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William MacKnight, *University of Massachusetts Amherst*

C. M. Brunette

S. L. Hsu

M. Rossman

N. S. Schneider

Thermal and Mechanical Properties of Linear Segmented Polyurethanes with Butadiene Soft Segments

C. M. BRUNETTE, S. L. HSU, M. ROSSMAN, W. J. MacKNIGHT, and N. S. SCHNEIDER*

*Polymer Science and Engineering Department
Materials Research Laboratory
University of Massachusetts
Amherst, Massachusetts 01003*

A series of segmented polyurethanes based on a hydroxyl terminated polybutadiene soft segment (HTPBD) have been prepared with varying hard segment content between 20 and 60 weight percent. These materials are linear and amorphous and have no potential for hydrogen bonding between the "hard" and "soft" segments. The existence of two-phase morphology was deduced from dynamic mechanical behavior and thermal analysis. Both techniques showed a soft segment glass transition temperature, T_{gs} , at -56°C and hard segment transitions between 20 and 100°C , depending on the urethane content. The low value of T_{gs} , only 8° higher than the T_g of free HTPBD and independent of hard segment concentration indicated nearly complete phase segregation. Depending on the nature of the continuous and dispersed phases, the urethanes behaved as elastomers below 40 weight percent hard segment or as glasslike materials at higher hard segment contents. The effect of thermal history on transitions of the HTPBD-urethanes was also investigated and the results suggest that the absence of hydrogen bonding to the soft segment must account for the extraordinary insensitivity to thermal history in dynamic mechanical, thermal and stress-strain behavior. Comparisons are made to the more common polyurethanes containing polyether and polyester soft segments.

INTRODUCTION

Considerable attention has been devoted toward understanding of the property-structure relationships in segmented polyurethanes in recent years. In general, these materials derive their unusual properties from the thermodynamic incompatibility of the component polymer segments and consequent phase separation. Typically, the soft segments are composed of a rubbery polymer, (i.e., polyester or polyether) with its glass transition temperature, T_{gs} , well below the use temperature. The hard segments, which are generally formed from the extension of an aromatic diisocyanate with a low molecular weight diol provide physical crosslinking and reinforcement for the soft phase and are responsible for the higher temperature performance.

The existence of phase segregation, caused by the clustering of hard and soft segments into separate domains, has been well documented (1-3). Consequently, many of the physical and mechanical properties, (i.e., enhanced modulus, high extensibility and resiliency)

have been interpreted in terms of a two phase system. Past studies have dealt primarily with the influence of hard and soft segment chemical structure and molecular weight on the extent of phase segregation and domain formation. Schneider (4) and Rustad (5) have shown that the choice of polyether rather than polyester soft segments and the use of 2000 rather than 1000 molecular weight leads to better phase segregation. Seefried, *et al.* (6) has illustrated that MDI-based polyurethanes, in contrast to TDI urethanes, possess a more perfect domain organization due to short range order including crystallinity and, consequently, show a higher extent of segregation between hard and soft segments. Through techniques such as differential thermal analysis, dynamic mechanical measurements, and X-ray studies, models of phase segregation and domain structure have been developed which are reasonably successful in accounting qualitatively for the many features of segmented polyurethanes (1-3). However, in most polyurethanes previously investigated, difficulties arise because the phenomena of interest are obscured by one or more of the following competing effects: 1) specific interactions between the hard and soft segment phase,

*Present address: Army Materials & Mechanics Center, Organic Materials Research Laboratory, Fibers & Polymers Division, Watertown, Massachusetts 02172.

via hydrogen-bonding, 2) crystallinity occurring in either or both the soft and hard segment phases, and 3) chemical crosslinking. It is therefore of interest to examine the structure-property relations in a series of segmented polyurethanes in which these added complexities are excluded.

