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Structure Relaxation and Metastable States at the Microphase Separation Transition in Diblock Copolymers: Experiments with Time-Resolved Small-Angle X-ray Scattering

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ABSTRACT: The kinetics of the microphase separation transition in a diblock copolymer of polystyrene/polyisoprene was studied with time-resolved small-angle X-ray scattering. Using synchrotron radiation it was possible to determine the structure factor in time intervals of 10 s. The relaxation of the structure factor after temperature jumps within the disordered regime was found to be wave vector dependent in accordance with Cahn–Hilliard theory. For quenches from the disordered into the ordered state an additional, slow process was found which consists mainly of a decrease in the width of the first-order reflection. It is interpreted as the perfectioning of the lamellar order. Whereas the corresponding relaxation time had been found to decrease strongly with supercooling for shallow quenches, it is found to increase again for deeper quenches.

1. Introduction

The properties of the microphase separation transition (MST) in diblock copolymers have been studied in great detail in recent years. Mainly scattering experiments with neutrons or X-rays were applied in studies of the structure of concentration fluctuations in such systems as they represent the most direct access to the ordering phenomenon of the MST. Various model systems have been used, with polystyrene/polyisoprene being one prominent example. It has the advantage of a rather large electron density difference between its components such that X-ray scattering experiments are easily feasible without further modification of the polymer. The preparation of well-defined samples of low polydispersity is possible using anionic polymerization. On the other hand, the repulsive interaction between polystyrene and polyisoprene monomers as described by the Flory–Huggins interaction parameter χ is large. One therefore has to use comparatively low molecular weight samples to expect the MST to occur at experimentally accessible temperatures. A further complication arises from the fact that the glass transition of the polystyrene domain in the ordered state is comparatively high and often prevents the formation of long-range order.[1] The MST therefore is difficult to observe. Early experiments on this system[2–4] have therefore mainly discussed the disordered state and the regime close to the MST.

Very recently, however, it was demonstrated that the MST was observable in nearly symmetric diblock copolymers of polystyrene/polyisoprene.[5] Small-angle X-ray scattering (SAXS) as well as measurements of the dynamic shear modulus defined the transition temperature of this system to a temperature interval better than ±2 K.

Whereas the static properties of diblock copolymers and of the MST have been extensively studied, very little is known about the kinetics of the phase transition. Some experiments have shown that long time scales may be involved in the transition to the ordered state.[6] A systematic approach to this problem should be a study of the time dependence of the change of concentration fluctuations. It would therefore require time-resolved small-angle scattering experiments. This method has been used earlier to investigate the ordering kinetics of block copolymers in solution.[7,8]

In the present work we report results from time-resolved SAXS on a bulk diblock copolymer of polystyrene/polyisoprene. Preliminary experiments at a fixed scattering angle on the same sample[9] had revealed the existence of two distinctly different time scales involved in the kinetics of the MST. In order to uniquely identify these processes, we have now investigated the time dependence of the structure factor after temperature jumps in the full wave vector regime using synchrotron radiation. Our aim is to clarify the mechanism of macrolattice formation at the MST.

In the following we will describe the experiments in some detail and collect the results on the equilibrium properties of the sample under study. The time-resolved SAXS experiments involve two series of data. They refer to quenches within the disordered state and across the phase transition temperature, respectively.

2. Experimental Section

2.1. Sample. The diblock copolymer of polystyrene/*cis*-1,4-polyisoprene was synthesized anionically and characterized for its composition and microstructure.[5,10] These data are compiled in Table 1. The equilibrium structure factor as measured in SAXS is discussed in refs 5 and 10. These measurements determine the phase transition temperature T_{ODT} and the so-called spinodal temperature T_{S} from an extrapolation of the temperature dependence of the structure factor obtained at high T. The ordered state is found to consist of lamellae with a period of $d = 16.2$ (±0.1) nm. The ordered domains comprise stacks of about 20 lamellae.

2.2. SAXS Experiments. The time-resolved SAXS experiments were carried out at the polymer beam line in Hasylab, DESY, Hamburg, Germany, using synchrotron radiation.

