

Polyurethane Elastomers Based on Molecular Weight Advanced Poly(ethylene Ether Carbonate) Diols. I. Comparison to Commercial Diols

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Synopsis

Poly(ethylene ether carbonate) diols (2025 mol wt) have been made by the molecular weight advancement of lower molecular weight oligomers and have been fabricated into polyurethane elastomers by reaction with 4,4'-MDI and 1,4-butanediol using the prepolymer method. Polymer structure has been delineated by carbon-13 NMR. Comparisons have been made to a series of elastomers based on other polyester and polyether polyols (2000 mol wt) under conditions where the only variable was the soft segment structure. 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. This lower ΔH_m leads to a significantly lower rubbery plateau modulus than the other polyester polyols. Phase mixing is increased by post-curing at 150°C. Organic solvent resistance is the most outstanding property. The poly(ethylene ether carbonate) diol produces a polymer with predominantly polyester polyol features.

INTRODUCTION

The structure of poly(ethylene ether carbonate) polyols has recently been delineated in sufficient detail to permit detailed understanding of their reactions under various conditions.^{1,2} When poly(ethylene ether carbonate) polyols are heated to elevated temperatures (> 180°C) at reduced pressures, molecular weight advancement occurs with the formation of diethylene glycol (DEG) and triethylene glycol (TriEG). As DEG and TriEG are removed as distillate, molecular weight builds in a controllable manner.³⁻⁶ These advanced polyols form rapidly with high CO₂ retention, relatively low polydispersity, and high purity.

This work examines the advancement of poly(ethylene ether carbonate) diols prepared by the monoethylene glycol initiated oligomerization of ethylene oxide and carbon dioxide. These molecular weight advanced poly(ethylene ether carbonate) diols are converted to isocyanate functional prepolymers and chain extended with 1,4-butanediol to form polyurethane elastomers. Their thermal and mechanical properties and morphologies are com-

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pared to similar elastomers made from commercial polyester and poly ether diols.

EXPERIMENTAL

Starting Materials

Monoethylene glycol (MEG), diethylene glycol (DEG), triethylene glycol (TriEG), tetraethylene glycol (TetraEG), ethylene oxide, Voranol 2120 brand poly(propylene glycol) [a 2000 molecular weight poly(propylene glycol)], B-2000 [a 2000 molecular weight poly(1,2-butylene glycol)], and Isonate 125M brand MDI [4,4'-methylene-di(phenylisocyanate)] were manufactured by The Dow Chemical Company. Tone 2000 is a 2000 molecular weight poly(caprolactone) diol manufactured by Union Carbide Corporation. Formrez 11-56 is a 2000 molecular weight diethylene glycol adipate manufactured by Witco Chemical Company. Terathane 2000 is a 2000 molecular weight poly(tetramethylene glycol) manufactured by DuPont. 1,4-Butanediol and 1,6-hexanediol were obtained from Aldrich Chemical Company.

Polyol 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

Carbon-13 NMR

Spectra were obtained on a Varian Gemini 300 NMR (75 MHz for carbon) using DMSO-*d*₆ as solvent.

Molecular Weight Determination

Molecular weight of the polyols (0.5 wt % in THF) was done by size exclusion chromatography (SEC) on Waters Ultrastayragel 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 glycols) and using a refractive index detector. Molecular weight of the polymers (0.25 wt % in DMF) was done by SEC on Waters Ultrastayragel 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.

Molecular Weight Advancement Procedure

Low molecular weight feed was synthesized by the monoethylene glycol initiated oligomerization of ethylene oxide and carbon dioxide⁷; catalyst was removed.^{6,8} The characteristics of the two batches of materials used as feed for the advancement process follow:

	CO ₂ (wt %)	Molecular weight data			Brookfield viscosity (cps, 24°C)	
		Peak	\bar{M}_n	\bar{M}_w		\bar{M}_w/\bar{M}_n
Feed 1	21.4	1100	779	1291	1.66	2490
Feed 2	20.2	1037	810	1383	1.71	3150

A given feed 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 (1000 g) 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.

Polymer Fabrication Procedure

A poly(ethylene ether carbonate) diol was placed in a reaction kettle (500 mL) equipped with an air stirrer, thermometer, septum port, vacuum inlet, temperature controller, and maintained under a nitrogen cover. The temperature was adjusted to 55°C and freshly distilled MDI was added by syringe. The temperature was raised to 80°C and maintained for 1 h. The isocyanate content was measured by reacting weighed samples with excess di-*n*-butylamine in toluene, digesting 10 min, and titrating with HCl (ASTM D-1638-74). The kettle was evacuated to about 1 mm Hg to degas the prepolymer. The degassed prepolymer (at 70°C) was quickly poured into a plastic cup and weighed. Catalyst [1 drop of a 15% dibutyltin dilaurate solution in a 2000 molecular weight poly(propylene glycol); 0.00192 wt % based on solids] and 1,4-butanediol (freshly distilled from calcium hydride, stored under nitrogen in silanized bottles, and degassed) were quickly added to give the required index (NCO : OH equivalent ratio; 1.03 for most experiments). The mixture was rapidly mixed without air entrainment (25–35 s), poured into 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

All plaques were aged at ambient temperature for 2 weeks prior to property measurements. All 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. Subambient work was done using a liquid nitrogen quench cooling cup. All 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. A length to thickness ratio of > 10 was used in order to negate the DMA's dependence on Poisson's ratio. Subambient work was done using a software programmable liquid nitrogen cooling accessory. The DSC and DMA modules were interfaced with a DuPont 9900 Thermal Analyzer for data reduction and analysis. Physical properties were measured using standard procedures: Shore A and Shore D hardness, ASTM E-140; flexural modulus, ASTM D-790; tensile properties, ASTM D-

638; notched Izod, ASTM D-256. Solvent resistance was measured at ambient temperature by a static soak test until solvent uptake reached equilibrium (6 days).

RESULTS AND DISCUSSION

Synthesis of Poly(ethylene Ether Carbonate) Diols

While previous articles in this series¹⁻⁶ have dealt with poly(ethylene ether carbonate) polyols derived from the glycol initiated oligomerization of ethylene carbonate, the poly(ethylene ether carbonate) polyols used in this work were made by the more economical route of the glycol initiated oligomerization of ethylene oxide and carbon dioxide.⁷ A series of experiments (1-kg scale) were carried out to make a quantity of molecular weight advanced poly(ethylene ether carbonate) polyol ($\bar{M}_n = 2000$) for polyurethane synthesis and at the same time to further study the molecular weight advancement process. Five batches of advanced polyols were prepared from low molecular weight feed by heating at 10 mm Hg vacuum with volatiles removal to pot temperatures between 225 and 235°C. Properties of these advanced poly(ethylene ether carbonate) diols are given in Table I. The number average molecular weight is approximately a linear function of pot temperature at the heat input and temperature range studied (Fig. 1). The advanced polyols have a higher CO₂ content than the feed due to a concentration effect. Brookfield viscosity has increased considerably over that of the feed due to molecular weight build. The five polyol batches were combined for use in the polyurethane elastomer fabrication. Diethylene glycol and triethylene glycol are the major products in the distillate (see Table II).

