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SYNTHESIS, CHARACTERIZATION AND PROPERTIES OF SEGMENTED POLYURETHANES CONTAINING MONODISPERSE HARD SEGMENTS

A Dissertation Presented

By

Tzuu-Heng Bernard Fu

Submitted to the Graduate School of the University of Massachusetts in partial fulfillment of the requirements for the degree of DOCTOR OF PHILOSOPHY

May 1985

Department of Polymer Science and Engineering
SYNTHESIS, CHARACTERIZATION, AND PROPERTIES OF SEGMENTED POLYURETHANES CONTAINING MONODISPERSE HARD SEGMENTS

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The research grant supported by Army is greatly appreciated. Above all, the great opportunity provided by the faculty and the facilities of the Department of Polymer Science and Engineering has made all this possible.
This dissertation concentrates the structure-property relationship of segmented polyurethanes containing monodisperse hard segments. There are four chapters in this dissertation.

Chapter I is a brief introduction of segmented polyurethanes in general. The importance of hard segment distribution as well as current status of other monodisperse hard segment systems are also described.

Chapter II covers the synthesis and characterization of monodisperse hard segments containing 2,4-toluene diisocyanate and 1,4-butanediol. Hard segment oligomers, up to six units, have been made and characterized by high performance liquid chromatography (HPLC), elemental analysis, proton NMR, C-13 NMR, and infrared spectroscopy. Thermal properties were reported.

Chapter III deals with the segmented polyurethanes based on the hard segments prepared in Chapter II and three types of soft segments. Thermal properties of these polyurethanes are dependent on the hard segment lengths. The effect of various soft segments are described. Dynamic mechanical measurements are generally in agreement with DSC results. Mechanical properties show a strong dependence on hard segment length as well as soft segment type.

Chapter IV gives suggestions for possible future work along the same line.
ABSTRACT
Synthesis, Characterization and Properties of
Segmented Polyurethanes Containing
Monodisperse Hard Segments
May, 1985
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Directed by: Professor William J. MacKnight

Hydroxy-terminated monodisperse hard segments of 2,4-toluene
diisocyanate (2,4-TDI) and 1,4-butanediol (BDL) were synthesized.
Segmented polyurethanes were prepared by reacting the hard segments
with various 2,4-TDI endcapped soft segments. Thermal, dynamic
mechanical, and mechanical properties were studied as a function of
hard segment length.

Hard segment dimers were prepared by endcapping 2,4-TDI with large
excess of BDL and purified by fractional precipitation. Other
oligomers were prepared by blocking-deblocking process using acetone
oxime as a blocking agent. The purities were verified by HPLC and
elemental analysis. The structures were confirmed by proton NMR, C-13
NMR, and IR. The Tg's of the hard segments were inversely
proportional to the reciprocal of their molecular weights. The Tm's
showed an odd-even effect relative to the number of 2,4-TDI units in
the hard segment.
Polybutadiene (PBD) polyurethanes were phase segregated to near completion with a constant soft segment Tg at about -60°C for all polymers. Hard segment Tg's increased with hard segment length but lower than the corresponding monodisperse oligomers. It was concluded that the hard segments were compatible in a blend of PBD polyurethanes containing two and six hard segment units.

Polycaprolactone (PCL) polyurethanes showed soft segment crystallinity which decreased with increasing hard segment length. The amorphous portion of soft segments were compatible with the hard segments and the Tg's increased as the hard segment length increased. The polymers showed acceptable mechanical properties due to the soft segment crystallinity and possible strain-induced crystallization. The polymer containing six hard segment units showed better mechanical properties due to improved phase segregation.

Polytetramethylene ether glycol (PTMEG) polyurethanes showed some soft segment crystallinity when three or lower hard segment units were incorporated. Two Tg's were found for those containing longer hard segments and assumed to arise from soft phase rich and hard phase rich phases. Phase segregation improved with increasing hard segment length. Mechanical properties were poor except that containing six hard segment units.
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CHAPTER I
OVERVIEW OF SEGMENTED POLYURETHANES

This chapter describes briefly about segmented polyurethanes and summarizes some of the views which have been generally accepted. Some controversial issues are also included to complete the whole picture. Detailed reviews can be found elsewhere [1-4] and will not be repeated.

Preparation and Reaction of Segmented Polyurethanes

Polyurethanes which contain alternating soft and hard segment units are called segmented polyurethanes. They are the reaction products of a macroglycol, a diisocyanate, and a short chain diol or diamine. They have become an important class of thermoplastic elastomers because of the wide selection of basic components and the variations in compositions, hence the variety of properties.

Urethane linkage can be formed from two basic reactions, one between an alcohol and an isocyanate (Eq.1), the other between an amine and a chloroformate (Eq.3) as shown below:

\[
\begin{align*}
\text{ROH} + \text{R'}\text{NCO} & \rightarrow \text{R'}\text{NHCOOR} & (1) \\
\text{R''OH} + \text{COCl}_2 & \rightarrow \text{R''OCOC}1 + \text{HCl} & (2) \\
\text{RNH}_2 + \text{R''OCOC}1 & \rightarrow \text{R''NHCOOR} + \text{HCl} & (3)
\end{align*}
\]

Chloroformate is formed from an alcohol and a phosgene (Eq.2). The first type of reaction is often used in forming urethane group because
no by-product is formed. The second type of reaction can be used in formulations where the relevant isocyanate is not available, as in the case when piperazine is used as a part of the hard segment.

Segmented polyurethanes are usually prepared in two ways. The first and most commonly used is a two-stage method where the macroglycols are endcapped with excess of diisocyanates, followed by the chain extension of the diols or diamines to form the polymer. The second method is a simpler, one-stage method where the stoichiometric amount of ingredients are reacted simultaneously. A typical example of the one-stage method is reaction injection molding (RIM) which has been used by automotive industries in producing bumpers. In order to form a linear polymer, the functionality of all components should be close to two and the molar ratio of OH to NCO should be close to one. The molar ratio of macroglycol/diisocyanate/diol is $1/n/(n-1)$ where $n$ is 2 or greater. Higher $n$ means higher hard segment content.

Side reactions can occur when excess free isocyanate reacts with the active hydrogen on the polyurethane and forms the allophanate linkage (Eq. 4).

\[ \text{H} \quad \text{C} = \text{O} \quad + \quad \text{R-} \text{NCO} \quad \rightarrow \quad \text{H} \quad \text{C} = \text{O} \]

Biuret linkages can occur between free isocyanate and urea groups (Eq. 5). Urea groups are formed if a diamine is substituted for a glycol in the formulation.
\[
\text{N-C-N-} + \text{R-NCO} \rightarrow \text{N-C-N-} \quad (5)
\]

Dimerization (Eq. 6) and trimerization (Eq. 7) are also possible, especially in the presence of specific catalysts.

\[
2 \text{R-NCO} \rightarrow \text{R-N} \quad (6)
\]

\[
3 \text{R-NCO} \rightarrow \text{O-C-C-N-O-R} \quad (7)
\]

**Soft Segments**

Macroglycols are usually hydroxy-terminated polyesters, polyethers, or to a lesser extent a polybutadiene. The molecular weights are in the range of 600 to 3000. The corresponding high molecular weight homopolymers should be flexible in nature because the "soft segments", which are rubbery at the normal service temperature, are the macroglycols extended by hard segments to several times of their original molecular weights.

Polyesters such as polytetramethylene adipate are usually prepared
by heating the glycol in a reactor to approximately 60-90°C. The carboxylic acid is added and heated in such a rate that water distilled out rapidly. The ratio of acid to hydroxyl component is such that the hydroxyl is in excess, so that nearly all the acid groups are consumed and the polyester is prepared in the desired molecular weight range. It is usually necessary to force the reaction to completion by heating to about 200°C while flushing with nitrogen or carbon dioxide under reduced pressure. Glycols with six or less carbons are usually used. However, because of its greater water sensibility, ethylene glycol is only used in a form of copolymer. Other type of hydroxy-terminated polyester such as polycaprolactone glycol is prepared by the base-catalyzed ring opening polymerization of ε-caprolactone using diethylene glycol as the initiator (Eq. 8).

\[
\text{HOCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} + (\text{CH}_2)_5\text{C}=\text{O} \rightarrow \text{H-(O(CH}_2)_5\text{CO})b-\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{O-(CO(CH}_2)_5\text{O})b-\text{H} \quad (8)
\]

Polyethers are prepared from ring opening polymerization using a glycol as an initiator. The most commonly found polyethers are polytetramethylene ether glycol (PTMEG) and polypropylene oxide glycol (PPO). Copolymers of ethylene oxide and propylene oxide are sometimes used to avoid the soft segment crystallization which detracts from elastomeric properties. The block copolymer of ethylene oxide and propylene oxide can be represented by the general structure.
In the preparation, propylene oxide is reacted with propylene glycol or water in the presence of a basic catalyst to form a poly(propylene oxide) homopolymer, which is then further reacted with ethylene oxide to form the block copolymer. The resulting polyether has a higher percentage of primary hydroxyl groups than does a poly(propylene oxide) glycol of comparable molecular weight.

Hydroxy-terminated polybutadiene (HTPBD) has gained some attention in recent years. It is prepared either from free radical or anionic polymerization. The hydroxyl functionalities are usually different from 2 which is required for a linear segmented polyurethane. However, polybutadiene with hydroxy functionality of two has recently been developed by Japan Synthetic Rubber Company. The polybutadiene soft segments are usually not crystallizable due to the coexistence of cis, trans, and vinyl structures. The content of isomers depends largely on the method and the condition of polymerization. Usually free radical polymerization gives higher trans content, whereas anionic polymerization forms more vinyl groups. The relative content of isomers can be determined by infrared spectroscopy by using the absorption bands at 910, 970, and 995 cm⁻¹ for vinyl, trans, and cis, respectively [5-7].

Molecular weight of soft segment has significant effect on the properties. Lower molecular weights are, in many cases, more
compatible with hard segments and result in a less phase separated, hence less desirable feature for thermoplastic elastomers. In addition, minor increase of the molar ratio of diisocyanate to macroglycol could result in the change from an elastomer to a plastic. Higher soft segment molecular weights, on the other hand, give materials with better tensile properties but with increasing tendency to cold harden, a phenomenon which is due to slow crystallization of the flexible blocks on standing [8]. However, this undesirable tendency can be avoided by the use of copolymers which possess structural irregularity. Soft segments with very high molecular weights reduce the hard segment content in the polymer which, in turn, decrease the degree of physical crosslinking as well as the reinforcement.

Hard Segments

Hard segments are essentially polyurethanes of diisocyanates and diols, which are formed due to the higher molar content of these two components than macroglycols. The molar ratio of NCO to OH is one or nearly one, whereas that of diol to macroglycol is usually greater than one.

Diisocyanates are usually prepared from the reduction of nitro compounds, followed by the reaction with phosgene and the subsequent de-hydrochlorination. In general, best properties are obtained from
aromatic diisocyanates although they tend to become yellowing after a period of service, which was attributed to the oxidation of aromatic amine from the degradation of polyurethane due to the effects of light and oxygen [9]. Among many available diisocyanates [10], 4,4'-diphenylmethane diisocyanate (MDI) and toluene diisocyanate (TDI) are generally used. TDI used to be the most popular diisocyanate. However, MDI has become the most widely used because it is less hazardous besides its superior high temperature properties.

MDI has symmetrical structure and is crystallizable when coupling with a symmetrical diol such as 1,4-butanediol (BDL). The higher melting temperature of this hard segment offers the higher service temperature of the polymer. The MDI-BDL based polyurethanes have thus far been the most intensively studied system. The crystallizable feature of this hard segment improves phase segregation which is responsible for many of the unusual properties of segmented polyurethanes.

Hard segments derived from 2,4-TDI and 1,4-butanediol are amorphous in nature due to the asymmetric structure of 2,4-TDI. Isomers of TDI are usually used together in commercial applications, with the 2,4- to 2,6-TDI ratio of 80/20 or 65/35, due to the difficulty in separation. The diols usually contain no more than six carbons with optimum properties found for 1,4-butanediol. MacKnight and Yang [11] have studied the thermal behavior of a series of pure hard segments obtained from polymerization of several diisocyanates
and diols. These results have provided useful information in selecting materials for specific service temperature. Similar survey can be used to predict the potential hard segments.

The diamine chain extenders are sometimes used for the fast curing which is desirable in the RIM process. Chain extenders such as 3,3'-dichloro-4,4'-diaminodiphenylmethane (MOCA), ethylene diamine, and hydrazine belong to this class. Polymers formed from diamine chain extenders are sometimes called "poly(urea)-urethanes" because the urea instead of urethane linkage is formed. These polyurea hard segments usually have higher Tm or Tg as compared to their polyurethane counterparts.

Hard segments are usually segregated from soft segments to form certain domains which are dependent on mutual hard segment affinity and enhanced by molecular arrangements that allow the formation of maximum number of stress-free hydrogen bonds. The structure and organization of the hard segment domains is known to have profound influence on the mechanical properties. Many structure-property studies have concentrated on the relations between the physical properties and the extent of phase segregation, hydrogen bonding, degree of ordering, chain conformation and packing, size and shape of the hard segment domains. On the other hand, relatively few studies are related to the sequence distribution of hard segment length and its influence on the morphology and the properties. In other words, most of the studies did not actually provide the structural evidence
of the final properties. It is the goal of this thesis to prepare segmented polyurethanes with well characterized hard segment structures and study the property dependence on structure.

**Hard Segment Distribution**

Hard segments are usually polydisperse and the sequence distribution depends on the reactivity and compatibility of reactants, the polymerization method, and the polymerization conditions such as solvent, catalyst, temperature, and extent of mixing.

The importance of the reactivity to hard segment distribution is unquestionable since segmented polyurethanes are formed from at least three reactants, each with different reactivities. Furthermore, the reactivity of two functional groups may be different within a reactant. For instance, 2,4-toluene diisocyanate has different activities in ortho and para positions: the para isocyanate is about 10 times higher than the ortho isocyanate towards an alcohol [12]. In general, the reactivity of the second functional group is reduced after the first is reacted. It has been shown that the reactivity of the first isocyanate in a symmetrical MDI is about three times higher than that of the second isocyanate towards n-butanol [13]. The decrease in reactivity is determined by two factors: (a) the electron withdrawing ability of the group attached to the isocyanate groups and (b) the interaction between the two functional groups. This variation
in reactivity has led to the deviation in sequence distribution from random distribution which was expected for PTMEG/MDI/ethylene diamine segmented polyurethanes when the two isocyanate groups were assumed to have the same reactivity [14].

Compatibility of reactants affects the hard segment distribution as evidenced in several polybutadiene based polyurethanes [15,16]. Brunette et al. [15] prepared PBD/2,4-TDI/BDL segmented polyurethanes in bulk and found two hard segment glass transitions for some compositions. A similar result was also reported earlier by Schneider and Matton [16]. The basic difference between these two studies is the difference in hydroxyl functionality of hydroxy-terminated polybutadiene which is 1.96 for the former and 2.3 for the latter. Apparently this bimodal distribution of hard segments is independent of the hydroxyl functionality. Xu et al. [17] studied Brunette's samples by separating them into sol and gel fractions from DMF at 70°C, followed by an infrared analysis. The polymers were found to include short and long hard segments and the dual hard segment Tg's was attributed to the incompatibility of two types of hard segments. The existence of relative long hard segment was originated from the incompatibility of polybutadiene and butanediol as evidenced in an optical microscopy study [18].

The sequence distribution of hard segments is also affected by the polymerization method. In the one-stage polymerization, the sequence distribution depends largely on the reactivities of macroglycol and
diol towards diisocyanate. In the two-stage polymerization the competing species are the diisocyanate and the endcapped macroglycol towards diol. The sequence distributions from these two types of polymerization are not expected to be the same. From a theoretical standpoint, Peebles [19,20] has shown that a two-stage method should lead to a narrower distribution of hard segment lengths as compared to that for a one-stage synthesis, providing the reaction of the first isocyanate moiety occurs at a faster rate than that of the second one.

Polymerization conditions should play an important role in the final hard segment distribution. It is apparent that good solvents or solvent pairs can provide a homogeneous condition which avoids the deviation caused by the incompatibility of reactants. Temperature affects the reactivity of the reactant in such a way that the difference in reactivity can be greatly reduced at certain elevated temperatures. The effect of catalyst on segmental distribution is less clear. In general the difference in reactivity is reduced as evidenced in the higher reaction rate when a catalyst is used. However, the segmental distribution will not be the same when different catalysts are used due to the differences in catalytic efficiency.

