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Synchrotron SAXS Studies of the Phase-Separation Kinetics in a Segmented Polyurethane

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ABSTRACT: Synchrotron small-angle X-ray scattering (SAXS) was used to investigate the kinetics of phase separation of a segmented polyurethane which was quenched from the homogeneous melt state to lower temperatures. The phase-separation process in the segmented polyurethane was very slow at most of the annealing temperatures, owing to the high viscosity of the system and low mobility of the hard segment. The phase-separation rate depended strongly on the annealing temperature, with the maximum rate being at an annealing temperature of around 80–107 °C. Further increase in the annealing temperature reduced the rate. The rate decrease could be attributed to an increase in the hard- and soft-segment compatibility at higher temperatures. The interdomain spacing did not change throughout the whole annealing process, a characteristic of segmented copolymers. However, the interdomain spacing increased with increasing annealing temperature. Both the phase-separation process and the peak intensity changes could be analyzed according to an equation of relaxation, which indicated that the phase separation in the segmented polyurethane system behaved like a relaxation process. The results are compared with the more restrictive Hashimoto theory.

Introduction

Segmented polyurethanes form microphase-separated structures due to the hard- and soft-segment incompatibility. The hard-segment domain acts as physical cross-linking points as well as fillers. This unique structure gives segmented polyurethanes very attractive properties. The structure–property relationships have drawn intensive attention both scientifically and industrially.[1]

Short-segmented copolymers show different behaviors in a variety of ways from long block A–B (or A–B–A) type copolymers such as styrene–butadiene(–styrene) copolymers.[1,2] Previous studies have concentrated on how the microphase structure could influence the mechanical properties. Obviously the macroscale superstructure should have a direct influence on the physical properties. Early reports have indicated that the superstructure, especially the spherulite structure, could not be formed by quenching the melt to lower temperatures.[3–5] Therefore, experiments on the superstructure were performed using samples either from solvent casting or from polymerization.[6–11]

It has been reported by us[12,13] that MDI–BD-based segmented polyurethanes could form spherulite structures by quenching the *melt* to annealing temperatures between 120 °C and the highest annealing temperature for spherulite formation (T_h). The T_h values were controlled by the hard- and soft-segment compatibility. The radius of the spherulite increased with increasing hard-segment content. It was also found that annealing at 135–140 °C resulted in the largest spherulite. The annealing time was 48 h. If the melt was quenched to room temperatures and stayed for 48 h before being jumped to higher annealing temperatures for another 48 h, no spherulite structures were observed. However, synchrotron small-angle X-ray scattering (SAXS) showed essentially similar SAXS curves whether the sample went through room temperature annealing or not.

The slow spherulite growth as well as the strong thermal history dependence of the structure suggests that a detailed study on the time dependence of the microphase-separated structure formation, crystallization, and spherulite growth should reveal new information on how segmented polyurethanes should be processed.

Wilkes and co-workers[14–16] used differential scanning calorimetry (DSC), mechanical testing, and SAXS to study the time dependence of the structural changes of segmented polyurethanes after the samples were annealed at high temperatures. Their studies showed that the structural changes were very slow in segmented polyurethanes, usually on the order of hours to days. While DSC and mechanical testing gave indirect evidence of the structural changes, their SAXS data on the phase-separation kinetics were basically reported only at a fixed scattering angle, simply due to a combination of the weak conventional X-ray source and single detector technique. Also by using DSC, Kwei[17] found that the phase separation proceeded logarithmically with time. The DSC results by Camberlin and Pascault[18] indicated that the time required to reach equilibrium was a function of chain mobility in such a way that the logarithm of the equilibration time was a linear function of the viscosity of the pure soft phase. Chee and Farris[19] proposed that the phase-separation process in segmented polyurethanes could be treated by first-order kinetics. More recently, Hsu and co-workers[20,21] used DSC and Fourier transform infrared spectroscopy (FTIR) to study the phase-separation process of segmented polyurethanes containing monodisperse hard and soft segments. The phase-separation process was treated like a crystallization process in the sense that it could be analyzed by using the well-known Avrami equation. The fastest process of phase separation occurred at a temperature close to 60 °C. It should be noted that, in a brief proceeding report, Galambos et al.[22] used synchrotron SAXS and wide-angle X-ray diffraction (WAXD) to study the phase-separation kinetics of a segmented polyurethane. They used the Avrami equation to describe the phase-separation and crystallization behavior. However, due to instrument limitation, the maximum controlled cooling rate was only

