

Thermoplastic Urethane Elastomers. II. Effects of Variations in Hard-Segment Concentration

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Synopsis

The dynamic mechanical properties of thermoplastic urethane elastomers have been characterized for polymers composed of varying hard-segment concentrations and for two different molecular weight polyester diols as soft segments. The urethane polymers based on an 830 \bar{M}_n polycaprolactone diol exhibited a progressive increase in glass transition temperature at increased levels of hard segments. In contrast, a similar series of polymers prepared with a 2100 \bar{M}_n polycaprolactone diol as the soft segment maintained a relatively constant glass transition temperature. These differences are attributed to the relative degree of phase separation between the constitutive blocks of the copolymer. The polymers of both series possessed two lower-temperature, secondary relaxations, which are ascribed to methylene sequence mobility within the polycaprolactone units and to possible disruption of interfacial associations between the hard- and soft-segment structures.

INTRODUCTION

Thermoplastic urethane elastomers are block copolymers composed of relatively immobile regions containing short polyurethane sequences connected to long and flexible polyether or polyester chains. The soft segments provide the flexible character of the polymer, while the degree of molecular association within the hard segments results in pseudocrosslinks that provide restraining forces which result in elastomeric properties of the polyurethanes. These polymers possess considerable hydrogen bonding capabilities for both intra- and intersegment interaction, and many characteristic responses have been attributed to them.¹⁻⁶ It is these interactions which give thermoplastic urethane elastomers practical modulus properties at normal service temperatures.⁷

The segmented nature of these thermoplastic urethane elastomers results in copolymers of $(AB)_n$ molecular structure, where A represents the soft segment and B corresponds to the hard segment. The structure, concentration, and organization of the hard segments have a dominant influence on the physical and mechanical properties of these urethane polymers. It has been shown that it is possible for the hard segments to undergo phase separation into regions termed domains.⁸⁻¹⁰ The extent of this microphase segregation appears to be dependent on the amount of association between the hard segment units and the relative degree of compatibility between the soft-segment chains and the hard-segment blocks.¹¹⁻¹⁵ These previous studies have shown

evidence for both crystalline and noncrystalline domains in various urethane elastomers.

The extent of compatibility between the segmented blocks of these urethane polymers is of particular interest when one considers soft segments based on polycaprolactone diols. Homopolymer polycaprolactone exhibits a unique ability to blend with a variety of both amorphous and crystalline polymers over wide composition ranges and is truly compatible with a number of different polymers.¹⁶ However, the influence of this compatibilization has not been considered in detail for segmented structures based on polycaprolactone sequences.

In this study, the dynamic mechanical properties of two series of thermoplastic urethane elastomers have been investigated. The sequence length of hard segments was varied over a wide range for polymers prepared with two different chain lengths of soft segments based on polycaprolactone diols. These properties were related to variations in the molecular structure of the urethane elastomers. The results of this investigation complement previous work which characterized the effects of variations in the sequence length of soft segments at constant hard segment concentration.¹⁷

EXPERIMENTAL

The thermoplastic urethane elastomers were prepared in a manner previously described.¹⁷ Stoichiometry was adjusted carefully so that the ratio of isocyanate to total hydroxyl was essentially equal to unity to prevent formation of primary crosslinks. The opacity of these elastomers increased at the progressively higher concentrations of hard segments.

The dynamic mechanical properties of these polymers were determined over the temperature range of -180°C to above 150°C using a recording torsional pendulum technique previously described.¹⁷ At ambient temperature, physical properties of the polymers were evaluated in accordance with standard ASTM procedures.

RESULTS AND DISCUSSION

The thermoplastic urethane polymers were prepared from polycaprolactone (PCP) diols, 4,4'-diphenylmethane diisocyanate (MDI), and 1,4-butanediol (BDO). A series of polymers was synthesized for each of two polycaprolactone diols having respective number-average molecular weights of 830 and 2100. For each series, the hard-segment concentration was changed by increasing the amount of MDI and BDO reacted relative to the polycaprolactone diol. The polymers are identified in relation to the number of moles of each intermediate contained in the polymer. For example, 1/2/1 refers to 1 mole of PCP, 2 moles of MDI, and 1 mole of BDO; while, correspondingly, 1/8/7 refers to 1 mole of PCP, 8 moles of MDI, and 7 moles of BDO. The influence of hard-segment concentration on the properties of the urethane polymers was investigated by keeping the sequence length of the soft segments constant and systematically varying the relative proportion of the MDI/BDO structures.

