

Polyurethane Elastomers Based on Molecular Weight Advanced Poly(Ethylene Ether Carbonate) Polyols.

III. Effects of Diisocyanate Modified Diols

ROBERT F. HARRIS,* MICHAEL D. JOSEPH, CARLA DAVIDSON, and CRAIG D. DEPORTER

Central Research—Advanced Polymeric Systems Laboratory, The Dow Chemical Company, Midland, Michigan 48674

SYNOPSIS

A series of diisocyanate-modified, molecular weight advanced poly(ethylene ether carbonate) diols has been prepared, characterized, and formulated into polyurethane elastomers using a prepolymer process. Properties were compared to a polyurethane elastomer control in which the only variable was the diisocyanate modification. The diisocyanate modification produces polymers with increased modulus (445–730% at 25°C), improved tensile strength and hardness properties and reduced (improved) coefficients of linear thermal expansion, while still passing the notched Izod impact test. The tensile strength at break increases with increasing number of urethane moieties in the soft segment and the elongation at break also increases. The plaques studied appear to have a three-phase morphology—a soft segment continuous phase containing amorphous hard segment, an amorphous hard segment phase plasticized by about 11% of the soft segment material, and a crystalline hard segment. The polymers based on the diisocyanate modified polyols are significantly more phase mixed than the control due to the increased amount of hard segment-soft segment interactions taking place. The improved properties of the polymers made with the modified polyols are due to their higher hydrogen bonding potential which gives more physically crosslinked polymers.

INTRODUCTION

Poly(ethylene ether carbonate) polyols are polymers which contain alternating blocks of carbon dioxide units and poly(ethylene glycol) units in their backbones. When these polyols are made using sodium stannate trihydrate as the catalyst, backbone hydrolysis studies¹ and carbon-13 NMR studies² have shown that these polyols contain predominantly carbon dioxide units and diethylene glycol (DEG) units with small quantities of triethylene glycol (TriEG) units and have $-\text{OC}(\text{O})\text{OCH}_2\text{CH}_2\text{OC}-\text{H}_2\text{CH}_2\text{OH}$ end groups. When these polyols are heated to elevated temperatures ($> 180^\circ\text{C}$) at reduced pressures, volatile impurities are removed, followed by molecular weight advancement and formation of DEG.^{3–6} As DEG is removed as distillate,

molecular weight builds in a controllable manner. This is thought to be a transesterification process in which $-\text{OC}(\text{O})\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ end groups on one molecule react with carbonate moieties on a second molecule with loss of DEG. These advanced polyols form rapidly with high CO_2 retention, relatively low polydispersity, and high purity.

Poly(ethylene ether carbonate) diols (2025 mol wt) made by the molecular weight advancement of lower molecular weight oligomers have been fabricated into polyurethane elastomers by reaction with 4,4'-MDI and 1,4-butanediol using the prepolymer method.^{7–9} The poly(ethylene ether carbonate) diol gives a polymer with a partially phase mixed morphology, a higher ambient temperature modulus, and a lower ΔH_m than the other polyester polyols studied. Resistance to organic solvents is their most outstanding property.

This work extends this research to the preparation of diisocyanate modified poly(ethylene ether carbonate) polyols, their molecular weight advance-

* To whom correspondence should be addressed.

ment, and the effects of using these modified polyols as soft segments in polyurethanes.

EXPERIMENTAL

Starting Materials

Isonate 125M brand MDI [4,4'-methylene-di(phenylisocyanate)] (freshly distilled just prior to use) and Voranate T-80 brand TDI (80 : 20 2,4 : 2,6 toluene diisocyanate) were manufactured by Dow Chemical Co. 1,4-Butanediol (freshly distilled from calcium hydride and stored under nitrogen in silanized bottles) and dibutyltin dilaurate were obtained from Aldrich Chemical Co. The poly(ethylene ether carbonate) diol starting material was prepared by the monoethylene glycol initiated oligomerization of ethylene oxide and carbon dioxide¹⁰ followed by removal of residual catalyst.^{6,11}

Isocyanate Modification

A given diisocyanate was added to the poly(ethylene ether carbonate) diol starting material under N₂ cover at ambient temperature. Reaction was finished by heating at 80°C for 2 h. After the isocyanate moieties were reacted (FTIR), the polyol structure was established by NMR.

Molecular Weight Advancement Procedure

The diisocyanate modified polyol and boiling stones were placed in a boiling flask equipped with a thermometer, heating mantle and down draft, water chilled condenser attached to a dry ice-isopropanol trap, and a vacuum source. The polyol was heated to 60–80°C to reduce viscosity and outgassed at about 50 mm Hg. The vacuum was then adjusted to 10 mm Hg and heating increased to effect fractionation and continued until the desired pot temperature was reached. The residue and distillate were weighed and analyzed.

Distillate Analysis

Capillary gas chromatograms were obtained on a Hewlett-Packard 5840A unit with a J&W Scientific Company DB-1 fused silica capillary column. 1,6-Hexanediol was used as an internal standard.¹

Polyol Characterization

NMR spectra were obtained on a Varian Gemini 300 NMR (300 MHz for hydrogen and 75 MHz for

carbon) using DMSO-d₆ as solvent. Viscosity/temperature profiles were obtained on a Brookfield Synchro-Lectric Digital Viscometer with a Brookfield Thermosel Heater using a HBTD #21 spindle. Temperature was controlled with a Model 84 Brookfield Programmable Temperature Controller.

Molecular Weight Determination

Molecular weight of the polyols (0.5 wt % in THF) was done by size exclusion chromatography (SEC) on Waters Ultrastyrigel 10², 10³, and 10⁴ Å columns in series at 25°C using tetrahydrofuran (THF) as the continuous phase (1.5 mL/min), calibrated with standard poly(ethylene glycol)s and using a refractive index detector. Molecular weight of the polymers (0.25 wt % in DMF) was done by SEC on Waters Ultrastyrigel 10³, 10⁴, and 10⁵ Å columns in series at 40°C using DMF as the continuous phase (1.0 mL/min) and a refractive index detector (calibrated against narrow molecular weight polystyrene standards). The system was interfaced to a Nelson Analytical 760 Series Intelligent Interface attached to an IBM AT computer for data collection and handling.

Polymer Fabrication

Polyurethane elastomers were prepared by the prepolymer process as previously described.⁸ All polymers were catalyzed with dibutyltin dilaurate (0.0013 wt % based on solids) using an index (isocyanate : hydroxyl equivalent ratio) of 1.03. They were fabricated in a preheated mold (6 in. × 6 in. × 70 mil) between Mylar sheets, pressured to 2000 psi, and cured at 121°C (250°F) for 1 h.

