

# Structure–Property Study of Polyurethane Anionomers Based on Various Polyols and Diisocyanates

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**ABSTRACT:** Polyurethane (PU) anionomers were prepared as aqueous dispersions using dimethylol propionic acid (DMPA) as the stabilizing moiety. The principal diols used were polytetrahydrofuran of molecular weight 1000 (PTHF1000) and cyclohexane dimethanol (CHDM). The diisocyanates used in this study were isophorone diisocyanate (IPDI), hydrogenated methylene bisphenylene diisocyanate (H<sub>12</sub>MDI), tetramethylene xylene diisocyanate (TMXDI), hexamethylene diisocyanate (HDI), and a 50 : 50 blend of IPDI and HDI. All these samples were neutralized using triethylamine (TEA) and chain-extended using hydrazine monohydrate. The dispersions were prepared at a NCO/OH ratio of 2 so that a comparison of their structure–property relationships could be made with respect to their mechanical and viscoelastic properties and solvent resistance. Also, two further samples were prepared of similar composition to the IPDI-based sample, but using poly(propylene glycol), PPG1000, and PTHF2000 polyols. The effects on the structure and properties of the PPG1000 and the higher molecular weight PTHF sample were compared with the PTHF1000 sample. Dynamic mechanical thermal analysis, tensile testing, solvent spot, and swelling studies were employed for the characterization of these materials. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 2035–2044, 1997

**Key words:** ionomer; polyurethane; structure–property relations

## INTRODUCTION

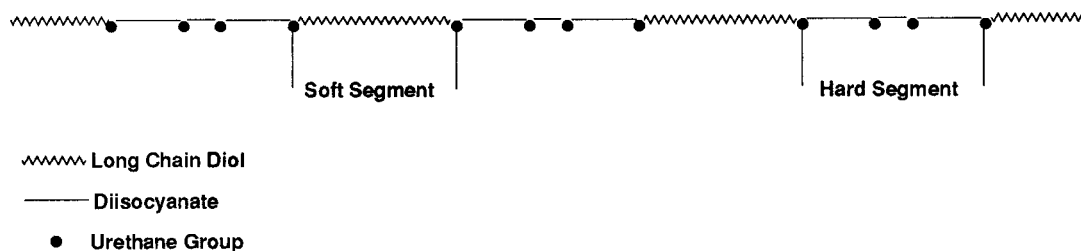
Environmental and legislative pressures have led to the partial replacement of solvent-borne polyurethanes (PUs), due to increasing concern over pollution and safety risks. This has resulted in the development of water-borne PU alternatives. These are finding increasing commercial usage.<sup>1–6</sup> They exist as a form of polymer dispersion stabilized by incorporating repeat units carrying pendant acid or tertiary nitrogen groups<sup>7–9</sup> into the

PU backbone. By completely or partially neutralizing or quaternizing these to form salts,<sup>10</sup> a stable dispersion is obtained. These have become known as PU ionomers and the ionic groups in the PU backbone exert considerable influence on the physical properties of the PU.<sup>11</sup>

PU are formed by a step-growth reaction<sup>12</sup> among a diisocyanate, a polyol, and the stabilizing group. There are a number of approaches for the preparation of these PU dispersions<sup>1,3</sup> including the acetone process, the melt-dispersion process, the prepolymer mixing process, and the ketimine process. A common feature of all these is that the first step is a conventional PU synthesis to obtain a low molecular weight prepolymer. The prepoly-

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**Figure 1** Representation of the ideal primary structure of a segmented PU.

mer is then chain-extended either before or more usually after dispersion in water. There are a number of diisocyanates that have been employed in the preparation of such PUs. Early structure–property studies were conducted on toluene diisocyanate (TDI)-based PU.<sup>13</sup> However, more recent studies have included PUs prepared using isophorone diisocyanate (IPDI),<sup>14–16</sup> hexamethylene diisocyanate (HDI),<sup>17</sup> and hydrogenated methylene bisphenylene diisocyanate (H<sub>12</sub>MDI).<sup>18</sup> Polyetherols and polyesterols<sup>19,20</sup> are commonly used as the soft polyol phase, although polyetherols are generally preferred due to their better hydrolytic stability and greater flexibility.

Microphase separation between incompatible soft polyol and hard urethane sequences can contribute to the unique properties of PU ionomers.<sup>21</sup> The potential driving force for the microdomain formation is a combination of hydrogen bonding between urethane and urea groups and the carboxylic acid group from the stabilizing group, the electrostatic interactions (Coulombic forces) between the ionic groups, as well as possible crystallization of both the hard and soft phases.<sup>22</sup> Factors affecting this microphase separation include the symmetry and type of diisocyanate, the molecular weight and type of polyol, and the ionic and urea group contents. Figure 1 shows a schematic representation of an ideal segmented PU. On the other hand, partial phase mixing can occur as a consequence of hydrogen-bond interactions between soft and hard domains. The degree of phase mixing can have a significant effect on the PU properties.

