

Properties of polyisobutylene polyurethane block copolymers: 3. Hard segments based on 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI) and butane diol

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A series of polyisobutylene (PIB) polyurethanes based on 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI) have been synthesized and their structure-property relationships have been investigated. The PIB glycol was synthesized by the 'inifer' technique. Sample compositions were designed for independent investigation of the effects on physical properties of hard segment content and soft segment molecular weight and for comparison with corresponding 4,4'-diphenylmethane diisocyanate (MDI) based PIB polyurethanes. Increasing hard segment content resulted in improved dynamic and tensile modulus while elongation at break was unaffected. Increasing soft segment molecular weight led to decreased mechanical properties attributed to larger domain sizes as indicated by small angle X-ray scattering (SAXS). Both the soft segment T_g and the extent of interfacial mixing as measured by SAXS were unaffected by hard segment content and soft segment molecular weight suggesting that the materials were highly phase separated. In comparison with corresponding MDI based materials the H₁₂MDI based polyurethanes exhibited less hard segment ordering, slightly less interfacial mixing, smaller domain sizes, and slightly better ultimate tensile properties.

(Keywords: polyisobutylene polyurethanes; block copolymers; H₁₂MDI; inifer; structure-property relationships; domain size)

INTRODUCTION

Conventional polyurethane block copolymers based on polyether or polyester soft segments suffer from poor environmental stability. Hydrocarbon soft segments, principally hydroxy-terminated polybutadienes and polyisobutylenes, have been introduced because of their superior hydrolytic stability and lower moisture permeability¹⁻³. Polyisobutylene is advantageous compared with polybutadiene as a soft segment material due to its enhanced oxidative stability^{1,2}. Polyurethane block copolymers are also known to suffer from poor stability to ultraviolet radiation⁴⁻¹¹. U.v.-induced degradation can cause reduction of molecular weight and tensile properties and yellowing, all of which can limit potential applications^{4,5}.

Polyurethanes based on aromatic hard segments often exhibit u.v. radiation induced discolouration¹¹ which has been related to the structure of the aromatic diisocyanate used in the polymer⁶. The degradation process has been attributed to the photodecomposition of urethane linkages to give conjugated azo- and possibly quinone-imide structures^{6,7,10}. However, replacing the aromatic diisocyanate with an aliphatic diisocyanate such as 4,4' dicyclohexylmethane diisocyanate (H₁₂MDI) removes the potential for conjugated structures and thus the corresponding polyurethane block copolymers

demonstrate improved light stability^{4,6}. Thus, from an environmental stability standpoint a polyurethane block copolymer based on polyisobutylene soft segments and H₁₂MDI would be almost ideal.

In previous studies of polyisobutylene polyurethanes^{1,12}, it was noted that in addition to improved environmental properties these materials are also of interest for structure-property studies. Polyisobutylene soft segments have no potential for hydrogen bonding and are less polar than the conventional polyether or polyester soft segments. Thus, polyisobutylene polyurethanes tend to be more completely phase separated than conventional polyurethanes^{1,12}. Despite the increased degree of phase separation, previous studies^{1,12} have shown that their mechanical properties were inferior compared with mechanical properties of conventional polyurethanes.

H₁₂MDI based polyurethanes, in addition to improved stability to u.v. radiation, are also of interest for structure property studies^{6,13-19}. In contrast to polyurethanes based on the corresponding aromatic diisocyanate, 4,4'diphenylmethane diisocyanate (MDI), polyurethanes based on H₁₂MDI generally exhibit less hard segment ordering or crystallinity^{14,18,19}. This lack of ordering has been attributed to the fact that H₁₂MDI is produced as a mixture of three isomers; *cis-trans*, *trans-trans* and *cis-cis*¹³⁻¹⁹. Because of the low degree of hard segment ordering, H₁₂MDI based polyurethanes are generally transparent, thereby creating potential additional

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applications^{16,17}. Recently, Byrne *et al.*¹⁷ have studied the effects of isomer content on the properties of an H₁₂MDI based polyether polyurethane. Byrne *et al.* studied three materials with 20, 30 (commercial material) and 70% *trans-trans* content respectively (all three materials had 5% *cis-cis* content). They noted that increasing the *trans-trans* content improved the material's hardness (Shore A), tensile modulus and elongation at break, while reducing flexibility. The lower *trans-trans* content materials exhibited a hard segment glass transition which was not observed for the 70% *trans-trans* material. Although no melting endotherms were reported, it is likely that the 70% *trans-trans* sample possessed hard segment crystallinity since it was opaque while the other materials were transparent.

Van Bogart *et al.* in a series of papers^{14,15,19} have compared the properties of H₁₂MDI based polyester polyurethanes with corresponding MDI based polyester polyurethanes. Generally, the effects of hard segment content and hard and soft segment length on the mechanical properties of the materials were similar for both the MDI and H₁₂MDI based materials. Increasing hard segment content led to increasing modulus and tensile strength, decreasing phase separation and extensibility. Increasing the segment length increased the degree of phase separation. The effect on the mechanical properties of segment length could not be directly observed due to differences in the hard segment content. As expected, the H₁₂MDI materials exhibited a lower degree of hard segment ordering. The H₁₂MDI materials also exhibited slightly higher ultimate tensile properties. This was attributed to a smaller hard segment domain size in the H₁₂MDI materials; small angle X-ray scattering data supported this assertion. Smith²⁰ has suggested that since smaller domains at equivalent volume fraction should have a higher surface to volume ratio they should be more effective at stopping catastrophic crack growth through the soft segment matrix.

The results of the investigations of Van Bogart *et al.*^{14,15,19} were inconclusive as to whether H₁₂MDI based polyurethanes are more completely phase separated than MDI based materials. Soft segment glass transition temperatures as measured by differential scanning calorimetry (d.s.c.) and dynamic mechanical spectroscopy were slightly lower for the H₁₂MDI based materials, indicating that they may be more completely phase separated than the MDI based materials. A similar conclusion was reached by Aitkens and Jeffs¹³ on polyethylene adipate based polyurethanes. However, Van Bogart *et al.* also noted that the H₁₂MDI hard segments appeared to inhibit soft segment crystallization to a greater extent than MDI based hard segments, suggesting that more hard segments are dispersed in the soft segment phase of the H₁₂MDI materials. The degree of phase separation as measured by small angle X-ray scattering (SAXS) was calculated for the MDI based materials, but the calculation could not be done for the H₁₂MDI based materials because of the similarity of the electron densities of the H₁₂MDI hard segments and the polyester soft segments¹⁵. Van Bogart *et al.*¹⁵ observed a narrower interphase for the H₁₂MDI materials but cautioned that rather than indicating the degree of phase separation, this property may be more closely related to hard segment unit flexibility and hard segment domain morphology. Recently, Wong *et al.*¹⁸ have suggested that the existence

of an observable high temperature glass transition in H₁₂MDI materials is indicative of an increased degree of phase separation relative to MDI based polyurethanes which generally do not exhibit an observable, hard segment glass transition. However, this reasoning does not seem to include the effect of the relative amount of amorphous material in the H₁₂MDI based polyurethane *versus* that in the MDI based material. Generally, one might expect H₁₂MDI hard segments to be more compatible with soft segments because of their aliphatic nature. Yet, the limited data available would seem to suggest the opposite conclusion. One possible explanation is that the more ordered structures in MDI based polyurethanes tend to 'exclude' more hard segments which then must be dispersed in the soft segment phase. The question of the degree of phase separation in MDI *versus* H₁₂MDI based polyurethanes will be investigated further in this study.

