Polyurethane Elastomers Based on Molecular Weight Advanced Poly(Ethylene Ether Carbonate) Polyols. IV. Effects of Poly(Propylene Glycol) Modified Diols

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

Central Research and Development, Materials Science & Development Laboratory, The Dow Chemical Company, Midland, Michigan 48674

SYNOPSIS

A series of polyurethane elastomers with a $(A\{BC\}_m)_n$ type of structure have been prepared and characterized based on poly(propylene glycol) modified poly(ethylene ether carbonate) polyols, where the poly(propylene glycol) content and block length were varied systematically. Strength and modulus properties showed a marked dependence on modifier level and exhibited synergistic property improvements at 25–50 wt % modifier, relative to both unmodified poly(ethylene ether carbonate) diol and poly(propylene glycol) controls. DMA results indicated an increased modulus for the modified plaques throughout the rubbery plateau region, with higher thermal dissociation temperatures. Excellent organic solvent resistance was maintained with 25–50 wt % poly(propylene glycol) modification in the soft segment. Chemical structure of the polyurethane elastomers was established by proton and ^{13}C-NMR spectroscopy. The morphology of these modified polyurethanes appears to be quite complex. Since the modified soft segments are block copolymers of blocks with a tendency toward immiscibility, some microphase separation within the soft segment domains of the polyurethane polymers might be expected. The soft segment T_g is highest where properties are maximized, suggesting changes in phase mixing. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Poly(ethylene ether carbonate) polyols are polymers that 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 studies[1] and ^{13}C-NMR studies[2] 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 $-OC(O)OCH_2CH_2OCH_2CH_2OH$ end groups. When these polyols are heated to elevated temperatures ($> 180°C$) 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 $-OC(O)CH_2CH_2OCH_2CH_2OH$ 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'-methylenedi(phenylisocyanate) (MDI) and 1,4-butanediol using the prepolymer method.[7-9] Poly(ethylene ether carbonate) diols gave polymers with a partially phase mixed morphology, a higher ambient temperature modulus, and a lower enthalpy of melting, ΔHm, than the other polyester polyols studied. Resistance to organic solvents was their most outstanding property. Diisocyanates have been

used to modify poly(ethylene ether carbonate) polyols and their urethane polymers studied.[10,11]

Recently this technology was extended to include other polyols in the reaction mixture during the molecular weight advancement process.[12] These polyol modifiers become chemically incorporated into the poly(ethylene ether carbonate) polyol backbone to yield a new class of compounds.[13,14] This work extends this research to the preparation and characterization of polyurethanes prepared from poly(propylene glycol) modified poly(ethylene ether carbonate) polyols.[15]

EXPERIMENTAL

Starting Materials

Isonate™ 125M brand MDI (4,4'-methylenedi(phenylisocyanate) (freshly distilled just prior to use), P-425 [a poly(propylene glycol) with a number-average molecular weight of approximately 425 g/mol], and tripropylene glycol (TPG) were manufactured by Dow Chemical Company. 1,4-Butanediol (freshly distilled from calcium hydride and stored under nitrogen in silanized bottles), P-725 [a poly(propylene glycol) with a number-average molecular weight of approximately 725 g/mol], and dibutyltin dilaurate were obtained from Aldrich Chemical Company. The poly(ethylene ether carbonate) diol starting material was prepared by the monoethylene glycol initiated oligomerization of ethylene oxide and carbon dioxide[16] followed by removal of residual catalyst.[6,17]

Polyol Modification/Molecular Weight Advancement Procedure

A given amount of poly(ethylene ether carbonate) diol, poly(propylene glycol) modifier, 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 mmHg. The vacuum was then adjusted to 10 mmHg and heating was increased to effect fractionation and continued until the desired pot temperature was reached. The residue and distillate were weighed and analyzed.

Analytical Procedures

Molecular weight of the polyols [0.5 wt % in tetrahydrofuran (THF)] was determined by size exclusion chromatography (SEC) on Waters Ultrastyragel™ 10^2-Å, 10^3-Å, and 10^4-Å columns in series at 25°C using THF as the continuous phase (1.5 mL/min), calibrated with standard poly(ethylene glycols) and using a refractive index detector. Molecular weight of the polymers (0.25 wt % in DMF) was determined by SEC on Waters Ultrastyragel 10^3-Å, 10^4-Å, and 10^5-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. NMR spectra (5 wt % in DMSO-d_6) were obtained on a Varian Gemini 300 instrument (300 MHz for proton and 75 MHz for carbon).

Polymer Fabrication

Polyurethane elastomers were prepared by the prepolymer process as previously described.[8] All polymers were catalyzed with dibutyltin dilaurate (0.0019 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 hr.

Mechanical and Thermal Properties

Procedures have been described.[8] All plaques were aged at ambient for two 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 2940 TMA, using a 0.05-N force and a macroexpansion probe. A heating rate of 5°C/min was used. Physical properties were measured using standard ASTM procedures.[8] Solvent resistance was measured at ambient by 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

Reaction Pathway for Modification of Poly(Ethylene Ether Carbonate) Polyols

When poly(ethylene ether carbonate) polyols are heated to elevated temperatures (> 180°C) at reduced pressures in the presence of a second polyol, the second polyol is incorporated into the backbone during the molecular weight advancement process to produce a higher molecular weight modified poly(ethylene ether carbonate) polyol. This reaction pathway is illustrated in Figure 1, where the modifiers (HOR'OH) are poly(propylene glycols). A similar process is applicable for higher functional polyols.

In the first step, a hydroxyl end group on the poly(propylene glycol) modifier molecule reacts with a carbonyl moiety on the poly(ethylene ether carbonate) diol. This is an equilibrium reaction in which the transient intermediate can either release the modifier molecule to reform the reactants or release DEG to form a modified poly(ethylene ether carbonate) diol (3) in which the modifier becomes chemically bonded to the poly(ethylene ether carbonate) diol and is present as an end group unit.

In the second step, the hydroxyl end group on the modified poly(ethylene ether carbonate) diol (3) reacts with a carbonyl moiety on the poly(ethylene ether carbonate) diol (1). This second transient intermediate can either release large poly(ethylene ether carbonate) diol molecules or release DEG to form a poly(propylene glycol) modified poly(ethylene ether carbonate) diol (4) in which the modifier becomes chemically bonded into the molecular weight advanced poly(ethylene ether car-
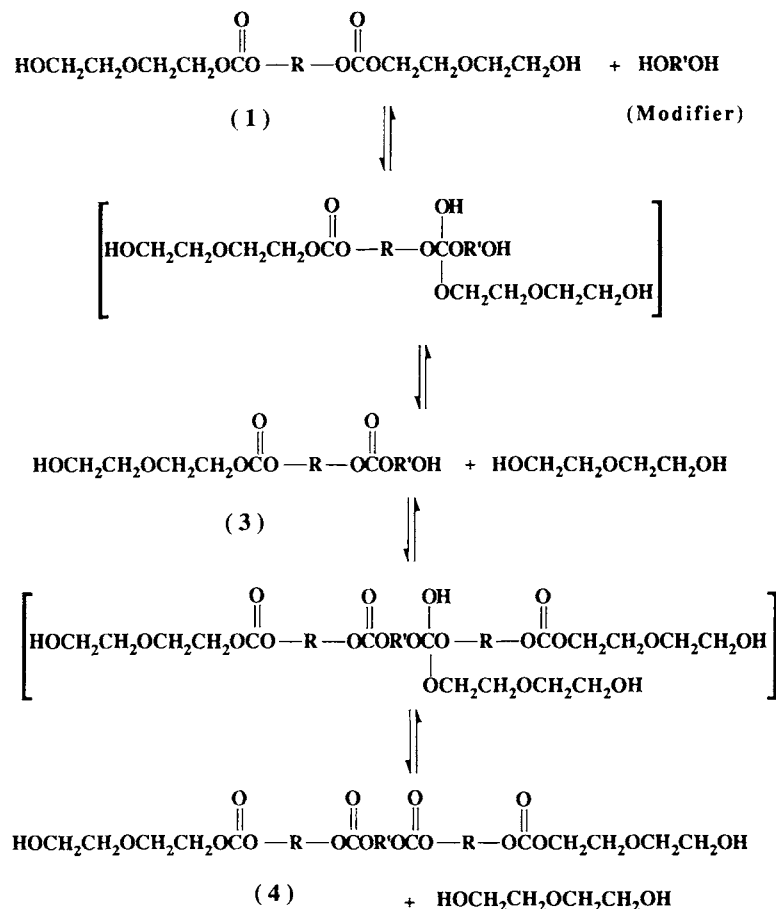
Figure 1   Proposed reaction pathway of modification process.

