

A New Criterion of Phase Separation: The Effect of Diamine Chain Extenders on the Properties of Polyurethaneureas

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Synopsis

A new criterion of phase separation of segmented polyurethaneureas is found by comparing the relative crystallinity of the soft segment of polyurethaneurea. This criterion is more sensitive than the conventional thermal transition temperature measurements. The difference of crystallinity can be distinguished even if the thermal transition temperatures are the same. The polymers are synthesized by coupling a prepolymer consisting of poly(tetramethylene oxide) (PTMO) and 4,4'-diphenylmethane diisocyanate (MDI) with different chain extenders, ethylenediamine (ED), 1,6-hexanediamine (HD), and 4,4'-methylenedianiline (MDA). The degree of phase separation is found to relate to the structure of the chain extender and the hard-segment content as indicated by the relative crystallinity and initial modulus. Several explanations are proposed to discuss the relationship between these factors.

INTRODUCTION

The segmented polyurethaneurea is a molecule which is constructed from an alternating sequence of two chemically different "hard" and "soft" segments. The hard segments are often composed of an aromatic diisocyanate reacted with a diamine chain extender, while the soft segments are a low-molecular-weight hydroxy-terminated polyether or polyester. Due to the incompatibility of the hard and soft segment, phase separation occurs. However, the degree of phase separation depends on many compositional variables such as type and molecular weight of the soft segment, type of isocyanate and chain extender, and the hard segment content.

A variety of characterization methods have been used to study the phenomenon of phase separation¹⁻⁶ in both polyurethanes and polyurethaneureas including modulus-temperature measurements, transmission infrared analysis, infrared dichroism, birefringence, thermal transition temperature measurements, small angle X-ray scattering, wide angle X-ray diffraction, and mechanical hysteresis behavior. Among these methods, the behavior of the thermal transition temperatures is one of the more conveniently applied criteria to study the degree of phase separation. Interaction between soft and hard segments can increase the glass transition temperature (T_g) of the soft segment and decrease the T_g of the hard segment. The degree of phase mixing is indicated by this shift of transition temperatures toward intermediate values.

In our previous studies, we reported the results of polyurethaneureas based on 2,4-tolylene diisocyanate (2,4-TDI) chain extended with ethylenediamine.²

The effects of different soft segment type (polyether and polyester) and molecular weight (1000 and 2000) and the effect of hard-segment content on the degree of phase separation were studied. It was found from thermal and X-ray analysis that, in 2,4-TDI based polyurethaneureas, phase separation was much better for polyether than for corresponding polyester polyurethaneureas. Extensive phase separation was observed both for the polyether polyurethaneureas with soft segment of molecular weight 1000 and 2000 (PTMO-1000 and PTMO-2000). Comparing the effect of molecular weight of the soft segment on the degree of phase separation, it was found that the higher the molecular weight of the soft segment, the better the phase separation. The degree of phase separation of polyurethaneureas was also found to be independent of hard-segment content based on the invariance of the transition temperatures. A criterion of "hydrogen bonding index" derived from transmission infrared analysis also indicated that the degree of phase separation was independent of the hard segment content.⁷ The phenomenon is different from polyurethanes extended with butanediol where the degree of phase separation varies significantly with hard-segment content. In general, the phase separation is poorer for the diol-type chain extender than the diamine-type.²

However, several of the compositional variables of polyurethaneureas have not been studied. These include the effect of the diamine chain extender on the degree of phase separation of polyurethaneureas and their mechanical properties. Also unknown is the effect of a higher-molecular-weight soft segment (for example, 2900) and different diisocyanate on the properties of polyurethaneureas. Therefore, a systematic study of these variables in relation to the thermal and mechanical properties of polyurethaneureas should improve the understanding of these materials and assist in their "design."

The majority of polyurethaneureas in this study were synthesized with 4,4'-diphenylmethane diisocyanate (MDI) and different chain extenders (ethylenediamine, 1,6-hexanediamine, 4,4'-methylenedianiline) and polyether soft segments of various molecular weights (1000, 2000, 2900). The hard segment concentration was also varied from 16% to 30% by weight to study the effect of this variable.

