

# The Thermal Analyses of Polymers.

## II. Thermomechanical Analyses of Segmented Polyurethane Elastomers\*

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### Synopsis

The development of new and more sensitive techniques in thermal analyses aids in a more complete understanding of the contributions of individual components in urethane elastomers regarding their mechanical and thermodynamic behavior. The behavior of various segments of the elastomers reported in this work illustrates a clearer interpretation of reasons for changes in mechanical behavior caused by changes in heat capacity, volume and tensile properties; the gross changes previously reported for polyurethane properties as a function of temperature are also confirmed with a more exact definition of their origin.

The sub-ambient temperature behavior and response of physical measurements near the melting point of the backbone polyol are largely a function of the so-called "soft block." The soft block does not contribute to the mechanical properties above the melting point of the polyol unless some urethane segments from the diisocyanate and extender are structured into the soft block, that is, excess diisocyanate and extender are added to build in the "hard" block. The extender and isocyanate influence for both low and high temperature properties is observed by the lack of molecular fit imparted to the backbone polyol as well as some crystallinity in the polymer hard block. The usual  $T_g$  transition reported in urethane elastomers corresponds to a first-order transition in the polyester or polyether backbone.

### INTRODUCTION

Polyurethane elastomers are an ideal class of polymers to study the effects of structure on properties of various combinations of reactive monomers, and thereby afford a systematic building of the desired polymer structure. Many of the changes in mechanical properties with varying diisocyanate polyester or polyether backbone and extender have been treated by Saunders<sup>1</sup> and by Saunders and Frisch.<sup>2</sup> Information regarding the low temperature mechanical behavior of urethane elastomers indicates that these properties are regulated to a large extent by the polyester or polyether backbone structure.<sup>3</sup> Tobolsky<sup>4</sup> has recently reported the effects of solvation by various plasticizers or swelling agents, demonstrating a pre-

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ferred solvation by a given agent for either the hard or soft block in the segmented urethane elastomer. He concludes that there is an undefined association among the segments regulating the low temperature behavior, as well as an association among the segments regulating the high temperature modulus behavior.

Slade and Jenkins<sup>5</sup> have shown some general changes which are observed by DTA and TGA analyses of various urethanes from differing combinations of di-isocyanates, polyesters, polyethers and diamine, and diol extenders. Their data indicated no significant changes by DTA until the region of decomposition corresponding to their TGA data for general polyurethane structures. Their report of no distinct endothermic changes in the DTA of the urethane appears to agree with the reported observation from X-ray analyses that no distinct crystallization is present in the segmented elastomers investigated.

This report illustrates the contributions by each component in the segmental buildup of a polyurethane elastomer and the change in the physical response of the segments on copolymerization with various diisocyanates to the changes in heat capacity, volume, and modulus which show excellent agreement. Furthermore, evidence is presented for some degree of molecular ordering (first order-type transition) in both the hard and soft blocks of the urethane elastomer.

## EXPERIMENTAL

A. *Thermomechanical Analyses:* Thermomechanical analyses were carried out in tension and expansion. A du Pont 940 Thermomechanical Analyzer, an instrument equipped with a probe and a linear variable differential transformer (LVDT) connected to the du Pont 900 console housing an amplifier, X-Y recorder and temperature programmer was modified to use a quartz probe as previously reported.<sup>6</sup>

1. *Expansion:* The expansion characteristics of the polyesters, polyethers, and polysiloxane backbones as well as the urethanes shown in Figure 6, were measured by placing the sample in a quartz tube (I.D. = 0.125 in., length, 1.0 in.) fitted with a flat-tipped quartz probe (D = 0.100 in.) in a piston-type arrangement. The sample (10 mg.) was mixed with silica, placed in the tube and heated with a load of 50 g to the melting point, shown as a penetration movement. The sample was then immediately quenched to  $-196^{\circ}\text{C}$  with liquid nitrogen while maintaining the 50 g load so that the sample could be compressed free from voids. The sample was then unloaded, and the probe was set at the maximum sensitivity of the instrument to a point where it rested lightly on the sample. The solid urethane elastomers were measured using the flat-tipped quartz probe (D = 0.100 in.) while the polymer sample rested on the quartz stage. The sample was heated at  $5^{\circ}\text{C}/\text{min}$ .