Suzuki and coworkers [14,21] have studied sequence distribution of a poly-(urea)urethane system containing polytetramethylene ether glycol (PTMEG), hydrazine (or ethylene diamine), and MDI. Number average molecular weight of the urea hard segment was determined by
volumetric analysis (titration) and elemental analysis after degradation by perchloric acid. It was found that Mn of the hard segment was smaller than that expected from the equal reactivity of two isocyanate groups in MDI as calculated in random copolymerization.

The sequence distribution of polyester based polyurethanes, on the other hand, have been determined by nuclear magnetic resonance (NMR) from several model compounds [22]. The resulting number average sequence lengths were in good agreement with calculated values.

These two techniques are, however, not very useful in determination of the actual hard segment distribution. First, only average hard segment length is obtained. Second, the depolymerization technique can only be applied to very few polyurethanes because it is difficult to break a specific bond without having other side reactions. Most of the structure-property studies can only therefore, relate morphology and properties to the hard segment content. The results of these studies will be significant only when the most probable hard segment distribution is obtained through random copolymerization. Otherwise, data interpretation will be based on conjecture.
Monodisperse Hard Segments

A. PTMEG/BDL/Piperazine Hard Segments

Harrell [23] has studied the physical properties as a function of segment sizes and distribution for a series of segmented polyurethanes with structures shown below:

\[ \cdots \left[ (\text{CH}_2)_4 \right]_m \left[ \begin{array}{c}
\text{O} \\
\text{N} \\
\text{O}
\end{array} \right] \left[ \begin{array}{c}
\text{O} \\
\text{N} \\
\text{O}
\end{array} \right] \left[ \begin{array}{c}
\text{O} \\
\text{N} \\
\text{O}
\end{array} \right] \left[ \begin{array}{c}
\text{O} \\
\text{N} \\
\text{O}
\end{array} \right] \cdots \]

where \( n = 1, 2, 3, \) and \( 4; \) \( m \) depends on the molecular weight of the soft segment. These polymers were prepared from the condensation polymerization of amino-terminated monodisperse hard segments and the bischloroformate of PTMEG. Monodisperse hard segments were prepared stepwise by a blocking-deblocking process using carboxenzyloxy as a blocking group which was removed later by hydrogenation.

These elastomers contain no N-H groups, hence no hydrogen bonding is possible. It was found that the melting points of the elastomers increased with increasing size of hard segment and asymptotically approached the melting point of the pure hard segment homopolymers. The heats of fusion of the hard segment were approximately constant indicating little variation in hard segment crystallinity within the series.

Various blends of the individual polymers containing monodisperse hard segments were made by casting films from solutions of pairs of
polymers. The polymer containing a hard segment having only one repeat unit gave an opaque film when cast from a solution containing three or four hard segment units. In these cases where opaque films were obtained the thermal fusion peaks were those of the individual polymers used in the blend. When clear polymer films were obtained, additional fusion peaks to those of the component polymers were noted by DSC. The DSC evidence together with the clarity of cast films indicated that compatibility occurred with hard segments having more than two repeat units in all the possible binary combinations. There are clearly a critical dependence of compatibility upon the hard segment length. A further series of polymers was also prepared in which the molecular weight distributions of the hard and soft segments were varied while maintaining the overall composition of the polymers. From an examination of their tensile behavior, it was shown that a hard segment of narrow distribution gave polymers of significantly higher modulus than one having a broader distribution. A narrow distribution of soft segments produced the polymers with greatest tensile strengths and elongation at break. The highest permanent set were obtained when both segments had broad distribution. It is not yet known if these conclusions apply also to polyurethanes elastomers containing strong hydrogen-bonded interactions.

The monodispersed polyurethanes prepared by Harrell were studied by Samuels and Wilkes [24] who investigated the rheo-optical and
mechanical properties. They found that the hard segment of the polyurethane showed spherulitic scattering and proposed a model for the polymer having a spherulitic structure. Wilkes et al. [25] studied the morphology of these polymers with scanning and transmission electron microscopy. Ng et al. [26] investigated the mechanical and thermal properties of Harrell's polymers.

B. MDI/BDL Hard Segments

Pure hard segments containing MDI and BDL have been prepared recently by several research groups: Macosko (University of Minnesota), Eisenbach (University of Freiburg, Germany), Pascault (France), and Cooper (University of Wisconsin), respectively [27-30]. However, at the time of this writing, no results have been published based on the polymers made from these hard segments. Techniques such as blocking-deblocking process and endcapping process as well as the combination of both are frequently used. As far as the type of the hard segments made, some are butanediol terminated while some are MDI terminated with suitable endcapping by alcohols. It should be noted that a comparison between these two types may not give significant meaning unless the number of MDI is the same and the alkyl terminal groups are comparable in length as butanediol. In addition, the hydroxyl groups in butanediol terminated oligomers should play a role in influencing structure organization, especially in short hard
segments because of the higher hydroxyl content. Since hard segments were prepared from different approaches by each research group with variations in terminal group, a discription of preparation and properties is given next.

Qin et al. [27] prepared the monodisperse hard segments by blocking-deblocking process using triphenylmethyl chloride as a blocking agent for 1,4-butanediol. This blocking group was removed by acid. The urethanes were formed from the reaction of an amine and a chloroformate, a procedure similar to that used by Harrell. Monodisperse oligomers B(MB)_n with n=1,2, and 3 were made. The heats of fusion of all annealed oligomers are in the neighborhood of 140 J/g which suggests a similar crystalline, hydrogen bonded structure for all oligomers.

Eisenbach and Gunter [28] prepared both types, namely, B(MB)_n and phenyl terminated M(BM)_n hard segments, where n=1,2, and 3. 1,4-Butanediol was blocked by 2,3-dihydropyran which was removed later by hydrolysis under acidic condition. According to the scheme, half of the hard segments were prepared by endcapping process which was developed by Kern et al. [29] who synthesized monodisperse hard segments containing hexamethylene diisocyanate and BDL. It was concluded that the miscibility of monodisperse hard segments is limited, and the hard segments crystallize in an extended chain without chain folding.

Camberlin et al. [30] prepared alkyl terminated monodisperse hard
segments by endcapping process, followed by GPC purification. The influence of chain ends on Tm have been studied systematically as a function of hard segment length. It was found that Tm increased with hard segment length, up to three units, for short chain ends. When long chain ends were incorporated, the Tm decreased as the hard segment length increased. Enthalpy and entropy decreased as the hard segment length increased.

Hwang et al. [31] synthesized ethyl terminated hard segments using excess endcapping method as well as blocking-deblocking technique. 1,4-Butanediol was blocked by chlorotrimethylsilane which was removed by reacting with anhydrous methanol under basic condition. Hard segments containing up to four BDL and five MDI have been made. However, the purities of these model hard segments are suspect since no direct evidence such as HPLC or GPC was given. It was found that the extrapolated Tm of BDL/MDI homopolymer with infinite molecular weight is 299°C which is much higher than most of the Tm's found in segment polyurethanes based on the same hard segments. The heat of fusion is 5.3 kcal/mol. Intrinsic viscosity measurements in dimethyl acetamide solutions revealed a Mark Houwink exponent of 1.43 suggesting that the model hard segments are rodlike in solution. Wide angle X ray diffraction showed that the hard segment crystallinity decreased as the oligomer length increased. Infrared spectroscopy studies showed that the distribution between C=O and N-H groups became broader with increasing segment length.
Segmented polyurethanes are usually phase segregated [30-34]. Clough et al. [32] studied both polyether and polyester based polyurethanes with MDI/BDL hard segments and came to the following important conclusions: (1) microphase segregation is greater for polyether-based polyurethanes than for the equivalent polyester-based polyurethanes, and (2) segregation into domains is enhanced by longer segment lengths. Techniques such as small angle X-ray scattering (SAXS), differential scanning calorimetry (DSC), electron microscopy, and dynamic mechanical measurements have been used to prove the existence of phase segregation of the microstructure.

The extent of phase segregation is determined by the type and composition of the formulation as well as the method and condition of polymerization. In other words, phase segregation is influenced by the segmental polarity difference, segmental length and crystallizability of either segment, and hydrogen bonding. It has generally been observed that longer block length results in higher degrees of phase segregation [34-38], higher hard segment content results in more hard segment mixing into the soft phase [35,38], and that polar soft segment which form strong interaction such as hydrogen bonding with the hard segment exhibit a higher degree of phase mixing [37,39,40].

Hard segments generally contain polar urethane groups and soft
segments contain less polar ester or ether groups, with the extreme
case of nonpolar hydrocarbons. Table 1-1 lists the cohesion energy,
therefore the segmental polarity of several important groups in
polyurethanes. Basically this polarity difference is the origin of
the segmental incompatibility which is responsible for phase
segregation. However, this factor is affected greatly by the fraction
of each phase and only comparable fraction can result in better phase
segregation. [Hard segment content can be increased either by reducing
the soft segment molecular weight or by increasing the molar content
of diisocyanate and diol] Usually the soft segment molecular weight
cannot be too low due to the possibility of phase inversion and the
better mixing between soft and hard phases. Therefore, higher soft
segment molecular weight is generally preferred and the possibility of
forming large number of long hard segments is increased if the hard
segment content is high. Although the actual sequence distribution of
hard segments is determined by many factors, it can be assumed that
higher hard segment content results in a longer average hard segment
length, providing the reactivities and compatibilities are comparable
for all the reactants. Longer segments of both phases improve the
crystallinity of crystallizable segments, thus improve the phase
segregation.

The role of hydrogen bonding to phase segregation is not very
clear, although it has been used as a semi-quantitative index for the
extent of phase mixing. It is certain that the distribution of
<table>
<thead>
<tr>
<th>Group</th>
<th>Cohesion energy (kcal/mole)</th>
<th>Volume* (cm³/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>- CH₂ -</td>
<td>0.68</td>
<td>21.8</td>
</tr>
<tr>
<td>- O -</td>
<td>1.00</td>
<td>7.3</td>
</tr>
<tr>
<td>- C(CH₃)₂ -</td>
<td>1.90</td>
<td>65.4</td>
</tr>
<tr>
<td>- C -</td>
<td>2.66</td>
<td>21.6</td>
</tr>
<tr>
<td>- C - 0 -</td>
<td>2.90</td>
<td>28.9</td>
</tr>
<tr>
<td>- C₆H₄ -</td>
<td>3.90</td>
<td>83.9</td>
</tr>
<tr>
<td>- C - N -</td>
<td>8.50</td>
<td>36.2</td>
</tr>
<tr>
<td>- O - C - N -</td>
<td>8.74</td>
<td>43.5</td>
</tr>
</tbody>
</table>

* based on small molecule liquids. The polymers have smaller volumes.
hydrogen bonding between the interphase and interurethane affects the phase mixing. More details about hydrogen bonding are given in the next section.

Not all the factors are required in achieving phase segregation. For example, piperazine based polyurethanes are free of hydrogen bonding but are phase segregated due to crystallization [24]. On the other hand, polybutadiene based polyurethane containing 2,4-TDI/BDL hard segments are phase segregated due to the large difference in segmental polarity and/or the lack of hydrogen bonding between two phases.

Above all, phase segregation is a desirable feature for segmented polyurethanes, but only to a certain extent. A complete phase segregation may diminish the adhesion between the two phases which results in poorer mechanical properties as in the case of many incompatible polymer blends.

**Hydrogen Bonding**

The typical polyurethane is extensively hydrogen-bonded [41]. The proton donor is the NH group of the urethane linkage. The hydrogen bond acceptor is either the carbonyl group of the urethane linkage or the ester carbonyl (or ether oxygen) of the soft segment. Another hydrogen acceptor could be the alkoxy group of the urethane linkage. The relative amounts of the two types of hydrogen bonds are determined
by the degree of microphase segregation, with increased phase
segregation favoring interurethane hydrogen bonding. The distribution
of NH bonding with respect to each type of acceptor is dependent on
many factors, including the electron-donating ability and relative
proportions and spatial arrangement of the various proton acceptor
groups in the polymer chain.

Direct measurement of the extent and nature of hydrogen bonding in
polyurethanes and its influence on physical properties is still in an
early stage of investigation. The strength of hydrogen bonding which
is indicated by its $\Delta H$ value, the distribution of different acceptor
functional groups, and the extent of phase segregation which is
reflected by the amount of interurethane hydrogen bonding remain
important parameters requiring further study and clarification of
their role in determining physical properties.

The literature concerning the nature and extent of hydrogen
bonding in polyurethane is extensive and has been reviewed by Seymour
et al. [41]. The principal objective of these studies is to determine
the distribution of hydrogen bonds among the various possible
acceptors. Infrared spectroscopy has proved to be a useful technique
for polyether, but not polyester, based polyurethanes by using the
different vibration frequencies for free and hydrogen-bonded groups.
In general, information can be obtained from N-H stretching and C=O
stretching. The free N-H stretching appears at about 3450 cm$^{-1}$
while that of the hydrogen bonded at about 3320 cm$^{-1}$. The
nonassociated and hydrogen bonded C=O absorbs around 1730 cm$^{-1}$ and 1700 cm$^{-1}$, respectively. The ratio of the molar extinction coefficient is 4.6 for the hydrogen bonded to the free amine stretching vibration and 1.05 for the hydrogen bonded to the free carbonyl stretching vibration [42].

It is generally found that in solid polyurethanes the majority of NH groups are involved in hydrogen bonding, but only part of the urethane C=O are hydrogen bonded [41,43]. The extent of soft-hard phase mixing can be qualitatively estimated as the fraction between the difference of hydrogen bonded N–H and hydrogen bonded C=O stretching. However, this usually overestimates the extent of phase mixing since there are other parameters involved: (1) the possibility of urethane alkoxyloxygen as a hydrogen acceptor, (2) the formation of hydrogen bonding at the domain-matrix interface, (3) the restructuring of hydrogen bonding, and (4) the dependence of hydrogen bonding on morphology, hence on the detailed thermal and mechanical history of the sample.

Boyarchuk has postulated urethane alkoxyloxygen as a hydrogen acceptor [44]. Sung and Schneider extended this viewpoint and studied the distribution of hydrogen bonding in a series of PTMEG (1000 Mn)/2,4-TDI/BDL polyurethanes [45]. They compared the extent of phase mixing derived from IR and DSC and found great discrepancies. The extent of phase mixing as calculated from the Fox equation [46] using observed Tg's was much higher than that from infrared results. In the
subsequent paper [47], they re-examined the system and found the new Tg's were 10 to 15 degrees lower in polymers of higher urethane content, indicating the great uncertainty in Tg determination. The observed Tg values were, however, still 15 to 25 degrees higher than that calculated from the copolymer equation assuming complete phase mixing. This indicates that either the copolymer equation is not applicable to this system or the Tg's were not determined correctly. Although no DSC trace was given in either study, it is likely that the phases were not completely mixed and resulted in a broad glass transition on the DSC scan. If this indeed is the case, the copolymer equation no longer holds since it is only applicable to compatible systems. Determination of Tg in such a system is, of course, difficult. Several problems remain. First, the fraction of hydrogen bonded C=O was overestimated based on the shape of C=O band in Figure 1 of reference 45. A better estimate will be about 2/3 of the values listed in Table III of ref. 45. For example, the fraction of hydrogen bonded CO should be 30 % instead of 46 % for 2,4-TDI-2. This will increase the fraction of hard-soft segment mixing from 18 % to about 25 %. Second, no direct evidence was given for the involvement of urethane alkoxy oxygen. Lastly, the role of allophanate, which is possibly formed due to the 5 % excess of diisocyanate in the composition, was not known.

Hydrogen bonding is likely to occur at the domain-matrix interface and should be treated differently from the actual phase mixing, i.e.,
the solubilization of hard segments into the soft segment phase. Therefore, the fraction of actual phase mixing should be less than that calculated from the difference between hydrogen bonded NH and hydrogen bonded CO. The interfacial hydrogen bonding is expected to be related to the size and shape of the hard segment domains [41]. If domain size is the only variable, the smaller domains should result in the higher concentration of interfacial hydrogen bonding. However, there should be a critical domain size below which no difference can be made from actual phase mixing. Various shapes of domains should affect the degree of interfacial interaction also.

Hydrogen bonding has been shown to influence morphological features such as chain ordering in partially crystalline polyurethanes [48]. The role of hydrogen bonds in determining mechanical properties is less clear. Studies of a number of hydrogen-bonded polymers have led to the general conclusion that the presence of such bonds does not necessarily enhance mechanical properties [49,50,51]. Other authors are of the opposite opinion [52].