EXPERIMENTAL

Materials

4,4'-Diphenylmethane diisocyanate (MDI) was kindly supplied by the Upjohn Co. Teracol® polyether glycols (PTMO 1000, 2000, 2900) were kindly provided by E. I. duPont de Nemours and Co. Analyzed reagent grade ethylenediamine (ED) was purchased from J. T. Baker Chemical Co., reagent grade 4,4'-methylenedianiline (MDA) and 1,6-hexanediamine (HD) were purchased from Eastman Kodak Co., 2,4-TDI, and spectrophotometric-grade *N,N*-dimethylacetamide (DMAC) were obtained from Aldrich Chemical Co. All materials were used as received.

Polymer Synthesis

The preparation of the various polyether polyurethaneureas was carried out by solution polymerization in DMAC. Samples were prepared by a standard two-step reaction. The glass resin kettle, equipped with mechanical stirrer, thermometer, condenser, drying tube, and inert gas inlet, is purged by nitrogen for 1 h. Then the solution of polyether soft segment in DMAC is added and purged for an additional 0.5 h at 80–90°C. The MDI is added slowly and the reaction mixture is stirred at 80–90°C for 3 h. The prepolymer solution is then cooled to room temperature, and a dilute solution of chain extender is added slowly with good stirring. The reaction mixture becomes viscous, and stirring is continued at room temperature for another hour. Because of the low reactivity of MDA chain extender, the reaction temperature is kept at 60°C for polyurethaneurea with MDA chain extender.

Polymer Characterization

1. *Thermal analysis:* Differential scanning calorimetry is carried out using a Perkin-Elmer DSC-II, equipped with a scanning auto zero accessory. The heating rate is 20°C/min. The sensitivity is 5 mcal/s. For the low temperature range from 150°K to 320°K, helium is used as a purge gas. Nitrogen is used for the ambient temperature range. Samples are cut directly from vacuum-dried, solvent-cast films to a weight of 10–20 mg. The glass transition temperature is determined by the change in heat capacity of one-half of its maximum value as suggested by the Perkin-Elmer Corp. The crystallinity of the soft segment of each sample is determined by measuring the area under the melting peak with planimeter and dividing by the weight of the sample. The relative crystallinity is the ratio of crystallinity of each sample to that of pure soft segment.

2. *Modulus measurement:* The modulus is determined by a Perkin-Elmer Thermomechanical Analyzer TMS-2. The sample preparation is very important in obtaining reproducible modulus values. Parallel sample edges are obtained using two safety razor blades clamped together for cutting. Samples are crimped firmly into the securing pins, taking care that the pins are perpendicular to the sample. The size of the sample is 0.3 in. × 0.1 in. The thickness of the sample is approximately 0.010 in. and is measured with a spring micrometer to the nearest 0.0001 in. The weight on the loading platform is adjusted to give near-zero loading weight. By adding several consecutive small weights from 2 g to 25 g and observing the extension in the region for which the stress-strain behavior of the polymer is nearly elastic, the modulus of the sample can be determined. In general, the modulus obtained here is an initial modulus because the strain level in this experiment is only a few percent.

3. *Gel permeation chromatography:* The molecular weight determinations is done with μ -Styragel columns using a Waters Associate Model 244 GPC. The polymer solution is first quenched in distilled water and dried in vacuum oven for 2 days at 50–60°C. The solid polymer is then dissolved in dimethylformamide (DMF) which contains 0.05M LiBr to make a 0.25% solution. The function of LiBr is to prevent the aggregation of polymers by increasing polymer/solvent interaction. The column set is calibrated with monodisperse polystyrene standards from Pressure Chemical. It should be pointed out that the molecular weight of polyurethaneureas determined here are reported in terms of the

polystyrene calibration. Absolute molecular weights are not determined because of the lack of suitable standards.

RESULTS

Thermal Transition Behavior

Table I shows the results obtained from GPC and DSC. The composition of samples is expressed as follows: The first number is the number average molecular weight of the soft segment, followed by the type of diisocyanate(s) and the chain extender. The last number is the weight percentage of hard segment content. The data indicate that all the polyurethaneureas are relatively high molecular weight, using polystyrene as a calibration standard. The molecular weight distribution of these samples is relatively narrow and very similar for most samples. It is therefore assumed that properties of these samples are determined by composition/morphology rather than the effect of molecular weight or its distribution. The molecular weight of 2000-MDI—ED-30 could not be determined because this sample was not completely soluble in DMF.