Polymer Fabrication

Hand-cast plaques were made using the prepolymer method. In the first step, isocyanate functional prepolymers were prepared using freshly distilled Isonate 125M and the molecular weight advanced poly(ethylene ether carbonate) diol. The degassed prepolymer was then chain extended with 1,4-butanediol, placed in a preheated mold, and cured for 1 h at 121°C (250°F). The first problem encountered was instability of the isocyanate functional prepolymers. Therefore,

TABLE I
Characteristics of Advanced Poly(Ethylene Ether Carbonate) Diols

Polyol number	Feed	Pot temp. (°C)	CO ₂ (wt %)	Molecular weight data			Viscosity (cps, 25°C)	
				Peak	\bar{M}_n	\bar{M}_w		\bar{M}_w/\bar{M}_n
A	1	225	22.9	3349	1829	3708	2.03	22,450
B	2	230	22.6	3599	1978	4209	2.13	29,900
C	2	230	22.8	3749	2021	4362	2.16	30,500
D	1	230	23.9	3553	2012	4194	2.09	36,100
E	1	235	23.7	4790	2278	4895	2.15	43,300
Composite			23.0	3810	2025	4275	2.11	32,500

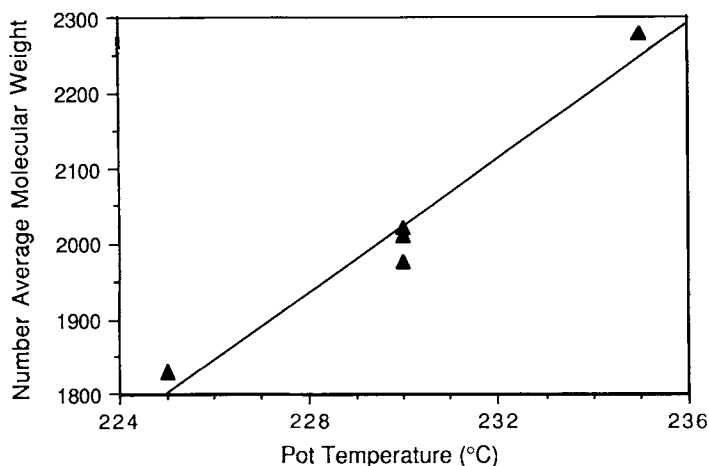
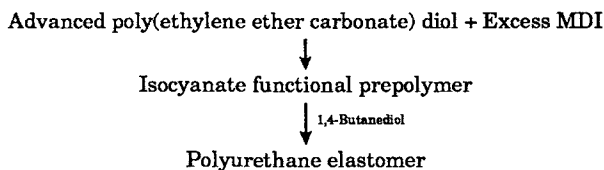


Fig. 1. Effect of pot temperature on molecular weight of advanced polyol.

a short study of the prepolymer stability using selected poly(ethylene ether carbonate) diols was carried out prior to polymer fabrication.

Polymerization Flowchart



Isocyanate Functional Prepolymers

The initial isocyanate functional prepolymers made were quite unstable and set up within minutes. This instability was a consequence of residual alkalinity in the polyols. The alkalinity was followed by the controlled polymerization rate (CPR) technique by titration with dilute (0.01 N) HCl.⁹ The reduction and/or removal of these impurities have been described.⁵⁻⁶

TABLE II
Product Weight and Distillate Composition

Polyol number	Composition (wt %)		Distillate assay (wt %)				
	Residue	Distillate	1,4-Dioxane	EC	DEG	TriEG	TetraEG
A	84.8	14.3	1.8	4.2	64.5	23.3	1.5
B	84.3	14.3	1.4	4.6	51.3	29.1	5.2
C	83.7	14.9	1.5	4.4	51.7	28.7	4.9
D	84.6	14.3	1.6	4.2	59.8	24.3	3.7
E	83.5	15.1	1.6	4.0	60.3	24.0	3.7

The stability of the isocyanate functional prepolymers (12% NCO based on reactants charged) was followed by measuring the isocyanate content as a function of time and CPR level (Fig. 2). Reaction is complete in < 1 h. Very little loss of isocyanate content occurs after the prepolymer reaction is complete using a polyol with a CPR of 2. Loss of isocyanate content becomes increasingly important as the CPR of the polyol is increased to 8 and 15. A polyol with a CPR value of 34 caused the prepolymer to set up in < 10 min.

The stability of the prepolymer could be enhanced considerably if the residual alkalinity was neutralized with a mildly acidic material such as benzoyl chloride (Fig. 3). Prepolymers based on polyols containing CPR values of 15 and 34 were stable at 80°C in the presence of 200 ppm benzoyl chloride. This stability was destroyed by the addition of catalytic amounts of dibutyltin dilaurate (Fig. 4). All of the useful prepolymers used in this study were stabilized by the presence of 200 ppm benzoyl chloride.

Effect of Isocyanate Index on Polyurethane Molecular Weight

It is well known that polyurethane formulations need to be slightly over indexed to obtain maximum properties. A short study was carried out to obtain the effect of index on polyurethane molecular weight through the range from 0.97 to 1.05 in a system formulated to about 44 wt % hard segment (see Table III). Polyurethane molecular weight is maximized at a 1.03 index.

Polyurethane Structure by Carbon-13 NMR

The structure of the highest molecular weight plaque, polyurethane III, was studied by carbon-13 NMR in DMSO- d_6 solution (2.5 wt %). An APT (associated proton test) spectrum is given in Fig. 5 and shows that there are only two carbon atoms attached to a single proton (the C-3 and C-4 carbon atoms

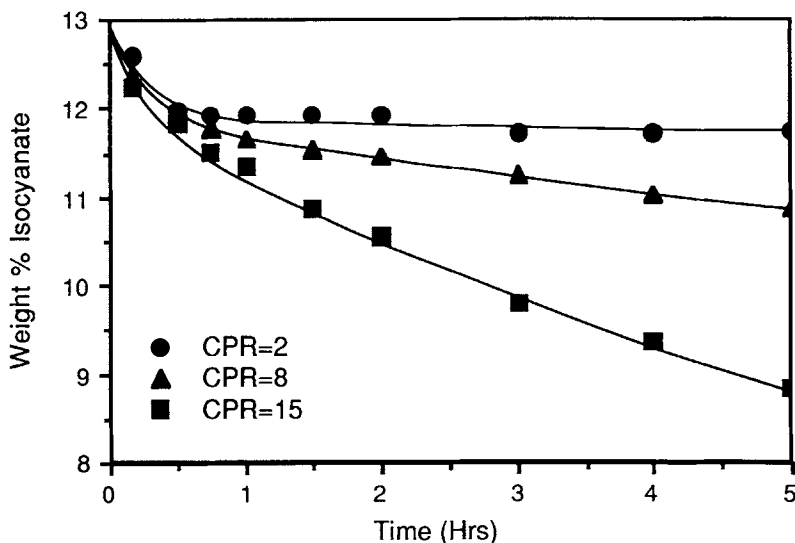


Fig. 2. Prepolymer stability vs. CPR at 80°C.

