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Properties of Segmented Poly(urethaneureas) Based on 2,4-Toluene Diisocyanate. 1. Thermal Transitions, X-ray Studies, and Comparison with Segmented Poly(urethanes)

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ABSTRACT: Polyether poly(urethaneureas) and polyester poly(urethaneureas) based on 2,4-toluene diisocyanate, ethylenediamine, and poly(tetramethylene oxide) or poly(butylene adipate) were synthesized to study the effect of the urea linkage in the hard segment on the extent of phase segregation, domain structure, and polymer properties. The experimental techniques utilized were differential scanning calorimetry and wide-angle and small-angle X-ray techniques. Phase segregation into the hard segment domains in the soft segment phase was observed in both the polyether and polyester series at all levels of urea content. In both series, the hard segment domains are amorphous with a very high T_g (165–190 °C), even in low-urea-content compositions. The T_g of the soft segment phase in the polyether series was found at approximately −55 °C for 1000 molecular weight polyether and −75 °C for 2000 molecular weight polyether. For the polyester series, the T_g of the soft segment phase was −10 to −30 °C for 1000 molecular weight polyester and −40 to −55 °C for 2000 molecular weight polyester. Comparison of the thermal transition behavior of poly(urethaneureas) was made with the comparable poly(urethanes) extended with butanediol. In general, the extent of phase segregation is dramatically improved, as is reflected by a much lower T_g of the soft segment phase and by a much higher T_g of the hard segment domain in poly(urethaneureas) extended with ethylenediamine than in poly(urethanes) extended with butanediol.

Thermoplastic poly(urethanes), which consist of alternating soft segment (aliphatic polyether or polyester) and hard segment (aromatic urethane), offer unique possibilties for tailor making their properties by varying their composition. Compositional variables are known to affect the degree of phase segregation, phase mixing, and hard segment domain organization, and accordingly the polymer properties.[1,2]

In our previous studies, we reported the results obtained on an extensive series of poly(urethanes) based on toluene diisocyanate extended with butanediol[3,4] where urethane (NHCOO) was the linkage in the hard segment in these polymers. The results on these polymers indicated that asymmetry in the diisocyanate structure, as in 2,4-toluene diisocyanate (2,4-TDI), leads to an amorphous hard segment domain, while in the symmetric 2,6-TDI poly(urethanes), the crystalline hard segment domain was observed. It was also found that in 2,4-TDI based poly(urethanes), extensive phase mixing occurs between hard and soft segment, except for the polymers which contain the 2000 molecular weight poly(tetramethylene oxide) soft segment. In general, the polyester soft segment was found to contribute to greater phase mixing than the polyether, despite the tendency of the polyester to crystallize more readily than polyether.[4] This behavior implied that the hydrogen bonding of urethane to polyester is stronger than that to polyether.

In polymers made from symmetrical diisocyanate, it is believed that poly(urethaneureas), which are extended with diamine, demonstrate better phase separation than poly(urethanes) extended with diol. For example, Bonart and his co-workers reported that poly(urethanes) composed of diphenylmethane diisocyanate, butanediol, and polyether in the molar ratio of 2:1:1 had mutually soluble hard and soft segments and showed no evidence of phase separation.[6] However, comparable ethylenediamine extended polymers, where urea (NHCONH) is the linkage in the hard segment, were phase separated at the same molar composition ratio, as evidenced by small-angle X-ray-scattering studies. Bonart tentatively suggested that a three-dimensional hydrogen bonding, where one carbonyl is involved with two NH groups, might be responsible for this difference. Also, Chang and Wilkes reported that in some polyether poly(urethaneureas) based on symmetrical diisocyanate and symmetrical diamine chain extender, a superstructure such as spherullite was observed despite the lack of appreciable crystallinity in the hard segment domains.[7]

Until now, it was not known whether poly(urethaneureas) made of asymmetric diisocyanate, such as 2,4-toluene diisocyanate, would exhibit better phase separation than similar poly(urethanes). Therefore, we have prepared four series of polyether poly(urethaneureas) and polyester poly(urethaneureas). Polyether poly(urethaneureas) are made of 2,4-TDI, ethylenediamine, and either 1000 or 2000 molecular weight poly(butylene adipate).

The effects of the urea linkage in the hard segment on the extent of phase separation, domain structure, and polymer properties are studied by employing various physicochemical techniques. In this report, we will first discuss the results obtained by thermal transition analysis, with both wide-angle and small-angle X-ray studies. Also, the comparison of thermal transition behavior of these polymers will be made with the comparable polymers extended with butanediol.