bonate) diol backbone. These equilibria reactions are controlled by using reaction conditions of elevated temperatures and reduced pressures where the DEG is removed as distillate as it forms. The relative amounts of (3) and (4) formed will depend on the ratio of the reactants and the relative reactivities of their hydroxyl end groups. Since the modified poly(ethylene ether carbonate) diol (4) contains hydroxyl end groups and carbonyl backbone moieties, it can continue this series of reactions to build even higher molecular weight products. As the molecular weight increases, the concentration of hydroxyl end groups decreases and higher temperatures (or reduced pressures) are required for further reaction at reasonable rates. A hydroxyl end group moiety can attack any carbonyl moiety in the backbone. This leads to a series of equilibria reactions in which only reactions at carbonyl moieties near the end of a molecule lead to molecular weight advancement by loss of DEG. However, transesterification can also occur, without release of volatile components, to equilibrate the modifier within the polymer backbone.[18,19]

A series of poly(propylene glycol) modified poly(ethylene ether carbonate) diols of about 2000 number-average molecular weight were prepared (Table I). The poly(propylene glycol) content and block length (molecular weights of 725, 425, and 192) were varied systematically.

Polymer Fabrication

Hand-cast plaques were made based on prepolymers with MDI, followed by chain extension with 1,4-butanediol.[8-10] The amount of poly(propylene glycol) modifier and its block length (molecular weight) in the soft segment were varied systematically. In several cases, different molecular weight poly(propylene glycols) were used at the same weight percent, so only block length was varied. The total soft segment block length, the hard segment block length, content, and structure were held constant. Identical procedures were used for plaque preparations and cures. Property differences should be a consequence of the amount of poly(propylene glycol) modifier and its block length in the soft segment.

The plaques prepared are described in Table II. All plaques were prepared using dibutyltin dilaurate (0.0019 wt %) as catalyst at an index of 1.03 (isocyanate–polyol equivalent ratio = 1.03:1) and a hard segment content of about 44 wt %. Size exclusion chromatography indicates that high-molecular-weight products were formed in all cases. Plaque molecular weight decreased with increasing amounts of poly(propylene glycol) modifier and was lowest for the 100% poly(propylene glycol) polymer. Plaque density decreased with increasing amounts of poly(propylene glycol) modification in the soft segment.

Polymer Structural Studies by NMR

The polyurethane elastomers were studied by nuclear magnetic resonance (NMR) for structure confirmation. The proton NMR spectrum of polyurethane elastomer IV-P, containing 49.1% P-725 in the soft segment of the polymer, is representative

Table I Properties of Poly(Propylene Glycol) Modified Polyols

Polyol Number	Modifier	wt % Modifier	Maximum Pot Temperature (°C)	Molecular Weight Data				CO_2 wt %	T_g (°C)
				Titration[a]	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$		
I	None	0	237	2330	2239	5114	2.28	30.0	−26
II	P-725	12.4	225	1840	1812	3787	2.09	26.5	−32
III	P-725	23.7	225	1977	1921	4555	2.37	23.7	−34
IV	P-725	49.1	225	2447	2413	5225	2.22	14.7	−45
V	P-725	72.1	216	1907	1904	4665	2.45	7.7	−57
VI	P-425	13.2	235	2075	2051	4495	2.19	26.2	−32
VII	P-425	25.2	235	2466	2317	5481	2.37	23.2	−34
VIII	P-425	51.2	235	2625	2545	5667	2.23	13.4	−41
IX	TPG	12.3	230	2050	2096	4628	2.21	25.0	−35
X	TPG	27.0	235	2596	2674	5924	2.22	20.4	−37

[a] By end group titration with phthalic anhydride in pyridine. P-725 and P-425 are poly(propylene glycols) of 725 and 425 molecular weight, respectively. TPG is tripropylene glycol.

Table II Description of Plaques Made Based on Poly(Propylene Glycol) Modified Polyols[a]

| Plaque Number	Modifier		% Isocyanate Content of Prepolymer	wt % Hard Segment	Plaque Density (g/cm^3)	CLTE[b] $\times 10^{-6}/°C$ $(25°)$	Molecular Weight Data		
							$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
I-P	None		9.90	43.5	1.27	188	141,500	230,100	1.63
II-P	12.4%	P-725	10.12	44.3	1.25	188	137,800	243,000	1.77
III-P	23.7%	P-725	9.99	43.4	1.25	185	126,800	264,300	2.09
IV-P	49.1%	P-725	10.48	43.6	1.20	177	86,500	172,900	2.00
V-P	72.1%	P-725	9.93	43.6	1.16	191	87,700	184,200	2.10
VI-P	13.2%	P-425	10.60	43.7	1.26	182	123,200	217,900	1.77
VII-P	25.2%	P-425	9.92	42.1	1.25	190	102,100	201,000	1.97
VIII-P	51.2%	P-425	10.45	42.4	1.21	199	75,800	136,500	1.80
IX-P	12.3%	TPG	10.03	43.5	1.26	183	112,000	186,200	1.66
X-P	27.0%	TPG	10.78	43.8	1.25	191	84,400	151,000	1.80
XI-P	100%	(V-2120)	10.00	43.6	1.12	199	49,800	89,140	1.79

[a] Dibutyltin dilaurate as catalyst (0.0019%), 1.03 index.
[b] Coefficient of linear thermal expansion.

and is given in Figure 2. The proton NMR structural assignments of the polyurethanes are given in Table III. Several of the structures are similar to structures previously described, making line assignments straightforward.[9,10] However, these structural features had not previously been described in the same molecule.