In this paper we extend our study of structure-property relationships of polyisobutylene polyurethanes to materials based on H₁₂MDI hard segments. As noted above, this combination of hard and soft segments should produce materials with excellent environmental stability. Two series of samples have been prepared based on two different polyisobutylene molecular weights, each with three levels of hard segment content (*Table 1*). The sample compositions were chosen to allow for separate investigation of the effects of hard segment content and soft segment molecular weight on the properties of H₁₂MDI based polyisobutylene polyurethanes. Experimental techniques used include d.s.c., dynamic mechanical spectroscopy, SAXS, and tensile testing. The polyisobutylene glycols used in this study were the same as those used previously¹² and the sample compositions were also designed to allow for comparisons of the properties of H₁₂MDI and MDI based materials. The use of polyisobutylene glycols produced by the 'inifer' technique which possess a number average functionality of 2.0^{21,22}, along with a solution polyurethane synthesis procedure, should serve to reduce functionality and reactant incompatibility problems encountered in a previous study¹ of polyisobutylene polyurethanes¹².

EXPERIMENTAL

Materials

The synthesis and purification of α,ω -dihydroxy polyisobutylene (PIB) has previously been described^{21,22}. 4,4'-dicyclohexylmethane diisocyanate (H₁₂MDI) (Mobay Chemical Co.) was vacuum distilled and stored under dry nitrogen before use. 1,4-butanediol (BD) (Fisher Scientific) was distilled over molecular sieves (3Å) under dry nitrogen and stored over molecular sieves (3Å).

Table 1 Composition of the materials used

Sample	wt % MDI	wt % MDI/BD
H-1800-6/5/1	41.1	52.9
H-1800-4/3/1	33.6	42.3
H-1800-3/2/1	28.4	34.9
H-4000-12/11/1	38.7	50.8
H-4000-8/7/1	31.2	40.5
H-4000-6/5/1	26.1	33.6

Xylene and *N,N*-dimethylformamide (DMF) (Fisher Scientific) were refluxed under dry nitrogen over calcium hydride and freshly distilled into amber bottles before use²³. Stannous octoate (M and T Chemicals) was used as received.

Synthesis of polyisobutylene polyurethane

The procedure used to synthesize H₁₂MDI based polyisobutylene polyurethanes was similar to the synthesis procedure described for MDI based polyisobutylene polyurethanes¹². However, to compensate for the lower reactivity of H₁₂MDI compared with MDI, catalyst and a slightly higher reaction temperature were used. Under a dry nitrogen atmosphere in a stainless steel enclosure, PIB glycol was dissolved in a mixture of dry DMF/xylene (25/75) to make a 20% w/v solution at 80°C. A stoichiometrically calculated amount of H₁₂MDI along with 0.15 wt% stannous octoate catalyst was added to the solution and stirred constantly with a glass rod for 1 h. Then the proper amount of BD was added with a microlitre syringe; the final NCO/OH ratio was 1.0. After stirring for an additional hour, the mixture was left overnight at 80°C. Subsequently, solvent was removed by evaporation in a vacuum oven at 70°C for one week.

Samples for physical testing were prepared by redissolving an appropriate amount of the polyisobutylene polyurethane in a xylene/DMF (80/20) mixture followed by spin casting at 70°C. The spin cast films were dried under vacuum for three days at 70°C. The resulting films were approximately 0.05 to 0.15 mm thick. The compositions of the various materials synthesized are shown in Table 1. The sample nomenclature, for example H-4000-4/3/1, indicates a polyisobutylene number average molecular weight (4000), an H₁₂MDI based hard segment (H), and a molar ratio (4/3/1) of H₁₂MDI to BD to PIB.

Characterization methods

Differential scanning calorimetry (d.s.c.) thermograms were recorded from -120° to 230°C using a Perkin-Elmer d.s.c. 2 equipped with a data processing unit. The heating rate was 20°C min⁻¹ and the quenching rate was 320°C min⁻¹. The data processing unit allowed automatic subtraction of the background and normalization of the thermograms for sample weight.

Dynamic mechanical data were obtained using a computer controlled Rheovibron DDV-II. Data were taken from -150°C until sample failure at a test frequency of 110 Hz and a temperature rise rate of 2°C min⁻¹.

Room temperature uniaxial stress-strain and stress hysteresis data were taken on an Instron table model tensile testing device. The rate of strain based on the initial guage length was constant at 33% min⁻¹. Samples were prepared using an ASTM D412 standard die. Hysteresis measurements were made by loading and unloading the sample at a constant rate of 33% min⁻¹, and were cyclically carried out to increasing strain levels.

Wide angle X-ray scattering experiments were performed using a Picker Model 3667A diffractometer in the reflectance mode. Intensity was scanned as a function of scattering angle from 2° to 40°.

Small angle X-ray scattering experiments were performed using the following apparatus and procedures.

X-rays were produced by a rotating anode X-ray generator operating at 40 kV accelerating potential and 50 mA emission current. After emission from the copper anode, the X-rays were passed through a nickel filter so that the X-ray wavelength was predominantly 0.1542 nm (CuK α). A modified Kratky compact SAXS camera was used to collimate the X-rays into a beam which was about 1.25 cm by 100 μ m at the sample. The collimation optics, the sample holder, and the scattering path were evacuated to eliminate scattering by air. The sample-to-detector distance was approximately 0.6 m. Scattered X-rays were detected by a one-dimensional position-sensitive detector and associated electronics. The SAXS data were collected by a multi-channel analyser and transferred to a computer for subsequent processing. Corrections were made to the data to take into account the detector sensitivity, the detector dark current, parasitic scattering, and sample absorption. Relative intensity data were converted to absolute intensity data by using a Lupolen (polyethylene) standard²⁴. In order to eliminate slit-length smearing effects, an experimentally measured slit-length weighting function was used to desmear the data by the iterative method of Lake²⁵. The range of overall sample thicknesses (several films were stacked together) was from about 0.9 mm to 1.3 mm. The range of linear attenuation coefficients was from about 0.4 mm⁻¹ to 0.5 mm⁻¹.

