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A Dynamic Mechanical Study of Phase Segregation in Toluene Diisocyanate, Block Polyurethanes

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The dynamic mechanical response of several toluene diisocyanate, polyurethane elastomers has been studied. A symmetrical hard-segment isomer and increasingly long hard and soft blocks promote phase segregation in these materials. The glass-transition temperature of the soft-segment phase is strongly influenced by the purity of the soft-segment phase and the overall degree of crystallinity. The high temperature δ relaxation is directly related to the average hard-segment length, while the plateau modulus between these relaxation regions strongly depends upon hard-segment content. Comparison of block polyurethane relaxations with corresponding loss processes of the hard- and soft-segment polymers indicates that the short block length and significant degree of intersegmental mixing contribute to poor phase organization in these block polyurethanes.

Linear polyurethane block copolymers have been objects of considerable research interest over recent years. These materials are composed of three parts, a diisocyanate, a low molecular weight chain extender (usually a diol but sometimes a diamine), and a low molecular weight rubbery polymer, frequently a polyether or polyester. The soft segment consists of the rubbery polymer while the diisocyanate and the chain extender form the hard segment. These materials are classified as thermo-

plastic elastomers since their resiliency at room temperature is characteristic of elastomers while their linear nature allows them to be processed with the ease of thermoplastics at higher temperatures.

Dynamic mechanical property studies have been successful in elucidating the molecular mechanisms underlying the mechanical behavior of these materials. Kajiyama and MacKnight (1, 2) proposed mechanisms for low temperature and glass-transition-region relaxations of three model hard-segment polyurethanes extended with diols containing from 2 to 10 methylene units. They observed relaxations attributable to motion of side chains, short-length main chain structures, and long main chain segments as well as crystal-crystal transitions. Dynamic mechanical investigations by Huh and Cooper (3) demonstrated the existence of a two-phase structure in 4,4'-diphenylmethane diisocyanate, MDI, polyurethanes, and examined the effects of composition, soft-segment molecular weight, and thermal history upon the relaxation mechanisms of this class of copolymers. Relaxations, in their notation, corresponding to a soft-segment T_g , α_n , soft-segment crystalline melting, α_c , hard-segment T_g , δ , and hard-segment melting, δ' , were observed in the polyurethanes studied. They concluded that the α_n and δ relaxations were influenced by the degree of crystallinity and the nature of the domain structure. The magnitudes of the α_c , δ , and δ' relaxations were found to be related to the size of the domain structures present. Similar studies were carried out on polyurethanes synthesized with structures that eliminated hydrogen-bonding effects and which allowed blocks of controlled, molecular weight distribution to be incorporated (4, 5). The major conclusions from this work are that a narrow, hard-segment molecular weight distribution in the phase-segregated systems increases the hard-segment glass transition, α_n , and the modulus between the hard- and soft-segment T_g while having little effect on the soft-segment glass transition, α_g . An examination of low temperature, dynamic mechanical properties of MDI polyurethanes with various soft segments was reported by Illinger and co-workers (6). They found that as urethane concentration increased, α_g remained constant but crystallization of the soft segment was inhibited. Ferguson and co-workers (7) have examined MDI-polyether block polyurethane chains extended with 1,3-diaminopropane as a function of hard-segment content.

Systematic studies on MDI polyurethanes with polycaprolactone soft segments over a wide range of soft-segment molecular weight and hard-segment concentration have been carried out by Seefried, Koleske, and Critchfield (8, 9). The glass transition was observed to shift to lower temperatures as the soft-segment chain length increased, and soft-segment crystallization was found to occur for the highest molecular weight polycaprolactone sample. The T_g of lower molecular weight, soft-segment samples

increased as the hard-segment content increased while the T_g of polyurethanes containing higher molecular weight soft segments was unchanged until extreme amounts of hard segments were introduced. The authors attributed the latter behavior to a high degree of phase segregation between blocks. This group also has compared MDI and toluene diisocyanate, TDI, hard segments over a more limited compositional range and studied the effects of different chain extenders on TDI polyurethane properties (10, 11). All TDI-containing polyurethanes studied by these workers displayed little or no phase segregation.

Schneider, Paik Sung, and co-workers have completed an extensive study of TDI polyurethanes (12, 13, 14, 15). This work differs from previous studies by the separate characterization of block polyurethanes prepared from the two isomers of TDI. These materials have been studied by thermomechanical analysis, TMA, DSC, x-ray scattering, and IR analysis in order to elucidate the structure of this particular class of polyurethanes. Their findings can be briefly summarized in terms of the degree of phase segregation exhibited. The glass-transition temperature of 2,4-TDI polyurethanes with polyether soft segments of about 1000 $\bar{M}_n$ showed a strong dependence on composition. Extensive hard- and soft-segment mixing was postulated in these materials. Similar polyurethanes based on the 2,6-TDI structural isomer displayed a highly ordered domain structure, indicated by a concentration invariant T_g and a strong high temperature transition attributed to melting of the easily crystallizable hard segment. An increase in soft-segment molecular weight from 1000 to 2000 induced phase segregation in the 2,4-TDI series and improved phase segregation in the 2,6-TDI series to the point that the soft segment exhibited some crystallinity. The soft-segment glass transition temperature, T_{gs} , was found to be a sensitive measure of the degree of phase segregation in these materials.

The systematic dynamic mechanical study reported here was undertaken to gain additional insight into the molecular relaxation processes which occur in TDI polyurethanes as well as to test the generality of findings developed from investigations of other chemical classes of segmented polyurethanes.