This article describes the synthesis and structure–property relationships of PU ionomers based on diisocyanates of differing structure prepared using the prepolymer mixing process.<sup>23</sup> These diisocyanates were IPDI, HDI, H<sub>12</sub>MDI, and tetramethylene xylene diisocyanate (TMXDI).<sup>24</sup> In the last case, few studies on this newer diisocyanate have been conducted. In addition to these, an IPDI/HDI blend was also investigated. The effect of polyol mo-

lecular weight and structure was also investigated for IPDI-based PU using PPG1000 and PTHF1000 and 2000 as the soft segment. With dimethylol propionic acid (DMPA) as the potential ionic center, the effect of the polyol and diisocyanate structure upon the viscoelastic and mechanical properties of these PUs of similar compositions were investigated and compared.

## EXPERIMENTAL

### Materials

Polytetrahydrofuran (PTHF) ( $M_n = 1000, 2000$  Aldrich) was dried at 0.1 mmHg and 80°C for 3 h before use. Poly(propylene glycol) (PPG) ( $M_n = 1000$  Aldrich) was used as received. DMPA (Aldrich), triethylamine (TEA, Aldrich), *N*-methyl-2-pyrrolidone (NMP, Aldrich), and cyclohexane dimethanol (CHDM, Aldrich) were used without further purification. The IPDI, HDI, and TMXDI (all Aldrich) had purities of 98%. The H<sub>12</sub>MDI (Aldrich) used in this study was a 90% mixture of isomers. Dibutyl tin dilaurate (DBTDL, Aldrich), used to catalyze the reaction, and the chain extender, hydrazine monohydrate (Aldrich), were used as received.

### Procedure

The specifications for the samples prepared in this study are presented in Table I. The prepolymer reaction apparatus consisted of a 250-mL flange flask and lid fitted with a nitrogen bubbler and inlet, a thermometer, and a stirrer paddle. The reaction temperature was controlled using a constant temperature oil bath. The CHDM, PTHF, and DMPA as a solution in NMP were weighed out into a clean, dry flask. The contents were then heated to 50°C with stirring to homogenize. At 50°C, the IPDI and the first portion of the catalyst, DBTDL, were added. The reaction temperature

**Table I Specifications of the Polyurethane Dispersions**

Polymer Code	Diisocyanate	Polyol <sup>a</sup>	DMPA (wt %)	CHDM (wt %)
Urethane dispersions <sup>b</sup>				
UR1	IPDI	PTHF1000	4.91	3.2
UR2	TMXDI	PTHF1000	4.92	2.8
UR 3	H <sub>12</sub> MDI	PTHF1000	4.93	2.5
UR 4	HDI	PTHF1000	4.92	4.2
UR 5	50IPDI : 50HDI	PTHF1000	4.91	3.7
UR 6	IPDI	PTHF2000	4.91	5.6
UR 7	IPDI	PPG1000	4.91	3.2

<sup>a</sup> Diol molecular weights: PTHF = 1000, 2000; PPG = 1000.

<sup>b</sup> All urethane prepolymers were prepared at a 2 : 1 NCO/OH ratio. All the prepolymers contained 10% by weight of NMP as the cosolvent. The final dispersion had a polymer solids content of 35% (w/w). All the samples were chain-extended to 98% mol NCO with hydrazine monohydrate.

was increased to 95°C, where it was maintained for 1 h. A further portion of the catalyst was then added and the reaction continued at 95°C for a further hour. The temperature was then lowered to 70°C and the experimental isocyanate number was determined using the standard dibutylamine back-titration method.<sup>25</sup> On achieving the theoretical NCO value, preneutralization of the carboxylic acid groups was carried out by the addition of the TEA. The temperature was maintained at 70°C for 30 min, at which point a prepolymer had now been prepared. Dispersion was carried out by slowly, adding the prepolymer via a funnel to a three-necked round-bottomed flask containing the water and the chain extender, hydrazine monohydrate. The flask was fitted with a stirrer and a condenser. Dispersion was carried out over a 40 min interval to ensure that the dispersion temperature did not exceed 40°C. The dispersion was then allowed to stir for a further 30 min. All the dispersions were prepared at 35 wt % solids.

Films from the samples were prepared by pouring the dispersion into a aluminum mold coated with a release agent. The films were allowed to dry at room temperature for 2 days. The residual water was removed by placing the films overnight into a vacuum oven at 25°C. These films were then used for DMTA, DSC, swelling, tensile testing, and wide-angle X-ray diffraction.

## Characterization

### Photon Correlation Spectroscopy

Particle sizes were determined for the dispersions by light scattering using a Malvern Autosizer model (Iic).

### Tensile Testing

Tensile properties were measured at room temperature using a Lloyds tensometer following the ASTM D-412 specifications. A crosshead speed of 50 mm/min was used throughout these investigations.

### Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) thermograms over the temperature range -100 to 150°C were obtained using a DuPont 910 apparatus at a heating rate of 20°C/min under nitrogen purging.

### Dynamic Mechanical Thermal Analysis

DMTA was undertaken over the temperature range -100 to 150°C using a Polymer Laboratories DMTA (Mark II) at a frequency of 10 Hz, a strain amplitude setting of  $\times 4$ , and a heating rate of 4°C/min. A single cantilever clamping system was used.

### Wide-Angle X-ray Spectroscopy

Wide-angle X-ray diffraction (WAXD) measurements were obtained using a Shimadzu Model XD-5 diffractometer operated at 30 kV and 20 mA over an angular range of 5° to 40° (2 $\theta$ ) at a scan rate of 4°/min. The smoothing time constant was 4 s.

### Infrared Spectroscopy

Infrared (IR) analysis was carried out using a Unicam Mattson 3000 FTIR spectrophotometer.

