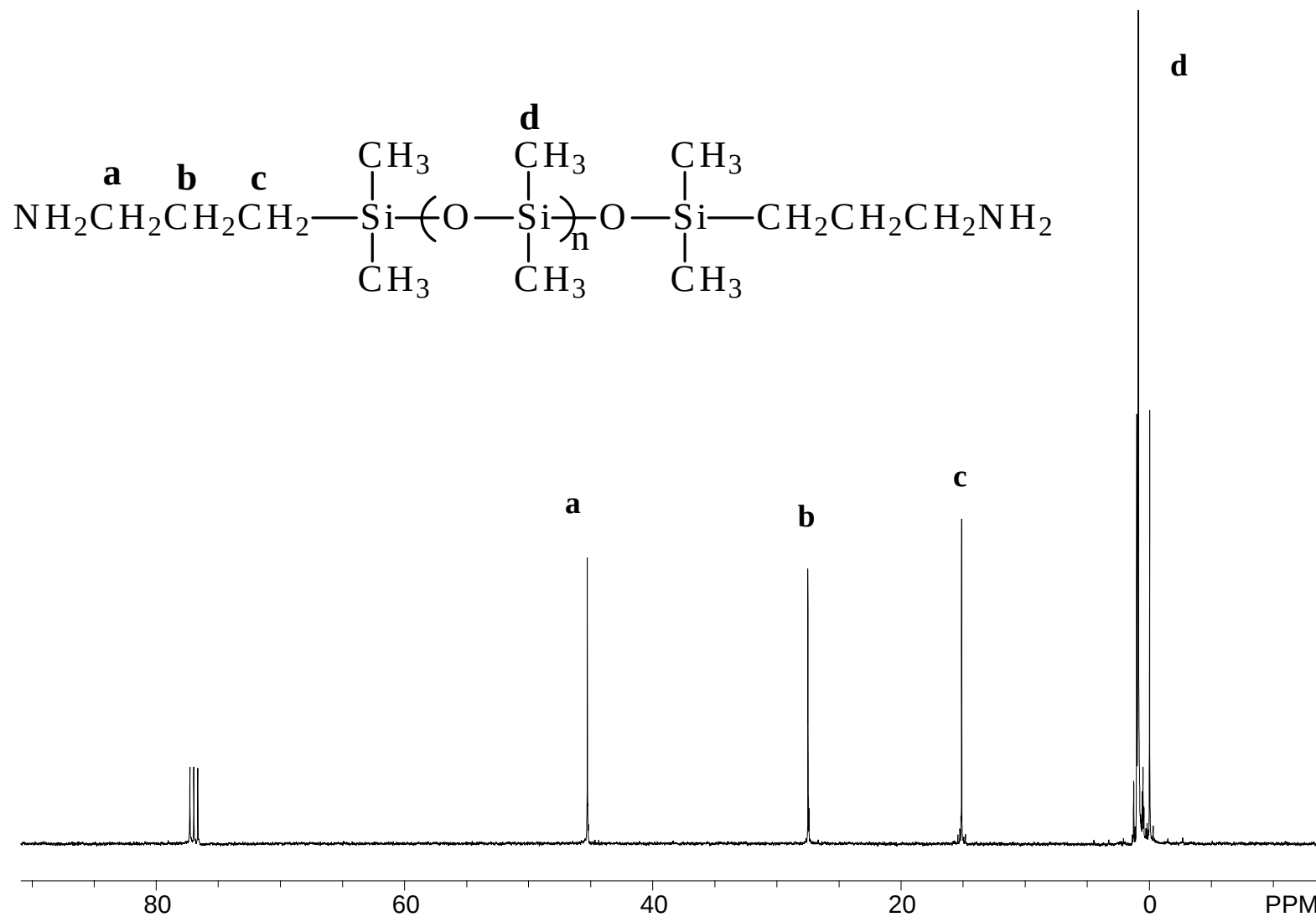


Figure 4.8 ^{13}C NMR spectrum of primary aminoalkyl terminated PDMS ($M_n=1528$)

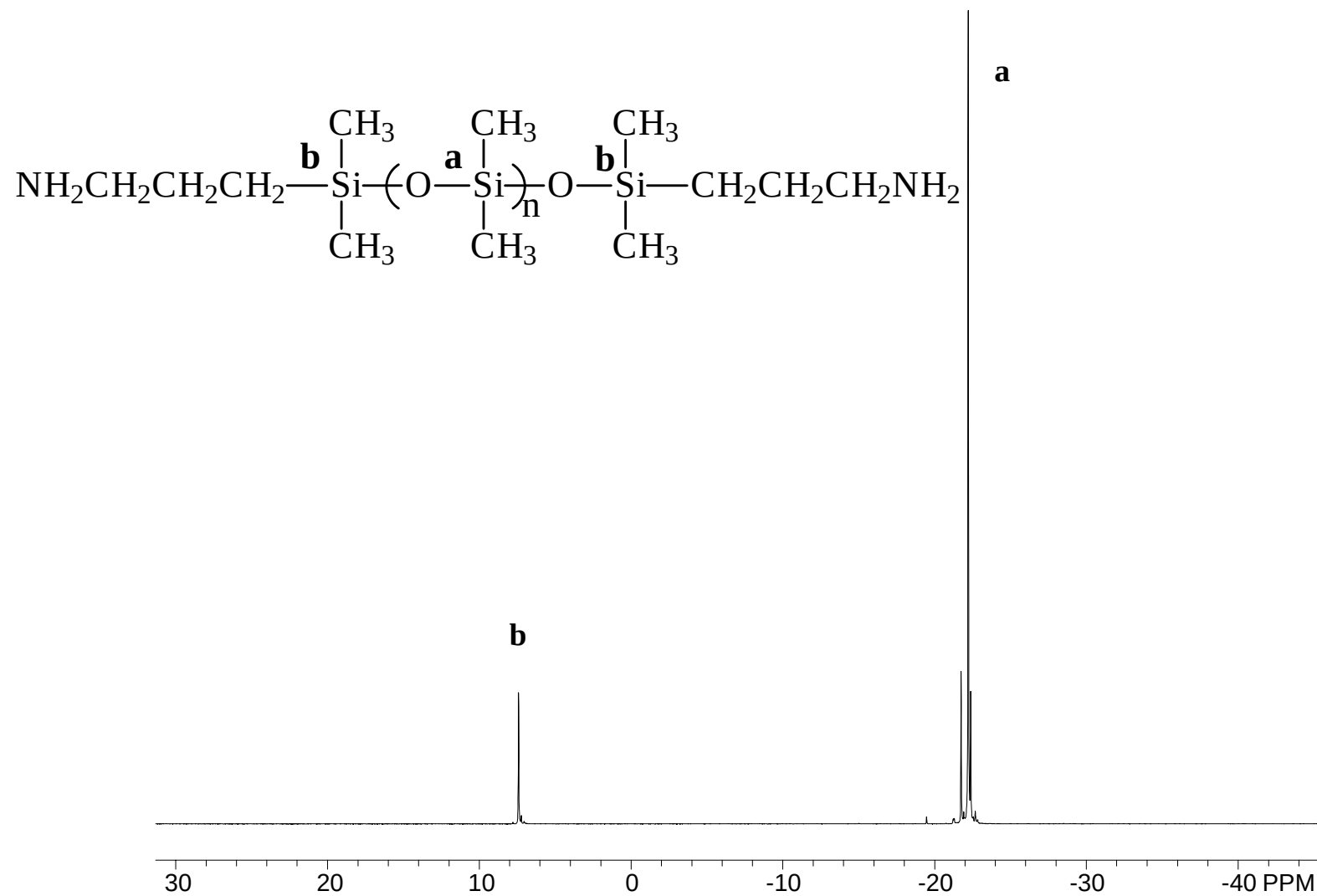


Figure 4.9 ^{29}Si NMR spectrum of primary aminoalkyl terminated PDMS($M_n = 1528$)

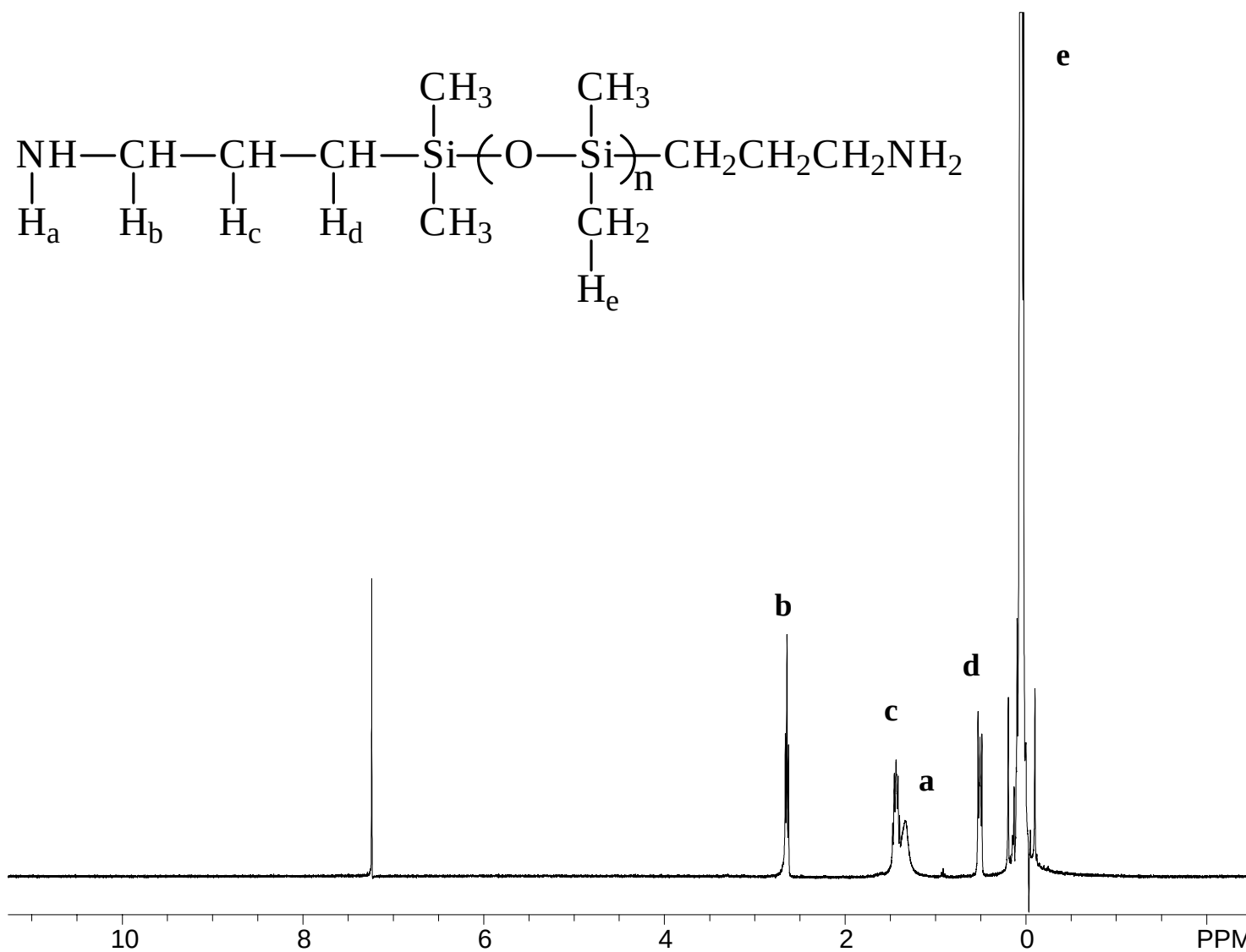


Figure 4.10 ^1H NMR spectrum of primary aminoalkyl terminated PDMS ($M_n=2897$)

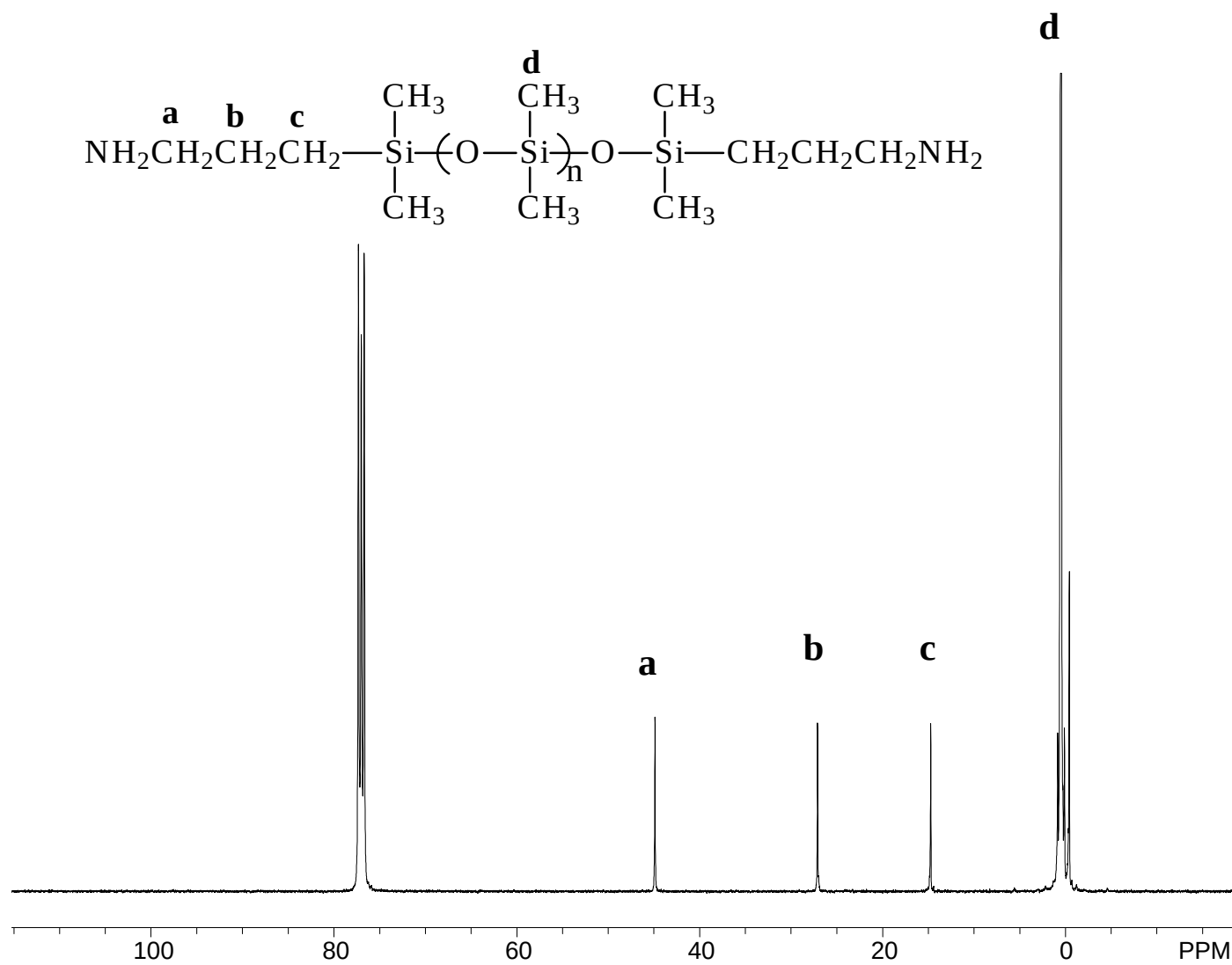


Figure 4.11 ^{13}C NMR spectrum of primary aminoalkyl terminated PDMS ($M_n=2897$)

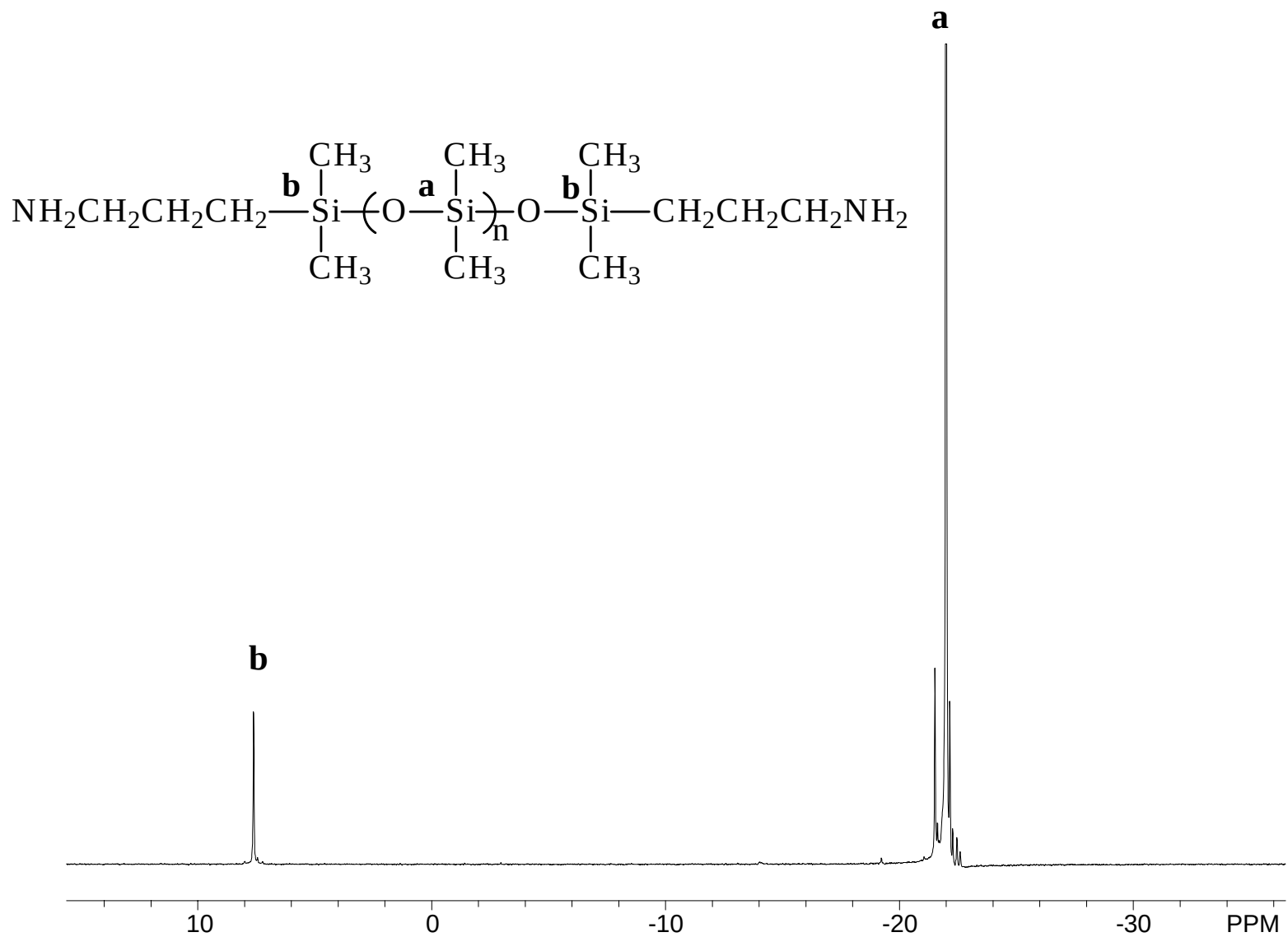


Figure 4.12 ^{29}Si NMR spectrum of primary aminoalkyl terminated PDMS ($M_n=2897$)

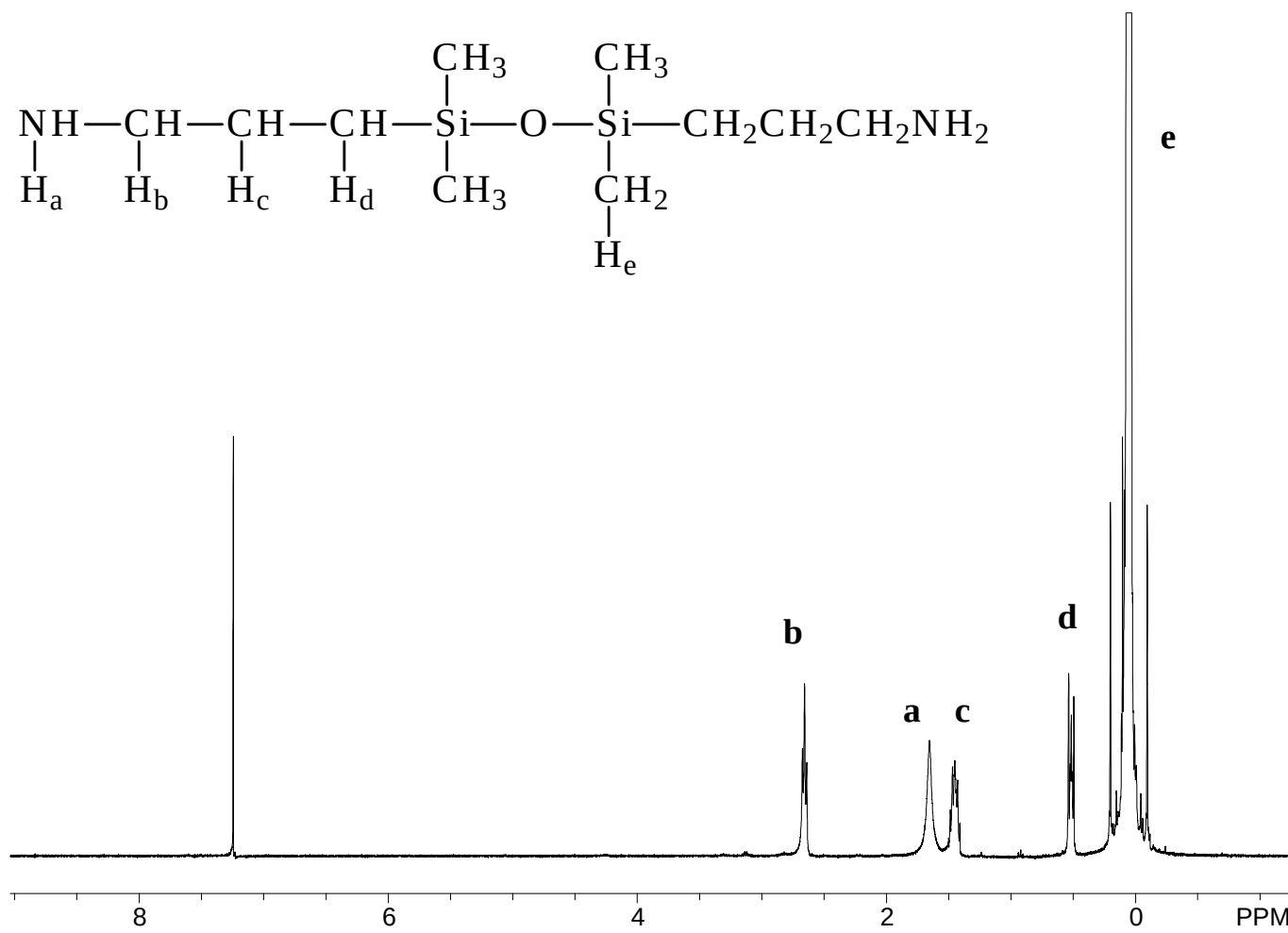


Figure 4.13 ^1H NMR spectrum of primary aminoalkyl terminated PDMS ($M_n=4229$)

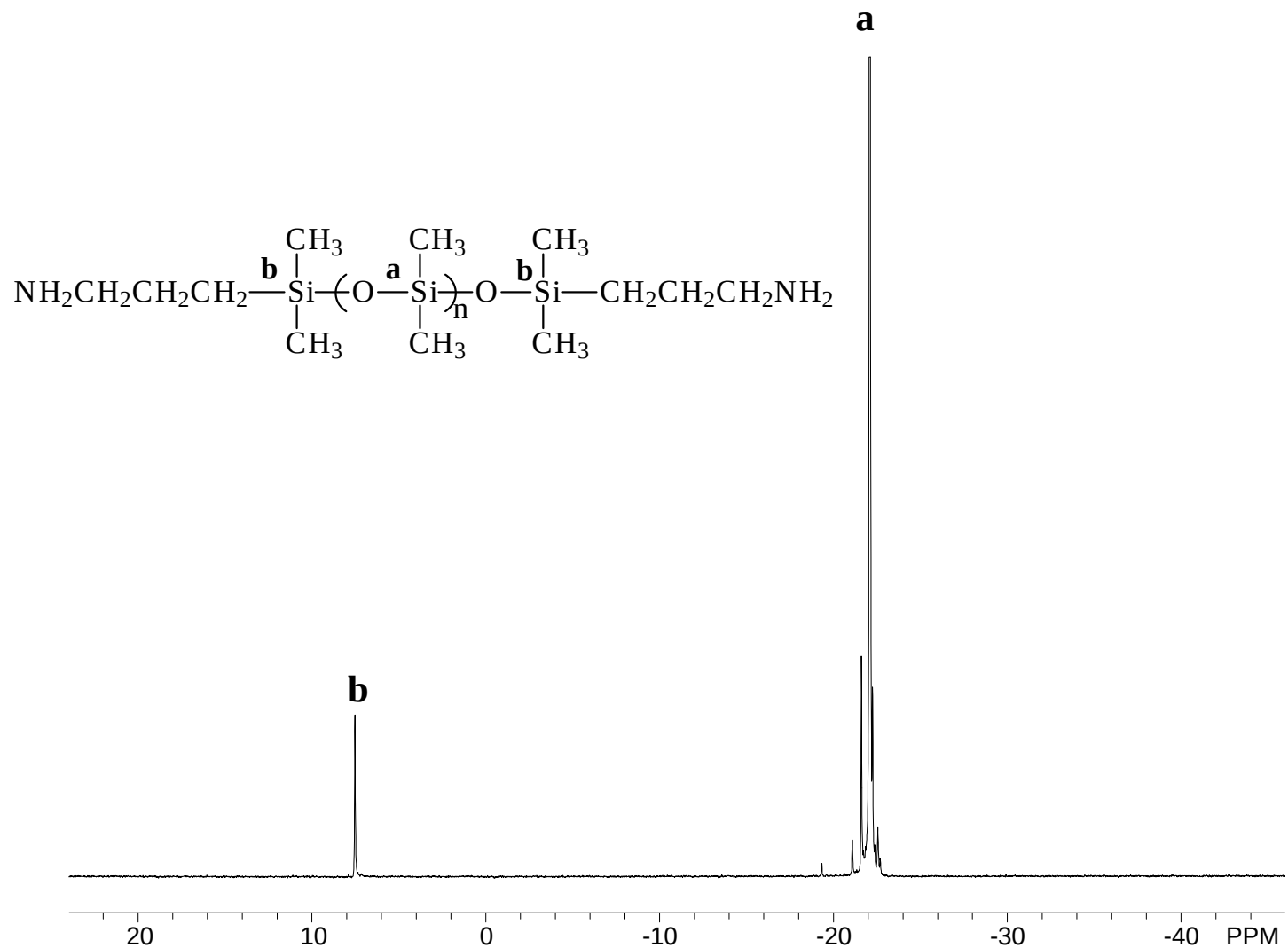


Figure 4.14 ^{29}Si NMR spectrum of primary aminoalkyl terminated PDMS ($M_n=4229$)

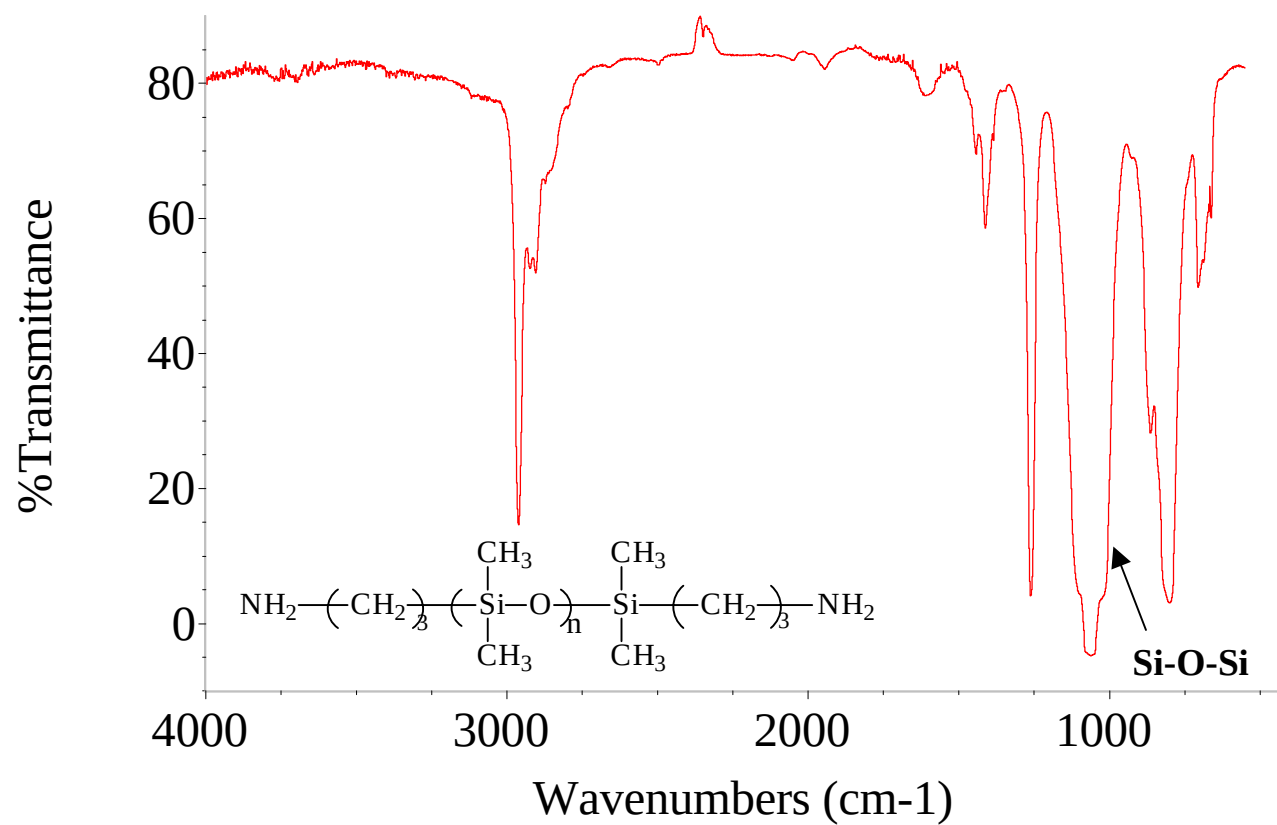


Figure 4.15 FTIR spectrum of primary aminopropyl terminated polydimethylsiloxane ($M_n=1528$)

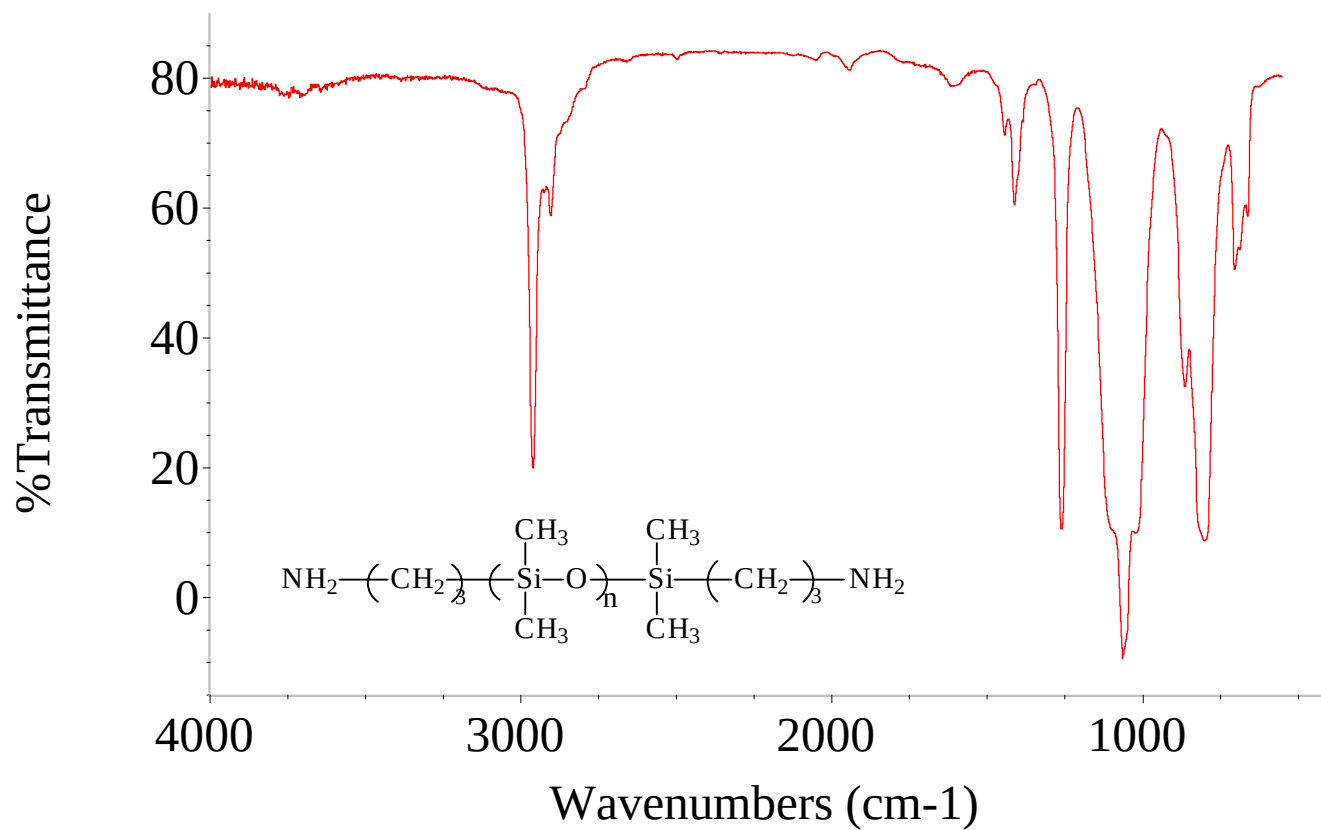


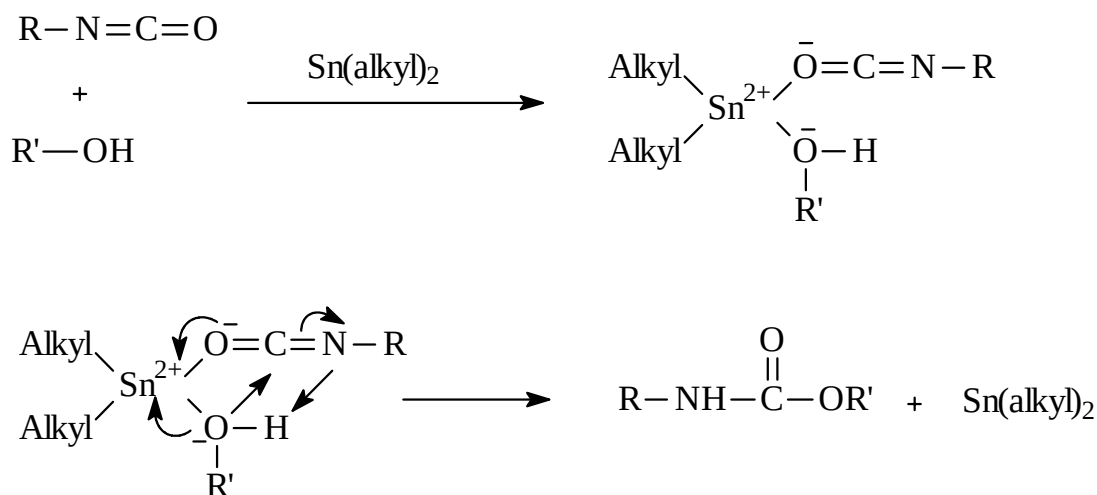
Figure 4.16 FTIR spectrum of primary aminopropyl terminated polydimethylsiloxane ($M_n=2897$)

4.2 Polymer Synthesis and Characterization

4.2.1 Synthesis of PTMO based segmented thermoplastic polyurethanes

Segmented thermoplastic polyurethanes can be synthesized via either bulk or solution polymerization, both of which can be conducted using a one-step or prepolymer 2-step process. In some cases, catalysts, such as tertiary amines and alkyl tin compounds, are added to accelerate the polyaddition reaction. An example of a divalent tin compound acting as a catalyst is illustrated in Scheme 4.1[14].

Bulk polymerization, either one-step or two-step, has been the main industrial process for polyurethane production.[12] On the other hand, solution polymerization has been used more frequently for the laboratory or experimental synthesis of polyurethanes. In this study, one step solution polymerization approach was used to synthesize both the PTMO based polyurethane control and the PDMS containing polyurethanes in order to compare the two polymer systems. The reason that solution polymerization was chosen over bulk polymerization is that PDMS is not miscible with PTMO, BD, and the resulting urethane linkage formed during the polymerization. It is, therefore, less likely that bulk polymerization will produce the well defined, high molecular weight polymers that are more apt to result from solution polymerization.



Scheme 4.1 Proposed mechanism for the alkyl tin catalyst in polyurethane synthesis

The polyurethane synthesis was conducted in a four-neck flask with a temperature controller. The reacting components, PTMO and BD, were not pre-dried. Instead, these two reagents were dissolved in a mixture of DMAc and toluene and the solution was

heated under reflux of toluene, usually at around 130°C. The toluene act as an azotrope to remove trace amounts of water that might come from the DMAc and reagents. If the PTMO has been on the shelf for some time, it can slowly pick up water. Therefore, it is very important to dry the PTMO in a vacuum oven at elevated temperatures, 100°C, before use, or use an azotropic solvent to remove small amounts of water. The same concern applies to the BD as well. The toluene was kept refluxing for 4 hours to completely remove the water in the system. After that, the toluene was removed from the solution since toluene is not a good solvent for the polyurethane. The solution was then cooled to 80°C and MDI was weighed and added to the PTMO solution quickly. The temperature rose 5-10°C after the addition of MDI because of the exothermic reaction. The solution temperature was then maintained at 100°C. During the whole reaction time, the solution temperature was controlled to around 100°C to avoid side reactions and the formation of by-products, as described in Chapter 1. An increase in viscosity was observed 30 minutes after the addition of MDI. In some cases, the solution became very viscous after adding MDI and some freshly distilled dry DMAc was added to dilute the reaction solution in order to promote polymerization. The viscous solution was stirred at 100°C for two hours to ensure the completion of reaction. The polymer solution was then precipitated into water in a blender. The white fibrous polymer was washed with water and dried in a vacuum oven at 100°C for 24 hours.

In order to obtain a high molecular weight polyurethane, the purity of the monomer is very important also. Thus, the MDI was typically freshly distilled and stored under nitrogen at 0°C. Also since the MDI can react with moisture in the air, the pure MDI was distributed into small bottles in the dry box and fresh MDI was used for each reaction.

The molar ratios of MDI, PTMO, and BD were altered in different experiments to produce samples with systematically varied hard segment content. The hard segment in the polyurethane control was derived from the MDI and BD. The theoretical hard segment content is equivalent to the weight percentage of MDI and BD charged.

$$\% \text{ Hard Segment Content} = \frac{\text{wt. of MDI} + \text{wt. of BD}}{\text{wt. of MDI} + \text{wt. of BD} + \text{wt. of PTMO}}$$

The polyurethanes synthesized with different hard segment contents are listed in Table 4.3. The hard segment content varied from 100% to 26%.

Table 4.3 Polyurethanes with different hard segment contents

Sample	PTMO:BD:MDI	Soft Segment %	M _n	M _w
PUR-1	0 : 1 : 1	0	17,000	44,000
PUR-2	1 : 3 : 4	40	22,500	53,900
PUR-3	2 : 2 : 4	63	32,000	67,000
PUR-4	3 : 1 : 4	74	29,600	86,000

By varying the ratio of the isocyanate group to the hydroxy group, the molecular weight of the resulting segmented thermoplastic polyurethane was also altered. These polyurethanes, displaying different molecular weights, are listed in Table 4.4. It should be noted that the molecular weight of the polyurethane increased when the ratio of the isocyanate group to the hydroxy group decreased from 1.02 to 1. A further decrease in the NCO/OH ratio resulted in a decrease in molecular weight.

Table 4.4 Molecular weights of polyurethanes obtained by varying the ratio of isocyanate group to hydroxy group

Sample No.	NCO/OH	Soft wt%	M _n	M _w
PU-1	1.02	63	11,100	21,900
PU-2	1.01	63	23,400	52,200
PU-3	1.005	63	32,600	67,100
PU-4	1.0	63	51,200	100,200
PU-5	0.99	63	39,100	82,300

It should also be noted that an excess of the isocyanate group in the polymerization reaction can cause the formation of allophanate, which results in

branching or crosslinking. However, all the polyurethanes in Table 4.4 were soluble in NMP and no significant increase in polydispersity was observed.