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20 °C/min. This means that the elapsed time of cooling the sample melt from 240 °C to the temperature region of 120–170 °C was 3–6 min, while the reported half-time of the process was only less than 1 min to less than 10 min. This cooling process became a nonisothermal kinetic process, and the starting point for the experiment contained substantial uncertainty. It should be mentioned that all the studies cited above except the one by Galambos et al. used indirect ways to follow the phase-separation process in segmented polyurethanes. Although SAXS should be an ideal technique for this purpose, conventional X-ray generators could not give time-resolved SAXS data with a satisfactory signal-to-noise ratio. This situation has been changed dramatically in recent years with the availability of high-flux synchrotron X-ray sources in combination with position-sensitive detectors.[23,24] The synchrotron SAXS setup at the SUNY X3A2 beamline, National Synchrotron Light Source (NSLS), Brookhaven National Laboratory (BNL),[25,26] is capable of reaching a small scattering angle of ~1–1.5 mrad which is very important for a decisive conclusion about the structure in segmented polyurethanes whose structure dimension could reach as large as ~50 nm.

Theoretically, although the phase-separation process has been a topic of intense concern in polymer blends,[27–29] very little attention has been paid to the segmented copolymer systems where the effect of intersegment connectivity is much stronger than that in long block A–B or A–B–A type copolymers. On the basis of the Ginzburg–Landau approach, Hashimoto[30] proposed a theory which could be used for A–B diblock copolymers, A–B–A triblock copolymers, and $-(\mathrm{A}-\mathrm{B})_n-$ multiblock copolymers as well as mixtures of block copolymers. His theory predicted an exponential increase in the scattered intensity during the early stages of phase separation. The theory was limited to the systems that did not involve solidification due to crystallization, hydrogen bonding, vitrification, etc. The phase-separation behavior in segmented polyurethanes is closer to a solid–liquid, instead of a liquid–liquid, phase separation. Unfortunately, to our knowledge, there has been no theory available for such systems. Therefore, we merely borrow the Hashimoto theory as a guide in order to treat the data of our segmented polyurethanes. Most studies were conducted by small-angle light scattering (SALS). SAXS should reveal the structural changes in more detail. By combining SAXS with SALS, the structural changes could be covered over a greater length scale.

In this paper, we report a detailed synchrotron SAXS investigation on the phase-separation kinetics in a segmented polyurethane after the melt was quenched to different annealing temperatures. We believe that this study should help clarify some of the diverse conclusions in the topic and once again indicate that the slowness in the time dependence of microphase structure formation in segmented polyurethanes should be taken into account carefully before any conclusion is drawn.

Experimental Section

Materials. The polyurethane used in this study consists of the following:

Hard segment: 4,4′-diphenylmethane diisocyanate (MDI) with 1,4′-butanediol (BD) as chain extender (MDI–BD). The hard-segment content is 50 wt %.

Soft segment: poly(tetramethylene oxide) (PTMO) end-capped with poly(propylene oxide) (PPO) with wt % PTMO:PPO = 70:30 (PPO–PTMO). The soft segment has a number-average molecular weight M_n of ~1000.

More details about the sample can be found in refs 13 and 31.

The sample notation is written as PTMO–PPO–PU-50 for 50 wt % hard-segment content in order to be consistent with ref 13.