2. *Tension:* The strain measurements vs. temperature at constant stress were carried out on cast elastomers.<sup>3</sup> The sample was cut from the elastomeric sheet (about 60 mils thick) and inserted in the hooks of the TMA

after punching in it holes about 0.250 in. apart. The hooks were set so that the sample was not in tension. The sample was then cooled to  $-196^{\circ}\text{C}$ , the hooks reset, and the sample loaded with 10 g.<sup>6</sup> The sample was heated at  $10^{\circ}\text{C}/\text{min}$ .

B. *Differential Thermal Analyses*: These measurements were carried out on the du Pont 900 thermal analysis system using their Differential Scanning Colorimeter cell at a heating rate of  $10^{\circ}\text{C}/\text{min}$ .

## RESULTS AND DISCUSSION

Measurements on the bulk properties of polyurethane elastomers have shown the effects of varying polyols and polyisocyanate structure. Generally single modulus changes are observed at low temperatures when the polyester or polyether backbone structure is changed, and the high temperature properties are influenced largely by the type of polyisocyanate and extender (glycol, diamine, etc.) or degree of crosslinking present in the urethane.<sup>1</sup> As thermal techniques for measuring changes in linear expansion and tensile strain improve, the observations of more phase changes and their correlation with changes in heat capacity yield more meaningful information on polymer behavior.

Thermomechanical analyses (TMA) have the same heating character as other modes of thermal analyses. Usually the use of a temperature scanning technique does not always allow true thermal equilibrium to occur. With the use of Differential Scanning Calorimetry, the temperature of a transition or heat change is increased as the heating rate is increased, usually above  $10^{\circ}\text{C}/\text{min}$ ., and hence, thermal equilibrium is only approached at slower heating rates, provided that the sample size is small. As the heating rate is decreased with DSC the resolution and sensitivity decrease, some appropriate rate must be selected.

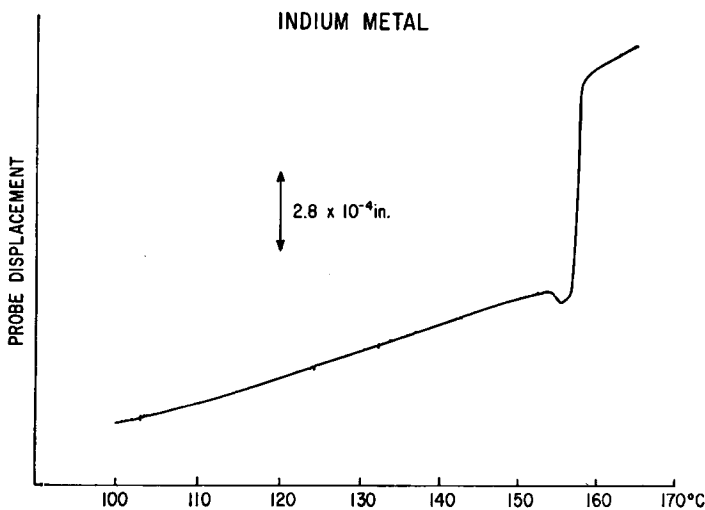


Fig. 1. Linear expansion behavior of indium metal.

The various modes of TMA must be used with appropriate heating rates to approach thermal equilibrium, provided small samples are used. In the expansion mode, heating rates greater than  $5^{\circ}\text{C}/\text{min}$  will increase the observed transition temperature, while for most samples and transitions, heating rates of  $5^{\circ}\text{C}/\text{min}$  or less do not change the transition temperatures but enhance their magnitude. Naturally, for the examination of multiple transitions over a very small temperature range, heating rates of  $1^{\circ}\text{C}/\text{min}$  are recommended.

Measurements in the tension mode can be made at  $10^{\circ}\text{C}/\text{min}$  with no appreciable change in the transition temperatures at lower rates. Lower heating rates will amplify the relative changes in strain rather than shifting their temperature of transition. Because of the appropriate relaxation times in polymers, measurements should be made on small samples at heating rates which approximate the relaxation times under the experimenter's conditions.

It is commonly accepted that the melting of pure metals represents a first-order transition which is illustrated in Figure 1 for the linear expansion of indium metal. The abrupt change in the linear expansion behavior of indium at  $156^{\circ}\text{C}$  is similar to the expansion behavior of urea and paraffins at their reported melting points.<sup>7</sup> Hence, we wish to define abrupt or discontinuous changes in expansion by the technique used in this study as tentative first-order transitions, and small changes in the slope of the expansion plot are termed tentatively as second-order transitions. This behavior is similar to that proposed by Bekkedahl<sup>8</sup> and others<sup>9</sup> for specific volume changes as a function of temperature, and has been described in detail elsewhere.<sup>7</sup> The confirmation of both of these first and second order transitions should show coincident changes in heat capacity at these temperatures. While the changes in heat capacity do not always appear as distinct endotherms usually associated with melting phenomena, the abrupt volume changes observed during linear expansion offer a clearer verification of first order behavior than DTA measurements.