RESULTS AND DISCUSSION

Thermal analysis

D.s.c. thermograms for the as cast H₁₂MDI materials are shown in Figure 1. Thermal transition data including values for the second heating (quenched run) following quenching from the first run are summarized in Table 2. Figure 1 and Table 2 indicate that the position and breadth of the soft segment glass transition is unaffected by hard segment content and by heating and quenching. This behaviour suggests that the materials are highly phase separated^{1,12}. The 1800 series materials do show a slight unexpected decrease in the soft segment glass transition temperature (*T_g*) with increasing hard segment content. Generally, polyurethanes exhibit an increase in *T_g* with increasing hard segment content that is attributed to an increase in the number of hard segments dispersed in the soft segment phase^{26,27}. Because of the high degree of incompatibility between the hard and soft segments it is likely that only the shortest hard segments (ones with one

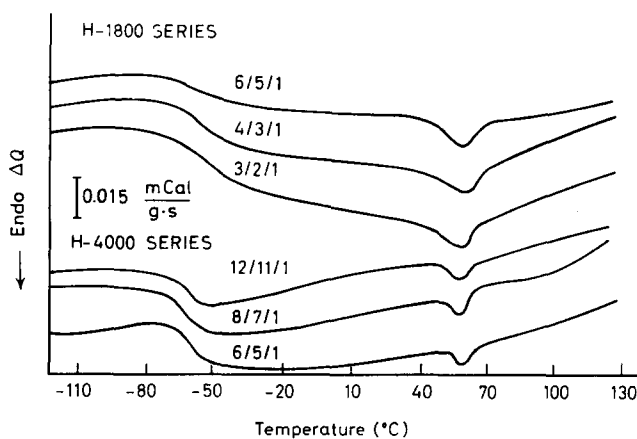


Figure 1 D.s.c. thermograms for the H-1800 and H-4000 series materials

Table 2 Thermal transitions (All values in °C)

Sample	First run ^c d.s.c.		T_g^a	Quench d.s.c.		Rheovibron (E'' MAX) T_g	First run d.s.c. T_1
	T_g^a	Breadth ^b		Breadth ^b	T_g^a		
H-1800-6/5/1	-57	30	-58	30	-43	60	
H-1800-4/3/1	-55	29	-54	27	-40	62	
H-1800-3/2/1	-44	28	-51	25	-40	60	
H-4000-12/11/1	-62	15	-62	14	-44	61	
H-4000-8/7/1	-61	14	-60	15	-43	61	
H-4000-6/5/1	-61	12	-61	12	-46	61	

^a D.s.c. T_g determined from midpoint of change in baseline height

^b T_g breadth determined by intersections of baselines and tangent through midpoint

T_1 Position of low temperature ordering endotherm

or two H_{12} MDI units) are dispersed in the soft segment phase. Since increasing the hard segment content also increases the average length of the hard segment units and reduces the number of short hard segments, the decrease in the soft segment T_g with increasing hard segment content may be a result of there being fewer short hard segments dispersed in the soft segment phase.

The effects of increasing soft segment molecular weight at equivalent hard segment content (thus increasing the average block length of both the hard and soft segments) on the soft segment glass transition can be discerned from the data in Table 2. The higher molecular weight (longer block length) 4000 series materials have a slightly lower glass transition temperature and a narrower transition region. Both of these effects would seem to be indicative of an increased degree of phase separation. However, it is likely that these effects are not due to an increase in the purity of the hard and soft phases but are the result of reduced interfacial effects with increasing segment length^{12,27,28}. Critchfield *et al.*^{27,28} have attributed the decrease in the soft segment T_g with increasing soft segment length in materials that do not exhibit a significant shift in T_g with hard segment content to increases in free volume and mobility. That is, there is a decreasing influence of chain end restrictions and interfacial effects as the soft segment chain length increases.

Figure 1 shows that all of the H_{12} MDI materials exhibit an endotherm at approximately 60°C. No other endotherms were observed in the temperature range (-120° to 230°C) studied. Also, no endotherms were observed on the quenched run. Similar endotherms to those seen on the initial run have been observed previously and attributed to ordering of hard segment regions as a result of room temperature ageing or annealing^{14,15,19}. This ordering is disrupted by heating to ~60°C and does not reform rapidly enough after quenching to be observed on the second heating run. Although, as discussed previously, H_{12} MDI/BD hard segments are generally not crystallizable they are capable of participating in paracrystalline types of ordering. Despite no evidence for hard segment crystallinity or a large degree of ordering, no hard segment glass transition¹⁸ was observed. This behaviour is not unusual^{1,14,15} and is not necessarily indicative of a low degree of phase separation. As stated above, the constancy of the soft segment T_g and the appearance of hard segment ordering indicate the presence of a high degree of phase separation.

In comparison with d.s.c. data on MDI based

polyisobutylene polyurethanes¹² the data shown here demonstrate that H_{12} MDI based PIB polyurethanes exhibit, as expected, a lower degree of hard segment ordering. The H_{12} MDI and MDI materials exhibit similar trends with respect to the effects of hard segment contents and soft segment molecular weight at equivalent hard segment contents on thermal transition behaviour. The position and breadth of the soft segment glass transition is almost identical for corresponding H_{12} MDI and MDI based materials. There is a slight trend especially in the 1800 series materials toward lower T_g values for the H_{12} MDI materials. Similar trends have been observed previously¹³⁻¹⁵ and may be indicative of a slightly higher degree of phase separation in H_{12} MDI materials or differences in morphology between MDI and H_{12} MDI materials leading to reduced interfacial effects in the H_{12} MDI based materials.

Dynamic mechanical analysis

Dynamic mechanical data are displayed in Figures 2-4 and E'' peak position data are recorded in Table 2. Using the position and breadth of the peak in the loss modulus (E'') curve (Figure 3, Table 2) as a measure of the position and breadth of the soft segment glass transition reveals trends in agreement with the d.s.c. data. The position and breadth of the glass transition are unaffected by hard segment content indicating a high degree of phase separation. Also, the 4000 series materials have slightly lower T_g values and exhibit a narrower transition zone (E'' data are not shown for the 4000 series samples) that is probably related to reduced interfacial effects at longer segment lengths.