This study continues the examination of polyurethanes based on a polybutadiene soft segment (7,8) to eliminate polar and hydrogen bonding interactions between hard and soft segment units. As in the prior study, the hard segment is based on 2,4 toluene diisocyanate and butanediol which is completely amorphous under all conditions. The distinguishing feature of the present work is the use of an anionically polymerized hydroxy terminated polybutadiene. This macroglycol has an average hydroxyl functionality of 1.97 which avoids crosslinking through the soft segment phase, a problem with the previously studied materials based on the free radical polybutadiene (ARCO R-45-M). In addition, the microstructure of the present macroglycol precludes the occurrence of any soft segment crystallinity. Thus, the structure of the hard domains, the nature of phase segregation and other morphological features can be studied in a simplified manner. The characterization techniques performed on these polymers include dynamic mechanical relaxation, stress-strain measurements and differential scanning calorimetry. Also, the thermal history dependence of these polybutadiene polyurethanes is studied and the results are compared to analogous polyurethanes containing polyether and polyester soft segments.

EXPERIMENTAL

Materials

The hydroxyl-terminated polybutadiene (HTPBD) used in this study was kindly provided by the Japan Synthetic Rubber Co. Infrared analysis yielded a vinyl content of 55 percent, a trans content of 35 percent and a cis content of 10 percent. The details of this analysis have been described previously (8). Gel permeation chromatography in tetrahydrofuran using a polystyrene calibration gave a number average molecular weight $M_n = 2200$ and weight average molecular weight $M_w = 3290$.

All polyurethanes were prepared in bulk by a two step method involving end capping the HTPBD with 2,4-toluenediisocyanate (TDI) (Aldrich) followed by reaction with the chain extender, 1,4 butanediol (BDL) (Aldrich). The end capping was carried out at 120°C for one hour under a nitrogen purge, after which the temperature was lowered to 80°C. Following the addition of the chain extender, the reaction mixture was degassed, poured between Teflon sheets and cured in the press at 120°C for 17 h. The resulting films, 0.40 mm in thickness, were allowed to stand at least one week before measurements were carried out. The composition and some characteristic properties of the resulting polyurethane samples are summarized in Table 1. This series of six samples ranges from a 2:1 to 10:1 equivalent ratio of TDI to HTPBD at a fixed NCO/OH ratio of approximately 1.05.

Table 1. Composition and Properties of HTPBD-Polyurethanes

Sample	Molar Composition TDI/BDL/PBD	Hard segment Weight percent	Properties
JSR-2	2.1/1.2/1.0	18	Clear, soft, tacky rubber
JSR-3	3.0/1.9/1.0	25	Translucent, rubbery, tough
JSR-4	4.1/3.1/1.0	32	Translucent, slightly elastic, tough
JSR-6	6.2/5.0/1.0	42	
JSR-8	8.4/7.2/1.0	49	Opaque, hard, slightly flexible
JSR-10	10.0/8.8/1.0	55	Opaque, hard

Measurements

Dynamic mechanical measurements were carried out on a Vibron Dynamic Viscoelastometer, Model DDV-II (Toyo Measuring Instruments Co.). The temperature range was from -160 to 150°C and the frequencies employed were 3.5, 11, and 110 Hz. Samples were heated at a nominal rate of 1.5 deg/min under a dry nitrogen atmosphere.

Thermal analysis of the soft segment glass transition temperature was made with the Perkin Elmer DSC-2, purged with He and chilled with liquid nitrogen. The DSC was calibrated for low temperatures using the crystal-crystal transformation of cyclohexane at 186°K. Runs were conducted on polymer samples of about 15 mg at a heating rate of 20°C/min and an attenuation of 5mcal/s. Heat capacity measurements at the soft segment glass transition were calibrated using a sapphire standard. The higher temperature scans were conducted from 250 to 450°K using the DSC-2 equipped with a two stage mechanical refrigerator unit. Glass transition temperatures were determined as the temperature corresponding to one half the increase in heat capacity at the transition.

Stress-strain data were obtained on an Instron Universal testing machine at an extension rate of 2cm/min. Rectangular-shaped specimens of the approximate average dimensions 50 × 3 × 0.40 mm were used. In cyclic stress-strain experiments, a single sample was submitted to increasing amounts of prestrain. The sample was extended by increments up to 20 percent, allowed to relax at zero load for 5 min, extended to 40 percent, etc. All data reported are averages of at least 5 tests on different samples.

