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Structural and Mechanical Properties of Polybutadiene-Containing Polyurethanes

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A series of segmented polyurethanes based on hydroxyl-terminated polybutadienes (HTPBD) and their hydrogenated derivatives (HYPBD) has been synthesized. Thermal, mechanical, and spectroscopic studies were carried out over a wide temperature range to elucidate the structure-property relationships existing in these polymers. Both thermal and dynamic mechanical response showed a soft segment T_g at -74°C for the unsaturated polyurethanes and at -69°C for the hydrogenated samples. In addition, two hard segment transitions are observed by differential scanning calorimetry (DSC) at 40 and 75°C and a softening region by thermal mechanical analysis (TMA) at 190°C . The low T_g , very close to that of the free HTPBD and HYPBD and independent of hard segment content, indicated that these polymers were well phase separated. Results of infrared analysis revealed that at room temperature, 90-95 percent of the urethane N-H groups formed hydrogen bonds. Since hydrogen bonding resides only within the hard segment domain in these butadiene-containing polyurethanes the extent of H-bonding served as additional evidence for nearly complete phase segregation. From dynamic mechanical studies, the plateau modulus above the soft segment T_g and stress-strain behavior depended upon the concentration of hard segments. A slight increase in the modulus, a moderate increase in stress (σ_b), and decrease in elongation accompanied a higher hard segment content. The thermal and mechanical response of these polyurethanes appears to be consistent with behavior observed for other phase segregated systems. Variations in behavior resulting from hydrogenation of the precursor prepolymer are discussed.

INTRODUCTION

Segmented polyurethanes incorporating a hydroxyl-terminated polybutadiene (HTPBD) soft segment offer the advantage of low moisture permeability and have been the subject of several studies aimed at exploiting this property for adhesives and electrical potting compounds (1-3). This class of materials is also of interest as a model system in which there is no possibility of hydrogen bonding between the hard and soft segment, in contrast to the more familiar polyester or polyether

polyurethanes. Since the hydrogen bonding interactions are limited to the hard segment components, studies of HTPBD-containing polyurethanes could shed further light on the role of hydrogen bonding in determining the extent of phase segregation, the stability of hard segment domain structure and related polyurethane properties.

Several recent publications have appeared which deal with the structure and properties of HTPBD polyurethanes. A study by Legasse (4) was concerned

with the morphology, transition behavior and especially the time dependent recovery of the hard segment transition after heating, but some aspects of the behavior reported were probably conditioned by the nature of the commercial coating formulation which was examined. The influence of HTPBD molecular weight on the mechanical properties of both nonsegmented and segmented polyurethane copolymers was studied by Ono and coworkers (5). They demonstrated that superior properties were obtained with segmented copolymers, reflecting the contribution of domain structure. In addition, it was shown that the tensile strength and related mechanical properties increased significantly below 3,000 HTPBD molecular weight, which corresponds to the molecular weight of the most commonly available HTPBD prepolymers (Arco). A study of the thermal transition behavior of a series of HTPBD polyurethanes, closely related in composition to those of the present study, was reported by Schneider and Matton (6). The HTPBD was Arco R45M, which has a number average molecular weight of 2,800, an average functionality between 2.1 and 2.3 hydroxyls per molecule and mixed chain microstructure consisting of 60 percent trans, 20 percent cis butadiene and 20 percent vinyl units. The low value observed for the soft segment T_g (-74°C) and the invariance of T_g with increasing hard segment content indicated that almost complete segregation of hard and soft segment units occurs in these polyurethane samples. In addition, two hard segment glass transitions were detected which suggested that some localization of the hard segments occurs according to size.

