Multiphase Structure of a Segmented Polyurethane: Effects of Temperature and Annealing

Yingjie Li,[†] Tong Gao,[†] Jian Liu,[†] Kung Linliu,[†] C. Richard Desper,[‡] and Benjamin Chu*,[†,§]

Departments of Chemistry and of Materials Science and Engineering, State University of New York at Stony Brook, Long Island, New York 11794-3400, and U.S. Army Materials Technology Laboratory, Watertown, Massachusetts 02172-0001

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ABSTRACT: The multiphase structure and related relaxations of a segmented polyurethane were characterized by using a combination of differential scanning calorimetry (DSC) and synchrotron small-angle X-ray scattering (SAXS). The results showed a soft-segment glass transition temperature ($T_{g,s}$) which is significantly higher than the $T_{g,s}$ (−84 °C) of the corresponding pure soft segment, suggesting an incomplete phase-separation behavior for the soft segment. The specimen lost its mechanical strength at above 200 °C while DSC indicated an endotherm at ~195 °C due to the hard-segment domain dissolution into the soft-segment matrix. Synchrotron SAXS scanning from 26 to 250 °C indicated that the sample structure remained stable with increasing temperature. A small change around 75 °C was attributed to the glass transition of the amorphous hard-segment domain. Phase mixing took place when the temperature was above 190 °C, in agreement with the DSC results. Synchrotron SAXS was also used to study the postannealing effects on the segmented polyurethane with a well-defined thermal history. The structural changes were irreversible upon annealing. Thermal postannealing did not have a significant effect on the multiphase structure once the structure development had reached equilibrium and interactions among the hard segments had reached a certain degree of strength. However, postannealing could promote perfection inside the hard-segment domain or further phase separation of some hard segments inside the soft-segment matrix. The structures from the samples which have not reached equilibrium or have very weak interactions among the hard segments could be changed dramatically by postannealing. The only way to change the existing structure entirely is to melt the sample. Although the phase-separation process in the segmented polyurethane was very slow, the phase mixing at high temperatures was extremely fast. Based on the Koberstein–Stein coiling/folding hard-segment model, a temperature- and interaction-dependent coiled hard-segment model could be used to interpret our observations. The mobility of the hard segment, the viscosity of the system, and the interaction between the hard segments are three key factors which control the structure in segmented polyurethanes.

I. Introduction

Segmented polyurethanes are a class of thermoplastic elastomers which form multiphase structures owing to the thermodynamic incompatibility between the hard and soft segments.[1] The hard segment usually consists of an aromatic diisocyanate such as 4,4′-diphenylmethane diisocyanate (MDI) extended by either a low molecular weight diol, such as 1,4-butanediol (BD), or a low molecular weight diamine. The soft segment usually consists of either a polyether or a polyester macroglycol with molecular weight between 600 and 3000. The hard segments, which act as cross-linking points and fillers, are in a crystalline state or an amorphous glassy state; the soft segments are in a rubbery state which gives the elasticity. The combination of hard and soft segments gives this class of materials very unique properties which can be changed by adjusting the chemical structure of the polymers and, equally importantly, by controlling the multiphase structure and morphology of the polymers during processing and other postpolymerization treatments. This is part of the reason why the structure–property relationships have drawn so much attention since the suggestion by Cooper and Tobolsky[2] that segmented polyurethanes consisted of multiphase structures.

The polymerization of segmented polyurethanes usually generates macromolecules which are polydisperse and have chemical compositional heterogeneity including hard-segment length distributions. All these structure characteristics are functions of polymerization conditions, and the multiphase structures are generally believed to be formed from nonequilibrium phase separations. Consequently, the structure and properties of segmented polyurethanes depend strongly upon the thermal history and processing conditions. It is very important from both basic and applied viewpoints to find out how the structures could be controlled via synthesis, thermal history, and processing conditions in order to get the expected mechanical properties.

In this paper, we are interested in (1) the temperature dependence of the structure and (2) how the structure can be affected by postannealing.

The multiphase structure and related relaxation of segmented polyurethanes have been studied by a variety of techniques such as differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA) and have been reviewed by Gibson et al.[1] Basically, a soft segment had a glass transition at around 50 to −20 °C, and the dissolution of the hard-segment domain occurred at ~200 °C. The phase structure depends upon many factors such as the hard-segment content, the soft-segment length, and annealing and processing conditions. It is difficult to carry out a detailed characterization of the structure and properties of the segmented polyurethane samples since the structure of the samples is a function of so many factors.

The postannealing effects on the structure of segmented polyurethanes have been studied by several groups. DSC studies by Seymour and Cooper[3] using compression-molded sheets of both poly(ester urethanes) and poly(ether urethanes) showed three endothermic peaks. Re-

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* To whom all correspondence should be addressed at the Chemistry Department.

[†] Department of Chemistry, State University of New York at Stony Brook.

[‡] U.S. Army Materials Technology Laboratory.

[§] Department of Materials Science and Engineering, State University of New York at Stony Brook.