The structure of the polyurethanes was identified by ^1H and ^{13}C NMR, which are provided in Figure 4.17 and Figure 4. 18, respectively. In the proton spectrum, urethane protons were observed at 9.51 ppm. The aromatic protons from the MDI showed at 7.52, 7.18 ppm. The methylene proton from MDI was assigned to the peak at 3.50 ppm. The methylene protons from BD were assigned to peaks at 4.13, and 1.73 ppm. The methylene protons from PTMO soft segments were observed at 1.57, 1.73, 3.39, 4.13 ppm. The ^{13}C NMR spectrum also verified the polyurethane structure.

The structure of the polyurethane control was also verified by FTIR spectroscopy. A typical FTIR spectrum of polyurethane is shown in Figure 4.19. The absorption bands around 3326 cm^{-1} (urethane N-H stretch), 1729 cm^{-1} (free urethane C=O), and 1701 cm^{-1} (H-bonded urea C=O) were assigned to the urethane linkage. The linkage at 1082 cm^{-1} (C-O-C) stretch showed the formation of the urethane linkage. A complete list of FTIR structure assignments is given in Table 4.5

Table 4.5 Assignments of FTIR Spectrum of PTMO based polyurethane (63% SSC)

Wavenumber (cm^{-1})	Assignment
3326	ν (N-H) (H-Bonded)
2940	ν_a (C-H) in CH_2
2855	ν_s (C-H) in CH_2
1729	ν (C=O) urethane non-bonded
1701	ν (C=O) urethane H-Bonded
1597	ν (C-C) aromatic ring
1530	ν (C-N) + δ (N-H) Amide II
1414	ν (C-C) aromatic ring
1313	ν (C-N) + δ (N-H)
1224	ν (C-N) + δ (N-H) Amide III
1115	ν_a (C-O-C) aliphatic ether
1082	ν (C-O-C) in hard segment (O=C-O-C)

ν =stretching mode, ν_a =asymmetric stretching, ν_s =symmetric stretching, δ = in-plane bending or scissoring

4.2.2 Synthesis of PDMS containing segmented thermoplastic polyurethanes

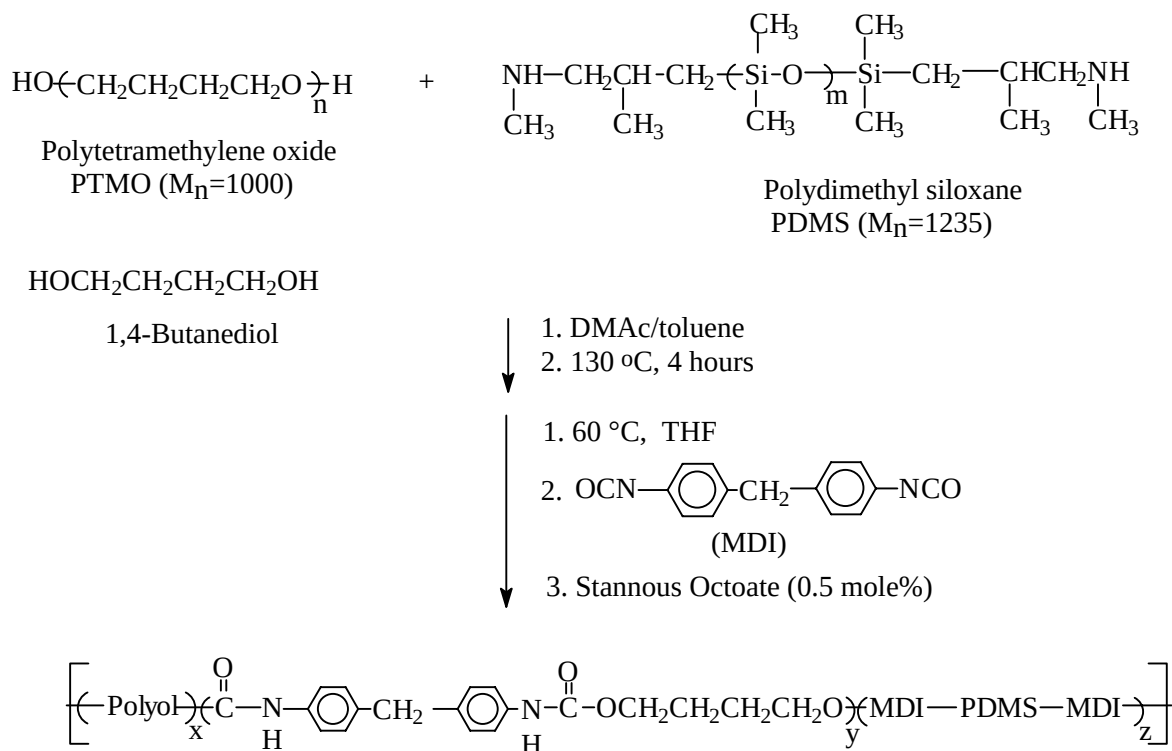
The incorporation of PDMS into polyurethanes has long been of interest because of the unique properties of PDMS, such as extremely low glass transition temperature (-123°C); very low surface energies (20-21 dynes/cm); hydrophobicity; good thermal and oxidative stability; high gas permeability; excellent atomic oxygen resistance; biocompatibility, low dielectric constant, and low solubility parameter.[221,222]

The literature contain a number of good examples of the versatility of PDMS incorporated polyurethanes. For example, the wear resistance of a polyurethane will be improved by blending with PDMS.[299] In addition, PDMS modified polyurethanes have a surface that is minimally attractive to the settlement of marine organisms. A polyurethane-polysiloxane hydrogel has been investigated for potential application in contact lenses because of the high oxygen permeability (up to 600 barrers) of PDMS.[300] Yet another example is that a siloxane based polyurethane ionomer has also been studied for use as a gas separation membrane.[301]

In the synthesis of siloxane-urethane copolymers, the large solubility differences between the PDMS soft segments and other urethane components make it very difficult to choose the right solvent or co-solvents for the polymerization reaction. However, this is a critical factor in this type of reaction (which is also true for many other polymerization reactions involving siloxane and any other organic monomers). This is because the molecular weight of the copolymer, which is essential to produce useful mechanical properties, is highly dependent on the choice of polymerization solvent. It is well known that PDMS is very non-polar and has a very low solubility parameter. It is not soluble in polar solvents such as DMAc, DMF, and NMP, which are the conventional solvents for polyurethane. To promote the homogeneity of the polymerization solution, co-solvents are usually used. One common co-solvent for polyurethane synthesis is DMF or DMAc. The other is usually a PDMS favored solvent such as THF, 2-ethoxyethyl ether (EEE), dioxane, and toluene. The combination of any two of these cosolvents and the ratio between the two can have a large effect on the polymerization reaction. The

synthetic method, one step or two-step, can also influence the solvent effect on the polymerization. In one step polymerization reaction, the soft segments PDMS and PTMO were first dissolved in co-solvents with chain extender BD to make a clear homogenous solution. However, the solubility of the solute changed dramatically after the addition of MDI, since polymerization took place and urethane linkages started to form. This dramatic solubility change can result in premature precipitation of the polyurethane if the solvent can no longer accommodate the polymer. Other factors that affect the molecular weight of the siloxane-urethane copolymer include reaction temperature, reaction time, and choice of catalyst.

The reaction scheme for synthesis of PDMS containing polyurethane via one step solution polymerization is illustrated in Figure 4.2, using DMAc/THF as co-solvents. The absolute molecular weights of the PDMS containing polyurethanes were measured by SEC with universal calibration. A detailed discussion of the SEC measurement of polyurethanes will be given in Section 4.3.



Scheme 4.2 Synthesis of PDMS containing segmented thermoplastic polyurethanes

To study the effect of a solvent on the molecular weight of a copolymer, two sets of polymers of exactly the same composition were synthesized in different solvents. Both sets of PDMS containing polyurethanes contained a total of 65% soft segment, which were composed of both PDMS and PTMO, but had different percentage content of the PDMS (15%-67%). The first set was synthesized in DMAc/THF co-solvents, illustrated in Table 4.6. The second set was synthesized in DMAc/ toluene, illustrated in Table 4.7.

Table 4.6 Molecular weights of PDMS containing polyurethanes synthesized from DMAc/THF

Sample ID	Soft Segment (%)	PDMS (%)	M _n (g/mole)	M _w (g/mole)
PUS15	63	15	26,000	54,000
PUS30	65	28	14,100	26,700
PUS40	65	42	14,400	33,200
PUS50	66	55	14,500	26,100
PUS60	67	67	14,200	27,600

Table 4.7 Molecular weights of PDMS containing polyurethanes synthesized from DMAc/toluene

Sample ID	Soft Segment (%)	PDMS (%)	M _n (g/mole)	M _w (g/mole)
PUS15'	63	15	13,200	24,000
PUS30'	65	28	14,100	26,700
PUS40'	65	42	14,400	33,200
PUS50'	66	55	14,500	26,100
PUS60'	67	67	14,200	27,600

From Table 4.6 and Table 4.7, it should be noted that the molecular weight of the polyurethane with low PDMS content (15%) changed dramatically, in fact almost doubled, when the co-solvents were switched from DMAc/toluene to DMAc/ THF.

However, when the PDMS content was above 28% the influence of the solvent didn't appear to be as significant. This is presumably due to the large solubility change once the polyurethanes with high PDMS content has formed, because it cannot be accommodated by either of the co-solvents. Thus, the molecular weight of polyurethanes with relatively high PDMS content, >28% PDMS, were solvent insensitive. In other words, the two co-solvents gave almost the same solvating power to these materials. A SEC chromatogram of the PDMS containing polyurethane is illustrated in Figure 4.20. It clearly shows that the polymer has a good unimodal distribution.

The effects of the ratio of the co-solvents, reaction time and catalyst on the molecular weight of the copolymer were also investigated to determine optimal reaction conditions. These results are provided in Table 4.9. The ratio of the co-solvent did play an important role in this type of reaction, as can be seen from the molecular weight change when the DMAc/ THF ratio was changed from 1:3 to 1:1. The 3 hours reaction time appeared to be sufficient for this type of reaction. This is not surprising since the PDMS was secondary aminoalkyl terminated and had a higher reactivity toward MDI than hydroxy terminated PTMO and BD. The reactivity differences among the components can result in some unique polymer structures. For example, since the reactivity of the secondary aminoalkyl terminated PDMS is higher than that of the PTMO and BD, its preferable reaction with MDI may result in a PDMS-MDI-PDMS structure. These structures are mainly consisted of PDMS and MDI. After most of the PDMS is consumed, the PTMO soft segments and the BD start to incorporate into the polymer chain. The choice of catalyst is also very important in determining molecular weight. For example, in the absence of a catalyst, the molecular weight reached only 8,500 g/mole after 3 hours. However, when a catalyst was added to the same reaction, the molecular weight of the copolymer was more than doubled in the same 3 hour period.

The structure of the PDMS containing polyurethanes was identified by ^1H and ^{13}C NMR. In the ^1H NMR spectrum, urethane protons were observed at 9.38 ppm and 8.09 ppm, due to urethane and urea linkages. The aromatic protons from the MDI appeared 6.93, 7.03, 7.37 ppm. The methylene protons from MDI were assigned to peak at 3.72 ppm. The methylene protons from BD were assigned to peaks at 4.00 and 1.58 ppm. The methylene protons from PTMO soft segments were observed at 1.43, 1.58, 3.24, 4.00

ppm. The protons from the aminoalkyl end-group of the PDMS were assigned to peaks at 0.32, 0.53, 0.82, 1.912.89, 3.09 ppm. The ^{13}C NMR also verified the structure of the polyurethane structure.

The structure of the PDMS containing polyurethane was also verified by FTIR spectroscopy. A typical FTIR spectrum of a PDMS containing polyurethane is shown in Figure 4.22. The absorption bands around 3320 cm^{-1} (urea N-H stretch) and 1645 cm^{-1} (H-bonded urea C=O) were assigned to the urea linkage. The peak at 3339 cm^{-1} (urethane N-H stretch), 1699 cm^{-1} (H-bonded urethane C=O), and 1080 cm^{-1} (C-O-C) stretch showed the formation of the urethane linkage. The peaks at 1258 cm^{-1} (sym. CH_3 bending), 1020 and 1106 cm^{-1} (Si-O-Si stretching), 803 cm^{-1} (CH_3 rocking) were assigned to the PDMS in the copolymer. A complete list of FTIR structure assignments is given in Table 4.8

The structural differences between the PDMS, the PDMS containing polyurethanes with different PDMS content, and polyurethane control can be clearly illustrated by FTIR spectroscopy. The major peaks that were monitored included a urea group at 1645 cm^{-1} , and a C-H group at 1258 cm^{-1} . The urea peak and C-H peak clearly increased with an increase of PDMS content in the polyurethanes.

In order to determine whether the PDMS was completely incorporated into the polyurethane backbone, the polyurethane was subjected to elemental analysis. The Si% in the polyurethane was calculated to be 13.7%, and was found to be 13.79%, which showed that the PDMS was completely incorporated into the polyurethane chains.

Table 4.8 Assignments of FTIR Spectrum of PDMS containing polyurethane (43% PDMS)

Wavenumber (cm ⁻¹)	Assignment
3339	ν (N-H) urethane H-Bonded
3320	ν (N-H) urea H-Bonded
2958	ν_a (C-H) in CH ₂
2857	ν_s (C-H) in CH ₂
1728	ν (C=O) urethane non-bonded
1699	ν (C=O) urethane H-Bonded
1645	ν (C=O) urea H-Bonded
1595	ν (C-C) aromatic ring
1530	ν (C-N) + δ (N-H) Amide II
1412	ν (C-C) aromatic ring
1312	ν (C-N) + δ (N-H) Amide III
1258	δ (C-H) in Si-CH ₃
1106	ν_a (Si-O-Si) in Si-O-Si
1080	ν_a (C-O-C) aliphatic ether
1020	ν_a (Si-O-Si) in Si-O-Si
803	ρ (C-H) in Si-CH ₃

ν =stretching mode, ν_a =asymmetric stretching, ν_s =symmetric stretching, δ = in-plane bending or scissoring, ρ =in-plane bending or rocking

Table 4.9 Effect of co-solvent ratio, reaction time and catalyst on the molecular weight of 15 wt% PDMS containing segmented thermoplastic polyurethanes

Sample ID	Solvent ¹	Catalyst (S.O) ²	Temperature (°C)	Time (Hours)	Concentration (wt%)	M _n (g/mole)	M _w (g/mole)
PUSI	D/T (1:3)	Y	60	3	30	21,000	39,600
PUSII	D/T (1:1)	Y	60	3	30	26,000	51,100
PUSIII	D/T (1:1)	Y	60	6	30	22,700	45,000
PUSIV	D/T (1:1)	N	60	3	30	8,500	15,500

1. DMAc/THF, 2. Stannous Octoate

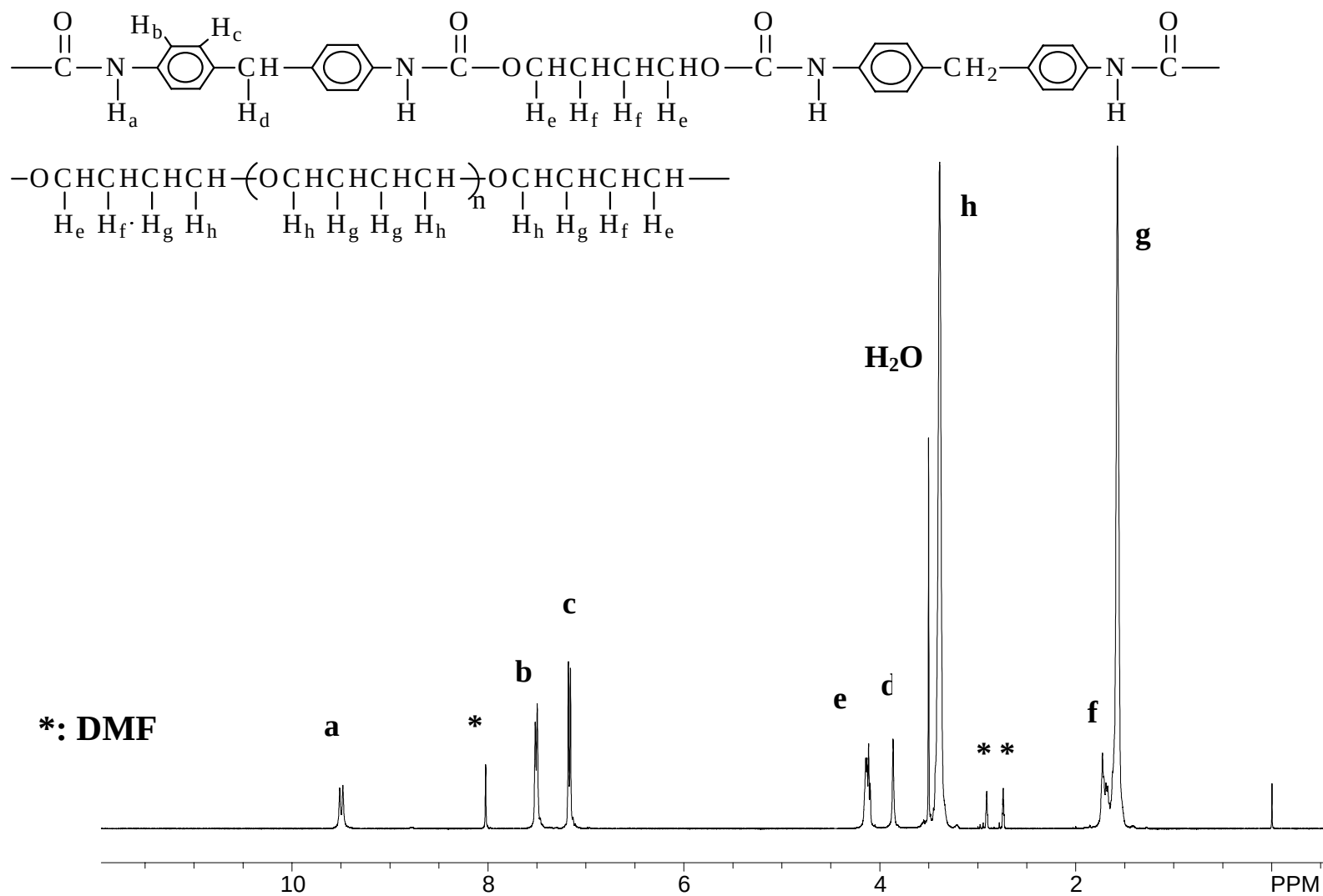


Figure 4.17 ^1H NMR spectrum of polyurethane control (63wt% soft segment)

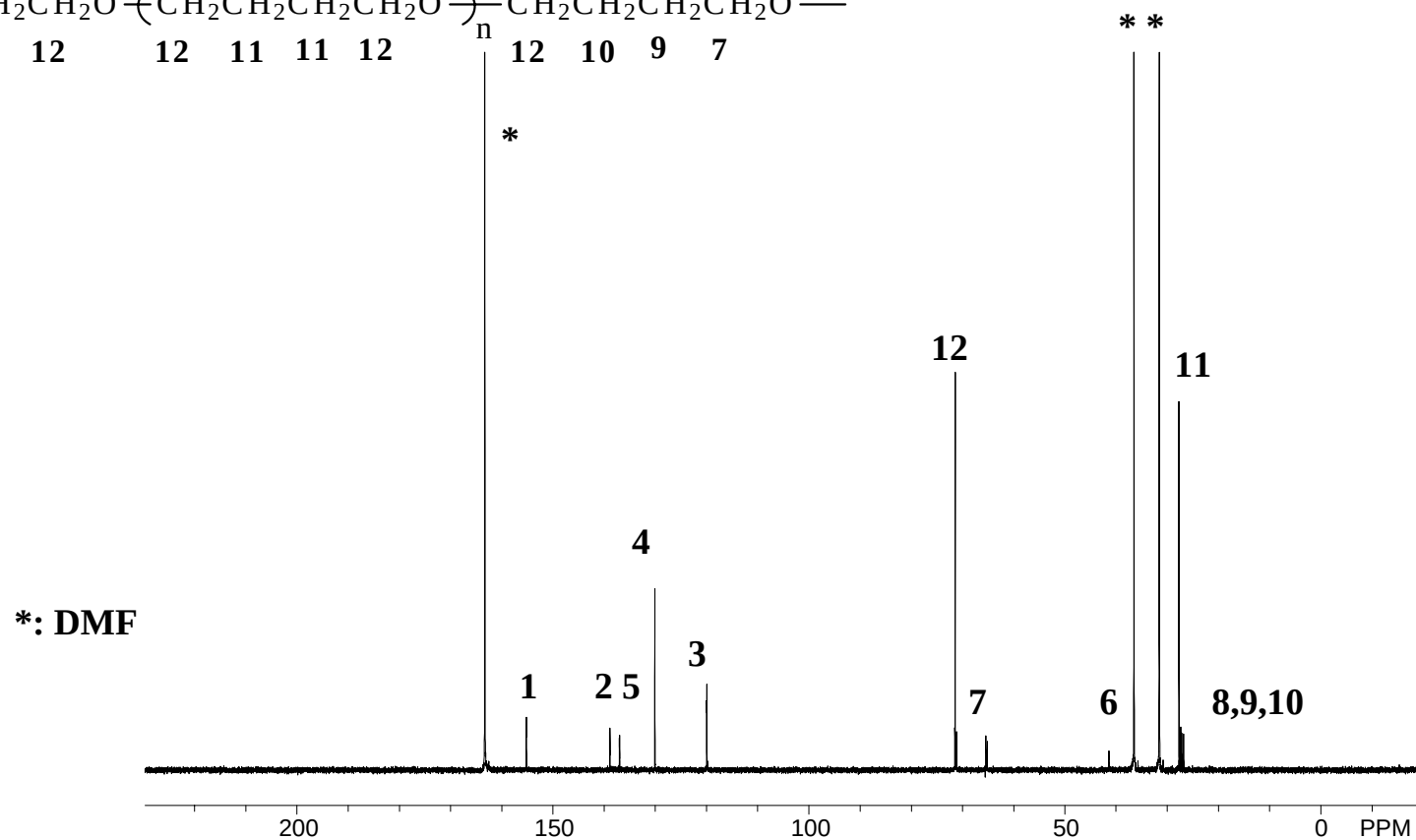
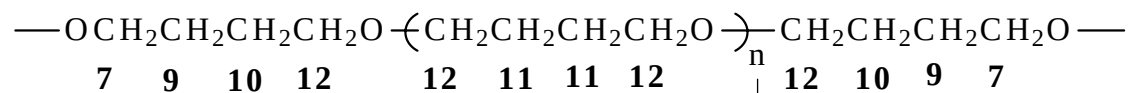
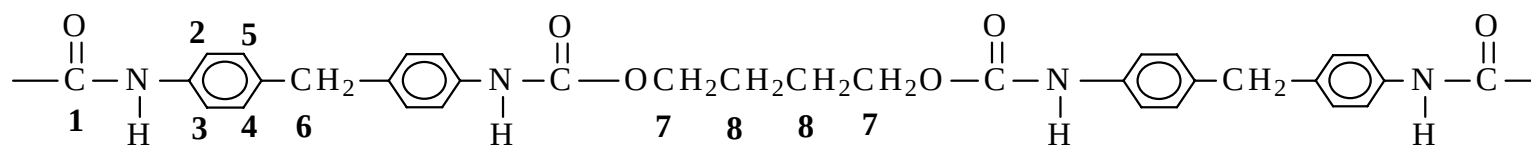


Figure 4.18 ^{13}C NMR spectrum of polyurethane control (63 wt% soft segment)

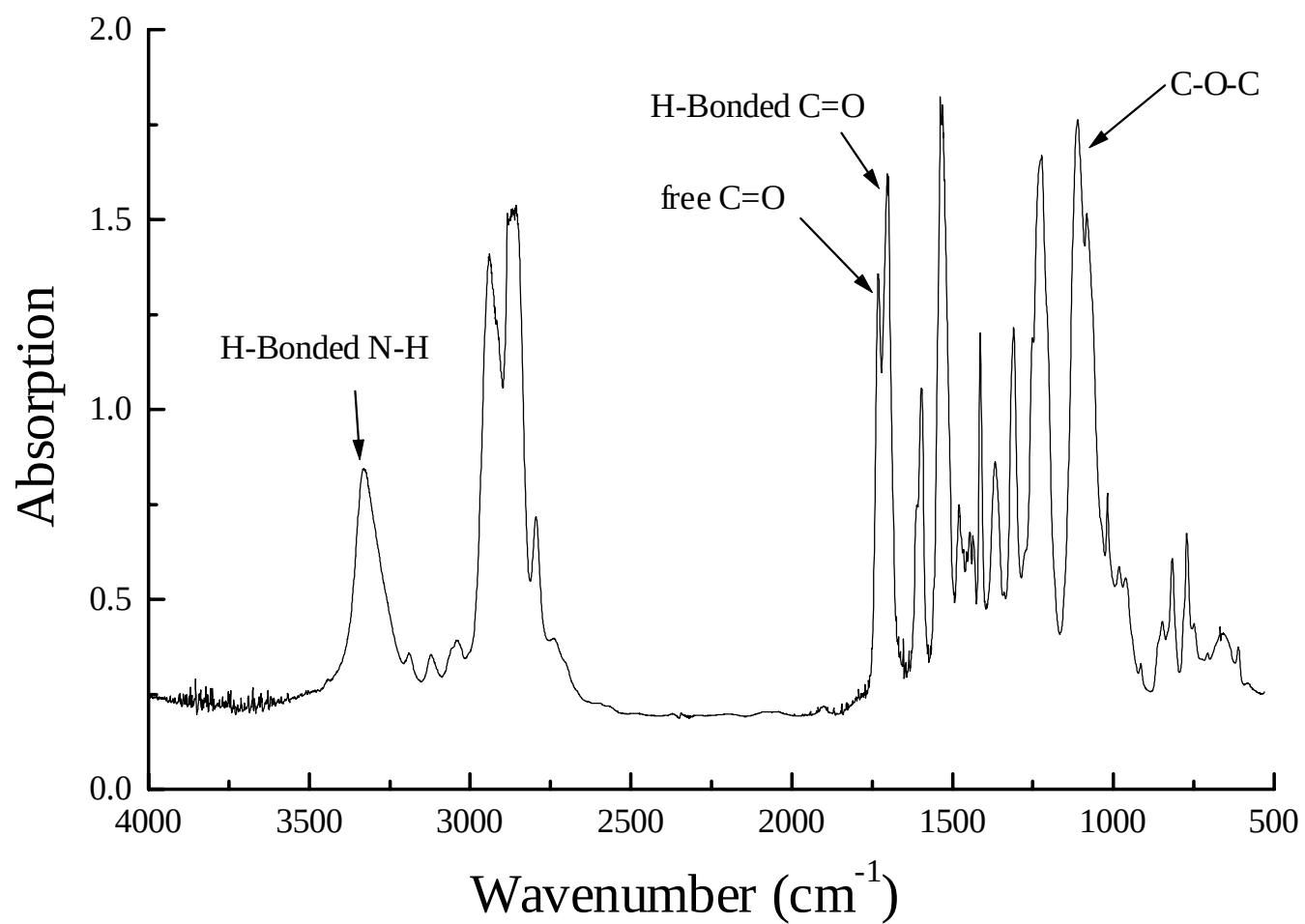


Figure 4.19 FTIR spectrum of PTMO based polyurethane control (63% soft segment)

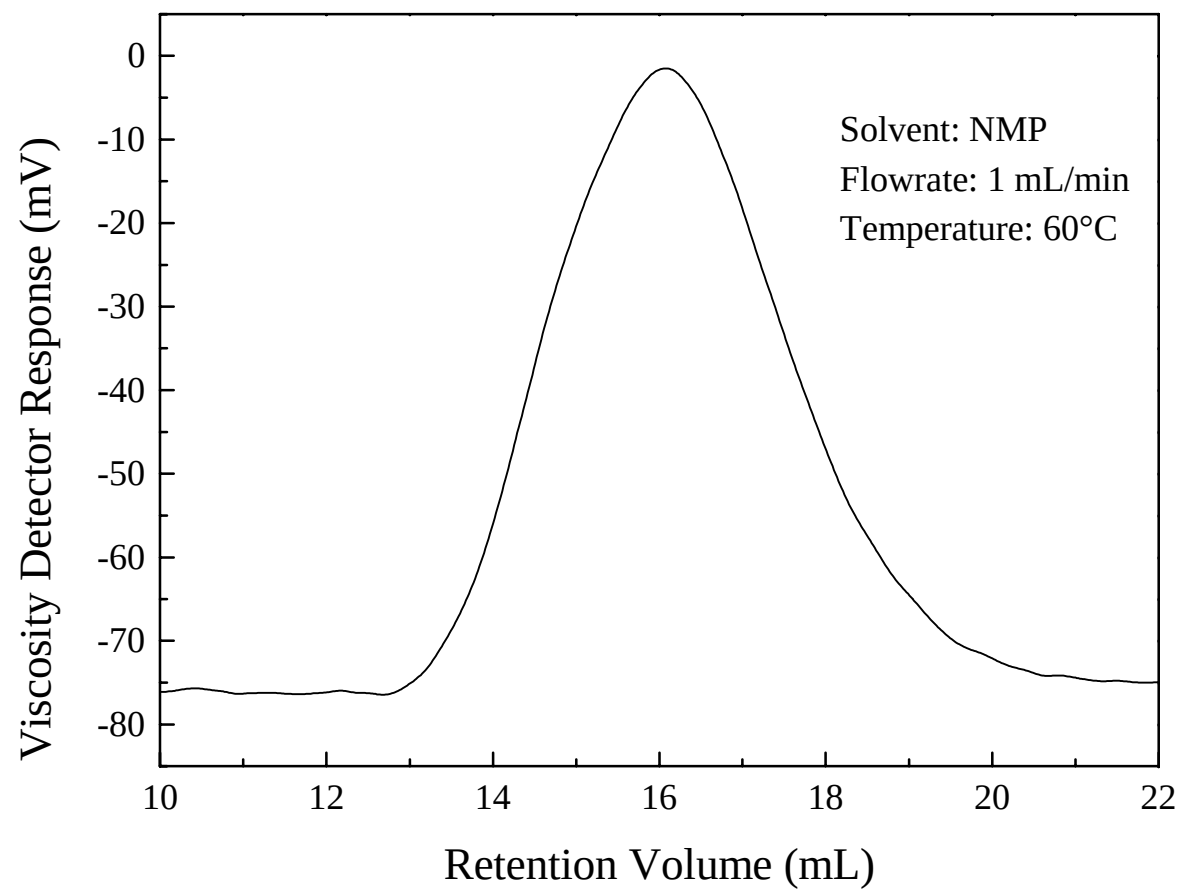


Figure 4.20 GPC chromatogram of PDMS containing segmented thermoplastic polyurethane

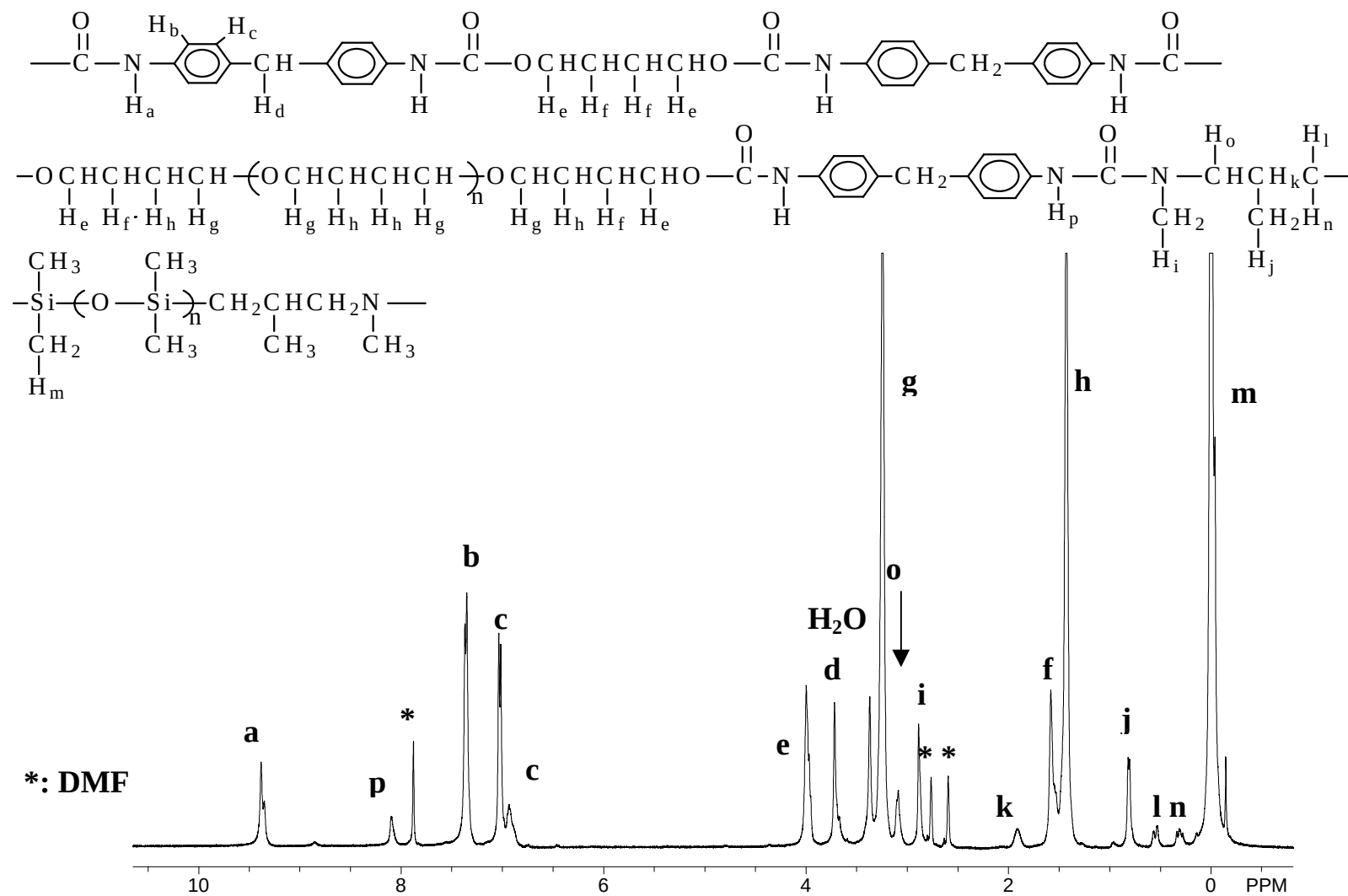


Figure 4.21 ^1H NMR spectrum of PDMS containing polyurethane (43 wt% PDMS)

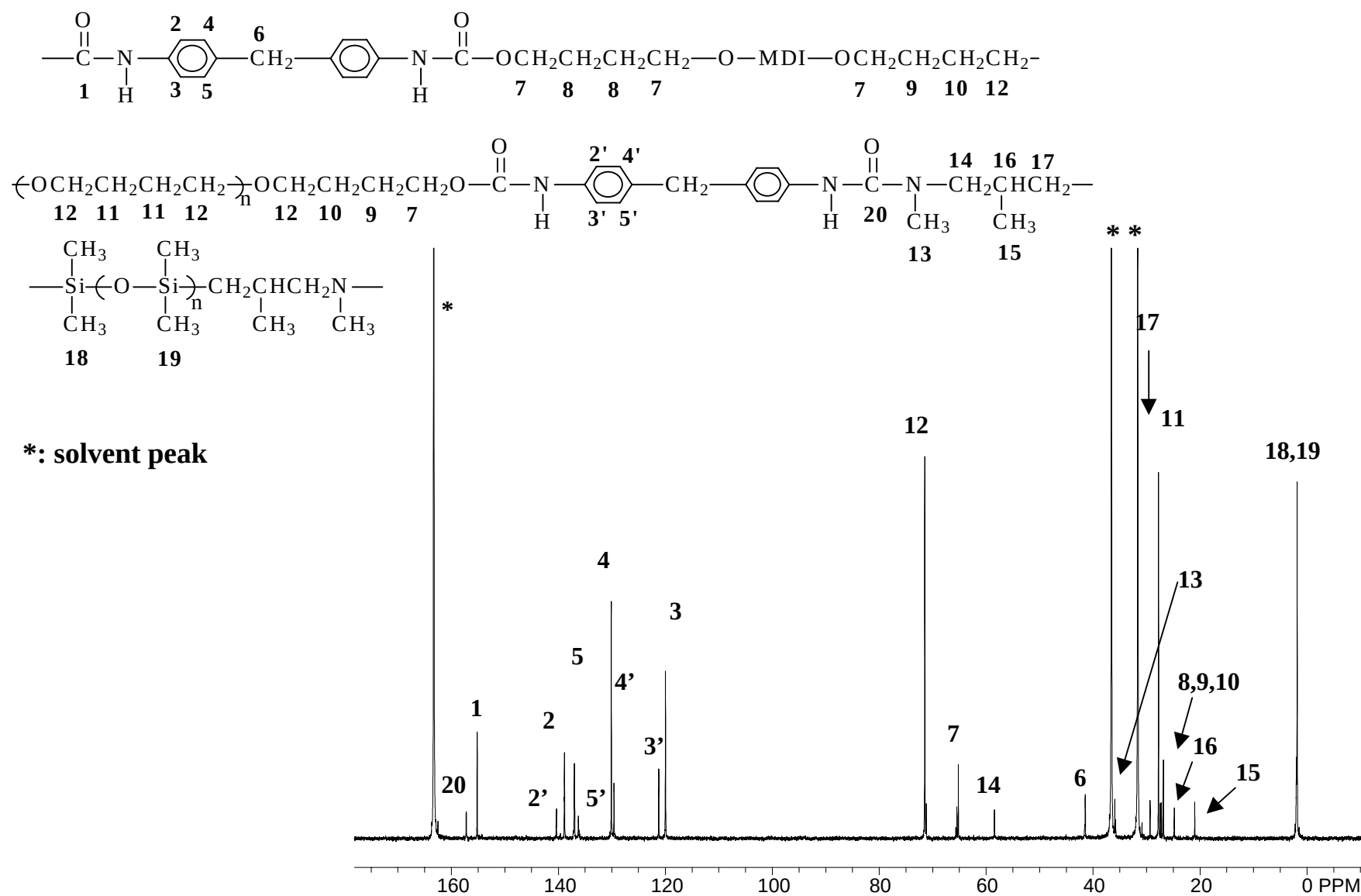


Figure 4.22 ^{13}C NMR spectrum of PDMS containing polyurethane (43 wt% PDMS)

