

Polyurethane Elastomers Based on Molecular Weight Advanced Poly(ethylene Ether Carbonate) Diols. II. Effects of Variations in Hard Segment Concentration

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Synopsis

A series of polyurethane elastomers were studied in which the soft segment composition was a molecular weight advanced poly(ethylene ether carbonate) diol (2025 mol wt) and the hard segment composition was based on MDI/1,4-butanediol. These polyurethane elastomers had a constant soft segment composition and block length, a constant hard segment composition, but a variable hard segment block length and concentration (31.9–65.2 wt % hard segment). Properties such as rubbery plateau modulus, solvent resistance, melting point, hardness, tensile strength, and hard segment run length all improve with increasing hard segment concentration. DMA and DSC data indicate a partially phase mixed morphology. However, phase mixing must occur at domain boundaries since the soft segment T_g is nearly invariant with hard segment concentration. Annealing studies indicate that the optimum post-cure temperature, for 1 h, is about 175°C.

INTRODUCTION

One family of polyurethane elastomers is block copolymers of $(AB)_n$ molecular structure, where A represents the soft segment and B represents the hard segment. The soft segments provide flexibility in the polymer backbone, while the hard segment units provide physical crosslinks by molecular association through hydrogen bonding. The structure, concentration, and organization of the hard segments have a dominant influence on the physical and mechanical properties of polyurethanes. However, the soft segment plays a key role in certain properties such as solvent resistance.

Poly(ethylene ether carbonate) polyols are soft segment materials that contain structural characteristics of both polyether polyols (ether moieties) and polyester polyols (carbonate ester moieties). Structural details of these materials have recently been delineated.^{1,2} When poly(ethylene ether carbonate) polyols are heated to elevated temperatures ($> 180^\circ\text{C}$) at reduced pressures, molecular weight advancement occurs with 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 CO_2 retention, relatively low polydispersity, and high purity.

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A previous article compared polyurethane elastomers made from these molecular weight advanced poly(ethylene ether carbonate) polyols to polyurethane elastomers made with various commercial polyether and polyester polyols under conditions where the hard segment structure and concentration were held constant.⁷ Resistance to organic solvents was found to be an outstanding property. This article examines the effects of variations in hard segment concentration on the properties of polyurethane elastomers, while holding the poly(ethylene ether carbonate) diol soft segment composition and block size constant.

EXPERIMENTAL

Starting Materials

Isonate 125M brand MDI [4,4'-methylene-di(phenylisocyanate)] (freshly distilled just prior to use) was manufactured by The Dow Chemical Company. 1,4-Butanediol (freshly distilled from calcium hydride and stored under nitrogen in silanized bottles) and dibutyltin dilaurate were obtained from Aldrich Chemical Company. Poly(ethylene ether carbonate) diols were prepared in two steps.⁷ First, low molecular weight feed ($\bar{M}_n = 800$) was prepared by the monoethylene glycol initiated oligomerization of ethylene oxide and carbon dioxide.⁸ Then, residual catalyst was removed,^{7,9} and the feed was advanced to a higher molecular weight ($\bar{M}_n = 2025$; 23.0 wt % CO₂; $T_g = -39^\circ\text{C}$).

Molecular Weight Determination

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 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.

Proton and Carbon-13 NMR

Spectra were obtained on a Varian Gemini 300 NMR (3–5 wt % in DMSO-*d*₆; 300 MHz for proton, and 75 MHz for carbon).

Polymer Fabrication

Polyurethane elastomers were prepared by the prepolymer process as previously described.⁷ All polymers were catalyzed with dibutyltin dilaurate (0.00192 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.⁷ 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. Physical properties were measured using standard ASTM procedures. Solvent resistance was measured at ambient temperature by a static soak test until solvent uptake reached equilibrium (6 days).

RESULTS AND DISCUSSION

Polymer Synthesis

Hand-cast plaques were made using the prepolymer method. The same poly(ethylene ether carbonate) diol was used in each plaque to keep the soft segment length and structure constant. The hard segment length was varied by making a series of plaques with hard segment compositions from 31.9 to 65.2 wt %. The structure of the hard segment was constant, being based on MDI and 1,4-butanediol.

The molecular weight of each polyurethane elastomer was measured by size exclusion chromatography (Table I). Molecular weights are highest for the polyurethanes with 35.7–43.5 wt % hard segment and are systematically reduced as the hard segment content is increased. There are only minor variations in the polydispersity of the polymers.

Carbon-13 NMR

The carbon-13 NMR spectrum of polyurethane III has been reported.⁷ However, supporting data is available from this study. Figure 1 gives the spectra of polyurethane I, containing the lowest hard segment content, and polyurethane VII, containing the highest hard segment content. All lines arising from 1,4-butanediol (25.3 and 63.9 ppm) and MDI (39.9, 118.7, 129.3, 135.9, 137.5, and 154.1 ppm) are intensified in the spectrum of polyurethane VII.

Proton NMR

The proton NMR spectrum of polyurethane VII is given in Fig. 2. Line assignment is straightforward due to the variations in line intensities by the

TABLE I
Effect of Hard Segment Content on Polyurethane Molecular Weight

Plaque number	Hard segment (wt %)	Density (g/cm ³)	Molecular weight data		
			\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
I	31.9	1.25	99,150	204,600	2.06
II	35.7	1.25	137,700	237,100	1.72
III	43.5	1.26	141,500	230,100	1.63
IV	49.1	1.26	91,500	175,000	1.91
V	54.9	1.27	94,200	176,000	1.87
VI	60.0	1.27	69,200	131,000	1.90
VII	65.2	1.28	67,000	125,000	1.87