There are two other features about hydrogen bonding. First, hydrogen bonding is reformable [48] and the reformation rate depends on the concentration of hydrogen acceptor and donor. Complete elimination of hydrogen bonding in bulk polymer is impossible if the system contains both hydrogen donor and acceptor unless the polymer is fully degraded. Second, hydrogen bonding is concentration dependent. Nakayama et al. [53] reported that as the polyether molecular weight
is increased from 2100 to 8390, the intensity of the bonded C=O peak relative to the nonbonded peak decreases. The bonded peak is no longer apparent at 8390 Mn, indicating that at this molecular weight, hydrogen bonds form primarily with the ether groups.

Temperature dependence of hydrogen bonding has been studied in several polyurethane systems. MacKnight and Yang [11] investigated the temperature dependence of hydrogen bonding from IR on three series of nonsegmented polyurethane homopolymers. It was found that these polyurethanes are hydrogen bonded to the extent of 75 % or less below their Tg and that the integrated absorbances of the N-H stretching vibration showed discontinuities at temperatures corresponding to the Tg or Tm of the polymers. Sung and Schneider [54] studied the temperature dependence of hydrogen bonding in PTMEG (1000 Mn)/2,4-TDI/BDL system where the free and bonded carbonyl absorptions showed little change from 0 to 150°C while 50 % of the NH groups had dissociated by 150°C. It was concluded that NH-to-ether hydrogen bonding was responsible for most of the hydrogen dissociation in the NH spectra. Hydrogen bond stability depends on the chain mobility which in segmented polyurethane is determined by the Tg or Tm of the hard segment domain and the soft segment matrix. It is apparent that the hydrogen bonding within the soft matrix is dissociated at the early stage and that at the hard domain is dissociated at the higher temperature. Values of ΔH for the bonded NH dissociation were reported to be 4 kcal/mole for the 2,6-TDI polymers and 3 kcal/mole.
for the 2,4-TDI polymers, independent of urethane content. Sung and Schneider concluded that the thermal behavior of hydrogen bonding is essentially independent of structure organization.

**Morphology**

Segmented polyurethanes usually do not display simple morphologies as that in styrene-butadiene block copolymers. Briber [55] compared the models of polyurethane hard segment microstructure which had been proposed previously and concluded that none can be used solely to interpret all the characteristics found for these (AmBn) type of materials. This is true because morphology is affected by a large number of factors such as hard segment and soft segment type, volume fraction, intermolecular bonding, molecular weight distribution, method and solvent of sample preparation as well as the thermal and mechanical history of the material. In addition, the hard segment domains are usually small because of the generally lower average segmental molecular weight. The difficulties are further complicated by the possible involvement of artifacts [56]. Much of the morphological data has been obtained from electron microscopy where the electron density difference between phases is crucial. The osmium tetroxide staining technique, which is useful in polymers containing unsaturated hydrocarbons, can only be applied to very limited number of segmented polyurethanes.
Cooper et al. [57] studied polyester and polyether polyurethanes by using transmission electron microscopy (TEM). Iodine was used to stain the hard phase. It was concluded that the hard domains were from 30 to 100 Å for both the polyester and polyether urethanes. This is considered somewhat small and the block lengths in the polymer are short. However, these micrographs may not represent the true morphology and has been criticized by Roche and Thomas [56]. The problem seems to arise from the unintentional defocusing of the objective lens. The same problem also occurred in other electron microscopy studies in different systems [25,58,59]. The true morphology of polyurethanes have been shown to be more complicated [60-63]. Schneider et al. [60] studied the MDI/BDL based segmented polyurethanes by TEM and found spherulites on the order of one micrometer, which was believed to arise from the crystallizable hard segments. Briber and Thomas [55,63] found three crystal forms in MDI/BDL hard segments in a polypropylene oxide based polyurethanes which was prepared by one-stage method. This is the only good electron microscopy evidence of crystalline hard segment domains.

Lagasse [59] studied the morphology of an amorphous crosslinked polybutadiene (PBD)/2,4-TDI/BDL system. The micro domains shown in the micrograph are actually the artifacts due to the defocusing of the microscope as discussed earlier. Chen [64], in realization of the defocusing problem, has carefully studied the linear PBD/2,4-TDI/BDL polyurethanes and found that for osmium tetroxide stained samples: 74%
of hard segment content showed meandering cylindrical PBD domains; 52% of hard segment content showed plate-like morphology with average interdomain distance of 130 Å; and 29% of hard segment content gave no reliable information. This work is thus far the only good evidence for amorphous hard segments.

Schneider et al. [32,65,66] have studied the structural organization and thermal transitions for several polyester and polyether urethanes. The soft segments were poly(butylene adipate) and PTMEG, respectively, and the hard segments were derived from MDI and BDL. Several transitions were detected from thermal analysis. In the polyether system, a transition at 205°C coincided with the melting of the birefringent region and is believed to be the polyurethane crystalline region. Such a transition was not observed in the polyester urethane. It was concluded that segregation of the soft segment and the urethane segments into domain structures occurs in both copolymers, but exists to a greater extent in the polyether system. They also reported that increasing the molecular weight of the PTMEG from 1000 to 1500 caused the soft segment glass transition temperature to decrease from -43°C to -55°C. This was interpreted as due to an increase in phase segregation in the molecular weight range. Lunardon et al. [67] studied the effect of molecular weight and molecular weight distribution of polyester based soft segments on the physical properties of polyurethanes. Their results showed the coexistence of three different phases: a soft phase, a mixed phase,
and a crystalline phase. The mixed phase depends on the molecular weight and MWD of the polyester segment. A decrease in the molecular weight of the polyester yields a higher level of crystallinity because the relative amount of hard segment increases.
References


45. C.S.P. Sung and N.S. Schneider, Macromolecules, 8, 68 (1975).
CHAPTER II
SYNTHESIS AND PROPERTIES OF MONODISPERSE
HYDROXY-TERMINATED OLIGOMERS OF 1,4-BUTANEDIOL
AND 2,4-TOLUENE DIISOCYANATE

Introduction

Segmented polyurethanes are alternating block copolymers containing soft and hard segments of various lengths. Soft segments are usually low glass transition temperature polyesters or polyethers with molecular weights ranging from 600 to 3000. Hard segments, being glassy or partially crystalline at ambient conditions are generally formed from the extension of a diisocyanate such as 2,4-toluene diisocyanate (2,4-TDI) or 4,4'-diphenylmethane diisocyanate (MDI) with a low molecular weight diol such as 1,4-butanediol (BDL).

The concept of phase segregation [1,2] with the hard segment domains dispersed in a rubbery matrix, has been accepted as the explanation for the thermoplastic elastomer properties of the segmented polyurethanes.

By changing the components and their relative ratios, a variety of segmented polyurethanes with different properties can be obtained. The properties depend largely on the glass transition temperature (Tg) or melting temperature (Tm) of both the soft and the hard segments; the domain size and shape, the crystallinity, and the internal
organization of the hard segments; and the compatibility between the soft and the hard segments. These factors are further related to the hard segment length and its distribution. The various segment lengths of regular segmented polyurethanes are mostly due to the differences in reactivities; polymerization conditions such as temperature, catalyst, mixing and solvent; and polymerization methods, either the one-stage or the two-stage process. Even in the randomly copolymerized segmented polyurethanes a distribution of hard segment lengths other than the statistically distributed is inevitable [3].

Techniques such as nuclear magnetic resonance (NMR) and depolymerization have been used to study the average sequence length of the hard segments in a limited number of polyurethanes. Suzuki et al. [4] obtained the average hard segment length of several polyester based polyurethanes by proton NMR using several model compounds. Suzuki and Ono [5] have depolymerized a poly(urea)-urethane elastomer with perchloric acid. The number average molecular weight of the urea segment was determined by elemental analysis and by volumetric analysis. However, the depolymerization technique can only be applied to very few polyurethanes due to the difficulty in breaking a specific bond. Since it is difficult to obtain the distribution of the segments, most of the structure-property studies can only relate morphologies and properties to the hard segment content instead of the actual segmental distribution. An alternate route to studying the structure-property relationships is to use a series of polyurethanes.
with controlled hard segment lengths. These polymers should provide important information about the domain sizes and shapes, mechanical properties, thermal properties, and transport phenomena as a function of the hard segment length.

Polyurethanes containing monodisperse hard segments can be prepared by condensation or addition polymerization from polyols and monodisperse hard segments, both with suitable end groups capable of forming urethane linkages. In general, there are two basic methods, namely the blocking-deblocking process and the excess endcapping process for the preparation of monodisperse hard segments. Harrell [6] studied the polytetramethylene ether glycol (PTMEG)/piperazine/BDL system where no hydrogen bonding was possible. He prepared hard segments, up to four units, by connecting piperazine and butanediol with phosgene. Amino-terminated hard segments were formed by the blocking-deblocking process using carbobenzyloxy blocking groups. Kern et al. [7] prepared hexamethylene diisocyanate (HMDI)/BDL hard segments by an endcapping process with a large excess of endcapping materials. Recently, monodisperse MDI/BDL hard segments have been studied more intensively. Camberlin et al. [8] prepared alkyl-terminated hard segments in order to study the chain end effects on the melting properties. Eisenbach and Gunter [9] and Macosko et al. [10] have successfully prepared monodisperse hard segments of the MDI/BDL system with hydroxyl end groups capable of forming segmented polyurethanes.
Our laboratory has studied [11] a completely amorphous polyurethane system containing polybutadiene soft segments and 2,4-TDI/BDL hard segments. The hard segments, unlike those of the MDI/BDL system, do not crystallize. Therefore, the effect of hydrogen bonding on properties can be determined more easily. In these bulk polymerized polyurethanes, two hard segment Tg's were observed. This is in accordance with the observations by Schneider and Matton [12], although the hydroxy functionality of the polybutadienes was different (1.97 vs. 2.3). Apparently the existence of two hard segments Tg's does not arise from chemical crosslinking. Later it was suggested [13] that the reactant incompatibility may cause a hard segment bimodal distribution and this is responsible for the two hard segment Tg's. A model of phase segregation was proposed by Chen et al. [14] on the same system. However, the compatibility of long and short hard segments remains unknown. It is one of our future goals to answer this question by blending segmented polyurethanes containing mododisperse hard segments of different lengths.

In this study, monodisperse hard segments based on 2,4-TDI and BDL are prepared and characterized. In the next chapter, we will discuss the properties of the segmented polyurethanes made from these hard segments and various types of soft segments.
Method

Dimers are prepared by endcapping 2,4-TDI with a large excess of BDL. Crude dimers are purified by fractional precipitation. Trimers and higher oligomers are prepared by a simple blocking-deblocking process taking advantage of the different reactivities of the isocyanate groups in 2,4-TDI and the characteristics of an oxime blocking group. It is well known [15] that the two isocyanate groups in 2,4-TDI are different in reactivities: para-isocyanate reacts about 10 times faster than ortho-isocyanate towards alcohols. This means the para-isocyanate group can be blocked while the ortho-isocyanate group remains free. Such a partially blocked 2,4-TDI enables us to incorporate a glycol into the molecule without using excess endcapping material. Oximes have been known [16] as blocking agents for preparing one-component blocked urethanes where the isocyanate groups are re-generated by heating. Guise et al. [17] have shown that oximes could be removed within 15 minutes at 100°C in such a blocked polyurethane. In this study, acetone oxime is chosen because its partially blocked 2,4-TDI adduct precipitates from the reaction medium, toluene, thus eliminating the need for purification. In addition, acetone oxime is soluble in water, which facilitates its removal after deblocking. Since acetone oxime is deblocked at elevated temperature, the re-generated isocyanate group can react with added butanediol to obtain the desired hard segments. Hard segments are hydroxy-terminated which avoids side reactions during purification.
Materials and Instruments

Both 1,4-butanediol (Aldrich Chemical) and 2,4-toluene diisocyanate (Sigma Chemical) were purified by vacuum distillation. Anhydrous toluene (Aldrich Chemical) and dibutyltin dilaurate (Alfa Chemical) were used as received. Acetone oxime (Aldrich Chemical) was distilled before use. HPLC grade dimethyl formamide (DMF) (Fisher Scientific) was purified by refluxing 24 hours, followed by distillation in the presence of TDI, calcium hydride, and TDI, respectively.

A Varian-T60 was used for proton NMR using 100% deuterated dimethyl sulfoxide (DMSO) (Aldrich Chemical) as a solvent for hard segments. Deuterated chloroform was used to analyze the adduct of 2,4-TDI and acetone oxime. C-13 NMR spectra were obtained with a Varian-CFT-20 using deuterated DMSO as a solvent. Infrared spectra were taken from a Perkin-Elmer 283 Infrared Spectrometer using KBr pellets. Differential Scanning Calorimetry (DSC) traces were obtained with a Perkin-Elmer DSC-2 equipped with a data station. Hard segments of 5 to 10 mg weight were used. The heating rate was 10°C/min and the cooling rate was either 320°C/min or 10°C/min. High performance liquid chromatograph (HPLC) results were obtained with a Perkin-Elmer Series 2 liquid chromatograph equipped with a data station using a μ-porasil silica gel column (Waters Associates) under the conditions: (THF as a solvent, UV detector at 254 nm, flow rate
1 ml/min, and room temperature). Thin layer chromatograph (TLC) results were obtained from a 20 cm x 20 cm silica plate (Fisher Scientific) using THF/hexane (60/40, v/v) solvent system.

**Synthesis**

Scheme 1 shows the synthesis of hard segments B(TB)n where B represents 1,4-butanediol and T represents 2,4-toluene diisocyanate. The adduct of acetone oxime and 2,4-TDI is abbreviated as AT.

(a) **BTB** 43.5 g of 2,4-TDI (0.25 mole) was added dropwise to 450 g of stirred BDL (5 moles) in a 1000 ml 3-neck flask at 100°C. The reaction was allowed to proceed for an additional two hours after 2,4-TDI was added completely. The excess butanediol was removed completely by vacuum distillation. The residue was dissolved in 2000 ml of methanol. Water was added until the solution became cloudy. The precipitate formed overnight was collected and analyzed by HPLC or TLC until the pure dimer was finally collected. The yield was 40 g (45%).

(b) **AT** 51 g of acetone oxime (0.7 mole) dissolved in 150 ml of dry toluene was added dropwise to 123 g of 2,4-TDI (0.7 mole) at 50°C in a 3-neck 500 ml flask equipped with a nitrogen inlet, a drying tube, and a mechanical stirrer. The reaction was allowed to proceed for an
Table 1

Synthesis of hydroxy-terminated hard segments of 1,4-butanediol and 2,4-TDI

<table>
<thead>
<tr>
<th>Key</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>B</td>
<td>1,4-butanediol</td>
</tr>
<tr>
<td>T</td>
<td>2,4-TDI</td>
</tr>
<tr>
<td>A</td>
<td>acetone oxime</td>
</tr>
<tr>
<td>AT</td>
<td>adduct of 2,4-TDI and acetone oxime</td>
</tr>
<tr>
<td>DBTDL</td>
<td>dibutyltin dilaurate</td>
</tr>
</tbody>
</table>

![Chemical structure](attachment:chemical_structure.png)
(b) $AT$

\[ \text{B(TB)$n$, n = 2, 3, 4, 5} \]

\[ 2AT + B(TB)$n-2 \xrightarrow{\text{DMF}, \text{DBTDL}, 25^\circ C} \text{ATB(TB)$n-2TA} \]

ex. $B \xrightarrow{100^\circ C} B(TB)n + 2A$
additional two hours before cooling to room temperature. The white precipitate formed upon cooling was collected and washed with portions of 500 ml of toluene. Toluene was removed in vacuo at 50°C. The yield was 122 g (70%).

(c) $B(TB)_n, \ n = 2, 3, 4, 5$ Since the procedures are generally the same for all oligomers, only the details for the trimer synthesis are described.