Dynamic Mechanical Measurements

As shown in Fig. 1, the relaxation behavior clearly illustrates the two phase nature of these HTPBD-containing polyurethanes of varying hard segment concentrations. All polymers of this family exhibit a constant low temperature relaxation at about -56°C, determined at 11 Hz from the temperature of the E'' loss maximum (see Table 2). This α_s relaxation is due to the onset of microbrownian segmental motion associated with the glass transition of the soft butadiene phase. Neither the temperature nor the activation energy, E_a , of the α_s relaxation varies with urethane content over the concen-

Fig. 1. Temperature dependence of the storage and loss modulus for HTPBD-polyurethanes.

tration range examined (see Table 2). This indicates that the development of a hard segment phase which gives rise to an additional relaxation (later to be discussed) has no effect on the mechanism of the α_s relaxation. The α_s relaxation is also characterized by a decrease in storage modulus of at least two orders of magnitude.

Above ambient temperatures, the loss processes vary systematically with urethane content. Samples of the lowest urethane concentration display a single weak transition at about 20°C, designated α_{1h} . At 42 wt percent hard segment, a second relaxation, designated α_{2h} , occurs at 75°C. As the hard segment content is further increased, the α_{2h} relaxation becomes much more prominent while the positions of both α_{1h} and α_{2h} relaxation are shifted some 15° to higher temperatures. The temperatures and activation energies for these transitions are summarized in Table 2. It is reasonable to believe that such transitions result from motions occurring within the hard segments. This could be supported by noting also the difference in E_a for α_s and α_h .

Consistent with findings for other phase segregated systems, the level of the storage modulus above α_s and the softening temperature increases with hard segment content. These effects, as well as the increase in the α_h

relaxation temperature, can be directly attributed to an increase in the hard segment length and a more well developed urethane domain structure which occurs with increasing hard segment content.

A final point to note lies in the temperature dependence of the mechanical loss ($\tan\delta$) illustrated in Fig. 2. As the hard segment content increases, the magnitude of the α_s relaxation decreases while that of the α_{2h} relaxation increases. In fact, the magnitude of the α_{2h} relaxation at the highest urethane content (JSR-10) is nearly equal to that of the α_s relaxation of the lowest urethane content (JSR-2). Such changes in the damping behavior of these materials clearly reflect changes in the relative amounts of the constituent phases present and a gross change in the character of the polymer. Further evidence for this behavior is presented in stress-strain data, to be discussed later.

Unlike the behavior of other polyurethanes (10,11), the dynamic mechanical properties of HTPBD-based polyurethanes were unaffected by thermal history. Samples were quenched to liquid nitrogen temperatures from 150°C and immediately retested and were also stored for one month prior to retesting. Figure 3 shows that the values of the various viscoelastic functions were essentially unchanged. The invariance of the activation energy, shape and temperature of the α_s re-

Fig. 2. Temperature dependence of the loss tangent for HTPBD-polyurethanes.

Sample	Relaxation	Temperature ^a (°C)	Activation ^b Energy (kJ/mole)	Softening Temperature (°C)
JSR-2	α_s	-57 (-45)	120 ± 20	35
JSR-3	α_s	-56 (-46)	140 ± 20	51
	α_{1h}	20		
JSR-4	α_s	-56 (-46)	110 ± 20	62
	α_{1h}	20		
JSR-6	α_s	-56 (-47)	110 ± 20	99
	α_{1h}	35	240 ± 10	
	α_{2h}	76 (84)	280 ± 20	
JSR-8	α_s	-56 (-48)	120 ± 30	114
	α_{1h}	56		
	α_{2h}	91 (102)	280 ± 20	
JSR-10	α_s	-55 (-47)	120 ± 10	138
	α_{1h}	60		
	α_{2h}	93 (105)	340 ± 10	

^aall determined at 11 Hz from E''_{max} ; () from $\tan \delta_{max}$.

^bdetermined from an Arrhenius dependent of frequency (3.5, 11, and 110 Hz) on temperature, to the 95 percent confidence level.