Experimental Section

Polymer Syntheses. 2,4-Toluene diisocyanate (2,4-TDI) was obtained from Aldrich Chemical Co. and vacuum distilled at 65 °C. Poly(tetramethylene oxides) (PTMO) of molecular weight 1000 and 2000 were obtained from Quaker Oats Co. Poly(butylene adipates) (PBA) of molecular weights 1000 and 2000 were from Hooker Chemical. Anhydrous ethylenediamine was purchased from Fisher Scientific Co.

The preparation of the polyether poly(urethaneureas) was carried out according to the method described by Lyman and co-workers, which involves the solution polymerization techniques due to the high reactivity of aliphatic diamine chain extender.[8] First, the solution of polyether was prepared in a 1:1 mixture of dimethyl sulfoxide and methyl isobutyl ketone, and 2,4-TDI was added to the solution. The prepolymer solution was stirred at 100 °C for 1.5 h, and ethylenediamine was added and stirred for an additional hour at 30–40 °C. The concentration of polymer in solution was 5–10%. The polymer was precipitated and dried in a vacuum oven at 50–60 °C for at least 1 week. The molar ratio of 2,4-TDI, ethylenediamine, and PTMO or PBA was varied in five equal steps from 2:1:1 to 6:5:1, without using excess diisocyanate. The copolymer of the hard segment analogue (2,4

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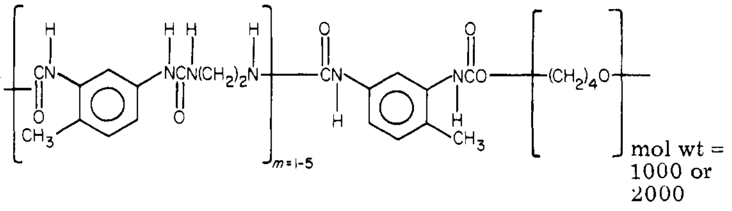
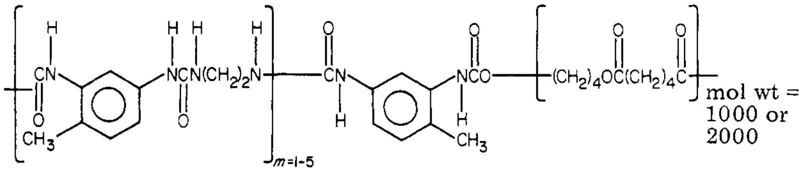
Chart I



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



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

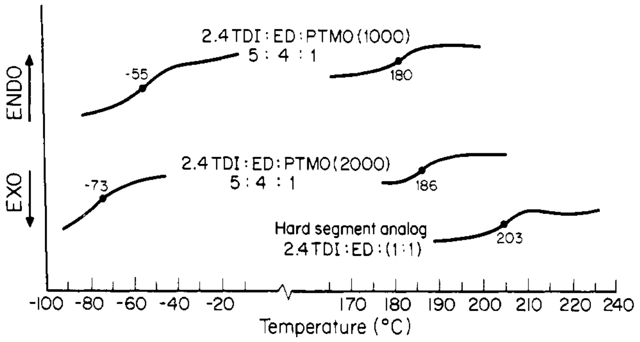


Figure 1. DSC scans of 2,4-TDI-ED-PTMO 1000 polyether poly(ureathaneurea) (5:4:1 composition), 2,4-TDI-ED-PTMO 2000 polyether poly(urethaneurea) (5:4:1 composition), and hard segment copolymer (2,4-TDI:ED=1:1).

TDI:ED=1:1) was made in a similar way as that used for segmented polymers. Chart I represents the chain structure of polyether poly(urethaneureas) and polyester poly(urethaneureas).

Polymer Characterization. Thermal Analysis. Differential scanning calorimetry was carried out on a Perkin-Elmer DSC II, equipped with the scanning Auto Zero Accessory. The heating rate was 20 °C/min. The sensitivity chosen was either 2 mcal/s of 5 mcal/s. For low-temperature scans ranging from 160 to 350 K, helium was used as a carrier gas, while argon was employed for high-temperature scans. The sample weight was approximately 10–35 mg.

Wide-Angle X-ray-Diffraction Studies. The X-ray-diffraction intensity was recorded as a function of diffraction angle, using a G.E. Model 11GN1 diffractometer with Cu Kα radiation. Film specimens were cast from dimethylformamide solutions. Film thickness varied from 25 to 200 μm.

Small-Angle X-ray-Scattering Studies. Small-angle X-ray-scattering patterns were initially recorded in photographic films by using the Cu Kα line for 7 h of exposure time. The distance between the sample and the film was 40 cm, and the thickness of the sample films was about 950 μm. After developing photographic plates, a densitometer (Jarrell-Ash No. 21-050) was used to scan the scattering intensity as a function of angle.