Experimental

Samples. Linear polyurethane block copolymers with hard segments composed of 2,4- or 2,6-TDI, and 1,4-butanediol, BD, and either 1040 or 2060 molecular weight poly(tetramethylene oxide), PTMO, soft segments were supplied through the courtesy of N. S. Schneider of the Army Materials and Mechanics Research Center, Watertown, MA. These polymers were prepared by a two-step process, first an endcapping of the PTMO with a 5% molar excess of TDI, followed by chain extension

2,6-T-xP Block Polyurethane

2,4-T-xP Block Polyurethane

Figure 1. Structure of the block polyurethane elastomers

with BD and additional TDI. All were found to be soluble in dimethylformamide. Hard- and soft-segment model polymers also were supplied. These materials were made in a one-step condensation reaction of a 2.5% molar excess of TDI with either BD or PTMO of 1090 molecular weight. Figure 1 shows a representation of the polymers studied. The hard segment is the material contained within the brackets with subscript m . The approximate value of the index i corresponds to 14, 15, and 28 for 1040, 1090, and 2060 molecular weight PTMO, respectively. For the pure, hard-segment material the index i is, of course, zero, while for the soft segment polymer m is likewise zero. Overall polymer M_n was estimated to be on the order of 13,000–25,000. Hard- and soft-segment polymers are designated first by the TDI isomeric structure followed by either BD for the hard segment or PTMO for the soft-segment polymers. For example, 2,4-TDI/PTMO refers to the 1090 molecular weight PTMO soft segment, which contains 14 wt% 2,4-TDI. The nomenclature used throughout the discussion for the block polyurethanes first refers to the TDI isomeric structure followed by the molecular weight of PTMO in thousands and finally the hard-segment content in weight percent if a specific polymer is designated. For example, 2,6-T-2P-60 indicates a block polyurethane with 60 wt% 2,6-TDI/BD hard segments and a 2060 molecular weight PTMO soft segment.

Characterization. Film samples about 0.25-mm thick were prepared by compression molding the polyurethanes under dry nitrogen at 180°C and 3 MPa pressure. After molding for 20 min, the samples were allowed to cool slowly in the press under dry nitrogen flow. Figure 2 shows the thermal history of the 180°C-molded films. No discoloration was observed when the samples were removed from the mold. The two soft-segment polyurethanes were compression molded at 120°C. The films were allowed to stand at least one week at room temperature in a dessicator before being evaluated with the Rheovibron DDV-IIB Dynamic Visco-

Figure 2. Thermal history of compression-molded polyurethane films

elastomer (Toyo Baldwin Co.). Samples were tested sequentially at 3.5, 11, 35, and 110 Hz while heating from -135° to 195°C at a nominal heating rate of $1.5^{\circ}\text{C}/\text{min}$ under a dry nitrogen atmosphere. Several samples were re-examined by the same procedure about 60 days after the first test. Apparent activation energies were determined for major relaxations from the Arrhenius dependence of frequency on inverse temperature. Least-squares lines were fitted to plots of $\log(\text{frequency})$ vs. T^{-1} and the activation energies to the 95% confidence level determined from the slopes. Thermal studies on the compression-molded films were carried out on a Perkin-Elmer DSC-2 differential scanning calorimeter at a heating rate of $20^{\circ}\text{C}/\text{min}$ and with a sensitivity of $5 \text{ mcal}/\text{sec}$.

Results

Hard- and Soft-Segment Polymers. The hard-segment polymer composed of 2,4-TDI/BD exhibited a single major α relaxation associated with the glass transition. The relaxation occurred at 108°C (11 Hz), as determined from the position of the loss modulus maximum. The storage modulus decreased from about 1.5 GPa to 50 MPa during the relaxation, and the loss of mechanical integrity and onset of flow was indicated by a rapid and unabated rise in $\tan(\delta)$ as the temperature rose above T_g . The apparent activation energy, E_a , determined from an Arrhenius dependence of frequency, ω , on temperature as shown in Equation 1, was

Figure 3a. Storage and loss modulus of 2,6-TDI/BD as a function of temperature at 110, 35, 11, and 3.5 Hz

Figure 3b. DSC scans of hard-segment polymers. (a) 2,4-TDI/BD; (b) quenched 2,6-TDI/BD; (c) 2,6-TDI/BD-annealed for 1 hr at 423 K.

$$\ln(\omega) = \frac{-E_a}{RT} + C \quad (1)$$

600 kJ/mol. The activation energy for the α relaxation agrees within experimental error with the value of 480 kJ/mol, determined by Kajiyama (16). No crystallinity is present in this hard-segment material, as shown by the DSC scan in Figure 3b which has no evidence of a melting endotherm.

The dynamic mechanical behavior of 2,6-TDI/BD was found to be similar to that of the 2,4-TDI/BD hard segment at low temperatures. Both showed a secondary γ relaxation at about -115° to -135°C , with an activation energy of about 30 kJ/mol. These processes correspond to the γ_1 and/or γ_2 relaxations, involving motions of methylene sequences which were observed for model hard segments by Kajiyama and MacKnight (2) and will not be subsequently considered. The α or glass-transition relaxation for 2,6-TDI/BD occurred at 105°C (11 Hz), with an activation energy of 510 kJ/mol. Above the α -loss peak, the storage modulus remained at a level of about 300 MPa, as can be seen in Figure 3a. This phenomenon can be attributed to the presence of crystallinity

in the 2,6-TDI/BD hard segment. The magnitude of the plateau in modulus was found to highly depend upon the thermal history of the sample. The results in Figure 3a represent the steady-state behavior of the fully annealed polymer. The width of the α -loss peak is about twice that of the 2,4-TDI/BD α -relaxation maximum. Broadening in the α -loss maximum by the introduction of crystallinity has been similarly observed for PET and PTFE (17). Crystalline structure in the 2,6-TDI/BD hard-segment polymer remained until the onset of the δ relaxation in dynamic mechanical experiments, about 212°C. The melting point, as determined from the maximum of the melting endotherm in Figure 3b, was found to be 200°C. The positions of the α relaxations for 2,4- and 2,6-TDI/BD are in good agreement with T_g values found from DSC studies, 102° and 93°C, respectively.