The present work is concerned with two related series of HTPBD samples, in one of which the HTPBD has been partially hydrogenated. In contrast to the previously reported work (6) where the samples were cured with 2,4-toluene diisocyanate (TDI) and bis(hydroxypropyl)aniline, the samples in the present study were cured with TDI and butanediol. Hydrogenation of the HTPBD was undertaken both as a means of improving the oxidative stability to meet the need of polyurethanes for long term electrical encapsulation and to study the influence on polyurethane properties. Results are presented for the thermal transition behavior of the samples containing the hydrogenated polybutadiene (HYPBD) and comparisons are made of the dynamic mechanical and mechanical properties of a set of HYPBD and PBD polyurethanes.

EXPERIMENTAL

Materials and Polymerization Conditions

The synthesis was carried out by a two step method involving end-capping the hydroxyl-terminated polybutadiene (PBD) (Arco, R45M) with a 5 percent molar excess of toluene-2,4-diisocyanate (TDI) (Aldrich) followed by reaction with the chain extender, 1,4 butanediol (BDL) (Aldrich).

A 100 ml reaction vessel equipped with a mechanical stirrer and vacuum outlet was charged with liquid prepolymer, evacuated and immersed in an oil bath at 120°C . After one hour, a weighed amount of TDI was added. The mixture was then stirred for one hour under

constant nitrogen flow, 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 (3 MPa pressure) at 120°C for 17 h.

Hydrogenation of Prepolymer

HTPBD (100 g) was dissolved in 500 ml of toluene in a 2 liter reactor sleeve. Approximately 0.5 g of Pd on activated charcoal catalyst was added and the sleeve was placed in the pressure reactor bomb assembly to which a hydrogen cylinder was connected. The vessel was purged with H_2 for 15 min and then pressurized with H_2 . The reaction was allowed to proceed until a pressure drop was attained which corresponded to the desired level of hydrogenation. The mixture was then filtered through a Buchner funnel and the catalyst residues were removed. The solvent was evaporated with a rotary evaporator, isolating the hydrogenated polybutadiene prepolymer (HT-HYPBD).

The extent of hydrogenation was determined by microanalysis for carbon and hydrogen and by proton nuclear magnetic resonance (NMR).

Infrared Analysis

Infrared spectra ($400\text{--}4000\text{ cm}^{-1}$) were obtained with a Nicolet 7199 Fourier Transform Infrared spectrometer. One hundred scans at 2 cm^{-1} resolution were signal averaged and stored on a disk for further analysis. Spectra of the prepolymer and its hydrogenated form were obtained from films cast from chloroform solution on KBr disks. Usually this technique yields sufficiently thin films for quantitative analysis. The criteria for the analysis is that Beer's law be obeyed; hence low absorptions are needed (7). Identical infrared spectra were also obtained for films cast as formed at 25°C . However, this technique usually yields thicker films, and hence higher absorbance values. Since the polyurethanes prepared were insoluble, the reaction mixtures were degassed and pressed between two KBr disks or aluminum plates. Samples thin enough for spectroscopic analysis can be obtained by this procedure.

Thermal Analysis

Measurements of the soft segment glass transition temperature were 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 $20^\circ\text{C}/\text{min}$ and an attenuation of 2 mcal/s. The higher temperature runs were carried out in a Perkin Elmer DSC-2 equipped with a two stage mechanical refrigeration unit. Scans were conducted from 240 to 420°K at $20^\circ\text{C}/\text{min}$ using an attenuation of 2 mcal/s. The samples were usually the same as those previously run in the low temperature DSC measurements. Glass transition temperatures were determined as the temperature corresponding to one half the increase in heat capacity at the transition. Penetrometer analyses were carried out employing the Perkin Elmer

TMS-1 on samples of approximately 50 ml thickness, using a probe weight of 25 g, heating rate of 10°C/min and an attenuation of 0.5 mil/in. Transition temperatures were estimated as the intersection of the two lines tangent to the curve preceding and following the region of softening.

Dynamic Mechanical Measurements

All measurements were carried out using a Vibron Dynamic Viscoelastometer (Toyo Measuring Instrument Co.) Model DDV II at a fixed frequency of 11 Hz. The temperature range was from -130 to 150°C and the samples were heated at a nominal rate of 1.5 deg/min under a dry nitrogen atmosphere.