Gel Permeation Chromatographic Results. Molecular weight distribution was obtained by running a dilute solution (0.25% in DMF which contains 0.01 M LiBr to prevent aggregation) through GPC (Waters Associates, high-pressure chromatograph). The number average molecular weight is found to be in the range of 10 000–43 000, as summarized in Table I.

Table I
Thermal Transitions of 2,4-TDI Based Polyether Poly(urethaneureas) and Polyester Poly(urethaneureas)

sample	M_n × 10^{-3}	urea,[a] wt %	T_{g1},[b] °C	T_{m1},[c] °C	T_{g2},[d] °C
Polyether Series					
2,4-TDI-ED-PTMO 1000					
2:1:1	21	29	−53		192
3:2:1	28	39	−54		190
4:3:1	33	47	−58		190
5:4:1	43	53	−55		180
6:5:1	27	57	−61		184
2,4-TDI-ED-PTMO 2000					
3:2:1	36	24	−76		180
4:3:1	34	30	−74		190
5:4:1	35	36	−73		186
6:5:1	25	40	−78		191
Polyester Series					
2,4-TID-ED-PBA 1000					
2:1:1	8	29	−17	45	165
3:2:1	13	39	−10	47	166
4:3:1	13	47	−33	48	185
5:4:1	16	53	−20	47	182
6:5:1	20	57	−38		177
2,4-TDI-ED-PBA 2000					
3:2:1	17	24	−41	51	176
4:3:1	18	30	−42	57	170
5:4:1	14	36	−45	62	194
6:5:1	31	40	−53	55	178

[a] Urea weight percent represents hard segment content. [b] T_g of the soft segment phase. [c] T_m of the crystalline soft segment, absent in polyether poly(urethaneureas). [d] T_g of the amorphous hard segment domain.

Results and Discussion

Polyether Poly(urethanes). Thermal Transition Behavior. A typical DSC scan for the 2,4-TDI-ED-PTMO 1000 series is illustrated in Figure 1. The T_g of the soft segment phase is clearly indicated at −55 °C. The T_g of the soft segment phase for the 2,4-TDI-ED-PTMO 2000 series is found to be even lower, approximately at −75 °C, as shown also in Figure 1. In both series, the soft segment phase was amorphous, since the melting endotherm near 40 °C was absent. As summarized in Table I, the soft segment glass transition temperatures for both series are independent of the increasing urea content (or increasing hard segment length). Since the T_g of the pure PTMO is −85 °C, the T_g in the 2,4-TDI-ED-PTMO 2000 series is elevated by only 10 °C, while for the PTMO 1000 series it is elevated by 30 °C. Therefore, in the PTMO 2000 series, the amount of solubilized hard segment in the soft segment phase is negligible, since anchoring the ends of the soft segment might raise the T_g to −75 °C. On the other hand, some hard segment must have been solubilized in the soft segment phase of the PTMO 1000 series to raise the T_g by 30 °C. As will be discussed in detail in a later section, the amount of intermixing of the hard segment in the soft segment in these poly(urethaneureas) is much

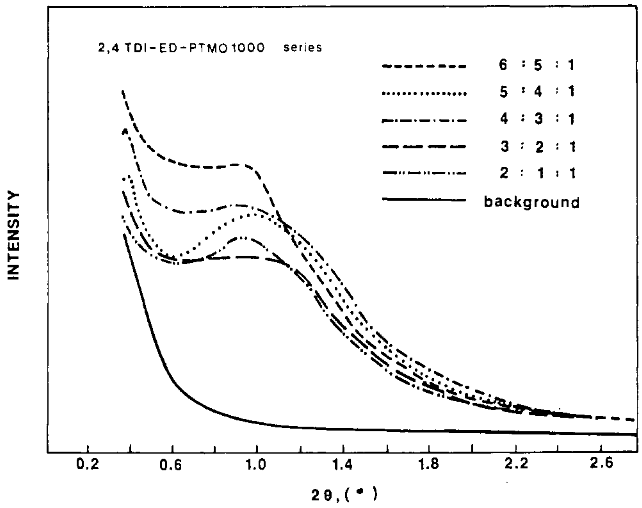


Figure 2. Angular dependence of SAXS for 2,4-TDI-ED-PTMO 1000 polyether poly(urethaneureas).