49.4 g of AT (0.2 mole), 9 g of BDL (0.1 mole) and 300 ml of DMF were placed in a 1000 ml 3-neck flask equipped with a nitrogen inlet, a condenser, and a drying tube. DBTDL (0.01 g) was added and the reactants were stirred for one hour at room temperature. A slight excess of AT might be needed since the AT used was not pure. After the reaction was completed, as evidenced by the IR spectrum, 180 g of BDL (2 moles) was added to the reaction mixture and the temperature raised and kept at 100°C with stirring for two hours. The solution was allowed to cool to room temperature and poured into 2000 ml of water containing 2 g of calcium chloride. The precipitate was collected and washed several times with water. The crude product was dissolved in 2000 ml of methanol and water added until the solution becomes cloudy. The precipitate was collected overnight. This fractional precipitation procedure was continued until the desired fraction of the hard segments as analyzed by TLC or HPLC was obtained. The yield was 46 g (75%).
Characterization

The structure of the adduct of 2,4-TDI and acetone oxime (AT) is confirmed by proton NMR (Fig. 2-1). Two types of methyl groups at 2.23 ppm and 2.07 ppm are observed. They are assigned to the methyl group attached to the benzene ring and the acetone oxime methyl group, respectively. The proton ratio is slightly lower than the expected ratio of 1:2. The deviation is due to the reaction between the ortho-isocyanate group and the acetone oxime. The amount of the side product formed can be calculated semi-quantitatively from the actual proton ratios. Our results show a purity of more than 90 % for the crude product. No attempt has been made to further purify this material. The singlet appearing at 8.06 ppm is assigned to the proton on the para-substituted urethane linkage. The ortho-urethane linkage, if it exists, should appear at 7.60 ppm as evidenced in one of our di-substituted samples. This peak can also be used as an indication of di-substitution. The peaks at 6.97 ppm and 7.17 ppm correspond to the aromatic protons.

The purity of the hard segments is analyzed by high performance liquid chromatography (HPLC) (Fig. 2-2) and thin layer chromatography (TLC). The hard segments of various lengths show different retention times and Rf values (Table 2-1) The retention times and Rf values decrease with increasing hard segment length due to the decreasing hydroxyl content. The UV absorptivity of each hard segment is found
Fig. 2-1. Proton NMR spectrum of the para-substituted adduct of 2,4-TDI and acetone oxime.
to be approximately the same. We may, therefore, conclude that the purity of the hard segments is better than 90% according to the HPLC traces. The purity is also apparent from the good agreement between calculated and observed values of the chemical compositions as shown in Table 2-2. Tolerance limit of the elemental analysis is ± 0.3 %.

The structure of the hard segments is confirmed by proton NMR. Fig. 2-3 shows the NMR spectrum of the dimer, BTB. The chemical shift assignments are listed in Table 2-3. The other hard segments show nearly the same chemical shifts but the proton ratios are different (Table 2-3). The triplet appearing at 4.33 ppm is assigned to the hydroxyl group adjacent to the methylene group (3.37 ppm). The intensities of these two peaks relative to the other peaks decrease as the hard segment length increases due to the lower content of CH₂OH groups in the longer hard segments. The spectrum of the hexamer, B(TB)₅, is shown in Fig. 2-4 for comparison. The proton ratios of each group are generally in good agreement with the calculated values. The lower value of the proton of the urethane linkage (NHCOO) is possibly due to the proton-deuterium exchange with the solvent, deuterated dimethyl sulfoxide. The hydroxyl group, however, shows complete proton-deuterium exchange with solvents such as deuterated acetone and methanol.

The structures of the hard segments are further supported by C-13 NMR. Fig. 2-5 shows the C-13 NMR spectrum of the dimer. All the peaks are identified using a variety of model compounds. The results
Table 2-1
Retention Times and Rf Values of Hydroxy-Terminated Hard Segments

<table>
<thead>
<tr>
<th>Oligomers</th>
<th>Retention time* (min)</th>
<th>Rf**</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimer</td>
<td>4.20</td>
<td>0.37</td>
</tr>
<tr>
<td>trimer</td>
<td>3.79</td>
<td>0.32</td>
</tr>
<tr>
<td>tetramer</td>
<td>3.70</td>
<td>0.28</td>
</tr>
<tr>
<td>pentamer</td>
<td>3.57</td>
<td>0.24</td>
</tr>
<tr>
<td>hexamer</td>
<td>3.47</td>
<td>0.20</td>
</tr>
</tbody>
</table>

* Based on the following conditions: (a) THF eluent (b) silica gel column (c) 1 ml/min flow rate and (d) UV detector at 254 nm.

** THF/hexane (60/40, v/v) on silica gel plate.
Table 2-2

Elemental Analysis of Hydroxy-Terminated Hard Segments

<table>
<thead>
<tr>
<th>Oligomers</th>
<th>Calculated</th>
<th>Found</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>dimer</td>
<td>57.63</td>
<td>7.34</td>
</tr>
<tr>
<td>trimer</td>
<td>58.25</td>
<td>6.80</td>
</tr>
<tr>
<td>tetramer</td>
<td>58.50</td>
<td>6.58</td>
</tr>
<tr>
<td>pentamer</td>
<td>58.64</td>
<td>6.46</td>
</tr>
<tr>
<td>hexamer</td>
<td>58.72</td>
<td>6.38</td>
</tr>
</tbody>
</table>

* by difference
Fig. 2-3. Proton NMR spectrum and the assignments of the dimer, BTB.
Table 2-3
Proton Ratios and Chemical Shifts of Hard Segments

<table>
<thead>
<tr>
<th>Peak</th>
<th>Dimer</th>
<th>Trimer</th>
<th>Tetramer</th>
<th>Pentamer</th>
<th>Hexamer</th>
<th>Chemical Shift(ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>(CH₂)₂</td>
<td>8(8)*</td>
<td>12(12)</td>
<td>16(16)</td>
<td>20(20)</td>
<td>24(24)</td>
</tr>
<tr>
<td>b</td>
<td>CH₃</td>
<td>3(3)</td>
<td>6(6)</td>
<td>9(9)</td>
<td>12(12)</td>
<td>15(15)</td>
</tr>
<tr>
<td>c</td>
<td>CH₂OH</td>
<td>4(4)</td>
<td>4(4)</td>
<td>4(4)</td>
<td>4(4)</td>
<td>4(4)</td>
</tr>
<tr>
<td>d</td>
<td>COOCH₂</td>
<td>4(4)</td>
<td>8(8)</td>
<td>12(12)</td>
<td>16(16)</td>
<td>20(20)</td>
</tr>
<tr>
<td>e</td>
<td>CH₂OH</td>
<td>2(2)</td>
<td>2(2)</td>
<td>2(2)</td>
<td>2(2)</td>
<td>2(2)</td>
</tr>
<tr>
<td>f,g</td>
<td>phenyl</td>
<td>3(3)</td>
<td>6(6)</td>
<td>9(9)</td>
<td>12(12)</td>
<td>15(15)</td>
</tr>
<tr>
<td>h,i</td>
<td>NH</td>
<td>2(1.7)</td>
<td>4(3.4)</td>
<td>6(5.4)</td>
<td>8(7.3)</td>
<td>10(8.4)</td>
</tr>
</tbody>
</table>

* observed values
Fig. 2-4. Proton NMR spectrum of the hexamer, B(TB)$_6$. Note the drastic decrease in OH peak (e) intensity.
Fig. 2-5. C-13 NMR spectrum and the assignments of the dimer, BTB.
are shown in Table 2-4. Again, the other hard segments show nearly the same chemical shifts but with different intensities. The intensities of peaks a and b decrease drastically as the hard segment length increases (Fig. 2-6). It should be noted that the two methylene groups represented by peaks b and c are inseparable in proton NMR but separable in C-13 NMR. The high intensity of peak c in the hexamer is due to the high content of the two internal methylene groups. The intensities of the other peaks change only slightly as expected.

The infrared spectrum of the dimer is shown in Fig. 2-7. The free NH stretching appears at 3460 cm\(^{-1}\), the hydrogen bonded NH stretching at 3330 cm\(^{-1}\), and the carbonyl group at 1700 cm\(^{-1}\) [18]. The OH absorption can not be separated clearly from bonded NH stretching. The other hard segments show similar spectra with changes in intensities.

The hard segments, after drying at 100°C for 24 hours, show a melting point during the first run. The quenched samples (320°C/min or 10°C/min cooling rate), on the other hand, show only glass transition temperatures (Fig. 2-8). Tg and Tm values are collected in Table 2-5. Fig. 2-9 shows the dependence of melting temperatures and glass transition temperatures on the hard segment length. The hard segment Tg's are inversely proportional to the reciprocal of the molecular weight, suggesting that the Flory-Fox relationship [19] is followed, with K= 32600. The extrapolated glass transition
Table 2-4

Calculated and Observed Carbon Chemical Shifts of Hard Segments

<table>
<thead>
<tr>
<th></th>
<th>Calculated*</th>
<th>Observed</th>
<th>Calculated**</th>
<th>Observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>a.</td>
<td>61.8</td>
<td>60.38</td>
<td>g.</td>
<td>125.66</td>
</tr>
<tr>
<td>b.</td>
<td>28.1</td>
<td>28.89</td>
<td>h.</td>
<td>130.29</td>
</tr>
<tr>
<td>c.</td>
<td>24.5</td>
<td>25.38</td>
<td>i.</td>
<td>114.95</td>
</tr>
<tr>
<td>d.</td>
<td>64.1</td>
<td>64.09</td>
<td>j.</td>
<td>136.54</td>
</tr>
<tr>
<td>e.</td>
<td>154.0</td>
<td>154.37</td>
<td>k.</td>
<td>114.95</td>
</tr>
<tr>
<td>f.</td>
<td>17.1</td>
<td>17.07</td>
<td>l.</td>
<td>137.31</td>
</tr>
</tbody>
</table>

* Based on the following model compounds: hexane, 1-hexanol, 1,6-hexanediol, carbamate of phenyl isocyanate and 1-hexanol, and butane.

** Based on the methyl dicarbamate of 2,4-toluene diisocyanate.
Fig. 2-7. Infrared spectrum of the dimer, BTB.
Fig. 2-8. Thermal behavior of the trimer: (A) first run showed the melting endotherm (B) quenched sample showed T_g only.
Table 2-5
Thermal Properties of Hydroxy-Terminated Hard Segments

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tm* (°C)</th>
<th>Tg** (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimer</td>
<td>115</td>
<td>9</td>
</tr>
<tr>
<td>trimer</td>
<td>122</td>
<td>45</td>
</tr>
<tr>
<td>tetramer</td>
<td>120</td>
<td>61</td>
</tr>
<tr>
<td>pentamer</td>
<td>136</td>
<td>70</td>
</tr>
<tr>
<td>hexamer</td>
<td>133</td>
<td>78</td>
</tr>
</tbody>
</table>

* Peak temperature
** Midpoint
Fig. 2-9. Molecular weight dependence of $T_g$ and $T_m$ in hard segments.
temperature of this hard segment with infinite molecular weight is 100°C. Such a trend was also found in solution polymerized segmented polyurethanes containing the same type of hard segments and a butadiene soft segment [20]. The Tm's of the hard segments show an odd-even effect relative to the number of TDI units. Even-numbered hard segments show higher melting temperatures than the neighboring odd-numbered hard segments. This may be attributed to the symmetrical structures of even-numbered hard segments, as shown in Fig. 2-10, due to the specific synthetic route.
Fig. 2-10. Structures of hydroxy-terminated hard segments: (A) dimer (B) trimer (C) tetramer (D) pentamer, and (E) hexamer.

\[
R = -N-C-O-(CH_2)_4-OH
\]

\[
\ldots = -N-C-O-(CH_2)_4-O-C-N-\]
References

20. B.H. Bengtson, W.J. MacKnight, C. Feger and N.S. Schneider, Polymer, in press.
CHAPTER III
STRUCTURE-PROPERTY RELATIONSHIPS OF SEGMENTED
POLYURETHANES CONTAINING MONODISPERSE HARD SEGMENTS

Introduction

Segmented polyurethanes are usually prepared from a two-stage method where the macroglycols are endcapped with excess of diisocyanates, followed by the chain extension with the stoichiometric amount of diols to obtain high molecular weight polymers. In the first stage, the macroglycols are extended by diisocyanates to some extent, which results in a change in their molecular weight distribution. Subsequent addition of diols extends the isocyanate-terminated soft segments to form polyurethanes containing one hard segment unit or, most probably, diols react with diisocyanates to form urethane oligomers of various lengths and connect to soft segments to form segmented polyurethanes. It is also possible that the hard segment units grow from isocyanate-terminated soft segments and connect to other soft segment units randomly. It is apparent that the segmental distribution, especially that of the hard segment, is complicated, even before other factors such as temperature, solvent, mixing, and catalyst are taken into account.

Actual sequence distribution of hard segments is important in determining polymer properties for several reasons. First, the glass
transition temperature [1] and melting temperature [2-5] increase with increasing hard segment length. Second, phase segregation improves with increasing segment length [6-10]. Third, the hard segment length affects morphology, with the possibility that longer hard segments form larger domains. However, sequence distribution of hard segments have not been studied extensively due to the lack of suitable techniques and appropriate model polymers. Nuclear magnetic resonance (NMR) has been used by Suzuki et al. [11] to obtain average sequence lengths of hard segments in some polyester based polyurethanes. The other technique, depolymerization, has been used by Suzuki and Ono [12] to obtain the average sequence length of hard segments in a PTMEG/MDI/hydrazine system. There are two shortcomings of these two techniques: (a) only the average sequence length is obtained and (b) the depolymerization technique can only be applied to few polymers due to the difficulty in breaking a specific bond.

Another feasible approach to overcome this difficulty is to prepare segmented polyurethanes with well characterized chain microstructures. Then the segmented polyurethanes can be prepared by reacting a soft segment with a hard segment of known structure. Monodisperse hard segments are suitable for this purpose and have been the subject of several recent investigations [1-5]. The goal of these studies is to simplify the rather complicated structure of conventional segmented polyurethanes so that their structure-property relationships can be established. Most of these studies are based on
hard segments containing MDI and BDL [2-4]. These hard segments are crystallizable due to their symmetrical structure. The other type of monodisperse hard segments based on 2,4-TDI and BDL has been prepared [1] and described in chapter II. These hydroxy-terminated hard segment oligomers are crystallizable by themselves, although they are expected to be amorphous once incorporated into the polymer. We intend to use these hard segments to study the dependence of properties on hard segment length without the influence of hard segment crystallization.

Properties of segmented polyurethanes generally depend on the type and content of both soft and hard segments as well as the method and condition of polymerization. The type of segment determines the crystallinity, the segmental polarity difference, and the secondary interactions such as hydrogen bonding. The molar content of the hard segment usually affects the hard segment length with higher content favoring longer hard segment sequences. Hard segments with higher weight contents, however, do not necessarily lead to the long hard segment sequences since soft segment molecular weights may be low and result in a low molar hard segment content. Polyurethanes prepared from the reaction of soft segments and monodisperse hard segments have several advantages over polydisperse polyurethanes. First, the method and condition of polymerization which affect the segmental distribution are less important. Second, properties can be expressed explicitly as a function of the hard segment length instead of the
hard segment content. Third, the morphology of a polymer such as domain size and size distribution can be more significantly related to hard segment length. It is apparent that if the hard segments are amorphous, the remaining parameters which affect the properties are the type of soft segment and the distribution of interphase and interurethane hydrogen bonding.

In order to study the effect of soft segment on properties, we have chosen three types of macroglycols in this study, namely, hydroxy-terminated polybutadiene (HTPBD), polytetramethylene ether glycol (PTMEG), and polycaprolactone glycol (PCL). Polyurethanes based on polyester, polyether, and polybutadiene show differences due to their different crystallinities and abilities for interphase hydrogen bonding. The carbonyl group of the polyester is a better hydrogen acceptor than the ether group of the polyether, whereas there is no hydrogen acceptor in polybutadiene. Therefore, the phase segregation is expected to increase in the order: polyester, polyether, and polybutadiene. Molecular weights of all macroglycols are around 2000, because only 2000 Mn HTPBD with hydroxy functionality of 1.96 was available. The other two were chosen to be in the same molecular weight range so that property comparisons are based on the same hard segment content as well as the same hard segment length.

The same HTPBD was previously used to prepare bulk polymerized segmented polyurethanes containing 2,4-TDI/BDL hard segments and those showed two hard segment Tg's [13] are in accordance with similar
observations reported by Schneider et al. [14]. Phase segregation is nearly complete in these bulk polymerized polyurethanes. A bimodal distribution of hard segments is present and has been attributed to the incompatibility between long and short hard segments [15] which originated from the large difference in polarity between butanediol and polybutadiene soft segment [16]. It is one of the goals of this study to investigate the compatibility between hard segments of different lengths by blending two polyurethanes, each containing monodisperse hard segments of a given length. Polybutadiene is ideal, not only because it is the original soft segment incorporated in the polyurethanes which showed the dual hard segment Tg's, but also because the phase mixing between the soft segment and the hard segment is minimal.