Both the 1800 and 4000 series materials exhibit an expected^{1,14,15} increase in modulus above the soft segment glass transition temperature with increasing hard segment content. However, as noted previously for other polyisobutylene polyurethanes^{1,12}, the storage modulus does not exhibit a well defined plateau primarily because hard domain cohesion is lost at relatively low temperatures. Losing dimensional stability at a low temperature compared with polyether or polyester polyurethanes may be an inherent feature of polyalkyl polyurethanes²⁹. The steep drop-off in the storage modulus between the soft segment glass transition and the point where dimensional stability is lost has also been observed previously^{1,12} and may be indicative of heterogeneity in the copolymer composition^{12,30}. Overlaying the storage modulus curves for the 1800 and 4000 series materials (Figures 2 and 4) shows that the 1800 series materials at roughly equivalent hard segment

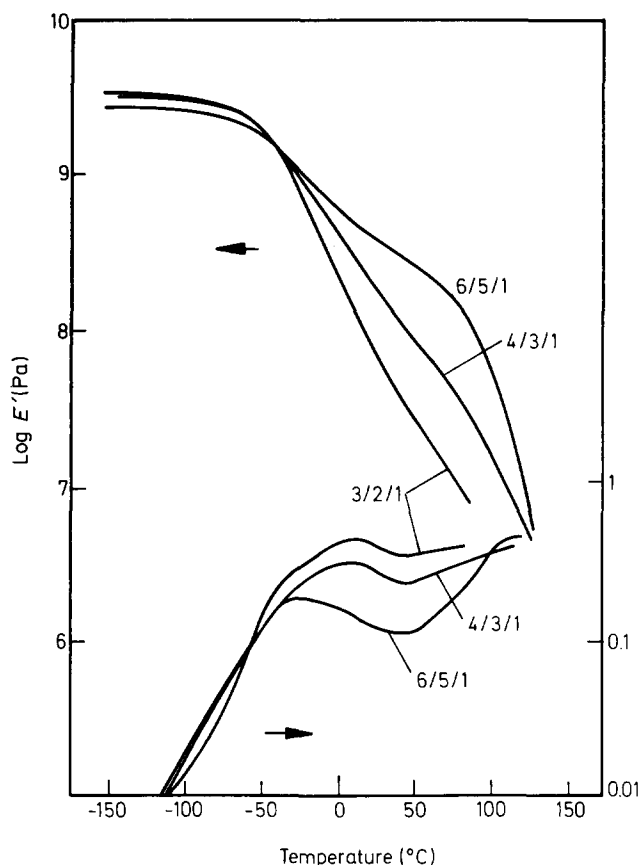


Figure 2 Storage modulus (E') and $\tan \delta$ curves for the H-1800 series materials

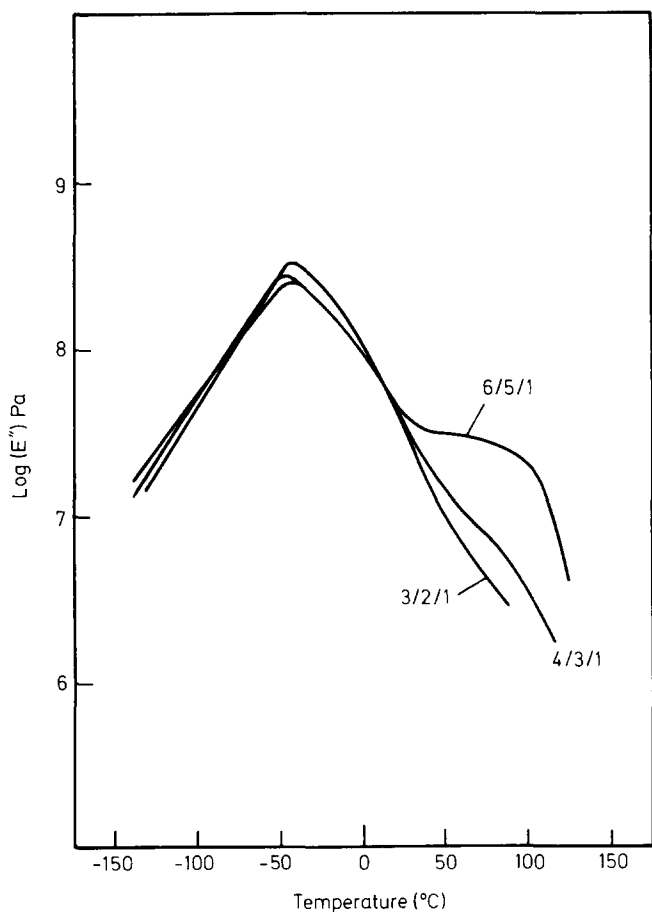


Figure 3 Loss modulus (E'') curves for the H-1800 series materials

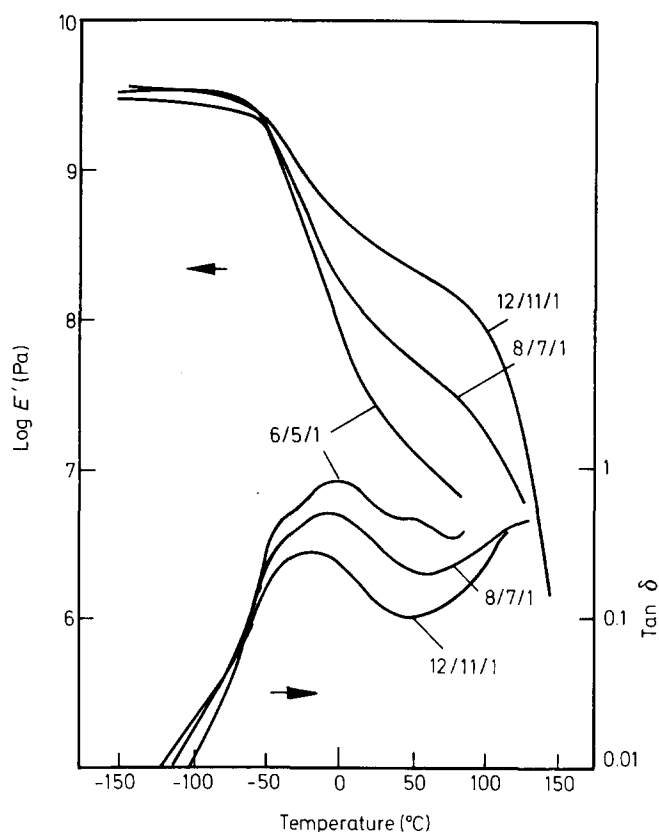


Figure 4 Storage modulus (E') and $\tan \delta$ curves for the H-4000 series materials

content (for example 1800-6/5/1, 52.9% and 4000-12/11/1, 50.8%) possess higher modulus values above the soft segment T_g .

In comparison with previously studied MDI based polyisobutylene polyurethanes^{1,2}, the H_{12} MDI materials exhibit similar trends in their dynamic mechanical behaviour with soft segment molecular weight and hard segment content. The MDI based materials also exhibited a trend of increasing modulus with decreasing soft segment molecular weight at equivalent hard segment content. In the case of the MDI materials^{1,2}, samples of higher segment molecular weight with both slightly lower and higher hard segment contents were compared with samples of lower segment molecular weight. Thus the difference in modulus could not be attributed to differences in hard segment content. In the MDI samples the fact that hard segment crystallinity also decreased with increasing soft segment molecular weight could account for the decrease in modulus. Another possible explanation is that shorter segment lengths give rise to smaller domains. Smaller domains at equivalent volume fractions may act more effectively as physical crosslinks and as a filler to improve modulus.