The typical DSC scans for these samples which appear in Figure 1 illustrate the difference in thermal transition behavior with changes in the soft-segment molecular weight. The glass transition temperatures of pure segment for different molecular weights 1000, 2000, and 2900 are in the range from -76°C to -80°C and is almost independent of the molecular weight of soft segment.⁸ However, the soft-segment glass-transition temperature of polyurethaneurea is sensitive to soft-segment molecular weight but insensitive to the nature of the chain extender and the hard-segment content, as shown in Table I. In the samples prepared with PTMO-2900, the T_g is around -74°C , which is very close to the T_g of -80°C for the free PTMO soft segment. The T_g changes only slightly, to -72°C , for the set of PTMO-2000 samples but increases to about -55°C in the samples with PTMO-1000. Because of the similar T_g of all the

TABLE I
Molecular Weight and Thermal Transition Temperatures of Polyurethaneureas

Sample	$M_w \times 10^{-4}$	$M_n \times 10^{-4}$	M_w/M_n	T_{g1}^b ($^{\circ}\text{C}$)	T_m^c ($^{\circ}\text{C}$)	T_{g2}^d ($^{\circ}\text{C}$)
2900-MDI-ED-16	8.0	5.9	1.35	-73	20	193
2900-MDI-ED-23	6.5	5.0	1.32	-75	17	195
2900-MDI-MDA-19	6.8	5.5	1.25	-74	21	—
2900-MDI-HD-18	10.8	8.0	1.36	-73	20	195
2900-MDI-HD-25	7.7	5.7	1.36	-75	20	193
2000-MDI-ED-22	24.8	13.8	1.80	-72	13	199
2000-MDI-ED-30 ^a	—	—	—	-72	12	203
2000-MDI-MDA-26	9.3	8.1	1.16	-69	19	—
2000-MDI-HD-24	22.6	16.6	1.35	-72	11	204
2000-TDI-ED-29	20.5	12.8	1.60	-72	8	190
1000-MDI-ED-23	34.0	20.8	1.64	-52	No	188
1000-MDI-ED-36	12.7	10.3	1.23	-56	No	189

^a This sample is not completely dissolved in DMF.

^b T_g of the soft segment phase.

^c T_m of the crystalline soft segment.

^d T_g of the hard segment domain.

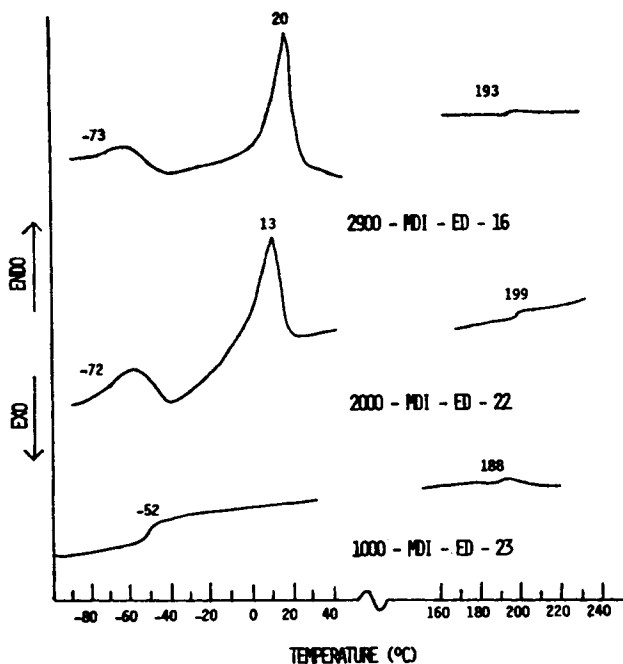


Fig. 1. DSC scan of polyurethaneureas with different molecular weight of the soft segment.

free PTMO soft-segments here, therefore, T_g is used as a measure of phase mixing of hard-segment units with soft-segment continuous phase; it is clear from these results that the degree of phase mixing is very low and almost the same for the PTMO-2000 and PTMO-2900 series but is much greater in PTMO-1000 samples.

