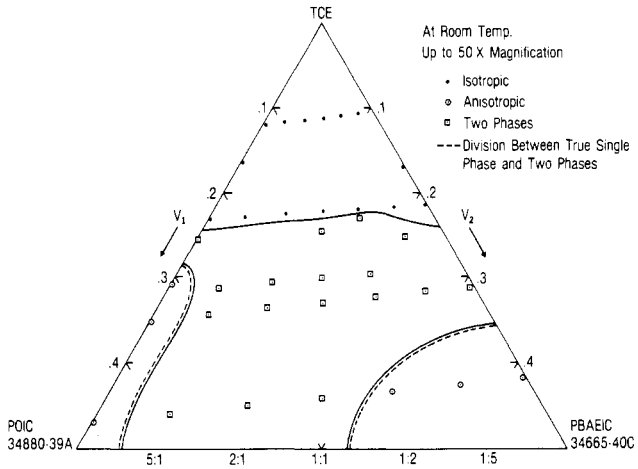

Figure 3. Ternary phase diagram of poly(octyl isocyanate)/poly(50% butyl + 50% *p*-anisole-2-ethyl isocyanate)/TCE. Same conditions and same legend as in Figure 1.

remove the isotropic inclusions completely.

The anisotropic single phase in Figure 3, containing substantial amounts of both poly(isocyanates), appears under high magnification as a truly single phase. Furthermore, the corresponding samples produced NMR spectra indicating them to belong to a single anisotropic phase on the molecular scale level. A detailed discussion of the NMR spectra of poly(isocyanates) in these and in additional phase diagrams is soon to be published.[11]

The existence of a single anisotropic solution containing substantial amounts of both poly(isocyanates) strongly supports, we believe, Flory's theory.[1-7]

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Shaul M. Aharoni
Allied Chemical Corporation
Morristown, New Jersey 07960

Received February 7, 1979

Hysteresis Behavior in Polyether Poly(urethaneureas) Based on 2,4-Toluene Diisocyanate, Ethylenediamine, and Poly(tetramethylene oxide)

Thermoplastic poly(urethanes) and poly(urethaneureas) are linear segmented copolymers which consist of alternating hard (aromatic urethane or urea) and soft (aliphatic polyether or polyester) segment units. The properties of these materials depend largely on the extent of microphase segregation of soft and hard segments which arises from their thermodynamic incompatibility. Compositional variables such as the symmetry in the diisocyanate structure,[1] the chain extender,[2] the molecular weight, and the molecular weight distribution[3] of the soft and the hard segments are known to have a strong influence on the extent of phase segregation, the domain organization, and thus the polymer properties.

Table I
Characterization of Polyether Poly(urethaneureas) Based on 2,4-TDI, Ethylenediamine, and Poly(tetramethylene oxide)

sample	$M_n \times 10^{-3}$	*e*	T_g,[b] °C	T_g,[d] °C
2,4-TDI-ED-PTMO 1000				
2:1:1[c]	21	29	−53	192
3:2:1[c]	28	39	−54	190
4:3:1[c]	33	47	−58	190
5:4:1[c]	43	53	−55	180
6:5:1[c]	27	57	−61	184
2,4-TDI-ED-PTMO 2000				
3:2:1[c]	36	24	−75	180
4:3:1[c]	34	30	−74	190
5:4:1[c]	35	36	−73	186
6:5:1[c]	25	40	−78	191

[a] Hard-segment content is equivalent to total urea content. [b] T_g of the soft-segment phase. [c] No crystallinity observed in these samples. [d] T_g of the amorphous hard segment domain. [e] Hard-segment content in wt % (footnote *a*).