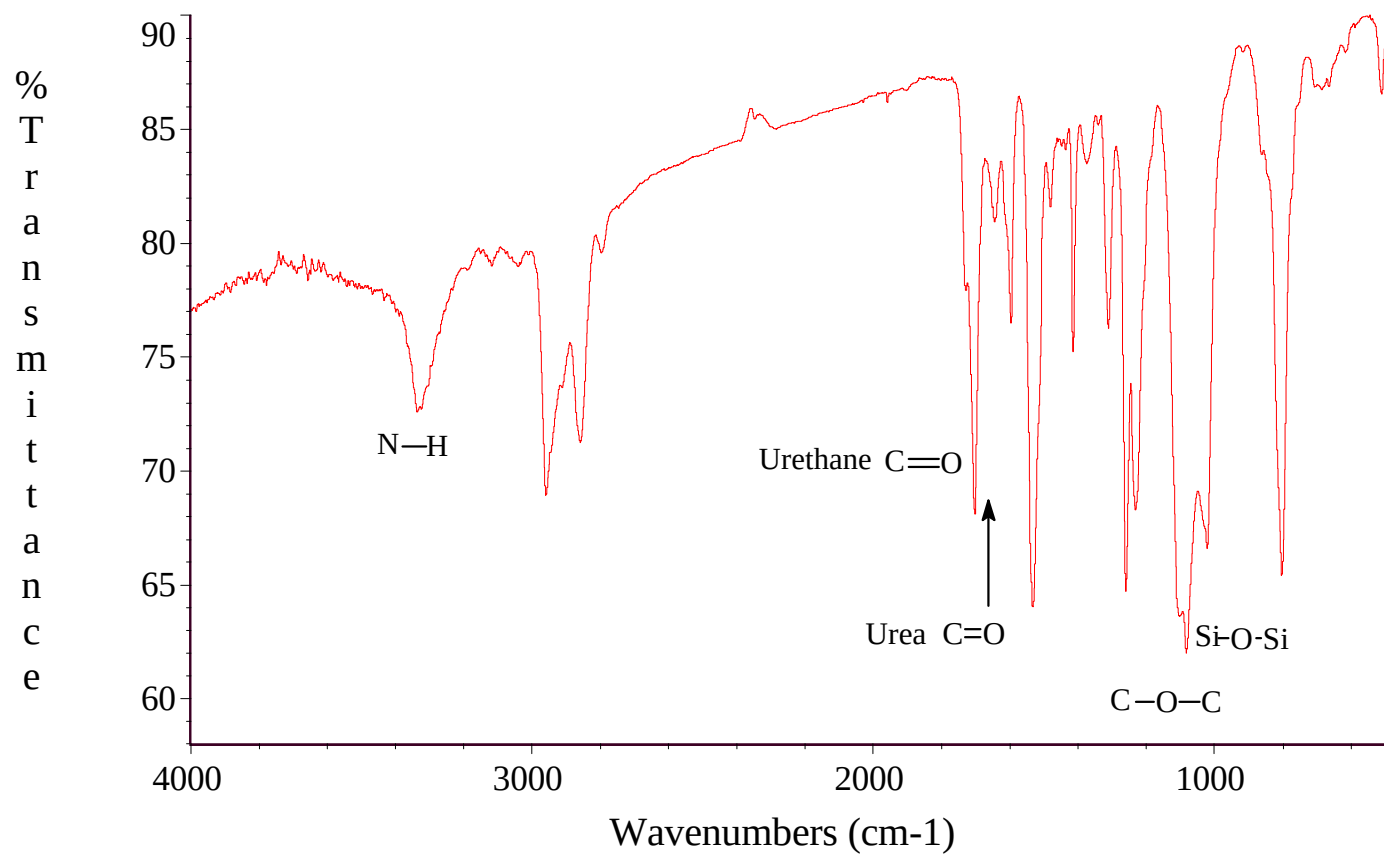
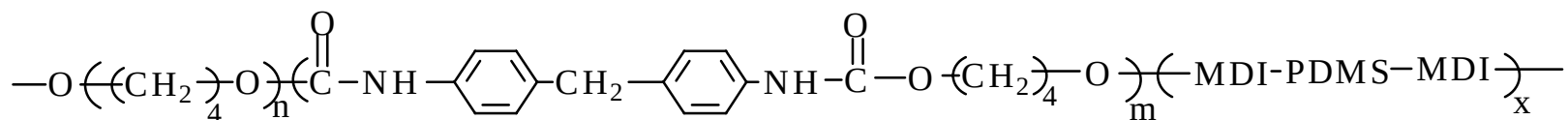


Figure 4.23 FTIR spectrum of PDMS containing polyurethane (43% PDMS)

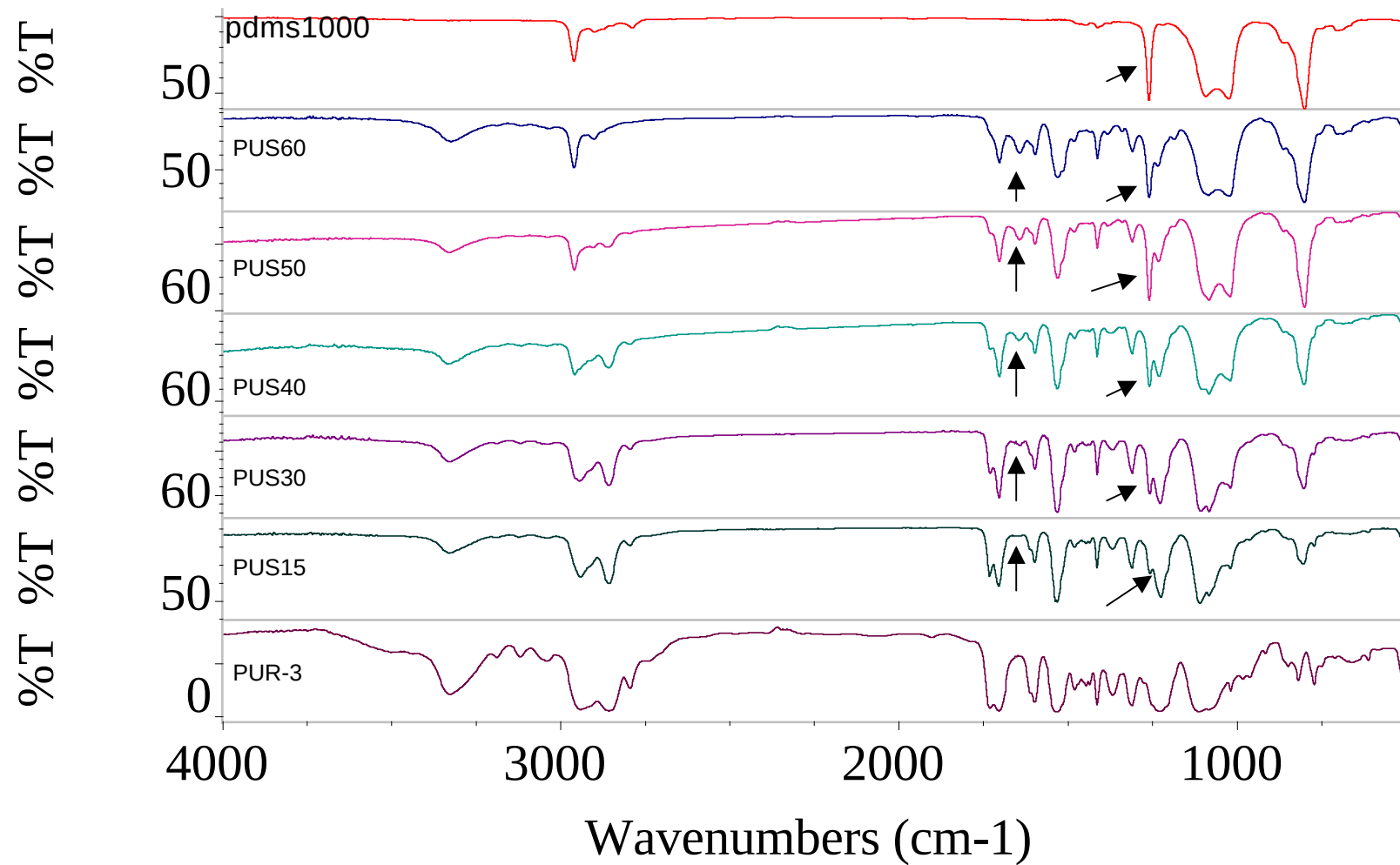


Figure 4.24 FTIR stack spectra of PDMS (pdms1000), PDMS containing polyurethanes (15-67%PDMS) (PUS15-PUS60), and polyurethane control (PUR-3)

4.3 SEC study of segmented thermoplastic polyurethanes

Size exclusion chromatography (SEC) is widely used to obtain molecular weight (MW) and molecular weight distribution (MWD). In the conventional mode, a SEC column is first calibrated with a polystyrene standard, whose molecular weight is known, in order to determine the relationship between elution volume and the molecular weight of the polystyrene standard. Then, the molecular weight of an unknown polymer is determined by comparing the elution volume of this polymer to that of the polystyrene standard, assuming the same elution volume results in the same molecular weight. Therefore, this molecular weight is actually referred to as the molecular weight compared to polystyrene. Obviously, the conventional method cannot yield the absolute molecular weight of a polymer since the elution volume is only directly proportional to the size of the polymer, which in turn is related to the hydrodynamic volume of the polymer. The hydrodynamic volume of a polymer is defined as the molecular weight of the polymer times the intrinsic viscosity of the polymer, as shown in the following equation:

$$V_h = [\eta] \times M$$

It can be clearly seen from the above equation that elution volume is directly proportional to the product of the intrinsic viscosity, $[\eta]$, and the molecular weight of the polymer. Therefore, the molecular weight of a polymer obtained by comparing it to polystyrene may, in fact, dramatically deviate from its true value.

In an effort to overcome this problem, a variety of detectors have been developed, the most important of which are the viscosity detector and the light scattering detector. Unfortunately, determining the molecular weight of segmented copolymer is somewhat more complicated.

In order to measure the absolute molecular weight of a polyurethane and a PDMS containing polyurethane, a universal calibration curve for the SEC system was constructed using a standard polystyrene with known molecular weight and measured intrinsic viscosity. The universal calibration curve is provided in Figure 4.25.

4.3.1 Polyurethanes with different molecular weights

Segmented thermoplastic polyurethanes of six different molecular weights were analyzed by SEC, using an on-line viscometric detector in combination with a regular concentration detector. This enabled the actual intrinsic viscosity distribution of the separated polymeric samples to be measured at the outlet of the chromatographic column. The chromatographs are illustrated in Figure 4.26.

Different polymer samples with the same elution volume will have the same hydrodynamic volume, as seen in the following relationship:

$$[\eta]_{sty,i} [M]_{sty,i} = [\eta]_{pu,i} [M]_{pu,i}$$

Thus, the absolute molecular weight of a polyurethane can be calculated based on the intrinsic viscosity value of each polyurethane fraction measured directly by the viscosity detector. These data can be processed by SEC software through universal calibration, to directly provide the absolute average molecular weight and molecular weight distribution of a polymer sample. The intrinsic viscosity $[\eta]$ and molecular weight from each data point were plotted in accordance with the log-log representation of the Mark-Houwink equation:

$$\log[\eta] = \log K + \alpha \log M$$

This plot is illustrated in Figure 4.27. The values K and α were obtained from the intercept and slope of the plot, and results are shown in Table 4.10. The molecular weight value of each polyurethane sample matches very well with its intrinsic viscosity and radius gyration values.

Since the chromatographic column can separate a single polyurethane sample into different fractions, the intrinsic viscosity of each fraction can be directly measured by the viscosity detector. The intrinsic viscosity distribution of a polyurethane sample is plotted against the elution volume and compared with polystyrene standard with the same elution volume. This plot is provided in Figure 4.28. It clearly illustrates that the intrinsic viscosity is much higher for the polyurethane than for the polystyrene standards at a given elution volume. The molecular weight of the polyurethane sample is

also plotted against the elution volume and compared with the polystyrene standard at the same elution volume in Figure 4.29. The true molecular weight of the polyurethane was found to be much lower than the corresponding polystyrene standard. In other words, the molecular weight of the polyurethane measured from SEC without universal calibration and intrinsic viscosity values is much higher than the true molecular weight. Therefore, comparing the molecular weight of the polyurethane and polystyrene could provide seriously misleading information.

Table 4.10 Molecular Weights and Mark-Houwink Parameters of Segmented Polyurethanes with Different molecular weights (SSC 63%)

Sample I.D.	M _n (g/mol)	M _w (g/mol)	M _w /M _n	[η] (dL/g)	log K	α	R _g (nm)
PU-1'	13,300	39,500	2.97	0.52	-2.62	0.52	8.16
PU-2'	19,100	46,000	2.41	0.58	-2.59	0.51	9.14
PU-3'	32,800	66,700	2.03	0.73	-2.67	0.53	11.23
PU-4'	39,900	94,900	2.38	1.16	-2.73	0.55	14.65
PU-5'	51,200	100,200	1.96	1.42	-3.08	0.63	16.14
PU-6'	64,000	146,400	2.29	1.57	-2.96	0.62	18.60

4.3.2 Polyurethanes with Different Compositions

Five polyurethane samples with different soft segment contents (SSC%) were analyzed by SEC. The average molecular weights and molecular weight distributions of the samples were calculated. The results are provided in Table 4.11.

The α parameters calculated from Mark-Houwink plots decrease with increasing soft segment content. Since α parameters represent the solvent quality, this trend indicates that polar NMP is a better solvent for the hard segments than for the soft segments.

Table 4.11 Molecular Weights and Mark-Houwink Parameters of Segmented Polyurethanes with Different Compositions

Sample I.D.	SSC (wt%)	M _n (g/mol)	M _w (g/mol)	M _w /M _n	[η] (dL/g)	log K	α
PU-00	0	15,100	27,400	1.82	0.71	-3.21	0.70
PU-20	20	22,000	40,800	1.86	0.82	-3.15	0.67
PU-40	40	29,500	57,400	1.95	0.94	-2.98	0.62
PU-60	60	39,900	94,900	2.38	1.16	-2.73	0.55
PU-80	80	23,700	46,400	1.96	0.57	-2.79	0.55

4.3.3 Siloxane Containing Segmented Polyurethanes

Five PDMS containing polyurethanes with similar soft segment concentration (~63 wt%SSC) but a different PDMS content (15% - 67wt %) were analyzed by SEC. In addition to the PTMO soft segment, a secondary amino alkyl terminated polydimethylsiloxane (PDMS) was used as a co-soft segment. The results are shown in Table 4.12.

From the results provided in Table 4.12 one notes that the intrinsic viscosity [η], the α value and the radius of gyration R_g all decrease with increasing PDMS content, except for sample PUS-67. This implies that the NMP solvent is a poor solvent for the siloxane segments (NMP is a non-solvent for the pure polysiloxane). Moreover, the intrinsic viscosity decreases with increasing PDMS content at the same hydrodynamic volume, which is illustrated in Figure 4.30.

Table 4.12 Molecular Weight and Mark-Houwink Parameters of Siloxane Containing Segmented Polyurethanes

Sample I.D.	PDMS (wt%)	M _n (g/mol)	M _w (g/mol)	[η] (dL/g)	log K	α	R _g (nm)
PUS-00	0	13,300	39,500	0.52	-2.62	0.52	8.16
PUS-15	15	16,200	33,700	0.51	-2.67	0.52	8.03
PUS-28	28	14,100	26,700	0.39	-2.45	0.46	6.77
PUS-42	42	14,400	33,200	0.36	-2.25	0.40	7.10
PUS-55	55	14,500	26,100	0.23	-2.47	0.42	5.72
PUS-67	67	12,900	27,100	0.20	-3.18	0.57	5.39

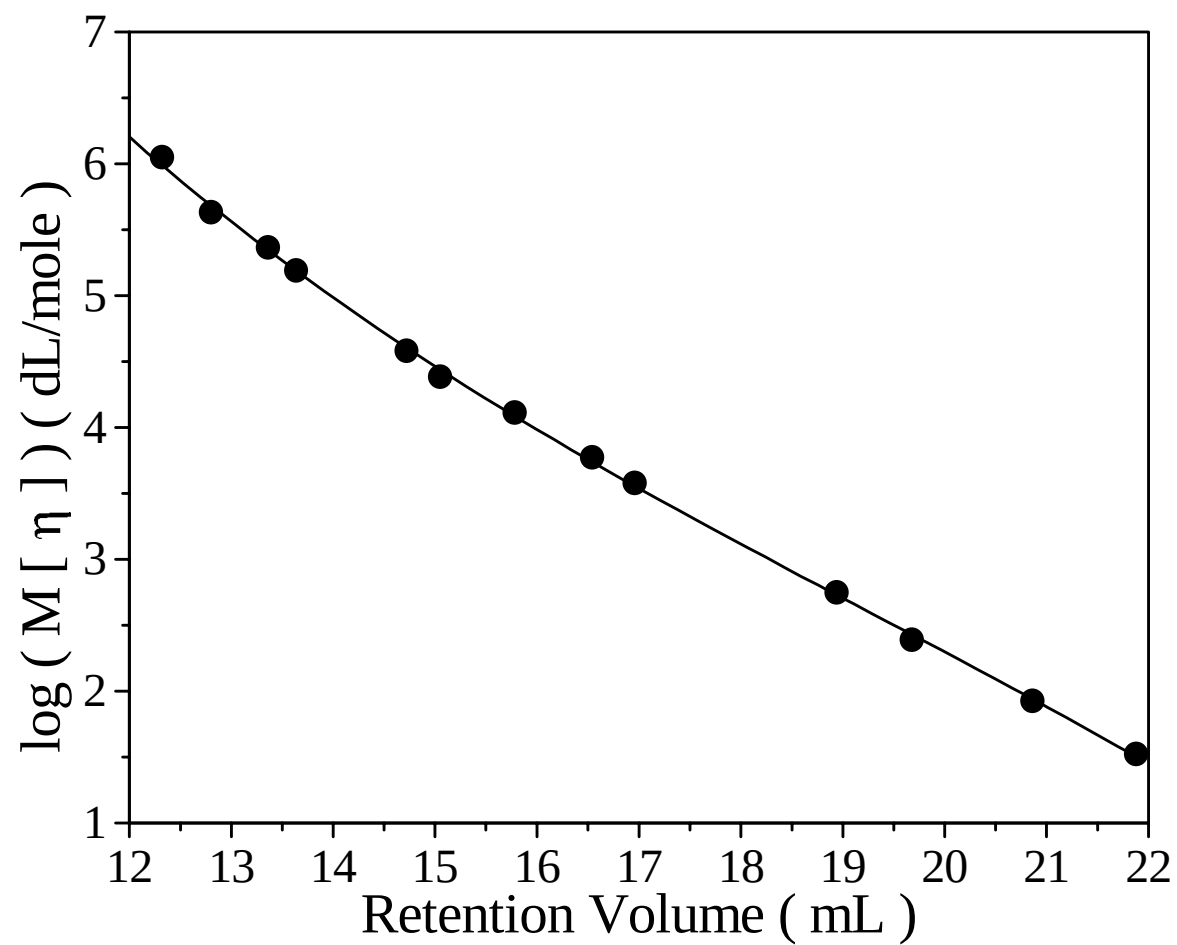


Figure 4.25 Universal calibration based on PS standards in NMP + 0.02M P_2O_5 systems at 60°C.

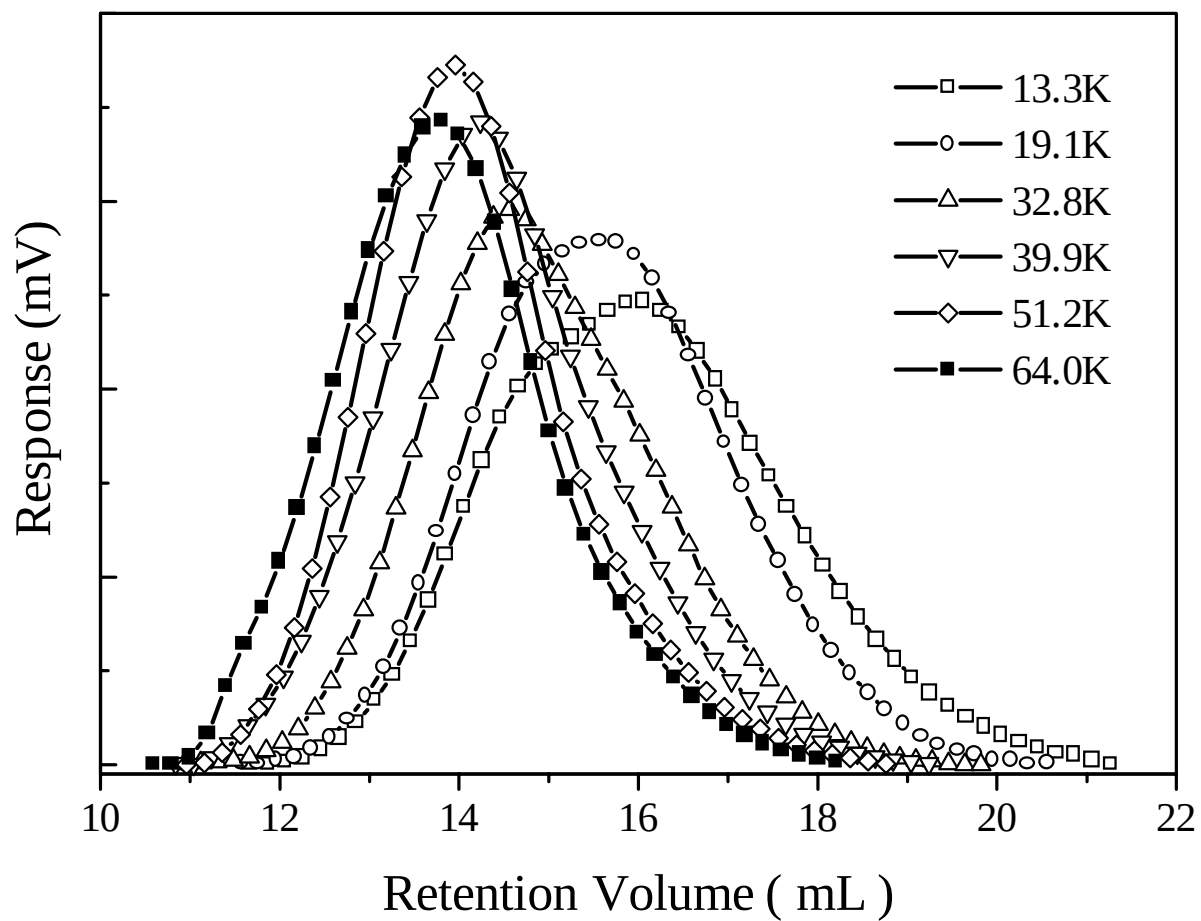


Figure 4.26 Chromatography of segmented polyurethanes with different molecular weight

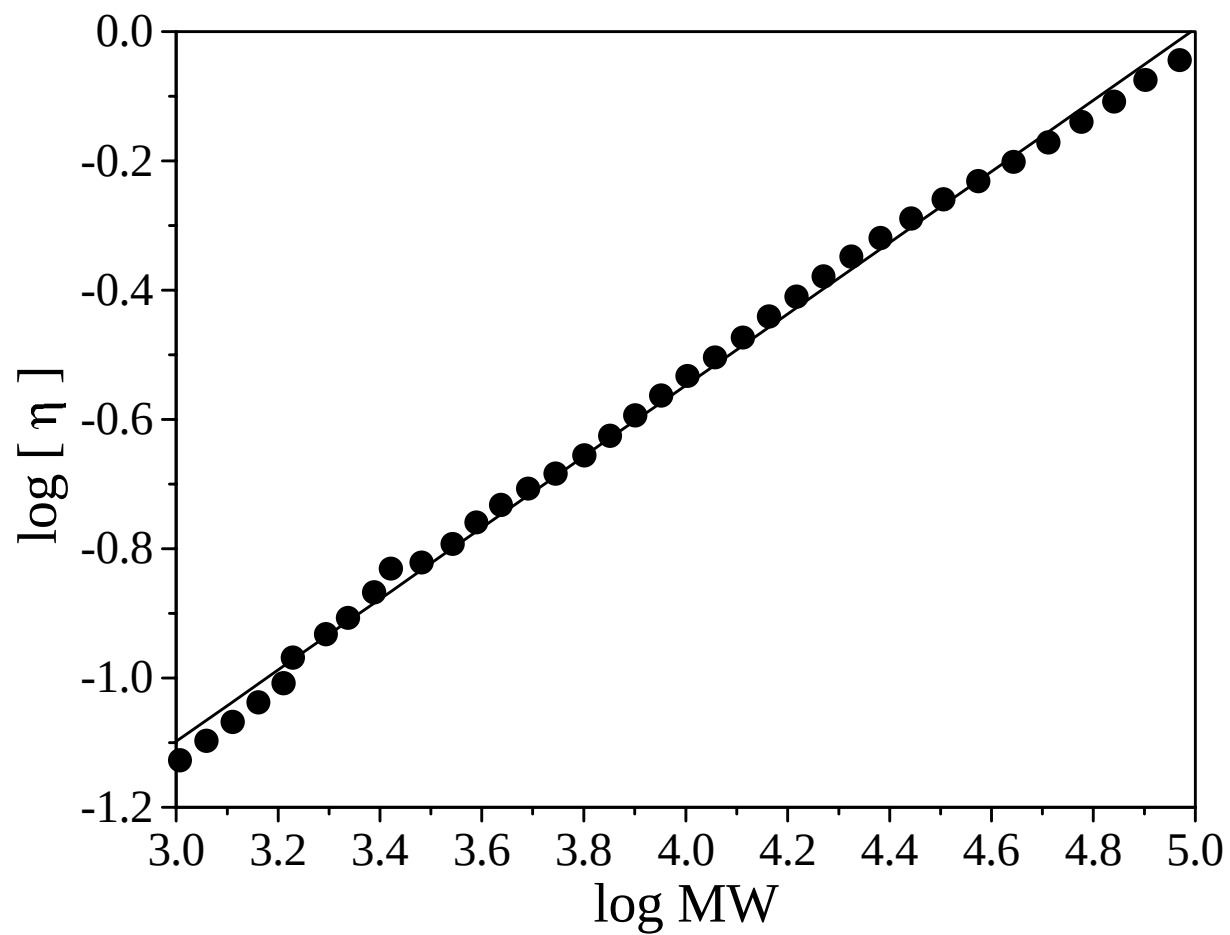


Figure 4.27 Mark-Houwink plot for segmented polyurethanes ($M_n=13,300$) in NMP with 0.02M P_2O_5 at 60°C.

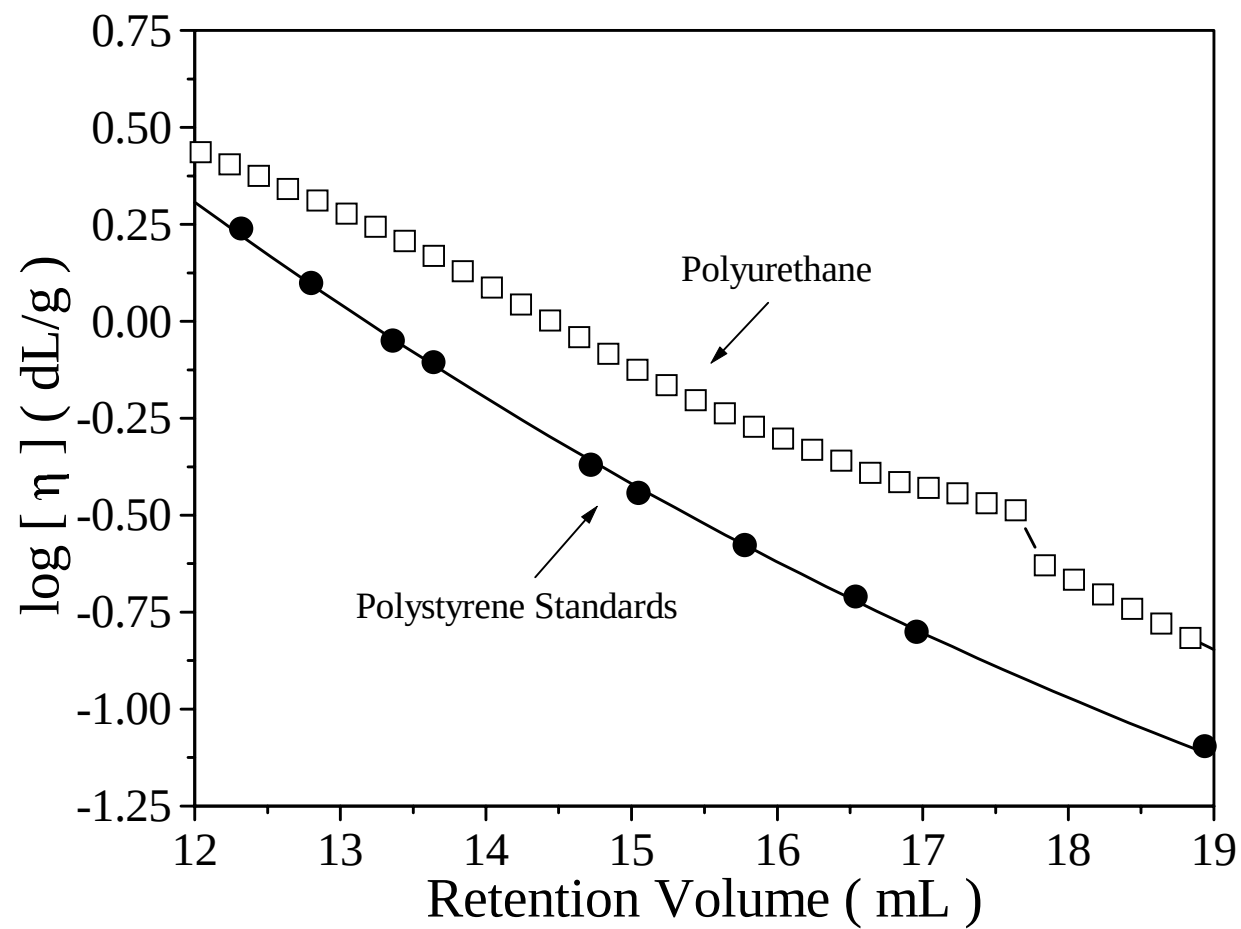


Figure 4.28 Intrinsic viscosity comparison of polyether urethane ($M_n = 39,900$) and polystyrene standards

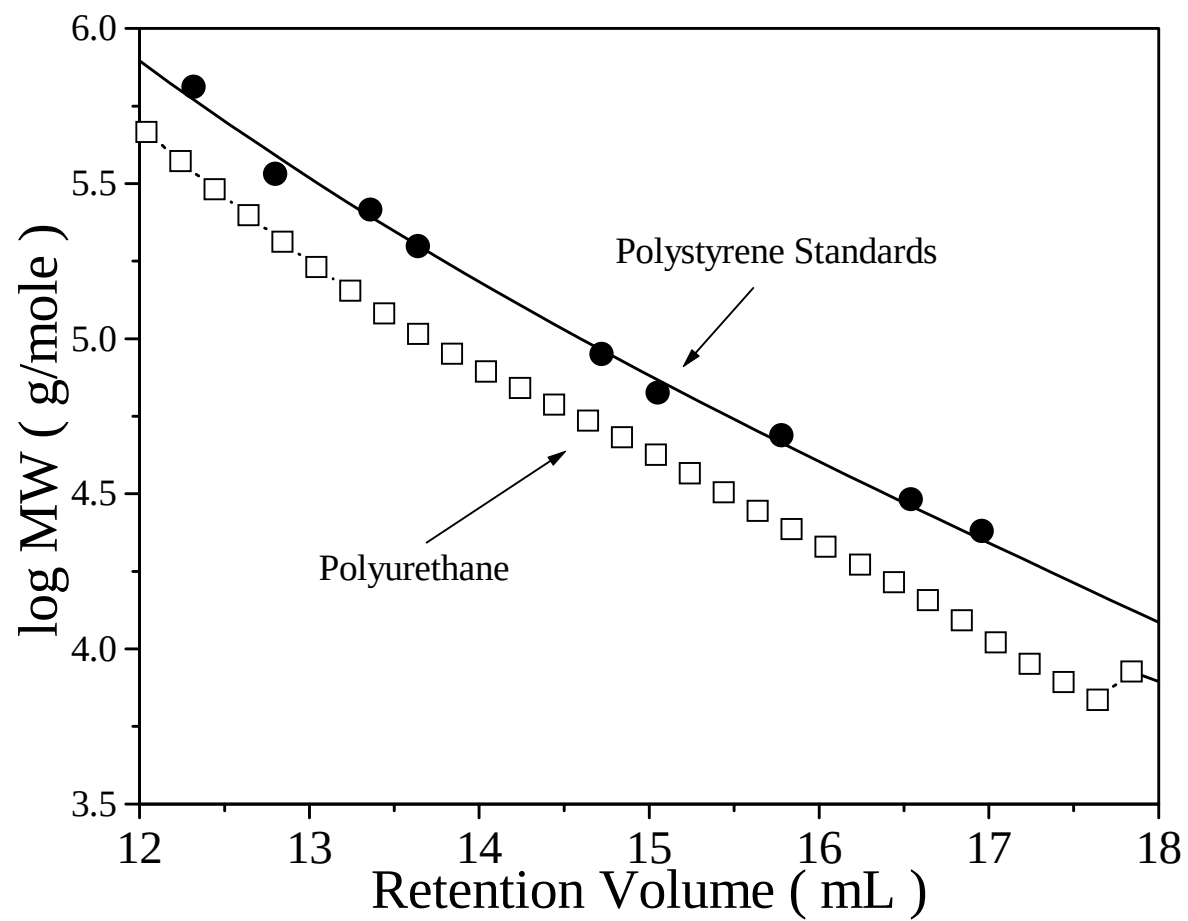


Figure 4.29 Molecular weight comparison of polyether urethane ($M_n = 39,900$) and polystyrene standards

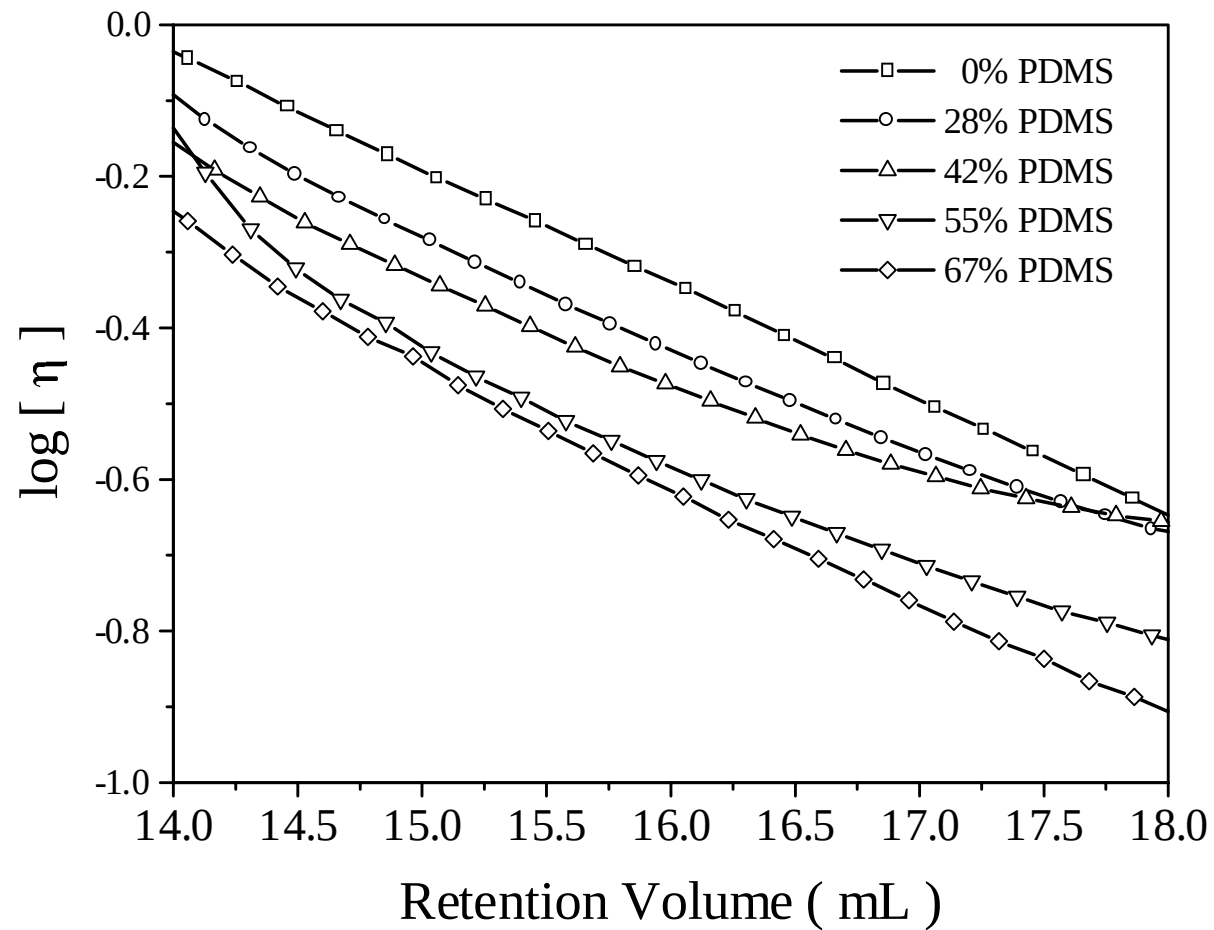


Figure 4.30 Intrinsic viscosity comparison of siloxane containing segmented polyurethanes with different PDMS contents

4.4 Structure-Property relationships of polyurethanes and PDMS containing polyurethanes

Segmented thermoplastic polyurethanes are a versatile group of multi-phase polymers that have excellent mechanical and elastic properties, good hardness, high abrasion and chemical resistance. Generally, segmented thermoplastic polyurethanes comprised of a low glass transition or low melting "soft" segment and a rigid "hard" segment that often has a crystalline melting point well above room temperature. The polyurethanes consisting of hard and soft segment combinations usually display a two-phase microstructure, which arises from the chemical incompatibility between the soft and the hard segments. The hard, rigid segment segregates into a glassy or semicrystalline domain and the polyol soft segment forms amorphous or semicrystalline matrixes in which the hard segments are dispersed in various ways at different contents. The hard domain in this two-phase microstructure can act as a physical crosslinking point and reinforcing filler and the soft segment behaves like a soft matrix. This phase separation results in the superior physical and mechanical properties, such as high modulus and high reversible deformation.

To study the structure-property relationships of the segmented polyurethanes and the novel PDMS modified segmented polyurethanes, they were subjected to a series of thermal and mechanical analyses.

4.4.1 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) is a commonly used tool for determine molecular organization changes, such as phase separation, glass transition and melting. As mentioned earlier in Chapter 2, the phase separation between the soft and the hard segments is the main reason for the polyurethanes' good physical properties. On the other hand, both the mechanical and thermal properties of polyurethanes can be affected dramatically by phase mixing. Interaction between the soft and hard segments can increase the glass transition temperature of the soft segment and decrease the T_g of the hard segments.

The DSC thermograms of the segmented polyurethane control and PDMS containing segmented polyurethanes are illustrated in Figures 4.31 and 4.32. The

polyurethane control sample consists of PTMO ($M_n=1000$) soft segments and MDI+BD hard segments. The glass transition temperature (T_g) of the soft segment was observed at -45°C . However, the hard segment showed a very broad glass transition, suggesting that the polymer possesses a two-phase morphology. Since the T_g of the soft segment in the polymer, -45°C , is higher than the T_g of its homopolymer, -81°C , the phase separation between the soft and the hard is not complete. On the other hand, the DSC thermograms of PDMS containing polyurethanes clearly showed the glass transition temperature of PDMS soft segment from -111°C to -120°C , depending on the PDMS content, indicating that the PDMS microphase separated from both the PTMO soft segment and hard segment phase. The broad transitions at -40°C and 100°C might be due to the glass transition of the PTMO and the hard segment, respectively.

4.4.2 Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) were used to determine the compositional dependence of the local scale motion, as well as the cooperative segmental motion that may exist in these segmented polyurethanes and PDMS containing polyurethanes. Figure 4.33 shows the overall dynamic behavior in terms of storage modulus (E') and dissipation factor ($\tan \delta$) as a function of temperature. The dynamic mechanical behavior also illustrates the two-phase nature of these materials. As shown in Figure 4.33, two low temperature transitions can be easily detected for the polyurethane. The secondary $\tan \delta$ peak near -120°C is designated as the γ relaxation. This peak corresponds to the short chain motion of the methylene sequences in the PTMO soft segment, known as methylene sequence cranking. The primary relaxation observed at -45°C is designated as the α relaxation and has been assigned to the glass transition temperature of the PTMO. In the PDMS containing polyurethane, the main glass transition of the PTMO soft phase is higher than that of the polyurethane control, suggesting complex microphase separation behavior. The PDMS $\tan\delta$ peak is observed around -100°C , but the principal soft $\tan\delta$ peak is moved somewhat higher. One possible explanation is that incorporation of PDMS segments promotes the phase mixing between the PTMO soft segments and hard segment, since the PDMS is completely incompatible with both of the other components. However, the shifting of the PDMS T_g to a higher temperature indicates that the PDMS

also did not completely phase separate from the other components. This is illustrated in Figures 4.34 and 4.35 and glass transition temperatures are summarized in Table 4.13. This phenomenon can be better understood by studying the polymerization process. During polymerization, the more reactive secondary aminoalkyl terminated PDMS and less reactive hydroxy terminated PTMO and BD were mixed together and MDI was added at once. Under this condition, more reactive PDMS will react with MDI first and form PDMS-MDI-PDMS-MDI sequences. Since PDMS forms its own phase, some MDI will be mixed with PDMS. Thus, the T_g of PDMS is also shifted to a higher temperature. The greater the PDMS content, the greater the likelihood of phase mixing to occur, and thus, the higher the T_g of the PDMS soft segment.

In both polyurethane and PDMS containing polyurethanes, the hard domain T_g was not detected, nor was any crystallization or melting transition observed. This might be due to greater hard/soft segment mixing present in these systems, which prevents the crystallization of either soft or hard segment.