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gion I peaked at ~70 °C, region II at 160 °C, and region III at 185 °C. Postannealing of the compression-molded sheets at 80 °C shifted peak I to a higher temperature, with peaks II and III unchanged. Further treatment continues this movement until the original peaks in regions I and II merged to form a single peak at the high-temperature side of the original peak II. Postannealing at 150 °C moved both peaks I and II into peak III. Also a sharp wide-angle X-ray diffraction (WAXD) ring was attributed to the formation of crystalline hard-segment structure. Further studies by Samuels and Wilkes[4] and by Seymour and Cooper[5] using samples without hydrogen-bonding ability showed similar phenomena, indicating that the multiple-endothermic phenomena were not due to the dissociation of hydrogen bonds. Rather, Seymour and Cooper proposed that all three peaks were morphological in origin. Peaks I and II represented the disordering of hard segments with a relatively short-range order that could be improved continuously by postannealing. Peak III was assigned to a relatively well-ordered microcrystalline structure by the hard segments. Jacques[6] studied the effects of postannealing at high temperatures (150–250 °C) on injection-molded samples. By using DSC, WAXD, infrared spectroscopy (IR), and DMA, his results showed that postannealing below 200 °C resulted in only long-range ordered hard-segment domains while postannealing at 200 °C and above resulted in the crystallization of hard-segment domains. Later in a series of studies on the postannealing effects by the Cooper group, Hesketh et al.[7] concentrated on postannealing-induced ordering at high temperatures (120–190 °C), and Van Bogart et al.[8] concentrated on postannealing between −10 and +120 °C. Basically, these studies reconfirmed the existence of three endothermic peaks. It should be noted that, in their experiments, the samples were held at 250 °C for 5 min and then cooled at a rate of 10 °C/min (not quenching at a rapid rate) to the desired annealing temperatures. Recently, Leung and Koberstein[9] studied the multiple-endothermic and phase-separation behavior in segmented polyurethanes by using DSC. Three regions of annealing temperature for segmented polyurethanes with high MDI–BD segment contents were observed. Annealing at or below 140 °C (defined as region I) showed no significant crystallization. Annealing at 140–190 °C (region II) gave rise to hard-segment crystallization. Annealing at and above ~200 °C showed phase mixing of noncrystalline hard segments and soft segments. It should be noted that in their annealing experiments, specimens were held at 240 °C for 1 min and then cooled at 10 °C/min (again not quenching at a rapid rate) to the desired annealing temperatures. Koberstein and Russell[10] used simultaneous SAXS/DSC to study the phase structure changes and the multiple-endothermic behavior in segmented polyurethanes. The results showed that the intermediate endotherm was associated with the onset of partial phase mixing. In their experiment, the specimens were heated at 10 °C/min to 250 °C then cooled to (once more not quenching at a rapid rate) the selected annealing temperatures, and annealed for 40 min. Galambos et al.[11] used the same technique to study the phase-separation, crystallization, and multiple-endothermic behavior. The observations wee essentially similar. Gibson et al.[12] performed SAXS experiments to investigate the multiphase structural changes of segmented polyurethanes upon postannealing. They found that annealing generally improved the degree of phase separation and increased the hard-segment domain size. Thicker interfacial regions were also observed in the annealed materials.

The studies mentioned above either used compression-molded specimens without indicating the thermal history of the specimens or used specimens which were *slowly cooled* to desired annealing temperatures, instead of quenching. It could be possible that the samples before postannealing might not be in an equilibrium state since the thermal history was not specified clearly. We believe that the effects of postannealing could depend upon the starting original structure. The slow cooling during the sample preparation represents a nonequilibrium kinetics which could produce different structures in response to the changing temperatures as well as the cooling rate based on the original structure. Therefore, it is not clear how the postannealing will affect the phase structure of segmented polyurethanes if we do not know what the original structure is. A sample with a well-defined thermal history could be used to find out the postannealing effects in a more decisive way. It is also necessary to know whether the original structure was achieved under equilibrium conditions. This requirement becomes even more obvious from one of our recent studies. In a previous paper[13] we investigated the phase-separation kinetics of a segmented polyurethane after the melt was quenched to the desired annealing temperatures. We found that the phase-separation process was very slow and could be accomplished in hours, depending upon the annealing temperature. Therefore, a well-designed experiment must carefully consider whether the time-dependent data are obtained from a system starting in some well-defined equilibrium state. On the other hand, phase separation immediately took place after thermal quenching so that slow cooling could become a nonisothermal process. It is desirable to investigate the reversibility of structural changes upon annealing using a sample with a well-defined thermal history. The results in this paper indicate that the structural changes upon annealing are irreversible. Thermal postannealing does not change the phase structure significantly, although ordering inside the hard-segment domain or further phase separation of some hard segments from the soft-segment matrix is possible. Therefore, all the experiments involving thermal history, thermal transition, or thermal characterization need to be carefully designed and interpreted; i.e., the thermal history of the sample is a dominant factor in the structural studies of segmented polyurethanes. It is equally important to understand the equilibrium rate in connection with time-dependent studies.

II. Experimental Section

II.1. Materials. The segmented polyurethane used in this study was prepared by a two-step bulk reaction process. The soft segment was poly(tetramethylene oxide) (PTMO) end-capped with poly(propylene oxide) (PPO) having PTMO:PPO = 70:30 wt % and an average molecular weight of about 1000 (PPO–PTMO). The hard segment was 4,4′-diphenylmethane diisocyanate (MDI) extended with 1,4-butanediol (BD). The hard-segment content was 50 wt %. The polymerization route was as follows: At 80 °C, MDI was added to vacuum dehydrated PPO–PTMO and prepolymerized for 0.5 h. Then BD was added and well mixed. After 1 min, the reaction mixture was poured into a Teflon mold and heated in an oven at 140 °C for 3 h and then at 80 °C for 12 h in order to complete the polymerization process. The sample was stored in a desiccator for more than 3 months before any experiment was performed. The sample, denoted as PPO–PTMO–PU-50, was characterized by elementary analysis, gel permeation chromatography (GPC), infrared spectroscopy (IR), and nuclear magnetic resonance (NMR).[14] The sample without any further treatment is known as the as-reacted sample.

All the annealing experiments were carried out in vacuum. GPC experiments were performed to make sure that thermal degradation was not a significant factor.

II.2. Instrumentation. DSC measurements were carried out by using a Perkin-Elmer Model DSC-2C instrument operated at

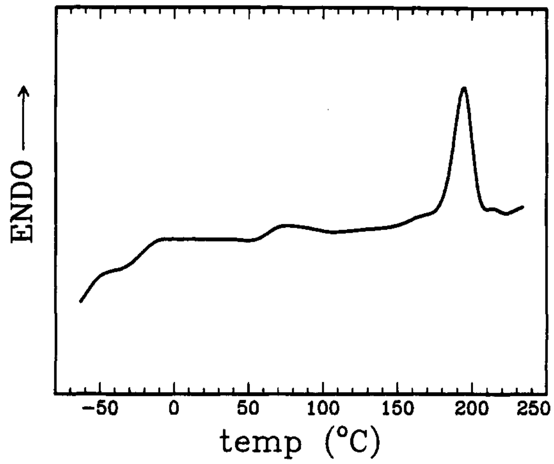

Figure 1. DSC thermogram of the PPO-PTMO-PU-50 as-reacted sample.

a 20 °C/min heating rate. A sample weight of about 10 mg was used for DSC experiments.

