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Properties of Segmented Polyether Poly(urethaneureas) Based on 2,4-Toluene Diisocyanate. 2. Infrared and Mechanical Studies

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ABSTRACT: IR spectra of two series of polyether poly(urethaneureas) based on 2,4-toluene diisocyanate, ethylenediamine, and either 1000 or 2000 molecular weight poly(tetramethylene oxide) were examined first to elucidate the state of the hydrogen bonding in the hard segment domain and at the interface between the domains and the soft segment phase. In both series, IR analysis suggests the presence of three-dimensional hydrogen bonding within their hard segment domains, where one urea carbonyl oxygen is bonded to two NH groups. The interface between domain and the soft segment matrix is quite sharp since most of the urethane carbonyl is free from bonding. Mechanical properties, specifically stress–strain behavior, hysteresis, and stress relaxation, are reported in this study to demonstrate the consequences of improved phase segregation and domain structure and to differentiate the morphologies of the two series. At the same urea content (30%), the domain in the PTMO 1000 sample is more interconnected than that in the PTMO 2000 sample, and, also, the soft segment phase of the former contains more solubilized hard segment than that of the latter. The PTMO 2000 sample, which has a better phase segregation than the PTMO 1000 sample, exhibits better mechanical properties, such as higher elongation at break, greater toughness, lower hysteresis, and a slower rate of stress relaxation, even though ultimate tensile strength is slightly lower.

In the preceding paper, we reported that the incorporation of urea linkage in the hard segment has a profound effect on the phase segregation and the domain structure of ethylenediamine extended poly(urethaneureas) based on an asymmetric diisocyanate, such as 2,4-toluene diisocyanate.[1] When compared with the analogous poly(urethanes) extended with butanediol, a drastic improvement in phase segregation and domain organization was observed, both in polyether poly(urethaneureas) and polyester poly(urethaneureas). In this study, we first investigated the IR spectra of polyether poly(urethaneureas) in order to elucidate the state of hydrogen bonding in the hard segment domain and at the interface between the domains and the soft segment phase. Also, the results on the mechanical properties, specifically tensile properties, hysteresis, and stress relaxation, are reported to demonstrate the consequences of improved phase segregation in polyether poly(urethaneureas).

Unlike styrene–butadiene–styrene block copolymers, which can be easily stained with osmium tetroxide, for polyurethanes or poly(urethaneureas) lacking crystallinity or superstructure, their morphologies by transmission electron microscopy are difficult to observe. This is mainly due to the smaller size of the domains and to the difficulty and the artifacts involved in the staining techniques.[2-4] Therefore, in this study, we have attempted to use the results of the mechanical properties to gain some information about the morphology and specifically to differentiate the morphology of two series of polyether poly(urethaneureas): one containing 1000 molecular weight polyether, the other containing 2000 molecular weight polyether.

Experimental Section

Polymers. Polyether poly(urethaneureas) based on 2,4-toluene diisocyanate (2,4-TDI), ethylenediamine (ED), and poly(tetramethylene oxides) (PTMO) of molecular weights 1000 and 2000 were prepared by a method described in a preceding paper.[1] The molar ratio of 2,4-TDI, ethylenediamine, and polyether (PTMO) was varied in five equal steps from 2:1:1 to 6:5:1 for the study of the effect of increasing urea content. The total urea content for each composition is listed in Table I.

Table I
Number of NH Groups, Urethane Carbonyl, and Urea Carbonyl in the 2,4-TDI-ED-PTMO 1000 Series or the 2,4-TDI-ED-PTMO 2000 Series

molar composition of 2,4-TDI-ED-PTMO	overall urea content		NH	no. of urethane C=O	no. of urea C=O
	for PTMO 1000	for PTMO 2000			
2:1:1	29		6	2	2
3:2:1	39	24	10	2	4
4:3:1	47	30	14	2	6
5:4:1	53	36	18	2	8
6:5:1	57	40	22	2	10

IR Studies. A thin polymer film (~ 2 μm in thickness) was cast directly on a NaCl plate from DMF solution and dried in a vacuum oven to remove the solvent completely. A Fourier Transform IR spectrophotometer (Digilab-14) was used to record the spectra.