Table 4.13 Glass transition temperatures (T_g) of PDMS containing segmented thermoplastic polyurethanes

Sample ID	PDMS wt %	T_g of PDMS Segment (°C) *	T_g of PTMO Segment (°C)*
PUR30	0	----	-45
PUS15	15	-104	-22
PUS30	28	-99	0
PUS40	45	-98	11
PUS50	55	-92	26

*Measured by DMA

4.4.3 Transmission electron Microscopy

The presence of a two-phase nature has been strongly suggested from the DSC and DMA results listed above. In order to confirm this hypothesis more directly, transmission electron microscopy was conducted. As shown in Figure 4.36, the unstained sample showed the PDMS soft segments appear to form a spherical phase of about 0.1 μm in diameter, when the PDMS content is low (15wt%). However, as the PDMS soft segment

content increases, the size of the spheres becomes smaller (Figure 4.37 and Figure 4.38). These phases eventually become co-continuous at higher PDMS concentration (55wt%) (Figure 4.39). The size of the spherical phase is fairly large, compared with the reported hard domain size of urethane, which usually range from 3-10 nm. The large domain size of PDMS could be explained by the mixing that occurs between the PDMS soft segment and the MDI, which can produce PDMS-MDI-PDMS structures. The DMA results also seem to support this argument. Thus, the incorporation of PDMS promotes phase mixing between the hard segment and the PDMS soft segment, causing the T_g of the PDMS to shift to a higher temperature.

4.4.4 Atomic Force Microscopy

The two-phase morphology of the PDMS containing segmented polyurethanes was corroborated by Atomic Force Microscopy (AFM). Solution cast films were cryo-ultramicrotomed at -120 °C and surfaces of the cross section were studied immediately by the AFM. The reason that the sample was studied so soon after cryo-ultramicrotoming is that the surface information obtained by the AFM may actually provide data about the bulk morphology. AFM micrographs of PUS15 and PUS55 are illustrated in Figure 4.41 and Figure 4.42, respectively. Both micrographs agree very well with the TEM results. In Figure 4.41, spherical phases can be observed that separate from the continuous phase. The size of this spherical phase is about the same as the spherical phase observed in TEM, which is attributed to the PDMS aggregate. On the other hand, the AFM micrograph of the PUS55 showed a more continuous structure. The interphase distance is also similar to the TEM value of about 40 nm. Therefore, from the AFM and TEM results, it can be concluded that the PDMS containing segmented polyurethane with low PDMS content forms a spherical morphology. On the other hand, a co-continuous morphology forms when the PDMS content is high ($\geq 55\%$).

4.4.5 Tensile Properties (Stress-Strain analysis)

All mechanical property tests were performed on dog-bone specimens that were prepared according to the procedure described in Chapter 3. The engineering stress-strain curves of PTMO based segmented thermoplastic polyurethanes are illustrated in

Figure 4.43 and tensile results are summarized in Table 4.14. All curves are shown up to the fracture stress point of the sample. Using the same hard segment concentration, the tensile strength increases with the total molecular weight but tends to level off when the molecular weight reaches 40,000 (M_n) as is often observed. All polyurethanes showed high ultimate elongation values up to 800%. The modulus is about the same for the four different molecular weight samples, since the hard segment content, which determines the modulus of the polymer, is unchanged.

Table 4.14 Stress-Strain Properties of PTMO based segmented thermoplastic polyurethanes

Sample ID	Film Thickness (inch)	M_n (g/mole)	Eng. Stress δ (psi)	Strain ϵ (%)	Modulus E (psi)
PUR20	0.0068	19,100	2541 $\pm$ 91	752 $\pm$ 22	2185 $\pm$ 180
PUR40	0.0079	39,900	7113 $\pm$ 1102	783 $\pm$ 66	1958 $\pm$ 144
PUR50	0.0076	51,000	7770 $\pm$ 854	807 $\pm$ 54	1892 $\pm$ 202
PUR60	0.0068	64,000	6897 $\pm$ 1050	843 $\pm$ 104	2280 $\pm$ 200

Stress-strain curves for the PDMS containing segmented polyurethanes are provided in Figure 4.44. All curves are shown up to the fracture stress point of the sample. All samples were elastomeric and had the same soft segment concentration, 65%. The stress, strain, and modulus values are shown in Table 4.15. A tensile strength value of 4857 psi and an ultimate elongation of 800% were obtained for the PUS15 (15wt% of PDMS). These values are comparable to the polyurethane control, which had a tensile strength of 6897 psi and 840% elongation. However, increasing the in PDMS content resulted in much lower tensile strength and modulus, which can be attributed to the low molecular weight of the these higher PDMS containing polyurethanes and the lose of strain induced crystallization from the PTMO. The low elongation of the 67% PDMS containing polyurethane may be a result of the low molecular weight of this polymer, while the much higher modulus can be explained by the significantly better hard domain

formation than seen in the other polymers. Despite some phase mixing with the PDMS, the hard domain of PUS60 can easily separate and form more pure hard domain than in other polyurethanes, in which PTMO often mixes with the hard segment to reduce the hard domain completion.

Table 4.15 Stress-Strain Properties of PDMS containing segmented thermoplastic polyurethanes

Sample ID	Film Thickness (inch)	M _n (g/mole)	Eng. Stress δ (psi)	Strain ϵ (%)	Modulus E (psi)
PUR60	0.0068	64,000	6897±1050	843±104	2280±200
PUS15	0.007	26,000	4857±599	794±59	2407±125
PUS30	0.0067	14,100	1855±199	560±138	1820±138
PUS40	0.0087	14,400	2554±160	494±22	2178±95
PUS50	0.0077	14,500	1695±120	326±29	2574±127
PUS60	0.0053	14,200	1760±114	149±21	7520±794

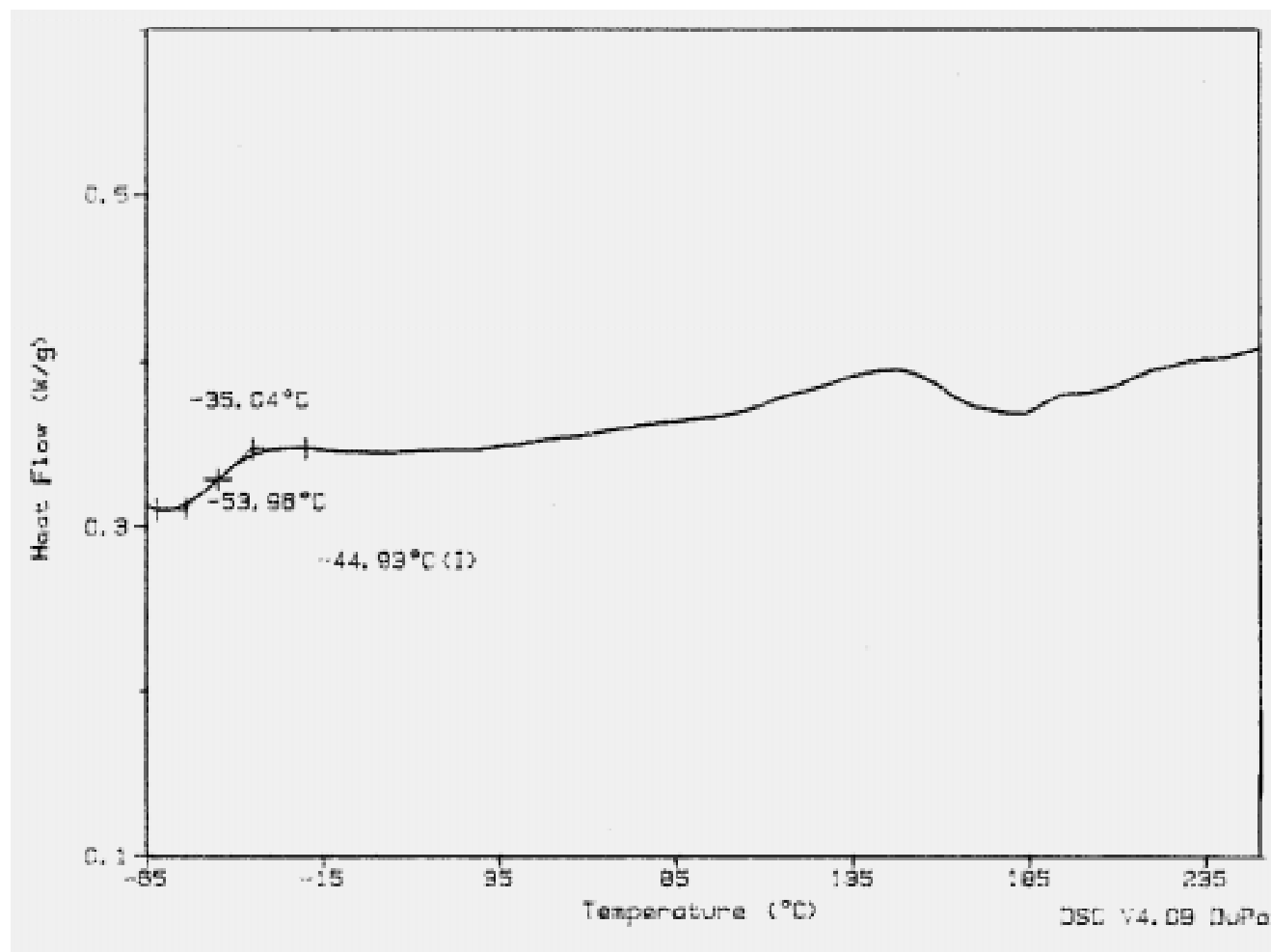


Figure 4.31 Dynamic scanning calorimetry (DSC) thermogram of PTMO ($M_n=1000$) based polyurethane, 2nd run on a Du Pont DSC

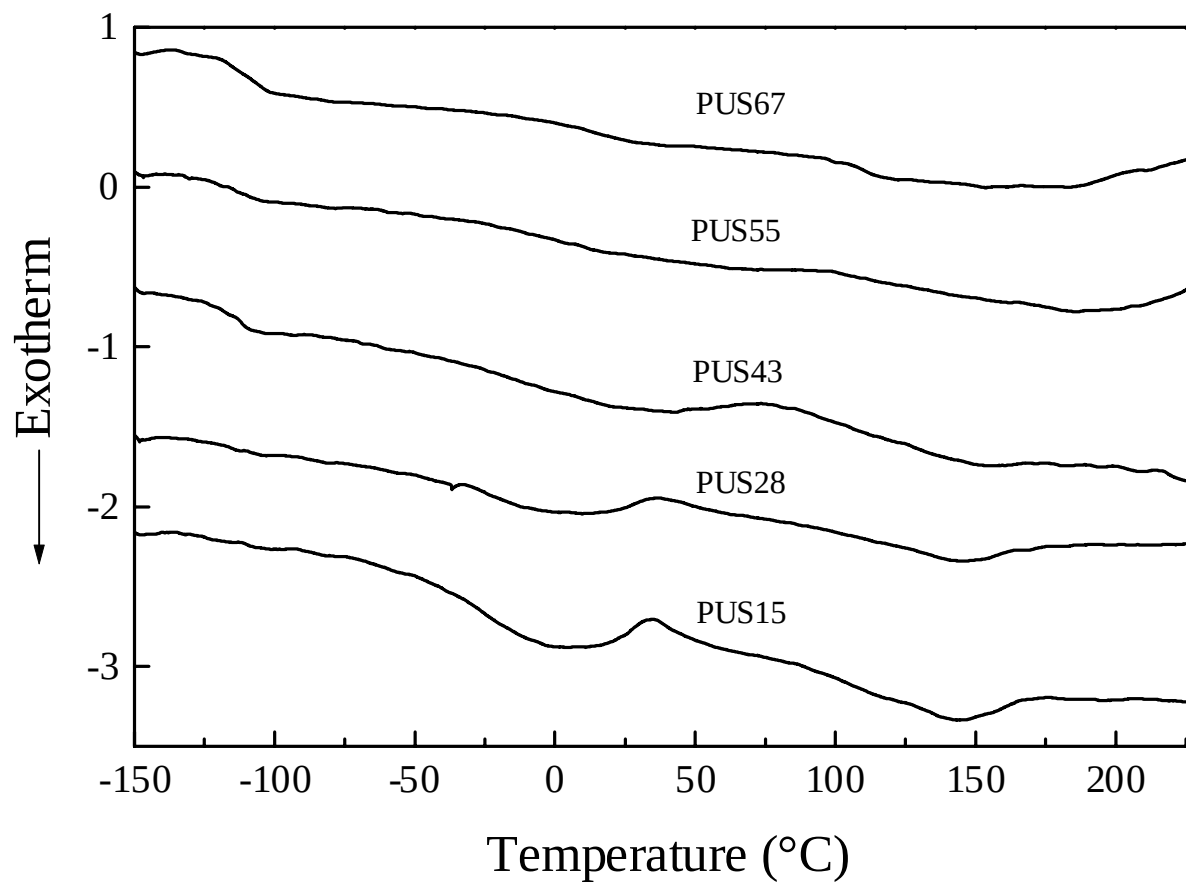


Figure 4.32 Dynamic scanning calorimetry (DSC) thermograms of PDMS containing segmented polyurethanes

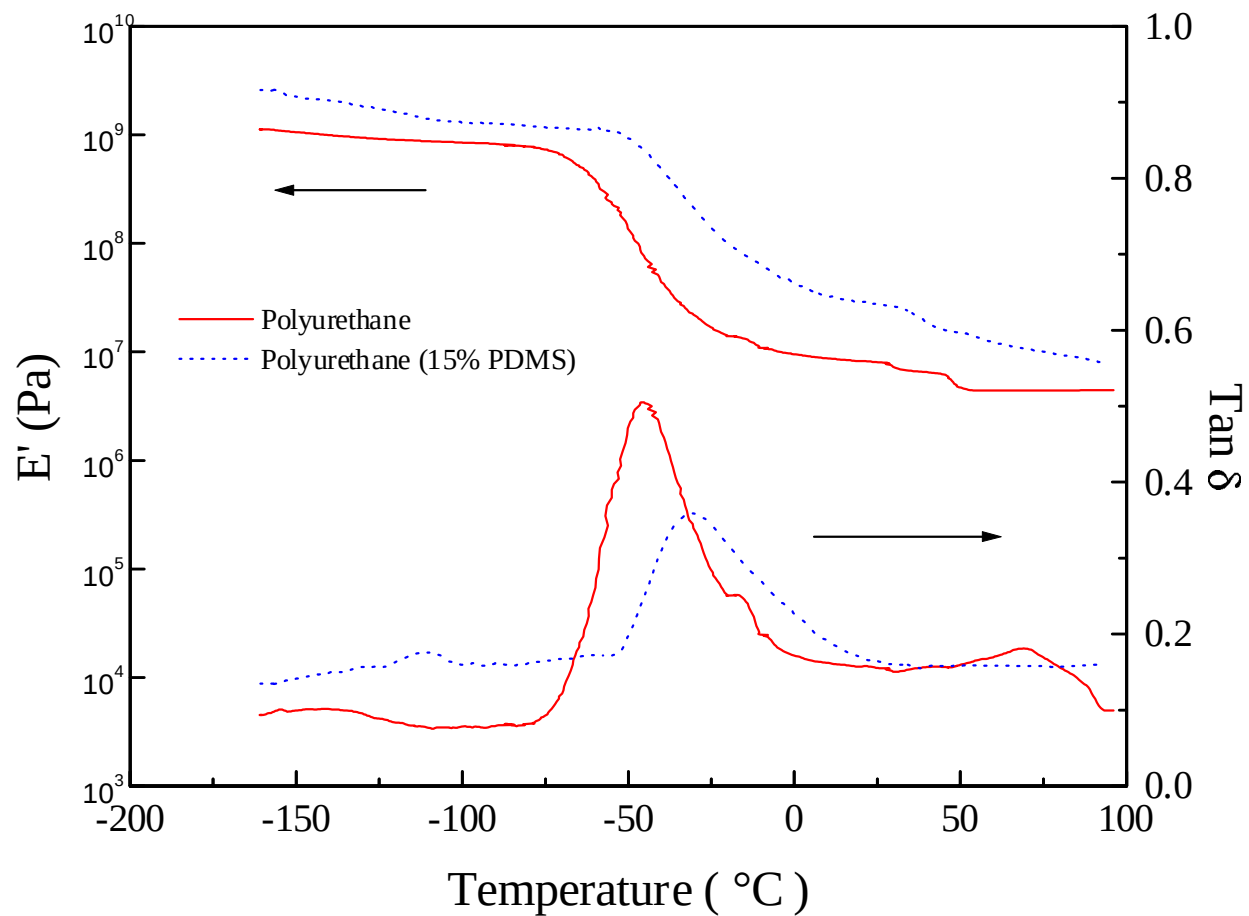


Figure 4.33 Dynamic mechanical analysis (DMA) thermograms of PTMO ($M_n=1000$) based polyurethane and PDMS containing segmented polyurethane

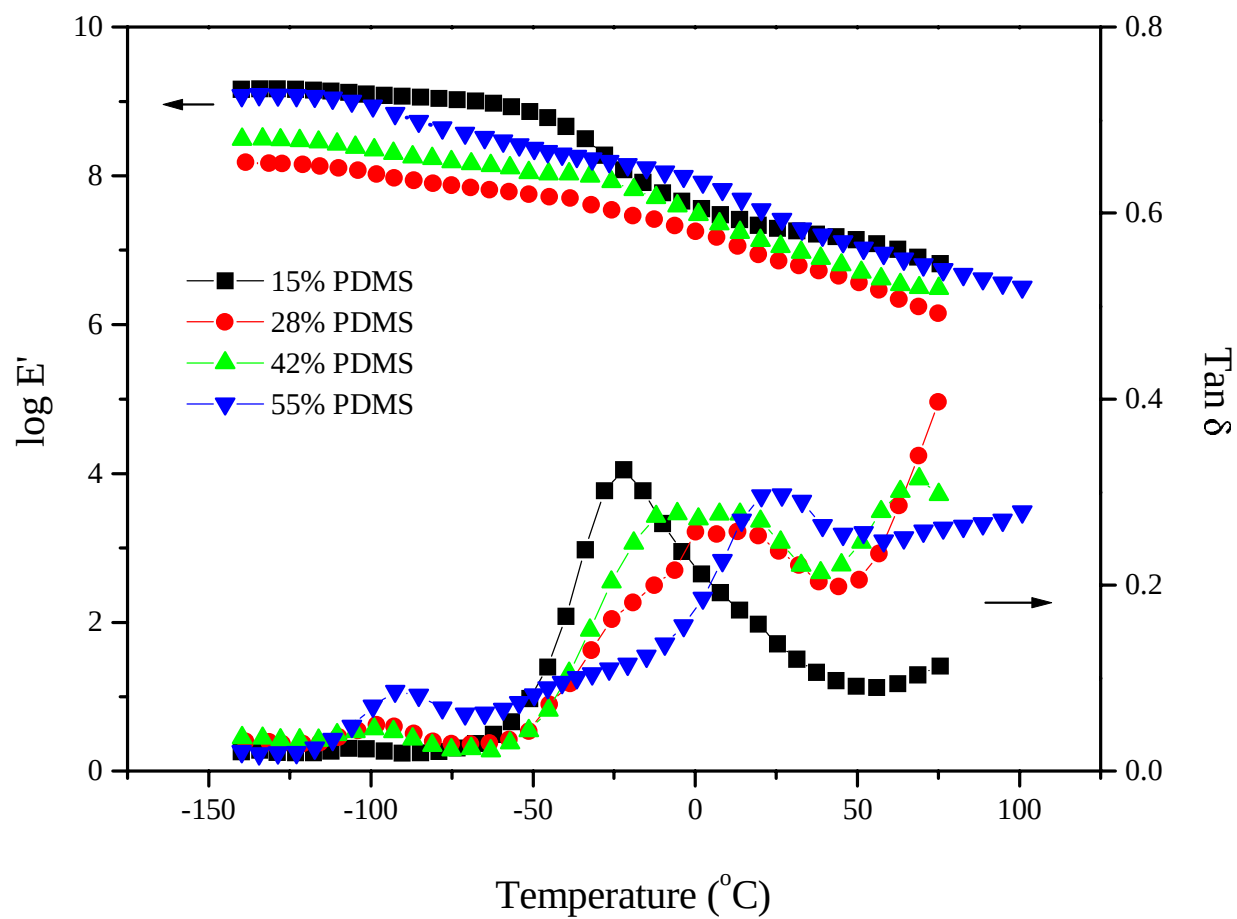


Figure 4.34 Dynamic mechanical analysis (DMA) thermograms of PDMS containing segmented polyurethanes

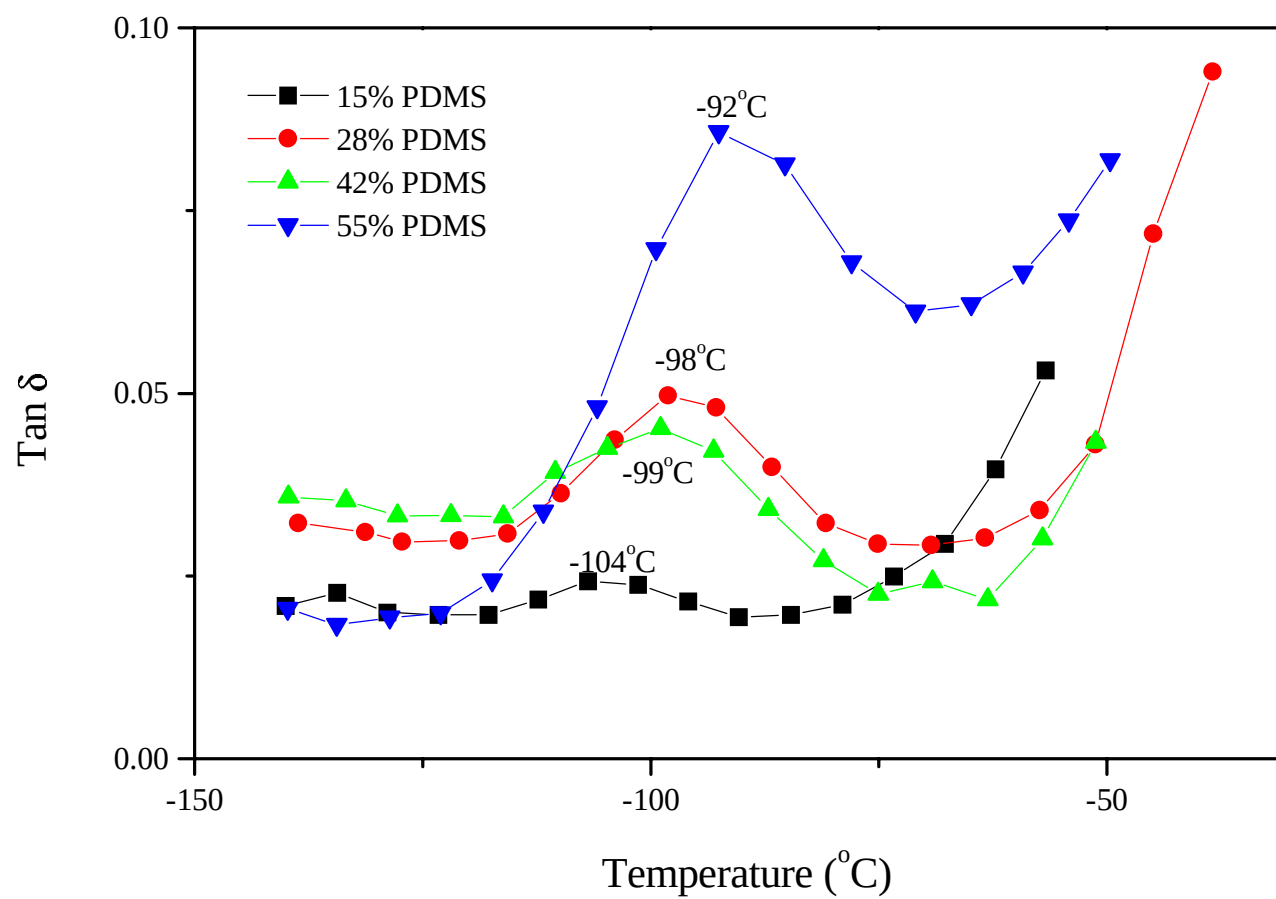


Figure 4.35 Dynamic mechanical analysis (DMA) thermograms of PDMS containing segmented polyurethanes

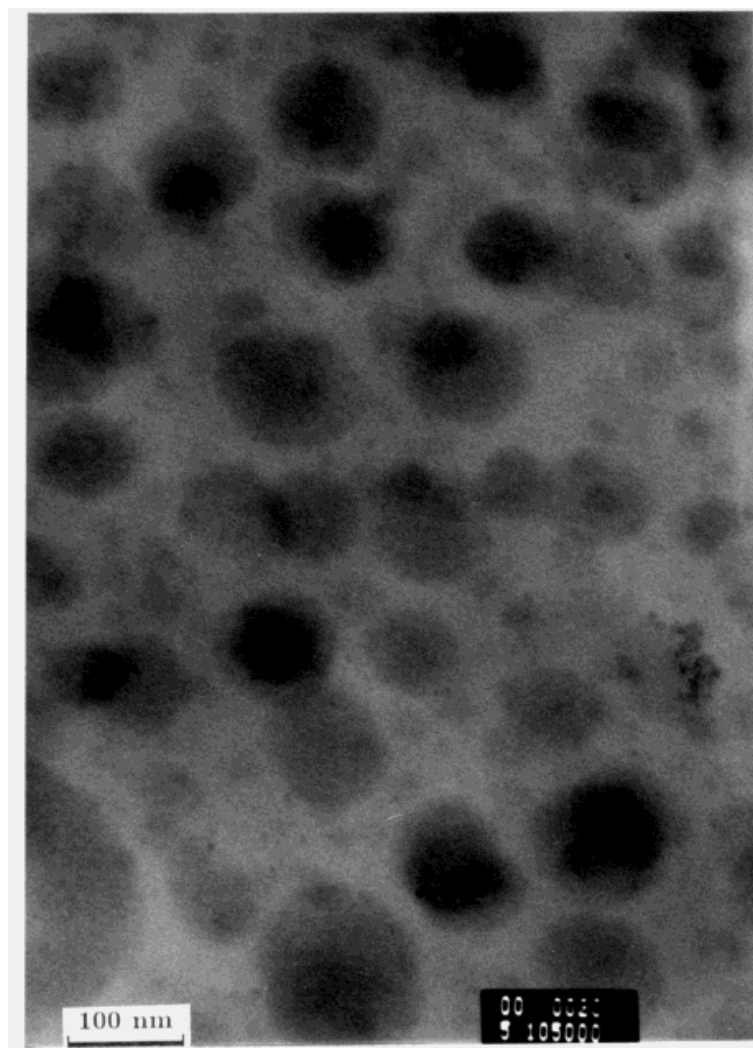


Figure 4.36 Transmission electron microscopy of PDMS containing polyurethane (15% PDMS)

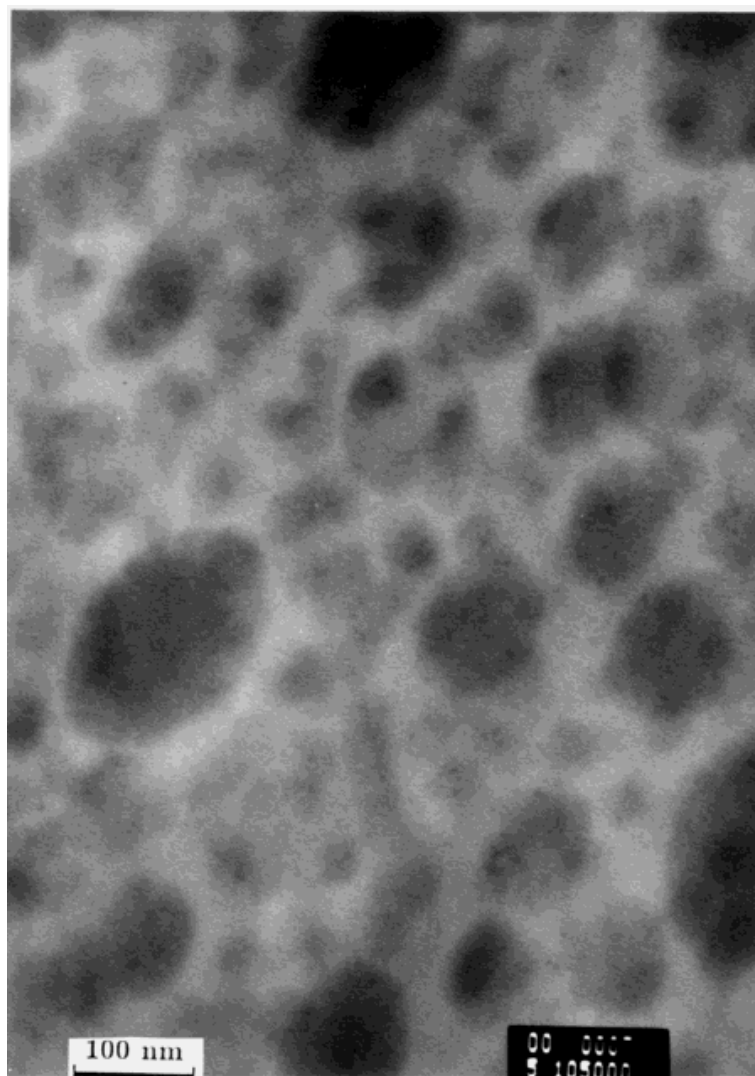


Figure 4.37 Transmission electron microscopy of PDMS containing polyurethane (28 % PDMS)

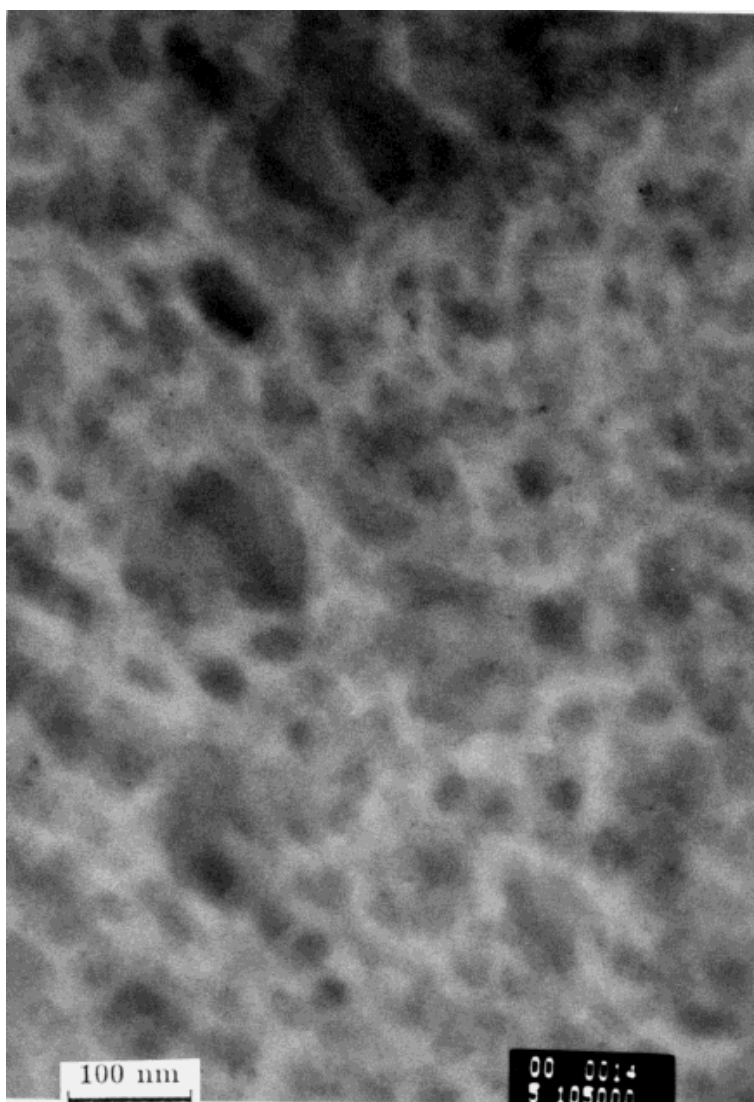


Figure 4.38 Transmission electron microscopy of PDMS containing polyurethane (45 % PDMS)

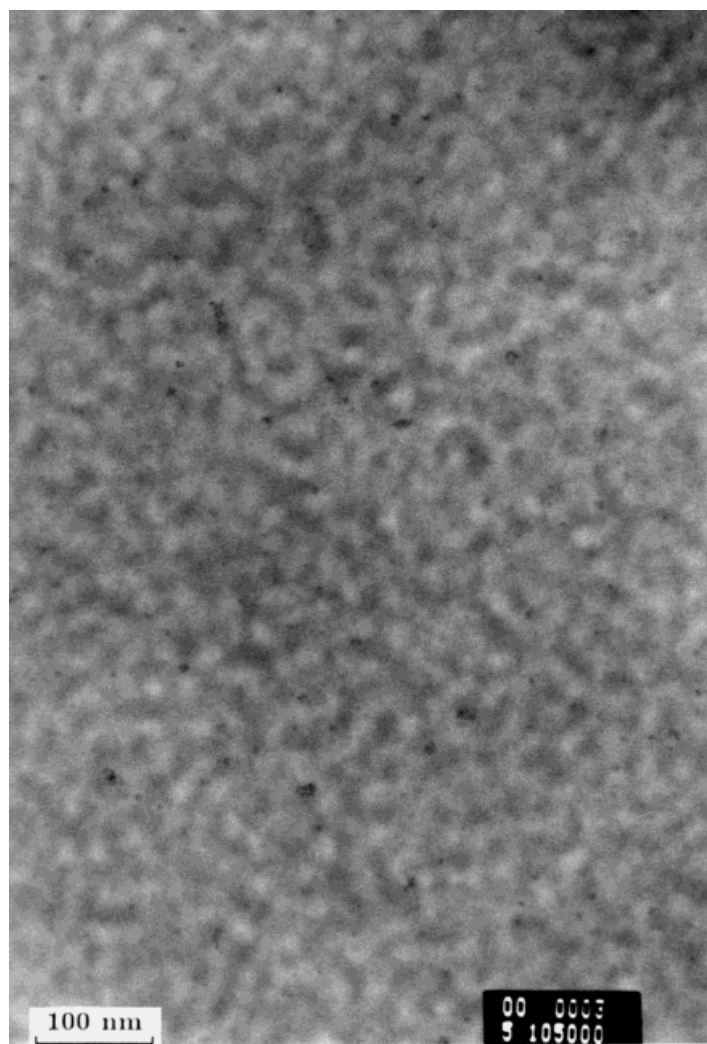


Figure 4.39 Transmission electron microscopy of PDMS containing polyurethane (55 % PDMS)

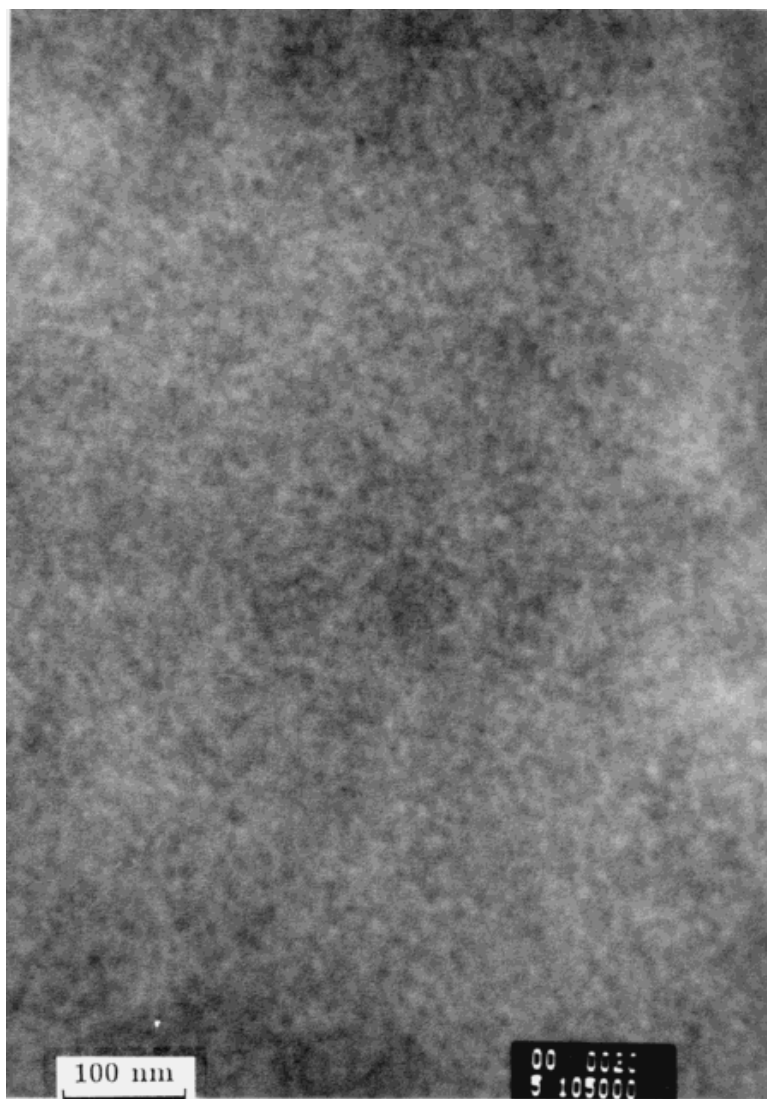


Figure 4.40 Transmission electron microscopy of PDMS containing polyurethane (67 % PDMS)

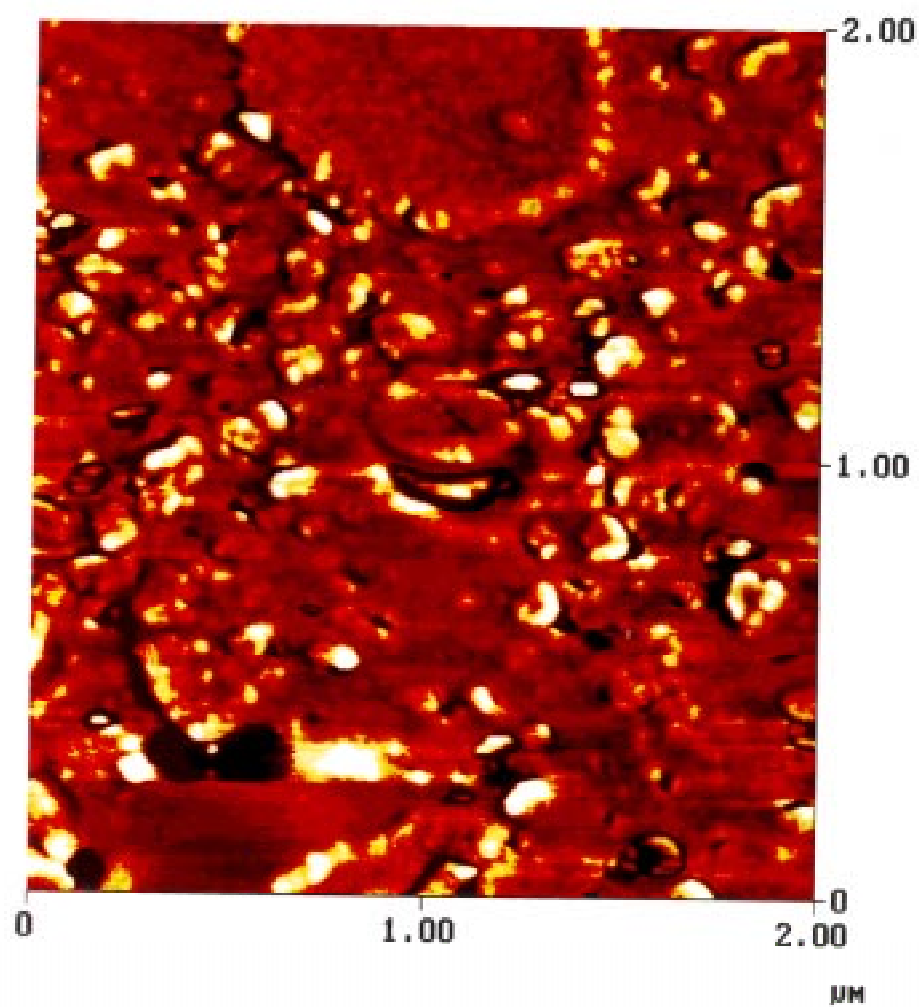


Figure 4.41 Atomic force microscopy (AFM) of PDMS containing polyurethane (15 % PDMS)

