

# The Effect of Annealing on the Thermal and Dynamic Mechanical Properties of Para-Tetramethyl Xylene Diisocyanate-Based Polyurethanes

G. M. STACK<sup>1,\*</sup> and L. L. BEUMEL<sup>2</sup>

<sup>1</sup>Naval Research Laboratory, Underwater Sound Reference Detachment, P.O. Box 568337, Orlando, Florida 32856, and <sup>2</sup>TRI/TESSCO, 3909 S. Summerlin Ave, Orlando, Florida 32806

## SYNOPSIS

A series of polyurethane elastomers based on the para-Tetramethyl Xylene diisocyanate group were annealed at temperatures from 100 to 180°C. These high-temperature exposures were found to raise significantly the peak melting point of the urethanes that contained crystalline hard segments. The corresponding enthalpy of fusion was found to decrease after annealing at the higher temperatures. In most cases, the annealings caused a slight increase in the soft-segment glass transition temperature, indicating that some increase in phase mixing had occurred. Dynamic mechanical measurements indicated that the annealings caused a slight reduction in the Young's modulus and a broadening of the loss-tangent peak. The broadening of the loss-tangent peak can be attributed to the increased phase mixing induced by the annealings. The large increases in melting point induced by annealing do not appear to significantly affect the subsequent dynamic mechanical properties.

## INTRODUCTION

Polyurethanes are linear segmented copolymers, which consist of alternating hard and soft segments. The soft segment is commonly a low molecular weight polyether or polyester chain. The hard segment is composed of diisocyanate molecules condensed with a low molecular weight diol or diamine. The properties of these materials are largely governed by the phase separation of the hard and soft segments of the polyurethane. This phase separation typically results in the formation of hard-segment domains, which are dispersed in a rubbery matrix.<sup>1</sup> Compositional variables are known to affect the degree of phase segregation, hard-segment domain organization, and consequently the polyurethane's

properties.<sup>2-3</sup> In addition, it has been found that high-temperature thermal treatment (annealing) can induce significant changes in the thermal properties of polyurethane elastomers.<sup>4-11</sup> These changes were attributed to an increase in the degree of order of the hard-segment domains and in some cases to a change in the extent of phase separation in the urethane. Factors such as the amount of time at the annealing temperature, the rate of cooling after annealing, and the time that the urethane was allowed to equilibrate at ambient temperature were found to affect the resultant thermal properties. These studies were mainly performed on polyurethanes based on aromatic isocyanates such as diphenyl methane diisocyanate (MDI) or toluene diisocyanate (TDI).

A class of diisocyanate molecules in which the isocyanate groups are bonded to aliphatic carbons is now commercially available.<sup>12-14</sup> In contrast to the aromatic isocyanate polyurethanes, there has been little systematic investigation of the effect of composition or thermal treatment on the properties of polyurethanes based on these aliphatic isocyanates. A series of polyurethane model compounds, based

\* Now employed at Eastman Chemical Co., P.O. Box 1972, Kingsport, Tennessee 37662. Correspondence should be addressed to: Technical Information Office, Department of the Navy, Naval Research Laboratory, Underwater Sound Reference Detachment, P.O. Box 568337, Orlando, Florida 32856.

on the meta and para isomers of the aliphatic isocyanate, tetramethyl xylene diisocyanate (TMXDI), have been prepared. A study of the effect of compositional parameters on the dynamic mechanical properties of these urethanes has been performed.<sup>12-13</sup> Many of the observed variations in dynamic mechanical properties of these urethanes were attributed to differences in the relative extent of phase separation present in the urethanes.

As an extension to this work, the effect of annealing on the structure and properties of these urethanes has been investigated. Polyurethanes based on the symmetric para isomer of TMXDI were used in these studies. Initially, the effect of annealing on the hard-segment organization was investigated by means of high-temperature calorimetric measurements. Calorimetric measurements were then made at lower temperatures to measure the soft-segment glass transition temperatures of the annealed polyurethanes. These results were used to determine if significant differences in the extent of phase separation had occurred during the annealing process. Finally, experiments were made on selected samples to determine the effects of annealing on the dynamic mechanical properties of these polyurethanes.

## EXPERIMENTAL

The polyurethane prepolymers were obtained from American Cyanamid Company. These prepolymers were synthesized by reacting an excess of diisocyanate with the polyol, as described previously.<sup>14</sup> Prepolymers were made with differing amounts of excess isocyanate in order to obtain polyurethanes with varying hard-segment contents. Polycaprolactone or hydroxy-terminated polybutadiene, each with a molecular weight of approximately 2000 g/mol, were used as the polyol soft segment. These prepolymers were cured into polyurethane elastomers using the liquid diamine, diethyl toluene diamine (DETDA), or the dialcohol, 1,4-butanediol. A small amount (0.01%–0.04%) of the metal catalyst, ferric acetylacetonate, was added to each of the curatives used. The prepolymer and curative were heated to 70°C and were degassed prior to mixing. To form a cured polyurethane, the prepolymer and curative were mixed thoroughly, degassed again and poured into a preheated mold. Once in the mold, the sample was degassed briefly to eliminate any remaining voids. The polyurethane was allowed to cure at 70°C for 24 h, was demolded, and was postcured at ambient conditions for at least two weeks. The composition

**Table I The Composition of Polyurethane Elastomers Studied**

Soft Segment Component	Hard Segment Content	Curative
Polycaprolactone	23%	Butanediol
Polycaprolactone Hydroxyterminated	30%	Butanediol
Polybutadiene	24%	Butanediol
Polycaprolactone	23%	DETDA
Hydroxyterminated Polybutadiene	24%	DETDA

of each of the polyurethanes used in this study are listed in Table I.

Calorimetric measurements were made using a Perkin Elmer model DSC-4 Differential Scanning Calorimeter. The polyurethane endotherms were measured from 50 to 250°C using a heating rate of 20°C/min and sample masses in the range of 10 mg. Additional low temperature scans from -100 to 100°C were made using liquid nitrogen as a coolant and a range of heating rates from 40 to 20°C/min. Annealings were performed directly in the DSC by heating at 10°C/min to a selected temperature and maintaining the sample at this temperature for a specific length of time. Larger samples, suitable for dynamic mechanical analysis, were annealed under vacuum in an oven that was preset at the selected temperature. The urethanes were maintained at ambient temperature for at least 48 h after annealing before any measurements were made.