Mechanical Studies. Test specimens were prepared by casting films from 5% polymer solution in DMF onto clean glass plates and drying them in a vacuum oven for 1 week. Tensile tests were carried out at a strain rate of 1.2%/s with an Instron Model 1122, using a 2-kg load cell. Hysteresis measurements were made by loading and unloading the strip specimens to an increasing strain level at each cycle. Strain levels were varied incrementally from 25 to 1050%. The percent hysteresis for a given cycle is calculated by taking the ratio of the area bounded by the loading–unloading curves to the total area under the loading curve. Stress–relaxation experiments were conducted at a constant strain of 3.5%. The decay in stress as a function of time was recorded.

Chart I shows the chemical structure of two series of polyether poly(urethaneureas) studied in this paper. It is noted from Chart I that the urea linkage is the bond within the hard segment domain, while the urethane linkage is only found as a bond to connect the hard segment domain and the soft segment phase, i.e., at the interface.

Results and Discussion

IR Studies. Figure 1 shows the IR spectra of the 2:1:1 composition of the 2,4-TDI-ED-PTMO 1000 series. Very similar IR spectra are observed for a 4:3:1 composition of the 2,4-TDI-ED-PTMO 2000 series. These two polymers

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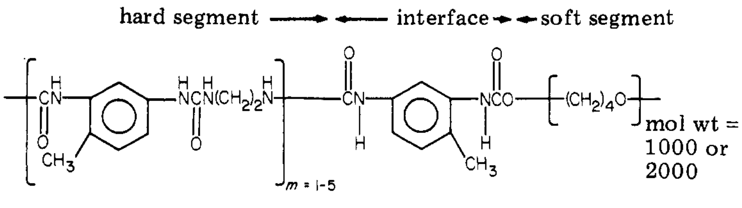
Chart I



2,4-TDI-ED-PTMO 1000 or 2,4-TID-ED-PTMO 2000 series

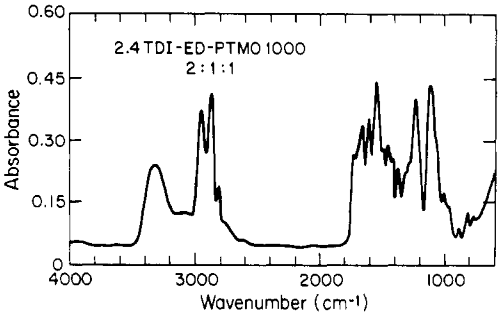


Figure 1. IR transmission spectra of polyether poly(urethaneurea) elastomers (the 2:1:1 composition of the PTMO 1000 series).

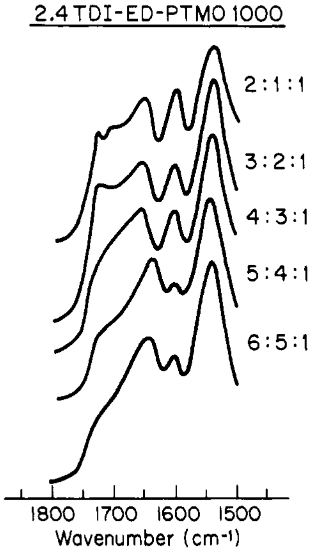


Figure 2. The carbonyl region of the IR transmission spectra of polyether poly(urethaneurea) elastomers as a function of increasing urea content (the PTMO 1000 series).

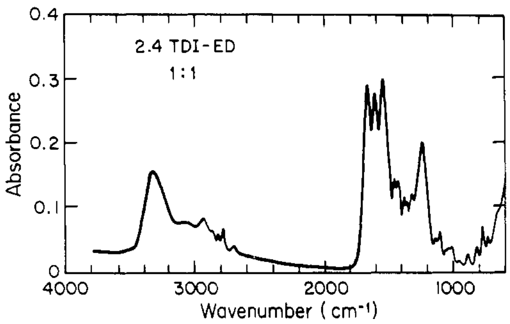
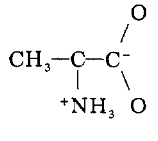


Figure 3. IR transmission spectra of the hard segment analogue (2,4-TDI-ED = 1:1).