Instrumentation. Synchrotron SAXS experiments were performed at the SUNY X3A2 beamline, NSLS, BNL. Detailed information about the instrumentation can be found elsewhere.[25,26] The setup includes a modified Kratky camera in combination with a Braun position-sensitive detector and a high-temperature jumper with temperature control to <±0.5 °C. A wavelength of 0.154 nm was used. The sample-to-detector distance was 1310 (±5) mm. The beam size at the sample holder was ~0.2 × 2 mm.[2] The effective width of the detector receiving window was ~2 mm. The synchrotron beam was focused onto the beam stop which was ~50 mm in front of the detector. Therefore, the smearing effect was negligible. The high-temperature jumper had double cells whose temperatures could be controlled outside the hutch by using a programmable temperature controller. The sample was first put into the low-temperature cell (measuring cell). The gas purge moved the sample into a melting cell at 221 °C, above the highest melting temperature from a DSC measurement. The sample was held in the melting cell for 2–3 min to erase all the thermal history. SAXS experiments found that this melting time was long enough for a completely homogeneous state.[32] Actually it should have been very interesting to check whether the scattering in the homogeneous state can be described by the Hashimoto theory. However, segmented polyurethanes are thermally not very stable. After a long annealing time period at high temperatures, thermal degradation could take place. On the other hand, we[32] have observed that the structural changes in the segmented polyurethane showed a fairly sharp transition once the temperature was above the hard-segment domain dissolution temperature (T_d). Beyond T_d, the scattered intensity became very weak and "featureless". This behavior is different from the A–B or A–B–A long block copolymers.

After the homogeneous melt was obtained, the gas purge moved the sample into the measuring cell at temperatures of 31, 80, 107, 135, and 167 °C, with a jumping time of less than 1 s. Measurements were started immediately after the jump. However, it took about 30–60 s for the sample to reach the exact sample cell temperature. Therefore, the first SAXS pattern contains a relatively higher uncertainty than the rest. This instrument limitation also restricted us from studying the phase-separation process at $t < 1$ min decisively. However, the uncertainty should not affect the conclusions since the whole process took hours to complete. Routine correction procedures were performed to get the excess scattered intensity. The absolute scattered intensity was not calculated. However, the Q values, although in relative scale, can be compared with each other.

The samples after the experiment did not show any kind of color change nor appreciable loss of mechanical strength.

Results and Discussion

Figure 1 shows the SAXS patterns after the homogeneous melt (221 °C) was quenched to an annealing temperature of 167 °C. The SAXS patterns for the sample after quenching to annealing temperatures of 31, 80, 107, and 135 °C are essentially similar in the sense that all of them showed a monotonic increase in the scattered intensity with elapsed time and in all the q values of the SAXS experiment, where $q = (4\pi/\lambda)\sin(\theta/2)$, with λ and θ being the wavelength of the X-ray and the scattering angle, respectively. The difference is that the scattering maximum shifts to higher q values with lower annealing temperatures. This means that the interdomain spacing decreases with decreasing annealing temperature. The scattering peak becomes more obvious in a plot of Lorentz-corrected scattered intensity Iq^2 versus, q, as shown in Figure 2. The applicability of the Lorentz correction has been justified by Ophir and Wilkes.[33] We also found that a one-dimensional correlation function analysis showed a periodic structure. The interdomain spacing values agreed very well with those obtained based on the Lorentz correction.[32] The distortion due to the Lorentz correction,

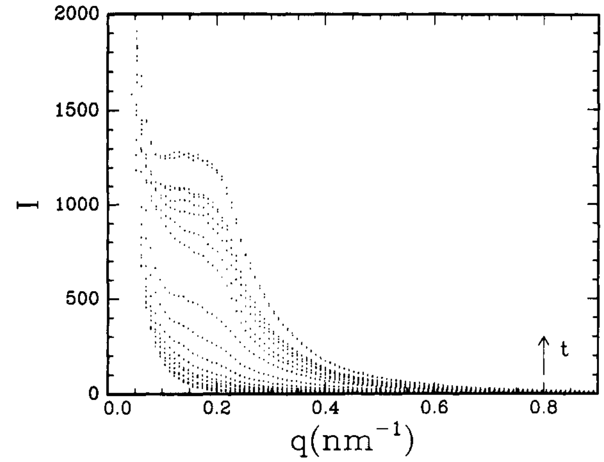

Figure 1. Time dependence of SAXS patterns after the homogeneous melt (221 °C) was quenched to 167 °C. The scattered intensity showed a monotonic increase with increasing elapsed time. The elapsed time was counted immediately after the sample was jumped from the melting cell to the measuring cell. From the bottom going upward, the curves represent, respectively, the SAXS pattern at the elapsed time of 13, 46, 85, 140, 237, 385, 750, 1240, 2187, 3388, 4153, 5183, 6776, 8270, 9390, 10 200, 14 980, and 15 450 s.