Tensile Testing

Stress-strain data were obtained on an Instron Model TM-SM table model universal testing instrument at an extension rate of 40 mm/min. Specimens were die-cut from a sheet of the polyurethane film 0.015 in. thick. A specimen gage length was about 1.5 in. long and 0.12 in. in width. 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. This test provides data at 0, 20, 40, 60 and 80 percent of the extension at break (ϵ_b). All data reported are averages of at least 5 tests on different samples.

RESULTS AND DISCUSSION

Two series of polyurethanes were prepared; one based on the HTPBD and the second on the HYPBD prepolymer. Each consisted of three samples with a stepwise increment of TDI and BDL relative to the prepolymer and an NCO/OH ratio of approximately 1.05, assuming a functionality of 2.1 hydroxyls per molecule for the prepolymer (see Table I).

The percent of hydrogenation of the prepolymer as determined by microanalysis and NMR was 65 percent.

Infrared Analysis

The infrared spectra confirmed the composition expected for the prepolymer. The strong 970 cm^{-1} and 910 cm^{-1} bands are generally associated with the C-H out of plane motion in the trans and 1,2 vinyl units, respec-

tively (8). In addition, the 995 cm^{-1} band was used to analyze the cis content (9). These normal motions are very localized and, therefore, suitable for quantitative analysis (8).

After hydrogenation, significant changes in the ratios of these bands are observed. For example, as shown in Figs. 1 and 2a, the integrated intensity of the 910 cm^{-1} band, assignable to 1,2 vinyl groups, decreased substantially compared to trans segments; the ratio of the integrated intensities of 910 cm^{-1} /970 cm^{-1} decreasing from about 0.35 to 0.11 in the hydrogenated form. The preferential hydrogenation of the vinyl groups is in accord with the fact that this moiety occurs in a pendant position on the polymer and should be more accessible to hydrogen. This finding is consistent with that of Mango, *et al.* in which the rate of hydrogenation of the vinyl double bond was found to be greater than that of the internal olefin (10). The cis units were also preferentially hydrogenated over the trans, although to a lesser extent than the vinyl group. In addition, the 1377 cm^{-1} band associated with methyl rocking motion was detected after hydrogenation (11).

The sequence length of the methylene units in the hydrogenated samples was also of interest. A medium intense band was found at 720 cm^{-1} , which is commonly associated with amorphous polyethylene (12, 13). This observation suggests that hydrogenation is quite extensive, consistent with the NMR studies, which showed a 65 percent saturation. In addition, a very weak band was observed at 729 cm^{-1} as shown in Fig. 2b. This band is the CH_2 rocking vibration component arising from the crystal field splitting associated with methylene sequences in an orthorhombic unit cell (14). The lack of extensive crystallinity as evidenced by the weak absorption band is probably due to the random placement of the hydrogenated 1,2 vinyl groups and residual unsaturated segments within the polymer chain.

The spectra associated with the unsaturated and hydrogenated PBD polyurethanes are much more complicated. As in the prepolymer, preferential hydrogenation of the cis and 1,2 vinyl groups was observed. This behavior is identical for the three samples of varying hard segment concentration. However, the bands in the 720-730 cm^{-1} region are barely observable above the background for any quantitative analysis. A survey spectrum of a typical PBD-containing polyurethane is

Table 1. Characterization Data for HTPBD-Containing Polyurethanes and their Hydrogenated Derivatives

Sample	Molar composition TDI/BDL/PBD	Urethane weight, percent	Dynamic (11 Hz) T_g (°C)		T_{max} for E'	Tensile stress (σ_b) psi	Ultimate elongation, percent
			From E''_{max}	From $\tan\delta_{max}$			
PU-Unsaturated							
R-50	4.2/3.1/1.0	27.2	-74.4	-64.8	30	570	340
R-51	6.5/5.3/1.0	37.9	-73.5	-63.2	61	1390	230
R-52	8.4/6.9/1.0	43.8	-73.7	-64.8	107	1410	150
PU-Hydrogenated							
HY-50	4.1/2.9/1.0	26.3	-69.5	-54.5	30	1220	410
HY-51	6.4/5.2/1.0	36.5	-69.5	-53.1	66	1350	380
HY-52	8.3/7.3/1.0	43.4	-68.8	-53.7	103	1920	260

Fig. 1 Infrared spectrum of HTPBD prepolymer.

