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A.F. Galambos, T.P. Russell and J.T. Koberstein

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22a NAME OF RESPONSIBLE INDIVIDUAL  
J.T. Koberstein

22b TELEPHONE (Include Area Code)  
(203)486-4716

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The Origin of Multiple Melting in Polyurethane Block Copolymers

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A. F. Galambos, T. P. Russell, and J. T. Koberstein,

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University of Connecticut  
Institute of Materials Science  
and Department of Chemical Engineering  
Storrs, CT 06269-3136

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**THE ORIGIN OF MULTIPLE MELTING IN  
POLYURETHANE BLOCK COPOLYMERS**

<p><u>A.F. Galambos*</u></p> <p>T.R. Russell</p> <p>J.T. Koberstein</p>	<p>Department of Chemical Engineering, Princeton University, Princeton, NJ 08544</p> <p>IBM Almaden Research Center, 650 Harry Road, San Jose, CA 95120,</p> <p>Dept. of Chem. Engr. and Inst. of Materials Sci., U. of Connecticut, Storrs, CT 06269.</p>
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The morphology of multiphase polymeric materials is often a strong function of temperature as well as thermal history. For example, the temperatures at which apparent multiple melting endotherms are observed in some materials are found to be sensitive to the thermal annealing conditions. The investigation of thermal history effects on polymer morphology has been hindered in part due to this sensitivity. That is, the structure of the material may change continually as a function of both annealing time and temperature. The difficulties involved in the characterization of thermal history effects may be overcome by performing thermal and structural analysis simultaneously during a particular temperature cycle. The availability of synchrotron radiation sources makes possible the collection of small and wide angle x-ray scattering data during a differential scanning calorimetry experiment. The technique is applied to examine the possible origins of multiple endotherms and annealing induced morphological changes in segmented polyurethane - poly(ether-ester) copolymers. The results of the polyurethane experiments are compared to thermal-mechanical measurements of softening behavior, from which a number of structure-property relations may be inferred.



\* Present address: HIMONT Research & Development Center, 800 Greenbank Rd., Wilmington, DE 19808

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A.F. Galambos

Dept. of Chemical Engineering, Princeton  
University., Princeton, NJ 08544

T.R. Russell

IBM Almaden Research Center, 650 Harry Road,  
San Jose, CA 95120

J.T. Koberstein

Dept. of Chem. Engr. and Inst. of Mat. Sci.,  
Univ. of Connecticut, Storrs, CT 06269.

**INTRODUCTION:** Segmented polyurethane block copolymers are linear copolymers with  $-(S_n-H_m)_p-$  chain architecture where S and H represent soft (rubbery) and hard (glassy or crystalline) segment sequences at use temperatures. Due to thermodynamic differences, the segments usually segregate to form an aggregated two-phase structure. When either or both of the sequences contain crystallizable units, the two-phase structure and resultant physical properties of the copolymer have been observed to be complex functions of temperature and thermal history<sup>1-3</sup>. This work examines the dependence of morphology and properties of a particular class of polyurethane block copolymer on both temperature and thermal history, relying primarily on the correlation of results from thermal analysis (DSC and TMA) with results from small- and wide-angle x-ray scattering (SAXS and WAXS).

The strength of this study arises from the ability to perform a number of these experiments simultaneously, through the use of the high flux x-ray source at the Stanford Synchrotron Radiation Laboratory (SSRL). Specimens placed in a DSC stage positioned in the x-ray beam were ramped in temperature and thermal transition data was recorded; the multiple thermal transitions commonly observed in these materials could be unambiguously correlated with morphological transitions observed directly by x-ray scattering.

**MATERIALS:** The materials examined in this study were comprised of a hard segment of 4-4' methyl-diphenyl-diisocyanate (MDI) chain extended with butane diol (BD or BDO), and a soft segment that was an amorphous copolymer of poly(propylene oxide) and poly(ethylene oxide) with a molecular weight of approximately 2000. The particular experiments reported here were performed on a material containing 60% by weight of the crystallizable MDI/BDO hard segment. This material is a commercially important polyurethane; previous studies have indicated that the hard

segment phase is continuous in this material<sup>4-5</sup>.