Dynamic mechanical properties were measured by means of a resonance method developed at our laboratory.<sup>15</sup> The principle of this method is based upon measuring the transmissibility of a mass-loaded rod with high internal damping undergoing longitudinal sinusoidal excitation. The sample is harmonically excited using discrete frequency excitation. By solving the equations of motion within the sample, Young's modulus and the loss tangent are obtained. The values obtained at resonance were also used as seed values to solve the equation of motion at frequencies other than resonance. This dynamic data is extrapolated to higher frequencies using a time-temperature superposition principle.<sup>16</sup> Lower temperature dynamic mechanical data were obtained on a Polymer Laboratories Dynamic Mechanical Thermal Analyzer (DMTA), at frequencies from 1 to 10 Hz. The sample chamber was cooled to -80°C using a liquid nitrogen cryogenic cooler

and data were taken while the sample was being heated to 50°C. Heating rates from 1 to 4°C/min and a strain of 4% were employed.

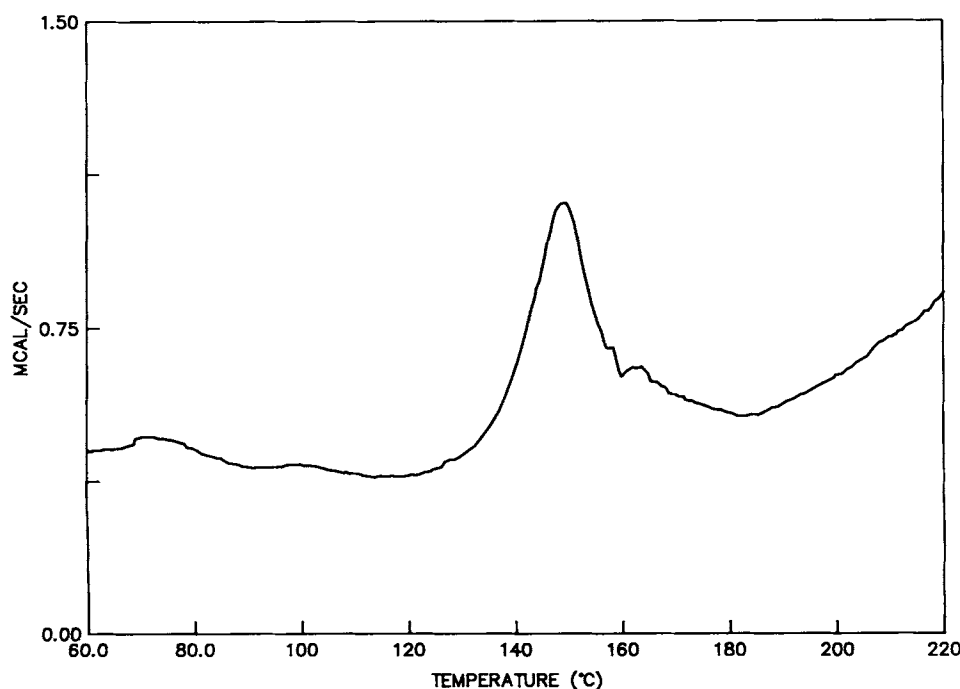
## RESULTS AND DISCUSSION

### Calorimetric Analysis

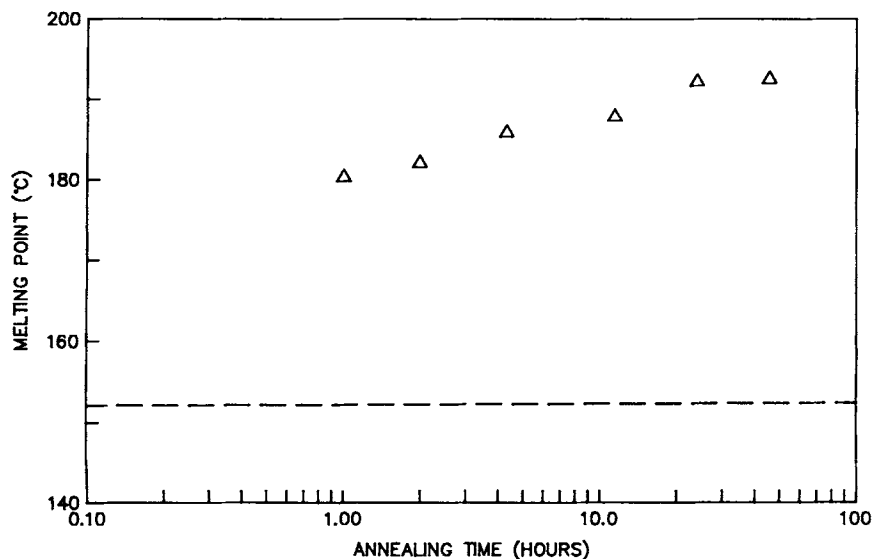
Initially, high-temperature DSC scans were run on each of the samples listed in Table I. No endothermic peaks were observed in the polyurethanes that had been obtained with DETDA as the curative. Poorly defined high-temperature transitions were observed in these urethanes, but these transitions could not be unambiguously attributed to the hard segment. A broad endothermic peak was observed in each of the polyurethanes that were cured with 1,4 butanediol. As an example, the DSC scan obtained from the polycaprolactone-based polyurethane, with a hard-segment content of 30%, is shown in Figure 1. A series of model compounds based on *para*-TMXDI have previously been found to form crystalline solids, which melted in the range from 150 to 200°C.<sup>17</sup> On the basis of those results, it is reasonable to attribute the endothermic peak observed in these *p*-TMXDI based urethanes to be due to the melting of microcrystalline domains within the ure-

thane. Although the breadth of this endothermic peak indicates that the melting occurs over a wide temperature range the endothermic peak temperature will be taken as the average melting point for each polyurethane. The DETDA used in the present study is actually a mixture of two isomers. This isomerism will result in the formation of unsymmetric hard segments and may explain the fact that no hard-segment crystallinity is formed in the DETDA-cured urethanes.