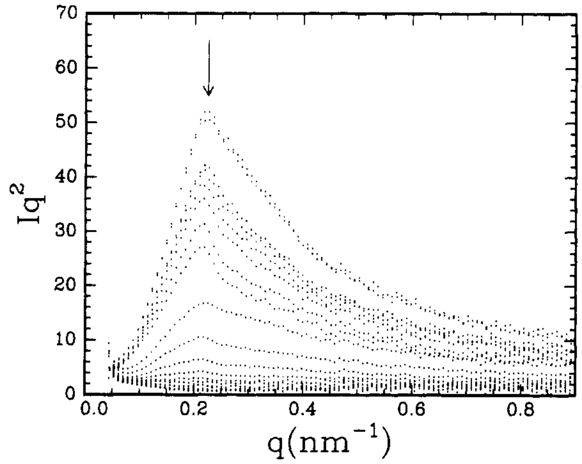

Figure 2. Time dependence of SAXS patterns shown in Figure 1 after the Lorentz correction (multiplying I by q^2). The peak position did not change with elapsed time.

if any, should not affect our conclusions. The interdomain spacing did not change throughout the whole phase-separation process, suggesting that the domain did not changed its size significantly in the direction perpendicular to the longitudinal dimension. The coiling of the hard segment (if Koberstein's model were accepted) remained unchanged during the phase separation. This is an important characteristic of short-segmented polyurethanes. The alternation of hard and soft segments restricted the structure reorganization of the hard segments which had already been segregated. In polymer blends, the scattering peak usually shifts to lower q values during the late stages of phase separation.[27-29] Here we see the effect due to the *connectivity* of the hard and soft segments.

In a polymeric system, the transition from one equilibrium state to another due to changes of thermodynamic variables can be considered as some type of relaxation process of the high system viscosity and the low segmental mobility. The equation of relaxation has the form

$$X_t = (x_\infty - x_t)/(x_\infty - x_0) = \exp(-t/\tau) \qquad (1)$$

where x is a physical quantity characteristic of the system, ∞, t, and 0 denote time at ∞, t and 0. τ is the relaxation time.

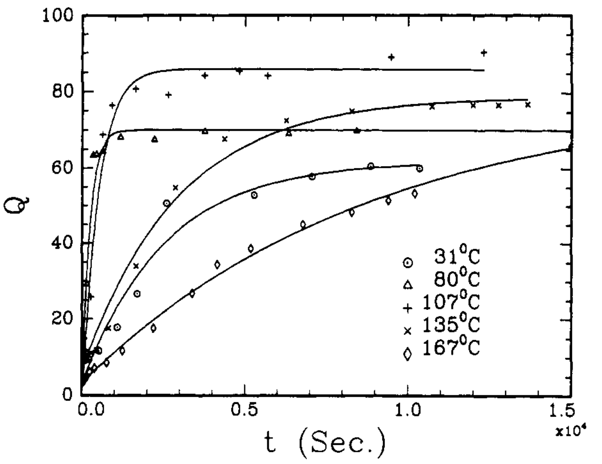

Figure 3. Time dependence of invariant Q versus t at different annealing temperatures. The solid lines represent the theoretical fitting of data with eq 1, suggesting that the phase-separation behavior could be treated as a relaxation process.