Synchrotron SAXS experiments were carried out at the State University of New York (SUNY) X3A2 beamline, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL). Details about the setup can be found in refs 15 and 16. A modified Kratky camera along with a Braun position-sensitive detector was used at an X-ray wavelength of 0.154 nm. The sample-to-detector distance was 1330 (±5) mm. The beam size at the sample position was $\sim 0.2 \times 2$ mm^2. The synchrotron beam was focused onto the beam stop which was ~40 mm in front of the Braun detector having a receiving window width of ~2 mm. Therefore, smearing effects on the SAXS patterns were negligible. Time-dependent experiments were performed by using a double-cell high-temperature jumper which had been described elsewhere.[13] The temperature precision was ±0.5 °C. Preliminary experiments were performed at the SAXS facility, SUNY at Stony Brook. Routine correction procedures, except for the absolute intensity calibration, were performed on SAXS data. As we are mainly interested in the structural changes of the segmented polyurethane as a function of temperature and annealing, the lack of absolute intensity calibration should not affect our conclusions.

III. Results and Discussion

Figure 1 shows the DSC thermogram of the as-reacted specimen of the segmented polyurethane. The base-line shift at -21 °C indicates the soft-segment glass transition. The glass transition temperature of pure PPO-PTMO ($T_{g,s,0}$) can be estimated by using the copolymer equation[17]

$$1/T_{g,s,0} = w_{PPO}/T_{g,PPO} + w_{PTMO}/T_{g,PTMO} \qquad (1)$$

where $T_{g,PPO}$ and $T_{g,PTMO}$ are, respectively, the glass transition temperatures of pure PPO (-75 °C)[18] and PTMO (-88 °C).[19] w_{PPO} and w_{PTMO} are, respectively, the weight fraction of PPO and PTMO. The calculated $T_{g,s,0}$ is -84 °C. (We note that eq 1 is valid for random polymers, while the soft-segment PPO-PTMO used in the present study is an A-B-A block copolymer. However, the block length was very short, and we did not observe any phase separation between PPO and PTMO. Equation 1 should be a reasonable approximation). Therefore, the glass transition temperature of the soft-segment matrix $T_{g,s}$ is above $T_{g,s,0}$ by 63 °C. The reasons are 2-fold. First, some hard segments are mixed inside the soft-segment matrix, resulting in an increase in the $T_{g,s}$ value. Second, the hard-segment domains act as cross-linking points which restrict the movements of the soft segments, thus increasing the $T_{g,s}$. The endotherm around 195 °C represents a dissolution of the hard-segment domains. Careful evaluation at around 70 °C reveals an endotherm along with a base-line shift. This behavior might be interpreted as a glass transition of the amorphous hard segment along with a dissolution of short-range ordered hard segments. It is noted that the glass transition of the amorphous hard-segment domains has not been observed in most of the DSC investigations. The absence of glass transition in most segmented polyurethanes is a typical example of how complex the systems are. First, the hard segment has a length distribution and the hard-segment domains have a size distribution. The domain size distribution tends to smear the glass transition of the hard-segment domains since bigger domains could have higher $T_{g,h}$, and smaller ones, lower $T_{g,h}$. Second, "domain-boundary matrix" and "mixing-in-domain" effects will also smear the glass transition and make it less sharp and less obvious.[20] Of course, all these factors depend upon sample polymerization and thermal history.

DMA and thermal-stimulated current discharge (TSDC) experiments were also performed. The results are in agreement with the DSC results.

For a system with spherical symmetry, the scattered intensity of X-rays is related to the so-called three-dimensional normalized correlation function by[21]

$$\gamma_3(r) = (1/Q)\int_0^\infty q^2 I(q)\,[\sin(qr)/(qr)]\,dq \qquad (2)$$

where $\gamma_3(r) = \langle \eta(\mathbf{r}_1)\,\eta(\mathbf{r}_2)\rangle / \langle \eta^2 \rangle$, with $r = |\mathbf{r}_1 - \mathbf{r}_2|$ and $\eta(\mathbf{r})$ being the local electron density fluctuations at position $\mathbf{r}$; q is the magnitude of the scattering vector, and $q = (4\pi/\lambda)\sin(\theta/2)$ with λ and θ being, respectively, the wavelength and the scattering angle; Q, the invariant, is defined by

$$Q = \int_0^\infty q^2 I(q)\,dq \qquad (3)$$

For an ideal two-phase system with a sharp interface, Q can be written as

$$Q_{id} = c\phi_1\phi_2(\rho_1 - \rho_2)^2 \qquad (4)$$

where ϕ_i and ρ_i are the volume fraction and electron density of the ith phase and c is a constant related to the instrument setup and the primary beam intensity. The physical importance of Q is that it is directly related to the mean-square fluctuations of the electron density. Therefore, the Q value can be used to calculate the *degree of phase separation* if scattering from the phases can be observed. For example, Q/Q_{id} can be used as an estimate of the overall degree of phase separation. In this study, only one sample was used. Therefore, Q_{id} has a fixed value, and the degree of phase separation can be estimated by using the Q value on a relative scale. It is not necessary to use the absolute value of Q for comparison purposes in the present case.

The assumption of spherical symmetry is not valid for many cases. For example, systems with lamellar structure obviously show local anisotropy. In such cases, a one-dimensional correlation function can be used.[21]

$$\gamma_1(r) = (1/Q)\int_0^\infty q^2 I(q)\cos(qr)\,dq \qquad (5)$$

The details of how to get correlation functions can be found elsewhere.[21,22]

The interdomain spacing d can be estimated from the position of the primary maximum of the correlation function, if the one-dimensional geometry is applicable. The other method is to use the Bragg equation

$$d = 2\pi/q_m \qquad (6)$$

where q_m is the q value at the position of a maximum in the scattering curve. However, if the system contains randomly oriented lamellar structures, the random arrangement of the one-dimensional repeating structure has to be corrected by performing the so-called Lorentz correction, i.e., by multiplying the scattered intensity with q^2. Then the peak position is determined from $I(q)\ q^2$ versus q, instead of $I(q)$ versus q.