Fig. 2a. Infrared spectrum of hydrogenated HTPBD prepolymer.

Fig. 2b. Infrared spectrum of hydrogenated HTPBD prepolymer showing the 729 cm^{-1} band.

Fig. 3. Survey infrared spectrum of HTPBD-containing polyurethane sample.

presented in Fig. 3 and the assignments of vibrational modes are collected in Table 2.

Two other regions of interest in the IR spectra of these polyurethanes are the N-H and carbonyl absorption regions. The major N-H absorption appears at 3310 cm^{-1} , typical for hydrogen bonded N-H groups. A small shoulder on the high frequency side of this peak at around 3440 cm^{-1} arises from non-bonded N-H groups. Similar observations are found in the carbonyl region; absorption bands at 1733 and 1710 cm^{-1} being assigned to the free and bonded carbonyl groups, respectively (see Fig. 4).

Studies of a series of MDI (p,p'-diphenyl methane diisocyanate) polyurethanes containing polyether soft segments by Seymour and coworkers (15) have shown that virtually all N-H groups were hydrogen bonded but that only 60% of the urethane carbonyl groups participated in hydrogen bond formation. Senich and MacKnight (20) found similar results whereby 88 percent of the N-H groups were hydrogen bonded and only

Table 2. Infrared Band Assignments for Segmented Polyurethanes Containing Polybutadiene Soft Segments^a

Frequency, cm^{-1}	Assignment ^b
3440 (w, sh)	free N-H str
3310 (s)	bonded N-H str
3200 (vw)	trans-bonded N-H str
3130 (vw)	cis-bonded N-H str
2955 (m, sh)	CH_2 asym. str
2925 (vvs)	CH_2 asym. str
2855 (vs)	CH_2 symm. str
1735-1710 (vs)	free and bonded C=O str
1600 (m)	C=C str in aromatic group
1535 (vs)	N-H bend + C-N str
1455 (s)	CH_2 bend
1230 (vs)	N-H bend + C-N str
1065 (s)	trans C-C symm str
995 (w)	cis = CH vib
965 (s)	trans = CH out of plane wag, tor
910 (w)	1,2 = CH_2 out of plane def.
816 (w)	C-H out of plane bend
	O
	$\parallel$
770 (w)	-C-O- out of plane bend
721 (w)	CH_2 out of phase rock

^aKey: s = strong; m = medium, w = weak; sh = shoulder; v = very.

^bRef.: Hsu, et al. (8), Binder (9), Cornel and Koenig (24), Johnstone (25), Neto and di Lauro (26).

Fig. 4. Infrared absorption peak at room temperature of the N-H and C=O region.

60 percent of the carbonyl groups were similarly associated in polyether-TDI segmented polyurethanes. The former authors suggest that the N-H groups also hydrogen bond to the soft segment at the interface of the phase separated structure or in the soft segment itself due to incomplete phase separation. In these butadiene-containing polyurethanes however, hydrogen bonding occurs only to urethane segments since the carbonyl in the urethane linkage and the urethane alkoxy oxygen are the only available proton acceptors. This simplifies matters considerably when one attempts to quantitatively determine hard and soft segment interactions. For the N-H and C=O stretching vibration, the fraction of hydrogen bonded and free N-H and carbonyl groups were resolved using a nonlinear least squares analysis for the fitting of Lorentzian curve shapes with a Gaussian approximation of the absorption bands. After taking into account the extinction coefficient difference (16), 90 percent of the N-H groups in the HY-51 polyurethane were found to be hydrogen bonded. This value varied slightly with hard segment content and was essentially the same in both the unsaturated and hydrogenated polyurethanes. Bonded N-H contents of 75 to 95 percent have been found for other polyurethanes at room temperature (15, 17, 18-20). As expected, comparable amounts of hydrogen bonded carbonyl groups were found in these polyurethanes, thus indicating that the alkoxy oxygen accounts for less than 5 percent of the N-H association. The role of hydrogen bonding in determining the mechanical properties for these polyurethanes is currently being studied.