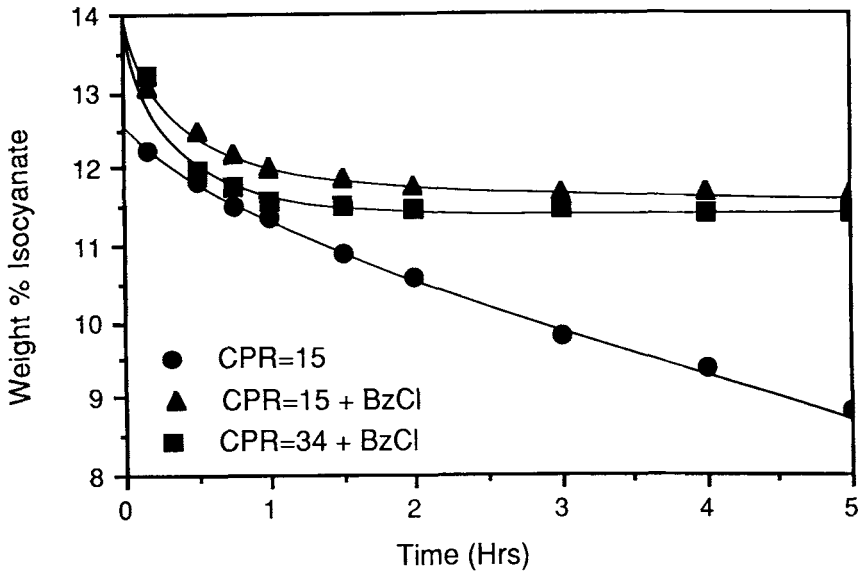


Fig. 3. Effect of 200 ppm benzoyl chloride on prepolymer stability at 80°C.

in the aromatic rings, as evidenced by two negative lines). A model hard segment (1,4-butanediol/4,4'-MDI polyurethane) was also prepared and studied to help in structural assignments.

Polyurethane III contains three different carbonyl moieties. Figure 6 compares the carbon-13 NMR spectra of the carbonyls in polyurethane III to the

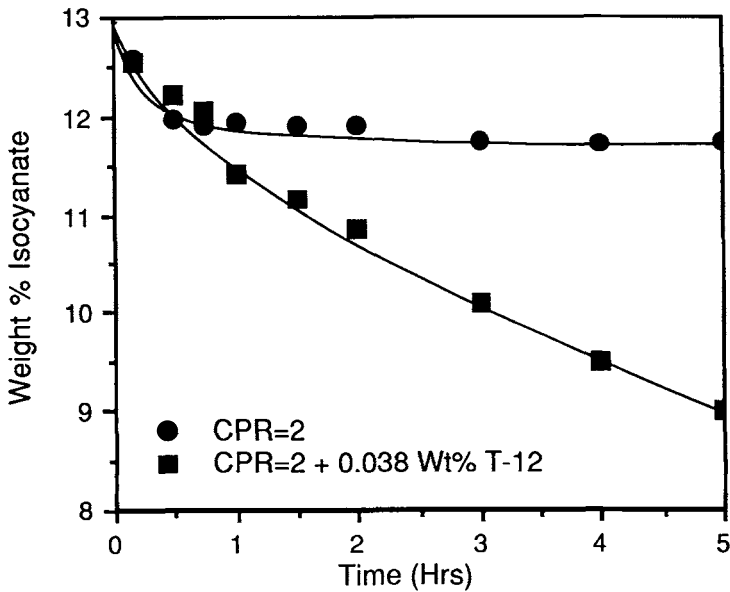


Fig. 4. Effect of dibutyltin dilaurate on prepolymer stability at 80°C.

TABLE III
Effect of Index on Polyurethane Molecular Weights

Plaque number	Hard segment (wt %)	Index	Molecular weight data		
			\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
I	43.9	0.97	68,200	117,600	1.73
II	44.2	1.00	78,800	143,700	1.82
III	43.5	1.03	141,500	230,100	1.63
IV	43.2	1.05	118,200	203,400	1.72

model hard segment and the starting poly(ethylene ether carbonate) diol. The three carbonyls are readily assigned as the carbonate carbonyl [155.1 ppm; only carbonyl present in the poly(ethylene ether carbonate) diol], the 1,4-butanediol urethane carbonyl (154.1 ppm; only carbonyl present in the model hard segment), and the poly(ethylene ether carbonate) diol urethane carbonyl (154.0 ppm).

Figure 7 shows the carbon-13 NMR spectra of polyurethane III, the model hard segment, and the poly(ethylene ether carbonate) diol starting material from 62 to 71 ppm. The only common line between the polyurethane III spectrum and the model hard segment spectrum is at 63.9 ppm and is assigned to the 1,4-butanediol carbon atoms attached to urethane moieties. The lines at 69.9, 68.2/68.3, and 66.8/66.9 ppm are part of the poly(ethylene ether carbonate) diol backbone and have previously been assigned as (1) carbon atoms both α and β to ether oxygen, (2) carbon atoms β to carbonate and α to ether oxygen, and (3) carbon atoms α to carbonate and β to ether oxygen, respectively.^{2,4,5} The lines in polyurethane III at 68.8/68.9 and 63.5/63.6 ppm [absent in the poly(ethylene ether carbonate) diol] are assigned to carbon atoms β to urethane and α to ether oxygen and to carbon atoms α to urethane and β to ether oxygen, respectively. These moieties are formed by the reaction of poly(ethylene ether carbonate) diol with MDI. A complete list of carbon-13 NMR structural assignments is given in Table IV. Line assignments for the hard segment portion of the polymer are consistent with reported values.^{10,11} Therefore, a well-defined polymer chemical structure was used for property evaluations.