The ^{13}C-NMR spectrum of polyurethane elastomer IV-P is given in Figure 3. Since the carbonyl carbon region of the spectrum is quite complicated, this region was expanded. Figure 4 compares the carbonyl carbon lines for polyurethane elastomers III-P, IV-P, and V-P, which contain 72.1, 49.1, and 23.7% P-725, respectively, in the polymer soft segment. A five-line pattern was obtained, which corresponds to (a) the carbonate carbonyl carbon atoms in the soft segment attached to only methylene carbon atoms (154.6 ppm),[8-10,12] (b) the carbonate car-
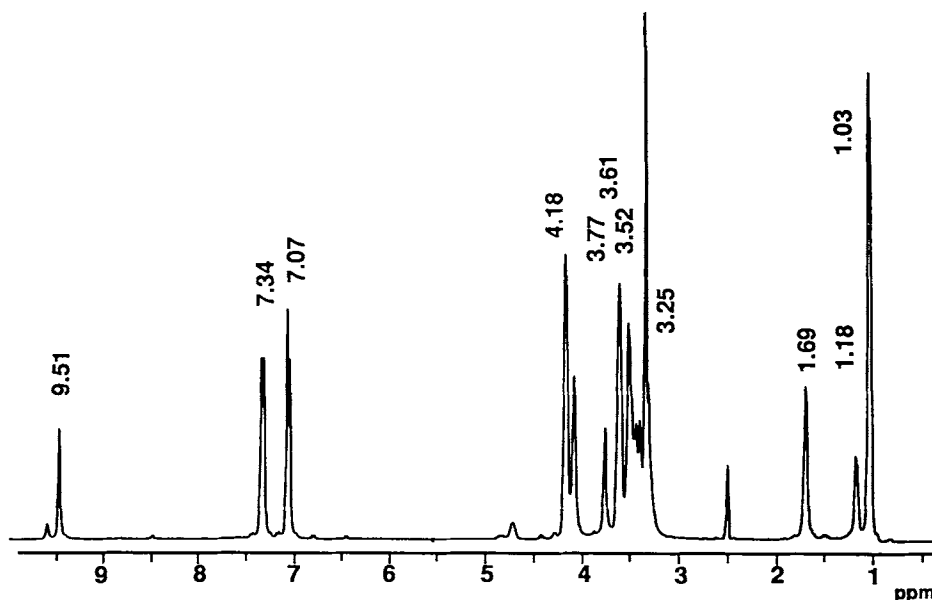
Figure 2 Proton NMR spectrum of polyurethane IV-P; 49.1% P-725 in the soft segment.

Table III   Proton NMR Structural Assignments of Polyurethanes

Chemical Shift[a] (ppm)	Structural Assignment
1.03	OCH(CH₃)CH₂O
1.18	C(O)OCH(CH₃)CH₂O
1.69	OCH₂CH₂CH₂CH₂O
3.25	OCH(CH₃)CH₂O
3.43	OCH(CH₃)CH₂O
3.52	OC(O)CH₂CH₂OCH₂
3.61	OC(O)CH₂CH₂OCH₂
3.77	ArCH₂Ar
4.09	OCH₂CH₂CH₂CH₂O
4.18	CH₂OCH₂CH₂OCH₂
7.07	Protons on aromatic carbon atoms
7.34	Protons on aromatic carbon atoms
9.51	Protons on urethane nitrogen atoms

[a] ppm from tetramethylsilane (TMS = 0); DMSO-d_6 as solvent.

bonyl carbon atoms in the soft segment attached to both methylene carbon atoms and methine carbon atoms (154.2 ppm),[12] (c) the urethane carbonyl carbon atoms in the hard segment formed by the reaction of MDI with 1,4-butanediol (153.6 ppm),[8,10] (d) the urethane carbonyl carbon atoms at the hard segment–soft segment interface formed by the reaction of MDI with primary hydroxyl moieties (153.4 ppm),[8,10] and (e) the urethane carbonyl car-

bon atoms at the hard segment–soft segment interface formed by the reaction of MDI with secondary hydroxyl moieties (153.1 ppm). The variations in line height as a function of composition further substantiate the line assignments.

Three different kinds of methyl carbon atoms are present in the polyurethane elastomers (Fig. 5). Large spectral lines (17.1/17.2 ppm) correspond to methyl groups in the poly(propyleneoxy) backbone.[12] Methyl groups on the methine carbon atoms attached to carbonate moieties[12] and to urethane moieties give lines at 16.3 and 16.9 ppm, respectively. The ¹³C-NMR structural assignments for all of the lines in the polyurethane spectra are given in Table IV.

Physical Properties

Several physical properties of the fabricated plaques are given in Table V. All plaques passed the notched Izod test. The tensile modulus values were unexpected (Fig. 6). Tensile modulus increased with increasing weight percent P-725 in the soft segment up to the plaque containing 23.7 wt %. Then, the tensile modulus decreased with further weight percent incorporation of P-725. The same trend occurred with the plaques containing P-425 and TPG in the soft segment. In the P-425 series, the tensile modulus was highest for the plaque containing 25.2 wt % P-425 in the soft segment; the plaque containing 51.2 wt % P-425 was markedly lower. In the TPG series, the tensile modulus was highest for the
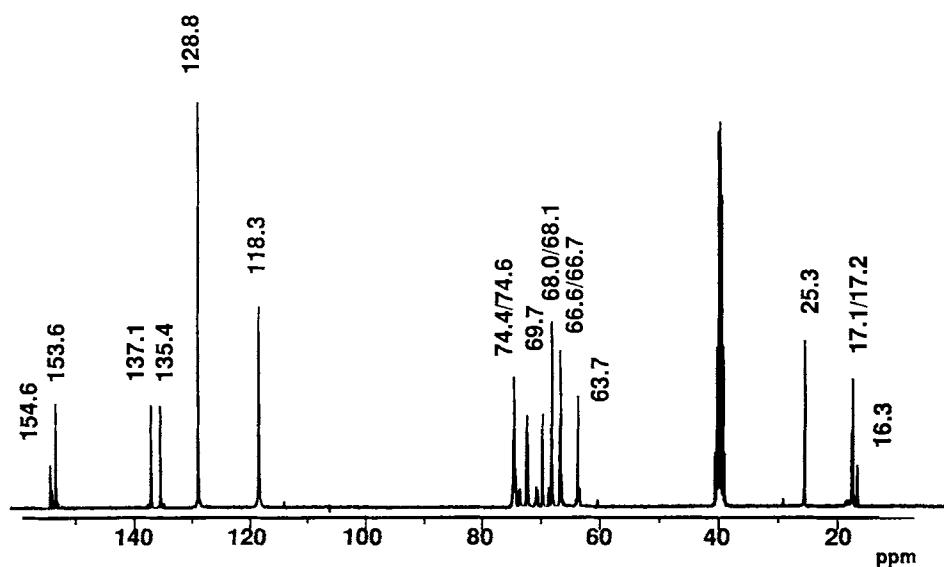
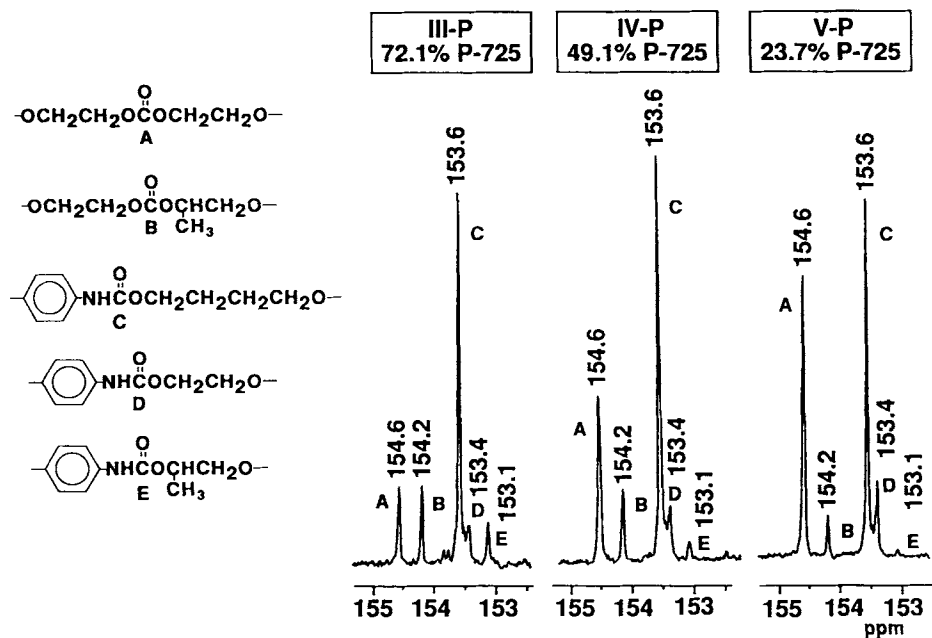**Figure 3**   ¹³C-NMR spectrum of polyurethane IV-P; 49.1% P-725 in the soft segment.