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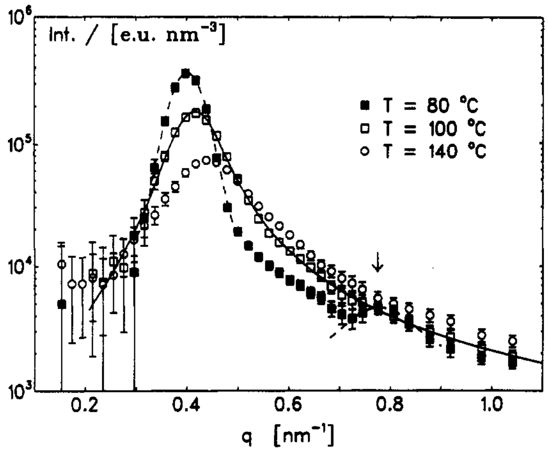

Figure 1. Equilibrium structure factor of the diblock copolymer for temperatures in the disordered and in the ordered state. The curves are fits of the RPA structure factor in the disordered state and of Gaussians representing Bragg peaks in the ordered state, respectively. The arrow indicates the position of the second-order maximum in the ordered state.

Table 1. Properties of the Diblock Copolymer

mol wt M_w	15 700
vol fraction polystyrene f	0.44
polydispersity M_W/M_N	1.04
transition temp T_{ODT} (°C)	89
spinodal temp T_S (°C)	115

Details about the instrumentation may be found elsewhere.[11] The experiments were performed in a double-focusing mirror monochromator camera at a wavelength $\lambda = 0.15$ nm. The scattered intensity was registered using a one-dimensional position-sensitive detector. For the time-resolved measurements it is essential to correct the intensities for fluctuations of the incoming beam. This was accomplished by a continuous measurement of the primary beam intensity and subsequent normalization.

The sample size was kept as small as possible to allow for rapid temperature changes. It was a pellet of 10 mg wrapped in thin aluminum foil and tightly fixed between two copper blocks. Temperature was controlled by pressing air of defined temperature through channels in the copper blocks. In this setup temperature changes of typically 70 °C were possible within times of change $\tau_T \leq 10$ s (see below and Figure 2).

Data were taken in time intervals of 10 s covering a regime of scattering vectors $0.1 \leq q = (4\pi/\lambda) \sin \theta/\text{nm}^{-1} \leq 1.45$, with 2θ denoting the scattering angle. Measurements at a given temperature were extended up to 20 min.

3. Results and Discussion

3.1. Static Structure Factor. In SAXS the intensity I measured at a scattering vector q is directly related to the correlation of concentration fluctuations of the same wave vector

$$I(q) = VKS(q) \qquad (1)$$

The contrast factor K in eq 1 is given by the squared electron density difference of polystyrene and polyisoprene and is therefore in general weakly dependent on temperature. V is the volume of a polymer chain. For a block copolymer in the disordered state the structure factor at temperature T, $S_T(q)$, has been calculated by Leibler[12] within the random-phase approximation (RPA). In this theory the interaction between segments of the different constituents of the diblock copolymer is described in terms of a Flory–Huggins parameter χ which is essentially inversely proportional to T. The result is

$$S_T(q) = \frac{N}{F(qR_g) - 2\chi N} \qquad (2)$$

The form function F is expressed in terms of Debye functions,[12] and N is the total number of chain segments of the polymer. $S_T(q)$ exhibits a maximum at a wave vector $q^* \approx 2/R_g$ with R_g = the radius of gyration of the polymer. Due to the temperature dependence of χ, the intensity of this maximum increases when T is lowered. If one takes the polydispersity of the sample and the finite resolution of the scattering experiment into account, one finds very good agreement between the RPA structure factor and the experimental scattering profiles.[3]

However, whereas the theory assumes the position of the maximum q^* to be independent of temperature, experiments have shown a shift of q^* to smaller values with decreasing temperature.[3,5] This has been interpreted as a stretching of the polymer chain as expressed in an apparent R_g. For our polymer q^* decreases by 10% when T is varied from 160 to 100 °C. At the MST a discontinuous step of about 10% is observed defining the disorder-to-order transition temperature T_{ODT}.[5]

Figure 1 compares the static structure factors for three temperatures: 140 °C which is in the disordered state, 100 °C which is close to the phase transition, and 80 °C which is in the ordered state. These data were obtained with a conventional Kratky camera and corrected for the slit smearing effect. Before each measurement the sample was annealed for a minimum of $^1/_2$ h at the given temperature. At both temperatures that refer to the disordered state the RPA structure factor (full curve) gives a good fit of the data if R_G is treated as an adjustable parameter. The shift in the q^* position between 140 and 100 °C is clearly seen in the figure. The ordered state then is characterized by a very different shape of the peak. It has lost its asymmetry and is now better described by a Gaussian as is typical for a Bragg peak. The intensity of the second-order peak at $2q^*$ is very small which is in part due to the structure factor: if both lamellae of polyisoprene and polystyrene were of exactly equal thickness, then the second-order peak would not appear at all.