### A. Thermal Behavior of Soft Block Polyol

Figures 2, 3, and 4 show the expansion characteristics for common polyols of molecular weight 2000 encountered in urethane technology, as well as, a rather unique polysiloxane. Figure 2 depicts the expansion behavior for poly(ethylene adipate) indicating transitions at  $-110^{\circ}$ ,  $-55^{\circ}$ ,  $-26^{\circ}$ ,  $3^{\circ}$ ,  $15^{\circ}$ , and  $34^{\circ}\text{C}$  with fusion completed at  $42^{\circ}\text{C}$ , and the data from differential scanning calorimetry agree with these values. It appears that the expansion changes at  $-26^{\circ}$ ,  $3^{\circ}$ ,  $15^{\circ}$ , and  $34^{\circ}\text{C}$  are those due to first-order type transitions. The change in expansion at  $-110^{\circ}\text{C}$  is probably that due to the glass transition of the poly(ethylene adipate). Figure 3 shows the linear expansion data for poly(oxybutylene) glycol, indicating changes in expansion at  $-155^{\circ}$ ,  $-89^{\circ}$ ,  $-54^{\circ}$ ,  $-32^{\circ}$ ,  $-5^{\circ}$ ,  $6^{\circ}$ ,  $24^{\circ}$ , and complete fusion at  $29^{\circ}\text{C}$ . Changes in specific heat at  $-153^{\circ}$ ,  $-87^{\circ}$ ,  $-45^{\circ}$ ,  $-8^{\circ}$ , and  $6^{\circ}$  substantiate the changes in expansion and offer excellent agreement.

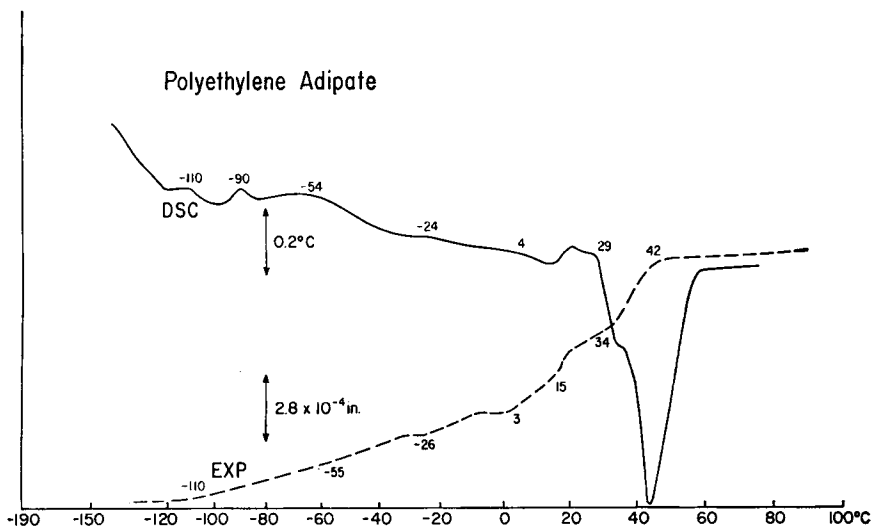


Fig. 2. The correspondence of expansion and heat capacity data for polyethylene adipate.

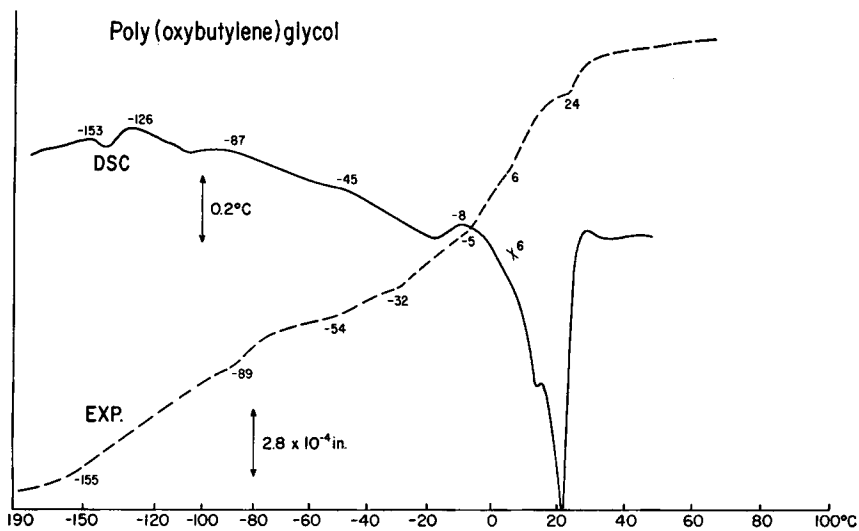


Fig. 3. The correspondence of expansion and heat capacity for poly(oxybutylene) glycol.