Comparisons to Plaques Made from Commercial Diols

A series of plaques were fabricated from commercial diols, using 4,4'-MDI and 1,4-butanediol as the hard segment at a content of about 43.5 wt %, in order to study a variety of soft segment structural types. Two polyester polyols—diethylene glycol adipate and poly(caprolactone) diol—and three polyether polyols—poly(propylene glycol), poly(1,2-butylene glycol), and poly(tetramethylene glycol)—were studied. Each material was a 2000 molecular weight diol. Since hard segment composition, diol molecular weight, fabrication procedure, heat histories, and cure conditions were constant, the differences seen in elastomer properties should be due to the structural differences in the various diols used in the polyurethane soft segments and the effects that these differ-

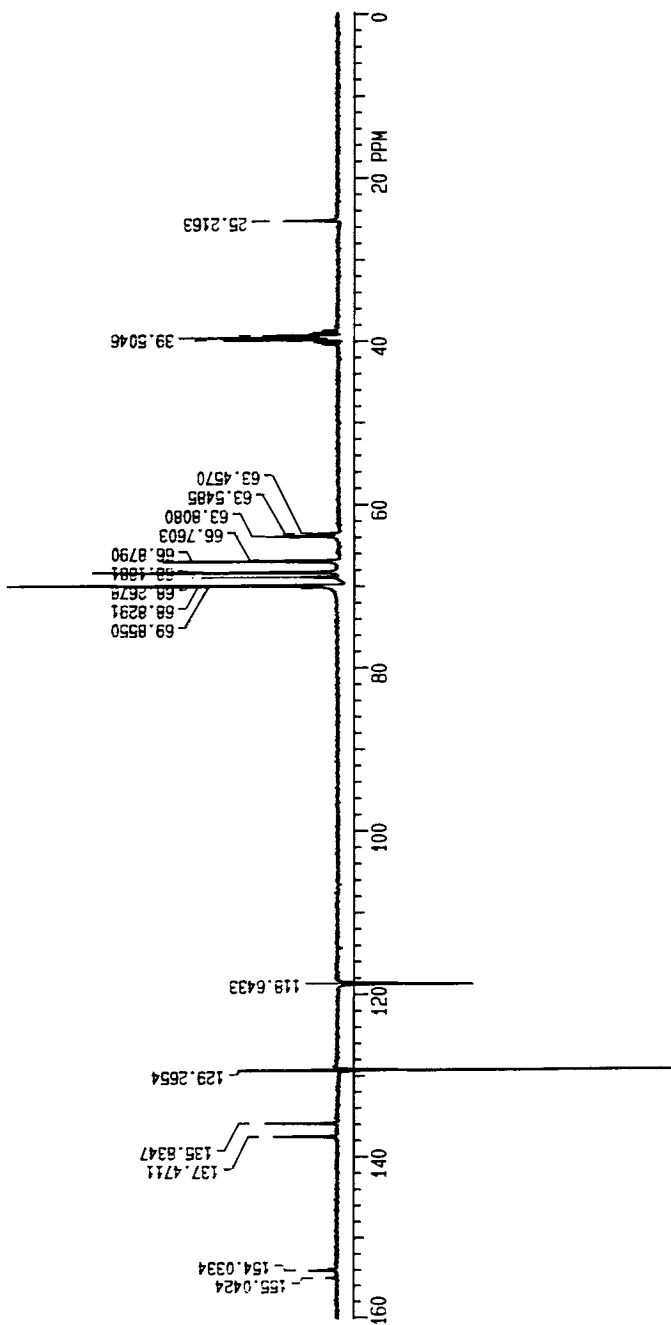


Fig. 5. Carbon-13 NMR spectrum of polyurethane III; associated proton test.

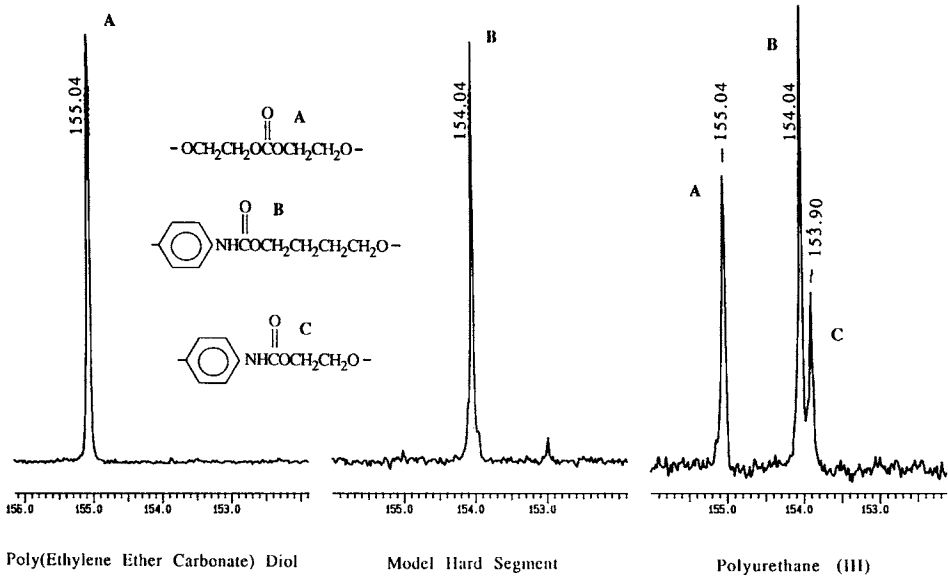


Fig. 6. Structural assignments of carbonyl carbon atoms in carbon-13 NMR spectra.

ences had on polymer morphology. Table V gives a list of the soft segment materials studied and the molecular weights of the resultant polyurethane elastomers. Figure 8 shows the structure of the soft segments studied.