have the same overall urea content (30%). In both series, the NH band in the region of 3200–3500 cm^{-1} appears completely hydrogen bonded, since only the peak at 3300–3310 cm^{-1} is visible, while the free NH peak at 3460 cm^{-1} is negligible. This was found to be true of other compositions of both series. However, IR spectra in the urethane and urea carbonyl region are more sensitive to the changes in the total urea content of the samples, as illustrated in Figure 2. Before we discuss the details of the urea and urethane carbonyl peaks in these poly(ureThaneureas), it will be useful to assign IR absorption peaks based on the previous studies and the results obtained with the copolymer of the hard segment analogue (2,4-TDI-ED 1:1). In MDI based poly(urethaneureas) extended with ethylenediamine, Ishihara and co-workers assigned a band at 1640 cm^{-1} due to the hydrogen-bonded urea carbonyl and a band at 1695 cm^{-1} for the free urea carbonyl.[5] In our earlier work on polyether poly(urethanes) extended with butanediol (2,4-TDI-BD-PTMO series), we assigned a peak at 1720 cm^{-1} for the hydrogen-bonded urethane carbonyl and a peak at 1740 cm^{-1} for the free urethane carbonyl.[6] In the IR spectra of the hard segment analogue, as shown in Figure 3, the NH group is completely hydrogen bonded, and the urea carbonyl peak appears at 1660 cm^{-1} as a strong, seemingly single peak. As expected, there is no urethane carbonyl absorption in the region of 1720–1740 cm^{-1} in this copolymer. Tentatively, we have assigned both 1640 and 1660 cm^{-1} peaks as due to the hydrogen-bonded urea carbonyl and a peak at 1695 cm^{-1} for the free urea carbonyl.

Figure 2 illustrates the expanded carbonyl region in the 2,4-TDI-ED-PTMO 1000 series. First, at a 2:1:1 molar composition, the urethane carbonyl absorption split into two peaks of similar intensity at 1740 and 1720 cm^{-1}. This result means that about 50% of the urethane carbonyl is hydrogen bonded, while the other 50% is free. The urea carbonyl peak appears at 1660 cm^{-1}, which corresponds to the hydrogen-bonded urea carbonyl. The free urea carbonyl must be of a negligible amount, since absorption at 1695 cm^{-1} is not observed. In a 3:2:1 and a 4:3:1 composition, which have greater amounts of urea content than a 2:1:1 composition, the urea carbonyl also occurs at 1660 cm^{-1}. Although there is clear evidence of the free urethane carbonyl at 1740 cm^{-1}, the peak at 1720 cm^{-1} is absent. This probably means that the amount of bonded urethane carbonyl decreases with increasing urea content. We were not able to deconvolute these spectra because of too closely overlapping peaks. With a further increase in the hard segment content, as in 5:4:1 and 6:5:1 compositions, the urea carbonyl peak is now shifted to 1640 cm^{-1}, which is assigned to a type of hydrogen bonded urea carbonyl. We will speculate later about the causes of this shift of the urea carbonyl peak from 1660 to 1640 cm^{-1}. No free urea carbonyl was observed in either 5:4:1 or 6:5:1 compositions. It is also noted that even at a 6:5:1 composition, much of the urethane carbonyl exists in the free form rather than being hydrogen bonded since a shoulder at 1740 cm^{-1} is present. The 2,4-TDI-ED-PTMO 2000 series shows very similar trends in the carbonyl region as observed in the 2,4-TDI-ED-PTMO 1000 series. Specifically, in the 2,4-TDI-ED-PTMO 2000 series, the urea carbonyl appears as completely hydrogen bonded, and the urea carbonyl peak exhibits a similar shift with 5:4:1 and 6:5:1 compositions as that in the PTMO 1000 series. Also, a peak corresponding to the free urethane carbonyl is present at 1740 cm^{-1}.