Polymers with 830 M_n Soft Segments

The physical properties of the urethane elastomers prepared with the 830 \bar{M}_n polycaprolactone diol as soft segment are given in Table I. As the hard-segment concentration of the polymers increases, the hardness and tear values increase and the elongation properties decrease. The magnitude of

TABLE I
Properties of Thermoplastic Urethane Elastomers Based
on 830 \bar{M}_n Polycaprolactone Diol

Mole ratio of PCP diol/MDI/BDO	1/2/1	1/3/2	1/5/4	1/8/7
Weight fraction MDI/BDO	0.42	0.52	0.66	0.76
Polymer Physical Properties				
Hardness, Shore D	40	50	70	80
100% Tensile stress, psi	800	3000	—	—
300% Tensile stress, psi	2500	—	—	—
Tensile strength, psi	6000	5000	1500	1000
Ultimate elongation, %	400	300	30	5
Die C tear, pli	—	800	1500	300
Glass Transition Temp., °C				
From G''	-10	8	24	50
From $\tan \delta$	-5	15	40	63

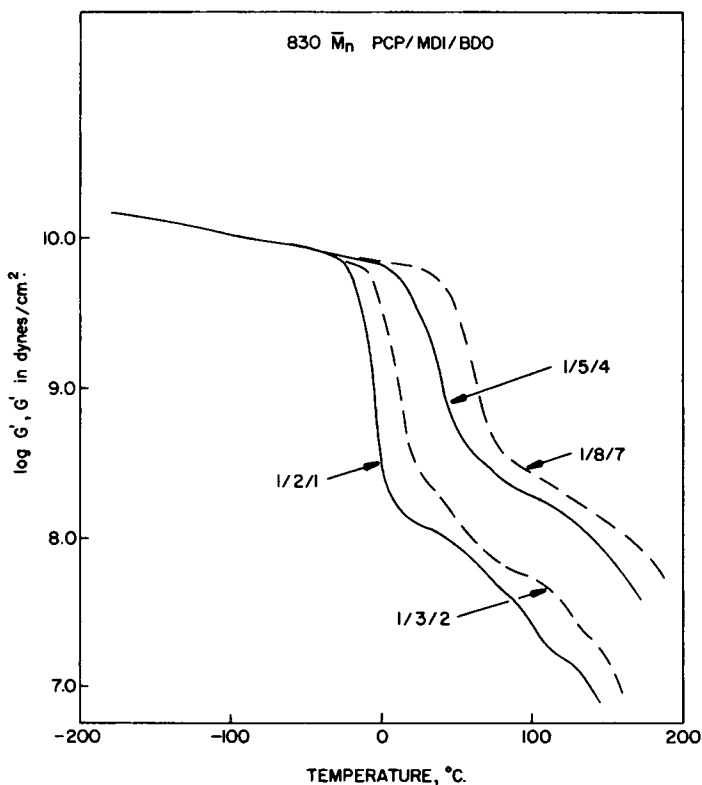


Fig. 1. Effect of hard-segment content on storage modulus properties of urethane polymers based on 830 \bar{M}_n polycaprolactone diol.