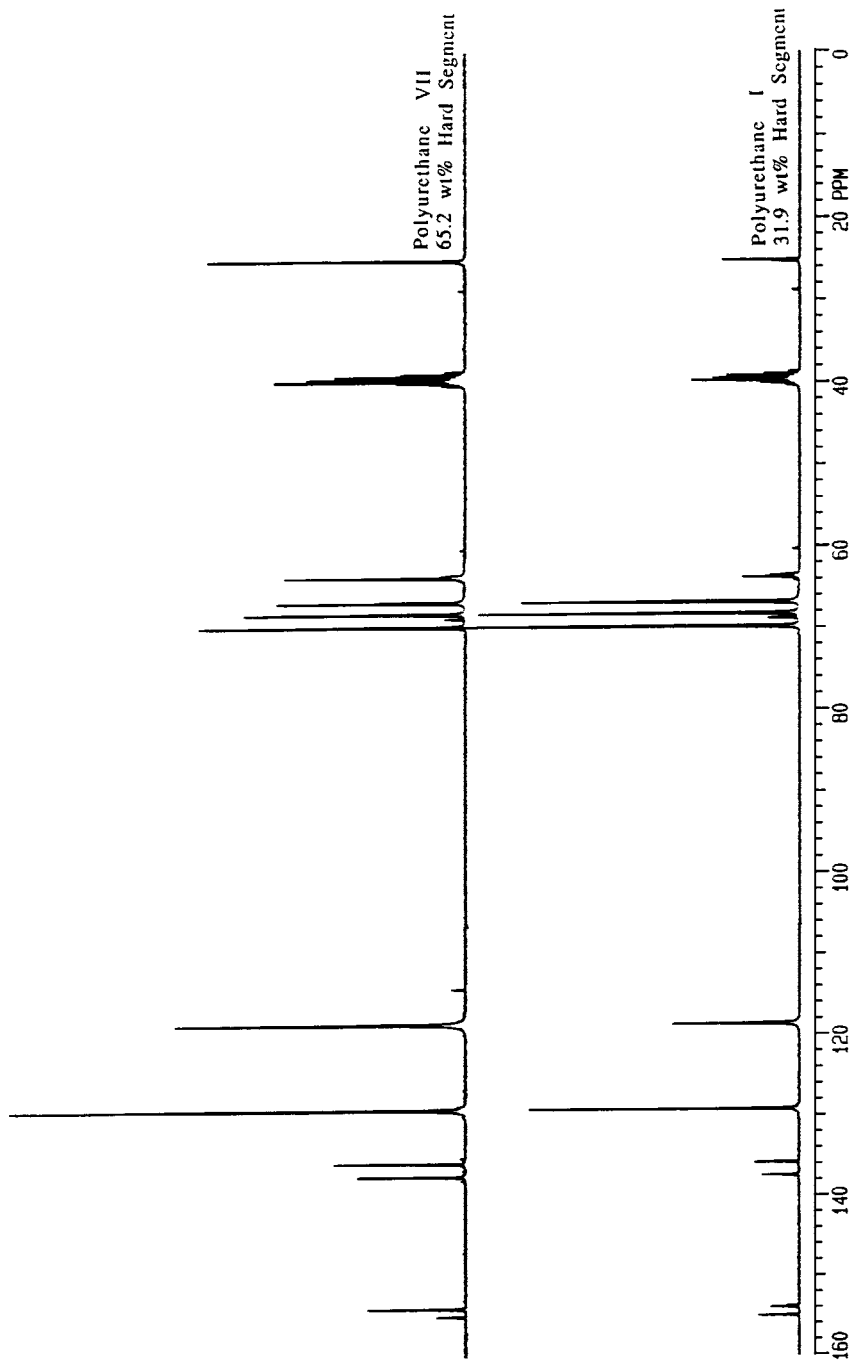


Fig. 1. Comparison of carbon-13 NMR spectra of polyurethanes containing 31.9 and 65.2 wt % hard segment.