Fig. 3. Dynamic mechanical response of JSR-6: (a) initial run; (b) quenched from 150°C and retested immediately; (c) quenched from 150°C and retested after one month.

laxation suggest there is little, if any, change in the composition of the soft segment phase on heating.

Thermal Analysis

A summary of the DSC transition temperatures for the six HTPBD-containing polyurethanes and the HTPBD prepolymer is presented in Table 3. These results are in good agreement with the dynamic mechanical studies. The soft segment glass transition is well defined and reproducible and appears at $-56 \pm 2^\circ\text{C}$ in all samples. Like the height of the α_s mechanical loss peak, the magnitude of the step change in the specific heat, (ΔC_p), accompanying the soft segment glass transition decreases with increasing wt percent of urethane. These ΔC_p values are listed in Table 3 and plotted vs weight fraction of hard segment in Fig. 4. Note that the intercept of the line lies very close to the ΔC_p value of the HTPBD prepolymer.

Since DSC gives quantitative results and since interactions between hard and soft segments are assumed sufficiently small that they may be ignored, the following equation based on a simple two-phase model can be used to calculate soft segment content (12,13):

$$f_{ss} = \frac{\Delta C_{pTg}}{\Delta C_{pTg}^0} = 1 - f_{hs}$$

where f_{ss} = soft segment fraction present per unit mass, ΔC_{pTg} = observed heat capacity change at T_{gs} for the polymer, ΔC_{pTg}^0 = the experimentally determined or extrapolated heat capacity change at T_{gs} for 100 percent soft segment phase, and f_{hs} = hard segment weight fraction. Using this equation, the ΔC_p values of the six polymers normalized to the ΔC_p of pure HTPBD are also plotted in Fig. 4 and are shown to lie very close to the ideal two-phase line.

This type of treatment has also been applied to semi-crystalline polymers (12). However, unlike these HTPBD-polyurethanes, deviations from the ideal two-phase behavior are generally observed indicating that interactions between the phases are important. In polyester and polyether urethanes where crystallinity is often present as is hydrogen bonding interactions between the two phases, deviations are also expected due to additional constraints imposed on the soft segment phase (4, 11).

The higher temperature transition behavior follows a general pattern, the details of which depend upon urethane content (see Table 3). The DSC scans for sam-

Fig. 4. Observed heat capacity change at T_{gs} for JSR samples of varying hard segment content, (open circles); normalized heat capacity change compared to ideal two-phase behavior, (closed circles).

ples of the lowest urethane content (JSR-2 and JSR-3) show only a single, diffuse transition in the vicinity of 20°C . This transition is reproducible in subsequent scans. For JSR-4, the initial trace shows two transition regions; a weak transition at 20°C (T_1) and a strong endothermic peak at 55°C (T_2). In the second scan, both transitions reappear but the excess enthalpy peak at T_2 disappears and the transition occurs about 5° higher. As mentioned earlier, both of these transitions can be attributed to the hard phase. T_1 and T_2 are also observed in the sample of the next highest urethane content, but now appear at 40 and 65°C , respectively. The T_1 transition is no longer discernible in a repeat scan and the enthalpy relaxation peak at T_2 disappears and the transition shifts to 80°C . Only one transition is evident in samples of the highest urethane concentration (JSR-8 and JSR-10) which appears at 75°C on first scan and 84°C on repeated scanning.

The systematic reduction in the strength and permanence of the T_1 transition with increasing hard segment content suggests that T_1 is due to phase segregated structures made up of shorter hard segment units and T_2 to phase segregated structures containing the longer hard segment units. Why two different populations of hard segments should occur in an amorphous system still remains unclear. However, two hard segment trans-