**Table II Dispersion and Film Characteristics of PU Samples Prepared Using PTHF and PPG**

	UR1 <sup>a</sup>	UR7 <sup>b</sup>
Particle size (nm)	57	58
Dispersion viscosity (Pa s)	0.38	0.02
MFT (°C)	< 1	< 1
pH	8.2	8.2
Tensile strength (MPa)	50.1	4.4
Initial modulus (MPa)	22.5	0.31
Elongation at break (%)	314	258
$T_{gs}^c$ (DMTA) (°C)	-52	-14
$T_{gh}^d$ (DMTA) (°C)	78	19
Solvent spot test <sup>e</sup>	33	10

<sup>a</sup> PU based on PTHF1000.<sup>b</sup> PU based on PPG 1000.<sup>c</sup>  $T_g$  of the soft segment.<sup>d</sup>  $T_g$  of the hard segment.<sup>e</sup> Solvent spot tests scored out of a maximum of 70.

### Swelling Studies

To measure swelling in water, 2-butanone, 2-propanol (IPA), dimethylformamide (DMF), and xylene, films were immersed in each liquid for 24 h at room temperature and the percentage swelling was determined by measuring the weight increase:

$$\% \text{ Swelling} = 100(W - W_0)/W_0$$

$W_0$  is the weight of the dried film and  $W$  is the weight of the film at equilibrium swelling.

### Solvent Spot Testing

The solvent resistance of the films was determined by exposing the film to a liquid droplet (approximately 1 cm in diameter) for 1 h. The remaining solvent was then removed and the film reexamined for deterioration. A grading system of 0–10 was employed, where 0 indicates total dissolution of the film and 10 represents total solvent resistance. The test liquids used were acetone, toluene, tetrahydrofuran, methanol, dichloromethane, water, and isopropanol. A film unaffected by these test liquids would score a maximum of 70.

## RESULTS AND DISCUSSION

### Effect of Varying the Polyol Structure

Table II shows some of the dispersion characteristics and film properties of two samples, one pre-

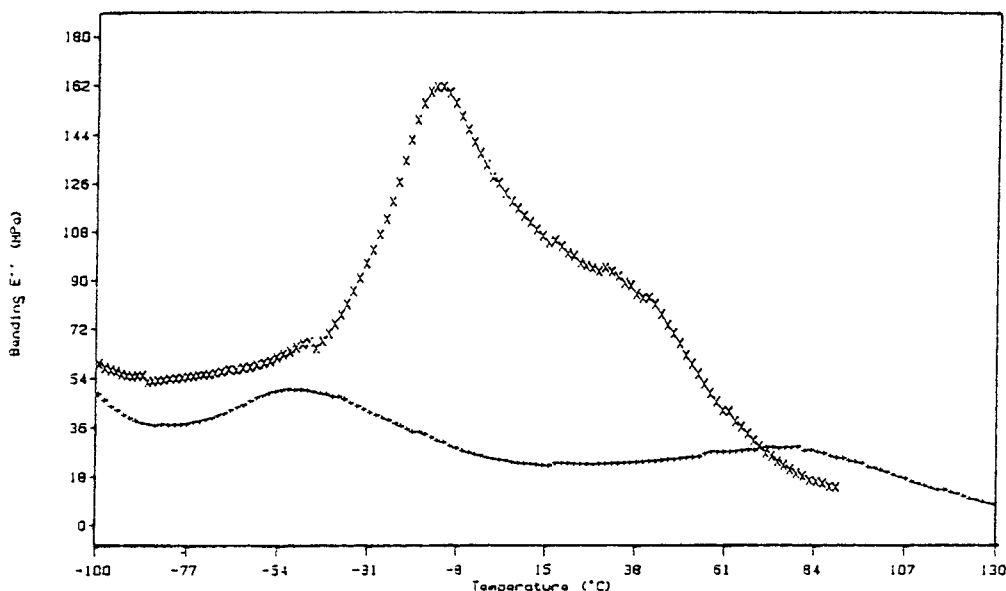
pared using PTHF (UR1) and the other incorporating PPG (UR7), both having an average molar mass of 1000. The samples were investigated by infrared spectroscopy and DMTA. The IR study employed a heated cell which allowed the investigation of band movement with increasing temperature. Of special interest was the —NH groups and the influence of temperature on their position. Table III outlines the —NH peak position at different temperatures. Shifting of the —NH band with increasing temperature was observed for both samples. This was attributed to the breakdown of hydrogen bonds between the hard segments or hard and soft segments. The movement of the —NH band to higher frequency is indicative of the formation of free unbonded —NH groups. A shoulder is seen to develop. This has been reported<sup>26</sup> as being representative of unbonded —NH groups. Increasing the temperature results in further shifting and what was once only a shoulder becomes the main —NH band. Relatively low temperatures, i.e., > 60°C, were required for the breakage of these bonds.

Figure 2 shows the DMTA traces obtained for UR1 (PTHF) and UR7 (PPG). It is clear that the change in polyol has a significant effect on the phase separation exhibited by the sample. The DMTA trace obtained for UR1 showed the soft ( $T_{gs}$ )- and hard ( $T_{gh}$ )-segment transitions reasonably clearly (see Table II). However, for UR7, only one broad peak with a high-temperature shoulder was identified. Hence, the segments in the PPG sample, UR7, are significantly more mixed than are those in UR1. It may be that the methyl side groups in PPG hinder the polymer chains aligning for hydrogen-bond formation, whereas in the case of PTHF, alignment of the polymer chains occurs more readily.