For a synchrotron SAXS experiment involving temperature changes, the difference between the thermal expansion coefficient of the two phases could give rise to a change in $(\rho_1 - \rho_2)$ which influences the Q value, according to eq 4. In segmented polyurethanes, the hard-segment domain has a lower thermal expansion coefficient than the soft-segment matrix. As the temperature is raised, the density of both phases is decreased. Therefore, the difference $(\rho_1 - \rho_2)$ is increased. This increase will result in an increase in the invariant (Q). In order to obtain the structural parameters, this effect has to be corrected.

Following Fisher et al.[23,24] and Gehrke et al.,[25] the thermal expansion coefficient is defined as

$$\alpha = \mathrm{d}\rho/\mathrm{d}T \qquad (7)$$

If the volume fractions ϕ_1 and ϕ_2 remain relatively constant, a combination of eqs 4 and 7 yields

$$[Q(T)/Q(T_0)]^{1/2} = 1 + [(\alpha_1 - \alpha_2)/|\rho_1(T_0) - \rho_2(T_0)|](T - T_0) \qquad (8)$$

where T_0 is any reference temperature; α_1 and α_2 are the thermal expansion coefficients of phases 1 and 2, respectively. From eq 8, a plot of $[Q(T)/Q(T_0)]^{1/2}$ versus $(T - T_0)$ should give a straight line if the structural changes other than thermal expansion do not take place in the system. A structural change would usually cause a change in $(\alpha_1 - \alpha_2)$ and therefore a corresponding slope change. It should be noted that a more rigorous approach would be to assume the weight fractions of the two phases remain relatively constant. However, eq 8 for the corresponding case then becomes complex with little gain in physical insight.

Figure 2 shows the synchrotron SAXS profiles of the as-reacted segmented polyurethane sample at different temperatures. The temperature precision was controlled to within 1 °C. The entire scan took about 100 min. Each step took about 4–5 min. The measurement time for each pattern was 200 s. With increasing temperature, the scattering peak gradually shifted toward lower q values. The scattered intensity first increased and then decreased at above 190 °C. Figure 3 shows that the invariant Q increased first with increasing temperature. Based on eq 8, $[Q/Q_{26\,°\mathrm{C}}]^{1/2}$ should be linearly proportional to T if there were no structural changes except the thermal expansion. The result shows that there was a small structural change around 70–90 °C, in agreement with the DSC result (Figure 1). The small bump in Figure 3 could possibly be due to the glass transition of the amorphous hard-segment domain along with breakage of the short-ranged ordered structure. The overall tendency of the curve from 26 to 180 °C was close to a straight line, indicating that during the temperature scan in this region, the structural changes were very small. The increase in Q due to thermal expansion should not generally be considered as a structural change. When the temperature was above ~185 °C, the Q value started to drop dramatically. We could attribute this drop to the phase mixing of the hard segments with the soft segments. The DSC results also showed the same transition temperature. The mixing process finished at ~220 °C. Figure 3 also shows that the interdomain spacing d (calculated from eq 6) increased with increasing temperature. A small structural change was observed around 70–90 °C. The d values showed an overall slow shift upward due to the thermal expansion of the two phases and could be distinguished from other more abrupt structural changes. The d values started to increase sharply when the temperature was above ~200 °C, again confirming the presence of phase mixing. Koberstein and Russell[10] observed this transition at ~160 °C, about 30 °C lower than that in the present study. The difference could probably be attributed to the difference in the thermal history of the samples.

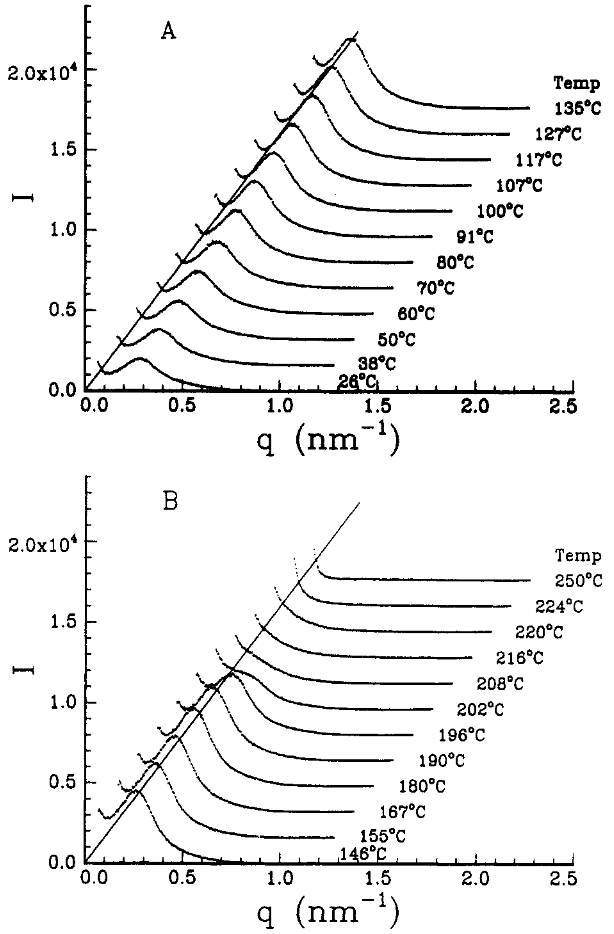

Figure 2. (A and B) SAXS patterns of the PPO–PTMO–PU-50 as-reacted sample as a function of temperature.