The model soft segment composed of 2,4-TDI/PTMO exhibited a single major α relaxation at -55°C (11 Hz), accompanied by a drop in the level of the storage modulus of two and one half orders of magnitude. An activation energy of 200 kJ/mol was determined for this relaxation. The 2,6-TDI/PTMO soft segment displayed quite different behavior from the 2,4-TDI/PTMO polymer, as can be seen from Figure 4a. An α relaxation can be observed to occur at -59°C (11 Hz), with an apparent activation energy of 260 kJ/mol. A subsequent α_c -loss process with a corresponding increase in the storage modulus by a factor of three can be seen to occur at about -30°C. This second relaxation can be attributed to crystallization of the soft segment above T_g , followed by annealing and finally complete melting at 9° to 13°C. Crystallization in the material during cooling to -135°C was inhibited by the rapid quenching process used for cooling the sample chamber. The DSC results for the 2,6-TDI/PTMO soft segment in Figure 4b confirm the interpretation of the dynamic, mechanical relaxation processes. A glass transition is indicated at -63°C, followed by a broad crystallization exotherm centered at -30°C and finally a melting endotherm at 10°C. The behavior of the 2,6-TDI/PTMO soft segment, containing no chain extender, is similar to that noted by Illinger (6) for an MDI/BD/PTMO polyurethane containing 24-wt% hard segments and 2000 $\bar{M}_n$ PTMO. The glass transition occurred at -100°C (110 Hz), followed by crystallization, completed at -45°C and finally melting at 30°C. The dynamic mechanical test results for the hard and soft segments are summarized in Table I.

2,4-TDI Polyurethanes. Two 2,4-T-IP samples with different hard-segment concentrations were studied and found to display a broad α -relaxation maximum, also characterized by a decline in storage modulus of about two and one half orders of magnitude, as shown in Figure 5, a plot of storage and loss modulus vs. temperature at 11 Hz. The position

Figure 4a. Temperature dependence of the storage and loss modulus of 2,6-TDI/PTMO at 110, 35, 11, and 3.5 Hz

Figure 4b. DSC scans of soft-segment polymers. (a) 2,4-TDI/PTMO, (b) 2,6-TDI/PTMO.

of the α relaxation varied with hard-segment content, ranging from 22°C for 2,4-T-1P-56 to 38°C for 2,4-T-1P-60, both at 11 Hz. The activation energies found for each sample are comparable, as can be seen from Table II, a summary of 2,4-TDI polyurethane data, on the order of 290 kJ/mol. The results from dynamic mechanical studies agree with the glass-transition temperatures found by Schneider and co-workers (12) from a TMA study of the same polyurethanes, as can be seen from Figure 6, a comparison of both sets of data.

The dynamic mechanical response of three 2,4-T-2P samples at 11 Hz is shown in Figure 7 for three hard-segment concentrations. A low temperature relaxation maximum, α_s , in the region of -68° to -54°C ,

Table I. Relaxations of Hard- and Soft-Segment Polymers

Sample	Relaxation	Temperature* (°C)	Activation Energy (kJ/mol)
2,4-TDI/BD	α	108	600 ± 140
2,6-TDI/BD	α	105	510 ± 70
2,6-TDI/BD	δ	212	—
2,4-TDI/PTMO	α	-53	200 ± 40
2,6-TDI/PTMO	α	-59	260 ± 50
2,6-TDI/PTMO	α_c	-30	—

* α and α_c determined from position of $E''_{\max}$, δ from $\log(E') = 1.25$ MPa, all at 11 Hz.

Figure 5. Storage and loss modulus as a function of temperature at 11 Hz for 2,4-T-1P with 56 and 60 wt % hard segments

Figure 6. Comparison of 11-Hz dynamic mechanical (open points) and DSC or TMA transition temperatures (filled points, Ref. 14) of 2,4-T-1P (triangles) and 2,4-T-2P (squares) polyurethanes as a function of hard segment wt %

with an activation energy of 120 kJ/mol, is apparent for each sample. The position of the α_s -relaxation maximum, given in Table II, can be seen to decrease slightly with increasing concentration of hard segments. Again, the dynamic mechanical data compares favorably with results from DSC studies on these materials by Schneider and Paik Sung (14), as can be seen in Figure 6. The same small decrease in transition temperature with increasing hard-block content is evident from both determinations. The storage modulus above the α_s relaxation can be seen to highly depend upon the hard-segment content. At 0°C for

Table II. Relaxations of 2,4-TDI Block Polyurethanes

Sample	Approximate Molar Ratio (TDI/BD/PTMO)	Relaxation	Temperature* (°C)	Activation Energy (kJ/mol)
2,4-T-1P-56	5/4/1	α	22	320 $\pm$ 50
2,4-T-1P-60	6/5/1	α	38	280 $\pm$ 20
2,4-T-2P-33	4/3/1	α_s	-62	120 $\pm$ 20
2,4-T-2P-39	5/4/1	α_s	-63	120 $\pm$ 20
2,4-T-2P-39	5/4/1	α_h	55	260 $\pm$ 30
2,4-T-2P-43	6/5/1	α_s	-64	120 $\pm$ 20
2,4-T-2P-43	6/5/1	α_h	68	270 $\pm$ 40

* Determined from position of $E''_{\max}$ at 11 Hz.

example, the storage modulus of 2,4-T-2P-43 is twice that of 2,4-T-2P-39, which in turn has a modulus five times that of 2,4-T-2P-33.