Figure 4   Structural assignments of carbonyl carbon atoms in ^{13}C-NMR spectra.

plaque containing 27.0 wt % TPG. Higher amounts of TPG were not possible in a 2000 molecular weight diol.

Not only was there a maximum in each tensile modulus versus weight percent modifier in the soft segment plot at about 25 wt % modifier, the magnitude of the effect increased with decreasing

block size: 12700, 15300, and 16100 psi at 725, 425, and 192 number-average molecular weight poly-(propylene glycol) blocks in the soft segment, respectively. This effect might be due to a specific kind of phase mixing when poly(propylene oxide) blocks are present. These poly(propylene glycol) modified poly(ethylene ether carbonate) diols produce
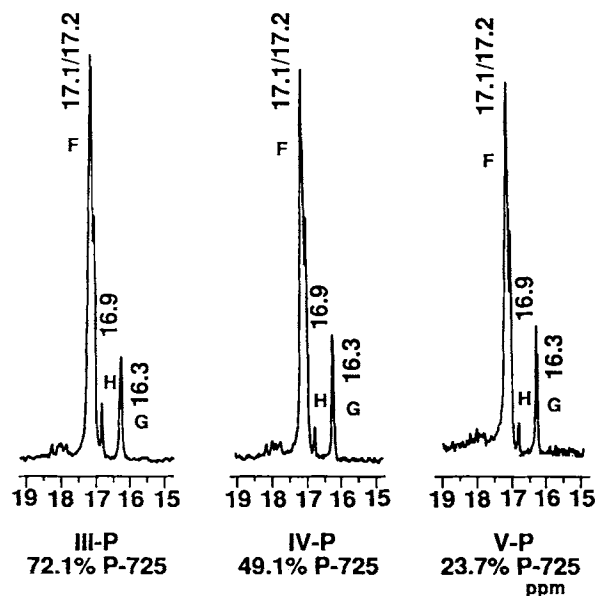

Figure 5   Structural assignments of methyl carbon atoms in ^{13}C-NMR spectra.

Table IV ^{13}C-NMR Structural Assignments of Polyurethanes

Chemical Shift[a] (ppm)	Structural Assignment
154.6	CH$_2$OC(O)OCH$_2$
154.2	CH$_2$OC(O)OCH(CH$_3$)CH$_2$O
153.6	ArNHC(O)OCH$_2$CH$_2$CH$_2$CH$_2$O
153.4	ArNHC(O)OCH$_2$CH$_2$O
153.1	ArNHC(O)OCH(CH$_3$)CH$_2$O
137.1	Aromatic carbon (1) attached to methylene
135.4	Aromatic carbon (4) attached to urethane
128.8	Aromatic carbon (2)
118.3	Aromatic carbon (3)
74.4/74.6	CH(CH$_3$)OCH$_2$CH(CH$_3$)OCH$_2$
74.1/74.2	CH(CH$_3$)OCH$_2$CH(CH$_3$)OC(O)O
73.5/73.7	CH(CH$_3$)OCH$_2$CH(CH$_3$)OC(O)NHAr
72.2/72.4	CH(CH$_3$)OCH$_2$CH(CH$_3$)OCH$_2$
70.5/70.7	CH(CH$_3$)OCH$_2$CH(CH$_3$)OC(O)O
69.7	CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$
68.6	CH(CH$_3$)OCH$_2$CH(CH$_3$)OC(O)NHAr
68.0/68.1	OC(O)OCH$_2$CH$_2$OCH$_2$
66.6/66.7	OC(O)OCH$_2$CH$_2$OCH$_2$
66.4/66.5	CH$_2$OC(O)OCH$_2$CH$_2$OCH$_2$CH$_2$OC(O)NHAr
63.7	ArNHC(O)OCH$_2$CH$_2$CH$_2$CH$_2$OC(O)NHAr
63.3/63.4	ArNHC(O)OCH$_2$CH$_2$O
39.9	ArCH$_2$Ar
25.3	ArNHC(O)OCH$_2$CH$_2$CH$_2$CH$_2$OC(O)NHAr
17.1/17.2	OCH(CH$_3$)CH$_2$O
16.9	NHC(O)OCH(CH$_3$)CH$_2$O
16.3	OC(O)OCH(CH$_3$)CH$_2$O

[a] ppm from tetramethylsilane (TMS = 0); DMSO-d_6 as solvent.

plaques with improved tensile strengths relative to both the unmodified poly(ethylene ether carbonate) diol and poly(propylene glycol) controls.

A similar trend was observed in the tensile strength versus elongation data (Fig. 7). In the P-725 series, the tensile strengths at 100, 200, and 300 % elongation each obtained a maximum value for the plaque containing 23.7 wt % poly(propylene glycol) in the soft segment. The tensile strength at break was highest for the plaque containing 12.4 wt % poly(propylene glycol) in the soft segment. These poly(propylene glycol) modified poly(ethylene ether carbonate) diols produced plaques with improved elongation properties relative to both the unmodified poly(ethylene ether carbonate) diol and poly-(propylene glycol) controls.

Plaques based on poly(ethylene ether carbonate) diols (carbonate ester backbone) are significantly harder than plaques based on poly(propylene glycols) (polyether backbone). When the soft segment was modified with poly(propylene glycols), there was a small enhancement in hardness at small modification levels, followed by a systematic reduction in hardness as poly(propylene glycol) modification was increased (Fig. 8).

Poly(ethylene ether carbonate) polyols produce polyurethanes with excellent organic solvent resistance when compared to polyurethanes based on polyester polyols. Polyether polyols give polyurethanes with much poorer organic solvent resistance than polyester polyol based polyurethanes. When poly(propylene glycols) are used to modify poly(ethylene ether carbonate) diols, the resultant

Table V Physical Properties of Plaques Made Based on Poly(Propylene Glycol) Modified Polyols

| Plaque Number	Modifier		Tensile Modulus (psi)	Tensile Strength at % Elongation				Elongation at Break (%)	Hardness (Shore D)	Notched Izod (ft lb/in.)
				100%	200%	300%	at Break			
I-P	None		9300	1355	1620	1835	2480	560	50	NB
II-P	12.4%	P-725	11,000	1630	1890	2070	3000	590	54	NB
III-P	23.7%	P-725	12,700	1890	2090	2300	2740	580	51	NB
IV-P	49.1%	P-725	12,100	1600	1820	1970	2600	330	50	NB
V-P	72.1%	P-725	8780	1340	1600	1780	2400	700	45	NB
VI-P	13.2%	P-425	12,500	1570	1745	1935	2340	575	52	NB
VII-P	25.2%	P-425	15,300	1500	1745	2010	2320	595	50	NB
VIII-P	51.2%	P-425	11,700	1375	1600	—	1620	220	46	NB
IX-P	12.3%	TPG	13,000	1210	1455	1655	2515	770	52	NB
X-P	27.0%	TPG	16,100	1780	1925	—	2000	200	54	NB
XI-P	100%	(V-2120)	8000	980	1270	1530	2260	580	40	NB