Thermal Analysis

The DSC and TMA results for the various hydrogenated (HYPBD) polyurethanes polybutadiene are summarized in Table 3. The last entry in the table cites the DSC results for the free hydrogenated polybutadiene. This material shows a well defined T_g at -70°C (see Fig. 5) which is about 11°C higher than the T_g (-81°C) determined on the precursor nonhydrogenated material. Above the T_g there is a diffuse but marked endothermal region extending from about -50 to 25°C

Table 3. Thermal Transitions (deg C) for Series of Polyurethanes Containing the Partially Hydrogenated Polybutadiene

Sample	T_g		Upper Transitions				
			DSC		TMA		
	DSC	TMA	T(1)	T(2)	T(1)	T(2)	T(3)
HY50	-68	-68	40	74	30	84	186
HY51	-72	-67	37	71	35	78	192
HY52	-69	-66	38	74	39	78	190
HY53	-72	-72	59	78	53	79	197
HYPBD	-70	Tm (Diffuse)	-50 to $+25^\circ$, Tm (Peak) 39°C				

and a broad but well defined melting endotherm with a peak at 39°C . The broadly distributed endothermal region, presumably due to melting of crystalline structure, suggests that the size distribution of the crystals is very large and that a preponderance of small imperfect crystals exists. The crystals have a polyethylene-like structure based on the infrared results. The behavior shown in Fig. 5 is repeatable on cooling and rescanning.

The polyurethane samples show T_g values of -65 to -72°C by DSC and about -68°C by TMA, both very close to that of the free HYPBD (Fig. 6). Above the soft

Fig. 5. DSC scan (160 to 340°K) on hydrogenated, hydroxyl terminated polybutadiene.

Fig. 6. DSC scan (150 to 400°K) on polyurethane sample HY-52. Run 1 initial scan; run 2 scan immediately after first run; run 3 rescan after several days at room temperature.

segment T_g , there is the endothermal region which also appears in the free HYPBD, but in the polyurethane samples the upper limit of the endotherm is 10° compared to 25°C with the free HYPBD and the melting peak at 39°C is absent. Instead, a T_g is observed at 35 to 40°C and a second T_g , dominated by a marked excess enthalpy peak, appears at 65 to 75°C . Both of these transitions can be attributed to the hard segment structure. The presence of two distinct transitions indicates that there may be segregation of the shorter and longer hard segment units (6). On a second DSC scan only the higher temperature T_g is observed but after several days at room temperature the lower temperature hard segment T_g reappears. The TMA results show parallel behavior (Fig. 7) with a very weak transition at 30 to 40°C , a moderate to strong reduction in modulus at 80°C and the final softening of the sample, due to the loss of allophanate crosslinking, at about 190°C . Unlike the DSC behavior, the lower hard segment T_g , although weak, is repeatable by TMA.

All of the above characteristics of the hard segment transition behavior, including the occurrence of an unstable lower temperature hard segment T_g , resemble the behavior reported previously (6) for the series of nonhydrogenated polybutadiene polyurethanes which were cured with bis-(2hydroxypropyl)aniline rather than butanediol.

Dynamic Mechanical Measurements

Results for the dynamic mechanical and tensile properties of the series of PBD and HYPBD polyurethanes are collected in Table 1.