The soft segment melting endotherm exhibits substantial changes in the samples of different soft segment molecular weight. The melting peak, which occurs at 30°C in pure PTMO, appears at 20°C in the PTMO-2900 series. It is shifted to significantly lower temperatures (about 12°C) in all but one of the PTMO-2000 series and is absent in the PTMO-1000 samples. There are also smaller changes in the magnitude of the endotherm within a series of samples of a given soft-segment molecular weight which will be considered in more detail later in this section.

The thermal transition temperature of the hard segment is not as easily observed as that of the soft segment phase. As shown in Figure 1, hard-segment glass-transition temperatures occur between 190°C and 200°C. It is very surprising that no high temperature transition is observed for polyurethaneureas with MDA as a chain extender. Because of the similar structure of diisocyanate and diamine, better hard-segment domain structure and a higher thermal transition temperature is expected in this case. It appears that these samples start decomposing before the hard-segment transition is detected. The attempt to obtain a crystallinity pattern from wide angle X-ray diffractometer is not successful. There is no crystallinity pattern observed for these samples. However, neither of these phenomena can be taken as absolute evidence that there is no hard segment crystallinity in these samples. Because these samples may start to decompose before the melting temperature is detected as indicated

by the irregular thermal pattern of DSC scan above 230°C, and the lack of WAXD peaks may be due to the small hard-segment contents of these samples.

Soft Segment Crystallinity

Because of the close transition temperatures, the degree of phase separation of polyurethaneureas with the same diamine type but different chain extenders is very difficult to distinguish by the shift of T_g . However, the relative crystallinity of the soft segment of polyurethaneureas can provide useful information about the degree of phase separation even in these cases. The basis for this assertion is that crystallization will be impeded in hydrogen bonding interactions between the soft-segment ether oxygen and the urethane or urea NH of phase-mixed hard-segment units. The relative crystallinity of the polyurethaneurea is determined by comparing the area under the melting peak of the DSC scan, normalized to unit weight of the soft segment, with that of pure soft segment. The results are summarized in Table II. Recall that samples with PTMO-1000 do not show any soft-segment crystallinity and, therefore, do not appear here. Also recorded in Table II are results which show that the crystallinity of the pure soft segment is slightly dependent on its molecular weight, being somewhat greater in pure PTMO-2900 than pure PTMO-2000.

First let us consider the data of a series of polyurethaneureas with a soft segment of molecular weight 2900, but with different chain extenders and hard-segment contents. It is found that relative crystallinity of soft segment is sensitive to both factors. For the same type of chain extender such as ethylenediamine or 1,6-hexanediamine, increasing the hard-segment content in the polyurethaneureas will decrease the crystallinity of the soft segment. For example, as the hard-segment content is increased from 16% to 23%, the relative crystallinity of the two 2900-MDI—ED samples has decreased from 52% to 37%. For the two 2900-MDI—HD samples, the relative crystallinity has decreased from 43% to 34% when the hard-segment content is increased from 18% to 25%.

TABLE II
Relative Crystallinity and Initial Modulus of Polyurethaneureas with Different Chain Extenders and Hard-Segment Contents

Sample	Area/mg	Relative crystallinity (%)	Initial modulus (psi)
PTMO(2900)	8.00	100	—
2900-MDI-ED-16	4.15	52	675
2900-MDI-ED-23	2.96	37	1661
2900-MDI-MDA-19	4.50	56	660
2900-MDI-HD-18	3.45	43	1173
2900-MDI-HD-25	2.72	34	2429
PMTO(2000)	7.81	100	—
2000-MDI-ED-22	2.72	35	1495
2000-MDI-ED-30	1.90	24	2939
2000-MDI-MDA-26	2.86	37	529
2000-MDI-HD-24	2.01	26	1621
2000-TDI-ED-29	0.23	3	6000

Within the same range of hard segment content (16–19%), the relative crystallinity varies with different chain extenders. It is highest (56%) for the polyurethaneurea with 4,4'-methylenedianiline as a chain extender and lowest (43%) for the polyurethaneurea with 1,6-hexanediamine as a chain extender. Similar trends are observed for the polyurethaneureas with a soft segment of molecular weight 2000. The relative crystallinity in this series is highest (37%) for the polyurethaneurea with 4,4'-methylenedianiline and lowest (26%) for 1,6-hexanediamine.