Mechanical and Thermal Properties

Procedures have been described.⁸ All plaques were aged at ambient temperature for 2 weeks prior to property measurements. Differential scanning calorimetry (DSC) samples were run on a DuPont 910 DSC in crimped aluminum pans using a heating rate of 10°C/min and a nitrogen atmosphere. Dynamic mechanical analysis (DMA) samples were run on a DuPont 983 DMA in a fixed frequency mode of 1.0 Hz using a heating rate of 3°C/min and a nitrogen purge. Thermal mechanical analysis (TMA) samples were run on a DuPont 943 TMA, using a 1.0 g load and a macroexpansion probe. A heating rate of 5°C/min was used. Physical properties were measured using standard ASTM procedures. Solvent resistance was measured at ambient temperature by

Table I Effect of Diisocyanate Modifier on Molecular Weight

Polyol No.	Diisocyanate Modifier	Modifier (wt %)	Molecular Weight Data			Brookfield Viscosity (cps; 25°C)	
			Peak	\bar{M}_n	\bar{M}_w		\bar{M}_w/\bar{M}_n
Starting polyol	—	0	1100	779	1291	1.66	2490
I	MDI	5.66	1677	1117	1937	1.74	9210
II	MDI	10.10	2419	1473	2736	1.86	31,100
III	MDI	18.00	5208	2602	5373	2.06	898,000
IV	TDI	5.74	2014	1189	2123	1.79	13,600

a static soak test until solvent uptake reached equilibrium (6 days).

Wide Angle X-Ray Spectroscopy (WAXS)

Data were obtained on a Siemens D-500 diffractometer equipped with a Co tube, primary beam monochromator, 1° slits, and position sensitive detector. Scans were obtained at a rate of 1°/min, using power settings of 40 kV at 25 mA.

RESULTS AND DISCUSSION

Synthesis of Diisocyanate-Modified Diols

A low molecular weight poly(ethylene ether carbonate) diol ($\bar{M}_n = 779$; prepared by the monoethylene glycol initiated oligomerization of ethylene oxide and CO₂) was reacted with various amounts of MDI to form a series of MDI modified diols (5.66–18.0 wt % MDI). An additional diol sample was modified with TDI (Table I). As expected, molecular weight increased with increasing diisocyanate modification, since the diisocyanate functions as a connecting unit between hydroxyl end groups. However, viscosity increases much more quickly than molecular weight.

Table II Effect of Pot Temperature on the Molecular Weight Advancement of Diisocyanate Modified Polyol II

Pot Temperature (°C)	Molecular Weight Data			
	Peak	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
Starting material	2419	1473	2736	1.86
200	2469	1510	2875	1.90
220	2905	1698	3477	2.05
230	3851	2014	4375	2.17
240	4340	2251	5295	2.35
252	6781	2876	7759	2.69

This is a consequence of intermolecular hydrogen bonding.

Molecular Weight Advancement of Diisocyanate Modified Diols

A portion of MDI modified polyol (II) was advanced to a series of higher molecular weight diols by heating at 10 mm Hg vacuum, with volatiles removed, to a pot temperature of 252°C, with sample removal at intermediate pot temperatures. Samples were removed from the reactor through a syringe port without interfering with the system pressure. The effect of pot temperature on molecular weight build is given in Table II and is shown graphically in Figure 1. There is a systematic increase in \bar{M}_n with increasing pot temperature which is represented by the following equation:

$$\bar{M}_n = -199.25T + 0.498T^2 + 21,437$$

$$\text{correlation coefficient} = 0.994$$

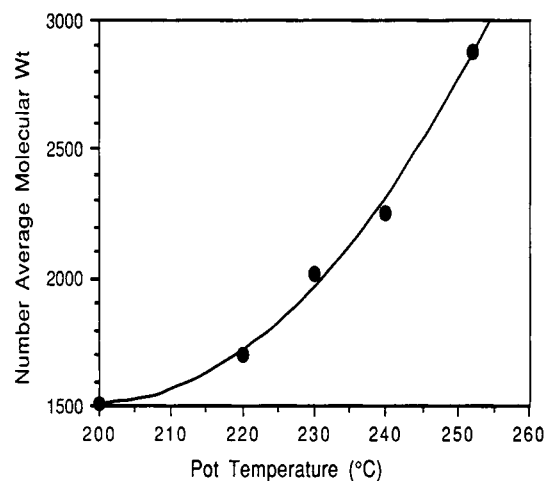
**Figure 1** Effect of pot temperature on the number average molecular weight during molecular weight advancement of diisocyanate modified polyol II.

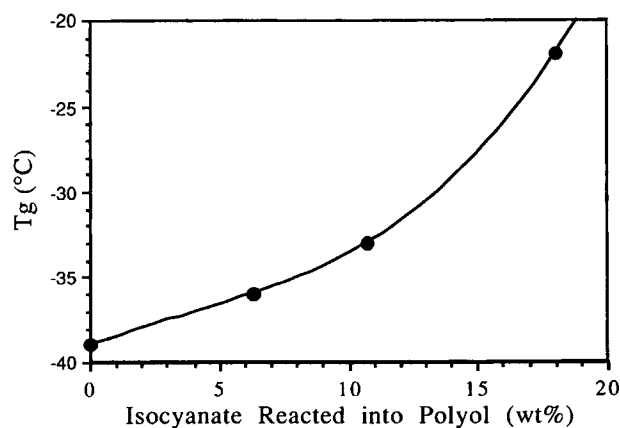
Table III Polyol Molecular Weights before and after Molecular Weight Advancement to a Pot Temperature of 230°C at 10 mm Hg

Sample No. ^a	Diisocyanate Modifier	Modifier (wt %)	Molecular Weight by OH Titration	Molecular Weight Data by SEC			CO ₂ (wt %)	T _g (°C)	Brookfield Viscosity (cps; 25°C)	
				Peak	\bar{M}_n	\bar{M}_w				\bar{M}_w/\bar{M}_n
I	MDI	5.66	880	1677	1117	1937	1.74	18.0	-46	9210
I-A	MDI	6.28	1852	4089	2103	4463	2.12	19.7	-36	63,300
II	MDI	10.10	1130	2419	1473	2736	1.86	20.4	-38	31,100
II-A	MDI	10.70	1690	3484	1912	3954	2.07	20.5	-33	106,400
IV	TDI	5.74	935	2014	1189	2123	1.79	19.6	-42	13,600
IV-A	TDI	6.29	1820	3700	2024	4370	2.16	20.2	-30	101,800

^a A = polyol after molecular weight advancement.