In the first series of experiments, the effect of annealing time on the subsequent thermal properties of a crystalline polyurethane was investigated. These studies were performed on the polycaprolactone-based polyurethane, whose DSC scan was shown in Figure 1. Samples of this urethane were annealed at 160°C for selected times and then were rapidly cooled at 20°C/min. The effects of these thermal treatments were then determined by subsequent heating of the annealed samples in the DSC. These results are summarized in Figures 2 and 3, in which the melting temperature and enthalpy of fusion of the endothermic peak are plotted as a function of annealing time. The peak temperature and enthalpy of fusion of the unannealed polyurethane are also shown in Figures 2 and 3, to serve as a reference. After the shortest annealing time of 1 h, the entire



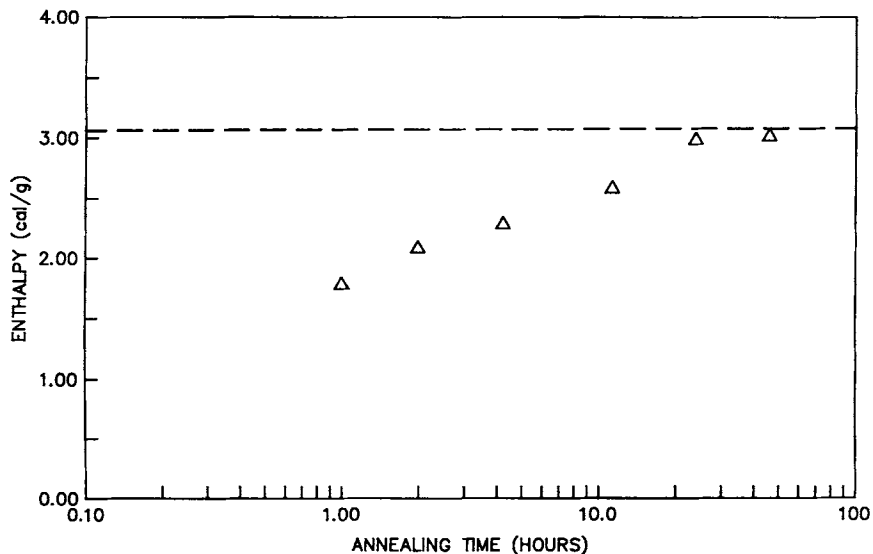
**Figure 1** Plot of the high-temperature DSC scan obtained for a polycaprolactone-based polyurethane containing a hard-segment content of 30% and cured with butanediol.



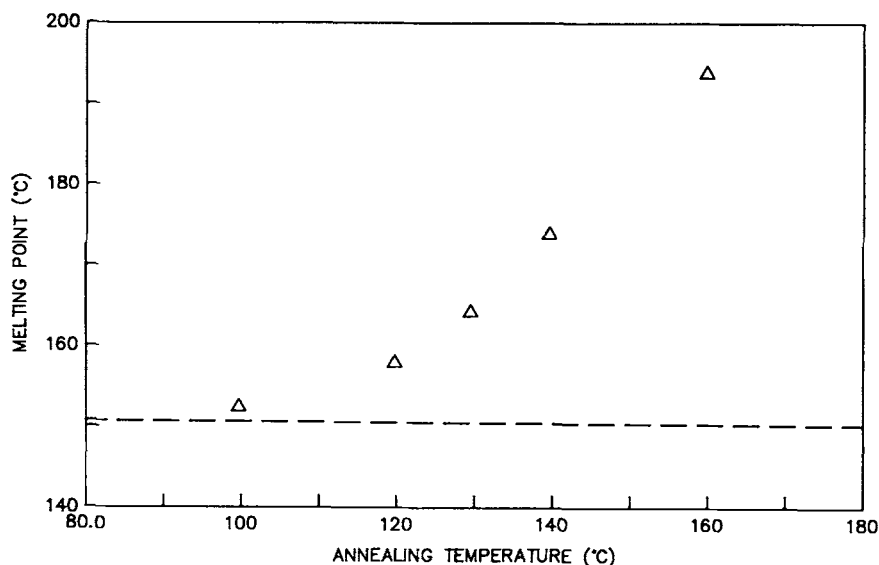
**Figure 2** Plot of the melting temperature as a function of annealing time for a polycaprolactone-based polyurethane annealed at 160°C. The peak temperature for the unannealed urethane is designated by the dashed line.

endothermic peak shifted to higher temperatures and the peak position increased by almost 30°C. Annealing for longer times caused a continuous increase in the peak position and, after the longest annealing time of 46 h, the peak temperature became more than 40°C higher than was measured for the unannealed urethane. Annealing for short times decreased the enthalpy of fusion of the endothermic peak. However, the enthalpy increased with in-

creasing annealing time and the sample annealed for the longest time had an enthalpy approximately equal to the unannealed sample. Both the melting temperature and enthalpy of fusion increased very slowly at the longer annealing times. These results indicate that the morphological changes induced by the annealing process have essentially been completed over this time scale. Therefore, an annealing time of 24 h was selected for the remaining experi-



**Figure 3** Plot of the enthalpy of fusion as a function of annealing time for a polycaprolactone-based polyurethane annealed at 160°C. The enthalpy of the unannealed urethane is designated by the dashed line.



**Figure 4** Plot of the melting temperature as a function of annealing temperature for a polycaprolactone-based polyurethane. The peak temperature of the unannealed polyurethane is designated by the dashed line.

ments. Several samples of this urethane were then annealed at 160°C for 24 h and were cooled to ambient temperature at cooling rates ranging from 1 to 40°C/min. The resultant melting point and enthalpy of fusion of the annealed urethanes was not found to be significantly affected by the rate of cooling. A cooling rate of 20°C/min was chosen for the remainder of the annealing experiments.