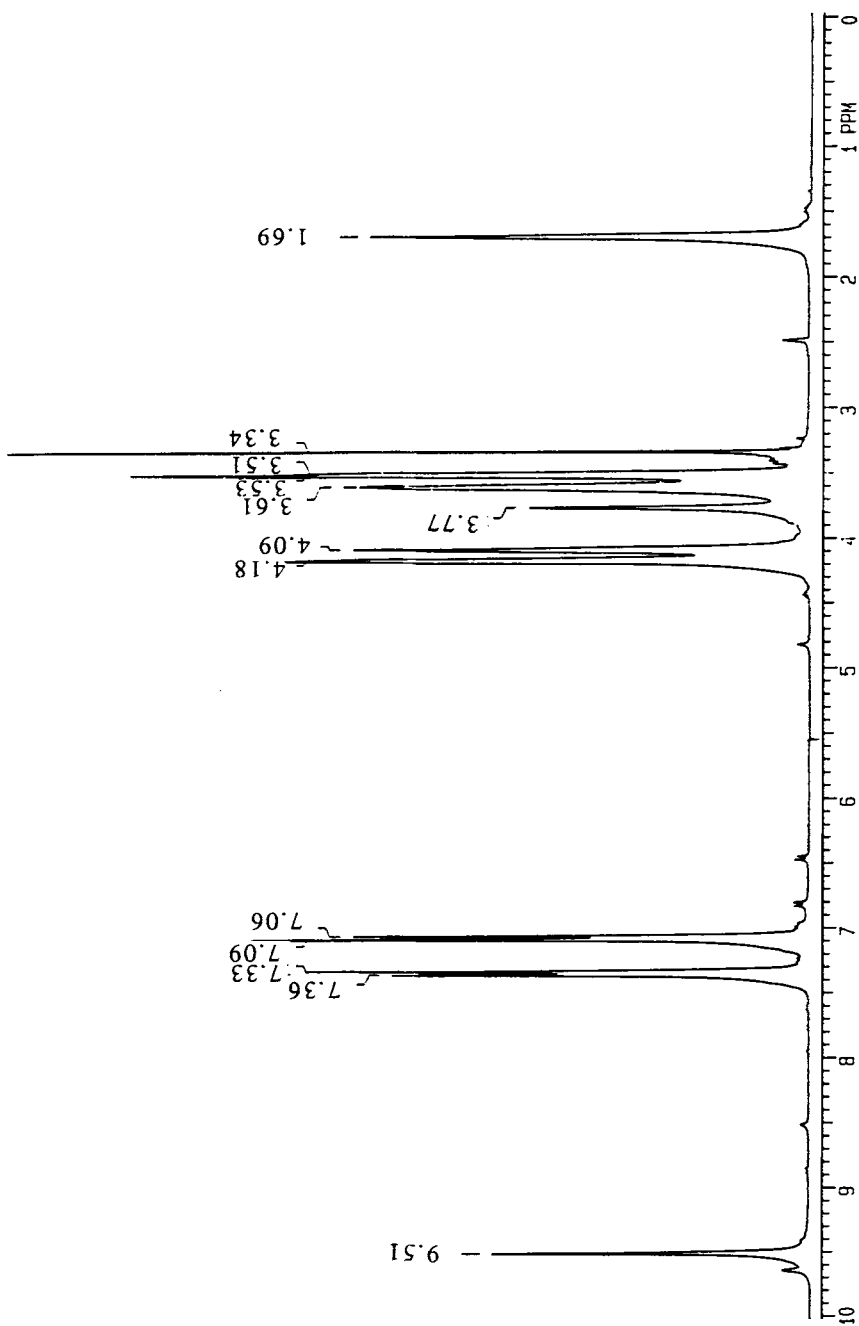


Fig. 2. Proton NMR spectrum of polyurethane containing 65.2 wt % hard segment.

TABLE II
Proton NMR Structural Assignments

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

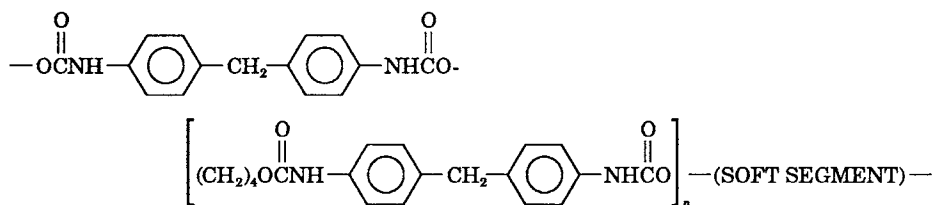
* ppm from tetramethylsilane (TMS = 0); DMSO- d_6 as solvent.

systematic variations in hard segment content. Structural assignments are given in Table II. Moisture present in the plaque gives a line at 3.34 ppm.

Polyurethane Elastomer Structure

This series of polyurethane elastomers has a constant soft segment composition and block length, a constant hard segment composition, but a variable hard segment block length and concentration. Table III shows the structural features of the hard segment. The average molecular weights and run lengths of the hard segment blocks are calculated from the amounts of reactants charged. The number of urethane moieties per average hard segment block length were calculated in order to better understand the variations in potential hydrogen

TABLE III
Variations in Hard Segment Run Lengths



Plaque number	Hard segment (wt %)	Soft segment (mol wt)	Hard segment (mol wt)	n	Urethane moieties per hard segment
I	31.9	2025	949	2.1	6.2
II	35.7	2025	1124	2.6	7.2
III	43.5	2025	1559	3.9	9.8
IV	49.1	2025	1953	5.0	12.0
V	54.9	2025	2465	6.5	15.0
VI	60.0	2025	3038	8.2	18.4
VII	65.2	2025	3794	10.4	22.8

bonding sites with hard segment content. This structure is consistent with the NMR line assignments.

Effect of Hard Segment Content on Properties

Since the hard segment content is the only variable in this study (fabrication procedure, heat history, and cure conditions were constant), any property changes should be the result of hard segment content and the effects hard segment content have on polymer morphology.

Solvent Resistance

Resistance to organic solvents is an outstanding property of poly(ethylene ether carbonate) polyol based polyurethane elastomers.⁷ The solvent resistance properties of the plaques made in this study are given in Table IV. Water, methanol, toluene, and methylethylketone were used to represent a variety of different solvent types. A static weight gain test was used to measure when equilibrium was obtained (< 6 days). The data show a systematic increase in solvent resistance in each solvent as the hard segment contents of the polyurethane elastomers are increased. It is the soft segment that absorbs solvent.

Modulus

Ambient temperature flexural and tensile modulus values (Table V) show a systematic increase in the stiffness of the polyurethane elastomers with increasing hard segment content. Figure 3 gives a plot (DMA) of flexural storage modulus (E') vs. temperature for each polyurethane elastomer. The modulus of the rubbery plateau region both increases and extends to higher temperatures as the hard segment content is increased.

Other Physical Properties

The effects of hard segment content on a variety of other physical properties are shown in Table V. Most of the polyurethane elastomers were nonbrittle materials. Only the two highest hard segment content materials broke under a notched Izod test. Hardness and tensile strengths increase with increasing

TABLE IV
Effect of Hard Segment Content on Solvent Resistance

Plaque number	Hard segment (wt %)	Solvent resistance (% wt gain after 6 days)			
		Water	Methanol	Toluene	MEK
I	31.9	6.9	14.6	17.4	Fell apart
II	35.7	5.1	13.3	14.7	41.4
III	43.5	4.6	11.7	11.7	30.3
IV	49.1	3.8	10.1	6.5	22.9
V	54.9	2.7	7.7	3.1	15.8
VI	60.0	1.6	5.3	1.4	9.3
VII	65.2	1.2	3.0	0.6	3.7