This process used to form diisocyanate-modified, molecular weight advanced poly(ethylene ether carbonate) polyols is quite general.¹² Polyols I, II, and IV were each advanced to higher molecular weight products (I-A, II-A, and IV-A, respectively) by heating to a pot temperature of 230°C at 10 mm Hg. The molecular weight of each polyol before and after advancement is given in Table III. The \bar{M}_n of these advanced polyols by SEC are all about 2000 under these conditions. The modifier content and CO₂ content increased during molecular weight advancement since these moieties are concentrated in the polyol due to distillate removal. There is a large increase in the ambient temperature viscosity.

The T_g of each polyol has also increased during the advancement process, due in part to removal of small molecules present prior to advancement and in part by the increase in molecular weight. The T_g's of the advanced polyols increase with increasing weight percent of the diisocyanate modifier (Fig. 2).

**Figure 2** Effect of MDI content on polyol glass transition temperature.

TDI increases the T_g more quickly since more urethane moieties are formed per unit weight (lower molecular weight), which results in more hydrogen bonding occurring.

The distillate composition is given in Table IV. Diethylene glycol (DEG) and triethylene glycol (TriEG) are the major components of the distillate, which is consistent with previous work.³⁻⁶ Monoethylene glycol (MEG) and ethylene carbonate are impurities in the starting polyol. 1,4-Dioxane is a decomposition product, which becomes increasingly important at higher temperatures and/or higher residual catalyst levels.⁶

Very volatile components in the distillate are collected in a dry ice trap (Table V). Acetone and water are a consequence of the catalyst removal process.^{6,11} Some 1,4-dioxane is also present in this trap.

Mass balances are given in Table V. The product represents ~ 90% of the polyol charged when the diisocyanate modifier is ~ 6.3 wt % and ~ 95% of the polyol charged when the diisocyanate modifier is 10.7%. Total accountability is excellent (~ 99.5%) in all cases.

Characterization of Molecular Weight Advanced Diols

Poly(ethylene ether carbonate) diols are rather viscous materials due largely to the carbonate ester moieties in their backbones. These carbonate moieties act as hydrogen bonding acceptor sites and undergo intermolecular hydrogen bonding with hydroxyl end groups. However, these hydrogen bonding sites are readily broken thermally, permitting the viscosity to be reduced easily by heating (Table VI). The amount of hydrogen bonding is enhanced considerably by the backbone urethane moieties formed

Table IV Analysis of Distillate Removed After Molecular Weight Advancement

Polyol No.	Components in Distillate (wt %)								Distillate Density (g/cc)
	MEG	Dioxane	EC	DEG	TriEG	TetraEG	Water	Total	
I-A	0.13	0.49	9.60	50.7	29.1	5.17	0.07	95.3	1.14
II-A	0.14	0.60	13.9	50.3	25.9	5.88	0.06	96.8	1.14
IV-A	0.10	0.37	10.4	51.4	27.7	6.74	0.07	96.8	1.14

Table V Mass Balance and Analysis of Dry Ice Trap After Molecular Weight Advancement

Polyol No.	Material Balance (wt %)						
	Components in Dry Ice Trap (wt %)			Product	Distillate	Dry Ice Trap	Unaccounted For
	Acetone	Dioxane	Water				
I-A	36.4	45.7	6.1	90.2	9.1	0.3	0.4
II-A	44.2	35.1	5.7	94.8	4.5	0.2	0.5
IV-A	44.4	31.7	10.1	91.3	8.0	0.2	0.5

during diisocyanate modification. At any given temperature, the viscosity of any diisocyanate modified diol is substantially greater than the viscosity of a corresponding unmodified diol (Fig. 3). The viscosities of the diisocyanate modified, molecular weight advanced polyols are all very similar.

The partial structure at the top of Table VII represents all of the carbon atom and hydrogen atom environments present in a MDI modified, molecular weight advanced poly(ethylene ether carbonate) diol. All line assignments have been made consistent with previous work to firmly establish the structure of these diols.^{2,8,9,13,14}

Table VI Effects of Temperature on Viscosity of Molecular Weight Advanced Polyols

Temperature (°C)	Viscosity of Advanced Polyol (cps)			
	Control ^a	I-A	II-A	IV-A
30	9880	26,400	42,960	43,520
40	4400	14,020	15,360	15,760
50	2180	5020	5960	6360
60	1168	2296	3000	3160
70	680	1552	1664	1768
80	468	932	1000	1068
90	320	620	640	696
100		436	440	476

^a The control is a molecular weight advanced poly(ethylene ether carbonate) diol which does not contain isocyanate modifier; $\bar{M}_n = 2025$.

Polymer Fabrication

Hand cast plaques were made based on prepolymers with MDI, followed by chain extension with 1,4-butanediol.^{8,9} The soft segment block length and content and the hard segment block length, content, and structure were held constant. Identical procedures were used for plaque preparation and cure. Property differences should be a consequence of the urethane moieties in the soft segments.

The plaques made are described in Table VIII. All plaques were made using dibutyltin dilaurate (0.0013 wt %) as catalyst at an index of 1.03 (isocyanate : polyol equivalent ratio = 1.03 : 1) and a

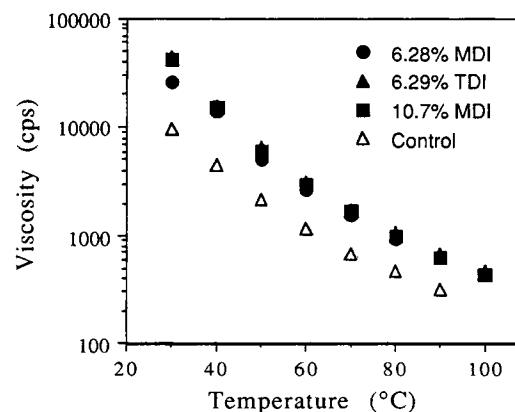
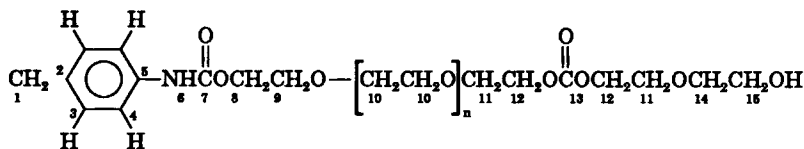
**Figure 3** Comparison of viscosities of molecular weight advanced poly(ethylene ether carbonate) polyols.