The results obtained after annealing this urethane with a hard-segment content of 30% at temperatures in the range from 100 to 160°C are shown in Figure 4. The lowest annealing temperature of 100°C causes only a slight increase in the melting point. Larger increases in the melting temperature are induced as the annealings are performed at progressively higher temperatures. At the highest annealing temperature of 160°C, the melting temperature is increased by more than 40°C above that observed in the unannealed sample. These increases in the melting temperature are comparable to those that have been observed in annealing studies of MDI-based polyurethanes.<sup>4-5</sup> However, in the MDI studies, it was the endothermic peak associated with the disruption of short range order in the urethane that was found to be increased by annealing. The endotherm, which corresponded to the melting of hard-segment crystallites, occurred at higher temperatures and was not appreciably affected by the annealing.<sup>5</sup> Annealing studies were also performed on this urethane after recrystallization from methylene chloride. This recrystallization was found to

raise the endothermic peak temperature from 151 to 175°C. The results obtained after annealing this recrystallized sample are summarized in Table II. Increases in the endothermic peak temperature are induced in the recrystallized sample after annealing, but the increase is smaller due to the higher melting temperature of the unannealed sample.

Annealing studies were performed on the other butanediol-cured polyurethanes listed in Table I; the results are summarized in Tables III-IV. The polycaprolactone-based polyurethane, with a lower hard segment of 23%, also underwent larger increases in

**Table II** The Effect of Annealing on a Polycaprolactone-Based Polyurethane Cured With Butanediol and Containing a Hard Segment Content of 30% After Recrystallization from Methylene Chloride

Annealing Temperature (°C)	Endothermic Peak Temperature (°C)	Enthalpy of Fusion (cal/g)	Glass Transition Temperature (°C)
Unannealed	174.6	3.3	-50.5
120	171.4	3.4	-50.4
130			-50.4
140	180.9	4.0	
150			-49.2
160	196.7	2.9	
170	201.0	2.3	-46.7

**Table III The Effect of Annealing on a Polycaprolactone-Based Polyurethane Cured With Butanediol and Containing a Hard Segment Content of 23%**

Annealing Temperature (°C)	Endothermic Peak Temperature (°C)	Enthalpy of Fusion (cal/g)	Glass Transition Temperature (°C)
Unannealed	134.8	1.6	-50.8
100	131.4	2.7	-50.9
120	150.9	2.3	-51.3
140	168.4	1.9	-50.9
150	174.9	1.6	
160	192.7	1.2	-48.2

its melting temperature after annealing. For this urethane, the position of its melting point was increased by over 50°C as the annealing temperature was increased from 100 to 160°C. An even larger increase in the melting temperature was induced in the polyurethane containing hydroxy-terminated polybutadiene as its soft block component. As shown in Table IV, the peak temperature underwent a continuous increase as the annealings were performed at progressively higher temperatures. The highest annealing temperature of 180°C caused an increase of over 60°C in the melting temperature.

The large increases in melting point can be explained by the assumption that these annealings cause an increase in the average size of the hard-segment crystallites. Alternatively, it is possible that annealing results in the formation of more distinctly defined hard-segment phases. Hard-segment phases, which are better organized and more phase separated than soft segment phases, would be expected to have a higher melting point. Without detailed morphological studies it is not possible to determine which of these mechanisms is the main cause for the observed melting point increases. However, it is likely that both of these morphological changes are occurring and contribute to the observed increases in melting point.

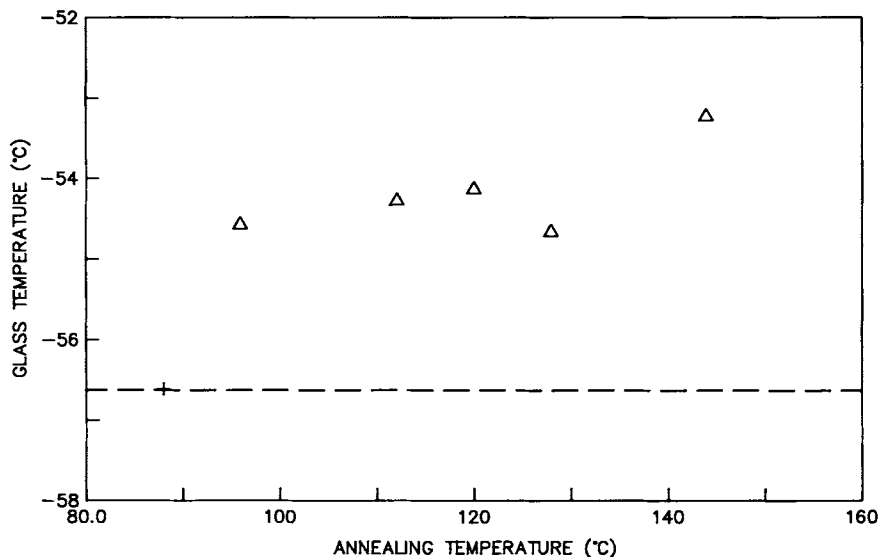
The enthalpy of fusion of the melting peak was also measured for each of the annealed polyurethanes. The measurement of the enthalpy is somewhat inaccurate due to the large breadth of the melting peaks. These estimated enthalpies of fusion for the annealed polyurethanes are listed in Tables II-IV. For the polycaprolactone-based polyurethane with 23% hard-segment content, the enthalpy of fusion is increased by the lower annealing temperatures. The enthalpy is found to decrease with in-

creasing temperature and the urethane annealed at the highest temperature is found to have a slightly lower enthalpy than the unannealed sample. Similar behavior is observed for the urethane with a higher, hard-segment content of 30%, as shown in Table II. For this urethane, the lower annealing temperatures cause only a slight increase in enthalpy and annealing at the highest temperature of 170°C, resulting in an enthalpy significantly less than is obtained in the unannealed urethane. The polyurethane based on hydroxy-terminated polybutadiene is found to undergo a continuous decrease in enthalpy as a function of annealing temperature. For this urethane, all of the annealed samples had a lower enthalpy of fusion than was measured before annealing. The observed decreases in enthalpy of fusion at the higher annealing temperatures may be partially due to a broadening of the melting curve. At these annealing temperatures, the peak of the melting curve is raised to a much higher temperature. Therefore, the melting of any remaining crystallites with lowering melting points would not be discernible from the baseline, which would result in an erroneously low enthalpy of fusion. However, it is clear that annealing does not cause large changes in the enthalpy, as was observed in previous annealing studies.<sup>4</sup> In MDI polyurethanes, annealing was found to increase the enthalpy of the endothermic peak by 200 to 300%.