smaller than in comparable poly(urethanes), implying much improved phase segregation in diamine extended polymers. The observation of T_g of the soft segment phase was reproducible even after the heating and cooling cycle. Higher temperature thermal transitions were not as easily observed as that for the soft segment phase. Only after increasing both sample weight to maximum capacity (~35 mg) and the sensitivity of the instrument was it possible to detect the T_g of the hard segment domain, as shown in Figure 1 between 180 and 190 °C. This is the reason why the entire DSC curve was not recorded, but rather short segments are shown in Figure 1. Beyond T_g of the domain, no crystallinity was observed up to 250 °C. As listed in Table I, the T_g of the hard segment domain was also independent of the urea content. This result seems to indicate that the domain organization is not further improved by a longer hard segment length. Even in the 2:1:1 molar composition of the 2,4-TDI-ED-PTMO 1000 series, the hard segment domain has equally high T_g as in the 6:5:1 molar composition. In order to ensure that the observed T_g of the hard segment domain is truly reflective of the amorphous domain, the DSC scan of the copolymer which consists of only 2,4-TDI and ethylenediamine was obtained and illustrated in the lowest part of Figure 1. The T_g is found at 203 °C for this hard segment analogue. The fact that the T_g of the hard segment domain in these series of 2,4-TDI-ED-PTMO was only 10–20 °C lower than that of the hard segment copolymer strongly suggests that the mixing of the soft segment in these domains, especially at a 2:1:1 molar composition, is quite small.

Small-Angle X-ray-Diffraction Studies. In order to provide more conclusive evidence of the presence of the domains in this series, small-angle x-ray-scattering studies were carried out. Figure 2 shows the angular dependence of the intensity in the small-angle region for the 2,4-TDI-ED-PTMO 1000 series, as obtained at room temperature. As can be clearly seen, all of the polymers which belong to this series exhibit the type of angular dependence which supports the presence of domain structure. Furthermore, the area under each curve is not drastically different. A quantitative analysis concerning domain organization and interfaces based on SAXS results are now in progress in collaboration with Professor G. L. Wilkes.

Wide-Angle X-ray-Diffraction Studies. Figure 3 represents WAXD curves of the 2,4-TDI-ED-PTMO 1000 series, along with those of pure soft segment and hard segment copolymer. All of the samples showed a rather broad band centered around a diffraction angle of 19°, which corresponds to 4–5 Å in d spacing. The WAXD curve of the hard segment copolymer, as shown in Figure 5, is very similar to those for the 2,4-TDI-ED-PTMO 1000 series. Therefore, it appears that the origin of this band may be due to short-range ordering in the hard segment domains. Similar results were observed by Chang and Wilkes[7] in Hylene-W (4,4′-dicyclohexylmethane diisocyanate) based poly(urethaneureas). The origin of two small peaks occurring at the diffraction angles of 26.5 and 29° appears to be spurious.

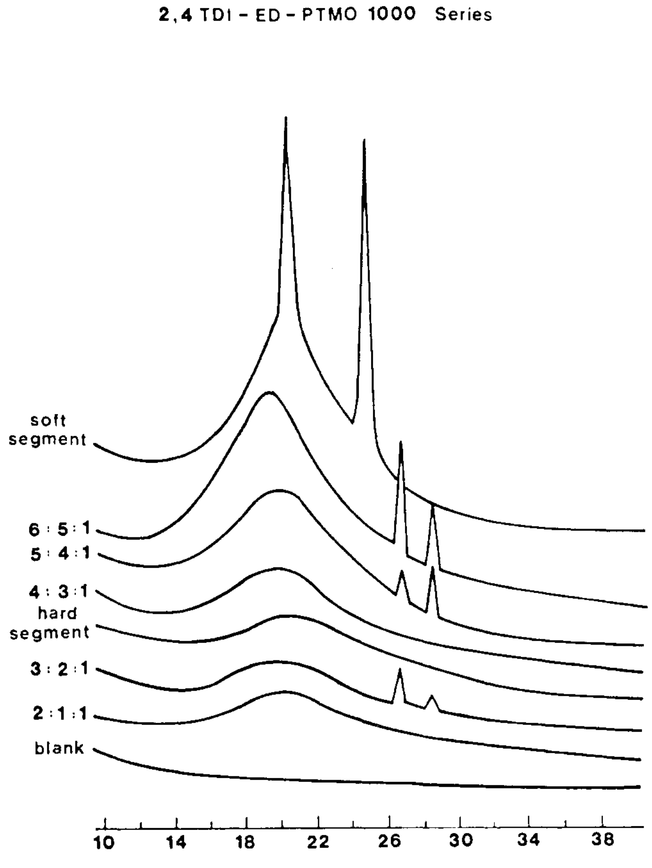


Figure 3. Angular dependence of WAXD for 2,4-TDI-ED-PTMO 1000 polyether poly(urethaneureas).