The expansion changes at  $-89^\circ$ ,  $-54^\circ$ ,  $-32^\circ$ ,  $-5^\circ$ ,  $6^\circ$ , and  $24^\circ\text{C}$  are first-order transitions, whereas that at  $-155^\circ$  is a second-order transition. The DSC scan also shows very sharp melting peaks at  $14^\circ$  and  $21^\circ\text{C}$  with completion of melting at  $29^\circ\text{C}$ . Trick and Ryan<sup>10</sup> have shown that the equilibrium melting point for high molecular weight poly(oxybutylene) glycol was dependent upon the degree of crystallization and post thermal treatment, with the highest melting point observed at  $51^\circ\text{C}$ .

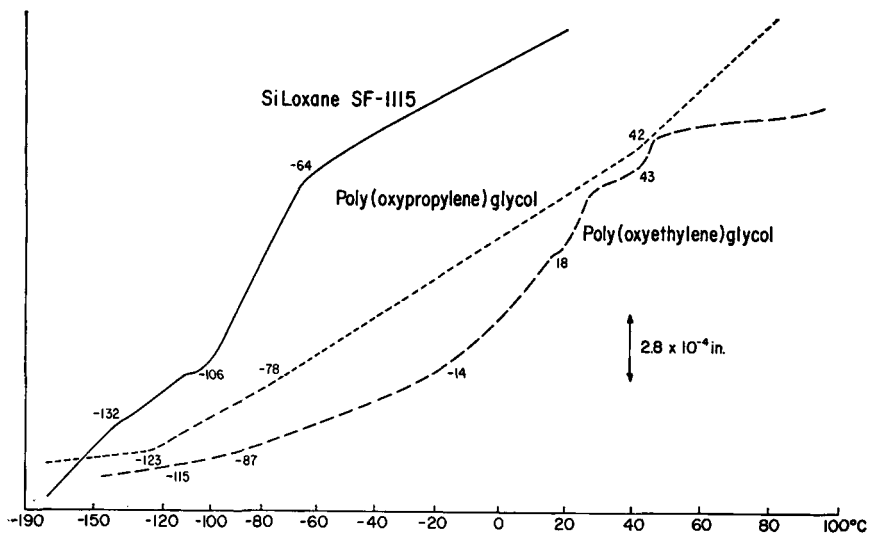
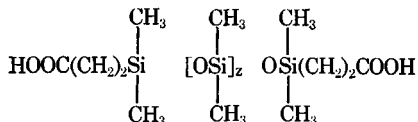


Fig. 4. The expansion behavior for poly(oxyethylene) glycol, poly(oxypropylene glycol), and siloxane SF-1115.

Poly(ethylene oxide) (Fig. 4) behaves somewhat differently as it exhibits a glass transition at  $-115^{\circ}$ , a second-order change at  $-87^{\circ}\text{C}$  and first-order changes at  $-14^{\circ}$ ,  $18^{\circ}$ , and  $43^{\circ}\text{C}$ , with melting occurring at approximately  $45^{\circ}\text{C}$ . The second-order change at  $-87^{\circ}\text{C}$  is probably due to residual low molecular weight glycol which typically shows a change in this temperature area similar to glycerine.<sup>7</sup> Polypropylene glycol, on the other hand, exhibits only two transitions, one at  $-123^{\circ}$  and one at  $-78^{\circ}\text{C}$ ; the former representing the  $T_g$  and the latter the temperature of fusion. The absence of more peaks corresponding to the other polyethers is probably due to the lack of crystallization in polypropylene glycol. The changes in heat capacity measured by the Differential Scanning Calorimeter cell showed a change at  $-67^{\circ}\text{C}$ . Finally, the expansion behavior for a polysiloxane (SF-1115) which is terminated by carboxyl groups is shown in Fig. 4. Its structure is approximately as shown below:



As with the polypropylene glycol, the polysiloxane shows one glassy transition, a first-order transition ( $-106^{\circ}\text{C}$ ) and a melting transition ( $-64^{\circ}\text{C}$ ), assigning the  $-132^{\circ}\text{C}$  transition to the glass transition. The first-order transition is unique for a polysiloxane liquid, for no first-order phase transitions have been reported at these low temperatures for siloxanes. Normally only the glassy behavior is observed which we see here at  $-132^{\circ}\text{C}$ .