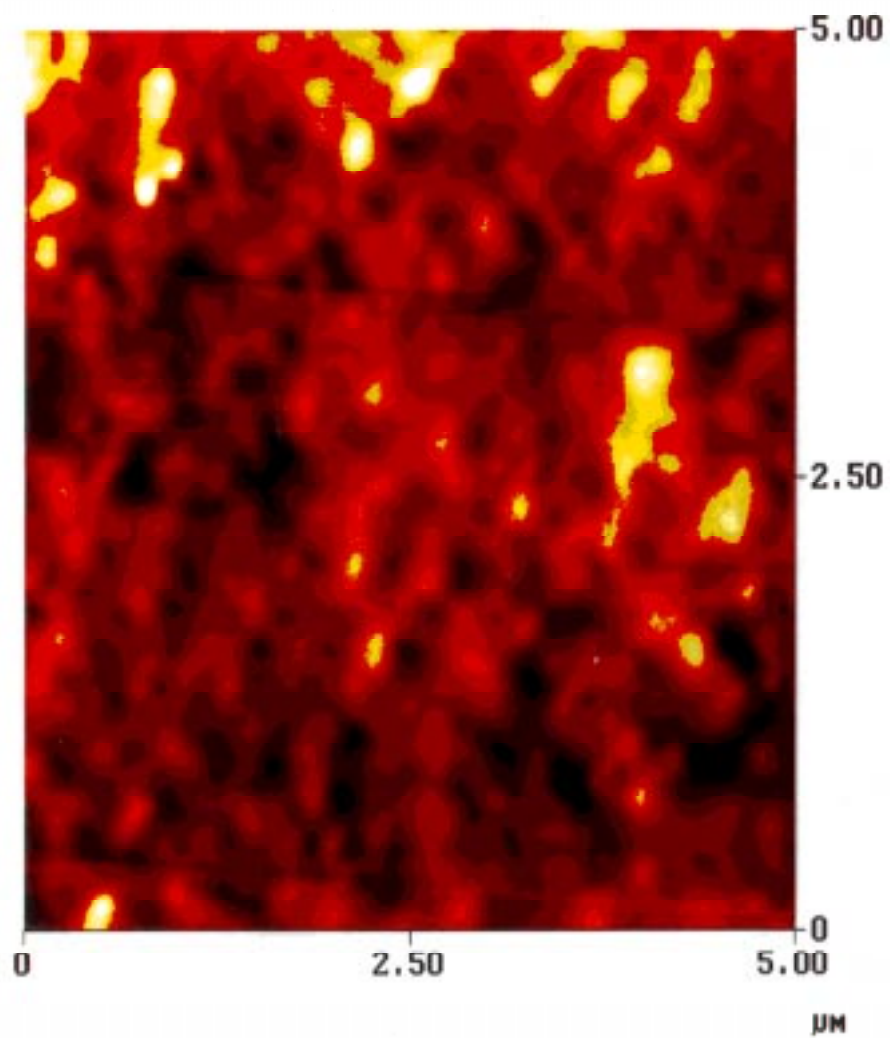


Figure 4.42 Atomic force microscopy (AFM) of PDMS containing polyurethane (55 % PDMS)

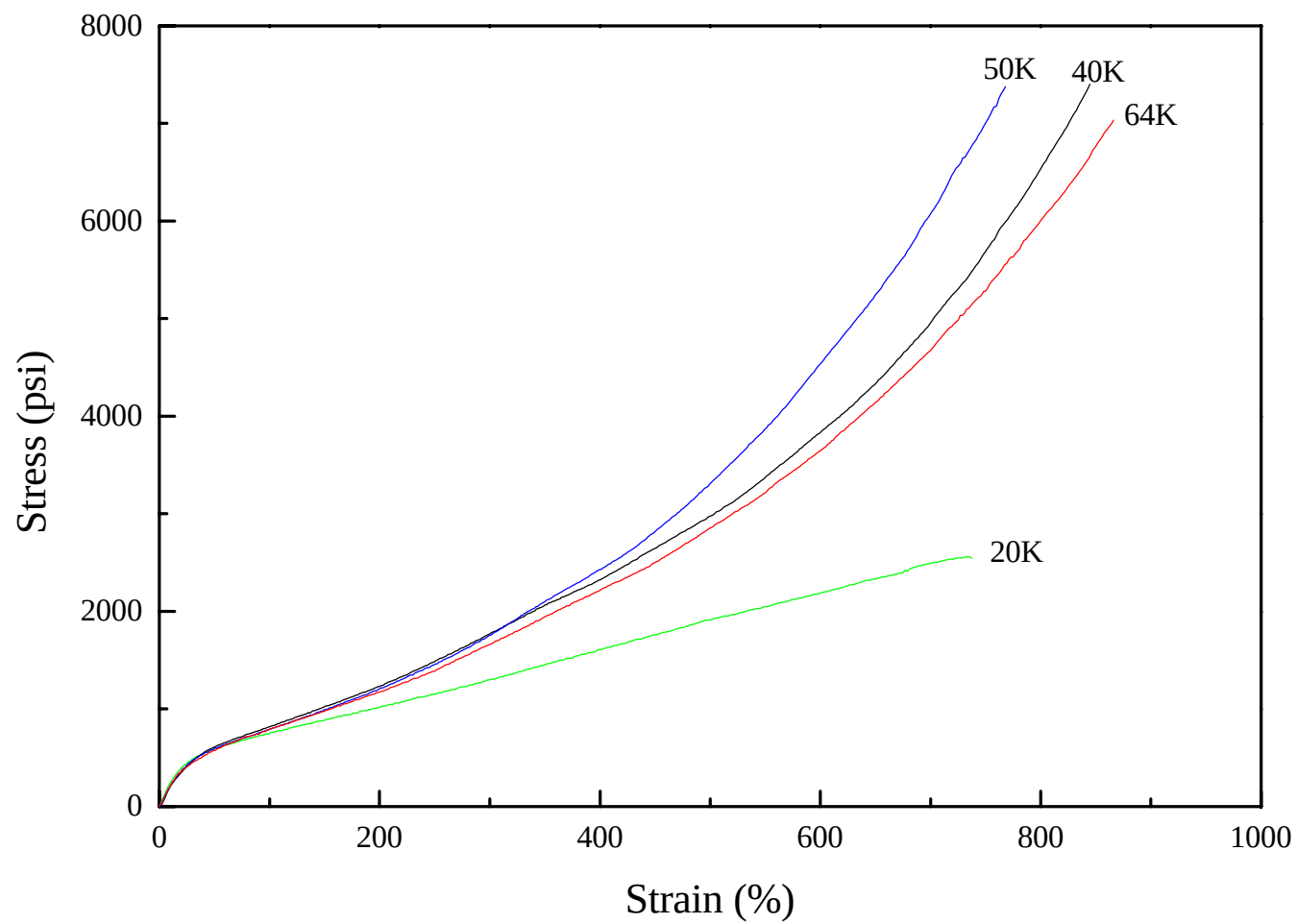


Figure 4.43 Stress-strain behavior of PTMO based segmented thermoplastic polyurethanes

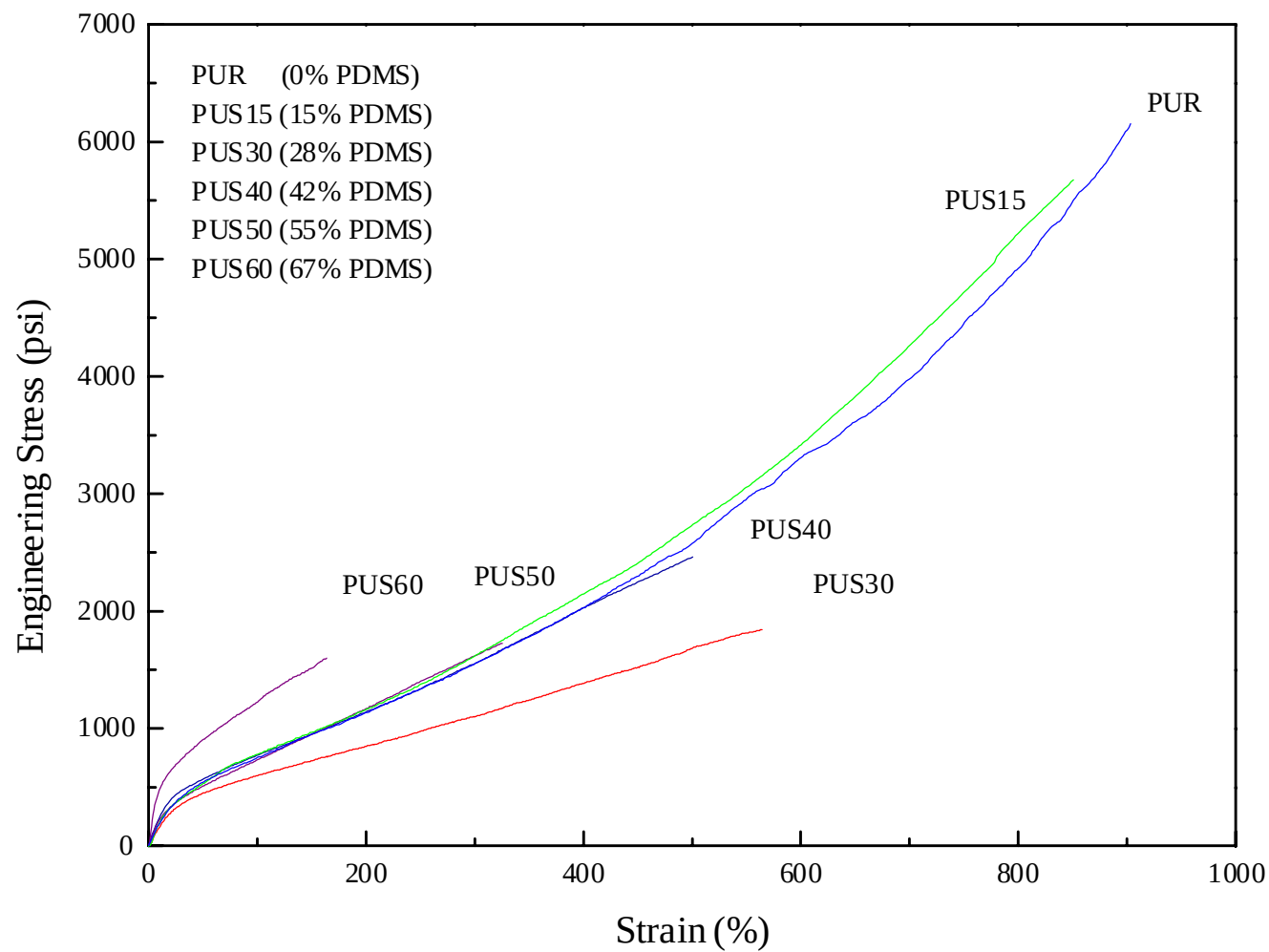


Figure 4.44 Stress-strain behavior of PDMS containing segmented thermoplastic polyurethanes

4.5 Thermal stability and degradation of polyurethanes and PDMS containing segmented thermoplastic polyurethanes

4.5.1 Thermogravimetric analysis

The thermal stability of PTMO based segmented polyurethanes was investigated using dynamic thermogravimetric analysis from 30°C to 700°C in air and nitrogen. The char yield, in air, was also used to measure a polymer's anticipated fire resistance. Char yield is an easily obtained and important measurement that correlates with the material's ability to sustain combustion. This is clearly illustrated in the Figure 2.16. A major objective of this research was to investigate the degradation and combustion process of polyurethanes and to determine whether one could reduce the risk of combustion by synthesizing polyurethane copolymers with PDMS segments, which produce significant char during degradation, thereby disrupting the combustion cycle.[306]

The test results of different PTMO based segmented polyurethanes containing the same soft segment concentration (63%), but varying molecular weights, are summarized in Table 4.16. The TGA thermograms of PTMO based segmented polyurethane in nitrogen and in air are provided in Figure 4.45 and Figure 4.47, respectively.

Table 4.16 Thermogravimetric analysis (TGA) of PTMO based segmented polyurethanes with same soft segment concentration but different molecular weights

Sample ID	M _n (g/mole)	Soft Seg. Content (%)	5% Weight Loss in N ₂ (°C)	Char Yield at 700 °C in N ₂ (%)	5% Weight Loss in Air (°)	Char Yield at 700 °C in Air (%)
PUR20	19,100	63	350	1.08	349	0
PUR30	32,000	63	350	1.93	348	0
PUR40	39,900	63	349	0	348	0
PUR50	51,000	63	341	1.27	341	0
PUR60	64,000	63	353	5.98	348	0

The 5% weight loss in both air and nitrogen are at around 350°C, almost identical for all samples. This indicates that the thermal stability of the PTMO based segmented polyurethanes with the same soft segment concentration does not significantly depend on molecular weight. Instead, thermal stability is more dependent on the stability of the urethane bond, which is the weakest linkage in the polyurethane structure. A detailed study of the thermal stability of urethane linkages will be discussed later. These samples produced small amounts of char yield in nitrogen, but no char yield at all in air at 700°C. The degradation of polyurethane in nitrogen and in air is somewhat different. In nitrogen, degradation is a two-step process, clearly illustrated in Figure 4.46, in which the first major weight loss occurs at 380°C and the second at 450°C. In air, however, degradation is a three-step process, illustrated in Figure 4.48. The first weight loss occurs at 379°C, the second at 443°C, and the third at 570°C. These different degradation processes in nitrogen and in air can be attributed to oxidative degradation in air. In other words, the degradation in air is a combination of both thermal and oxidative degradation, instead of pure thermal degradation.

The thermal stability of PTMO based segmented polyurethanes with different soft segment concentrations was also investigated by TGA. The TGA thermograms are illustrated in Figure 4.49 and the results are summarized in Table 4.17.

Table 4.17 Thermogravimetric analysis (TGA) of PTMO based segmented polyurethanes with different soft segment concentrations (0-74%)

Sample ID	M _n (g/mole)	Soft Seg. Content (%)	5% Weight Loss in N ₂ (°C)	Char Yield at 700 °C in N ₂ (%)	5% Weight Loss in Air (°C)	Char Yield at 700 °C in Air (%)
PUR-1	17,000	0	308	32.7	312	0
PUR-2	22,500	40	326	10.9	319	0
PUR-3	32,000	63	331	7.8	325	0
PUR-4	29,600	74	326	8.2	306	0

The thermal stability, in terms of 5% weight loss, of each polyurethane sample is very similar in nitrogen and air, except the PUR-4 sample. The thermal stability of the PUR-1, which had 100% hard segment concentration, is very different from the rest of the samples that contained the PTMO soft segment. Although the 5% weight loss temperature of the PUR-1 is lower than those of other samples, it tends to give more char yield over a wide temperature range. This can be explained by the higher urethane linkage concentration in the PUR-1, which is again the weakest linkage in a polyurethane. The char formation at higher temperatures may also be caused by the crosslinked network generated from the hard segment. All samples, however, gave no char yield in air at 700 °C, which reflects the poor thermal oxidative stability of the polyurethanes.

The thermal stability of the PDMS containing segmented polyurethanes was investigated using dynamic thermogravimetric analysis from 30°C to 700°C in air and nitrogen. The results of testing polyurethanes with the same soft segment content (65%), but different PDMS concentrations, are summarized in Table 4.18. The TGA thermograms of PDMS containing segmented polyurethanes in nitrogen and in air are provided in Figure 4.50 and Figure 4.52, respectively.

Table 4.18 Thermogravimetric analysis (TGA) of PDMS containing segmented polyurethanes with different PDMS concentrations (0-67%)

Sample ID	M _n (g/mole)	PDMS Content (%)	5% Weight Loss in N ₂ (°C)	Char Yield at 700 °C in N ₂ (%)	5% Weight Loss in Air (°C)	Char Yield at 700 °C in Air (%)
PUR	32,000	0	331	7.8	325	0
PUS15	14,500	15	345	8.9	344	3.4
PUS30	14,100	28	332	5.4	340	5.9
PUS40	14,400	45	328	8.8	327	8.7
PUS50	14,500	55	308	7.4	305	10.9
PUS60	14,200	67	302	4.9	321	14.3

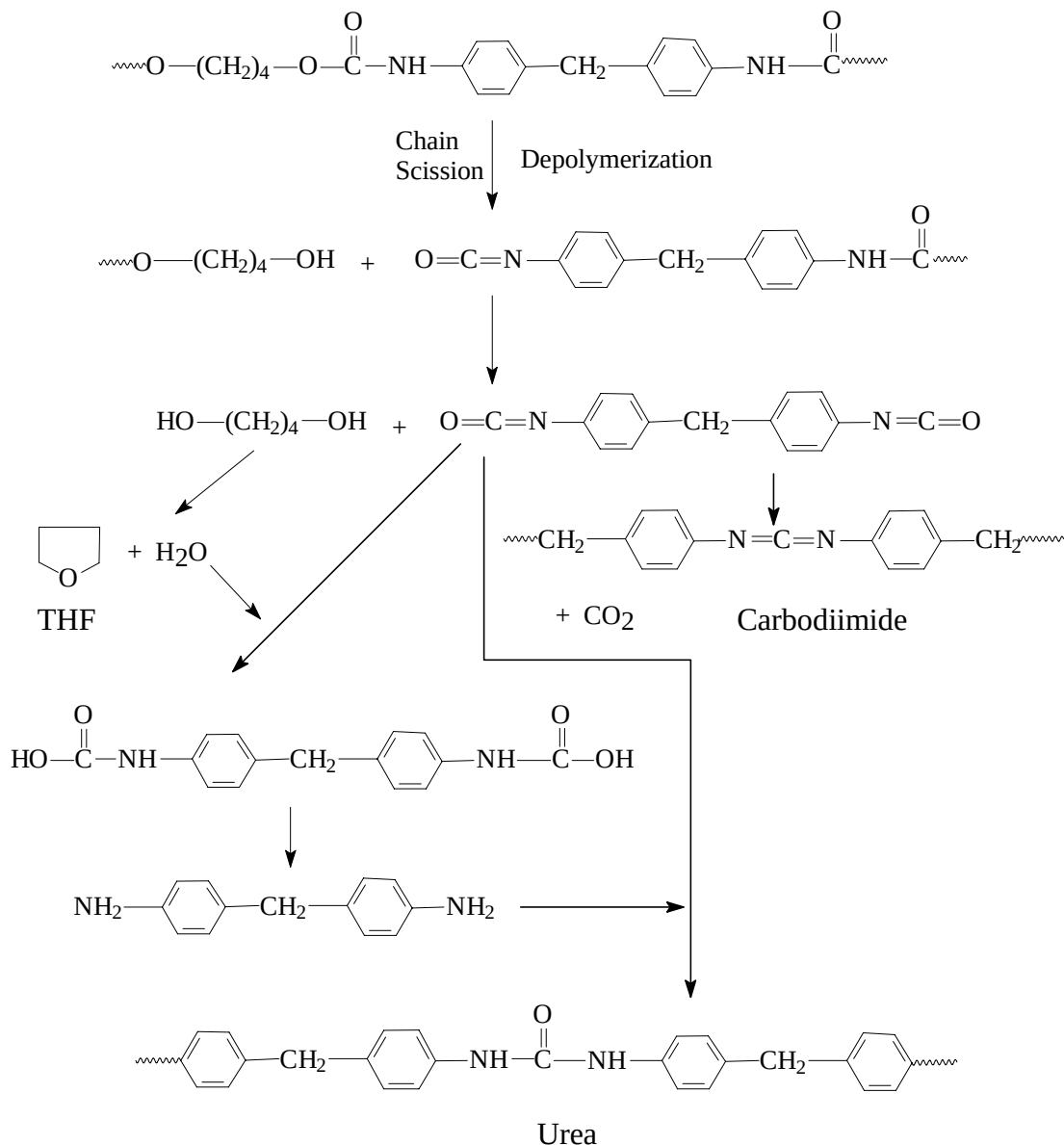
The 5% weight loss for a PDMS containing polyurethane is similar to PTMO based segmented polyurethane, both in nitrogen and in air, suggesting that the incorporation of PDMS doesn't significantly impact initial decomposition. This is not surprising because the thermally weakest link is the urethane bond, which starts to dissociate at around 200 °C. Like the polyurethane control, the thermal degradation of PDMS containing segmented polyurethanes in nitrogen is a two-step process, while the thermal oxidative degradation is a three step process. These degradation processes are clearly demonstrated in the thermogram derivative curves illustrated in Figure 4.51 and 4.53, respectively. It also can be seen in Figure 4.54, which shows that for the same soft segment concentration, the PDMS containing polyurethane has lower weight loss over a wide temperature range, and higher char yield at 700°C, than the PTMO based polyurethane control. Moreover, grayish char formation at 700°C was observed, which increased with PDMS content in the polyurethane as shown in Table 4.18. In fact, the char yield at 700°C in air increased almost linearly with the silicon content in the polymer, as illustrated in Figure 4.55. This suggests that complex silicates are indeed formed upon pyrolysis in air.

4.5.2 High temperature FTIR

The thermal degradation processes of PTMO based segmented polyurethanes and PDMS containing segmented polyurethanes were further studied by high temperature FTIR. The samples were cast onto the KBr discs, which were inserted into a heating cell. The heating cell was then put into the sample holder and connected to a temperature controller. The temperature of the cell was controlled manually through a temperature controller. The FTIR spectra were collected at different temperatures to follow the degradation of the polyurethane and the PDMS containing polyurethane. The sample films in the cell were heated from room temperature to 300 °C while the FTIR data were collected.

Apparently, the degradation of a polyurethane first undergoes a de-polymerization reaction, as illustrated in Scheme 4.3.[248] The primary degradation products, diisocyanate and diol, can then generate secondary degradation products. For example, the diisocyanate can react with water to form diamine or react with itself to form

carbodiimide. These reactions can be followed by FTIR spectroscopy at elevated temperature. The FTIR spectra of a polyurethane and a PDMS containing polyurethane at elevated temperatures are illustrated in Figure 4.56-4.61.



Scheme 4.3 Thermal Degradation mechanism of polyurethane[248]

For both samples, an increase in temperature results in hydrogen bond breakage, as indicated by the shifting of the hydrogen-bonded N-H stretch to a non-bonded N-H,

and the hydrogen-bonded C=O stretch to a non-bonded C=O. The appearance of isocyanate groups was observed at around 200°C. The isocyanate peak reaches its maximum at 300°C, and further increases in temperature results in a decrease of the isocyanate peak, which may be caused by the formation of carbodiimide, or by reacting with newly formed diamine to generate urea. Though the carbodiimide peak, which should be at 2137 cm⁻¹, can not be detected, a new amine peak and urea peak were observed at high temperatures in the PDMS containing polyurethane. These are shown in Figure 4.59 and Figure 4.61.

4.5.3 GC-Mass pyrolysis

Polymer degradation studies were conducted to compare the behaviors of the polyurethane control and the PDMS containing polyurethanes. It is important to understand how these polymers degrade for several reasons. First, a better understanding of polymer degradation will assist in designing polymers with increased thermal stability. Second, identifying the volatile byproducts and the composition of the residual char will provide important information for polymer applications.

The PTMO based segmented polyurethanes and PDMS containing segmented polyurethanes were decomposed in helium at 400°C. Their volatile by-products were separated by gas chromatography and analyzed using mass spectrometry. The gas chromatograms are shown in Figure 4.62 and Figure 4.63 and every major peak is identified. It is critical when analyzing these polymers to quickly sweep the volatiles through the pyrolysis injector so that further degradation of the reaction product does not occur. Otherwise, secondary degradation will generate a number of extra volatiles and render interpretation difficult.

The primary volatiles generated from polyurethane degradation are PTMO oligomers with varying molecular weights and MDI, consisting of different isomers. However, in addition to the above volatiles, the decomposition of PDMS containing polyurethane gave cyclic siloxanes: D₃, D₄,. These are generated via a backbiting process of the PDMS oligomer once the urethane bond has dissociated.

4.5.4 Cone Calorimetry Analysis

Quantitative measurements of fire resistance was based on cone calorimetry in cooperation with Dr. U. Sorathia of Naval Surface Warfare Center. Cone calorimetry determines the amount of heat released by a polymer due to combustion under a specific applied heat flux. The results are shown in Table 4.19. The heat release rate of the 15% siloxane modified samples dropped 67%, compared with the polyurethane control. It should be noted that as the siloxane content was increased from 15wt% to 67wt%, the heat release rate didn't appear to further change. This suggests that desirable physical properties could be maintained while improving fire resistance. However, further verification of this phenomenon is needed. The reduction in the peak heat release rate was attributed to the formation of a silicate-like material that was generated by the oxidation of the PDMS segments on the polymer surface, which cuts off the heat transfer from the flame as well as diffusion of volatile byproducts into the flame. Since the PDMS has very low surface energy, it formed a PDMS enriched surface even at very low bulk content, which will be discussed more thoroughly in the next section. This might account for the fact that the peak heat release rate did not further decrease when PDMS content was increased.

Table 4. 19 Cone calorimetry test with a heat flux of 25KW/m²

Sample	Soft Segment (wt%)	PDMS (wt%)	Peak Heat Release Rate (KW/m ²)
PUR1	63	0	2671
PUS15	63	15	825
PUS30	65	28	1118
PUS40	65	42	818
PUS60	67	67	776

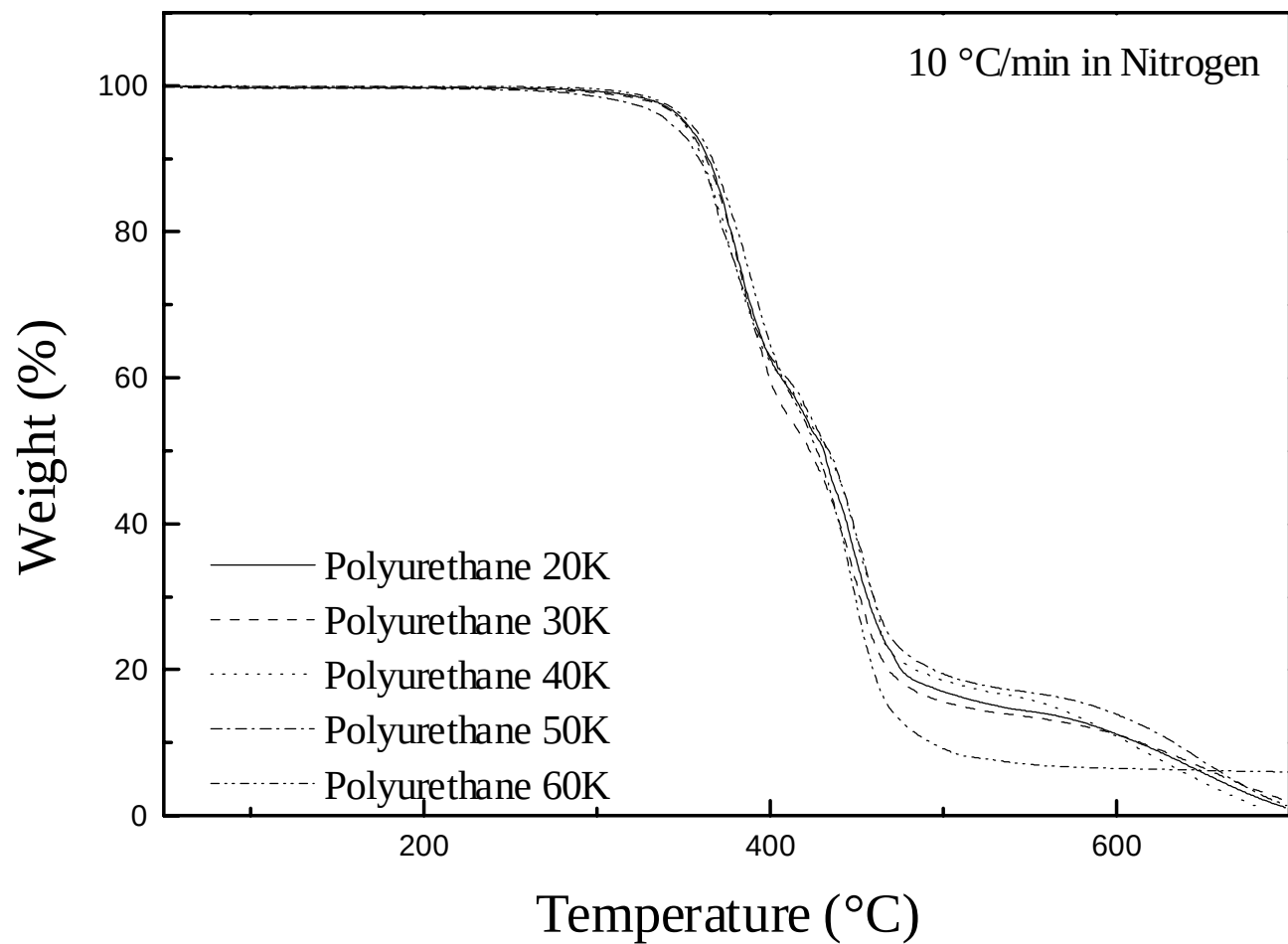


Figure 4.45 TGA thermograms of PTMO based segmented polyurethanes (63% SSC) in N₂

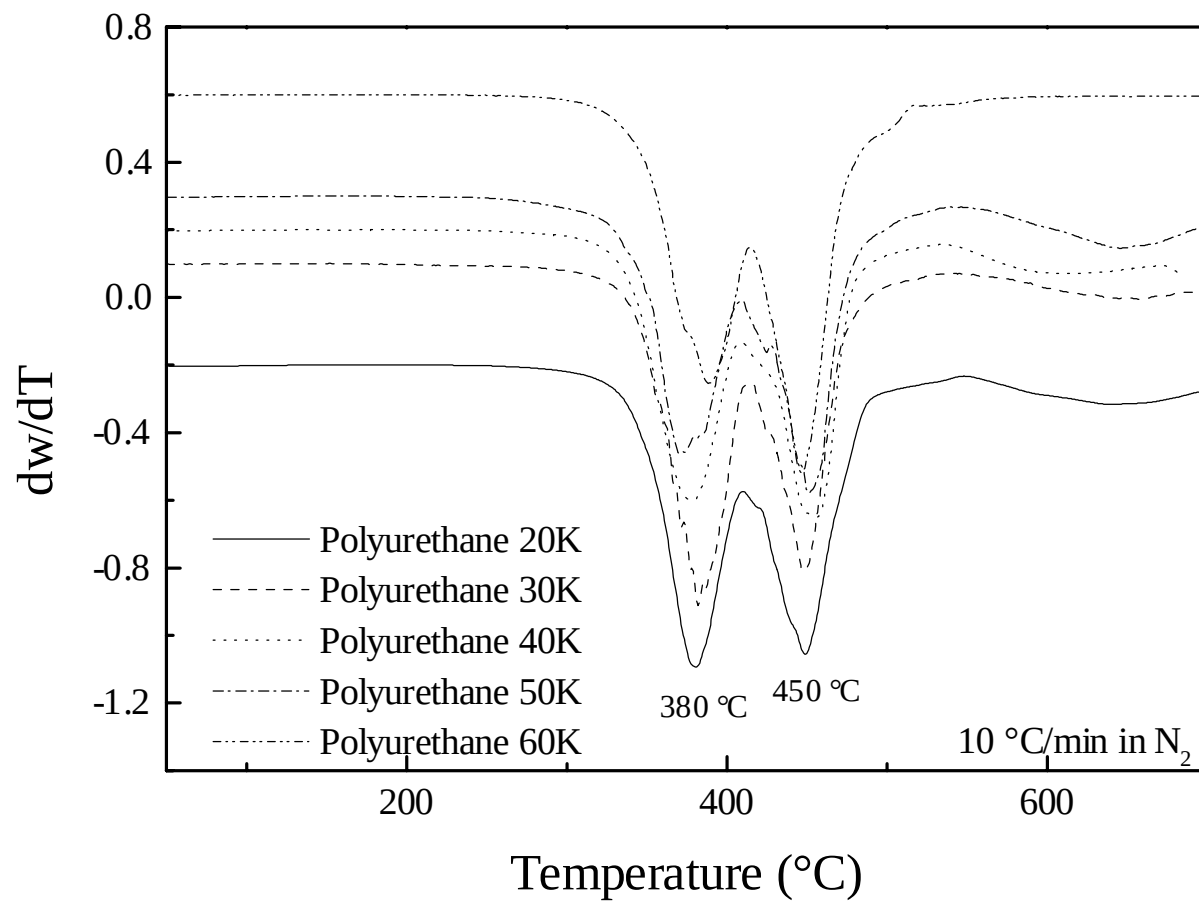


Figure 4.46 TGA thermogram derivative curves of PTMO based segmented polyurethanes (63% SSC) in N_2

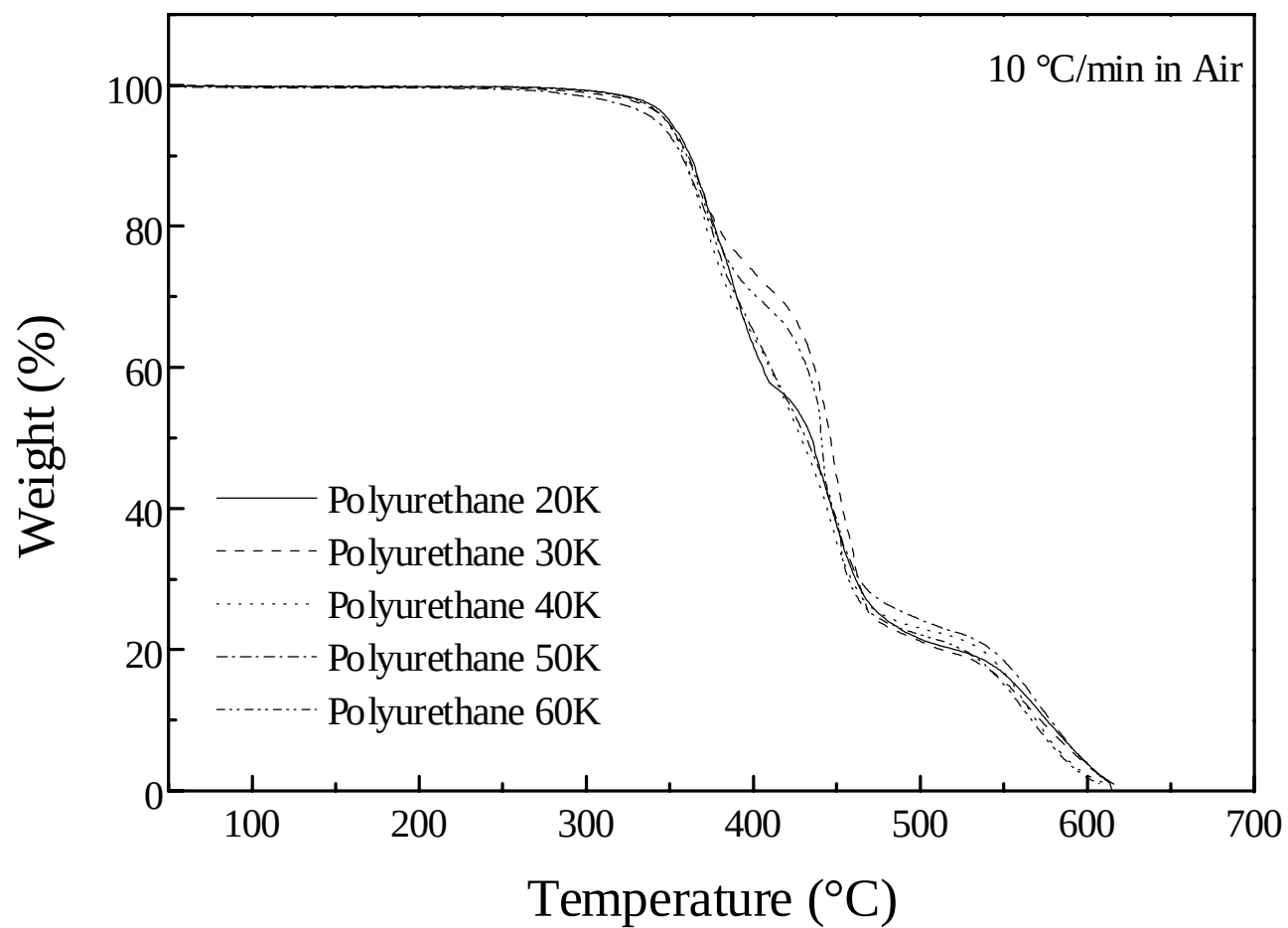


Figure 4.47 TGA thermograms of PTMO based segmented polyurethanes (63% SSC) in air

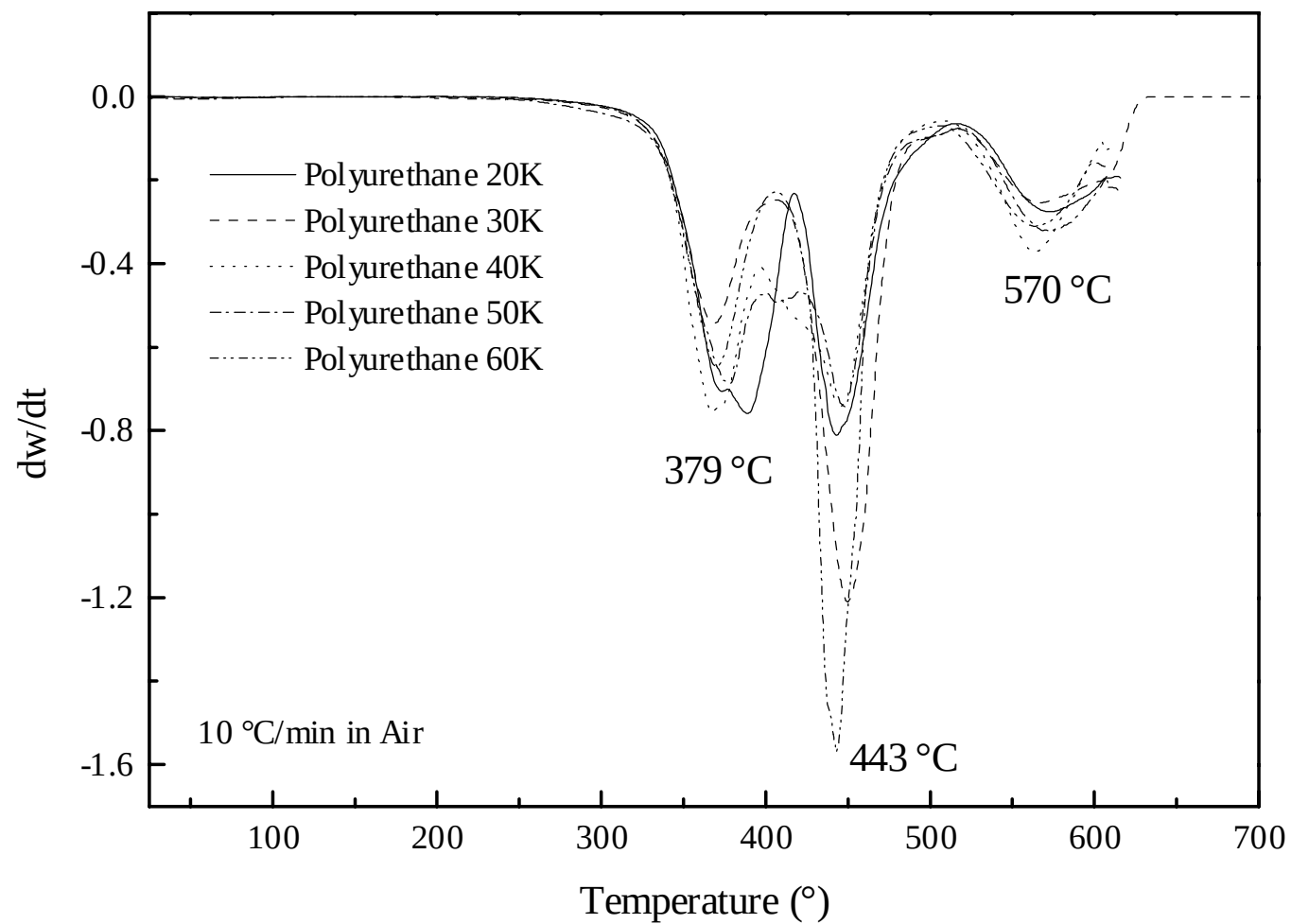


Figure 4.48 TGA thermogram derivative curves of PTMO based segmented polyurethanes (63% SSC) in air