TABLE V
Effect of Hard Segment Content on Physical Properties^a

Plaque number	Hard segment (wt %)	Notched Izod (ft.-lb./in.)	Shore hardness		Modulus		Yield strength (psi)	Tensile at elongation			At break	
			A	D	Flexural (psi)	Tensile (psi)		100% (psi)	200% (psi)	300% (psi)	Strength (psi)	Elong (%)
I	31.9	NB	89	33	4,500	4,500	NO	615	—	—	645	150
II	35.7	NB	93	40	4,930	4,900	NO	790	1020	1240	1600	475
III	43.5	NB	97	47	9,300	9,300	NO	1355	1620	1835	2480	560
IV	49.1	NB	100	56	24,900	25,000	NO	2250	2445	2590	2970	525
V	54.9	NB	> 100	66	44,350	44,000	3160	3155	3150	3145	3150	400
VI	60.0	2.70	> 100	70	71,100	71,000	3560	3550	3410	3425	3390	325
VII	65.2	1.77	> 100	75	ND	ND	ND	ND	ND	ND	ND	ND

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

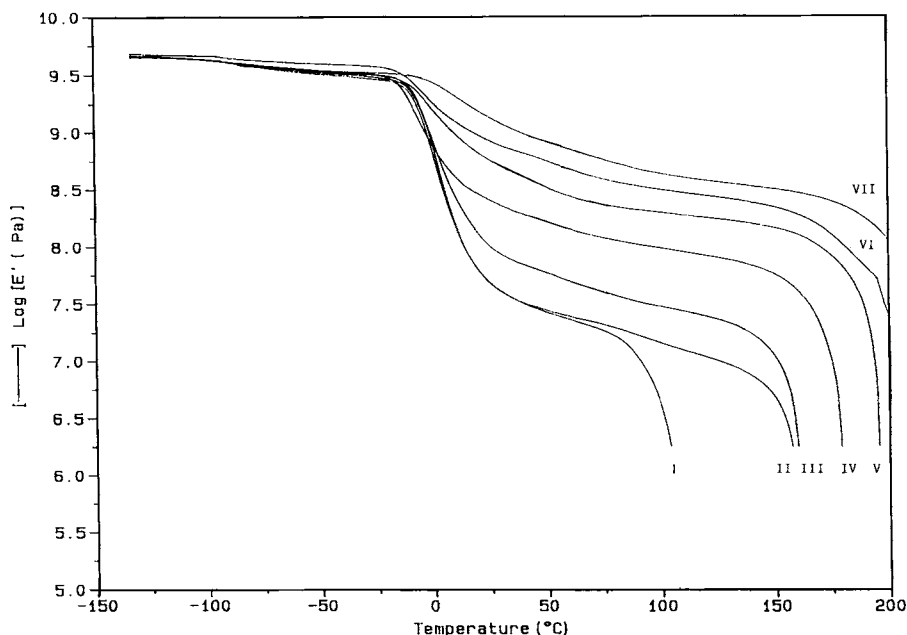


Fig. 3. Flexural storage modulus (E') vs. temperature by DMA.

hard segment content. The shape of the stress-strain curves change with the higher hard segment content materials (V and VI), and a yield point is observed. Tensile properties were not measured for (VII). Tensile strengths increase with increasing hard segment contents at 100, 200, and 300% elongations. Elongation at break is highest for intermediate hard segment content materials (polyurethanes II-V). The materials become too brittle at the higher hard segment contents.

Polymer Morphology

The flexural storage modulus (E') curves (Fig. 3) show that as the hard segment content is increased, the soft segment glass transition (T_g) becomes broader, and the hard segment melting point increases. A plot of hard segment dissociation temperature (temperature at which $E' = 1.78$ MPa) vs. hard segment content is shown in Fig. 4. This increase in melting point is probably due to the increase in the number of higher run length hard segment chains in the hard segment domains that occur as the hard segment content of the polymer is increased.

The flexural loss modulus data (E'') for the polyurethane elastomers are given in Fig. 5. The data show a relatively constant soft segment glass transition temperature. The polyurethane elastomer with the highest hard segment content (VII) has a somewhat higher soft segment T_g . These T_g data are consistent with the DSC results (Table VI). Figure 5 also reflects the progressive influence of the hard segment structure on the mobility of the soft segment units as indicated by the gradual broadening of the glass transition region.

The $\tan \delta$ curves for the polyurethane elastomers (Fig. 6) indicate the glass transition region already discussed. A β -type transition is observed at about

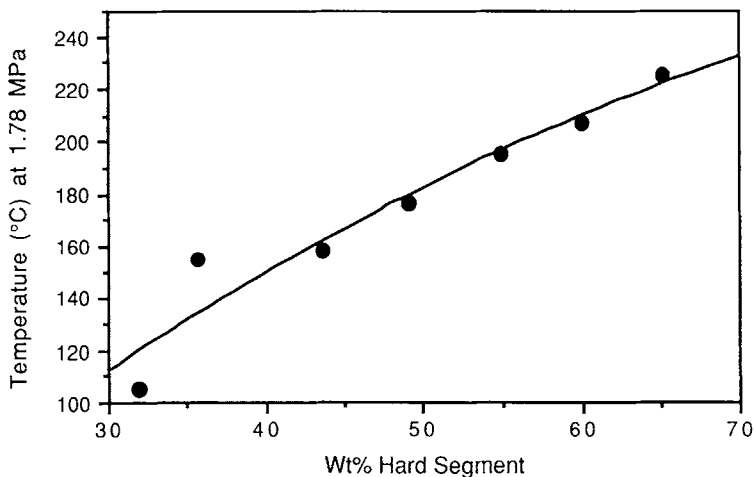


Fig. 4. Effect of hard segment content on hard segment dissociation temperature (DMA).

-75°C for all of the elastomers. This β transition, which in poly(propylene glycols) is normally associated with rotation of pendant methyl groups, is probably due to rotation of the carbonate carbonyl moieties about the C—O bonds. This type of transition has been seen in bisphenol A and polyester polycarbonates.¹⁰ An additional transition region at about 75°C is apparent in the three higher hard segment materials. This could be due to moisture devolatilization.