Solvent Resistance

The solvent resistance of these plaques is given in Table VI. Water, methanol, toluene, and methylethylketone were used to represent a variety of different

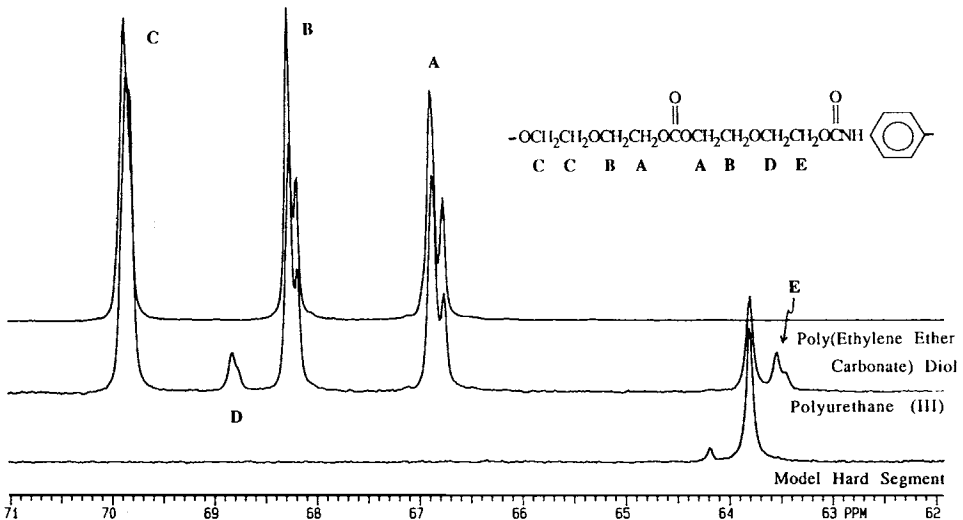


Fig. 7. Comparison of carbon-13 NMR spectrum of polyurethane III to poly(ethylene ether carbonate) diol and model hard segment.

TABLE IV
 Carbon-13 NMR Structural Assignments of Polyurethane III

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

^a ppm from tetramethylsilane (TMS = 0); DMSO-*d*₆ as solvent.

solvent types. A static weight gain test was employed to measure when equilibrium was attained (< 6 days). Polyurethane III has the poorest solvent resistance to water due to the polar nature of the poly(ethylene glycol) and carbonate ester moieties in the soft segment backbone. However, organic solvent resistance is quite different. The polyether polyol soft segments give the poorest organic solvent resistance. Polyester polyols are known for superior solvent resistance and the results of these studies bear this out. However, polyurethane III is clearly superior in resistance to the organic solvents tested relative to the plaques containing polyester soft segments.

 TABLE V
 Effect of Soft Segment Structure on Molecular Weight

Plaque number	Diol used in soft segment	Hard segment (wt %)	Molecular weight data		
			\bar{M}_n	\bar{M}_w	PDI
III	Poly(ethylene ether carbonate) diol	43.5	141,500	230,100	1.63
V	Formrex 11-56 ^a	43.6	100,535	178,825	1.78
VI	Tone 2000 ^b	43.3	187,560	410,650	2.19
VII	Terathane 2000 ^c	44.0	92,500	183,300	1.98
VIII	Voranol 2120 ^d	43.6	49,800	89,140	1.79
IX	B-2000 ^e	43.6	55,230	122,800	2.23

^a Diethyleneglycol adipate ($\bar{M}_n = 2000$).

^b Poly(caprolactone) diol ($\bar{M}_n = 2000$).

^c Poly(tetramethylene glycol) ($\bar{M}_n = 2000$).

^d Poly(propylene glycol) ($\bar{M}_n = 2000$).

^e Poly(1,2-butylene glycol) ($\bar{M}_n = 2000$).

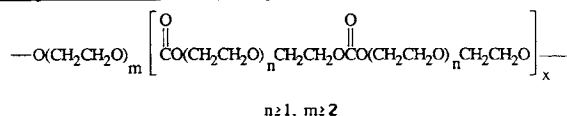
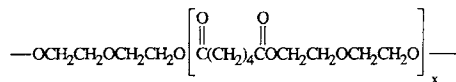
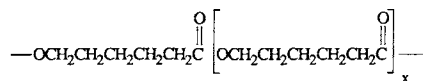
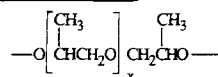
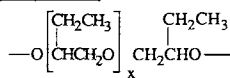
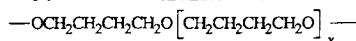
Poly(ethylene ether carbonate) DiolDiethyleneglycol Adipate (Formrez™ 11-56)Poly(caprolactone) Diol (Tone™ 2000)Poly(propylene glycol) (Veranol™ 2120)Poly(1,2-butylene glycol) (B-2000)Poly(tetramethylene glycol) (Terathane™ 2000)

Fig. 8. Soft segment structures.

Modulus

Ambient temperature flexural and tensile modulus values (Table VII) show that polyurethane III has a modulus intermediate between that of the plaques made with the other polyether and polyester polyols. Figures 9 and 10 show flexural storage modulus (E') curves (by DMA) comparing polyurethane III

TABLE VI
Effect of Backbone Structure of Soft Segment on Solvent Resistance

Plaque number	Hard segment (wt %)	Solvent resistance (% wt gain after 6 days)			
		Water	Methanol	Toluene	MEK
III	43.5	4.6	11.7	11.7	30.3
V ^a	43.6	2.0	12.5	23.9	49.7
VI ^b	43.3	0.8	11.8	41.2	54.3
VII ^c	44.0	1.1	19.6	54.8	50.0
VIII ^d	43.6	2.2	43.2	79.9	149.2
IX ^e	43.6	0.7	23.0	79.5	153.1

^a Based on diethyleneglycol adipate ($\bar{M}_n = 2000$).

^b Based on poly(caprolactone) diol ($\bar{M}_n = 2000$).

^c Based on poly(tetramethylene glycol) ($\bar{M}_n = 2000$).

^d Based on poly(propylene glycol) ($\bar{M}_n = 2000$).

^e Based on poly(1,2-butylene glycol) ($\bar{M}_n = 2000$).

TABLE VII
Effect of Backbone Structure of Soft Segment on Physical Properties^a

Plaque number	Hard segment (wt %)	Notched Izod (ft.-lb/in.)	Shore hardness		Modulus		Tensile at elongation			At break	
			A	D	Flexural (psi)	Tensile (psi)	100% (psi)	200% (psi)	300% (psi)	Strength (psi)	Elong (%)
III	43.5	NB	97	47	9,300	9,300	1355	1620	1835	2480	560
V ^b	43.6	NB	92	46	13,200	13,000	2200	2820	—	ND	ND
VI ^c	43.3	NB	99	53	13,000	13,100	1250	1530	1800	5175	1315
VII ^d	44.0	NB	99	49	9,900	9,800	1335	1550	1810	4020	1200
VIII ^e	43.6	NB	85	40	8,000	8,000	980	1270	1530	2260	580
IX ^f	43.6	NB	85	42	6,420	ND	ND	ND	ND	ND	ND

^a NB = no break; ND = not determined.

^b Based on diethyleneglycol adipate ($\bar{M}_n = 2000$).

^c Based on poly(caprolactone) diol ($\bar{M}_n = 2000$).

^d Based on poly(tetramethylene glycol) ($\bar{M}_n = 2000$).

^e Based on poly(propylene glycol) ($\bar{M}_n = 2000$).

^f Based on poly(1,2-butylene glycol) ($\bar{M}_n = 2000$).