**EXPERIMENTAL:** X-ray scattering/DSC experiments were performed on Beam Line I-4 of the Stanford Synchrotron Radiation Lab (SSRL). Details of the beam line setup are available in the literature<sup>6</sup>; for purposes of this study the most important considerations were that the x-ray source at SSRL was intense enough to allow statistically meaningful x-ray spectra to be obtained on time scales of several seconds, and that the beam collimation was such that the beam size was approximately 1 mm<sup>2</sup> at the sample position, small enough to pass through the optical path of a Mettler FP84 DSC/microscopy stage without impingement. Samples which were run at the synchrotron in simultaneous scattering/DSC experiments were also run in parallel on a Perkin-Elmer DSC-4 using a similar annealing cycle.

The thermal conditioning cycle of the annealing experiments performed in the x-ray beam was as follows: Samples were heated at 20° C/min to 240° C, above all observed DSC endotherms, and held there for one minute to ensure a homogeneous melt state. After melting, specimens were cooled at 20° C/min (the maximum controlled cooling rate of the Mettler FP80/FP84) to the annealing temperature and held there for one hour. WAXD and SAXS spectra were collected during all stages of the annealing experiments to monitor changes in microstructure during annealing and the various cooling processes. After annealing, samples were cooled to room temperature and then scanned at 20° C/min to 240° C to observe the morphological transitions associated with the multiple DSC endotherms. The observed melting (DSC), and softening (TMA) behavior of these particular polyurethanes after thermal conditioning appears in Figure 1.

### **RESULTS AND DISCUSSION:**

**1. Kinetic Studies:** The kinetics of phase separation and crystallization were assessed in this system by evaluating the degree of phase separation and fractional crystallinity directly from scattering spectra collected as a function of time during annealing. For SAXS data this was accomplished by calculating the integrated second moment of the scattering curve, known as the Invariant; for WAXD spectra fractional crystallinity was evaluated by comparison of spectra to standards of zero and high crystallinity. The absolute value of deviation from these standards therefore served as a measure of relative crystallinity. As a function of annealing time, both relative crystallinity and degree of phase separation increased in a sigmoidal fashion well described by the Avrami equation of crystallization kinetics. One convenient kinetic parameter used to describe the kinetics of structural development in this system was the half-time to full development, or the time required for the structure to reach one half of its final value. This parameter is plotted as a function of annealing temperature for SAXS and WAXD data in Figure 2. Briefly, the structure developed during annealing was found to be a strong function of annealing temperature in three basic temperature regions. Region I covered annealing temperatures at or below 130° C, and was typified by the rapid development of phase separated structure with little evidence of ordered hard segment crystalline structure. This was confirmed by the WAXD spectra of Figure 3, specifically that of the sample annealed at 120° C, which indicates that at these low

temperatures hard segment order can at best be described as para-crystalline. The second region of annealing temperature, Region II, which comprised annealing temperatures between 130 and 185°C, was typified by the development of both phase separated and crystalline structure. As annealing temperature increased in this region, the kinetics of structural development slowed markedly, until at 187°C, no development was observed after one hour of annealing; this temperature marked the lower boundary of Region III of annealing behavior.

The next phase of this study correlated the kinetic behavior observed in these annealing studies with the appearance of specific endotherms in DSC traces of the annealed materials, and with the softening point behavior in scanning temperature studies of the annealed samples.

**2. Scanning Temperature Studies:** Careful examination of the DSC traces of Figure 1 reveals the presence of four distinct endotherms in the DSC behavior of the annealed polyurethanes of this study. The first endotherm appears as a small peak 30°C above the annealing temperature, and increases with annealing temperature until it merges with a higher temperature peak at an annealing temperature of 180°C. A second endotherm appears only for annealing in Region I (120°C and below), this endotherm will therefore be termed Peak I; this endotherm has a peak temperature of 190°C and does not move with annealing temperature, rather it simply disappears as annealing temperature is increased and crystalline structure begins to develop in the system. The development of crystalline MDI/BD structure in these materials is promoted by annealing in a temperature range between about 135 and 185°C; annealing in this temperature range results in the simultaneous appearance of high temperature endotherms (205 to 225°C peak temperatures) and a WAXD pattern typical of the crystal structure termed Type II in the crystallographic studies of Briber and Thomas<sup>7</sup>. One interesting aspect of this crystallization behavior is that in the lower annealing temperature range of Region II, termed Region IIA – covering annealing temperatures between 135 and 155°C, the rapid development of both phase separated and crystalline structure promotes a higher melting temperature form of Type II crystallites. As the annealing temperature increases, the kinetics of crystallization and phase separation slowed considerably, and this higher melting endotherm is replaced by a lower melting point transition, which becomes the only transition observed in DSC behavior at annealing temperatures between 180 and 185°C. This unusual behavior cannot be explained in terms of different crystalline polymorphs, as the scanning WAXD data of this study indicate that only the Type II crystal form is present in these annealing materials during these endothermic events. At present no conclusive explanation can be offered for this crystallization behavior, except that it may relate to the crystallization of hard segment units both before and after phase separation in this rapidly phase separating system. In this regard it may be related to the different melting points of crystalline entities that have formed from the homogeneous melt and those which formed in the bulk hard segment domain after phase separation.