NB = no break.
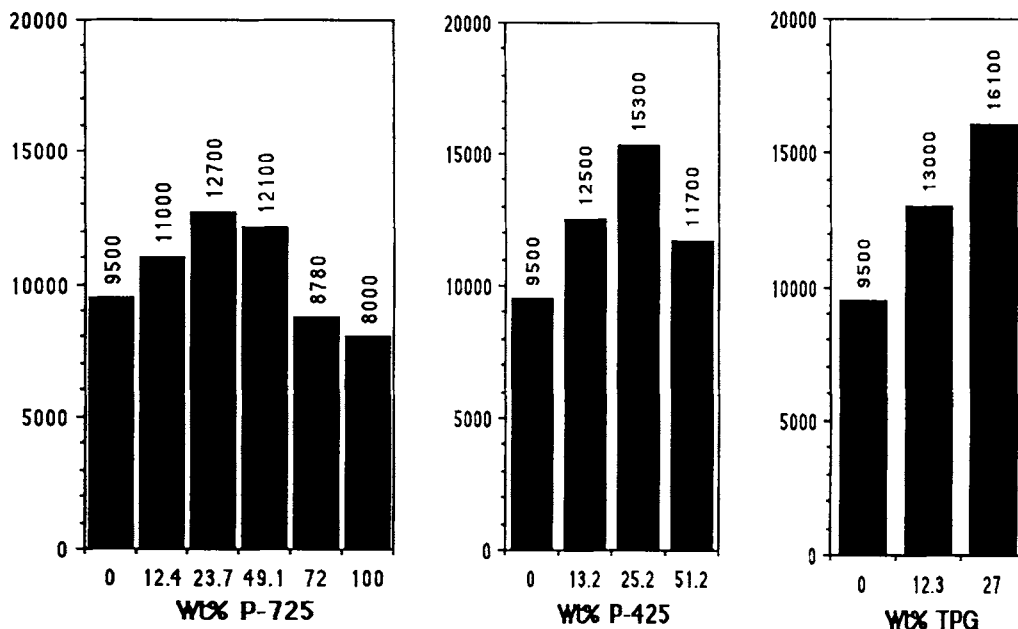
Figure 6 Effect of weight percent modifier in the soft segment on tensile modulus of polyurethane plaques.

plaques had poorer organic solvent resistance as the amount of poly(propylene glycol) in the soft segment was increased. However, this was not a linear relationship (Table VI). The data are plotted in Figure 9 and show that poly(propylene glycol) levels of 25–50 wt % can be used before substantial loss in solvent resistance is experienced.

Thermal Properties

Figure 10 shows a series of DSC scans that compare different soft segment modifiers at the same concentration (essentially 25 wt % modification) to end points with 0 and 100% modification levels. All the scans show a subambient T_g and an endotherm due
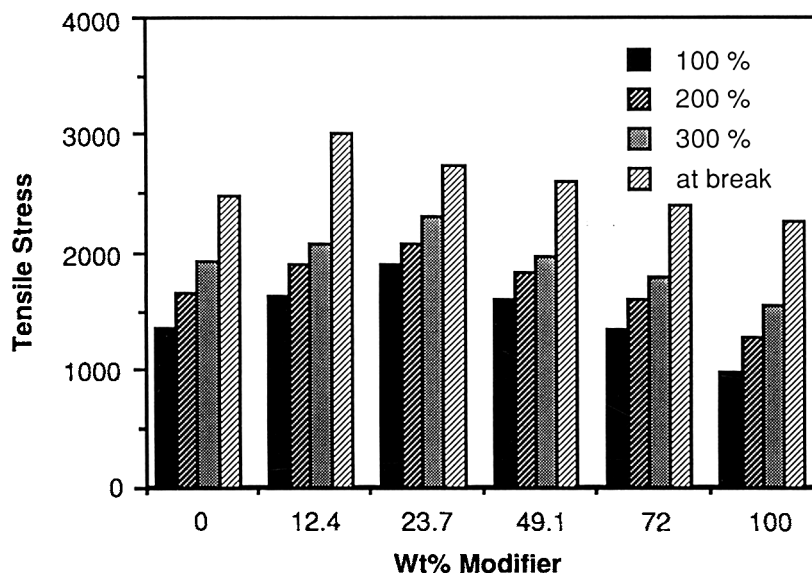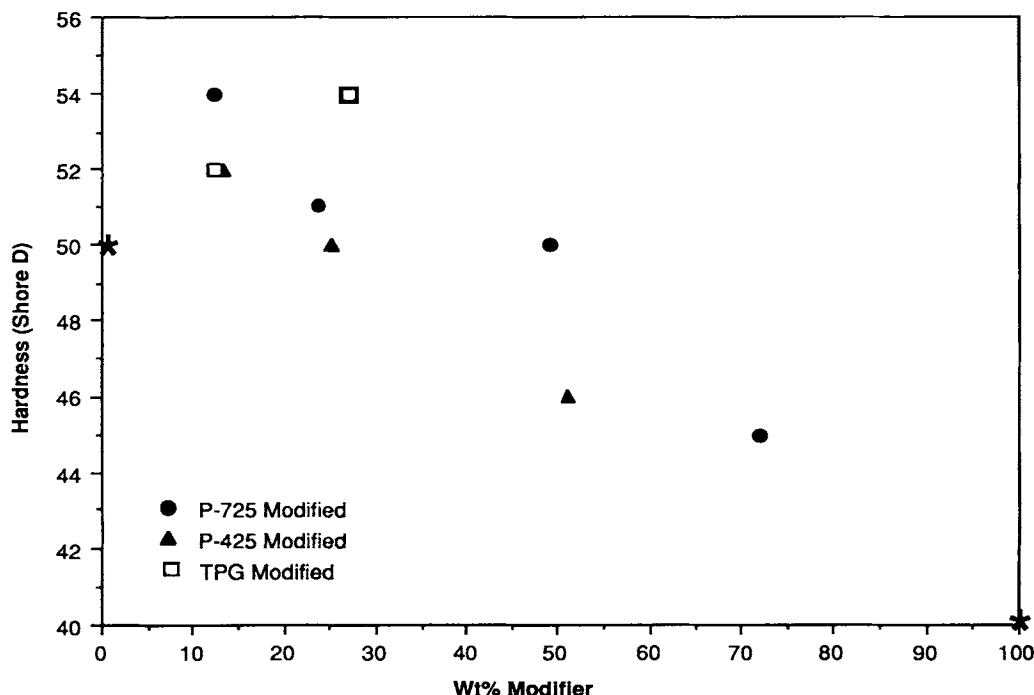

Figure 7 Effect of weight percent modifier in the soft segment on tensile strength at elongation of polyurethane plaques.

Figure 8   Effect of weight percent modifier in the soft segment on shore D hardness of polyurethane plaques.

to the hard segment melt. It is helpful at this point to keep in mind that at a given modifier concentration, there will be a different number of modifier blocks along the soft segment's backbone depending on the modifier's block length. The scans for samples III-P, VII-P, and X-P show virtually identical thermal characteristics by DSC analysis, indicating similar morphological properties. Since the concen-

tration of modifier in these samples was kept constant, the only variables were the block length of the modifier and the number of these blocks along the polymer backbone. These scans would then indicate that the combination of modifier block length and number of blocks has little effect on polymer morphology at this modifier concentration.