We can derive at least two important observations from the features of the IR spectra. First, the fact that much of the urethane carbonyl, which is only present at the interface between the hard segment domain and the soft segment phase, is free from hydrogen bonding strongly suggests that the interface must be fairly sharp. Second, in both of these series, both NH and urea carbonyl groups are almost completely hydrogen bonded. Since we can assume that the polymer is for the most part a linear molecule (which is expected from the exact stoichiometry used in the synthesis and supported by the solubility in DMF of even 6:5:1 composition), there are approximately twice as many NH groups per each urea carbonyl in all of the compositions as are indicated in Table I for both the 2,4-TDI-ED-PTMO 1000 series and the 2,4-TDI-ED-PTMO 2000 series. For example, at a 2:1:1 composition, there are 6 molar NH groups, 2 molar urethane carbonyls, and 2 molar urea carbonyls. Since only half of the urethane carbonyl (1 molar group) is bonded to presumably 1 molar NH group, the rest of the NH groups (5 molar) should be bonded to other acceptors, such as urea carbonyl, nitrogen in adjacent NH groups, or polyether oxygen. Thermal transition studies reported in the preceding paper indicated that the mixing of the hard segment in the soft segment phase is likely to be small in the PTMO 1000 series and negligible in the PTMO 2000 series. Therefore, we can assume that the hydrogen bonding of NH groups to polyether is small, which means that most of the NH groups should be bonded to either nitrogen in the NH groups or to the urea carbonyl. Blackwell and Gardner reported recently by X-ray crystallographic studies that in the hard segment of MDI-butanediol hydrogen bonding does not occur either to the urethane ester oxygen or to the nitrogen.[7] In view of this finding, it may be unlikely that the nitrogen atom in the urea hard segment will be the hydrogen bond acceptor. This leaves 2 molar urea carbonyls which are a much stronger hydrogen bond acceptor than nitrogen to be bonded to most of the 5 molar NH groups. We speculate that the most likely way that this can be accommodated may be for each urea carbonyl to be bonded to two NH groups. This type of 3-D hydrogen bond should also occur, if at all, in all of the compositions in our polymers as indicated by the stoichiometry in Table I, but to a greater extent in compositions such as 5:4:1 and 6:5:1, since they tend to have longer hard segment lengths. Perhaps the shift in the hydrogen bonded urea carbonyl from 1660 to 1640 cm^{-1} with 5:4:1 and 6:5:1 compositions is due to the increased number of this type of 3-D hydrogen bonding. However, it is not clear why the urea carbonyl peak occurs at 1660 cm^{-1} rather than at 1640 cm^{-1} for the hard segment analogue, since similar types of hydrogen bonding would be expected. More direct evidence for this type of 3-D hydrogen bonding could come from X-ray crystallographic studies with the model compounds made of MDI and ethylenediamine, since the hard segment analogue made of 2,4-TDI and ethylenediamine is amorphous. However, a similar type of 3-D hydrogen bonding, where one carbonyl is bonded to two NH groups, has been observed before in other organic and biological molecules. Simpson and Marsch studied the crystal structure of L-alanine by X-ray diffraction and deduced that L-alanine existed as a zwitterion structure, as such,



$$\mathrm{CH_3-\underset{{}^{+}NH_3}{\underset{|}{C}}-\overset{\overset{O}{/}}{\underset{\underset{O}{\backslash}}{C^-}}}$$

where one of the carbonyl oxygens is bonded to one NH group and the other carbonyl oxygen is bonded to two NH groups.[8] Similar results were obtained by Bodor et al[9] with an organic, nonbiological amino acid, ϵ-aminocaproic acid, which is the precursor to Nylon 6. Also, Bonart and his co-workers[10] suggested the same type of 3-D hydrogen bonding for MDI-based polyether poly(urethaneureas) but without showing IR spectra.