The last region of characteristic annealing behavior, termed Region III, covers annealing temperatures of about 190°C and above, and is typified by the absence of either phase separated or crystalline development on the

one hour time scale of these experiments. Specimens quenched and reheated after annealing in this temperature region take on much of the characteristic DSC behavior of specimens quenched directly from the melt at 240°C, indicating that the homogeneous melt state is quite stable in this region of annealing temperature. The drastic change in the nature of the structuring process with such a small change in temperature, combined with the fact that the pure hard segment crystallizes readily at this temperature<sup>9</sup>, supports the claim<sup>8</sup> that this is the thermodynamic phase mixing/demixing temperature of the soft and hard segments of this system in the absence of hard segment crystallinity.

The morphological origin of each of the endotherms discussed previously can be determined directly by the use of the powerful technique of combined DSC/x-ray scattering. SAXS and WAXD data relating to the degree of phase separation and fractional crystallinity as a function of temperature for specimens annealed in each of the regions of annealing behavior discussed previously has been collected and plotted along with the DSC trace in Figure 4. Thus it is evident from SAXS and WAXD/DSC for materials annealed at low temperatures (Region I – 120° anneal in Fig. 4) that very little crystalline structure, as detectable by WAXD, is present in these materials, and microphase mixing is concurrent with the appearance of Peak I at about 180 to 190°C. For specimens annealed at higher temperatures (Region II – 135 to 185°C, typified by 155 and 180°C anneal in Fig. 4) significant crystalline structure develops, as illustrated by the WAX diffraction patterns of Figure 3, and crystalline melting is accompanied by microphase mixing at higher temperatures, between 205 and 230°C. In this sense, crystalline structure serves to stabilize the microphase structure of the materials, which would otherwise phase mix at 190°C. Annealing for one hour at temperatures above 190°C produces little phase separated or crystalline structure in the materials, as evidenced by the similarity of the melting and phase mixing behavior to that of specimens annealed in Region I of annealing temperature.

Thermal-mechanical analysis (TMA) by penetration probe testing (Figure 1) correlates well with observation of crystalline melting and phase mixing behavior, as materials soften as they undergo segmental mixing. One illustration of the importance of thermal history on the mechanical properties of these materials may be taken from softening point data: Specimens annealed in Region IIB, at 180°C, have a softening point about 40°C higher than materials annealed in Region I at 120°C.

**SUMMARY:** The use of thermal analysis combined with real time SAXS and WAXD analysis has proven to be a powerful tool for the determination of morphological transitions in segmented MDI/BDO-based polyurethane block copolymers. In this study these combined techniques were first used to monitor the morphology of these materials during the course of microphase structural development in isothermal annealing experiments, and then employed during subsequent DSC temperature scans to determine the temperature dependence of the structure developed by annealing. In this way these experiments serve as the basis for structure – property relationships for this class of material.

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Figure 1 - DSC and TMA penetration probe results for PU60 as a function of the annealing temperatures listed at the left. All results were acquired at a scan rate of 20° C/min.