Table VII NMR Structural Assignments for MDI Modified Poly(Ethylene Ether Carbonate) Diols

Structural Assignment	Carbon Chemical Shift ^a	Proton	
		Chemical Shift ^a	Multiplicity
1	39.9	3.74	Singlet
2	137.5	—	—
3	129.3	7.05	Doublet
4	118.6	7.32	Doublet
5	135.9	—	—
6	—	9.63	Singlet
7	154.0	—	—
8	63.5/63.6	4.14	Singlet
9	68.8/68.9	3.57	Singlet
10	69.9	3.47	Singlet
11	68.2/68.3	3.57	Singlet
12	66.8/66.9	4.14	Singlet
13	155.1	—	—
14	72.4/72.5	3.57	Singlet
15	60.3	3.42	Singlet

^a ppm from tetramethylsilane (TMS = 0); DMSO-d₆ as solvent.

hard segment content of about 44 wt %. Size exclusion chromatography indicates that substantial molecular weight products are formed using MDI. The TDI product was highly swollen in DMF, indicating that some crosslinking had occurred. All plaques have essentially the same density. Thermal mechanical analysis shows that the coefficients of linear thermal expansion (CLTE) decrease (improve) with increasing soft segment modification. This is thought to be a consequence of soft segment-hard segment interactions which enhance dimensional stability.

Polymer Structural Studies by Carbon-13 NMR

The polyurethane elastomers containing MDI modification in their soft segments were studied by NMR for structure proof. The proton NMR spectrum and the carbon-13 NMR spectrum of polyurethane elastomer II-P are given in Tables IX and X, respectively. All structural assignments are given in the tables and are consistent with previously reported values.⁷⁻⁹ The MDI residues in the hard segment and in the soft segment are not distinguishable by these studies.

Table VIII Description of Plaques Made Based on Diisocyanate Modified Polyols^a

Plaque No.	% Modifier in Soft Segment	% Isocyanate Content of Prepolymer	Wt % Hard Segment	Plaque Density (g/cc)	CLTE ^b × 10 ⁻⁶ /°C (25°C)	Molecular Weight Data		
						\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
Control	0	9.90	43.5	1.27	181	141,500	230,100	1.63
I-P	6.28% MDI	10.00	44.6	1.27	173	153,100	498,400	3.27
II-P	10.70% MDI	9.77	44.8	1.27	158	164,500	469,500	2.86
IV-P	6.29% TDI	9.90	43.9	1.28	178	s ^c	s ^c	s ^c

^a Dibutyltin dilaurate as catalyst (0.0013 wt %), 1.03 index; control = no soft segment modification.

^b Coefficient of linear thermal expansion.

^c s = plaque was highly swollen in DMF, but not completely dissolved.

Table IX Proton NMR Structural Assignments for Polyurethane II-P

Chemical Shift ^a	Structural Assignment
1.69 ppm	Protons on central carbon atoms of 1,4-butanediol
3.52 ppm	Protons on carbon atoms α to carbonyl and β to ether oxygen
3.61 ppm	Protons on carbon atoms β to carbonyl and α to ether oxygen
3.77 ppm	Protons on methylene carbon atoms of MDI
4.09 ppm	Protons on terminal carbon atoms of 1,4-butanediol
4.18 ppm	Protons on carbon atoms both α and β to ether oxygen
7.07 ppm	Protons on aromatic carbon atoms of MDI
7.34 ppm	Protons on aromatic carbon atoms of MDI
9.51 ppm	Protons on urethane nitrogen atoms of MDI

^a ppm from tetramethylsilane (TMS = 0); DMSO-d₆ as solvent.

Physical Properties

Several physical properties of the fabricated plaques are given in Table XI. All plaques pass the notched Izod test. Modulus, strength, and hardness properties all increase with increasing diisocyanate content in the backbone of the soft segment (Fig. 4). The increase in flexural modulus (25°C) is particularly dramatic. As the MDI in the soft segment is increased from 0 to 6.28 to 10.7 wt %, the modulus increases by 445 and 730%, respectively. Not only has the tensile strength at break increased with increasing number of urethane moieties in the soft segment, but the elongation at break has also increased (highest with either MDI or TDI modification at ~ 6.3 wt %).

Diisocyanate modification improves solvent resistance to water and toluene but has little effect on solvent resistance to methanol and methylethylke-

tone (Table XII). However, even plaques made from unmodified poly(ethylene ether carbonate) polyols have excellent organic solvent resistance when compared to plaques made from polyester polyols.⁸

Polymer Morphology

Previous work^{8,9} has shown that polyurethanes made with unmodified poly(ethylene ether carbonate) polyols as the soft segment, the control for this study, show a partially phased mixed morphology. This can be explained as a result of the high potential for hydrogen bonding of these polyols, which creates a high virtual crosslink density within the polyurethane. These virtual crosslinks increase the amount of soft segment-soft segment and, more importantly, hard segment-soft segment interactions, which in turn can lead to increased phase mixing.

The incorporation of low levels of MDI or TDI

Table X Carbon-13 NMR Structural Assignments of Polyurethane II-P

Chemical Shift ^a	Structural Assignment
155.1 ppm	Carbonate carbonyl
154.1 ppm	1,4-Butanediol urethane carbonyl
154.0 ppm	Poly(ethylene ether carbonate) diol urethane carbonyl
137.5 ppm	Aromatic carbon (1) attached to methylene moiety
135.9 ppm	Aromatic carbon (4) attached to carbonyl moiety
129.3 ppm	Aromatic carbon (2)
118.7 ppm	Aromatic carbon (3)
69.9 ppm	Carbon atom both α and β to ether oxygen
68.8/68.9 ppm	Carbon atoms β to urethane and α to ether oxygen
68.2/68.3 ppm	Carbon atoms β to carbonate and α to ether oxygen
66.8/66.9 ppm	Carbon atoms α to carbonate and β to ether oxygen
63.9 ppm	1,4-Butanediol carbon atom attached to urethane moiety
63.5/63.6 ppm	Carbon atoms α to urethane and β to ether oxygen
39.9 ppm	Methylene carbon atoms between aromatic rings
25.3 ppm	1,4-Butanediol center carbon atoms

^a ppm from tetramethylsilane (TMS = 0); DMSO-d₆ as solvent.