In the following we will now discuss the time-resolved SAXS after temperature jumps that start at $T = 140$ °C in the disordered state and lead to a new equilibrium either in the disordered or in the ordered state (see Figure 1).

3.2. Time Dependence of Temperature. The initial state of the sample is prepared by annealing it for 15 min at $T_0 = 140$ °C. No further variation of the structure factor is observed after this time. The temperature is then rapidly changed to its final value T_f, and the time dependence is shown in Figure 2. It is phenomenologically described by

$$T(t) = \frac{T_0 + T_f}{2} - \frac{T_0 - T_f}{2} \tanh \frac{t}{\tau_T} \qquad (3)$$

The values found for τ_T are typically 5 s for T_f above 100 °C and 7 s for the jumps to lower temperatures.

3.3. Relaxation of the Structure Factor within the Disordered State. It is observed in Figure 1 that a change of temperature from 140 to 100 °C within the disordered state results in drastic variation of the intensity in the regime of the peak in the scattering function. As both equilibrium states are well described within the RPA theory, we use the RPA structure factor equation (2) to calculate the response of the system to a steplike change of temperature $T_0 \rightarrow T_f$. Temperature enters eq 2 through

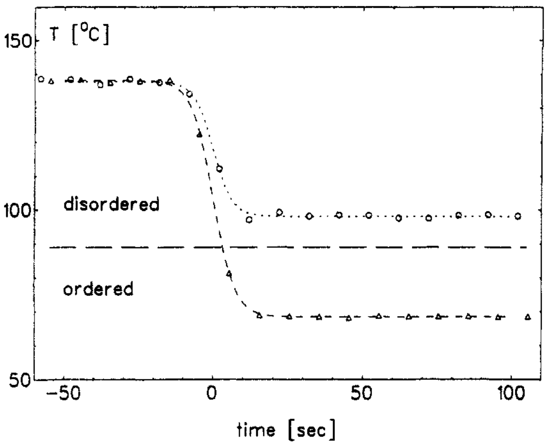

Figure 2. Time dependence of temperature during a quench. The curves are fits of eq 3.

the interaction parameter χ

$$\chi = A + B/T \quad (4)$$

The validity of eq 4 has been shown for polystyrene/polyisoprene, and the parameters A and B are known although they depend slightly on the composition f of the block copolymer.[3] In a linearized theory the time-dependent structure factor is then controlled by a first-order differential equation.[13]

$$\frac{dS_T(q,t)}{dt} = -\frac{2}{\tau_q}(S_{T_0}(q,t) - S_T(q,t)) \quad (5)$$

The subscript T or T_0 denotes the temperature that the structure factor S refers to.

Together with the boundary condition $S(q,t=0) = S_{T_0}(q)$ and $S(q,t\to\infty) = S_T(q)$, the solution of eq 5 is

$$S(q,t) = S_{T_0}(q)\exp[-(2t/\tau_q)] + S_T(q)\{1 - \exp[-(2t/\tau_q)]\} \quad (6)$$

The structure factor of the initial state given by $T = T_0$ decays with the rate $\tau_q^{-1}/2$, and the new equilibrium is attained with the same rate constant. The time τ_q is given by a diffusive law

$$\frac{1}{\tau_q} = \frac{\Lambda(q)\, q^2}{S_T(q)} \quad (7)$$

Equation 7 implies that the relaxation of the system into its new equilibrium after the temperature jumps is governed by the susceptibility that belongs to the final temperature T and is given by the static structure factor $S_T(q)$. The coefficient $\Lambda(q)$ may in general depend on wave vector q, as the relaxation involves segmental diffusion over length scales that lie in the regime of the internal modes of the polymer molecule.

In Figure 3 we show the result of a time-resolved SAXS experiment after a temperature jump from 140 to 100 °C. The peak height increases strongly and reaches its plateau value after approximately 20 s. Only every second data set is shown in the figure. In order to compare these data with eq 6, it is necessary to analyze the time dependence of the intensity at a fixed scattering vector q.