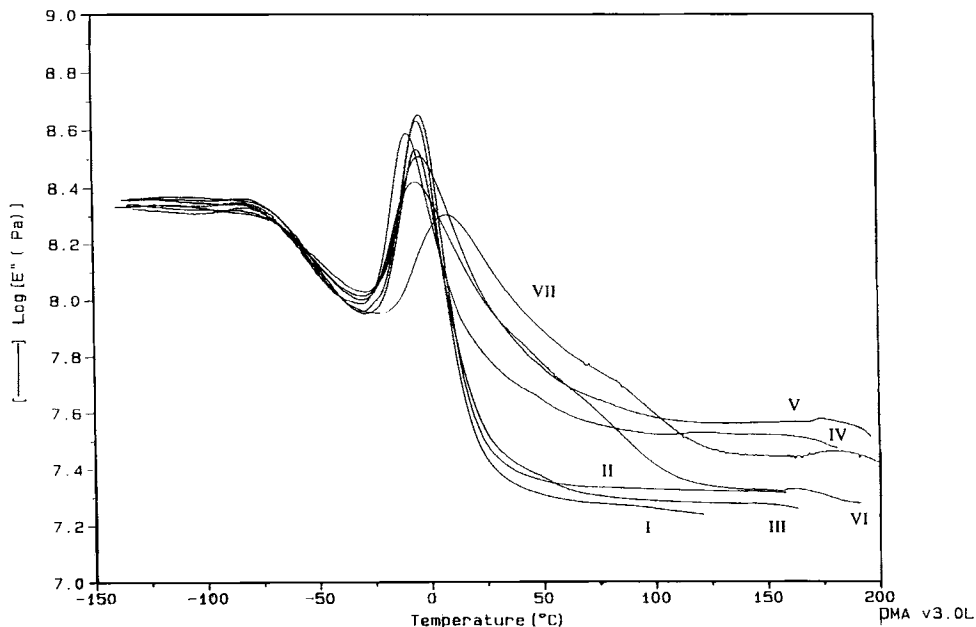


Fig. 5. Flexural loss modulus (E'') vs. temperature by DMA.

TABLE VI
Effect of Hard Segment Content on Thermal Properties

Plaque number	Hard segment (wt %)	First DSC scan		Second DSC scan		T_m (°C) First DSC scan	ΔH_m (J/g)	
		T_g (°C)	ΔC_p^a (J/g °C)	T_g (°C)	ΔC_p^a (J/g °C)		First DSC scan	Second DSC scan
I	31.9	-18	0.50	-5	0.57	120	1.9	0
II	35.7	-19	0.45	-1	0.47	169	6.2	7.1
III	43.5	-20	0.44	+7	0.50	167	12.8	5.3
IV	49.1	-20	0.32	+14	0.48	175	15.8	10.4
V	54.9	-19	0.31	+23	0.44	188, 218	23.7	9.0
VI	60.0	-17	0.27	+26	0.43	209, 220	29.8	15.8
VII	65.2	-12	0.20	+37	0.44	220	36.9	17.4

^a Not corrected for heat flow in sample pan.

The results of the DSC scans for polyurethanes I–VII are summarized in Table VI. In each case, the sample was heated to 250°C (first scan), then quenched with liquid nitrogen to -150°C, and scanned a second time up to 250°C. In some of the first scans there is a broad, shallow endotherm at about 75°C. This transition is also observed in some of the tan δ curves and is believed to be due to the volatilization of moisture picked up by the plaque as it sat at ambient temperature and humidity, since it is not present on the second scan and can be removed from the first scan by drying the sample in a vacuum oven

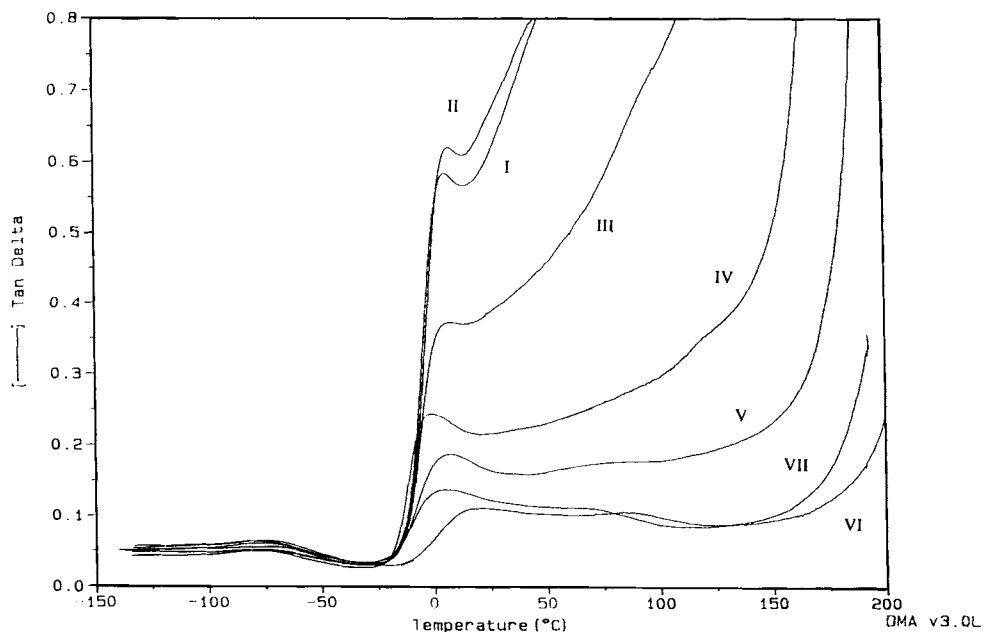


Fig. 6. Tan δ vs. temperature by DMA.

before running a DSC scan. A line due to water is also seen in the proton NMR spectra (3.34 ppm).

