Thermoplastic Urethane Elastomers. I. Effects of Soft-Segment Variations

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Synopsis

A series of thermoplastic urethane elastomers with soft segments of varying sequence length was prepared and their dynamic mechanical properties were characterized over a wide temperature range. The polymers were prepared using various molecular weight polycaprolactone diols as the soft segment and 4,4'-diphenylmethane diisocyanate and 1,4-butanediol as the hard segment. The urethane elastomer exhibited soft-segment crystallization when a polycaprolactone diol greater than 3000 $\bar{M}_n$ was used. The glass transition temperature of these materials progressively shifted to lower temperatures as the chain length of the soft segment was increased. This dependence was interpreted in terms of a molecular weight relationship similar to that associated with amorphous homopolymers. The dynamic mechanical properties of these polyurethanes appear to be consistent with responses observed for compatible copolymers.

INTRODUCTION

On a molecular basis, thermoplastic urethane elastomers may be described as linear block copolymers of the $(AB)_n$ type. One block of the polymer chain consists of a relatively long, flexible polyester or polyether diol in the typical number-average molecular weight range of 1000 to 3000. These amorphous polyol blocks are usually termed the soft segments since they impart the elastomeric character to the polymer. The second block of the copolymer is commonly referred to as the hard segment and is formed by the reaction of aromatic diisocyanates with low molecular weight diol or triol chain extenders. Due to the polar nature of the urethane groups in the hard segments and their ability to form hydrogen bonds, these hard segments are capable of intermolecular associations and possible domain segregation.[1-3] The thermally reversible network structure of these copolymers provides for the elastomeric or apparent crosslinked nature of these polymers.

Several studies have been performed with regard to the various relationships of molecular structure and physical properties for thermoplastic urethane elastomers.[4-14] In a general sense, the dynamic mechanical properties of these polymers may be interpreted in terms of corresponding modifications in either the hard or soft segments. Typical of responses observed for block copolymers, the lower temperature glass transition region for these elastomers appears to be influenced primarily by the degree of flexibility of the amorphous, soft segments and their interactions with the hard segments. The higher temperature relaxation region is controlled mainly by the extent

of association of the rigid, hard segments. In addition, the relative concentration of the hard and soft segments affects the level of the plateau modulus at temperatures between the major relaxation regions.

This study characterizes the temperature dependence of dynamic mechanical properties for thermoplastic urethane elastomers based on a polyester soft segment and a hard segment comprised of an aromatic dissocyanate and a polyether diol chain extender. Systematic variations were made in the chain length of the soft segment. The dynamic mechanical spectra were correlated with the molecular structure changes of the copolymers.

EXPERIMENTAL

Polymer Preparation

Polycaprolactone diols (PCP) marketed by Union Carbide Corporation were added individually to a 500-ml reaction flask equipped with a heating mantle, stirrer, thermometer, and vacuum inlet. Each diol was heated to 100°C and degassed for 1 hr at 1–2 mm Hg to remove water and dissolved gases. The temperature of the diol was then increased to 175°C while degassing was continued. The 1,4-butanediol (BDO) was dried by distillation and added to the polycaprolactone diol with stirring. Finally, the solid, flaked 4,4-diphenylmethane dissocyanate (MDI) was added. The mixture was stirred vigorously for about 30 sec, was transferred to a metal mold at 175°C, which was previously treated with a release agent, and was placed in an oven and cured at 140°C for 3 hr. After removal from the oven, the respective thermoplastic urethane polymers were removed from the mold and postcured for one week at ambient temperature. The polymers were granulated with a Wiley mill using solid carbon dioxide as coolant. Test plaques were compression molded from the granules at 175°C and were characterized for dynamic mechanical properties approximately three to five days after molding. The standard physical properties of these thermoplastic urethane elastomers were determined at ambient temperature in accordance with prescribed ASTM methods.

Dynamic Mechanical Properties

The temperature dependence of dynamic mechanical properties were determined with a recording torsional pendulum similar to that described by Nielsen.[15] Test specimens were approximately 0.50 in. long, 0.25 in. wide, and 0.060 in. thick. Beginning at subambient temperatures, torsional response data were obtained at 10°C intervals, except in the major transition region where the temperature intervals were decreased to 2.5°C. The test specimens were held for about 10 min at each temperature to ensure thermal equilibrium. In the vicinity of the major glass transition, the frequency varied from 1 to 2 hertz.