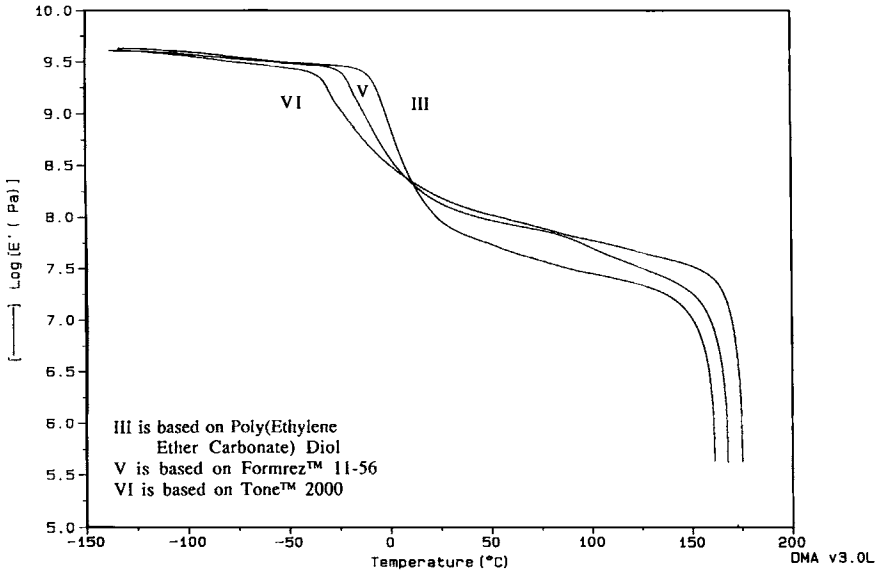


Fig. 9. Flexural storage modulus (E') curves of polyurethanes based on polyester polyols.

to the other polymers. Polyurethane III shows a much lower rubbery plateau modulus than polyurethanes V and VI (made with the other polyester polyols) but has a higher modulus in the -25 to 5°C range (Fig. 9). The loss in modulus at higher temperatures leads to somewhat lower use temperatures, while the extended glassy range should result in poorer low-temperature properties.

Polyurethane III shows a higher modulus than polyurethanes VIII and IX (made with the epoxide based polyether polyols) in the -50 to 50°C range and

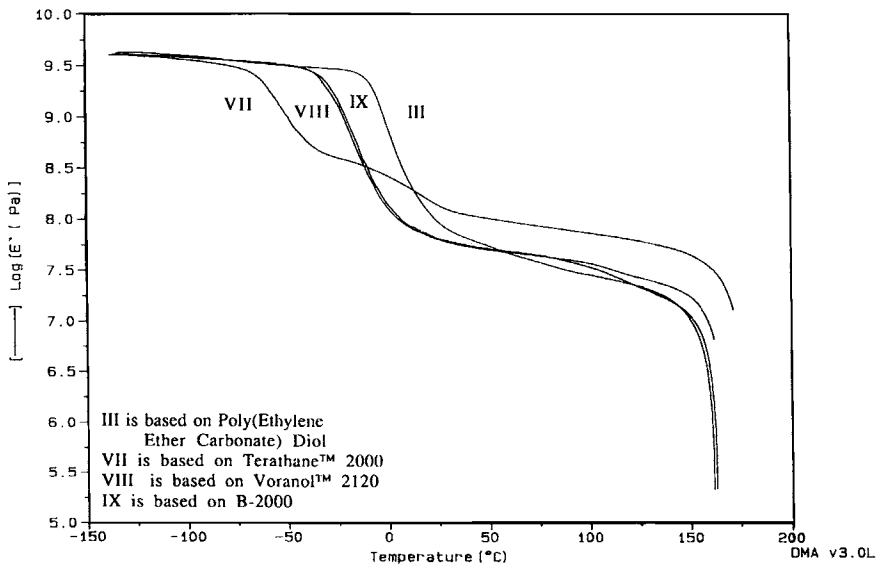


Fig. 10. Flexural storage modulus (E') curves of polyurethanes based on polyether polyols.

a somewhat lower rubbery plateau modulus. These differences are a result of differences in morphologies of the polymers and are discussed later.

Other Physical Properties

The effects of backbone structure of the soft segments on a variety of other physical properties are shown in Table VII. All of the elastomers passed the notched Izod test (no break). Polyurethanes VIII and IX, based on V-2120 and B-2000 (polyether polyols), have the lowest hardness. Polyurethane III has about the same hardness as polyurethanes V and VI, the other polyester polyol based elastomers. Polyurethane III has good strength at relatively low elongation, but it has a lower elongation at break than some of the other elastomers studied.

Polymer Morphology

As with all polyurethane block copolymers, polymer morphology, and thus thermal and physical properties, is influenced to a large extent by the degree of separation of the hard segment and soft segment blocks. This phase separation is governed primarily by the soft segment-soft segment, hard segment-hard segment, and soft segment-hard segment interactions.

These types of interactions can vary greatly between polyurethane elastomers made with polyether polyol soft segments and those made with polyester polyol soft segments.¹²⁻¹⁴ The poly(ethylene ether carbonate) diol starting material can be considered as an ester modified polyether polyol or as an ether modified polyester polyol. Therefore, polyurethane III has structural features in its soft segment of both polyester polyols (carbonate ester moieties) and polyether polyols (ether oxygen moieties).

Polyester Polyols

Polyurethane elastomers containing soft segments based on adipate esters¹⁵⁻¹⁷ and poly(caprolactone) diols^{16,18-21} have been studied by several workers. The DMA and DSC data for the polyurethane elastomers made with the polyester polyols of this study (Figs. 9 and 11) show some clear structure/property relationships. It should be kept in mind at this point that any differences in these polymers should be due to the differences in soft segment structures and their interactions with the hard segments.

An important feature of the soft segments is their density of potential hydrogen bonding sites (carbonyl and ether oxygen moieties). One way to compare soft segments is to compare the number of carbonyl moieties and ether oxygen moieties per soft segment unit (see Table VIII). The soft segment of polyurethane III has only about half the carbonyl moieties of the polyester polyol based elastomers of this study but has a much higher number of ether oxygen moieties. These short run lengths of poly(ethylene glycol) units in the soft segment of polyurethane III, in combination with the carbonate moieties, can enhance soft segment-soft segment interactions. The efficiency of these interactions are dependent on structural arrangements and steric factors.