First and second DSC thermograms for polyurethane V are given in Fig. 7 and are typical of these polyurethane elastomers. The increase in soft segment T_g , the crystallization exotherm, and the reduced melt endotherm in the second scan are readily apparent.

The soft segment glass transition temperatures obtained for both the first and second DSC scans are plotted vs. hard segment content in Fig. 8. Although these polyurethane elastomers are partially phase mixed,⁷ most of the mixing must occur at domain boundaries since the soft segment T_g (first scan) is nearly invariant with hard segment composition. However, the second DSC scan indicates a highly phase mixed morphology. The soft segment glass transition temperatures (second scan) increase with increasing hard segment content. Therefore, they were analyzed by the Fox relationship¹¹:

$$1/T_{g1,2} = (w_1/T_{g1}) + (w_2/T_{g2})$$

where $T_{g1,2}$ is the glass transition temperature of a copolymer containing weight fractions w_1 and w_2 of units 1 and 2, which, respectively, have homopolymer glass transition temperatures T_{g1} and T_{g2} . Utilizing the T_g of the poly(ethylene ether carbonate) diol ($T_g = -39^\circ\text{C}$) and the T_g of the MDI/BDO hard segment units ($T_g = 125^\circ\text{C}$),¹² the Fox equation was used to calculate the theoretical glass transition temperatures of the polyurethane elastomers based on the different hard segment/soft segment compositions studied. The solid line in Fig. 8 shows the results of these calculations and corresponds to complete phase

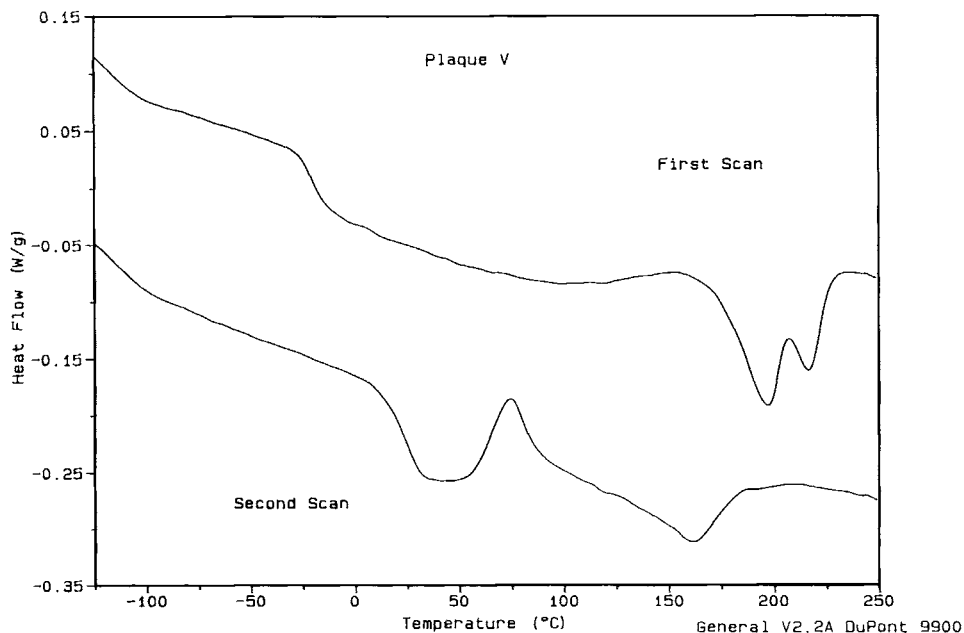


Fig. 7. First and second DSC scans of polyurethane V (54.9 wt % hard segment).

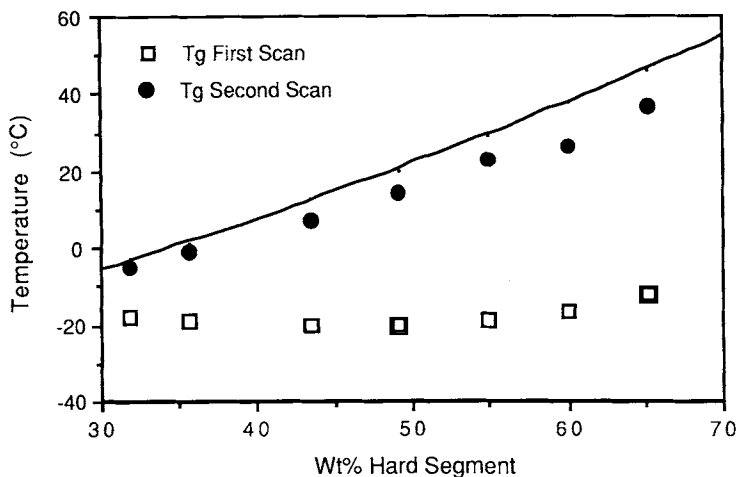


Fig. 8. Comparison of soft segment T_g during first and second DSC scans to predicted curve at 100% phase mixing.

mixing. The data points (second DSC scan) are slightly below the theoretical curve indicating nearly 100% phase mixing under these conditions.

The changes in heat capacity (ΔC_p) of the soft segment glass transition regions for the first and second DSC scans are plotted vs. hard segment content in Fig. 9. These transitions broaden with increasing hard segment content, consistent with the DMA results. The second scan glass transition temperatures are broader, taller, and occur at a higher temperature than those of the first scans.

Information about the melt endotherms (ΔH_m) of these polyurethane elastomers is given in Table VI. There is a systematic increase in the heat of melting as the hard segment content of the polyurethane elastomer increases.