The experimental mechanical damping data were taken in triplicate, and an average value of the logarithmic decrement was used to calculate the mechanical loss, tan δ. The real and imaginary components, G' and G'', respectively, of the complex dynamic shear modulus were calculated from the period of oscillation and the damping data at each temperature.

RESULTS AND DISCUSSION

Polymer Physical Properties

The urethane elastomers were based on polycaprolactone diols (PCP), 4,4'-diphenylmethane diisocyanate (MDI), and 1,4-butanediol (BDO). The number-average molecular weight ($\bar{M}_n$) of the PCP soft segments was varied in the range of 340 to 3130. For each polymer the theoretical sequence length of the hard segments was kept constant by fixing the molar ratio of the intermediates PCP/MDI/BDO at 1/2/1. Thus, as the molecular weight of the PCP soft segments was increased, the weight fraction of hard segment in the polymers sequentially decreased.

Physical properties of these urethane elastomers at ambient temperature are given in Table I. As the sequence length of the soft segment increases, the hardness, tensile modulus, and tear properties tend to decrease. As expected, the ultimate elongation values for this series of polymers increases with increasing weight fraction of soft segment in the elastomer.

Soft Segment Crystallization

All of these urethane elastomers were transparent, except the material based on the 3130 $\bar{M}_n$ polycaprolactone diol, which crystallized on aging. High molecular weight polycaprolactone homopolymer is a partially crystalline material with a melting point of 60°C.[15] The ability of this polycaprolactone diol to crystallize within the urethane elastomer network is reflected in the polymer physical properties as shown in Table I. A sample of the urethane polymer prepared with the 3130 $\bar{M}_n$ polycaprolactone diol was warmed to about 55°C and then quenched in liquid nitrogen to ensure vitrification and the presence of amorphous soft segments. For these quenched and annealed samples, comparison of the temperature dependences of the real component of the complex dynamic shear modulus G' is shown in Figure 1. The annealed polymer exhibited only a minor decrease in modulus values as the temperature was varied in the transition region, whereas the quenched sample showed a decrease of about 2.5 orders of magnitude in this temperature

TABLE I
Properties of Thermoplastic Urethane Elastomers Polycaprolactone
Diol/MDI/BDO at 1/2/1 Molar Ratio

Polycaprolactone diol molecular weight $\bar{M}_n$	340	530	830	1250	2100	3130
Weight fraction MDI/BDO	0.63	0.53	0.43	0.32	0.22	0.16
Polymer Physical Properties						
Hardness, Shore A	—	95	90	80	65	50
100% Tensile stress, psi	—	2000	500	400	300	1000
300% Tensile stress, psi	—	—	2500	1000	600	1500
Tensile strength, psi	—	4000	6000	6000	5000	4500
Ultimate elongation, %	—	250	400	500	600	700
Graves tear, pli	—	700	500	350	250	500
Reduced viscosity, 30°C DMF, 0.2 g/dl	1.16	1.44	1.36	1.57	1.57	0.98
Glass Transition Temperatures, °C						
From G''	53	25	-10	-27	-40	-35(-45)[a]
From tan δ	65	35	-5	-20	-35	-20(-40)[a]

[a] Values in parenthesis obtained from sample which was warmed and quenched in liquid nitrogen.
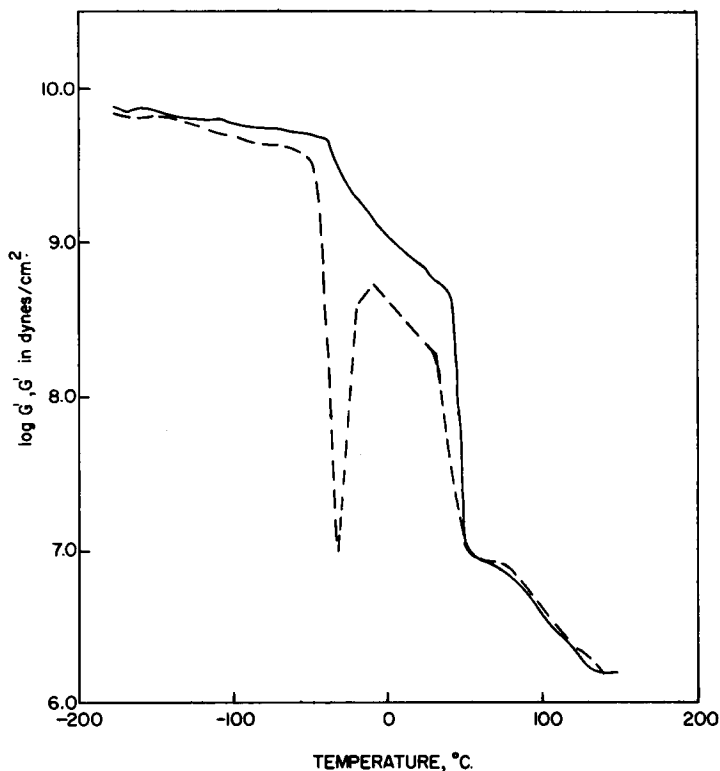
Fig. 1. Comparison of storage modulus properties for annealed (———) and quenched (- - -) samples of the urethane polymer based on 3130 $\bar{M}_n$ polycaprolactone diol.