Hence, it would seem that for extreme temperature properties a hydroxyl-

terminated polysiloxane could be a suitable starting backbone for low temperature behavior. Apparently the high temperature properties would depend upon the type and amount of isocyanate and other curing agent used. The absence of secondary bonding in the backbone of the siloxane would indicate a low level of mechanical property behavior whereas the polyethers, particularly poly(tetramethylene) glycol and poly(oxyethylene) glycol, would indicate a somewhat higher mechanical level of properties, with the polyester backbone exhibiting the highest degree of mechanical behavior because of its high degree of crystallinity.

### B. Thermal Behavior of Polyurethane Elastomers

When viewing the structure-property relationships of polyurethanes, it is easy to understand the effect of changes in structure when these are studied as a function of the thermal response of the urethane extension of the polyol backbone. Figure 5 shows the expansion and heat changes associated with the thermal analysis of poly(butylene adipate). The changes in linear expansion at  $-118^\circ$ ,  $-67^\circ$ ,  $-35^\circ$ , and the onset of melting at  $25^\circ\text{C}$  as well as the completion of crystalline melting at  $60^\circ\text{C}$  correlate well with the changes in heat capacity at or near the same temperatures. The change in expansion and heat capacity at  $-118^\circ\text{C}$  probably originates from the segmental motion identified with the glass transition. There are first-order changes in expansion at  $-67^\circ$  and  $-35^\circ\text{C}$ , indicating that the normal phase change attributed to  $T_g$  in polyurethanes can originate as a first-order change in the polyol backbone. These first-order changes in the polyester backbone are reflected in a significant modulus drop in a polyurethane made from poly(butylene adipate).

In considering the polyol backbone as the basic structure for the seg-

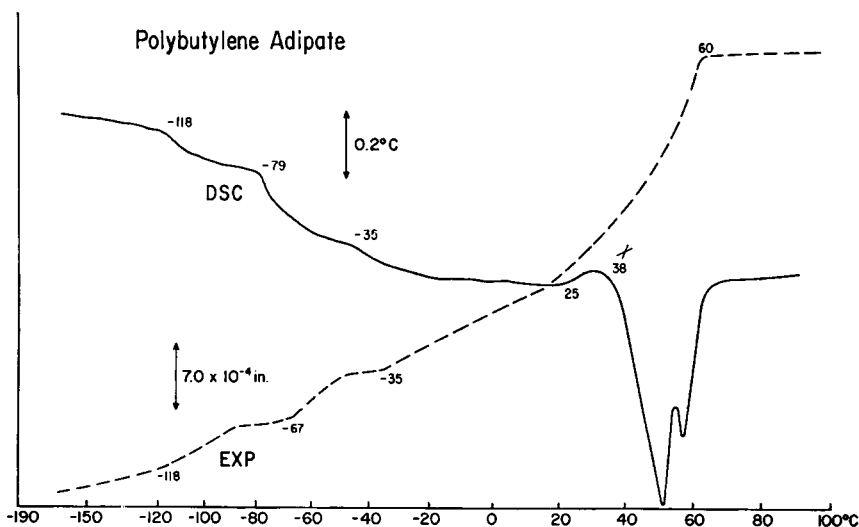


Fig. 5. The expansion and heat capacity behavior of poly(butylene adipate).