A comparison of modulus values of MDI and H_{12} MDI based materials at identical soft segment molecular weights and composition ratios did not show a conclusive trend. Generally, at room temperature the H_{12} MDI based materials has slightly higher modulus values. In the 4000 series the H_{12} MDI samples also appeared to have slightly higher modulus at high temperatures. However, it should be noted that the H_{12} MDI materials have a slightly higher hard segment content than the corresponding MDI samples. Also in contrast to the 4000 series behaviour, MDI based 1800 series materials possess a greater high temperature modulus than their H_{12} MDI

based counterparts. This is simply a result of the MDI samples maintaining dimensional stability to a higher temperature and may be attributable to their increased degree of hard segment ordering especially since the 1800 series MDI materials exhibited a much higher degree of ordering at high temperature than the 4000 series MDI materials.

Tensile properties

Stress-strain curves for the H₁₂MDI based materials are displayed in Figure 5. Tensile properties along with stress-hysteresis values are summarized in Table 3. Figure 5 and Table 3 show that these materials exhibit rather low elongations at break and tensile strengths compared with conventional polyurethane elastomers. This behaviour has been observed and discussed previously for other polyisobutylene polyurethanes^{1,12} and will not be discussed here.

From Table 2 and Figure 5 it can be seen that increasing hard segment content results in increasing modulus, tensile strength and hysteresis with little change in elongation at break. Similar trends have been reported for polyisobutylene polyurethanes^{1,12,20,28} except that elongations at break normally decrease with increasing hard segment content. The increase in strength and modulus is usually attributed to an increased filler and physical crosslinking effect with an increase in the fraction of hard segment phase. Hysteresis at low strain levels is related to the hard segment domain interconnectivity^{31,32}. Thus since increasing hard segment content generally leads to increased hard segment domain interconnectivity, stress-hysteresis values also generally increase with hard segment content³¹. The hysteresis values observed here are higher than those seen for corresponding MDI based samples¹². This trend could be ascribed to the H₁₂MDI materials possessing lower molecular weight¹ but is more likely a result of reduced domain cohesion. H₁₂MDI based polyester polyurethanes have been shown by infra-red dichroism experiments¹⁴ to exhibit greater hard segment orientation than corresponding MDI based materials. In that study¹⁴, the authors suggested that the amorphous H₁₂MDI hard segment domains should be more easily disrupted than the ordered MDI hard segment domains.

The effect of soft segment molecular weight on tensile properties can be easily seen from Figure 5. The higher molecular weight 4000 series materials exhibit lower moduli, tensile strengths and elongations at break. Similar results were observed previously for MDI based polyisobutylene polyurethanes¹². From Table 3 it can also be seen that increasing soft segment molecular weight leads to lower stress-hysteresis values at equivalent hard segment content. This could be a result of the longer soft segments being able to undergo larger deformations before sufficient stress is transferred to disrupt the hard segment domains.

A direct comparison of tensile properties for corresponding MDI¹² and H₁₂MDI based polyisobutylene polyurethanes shows that in most cases the H₁₂MDI based materials exhibit better ultimate properties. This trend has also been observed previously for polyester polyurethanes and based upon SAXS analysis was attributed to smaller hard segment domains in H₁₂MDI based samples^{14,15}. Smith²⁰ has suggested that smaller hard segment domains (at equivalent volume fractions) should be more effective at stopping

catastrophic crack growth through the soft segment matrix. Smaller domain size may also explain why shorter segment length materials exhibit superior tensile properties¹². In studies on conventional polyurethanes it has been found that decreasing soft segment molecular weight (and thus hard and soft segment lengths) below about 1500 and 2000 leads to reduced tensile properties^{15,26-28}. Most likely this is an effect of decreasing phase separation and decreasing ability of the soft segments to crystallize under strain and is not due to the hard segment domains becoming too small to effectively strengthen the material¹². Since polyisobutylene polyurethanes do not demonstrate a marked improvement in either the degree of phase separation or the ability of the soft segments to crystallize under strain with increasing soft segment molecular weight (in the range 1000-2000) it is not surprising that optimum properties appear to be obtained at lower soft segment molecular weights¹². The effect of domain size on

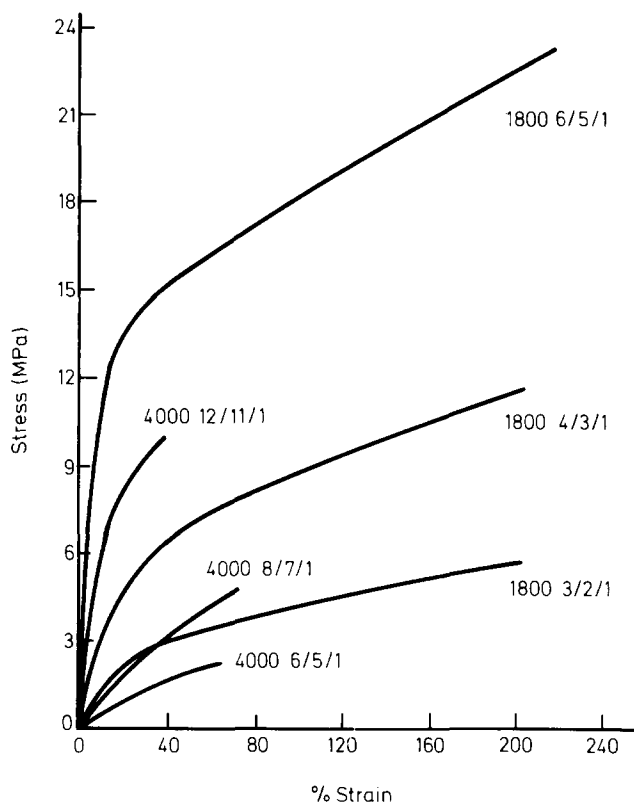


Figure 5 Stress-strain curves for the H-1800 and H-4000 series materials

Table 3 Tensile properties

Sample	E ₁₀₀ (MPa)	σ _b (MPa)	ε _b %	% Hysteresis at 20% strain
H-1800-				
6/5/1	18	23	220	70
4/3/1	8.7	12	200	50
3/2/1	4.4	5.2	200	45
H-4000-				
12/11/1	—	10	40	50
8/7/1	—	4.6	70	30
6/5/1	—	2.4	70	30

E₁₀₀ Secant modulus at 100% elongation
 σ_b Engineering stress at break
 ε_b Elongation at break