A low-temperature transition was observed in each of the urethanes listed in Table I and was attributed to the glass transition of the polycaprolactone or polybutadiene soft segment. The position of this glass transition was measured subsequent to the high-temperature exposures. The results obtained for the polycaprolactone-based polyurethane with 30% hard-segment content are summarized in Figure 5. The lowest annealing temperature of 100°C

**Table IV The Effect of Annealing on a Hydroxyterminated Polybutadiene-Based Polyurethane Cured With Butanediol and Containing a Hard Segment Content of 24%**

Annealing Temperature (°C)	Endothermic Peak Temperature (°C)	Enthalpy of Fusion (cal/g)	Glass Transition Temperature (°C)
Unannealed	141.8	2.8	-77.4
120	151.9	2.5	-76.4
140	178.3	1.9	-76.1
160	204.3	1.9	-75.6
180	217.6	1.4	-75.4

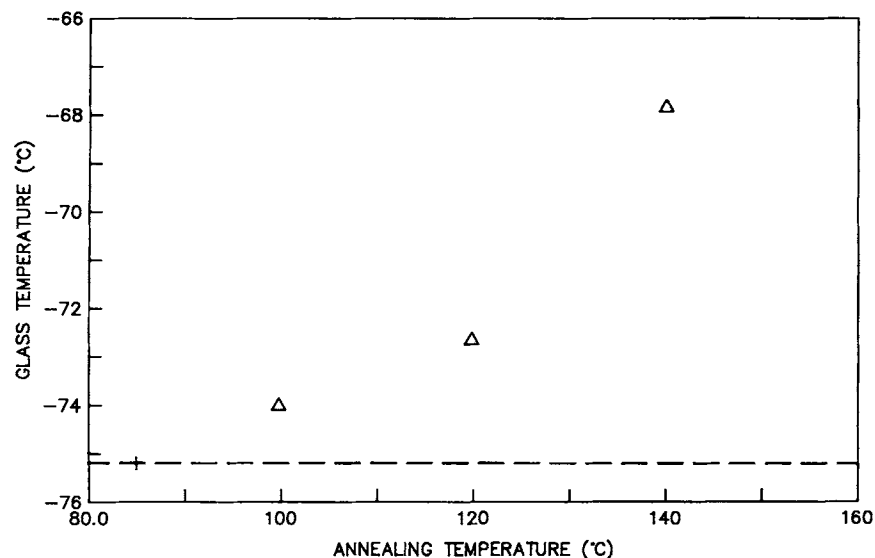


**Figure 5** Plot of the glass transition temperature as a function of annealing temperature for a polycaprolactone-based polyurethane. The glass transition temperature of the unannealed urethane is designated by the dashed line.

induces a significant increase in the glass transition temperature. Increasing the annealing temperature to 160°C causes further increases in the glass transition temperature. Over the range of annealing temperatures, an increase of almost 4°C in the glass transition temperature is induced. The effects of annealing on the glass transition temperatures of the other butanediol-cured polyurethanes are summarized in Tables II–IV. The polycaprolactone-based polyurethane with 23% hard-segment content was found to have its glass transition temperature relatively unaffected by the lower annealing temperatures. However, a significant increase in the glass transition was observed after annealing at higher temperatures. Annealing at the highest temperature of 160°C was found to increase the glass transition temperature of the polycaprolactone soft segment by 2.6°C. The urethane based on hydroxy-terminated polybutadiene exhibits a continuous increase in its glass transition temperature as a function of annealing temperature. However, only a 2°C increase in glass transition temperature is observed for this urethane over the entire range of annealing temperatures. In the annealing studies of MDI-based polyurethanes, a much larger increase in the soft-segment glass transition was found if DSC scans were made immediately after cooling from the annealing temperature.<sup>5</sup> However, if the sample was allowed to equilibrate at ambient temperature for at least 24 h, then the increase in glass transition temperature was on the order of 2–3°C, which is comparable to the present results.

An increase in the glass transition temperature of a polyurethane soft segment normally indicates that there is an increased amount of mixing between the hard- and soft-segment phases of the polyurethane. The small increases of 2 to 4°C in the glass transition temperature suggest that annealing may induce the mixing of a few hard segments into the soft-segment phase. Such a phase mixing is consistent with the previous discussion of the morphological changes induced by annealing. If the hard-segment crystallites increase in size, it is likely that some of the smaller hard segments could not be incorporated into these larger crystallites and would dissolve into the soft segments. Similarly, if annealing causes the formation of better defined hard-segment phases, some of the smaller hard segments may be excluded.

Low-temperature DSC scans were also made on the samples of the polycaprolactone-based polyurethane, which had been annealed at 160°C for various annealing times. The glass transition temperature was found to increase as a function of annealing time and was close to a limiting value at the longer annealing times. This behavior is very similar to the effect of annealing time on the melting point and enthalpy of fusion, which had been shown in Figures 2 and 3. The effect of the rate of cooling from the annealing temperature on the resultant glass transition temperature was also investigated. The same polycaprolactone-based urethane with a hard-segment content of 30% was used in this study. Several samples of this urethane were annealed at 160°C for 24 h and then were cooled at a range of rates



**Figure 6** Plot of the glass transition temperature as a function of annealing temperature for a polybutadiene-based polyurethane cured with DETDA. The glass transition temperature of the unannealed urethane is designated by the dashed line.

from 1 to 40°C/min. The glass transition temperature of the resultant urethanes were not found to vary significantly as a function of the cooling rate employed.