Table 3. Effect of Thermal History on Transitions in HTPBD-Polyurethanes by DSC

Sample	$T_{gs} (^\circ\text{C})$	ΔC_p (cal g ⁻¹ °K ⁻¹)	Upper transitions, T_1 and T_2 ($^\circ\text{C}$) ^a		
			1st Run	After 24 h	After 24 days
JSR-2	-58 (-57)	.125	20(d)	20w	20(d)
JSR-3	-56 (-56)	.118	20(d)	20w	20(d)
JSR-4	-58(-58)	.097	20(20) 55(58w)	22 54	20(22) 54(57)
JSR-6	-55 (-54)	.084	40(a) 65(80)	42 74	39(a) 64(83)
JSR-8	-55 (-54)	.076	74(84)	83	74(82)
JSR-10	-56 (-54)	.070	75(84)	83	74(84)
JHTPBD	-65 (-65)	.155			

^a Values in bracket, transition observed in second scan; d—indicates the transition was diffuse; w—that it was weak; a—that it was absent.

itions have been observed in other HTPBD-containing polyurethanes under conditions where the lower transition was clearly identifiable with shorter hard segments containing up to three TDI repeat units (7).

The effect of thermal history on T_{gs} , T_1 and T_2 was also studied. Thermal cycling of the materials to 150°C produces no change either in the position or shape of T_{gs} . The absence of thermal history effects on T_{gs} is consistent with the dynamic mechanical results reported earlier. The effects of thermal history on T_1 and T_2 are illustrated in Fig. 5. Scans were made after different storage times at 25°C as noted on the figure. As mentioned earlier, two transitions are observed in samples of intermediate composition. For JSR-4, the T_1 transition region is only slightly affected by thermal treatment, recovering readily after the initial scan. The time scale for recovery of the endothermic peak at T_2 , however, is far longer. Following heat treatment, this endothermic peak is replaced by a weak step change in specific heat that increases in strength over a period of approximately 24 days before assuming its original appearance. This time-dependent behavior is believed to be caused by a simple densification process within the hard segment domains (14). A comparable time scale was required for the recovery of the T_2 transition in the higher urethane samples.

Stress-Strain Measurements

The effect of hard segment content on the stress-strain behavior of these polyurethanes was also investigated. The results are summarized in Table 4.

From Fig. 6 it is clear that the mechanical properties of these materials change only slightly when the hard segment content increases from 18 to 32 wt percent but change profoundly between 32 (JSR-4) and 42 wt percent hard segment (JSR-6). In fact, below 32 wt percent the polymers are clearly elastomeric with extensions of > 1000 percent and recover almost completely when the stress is removed. Above 42 wt percent hard segment, they exhibit elongations to break, ϵ_b , of less than 80 percent and show permanent set. Such a marked change in the characteristics of the polymer is probably due to inversion of hard and soft phases. Very likely, the films have a different morphology consisting of soft segment domains in a hard segment rich matrix.

In agreement with our dynamic mechanical and DSC studies, the stress-strain behavior of these PBD-based polyurethanes is unaffected by thermal treatment. Here the samples were annealed at 150°C for as long as two

Fig. 5. DSC scans of JSR-4 taken at different times following quenching.

Fig. 6. Stress-strain response of HTPBD-polyurethanes.

hours followed by air quenching. In contrast, the mechanical properties of a series of polyester and polyether polyurethanes were shown to be highly time dependent (i.e., materials harden with time and increase in toughness) when tested under similar conditions (10).

Cyclic Instron tests were also performed on these materials. If the sample is not strained to break, but relaxed to zero stress, stress softening or hysteresis is observed (see Fig. 7). With the exception of JSR-10 which was too brittle to test, all samples show a decrease in stress on repeated straining. Moreover, the higher

Table 4. Stress-Strain Properties of HTPBD Polyurethanes

Sample	Tensile strength (σ_b) psi		Elongation (ϵ_b) percent	Percent recovery ^a
	True σ_b	Engineering σ_b		
JSR-2	4,440	410	1000	95
JSR-3	10,060	600	1620	90
JSR-4	6,010	480	1160	89
JSR-6	3,310	620	430	85
JSR-8	650	390	70	75
JSR-10	440	390	15	—

^a All determined at 90 percent ϵ_b .

the hard segment content, the higher the percent hysteresis, presumably due to greater plastic deformation occurring within the hard phase. This stress softening behavior is characteristic of phase separated materials (15).