The reproducibility of the phenomena for both series (PTMO-2000, -2900), supports the conclusion that the structure of the chain extender has a systematic effect on the relative crystallinity of the soft segment of polyurethaneurea. This might be explained on the basis that an aliphatic chain extender such as 1,6-hexanediamine, which has a molecular structure more similar to that of the soft segment, will promote phase mixing. An aromatic chain extender, such as 4,4'-methylenedianiline, which has a structure significantly different from that of the soft segment, would be less compatible with the soft-segment phase. It should be noted that the results also suggest that the degree of phase mixing of polyurethaneureas can differ for different chain extenders even if the same soft- or hard-segment transition temperatures are observed. Therefore, the relative crystallinity proves to be a more sensitive criterion for distinguishing the degree of phase separation than the thermal transition temperature measurements in these highly segregated material.

Modulus Behavior

Figure 2(a) is a typical example of the initial tensile modulus measurement of polyurethaneurea by TMA, and Figure 2(b) is a corresponding plot of the stress-strain curve derived from the experimental data. As shown in Figure 2(b), the stress-strain behavior of the polymer is almost linear in this strain level; therefore, an initial modulus can be obtained accurately. It is clear from the data of Table II that the initial modulus of polyurethaneureas increased as expected with increasing hard-segment content if the molecular weight of the soft segment and the nature of the chain extender are the same. The extent to which the changes in the initial tensile modulus can be correlated directly with the increase in hard-segment content, without regard to the nature of the diamine, is indicated in Figure 3. The data for the PTMO-2900 series show a distinct linear correlation with the hard-segment content. For the PTMO-2000 series there is a similar trend toward increasing modulus values with increasing hard-segment content, but the correlation is much poorer. Actually, in both the PTMO-2900 and PTMO-2000 series there are examples of large changes in modulus for samples of approximately the same hard-segment content but with different diamine extenders. This suggests that varying the nature of the diamine produces some change in structure which has a significant effect on certain physical properties. Since it has already been shown that there is a change in relative soft-segment crystallinity with the choice of diamine, some correlation might be expected between crystallinity and modulus. In fact, the data of Table II show that, at least qualitatively, there is an inverse relation between relative crystallinity and modulus. Within a series of a given soft-segment molecular weight, samples with smaller relative crystallinity invariably have the higher initial modulus.