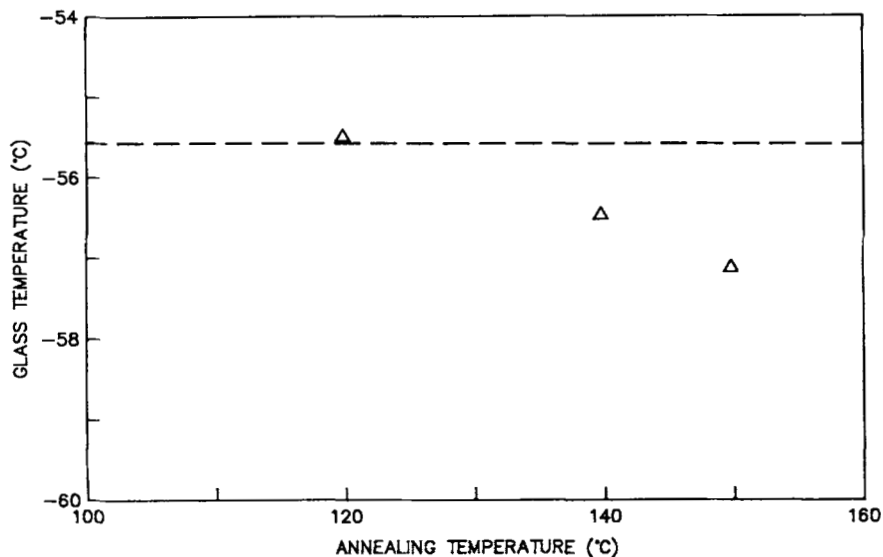
Annealings were also performed on the two polyurethanes listed in Table I, which had been made with the diamine curative, DETDA. No endothermic peaks were observed in the DSC scans of the annealed urethanes as was the case for the unannealed samples. The soft-segment glass transition temperatures of these urethanes were also measured subsequent to annealing. The polyurethane based on hydroxy-terminated polybutadiene was found to have its glass transition temperature increased by these annealings as shown in Figure 6. The observed increases are even greater than the increases observed for the corresponding crystalline polyurethane, which was made using butanediol as the curative. The results obtained for the DETDA-cured polyurethane, based on polycaprolactone, are summarized in Figure 7. In this case, the annealings cause a slight decrease in the glass transition temperature of the urethane.

### Dynamic Mechanical Measurements

Dynamic mechanical measurements were made on selected polyurethanes both before and after high-temperature annealings. These measurements were made as a function of frequency on the resonance apparatus and over a wide range of temperatures by

means of the Polymer Laboratories DMTA. The initial measurements were made on the polycaprolactone-based urethane with 30% hard-segment content, which was cured with butanediol. The dynamic Young's modulus of this urethane, measured before and after annealing at 150°C, is shown in Figure 8 as a function of frequency. At this reference temperature of 5°C, the soft-segment glass transition would occur at a very high frequency. The increase in modulus at the higher frequencies is due to the approach of this glass transition. It is apparent from Figure 8 that the modulus is not significantly changed by the annealing. This observation is surprising because of the large increase in melting point that is induced by annealing. This increase in melting point indicates that improved organization of the hard phases has occurred. The hard-segment phases provide mechanical reinforcement in a polyurethane and help to give it a higher rubbery modulus. These more ordered hard segments would be expected to provide greater reinforcement and should result in an increase in the modulus. In actuality, the modulus of the annealed polyurethane is slightly lower at the lower frequencies in Figure 8. The corresponding loss tangents of these polyurethanes, both before and after annealing, are plotted in Figure 9. The thermal treatment is seen to cause a slight increase in the loss tangent over the entire frequency range of measurement. This observation is consistent with the previous assumption that the annealing causes an increase in the



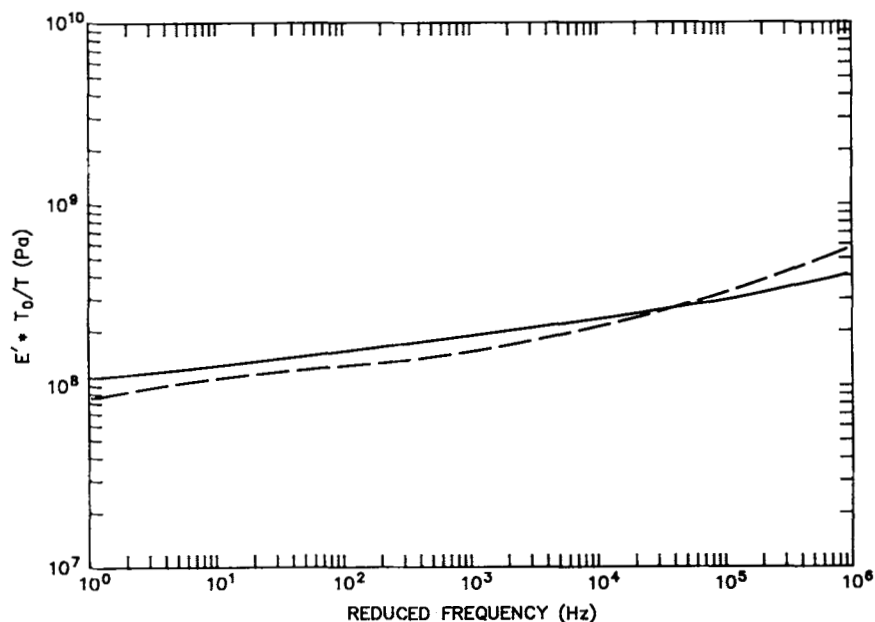


**Figure 7** Plot of the glass transition temperature as a function of annealing temperature for a polycaprolactone-based polyurethane cured with DETDA. The glass transition temperature of the unannealed urethane is designated by the dashed line.

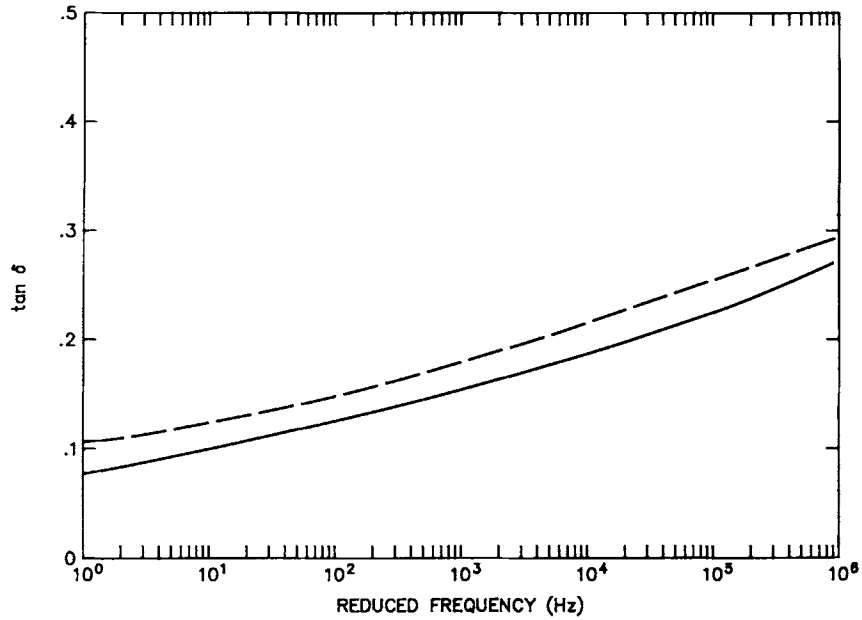
phase mixing between the hard and soft segments. A more phase-mixed system would have the high loss associated with the soft-segment glass transition broadened to higher temperatures and lower frequencies and would result in a higher loss tangent over the range of frequencies plotted in Figure 9.