The predominantly phase-mixed structure of UR7 resulted in a lower tensile strength and initial modulus than those of UR1. UR1 possessed properties of a strong, tough material, while maintaining a high degree of elasticity, presumably a reflection of the two-phase morphology. Im-

**Table III IR Peak Positions for UR1 and UR7 at Different Temperatures**

Sample	RT	40°C	60°C	80°C
UR1				
—NH (cm <sup>-1</sup> )	3319	3321	3323	3323
UR7				
—NH (cm <sup>-1</sup> )	3321	3323	3325	3327



**Figure 2** Loss modulus versus temperature for the PTHF1000 sample [(+) UR1] and the PPG1000-based sample [(x) UR7].

provement in solvent resistance for UR1 in comparison to UR7 is most likely due to the reinforcement by the hard-segment domains.

### The Effect of Polyol Molecular Weight

Here, to maintain the same NCO/OH ratio and hard fraction content for comparison with the PTHF1000 sample, the level of CHDM and IPDI were increased and decreased accordingly. See Table I for details of the CHDM contents of these samples. So, for the PTHF2000-derived sample, it is important to note that almost twice as much CHDM is present, and this is expected to significantly influence the properties exhibited by the sample. Table IV shows some of the dispersion characteristics and film properties of the two samples: one prepared using PTHF of 1000 (UR1) and the other of 2000 (UR6) molar mass.

The particle-size results shown in Table IV indicate that the particle size decreases slightly as the molecular weight of the soft segment increases. This is consistent with results reported by other workers.<sup>14</sup> The increased flexibility of the soft segment results in decreasing particle size because the PU chains lose their rigidity and strength, not solely by their fractional increase in weight, but also from the reduced number of urethane linkages, which with the isocyanate segment form the hard domains.<sup>27</sup> Other important factors to consider are the prepolymer viscosities

(see Table IV) which are significantly different at 70°C. The higher prepolymer viscosity for UR6 will increase the resistance to droplet formation.

Comparing the DMTA data in Table IV, an increase in the degree of phase separation was apparent for UR6 due to its lower soft-segment  $T_g$  (see Fig. 3). The increase in molecular weight of the UR6 soft segment facilitates this increase in phase separation. It was thus interesting to find out whether this situation would lead to soft-segment crystallization. Examination by DSC and

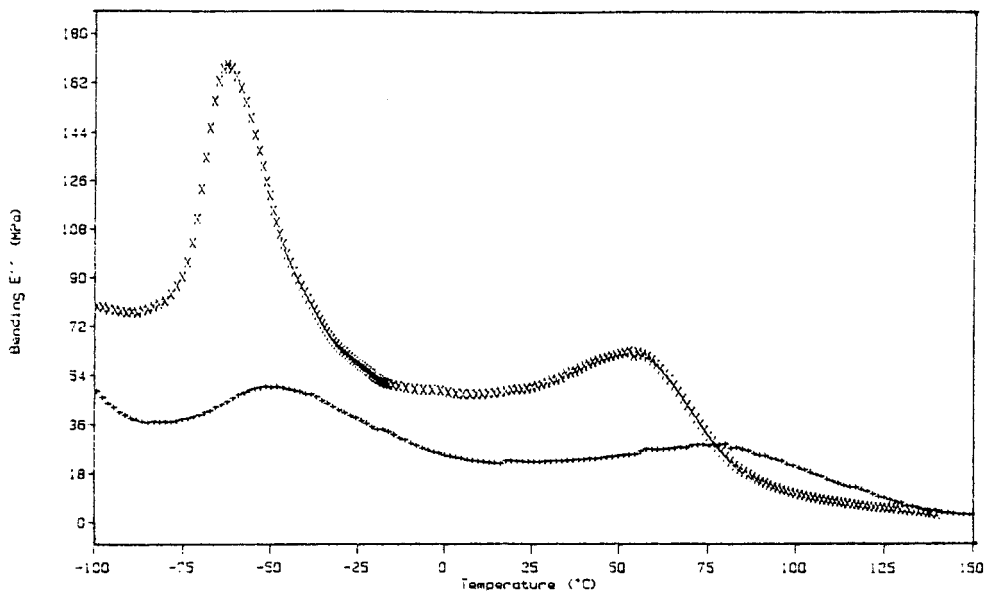
**Table IV** Dispersion and Film Properties for Materials with Polyol of Increasing Molecular Weight

	UR1 <sup>a</sup>	UR6 <sup>b</sup>
Particle size (nm)	57	51
Dispersion viscosity (Pa s)	0.38	0.43
Prepolymer viscosity at 70°C (Pa s)	3.48	6.01
MFT (°C)	< 1	< 1
pH	8.2	8.3
Tensile strength (MPa)	50.1	20.6
Initial modulus (MPa)	22.5	2.5
Elongation (%)	314	250
$T_{gs}$ (DMTA) (°C)	-52	-63
Solvent spot <sup>c</sup>	33	24

<sup>a</sup> PU based on PTHF1000.

<sup>b</sup> PU based on PTHF2000.

<sup>c</sup> Solvent spot tests scored out of a maximum of 70.