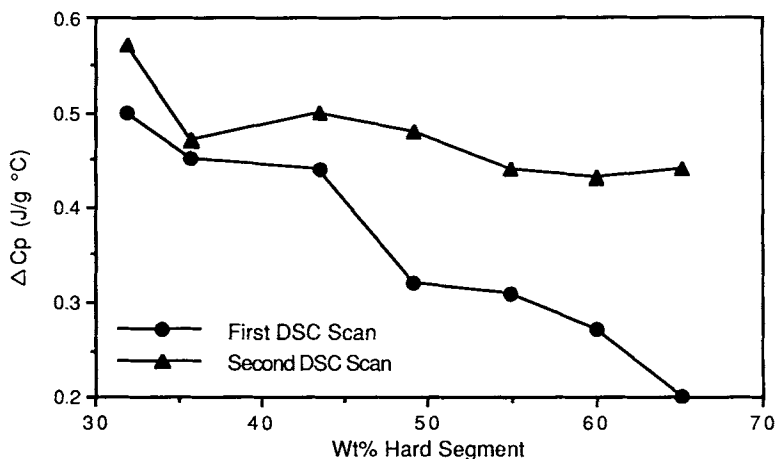


Fig. 9. Effect of hard segment concentrations on the size of soft segment transition regions during first and second DSC scans.

Figure 10 is a graph of the size of these melt endotherms for the first and second DSC scans vs. hard segment content. The second scans show a smaller hard segment melt endotherm because part of the hard segment remains amorphous and is dissolved in the soft segment. It is this amorphous hard segment that causes the soft segment T_g to be shifted to a higher temperature and to increase in size on the second DSC scan. In one experiment, polyurethane V ($T_g = -18$) was heated to 250°C and quenched to -150°C . A second scan ($T_g = 22^\circ\text{C}$) was stopped after the crystallization exotherm had occurred (100°C) but prior to any melting of the hard segment. Subsequent cooling (to -150°C) and reheating to 250°C showed the soft segment T_g shifting downward to 8°C , consistent with less amorphous hard segment dissolved in the soft segment.

What is particularly interesting about these polyurethanes, as opposed to polyurethane elastomers made with conventional polyether polyol soft segments, is that when there is any amorphous hard segment present, it is completely dissolved in the soft segment and shows no distinct hard segment T_g regardless of the hard segment content of the polymer. Any amorphous hard segment, which is not dissolved in the soft segment, would be expected to have a hard segment T_g at about 125°C . This high degree of hard segment solubility in the soft segment is probably due to the increased hydrogen bonding potential inherent in the poly(ethylene ether carbonate) diols.

Annealing Studies

Polyurethane V (54.6 wt % hard segment) was annealed at various temperatures up to 200°C in order to see what effect annealing had on morphology. Results are summarized in Table VII. Figure 11 shows the first DSC thermograms for non-post-cured polyurethane V and for polyurethane V samples after they were annealed at various temperatures. The annealing was done in the DSC, and then the sample was cooled and run immediately. The first sample was dried in a vacuum oven at 130°C for 16 h. This removes atmospheric moisture that the sample picks up from sitting at ambient temperature and humidity, and which would otherwise show up on the DSC thermogram as a

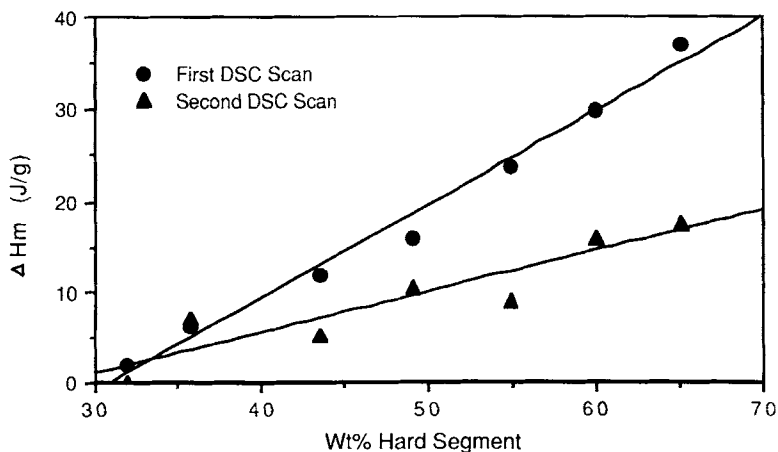


Fig. 10. ΔH_m vs. wt % hard segment for first and second DSC scans.

TABLE VII
Effect of Annealing on Thermal Properties of Polyurethane V

Annealing conditions	T_g (°C)	ΔC_p^a (J/g °C)	T_m (°C)	ΔH_m (J/g)
Polyurethane V	-19	0.31	188, 218	23.7
Vacuum dried at 130°C/16 h	-13	0.40	197, 216	29.2
Annealed at 150°C/1 h	-12	0.44	196, 215	29.9
Annealed at 175°C/1 h	-10	0.43	199, 215	29.1
Annealed at 190°C/1 h	-4	0.47	208, 214	23.4
Annealed at 200°C/1 h	-2	0.50	222	15.6

^a Not corrected for heat flow in sample pan.

broad, shallow endotherm centered at about 75°C. This sample shows hard segment melt endotherms at 197 and 216°C.

Three significant events are observed when the DSC thermograms (Fig. 11 and Table VII) are compared. First, the endothermic transitions (melts) disappear below the annealing temperature causing a narrowing of the melt endotherms. Second, the soft segment T_g increases in height and temperature as the annealing temperature is increased and the melt endotherm is narrowed. Third, the total area of the melt endotherms, measured in joules per gram, remain relatively constant when the annealing temperature is kept below the first peak melting point of 197°C.

When the sample is annealed above the onset temperature of the melt, the portion of the endotherm below the annealing temperature disappears, and that fraction of the sample that it represents is assumed to have become amorphous and dissolved in the soft segment, which is what causes the soft segment T_g to increase in both size and temperature.