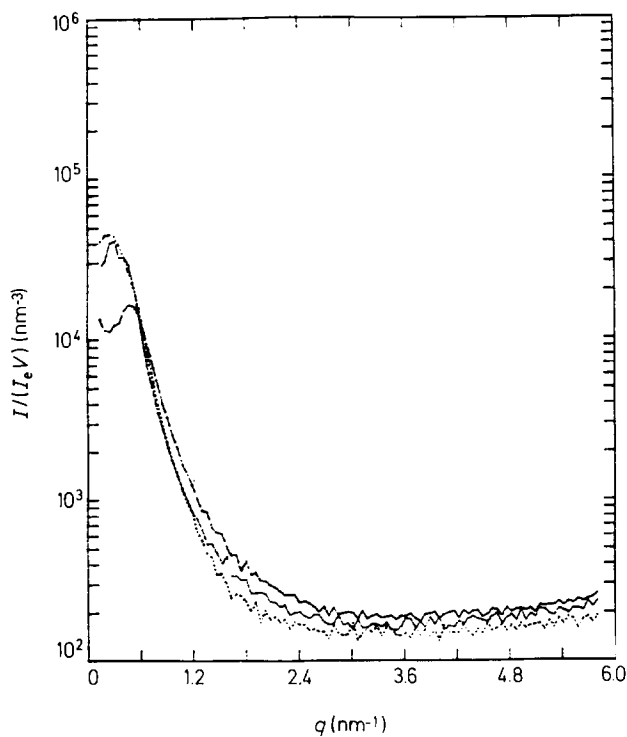


Figure 6 Desmeared and corrected SAXS curves for the H-1800 series materials: (—) 6/5/1; (····) 4/3/1; (-·-·-) 3/2/1

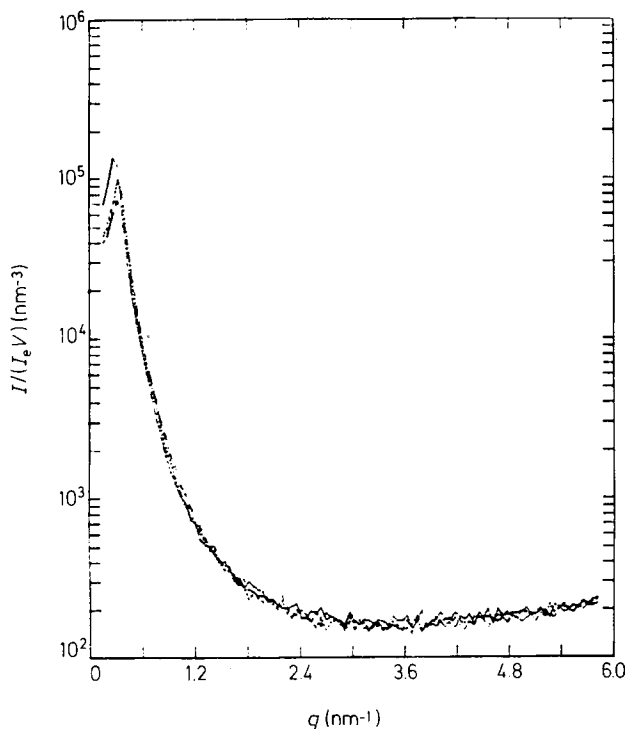


Figure 7 Desmeared and corrected SAXS curves for the H-4000 series materials: (—) 12/11/1; (····) 8/7/1; (-·-·-) 6/5/1

mechanical properties will be discussed further based on the results of the SAXS analysis presented in the next section.

Small angle X-ray scattering

Desmeared and corrected SAXS curves are presented in Figures 6 and 7 for the 1800 and 4000 series respectively. The absolute intensity normalized for the scattering from an electron (I_e) and the scattering volume (V) is plotted as

a function of q , the magnitude of the momentum transfer vector. By definition, $q = (4\pi/\lambda)\sin\theta$ where λ is the wavelength of the X-rays and 2θ is the scattering angle. Figures 8 and 9 show model fits to the experimental data for samples H-1800-4/3/1 and H-4000-8/7/1. Table 4 summarizes some of the morphological parameters extracted from analysis of the SAXS data. The method of analysis used in this study has been described in detail^{1,2} and will only be discussed briefly here.

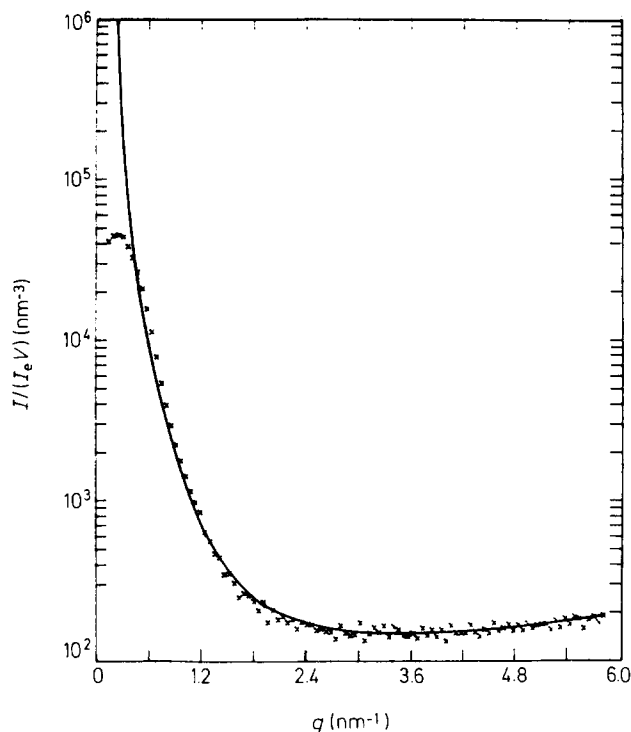


Figure 8 Experimental SAXS data and model fit for sample H-1800-4/3/1: (X) experimental data (—) modelled data

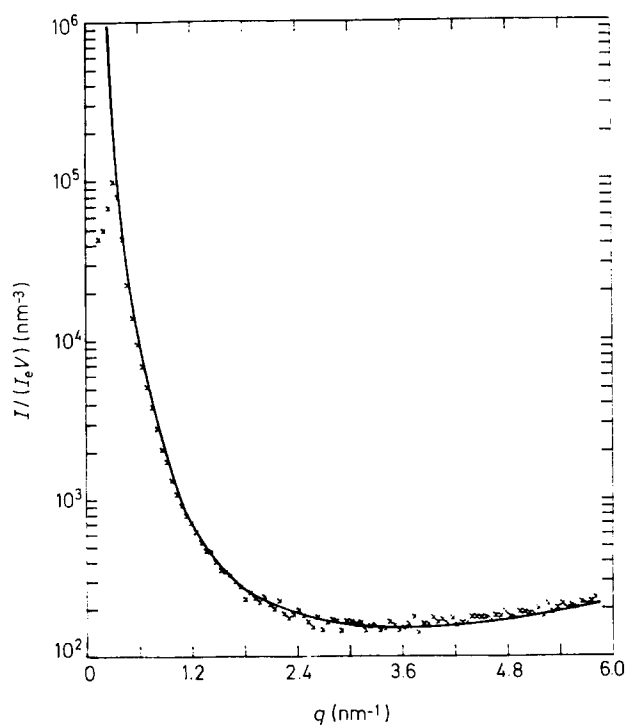


Figure 9 Experimental SAXS data and model fit for sample H-4000-8/7/1: (X) experimental data (—) modelled data