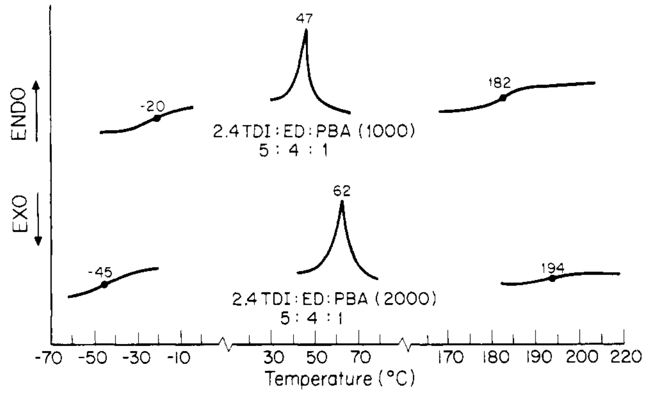


Figure 4. DSC scans of 2,4-TDI-ED-PBA 1000 polyester poly(urethaneurea) (5:4:1 composition) and 2,4-TDI-ED-PBA 2000 polyester poly(urethaneurea) (5:4:1 composition).

Polyester Poly(urethaneureas). Thermal Transition Behavior. A typical DSC scan for the 2,4-TDI-ED-PBA 1000 series is illustrated in Figure 4. The T_g of the soft segment phase ranges from −10 to −38 °C, decreasing slightly with increasing urea content, as summarized in Table I. Also noticed in the DSC scans is the presence of

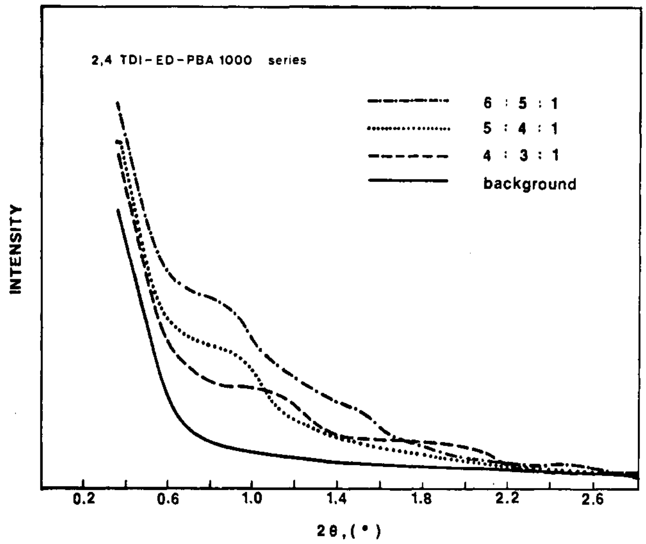


Figure 5. Angular dependence of SAXS for 2,4-TDI-ED-PBA 1000 polyester poly(urethaneureas).

a certain amount of the crystalline soft segment, which melts at 45 °C, except for the 6:5:1 molar composition.

Even though the T_g of the soft segment in this series was higher than those for the 2,4-TDI-ED-PTMO 1000 series, it was much lower than that for polyester poly(urethanes) extended with butanediol. Therefore, the phase segregation must have been improved in comparison to polyester poly(urethanes). Figure 4 illustrates the high-temperature DSC scan for the 2,4-TDI-ED-PBA 1000 series. The T_g of the hard segment domain was observed at 165–185 °C for all of the samples in this series, again after increasing the sample weight and the sensitivity of the instrument. For the 2,4-TDI-ED-PBA 2000 series, the T_g of the soft segment phase is observed from −40 to −53 °C, decreasing slightly with increasing urea content, as shown in Figure 4. When compared with the T_g of the pure PBA which is −65 °C, the T_g of this series is only raised by 10–25 °C. When compared with the T_g of the PBA 1000 poly(urethaneureas), the effect of increasing the PBA molecular weight is obvious, i.e., higher molecular weight improves phase separation. This behavior is also reflected in the presence of the crystallinity of the soft segment whose melting point is slightly higher than those observed in the PBA 1000 series. As illustrated in Figure 4, the T_g of the hard segment domain is observed at temperatures ranging from 165 to 194 °C.

Small-Angle X-ray-Scattering Studies. Figure 5 shows the angular dependence of the intensity in the small-angle region for polymers in this series, as obtained at room temperature. All of the polymers in this series exhibit the type of angular dependence which implies the presence of domain structure, even though the integrated area under the curve is smaller than that for the 2,4-TDI-ED-PTMO 1000 series.

Wide-Angle X-ray-Diffraction Studies. Figure 6 represents WAXD curves of the 2,4-TDI-ED-PBA 1000 series. For samples of composition ranging from 2:1:1 to 4:3:1, a small extent of soft segment crystallinity is observed, but not in 5:4:1 and 6:5:1 molar compositions. The 5:4:1 samples showed small amounts of soft segment crystallinity by DSC. It appears that the amount of soft segment crystallinity in the 5:4:1 sample is too small to produce peaks in WAXD under the experimental condition. The hard segment is again amorphous in this series, since only a broad peak at 19° is observed as in polyether poly(urethaneureas). Two small peaks at diffraction angles of 26.5 and 29° appear spurious.