Polycaprolactone glycol (PCL), a polyester, was chosen because it has been endcapped successfully with 2,4-TDI [17]. Polycaprolactone (PCL) was used in a series of studies of dynamic mechanical properties for MDI/BDL, TDI/BDL, and TDI/HBPA (Hydrogenated Bisphenol A) based polyurethanes [18-21]. In a PCL/MDI/BDL (molar ratio 1/2/1) system, the soft segment was crystallizable when the polycaprolactone glycol molecular weight (Mn) exceeded 3000. Polycaprolactones with Mn lower than 3000 were found to be compatible with the hard segments. The Tg's increased with hard segment content and agreed with that calculated by the Fox equation when Tg's were taken to be \(-60^\circ C\) for PCL and \(125^\circ C\) for MDI/BDL hard segments [18]. For higher hard
segment contents, the compatibility depended on the molecular weight of the soft segment. It was found that Tg's increased with hard segment content when 830 Mn PCL was used, whereas the Tg's were independent of hard segment content when Mn was 2100. This was attributed to better phase segregation in the 2100 Mn series [19]. However, when MDI was replaced by a mixture of 2,4- and 2,6-TDI (80/20, w/w) with PCL Mn = 2100, the Tg's increased with hard segment content, indicating considerable interphase mixing [20]. No information was given regarding soft segment crystallinity and the degree of phase segregation. Similar results were found when 1,4-butandiol was replaced by hydrogenated bisphenol A [21].

Polytetramethylene ether glycol (PTMEG) has been the soft segment of choice for polyether based segmented polyurethanes due to its good resistance to humidity and superior mechanical properties. The transition behavior of PTMEG/TDI/BDL polyurethanes has been studied by Sung and Schneider [22-25]. It was found that the phase segregation increased with increasing soft segment molecular weight and greater phase mixing occurred in polyester than in polyether. The amorphous 2,4-TDI/BDL hard segments were compatible with PTMEG of 1000 Mn and showed the Tg dependence on hard segment concentration although the observed Tg's were 15 to 25 degrees higher than that calculated from the Fox equation, assuming complete phase mixing. The observed Tg's were 28 to 66 degrees higher than that calculated from the Fox equation when the extent of hard segment-soft segment mixing was
obtained from infrared results. Apparently the extent of phase mixing can not be determined from the hydrogen bonding analysis of infrared results. When the soft segment molecular weight was increased to 2000 Mn, phase segregation was improved as evidenced by the existence of low glass transition temperatures. The hard segment Tg's obtained from thermomechanical analysis (TMA) were between 45°C and 65°C with little dependence on hard segment concentration. Higher Tg's were also found, which were attributed to the possible formation of allophanate and biuret linkages.

Senich and MacKnight [26] have studied the dynamic mechanical properties of segmented polyurethanes based on 2,4-TDI/BDL and 2,6-TDI/BDL hard segments and PTMEG soft segment with Mn of 1000 and 2000. In PTMEG (2000 Mn)/2,4-TDI/BDL system, three compositions were studied with molar ratios of 1/4/3, 1/5/4, and 1/6/5, respectively. The transition temperatures as determined from the loss modulus at 11 Hz showed a soft segment relaxation at -63°C for three compositions, whereas the hard segment transition increased from 55°C for 1/5/4 composition to 68°C for 1/6/5 composition, indicating improved phase segregation as the hard segment content increased.

In this study, properties are investigated with structural variations. This includes studies of thermal, dynamic mechanical, and stress-strain properties as functions of hard segment length as well as various types of soft segments.
Experimental

Materials. 2,4-Toluene diisocyanate (Fluka A G) was purified by vacuum distillation. Anhydrous hexane (Aldrich, less than 0.005 % water) was used as received. Tetrahydrofuran (THF) (Aldrich, HPLC grade) and dimethyl formamide (DMF) (Fisher Scientific, spectrophotometric grade) were purified by refluxing 24 hours, followed by distillation in the presence of TDI, calcium hydride, and TDI, respectively.

Some of the properties of macroglycols were evaluated in this laboratory and the results are shown in Table 3-1. Number average molecular weight (Mn) was determined by hydroxyl equivalent weight method (ASTM-E222, reflux method), assuming hydroxyl functionality of 2. Molecular weight (Mn) and molecular weight distribution (MWD) was determined from gel permeation chromatography (GPC) by using polystyrene standards.

Hydroxy-terminated polybutadiene (HTPBD, lot number LP-R-1), kindly supplied by Japan Synthetic Rubber Company, has Mn of 2120 and functionality of 1.96. The GPC trace shows a bimodal distribution with MWD of 1.23. The micro-structure shows 19% of cis-1,4, 31% of trans-1,4, and 50% of 1,2-vinyl contents. Polycaprolactone (Polysciences) has Mn of 2060 and MWD of 1.47. Polytetramethylene ether glycol (Polysciences) has Mn of 1840 and MWD of 1.44.
Polymer synthesis. Segmented polyurethanes containing monodisperse hard segments were prepared according to scheme I. The synthesis of hydroxy-terminated hard segments of 2,4-toluene diisocyanate and 1,4-butanediol has been described elsewhere [1]. The polymers are synthesized in two steps: first, the endcapping of macroglycols with 2,4-TDI and second, the addition polymerization from hydroxy-terminated hard segments and isocyanate-terminated soft segments.

a. Endcapping of macroglycols with 2,4-toluene diisocyanate.

Endcapping procedures are the same for all three types of macroglycols. For endcapping of polycaprolactone (PCL), 50 g of PCL (ca. 2.5x10^-2 mole) was placed in a separatory funnel equipped with pressure equalizing tube and 17.4 g of 2,4-TDI (0.1 mole) was placed in a 250 ml round bottom flask. The whole system was kept under vacuum for three hours with the funnel section heated by a heating band at about 100°C in order to remove moisture. The flask was then flushed with dry nitrogen and heated in an oil bath at 100°C without further use of vacuum. PCL was added dropwise into 2,4-TDI with stirring. The reaction was allowed to proceed for another 3 hours after the complete addition of PCL to insure endcapping.

Excess 2,4-TDI was stripped by continuous liquid-liquid extraction from hexane in an apparatus shown in Fig. 3-1(A) since endcapped PCL is less soluble than 2,4-TDI in hexane. The reaction flask containing
Scheme I

(A) **Endcapping of Prepolymers by 2,4-TDI**

P: HTPBD, PTMEG, PCL.

\[ P + \text{ex. T} \xrightarrow{\text{100°C}} \text{TPT + ex. T} \xrightarrow{\text{TDI stripping}} \text{TPT} \]

HTPBD: \[ \text{HO}((\text{C=C-C})_m-(\text{C-C})_n\text{OH}) \]

PTMEG: \[ \text{HO((CH}_2)_4\text{O)-R-(O(CH}_2)_4\text{OH}) \]

PCL: \[ \text{HO((CH}_2)_5\text{OC)}\text{R-(CO(CH}_2)_5\text{OH}) \]

(B) **Polymerization of Segmented Polyurethanes Containing Monodisperse Hard Segments**

\[ \text{TPT + B(TB)}_n \xrightarrow{\text{THF}} [\text{P-T-B(TB)}_n\text{T}] \]

\[ \begin{align*}
n = 0, & \quad \text{monomer} \\
n = 1, & \quad \text{dimer} \\
n = 2, & \quad \text{trimer} \\
n = 3, & \quad \text{tetramer} \\
n = 4, & \quad \text{pentamer} \\
n = 5, & \quad \text{hexamer} \end{align*} \]
Fig. 3-1. Liquid-liquid extraction apparatus for removing excess 2,4-TDI from TDI endcapped macroglycols: (A) for T(PCL)T and T(PTMEG)T; (B) for T(PBD)T.
the reaction mixture was placed in an oil bath at 50°C. Hexane was added through the inner tube to strip 2,4-TDI from the mixture. Excess 2,4-TDI was removed completely in about two days with this continuous extraction. The same apparatus was also used to strip excess 2,4-TDI from endcapped PTMEG.

The stripping procedures are different for PBD since it is soluble in hexane. The other type of liquid-liquid extraction apparatus as shown in Fig. 3-1(B) was used. The reaction mixture after endcapping was diluted with anhydrous hexane to about 200 ml. The heavier, anhydrous DMF from the solvent flask passed through the hexane layer and removed 2,4-TDI from the mixture due to the better solubility of 2,4-TDI in DMF.

b. Synthesis of segmented polyurethanes containing monodisperse hard segments. Synthesis procedures are the same for all types of segmented polyurethanes. For the synthesis of PCL polyurethane containing three hard segment units, 5 g of endcapped PCL (2.1x10^-3 mole) and about 50 mg of dibutyltin dilaurate (DBTDL) were dissolved in 25 ml of THF in a 125 ml three-neck round bottom flask which was equipped with a nitrogen inlet, a separatory funnel and a drying tube. 1.3 g of BTBTB trimer (2.1x10^-3 mole) was dissolved in 45 ml of THF in the separatory funnel. About half of the trimer was added to the reaction flask with stirring at room temperature. The rest of
the trimer was added dropwise over four hours. The completeness of polymerization was monitored by the disappearance of isocyanate absorption from the infrared spectrum.

The reaction mixture was poured slowly into 2000 ml of methanol with stirring. The polymer collected was washed again with a small amount of methanol to remove traces of the excess trimer, followed by drying in vacuo at 50°C.

**Measurements**

**Polymer characterization.** The number average molecular weights of TDI endcapped macroglycols were determined from gel permeation chromatography (GPC) and an isocyanate equivalent weight method (modified ASTM D1638-59T). Polymers were characterized by GPC and infrared spectroscopy. GPC results were obtained from a Waters apparatus in tetrahydrofuran (THF) using polystyrene standards. Infrared spectra were obtained from a Perkin-Elmer 283 infrared spectrometer from a thin film cast from THF solution on a KBr pellet.

**Sample preparation.** Polyurethane samples were compression molded at 3 MPa with temperature variations shown in Table 3-2. The samples were stored about two weeks for dynamic mechanical property tests and about eight weeks for thermal and mechanical property tests.
Experimental methods. DSC scans over the temperature range of -140°C to 180°C were recorded by using a Perkin-Elmer DSC-II linked to a Perkin-Elmer Thermal Analysis Data Station. Sample weights were 20±5 mg. The experiments were carried out at a heating rate of 20°C/min under a helium purge. Cyclohexane and indium were used as thermal standards. The glass transition temperatures were taken to be the midpoint of the step in heat capacity. The peak temperatures were used for melting temperatures.

The dynamic mechanical properties were measured by using a computerized dynamic mechanical thermal analyzer (DMTA) instrument of Polymer Laboratories, England. Samples were measured at 1 Hz frequency with heating rate of 5°C/min in several temperature ranges. The dimensions of the samples were about 40x19x1.6 in millimeter. A double cantilever bending geometry was used.

Uniaxial stress-strain responses were measured with an Instron universal testing machine at room temperature, with a crosshead speed of 1 cm/min. Sample thickness was about 0.015 in with a gauge length of 2.5 cm. The engineering stress was calculated using the initial cross-sectional area.

Stress hysteresis was measured by loading and unloading the specimen at a crosshead speed of 1 cm/min. The unloaded samples were kept at unstrained state for five minutes before the next loading cycle. These experiments were carried out at increasing strain levels.
Results and Discussion

A. Polymer Characterization

Endcapped macroglycols. The number average molecular weights obtained from both GPC and isocyanate equivalent weight determination are shown in Table 3-1. The results from these two techniques are not quite consistent. The equivalent weight method seems to be more reliable in this molecular weight range unless more sophisticated GPC techniques are used. Results of Mn from vapor phase osmometry (VPO) (not shown) are between 2000 to 4500 without acceptable consistency. It is apparent that T(PBD)T was highly chain extended, whereas the other two endcapped macroglycols were still in the neighborhood of 2000 Mn. The chain extension of PBD possibly originates from impurities such as 2,6-TDI (in 2,4-TDI) and amines or water remaining in the extracting solvent, DMF; reaction due to the C=C bonds in polybutadiene; or the formation of allophanate linkages. Further investigation is needed to establish a room temperature endcapping process in the presence of a solvent such as toluene and a catalyst. Lower reaction temperatures are in general more favorable if reactive groups capable of side reactions are present. Another problem arises from the very limited supply of PBD with functionality near two, which restricts the development of optimum conditions for endcapping. Nevertheless, polymers based on the highly chain extended PBD were prepared. Due to
Table 3-1

**Mn of Hydroxy and Isocyanate-Terminated Soft Segments**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Equivalent Weight Method</th>
<th>G P C (MWD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBD</td>
<td>2,200</td>
<td>2,200(1.23)</td>
</tr>
<tr>
<td>T(PBD)T*</td>
<td>6,800</td>
<td>8,500(2.20)</td>
</tr>
<tr>
<td>PCL</td>
<td>2,060</td>
<td>1,630(1.46)</td>
</tr>
<tr>
<td>T(PCL)T*</td>
<td>2,150</td>
<td>2,900(1.60)</td>
</tr>
<tr>
<td>PTMEG</td>
<td>1,840</td>
<td>1,960(1.48)</td>
</tr>
<tr>
<td>T(PTMEG)T*</td>
<td>2,130</td>
<td>2,180(1.70)</td>
</tr>
</tbody>
</table>

* Macroglycol endcapped with 2,4-toluene diisocyanate. The GPC samples were capped with methanol and dried before measuring.
the very highly phase segregated nature of PBD based polyurethanes, it is expected that the thermal properties are not much affected by high molecular weight soft segment. On the other hand, the mechanical properties are no doubt quite different from those with lower molecular weight soft segments.

Polymers. Table 3-2 summarizes the general properties of segmented polyurethanes containing various hard segment lengths and different types of soft segments. Polymers synthesized at room temperature are almost free of colored contaminants which occurred in polymers prepared at reflux temperature of the solvent, namely, 69°C for THF. Polymers are designated as, for example, PCL-2BT where PCL represents the polycaprolactone soft segment and 2BT represents two hard segment units with each unit comprises 2,4-toluene diisocyanate (T) and 1,4-butanediol (B). There is an extra 2,4-TDI in each repeat unit which, in this study, is also considered a part of the hard segment. Infrared spectra which represent polyurethanes based on three types of soft segments are shown in Figs. 3-2, 3-3 and 3-4. In each figure the top spectrum is from the polymer while the bottom spectrum is from the 2,4-TDI endcapped soft segment. The disappearance of the isocyanate band at about 2250 cm\(^{-1}\) before precipitating from methanol is the indication of complete polymerization. In addition, the relatively intense N-H and C=O peaks in the polymers indicate that hard segments have been incorporated. Number average molecular weights and
<table>
<thead>
<tr>
<th>sample</th>
<th>urethane (wt %)</th>
<th>transparency</th>
<th>properties</th>
<th>molding temperature(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL-1BT</td>
<td>18</td>
<td>opaque</td>
<td>soft plastic</td>
<td>60</td>
</tr>
<tr>
<td>PCL-2BT</td>
<td>26</td>
<td>opaque</td>
<td>soft plastic</td>
<td>60</td>
</tr>
<tr>
<td>PCL-3BT</td>
<td>33</td>
<td>opaque</td>
<td>med. soft plastic</td>
<td>60</td>
</tr>
<tr>
<td>PCL-4BT</td>
<td>38</td>
<td>opaque</td>
<td>plastic</td>
<td>60</td>
</tr>
<tr>
<td>PCL-5BT</td>
<td>43</td>
<td>translucent</td>
<td>tough elastomer</td>
<td>60</td>
</tr>
<tr>
<td>PCL-6BT</td>
<td>47</td>
<td>transparent</td>
<td>tough elastomer</td>
<td>120</td>
</tr>
<tr>
<td>PTMEG-1BT</td>
<td>19</td>
<td>translucent</td>
<td>soft rubber</td>
<td>60</td>
</tr>
<tr>
<td>PTMEG-2BT</td>
<td>27</td>
<td>translucent</td>
<td>soft rubber</td>
<td>60</td>
</tr>
<tr>
<td>PTMEG-3BT</td>
<td>34</td>
<td>translucent</td>
<td>soft, tacky rubber</td>
<td>60</td>
</tr>
<tr>
<td>PTMEG-4BT</td>
<td>39</td>
<td>translucent</td>
<td>soft, tacky rubber</td>
<td>60</td>
</tr>
<tr>
<td>PTMEG-5BT</td>
<td>44</td>
<td>transparent</td>
<td>rubber</td>
<td>120</td>
</tr>
<tr>
<td>PTMEG-6BT</td>
<td>48</td>
<td>translucent</td>
<td>tough elastomer</td>
<td>120</td>
</tr>
<tr>
<td>HTPBD-1BT</td>
<td>6</td>
<td>translucent</td>
<td>viscous liquid</td>
<td>145</td>
</tr>
<tr>
<td>HTPBD-2BT</td>
<td>9</td>
<td>translucent</td>
<td>soft rubber</td>
<td>145</td>
</tr>
<tr>
<td>HTPBD-3BT</td>
<td>12</td>
<td>transparent</td>
<td>rubber</td>
<td>145</td>
</tr>
<tr>
<td>HTPBD-4BT</td>
<td>15</td>
<td>transparent</td>
<td>rubber</td>
<td>145</td>
</tr>
<tr>
<td>HTPBD-5BT</td>
<td>18</td>
<td>transparent</td>
<td>tough rubber</td>
<td>145</td>
</tr>
<tr>
<td>HTPBD-6BT</td>
<td>20</td>
<td>transparent</td>
<td>rubber</td>
<td>145</td>
</tr>
</tbody>
</table>
Fig. 3-2. Infrared spectra of (A) PBD-4BT and (B) T(PBD).
Fig. 3-3. Infrared spectra of (A) PCL-5BT and (B) T(PCL)T.
Fig. 3-4. Infrared spectra of (A) PTMEG-5BT and (B) PTMEG.
Table 3-3
Mn, Mw and MWD of Polyurethanes from GPC