Figure 8 represents the temperature dependence of the tensile storage and loss moduli (E' and E'') for the various PBD and HYPBD-containing polyurethanes. Both series display a single major relaxation, labeled α , and are characterized by a decrease in modulus from about 1000 to 10 MPa over a narrow temperature range. The α relaxation occurs at -74°C for the unsaturated polymers and at -69°C for the hydrogenated ones, all determined at 11 Hz from the position of the E'' loss maximum. This α relaxation is associated with the glass transition temperature of the soft (butadiene) segment. Its temperature is independent of hard segment content, indicating that these polyurethanes are well phase separated. This conclusion is further substantiated by

Fig. 7. TMA scan on polyurethane sample HY-51.

Fig. 8. Temperature dependence of the storage and loss modulus for (a) HTPBD-containing polyurethanes and (b) their hydrogenated derivatives at 11 Hz.

the fact that the soft segment T_g of the unsaturated polymer is only 7°C higher than that obtained for the pure HTPBD. The slight elevation in T_g above that of free polybutadiene can be accounted for by an anchoring effect imposed by the hard segment on the soft segment phase and/or by small amounts of intermixing between the two phases.

Further examination of Fig. 8 shows that as hard segment content increases, the storage modulus at temperatures above the α relaxation temperature also increases. A corresponding decrease in intensity of the $\tan \delta$ peak accompanies such changes in hard segment content. These effects are much less marked in the case of the hydrogenated polymer than in the unsaturated polymers. The temperature at which the limit of measurement was reached, corresponding to a modulus value of roughly 10 MPa, showed a corresponding increase with hard segment content for both series. These observations are consistent with findings for other phase segregated systems (21). The latter effect can be directly attributed to an increase in hard segment density and, possibly, improved organization which occurs with increasing hard segment content.

A more direct comparison between the hydrogenated and nonhydrogenated polymers can be made by inspection of the temperature dependence of the loss tangent shown in Fig. 9 for the various samples. It is at once apparent that all the hydrogenated polymers show a

Fig. 9. Temperature dependence of the loss tangent for (a) HTPBD-containing polyurethanes and (b) their hydrogenated derivatives at 11 Hz.

decrease in intensity and a broadening of the $\tan \delta$ peak compared to the unsaturated polymers. Moreover, the temperature of this relaxation is shifted to higher temperatures by approximately 10°C in the hydrogenated series. This effect may be attributed to the presence of soft segment crystallinity in the hydrogenated polyurethanes. The soft segment crystallinity acts to increase the temperature of the α relaxation and to change its shape. Such effects are also observed in other semicrystalline polymers such as polyethylene, polypropylene and poly(ethylene terephthalate) (22, 23). Soft segment crystallization and melting in these hydrogenated polymers were also observed in our thermal studies.

No conclusive evidence of a hard segment glass transition, which was found to occur between 30 and 100°C by DSC determination, is observable in the various dynamic mechanical relaxation measurements of both hydrogenated and unsaturated polymers. However, increasing the hard segment content increases the softening point presumably because of an increase in the hard segment sequence lengths.

Stress-Strain Measurements

The results of tensile tests performed at room temperature on films of hydrogenated and unsaturated polyurethanes are shown in Fig. 10 and summarized in

Fig. 10. Stress-strain response of HTPBD-containing polyurethanes (—) and their hydrogenated derivatives (---).

Table 1. In both series, as the percentage of hard segment increases, several systematic changes occur in the tensile properties. First, the initial modulus (slope of stress-strain curve) increases, indicating the greater rigidity imposed by the hard segment. The stress level during extension also increases with hard segment content, again showing the effects of the less mobile hard segment domains which have difficulty sliding past one another. As expected, the ultimate elongation values for the two series of polymers decreases with increasing weight fraction of hard segment.

With the exception of sample 51, the initial modulus and stress level at break was higher in the hydrogenated samples than in the unsaturated ones. The ultimate elongations were also significantly higher. The two concurrent effects give rise to an increase in the toughness of the material, as determined by the areas under the curves.