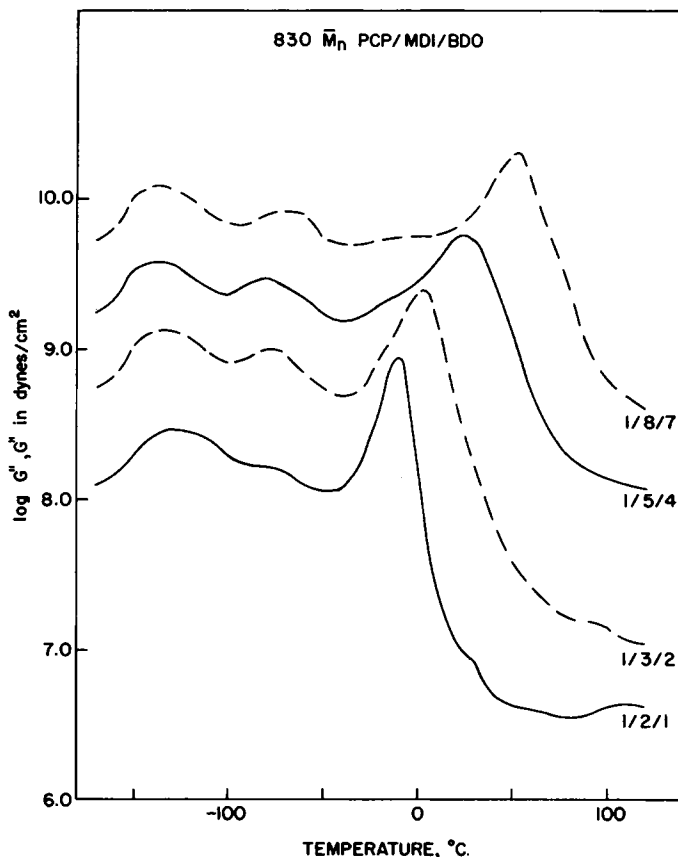


Fig. 2. Effect of hard-segment content on loss modulus properties of urethane polymers based on 830 \bar{M}_n polycaprolactone diol. For clarity, all curves except that for the 1/2/1 polymer are displaced vertically from each other.

these properties correspond to the relative position of the polymer glass transition temperature with regard to the ambient test temperature.

The temperature dependences of the dynamic storage modulus G' , shown in Figure 1 for these polymers, substantiate the relative position of the glass transition temperatures with regard to physical properties observed at ambient temperature. The increase in hard-segment concentration shifts the occurrence of the sharp modulus decrease to higher temperatures. In addition, as the concentration of hard segments is increased, the modulus in the rubbery plateau region is increased. Figure 2 compares the dynamic loss modulus G'' properties of the polymers as a function of temperature. Not only does an increased hard-segment concentration shift the glass transition to higher temperatures, but it also considerably increases the breadth over which the relaxations contributing to the glass transition occur. A secondary relaxation maximum is observed at about -130°C , which corresponds to rotational mechanisms occurring for sequential methylene units.¹⁸ This peak also has been observed with polyether soft segments in urethane elastomers.¹² At temperatures near -70°C , another secondary relaxation exists, and it becomes more prominent as the concentration of hard segments is increased.

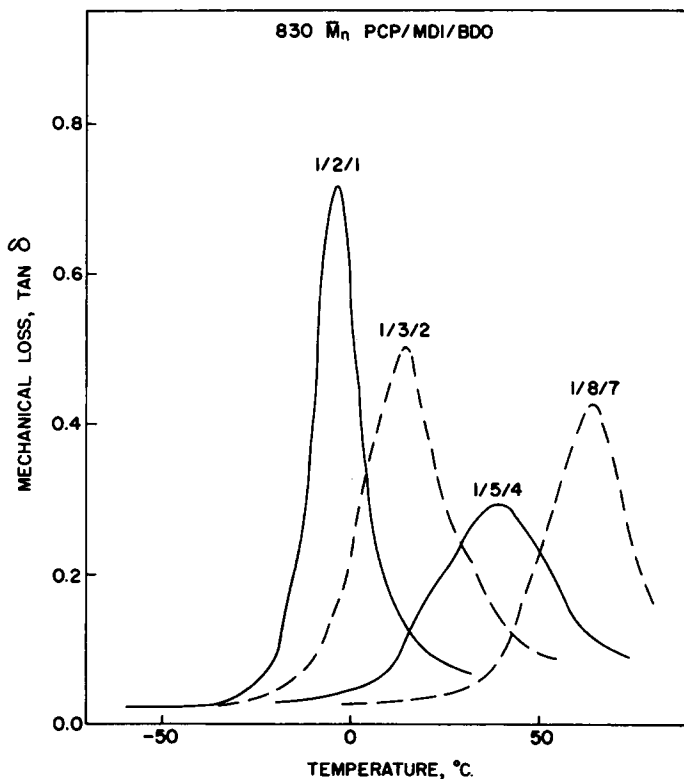


Fig. 3. Effect of hard-segment content on mechanical loss modulus properties of urethane polymers based on 830 \bar{M}_n polycaprolactone diol.