On further examination of Figure 7, an α_h relaxation can be noted that becomes increasingly prominent as hard-segment content increases from 33 to 43 wt%. The α_h -loss process for 2,4-T-2P-43 is comparable in breadth to the α_s relaxation and has an apparent activation energy of about 270 kJ/mol. The position of α_h rose about 13°C as the hard-segment content increased from 39 to 43 wt%.

Several 2,4-T-2P samples were reevaluated and gave results identical within experimental error to the first determination, indicating that thermal history has a negligible effect on these polyurethanes.

2,6-TDI Polyurethanes. Three 2,6-T-1P samples of varying hard-segment content were studied and exhibited the dynamic mechanical response displayed in Figure 8. An α_s relaxation can be noted at -64°C (11 Hz) for 2,6-T-2P-31, which progressively broadened as the quantity of hard segments incorporated into the polyurethane increased. The activation energy of the α_s process was found to decrease as hard-segment content increased, as can be noted from Table III. The level of the storage modulus above α_s was found to highly depend upon the composition of the polyurethane, increasing from 2,6-T-1P-31 to 2,6-T-1P-42 by about 250% at 0°C and by a like amount from 2,6-T-1P-42 to the next member of the series. A final point to note is the high temperature behavior of these polyurethanes. The storage modulus shows a region of rapid decline not matched by the loss modulus. This leads to a rapid rise in the loss tangent vs. temperature curves, not shown, corresponding to the onset of a softening or flow δ -relaxation process. The temperature at which the storage modulus reached a value of 1.25 MPa was taken as an arbitrary indication of the loss of mechanical integrity and melting of the hard segments of these polyurethanes. The temperatures of both α_s - and δ -relaxation processes are plotted against hard-segment content and compared with the data of Schneider and co-workers (12) in Figure 9. The α_s relaxation occurs at increasingly higher temperatures as hard-segment content increases while the T_{gs} determined from DSC measurements shows a slight decrease. Both sets of data show the same trend for the higher temperature, hard-segment melting transition.

The dynamic mechanical properties of four 2,6-T-2P samples containing from 19 to 43 wt% hard segments are summarized in Figure 10. A low temperature α_s relaxation is apparent at about -70°C for all compositions examined. The transition temperatures of these loss maxima and the associated activation energies are given in Table III. A second process, the α_c relaxation, can be noted as a shoulder on the high temperature side of the α_s -loss maximum. The conclusion of this relaxation is marked by a change in slope of the loss modulus vs. temperature plots

Figure 7. Temperature dependence of the storage and loss modulus of 2,4-T-2P at 11 Hz for 33, 39, and 43 wt % hard-segment concentration

Figure 8. Storage and loss modulus of 2,6-T-1P vs. temperature at 11 Hz for polyurethanes containing 31, 42, and 56 wt % hard segments

Figure 9. Comparison of 11-Hz dynamic mechanical (open points) and DSC or TMA transition temperatures (filled points, Ref. 13) of 2,6-T-1P polyurethanes as a function of hard-segment content

at about 2° to 7°C. This relaxation can be more clearly observed in a plot of storage and loss modulus vs. temperature at 11 Hz for two polyurethanes, 2,6-T-1P-31 and 2,6-T-2P-33, shown in Figure 11. These polymers have about the same hard-segment content and differ only in the soft-segment molecular weight. The α_c -relaxation peak can be observed in the 2,6-T-2P polyurethane as an elevation in the loss modulus over the region from about -40° to 7°C. The storage modulus of the sample with a higher molecular-weight soft segment can be seen to be about double that of 2,6-T-1P over the same temperature range. The increase in storage modulus above α_s can be attributed to reinforcement of the soft-segment phase by crystallization above its T_g . This enhancement of strength continues up to a temperature of about 7°C, the region where soft-segment melting was found to occur in the 2,6-TDI/PTMO soft-segment polymer. The α_c relaxation is also apparent in loss tangent vs. temperature curves, not shown. The intensity of the α_s relaxation is approximately equal to that of the α_c relaxation from the $\tan(\delta)$ data, and the two processes exhibit considerable overlap.

Returning to the 2,6-T-2P in Figure 10, the storage modulus above α_c and the position of the δ relaxation, the temperature at which the storage modulus reached 1.25 MPa, can be seen to depend upon hard-

Figure 10. Temperature dependence of the storage and loss modulus of 2,6-T-2P at 11 Hz for polyurethanes containing 19, 27, 33, and 43 wt % hard blocks

Figure 11. Comparison of the storage and loss modulus of 2,6-T-1P-31 (squares) and 2,6-T-2P-33 (triangles) as a function of temperature