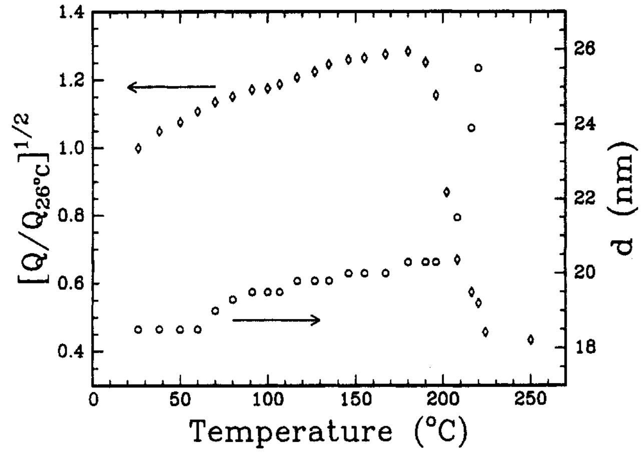

Figure 3. Square root of the normalized integrated scattered intensity and interdomain spacing (d) of the PPO–PTMO–PU-50 as-reacted sample as a function of temperature.

Correlation function analysis was employed to investigate the phase structure of the segmented polyurethane. The Debye–Bueche theory[26] was used to extend the low q region, and the Porod–Ruland theory,[21] the high q limit. The correlation function was not sensitive to the models used in the low-angle region, partially because our experimental data were already fairly close to the zero scattering angle; i.e., our SAXS profiles could already reach very small values of q. With the high flux of the

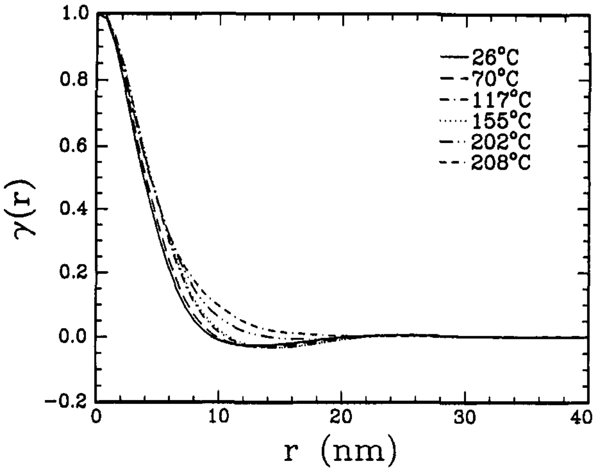

Figure 4. Three-dimensional correlation function of the PPO–PTMO–PU-50 as-reacted sample as a function of temperature.

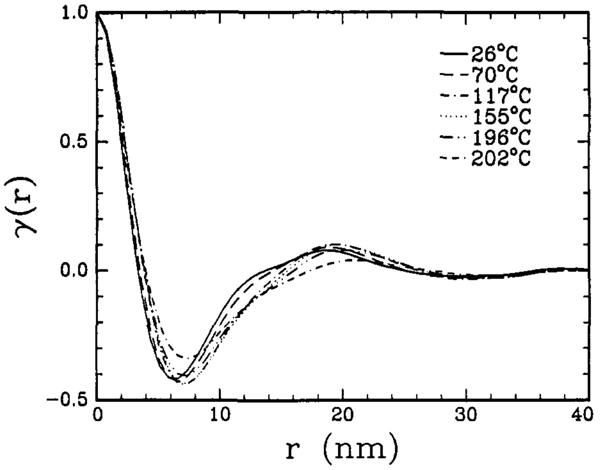

Figure 5. One-dimensional correlation function of the PPO–PTMO–PU-50 as-reacted sample as a function of temperature.

synchrotron X-ray source, ~300 s of data accumulation yielded adequate precision for the correlation function analysis without smoothing. Both three- and one-dimensional correlation functions were computed. Figures 4 and 5 show the corresponding results for the as-reacted sample. If the system were totally random, the three-dimensional correlation function analysis could be used. As shown in Figure 4, the system did not follow this relation. The position of the first maximum gave the interdomain spacing. However, the three-dimensional correlation functions show very broad peaks which make the determination of the peak position difficult. The one-dimensional correlation functions in Figure 5 show a typical two-phase structure. The interdomain spacing calculated from the one-dimensional correlation function was 19.0 nm at 26 °C. The interdomain spacing calculated from the Lorentz-corrected SAXS pattern was 18.5 nm at 26 °C, in good agreement with the one-dimensional correlation function analysis. The phase structure in segmented polyurethanes is believed to be close to lamella, at least on a local scale. Our recent investigation[27] indicated that spherulite structures could be formed if the segmented polyurethane melt was quickly quenched to annealing temperatures above 120 °C. Therefore, an analysis based on the one-dimensional correlation function should be more appropriate.

As shown in Figure 5, the phase structure did not show significant changes except that the first maximum was shifted to a greater value, indicating that the interdomain spacing increased with increasing temperature. The phase contrast increased slightly due to the difference in the thermal expansion coefficient of the two phases. It is interesting to note that there was a shoulder at $r \sim 11.5$ nm. A similar shoulder was observed by Koberstein and Stein.[28] The exact nature of this shoulder is not yet clear, although it could be due to the fact that the thermal history involved two different polymerization temperatures, i.e., 140 °C (3 h) and 80 °C (12 h). At temperatures above ~200 °C, the one-dimensional correlation functions showed some ripples. On the other hand, the three-dimensional correlation function changed closer to an exponential decay, as shown in Figure 4. This behavior could imply that when substantial phase mixing took place, the system could become more and more random.

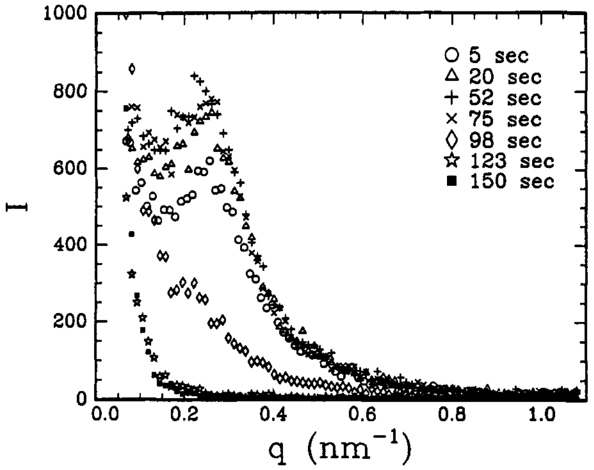

Figure 6. SAXS patterns of the PPO–PTMO–PU-50 as-reacted sample after being jumped from room temperatures to 221 °C.