Dynamic mechanical measurements were also

made on the same two samples as a function of temperature at a frequency of 1 Hz on the DMTA. The dynamic Young's moduli and loss tangents, measured as a function of temperature, are shown in Figure 10. Similar to the high-frequency results, the annealed sample has a slightly lower modulus over a wide temperature range. At temperatures below



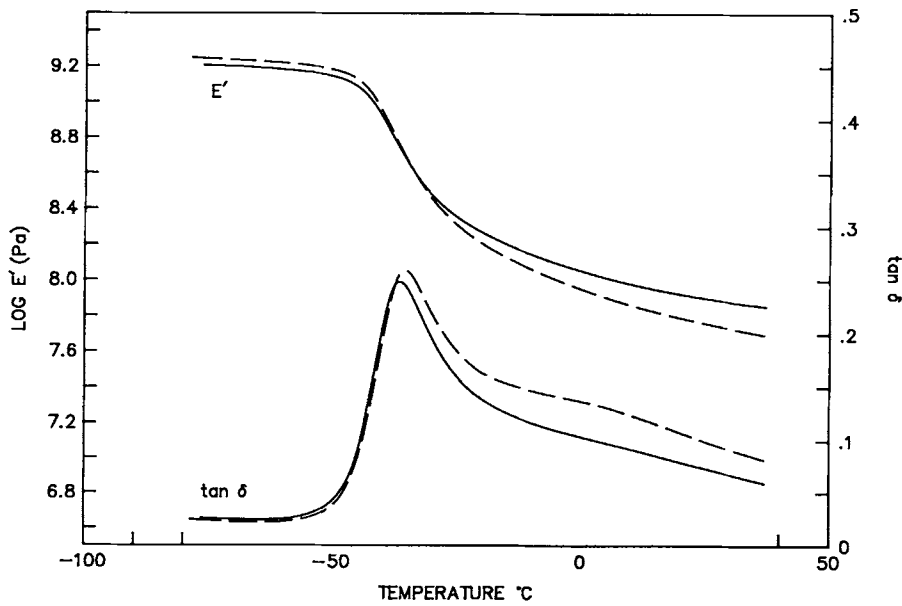
**Figure 8** Plot of the dynamic Young's modulus as a function of frequency at 5°C for a polycaprolactone-based urethane; as cured (solid line), after annealing at 150°C (dashed line).



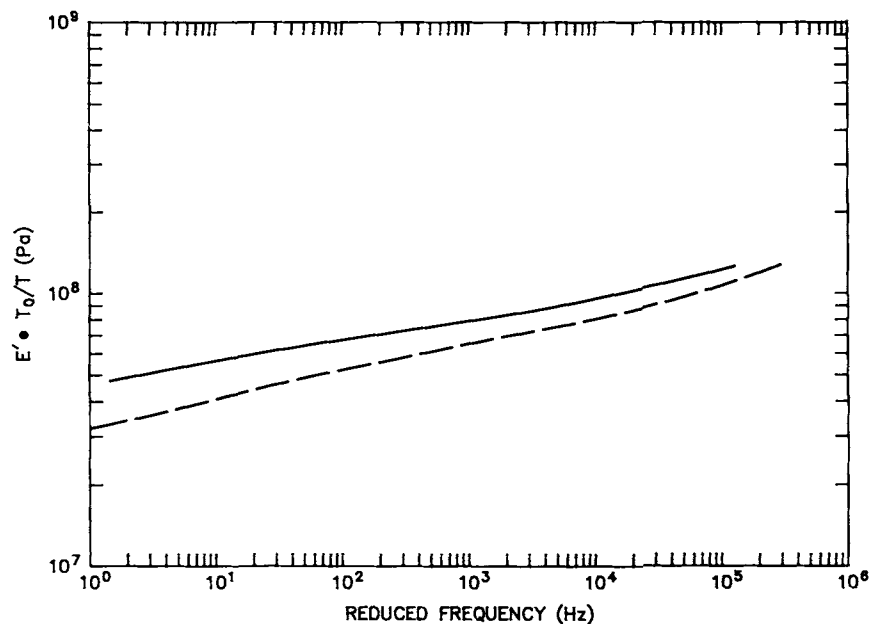
**Figure 9** Plot of the loss tangent as a function of frequency at 5°C for a polycaprolactone-based urethane; as cured (solid line), after annealing at 150°C (dashed line).

-50°C, the moduli became virtually the same. This is the region below the glass transition of the polycaprolactone soft segment. The entire peak in the loss-tangent curve associated with the soft-segment glass transition can be observed in Figure 10. The peak of the tan-delta curve is shifted to higher tem-

peratures in the annealed sample. This observation is consistent with the increase in the glass transition measured by calorimetry. It is also clear that the annealed sample has a slightly greater loss tangent at higher temperatures, which is consistent with the premise that the annealing promotes increased



**Figure 10** Plot of the dynamic Young's modulus and loss tangent as a function of temperature measured at 1 Hz for a polycaprolactone-based urethane; as cured (solid lines), after annealing at 150°C (dashed lines).