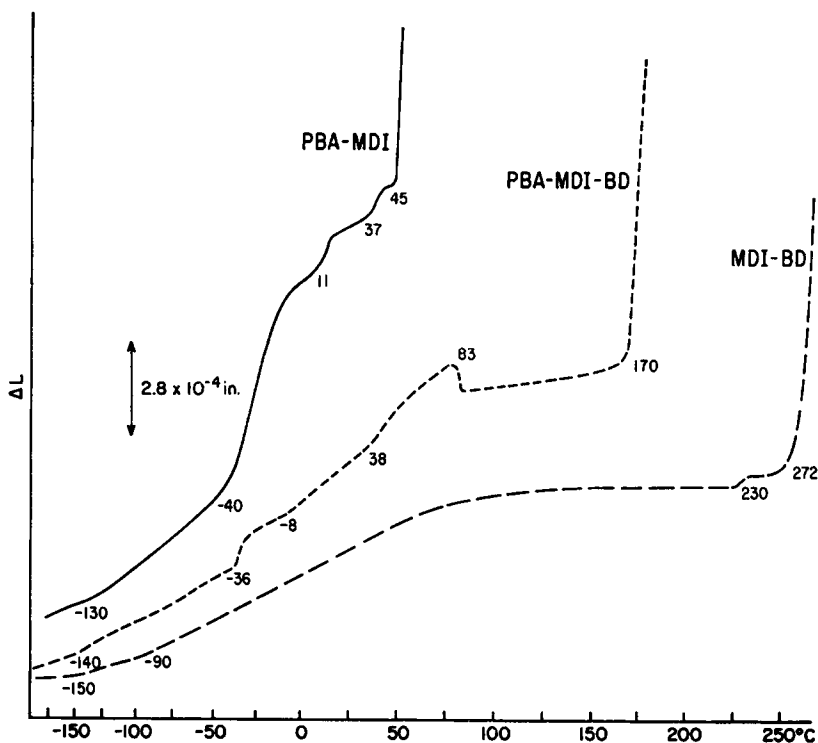


Fig. 6. The expansion behavior of PBA-MDI, PBA-MDI-BD, and MDI-BD polyurethanes.

mented elastomer, the effect of reaction of this polymeric substrate with a diisocyanate should cause some morphological changes in the thermal characteristics of the polyester backbone. In Figure 6 is shown the expansion curve from the poly(butylene adipate) extended with an equivalent amount of MDI. Here, the changes in expansion at  $-118^{\circ}$  and  $-35^{\circ}\text{C}$  are shifted to  $-130^{\circ}$  and  $-40^{\circ}\text{C}$ , respectively. The change in expansion at  $-67^{\circ}\text{C}$  in the native polyol is no longer observable, and it is probably merged with the  $-35^{\circ}\text{C}$  transition in the polyester, resulting in the  $-40^{\circ}\text{C}$  transition which is apparently much sharper than the  $-35^{\circ}$  or  $-67^{\circ}\text{C}$  transition. A new transition occurs near  $11^{\circ}\text{C}$  and the onset of melting shifts from  $25^{\circ}$  to  $37^{\circ}\text{C}$  with complete melting at  $45^{\circ}\text{C}$ . Consequently, reacting the poly(butylene adipate) with MDI lowers the melting point of the polyester backbone. The shifting of the  $-118^{\circ}\text{C}$  change in expansion of the poly(butylene adipate) to  $-130^{\circ}\text{C}$  for the polymer from the reaction with MDI is probably due to the poorer fit of the polyester segments in forming a high molecular weight polyurethane. Also, the shift from  $-35^{\circ}\text{C}$  to a more emphatic change at  $-40^{\circ}\text{C}$  in the urethane reflects again the lowering of a phase transition by molecular constraints. While it appears that the changes in linear expansion at  $-118^{\circ}\text{C}$  confirm the glassy transition for the



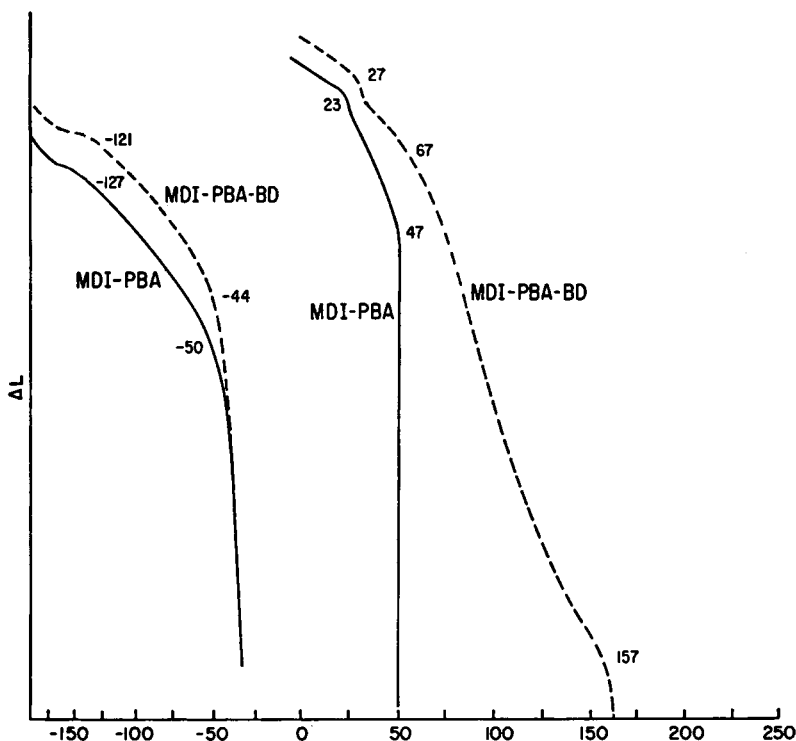


Fig. 7. The tensile strain behavior of PBA-MDI and PBA-MDI-BD polyurethanes.