**Figure 3** Loss modulus versus temperature plots for samples (+) UR1 and (x) UR6 of similar composition but containing PTHF1000 and PTHF2000, respectively.

WAXD provided no evidence for crystallinity in either domain. This is consistent with similar studies<sup>28</sup> of PU systems employing PTHF polyols of increasing length.

The mechanical properties of these two samples complement the WAXD and DSC results. The results from tensile testing are also shown in Table IV. It is apparent that an increase in polyol molecular weight results in reduced tensile strength, modulus, and elongation at break. In the absence of domain crystallinity, as shown previously, it is the reduction in the number of urethane linkages in UR6, as a consequence of PTHF2000 incorporation, and not the increase in CHDM content that has the predominant effect upon mechanical properties. This is also complemented by the increased flexibility of the higher molecular weight polyol. This explanation may also be applied to explain the large difference in the solvent resistance of these two films shown by the solvent spot test experiments. The solvent primarily attacks the soft domains but is retarded by the hard segments. Hence, the greater the degree of phase separation, the more susceptible the film is to solvent attack. It has been shown here that UR6 has a poorer resistance to solvent than has UR1 and this is consistent with the above. Other studies that investigated the microstructure of polyurethanes were conducted by Sreenivasan.<sup>29</sup> He discovered that he could estimate the hard-segment content in PUs from solvent ab-

sorption. A modified version of this method was used for the examination of UR1 and UR6. The results from the swelling studies indicated that higher swelling was observed for UR6 in all solvents tested. This could be a result of the increased phase separation, compared to UR1, as discussed above.

#### Effect of Diisocyanate Structure

The properties obtained for a number of PUs prepared using different diisocyanates are shown in Table V and Figure 4. The HDI prepolymer was successfully prepared, but on chain extending the prepolymer, gelation resulted. HDI also appeared to be more reactive than were the other diisocyanates used in this study, achieving the calculated prepolymer %NCO value in only 1 h with half the normal amount of catalyst. This suggests that the prepolymer viscosity is high prior to chain extension with biuret and allophanate groups being present. On chain extending the prepolymer, a 3-dimensional network is believed to have been produced, resulting in a high molecular weight gel. To overcome this, a larger NCO/OH ratio may be used in order to lower the molecular weight of the prepolymer so that it may be chain-extended. Chen and Chan described the preparation<sup>30</sup> of a NCO-terminated prepolymer derived from HDI using a 6 : 1 NCO/OH ratio. In fact, few articles have been published in the open literature<sup>31</sup> on

**Table V Dispersion and Film Properties of Samples Prepared from PTHF1000 and Different Diisocyanates**

Property	UR1 IPDI	UR2 TMXDI	UR3 H <sub>12</sub> MDI	UR5 HDI/IPDI
pH	8.2	8.2	8.9	8.7
Particle size (nm)	57	36	41	62
Viscosity (Pa s)	0.38	0.05	0.44	0.11
MFT (°C)	< 1	< 1	< 1	< 1
Tensile strength (MPa)	50	6.1	10.8	23.2
Elongation (%)	314	457	187	269
T <sub>g</sub> DMTA (°C)	-52	-19.1	-41	-47
Solvent spot	33	24	30	51
% Swelling in				
2-Butanone	133	D	92	79
Isopropanol	231	51	41	77
Water	36	108	22	38
DMF	D	D	D	130
Xylene	84	132	63	64

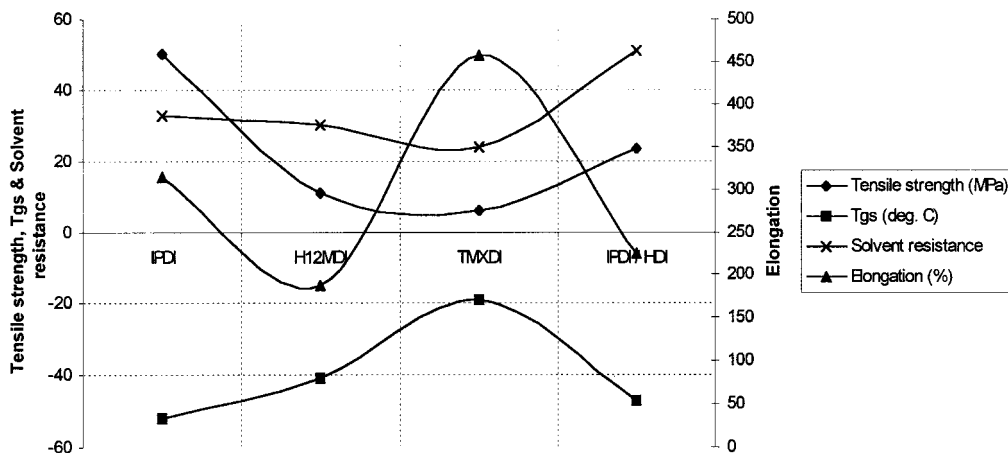
All prepolymers were prepared at a NCO/OH ratio of 2 and then 98% chain-extended.

HDI ionomers because of their readiness to form high molecular weight branched materials. Most work has been confined to cationomers,<sup>32,33</sup> commonly studied as solutions in MEK, rather than water-borne dispersions. Hence, for this study, no HDI-derived PU of similar composition to the other samples could be prepared.