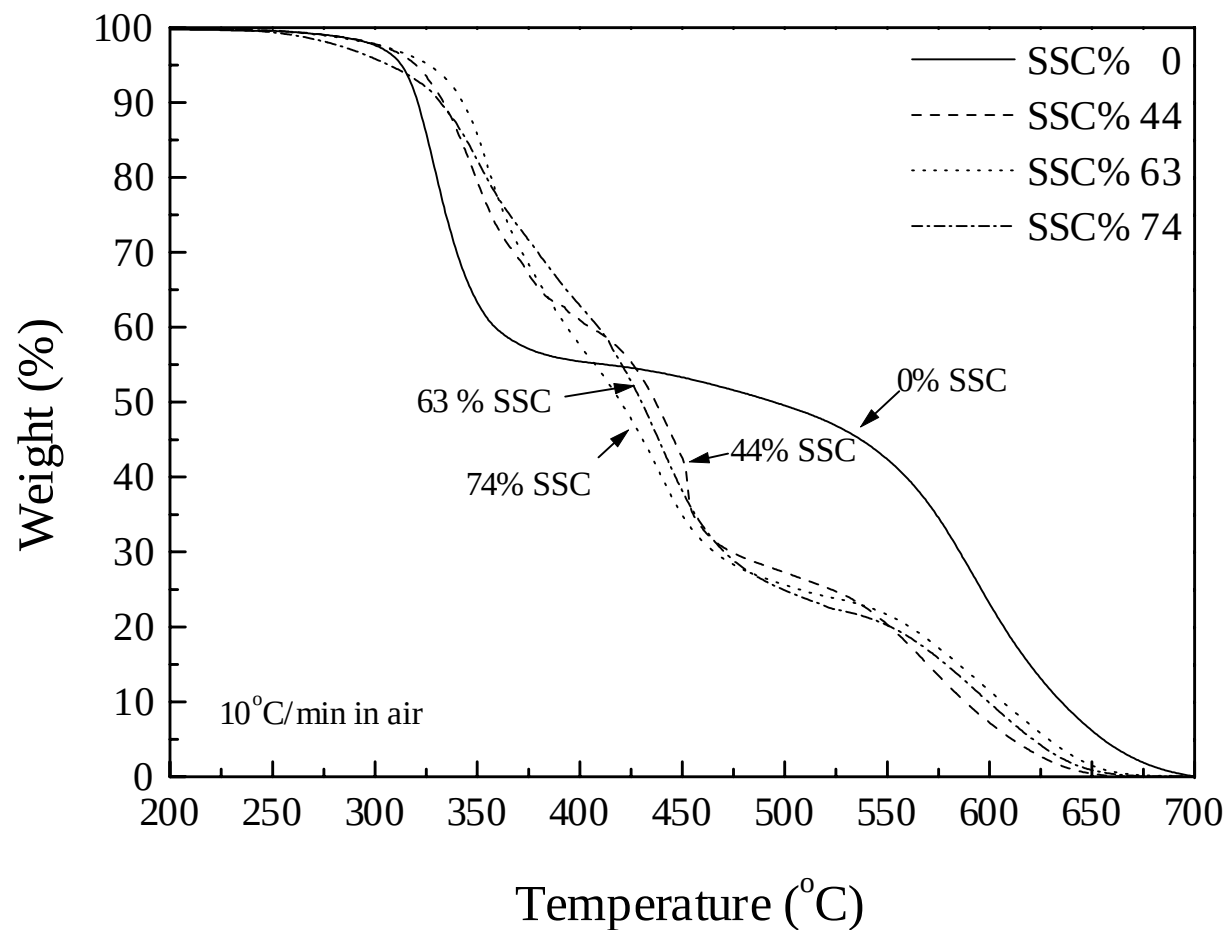


Figure 4.49 TGA thermograms of PTMO based segmented polyurethanes with different soft segment concentrations (0-80%) in air

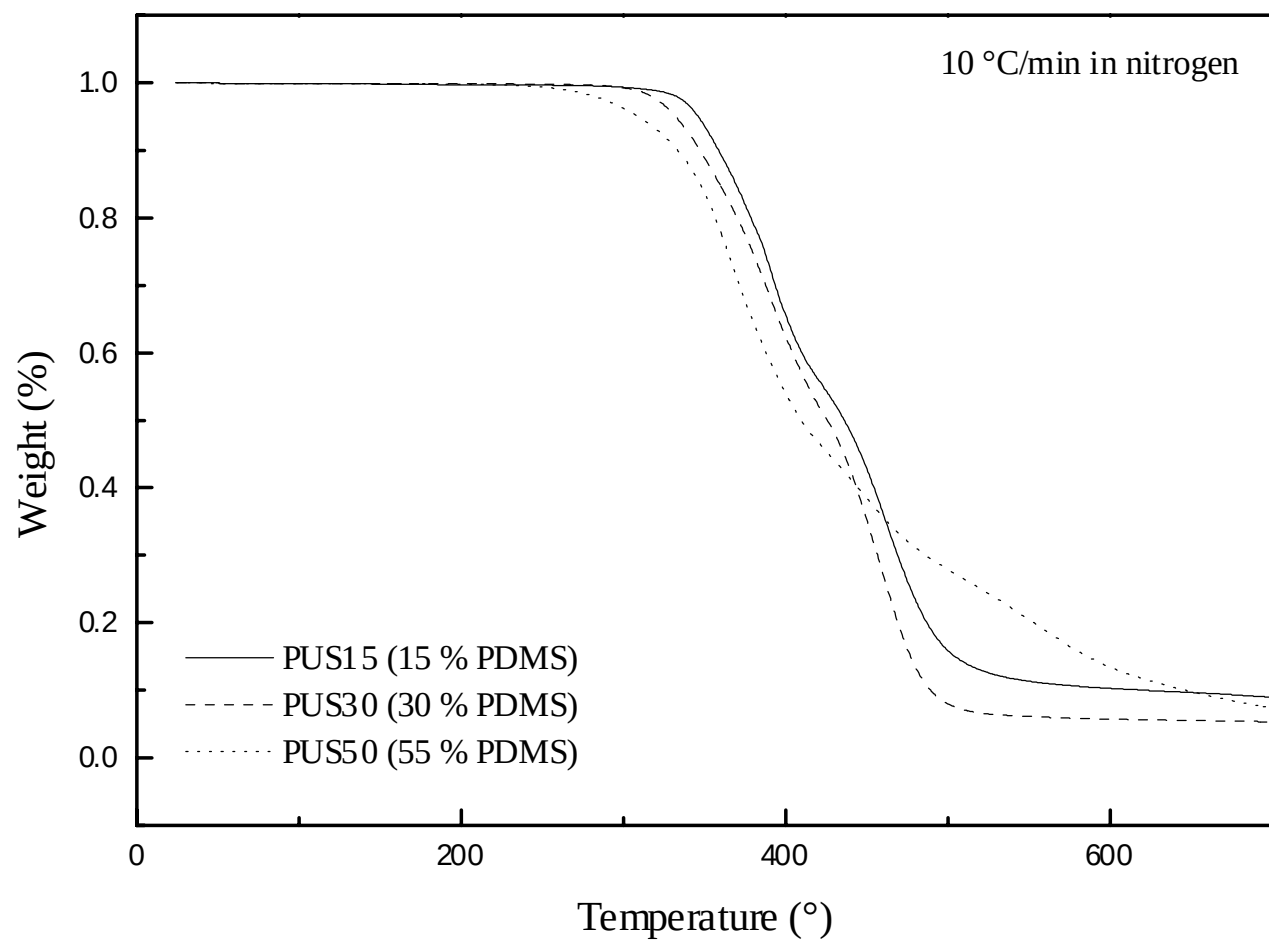


Figure 4.50 TGA thermograms of PDMS containing segmented polyurethanes with same soft segment content (63% SSC), but different PDMS contents (15-55%) in N₂

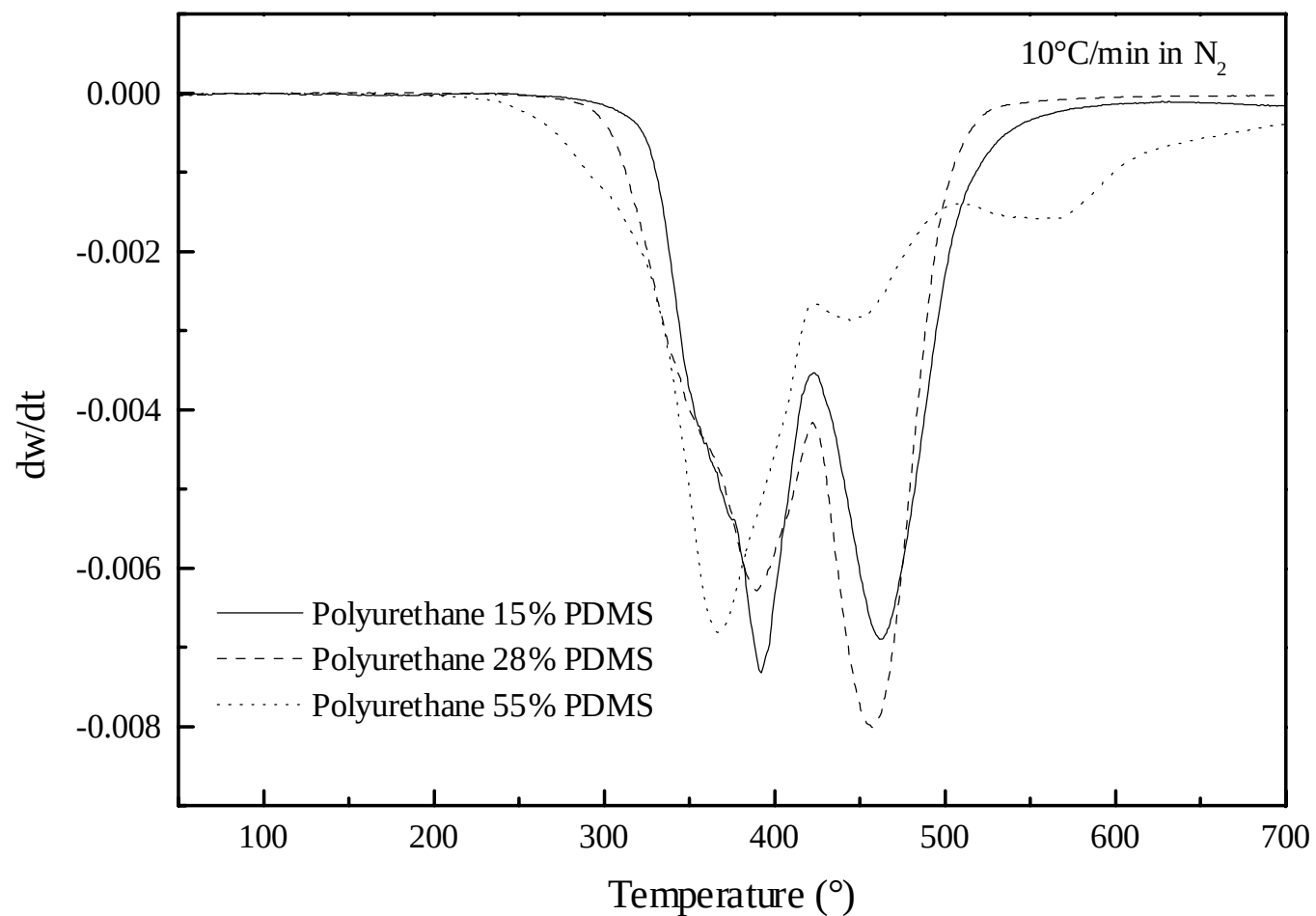


Figure 4.51 TGA thermogram derivative curves of PDMS containing segmented polyurethanes with same soft segment content (63% SSC), but different PDMS contents (15-55%) in N₂

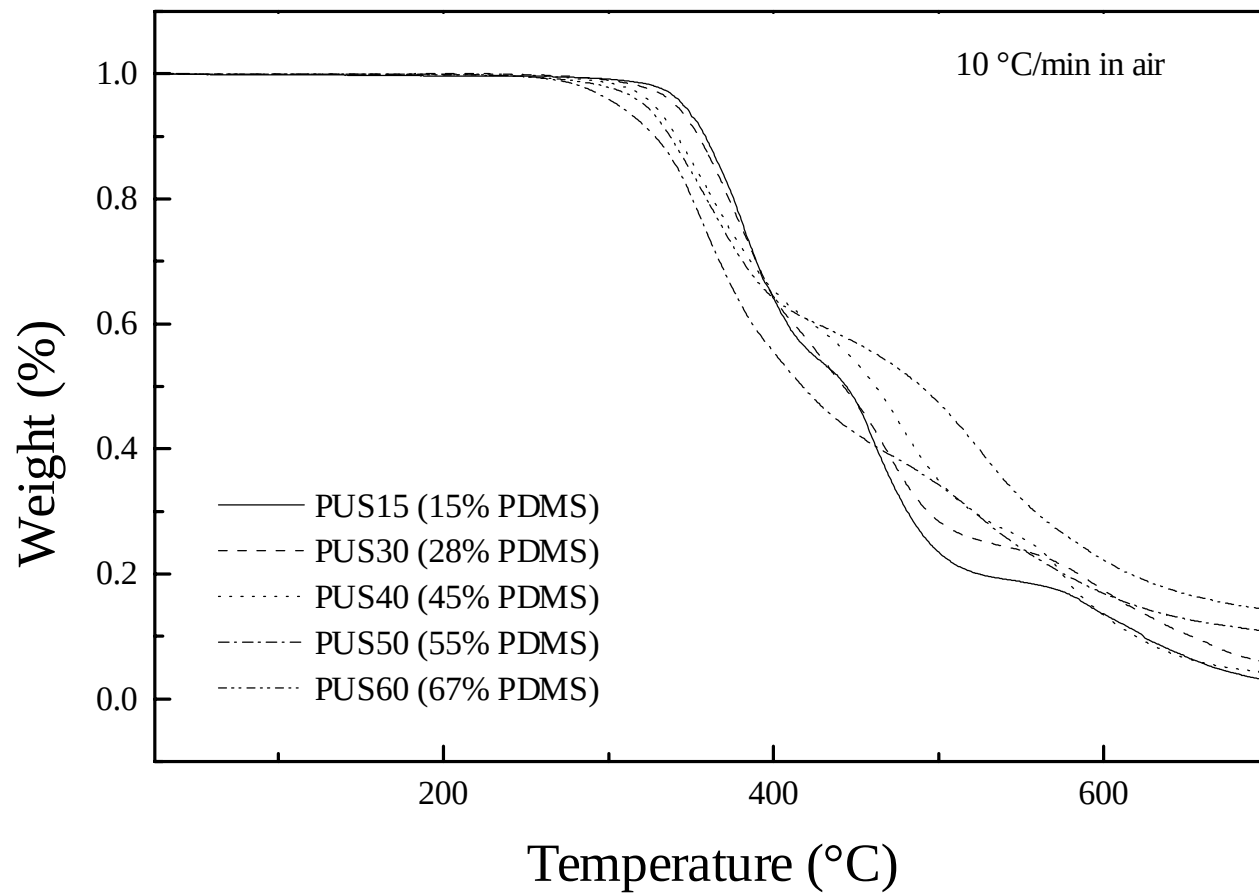


Figure 4.52 TGA thermograms of PDMS containing segmented polyurethanes with same soft segment content (63% SSC), but different PDMS contents (15-55%) in air

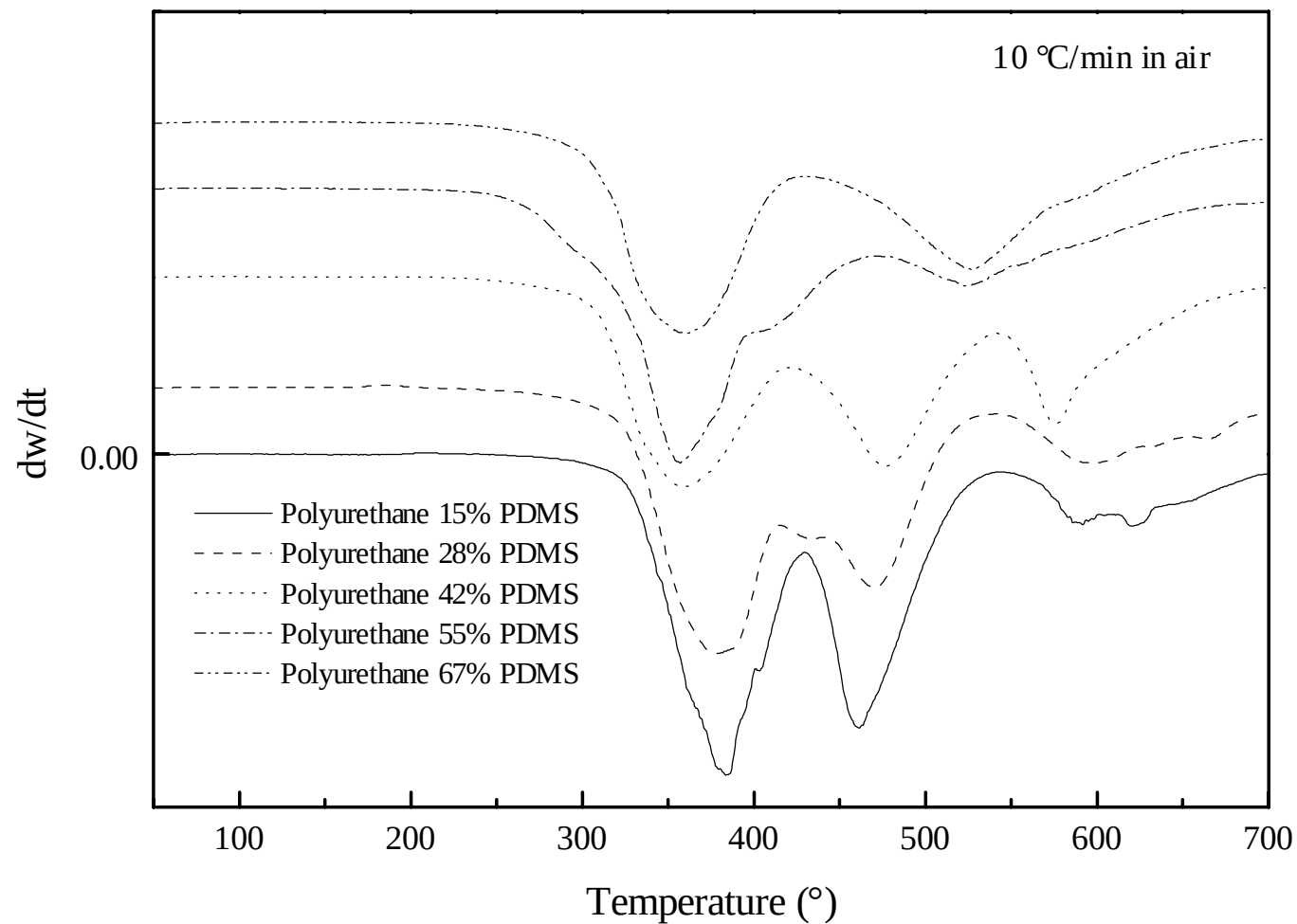


Figure 4.53 TGA thermogram derivative curves of PDMS containing segmented polyurethanes with same soft segment content (63% SSC), but different PDMS contents (15-55%) in air

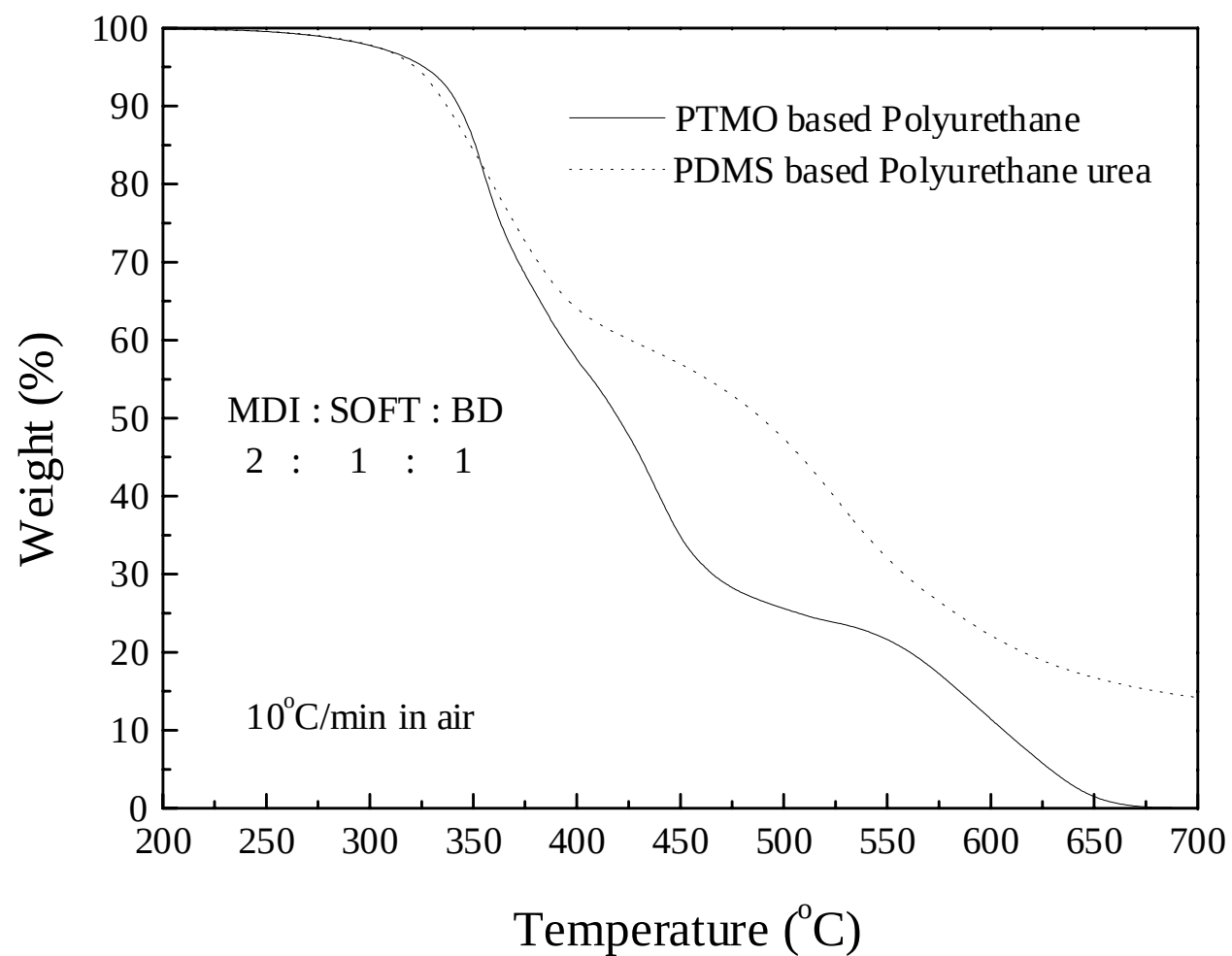


Figure 4.54 TGA thermograms PTMO and PDMS based segmented polyurethanes with same soft segment content (63% SSC) in air

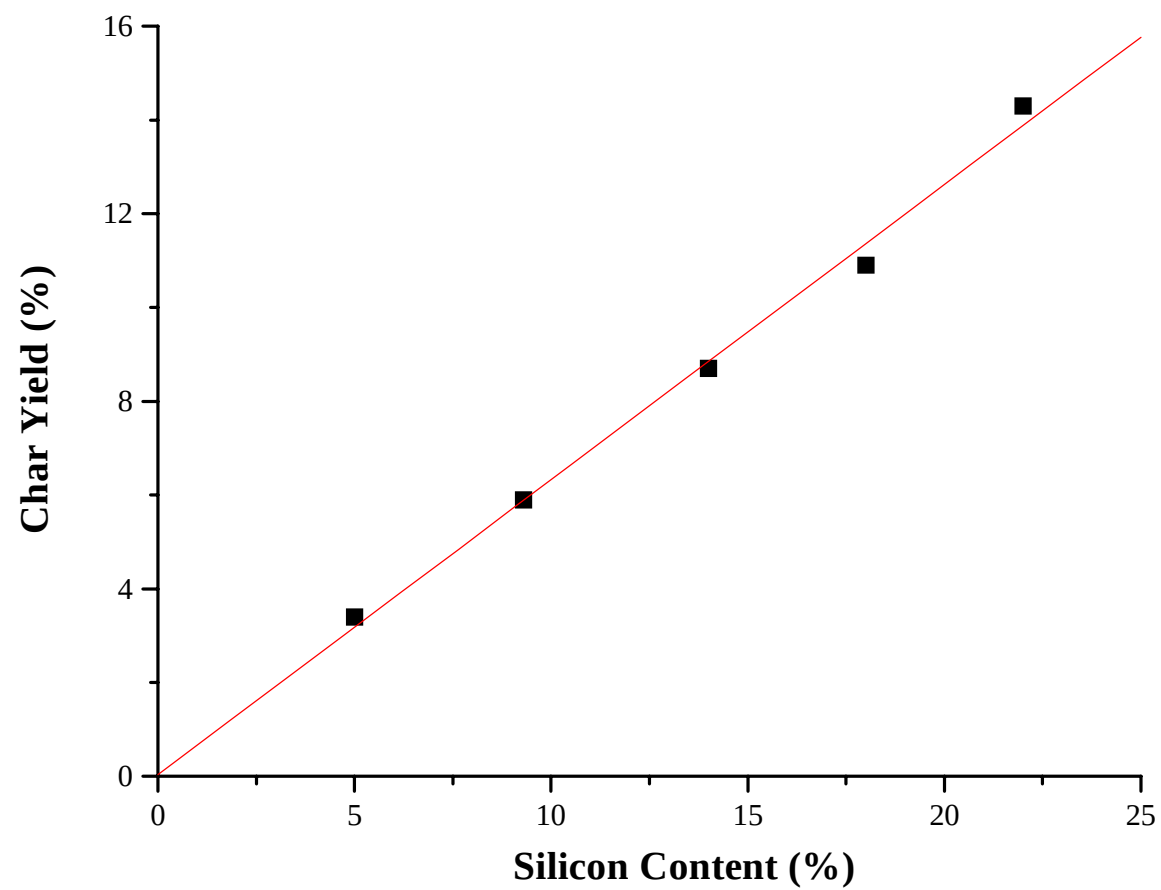


Figure 4.55 Char yields of PDMS containing polyurethanes at 700 °C in air vs silicon content

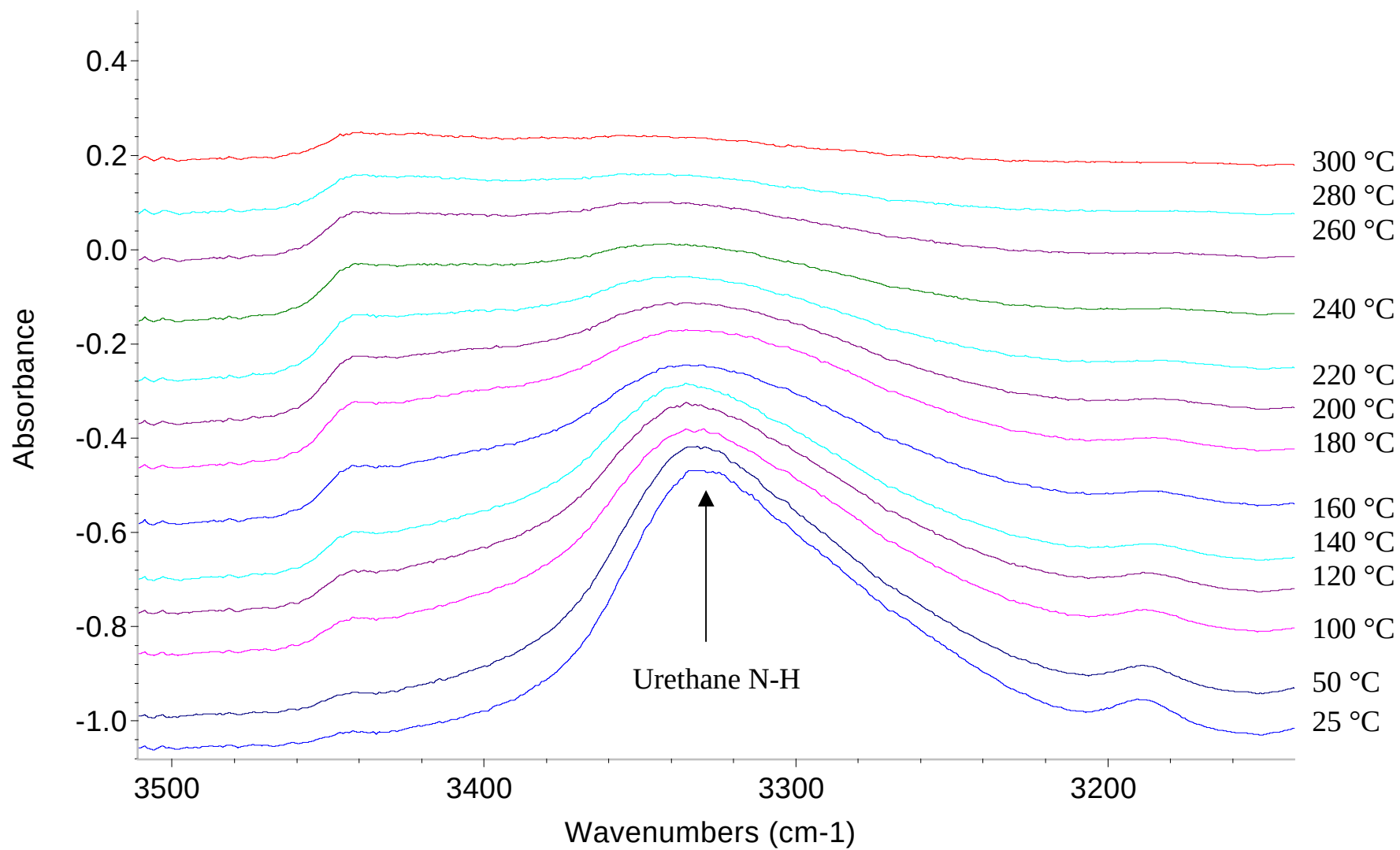


Figure 4.56 FTIR spectra of PTMO based segmented polyurethane at elevated temperature: N-H stretch

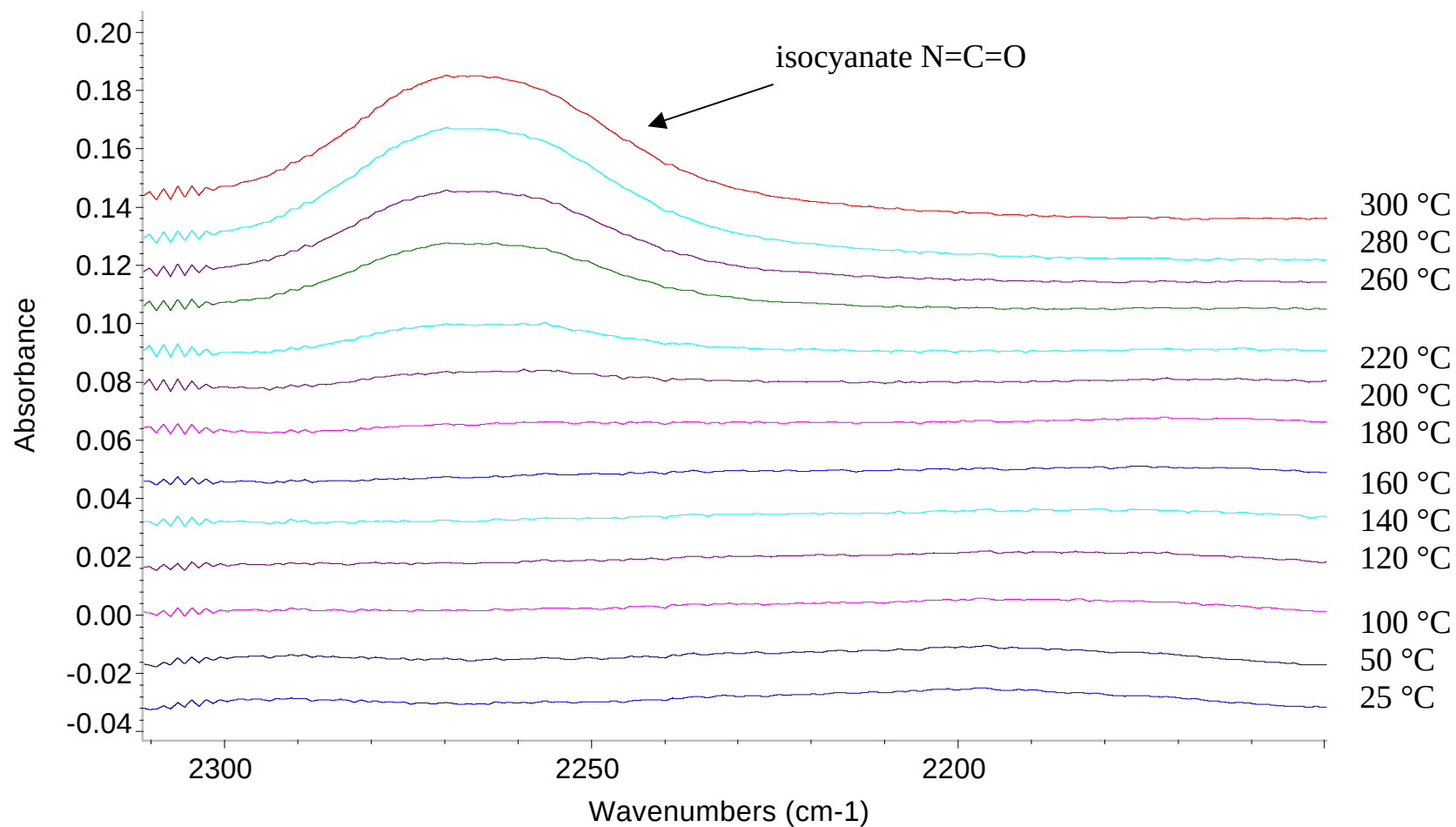


Figure 4.57 FTIR spectra of PTMO based segmented polyurethane at elevated temperature: N=C=O stretch

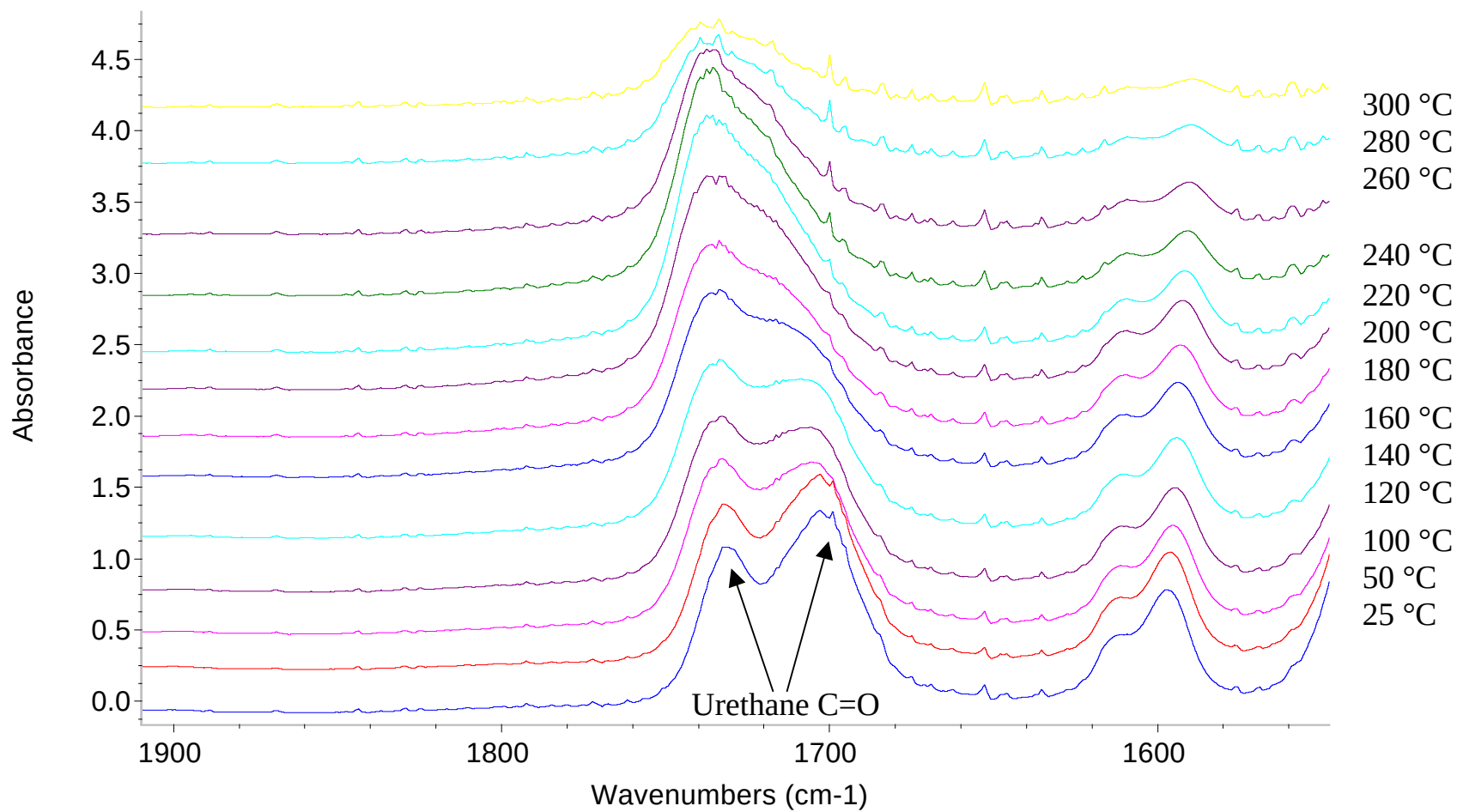


Figure 4.58 FTIR spectra of PTMO based segmented polyurethane at elevated temperature: C=O stretch

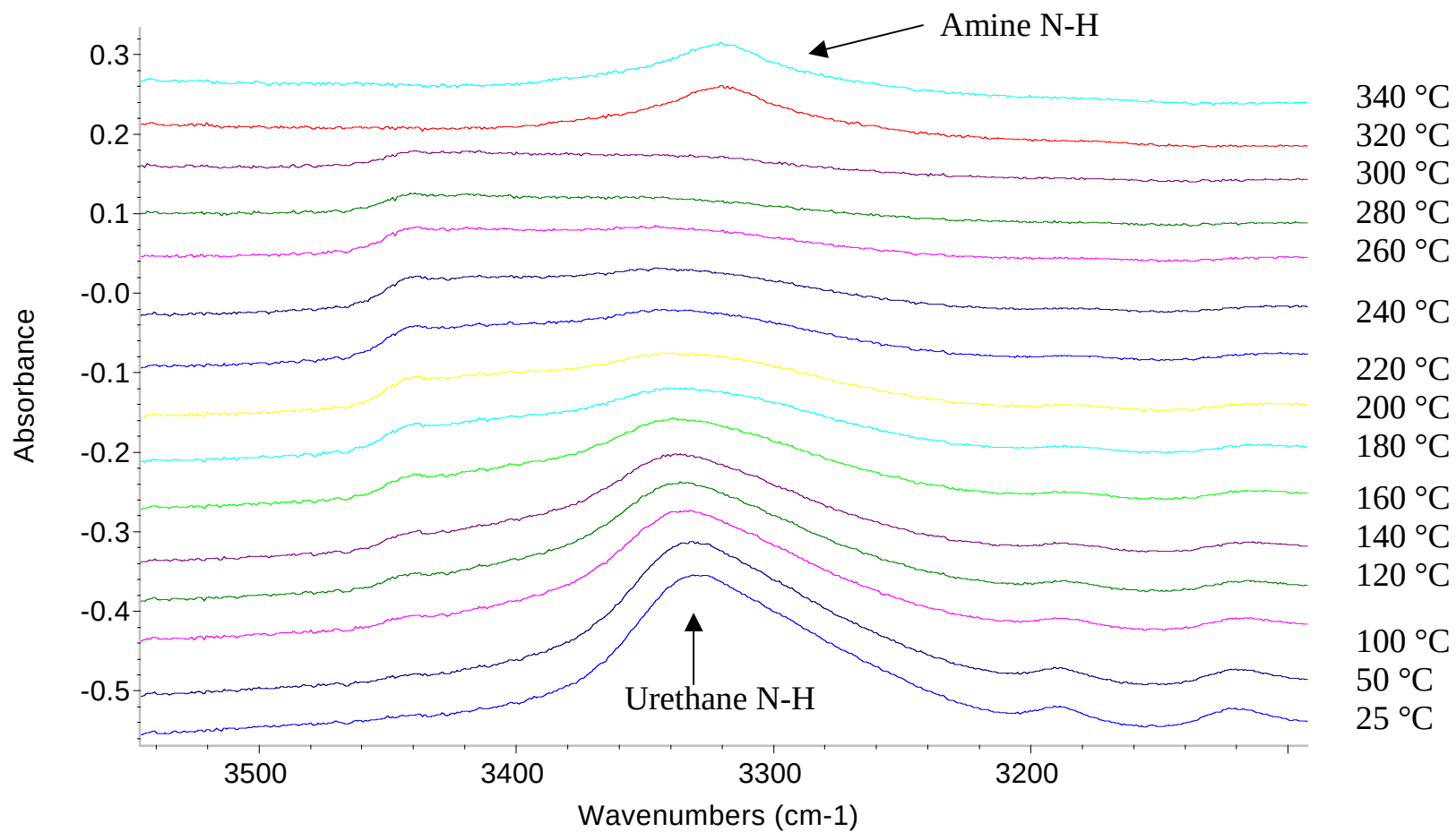


Figure 4.59 FTIR spectra of PDMS containing segmented polyurethane at elevated temperature: N-H stretch