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn</th>
<th>Mw</th>
<th>MWD</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBD-T</td>
<td>22,000</td>
<td>48,800</td>
<td>2.2</td>
</tr>
<tr>
<td>PBD-BT</td>
<td>22,500</td>
<td>74,800</td>
<td>3.3</td>
</tr>
<tr>
<td>PBD-2BT</td>
<td>16,400</td>
<td>44,600</td>
<td>2.7</td>
</tr>
<tr>
<td>PBD-3BT</td>
<td>16,400</td>
<td>39,500</td>
<td>2.4</td>
</tr>
<tr>
<td>PBD-4BT</td>
<td>9,600</td>
<td>30,600</td>
<td>3.2</td>
</tr>
<tr>
<td>PBD-5BT</td>
<td>14,800</td>
<td>39,200</td>
<td>2.6</td>
</tr>
<tr>
<td>PBD-6BT</td>
<td>9,000</td>
<td>41,200</td>
<td>4.6</td>
</tr>
<tr>
<td>PTMEG-T</td>
<td>12,300</td>
<td>28,300</td>
<td>2.3</td>
</tr>
<tr>
<td>PTMEG-BT</td>
<td>18,200</td>
<td>58,400</td>
<td>3.2</td>
</tr>
<tr>
<td>PTMEG-2BT</td>
<td>39,400</td>
<td>88,100</td>
<td>2.2</td>
</tr>
<tr>
<td>PTMEG-3BT</td>
<td>37,300</td>
<td>63,600</td>
<td>1.7</td>
</tr>
<tr>
<td>PTMEG-4BT</td>
<td>41,400</td>
<td>94,000</td>
<td>2.3</td>
</tr>
<tr>
<td>PTMEG-5BT</td>
<td>53,000</td>
<td>163,000</td>
<td>3.0</td>
</tr>
<tr>
<td>PTMEG-6BT</td>
<td>24,600</td>
<td>76,000</td>
<td>3.0</td>
</tr>
<tr>
<td>PCL-T</td>
<td>7,700</td>
<td>22,000</td>
<td>2.8</td>
</tr>
<tr>
<td>PCL-BT</td>
<td>35,500</td>
<td>132,000</td>
<td>3.7</td>
</tr>
<tr>
<td>PCL-2BT</td>
<td>20,400</td>
<td>41,200</td>
<td>2.0</td>
</tr>
<tr>
<td>PCL-3BT</td>
<td>30,100</td>
<td>67,000</td>
<td>2.2</td>
</tr>
<tr>
<td>PCL-4BT</td>
<td>26,500</td>
<td>70,400</td>
<td>2.7</td>
</tr>
<tr>
<td>PCL-5BT</td>
<td>44,000</td>
<td>156,000</td>
<td>3.5</td>
</tr>
<tr>
<td>PCL-6BT</td>
<td>19,800</td>
<td>35,600</td>
<td>1.8</td>
</tr>
</tbody>
</table>
molecular weight distributions of the polyurethanes are listed in Table 3-3. Polyurethanes based on polycaprolactone and polytetramethylene ether glycol show molecular weights ranging from 20,000 to 50,000. Number average molecular weights of PBD based polyurethanes are lower than 20,000.

B. Thermal Properties

PBD polyurethanes. Thermal properties of PBD polyurethanes are summarized in Table 3-4. The two-phase behavior of these materials is clearly shown in Fig. 3-5. The lower Tg is the relaxation of the soft segment. The closeness of these Tg's to that of hydroxy-terminated polybutadiene (HTPBD) indicates that the phase segregation is nearly complete. Hard segments are amorphous as expected. The Tg's increase with increasing hard segment length and are lower than the corresponding hydroxy-terminated hard segment oligomers as shown in Table 3-5. The decrease of hard segment Tg's due to the presence of polybutadiene soft segments is not correlated to the behavior of the hydroxy-terminated hard segment oligomers. There are two possible explanations. First, the hard segment in the polymer has a diisocyanate on both ends; for instance, the dimer BTB becomes TBTBT in the polymer, which may have different Tg from that of BTB. Therefore the effect of chain ends should be compared with diisocyanate terminated oligomers. Second, the hydroxyl groups of the
Table 3-4

Thermal Properties of PBD Polyurethanes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Low Tg, °C</th>
<th>High Tg, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTPBD</td>
<td>-64</td>
<td>--</td>
</tr>
<tr>
<td>PBD-T</td>
<td>-59</td>
<td>--</td>
</tr>
<tr>
<td>PBD-BT</td>
<td>-64</td>
<td>--</td>
</tr>
<tr>
<td>PBD-2BT</td>
<td>-61</td>
<td>3</td>
</tr>
<tr>
<td>PBD-3BT</td>
<td>-58</td>
<td>31</td>
</tr>
<tr>
<td>PBD-4BT</td>
<td>-59</td>
<td>54</td>
</tr>
<tr>
<td>PBD-5BT</td>
<td>-61</td>
<td>55</td>
</tr>
<tr>
<td>PBD-6BT</td>
<td>-62</td>
<td>58</td>
</tr>
</tbody>
</table>
Fig. 3-5. Two-phase behavior in PBD polyurethanes (PBD-xBT) and the dependence of hard segment Tg on hard segment length.
hard segments affect Tg's extensively. This is evident when the hydroxyl groups are replaced by other functional groups as in the case of aceto-terminated hard segments which have much lower Tg values as shown in Table 3-5. It seems reasonable to compare Tg's of similar structures such as a PBD-2BT with structure -(PTB)+ versus the aceto-terminated tetramer RTBTBTR where R is CH$_3$COO(CH$_2$)$_4$-. The differences is 27°C between the Tg of PBD-2BT and the aceto-terminated tetramer, 12°C between PBD-3BT and the aceto-terminated pentamer, and only 2°C between PBD-4BT and the aceto-terminated hexamer. This suggests that the effect of chain ends depends on the hard segment length. It is pronounced for lower hard segment units, but nearly negligible as the hard segment length increases to four units. The observed Tg's for some hard segments may be different from the actual values due to the excess enthalpy relaxation [27].

The thermal behavior of several blends of these polyurethanes are included in Table 3-6. The compatibility between a dimer and other hard segment oligomers was studied. A blend of PBD-2BT and PBD-6BT was prepared from THF with a 3/1 (w/w) ratio, followed by drying in air and then in vacuo. Fig. 3-6 shows the DSC traces of PBD-2BT, PBD-6BT, and the blend of both. The Tg of the blend is 32°C which is between the 3°C and the 48°C of PBD-2BT and PBD-6BT, respectively. The hard segments are therefore compatible, at least for hard segments less than 6 units in length. The broad transition,
Table 3-5
Comparison of Hard Segment Tg (°C) in PBD Polyurethanes and Oligomers

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg</th>
<th>Tg'</th>
<th>Tg&quot;</th>
<th>Tg - Tg'</th>
<th>Tg - Tg&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimer</td>
<td>3</td>
<td>9</td>
<td>-36</td>
<td>-6</td>
<td>39</td>
</tr>
<tr>
<td>trimer</td>
<td>31</td>
<td>45</td>
<td>8</td>
<td>-14</td>
<td>23</td>
</tr>
<tr>
<td>tetramer</td>
<td>54</td>
<td>61</td>
<td>30</td>
<td>-7</td>
<td>24</td>
</tr>
<tr>
<td>pentamer</td>
<td>55</td>
<td>70</td>
<td>43</td>
<td>-15</td>
<td>12</td>
</tr>
<tr>
<td>hexamer</td>
<td>58</td>
<td>78</td>
<td>56</td>
<td>-20</td>
<td>2</td>
</tr>
</tbody>
</table>

Tg: polybutadiene based polyurethanes.

Tg': hydroxy-terminated hard segments.

Tg": aceto-terminated hard segments.
### Table 3-6

Hard Segment Compatibility Study from PBD Polyurethane Blends

<table>
<thead>
<tr>
<th>Blend (w/w)</th>
<th>Low Tg, °C</th>
<th>High Tg, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBD-2BT, PBD-6BT (3/1)</td>
<td>-59</td>
<td>32</td>
</tr>
<tr>
<td>PBD-3BT, PBD-6BT (5/3)</td>
<td>-59</td>
<td>38</td>
</tr>
<tr>
<td>PBD-2BT, PBD-5BT (3/1)</td>
<td>-60</td>
<td>35</td>
</tr>
<tr>
<td>PBD-2BT, PBD-4BT (3/2)</td>
<td>-58</td>
<td>37</td>
</tr>
</tbody>
</table>
Fig. 3-6. Compatibility study of hard segments (2,4-TDI/BDL) of different lengths. The blend of PBD-2BT and PBD-6BT showed a broad transition between that of the respective polymers.
however, indicates that micro-phase incompatibility may occur. The bimodal distribution of the hard segments in some bulk polymerized polybutadiene based polyurethanes has been attributed to the incompatibility of short and long hard segments [13-16]. If this is indeed the case, the second hard segment glass transitions in those polyurethanes should arise from hard segment sequences longer than six units.

PCL polyurethanes. Table 3-7 shows the thermal properties of PCL polyurethanes. Polycaprolactone glycol with Mn of 2000 is easily crystallizable as shown in Fig. 3-7 with a melting temperature at 50°C compared to polycaprolactone homopolymer which melts at 60°C [28]. No glass transition was observed even after the sample was quenched (320°C/min) in the DSC. The quenched PCL showed two melting peaks at 39°C and 48°C, which could be due to crystallite size distribution. Pure soft segments (PCL-T) of higher molecular weight were obtained by coupling PCL with 2,4-TDI. They showed only melting behavior in the first DSC scan. Subsequent quench and re-scan showed a Tg at -58°C, a recrystallization peak at -29°C, and a melting peak at 44°C (Fig. 3-8). The Tg is close to that previously reported (-60°C [28]). The DSC traces of PCL polyurethanes are shown in Fig. 3-9. Soft segments were crystallizable for polymers containing five or less hard segment units. Since the samples were annealed at room temperature for a period of time, the first run DSC
Table 3-7
Thermal Properties of PCL Polyurethanes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
<th>Heat of fusion (cal/g)</th>
<th>Crystallinity (%)*</th>
<th>Calculated Tg**(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL</td>
<td>--</td>
<td>49</td>
<td>(24.1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCL-T</td>
<td>--</td>
<td>43</td>
<td>(24.1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCL-BT</td>
<td>-12</td>
<td>47</td>
<td>(11.9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PCL-2BT</td>
<td>-2</td>
<td>46</td>
<td>(11.9)</td>
<td>69</td>
<td>1 (6)</td>
</tr>
<tr>
<td>PCL-3BT</td>
<td>3</td>
<td>48</td>
<td>(9.4)</td>
<td>63</td>
<td>4 (10)</td>
</tr>
<tr>
<td>PCL-4BT</td>
<td>10</td>
<td>47</td>
<td>(8.3)</td>
<td>55</td>
<td>13 (19)</td>
</tr>
<tr>
<td>PCL-5BT</td>
<td>12</td>
<td>47</td>
<td>(6.8)</td>
<td>52</td>
<td>14 (21)</td>
</tr>
<tr>
<td>PCL-6BT</td>
<td>-38, 66</td>
<td>--</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Soft segment crystallinity based on the following values:
  soft segment Mn= 2000; heat of fusion of 100% crystallinity
  PCL= 24.1 cal/g.

** Calculated Tg based on Tg= -60°C for PCL and 100°C for
  2,4-TDI/BDL hard segment. Numbers in parentheses based on
  Tg= 120°C for the hard segment.
Fig. 3-7. Thermal properties of polycaprolactone glycol (PCL) of 2000 Mn before and after quench.
Fig. 3-8. DSC scans of polycaprolactone pure soft segment (PCL-T) before (top) and after (bottom) quench.
Fig. 3-9. Thermal properties of PCL polyurethanes (PCL-xBT) as a function of hard segment length. The soft segments are crystallizable until the hard segment reaching six units.
can be considered close to equilibrium as far as crystallinity is concerned. The relative crystallinities were calculated from the ratios of the observed heats of fusion to the value of 24.1 cal/g which was found for both PCL and PCL-T in this study. This heat of fusion is different from that calculated by Robeson and Joesten [29], namely between 32.5 to 36 cal/g for a polycaprolactone of 100% crystallinity from the studies of PVC-PCL blends. The soft segment crystallinity decreases as the hard segment length increases as shown in Table 3-7. No hard segment Tg was observed due to the high compatibility of PCL and the hard segments. The Tg's are close to the melting peak and can only be determined from the baseline change below and above the melting temperatures. Table 3-7 shows that the Tg increases as the hard segment length increases and is relatively close to that calculated from the Fox equation [30]:

\[
\frac{1}{T_g} = \frac{W_h}{T_{g,h}} + \frac{W_s}{T_{g,s}}
\]

where Tg is the glass transition temperature of the copolymer and Wh andWs are the weight fractions of the hard segment and the amorphous soft segment with glass transitions of Tg,h and Tg,s, respectively. The amorphous fractions of soft segment are calculated from the crystallinity results from DSC. Glass transition temperatures were assumed to be -60°C for the soft segment and 100°C for the hard segment. The latter is based on the extrapolated value from the hydroxy-terminated hard segment oligomers. Another set of calculated values are also given based on Tg = 120°C for 2,4-TDI/BDL hard
segments. The reason for this is given later. It should be mentioned that the observed Tg's may not be very accurate since the observed heat capacity steps are very broad. Because of the interference of the crystallization process, it is probably impossible to ascertain the equilibrium degree of phase mixing of amorphous hard and soft segments below the soft segment Tm, although the results indicate a strong phase mixing of the amorphous soft segment and the hard segment. At a hard segment length of six units, a completely different behavior is observed for the sample annealed at room temperature for two months. The soft segment appears to be not crystallizable. There is some incompatibility between soft and hard segments. A lower Tg is observed at -38°C which is the result of limited soft segment-hard segment mixing. The higher transition at 66°C, which is not very well defined, may be the Tg of the hard segment with a large excess enthalpy relaxation. The well annealed PCL-6BT (four months at room temperature), however, also shows the soft segment crystallinity.