region. A portion of the amorphous material then crystallized, as indicated by the rather abrupt modulus increase. Once a quasi-equilibrium was established, the modulus gradually decreased until temperatures near the melting point of the polycaprolactone segments were reached. In this region, the modulus values of both the quenched and annealed polymers rapidly decreased.

As presented in Table I, the data obtained with these quenched and annealed samples indicate that a difference of 10°C exists between the glass transition temperatures determined from the imaginary component, G'', of their complex dynamic shear modulus. The mechanical loss, tan δ, properties shown in Figure 2 reflect in the transition region the relative magnitude of the amorphous material present in each polymer. The temperature for the major loss peak in these mechanical loss data is −40°C for the quenched polymer and −20°C for the annealed polymer. Large differences in the transition temperatures determined from G'' and tan δ spectra may indicate the relative influence of polymer crystallinity on the transition region.[16]

Dynamic Mechanical Properties

The variations in physical properties at ambient temperature may be more readily interpreted when the temperature dependence of the polymer dynamic mechanical properties are considered. The G' properties of these urethane
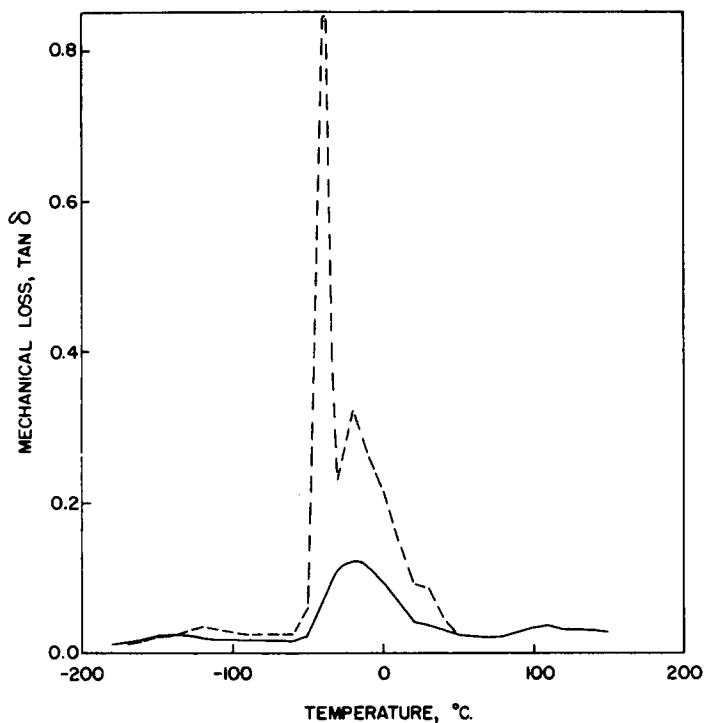
Fig. 2. Comparison of mechanical loss properties for annealed (———) and quenched (- - -) samples of the urethane polymer based on 3130 $\bar{M}_n$ polycaprolactone diol.
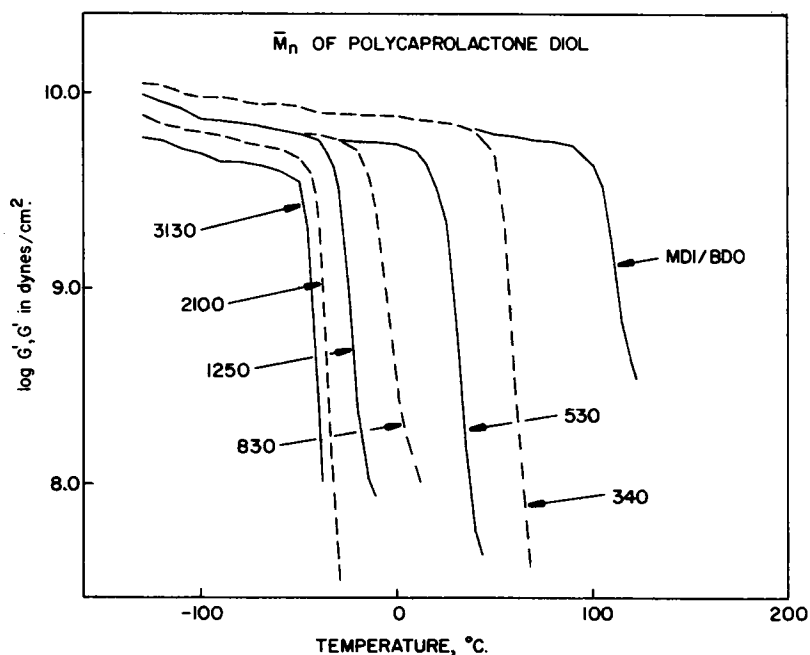