Table XI Physical Properties of Plaques Made Based on Diisocyanate Modified Polyols

Plaque No.	Hardness (Shore D)	Notched Izod (ft lb/in.)	Flexural Modulus E' (psi, 25°C)	Tensile Strength at % Elongation				Elongation at Break (%)
				100%	200%	300%	At Break	
Control	48	NB	14,500	1440	1720	1970	2260	460
I-P	51	NB	64,600	1730	2160	2520	4120	770
II-P	60	NB	106,000	2230	2610	2950	3470	530
IV-P	58	NB	38,200	1780	2190	2540	3860	700

* Control = no soft segment modification; NB = no break.

along the polyol backbone, as was done in this study, causes an average of 1–2 urethane moieties to be added along the backbone of each polyol chain (~ 2000 molecular weight). These urethane moieties are very good sites for hydrogen bonding to

take place and further increase the density of virtual crosslink sites in these polyols.

DMA data for the control and polyurethanes I-P, II-P, and IV-P are given in Figures 5–7 for the flexural storage modulus, flexural loss modulus, and

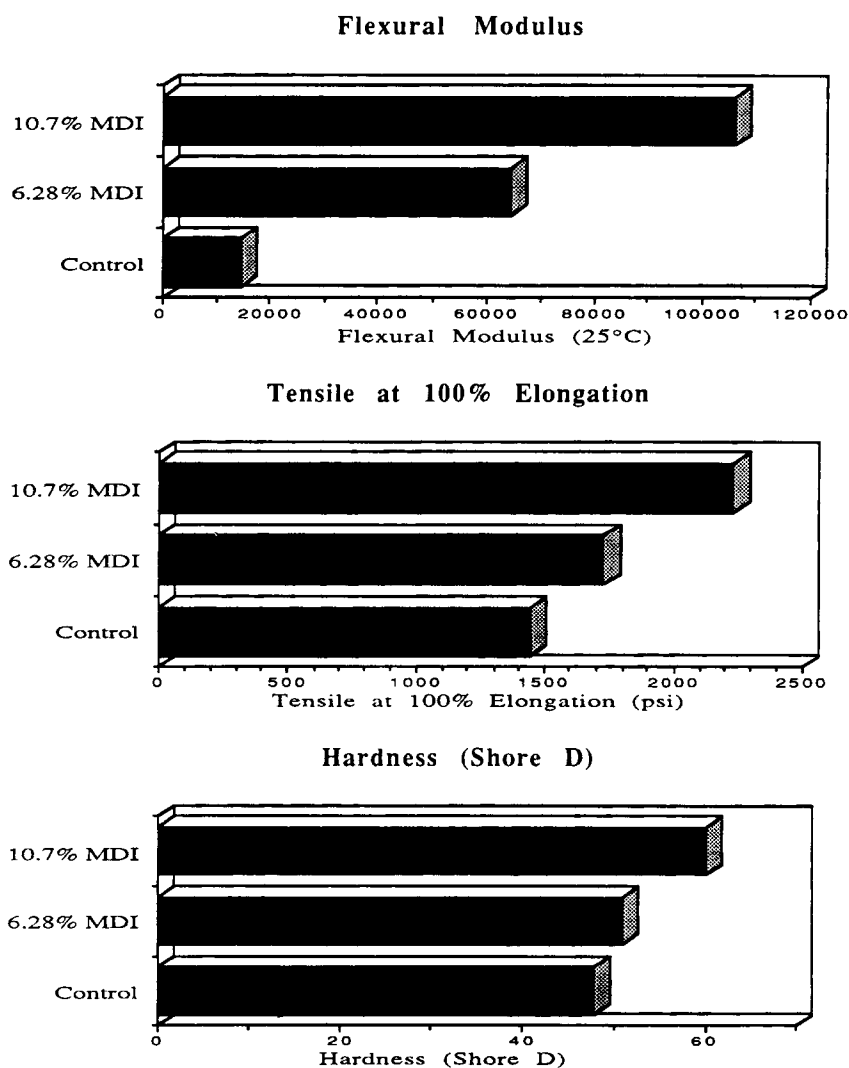


Figure 4 Effect of diisocyanate in soft segment on polymer properties.

Table XII Effect of Diisocyanate Modifier in Soft Segment on Solvent Resistance

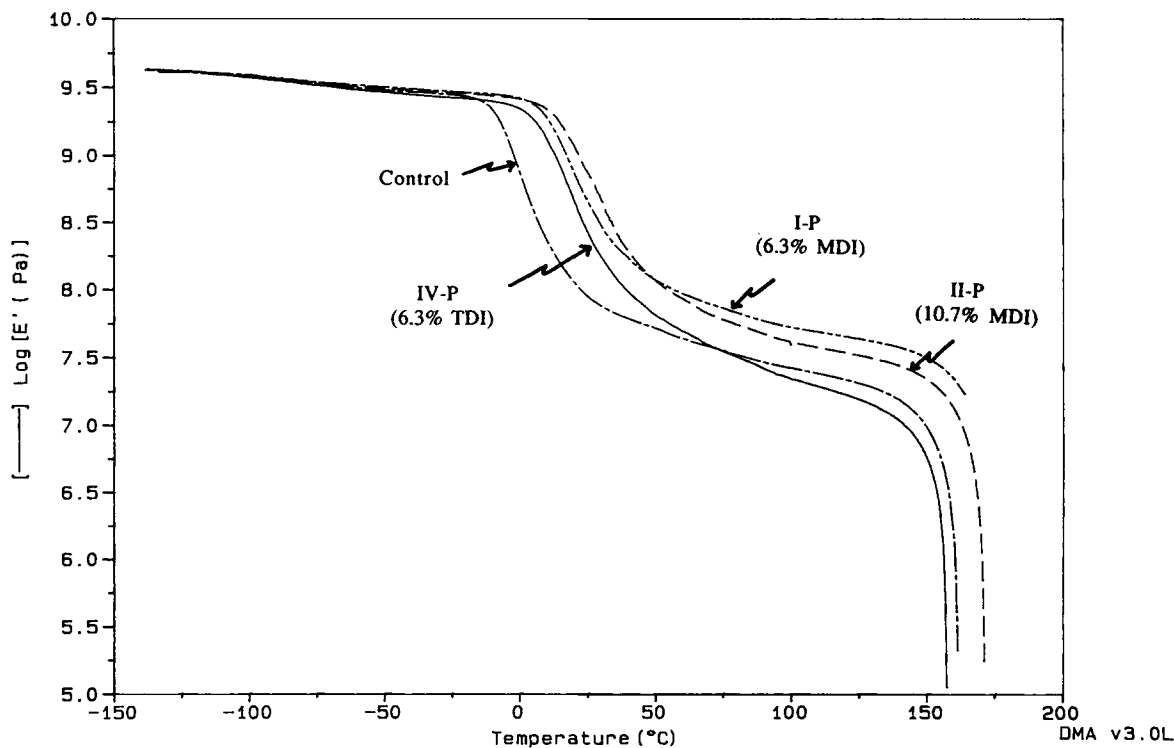
Plaque No.	Soft Segment Diisocyanate Modifier	Solvent Resistance (% wt Gain after 6 days)			
		Water	Methanol	Toluene	MEK
Control	None	4.6	11.7	11.7	30.3
I-P	6.28% MDI	3.5	11.7	5.6	28.5
II-P	10.70% MDI	2.8	11.5	3.7	29.4
IV-P	6.29% TDI	3.8	12.5	5.2	28.6