In Figure 11 and Table VII data are presented for

**Table VI   Effect of Poly(Proplyene Glycol) Modifier in Soft Segment on Solvent Resistance**

Plaque Number	Soft Segment Modifier		Solvent Resistance (% Weight Gain after 6 Days at 25°C)			
			Water	Methanol	Toluene	MEK
I-P	None		4.6	11.7	11.7	30.3
II-P	12.4%	P-725	4.0	12.2	17.9	37.0
III-P	23.7%	P-725	1.9	12.6	20.4	43.1
IV-P	49.1%	P-725	1.9	19.2	35.2	58.1
V-P	72.1%	P-725	1.9	27.3	51.6	100.0
VI-P	13.2%	P-425	4.4	12.3	16.6	35.6
VII-P	25.2%	P-425	1.9	12.4	20.8	51.2
VIII-P	51.2%	P-425	2.0	18.9	37.3	100.5
IX-P	12.3%	TPG	4.4	11.7	18.6	37.8
X-P	27.0%	TPG	1.9	14.4	19.3	42.5
XI-P	100%	(V-2120)	2.2	43.2	79.9	149.2
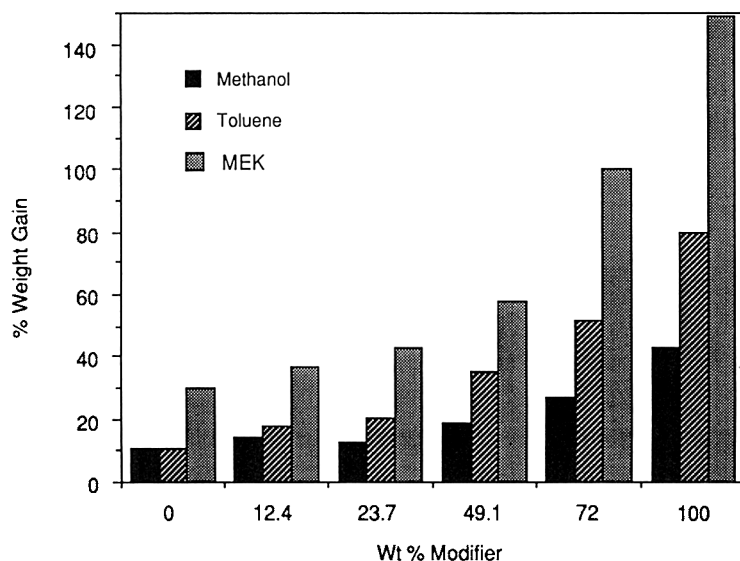
Figure 9   Effect of weight percent P-725 modifier in the soft segment on organic solvent resistance of polyurethane plaques.

a series of DSC scans comparing different concentrations of the P-725 modifier and the effect on morphology. As the poly(propylene oxide) character of the soft segment is increased, the soft segment T_g increases from $-20°C$, showing a maximum at $-13°C$ (25% P-725 level), and then starts decreasing

to a minimum of $-33°C$ (Fig. 12). When looking at the shape of the hard segment melt endotherm, one sees that as the poly(propylene oxide) character of the soft segment is increased, the broad, shallow shape, and temperature of the 100% modified soft segment endotherm is systematically approached.
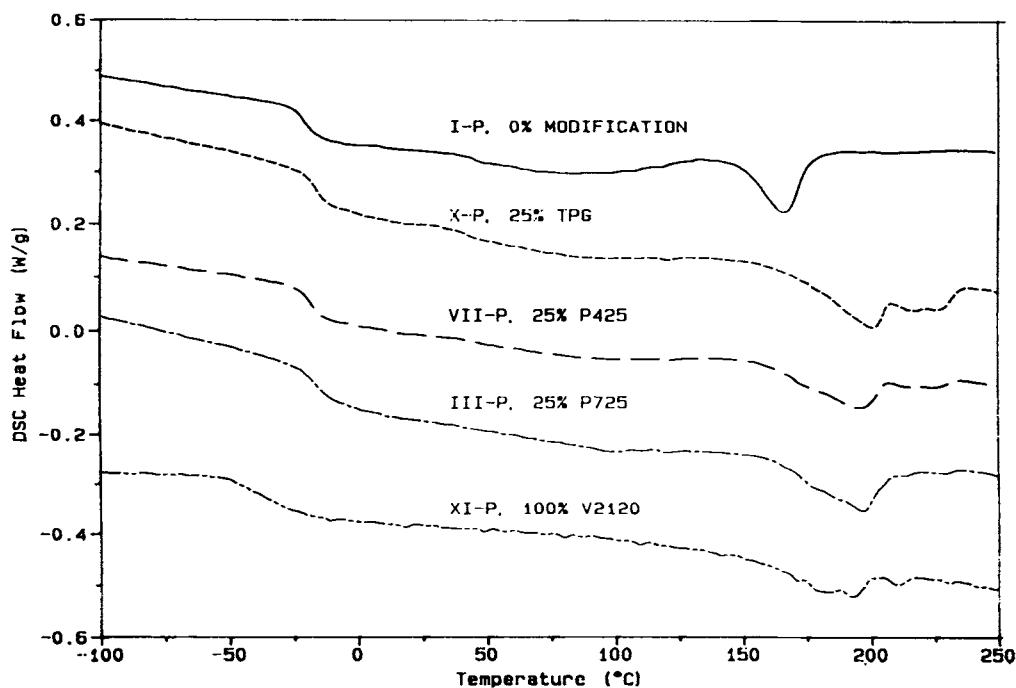
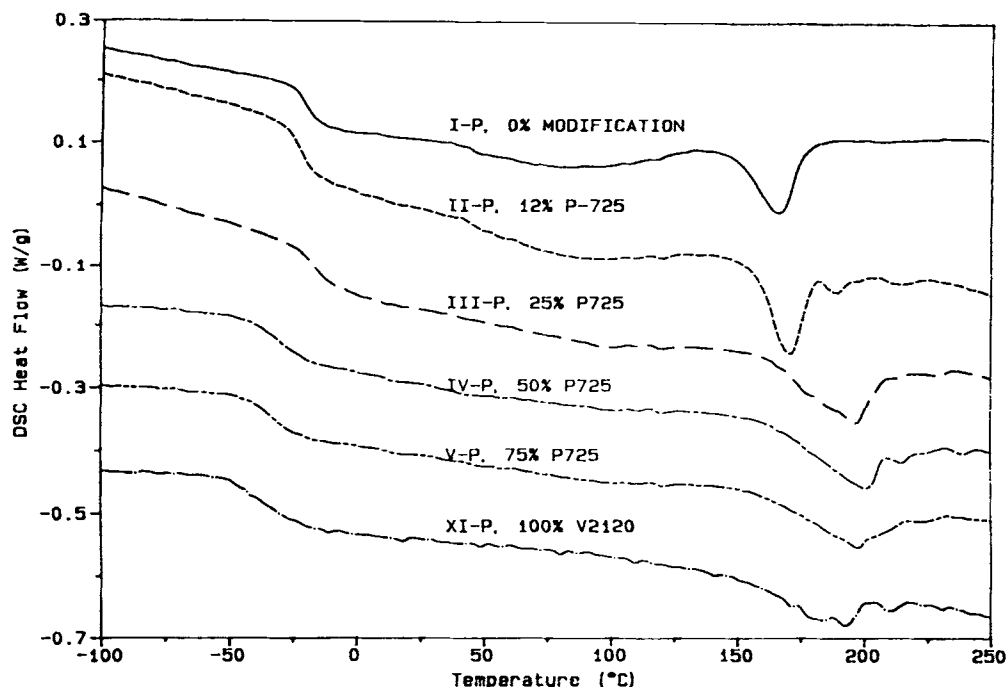**Figure 10**   DSC thermograms for 25% modification level of the soft segments.

Figure 11 DSC thermograms for P-725 modified soft segment polymers.

The percent crystallinity is quite low (2–3%) for all of the polymers based on poly(propylene glycol) modified diols.

Flexural storage moduli as a function of temperature for the P-725 modified plaques and the 0 and 100% end points, as determined by DMA, are plotted in Figure 13. Flexural loss moduli as a function of temperature for the same P-725 modified plaques are plotted in Figure 14. The 0 and 100% modified samples show a lower plateau modulus and lower hard segment thermal dissociation temperature (Fig. 15) than the P-725 modified samples. This synergistic effect on modulus is thought to be a result of the $(A\{BC\}_m)_n$ type of structure (see Polymer Morphology section). This same type of effect is

seen with the coefficient of linear thermal expansion (CLTE) data (Fig. 16), but the peak appears at the 50% P-725 modification level as opposed to 12% for the 25°C flexural storage modulus values (Table II).