Fig. 3. Effect of soft-segment molecular weight on the storage modulus properties of urethane polymers based on various polycaprolactone diols.
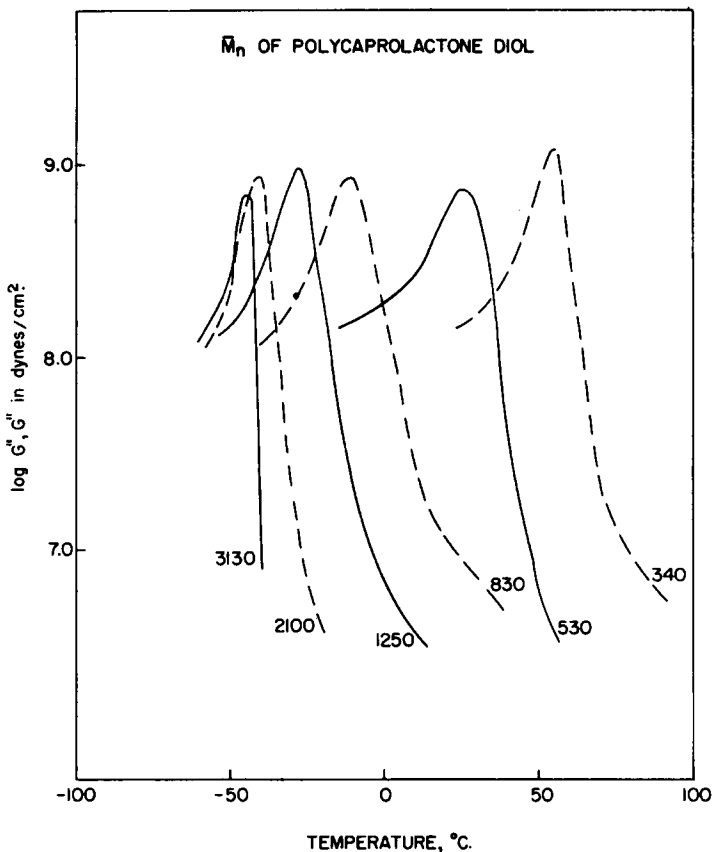
Fig. 4. Effect of soft-segment molecular weight on the loss modulus properties of urethane polymers based on various polycaprolactone diols.

polymers are shown as a function of temperature in Figure 3. A substantial decrease in the respective modulus properties for each polymer corresponds to the transition from the brittle, glassy state to the elastic, rubbery state. An increase in the molecular weight of the soft-segment polycaprolactone diol shifts this modulus decrease to progressively lower temperatures.

Polymer glass transition temperatures are generally determined precisely by the maximum occurring in the G'' modulus variations with temperature. Figure 4 compares the G'' spectra obtained for these urethane elastomers, and the corresponding glass transition temperatures are summarized in Table I. The mechanical loss data presented in Figure 5 further emphasize the influence of the sequence length of the polycaprolactone soft segments on the glass transition properties of the respective polymers. The magnitude of the mechanical loss peak usually reflects the relative amount of amorphous material in the polymer undergoing the transition from the glass to the rubbery state. It is not readily explainable why this parameter passes through a minimum as the molecular weight of the polycaprolactone diol is varied.