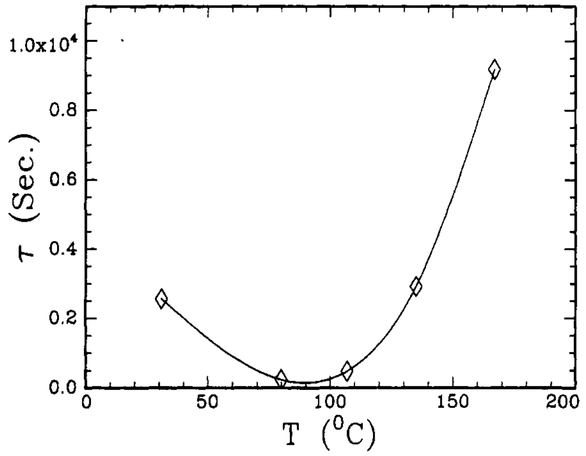

Figure 4. Temperature dependence of the relaxation time τ based on the results presented in Figure 3 which were fitted to eq 1. The solid line is only for guiding the eyes.

In this paper the integrated scattered intensity, Q, called invariant, was used as x. Q can be expressed by[34]

$$Q = \int_0^\infty I(q)\, q^2\, \mathrm{d}q \qquad (2)$$

$$Q \propto \phi_1\phi_2(\rho_1-\rho_2)^2 \qquad (3)$$

where ϕ_i and ρ_i are the volume fraction and the electron density of the ith phase, respectively.[35] The Q value gives an estimate of the degree of phase separation.[36] An increase in the Q value means an increase in the degree of phase separation. The results are shown in Figure 3. Solid lines represent the fitting curves based on eq 1. From the fitting τ can be calculated. The half-time $t_{1/2}$ for the process, corresponding to $X_{t_{1/2}}$, is equal to $\tau \ln 2$. $t_{1/2}^{-1}$ can be used as an indication of the changing rate of the process. Therefore, the τ value is a direct measure of the quickness of the changing process. The τ value as a function of annealing temperature is shown in Figure 4. The fastest rate happens in the annealing temperature region of 80–107 °C. This behavior can be understood in the following way. At annealing temperatures lower than 80 °C, the very high viscosity of the system slows down the phase-separation process. At annealing temperatures higher than 107 °C, the compatibility between the hard segment and the soft segment is increased. The thermodynamic driving force for the phase separation is gradually removed with increasing annealing temperature. In addition, an increase in the contractile force of the soft segment due to an increase in the annealing temperature tries to pull more hard segments out of the hard-segment domains. The entropy increase favors phase mixing at high annealing temperatures.[14]

Chee and Farris[19] and Galambos et al.[22] found evidence of a two-stage process in the phase separation of their segmented polyurethanes. A relaxation equation with multi-relaxation time parameters could also have been used here and would definitely improve the fitting of the phase-separation process, especially at the late stages. However, the introduction of a second relaxation time would require two more fitting parameters. The use of more parameters could be meaningful only if the data were of very high quality. By taking into account the uncertainties of our data, we prefer to use a single-relaxation time equation which could already give us the key information as to what was happening during the phase-separation process.

The linearized phase-separation theory in polymer blends generally predicts the following two behaviors:[27-29]

1. The scattered intensity $I(q,t)$ increases in an exponential form

$$I(q,t) = I(q,0) \exp[2R(q)t] \qquad (4)$$

where $R(q)$ is the growth rate and depends upon q. Therefore, a plot of log I vs t should give a straight line during the early stages of phase separation.

2. The scattered intensity and/or the growth rate $R(q)$ as a function of q show a maximum whose position q_m is independent of time t.

This theory has found success during the early stages of phase separation by SALS. For late stages of the phase separation, the following scaling relations are expected:[27-29]

$$I = I(q_m,t) \sim t^{-\alpha} \qquad (5)$$

and

$$q_m \sim t^{-\beta} \qquad (6)$$

where exponents α and β are scaling constants. The linearized theory neglects the random thermal force. Deviations from the theory are expected to occur at larger q values which correspond to the q range of SAXS. In the Binder theory,[37,38] the effect of thermal fluctuations was considered and the evolution of the structure factor $S(q,t)$ (proportional to the scattered intensity) after a temperature jump could be described by

$$S(q,t) = S_x(q) + (S(q,t{=}0) - S_x(q)) \exp(2\tau_q^{-1}t) \qquad (7)$$

where $2\tau_q^{-1}$ is the relaxation rate and $S_x(q)$ is a "virtual" structure factor. Equation 7 is essentially identical to eq 1 mathematically. If $S_x(q) = 0$, eq 7 is reduced to eq 4. However, this is obviously not the case in the segmented polyurethane system.