DSC results on the polyester polyol monomers, their model soft segments (MDI reaction products), and the polyurethane elastomers of this study are

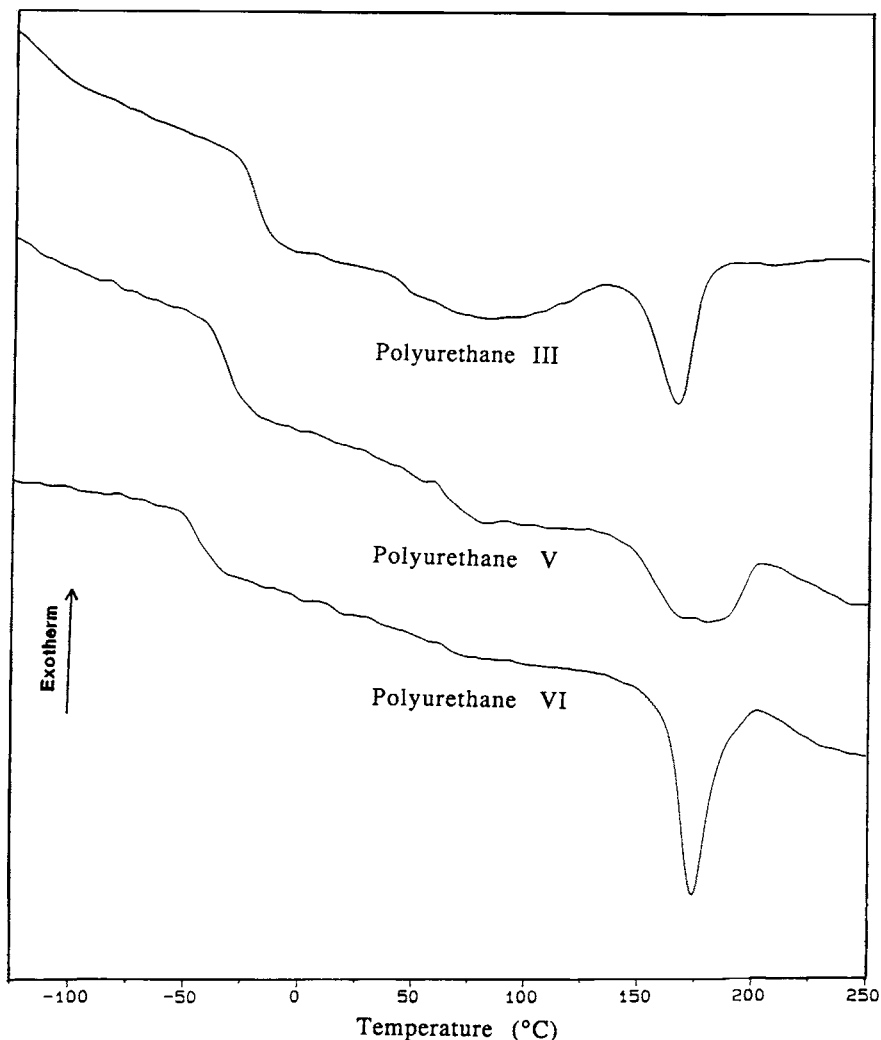


Fig. 11. DSC scans of polyurethanes based on polyester polyols.

summarized in Table IX. When comparing polymer properties, going from polyurethane VI (made with Tone 2000) to polyurethane V (made with Formrez 11-56) to polyurethane III [made from poly(ethylene ether carbonate) diol], the temperature of the soft segment glass transition (T_g) increases, the amount of amorphous hard segment material present in the soft segment increases (as indicated by the ΔC_p of the subambient T_g) and the heat of melting (ΔH_m) of the hard segment decreases. This could be due to a decrease in the percent crystallinity of the hard phase, to an increase in the amount of amorphous hard segment in the soft phase, or both. However, if the percent crystallinity decreases and the amorphous hard segment does not dissolve in the soft segment, a hard segment T_g ($\sim 110^\circ\text{C}$) should be observed. Since a hard segment T_g is not observed, an increase in the amount of the amorphous hard phase in the soft segment must be the dominant effect. This indicates that polyurethane III is

TABLE VIII
Hydrogen Bonding Moieties in Different Soft Segment Materials

Diol used in soft segment	CO ₂ (wt %)	<i>x</i>	Carbonyl units/soft segment	Ether oxygen units per soft segment	Total H bonding sites
Poly(ethylene ether carbonate) diol	23.0	5.5	11.0	22.0	33.0
Diethyleneglycol adipate	40.7	8.8	17.6	9.8	27.4
Poly(caprolactone) diol	38.6	17.2	17.2	0	17.2
Poly(propylene glycol)	0	33.2	0	33.2	33.2
Poly(1,2-butylene glycol)	0	26.5	0	26.5	26.5
Poly(tetramethylene glycol)	0	26.5	0	26.5	26.5

the most phase mixed polymer due to the increased virtual crosslinking brought about primarily by the carbonyl moieties and to a lesser extent by the ether oxygen moieties. As these polymers become more phased mixed, their rubbery plateau moduli decrease (Fig. 9). This is due to the weaker internal cohesive forces brought about by the lower volume fraction of hard phase in poorer phase separated polymers.

Polyether Polyols

Since the soft segment of polyurethane III contains ether oxygen moieties, which give it some of the structural features of a polyether polyol, its morphology was compared to polyurethane elastomers made with the polyether polyols Terathane 2000, Voranol 2120, and B-2000 (polyurethane VII, VIII, and IX, respectively). Polyurethane elastomers containing soft segments based on poly(tetramethylene glycols)^{15,22,24} and poly(propylene glycols)^{14,23-26} have been studied by numerous workers. Figure 8 shows the polyol structures being compared in this study. Figures 10 and 12 show the DMA and DSC scans for these polymers.

When compared to the epoxide based polyols (Voranol 2120 and B-2000), the poly(ethylene ether carbonate) diol gives a polymer with a lower ΔH_m , a lower melting point, and a higher soft segment T_g (Table IX). These differences can be explained in terms of partial phase mixing of polyurethane III due to virtual crosslinking through soft segment-hard segment interactions involving primarily the carbonyl oxygen moieties and to a lesser extent the ether oxygen moieties.

By comparison, polyurethane VII, made with Terathane 2000, shows partial soft segment crystallinity (Fig. 12) and a very low T_g for the part of the soft phase that is amorphous. The relatively long, straight-chain hydrocarbon between ether oxygen atoms is responsible for the soft segment being able to partially crystallize. These factors give a very phase separated morphology that allows this polymer to have the highest ΔH_m of all the polymers studied. This also gives this polymer the highest rubbery plateau modulus of the polymers studied including those made with the polyester polyols.