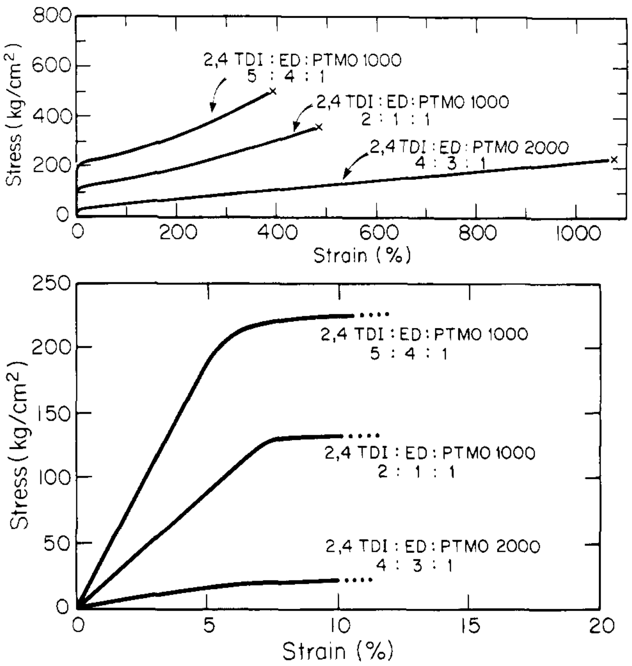


Figure 4. Stress–strain behavior of polyether poly(urethaneurea) elastomers (strain rate = 1.2%/s). (a, top) Overall stress–strain curves until fracture; (b, bottom) initial portion of the stress–strain curves.

Mechanical Properties. While the IR spectra of the 2,4-TDI-ED-PTMO 1000 series and the 2,4 TDI-ED-PTMO 2000 series are similar, as discussed in the preceding section, the mechanical properties are found to be quite different between the series. We attribute this difference to the differences in morphology. We will discuss the results first and elaborate on our interpretation later.

Figure 4a shows the stress–strain curves obtained with two samples from the 2,4-TDI-ED-PTMO 1000 series and one sample from the 2,4-TDI-ED-PTMO 2000 series. The tensile modulus for two samples in the PTMO 1000 series is much greater than that for a PTMO 2000 sample. This behavior is more clearly shown in Figure 4b, which represents the initial portion of the curve with better accuracy. Tensile modulus, tensile strength, and elongation at the break depend strongly on the composition of the polymer. Within the PTMO 1000 series, the tensile modulus and tensile strength were relatively high, and they increase with increasing urea content, while elongation at the break decreases slightly. Specifically, with a 2:1:1 composition, the tensile modulus and the tensile strength were 2000 and 400 kg/cm^2, respectively, and the elongation at break was 500%. With a 5:4:1 composition, the tensile modulus was 4000 kg/cm^2, the tensile strength was 500 kg/cm^2, and the elongation at the break was 400%. With a 4:3:1 composition of the PTMO 2000 series, which has the same overall urea content as a 2:1:1 composition of the PTMO 1000 series, the tensile modulus was about 200 kg/cm^2 (one tenth of that of the latter), and the tensile strength was 250 kg/cm^2, which is lower than that for the PTMO 1000 analogue. However, the elongation at break was 1100%.

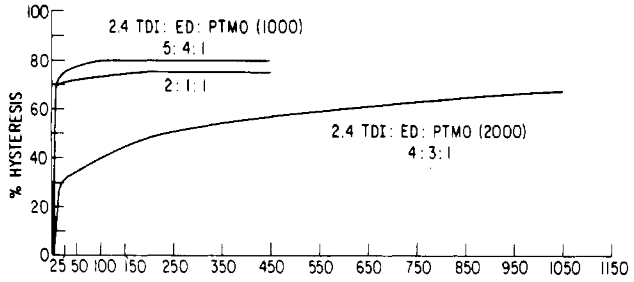


Figure 5. Percent hysteresis as a function of strain in polyether poly(urethaneurea) elastomers.

Whereas the two curves corresponding to the 2,4-TDI-ED-PTMO 1000 series show a marked deviation from the behavior of unfilled vulcanized rubber, the curve corresponding to a 2,4-TDI-ED-PTMO 2000 sample exhibits a smaller degree of deviation.

Sêquela and Prud'homme have shown recently that in styrene–isoprene–styrene or styrene–butadiene–styrene triblock polymers, the specimens with discrete and well-isolated spherical hard domains exhibit the stress–strain behavior close to unfilled vulcanized rubber, while the specimens with other morphologies deviated from rubber-like behavior.[11] Based on their findings, we suggest that domains in the PTMO 2000 series are better separated than those in the PTMO 1000 series. In order to provide more conclusive evidence for this proposed difference in domain morphology, we carried out hysteresis experiments.