DISCUSSION

Based on the chemically dissimilar nature of the hard and soft segment components, the existence of nearly compositionally pure phases in these materials is not surprising. The morphology of PBD-polyurethanes, as shown by Legasse (14) and inferred from our results resembles that of S-B-S and S-I-S block copolymers. In these systems, the hard and soft segments undergo microphase separation to form individual domains largely composed of one type of segment (i.e., hard segment domains dispersed in a soft segment matrix) (16,17). The morphology of such a domain structure may be contrasted to that of polyester and polyether polyurethanes. Experimental evidence suggests that for these materials, separation into discrete microphase regions does not occur but rather the hard segments form an interlocking continuous network with regions rich in soft segments (18,19). Consequently, the inherent properties of the individual segments, i.e., crystallinity, chemical structure, molecular weight, etc., are likely to be determinants of the extent of phase separation and resultant morphology. This line of reasoning is further exemplified in their time-dependent thermal and mechanical behavior. For polyester and polyether urethanes, changes in soft segment glass transition temperature, degree of phase separation and room temperature modulus are observed following heat treatment. These results have been attributed to the temporary disruption of domain structure and increased mixing of hard and soft segments (10). This mixing process is promoted in part by hydrogen bonding between the urethane segments and ester or ether functional groups of the soft segment (20). While this model explains well time-dependent phenomena in polyester and polyether urethanes, it bears little application to HTPBD-based polyurethanes where the lower transition temperature

remains insensitive to thermal cycling. Legasse (14), working on a series of crosslinked HTPBD-polyurethanes proposes that the reversible thermal history dependence in these HTPBD systems is related to physical changes within the hard segment domains and independent of the soft segment matrix. Since no thermally activated mixing occurs between the two phases, two distinct regions prevail rather than a continuum of compositions. Although this behavior has been attributed to either the presence of chemical crosslinks or absence of hydrogen bonding to the soft segment (14,21), this present study on linear HTPBD-urethanes confirms the latter—that the absence of hydrogen bonding between hard and soft segments must account for the absence of thermal history effects in these polymers as compared to polyester and polyether polyurethanes.

CONCLUSIONS

The glass transition temperature of the HTPBD soft segment appears at -56°C by both DSC and rheovibron measurements. The value of T_{gs} in these polyurethanes as compared to a value of -64°C for the pure HTPBD and its invariance with increasing urethane content indicate that phase segregation is very nearly complete. Since TDI-BD form amorphous hard segment regions, the driving force for phase segregation must come from the extreme incompatibility of the apolar soft segment and the strongly polar hard segment units. In addition, there is no hydrogen bonding contribution to increase the compatibility between the two phases.

The unusual transition behavior above ambient temperatures is related to the nature of the dispersed hard segment phase. Only a T_1 (α_{1h}) transition region is evident in samples of lowest urethane content; both T_1 and T_2 (α_{2h}) appear in samples of intermediate content while only T_2 appears in highest urethane samples. These transitions above T_{gs} are also the result of the extreme degree of phase segregation, with T_1 arising from the localization of shorter hard segment units, which in polyester or polyether polyurethanes would remain soluble in the soft segment phase and T_2 from domains containing longer hard segment units. This systematic change in transition behavior with urethane content is also reflected in stress-strain properties whereby the polyurethane changes from a tough elastomeric material to a more brittle, though low modulus, plastic. This is undoubtedly due to inversion of the continuous and dispersed phases which occurs in the system at approximately 40-50 weight percent of hard segment.

Another significant feature of these HTPBD-polyurethanes is their completely reversible nature following thermal treatment. In contrast with previous findings on polyester and polyether urethanes, the time dependence in dynamic mechanical and thermal behavior was not accompanied by any measurable change in the T_g of the soft segment phase. This difference in behavior is largely attributed to the absence of urethane hydrogen bonding to the soft segment in HTPBD-based polyurethanes.

Fig. 7. Cyclic stress-strain curve for JSR-6 extended 20, 40, 60 and 80 percent ϵ_h .

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