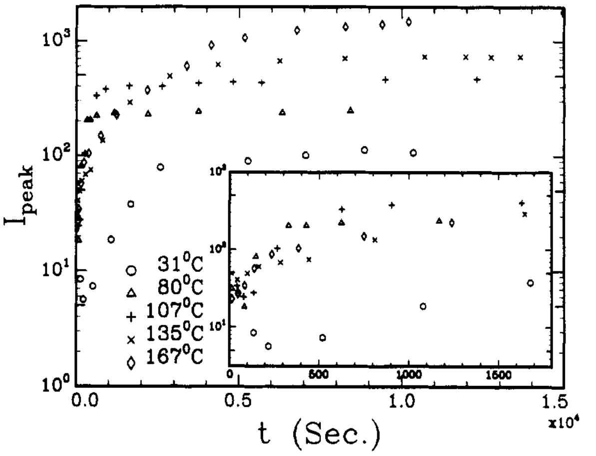

Figure 5. Time dependence of logarithmic peak intensity (peak position fixed) versus t at different annealing temperatures where the peak positions were determined from the Lorentz-corrected scattering curves with q_{peak} = 0.225 nm^{-1} for 167 °C, q_{peak} = 0.33 nm^{-1} for 135 °C, q_{peak} = 0.45 nm^{-1} for 107 °C, q_{peak} = 0.52 nm^{-1} for 80 °C, and q_{peak} = 0.747 nm^{-1} for 31 °C. The inset is a plot of SAXS behavior during the early stages of phase separation. If the Hashimoto theory holds in this case, ln I vs t should give a straight line, at least during the early stages.

A key structural difference between polymer blends and block copolymers is that, in block copolymers, the different blocks are connected together by chemical bonds. This *connectivity* effect was obviously important in the phase separation of block copolymer systems. Hashimoto[30] started from the time-dependent Ginzburg–Landau approach and used the coarse-grained free-energy functional equation derived by Leibler[39] for block copolymer systems. The theory is also a linearized one and omits the random thermal force. The Hashimoto theory predicts an exponential growth of the scattered intensity and time-independent q_m for early stages of phase separation of block copolymer systems. The mathematical form for the equation for the scattered intensity in the Hashimoto theory is identical to eq 4, which means that the Hashimoto theory predicts no difference, at least mathematically, as far as the scattered intensity growth is concerned. The Hashimoto theory also predicts a time-independent q_m during the early stages of phase separation. The value of q_m is associated with the molecular connectivity. To our knowledge, this is the only theory which is considered valid for block copolymer systems. The Hashimoto theory was successful in predicting the time evolution behavior of the SAXS results after a temperature jump from 190 to 30° for 55 wt % SBS block copolymer (M_n = 58 000) solution in dipentene. Obviously the time independence of q_m in the phase-separation process of the segmented polyurethane is consistent with the theory. Furthermore, the scattered intensity measured at the peak position which did not change throughout the whole process was used to test the theory. The fitting was poor for all the annealing temperatures, even at the early stages of phase separation (Figure 5). Instead, the scattered intensity could, once again, be fitted to eq 1. Figure 6 shows the time dependence of peak intensity (fixed q values) versus time at different quenching depths. The solid lines are the fitting curves according to eq 1. The τ values fitted from the equation, shown in Figure 7, are very close to those values fitted from the $Q \sim t$ curves which are shown in Figure 3. The SAXS behavior at other q values was similar to that at the peak position. Figure 8 shows the τ values as a function of q at different annealing temperatures. The τ values are all positive, indicating that all over the SAXS q range the scattered intensity shows a monotonic increase with elapsed time. At a fixed annealing temperature, the q dependence of τ is not very obvious, although it appears that there is a maximum, and the maximum shifts to higher q values with decreasing annealing temperatures (Figure 8). The small q dependence of the τ values means that structures of different length scales do not "aggregate" together during later stages of phase separation. In other words, postrestructuring is not significant. This could be due to the strong effect of connectivity in the segmented polyurethane system as well as the entanglement of the molecular chain in the bulk state. Such behavior cannot