The presence of the hard segment domains is widely recognized as being responsible for the high tensile strength and modulus exhibited by these materials. However, the presence of the domains was also throught to be responsible for the stress softening, a serious deficiency in many applications under cyclic loading conditions due to the heat buildup.[4] Several attempts to minimize this problem have been made.[5] One successful method was to cross-link the polymer with triol.[4] This treatment disrupts the domain structure, thereby reducing hysteresis under cyclic loading. However, this also leads to a reduction in the modulus and the tensile properties. Moreover, the polymer is no longer thermoplastic. An alternate way has been reported where orientation followed by heat setting is used which presumably breaks the interconnectivity of the domain and reduces the heat buildup problem.[6]

In our continuing studies of segmented poly(urethanes) and poly(urethaneureas) toward establishing structure–property relationships, we have recently reported that the incorporation of the urea linkage via ethylenediamine (ED) as a chain extender leads to a drastic improvement in microphase segregation and domain structure, even with asymmetric diisocyanate such as 2,4-toluene diisocyanate (2,4-TDI).[2,7,8] For example, in polyether poly(urethaneureas) consisting of 2,4-TDI, ED, and PTMO (poly(tetramethylene oxide), mol. wt. 1000 or 2000), the phase segregation and domain structure were greatly improved as compared with diol extended analogues.[2] This was evidenced by the lower T_g of the soft-segment phase and the higher T_g of the amorphous hard-segment domain. The presence of the amorphous domain was also supported by small-angle X-ray scattering studies.[2] Between the PTMO 1000 and the PTMO 2000 series, polymers containing 2000 molecular weight polyether exhibited better phase segregation, as illustrated in Table I. The T_g of the soft-segment phase for 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 indicates that the amount of the solubilized hard segment in the soft segment phase in the PTMO 2000 series is very small if any, because tying down both ends of the soft segment would likely contribute to

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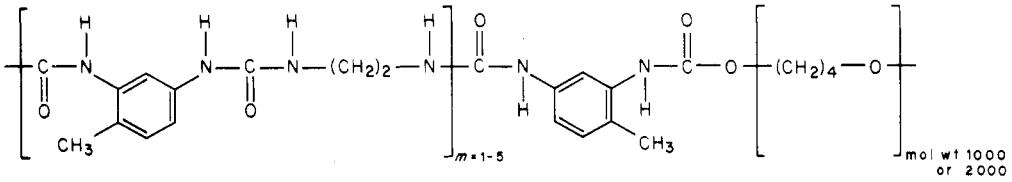
Scheme I



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

Table II
Mechanical Properties of Polyether Poly(urethaneureas) at Room Temperature

sample	modulus, kg/cm²	tensile strength, kg/cm²	elong. at break, %
2,4-TDI-ED-PTMO 1000			
2:1:1	2000	400	500
5:4:1	4000	600	400
2,4-TDI-ED-PTMO 2000			
4:3:1	200	250	1100

a few degrees raise in the T_g. On the other hand, the amount of the solubilized hard segment in the PTMO 1000 series should be considerable since the T_g is raised by 25 °C. Both in the PTMO 1000 and 2000 series, the T_g of the soft segment was relatively independent of the increasing urea content.

It is to be noted for Table I that the very high T_g of the amorphous hard segment domain is observed in the temperature range of 180–190 °C, regardless of the length of the hard segment or the soft segment. We conclude from this behavior that the domain is probably well organized, containing small amounts of solubilized soft segment.

In the process of studying mechanical properties of these materials, we have recently observed that the hysteresis properties are very sensitive to the degree of phase mixing and probably the domain morphology. In fact, moderately low hysteresis can be observed in the polymers containing PTMO 2000 as the soft segment. We wish to report this observation in this communication.

Experimental Section. Two series of the polyether poly(urethaneureas) were synthesized as described earlier.[2] The chemical structure of the polymer is shown in Scheme I. Table I summarizes the characteristics of the polymers. In the sample designation, the numbers represent the molar ratios of 2,4-TDI, ED, and PTMO in sequence. Tensile hysteresis measurements were made by using an Instron (Model 1122) by loading and unloading the strip specimens at constant cross-head speed to an increasing strain level at each cycle.[8] The initial strain rate was 1.2%/s and the strain levels were varied from 25% to 1050%. The percent hysteresis for a given cycle is calculated by the ratio of the area bounded by the loading–unloading curves to the total area under the loading curve. The area was calculated using a planimeter.