The quenched PCL polyurethanes exhibited only glass transition behavior. Table 3-8 shows that the Tg's increase with increasing hard segment length and only one glass transition is observed for each polymer as shown in Fig. 3-10. The Tg's were plotted against hard segment content as shown in Fig. 3-11. It is apparent that the Fox relationship is followed when soft segment Mn= 2000 is assumed and Tg = -60°C and 100°C for soft segment and hard segment,
<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg, °C</th>
<th>Crystallization</th>
<th>Tm, °C(cal/g)</th>
<th>Calculated Tg*, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL</td>
<td>--</td>
<td></td>
<td>39(4), 47(20)</td>
<td></td>
</tr>
<tr>
<td>PCL-T</td>
<td>-58</td>
<td>-29</td>
<td>44(19)</td>
<td>-42 (-41)</td>
</tr>
<tr>
<td>PCL-BT</td>
<td>-41</td>
<td>--</td>
<td>--</td>
<td>-34 (-32)</td>
</tr>
<tr>
<td>PCL-2BT</td>
<td>-33</td>
<td>--</td>
<td>--</td>
<td>-26 (-24)</td>
</tr>
<tr>
<td>PCL-3BT</td>
<td>-25</td>
<td>--</td>
<td>--</td>
<td>-19 (-16)</td>
</tr>
<tr>
<td>PCL-4BT</td>
<td>-15</td>
<td>--</td>
<td>--</td>
<td>-14 (-8)</td>
</tr>
<tr>
<td>PCL-5BT</td>
<td>-6</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>PCL-6BT</td>
<td>0</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
</tbody>
</table>

* Calculated Tg based on Tg = -60°C for PCL and 100°C for 2,4-TDI/BDL hard segment. Numbers in parentheses based on Tg = 120°C for the hard segment.
Fig. 3-10. Thermal properties of quenched PCL polyurethanes (PCL-XBT) as a function of hard segment length. Only a single Tg is observed in each polymer.
Fig. 3-11. Glass transition temperatures of quenched PCL polyurethanes as a function of hard segment content. The calculated values from Fox copolymer equation are shown using $T_g = 120\,^\circ C$ (dotted line) and $100\,^\circ C$ (solid line) for hard segment.
respectively. A higher hard segment Tg= 107°C has been used by other investigators [23]. The Tg's are close to that calculated when the hard segment is three units or lower. However, when the hard segment length increases, the observed Tg's are a few degrees higher than the calculated values and fit better for the curve obtained from Tg = 120°C of 2,4-TDI/BDL homopolymer. At this juncture, it seemed necessary to determine the actual Tg of the hard segment with infinite molecular weight. Therefore, the relationship between Tg and molecular weight of hard segments was re-examined. It was found that the Tg of the hard segment with infinite molecular weight could be extrapolated exponentially to 120°C from both hydroxyl and aceto-terminated hard segments as shown in Fig. 3-12. Here the molecular weights of aceto-terminated hard segments are higher than that of the hydroxyl-terminated hard segments due to the two additional acetyl groups. The extrapolated Tg from the exponential curve is higher than that from the straight line as expected from the Fox-Flory relationship [31]:

\[ Tg = Tg^* - \frac{K}{Mn} \]

where Tg and Tg* are the glass transition temperatures of a homopolymer with Mn and infinite molecular weights, respectively. K is a constant. We do not intend to draw any conclusion about the hard segment Tg of 2,4-TDI/BDL due to the lack of monodisperse oligomers of higher molecular weights. However, the Tg's of quenched PCL polyurethanes can be explained more adequately with hard segment Tg of 120°C if the copolymer equation is to be followed.
Fig. 3-12. Determination of 2,4-TDI/BDL hard segment Tg with infinite molecular weight from hydroxy (filled circles) and aceto- (opened circles) terminated monodisperse hard segments.
PTMEG polyurethanes. Fig. 3-13 shows that polytetramethylene ether glycol with Mn = 2000 is highly crystalline with a melting peak at 34°C and no observable Tg. The as polymerized pure soft segment (PTMEG-T) from the coupling of PTMEG and 2,4-TDI does not show Tg, rather, there is a crystallization peak at -37°C, followed by a melting peak at 14°C and the major melting peak at 33°C, the same as that in PTMEG itself. The quenched PTMEG-T, however, shows a Tg at -78°C, a crystallization peak at -43°C and a melting peak at 19°C. The original melting peak of PTMEG at 33°C is not observed. DSC traces of PTMEG polyurethanes are shown in Fig. 3-14. The results are summarized in Table 3-9. Soft segments are crystallizable for polymers containing three or less hard segment units. PTMEG-BT has a Tg at -57°C and two melting peaks at 18°C and 44°C. The increase in Tg of about 20 degrees compared to the pure soft segment is presumably the result of soft segment-hard segment mixing. PTMEG-2BT shows a soft segment melting peak at 40°C and a not very well defined Tg at -53°C. The crystallinity of the soft segment is estimated to be 14 % from the ratio of the experimental heat of fusion to 53 cal/g, the heat of fusion of 100% crystalline poly(tetramethylene oxide) [32]. The calculated Tg from the amorphous portion of the soft segments and hard segments from the Fox equation is -49°C assuming soft segment Mn = 1900 and Tg = 120°C and -84°C [33] for hard and soft segments, respectively. The good agreement between the observed and the calculated values suggests
Fig. 3-13. Thermal properties of polytetramethylene ether glycol (PTMEG) (top) and the pure soft segment PTMEG-T before (middle) and after (bottom) quench.
Fig. 3-14. Thermal properties of PTMEG polyurethanes (PTMEG-xBT) as a function of hard segment length. Phase segregation improves with increasing hard segment length.
Table 3-9

Thermal Properties of PTMEG Polyurethanes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg, °C</th>
<th>Crystallization</th>
<th>Tm, °C (cal/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMEG</td>
<td>--</td>
<td>-37</td>
<td>14, 34</td>
</tr>
<tr>
<td>PTMEG-T</td>
<td>--</td>
<td>-37</td>
<td>14, 33</td>
</tr>
<tr>
<td>PTMEG-BT</td>
<td>-57</td>
<td></td>
<td>18, 44</td>
</tr>
<tr>
<td>PTMEG-2BT</td>
<td>-53</td>
<td></td>
<td>40 (5.6)</td>
</tr>
<tr>
<td>PTMEG-3BT</td>
<td>-61, -18</td>
<td></td>
<td>40 (0.8)</td>
</tr>
<tr>
<td>PTMEG-4BT</td>
<td>-45, -2</td>
<td></td>
<td>--</td>
</tr>
<tr>
<td>PTMEG-5BT</td>
<td>-52, 12</td>
<td></td>
<td>--</td>
</tr>
<tr>
<td>PTMEG-6BT</td>
<td>-74, 70</td>
<td>-46</td>
<td>23</td>
</tr>
</tbody>
</table>
extensive phase mixing between the hard segments and the amorphous soft segments. The melting peak in PTMEG-3BT is relatively small (apparent 2% crystallinity) compared to that of PTMEG-2BT. There appear to be two broad glass transition regions with the midpoints at -61°C and -18°C, respectively. This dual Tg behavior becomes more pronounced in PTMEG-4BT and PTMEG-5BT. PTMEG-4BT shows two Tg's at -45°C and -2°C while PTMEG-5BT shows them at -52°C and 8°C. This behavior can be rationalized as the result of the presence of a soft phase rich and a hard phase rich phases due to incomplete phase mixing. The difference between the Tg's of these two phases is the same for both PTMEG-3BT and PTMEG-4BT, namely, 43°C, but the observed Tg's were lower in PTMEG-3BT. The Tg differences between the two phases was greater in PTMEG-5BT, indicating better phase segregation. For PTMEG-6BT, a different behavior was observed. There is a well defined Tg at -74°C which is very close to that of the pure soft segment, namely, -78°C. A crystallization peak occurred at -46°C and a melting peak at 23°C. A higher hard segment Tg was observed at 70°C. This suggests that the phase segregation is nearly complete in PTMEG-6BT.

The dependence of the thermal behavior of PTMEG polyurethanes on hard segment length is readily evident. The soft segment crystallinity decreases as the hard segment length increases up to four units which do not show any crystallinity. On the other hand, the Tg increases from -78°C to -57°C for PTMEG-6BT and -53°C for
PTMEG-2BT as expected. As the hard segment length increases, the compatibility between the soft and hard segments decreases and the segments separate into different phases. The Tg difference between these phases becomes larger as the hard segment length increases due to the higher hard segment Tg and the better phase segregation of the soft phase for the longer hard segments. However, the two phases present are not pure until the hard segment length increases to six units.

Polydisperse PTMEG polyurethanes with Mn= 2000 do not show soft segment crystallinity [24], in contrast to the polymers investigated in this study. Several reasons may be cited for this different behavior. First, phase segregation is better in monodisperse polymers, possibly due to the greater ease of domain formation from the same hard segment length. Second, the interference of longer hard segments to the soft segment ordering is greater than that of the shorter hard segments as can be seen from the decreasing crystallinity as the hard segment length increases. Third, the composition containing low hard segment content such as 1/2/1 molar ratio must contain hard segments of four units or higher, otherwise the polydisperse polyurethanes would show some soft segment crystallinity.

PTMEG polyurethanes with crystallizable soft segments were quenched in DSC and re-scanned. The results are shown in Table 3-10 and Fig. 3-15. Polymers with short hard segment show Tg's around -50°C. However, the quenched PTMEG-6BT showed a low Tg at -78°C.
Table 3-10
Thermal Properties of Quenched PTMEG Polyurethanes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg, °C</th>
<th>Crystallization</th>
<th>Tm, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMEG</td>
<td>--</td>
<td>--</td>
<td>14, 34</td>
</tr>
<tr>
<td>PTMEG-T</td>
<td>-78</td>
<td>-44</td>
<td>19</td>
</tr>
<tr>
<td>PTMEG-BT</td>
<td>-53</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PTMEG-2BT</td>
<td>-51</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PTMEG-3BT</td>
<td>-47</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PTMEG-6BT</td>
<td>-78, 1</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
Fig. 3-15. DSC scans of quenched PTMEG polyurethanes. Note that PTMEG-6BT is phase segregated even after quench.
and a high Tg at 1°C with an excess enthalpy relaxation peak. It is apparent that the short hard segments were readily miscible with the soft segments at elevated temperatures, whereas the longer hard segments were only partially miscible with the soft segments and a pure soft segment phase is present as evidenced from the Tg at -78°C.

C. Dynamic Mechanical Properties

**PBD polyurethanes.** The results of the dynamic mechanical properties studies of the PBD polyurethanes are summarized in Table 3-11. The Tg's of the PBD phase are clearly observed in Figs. 3-16 and 3-17 from loss tangent and Log E'', respectively. The values from loss tangent (-36±1°C) are higher than that from Log E'' (-42±3°C), but both are within a small range. The hard segment glass transitions were observed in Log E''. Here broad transitions were observed for PBD-5BT and PBD-6BT, with peak temperature at about 70°C while a narrow transition was observed in PBD-3BT with peak temperature at 39°C. PBD-5BT shows a broad peak in loss tangent which is due to the partial cross-linking during sample preparation. PBD-3BT also shows a less well defined loss tangent peak around 50°C due to a slight crosslinking. Log E' (Pa) are around 11 in the glassy state. The moduli decrease 2 to 3 orders of magnitude above glass transition region and a plateau region extends for another 70 to 100 degrees.
### Table 3-11

Dynamic Mechanical Properties of PBD Polyurethanes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Low Tg (°C)</th>
<th>High Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Log $E''$</td>
<td>Tan $\delta$</td>
</tr>
<tr>
<td>PBD-3BT</td>
<td>-45</td>
<td>-37</td>
</tr>
<tr>
<td>PBD-4BT</td>
<td>-39</td>
<td>-35</td>
</tr>
<tr>
<td>PBD-5BT</td>
<td>-41</td>
<td>-35</td>
</tr>
<tr>
<td>PBD-6BT</td>
<td>-44</td>
<td>-37</td>
</tr>
</tbody>
</table>
Fig. 3-16. Storage modulus and loss tangent of PBD polyurethanes (PBD-\(x\)BT) as a function of hard segment length. Note that PBD-5BT and PBD-3BT are crosslinked.
Fig. 3-17. Loss modulus of PBD polyurethanes as a function of hard segment length. The curves are displaced vertically for clarity except PBD-XBT.
The range of the plateau for PBD-6BT is about 30 degrees greater than that in PBD-3BT.

The phase segregation is apparent. The relatively strong loss tangent peak of the soft segment is believed to be from the higher soft segment content due to soft segment chain extension in the endcapping process. The three samples shown in Figs. 3-16 and 3-17 are different in nature: PBD-6BT is linear; PBD-3BT is slightly crosslinked; and PBD-5BT is moderately crosslinked. The crosslinked PBD-5BT showed thermal stability even at 150°C, whereas the linear PBD-6BT lost its integrity at about 90°C. The slightly crosslinked PBD-3BT showed poorer thermal stability than PBD-6BT, possibly due to the lower hard segment Tg. It should be noted that the transition temperatures obtained from this study are about 20 degrees higher than that obtained from DSC, possibly due to the inherent characteristics of the instrument, DMTA.

**PCL polyurethanes.** Table 3-12 lists the dynamic mechanical properties of PCL polyurethanes. Fig. 3-18 shows the change of storage modulus and loss tangent as a function of temperature for polycaprolactone based polyurethanes. The modulus of PCL-2BT was constant up to -15°C and decreased by one order of magnitude within a range of 50 degrees, followed by a modulus change of 2.5 orders of magnitude at 40°C, the melting point of the soft segment. This behavior is similar to that reported for PCL/MDI/BDL (molar ratio 1/3/2)
### Table 3-12

Dynamic Mechanical Properties of PCL Polyurethanes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (°C)</th>
<th>Tan δ</th>
<th>Log E&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL-2BT</td>
<td></td>
<td>18 (broad)</td>
<td>-35, -6</td>
</tr>
<tr>
<td>PCL-3BT</td>
<td></td>
<td>24 (broad)</td>
<td>-75, -2</td>
</tr>
<tr>
<td>PCL-4BT</td>
<td></td>
<td>30 (broad)</td>
<td>-70, 5</td>
</tr>
<tr>
<td>PCL-5BT</td>
<td></td>
<td>5, 30</td>
<td>-60, -3</td>
</tr>
<tr>
<td>PCL-6BT</td>
<td></td>
<td>7</td>
<td>-60, -10</td>
</tr>
</tbody>
</table>
Fig. 3-18. Storage modulus and loss tangent of PCL polyurethanes (PCL-xBT) as a function of hard segment length. Samples were tested two weeks after compression molding.
polyurethanes, where the E' curve showed a sharp drop in modulus at approximately 40°C [8]. It is apparent that the partially crystalline polycaprolactone soft segments in this system reinforce the polymer above the soft segment Tg. The broad peak from loss tangent has a peak temperature of 18°C. The modulus change of PCL-3BT is similar to that of PCL-2BT. The Tg from loss tangent appears at 24°C. In PCL-4BT, there is a greater modulus decrease within the same glass transition region as that in PCL-3BT. This can be explained as arising from the lower crystallinity in PCL-4BT. The loss tangent peak appears at 30°C. The decrease of modulus in PCL-5BT is even greater than that containing shorter hard segments in the temperature range of -10°C to 35°C. PCL-5BT shows two loss tangent peaks: one at 5°C and the other at 33°C. The modulus of PCL-6BT decreases about 2 orders of magnitude between -20°C and 30°C. The subsequent decrease of modulus is moderate until 55°C, followed by a slightly faster decrease of modulus. The loss tangent peak appears at 7°C.

It was found that the difference between the temperatures of the loss tangent and E'' peaks are not consistent from sample to sample. The difference is about 25 degrees for shorter hard segments and about 15 degrees for longer hard segments. The Log E'' of PCL-2BT in Fig. 3-19 shows a small peak at -35°C and a large, broad peak at -6°C. In PCL-3BT, two peaks were observed in Log E'': a small peak at -75°C and a broad peak at -2°C. Log E'' of PCL-4BT shows a small peak at
Fig. 3-19. Loss modulus of PCL polyurethanes (PCL-xBT) as a function of hard segment length. The curves are displaced vertically for clarity except PCL-6BT.
-70°C and a larger peak at 5°C. Similar behavior is also found in PCL-5BT and PCL-6BT.

The results from these dynamic mechanical measurements are generally in agreement with DSC studies. The glass transition temperatures occurred below the melting temperature and increased with hard segment length up to six hard segment units where soft segments are no longer crystallizable. The behavior of PCL-5BT is different from that obtained in DSC studies where only one Tg at higher temperatures was found in addition to the melting peak. The polymer showed behavior intermediate between that of PCL-4BT and PCL-6BT. This is understandable since the samples for dynamic mechanical measurements were annealed at room temperature for two weeks, whereas the samples for DSC were stored for eight weeks before testing. Apparently the soft segment crystallinity was not fully developed after two weeks at room temperature.