The observed times of change are only 3–4 times longer than the time τ_T for the change of temperature. We therefore use the functional form of eq 3 for $I_q(t)$ instead of the exponential in eq 6 to obtain the times of change τ_q for the intensity at each scattering vector q. A more detailed description of $I_q(t)$ in the case of a nonideal temperature jump would afford us to assume a mechanism for the variation of τ with time t in the derivation of eq 6 as has been done in other studies.[7] In view of the limited experimental information on the detailed shape of $I_q(t)$, however, we restrict ourselves to the above-described approximate procedure.

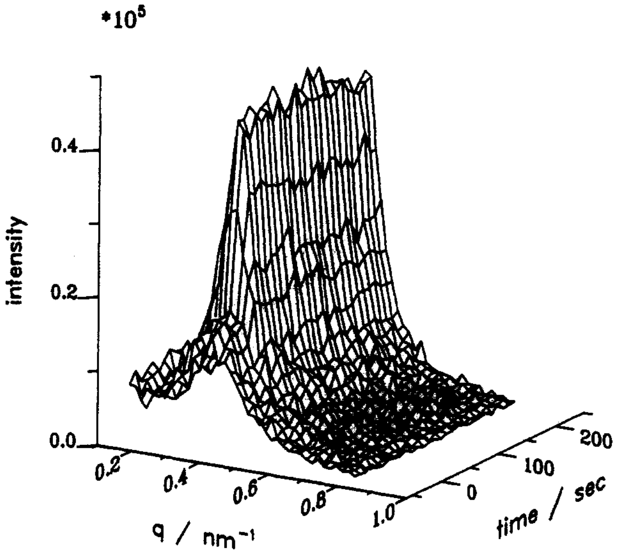

Figure 3. Example of a temperature jump within the disordered state, 140 °C → 100 °C.

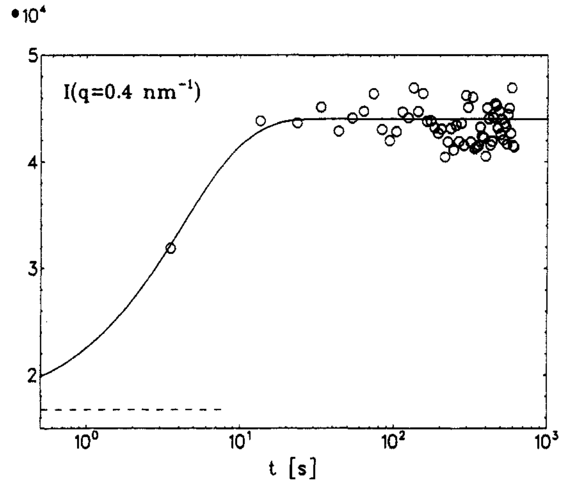

Figure 4. Intensity at fixed scattering vector q for the jump 140 °C → 100 °C. The full curve corresponds to a fit of eq 3 for $I_q(t)$ and allows us to determine τ_q. Note that the start-off level $I(t=0)$ (dotted line) is known.

In order to improve statistics the data have been averaged over two measured points. Figure 4 shows a satisfactory agreement between the form of eq 3 and the data. A slowing down of the relaxation is observed at the q^* of the structure factor. Moreover, in general the relaxation times τ_q are significantly larger than the finite width of the temperature jump τ_T.

In the following we restrict attention to those relaxation times τ_q for which $\tau_q \geq \tau_T$ and the above-described approximation is valid. The observed τ_q show a strong wave-vector dependence, and in Figure 5 we compare τ_q with $S_T(q)/q^2$ as suggested by eq 7. The transport coefficient $\Lambda(q)$ does not seem to carry an intrinsic q dependence although internal modes of the polymer would be expected to contribute to the relaxation.

The temperature dependence of the τ_q is rather weak. The process is also observed after T-jumps across T_{ODT}, and there is no abrupt change in τ_q at T_{ODT}.