Cyclic Instron tests were also performed on these samples and the results are shown in Fig. 11. Readily apparent are two characteristics of stress softening. First, upon subsequent straining, lower stress levels are observed at all extensions lower than the maximum previously applied, and second, at strain levels higher than those previously reached, the stress levels are apparently unaffected by prestraining. Both the hydrogenated and unsaturated materials behave similarly in this respect, the only noticeable difference is that HY-51 shows more permanent set than R-51. This stress-softening behavior is characteristic of phase separated materials and several interpretations of the phenomena are cited, including disruption of the polymer structure and of the reinforcing mechanism, chain slippage and chain breakage (21).

CONCLUSIONS

The results obtained for the soft segment T_g by DSC, TMA and from the rheovibron measurements (E' or $\tan \delta$) are in good agreement. The low value of T_g for both the PBD and HYPBD-containing polyurethane, very close to the respective values for the free PBD or HYPBD, and the invariance of T_g with increasing urethane content attest to the fact that these samples are

Fig. 11. Cyclic stress-strain curves for (a) R-51 (HTPBD-containing polyurethane); and (b) HY-51 (hydrogenated derivative) extended 20, 40, 60, and 80 percent ϵ_b .

all well phase segregated. Moreover, IR analysis indicates that 90-95 percent of the urethane N-H groups are hydrogen bonded. Since the hydrogen bonding interactions are limited to the hard segment components, the high extent of interurethane hydrogen bonding serves as additional evidence that the hard segment phase in these polyurethanes is relatively free of intermixed soft segments.

As observed in the IR spectra, the partial hydrogenation (65 percent by NMR) of the prepolymer involves preferential saturation of 1,2 vinyl and cis double bonds. It is surprising under the circumstances that any crystallinity develops. Nonetheless, the DSC measurements indicate a broad melting peak at 39°C. Since the chain structure is chemically heterogeneous, the crystalline material must involve only small regions of

the chain leading to very small crystallite sizes. Only a very weak infrared absorption can be detected at 729 cm^{-1} , which is a characteristic absorption for crystalline polyethylene. In the HYPBD polyurethane samples the broad low temperature melting process is observed but not the melting peak, suggesting that either the additional constraints on mobility or the very slight amount of phase mixing interferes with crystallization.

Two hard segment transitions are observed, by DSC, at 40 and 75°C. In TMA the lower transition is weak and the upper transition moderately strong. Two hard segment transitions have been observed in other PBD-containing polyurethanes under conditions where the lower temperature transition was clearly identifiable with shorter hard segments containing up to three TDI repeat units (4). The occurrence of two hard segment transitions is the result of the high degree of phase segregation. Short hard segment units, which in polyether or polyester polyurethanes would be mixed with the soft segment phase, are phase separated in these PBD polyurethanes.

In the dynamic mechanical results only the low temperature T_g is clearly evident. The $\tan \delta$ peak for the HYPBD containing polyurethanes is considerably broadened, probably reflecting the interplay of the T_g and the broad melting process observed by DSC. The main effect of the increasing hard segment content is to increase the storage modulus above the glass transition and also the upper temperature limit at which the vibron measurements can be made. More important evidence of the effect of soft segment hydrogenation is seen in the comparison of mechanical properties. Generally, it appears that hydrogenation of the soft segment results in a significant increase in the ultimate elongation and the breaking strength and, therefore, in the toughness of these polyurethanes measured as the area under the stress-strain curve. In view of the low tensile and tear strength of the PBD polyurethanes, this is a welcome improvement in properties. The gain is presumably due to crystallinity within the soft segment which develops upon hydrogenation of the precursor prepolymer. The soft segment crystallinity acts to increase the temperature of the α relaxation and change its shape. Further, the presence of crystallites in the soft segment of the hydrogenated urethane polymers results in the enhancement of the stress values at a given strain due to these regions acting as tie-points. The comparable levels of hysteresis observed in the cyclic stepwise extension curves for PBD and HYPBD polyurethanes, however, indicate that the small level of crystallinity does not interfere with the elastic recovery of the HYPBD-containing polyurethanes.

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