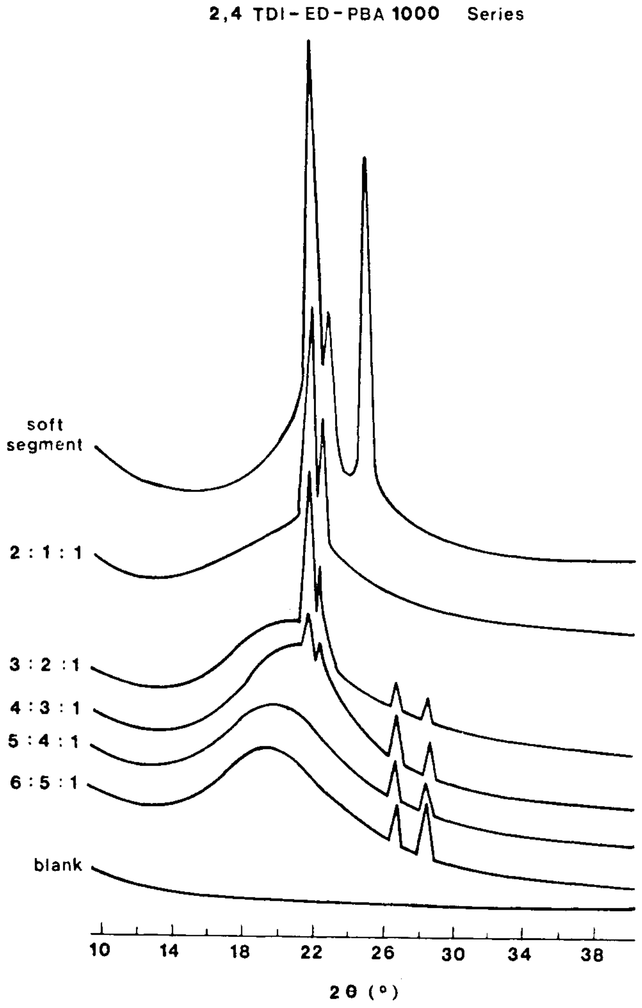


Figure 6. Angular dependence of WAXD for 2,4-TDI-ED-PBA 1000 polyester poly(urethaneureas).

Comparison with Poly(urethanes) Extended with Butanediol. In this section, we will compare the thermal transition behavior of poly(urethaneureas) extended with ethylenediamine with the previously reported values for poly(urethanes) extended with butanediol.[1,4,9] The major difference between these two series is the presence of urea linkage vs. urethane linkage in the hard segment. One may be concerned about the effect of the butyl group in poly(urethanes) vs. the ethyl group in poly(urethaneureas). In the work reported by Bonart and co-workers, the hard segment softening point in the MDI-ED-PBA 2000 series was 187 °C, while that for the MDI-BD(butylenediamine)-PBA 2000 series was 179 °C.[10] There result implies that in poly(urethaneureas) the effect of changing ethylenediamine to butylenediamine is small. Therefore, the major difference between poly(urethanes) extended with butanediol and poly(urethaneureas) extended with ethylenediamine can be interpreted due to the difference of urea linkage vs. urethane linkage.

Figure 7 compares the T_g of the soft segment phase of poly(urethanes) extended with butanediol with those of poly(urethaneureas) extended with ethylenediamine. We will discuss the PTMO 1000 series first. In 2,4-TDI-BD-PTMO 1000, the T_g varies from −36–23 °C with increasing urethane content. This corresponds to an elevation from the T_g value of the free soft segment (−85 °C), in the range of 49–108 °C. The increase in T_g in these poly(urethanes) explains the progressive change observed in properties. Previous IR analysis indicated that in these poly(ure-

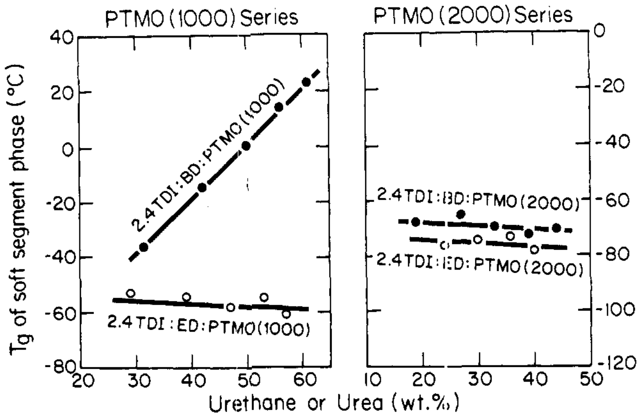


Figure 7. Comparison of T_g of the soft segment phase in polyether poly(urethanes) and poly(urethaneureas).