The temperature dependences of mechanical loss properties of the polymers are shown in Figure 3 and reflect the shift in glass transition temperature and relaxative peak broadening associated with increasing hard-segment contents. The increase in intensity of the mechanical loss peak at high hard-segment concentrations has been observed previously for other urethane elastomers.¹³ It was suggested to arise from increased free volume in the soft-segment regions as the hard segments became more structurally ordered.

Previous studies have shown that the glass transition temperatures of thermoplastic urethane elastomers which vary in sequence length of soft segments may be described by a relationship usually applied to compatible copolymers.¹⁷ The glass transition temperatures of these polymers which vary in hard-segment content were analyzed according to the Fox relationship¹⁹:

$$1/T_{g_{1,2}} = (w_1/T_{g_1}) + (w_2/T_{g_2}) \quad (1)$$

where $T_{g_{1,2}}$ is the glass transition temperature of a copolymer containing weight fractions w_1 and w_2 of units 1 and 2, which respectively have homopolymer glass transition temperatures T_{g_1} and T_{g_2} . The glass transition temperatures obtained from G'' for these urethane elastomers are given in Table I as a function of hard-segment concentration. Utilizing the previously obtained glass transition temperatures of -60°C for the polycaprolactone diol soft segment²⁰ and 125°C for the hard segment MDI/BDO units,¹⁷ eq. (1) was used to calculate the glass transition temperatures of the various urethane

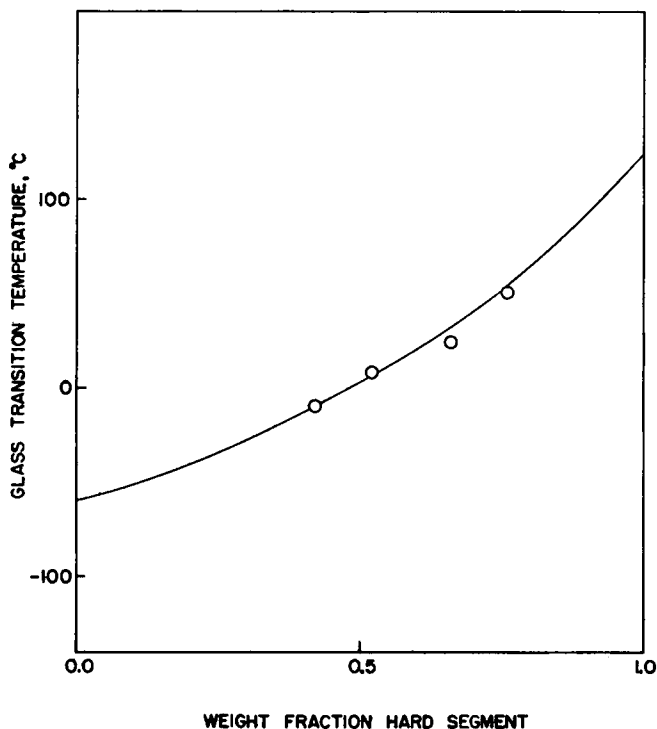


Fig. 4. Glass transition temperatures of urethane polymers based on 830 \bar{M}_n polycaprolactone diol are compared with calculated curve determined from eq. (1).

elastomers based on different ratios of hard- and soft-segment concentrations. As shown in Figure 4, the calculated curve determined by the Fox relationship adequately describes the variation in the experimental glass transition temperatures of the polymers.

Polymers with 2100 M_n Soft Segments

The influence of increasing hard-segment content also was investigated for a series of urethane polymers based on the 2100 \bar{M}_n polycaprolactone diol as the soft segment. As shown in Table II, the physical properties trends obtained with these polymers were similar to those of the series prepared with the 830 \bar{M}_n polycaprolactone diol. Increasing hard-segment content produces increased hardness, tensile stress, and tear values, while reducing elongation properties.