After the phase structure and related transitions of the segmented polyurethane were characterized, it became interesting to see how postannealing will affect the phase structure of the segmented polyurethane after the samples were thermally annealed at certain temperatures for 48 h. The as-reacted sample was not used for this purpose because the as-reacted sample used two polymerization temperatures. In order to start from a sample with a well-defined thermal history, the as-reacted samples were melted at 221 °C and then quenched to the desired annealing temperatures. The samples were annealed at the annealing temperatures for 48 h. Then part of the samples was further annealed at different temperatures (postannealing; also for 48 h) in order to investigate the postannealing effects. First of all, the as-reacted samples had to be melted and had to become homogeneous after the annealing at 221 °C for 3–4 min. Obviously, if a sample were not completely melted, the residual structure would definitely affect the conclusions on the annealing effects. In the study by Leung and Koberstein,[9] a copolymer equation was used to check whether the starting samples were homogeneous. We used a SAXS experiment to check the short annealing time at 221 °C. Figure 6 shows SAXS profiles of the as-reacted sample after it was jumped from room temperature (25 °C) to 221 °C. The scattered intensity increased first as the sample reached the temperature of the thermal bath (221 °C). The increase was, once again, due to the difference in the thermal expansion coefficient of the hard- and soft-segment domains. When the sample reached 221 °C, which was above the highest dissolution temperature of the hard-segment domain from DSC or SAXS measurements, the scattered intensity dropped very quickly. The time for the sample to reach a homogeneous state in our temperature jump apparatus was about 90 s. The scattering patterns remained basically unchanged for another 2–3 min before an upturn at the low scattering angle started to grow. The small-angle upturn could probably be used

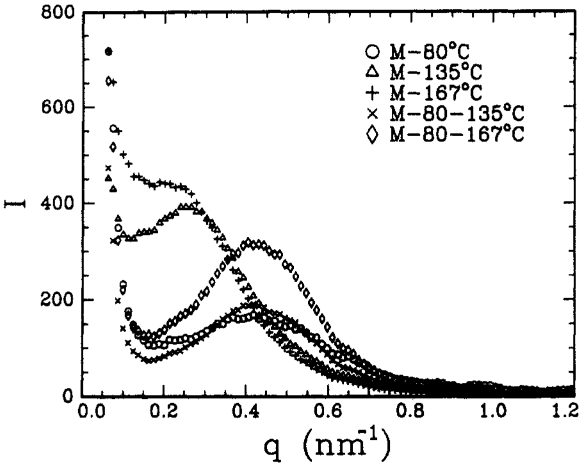

Figure 7. SAXS patterns of PPO-PTMO-PU-50 samples with different thermal treatments in order to study the effects of postannealing on the structure of 80 °C annealed samples. M-80-135 denotes the following sample history: quench the melt to 80 °C and anneal at 80 °C for 48 h. Then jump the temperature from 80 to 135 °C and anneal the sample at 135 °C for 48 h. All SAXS measurements were performed at room temperature.

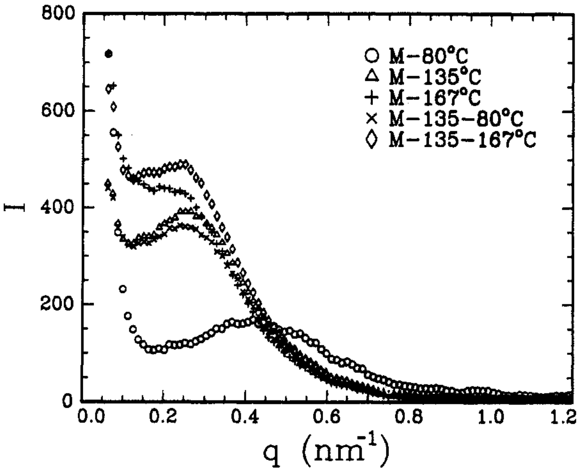

Figure 8. SAXS patterns of PPO-PTMO-PU-50 samples with different thermal treatments in order to study the effects of postannealing on the structure of 135 °C annealed samples.

as an indication of some degradation reaction. A small amount of air bubbles was found after about 7–8 min of annealing at 221 °C. SAXS experiments on the melting process at 231, 241, 251, and 261 °C were also performed. The behavior was similar to that observed at 221 °C except that the time required for the sample to become homogeneous was reduced from about 90 s for 221 °C to about 60 s at higher temperatures. We used a melting time of 2–3 min in order to ensure our material to have a homogeneous state.[29]

The homogeneous melt was then quenched to different annealing temperatures in less than 30 s. The cooling rate was not a constant. Rather it followed an exponential decay in the temperature vs time plot. The time required to cool the sample to the annealing temperatures depended upon the difference between the melting temperature and the annealing temperatures. The annealing time was 48 h to make sure that the structural development could have sufficient time to reach equilibrium. Based on our phase-separation kinetics studies,[13] the 48-h annealing time could be shown to be enough. SAXS curves in Figures 7–9 show the effect of postannealing on the phase structure of the segment polyurethane, measured at room temperature after an additional 48 h of postannealing time. As a comparison SAXS profiles of the sample annealed at 80, 135, and 167 °C are also plotted in the three figures.

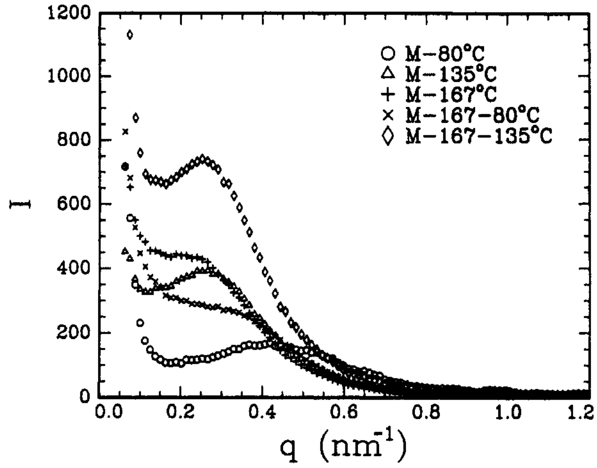

Figure 9. SAXS patterns of PPO-PTMO-PU-50 samples with different thermal treatments in order to study the effects of postannealing on the structure of 167 °C annealed samples.