$\tan \delta$ traces, respectively. Plaques made from the diisocyanate modified polyols have a much higher flexural storage modulus (E') than the control above the glassy region. The only exception is the plaque made from the TDI modified polyol (IV-P), which crosses the control curve at about 70°C (Fig. 5). Plaques made from the MDI modified polyols should have superior high temperature properties.

The flexural loss modulus (E'') data (Fig. 6) show a large increase in the soft segment glass transition temperature when going from the control plaque to the plaques based on the diisocyanate modified poly (ethylene ether carbonate) diols. This same increase in soft segment T_g is evident for the DSC data given in Table XIII. The first scans typically show a subambient T_g , a broad, shallow endotherm

centered around 75°C, and a hard segment melt at about 170°C. There is a large increase in the soft segment glass transition temperature when going from the control plaque to the plaques based on the diisocyanate modified poly (ethylene ether carbonate) diols.

The broad, shallow endotherm seen around 75°C was assumed to be due to volatilization of atmospheric moisture, picked up by the plaques as they sat at ambient temperature and humidity. To make sure of this, plaques were annealed at 125°C for 15 min, and then cooled to -150°C under nitrogen and reheated to 250°C. Figure 8 shows a DSC of plaque IV-P that was subjected to this heat history. After the annealing removes the moisture, a T_g can be seen more clearly at about 50°C. It should be noted

**Figure 5** Flexural storage modulus (E') vs. temperature by DMA.

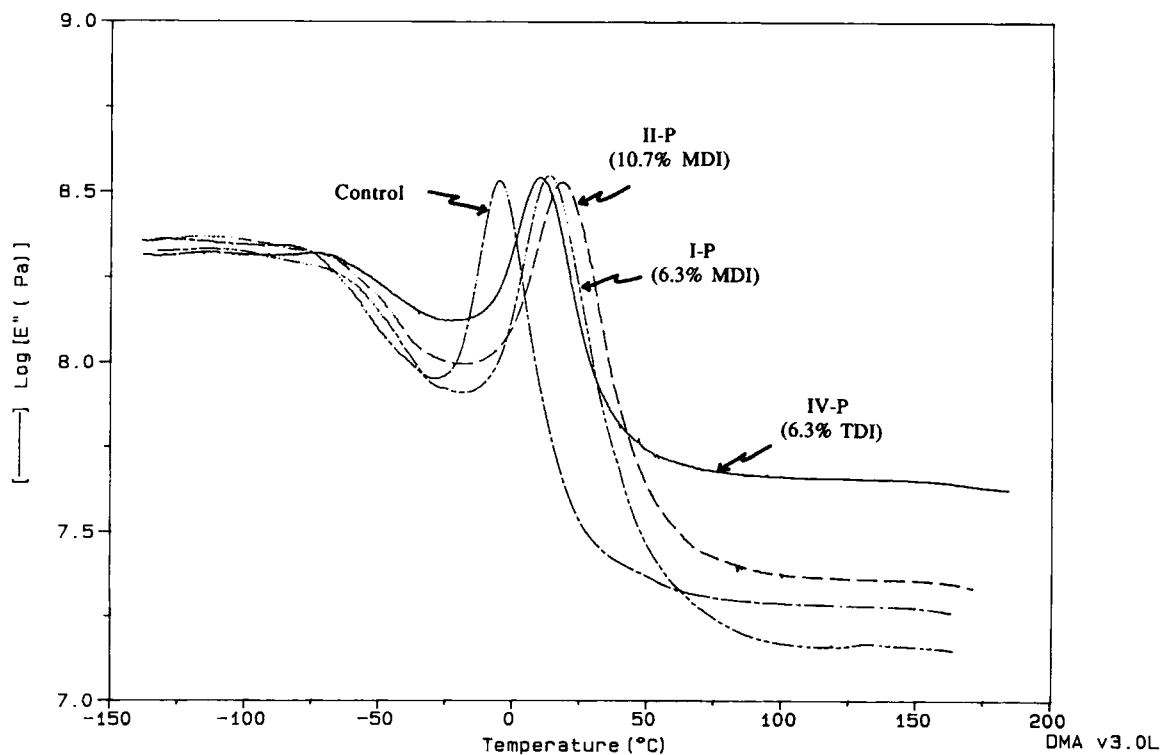


Figure 6 Flexural loss modulus (E'') vs. temperature by DMA.