The dynamic storage modulus G' data presented in Figure 5 show that the initial decrease in modulus properties occurs within a small temperature range for the polymers of increasing hard-segment content based on the 2100 \bar{M}_n polycaprolactone diol. However, the urethane elastomers of higher hard-segment content exhibit much broader and less drastic modulus changes with temperature and have higher modulus values at elevated temperatures.

The dynamic loss modulus G'' data for these polymers are given in Figure 6. Comparison of these curves shows the relative constancy of the polymer glass transition temperatures, and it reflects the broadening of the glass tran-

TABLE II
Properties of Thermoplastic Urethane Elastomers Based on 2100 \bar{M}_n
Polycaprolactone Diol

Mole ratio of PCP Diol/MDI/BDO	1/2/1	1/3/2	1/4/3	1/5/4	1/6/5	1/8/7	1/10/9	1/15/14	1/20/19
Weight fraction MDI/BDO	0.22	0.31	0.38	0.43	0.49	0.56	0.61	0.70	0.76
Polymer Physical Properties									
Hardness									
Shore A	65	85	90	95	—	—	—	—	—
Shore D	—	30	40	45	55	60	60	—	—
100% Tensile stress, psi	300	600	1000	2000	2500	5500	—	—	—
300% Tensile stress, psi	600	1000	2000	3500	5000	—	—	—	—
Tensile strength, psi	5000	5000	7500	7000	6500	6000	3000	—	—
Ultimate elongation, %	600	600	500	450	350	150	25	—	—
Die C tear, pli	250	400	500	600	750	1000	1200	—	—
Glass Transition Temp., °C									
From G''	-40	-40	-32	-30	-30	-30	-30	+30	+30
From $\tan \delta$	-35	-30	-23	-17	-14	-5	+30	+55	+65

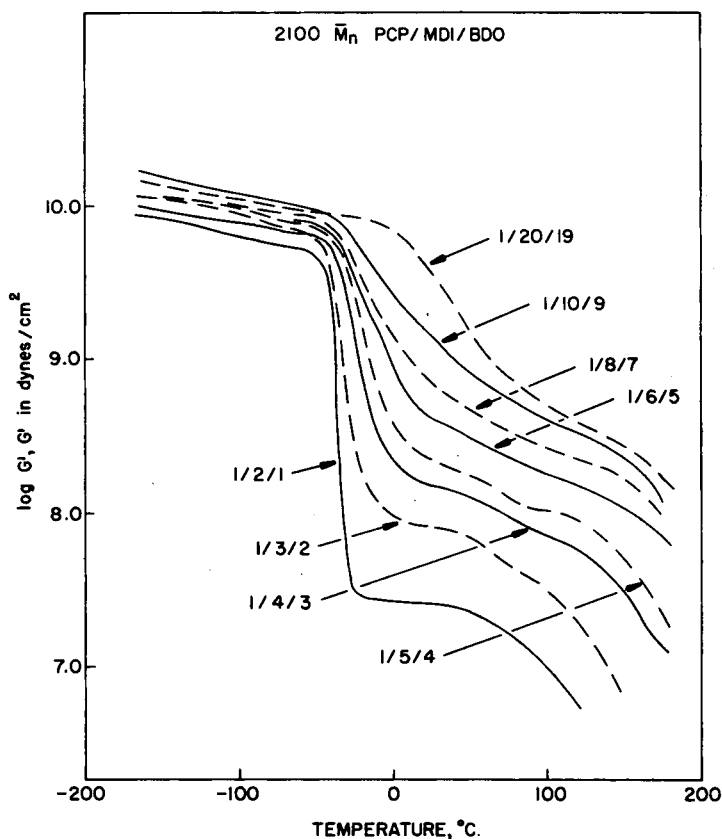


Fig. 5. Effect of hard-segment content on storage modulus properties of urethane polymers based on 2100 \bar{M}_n polycaprolactone diol.