First, the starting structure had very significant effects on the phase structure. As the annealing temperature was increased the scattering peak shifted to lower scattering angles, indicating increasing interdomain spacing. The degree of phase separation first increased with annealing temperature and later decreased slowly as the annealing temperature was raised to 167 °C, in agreement with the observations of our earlier reports.[27,30]

From Figure 7, the postannealing at 135 °C of the 80 °C-annealed sample and postannealing at 167 °C of the 80 °C-annealed sample resulted in an increase in the scattered intensity. The shapes of the three scattering curves were very similar. The increase in the scattered intensity could be attributed to the ordering inside the hard-segment domain, thus increasing the electron density contrast between the hard-segment domain and the soft-segment matrix. The postannealing at 135 or 167 °C of the 80 °C-annealed sample generated samples which were by no means identical or close to the 135 °C-annealed sample or the 167 °C-annealed sample, respectively. Therefore, the first annealing from melt is a decisive step. The change in the phase structure is irreversible.

Figure 8 shows that the postannealing at 80 and 167 °C of the 135 °C-annealed sample produced very little structural change.

In Figure 9, the postannealing at 135 °C of the 167 °C-annealed sample again shows little change except for an increase in the Q value. The postannealing at 80 °C of the 167 °C-annealed sample showed a decrease in the interdomain spacing. This change can be explained in the following way. The 167 °C-annealed sample had more short hard segments dissolved in the soft-segment matrix. During the 80 °C postannealing these short hard segments became thermodynamically incompatible with the soft segments and would separate from the soft-segment matrix and caused a decrease in the d value.

Although the postannealing effects of those samples annealed at other elevated temperatures were very small, significant postannealing effects were observed in those samples first annealed at a temperature below the glass transition temperature of the hard-segment domain. In an early paper,[27] we have shown that when the samples were quenched from the melt to room temperatures (25 °C) and remained at 25 °C for 24 h and then postannealed at higher temperatures above the glass transition temperature of the hard-segment domain, the structure was very close to those samples without the room temperature annealing, although no spherulites were observed.

The above results show that the structure of segmented polyurethanes is largely decided by the first annealing,

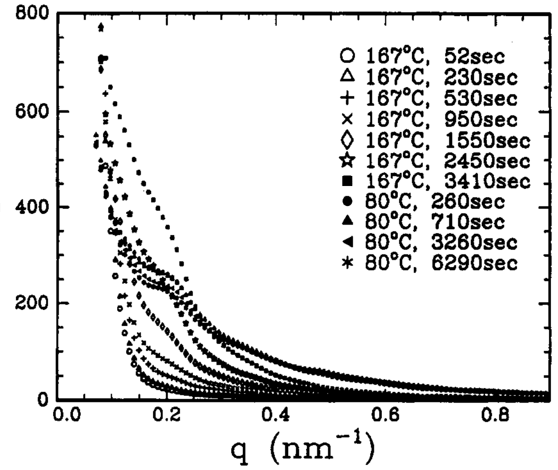

Figure 10. SAXS patterns of PPO-PTMO-PU-50 after jumping from the melt state (221 °C) to 167 °C for 3600 s and then jumping to 80 °C.

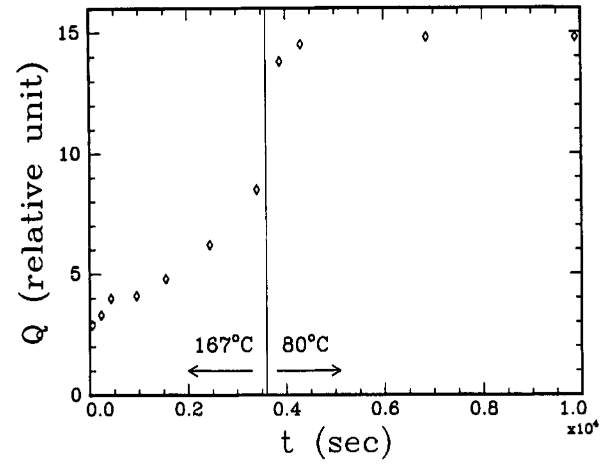

Figure 11. Integrated scattered intensity of PPO-PTMO-PU-50 under different times and temperatures.

starting from the melt. The second annealing has a very small effect. The structural changes are irreversible. Generally, if the postannealing temperature is lower than the first annealing temperature, the hard-segment domains remain basically unchanged. However, some of the hard segments may phase separate from the soft-segment matrix. If the postannealing temperature is higher than the first annealing temperature, the soft-segment matrix changes very little while the hard-segment domains may undergo further perfection, with the overall shape of the hard-segment domains basically unchanged. However, if the system has not reached an equilibrium state in the first annealing, postannealing will change the structure dramatically. Also the change occurs mainly in those domains which have not reached an equilibrium state in the first annealing. This statement can be proved in the following experiments.

The sample was melted at 221 °C first and then jumped to 167 °C. Figure 10 shows the phase-separation process. After 1 h of annealing, the sample was jumped to 80 °C. The scattered intensity at higher q values started to grow, while the scattered intensity at lower q values decreased a little. The phase-separation process at 80 °C has been found to be much faster than that at 167 °C. Figure 11 showed two different processes. It is clear that the phase separation at 80 °C mainly happened in those parts where phase separation had not taken place. The portion where phase separation had taken place remained basically unchanged during the annealing. When the melt was first quenched to 80 °C and annealed for 1380 s and then fast heated to 167 °C, the scattered intensity at lower q values started to increase. The scattered intensity at higher q values decreased slightly (Figure 12). The two different phase-separation processes were once again observed, as shown in Figure 13.