polyester backbone, the apparent glass transition for the poly(butylene adipate)-MDI urethane elastomer is probably  $-130^{\circ}\text{C}$ . The abrupt changes in expansion near  $-40^{\circ}\text{C}$  for the urethane and  $-35^{\circ}\text{C}$  for the polyester indicates that some type of first-order phenomenon is occurring, illustrating a behavior similar to Figure 1.<sup>7</sup>

Curve 2 in Figure 6 illustrates the effect of adding hard block sequences to the polyester backbone, and represents a polyurethane made from 1.0 mole polyester, 3.2 moles MDI and 2.0 moles of 1,4-butanediol. The changes in expansion again shift downward in temperature for the low temperature transition, that is, the glass transition for the urethane elastomer in Curve 2 is now  $-140^{\circ}\text{C}$ , maintaining approximately the same temperature for the apparent first-order transition near  $-40^{\circ}\text{C}$ . A third expansion change occurs at  $-8^{\circ}\text{C}$ , and the change in expansion at  $38^{\circ}\text{C}$  corresponds with the onset of melting for the poly(butylene adipate)-MDI copolymer. When adding the excess MDI and BD, hard block sequences are formed in the urethane, and we see the expansion response to the hard block sequences indicated as a softening at  $83^{\circ}$  and a complete melting of the polymer at  $170^{\circ}\text{C}$ . Curve 3 illustrates a copolymer formed from MDI and BD to illustrate the hard block sequence by itself. Here again the secondary transition is now at  $-90^{\circ}\text{C}$ . There is a relaxation near  $80^{\circ}\text{C}$ ;

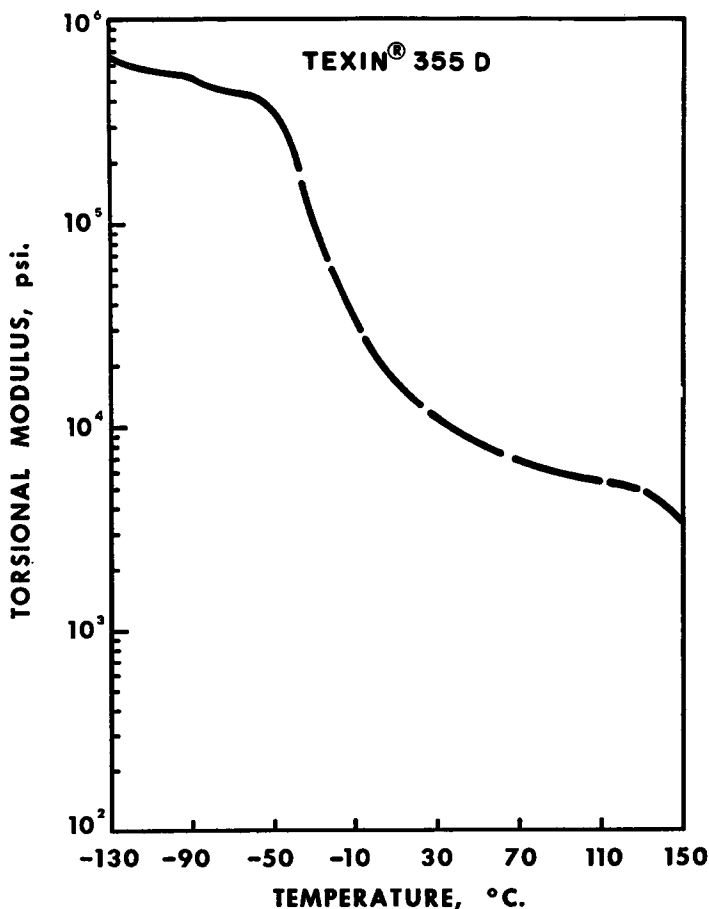


Fig. 8. Torsional modulus versus temperature for MDI-PBA-glycol polyurethane (Texin 355D).

however, there are no significant volume changes until 230°C and 272°C, the latter of which is the melting point of the copolymer. It is readily apparent then that the normal urethane elastomer represented by Curve 2 is truly a hybrid of soft block indicated by Curve 1 and hard block behavior indicated by Curve 3 (Fig. 6), and it would be reasonable to expect that the effects of each are additive on the formulated urethane elastomer. The MDI-BD copolymer is a hard crystalline substance, whereas the poly-(butylene adipate)-MDI copolymer is a very soft cheesy elastomer.