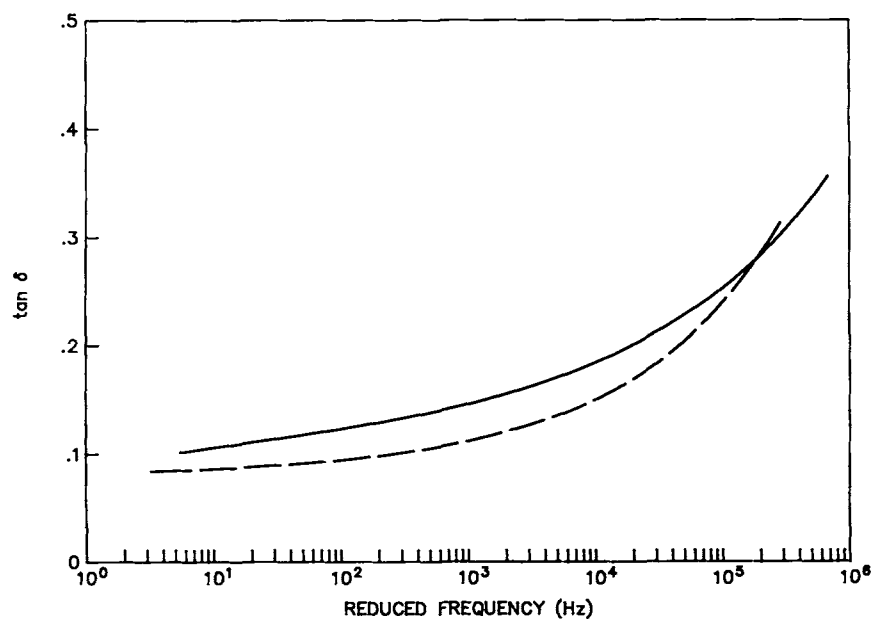


**Figure 11** Plot of the dynamic Young's modulus as a function of frequency at 5°C for a polybutadiene-based urethane; as cured (solid line), after annealing at 150°C (dashed line).

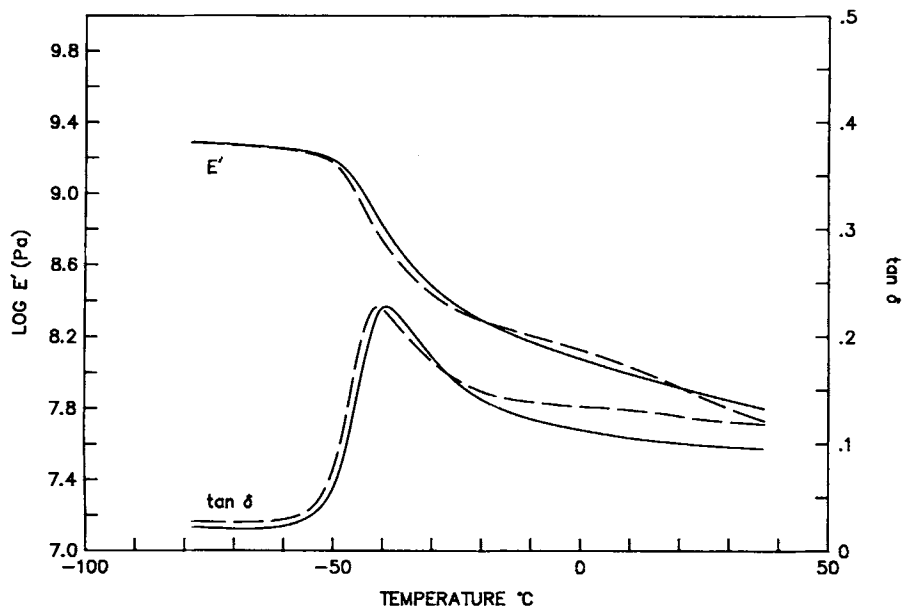
phase mixing and therefore a broadening of the loss-tangent peak.

The effect of annealing on the dynamic mechanical properties of the butanediol-cured polyurethane, which has polybutadiene as its soft segment, was also investigated. The dynamic Young's modulus of

this urethane is plotted as a function of frequency in Figure 11 before and after annealing at a temperature of 160°C. The corresponding loss tangents are shown in Figure 12. The high-temperature annealing caused a more significant decrease in the Young's modulus of this polyurethane than was ob-



**Figure 12** Plot of the loss tangent as a function of frequency at 5°C for a polybutadiene-based urethane; as cured (dashed line), after annealing at 150°C (solid line).



**Figure 13** Plot of the dynamic Young's modulus and loss tangent as a function of temperature measured at 1 Hz for a DETDA-cured polyurethane; as cured (solid lines), after annealing at 160°C (dashed lines).

served for the polycaprolactone-based polyurethane. In the polybutadiene-based polyurethane, a significant reduction in the enthalpy of fusion occurred at the higher annealing temperatures. This decrease in enthalpy indicates that a reduction in the amount of hard-segment crystallinity has occurred. The observed decrease in modulus is likely to be due to this decrease in crystallinity. The increase in the loss tangent, induced by the annealing shown in Figure 12, is comparable to the increase observed for the polycaprolactone-based polyurethane.

Dynamic mechanical measurements were also made on the polycaprolactone-based polyurethane that was cured with DETDA. The effect of annealing this urethane at 160°C is summarized in Figure 13. For this sample, the Young's modulus is virtually unaffected by the high-temperature exposure. This result supports the explanation that the reduction in modulus observed in the butanediol-cured urethanes is due to a reduction in the amount of their hard-segment crystallinity induced by the annealing. In the calorimetric experiments, no hard-segment crystallinity was found in this DETDA-cured urethane. Examination of Figure 13 also indicates that the loss-tangent peak is shifted to a lower temperature by the annealing. This decrease is consistent with the calorimetric result that annealing caused a slight reduction in the glass transition temperature of the soft segment. It is also clear that the annealing causes a broadening of the loss-tangent curve at high

temperatures. This increase cannot be explained by an increase in the amount of phase mixing since the annealing caused a lowering of the glass transition temperature. It is therefore likely that some other morphological change is occurring in the sample. However, since the change in the loss tangent is fairly small, it would be difficult to determine the exact cause for this increase.

## CONCLUSIONS

High-temperature annealing increases the degree of order of the hard-segment phases of crystalline polyurethanes as is evident by an increase in their DSC peak melting points. These thermal treatments also result in more of the hard segments of the polyurethane being incorporated into the soft-segment phases. This increased phase mixing results in an increase in the glass transition temperature of the soft segment and a broadening of the loss-tangent curve. The ordering of the hard segments induced by annealing does not significantly affect the subsequent dynamic mechanical properties, and a slight reduction in modulus is observed after annealing.

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