Thermoplastic Urethane Elastomers. III. Effects of Variations in Isocyanate Structure

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Synopsis

The dynamic mechanical properties of thermoplastic urethane elastomers have been compared for materials based on different diisocyanate structures, either 4,4'-diphenylmethane diisocyanate (MDI) or an isomeric ratio of tolylene diisocyanate (TDI). Two comparable series of polymers were prepared with a polycaprolactone diol as the soft segment and varying concentrations of hard segments based on the respective diisocyanates and 1,4-butanediol. Over the composition range studied, the polymer glass transition temperatures increased for the TDI-based polyurethanes, but remained relatively constant for the series containing MDI. Differences in the degree of macroscopic order within the hard segments, due to variations in the symmetry of the diisocyanate structures, are suggested as an explanation of these dynamic mechanical properties.

INTRODUCTION

Previous studies of thermoplastic urethane elastomers have characterized the effects of variations in soft-segment molecular weight and hard-segment concentration on the dynamic mechanical properties of the respective polymers.[1,2] At a fixed molar concentration of hard segments, the glass transition temperature of the block copolymers decreased as the molecular weight of the soft segments increased. This variation was interpreted in terms of relative increasing flexibility for the amorphous soft-segment structures. In contrast, increasing hard-segment concentrations affect the glass transition temperature of the urethane polymers in a manner which is dependent on the molecular weight of the respective polycaprolactone soft segments. For polycaprolactone soft segments of 830 $\bar{M}_n$, the glass transition temperature of the polymers progressively increases with higher hard-segment concentrations. However, for polycaprolactone soft segments of 2100 $\bar{M}_n$, the glass transition temperature of the polymers is relatively insensitive to hard-segment concentration. These property variations may be ascribed to differences in the extent of microphase segregation and the perfection of domain organization within the block copolymer structure.

In the preparation of linear thermoplastic urethanes, a diisocyanate structure usually is reacted with a low molecular weight diol to form the hard segment of the polymer. The soft segments, commonly a polyether or polyester diol of relatively high molecular weight, are linked chemically to the hard segments by reaction with the diisocyanate. Generally, the diisocyanate of

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choice has been 4,4′-diphenylmethane diisocyanate (MDI), a structure of high aromatic content.

This study characterizes the dynamic mechanical properties of thermoplastic urethane elastomers based on an isomeric ratio of tolylene diisocyanate (TDI). For a series of polyurethanes of varying hard-segment concentration, the effect of diisocyanate structure on polymer properties is considered by comparison of elastomers prepared with the isomeric TDI mixture or MDI.

EXPERIMENTAL
Polymer Preparation

A polycaprolactone diol (PCP) having a number average molecular weight of 2100 and marketed by Union Carbide Corporation (PCP-0240) was used as the soft segment structure of the thermoplastic urethane elastomers. For the low molecular weight diol component of the polymer hard segments, 1,4-butanediol (BDO) was selected. Preparation of the urethane polymers based on 4,4′-diphenylmethane diisocyanate (MDI) has been previously described.[1] A similar series of polymers were prepared using a commercial tolylene diisocyanate (TDI), which is an 80/20 mixture by weight of 2,4-TDI and 2,6-TDI isomers. Preparation of these materials was similar to that for the polymers based on MDI.

Polymers of PCP/MDI/BDO and PCP/TDI/BDO were prepared at molar ratios of 1/4/3, 1/6/5 and 1/8/7. Stoichiometry of the reactants was controlled carefully so that the ratio of the respective diisocyanate to total hydroxyl requirements was essentially unity to prevent the formation of primary crosslinks.

Polymer Properties

Physical properties of the polymers at ambient temperature were evaluated in accordance with standard ASTM procedures. The temperature dependences of the polymer dynamic mechanical properties were determined with a recording torsional pendulum and a technique previously described.[1]

RESULTS

A comparison of physical properties at ambient temperature for the urethane elastomers based on MDI and TDI is given in Table I. As previously noted for the MDI-based polymers,[2] hardness, tensile stress, and tear resistance values increase and ultimate elongations decrease as the hard-segment concentration is increased in the TDI-based polymers. At equal molar concentrations of hard segments, the polymers prepared with TDI exhibit lower strength properties, i.e., tensile stress and tear resistance, and greater extensibilities than the polymers prepared from MDI.