In Figure 7 are shown the changes in tensile strain at constant stress according to conditions previously reported.<sup>6</sup> Only slight differences are noticeable when measured under stress near -121°, -44°C and +27°C. The correspondence between the expansion and tensile measurements is good, and the effect of stressing the sample shows in the observation of each transition at a somewhat higher temperature than when measured in ex-

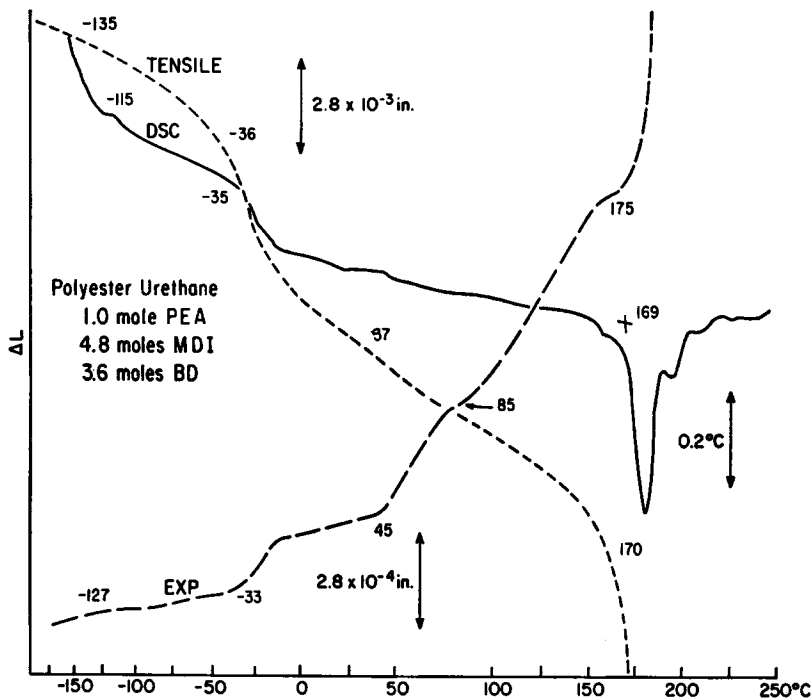


Fig. 9. The correspondence of expansion, tensile strain, and heat capacity data for a polyester urethane.

pansion. The changes near  $-121^{\circ}\text{C}$  are due to the glass transition of the bulk polymer, whereas those near  $-44^{\circ}\text{C}$  originate from a first-order change in the polyester backbone. The tensile changes near  $27^{\circ}\text{C}$  are not readily explainable, but those near  $67^{\circ}\text{C}$  are most likely due to the complete fusion and increased mobility of the polyester backbone. The  $157^{\circ}\text{C}$  change in strain is the usual onset of fusion.

The torsional modulus vs. temperature for a poly(butylene adipate)-MDI-glycol extended polyurethane elastomer is shown in Figure 8 (Texin 355D). The Texin urethane elastomer shows the  $-90^{\circ}\text{C}$  transition typical of the  $T_g$  assigned to the PBA backbone, wherein the presence of excess urethane groups restricts the normally low temperature of segmental motion, raising the  $T_g$  from  $-118^{\circ}\text{C}$  for the soft block to  $-90^{\circ}\text{C}$  for the bulk urethane elastomer. The incorporation of hard block urethane segments will raise the bulk  $T_g$ , and this glassy behavior has been identified with changes in mechanical, expansion, and heat capacity data.<sup>7</sup> The modulus drop at this temperature is about 200,000 psi, whereas the modulus change near  $-40^{\circ}\text{C}$  is about 350,000 psi. A first-order transition is likely to cause a greater modulus drop than a second-order transition.

In Figure 9 are shown the correspondence of expansion, heat capacity and tensile strain data for an MDI-poly(ester-urethane). The correspondence

in these properties is excellent, and observation of the discrete endotherms in the region of polymer melting gives credence to the fact that urethanes can be partially crystalline.

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