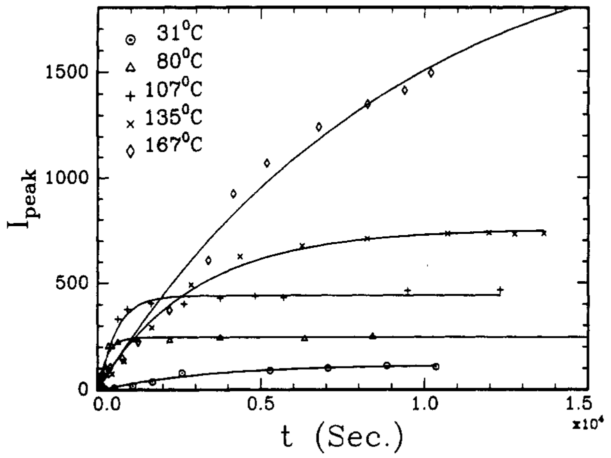

Figure 6. Time dependence of peak intensity (peak position fixed) versus t at different annealing temperatures where the peak positions were determined from the Lorentz-corrected scattering curves with $q_{peak} = 0.225$ nm^{-1} for 167 °C, $q_{peak} = 0.33$ nm^{-1} for 135 °C, $q_{peak} = 0.45$ nm^{-1} for 107 °C, $q_{peak} = 0.52$ nm^{-1} for 80 °C, and $q_{peak} = 0.747$ nm^{-1} for 31 °C. The solid lines represent the theoretical fitting based on eq 1.

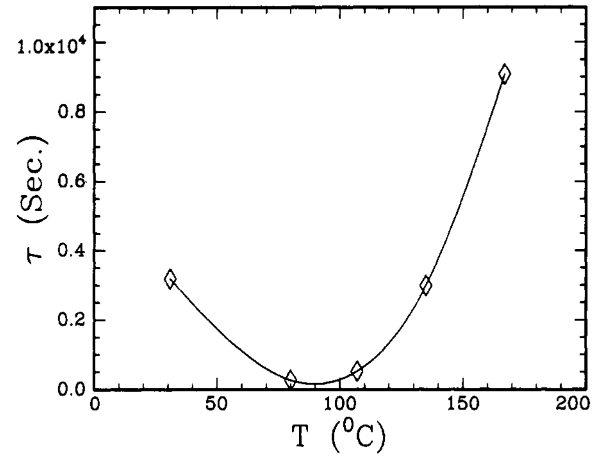

Figure 7. Temperature dependence of the relaxation time τ based on the results presented in Figure 6 which were fitted to eq 1. The solid line is only for guiding the eyes.

be described by the scaling relations expressed in eqs 5 and 6 for the late stages of phase separation.

As we have pointed out before, the phase-separation behavior in the segmented polyurethane system involves at least one- or two-dimensional ordering of the hard segments at high annealing temperatures as well as hydrogen-bonding formation. All these phenomena may take place even during the early stages of phase separation. Therefore, the phase-separation process could be more like a solid–liquid phase separation. The solidlike hard-segment aggregates tend to yield a high system viscosity due to the low hard-segment mobility which could reduce the phase-separation rate and exhibit deviations predicted by a liquid–liquid phase-separation theory of the type proposed by Hashimoto.[27] With high system viscosity and low segment mobility, the phase separation is like a relaxation process which could be described by eq 1.