The temperature dependences of the dynamic storage modulus G' are compared in Figure 1 for these two series of polymers. In contrast to the MDI-based polymers, the rapid decrease in modulus values associated with the

TABLE I
Effect of Isocyanate Structure on the Physical Properties of Thermoplastic
Urethane Elastomers

Components[a]	PCP/MDI/BDO			PCP/TDI/BDO		
Molar ratio of components	1/4/3	1/6/5	1/8/7	1/4/3	1/6/5	1/8/7
Weight fraction hard segment	0.38	0.49	0.56	0.32	0.42	0.49
Polymer Physical Properties						
Hardness, Shore A	90	—	—	60	65	85
Shore D	40	55	60	—	—	—
100% Tensile stress, psi	1000	2500	5500	200	300	600
300% Tensile stress, psi	2000	5000	—	300	500	2000
Tensile strength, psi	7500	5500	6000	2000	4000	9000
Ultimate elongation, %	500	350	150	600	500	400
Graves tear, pli	600	800	900	150	200	300
Glass Transition Temperatures, °C						
From G''	−32	−30	−30	−20	0	10
From tan δ	−23	−14	−5	−10	10	20

[a] PCP represents polycaprolactone diol of 2100 $\bar{M}_n$, BDO represents 1,4-butanediol, MDI represents 4,4'-diphenylmethane diisocyanate, and TDI represents 80/20 mixture of 2,4- and 2,6-isomers of tolylene diisocyanate.

glass transition shifts to progressively higher temperatures as the hard segment concentration increases for the series of TDI polymers. The magnitude of the rubbery plateau modulus is seen to be greater for the respective polymers based on MDI.
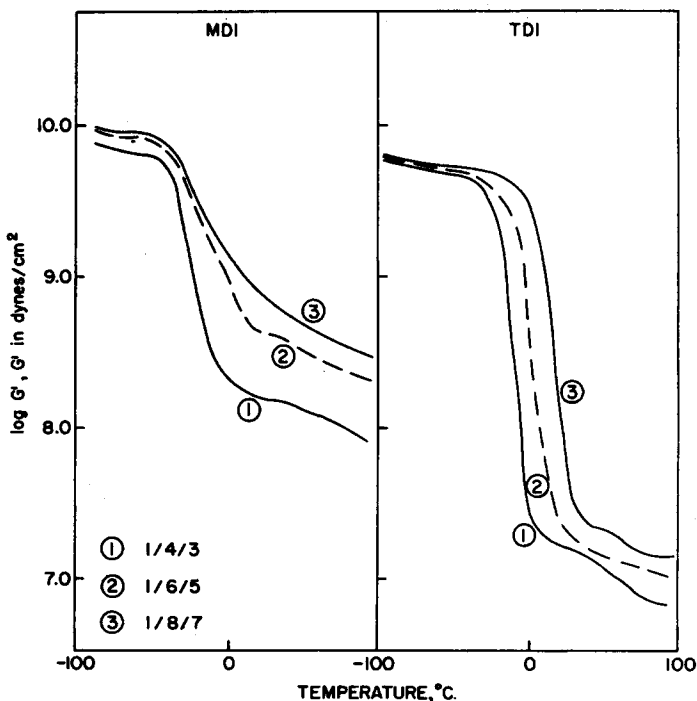