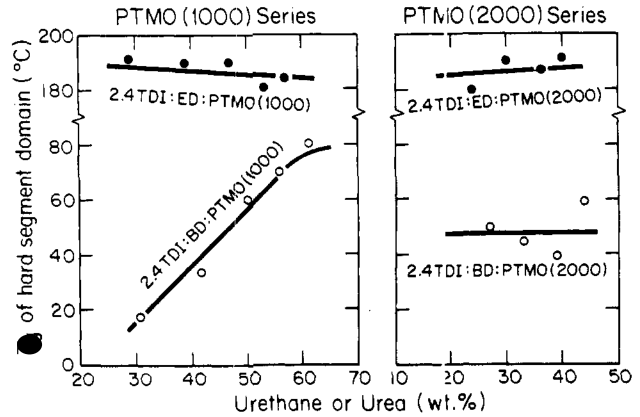


Figure 8. Comparison of T_g of the hard segment domain in polyether poly(urethanes) and poly(urethaneureas).

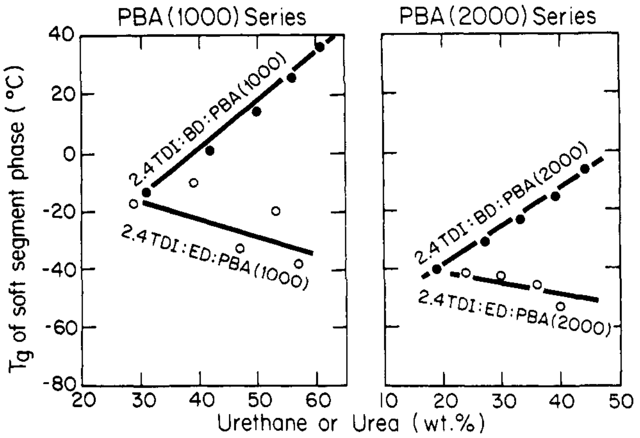


Figure 9. Comparison of T_g of the soft segment phase in polyester poly(urethanes) and poly(urethaneureas).

thanes), increasing urethane content elevates the T_g of the mixed soft segment phase by providing more NH groups available for hydrogen bonding with the soft segment. On the other hand, in the 2,4-TDI-ED-PTMO 1000 series, the T_g of the soft segment phase is much lower (about −55 °C) and independent of the urea content. Therefore, the improvement in phase segregation in the PTMO 1000 series in poly(urethaneureas) is dramatic. Increasing the molecular weight of the polyether soft segment from 1000 to 2000 produces an improvement in phase segregation, at least in terms of T_g of the soft segment phase, as can be seen in Figure 7. The improvement in poly(urethanes) is more pronounced than that in poly(ureas) as compared with the values for the respective PTMO 1000 series. The T_g of poly(urethanes) is already quite low (about −70 °C), while that of poly(urethaneureas) is even lower (about −75 °C). In both of these PTMO 2000 series, the amount of solubilized hard segment in the soft segment phase would be expected to be small. The fact that the soft segment phase is relatively pure does not seem to guarantee that the hard segment domains will be pure, as will be discussed later.

Figure 8 compares the T_g of the hard segment domain. In the PTMO 1000 series of poly(urethanes), the T_g of the hard segment domain increases from 18 to 80 °C with increasing urethane content. This result has been interpreted as meaning that the amorphous hard segment domain structure improves with increasing urethane content, based on small-angle X-ray-scattering studies which provided independent evidence of domain structure in the three samples of higher urethane content. This trend of improving domain structure with increasing urethane content might appear in contradiction to our earlier statement that the mixing of the hard segment in the soft segment phase increases with increasing urethane content. Perhaps this apparent contradiction can be resolved if we envision a morphology for the 2,4-TDI-BD-PTMO 1000 series such that the hard segment domain is also impure and contains the solubilized soft segment. This is reasonable to assume since the T_g of the domain is much lower than that of the pure hard segment copolymer. As the length of the hard segment increased, apparently the amount of the solubilized soft segment in the domain must decrease, thus resulting in the improvement of the domain structure. This may be attributed to the increasing amount of interurethane hydrogen bonding in the domain at the higher urethane content, with the effect of excluding the soft segment from the domain. However, by no means is the hard segment domain, even at the highest urethane content (6:5:1 composition), pure. Also, due to the polydispersity of the hard segment length, some of the shorter hard segments may not be incorporated in the domain, but rather find themselves in the soft segment phase. Apparently, this availability of the solubilized hard segment must increase as the urethane content increases, thus resulting in the elevation of the T_g of the soft segment phase.