The Hashimoto theory is based on a linearized approximation which is valid only in the very early stages before crystallization or hydrogen-bonding effects appear and before the random thermal noise is significant as experienced in a deep quench; therefore, it may be argued that the early stages we showed in Figure 5 were still not early enough. Perhaps we should try a time scale shorter than 100 s. However, our SAXS data showed that the changes during the first 100 s were very minor and involved only a very small portion of the phase-separation process. Thus, in our kinetic studies we were not concerned with only the early stages but more on an overview of the structure development toward the final equilibrium.

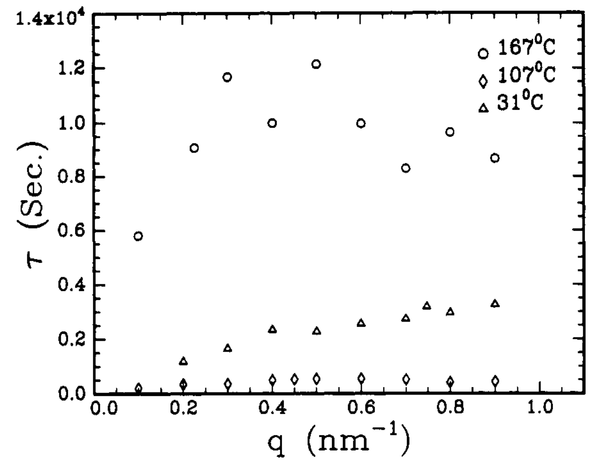

Figure 8. Values of τ as a function of scattering vector q for different annealing temperatures.

Another important point which we want to point out is that the poor fitting of the Hashimoto theory could also possibly be due to the strong connectivity effect between the soft and hard segments in this segmented polyurethane system. Generally, the connectivity in short-segmented copolymers is much stronger than that in long block A–B or A–B–A copolymers. For example, the SBS block copolymer with $M_n = 58\,000$ used in Hashimoto's study contains only two connecting points. The segmented polyurethane sample used in our study contains about 40 connecting points. This strong connectivity is obviously responsible for the slow phase-separation kinetics of the segmented polyurethane system. Therefore, the degree of connectivity should be explicitly included in an improved theory.

Since eqs 1 and 7 are mathematically similar, our SAXS intensity results could also be described by eq 7, which does not necessarily mean that the Binder theory could be used to interpret the SAXS behavior of the segmented polyurethane system.

Conclusion

The phase-separation process in the segmented polyurethane was very slow at most of the annealing temperatures, owing to the high polymer viscosity and low mobility of the hard segments. It would usually take hours to reach equilibration, depending upon the annealing temperature. The interdomain spacing did not change throughout the whole process, which might be a major difference between short-segmented copolymers and homopolymers or polymer blends. The interdomain spacing increased with increasing annealing temperature. Both the phase-separation process and the peak intensity (fixed q value) changes could be treated as a relaxation process. The Hashimoto theory gave a poor fitting even during the early stage of phase separation. These results clearly indicate that, in an investigation of the structure–property relationships in segmented polyurethanes, special care has to be taken to find out whether the results are obtained from the system in the equilibration state.

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(35) The structure in the segmented polyurethane could have three different types of phases. However, the two-phase assumption is used due to the small difference between the amorphous hard-segment domain and the crystalline hard-segment domain. WAXD patterns did not show significant diffraction peaks even though the spherulite structure had been observed.[31] The applicability of the two-phase approximation was also used by Cooper and co-workers (*J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 885) and Leung and Koberstein (*J. Polym. Sci., Polym. Phys. Ed.* **1985**, *23*, 1883).

(36) Although the value of $\phi_1\phi_2$ will change during the phase-separation process, the change in the magnitude of $\phi_1\phi_2$ will be small, because of the mathematical characteristics of $\phi_1\phi_2 = \phi_1(1 - \phi_1)$. The demixing between the soft and hard segments will cause an increase in $(\rho_1 - \rho_2)$.[2] Therefore, an increase in Q is expected (see also: Koberstein, J. T.; Russell, T. P. *Macromolecules* **1986**, *19*, 714).

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