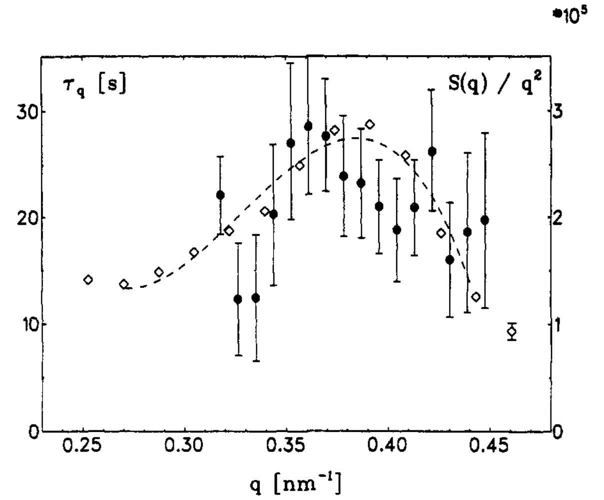

Figure 5. Relaxation times τ_q in comparison with the static structure factor according to eq 7 for the example of the jump 140 °C → 100 °C. The broken line is a guide line for the eye. τ_T for this jump is 6.5 s.

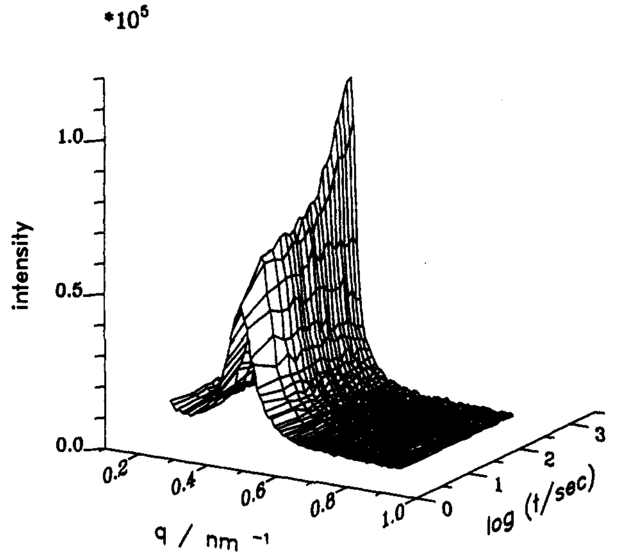

Figure 6. Example of a temperature jump from the disordered state into the ordered state: 140 → 70 °C. The two processes on short and long time scales are clearly discernible.

4. Temperature Jumps across the Disorder-to-Order Transition

For temperatures T that are below the phase transition temperature T_{ODT} the early state of the changes in $S(q)$ is analogous to the curves shown in Figure 4. For longer times, however, a different variation of I with t is found. It is phenomenologically described as an additional increase of intensity as was done for the scattering vector q^* in ref 9. However, for increasing wave vector the additional term becomes smaller or even negative at $q \geq 2.5q^*$. The variation of $S(q,t)$ on two time scales is clearly demonstrated in Figure 6. In a description of the time dependence of the structure factor we are therefore led to the following two-step procedure.

For the short time behavior we continue to use the exponential description of eq 6 for the variation of intensity with time at a given q position. $\tau_{q^*}(T)$ continues smoothly through T_{ODT} without significant change, thus indicating that the underlying process is not directly coupled to the disorder-to-order transition. The short-time process is a modification of the amplitude of concentration fluctuations in the system. However, the structure factor $S_T(q)$ (refer to eq 6) that is obtained after approximately 50 s is only metastable. Its form is still similar to the high-T structure factor: it is fairly well described by a Lorentzian

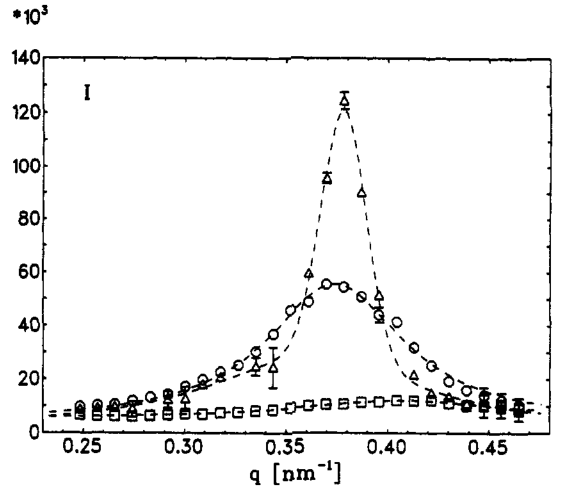

Figure 7. Initial disordered state (□); the metastable state $S_T(q)$ as described by eq 6 (○); the final state of the structure factor after a jump of 140 → 70 °C (△).