Fig. 1. Effect of hard-segment content on storage modulus properties of urethane polymers based on 2100 $\bar{M}_n$ PCP diol/MDI or TDI/BDO.
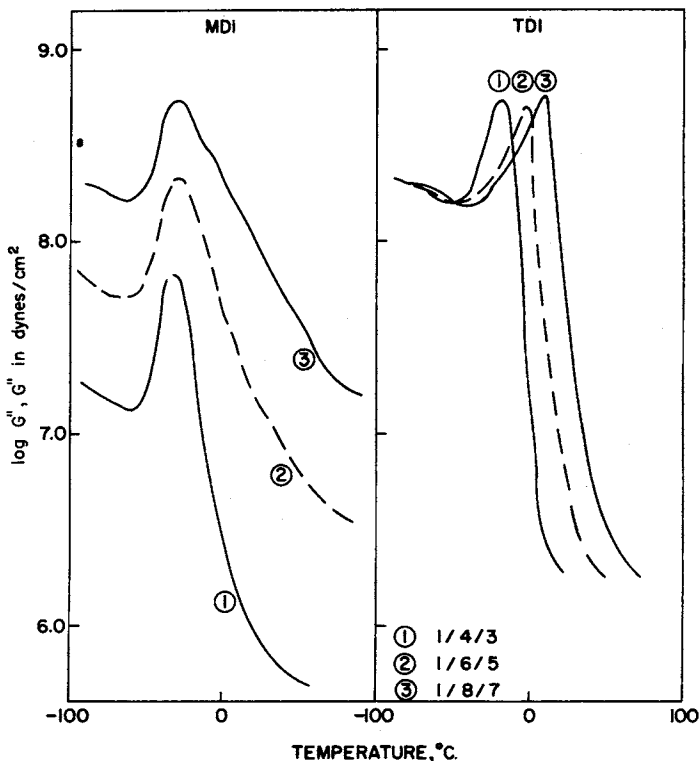
Fig. 2. Effect of hard-segment content on loss modulus properties of urethane polymers based on 2100 $\bar{M}_n$ PCP diol/MDI or TDI/BDO. For clarity, the curves for the MDI-based polymers are displaced vertically downward from each other.

The effect of hard-segment concentration on the glass transition temperature of the polymers prepared with MDI and TDI is clearly shown in Figure 2. For the MDI-based polymers, the temperature of the peak maximum corresponding to the glass transition remains constant, but the peak broadens at higher hard-segment concentrations. However, the converse trends are apparent for the TDI-based polymers. For this series, the temperature of the glass transition shifts to higher values, and there does not appear to be any marked peak broadening as the hard-segment concentration is increased.

Relationships similar to the above are observed for the mechanical loss properties of these polymers, as shown in Figure 3. Considerable broadening and loss of intensity for the glass transition peak are seen for the MDI-based polymers at increased levels of hard segment. The comparable polymers of the TDI series exhibit a much higher level of mechanical loss at the peak maximum, and this intensity does not change appreciably with hard-segment concentration. However, the temperature of the transition peak increases without any significant peak broadening as the hard-segment concentration increases in the TDI series.

DISCUSSION

The molecular structure of the urethane polymers prepared with MDI and TDI differs primarily with regard to the symmetry of the diisocyanate link-
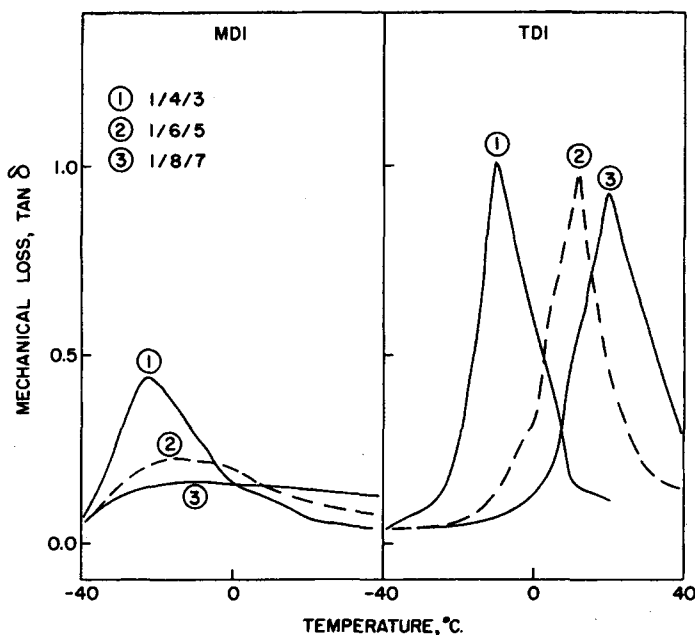
Fig. 3. Effect of hard-segment content on mechanical loss properties of urethane polymers based on 2100 $\bar{M}_n$ PCP diol/MDI or TDI/BDO.