Table III. Relaxations of 2,6-TDI Block Polyurethanes

Sample	Approximate Molar Ratio (TDI/BD/PTMO)	Relaxation	Temperature ^a (°C)	Activation Energy (kJ/mol)
2,6-T-1P-31	2/1/1	α_s	-64	170 ± 20
2,6-T-1P-31	2/1/1	δ	120	—
2,6-T-1P-42	3/2/1	α_s	-54	120 ± 40
2,6-T-1P-42	3/2/1	δ	157	—
2,6-T-1P-56	5/4/1	α_s	-48	70 ± 20
2,6-T-1P-56	5/4/1	δ	183	—
2,6-T-2P-19	2/1/1	α_s	-69	140 ± 20
2,6-T-2P-19	2/1/1	δ	97	—
2,6-T-2P-27	3/2/1	α_s	-71	180 ± 20
2,6-T-2P-27	3/2/1	α_c	-31	—
2,6-T-2P-27	3/2/1	δ	137	—
2,6-T-2P-33	4/3/1	α_s	-71	180 ± 30
2,6-T-2P-33	4/3/1	α_c	-19	—
2,6-T-2P-33	4/3/1	δ	160	—
2,6-T-2P-39	5/4/1	α_s	-72	160 ± 20
2,6-T-2P-39	5/4/1	α_c	-9	—
2,6-T-2P-39	5/4/1	δ	154	—
2,6-T-2P-43	6/5/1	α_s	-66	70 ± 20
2,6-T-2P-43	6/5/1	α_c	-8	—
2,6-T-2P-43	6/5/1	α_h	60	270 ± 90
2,6-T-2P-43	6/5/1	δ	177	—

^a α_s determined from E''_{max} , α_c and α_h from $\tan(\delta)_{max}$, δ from $\log(E') = 1.25$ MPa, all at 11 Hz.

segment concentration in a manner similar to that observed for the 2,6-T-1P polyurethanes. The α_s - and δ -relaxation temperatures at 11 Hz are plotted as a function of hard-segment content in Figure 12 and compared with TMA and DSC results of Schneider and Paik Sung (14). There is good agreement between the α_s -loss process and the T_{gs} transition, and both the δ relaxation and the hard-segment melting transition show a similar trend, with the exception of 2,6-T-2P-39.

Thermal history was found to have an effect on 2,6-T-2P dynamic mechanical properties. For the two samples retested after the first experiment to 190°C, the α_s relaxation was shifted to a higher temperature after thermal treatment while the storage modulus increased by about 50% over the temperature interval from -80° to 130°C. The δ relaxation was not affected by heating to 190°C. Table IV summarizes the dynamic mechanical data for both of the retested 2,6-T-2P polyurethanes. The apparent activation energy of the α_s relaxation increased significantly after the first determination, as can be seen from Figure 13, a plot of activation energy vs. hard-segment content.

Table IV. Relaxations of Thermally Treated 2,6-TDI Polyurethanes

Sample	Relaxation	Temperature* (°C)	Activation Energy (kJ/mol)
2,6-T-2P-39	α_s	-64	310 ± 40
2,6-T-2P-39	α_c	-3	—
2,6-T-2P-39	δ	154	—
2,6-T-2P-43	α_s	-64	200 ± 30
2,6-T-2P-43	α_c	-2	—
2,6-T-2P-43	α_h	71	310 ± 50
2,6-T-2P-43	δ	174	—

* α_s determined from E''_{max} , α_c and α_h from $\tan(\delta)_{max}$, δ from $\log(E') = 1.25$ MPa, all at 11 Hz.

Figure 12. Comparison of 11-Hz dynamic mechanical (open points) and DSC or TMA transition temperatures (filled points, Ref. 14) of 2,6-T-2P polyurethanes as a function of hard-segment concentration

Figure 13. Apparent activation energy of the α_h relaxation in 2,6-T-2P polyurethanes as a function of hard-segment content from the first (filled points) and second determination (open points)

An additional relaxation can be detected in plots of the loss tangent as a function of temperature for 2,6-T-2P-43, not shown. The α_h relaxation occurred at 60°C (11 Hz) in the first examination of this sample. A weak α_h relaxation can be detected in the loss modulus vs. temperature plots in Figure 13, but the process is more readily apparent in the $\tan(\delta)$ data. Upon retesting of this sample, the α_h dispersion was shifted to 71°C. The activation energy for the α_h relaxation did not change significantly with thermal history and was extremely weak or undetectable in 2,6-T-2P samples which contained less than 43 wt% hard segments.

Discussion

Hard- and Soft-Segment Polymers. The structure of the diisocyanate component has a significant influence on dynamic mechanical properties of both hard- and soft-segment polymers. Both 2,4- and 2,6-TDI/BD α relaxations occur at about the same temperature and have a comparable activation energy. However, the symmetrical structure of

2,6-TDI/BD facilitates crystallization of the hard-segment polymer, which has the effect of broadening the α relaxation when compared with that of the totally amorphous 2,4-TDI/BD (*see* Figure 3b). The semicrystalline nature of the 2,6-TDI hard segment provides modulus reinforcement above the α relaxation to about 212°C. This behavior can be compared with that of a MDI/BD hard segment studied by Illinger et al. (6), which displayed an α relaxation at 110°C (110 Hz) and a second relaxation, attributed to melting, at about 170°C (110 Hz). The symmetrical TDI hard segment maintained a higher modulus above the α relaxation to a higher temperature than did the MDI/BD hard segment studied by these workers.

The soft-segment polymers studied consisted of 1090 $\overline{M}_n$ PTMO chains, corresponding to about 75 carbon and oxygen atoms each, in an alternating arrangement with diisocyanate molecules. This material was thought to be representative of the soft segment, as the single urethane units do not function as hard segments in block polyurethanes (18). The glass transition for both isomers was found to be in the region -50° to -60°C, above the literature value for high molecular-weight PTMO, -84°C (19). The elevation of the soft-segment T_g over that of the pure PTMO homopolymer can be attributed to a combination of the copolymer effect and effective crosslinking of the PTMO ether oxygens by hydrogen bonding with the diisocyanate amine group, an association which has been found to be significant for block copolyurethanes (13, 14, 15).