$$S^{\mathrm{L}}(q) = \frac{S^{\mathrm{L}}(q^*)}{1 + \xi^2(q - q^*)^2} \tag{8}$$

with a correlation length ξ on the order of nanometers. Equation 8 is also known to be an adequate description of the disordered state[3] in a limited interval of scattering vectors. The development of the metastable state after a temperature jump below T_{ODT} is demonstrated for the example of T = 70 °C in Figure 7. Immediately after the quench, the structure factor is still of the form that is characteristic for the disordered state. Its correlation length is ξ = 24 nm. It relaxes according to eq 6 to a metastable state with ξ = 60 nm. The values $S_T(q)$ refer to the parameters obtained from fitting eq 6 to the data at a given scattering vector q. The peak in $S(q)$ has shifted its maximum position q^* to smaller values, and it has gained in intensity. These findings agree with the observations made for the structure factor relaxation in the disordered regime.

We now turn to a discussion of the long-time behavior of the structure factor relaxation after temperature jumps from 140 °C to $T < T_{\mathrm{ODT}}$. A close inspection of the curves reveals a change of the peak shape from Lorentzian at short times to a narrow reflection at long times, as is demonstrated in parts a and b of Figure 8. In order to describe the transition between these two states quantitatively, we fit each data set at a given time t with the sum of a Lorentzian and Gaussian contribution. These two components refer to the liquidlike structure of concentration fluctuations as described by eq 8, on the one hand, and to the scattering from the lamellar order, on the other hand.

We assume the system to consist of lamellar domains without orientational order containing a large degree of disorder. The ordered lamellae will give rise to a Bragg reflection which we model as a Gaussian. The remaining disorder shows up as diffuse scattering and is represented as a Lorentzian contribution to the scattering function.

$$S(q,t) = S^{\mathrm{L}}(q,t) + S^{\mathrm{G}}(q,t) \tag{9}$$

with

$$S^{\mathrm{G}}(q) = \frac{A_{\mathrm{G}}}{(2\pi\sigma^2)^{1/2}} e^{-(q-q^*)^2/2\sigma^2} \tag{10}$$

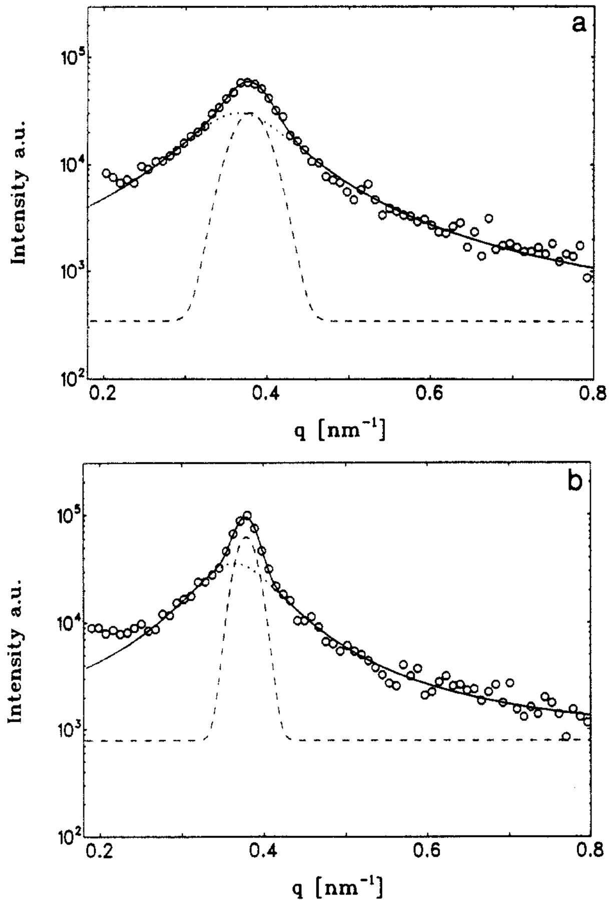

Figure 8. Relaxation of the structure factor on a long time scale. Peak shape after 35 s (a) and 580 s (b). The peak changes from a Lorentzian (dotted line) to a Gaussian (broken line) shape (see eq 9).