The question then arises as to why the total area of the melt endotherm, when annealed below 197°C, remains relatively constant if the hard segment is losing crystalline material to the amorphous state. One explanation for this could be that of the material that becomes amorphous, part stays amorphous and dissolves in the soft segment and part crystallizes into a higher-order crystal, which has a greater ΔH_m , and thus the overall heat of melting for the endotherm remains relatively constant even though there is less crystalline material present.

The data from this annealing study would seem to indicate that the optimum post-curing temperature, for one hour, for this polymer is about 175°C. The rubbery plateau region can be extended 25°C higher when post-cured at 175°C without losing crystallinity. Post-curing at higher temperatures increases the temperature range of the rubbery plateau region but decreases the ΔH_m of the sample, which influences physical properties such modulus, impact strength, etc.

SUMMARY AND CONCLUSIONS

A series of polyurethane elastomers were studied in which the soft composition was a molecular weight advanced poly(ethylene ether carbonate) diol

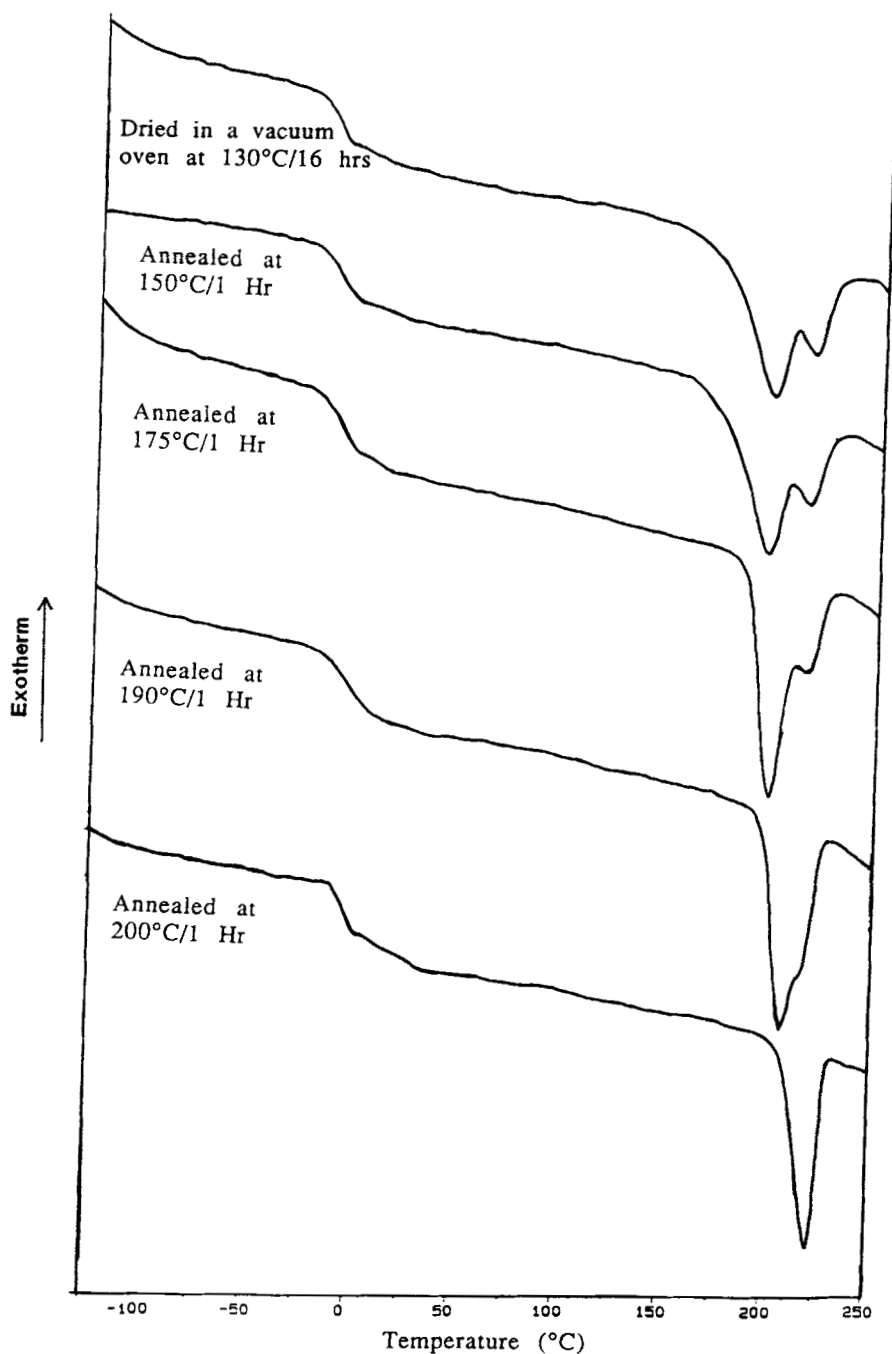


Fig. 11. Effect of annealing conditions on polyurethane V DSC scans.

(2025 mol wt) and the hard segment composition was based on MDI/1,4-butanediol. These polyurethane elastomers had a constant soft segment composition and block length, a constant hard segment composition, but a variable hard segment block length and concentration (31.9–65.2 wt % hard segment).

Properties such as rubbery plateau modulus, solvent resistance, melting point, hardness, tensile strength, and hard segment run length all improve with increasing hard segment concentration. Impact properties suffer at the highest hard segment concentrations (60.0 and 65.2 wt %). DMA and DSC data indicate a partially phase mixed morphology. However, phase mixing must occur at domain boundaries since the soft segment T_g is nearly invariant with hard segment concentration. The poly(ethylene ether carbonate) diol blocks show a high compatibility with any amorphous hard segment blocks present. Samples that are melted and then quenched quickly are nearly 100% phase mixed. Annealing studies indicate that the optimum post-cure temperature, for 1 h, is about 175°C.

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