Above the α -relaxation process, the 2,4-TDI/PTMO polymer displayed a short rubbery plateau at a storage modulus of about 5 MPa while 2,6-TDI/PTMO was capable of crystallization, as evidenced by the α_c -loss process. This difference in dynamic mechanical properties demonstrates the effect of a symmetric diisocyanate structure upon soft-segment properties. As previously discussed, single urethane links can sometimes be incorporated into the soft-segment phase. The introduction of only one of these diisocyanate molecules between two long PTMO chains inhibits crystallization if the diisocyanate is asymmetric. In the case of a symmetric diisocyanate, soft-segment crystallization above T_g can readily occur. The crystals formed were found to melt about 30°C below the reported melting point for PTMO homopolymer, 37°–43°C (19), possibly because of disruption of the crystal structure by the bulky diisocyanate units.

The α Relaxation of 2,4-T-1P. Only the 2,4-T-1P block polyurethanes exhibited a single major α relaxation which had a strongly composition-dependent position. Similar behavior was observed by Seefried and co-workers (10) for polyurethanes containing a TDI/BD hard segment and a 2100- $\overline{M}_n$ polycaprolactone hard segment. The extreme

dependence of the α process on hard-segment content suggests that the amount of hard urethane segments mixed with the soft segment is extensive. The location of the α relaxation cannot be predicted from the hard- and soft-segment-polymer relaxation temperatures and polyurethane composition by the use of the copolymer equation. Schneider and Paik Sung (14) have shown that the difference between the observed T_g and that predicted from the copolymer equation can be accounted for by considering hydrogen bonds between hard and soft segments as crosslinks which elevate the glass transition of the soft-segment phase. Hydrogen-bond crosslinking should affect the soft segment, main chain microBrownian motion through a reduction in free volume. A corresponding increase in the temperature and activation energy of the α -relaxation process is predicted with increasing crosslink density. Such effects can be observed in the dielectric relaxation data of Scott and co-workers (20) on a series of increasingly crosslinked natural rubber samples. An increase in the activation energy for the α process in 2,4-T-1P by about 50% over that for 2,4-TDI/PTMO can be noted. These results are consistent with the crosslinking assumption of Schneider and Paik Sung.

Estimates of the quantity of hard segments incorporated in the soft segment phase do not approach the total hard-segment content of the 2,4-T-1P polyurethanes. These materials were found to give rise to a small angle, x-ray-scattering intensity maximum which became more pronounced as the hard-segment content increased (15). The x-ray results indicate that these materials display some phase segregation, but no hard-segment relaxation could be detected by dynamic mechanical testing as carried out in this study because of the low modulus of these materials above the α relaxation. Additional experiments to characterize the dynamic mechanical properties of 2,4-T-1P samples supported by an elastic spring above the α -relaxation process are currently underway.

Soft-Segment Relaxations. The remaining polyurethanes studied exhibited a low temperature, α_s -relaxation much less sensitive to sample composition than the 2,4-T-1P polyurethanes. This relaxation process can be attributed to the glass transition which occurs in soft-segment domains of the phase-separated structure. The α_s relaxation of 2,4-T-2P occurred about -63°C and was not a strong function of hard-segment content over the concentration range examined. An increase in soft-segment block length caused a dramatic improvement in phase separation of 2,4-TDI polyurethanes.

The increase in the α_s -relaxation temperature for 2,6-T-1P samples with increasing hard-segment content is caused by extreme broadening of the relaxation maximum attributable to increasing hard block crystallinity. These effects are similar to changes in dynamic mechanical and

dielectric glass-transition relaxation processes in nylon, PET, and other semicrystalline polymers as the amount of crystallinity increases (21). Huh and Cooper (3), Seefried and co-workers (9,10), and Ferguson (7) have observed similar effects in dynamic mechanical studies of MDI polyurethanes. The activation energy of the α_s process in 2,6-T-1P was found to decrease significantly as the hard-segment content increased, again reflecting the influence of the increasingly crystalline hard segment on soft-segment motions. Similar results have been noted for the decrease in activation energy of the PET α relaxation with increasing degree of crystallinity (21, 22).

The 2,6-T-2P polyurethanes exhibited the lowest temperature α_s relaxation of any of the block polyurethanes studied. A slight increase in activation energy and decrease in the temperature of the α_s relaxation occurred when the hard-segment content increased from 19 to 27 wt%. This behavior can be attributed to the increasing purity of the soft-segment phase. As the hard-segment content increases the hard-block-sequence length also increases, and the longer hard segments display a greater tendency to form a more highly organized separate phase in preference to mixing with the soft-segment material. When a well-developed, hard-segment phase has formed in 2,6-T-2P-43, the crystalline regions exert a similar broadening effect on the α_s relaxation to that noted for highly crystalline 2,6-T-1P polymers. The activation energy was found to decrease significantly and the α_s -relaxation temperature increased for the 2,6-T-2P-43 sample.

Upon repetition of the dynamic mechanical tests, the activation energy for the α_s relaxation of the two highest hard-segment content 2,6-T-2P polyurethanes showed an increase of about 250% over the first determination, as can be seen from Figure 13. The increase in activation energy and corresponding narrowing of the α_s relaxation can be understood in terms of a change in composition of the soft-segment phase on heating. Longer length hard segments are transferred from the soft-segment to the hard-segment phase during the thermal treatment. This leads to a narrower distribution of relaxation times and a corresponding narrowing of the α_s -loss process when the same samples are reevaluated. Changes in the α_s -relaxation temperature from run to run may not be significant in light of the change in breadth of the loss process.