Glass Transition Temperatures

It is apparent from these studies that the glass transition temperature and associated low-temperature properties of these thermoplastic urethane elas-
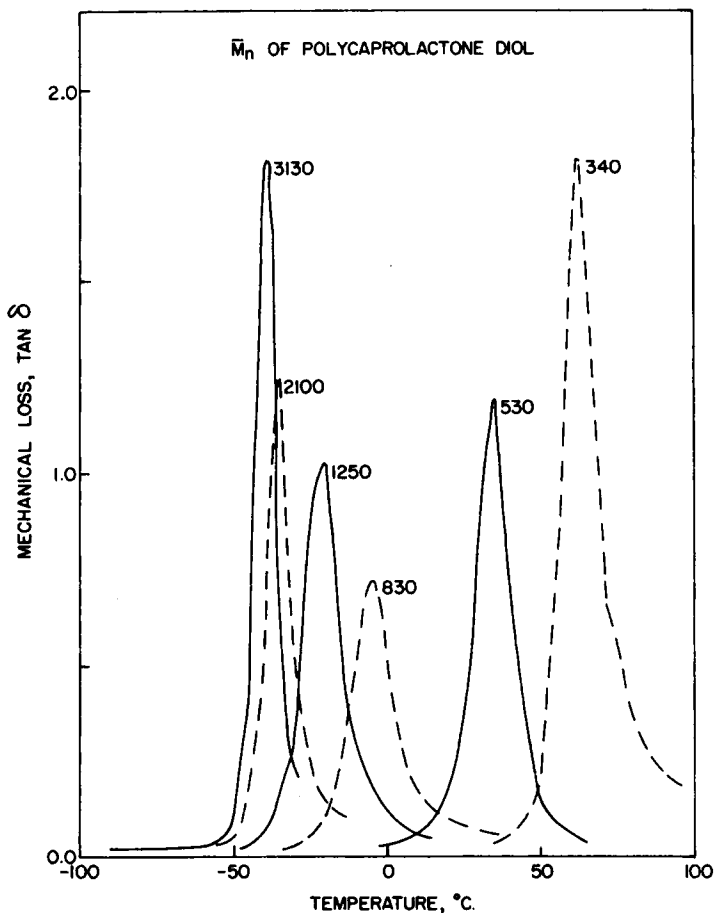
Fig. 5. Effect of soft-segment molecular weight on the mechanical loss properties of urethane polymers based on various polycaprolactone diols.

tomers are strongly dependent on the sequence length of the polymer soft segments. The effect of molecular weight on the glass transition temperatures of amorphous homopolymers has been shown by Fox and Flory[17] to be a reciprocal relationship:

$$T_g = T_g^\infty - K_g/\overline{M}_n \qquad (1)$$

where T_g is the glass transition temperature of an amorphous polymer with number-average molecular weight $\overline{M}_n$, T_g^∞ represents the glass transition temperature for a polymer of infinite molecular weight, and K_g is a constant. The decrease in T_g for lower molecular weight polymers has been interpreted as due to additional free volume associated with the chain ends of the molecules and is proportional to their concentration. Recently, an empirical correlation between K_g and T_g^∞ has been shown for a variety of common polymers.[18]

For these linear urethane elastomers, the chain ends of the polycaprolactone diols do not possess increased mobility. Rather, the mobility should be decreased due to their chemical attachment to the rigid, hard segments of the molecule. Hence, as the molecular weight of the polycaprolactone diol or se-
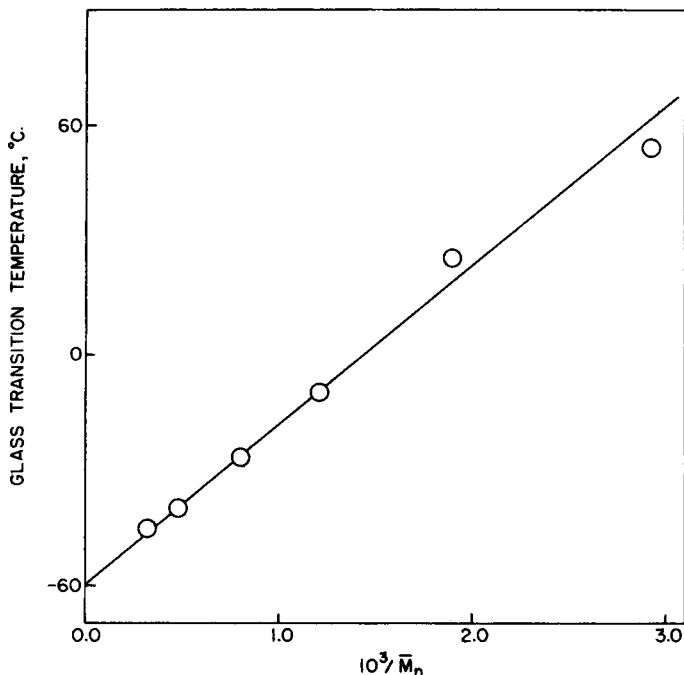
Fig. 6. Glass transition temperatures of urethane polymers as a function of reciprocal molecular weights for polycaprolactone diols.