Polymer Morphology

In general, polyurethane elastomers are block copolymers of $(AB)_n$ molecular structure, where A represents the hard segment blocks and B represents the soft segment blocks. The soft segment provides flexibility in the polymer and is generally the continuous phase, while the hard segment blocks provide physical crosslinks by molecular association through hydrogen bonding. The structure, concen-

Table VII   Summary of DSC and WAXS Data for Polyurethanes Made from P-725 Modified Polyols

| P-725 in Diol (wt %)	CO₂ in Diol (wt %)	T_g by DSC (°C)	T_g Width (°C)	T_m (°C)	ΔHm (J/g)	WAXS (% Crystallinity)
0	30.0	−20	30.4	166	12.0	9.2
12.4	26.5	−18	39.3	170	17.8	1.8
23.7	23.7	−13	55.4	196	17.7	2.5
49.1	14.7	−30	37.5	199	16.6	2.1
72.1	7.7	−31	34.8	196	13.4	2.6
100	0	−33	48.0	192	11.5	2.1
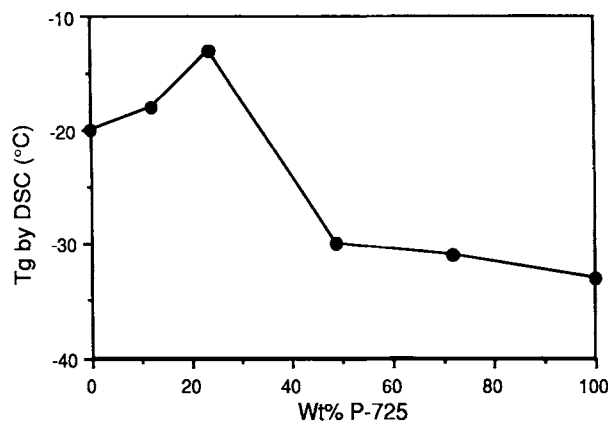
Figure 12 Effect of weight percent P-725 modifier in the soft segment on glass transition temperature of polyurethane plaques.

tration, and organization of the soft segment blocks have a large influence on the physical and mechanical properties of the polymer. The degree of phase separation between the hard segment and soft segment blocks, as well as the types of soft segment–soft segment and soft segment–hard segment interactions, influence polymer properties significantly.

The soft segment blocks used in this study are themselves a type of block copolymer, made of poly(ethylene ether carbonate) and poly(propylene oxide) blocks, which in effect gives an $(A\{BC\}_m)_n$ type of block copolymer. This linear, three-block copolymer shows some interesting physical properties as a result of the varied types of morphologies possible.

The morphology of these modified polymers appears to be quite complex, as expected due to the block copolymer nature of the soft segments. The fact that many thermal and physical properties of these polymers show a maximum in behavior when the modifier content of the soft segment is increased in a systematic manner was unexpected. The basis for these maxima in property values at about a 25% modification level may revolve around the immiscibility of poly(ethylene ether carbonate) polyols and poly(propylene glycols). Neat mixtures of these two types of polyols are immiscible.[12] However, their block copolymers are single-phase materials in all proportions studied.[12] By carrying this tendency toward immiscibility through to the soft segment of the polymer, we can try to explain some of the properties observed.
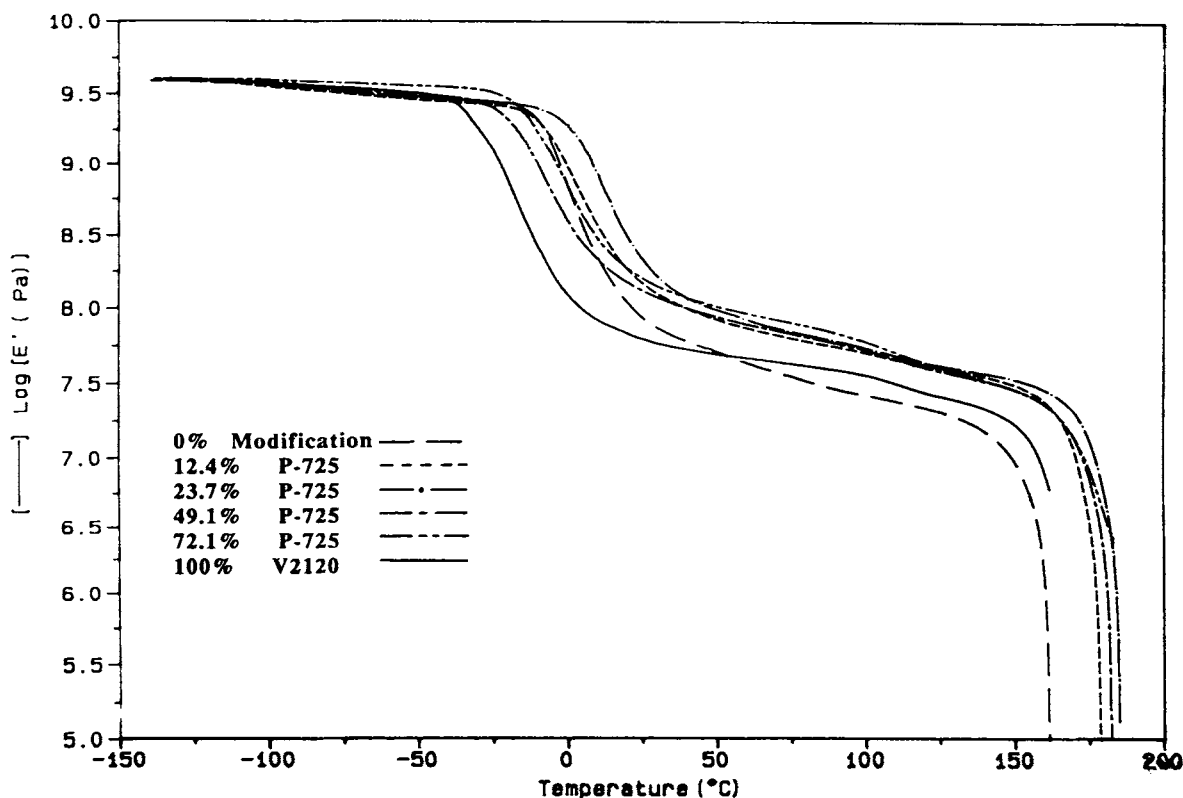
Figure 13 Flexural storage modulus vs. temperature for P-725 modified soft segment polymers.
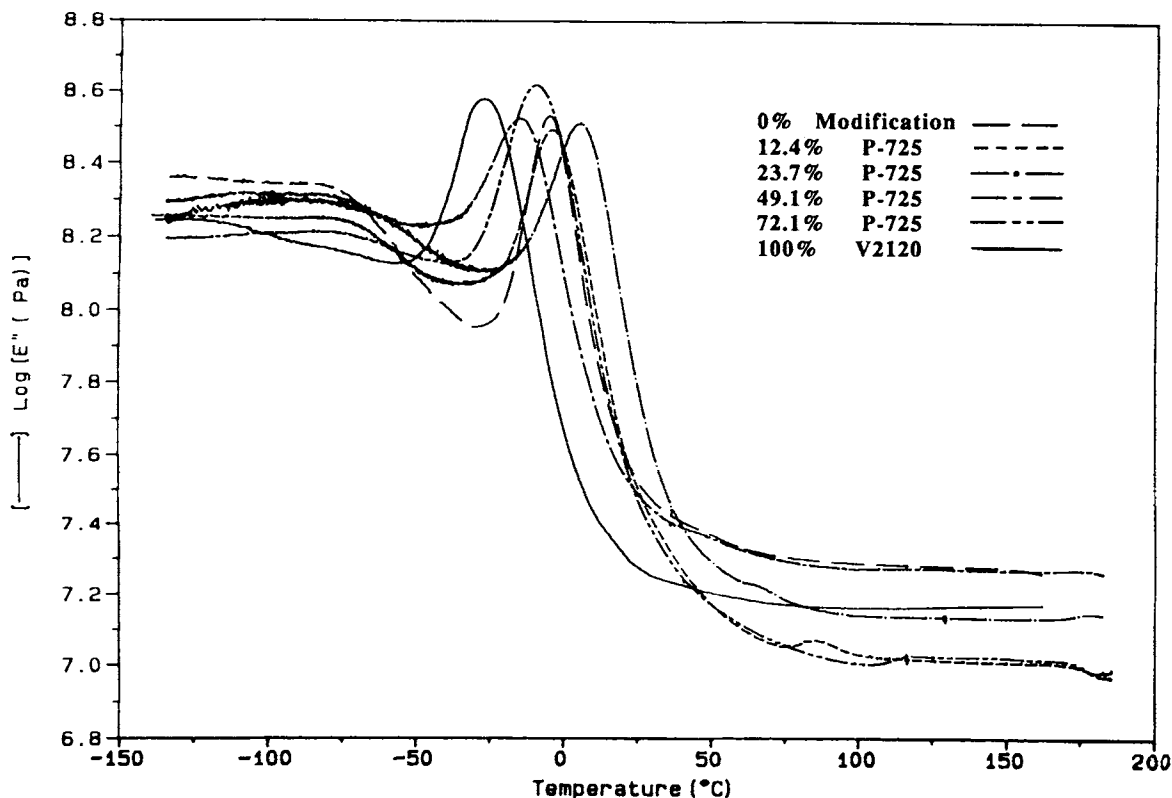
Figure 14 Flexural loss modulus vs. temperature for P-725 modified soft segment polymers.