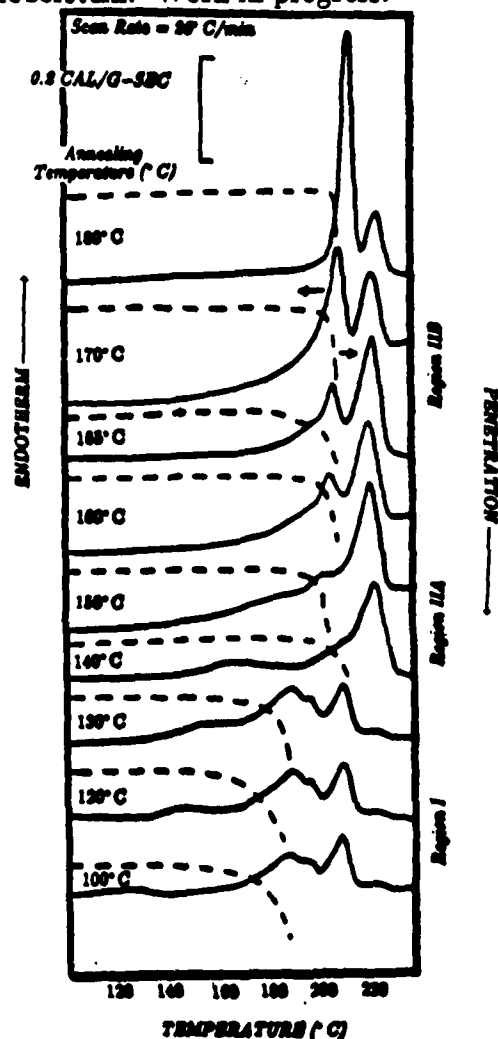


Figure 2 – WAXS spectra of annealed PU60 at annealing temperatures

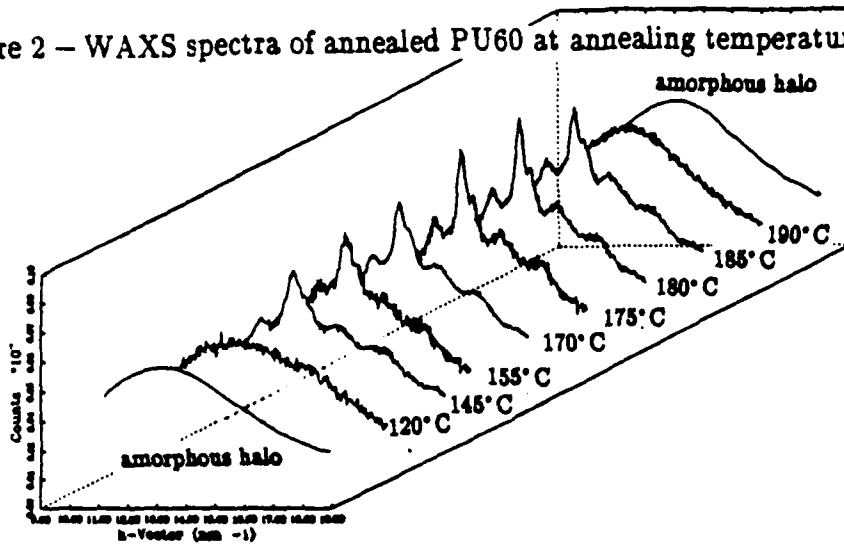


Figure 3 – Half-time to full structural development vs. annealing temp.

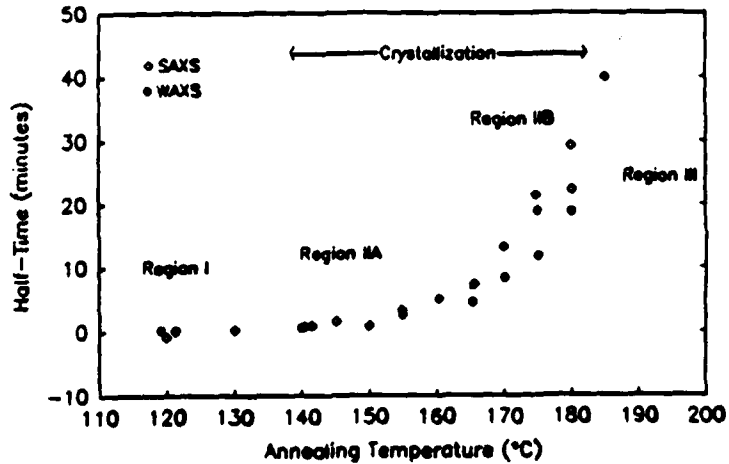


Figure 4 – SAXS and WAXS/DSC for Region I, IIA, IIB, and III annealing