sition region for elastomers of increased hard-segment concentration. At high levels of hard-segment content (1/15/14 and 1/20/19), the glass transition peak is shifted to a higher temperature. For all of the polymers, the secondary relaxation maximum for methylene sequence units is observed at

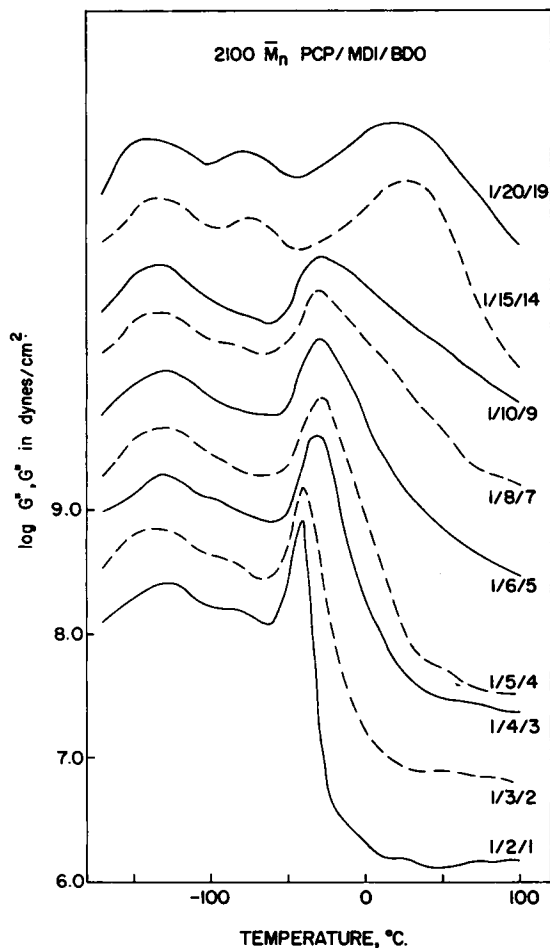


Fig. 6. Effect of hard-segment content on loss modulus properties of urethane polymers based on 2100 \bar{M}_n polycaprolactone diol. For clarity, all curves except that for the 1/2/1 polymer are displaced vertically from each other.

-130°C. However, the additional relaxation maximum near -70°C is present only for the highest members studied in this series. This peak has been observed previously with other thermoplastic urethane polymers,²¹ but its origin was not discussed. The existence of this transition in various polymers of the two series studied suggests that it may arise from the disruption of associations between the hard and soft segments.

In contrast to the relative temperature insensitivity observed for the G'' peaks, the mechanical loss peaks usually associated with the glass transition temperature, shown in Figure 7, exhibit a progressive increase to higher temperatures as the polymer hard-segment content increases. For the elastomers of lower hard-segment concentration, the magnitude of the loss peak decreases, and its breadth increases considerably as the relative proportion of the amorphous soft segments in the respective polymers decreases. The loss peak shifts to higher temperature and increases in intensity for the two polyurethanes of highest hard-segment concentration.