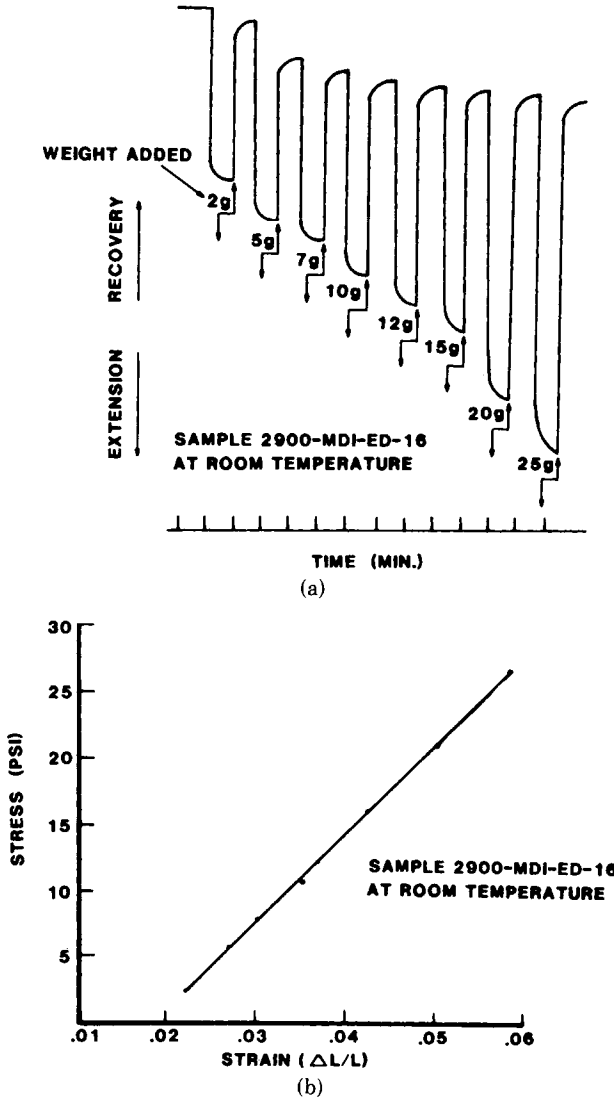


Fig. 2. (a) Experimental measurement of the initial tensile modulus of polyurethaneureas. (b) Corresponding plot of the stress-strain curve from the experimental data.

A plot of modulus data against relative crystallinity is presented in Figure 4. The correlation for PTMO-2900 samples is comparable to a plot of modulus against hard segment content, while, for PTMO-2000 samples, the correlation is much improved and accommodates all samples. The extreme example is represented by 2000-TDI—ED-29. The T_g of this sample is -72°C with a small melting peak near 8°C . Both transition temperatures are close to polyurethaneureas based on MDI. However, the relative crystallinity is only 3%, much smaller than the value in comparable MDI-based polyurethaneureas, indicating that phase mixing is greater in polyurethaneureas from 2,4-TDI than from MDI. The initial modulus (6000 psi) is the highest value for any sample in Table II, but is still in good agreement with the relative crystallinity, as indicated in Figure 4.

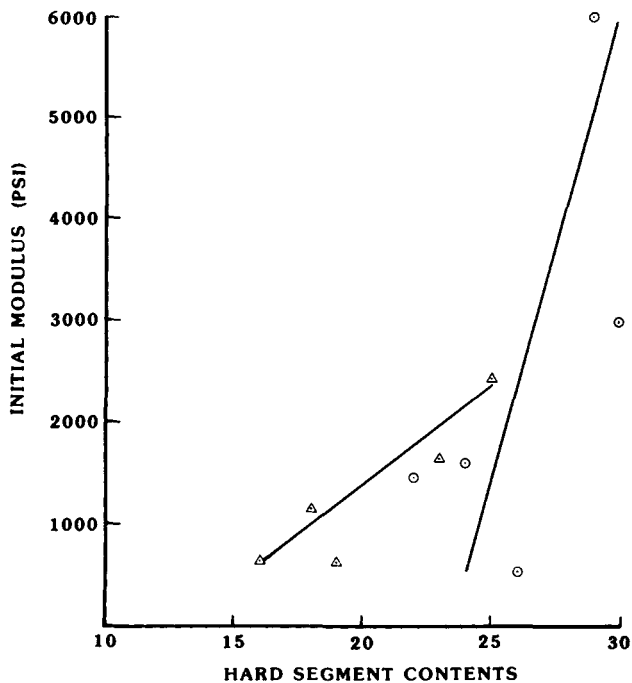


Fig. 3. Initial modulus vs. hard-segment content of polyurethaneureas. (○) PTMO-2000 series, (△) PTMO-2900 series.

DISCUSSION AND CONCLUSION

This study has confirmed that these polyurethaneureas investigated are highly phase-separated materials, especially for the PTMO-2000 and PTMO-2900 series, judging by the soft-segment T_g . Nonetheless, varying the diamine chain extender causes systematic changes in the relative soft-segment crystallinity. These changes can be rationalized as due to small variations in phase mixing,

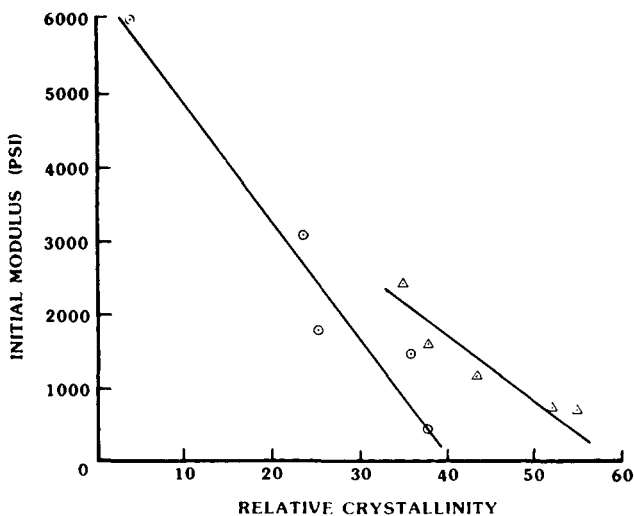


Fig. 4. Initial modulus vs. relative crystallinity of polyurethaneureas. (○) PTMO-2000 series, (△) PTMO-2900 series.