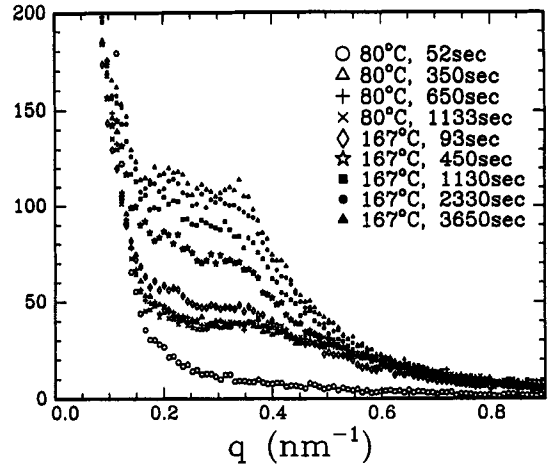

Figure 12. SAXS patterns of PPO-PTMO-PU-50 after jumping from the melt state (221 °C) to 80 °C for 1380 s and then fast heating at a heating rate of ~50 °C/min to 167 °C.

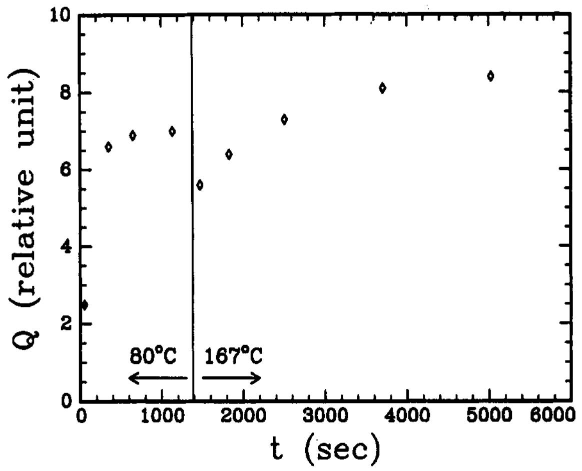

Figure 13. Integrated scattered intensity of PPO-PTMO-PU-50 under different times and temperatures.

The original model of the hard-segment chain was proposed by Bonart,[31] who stated that the hard-segment chains were in an extended state. Recently, Van Bogart et al.[32] and Koberstein and Stein[28] have concluded from their experiments that the hard-segment chains must be in a coiled or even folded configuration. In particular, Koberstein and Stein proposed a model which stated that the thicknesses of the hard-segment domains were controlled by the minimum critical sequence length insoluble in the soft-segment matrix. Hard segments longer than this critical length had to adopt either a coiled or folded configuration in order to keep themselves inside the hard-segment domain. Hard segments shorter than this critical length were mostly dissolved in the soft-segment matrix.

In an earlier study,[13] we found that after the melt was quenched to different temperatures the phase-separation process was very slow. It took hours to accomplish. The process could be described by an equation of relaxation, suggesting that the process could be controlled by the mobility of the hard segments and the system viscosity. The above experimental results, combined with earlier kinetics studies, led us to the following proposition:

1. The Koberstein–Stein model could be extended to explain the annealing effects. The hard segments are essentially coiled or folded. The degree of coiling or folding is temperature-dependent. The hard segments extend gradually with increasing annealing temperature. This

can explain the increase in interdomain spacing with increasing annealing temperature.

2. The mobility of the hard segment and the viscosity of the system are two important factors controlling the phase-separation process. When the melt is quenched to below the glass transition temperature of the hard-segment domain, most of the hard segments do not have enough mobility to reach an equilibrium state. When the sample is later postannealed at higher temperatures, the mobility of the hard segments is increased and the viscosity of the system is decreased. The hard segments may then be able to rearrange and to form phase-separated structures.

3. The interaction between the hard segments is another factor which could affect the hard-segment domain stability. As the annealing temperature is increased the hard segments extend and interact more strongly. The interaction among the hard segments in the segmented polyurethane system is usually very strong, giving rise to the good mechanical properties of the material. However, the strong interactions may not be solely due to the crystallization of the hard segments. When the samples were postannealed at temperatures higher than the first annealing temperature, the hard segments which have not reached strong enough interactions will rearrange to a more ordered structure in order to increase their interaction level. When the sample was postannealed at temperatures lower than the first annealing temperature, the critical length of the hard segment decreased.[10] Those hard segments longer than the new critical length would separate from the soft-segment matrix. The original hard-segment domain would remain unchanged because the temperature could not provide the hard segments enough energy to overcome the interaction barrier. When the sample was postannealed at below the glass transition temperature of the hard-segment domain, the system was basically frozen and no significant postannealing effects would be observed. No observable structural changes were determined whether the measurements were performed at annealing temperatures or at room temperatures, if the thermal expansion effects on the structures had been corrected.

IV. Conclusion

A combination of DSC and synchrotron SAXS has been used to characterize the multiphase structure of a segmented polyurethane. The sample showed a glass transition of soft-segment matrix, a glass transition of hard-segment domain, and a dissolution of the hard-segment domain into the soft-segment matrix. The material basically showed good temperature stability. The increase in Q and d due to thermal expansion of the two phases should not be considered as a phase structure change. The postannealing effects on the samples with a well-defined thermal history were studied by synchrotron SAXS. The structural changes were irreversible. Once the system reached an equilibrium state and a certain degree of interaction, postannealing could only produce small effects. Based on the temperature-dependent coiled/folded hard-segment chain model, mobility of the hard segments, viscosity of the system, and the interaction between hard segments are responsible for the multiphase structures.

We want to emphasize that in a well-designed experiment, the thermal history of the sample has to be well specified because it will dominate the annealing effects. In kinetic studies the sample should start from an equilibrium state because the time for the system to reach equilibrium could usually be very long.

The viscosity–mobility interaction argument could be further tested by using samples with different hard-segment flexibilities. These samples have been synthesized by intentionally changing the chemical structure of the hard segments. The synchrotron SAXS and DSC results on these systems will be presented in a later report.

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