Table 4 SAXS parameters

Samples	Interdomain spacing (nm)	l_p (nm)	σ (nm)	d	d	d	$\overline{\Delta\rho^{2'}}^a$	$\overline{\Delta\rho^{2'}_{ideal}}^b$	$\overline{\Delta\rho^{2''}}^c$
				$\overline{\Delta\rho^{2'}_{ideal}}^+$	$\overline{\Delta\rho^{2'}}$	$\overline{\Delta\rho^{2''}}$	$\overline{\Delta\rho^{2'}_{ideal}}$	$\overline{\Delta\rho^{2''}}$	$\frac{\overline{\Delta\rho^{2''}}}{\overline{\Delta\rho^{2'}}} - 1$
H-1800-6/5/1	13.2	3.6	0.1	2.11	0.57	0.60	0.27	2.53	0.05
	4/3/1	13.0	3.7	0.4	1.98	0.53	0.64	2.08	0.22
	3/2/1	10.7	2.5	0.2	1.79	0.58	0.66	1.71	0.13
H-4000-12/11/1	20.6	5.2	0	2.10	0.61	—	0.29	2.46	—
	8/7/1	17.9	4.8	0	1.94	0.60	—	2.23	—
	6/5/1	17.3	4.6	0	1.74	0.63	—	1.78	—

l_p Porod's inhomogeneity length

σ interfacial thickness parameter

$\overline{\Delta\rho^{2'}_{ideal}}$ Calculated electron density variance assuming pure phases and sharp interfaces

$\overline{\Delta\rho^{2'}}$ Actual electron density variance excluding thermal density fluctuations

$\overline{\Delta\rho^{2''}}$ Actual electron density variance excluding thermal density fluctuation and diffuse interface effects

a A measure of the overall degree of phase separation

b A measure of the amount of segmental mixing in domains

c A measure of the amount of interfacial mixing

d (moles electrons/cm³)² × 10³

+ Values for the mass density of the PIB and H₁₂MDI/BD phases used to calculate $\overline{\Delta\rho^{2'}_{ideal}}$ were 0.917 (36) and 1.13 (37) g/cm³ respectively.

The model curves shown in *Figures 8* and *9* are the result of a non-linear regression of the parameters describing Porod's law modified for interfacial thickness and a Vonk type wide angle X-ray background^{12,33,34}. The fit ranges for H-1800-4/3/1 and H-4000-8/7/1 were from $q = 1.21\text{--}5.7\text{ nm}^{-1}$ and $q = 0.88\text{--}5.7\text{ nm}^{-1}$ respectively. The lower limit for q was chosen based on a criterion developed by Ruland for the low angle validity of Porod's law^{12,34,35}. As shown in *Figures 8* and *9* there is good agreement between the experimental data and the model over the desired fit range. For sample H-1800-4/3/1, the model deviates markedly from the data at lower q values (outside the fit range) while the model for sample H-4000-8/7/1 provides a good fit right up to the peak in the scattering curve. Similar behaviour was observed for the corresponding MDI based materials¹² and confirms the observation³⁴ that Porod's law in some cases holds to much lower q values than predicted by Ruland's criterion^{12,34,35}.

The SAXS parameters in *Table 4* and the SAXS curves in *Figures 6* and *7* show distinct trends with hard segment content and soft segment molecular weight. The peak position moves to smaller angles with increasing hard segment content and is reflected in increasing interdomain spacings (*Table 4*) which are associated with increasing domain size. This trend is also reflected in the inhomogeneity length (l_p) values (*Table 4*). Increasing the soft segment molecular weight (or equivalently the hard and soft segment block lengths) results in much larger domain sizes as measured by the interdomain spacing and inhomogeneity length. These data in combination with the stress-strain results support the idea that smaller domains at equivalent volume fractions are more efficient at stopping catastrophic crack growth²⁰. A comparison of the inhomogeneity lengths of these H₁₂MDI based PIB polyurethanes and the corresponding MDI based materials¹² reveals that the H₁₂MDI based materials have smaller values indicating smaller domain sizes or larger interfacial areas per unit volume. As noted in the previous section, the H₁₂MDI based materials also generally have better ultimate tensile properties.

The calculated electron density variance assuming complete phase separation ($\overline{\Delta\rho^{2'}_{ideal}}$) shows the usual

decrease with decreasing hard segment content due to the fall-off of the term containing the product of the volume fractions of the two phases¹². The actual electron density variances with corrections for thermal density fluctuations ($\overline{\Delta\rho^{2'}}$) and thermal density fluctuations and interfacial mixing ($\overline{\Delta\rho^{2''}}$) do not show a distinct trend with hard segment content. Similarly the values for a Cahn Hilliard type of interfacial thickness (σ)^{1,12} do not show a distinct trend. As shown in *Table 4*, for the 4000-series materials, $\overline{\Delta\rho^{2'}}$ and $\overline{\Delta\rho^{2''}}$ are identical since the best fits provide no interfacial mixing contribution to $\overline{\Delta\rho^{2'}}$ to remove. The values of the interfacial thickness, σ , and the degree of interfacial mixing $\overline{\Delta\rho^{2''}}/\overline{\Delta\rho^{2'}} - 1$ are low compared to conventional polyurethanes^{15,34}, indicating a higher degree of phase separation, but are similar to values observed for the corresponding MDI-based materials¹². Except for sample H-1800-4/3/1 the σ values are slightly lower for the H₁₂MDI based materials compared with the corresponding MDI based samples¹². A similar trend has been observed previously¹⁵ and attributed to the fact that H₁₂MDI based hard segments are more flexible than MDI based hard segments and would have less of a tendency to protrude from the hard segment domains.

As noted previously¹², the absolute values of the parameter describing the degree of phase separation $\overline{\Delta\rho^{2'}}/\overline{\Delta\rho^{2'}_{ideal}}$ and the degree of phase mixing in domains $(\overline{\Delta\rho^{2'}_{ideal}}/\overline{\Delta\rho^{2''}}) - 1$ are highly dependent on the calculated values of $\overline{\Delta\rho^{2'}_{ideal}}$ which in turn depend on values used for the densities of the pure phases. Thus the validity of direct comparisons of these values to values obtained for other polyurethane materials is questionable. In any event, the values for the degree of phase separation are similar to the values obtained for a conventional polyether polyurethane³⁴ and corresponding MDI based PIB polyurethanes¹², while in both cases the values for the degree of phase mixing in domains are higher. The relative trends in the data are however independent of the choice of density values. The degree of phase separation decreases and the degree of segmental mixing increases with increasing hard segment content. Increasing hard segment content is generally thought to

lead to a higher degree of phase mixing due to more hard segments dispersed in the soft segment phase^{26,27}; however, this argument is not supported by the d.s.c. data which should show an increasing soft segment T_g with increasing hard segment content. Similar anomalous behaviour was observed for the corresponding MDI based PIB polyurethanes and was attributed to increased mixing of soft segment in the hard segment domains¹². It was suggested that since higher hard segment content materials have longer hard segment block lengths, the increased degree of mixing in domains with increasing hard segment content might be related to the difficulty of packing less mobile, longer hard segments into compact hard segment domains. This concept was also strengthened by the fact that for the MDI materials increasing the hard segment block length at fixed hard segment content (by increasing the soft segment molecular weight) also resulted in a lower degree of phase separation and a higher degree of segmental mixing in domains. The H₁₂MDI materials however do not show a similar distinct trend.