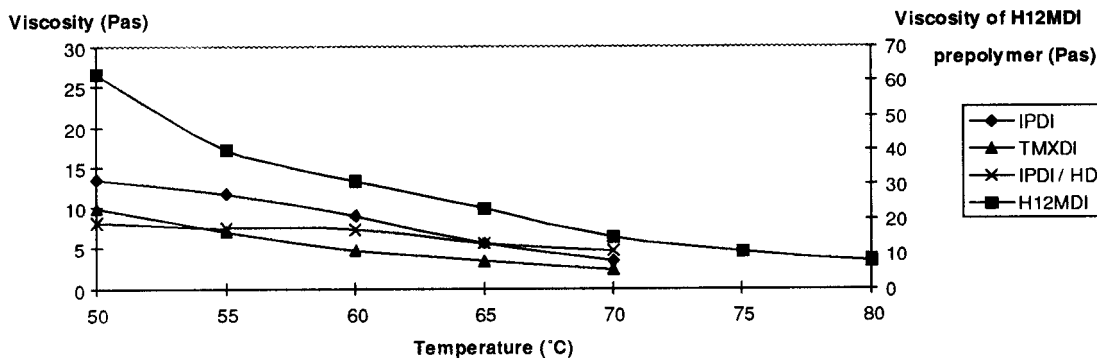
Viscosity measurements were determined for the prepolymers of IPDI, TMXDI, and H<sub>12</sub>MDI, at a constant NCO/OH ratio, at increasing temperatures. Figure 5 shows the results and highlights the significant differences in prepolymer viscosity obtained when using these different diisocyanates. The prepolymer viscosities at the 70°C dispersion temperature can be seen in Figure 6. The

low viscosity of the TMXDI-derived prepolymer makes processing much easier than in the IPDI and H<sub>12</sub>MDI prepolymers, where the viscosity is significantly higher. Hence, dispersions may be prepared at higher solids content when using TMXDI since the prepolymer viscosity remains relatively low. Another advantage of the TMXDI's lower prepolymer viscosity is the reduced need for a cosolvent. It has been reported<sup>24</sup> that TMXDI-derived PUs may be prepared without the necessity for a cosolvent. This, of course, is significant with the tightening laws on the emission of solvents.

DMTA was employed to elucidate differences in phase separation. See Figure 7, where it is clear



**Figure 4** Film properties of PUs prepared using different diisocyanates.



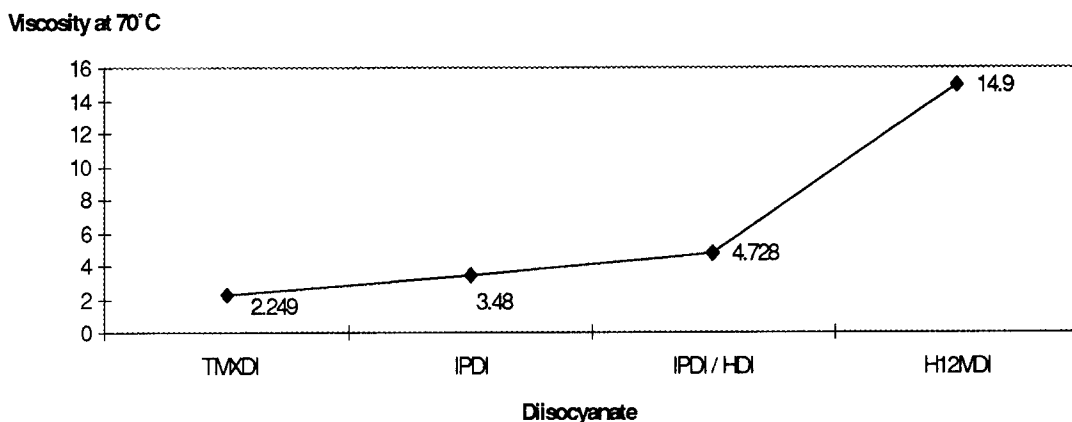
**Figure 5** Viscosity versus temperature plots for prepolymers prepared from different diisocyanates.

that these samples possess very different phase morphologies. The soft-segment  $T_g$  ( $T_{gs}$ ) for the samples are in the increasing order of IPDI < IPDI/HDI < H<sub>12</sub>MDI < TMXDI. It is apparent from these studies that on blending HDI, an aliphatic diisocyanate, with IPDI the degree of phase separation decreases and the  $T_g$  of the soft domain moves to a higher temperature. The symmetrical structure of HDI favors crystallization of the hard domains, which is common in HDI-derived PUs. However, in the case of the blend, DSC studies showed that crystallization of the hard segments is inhibited by the presence of the IPDI units, and the low molecular weight of the PTHF polyol makes complete phase separation difficult. Thus, the higher soft-segment  $T_g$  for the blend is most probably the consequence of disrupting the hard domain with the inclusion of HDI.