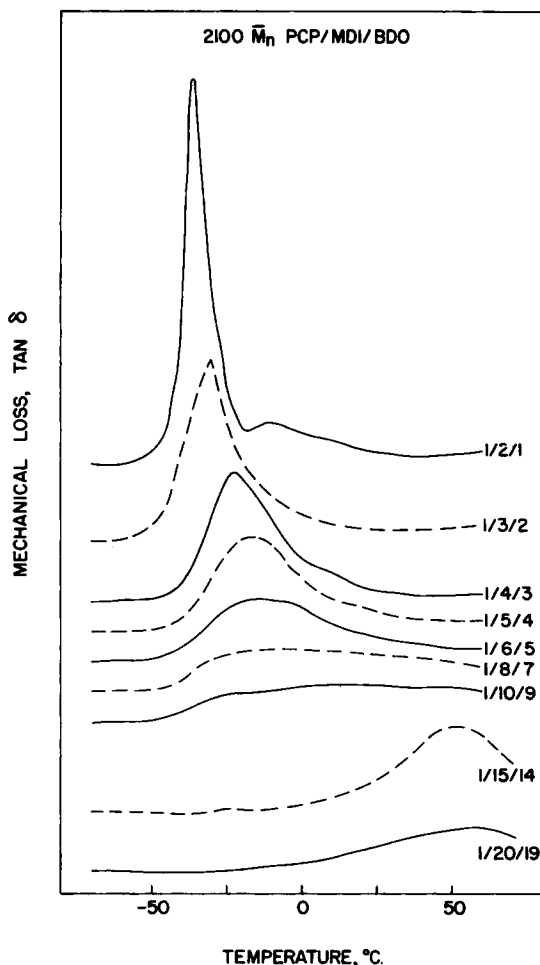


Fig. 7. Effect of hard-segment content on mechanical loss properties of urethane polymers based on 2100 \bar{M}_n polycaprolactone diol. For clarity, all curves except that for the 1/20/19 polymer are displaced vertically from each other.

Influence of Hard Segments

The amorphous state environment of soft-segment units in thermoplastic urethane elastomers is clearly influenced by the proportionate concentration of the rigid, hard-segment structures. The interface of these hard- and soft-segment regions cannot be distinct, but rather it must exhibit gradual changes. In addition, the degree of segregation between the molecular blocks of these copolymers appears to be dependent on the sequence length of the soft segments. Different interpretations have been ascribed to the influence of soft-segment molecular weight on domain formation and the dynamic mechanical properties of urethane elastomers.

For the series of urethane polymers containing the 830 \bar{M}_n polycaprolactone diol as the soft segment, increasing the relative hard-segment concentration produces responses typical of compatible copolymers, i.e., an increase in the glass transition temperature corresponding to changes in hard-segment

levels. At this soft-segment molecular weight, the hard segments exert considerable restrictions on the mobility of the amorphous regions. In contrast, the urethane polymers based on the 2100 \bar{M}_n polycaprolactone diol as the soft segment exhibit properties at increased hard-segment concentrations which are similar to those observed for partially crystalline polymers. Previous studies of similar urethane elastomers based on relatively low hard-segment concentrations and various molecular weight polycaprolactone diols showed that the polyester soft segments tended to crystallize for 3100 \bar{M}_n polycaprolactone diols, but not for 2100 or lower molecular weight polycaprolactone diols.¹⁷ As shown in Table II, the temperature difference between the major transition peaks obtained from G'' and $\tan \delta$ spectra of the 2100 \bar{M}_n materials becomes greater as the extent of apparent partial crystalline character in the polymer increases. In addition, the magnitude of the mechanical loss peak decreases and the modulus of the rubbery plateau increases. The progressive influence of those hard-segment structures on the mobility of the amorphous soft-segment units is noted by the gradual broadening of the glass transition responses. It is only at a considerable hard-segment content, weight fraction greater than approximately 0.60, that the glass transition temperature of the soft segments is shifted to a higher temperature.

CONCLUSIONS

The dynamic mechanical properties of thermoplastic urethane elastomers are influenced significantly by the structure and organization of the hard segments. Localized mobility within the amorphous soft segments is unaffected by the hard segments, since all of the polymers possess a relaxation associated with methylene sequences. However, cooperative motions within the soft segments which control the glass transition temperature are modified to various extents which depend on the relative sequence length of the soft segments. Polymers based on relatively low molecular weight polycaprolactone diols exhibit progressively greater interactions between the structural domains at higher hard-segment levels. For polymers containing longer sequence length of soft segments, the degree of interaction between the phases appears to be less pronounced. An additional secondary relaxation arises at higher hard-segment concentrations. This relaxation is thought to be related to molecular associations between the hard and soft segments.

These data suggest that the extent of microphase separation between the hard and soft segments of these thermoplastic urethane elastomers is significantly influenced by the sequence length of the soft segments. For relatively short sequence lengths, the segments of the polymers exhibit compatible behavior, while longer sequence lengths result in incompatible responses for the respective segments. Similar structure-property relationships have been observed for thermoplastic elastomers other than urethanes, which are based on segmented copolymers of A-B-A molecular structure.²²

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