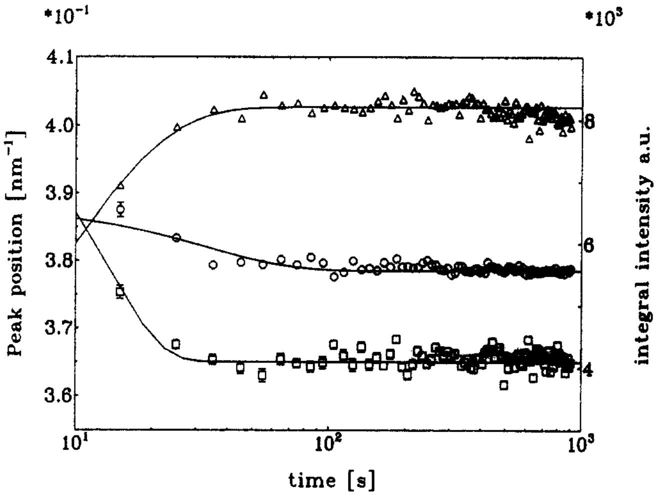

Figure 9. Time dependence of peak-shape parameters varying on a short time scale for the example of a jump of 140 → 70 °C: (△) integral peak intensity; (○) center of the Gaussian component; (□) center of the Lorentzian component.

The full width at half-maximum (fwhm) of the Gaussian component is 2.36σ. Equation 9 indeed represents an excellent description of the data as may be seen in Figure 8. The time t enters eq 9 implicitly through its parameters q_L^*, q_G^*, ξ, σ, $S^L(q^*)$, and A_G. In addition a flat background taken into account which is mainly due to scattering by density fluctuations.

The time dependence of the structure factor may now be discussed in terms of the shape parameters contained in eq 9. They are displayed for the example of T = 70 °C in Figures 9 and 10.

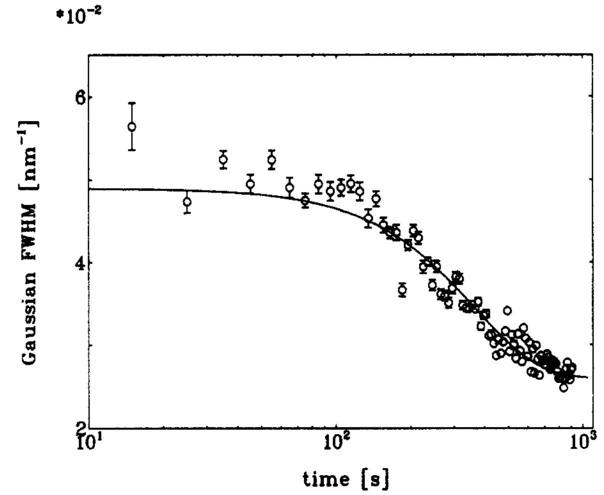

Figure 10. Time dependence for the full width at half-maximum (fwhm) of the Gaussian component (compare Figure 9). Its variation with time defines the slow relaxation time τ_{SF}.

The position q^* of both peaks does not coincide, but both parameters q_L^* and q_G^* relax rapidly and are then constant. A similar behavior is found for the correlation length ξ and the total peak intensity. This leads to the conclusion that at short times concentration fluctuations are built up and therefore intensity and correlation length increase. There is only one quantity that changes on a long time scale and accounts for the obvious change of the scattering profile as shown in Figure 8a,b. The fwhm of the Gaussian component decreases at a constant overall intensity, thus giving rise to an increase of the intensity at the peak position $I(q^*)$. This variation of σ with t is shown in Figure 10.

The detailed time dependence of σ is described by an Avrami type law.

$$\sigma(t) = \sigma_\infty + \sigma_0 \exp[-(t/\tau_{SF})^\beta] \tag{11}$$

The exponent β is clearly different from 1. Our fits result in $\beta \approx 2$. This finding agrees with the report of ref 9 for the time variation of $S(q^*,t)$. A recent theory for the process of structure formation in diblock copolymers[14] proposes β = 4 based on the assumption of a spherical droplet of the ordered phase growing into the disordered medium. We call τ_{SF} the typical time for structure formation.

The physical significance of the decrease of σ is the increasing thickness of the ordered lamellar domains D. Taking the Gaussian form of the peak into account, we may write

$$\sigma^2 = \sigma_{Res}^{\ 2} + (2\pi/D)^2 \tag{12}$$

σ_{Res} is the instrumental resolution. From measurements of Bragg reflections from cornea, we have determined $\sigma_{Res} \approx 0.02$ nm^{-1}. The domain thickness D is then found to vary between 160 and 380 nm during the relaxation.