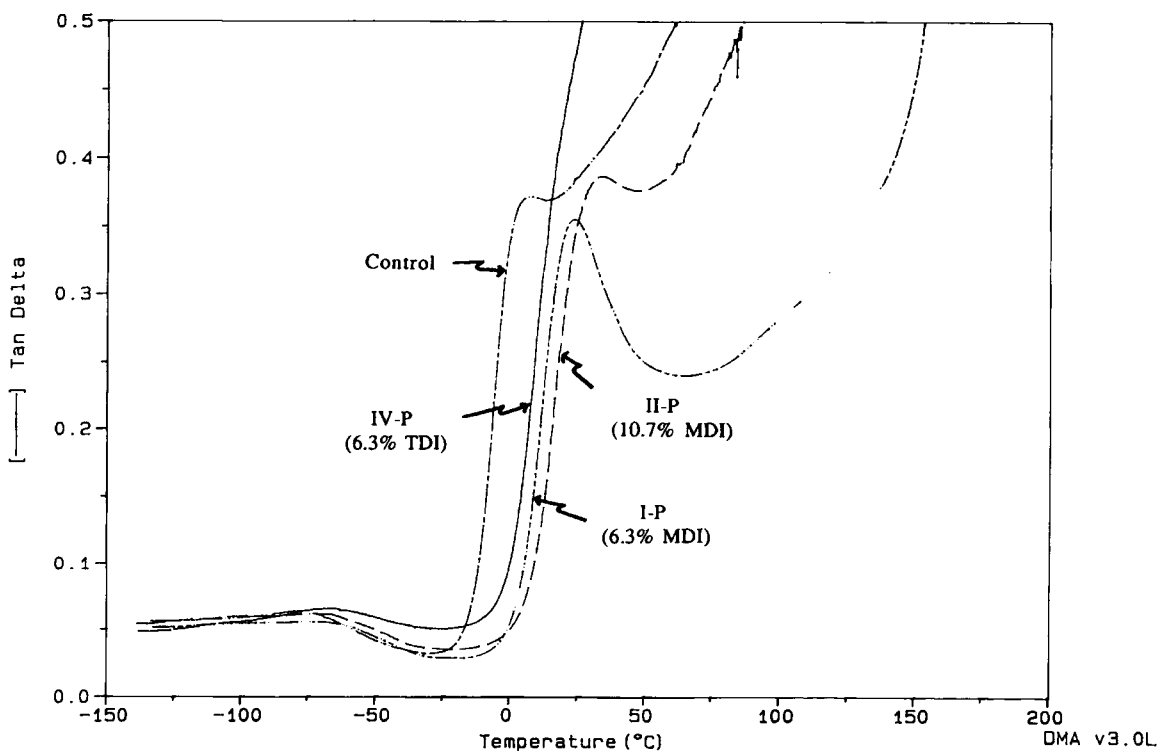


Figure 7 $\tan \delta$ vs. temperature by DMA.

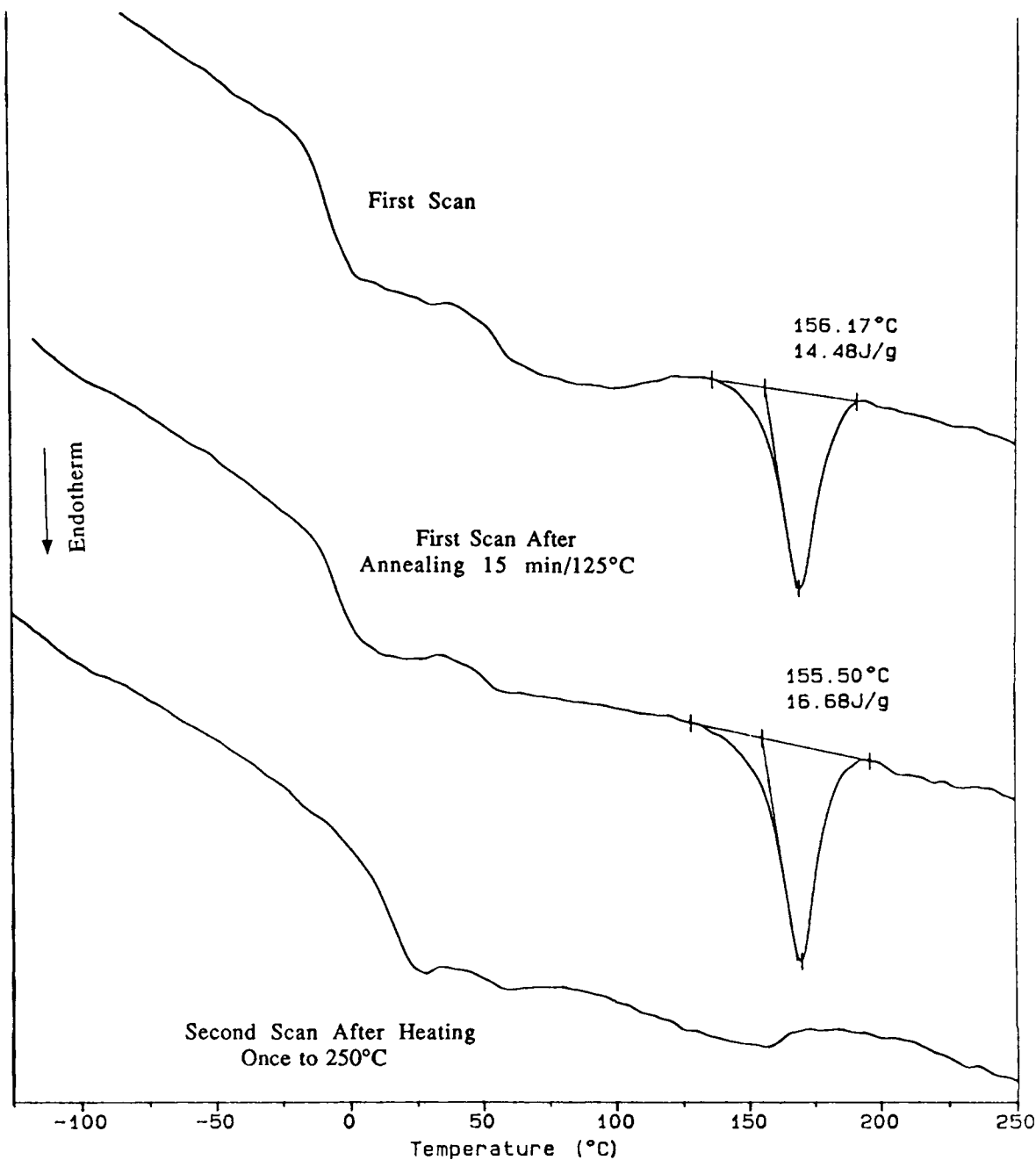


Figure 8 Effect of annealing on DSC scan of plaque IV-P.

that if the plaque is annealed too long or at too high a temperature, this T_g begins to disappear, and, as it does, the soft segment T_g increases and the ΔH_m increases (plaque IV-P in Figure 8 can be seen to be beginning this behavior), indicating that the T_g is due to amorphous hard segment plasticized by some of the soft segment. All the plaques showed this type of behavior when annealed.