UR2 appears from this study to be more phase-mixed compared to the other PUs. The asymmetrical structure and the steric hindrance of the isocyanate group by the  $\alpha$ -methyl group result in

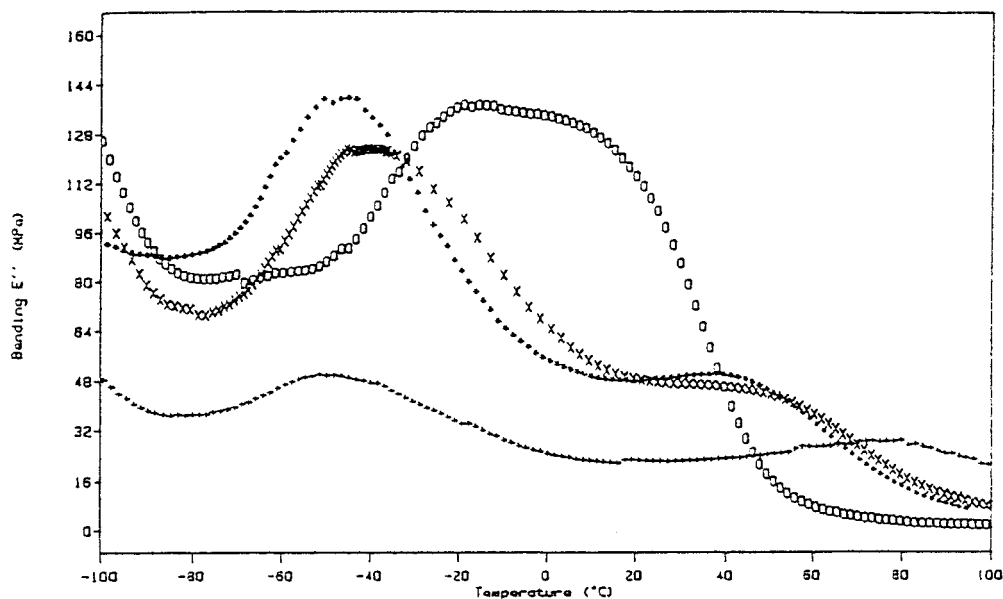
TMXDI-derived PUs possessing unique properties. Formation of allophanate, biuret, and trimer forms are not feasible. These two factors combined do not favor hard-segment alignment and the formation of crystalline domains.<sup>34</sup> The symmetrical structure of H<sub>12</sub>MDI favors phase-separated domains and hard-phase crystallization. However, the relatively low molecular weight of PTHF and the existence of isomers of H<sub>12</sub>MDI prohibit crystallization in both hard and soft domains. The morphology of H<sub>12</sub>MDI is governed by the hard/soft fraction and the number of interchain interactions. It has a higher soft-phase  $T_g$  compared to that for the IPDI-derived PU, UR1, suggesting that there are significantly more hard-soft phase interactions than in the latter, and, hence, a higher degree of phase mixing is deduced.

The mechanical properties and solvent resistance of these PUs were examined and compared. The results are outlined in Table V. A trend corresponding to the DMTA results was observed from a study of tensile strength. UR1 had the highest



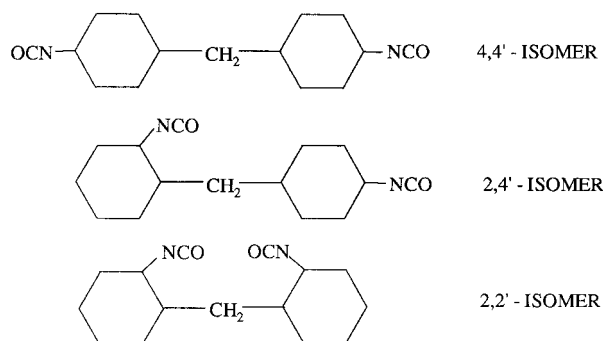
**Figure 6** Viscosity at 70°C of the prepolymers prepared from different diisocyanates.





**Figure 7** Loss modulus versus temperature plots for samples (+) UR1, (O) UR2, (X) UR3, and (\*) UR4 based on IPDI, TMXDI, H<sub>12</sub>MDI, and 50IPDI/50HDI, respectively.

ultimate tensile strength, but the IPDI/HDI blend, UR5, exhibited poorer mechanical properties. The H<sub>12</sub>MDI sample, UR3, however, having more separated domains tended to possess increased strength compared with UR2, but significantly lower elongation. H<sub>12</sub>MDI consists of a number of isomers in addition to the 4,4-isomer (cf. MDI), i.e., 2,4- and 2,6-. Although the 4,4-isomer is in the majority, these other two forms are also present, unless more pure grades are used. The three isomers are shown in Figure 8. The closer the two —NCO groups are to 180° to one another, i.e., the 4,4-isomer, the better the packing and greater the cohesion of the hard phase.<sup>35</sup> This leads to an improvement in the strength of the PUs. Hence, the presence of these two other forms of H<sub>12</sub>MDI form less well-packed



**Figure 8** The isomers of H<sub>12</sub>MDI.

hard domains than does the 4,4-isomer, which has a detrimental effect on the overall strength of the PU.

The solvent resistance of the films was determined by the solvent spot tests and a study of % swelling in a number of solvents. The results from these are shown in Table V. The swelling behavior for samples UR1 (IPDI) and UR3 (H<sub>12</sub>MDI) were similar in all the solvents. However, UR2 (TMXDI) appeared to swell to a greater extent, and in some instances, the film was dissolved completely. The inability of TMXDI to form biurets and allophanates resulting in branching and crosslinking leads to the observed swelling phenomena. There may also be a contribution from the difference in the hardness of the IPDI and H<sub>12</sub>MDI films and the TMXDI film, resulting from increased phase separation in the former two films. The UR5 blend also showed similar swelling phenomena, except with DMF, where the film did not dissolve as it had done previously for the other samples. In fact, superior solvent spot results were also observed for the blend.