Finally we turn to a discussion of the temperature dependence of the structure formation time τ_{SF}. Figure 11 displays our results in comparison with those of ref 9. The agreement between both experiments is very good considering the fact that ref 9 determined only the intensity at q^*, whereas the present experiments extract τ_{SF} from the thickness of the ordered domains. The figure also includes results for quenches starting from T_0 = 100 °C. There is no dependence for τ_{SF} on the initial temperature T_0.

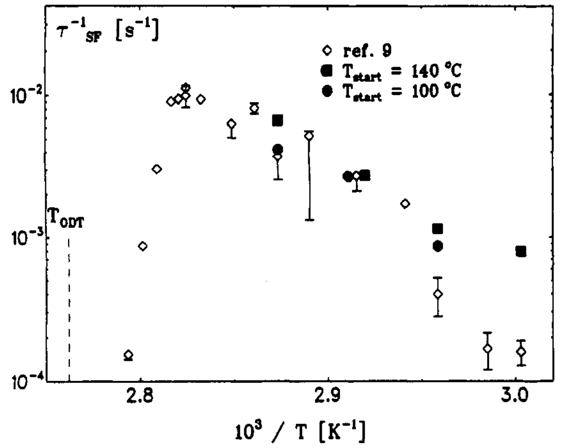

Figure 11. Slow relaxation time τ_{SF} together with the results of ref 9.

Our results do not refer to very small supercooling $\delta = T_{ODT}/T - 1$. It is seen in Figure 11 that τ_{SF} increases with supercooling, whereas close to T_{ODT} the opposite behavior should be expected.[14]

$$\tau \sim \delta^{-3/4} \exp(1/(\delta\xi_N)^2)$$

ξ_N is a correlation length measured in units of R_g.[14] At small δ the exponential term is expected to dominate, resulting in $\ln \tau \propto (\delta\xi)^{-2}$, which is not in agreement with the results of ref 9. Heterogeneous nucleation may be responsible for the stronger decrease of τ with supercooling.

The temperatures T in our experiment are in the regime $\delta > 3 \times 10^{-2}$ which is obviously controlled by the growth of ordered regimes in the proximity of the glass transition of the polystyrene-rich domain. The apparent activation energy for τ_{SF}^{-1} is 290 kJ/mol[9] and therefore of the typical magnitude of polystyrene 30K above its glass transition temperature.

In order to determine T_g for the polystyrene domain, we have performed DSC measurements on the block copolymer. The sample was annealed at 80 °C for 24 h, then cooled to −100 °C, and heated at 10 K/min. It displays two glass transitions at −60 and 70 °C as would be expected for this sample with $T_{ODT} > T_g^{PS}$.[1] The observed slowing down of structure formation for low temperatures may therefore be related to the glass transition of the polystyrene domains.

5. Conclusion

The formation of an ordered lamellar structure in nearly symmetric diblock copolymers proceeds on two well-separated time scales. Following a quench from the disordered state to temperatures below T_{ODT}, the supercooled liquid relaxes into a metastable state with a time τ on the order of seconds. The process is well described within linear theory, and in particular the slowing down of the relaxation in the vicinity of the peak of the structure factor is experimentally well confirmed. The lifetime of the metastable state depends on the depth of the quench, and for the polystyrene/polyisoprene system it is influenced by the glass transition of the polystyrene domain.

As a microscopic picture for the two processes involved in structure formation, we suggest the separation of the two components on the scale of the radius of gyration to be responsible for the short time relaxation. Accepting the value of T_S as determined from the high-temperature experiments on our block copolymer, one expects the system to be in a state for which the homogeneous melt cannot exist. This local demixing creates contrast and is therefore responsible for the observed increase of the overall intensity. However, the correlation of concentration fluctuations, i.e., the formation of long-range order, is not yet achieved.

In the second step the domains thus formed order onto a lattice just in the same manner as molecules crystallize from the melt. The process therefore carries some characteristics of a nucleation and growth phenomenon, in particular the Avrami type time dependence of the size of the ordered domains. The strong dependence of τ_{SF} on supercooling for $\delta \leq 3 \times 10^{-2}$ observed earlier does not conform to the assumption of homogeneous nucleation.

An alternative approach to an understanding of the slow process of structure formation is based on a redistribution of the transition layers between the microphases. This model will be outlined in detail in a separate publication.

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