In the PTMO 2000 series, again the T_g's of the domain in poly(urethaneureas) are about 185 °C, and thus are much higher than those of similar poly(urethanes). In fact, the T_g's of the domain in 2,4-TDI-BD-PTMO 2000 are surprisingly low (about 50 °C), since one may expect the relatively pure domain since the soft segment phase is relatively pure. The results, however, indicate that even when the soft segment phase does not contain much of the solubilized hard segment, the hard segment domain can contain some of the solubilized soft segment. The T_g of the domain in the 2,4-TDI-BD-PTMO 2000 series is either equal to or higher than that of the 2,4-TDI-BD-PTMO 1000 series when compared at the same urethane contents (compare the first two points in the PTMO 1000 series and all of the points in the PTMO 2000 series). This is expected since the increase in the soft segment molecular weight from 1000 to 2000 produces improvement in phase segregation. The last three points in the PTMO 1000 series appear slightly higher than any of the T_g values for the PTMO 2000 series. We do not have the PTMO 2000 poly(urethanes) in a similar range of urethane content (between 50 and 60% by weight) for direct comparison.

In polyester-containing polymers, Figure 9 compares the T_g of the soft segment phase of poly(urethanes) extended with butanediol with those of poly(urethaneureas) extended with ethylendiamine. A distinguishing feature of Figure 9 is the contrast of the T_g as a function of hard

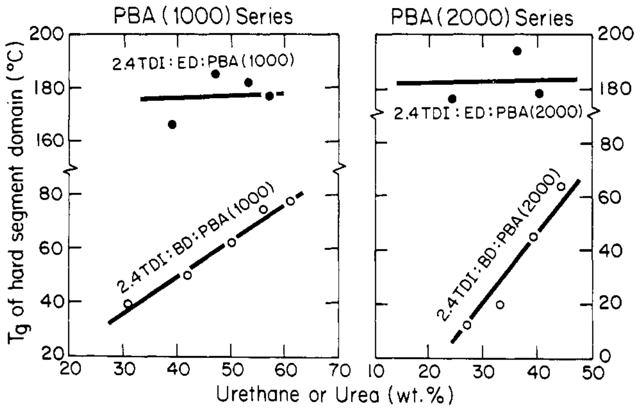


Figure 10. Comparison of T_g of the hard segment domain in polyester poly(urethanes) and poly(urethaneureas).

segment content. In poly(urethanes) such as 2,4-TDI-BD-PBA 1000 or 2,4-TDI-BD-PBA 2000, the T_g of the soft segment phase is progressively increased as a function of urethane content. This suggests that more hard segment is solubilized in the soft segment phase as the urethane content increases. In contrast, the T_g of the soft segment phase of the 2,4-TDI-ED-PBA 1000 series or the 2,4-TDI-ED-PBA 2000 series decrease, which means a smaller amount of hard segment is solubilized in the soft segment phase with increasing urea content. Therefore, both in the PBA 1000 and the PBA 2000 series, the improvement of phase segregation in poly(urethaneureas) is obvious when compared with analogous poly(urethanes). Figure 10 compares the T_g of the hard segment domain of two series of polymers. Again both in the PBA 1000 and the PBA 2000 series, the hard segment domain in poly(urethaneureas) is much better organized, as evidenced by the presence of high temperature T_g of the domain in comparison to much lower values for poly(urethanes). Furthermore, the T_g of the domain in poly(urethaneureas) is independent of the urea content, while a strong dependence of the T_g of the domain is observed in analogous poly(urethanes).

Conclusion

We have studied the effect of having urea linkages in the hard segment on the phase segregation and domain structure of polyether poly(urethaneureas) and polyester poly(urethaneureas) based on 2,4-toluene diisocyanate. The effect is dramatic when compared with analogous poly(urethanes), which have urethane linkage in the hard segment. The most pronounced effect is reflected in the high T_g of the hard segment domain (170–190 °C) both in polyether and polyester poly(urethaneureas). The presence of the amorphous domain is observed not only in high-urea-content compositions, but also in low-urea-content compositions, for example, at 30% urea content, as supported by thermal transition studies and small-angle X-ray-scattering studies. The extent of phase segregation, as judged by the extent of solubilized hard segment in the soft segment phase, is also improved greatly in poly(urethaneureas) as compared with poly(urethanes). Thus, in general, a much lower T_g of the rubbery soft segment phase is observed in poly(urethaneureas). Polyether poly(urethaneureas) are even better than polyester poly(urethaneureas) in this respect; thus, polyether polymers offer better low-temperature flexibility than polyester polymers. Increasing the molecular weight of the soft segment from 1000 to 2000 improves phase segregation, both in the polyether and the polyester series. Both in polyether and polyester poly(urethaneureas), the thermal transition behavior is rather insensitive to the total urea content, both in the T_g of the soft segment phase and in the T_g of the hard segment domain, while a strong dependence was usually observed in poly(urethanes) extended with butanediol.

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