Analysis of the DSC data was done by using the Fox equation¹⁵:

$$1/T_{gm} = (w_1/T_{g1}) + (w_2/T_{g2})$$

where T_{gm} is the glass transition temperature of a copolymer containing weight fractions w_1 and w_2 of units 1 and 2, which have homopolymer glass transition temperatures T_{g1} and T_{g2} , respectively. Units 1 and 2 refer to the polyol soft segment phase and the MDI/BDO hard segment phase, respectively. A value of 100°C was used for T_{g2} and the T_{g1} values

Table XIII Effect of Modifying the Soft Segment Backbone on Thermal Properties

Plaque No.	% Modifier in Soft Segment	First DSC Scan		Second DSC Scan		T_m (°C) First DSC Scan	ΔH_m (J/g)		Percent Crystallinity (WAXS)
		T_g (°C)	ΔC_p^a (J/g °C)	T_g (°C)	ΔC_p^a (J/g °C)		First DSC Scan	Second DSC Scan	
Control	None	-20	0.44	7	0.50	167	12.8	5.3	4
I-P	6.29% MDI	-7	0.43	13	0.52	170	15.7	5.5	3
II-P	10.70% MDI	-8	0.42	22	0.48	171	15.2	1.1	7
IV-P	6.28% TDI	-7	0.43	16	0.53	173	15.7	0	6

^a Not corrected for heat flow in sample pan.

were -39, -36, -33, and -30°C for the control and plaques I-A, II-A, and IV-A, respectively.

By using the known hard and soft segment concentrations for each polymer and WAXS data (Table XIII) to determine how much of the hard segment is crystalline, the Fox equation can be manipulated to give an approximation of the distribution of hard segment material and soft segment material in each of the amorphous transitions seen in the DSC scans. The results of the analyses are shown in Table XIV and can give some insight into the amount of phase mixing taking place. We can only get approximate values due to the limitations of the Fox equation when working with polymers that have as high a degree of intermolecular hydrogen bonding as these polymers do and to the scatter in WAXS data.

The plaques studied seem to have a three phase morphology. The first phase is primarily an amorphous soft segment phase containing amorphous hard segment well dispersed throughout with the soft segment being the continuous phase. The amount of hard segment material in the continuous phase is significantly increased in plaques based on the diisocyanate modified diols (increased phase

mixing). The second phase accounts for the majority of the amorphous hard segment material plasticized by about 11% of the soft segment material, which decreases its T_g by about 50°C. The third phase is the crystalline hard segment. The amount of crystallinity is quite low due to the increased amount of hard segment-soft segment interactions taking place. The properties of the polymers made with the modified polyols show significant differences when compared to the control due to their higher hydrogen bonding potential which gives a more physically crosslinked polymer.

CONCLUSIONS

Poly(ethylene ether carbonate) polyols can be modified with diisocyanates and advanced to higher molecular weights under conditions of elevated temperatures and reduced pressures where diethylene glycol is removed as distillate. A series of diisocyanate modified, molecular weight advanced poly(ethylene ether carbonate) diols has been prepared and characterized by molecular weight, carbon-13 NMR, and viscosity relationships.

Table XIV Approximate Distribution of Hard Segment and Soft Segment Material among Phases Based on Analyses Using the Fox Equation

Plaque No.	% Modifier in Soft Segment	Continuous Phase				Plasticized Hard Segment Phase				Crystalline Phase Wt % HS ^a
		T_g (°C)	Wt % SS ^a	Wt % HS ^a	Wt Ratio (SS/HS)	T_g (°C)	Wt % SS ^a	Wt % HS ^a	Wt Ratio (SS/HS)	
Control	None	-20	84.1	28.7	(79/21)	52	15.9	62.1	(25/75)	9.2
I-P	6.29% MDI	-7	89.3	47.6	(70/30)	56	10.7	45.6	(23/77)	6.8
II-P	10.70% MDI	-8	89.2	39.3	(74/26)	58	10.8	45.0	(23/77)	15.7
IV-P	6.28% TDI	-7	89.0	38.5	(75/25)	58	11.0	47.8	(24/76)	13.7

^a Wt % of total available hard segment material (HS) or soft segment material (SS) in a given phase.

These diols were formulated into polyurethane elastomers using a prepolymer process and the resultant polymers were characterized structurally by proton and carbon-13 NMR. Properties were compared to a polyurethane elastomer control in which the only variable was the diisocyanate modification. The diisocyanate modification produces polymers with increased modulus (445–730% at 25°C), improved tensile strength and hardness properties, and reduced (improved) coefficients of linear thermal expansion, while still passing the notched Izod impact test. The tensile strength at break increases with increasing number of urethane moieties in the soft segment and the elongation at break also increases (highest with either MDI or TDI modification at ~ 6.3 wt %).

The plaques studied appear to have a three phase morphology—a soft segment continuous phase containing amorphous hard segment, an amorphous hard segment phase plasticized by about 11% of the soft segment material and a crystalline hard segment. The polymers based on the diisocyanate modified polyols are significantly more phase mixed than the control due to the increased amount of hard segment–soft segment interactions taking place. The improved properties of the polymers made with the modified polyols are due to their higher hydrogen bonding potential which gives more physically crosslinked polymers.

REFERENCES

1. R. F. Harris, *J. Appl. Polym. Sci.*, **37**, 183 (1989).
2. R. F. Harris and L. A. McDonald, *J. Appl. Polym. Sci.*, **37**, 1491 (1989).
3. R. F. Harris, U.S. Pat. 4,709,069 (1987).
4. R. F. Harris, *Polym. Prepr. Div. Polym. Chem. Am. Chem. Soc.*, **29**(2), 418 (1988).
5. R. F. Harris, *J. Appl. Polym. Sci.*, **38**, 463 (1989).
6. R. F. Harris, *J. Appl. Polym. Sci.*, **40**, 1265 (1990).
7. R. F. Harris, M. D. Joseph, C. Davidson, C. D. DePorter, and V. A. Dais, *Polym. Prepr. Div. Polym. Chem., Am. Chem. Soc.*, **30**(2), 235 (1989).
8. R. F. Harris, M. D. Joseph, C. Davidson, C. D. DePorter, and V. A. Dais, *J. Appl. Polym. Sci.*, **41**, 487 (1990).
9. R. F. Harris, M. D. Joseph, C. Davidson, C. D. DePorter, and V. A. Dais, *J. Appl. Polym. Sci.*, **41**, 509 (1990).
10. M. O. Myers, U.S. Pat. 4,686,276 (1986).
11. D. G. Prior, U.S. Pat. 4,528,364 (1985).
12. R. F. Harris, U.S. Pat. 4,861,909 (1989).
13. C. Delides, R. A. Pethrick, A. V. Cunliffe, and P. G. Klein, *Polymer*, **22**, 1205 (1981).
14. K. H. Matthews, A. McLennaghan, and R. A. Pethrick, *Br. Polym. J.*, **19**, 165 (1987).
15. T. G. Fox, *Bull. Am. Phys. Soc.*, **2**, 123 (1956).

Received October 16, 1989

Accepted November 7, 1990