quence length of the soft segment increases, the restrictive influences of the hard-segment structures should become less important and, accordingly, the glass transition of the polymer should occur at a lower temperature. A plot of polymer glass transition temperature versus reciprocal molecular weight of the soft segments is shown in Figure 6 for the urethane elastomers prepared with various molecular weight polycaprolactone diols. In contrast to the usual plots for most amorphous polymers, the slope of the linear relationship is positive due to the anchoring effects described for the soft-segment end group restrictions. A similar dependence has been observed in a series of polystyrenes having trichlorotriphenyl methyl endgroups for which T_g actually increased with decreasing molecular weight.[19] From Figure 6, the predicted value of T_g^{∞} is $-60°$C and corresponds to the glass transition temperature observed experimentally for high molecular weight amorphous polycaprolactone homopolymer.[16]

Since the glass transition temperature of these thermoplastic urethane elastomers varied with the relative concentration of the hard and soft segments, it was of interest to analyze these properties with regard to compatible polymer relationships. The glass transition temperature of compatible copolymers may be predicted by the Fox relationship[20]:

$$1/T_{g1,2} = (w_1/T_{g1}) + (w_2/T_{g2}) \tag{2}$$

where $T_{g1,2}$ is the glass transition temperature of a copolymer containing weight fractions w_1 and w_2 of the structural units for which the respective homopolymers have glass transitions T_{g1} and T_{g2}.

Using the extrapolated value of −60°C for the glass transition temperature of the polycaprolactone soft-segment portion of the thermoplastic urethane elastomers and appropriate rearrangement of eq. (2), a value for the glass transition temperature of the MDI/BDO hard segment may be obtained graphically. This extrapolated value was +125°C, which is in good agreement with values obtained by experimental determinations for the glass transition temperature of MDI/BDO polymers.[8,21] Figure 7 shows the general agreement of the observed glass transition temperatures for the urethane polymers of varying soft segment content with the Fox equation for compatible copolymers. The data points are higher than the calculated curve for the lower molecular weight polycaprolactone soft segments. However, this may be due to the anchoring effect of the hard segments, which would be expected to have the most influence in this composition region.

CONCLUSIONS

The study of dynamic mechanical properties of thermoplastic urethane elastomers have revealed effects of composition and structure on transition phenomena. These block copolymers exhibit segmented domain structure which leads to soft-segment crystallization when the molecular weight of the polycaprolactone diol is greater than 3000. The glass transition temperature of the elastomer shifts to higher temperatures as the sequence length of the soft segments is decreased. This may be interpreted as a molecular weight effect for the soft segments which are attached to the relatively immobile hard segments. In addition, the glass transition temperatures are in good
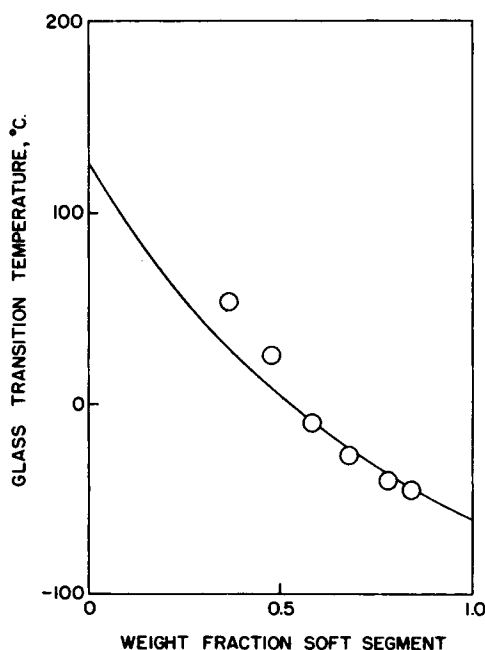

Fig. 7. Glass transition temperatures of urethane polymers as a function of weight fraction of soft segments. Solid curve was calculated from the Fox equation for compatible copolymers.

agreement with calculated values obtained from a relationship for compositional variations of a compatible copolymer.

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