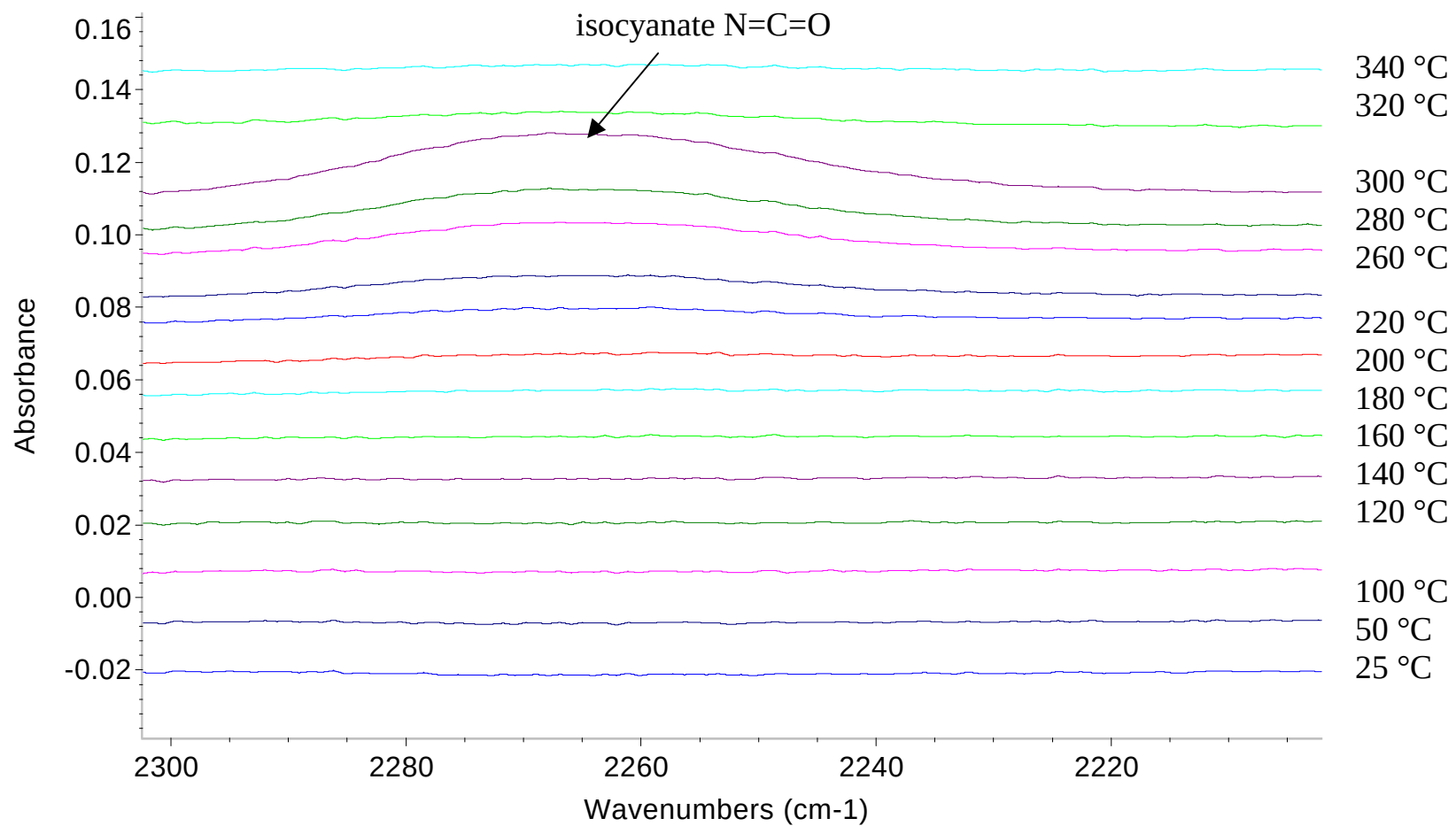


Figure 4.60 FTIR spectra of PDMS containing segmented polyurethane at elevated temperature: N=C=O stretch

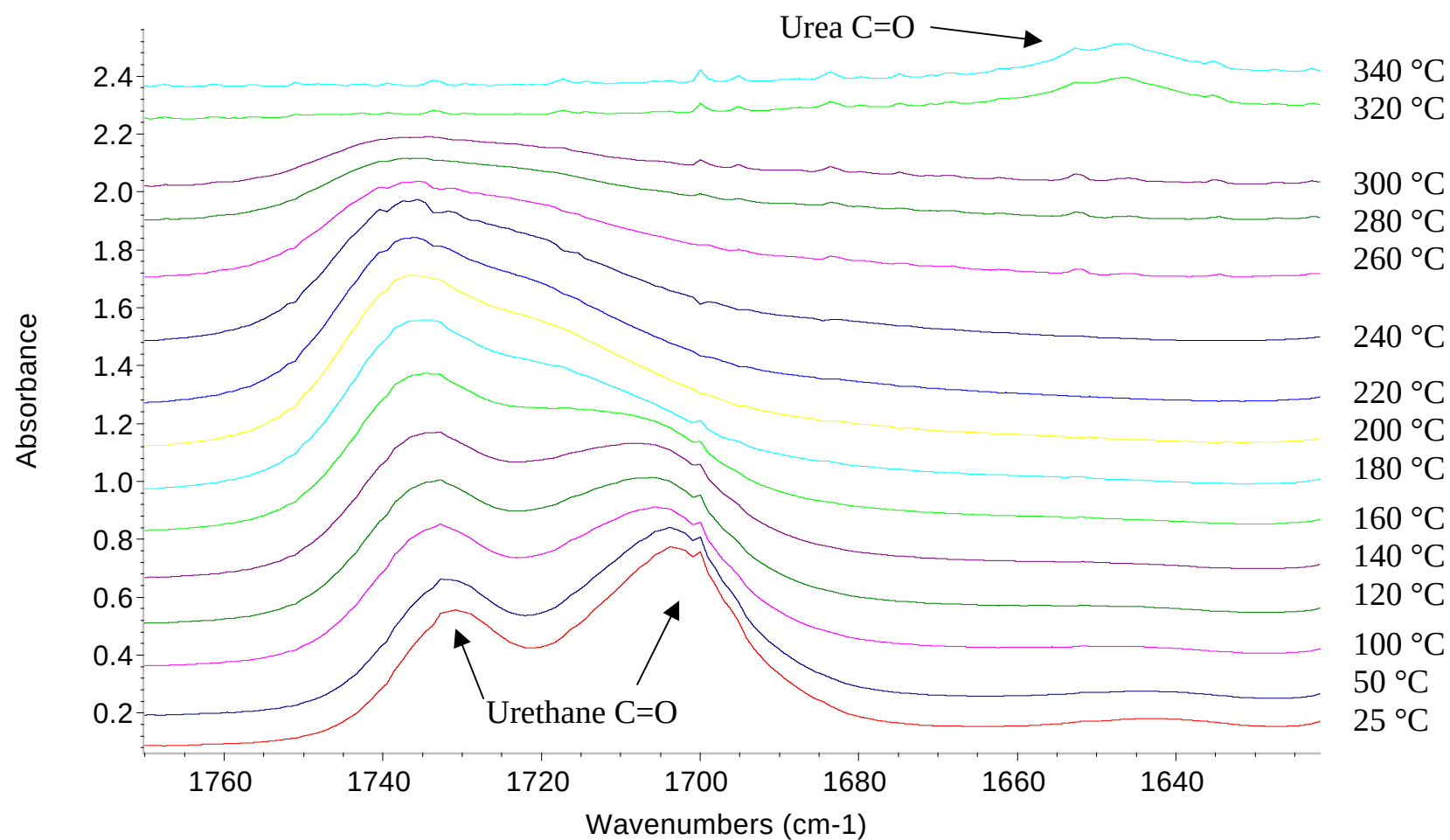


Figure 4.61 FTIR spectra of PDMS containing segmented polyurethane at elevated temperature: C=O stretch

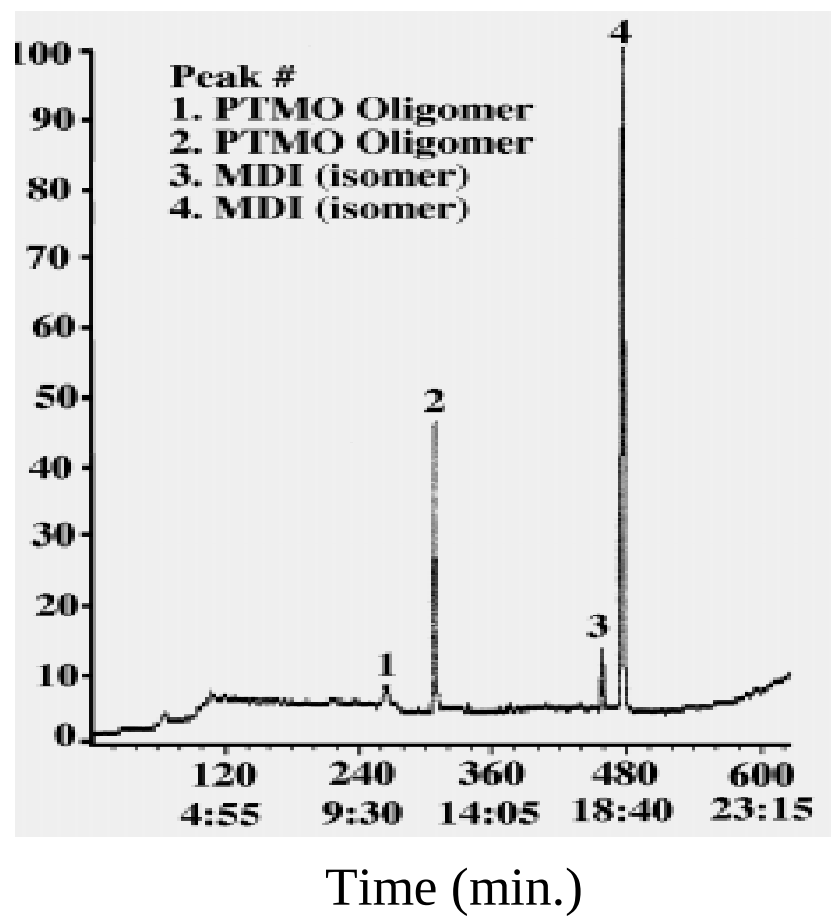


Figure 4. 62 Gas chromatographic analysis of PTMO based segmented polyurethane degraded at 450 °C in helium atmosphere

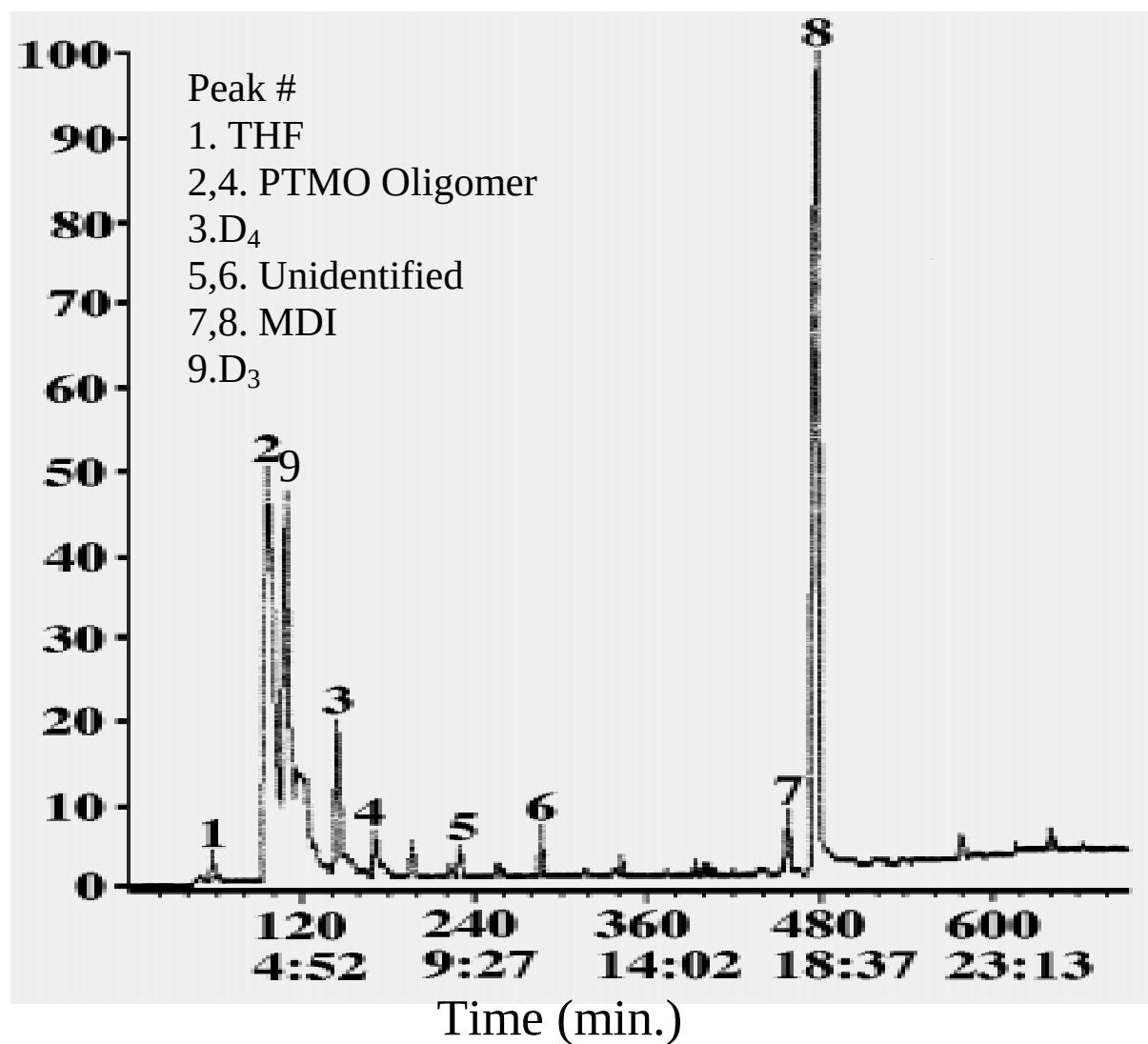


Figure 4. 63 Gas chromatographic analysis of PDMS containing segmented polyurethane degraded at 450 °C in helium atmosphere

4.6 Surface analysis of PDMS containing segmented polyurethanes

4.6.1 Electron Spectroscopy for Chemical Analysis

Many researchers have been interested in the novel surface properties exhibited by siloxane containing segmented copolymers. The surface segregation of the low surface energy segments (e.g. PDMS) has been widely reported.[221,222] Essentially, the low surface energy properties of siloxane provide a thermodynamic driving force for migration to the copolymer air or vacuum interface. XPS spectroscopy studies conducted on these copolymers showed that the surface compositions were predominately siloxane, even when the amount of siloxane incorporated during the synthesis was relatively small. This has been confirmed in the PDMS containing segmented polyurethane systems by an XPS angular dependent study of these polymers, which was performed by changing the escape angle of the photo-electrons from 90° to 15°. The depth of analysis decreased with the decreased angle between the analyzer slit and the sample plane. Three take off angles, 15°, 45°, and 90° were used, which correspond approximately to sampling depths ranging from 1 to 6 nm. Quantitative results have been plotted in Figure 4.64 and Figure 4.65. For all five samples, the silicon atom concentration increased dramatically from the calculated bulk value to the surface, suggesting PDMS enrichment throughout the XPS sampling depth. The ESCA results of the five PDMS containing polyurethanes are summarized in Table 4.20-4.24.

Table 4.20 Quantitative XPS study of angular dependant profile of PDMS containing segmented thermoplastic polyurethane (15% PDMS)

Angle	O%	Si%	N%	C%
15 °	22.9	14.2	1.99	60.9
45 °	21.3	9.86	2.91	65.9
90 °	21.3	7.45	3.53	67.7
bulk	18.0	2.58	3.9	75.4

**Table 4.21 Quantitative XPS study of angular dependant profile of PDMS
containing segmented thermoplastic polyurethane (28% PDMS)**

Angle	O%	Si%	N%	C%
15 °	21.6	15.5	1.66	61.0
45 °	20.8	13.6	2.70	62.0
90 °	20.5	12.6	2.80	63.6
bulk	17.8	4.90	4.30	73.0

**Table 4.22 Quantitative XPS study of angular dependant profile of PDMS
containing segmented thermoplastic polyurethane (45% PDMS)**

Angle	O%	Si%	N%	C%
15 °	22.2	17.6	1.84	56.7
45 °	21.0	17.7	2.93	56.5
90 °	21.3	16.9	3.1	57.4
bulk	17.6	7.49	4.68	70.2

**Table 4.23 Quantitative XPS study of angular dependant profile of PDMS
containing segmented thermoplastic polyurethane (55% PDMS)**

Angle	O%	Si%	N%	C%
15 °	23.6	20.3	1.58	54.5
45 °	22.0	19.4	2.48	56.1
90 °	22.4	18.4	2.66	56.6
bulk	17.3	10.0	5.00	67.7

Table 4.24 Quantitative XPS study of angular dependant profile of PDMS containing segmented thermoplastic polyurethane (67% PDMS)

Angle	O%	Si%	N%	C%
15 °	21.7	17.6	2.13	58.6
45 °	21.0	15.3	3.36	60.4
90 °	20.6	13.9	4.16	61.3
bulk	17.1	12.6	5.43	64.9

For the polyurethanes with lower PDMS content (15wt%), the angle-dependent PDMS concentration was much more drastic than for those with higher PDMS content. In other words, the high PDMS content polyurethanes had less of an effect on surface siloxane concentration with depth throughout the sampling depth profile. This indicates that a uniform siloxane surface layer might have formed on the polyurethanes with higher PDMS content.

This is further illustrated by the XPS surface analysis of the PDMS containing polyurethanes before and after exposure to 700°C. Figure 4.66 qualitatively compares the nature of the surface of the PUS40 (45wt% PDMS) before and after its exposure to 700°C via their Si2p peak. The Si2p peak of PDMS was observed at 102.1 eV as a result of the presence of O-Si-O on the surface before exposure to 700°C. However, after the sample had been heated to 700 °C in the TGA in air, the XPS surface analysis showed that the Si2p peak had shifted from 102.1 eV to 103.5 eV, becoming SiO₂. This indicates that the PDMS on the surface had been oxidized to complex silicates during the heating process. This conversion of PDMS to complex silicate is very helpful for improving the fire resistance of a polyurethane, since the surface formation of a complex silicate can act as a protective layer to retard the further burning of the solid polymer beneath it.

4.6.2 Contact angle analysis

The copolymer surface composition were also evaluated in a semi-quantitative manner through the use of contact angle measurements. The polyurethane control and

the PDMS containing polyurethane were analyzed and the contact angle values are summarized in Table 4.23. A significant increase in contact angle was observed between the unmodified control and the 15wt% PDMS containing polyurethane. The extremely large contact angle obtained for the PDMS containing polyurethane indicates the presence of a largely hydrophobic surface. In fact, the copolymer contact angles approaches those of pure PDMS.

Table 4.25 Water advancing contact angles of PDMS containing segmented polyurethanes

Sample ID	PDMS wt%	H ₂ O Contact Angle
PUR	0	79
PUS15	15	104
PUS28	28	104
PUS45	43	106
PUS55	55	108

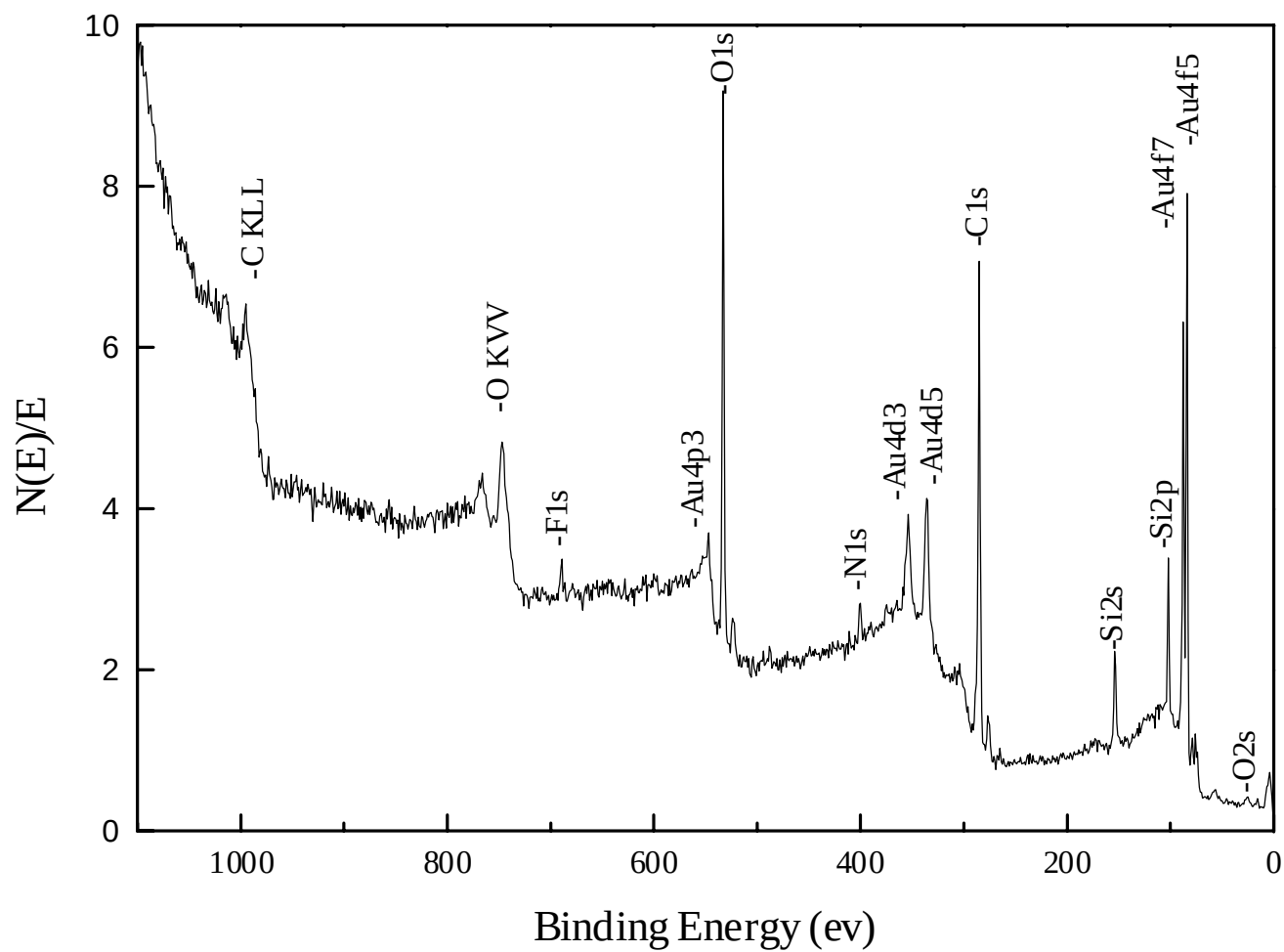


Figure 4.64 ESCA wide scan spectrum of PDMS containing segmented polyurethane

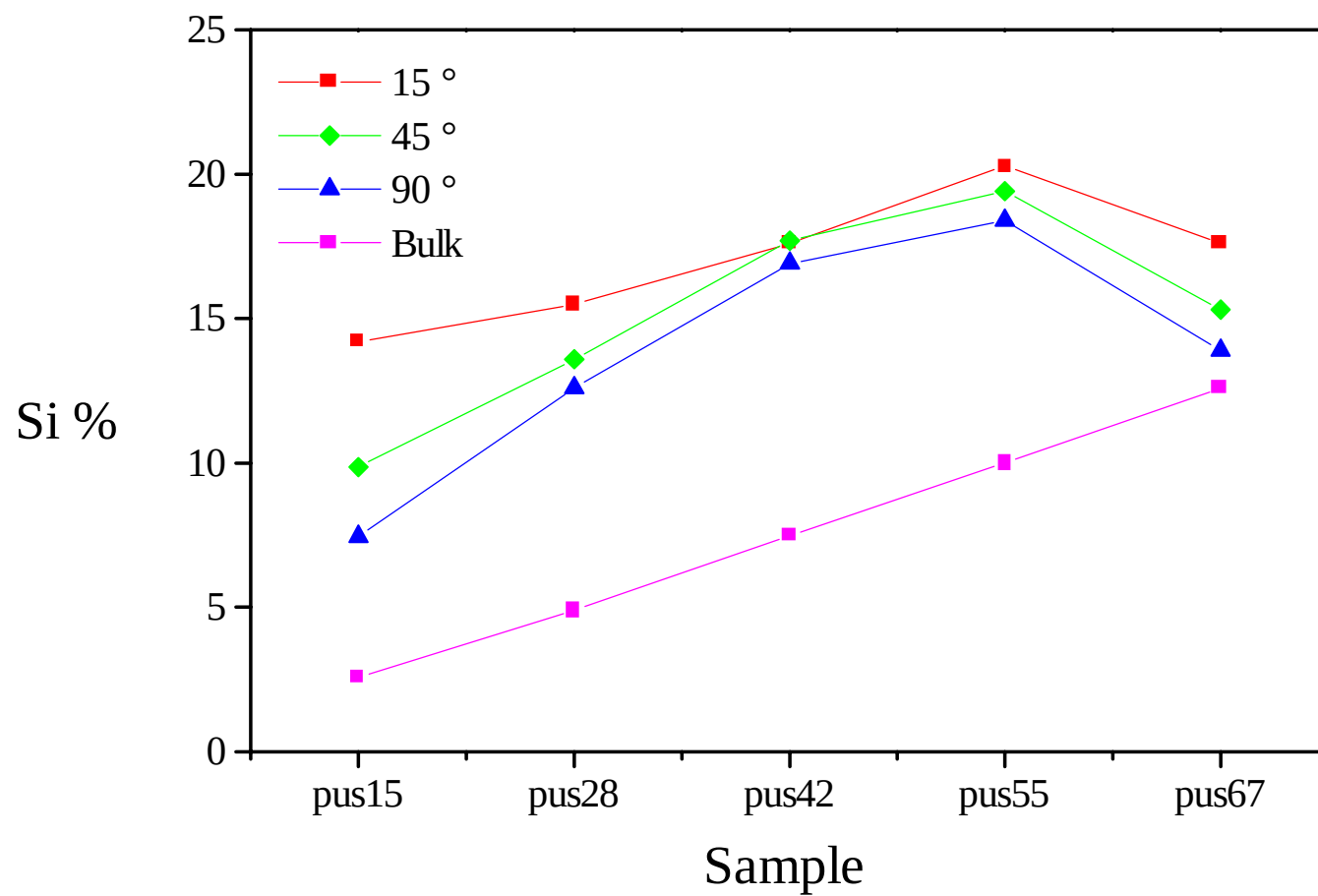


Figure 4.65 Surface enrichment of PDMS for PDMS containing segmented polyurethanes with different PDMS contents (15- 67%)

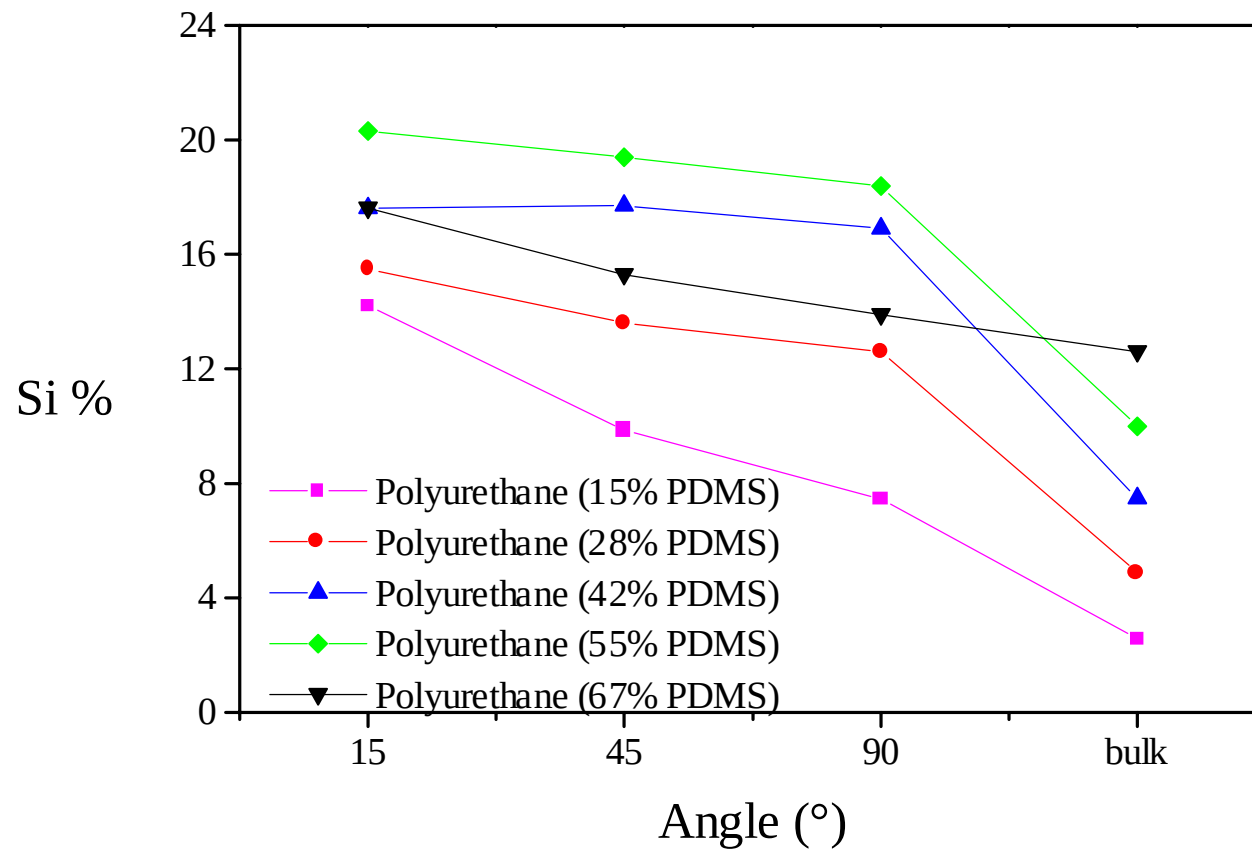


Figure 4.66 Surface enrichment of PDMS for PDMS containing segmented polyurethanes with different PDMS contents (15- 67%)

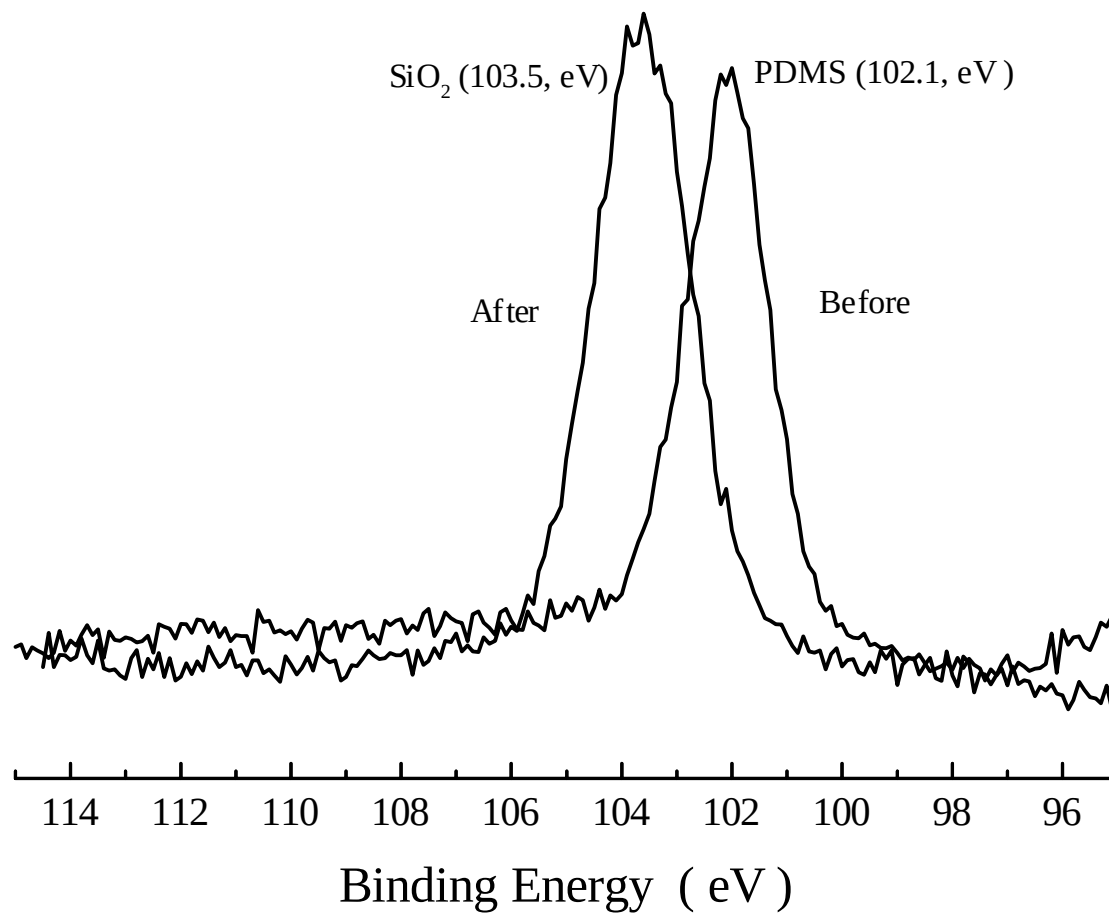


Figure 4.67 XPS analysis of PDMS containing polyurethane before and after exposure to 700 °C

4.7 Synthesis and characterization of PDMS based polyureas

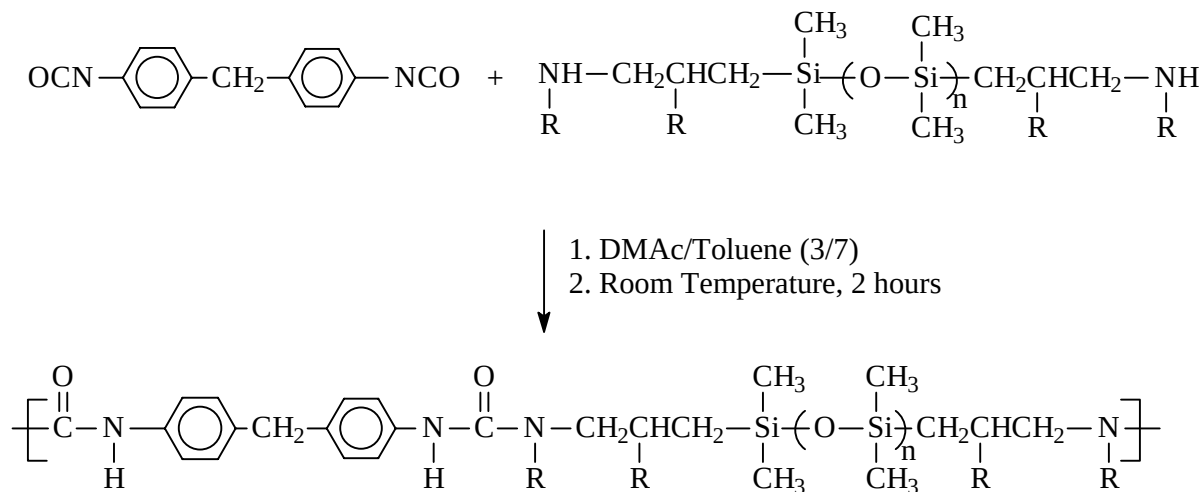
Polyorganosiloxanes have been recognized as one of the most important inorganic backbone polymers since they were first commercially introduced in 1940. Among them, polydimethylsiloxane (PDMS) is the most widely used, because of its many unique properties, including the extremely low glass transition temperature ($T_g = -123^\circ\text{C}$), low surface tension, low solubility parameter, low dielectric constant, as well as its transparency to visible and UV light, resistance to ozone and atomic oxygen, high permeability to various gases, and biocompatibility. Another advantage of the polydimethylsiloxane is that their attractive properties vary only slightly over a wide temperature range. Unfortunately, PDMS has poor mechanical strength even with very high molecular weight. Generally, PDMS must be chemically crosslinked and reinforced with finely divided high surface silica to develop useful elastic modulus and tensile strength. However, the crosslinking and addition of silica filler may complicate the processing of these materials.

Besides crosslinking, another effective way to improve the mechanical strength of PDMS is to chemically connect it to a hard glassy or crystalline segment, in other words, to synthesize block or segmented copolymers that contain both soft and hard segments. This approach has been used to make a number of PDMS containing copolymers. In fact, the first siloxane-urea copolymer was prepared in our group by reacting aminopropyl-terminated PDMS with MDI (4,4'-diphenylmethane diisocyanate) in solution.

4.7.1 Synthesis of PDMS based polyureas

To compare with previous results, polyureas were synthesized from both primary aminopropyl and secondary aminoisobutyl terminated PDMS, by a by direct reaction of diamine (primary or secondary) terminated PDMS with MDI at room temperature. The siloxane concentration and hard segment concentration were controlled by varying the molecular weight of the PDMS soft segment, i.e. soft segment length. The synthetic route is illustrated in Scheme 4.3. In order to make a homogenous reaction solution, it is very important to use a mix of solvents, i.e. DMAc and toluene. The reagents, PDMS and MDI, need to be dissolved in the appropriate solvent prior to the reaction. Thus, the MDI was first dissolved in a DMAc/toluene mixture (2:3), and the PDMS was dissolved

in toluene. The reaction starts by adding the PDMS solution into the MDI solution using an addition funnel. It is important to use a mixed solvent to dissolve the MDI before adding the PDMS. Otherwise, the PDMS solution will immediately precipitate because of the solubility differences.



R=H, Primary amine terminated PDMS, $M_n=1528, 2897, 4229$

R=CH₃, Secondary amine terminated PDMS, $M_n=1235, 3383$

Scheme 4.4 Synthesis of PDMS based polyureas

Due to the high reactivity of the aminoalkyl group toward the isocyanate group, the polymerization proceeded smoothly at room temperature without the use of a catalyst. The molecular weight of these polyureas were found to be high according to their intrinsic viscosity measured in THF, as illustrated in Table 4.24. The intrinsic viscosity values for the polyureas synthesized from secondary aminoalkyl terminated PDMS were lower than that of primary aminoalkyl terminated PDMS. This difference may result from the hydrogen bonding differences between the two polyureas, which can reduce the flexibility of the chain and increase solution viscosity, rather than the molecular weight difference.

4.7.2 Structural identification

The structure of the polyureas were identified by ^1H NMR and FTIR spectra, illustrated in Figure 4.67 and Figure 4.68, respectively. In the ^1H NMR spectrum, urea protons were observed at 6.3 ppm. The peaks at 3.9, 7.1, and 7.3 ppm are due to aromatic protons and benzyl protons on MDI. The protons of the PDMS end groups were observed at 3.2, 3.0, 2.0, 1.0, 0.6, and 0.4 ppm. The protons associated with methyl group attached to silicon showed a large peak at 0.1 ppm.

Table 4.26 Intrinsic viscosities and glass transition temperatures of PDSM based polyureas

Sample	End Group	PDMS (g/mole)	PDMS wt%	η (dL/g), 25°C, THF	T_g (°C)
PUE1	Secondary aminoalkyl	1235	82	0.40	-103
PUE2	Secondary aminoalkyl	3363	92	0.42	-116
PUE3	Primary aminoalkyl	1528	86	0.83	-112
PUE4	Primary aminoalkyl	2897	92	0.45	-119
PUE5	Primary aminoalkyl	4229	94	0.64	-119

FTIR spectra verified the existing of the polymer structure. The absorption bands around 3320 cm^{-1} (urea N-H stretch) and 1645 cm^{-1} (H-bonded urea C=O) are assigned to the urea linkage. The peaks at 1260 cm^{-1} (sym. CH_3 bending), 1020 and 1100 cm^{-1} (Si-O-Si stretching), 803 cm^{-1} (CH_3 rocking) are assigned to the PDMS in the copolymer. However, the absorption band for C-N stretch in primary aminoalkyl terminated polyurea 1560 cm^{-1} was found to be different from that of secondary aminoalkyl terminated polyurea, which was around 1519 cm^{-1} .