Post-Cure Studies

Samples of all the polymers studied were post-cured for 1 h at 150°C in order to observe the effects on polymer morphology (Table X). The hard seg-

TABLE IX
Summary of DSC Data (First Scans) on Polyurethane Elastomers^a

Plaque number	Diol used in soft segment	Polyol T_g (width) (°C)	Model soft segment		Plaque soft segment		T_m (°C)	ΔH_m (J/g)
			T_g (width) (°C)	ΔC_p^b (J/g °C)	T_g (width) (°C)	ΔC_p^b (J/g °C)		
III	Poly(ethylene ether carbonate) diol	-39 (19)	-22 (20)	0.73	-20 (30)	0.40	167	12.8
V	Formrez 11-56	-50 (20)	-34 (23)	0.70	-30 (30)	0.37	170	14.7
VI	Tone 2000	-65 (17)	-46 (17)	0.36	-45 (30)	0.26	173	17.2
VII	Terathane 2000	-78 ^c (ND)	ND		-73 (20)	0.25	174	18.0
VIII	Voranol 2120	-68 (10)	ND		-45 (31)	0.36	170	15.6
IX	B-2000	-71 (15)	ND		-44 (19)	0.22	168	12.7

^a ND = not determined.

^b Not corrected for heat flow in sample pan.

^c $T_m = 28^\circ\text{C}$, $\Delta H_m = 100 \text{ J/g}$.

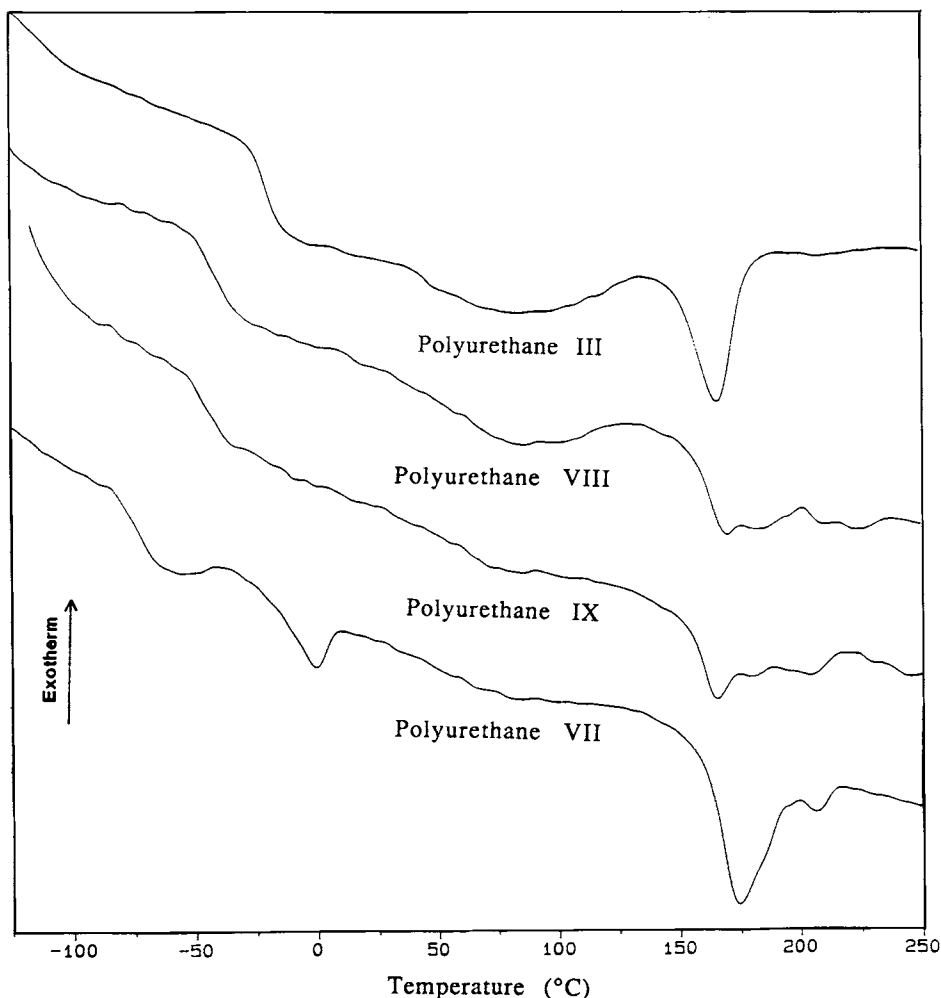


Fig. 12. DSC scans of polyurethanes based on polyether polyols.

ment melt endotherms became sharper, but their areas were relatively unchanged. While the polymers made with polyether polyols showed no significant changes, the polymers made with polyester polyols, including polyurethane III, showed an increase in the soft segment T_g of about 10°C , indicating that some additional phase mixing was taking place. This was probably due to the shorter run length hard segments melting and dissolving in the amorphous soft segment.

SUMMARY AND CONCLUSIONS

Poly(ethylene ether carbonate) diols (2025 mol wt) have been made by the molecular weight advancement of lower molecular weight oligomers and have been fabricated into polyurethane elastomers by reaction with 4,4'-MDI and 1,4-butanediol by the prepolymer method. Polymer structure has been delineated by carbon-13 NMR. This polyurethane elastomer has been compared to a series

TABLE X
Effect of Post-curing at 150°C on Soft Segment T_g

Plaque number	Diol used in soft segment	Non-post-cured T_g (°C)	Post-cured T_g (°C)	ΔT_g (°C)
III	Poly(ethylene ether carbonate) diol	-20	-11	9
V	Diethyleneglycol adipate	-31	-22	10
VI	Poly(caprolactone) diol	-43	-34	9
VII	Poly(tetramethylene glycol)	-74	-73	1
VIII	Poly(propylene glycol)	-40	-38	2
IX	Poly(1,2-butylene glycol)	-44	-41	3

of elastomers based on other polyester and polyether polyols (2000 mol wt) under conditions where the only variable was the soft segment structure.

Some clear structure/property relationships are evident in this study. The poly(ethylene ether carbonate) diol with its potential for high virtual crosslink density gives a polymer with a partially phase mixed morphology. This phase mixing leads to a lower ΔH_m than that seen in polymers made with the other polyester polyols but only slightly lower ΔH_m than polymers made with the epoxide based polyether polyols. This partially phase mixed morphology, with its higher soft segment T_g , is what gives polymers made with the poly(ethylene ether carbonate) diol a higher modulus than the epoxide based polyether polyols over the -50 to 50°C range. The lower volume fraction of hard phase in polyurethane III is responsible for it having a significantly lower rubbery plateau modulus than the other polyester polyols. Organic solvent resistance is the most outstanding property.

The post-cure and T_g shift data, along with the solvent resistance and physical property data, indicate that the poly(ethylene ether carbonate) diol produces a polymer with predominantly polyester polyol features.

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