Only the 2,6-T-2P polyurethanes exhibited a relaxation associated with crystallization and later melting of the soft segments. The position of the crystallization maximum was estimated from the location of $\tan(\delta)_{\max}$ and was somewhat difficult to characterize accurately because of extreme overlapping of the α_s and α_c relaxations, as evident in Figure 10. Melting occurred over the region 2°–7°C in all samples. Phase segregation in 2,6-T-2P samples was well developed to the point that the

small amount of hard-segment mixing in the soft segment resulted in freedom from restrictions of hard-segment hydrogen bonding and permitted the soft segment to crystallize above its glass transition.

Hard-Segment Relaxations. For the 2,6-TDI polyurethanes, the δ -relaxation temperature increased with increasing hard-segment content as did the α_h -relaxation temperature of 2,4-T-2P. This effect can more accurately be ascribed to an increase in hard-block length as hard-segment content increased. The longer hard-segment lengths can form a more ordered structure which melts or dissociates at higher temperatures. Peebles (23) has shown that the hard-block length is actually greater than that which would be predicted on a molar basis for a two-stage polyurethane reaction similar to the procedure used to synthesize the materials characterized in this study. Using the number average hard-segment length at 99% conversion and a μ value of three from Peebles' results, the equation given by Flory (24) can be used to obtain the melting temperature for an infinite chain (Equation 2). A plot of

$$\frac{1}{T_m} = \frac{2R}{n\Delta H_u} + \frac{1}{T_m^\infty} \quad (2)$$

the inverse of the δ relaxation temperature against the inverse of the hard-segment length, n , is shown in Figure 14. The δ -relaxation temperatures for both 2,6-TDI polyurethanes were found to fit a straight line with identical values of T_m^∞ , within experimental error, of 222°C for 2,6-T-2P and 227°C for 2,6-T-1P. The hard-segment δ relaxation depends upon chain length and is depressed over the value for an infinite chain only by the presence of end groups, in this case the soft segments which cannot enter the hard-segment crystals.

Figure 14. Reciprocal of average hard segment length vs. $1/T$ for the 2,6-TDI-polyurethane δ relaxation

From the slope of the lines, the heat of fusion per repeat unit, ΔH_u , was calculated as 64 J/g for 2,6-T-2P and 82 J/g for 2,6-T-1P. The hard segment in 2,6-T-1P is more highly organized as the heat of fusion per segment, the unit contained within the brackets with subscript m in Figure 1, is about 25% higher than the value for 2,6-T-2P. This could occur if a greater amount of soft segment is mixed in the hard-segment phase of 2,6-T-2P. Some caution should be exercised in the interpretation of the heat of fusion results, however, as the equation given by Flory applies to the melting temperature while the δ -relaxation temperature, which has no thermodynamic basis, was used in this study.

Harrell (18) has noted that the melting point increased with hard-block length while the degree of crystallinity did not change in a DSC study of nonhydrogen-bonding polyurethane elastomers. The degree of organization in a hard-segment polymer was found to be superior to that of a hard segment in a block polyurethane. A value of ΔH_u of about 40 J/g was determined for these materials, considerably less than for the 2,6-TDI hard segments attributable to the absence of hydrogen-bonding interactions in the piperazine-containing samples.

The δ relaxation, as defined in this study, did not exceed 185°C while the 2,6-TDI/BD hard segment had a melting temperature of about 212°C. The crystalline hard-segment domains in 2,6-TDI polyurethanes can be seen to be more poorly organized than in the hard-segment polymer because of their shorter lengths and the possibility of inclusion of soft segments into the hard-segment-domain regions. Similar results that show an increasing hard-segment melting relaxation have been reported by Ferguson and co-workers (7) for MDI polyurethanes of increasing hard-segment concentration.

The increase in the α_h -relaxation temperature with increasing hard-segment content for 2,4-T-2P parallels the results of Kraus and Rollman (25), who studied S-B-S and S-I-S block copolymers of varying block molecular weight. They found that as block length increased, the hard-segment relaxation shifted to higher temperatures while the soft-block relaxation shifted to lower temperatures. They also demonstrated that the hard-segment relaxation can be lowered by mixing of soft segment into the hard-segment phase at a given hard-block length. By using the theory of Meier (26), they concluded that samples which contained no compositionally pure phases could still give rise to typical block copolymer, dynamic mechanical relaxation behavior. The existence of compositionally pure phases in 2,4-T-2P polyurethanes is doubtful. Schneider and Paik Sung (14) have estimated that about 11–19 wt% hard segment is mixed into the soft phase in 2,4-T-2P polyurethanes. The hard-segment α_h -relaxation occurs at a much lower temperature in 2,4-T-2P polyurethanes than in the pure hard segment, indicating that a compositionally pure hard-segment phase may not be present. The exist-

ence of specific interactions of the hard and soft segment by hydrogen bonding further enhances the presumption that 2,4-T-2P polyurethanes contain no pure hard or soft phase but consist primarily of interlayer material.

The α_h relaxation in 2,6-TDI block polyurethanes could only be clearly observed for 2,6-T-2P-43. This sample contained sufficiently well-developed hard-segment domains that both an amorphous α_h and a crystalline melting δ relaxation were detectable. During the second examination of this sample, the α_h relaxation increased by about 10°C but did not change in intensity, an effect which can be attributed to the presence of a slightly greater degree of crystallinity in the hard segment after thermal treatment.