## CONCLUSIONS

These results indicate that there are a great many differences in structure and properties in the studied samples. Clearly, the architecture of the

PU can be manipulated to obtain properties to suit a range of applications. It has been shown that both the structure and molecular weight of the polyol, in addition to the structure of the diisocyanate (aliphatic, cycloaliphatic, aromatic), can have a significant effect on the structure and properties of PUs of similar composition.

It appears that the IPDI systems possessed superior mechanical properties, as a consequence of their increased phase-separated structure. TMXDI-derived PUs were shown to produce prepolymers of low viscosity and PUs possessing highly elastomeric properties. It was also shown that PUs with mixed HDI/IPDI blends could be prepared using HDI and IPDI diisocyanates, although the HDI-derived PU could not be prepared at a similar composition.

## REFERENCES

1. R. Arnoldus, *Surface Coatings*, J. Wilson, Ed., Elsevier, London, 1990, p. 179.
2. J. W. Rosthauser and K. Nachtkamp, *J. Coat. Fabrics*, **16**, 39 (1986).
3. D. Dietrich, *Adv. Org. Coat. Sci. Technol. Ser.*, **1**, 55 (1979).
4. D. Lorenz and K. H. Reinmbller, *Coll. Polym. Sci.*, **259**, 367 (1981).
5. B. K. Kim, T. K. Kim, and M. Y. Lee, *J. Appl. Polym. Sci.*, **43**, 393 (1991).
6. P. L. Jansse, *Polym. Paint Colour J.*, **181**, 398, 1991.
7. P. Markusch, U.S. Pat. 4,408,008 (1983).
8. Y. Matoba, A. Hashimoto, and M. Sugahara, U.S. Pat. 4,237,247 (1980).
9. P. Markusch, K. Noll, and D. Dietelich, U.S. Pat. 4,238,378 (1980).
10. R. Longworth, *Developments in Ionic Polymers-I*, A. D. Wilson and H. J. Prosser, Eds., Applied Science, London, 1983, p. 53.
11. C. Geraldine and A. Eisenberg, *Ind. Eng. Chem. Prod. Res. Dev.*, **20**, 271 (1981).
12. R. Satguru and J. C. Padget, paper presented at the 20th Water-Bourne, Higher Solids, and Ponder Coatings Symposium, Feb. 24–26, 1993, New Orleans, LA.
13. K. C. Frisch, *Appl. Polym. Sci.*, **54**, 828 (1980).
14. Y. M. Lee, J. C. Kim and B. K. Kim, *Polymer*, **35**, 1095 (1994).
15. C. K. Kim and B. K. Kim, *J. Appl. Polym. Sci.*, **43**, 2295 (1991).
16. A. Mirceva, T. Malavasic, and V. Osredkar, *J. Mol. Struct.*, **219**, 371 (1990).
17. B. K. Kim and Y. M. Lee, *Colloid Polym. Sci.*, **270**, 956 (1992).
18. M. L. Lee, T. K. Kim, and B. K. Kim, *Polym. Int.*, **28**, 157 (1992).
19. F. M. Ball, *Treat. Coat.*, **1**, 323 (1972).
20. J. H. Saunders, *Rubb. Chem. Technol.*, **33**, 1266 (1960).
21. J. W. C. Van Bogart, A. Lilacnikul, and S. L. Cooper, *Adv. Chem. Ser.*, **3**, 176 (1979).
22. H. Xiao, H. X. Xiao, K. C. Frisch, and N. Malwitz, *J. Appl. Polym. Sci.*, **54**, 1643 (1994).
23. G. Oertel, *Polyurethane Handbook*, 2nd ed., Carl Hanser Verlag, Munich, 1993.
24. R. D. Cody and U. S. Askew, in *Water-borne and Higher Solids Coatings Symposium*, New Orleans, LA, Feb. 21–23, 1990.
25. D. J. David and H. B. Staley, *Analytical Chemistry of Polyurethanes*, High Polymer Series, Part 3, Wiley-Interscience, New York, 1969.
26. C. S. Sung and N. S. Schneider, *Macromolecules*, **8**, 68 (1975).
27. S. L. Hsu, H. X. Xiao, H. H. Szmant, and K. C. Frisch, *J. Appl. Polym. Sci.*, **29**, 2467 (1984).
28. H. X. Xiao, S. Yang, J. A. McLean, and K. C. Frisch, in *Waterborne & Higher Solids, and Powder Coatings Symposium*, New Orleans, LA, Feb. 24–26, 1993.
29. K. Sreenivasan, *Polym. J.*, **22**, 620 (1990).
30. S.-A. Chen and W.-C. Chan, *J. Polym. Sci. Part B Polym. Phys.*, **28**, 1499 (1990).
31. C. K. Kim, B. K. Kim, and H. M. Jeong, *Colloid Polym. Sci.*, **269**, 895 (1991).
32. V. Sreenivasulu and K. T. Joseph, *Polym.-Plast. Technol. Eng.*, **32**, 501 (1993).
33. W.-C. Chan, *Polym. Bull.*, **30**, 705 (1993).
34. H. Manock, *Surf. Coat. Int.*, **9**, 348 (1993).
35. Z. Wirpsza, *Polyurethanes: Chemistry, Technology & Applications*, Polymer Science Series, Ellis Horwood, New York, 1993.