Hysteresis under cyclic loading conditions, a serious deficiency in many applications of polyurethanes, due to heat buildup, is related to the interconnectedness of the hard segment domain.[12,13] The breaking of the interconnected hard segment domain through mechanical orientation and heat setting leads to the reduced hysteresis.[14] Therefore, the hysteresis measurement is expected to detect the differences in domain morphology between the PTMO 1000 series and the PTMO 2000 series. Since the preliminary results of the hysteresis were reported in an earlier communication,[15] only a summary figure (Figure 5) is presented here, which shows the percentage of the hysteresis as a function of strain imposed in an incremental manner. For both samples of the 2,4-TDI-ED-PTMO 1000 series, the percent hysteresis quickly reaches about 70% and stays constant between 75 and 80%, even with a further increase in the elongation. There is no difference in the curve between a 2:1:1 composition and a 5:4:1 composition which contains about twice the total urea content. From this, it can be suggested that the hard segment domain is considerably interconnected in the 2,4-TDI-ED-PTMO 1000 series.

In contrast, the hysteresis value in the 2,4-TDI-ED-PTMO 2000 series is distinctly lower than that of two members of the PTMO 1000 series. A 4:3:1 composition of the PTMO 2000 series, which has the same overall urea content as a 2:1:1 composition of the PTMO 1000 series, exhibits a much lower hysteresis. As illustrated in Figure 5, the initial hysteresis value for this sample of the PTMO 2000 series is around 30% and increases slowly with a further elongation up to 65–70% at 1050% elongation. The overall results on the hysteresis behavior then support our hypothesis about the differences in the domain morphology between the PTMO 1000 and the PTMO 2000 poly(urethaneureas). A difference in the domain morphology would likely lead to a significant difference in the ultimate tensile properties. As Smith[16] and Cooper[17] speculated, interconnected or interlocked domain morphology would exhibit higher ultimate tensile strength than separated domain morphology. This is borne out by our data that the tensile strength for a 2:1:1 sample of the PTMO 1000 series is considerably higher than that for a 4:3:1 sample of the PTMO 2000 series.

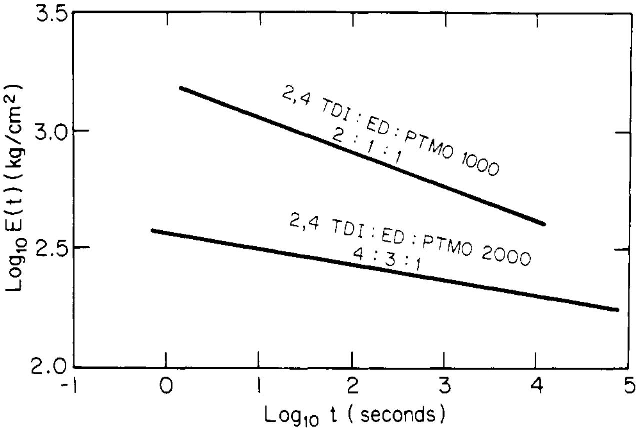


Figure 6. Stress relaxation at room temperature for polyether poly(urethaneureas).

Thermal transition studies, reported in the preceding paper,[1] showed that the T_g of the rubbery phase of the PTMO 1000 series is around −55 °C, while that for the PTMO 2000 series is −75 °C, which is only a few degrees higher than the T_g of the free soft segment. This result may be interpreted as indicating that the amount of the solubilized hard segment in the rubbery soft segment phase in the PTMO 2000 series is negligible, because tying down both ends of the soft segment would likely raise the T_g by a few degrees, while the amount of the solubilized hard segment in the soft segment phase, as in the PTMO 1000 series, should be considerable, since the T_g is rasied by 25 °C. Some of the solubilized hard segment in the PTMO 1000 series would be expected to be the chain ends. Therefore, the number of chain ends in the rubbery soft segment phase of the PTMO 1000 series would be greater than that in the PTMO 2000 series. If so, the stress in the PTMO 1000 series would likely relax faster than that in the PTMO 2000 series due to the greater viscous flow. In order to provide more support for this interpretation of the soft segment structure, we carried out stress–relaxation experiments by rapidly stretching and holding the samples at a small strain of 3.5%, which is within the range of the linear portion of the stress–strain curve. At such a small strain, Cooper et al.[18] have shown from IR dichroism studies that the orientation of either hard segment domain or soft segment is negligible. The result of the stress–relaxation is plotted in Figure 6, where the plots of log $E(t)$ vs. log t result in approximately straight lines for both series. As expected from the stress–strain curve, the initial stress for the PTMO 1000 sample is higher than that for the PTMO 2000 sample. Also, the decay in stress was much faster for a 2:1:1 sample of the PTMO 1000 series than for a 4:3:1 sample of the PTMO 2000 series. The logarithm of the modulus expressed as a percentage of initial modulus vs. log t produced straight lines for both series, as shown in Figure 7. This linearity enables the application of the central limit theorem[19] to obtain a quantitative analysis of the data. The time required for the 50% stress–relaxation is compared for both series. For a 2:1:1 sample of the PTMO 1000 series, the value of log t is 2.53, corresponding to a mean relaxation time of 325 s, while for a 4:3:1 sample of the PTMO 2000 series, log t is found to be 3.95, corresponding to 8910 s. Therefore, there is at least an order of magnitude of difference in the rate of stress–relaxation between the PTMO 1000 series