4.7.3 Thermal analysis

The thermal transitions of the polyureas were characterized by DSC and DMA as shown in Figure 4.69, Figure 4.70, and Figure 4.71. In the DSC thermogram, only the glass transition temperature of the PDMS was detected, and the T_g was found to decrease with decreasing PDMS block length. No thermal transition was detected for the hard segment. However, in the DMA thermogram of the polyurea made from primary aminoalkyl terminated PDMS (Figure 4.70), two thermal transitions were clearly detected. The low temperature transition at -110°C is due to the T_g of the PDMS, and the high temperature transition at -85°C can be attribute to the T_g of hard segment. This clearly indicates that PDMS based polyureas have a two-phase morphology, even though the hard segment length was very short and hard segment concentrations were very low. This two-phase morphology probably account for the fact that these materials are exceptional strong, considering the small amount of PDMS they contain. Moreover, the storage moduli of these polyureas increase with a decrease in PDMS content, i.e., an increase in hard segment content. The DMA thermogram of the polyurea made from secondary aminoalkyl PDMS also showed two transitions: the low temperature transition at -99°C as a result of the T_g of the PDMS, and the high temperature transition resulting from the T_g of the hard segment. It should be noted that the T_g of the PDMS in polyurea is much lower than that of the PDMS in the polyurea made from primary aminoalkyl terminated PDMS, which enhances hydrogen bonding. On the other hand, the T_g of the hard segment is drastically lower than the primary analogue. This suggests that the soft segment PDMS experiences a better phase mixing with the hard segment if the end-group is a secondary aminoalkyl. This difference in phase mixing might also contribute to the hydrogen bonding variation caused by the different end-group. The primary aminoalkyl terminated PDMS, once reacted with MDI, can generate urethane linkages that hydrogen bond much more effectively with other urethane linkage than the corresponding secondary one. It is clear that stronger hydrogen bonding can promote the aggregation of the hard segment, and phase separation between the soft and the hard segments.

The thermal stability of the polyureas was analyzed by TGA and the results are summarized in Table 4.25. The thermal stability in terms of 5% weight loss increased with PDMS block length, both in air and nitrogen. This is because the weakest point in a

polyurea is its hard segment, which decreases with increasing PDMS block length. This is clearly demonstrated in the TGA thermogram and the thermogram derivative curves shown in Figure 4.73 to Figure 4.76. The polyureas displayed two-step degradation both in air and in nitrogen. The maximum weight loss rate, which is shown as the peak in the TGA derivative curves, occurred at about the same temperature, regardless of the atmosphere. The char yield at 700°C are higher in air than in nitrogen for all the polyureas because of the formation of a silicate-like material that enhances char yield in air.

Table 4.27 TGA results of PDMS based polyureas

Sample	PDMS wt%	5% Weight Loss in Air	Char Yield at 700 °C in air	5% Weight Loss in N ₂	Char Yield at 700 °C in air
PUE1	82	298	13.2	313	6.5
PUE3	86	322	20.8	323	6.5
PUE4	92	334	20.0	338	7.5
PUE5	94	340	15.6	344	0.5

4.7.4 Surface analysis

The surface composition of the polyureas were investigated by ESCA at three take off angles: 15°, 45°, 90°. The silicon concentrations were converted to PDMS content based on the different silicon concentrations in the PDMS oligomers, as shown in Table 4.26. No obvious angular dependence or surface enrichment of silicon was observed for these samples due to the high concentration (>86) of PDMS in these polymers except for the PUE1. The higher percentage of PDMS on the surface of the PUE1 compared to the PUE2, which has a similar PDMS bulk concentration, might be due to the lack of hydrogen bonding in the PUE1, resulting in higher PDMS segment mobility.

Table 4.28 Surface compositions of polyureas measured by XPS

Sample	PDMS wt% in bulk	PDMS wt% measured at 15 °	PDMS wt% measured at 45 °	PDMS wt% measured at 90 °
PUE1	82	92.5	87.8	84.9
PUE3	86	76.5	80.2	80.9
PUE4	92	89.4	88.1	88.4
PUE5	94	92	92.3	95.1

4.7.5 Tensile properties

All polyureas can produce clear films. The films used to test tensile strength were prepared by solution casting from THF. The films were then dried at room temperature for 6 hours before further drying at 80 °C in vacuum oven for 24 hours. The films were aged at room temperature for over a week before testing. All the polyureas showed good elasticity and toughness, and their tensile properties are illustrated in Figure 4.77. However, the polyureas made from secondary aminoisobutyl terminated PDMS differ dramatically in mechanical strength from those made from primary aminopropyl terminated PDMS. Moreover, the polyureas made from primary aminoalkyl terminated PDMS showed excellent tensile strength and elongation, considering that they contained over 86% PDMS. The polyureas made from primary aminoalkyl terminated PDMS also demonstrated higher modulus than the corresponding secondary analogue. We attribute these drastic tensile property differences to the lack of hydrogen bonding in the secondary aminoalkyl terminated PDMS polyureas. This is an excellent example of how important hydrogen bonding can be in determining the physical properties of polymers, even at very low concentration.



- a: Polyurea based on primary amino alkyl terminated PDMS
b: Polyurea based on secondary amino alkyl terminated PDMS

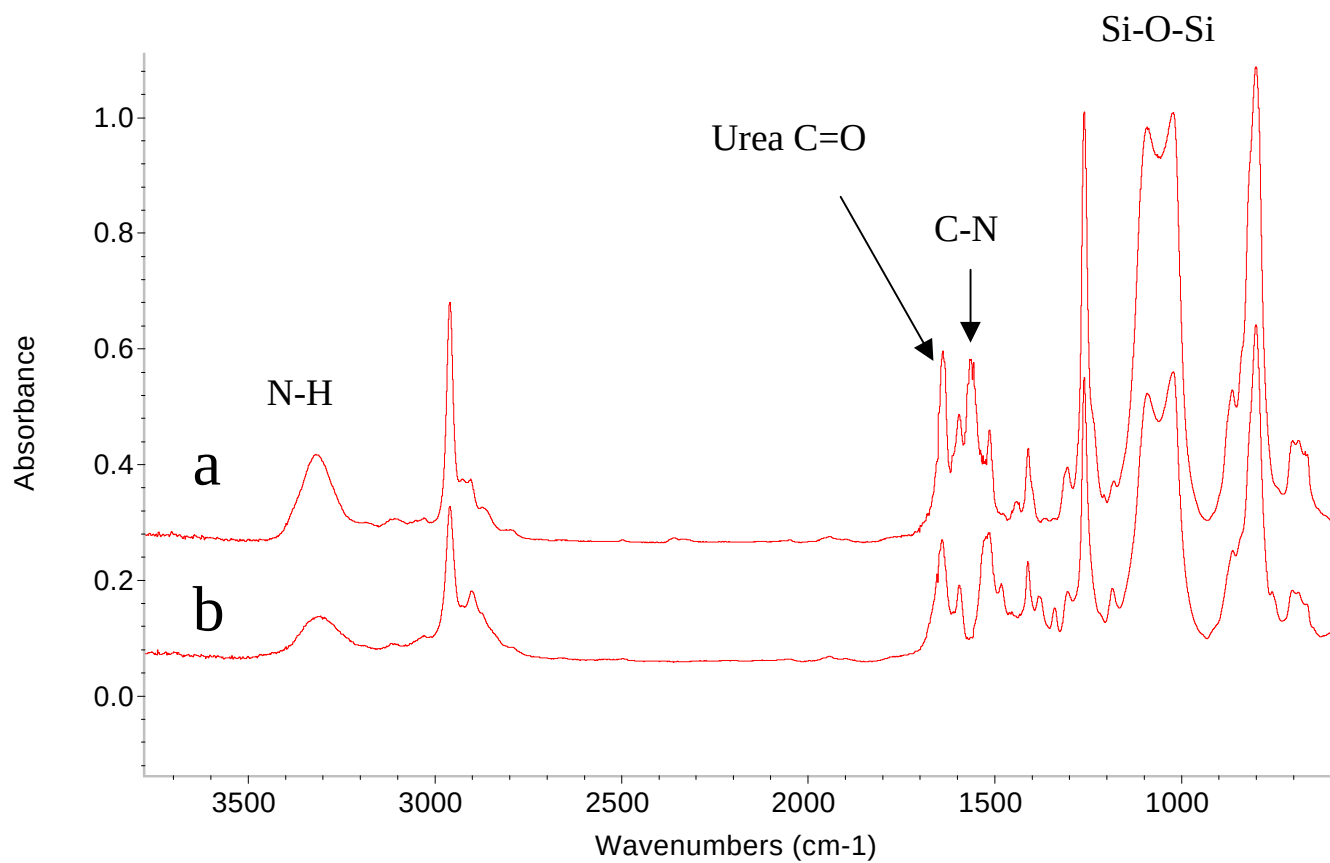


Figure 4.69 FTIR spectra of PDMS based polyureas

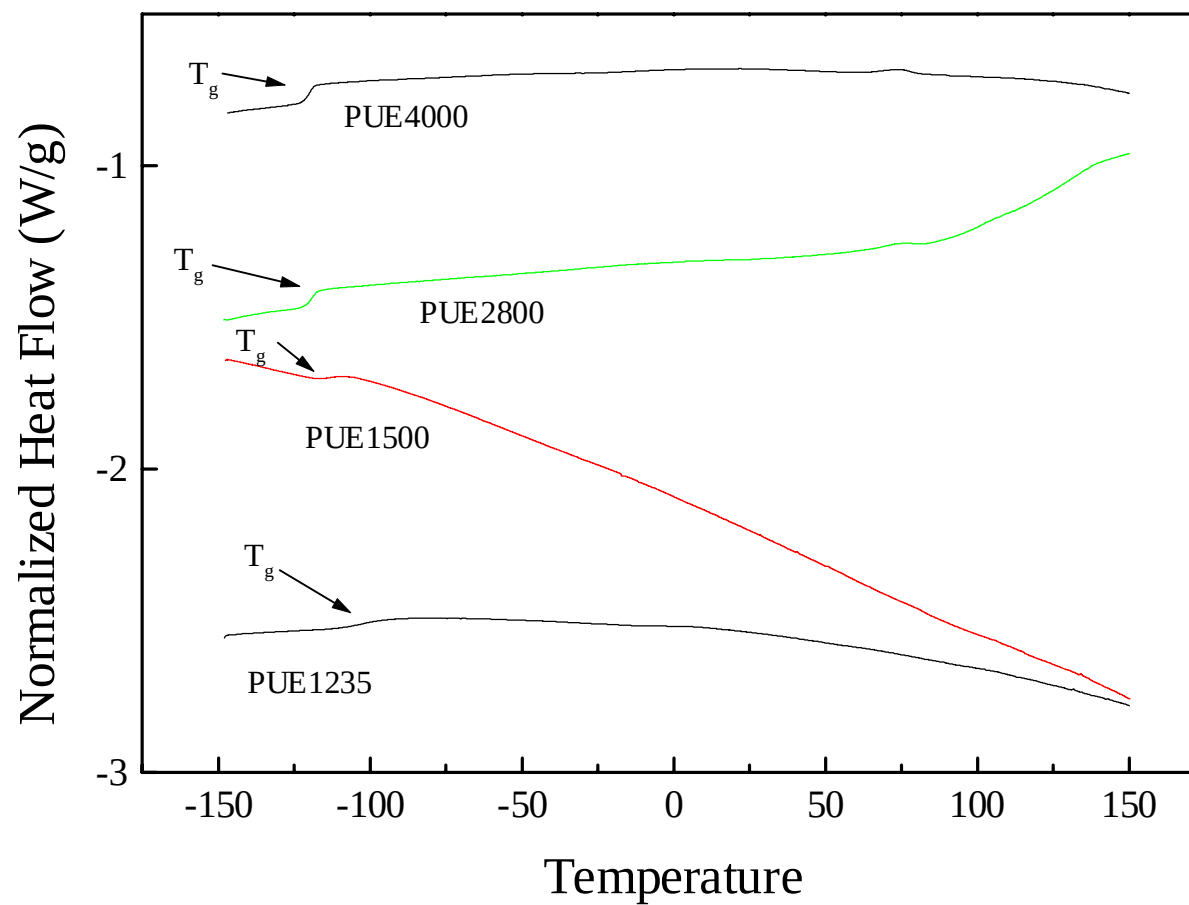


Figure 4.70 DSC thermograms of PDMS based polyureas

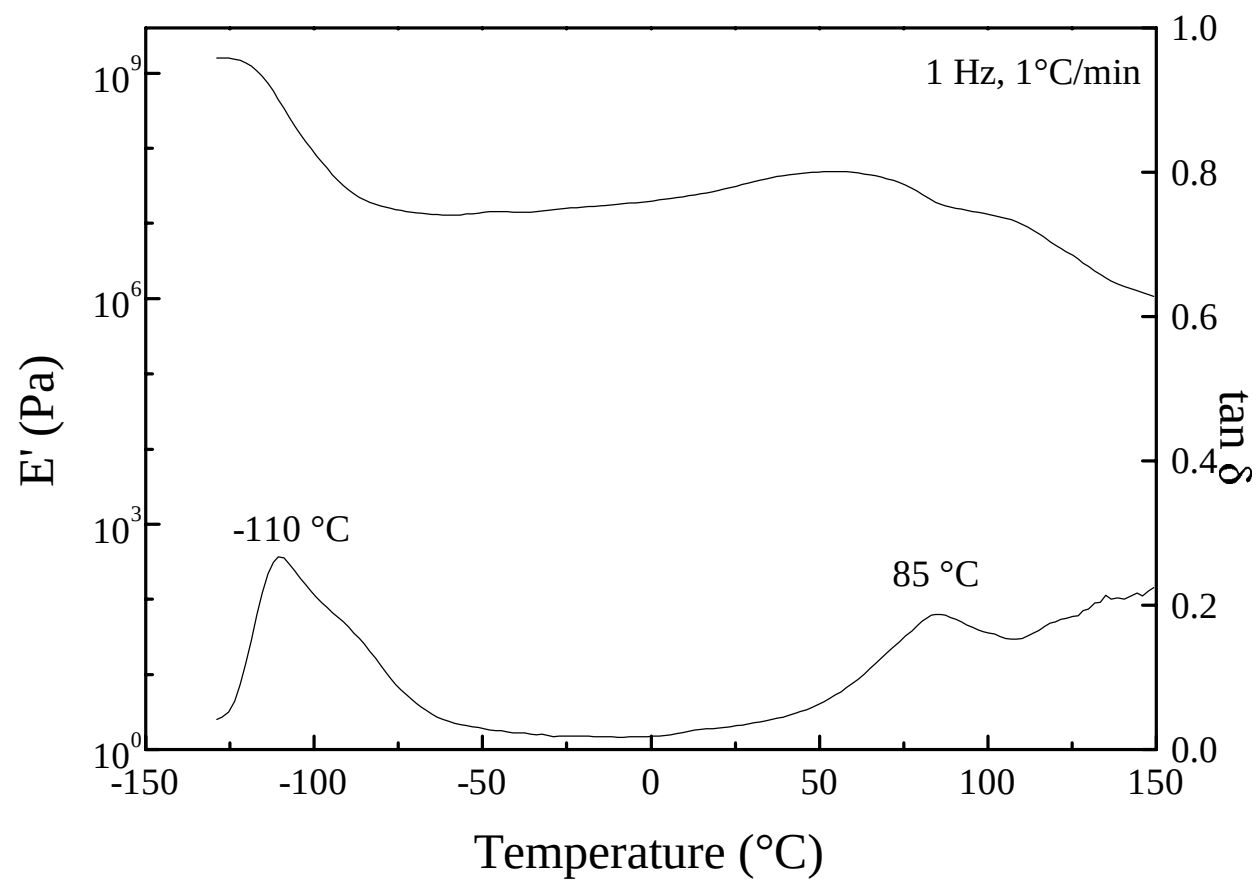


Figure 4.71 DMA thermograms of PDMS (primary aminoalkyl terminated) based polyureas

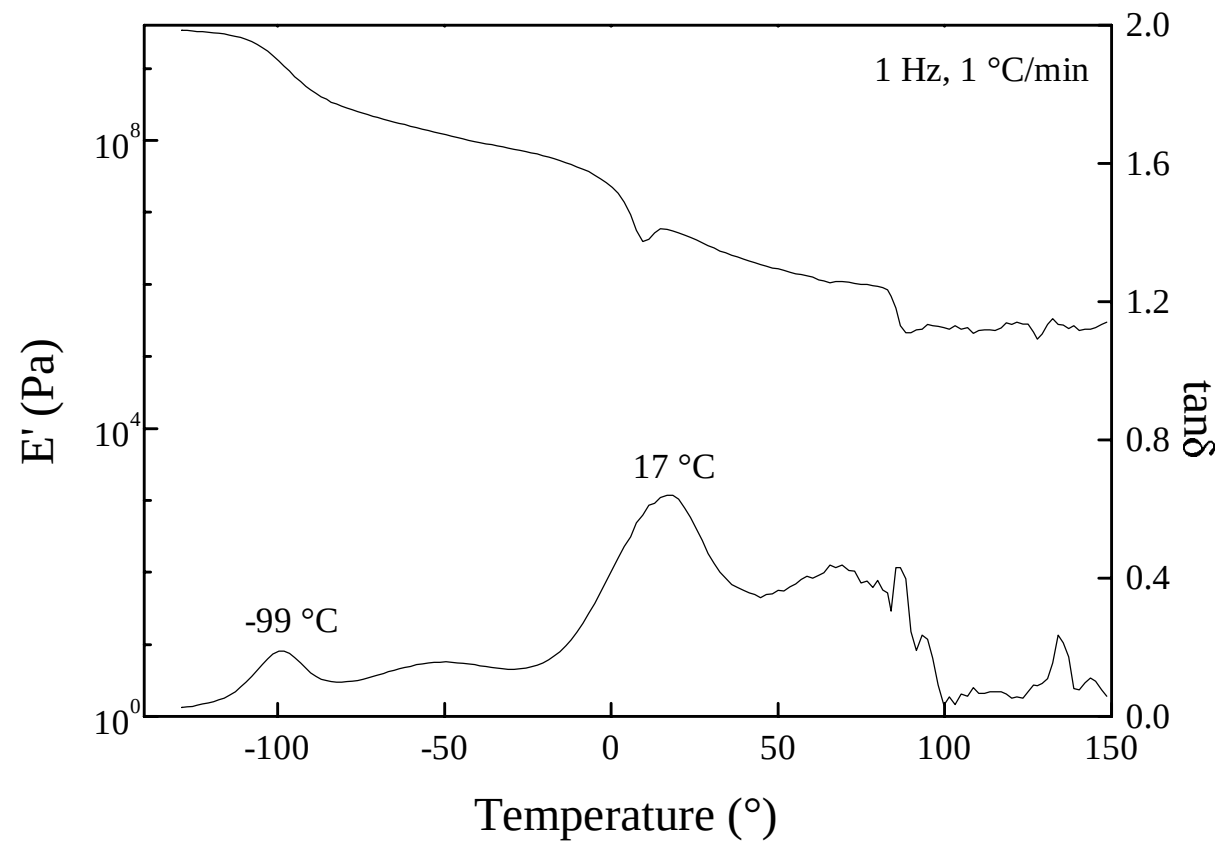


Figure 4.72 DMA thermograms of PDMS (secondary aminoalkyl terminated) based polyureas

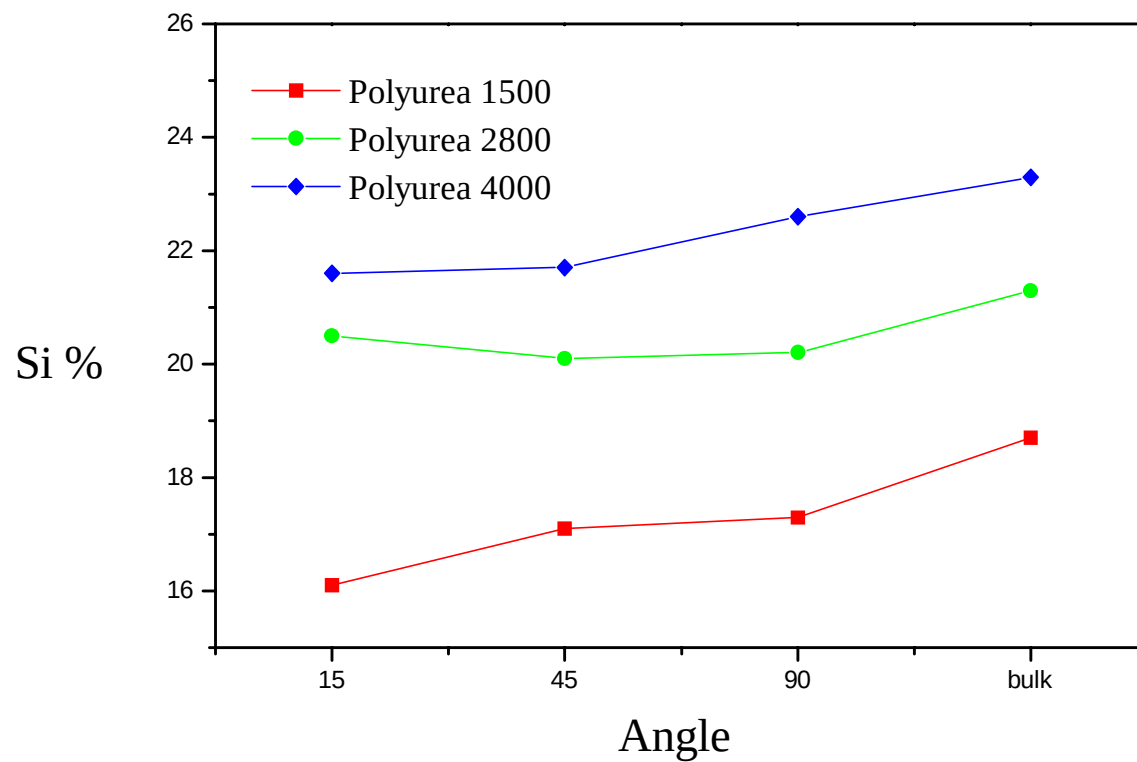


Figure 4.73 Quantitative XPS study of angular dependant profile of PDMS based polyureas

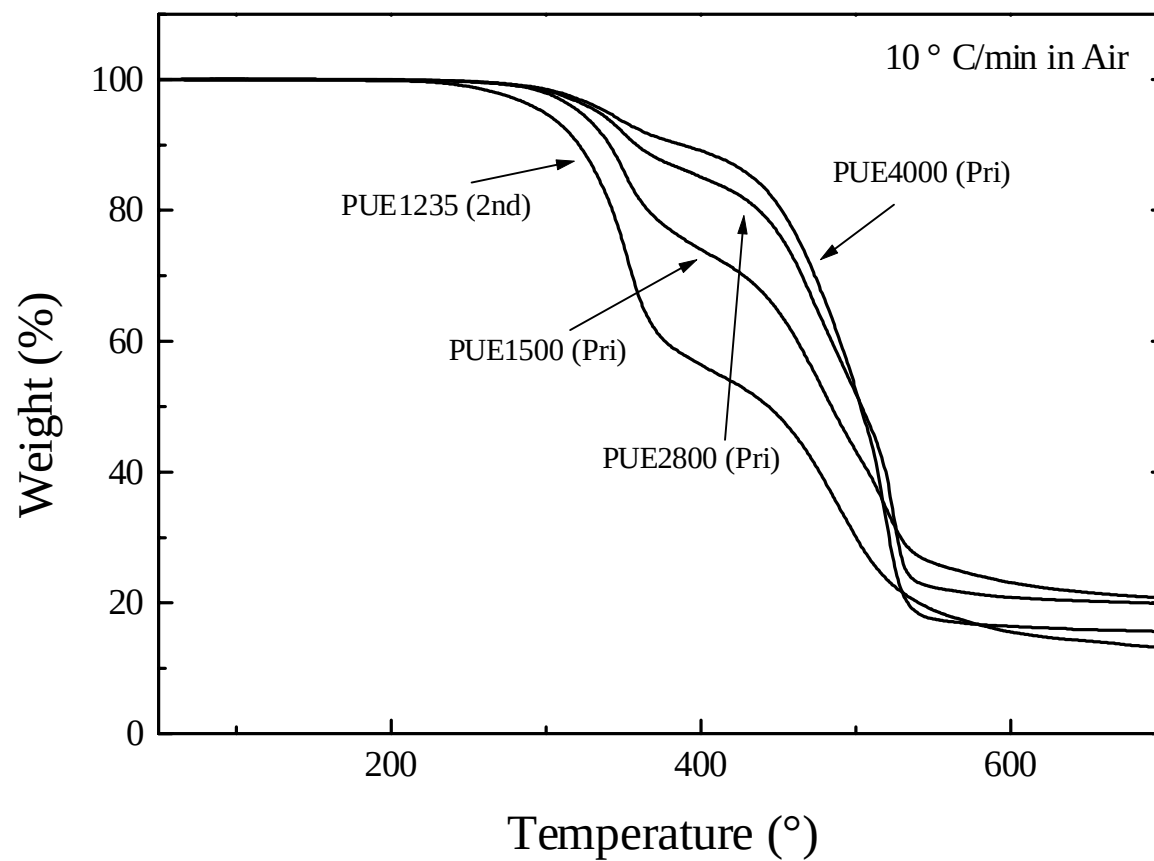


Figure 4.74 TGA thermograms of PDMS based polyureas in air

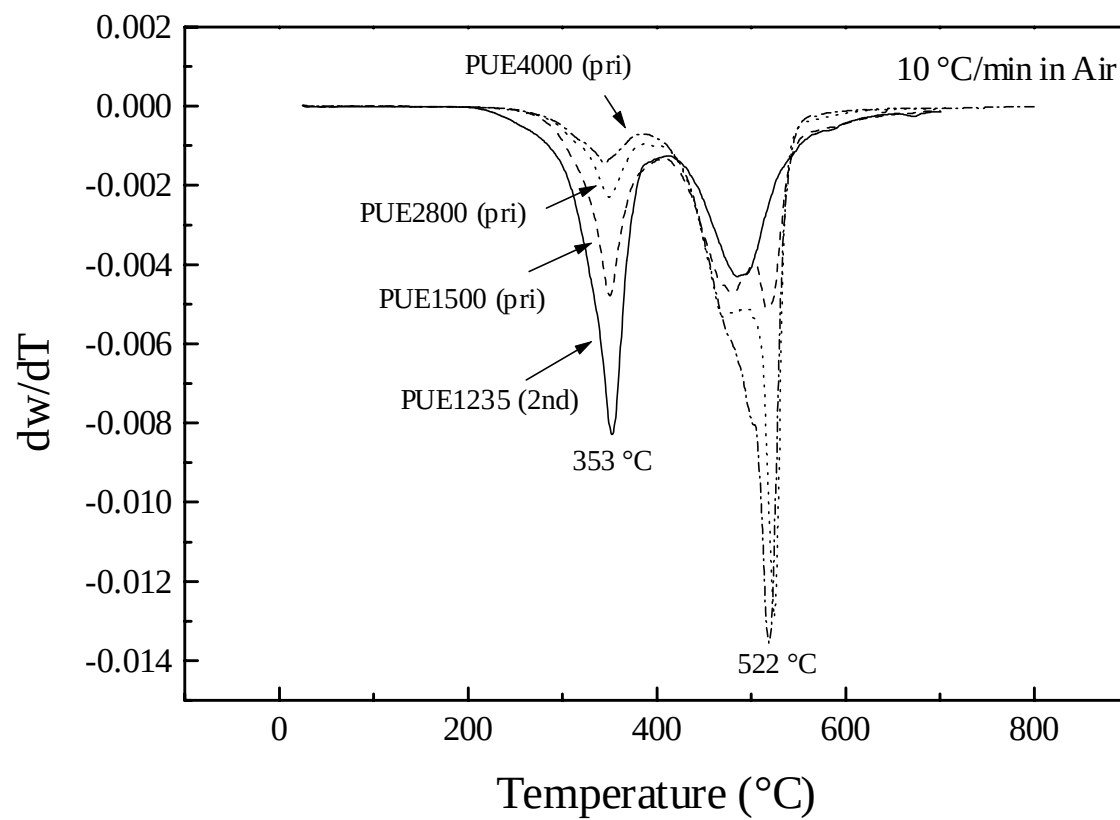


Figure 4.75 TGA thermograms derivative curves of PDMS based polyureas in air

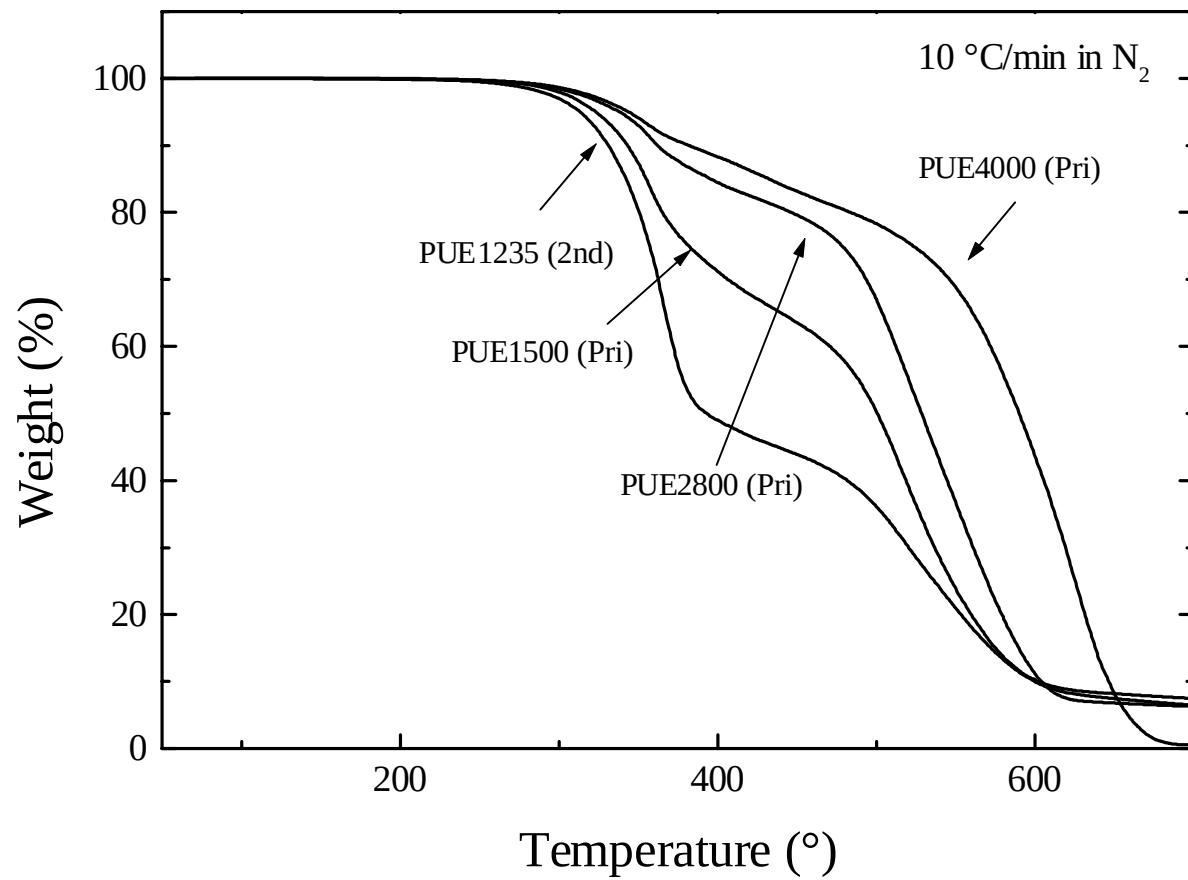


Figure 4.76 TGA thermograms of PDMS based polyureas in nitrogen

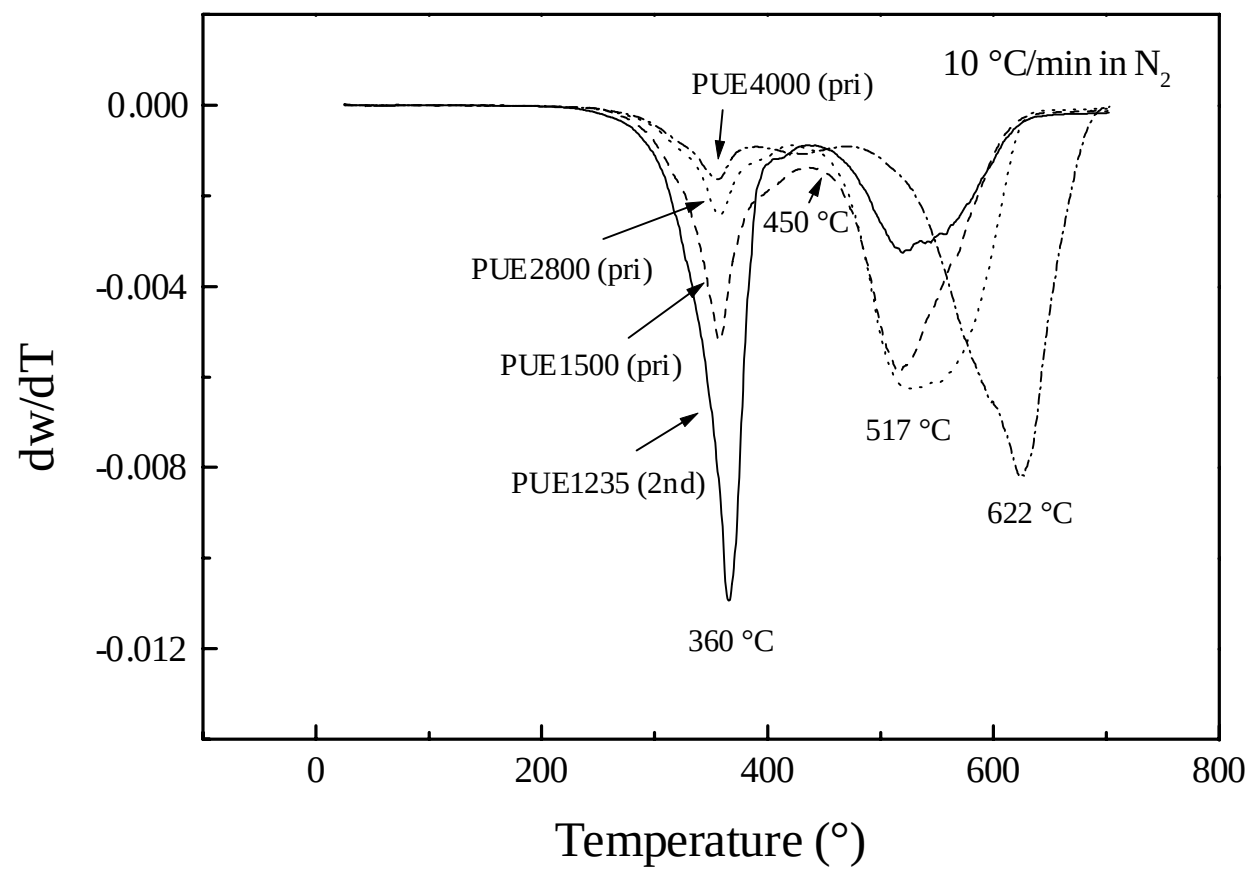


Figure 4.77 TGA thermograms derivative curves of PDMS based polyureas in nitrogen

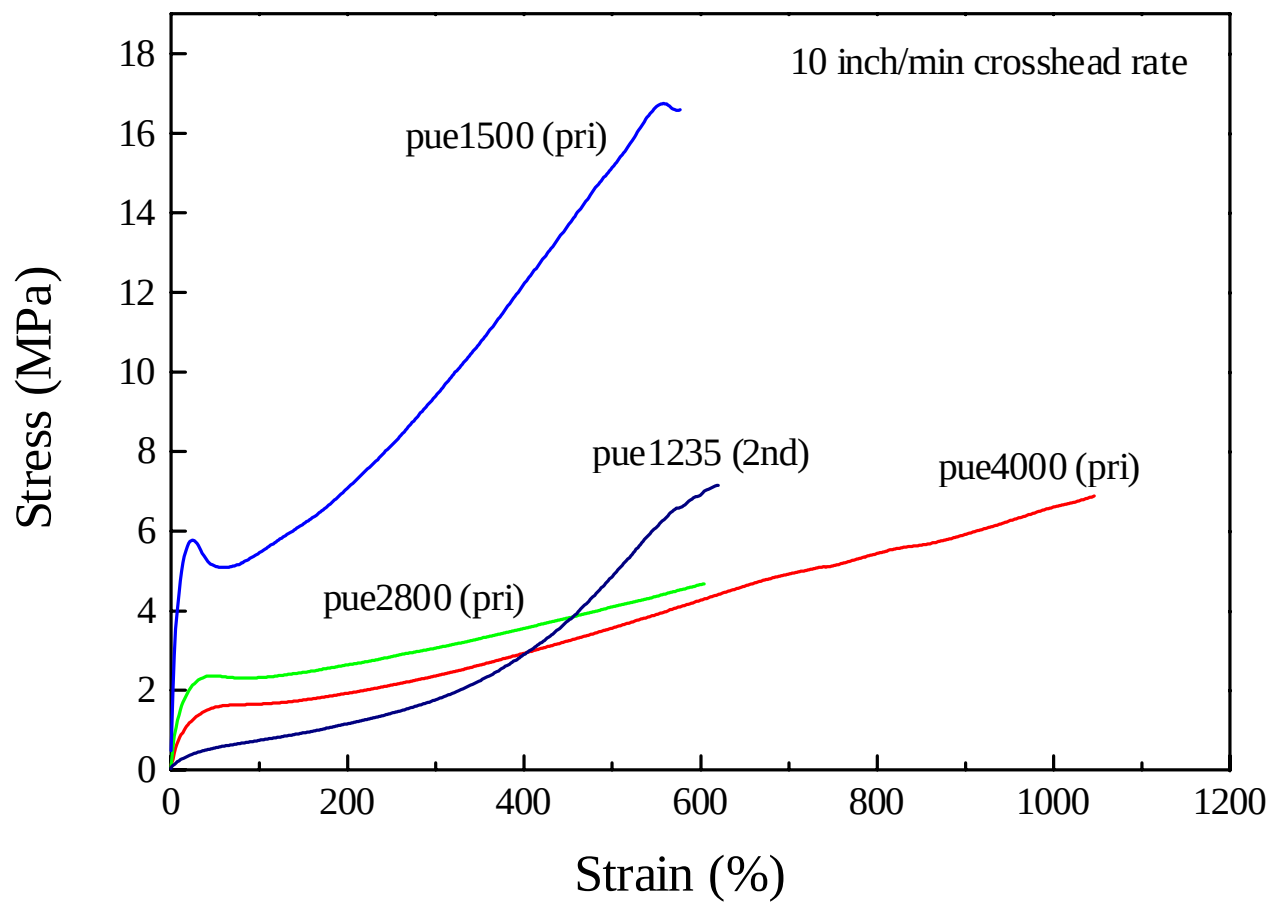


Figure 4.78 Stress-strain behavior of PDMS based polyureas

Chapter 5 Conclusions

Randomly coupled segmented siloxane-urethane copolymers were synthesized from PTMO, secondary aminoalkyl terminated polydimethylsiloxane, BD, and MDI. The microphase separation of the PDMS soft segments from the PTMO and hard segments was clearly demonstrated, even though some phase mixing between the PDMS and the hard segments still existed. While the thermal stability of the PDMS based polyurethanes was similar to the polyurethane control, the char yield at 700°C in air was higher than the polyurethane control and increased with silicon content. Cone calorimetry results showed that even with 15wt% PDMS content, the peak heat release rate could be reduced to one third of that of the polyurethane control. Further increases in PDMS concentration did not reduce the peak heat release rate accordingly. These results are attributed to the low surface energy of the PDMS soft segment, which tends to migrate to the air-polymer interface and form a PDMS enriched surface. This PDMS enriched surface can be formed even when the total PDMS content is relatively low. This PDMS layer can then be oxidized to a layer of silicate-like material upon heating in air, which protects the underlying polymer from pyrolysis. Moreover, for the 15wt% PDMS composition, the mechanical properties of the polyurethane copolymer were comparable to the higher molecular weight polyurethane control. This suggests that modifying a polyurethane with a small amount of PDMS will only affect the surface of the polymer and thus reduce flammability, leaving the bulk properties intact.

PDMS based polyureas have been synthesized with a PDMS-MDI alternating structure. The PDMS content in the polyureas was varied by changing the molecular weight of the PDMS segments which were as high as 94%. Although the hard segment block is short (only coming from the MDI) and content is low, it can still form a second phase. The tensile properties of these polyureas were shown to be excellent, even when they contained a large amount of PDMS. The polyureas made from the primary aminoalkyl terminated PDMS were found to be much stronger than the polyureas made from the secondary analogue. Moreover, the siloxane T_g of the PDMS in the polyureas made from primary aminoalkyl terminated PDMS was also found to be lower than the

secondary analogue. These drastic property differences between the polyureas made from the primary amine end group and the secondary amine end group are attributed to better hydrogen bonding in the former. This research provided valuable evidence about the importance of hydrogen bonding, even at very low concentrations, in determining the property of polymers.

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Vita

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