Degree of Phase Segregation. The relative degree of phase segregation of the various block polyurethanes studied can be estimated from their dynamic mechanical response. The 2,4-T-1P samples displayed the least amount of phase segregation by virtue of the highly composition-dependent α relaxation. The 2,6-T-2P polyurethanes possessed the soft-segment phase of greatest purity as evidenced by the temperature of the α_s relaxation, closest to that of the PTMO homopolymer, as well as the ability of the soft segment to crystallize above its T_g . The soft-segment domains in 2,4-T-2P and 2,6-T-1P polyurethanes are intermediate in purity, with the 2,6-T-1P samples containing a slightly greater amount of hard segment mixed into the soft segment than 2,4-T-2P, which inhibited soft-segment crystallization. The hard-segment domains in 2,4-T-2P are clearly the least organized. A large hard-segment concentration was found to be necessary in order for a well defined, α_h -relaxation process to occur. The 2,6-TDI polyurethanes contained highly ordered hard segments because of the ability of the hard blocks to crystallize. The 2,6-T-1P polyurethanes appear to be the more highly ordered of the two, as these materials exhibit a higher temperature δ relaxation for a given hard-segment length and a higher heat of fusion per segment. The degree of phase segregation in the polyurethanes studied is not nearly as well developed as in some nonpolar block copolymers of higher block molecular weight. The polyurethanes display broad relaxation processes characteristic of poorly defined phases. No pure component phases are thought to exist in these materials. From their dynamic mechanical response, the degree of mixing in each phase can be seen to depend on soft-block molecular weight and hard-segment structure.

Effects of Phase Segregation on Modulus. The magnitude of the modulus between α_s and α_h for 2,4-T-2P or δ for 2,6-TDI block polyurethanes was found to highly depend upon hard-segment content. The presence of a plateau region in modulus-temperature plots has been attributed to phase segregation in block copolymers (27). The hard

Figure 15. Comparison of the storage and loss modulus of 2,4-T-2P-43 and 2,6-T-2P-43 as a function of temperature at 11 Hz

phase can act to reinforce the plateau modulus in a manner similar to that of fillers in crosslinked elastomers. The hard phase also is thought to act as a crosslinking or anchoring region for the soft segments, a mechanism which gives rise to a plateau in modulus above the soft segment T_g . An increase in hard-segment content can induce a higher value of the plateau modulus through either of these mechanisms.

The nature of the hard-segment domains, either crystalline or amorphous, does not appear to be important to plateau modulus enhancement in TDI block polyurethanes, provided that the hard-block length is sufficient. This is illustrated in Figure 15, a modulus vs. temperature comparison of 2,4- and 2,6-T-2P-43. Both polyurethanes exhibit identical storage moduli in the region between the 2,6-T-2P-43 α_c and 2,4-T-2P-43 α_h relaxations. The difference in modulus between α_h and α_c can be accounted for by crystallinity of the soft segment in the 2,6-TDI sample. A comparison of these two polyurethanes containing 39 wt% hard segments indicates that the plateau modulus is much lower for 2,4-T-2P-39. A well developed, α_h -relaxation maximum was not present in this sample. A hard segment capable of crystallization can increase the temperature range of plateau modulus enhancement or be a more efficient method of increasing the plateau modulus, but an equal effect can be provided by a well developed, glassy urethane domain structure.

The plateau modulus in 2,6-TDI polymers was found to depend on hard-segment content rather than on hard-block length. Comparisons of the modulus levels between two 2,6-TDI samples with the same hard-segment content, such as in Figure 11, show that the plateau modulus of the 2,6-T-2P polyurethanes is only about 10% higher at temperatures above the soft-segment melting point. In contrast, for two block polyurethanes with the same hard-block length, such as 2,6-T-1P-42 and 2,6-T-2P-27, the plateau modulus of the 2,6-T-1P sample is about 250% greater.

Conclusions

The structure of the diisocyanate moiety has a significant effect on hard- and soft-segment dynamic mechanical response, which also is reflected in the properties of the block polyurethanes studied. An asymmetric 2,4-TDI hard segment displays only an amorphous α relaxation while a symmetric 2,6-TDI hard segment has a broadened glass-transition relaxation and is capable of crystallization, retaining a high modulus to the melting temperature, about 212°C. Similarly for soft-segment polymers, the relaxation associated with the glass transition occurs at low temperatures for both 2,4- and 2,6-TDI/PTMO, but the latter crystallizes above T_g and later melts at about 10°C.

The dynamic mechanical response of TDI block polyurethanes is sensitive to the degree of phase segregation in these materials. Polyurethanes composed of 2,4-T-1P contain a highly nonhomogeneous soft-segment phase, as evidenced by the compositionally dependent, α -relaxation temperature. A doubling in the soft-segment molecular weight causes phase segregation to occur in 2,4-T-2P, as a relaxation process associated with each phase is evident. The 2,6-TDI block polyurethanes studied are also phase segregated, displaying an α_s relaxation corresponding to the soft-segment T_g and a δ relaxation, associated with hard-block melting. The α_s -relaxation temperature is affected by soft-segment-phase purity and the degree of crystallinity. The δ -relaxation temperature increases with increasing hard-block length. The level of the plateau modulus between the low- and high-temperature relaxations in phase-segregated polyurethanes strongly depends upon hard segment content.

The 2,6-T-2P samples display an additional α_c relaxation associated with crystallization of the soft segment above its glass transition, suggesting that the soft-segment phase is relatively free of intermixed hard blocks. A hard-segment glass transition was observed for the polyurethane sample in this series with the highest hard-segment content, indicating that hard-block organization also is well developed in these materials. The 2,6-T-1P polyurethanes however, contain fewer soft segments mixed in the hard-block domains than the 2,6-T-2P samples.

Comparison of the block copolyurethane relaxations with corresponding loss processes of the hard- and soft-segment polymers indicates that the organization of phases in block polyurethanes is inferior because of the short block length and significant amount of intersegmental mixing in the domains. Samples with crystallizable hard segments and the higher block length, amorphous samples are composed of domains with a sufficiently small degree of mixing that typical block copolymer, dynamic mechanical response is exhibited.

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