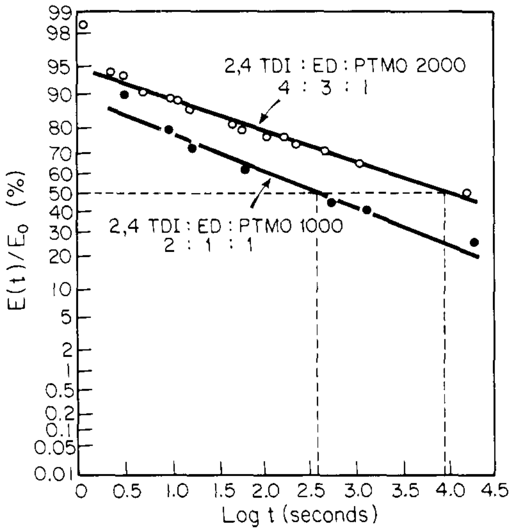


Figure 7. Stress relaxation data on the probability coordinate vs. the log of the time for polyether poly(urethaneureas).

and the PTMO 2000 series. This result appears to be consistent with our interpretation of the elevation of the T_g in the soft segment phase attributed to the solubilized hard segment.

Conclusion

Results obtained in this study by IR and mechanical studies on two series of polyether poly(urethaneureas) provide more insight into the morphology of these phase-segregated systems.

In the 2,4-TDI-ED-PTMO 1000 samples, and to a greater extent in the 2,4-TDI-ED-PTMO 2000 samples, three-dimensional hydrogen bonding may exist within their hard segment domains, where one urea carbonyl oxygen is hydrogen bonded to two NH groups, as suggested by IR studies. Perhaps this type of three-dimensional hydrogen bond formation may provide the driving force for much improved phase segregation, even at low urea content, and the fast kinetics[20] of phase segregation generally observed with poly(urethaneureas). It is noted that this type of 3-D hydrogen bonding has not been detected in poly(urethanes) extended with diol. IR studies also indicated that the interface between the hard segment domain and the soft polyether matrix is quite sharp, since most of the urethane carbonyl is free from bonding.

In general, the morphology for both the PTMO 1000 series and the PTMO 2000 series is that of hard segment domains dispersed in the continuous matrix of the polyether soft segment phase in the range of urea content we studied. The hard segment domain in both series is quite pure. However, there are distinct differences in the detailed morphology between the PTMO 1000 sample and the PTMO 2000 sample if we compare them at the same urea content (e.g., a 2:1:1 sample of the PTMO 1000 series vs. a 4:3:1 sample of the PTMO 2000 series). For example, the hard segment domain of the PTMO 1000 sample is more interconnected than that of the PTMO 2000 sample, as indicated by the stress–strain curve and the hysteresis behavior. Also, in the PTMO 1000 sample, the soft segment phase contains some solubilized hard segment, while it is absent in the PTMO 2000 sample.

As a result, the PTMO 2000 sample with the improved segregation leads to excellent mechanical properties such as higher elongation at the break, lower hysteresis, a greater toughness value (as expressed by the area under the stress–strain curve), and a slower rate of stress–relaxation, even though the ultimate strength is somewhat lower, as compared with the PTMO 1000 sample.

Future work with these materials involves quantitative small-angle X-ray scattering and IR dichroism to provide more information on the morphology and the structure–property relationships.

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