In these polymers the soft segment is the continuous phase. Since the modified soft segment is a block copolymer made of two blocks with a tendency toward immiscibility, we might expect to get some micro phase separation within the soft segment domains of the polymer and the introduction of a phase

continuity variable within the soft segment domain. At 0 wt % modification, we have an unmodified poly(ethylene ether carbonate) polyol that forms the continuous phase and can interact with itself and the hard segment blocks. Previous work[8,9] has shown that this polyol can have strong hydrogen
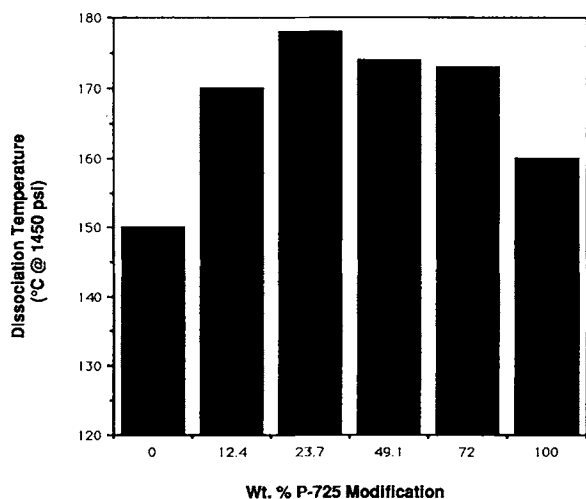

Figure 15 Effect of wt % P-725 modifier in the soft segment on dissociation temperature.
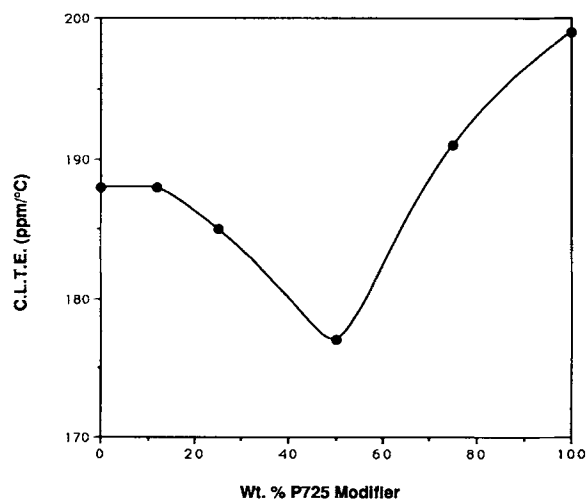

Figure 16 CLTE vs. wt % P-725 modifier in the soft segment.

bonding interactions with itself and the hard segment leading to phase mixing.

In the case of the P-725 modified soft segment, as we put in a small amount of poly(propylene oxide) modifier, the soft segment T_g begins to increase in temperature and the size of the melt endotherm begins to increase. One could hypothesize that this is due to the poly(ethylene ether carbonate) blocks decreasing their amount of interaction with the highly amorphous hard segment in favor of inter- and intramolecular interactions with the poly(propylene oxide) modifier along its backbone, causing the T_g to increase as a result of micro phase mixing within the continuous soft segment phase of the polymer. As the amount of poly(propylene oxide) modifier is increased to 25%, the above-mentioned effect becomes more pronounced.

The peaking behavior seen in the modulus, T_g, and CLTE data could then be a result of the poly(propylene oxide) modifier reaching a high enough concentration that it then becomes the dominant continuous phase within the polymer. At this point the, the T_g begins to decrease again and the polymer starts to assume the characteristics of the 100% poly(propylene oxide) soft segment polymer.

CONCLUSIONS

A series of polyurethane elastomers have been prepared and characterized based on poly(propylene glycol) modified poly(ethylene ether carbonate) polyols. The poly(propylene glycol) content and block length (number-average molecular weights of 725, 425, and 192) were varied systematically in the 2000 number-average molecular weight diol. These polyurethane elastomers have a $(A\{BC\}_m)_n$ type of structure. Chemical structure of the polyurethane elastomers was established by proton and ^{13}C-NMR spectroscopy.

Several properties showed a marked dependence on modifier level and exhibited synergistic property improvements at 25–50 wt % modifier. Plots of tensile modulus versus weight percent modifier in the soft segment exhibited maximum values at about 25 wt % modifier, the magnitude of the effect increased with decreasing block size. A similar trend was observed in tensile strength versus elongation. These poly(propylene glycol) modified diols produced plaques with improved tensile strengths relative to both unmodified poly(ethylene ether carbonate) diol

and poly(propylene glycol) controls. DMA results indicated an increased modulus for the poly(propylene glycol) modified plaques throughout the rubbery plateau region, relative to unmodified controls, with higher thermal dissociation temperatures. The excellent organic solvent resistance of poly(ethylene ether carbonate) polyol-produced polyurethanes was maintained with 25–50 wt % poly(propylene glycol) incorporation in the soft segment. The CLTE values are lowest at about 50 wt % incorporation of poly(propylene glycol).

The morphology of these modified polyurethanes appeared to be quite complex. Since the modified soft segments are block copolymers of two blocks with a tendency toward immiscibility, some microphase separation within the soft segment domains of the polymers might be expected. The soft segment T_g is highest where properties are maximized, suggesting changes in phase mixing.

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. Prepri. (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. Prepri. (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. R. F. Harris, M. D. Joseph, C. Davidson, and C. D. DePorter, *J. Appl. Polym. Sci.*, **42**, 3241 (1991).
11. R. F. Harris, U.S. Pat. 4,861,909 (1989).
12. R. F. Harris, *J. Appl. Polym. Sci.*, **41**, 1937 (1990).
13. R. F. Harris, U.S. Pat. 4,686,273 (1987).
14. R. F. Harris, U.S. Pat. 4,795,810 (1989).
15. R. F. Harris, U.S. Pat. 4,948,862 (1990).
16. M. O. Myers, U.S. Pat. 4,686,276 (1986).
17. D. G. Prior, U.S. Pat. 4,528,364 (1985).
18. R. F. Harris and D. G. Prior, U.S. Pat. 4,686,274 (1987).
19. R. F. Harris, *J. Appl. Polym. Sci.*, **44**, 605 (1992).