Results and Discussion. Before we discuss the hysteresis behavior, it would be useful to comment on other mechanical properties of these polyether poly(urethaneureas). As summarized in Table II, modulus, tensile strength, and elongation at break depend strongly on the composition of the polymer. Within the PTMO 1000 series, the modulus and the tensile strength were quite high and they increase with increasing hard-segment content, while the elongation at break decreases slightly. Mechanical properties of these poly(urethaneureas) are in general much better than those of unfilled vulcanized rubber. For example, the tensile strength is at least one order of magnitude greater than that of unfilled vulcanized rubber. Moreover, the general shape of the stress–strain curve of the PTMO 1000 samples deviates from those of unfilled vulcanized rubber. In the PTMO 2000 series, the modulus and tensile strength are somewhat lower than the PTMO 1000 series, but elongation at break is much greater than the analogous PTMO 1000 series. The deviation in the shape of the stress–strain curve from the behavior of unfilled vulcanized rubber in the PTMO 2000 series is much less than that for the PTMO 1000 series. In a recent work of Séquéla and Prud'homme[9] with SIS and SBS block copolymers, they have shown that the specimens with spherical microdomains, which are discrete and well isolated, exhibit the mechanical behavior close to unfilled vulcanized rubber, while the specimens with connected domain morphology deviated from rubber-like behavior. Borrowing from their analogy, we conclude that in the PTMO 2000 series, the domains are less interconnected than those in the PTMO 1000 series.

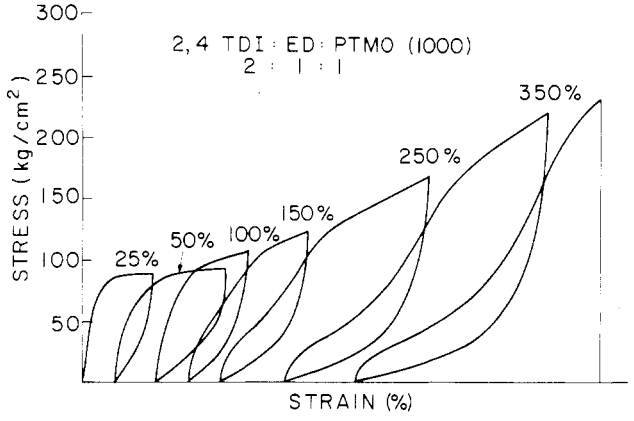


Figure 1. Stress–strain curves for successively increasing cyclic deformation of a 2:1:1 composition sample polyether poly(urethaneurea) elastomer based on 2,4-TDI–ED–PTMO 1000 (for the first two elongations of 25 and 50%, the chart speed was 2.5 times faster than the rest of the experiment in order to insure accuracy in planimeter measurement).

With this background information stated, we will now discuss the hysteresis behavior observed in these samples. Figure 1 illustrates the hysteresis behavior for a sample of the 2:1:1 (2,4-TDI–ED–PTMO 1000) composition. It is clear that the extent of the permanent set is increased at a greater strain level, and a large amount of hysteresis is observed. For a sample of 5:4:1 (2,4-TDI–ED–PTMO 1000) composition, which contains about twice the hard segment content when compared to the 2:1:1 composition, a similar hysteresis behavior is observed. In fact, the percent hysteresis as a function of strain for these two samples is almost identical as illustrated in Figure 2. The hysteresis value quickly reaches about 70% and stays constant between 75 and 80%, even with a further increase in the elongation.

On the other hand, with the poly(urethaneureas) con-

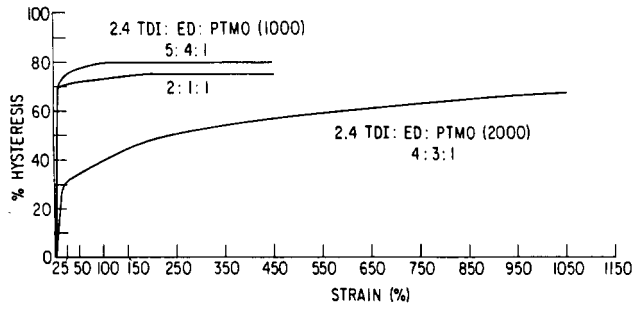


Figure 2. Percent hysteresis as a function of strain in polyether poly(urethaneurea) elastomers.