The properties of quenched samples are listed in Table 3-13. The values from Log E" are closer to that observed in DSC, and the same trend was found: Tg increased with increasing hard segment length. A comparison of the quenched and room temperature annealed PCL-4BT samples was made in Fig. 3-20. The lack of an abrupt change of modulus from 35°C to 45°C in the quenched samples indicates the disappearance of soft segment crystallinity, accompanied by the large increase of the loss tangent peak which occurred at lower temperature. The dependence of Log E', Log E", and loss tangent of
Table 3-13

Dynamic Mechanical Properties of Quenched PCL Polyurethanes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (°C)</th>
<th>Tan δ</th>
<th>Log E''</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL-3BT</td>
<td>-8</td>
<td></td>
<td>-21</td>
</tr>
<tr>
<td>PCL-4BT</td>
<td>2</td>
<td></td>
<td>-14</td>
</tr>
<tr>
<td>PCL-5BT</td>
<td>5</td>
<td></td>
<td>-13</td>
</tr>
</tbody>
</table>
Fig. 3-20. Comparison of dynamic mechanical properties of PCL-4BT polyurethane before (broken line) and after (solid line) quench.
quenched PCL-3BT and PCL-5BT on temperature are similar to PCL-4BT.

Seefried et al. [18] have studied the dynamic mechanical properties of several compositions of PCL polyurethanes containing 2,4- and 2,6- TDI (80/20) and 1,4-butanediol. The soft segment molecular weight was 2100, a value close to this study. It was found that the glass transitions increased with increasing hard segment content, indicating extensive soft segment-hard segment mixing. The Tg's are about 5 to 10 degrees higher than that calculated from the Fox equation assuming complete phase mixing with Tg = -60°C for polycaprolactone soft segment and Tg = 120°C for 2,4-TDI/BDL hard segment. The higher results of the Tg's compared to this study could be due to either the inherent characteristics of the instrument, a torsional pendulum, or to incomplete phase mixing. The effects of these two factors can not be determined unless relevant information from other techniques such as DSC is given. It is usually difficult to detect the hard segment Tg from dynamic mechanical measurements due to the softening of the thermoplastic elastomer above its glass transition temperature. Nevertheless, phase segregation must exist due to the relatively high tensile strength (2000 psi for 1/4/3 composition) which could not be expected for an amorphous polymer with a single Tg at -10°C as reported. It is apparent that the soft segments are not crystalline since there was no large modulus drop at 40°C. The high tensile strength of the polydisperse system can be attributed to the presence of long hard segments which has high Tg's
and good phase segregation from the soft segment phase. Another possibility is that samples for dynamic mechanical and mechanical properties were subjected to different annealing conditions, similar to the situation in this study. All of this indicates that the segmented polyurethanes containing monodisperse hard segments are useful in interpreting the data from a polydisperse system.

PTMEG polyurethanes. Table 3-14 summarizes the dynamic mechanical properties of PTMEG polyurethanes. Fig. 3-21 shows Log E' and loss tangent of these materials. The moduli at temperatures below the glass transition are between 11 and 11.5 MPa. The moduli of PTMEG-3BT and PTMEG-4BT begin to decrease at -40°C. However, the modulus of PTMEG-4BT is 0.5 to 1 order of magnitude higher than that in PTMEG-3BT at the same temperature. The Log E' of PTMEG-5BT is the highest in these series in all temperature regions: about one order of magnitude higher than that in PTMEG-4BT in the glass transition region. There is a small decrease of modulus from -60°C to 0°C, followed by a sharper decrease from 0°C to 40°C. PTMEG-6BT clearly shows two transitions, but the second transition is not as sharp as that in PTMEG-5BT. All four of these polyurethanes exhibited a rather broad rubbery plateau. For each polymer there is a well-defined but broad loss tangent peak and the peak values increase as the hard segment length increases. The shape of the loss tangent in PTMEG-6BT is broader than the others, which indicates a different behavior. The
Table 3-14
Dynamic Mechanical Properties of PTMEG Polyurethanes

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tg (°C)</th>
<th>Tan δ</th>
<th>Log E&quot;</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTMEG-3BT</td>
<td>-6</td>
<td>-35, -25 (shoulder)</td>
<td></td>
</tr>
<tr>
<td>PTMEG-4BT</td>
<td>4</td>
<td>-20, -10 (shoulder)</td>
<td></td>
</tr>
<tr>
<td>PTMEG-5BT</td>
<td>17</td>
<td>-55, -5 (shoulder)</td>
<td></td>
</tr>
<tr>
<td>PTMEG-6BT</td>
<td>21</td>
<td>-58 0 (shoulder)</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 3-21. Storage modulus and loss tangent of PTMEG polyurethanes (PTMEG-\(x\)BT) as a function of hard segment length. Samples were tested two weeks after compression molding.
Fig. 3-22. Loss modulus of PTMEG polyurethanes (PTMEG-xBT) as a function of hard segment length. The curves are displaced vertically for clarity except PTMEG-6BT.
Tg's from Log $E''$ are not well defined as shown in Fig. 3-22 and there seems to be a peak and a shoulder for each polymer. The peak can be interpreted as due to relaxation arising from the soft segment rich region while the shoulder is from the hard segment rich phase, similar to the behavior observed in DSC. It has to be mentioned again that the samples were examined only about two weeks after compression molding, as compared to about two months of room temperature annealing for the DSC samples. Therefore the results obtained from these DMTA measurements are nonequilibrium results. The Tg's increase with the hard segment length as evidenced by the Tg of $-6^\circ$C for PTMEG-3BT and the Tg of $21^\circ$C for PTMEG-6BT from loss tangent data.

D. Mechanical Properties

PBD polyurethanes. Table 3-15 summarizes the stress-strain properties of the three types of polyurethanes. Fig. 3-23 shows the stress-strain curves for PBD based polyurethanes. Since the molecular weights are so low for the PBD based polyurethanes that what we have obtained is essentially an ABA block copolymer where A is the hard segment and B is the (extended) soft segment rather than an (AB)n block copolymer which is the case for the PCL and PTMEG based polyurethanes. Tensile strengths are high for crosslinked PBD-5BT and low for the others as expected from the long soft segment and the low molecular weights. The elongation at break is also lower than the PBD
Table 3-15

Stress-Strain Properties of Polyurethanes

<table>
<thead>
<tr>
<th></th>
<th>Tensile Strength (MPa)</th>
<th>Elongation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBD-3BT</td>
<td>2.3</td>
<td>560</td>
</tr>
<tr>
<td>PBD-4BT</td>
<td>1.1</td>
<td>240</td>
</tr>
<tr>
<td>PBD-5BT</td>
<td>6.4</td>
<td>200</td>
</tr>
<tr>
<td>PBD-6BT</td>
<td>1.8</td>
<td>200</td>
</tr>
<tr>
<td>PCL-2BT</td>
<td>4.0</td>
<td>880</td>
</tr>
<tr>
<td>PCL-3BT</td>
<td>5.6</td>
<td>1330</td>
</tr>
<tr>
<td>PCL-4BT</td>
<td>6.1</td>
<td>1320</td>
</tr>
<tr>
<td>PCL-5BT</td>
<td>7.5</td>
<td>1600</td>
</tr>
<tr>
<td>PCL-6BT</td>
<td>16.0</td>
<td>800</td>
</tr>
<tr>
<td>PTMEG-3BT</td>
<td>0.5</td>
<td>1760</td>
</tr>
<tr>
<td>PTMEG-4BT</td>
<td>0.5</td>
<td>2100</td>
</tr>
<tr>
<td>PTMEG-5BT</td>
<td>4.0</td>
<td>1600</td>
</tr>
<tr>
<td>PTMEG-6BT</td>
<td>7.7</td>
<td>1140</td>
</tr>
</tbody>
</table>
Fig. 3-23. Stress-strain response of PBD polyurethanes (PBD-xBT) as a function of hard segment length. Note that PTMEG-5BT and PTMEG-3BT are crosslinked.
based polyurethanes with polydisperse hard segments. The hysteresis test of PBD-4BT, shown in Fig. 3-24, indicates a high recovery after strain.

**PCL polyurethanes.** All PCL polyurethanes except PCL-6BT showed plastic deformation and yielding behavior as shown in Fig. 3-25. This can be explained as arising from the crystallized soft segment. These polymers show little change in stress with strain until about 800% elongation where the stress begins to increase. This could be due the strain-induced crystallization of the soft segment as is indicated from an increased opacity of the samples at higher strains. Both the tensile strength and the elongation increase with the hard segment length, contrary to most cases. PCL-6BT behaves very differently from the others. No necking occurred and stress increases rapidly with strain until 80% elongation, followed by a moderate increase in stress to 8 MPa at 400% elongation. The material, up to this point, behaves like a typical rubber. The tensile stress increased to 16 MPa at 800% elongation where the sample breaks. The hysteresis of two different PCL polyurethanes are shown in Fig. 3-26. Here necking occurred at the first strain of PCL-5BT, followed by a very low recovery accompanied with a large absorption of energy. Necking did not occur on the second strain, but the recovery remained low with large loss of energy. No necking was observed in PCL-6BT. The recovery is higher than that of PCL-5BT, which occurs because of the good phase segregation between hard and soft segments in this polymer
Fig. 3-24. Hysteresis study of PBD-4BT polyurethane.
Fig. 3-25. Stress-strain response of PCL polyurethanes (PCL-xBT) as a function of hard segment length.
Fig. 3-25. Hysteresis studies of PCL-5BT (top) and PCL-6BT (bottom) polyurethanes.
compared to other PCL polyurethanes, where phase segregation occurs because of the crystallization of the soft segment. Both PCL-5BT and PCL-6BT broke at lower elongation in the cyclic test.

PTMEG polyurethanes. Fig. 3-27 shows the relatively low tensile strength and high elongation of PTMEG-3BT and PTMEG-4BT. This can be explained as due to relatively poor phase segregation and low Tg's as observed in DSC. PTMEG-5BT shows better tensile strength and toughness with comparable elongation at break, which could be due to better phase segregation, the higher hard segment Tg, and the higher hard segment content. The mechanical properties of PTMEG-6BT are much better than the others because of the near complete phase segregation. Hysteresis tests of PTMEG-5BT and PTMEG-6BT are shown in Fig. 3-28. The recovery and energy loss are between that of PBD based and PCL based polyurethanes.
Fig. 3-27. Stress-strain response of PTMEG polyurethanes (PTMEG-xBT) as a function of hard segment length.
Fig. 3-28. Hysteresis study of PTMEG-5BT (top) and PTMEG-6BT (bottom) polyurethanes.
CONCLUSIONS

Segmented polyurethanes based on monodisperse hard segments containing 2,4-toluene diisocyanate and 1,4-butanediol were prepared. The hard segments were compatible when PBD polyurethanes containing two and six hard segment units were mixed. However, the broad glass transition observed in DSC suggests that a microphase segregation may occur. The previously reported bimodal distribution of hard segments should, therefore, arise from hard segments longer than six units.

The effect of the hard segment length as well as the type of soft segment in phase segregation has been demonstrated by DSC. The nearly complete phase segregation has been found for polybutadiene polyurethanes due to the nonpolar nature of polybutadiene soft segments. The increased polarity of polytetramethylene oxide soft segments and the ability of the ether oxygen to accept a hydrogen improve the soft segment-hard segment phase mixing. The phases are compatible when the hard segments are two units or lower in length. When the hard segment increases to three units the phases begin to separate into soft segment rich and hard segment rich regions. This behavior becomes more pronounced as the hard segment length increases. Almost complete phase segregation behavior was observed when the hard segments are six units in length. The polar nature of polycaprolactone soft segments and the better interphase hydrogen
bonding enables the soft segment to mix with those hard segments extensively. The soft segments are crystallizable when the hard segment are five units or less. However, the amorphous portion is nearly completely mixed with the hard segments until they are six units in length where the hard segment phase is strongly separated from the soft segment phase.

Dynamic mechanical measurements are in agreement with the results from DSC. The loss tangent peak of the polybutadiene phase is almost constant in all compositions, indicating the relatively pure soft phase in polybutadiene based polyurethanes. Hard segment Tg's are usually not detectable unless the polymer is crosslinked. Hard segment Tg's were observed in two of the crosslinked polymers which were formed unintentionally during sample preparation. The effect of phase mixing in PTMEG based polyurethanes is clearly shown in mechanical properties which are consistent with the findings in thermal and dynamic mechanical studies. The tensile strengths of polybutadiene based polyurethanes are far below the expected values due to the soft segment chain extension during the macroglycol endcapping process. However, they are better than PTMEG polyurethanes containing hard segments of no more than four units in length because of the nearly complete phase segregation in PBD polyurethanes.

The tensile strength of PTMEG based polyurethanes depend on the degree of phase segregation as well as the hard segment length. The tensile strength is low when hard segment units are four or below, due
to the low Tg's. It increases when the phase segregation is improved and the Tg of the hard segment rich fraction is close to room temperature. Phase segregation becomes more complete when the hard segment is six units long and much better mechanical properties were observed as expected.

Polycaprolactone based polyurethanes have the best tensile strength and toughness, which is attributed to the soft segment crystallinity and the possible strain-induced crystallization of the soft segments. The amorphous portions of the soft segments are mixed with hard segments with Tg's lower than the melting temperatures of the soft segments. This is evident from the modulus decrease at 40°C in the dynamic mechanical measurements. The phase mixing behavior changes drastically when the hard segment is six units long and the soft segment is not crystallizable and two amorphous phases are present. Mechanical properties were greatly improved due to the phase segregation.
References

1. B. Fu, C. Feger, W.J. MacKnight, and N.S. Schneider, Polymer, in press.


Although the synthesis and properties of segmented polyurethanes containing monodisperse 2,4-TDI/BDL hard segments have been described, it is obvious that the studies are only at the preliminary stage. The synthetic method developed for hard segment oligomers has made it possible to prepare segmented polyurethanes containing 2,4-TDI/BDL hard segments with various types of soft segments in several molecular weight ranges as long as the macroglycols are endcapped and free of excess 2,4-TDI. The future work can be stressed on two aspects, namely, the synthesis and the properties.

Since the polybutadiene based polyurethanes are less satisfactory as compared to the polyurethanes based on other soft segments, it is desirable to prepare more acceptable polyurethanes containing PBD soft segments and 2,4-TDI/BDL monodisperse hard segments. The very limited supply of hydroxy-terminated polybutadiene with hydroxyl functionality of two has called for the need of self-sufficient preparation for this material. Hard segment oligomers containing higher units can also be made by the technique described in chapter II except using different solvents for fractional precipitation. As a matter of fact, hard segment oligomers, up to ten units, have been prepared. The purity, however, was suspect due to the poor resolution of HPLC and the less efficient solvent system for fractional precipitation. Dimethyl
formamide was used to dissolve crude oligomers and water added to precipitate the fractions of oligomers. This solvent/non-solvent system did not separate oligomers as easily as the methanol/water system did in lower hard segment oligomers. Therefore, the conditions for both the fractional precipitation and HPLC should be optimized for hard segment oligomers containing more than six units.

In contrast to the investigation of the property dependence on the hard segment length, it is interesting to study the property dependence of soft segment molecular weight with certain hard segment length. The crystallinity and degree of phase mixing usually depend largely on the soft segment length.

The controversial issue whether the narrow or broad distribution of hard segments gives better mechanical properties can be justified by comparing polymers of the same molar content but with different polydispersities. However, the investigation should cover different types of soft segments as well as different lengths of hard segments before a conclusion is made.

Hard segment sequence distribution in polybutadiene based polyurethanes can be studied by using soft segment degradation technique, namely, ozonolysis. The hard segments can be separated from degraded samples by chemical means such as extraction or chromatography. The sequence distribution can be obtained from GPC or HPLC by using the standards: the degraded polyurethanes which contain monodisperse hard segments.
It is important to know the thermal stability of hydroxy-terminated hard segments since the hard segment distribution could become polydisperse after heat treatment as in the case of MDI/BDL monodisperse hard segment oligomers. This can be done by placing samples in the oven for a certain period of time at various temperature ranges. The samples should be run under two conditions: one in the air and the other under nitrogen flush. The reason for this is to optimize the conditions for sample preparation by compression molding. The heat treated samples can be analyzed by HPLC using silica gel column and THF solvent, with UV or RI detector.

The influence of hydrogen bonding to phase mixing can be studied through a well designed system which contains amorphous polyether soft segments and monodisperse hard segments. One of the best candidates of soft segment is polypropylene oxide (PPO) with Mn=1000, 2000, and 3000. PPO is not only amorphous but also available with a narrow molecular weight distribution. The degree of phase mixing can therefore be calculated more accurately from DSC data by using the Fox equation, where the weight fraction is used for calculation. The degree of interphase hydrogen bonding is obtained from infrared results by the difference of the hydrogen bonded NH absorption and that of the CO absorption.

The effect of hard segment length on the phase boundary can be studied by using small angle X-ray scattering (SAXS). Other studies include dielectric measurement, transport phenomena, morphology as
well as the correlation of the hard segment domain size and shape to the mechanical properties.