ages. The isocyanate groups of MDI are symmetrically situated at the para positions of the aromatic rings, and this allows relatively close association of these segments when reacted in a urethane polymer. Previous studies of MDI-based urethane elastomers prepared at relatively low hard-segment concentrations 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.[2]

The mixture of TDI isomers contains a high proportion of the asymmetrical isomer, 2,4-TDI, which can result in head-to-tail isomerization within the urethane structure. Studies of thermoplastic polyether urethane polymers prepared with 2,4- and 2,6-TDI have shown that 2,4-TDI-based polymers are amorphous, whereas 2,6-TDI results in materials which exhibit partially crystalline character by wide angle x-ray diffraction analysis.[3] The glass transition temperatures of hard segments based on BDO and these isomeric TDI structures are comparable[4] and only slightly lower than the value of 125°C obtained for similar materials prepared with MDI.[1]

The amorphous character of the hard segments containing the isomeric TDI units may result in considerable intermixing of this phase with the soft segments. These hard segment–soft segment interactions can produce restrictions on the relative mobility of the polyol units and increase the glass transition temperature of the urethane polymer. In contrast, the hard segments based on MDI possess a more perfect domain organization due to their crystalline nature. Hence, this higher extent of segregation between the hard and soft segments results in little effect on the glass transition temperature of the amorphous polyol structures. The higher degree of order within the MDI hard segments is reflected by an increased magnitude of the rubbery plateau

modulus in comparison with that obtained for similar urethane polymers based on the TDI isomeric mixture.

Qualitative estimations[5,6] have revealed that a high proportion of N–H groups are hydrogen bonded with various proton acceptors of urethane polymers. Recent studies of thermoplastic urethane elastomers based on the respective isomers of TDI have shown that urethane hydrogen bonding to the polyester carbonyl is stronger than to the polyether oxygen atom of the soft segments.[7] The extent of interaction between the hard and soft segments may be estimated by assuming that the intersegmental hydrogen bonds are pseudocrosslinks which increase the glass transition temperature of the soft segments in the urethane polymer.[4] The extent of hydrogen bonding between urethane N–H groups of the hard segments and the ester units of the soft segments may be calculated according to the following equation:

$$(T_g - T_{g1})/T_{g1} = KX_c/(1 - X_c) \tag{1}$$

where T_g is the glass transition temperature of the urethane polymer, T_{g1} is the glass transition temperature of the soft segment, X_c is the mole fraction of ester units which are hydrogen bonded to the urethane N–H groups, and K is constant having values[4] in the range of 1.2 and 1.5. The amount of hydrogen-bonded crosslinks necessary to produce the increase in the glass transition temperature of each TDI-based urethane polymer was calculated assuming a glass transition temperature of 213°K for the soft-segment polycaprolactone diol of 2100 $\bar{M}_n$.[1] The mole fraction of hydrogen-bonded caprolactone units ranged from approximately 0.1 to 0.2 and increased with higher hard-segment concentrations in the polymer. These values are comparable to those obtained with polyester urethane elastomers prepared with poly-(butylene adipate) soft segments and 2,4-TDI.[7]

CONCLUSIONS

The extent of interaction between the hard and soft segments of thermoplastic urethane elastomers may be ascribed to changes in the glass transition temperature of the respective polymers as the relative concentration of the components are varied. A high degree of phase separation results in minor effects on the glass transition temperature of the amorphous soft segments. Increased intermixing of the hard and soft segments produces restrictions on the relative mobility of the soft segments, which may be described as due to the effect of hydrogen-bonded crosslinks. The symmetry of the diisocyanate structures which form the hard segments is a dominant factor with regard to the extent of this domain segregation.

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