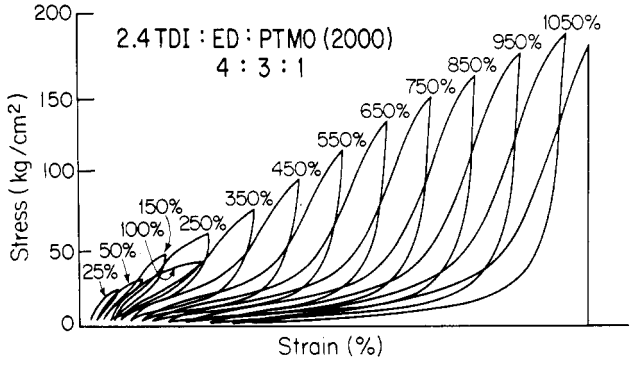


Figure 3. Stress–strain curves for successively increasing cyclic deformation of a 4:3:1 composition sample polyether poly(urethaneurea) elastomer based on 2,4-TDI–ED–PTMO 2000 (for the first three elongations of 25, 50, and 100%, the chart speed was 2.5 times faster than the rest of the experiment in order to insure accuracy in planimeter measurement).

taining 2,4-TDI, ED, and 2000 molecular weight PTMO polyether, the hysteresis behavior is clearly different from that of two members of the PTMO 1000 series. As illustrated in Figure 3, the permanent set for the PTMO 2000 sample is much less when compared with the PTMO 1000 series. Also, in spite of the same overall urea content, the 4:3:1 sample of the PTMO 2000 series exhibits a much lower hysteresis than the 2:1:1 sample of the PTMO 1000 series, as illustrated in Figure 2. In the PTMO 2000 series the initial hysteresis value is around 30% and increases slowly with a further elongation up to 65–70% at a 1050% elongation. It is interesting to note that the hysteresis behavior is independent of the total urea content within the range of 29 to 54% (as indicated by the total weight of diisocyanate and ethylenediamine) in the PTMO 1000 series, while the tensile properties are considerably different. This suggests that the interconnection of the hard segments may not necessarily increase with greater urea content in the PTMO 1000 series. In contrast, Cooper et al. found[10,11] that the orientation and hysteresis were very sensitive to the overall diisocyanate content in polyether poly(urethanes) based on MDI, butanediol, and PTMO 1000. They interpreted this behavior as a change from an independent hard segment domain at low urethane content to the interconnected hard segment at higher urethane content. With the PTMO 2000 polymer, which has virtually no solubilized hard segment in the soft segment phase, and which is likely to have the domains less connected than the PTMO 1000 polymer, the hysteresis is lower. This behavior seems to be consistent with the phenomena observed with SIS and SBS systems, since Séquéla and Prud'homme report in their extensive studies that the specimens with isolated spherical domain show little stress softening while specimens with interconnected spherical domain or cylindrical structure showed stress softening on repeated extensions.[9]

We believe that the further support for the different degree of interconnectivity of domains in these PTMO series could come from a quantitative investigation of small-angle X-ray scattering, which is in progress,[12] along with the stress relaxation experiment and the scanning transmission electron microscopic work.

Acknowledgment. The generous support of the Whitaker Health Sciences Fund is greatly appreciated. The authors thank Professor G. W. Wilks and S. L. Cooper for pointing out orientation and heat setting as a way of reducing hysteresis and other helpful comments. T.W.S. also acknowledges the support of the Undergraduate Research Opportunities Program Office at M.I.T. We would also extend our gratitude to Professor C. K. Rha of M.I.T. for the use of Instron and much encouragement during the course of this work.

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(12) In collaboration with Professor G. W. Wilks.

C. S. Paik Sung,* T. W. Smith, C. B. Hu, and Nak-Ho Sung

Department of Materials Science and Engineering
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
Department of Chemical Engineering
Tufts University
Medford, Massachusetts 02155

Received August 11, 1978