SUMMARY

A series of H₁₂MDI based PIB polyurethanes have been synthesized and their structure-property relationships studied using d.s.c., SAXS and dynamic mechanical and tensile testing. The sample compositions were designed for independent investigation of the effects of hard segment content and soft segment molecular weight on the material properties and for comparison with MDI based materials. Increasing hard segment content increased the dynamic and tensile modulus as expected but did not significantly affect the elongation at break. The purity of the soft segment phase as measured by the position of the soft segment glass transition and the extent of interfacial mixing were unaffected by hard segment content. Increasing soft segment molecular weight lowered the soft segment T_g slightly due to reduced interfacial effects. The extent of phase mixing was relatively unaffected by soft segment molecular weight. Increasing soft segment molecular weight led to lower ultimate tensile properties that were attributed to larger domains (as measured by SAXS) in the higher soft segment molecular weight materials. In comparison with corresponding MDI based materials, the H₁₂MDI based samples for the most part exhibited similar trends with hard segment content and soft segment molecular weight.

Direct comparison of the properties of these H₁₂MDI based PIB polyurethanes with the properties of the corresponding MDI based materials leads to several interesting conclusions. The soft segment T_g is generally slightly lower in the H₁₂MDI based materials as is the degree of interfacial mixing. This was interpreted not as direct evidence for a higher degree of incompatibility in the H₁₂MDI materials but as a consequence of the difference in flexibility between the two hard segment types, and the possible exclusion of short MDI hard segments from ordered hard segment domains. The H₁₂MDI materials, as expected, exhibited a much lower degree of hard segment ordering ascribed to the presence of hard segments which are formed from mixtures of the three isomeric forms of the diisocyanate. Finally, the H₁₂MDI based materials which contain smaller domains

as measured by SAXS possessed better ultimate tensile properties than equivalent MDI based systems.

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REFERENCES

- 1 Speckhard, T. A., Ver Strate, G., Gibson, P. E. and Cooper, S. L. *Polym. Eng. Sci.* 1983, **23**, 337
- 2 Chang, V. S. C. and Kennedy, J. P. *Polym. Bull.* 1983, **8**, 69
- 3 Arnold, Jr., C. J. *J. Elast. Plast.* 1974, **6**, 238
- 4 Brauman, S. K., Mayorla, G. D. and Heller, J. *Ann. Biomed. Eng.* 1981, **9**, 45
- 5 Hummel, D. O., Ellinghorst, G., Katchatryan, A. and Stenzenberger, H. D. *Angew. Makromol. Chem.* 1979, **82**, 103
- 6 Schollenberger, C. S. and Stewart, F. D. *Adv. Urethane Sci. Tech.* 1973, **2**, 71
- 7 Schultze, H. *Makromol. Chem.* 1973, **172**, 54
- 8 Tarakanov, O. G., Neuskij, L. V. and Beljakov, V. K. *J. Polym. Sci.-C* 1968, **23**, 193
- 9 Osawa, Z., Cheu, E. L. and Ogiwara, Y. *Polym. Lett.* 1975, **13**, 535
- 10 Beachell, H. C. and Chang, I. C. *J. Polym. Sci.-A1* 1972, **10**, 503
- 11 Craig, R. G., Koran, A. and Yu, R. *Biomater.* 1980, **1**, 112
- 12 Speckhard, T. A., Gibson, P. E., Cooper, S. L., Chang, V. S. C. and Kennedy, J. P. *Polymer* 1984, **25**, 55
- 13 Aitkens, R. R. and Jeffs, G. M. F. *Polymer* 1977, **18**, 198
- 14 Van Bogart, J. W. C., Lilaonitkul, A., Lerner, L. E. and Cooper, S. L. *J. Macromol. Sci.-Phys.* 1980, **17**, 267
- 15 Van Bogart, J. W. C., Gibson, P. E. and Cooper, S. L. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 65
- 16 Byrne, C. A., McHugh, E. A., Matton, R. W., Wong, S. W. and Frisch, K. C. *Am. Chem. Soc. Org. Coat. Prepr.* 1982, **47**, 49
- 17 Bryne, C. A., Mack, D. P. and Cleaves, M. A. *Am. Chem. Soc. Polym. Prepr.* 1983, **50**, 58
- 18 Wong, S. W., Cormier, G. J., Frisch, K. C., Schneider, N. S. and Byrne, C. A. *Am. Chem. Soc. Polym. Prepr.* 1983, **50**, 63
- 19 Van Bogart, J. W. C., Bluemke, D. A. and Cooper, S. L. *Polymer* 1981, **22**, 1428
- 20 Smith, T. L. *Polym. Eng. Sci.* 1977, **17**, 129
- 21 Ivan, B., Kennedy, J. P. and Chang, V. S. C. *J. Polym. Sci. Chem. Edn.* 1980, **18**, 3177
- 22 Fehervari, A., Kennedy, J. P. and Tudos, F. *J. Macromol. Sci. Chem.* 1981, **15**, 215
- 23 Trisler, J. C., Freasier, B. F. and Wu, S. M. *Tetrahedron Lett.* 1974, 687
- 24 Kratky, O., Pilz, I. and Schmitz, P. J. *J. Colloid Interface Sci.* 1966, **21**, 24
- 25 Lake, J. A. *Acta. Crystallogr.* 1967, **23**, 191
- 26 Schneider, N. S. and Paik Sung, C. S. *Polym. Eng. Sci.* 1977, **17**, 73
- 27 Seefried, Jr., C. G., Koleske, J. V. and Critchfield, F. E. *J. Appl. Polym. Sci.* 1975, **19**, 2503
- 28 Zdrahala, R. J., Hager, S. L., Gerkin, R. M. and Critchfield, F. E. *J. Elast. Plas.* 1980, **12**, 225
- 29 Ryan, P. W. *Br. Polym. J.* 1971, **3**, 145
- 30 Nielsen, L. E. *J. Am. Chem. Soc.* 1953, **75**, 1435
- 31 Wang, C. B. and Cooper, S. L. *Macromolecules* 1983, **16**, 775
- 32 Paik Sung, C. S., Smith, T. W. and Sung, N. H. *Macromolecules* 1980, **13**, 117
- 33 Ruland, W. *J. Appl. Crystallogr.* 1971, **4**, 70
- 34 Koberstein, J. T. and Stein, R. S. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 2181
- 35 Ruland, W. *Colloid Polym. Sci.* 1977, **255**, 417
- 36 Wood, L. A., Bekkedahl, N. and Roth, F. L. *Ind. Eng. Chem.* 1942, **34**, 1291
- 37 Van Bogart, J. W. C. *Ph.D. Thesis*, Univ. of Wisconsin, 1981