which suggests that the use of relative soft-segment crystallinity is a more sensitive criterion of phase mixing than the soft-segment T_g in such highly phase-separated materials. In addition, there are large accompanying changes in the initial modulus of the samples with differences in hard-segment content and choice of diamine chain extender. Within a series of a given PTMO molecular weight there is some evidence of a correlation between modulus and hard-segment content almost independent of the nature of the diamine. The correlation is stronger in the PTMO-2900 series but less satisfying in the PTMO-2000 series. On the other hand, the initial modulus correlates equally well with relative percent crystallinity in both PTMO series, including samples with different diamines at approximately the same hard-segment content which show substantial differences in modulus. This is not to say that the relative crystallinity is itself the controlling factor, but rather that the changes in composition which result in a decrease in relative crystallinity also produce an increase in modulus. The problem is to provide a structural model capable of accounting for the correlated changes in these two quantities.

It is possible that the variations in relative soft segment crystallinity and attendant initial modulus changes are due to changes in morphology with diamine type. In related studies of polyurethaneureas chain-extended with TDI and ED,^{2,3} marked differences in the stress-strain curve were observed for samples based on PTMO-1000 compared to PTMO-2000. The latter samples had initial modulus values only 1/10 that of the PTMO-1000 samples of equivalent hard-segment weight content. The difference in initial modulus and other mechanical properties was attributed to the fact that the PTMO-1000 samples contained interconnected domain structure whereas in the PTMO-2000 samples the domain structure was discrete.^{2,3,5} No such gross alteration in morphology is expected to result from the change in diamine in the present set of samples. Since the T_g values of samples in Table II are nearly the same as those reported by Sung and Hu for their PTMO-2000 samples, the morphology of the present samples must correspond to that of discrete domain structure. This is reinforced by the modulus values which are more nearly in accord with that reported by Sung and Hu for their PTMO-2000 samples.³ Nonetheless, it is possible to conceive of small changes in the discrete morphology, involving the shape factor for the dispersed domains, which could influence the modulus results. The effect of the asymmetry of filler particles on the modulus of the matrix phase has been described as equivalent to the effect of particle asymmetry on solution viscosity.⁹ Changes in discrete particles shape factors would be expected to influence the initial modulus but would have little effect on the matrix T_g , consistent with the present experimental results. However, such a model does not seem to provide an explanation of the variations in soft-segment crystallinity with diamine choice.

The concept of phase mixing which has been emphasized in the earlier discussion of results appears to be capable of explaining the correlation between the reduction in crystallinity and corresponding modulus increase, at least on a qualitative basis. Quantitative infrared analysis¹⁰ has not only provided direct evidence for phase mixing but has shown that mixed hard-segment units are hydrogen-bonded to the ether group of the PTMO soft segment. It has also been suggested that these hydrogen-bonding interactions in polyurethaneureas contribute to the increase in the soft-segment glass-transition temperature re-

sulting from phase mixing. The presence of specific interactions of this type between hard- and soft-segment units would also be expected to interfere with the ability of the soft segment to crystallize as assumed earlier. Thus, in principle, the hydrogen-bonding interactions could provide the basis for an inverse correlation between modulus and percent soft-segment crystallinity. Moreover, urea segments, if mixed with the soft-segment phase, should result in more effective hydrogen-bonding interactions than the urethane hard segment, due to the two NH groups carried by each urea hard-segment unit.

It is not suggested that the model be pressed too far. The main purpose of the discussion is to emphasize the complexity of the structure-property relations which arise in the polyurethaneureas and to call attention to the need to consider the possibility of subtle morphological changes as well as phase mixing and specific intersegmental interactions in arriving at an explanation of changes in transition temperature, crystallinity, and modulus behavior.

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