Metastable States below the Order–Disorder Transition in a Symmetric Diblock Copolymer. A Time-Resolved Depolarized Light Scattering Study

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ABSTRACT: Depolarized light scattering has been used to study the ordering kinetics in a symmetric poly(styrene-*b*-isoprene) copolymer melt. The depolarized intensity variation with time following a quench from the disordered phase provides an estimate of the grain size which is consistent with the result from the SAXS experiment. The mechanism of grain relaxation is discussed in terms of rotational motions in the mobile environment. The dissolution of the initially ordered structure is much faster ($t < 10^2$ s) than the ordering process.

Introduction

The microphase separation or the order–disorder transition (ODT) in diblock copolymers has mainly been studied by small-angle X-ray scattering (SAXS), small-angle neutron scattering (SANS) and rheology.[1–4] Rheology[3,5,6] and SAXS[6,7,8] have also been used to study the ordering kinetics in symmetric diblock copolymers and recently[6] in graft copolymers and terpolymers. These experiments[3–8] have shown that the ordering process can be studied over a narrow temperature range below the T_{ODT} and provided information on the effect of chain architecture and on the nature of the ordering mechanism. In the case of symmetric poly(styrene-*b*-isoprene) copolymers, this temperature interval was ~12 K below the ODT where the ordering proceeds by heterogeneous nucleation and growth of grains with lamellar microstructure.[5] Other experiments like birefringence[9–13] and depolarized light scattering (DLS)[14] have been shown to be sensitive to the formation of ordered structures which are called domains or grains. In the former studies,[12,13] it was shown that the scattered power and the angular spread of the diffracted intensity from a sample held between crossed polarizers are related to a characteristic grain size whereas the latter method (DLS)[14] was sensitive to the formation of grains of cylinders in an asymmetric diblock copolymer in a common solvent. The static measurements above were very sensitive to the thermal history of the sample, which implied that kinetic effects associated with the observed hysteresis were present.

In the present work we utilize DLS to study, for the first time, the ordering kinetics in a symmetric poly(styrene-*b*-isoprene) (SI) copolymer melt. The sample orders at 359 K as revealed by SAXS and rheology and has a lamellar microstructure. We have shown that it is possible to study, by DLS, the metastable states in an undercooled diblock copolymer melt and provide a rough estimate of the grain size which is consistent with the SAXS result. A possible mechanism of relaxing the orientation fluctuations near and below ODT is discussed.

Experimental Section

The SI copolymer is identical to the one used in the SAXS and dynamic mechanical studies.[5] It has a number-average molecular weight $\bar{M}_n = 12\,200$ and a polydispersity $\bar{M}_w/\bar{M}_n = 1.06$, and the volume fraction of PS is $f_{PS} = 0.51$. Two glass-transition temperatures (T_g) have been identified by DSC, with the high-T_g at 334 K. In the ordered phase the diblock has a lamellar microstructure with a lamellar thickness of 127 Å and a domain thickness of ~700 Å estimated from the peak position and peak width, respectively. The ODT has been identified in SAXS from the drop of the peak intensity $I(Q^*)$ and the discontinuity in the peak width at $T_{ODT} = 359 \pm 2$ K. The interaction parameter has been evaluated by fitting the experimental intensity profiles to the mean-field theory, at temperatures above the T_{ODT}, including polydispersity corrections: $\chi = 0.0434 + 9.2/T$. The calculation of χ was based on the statistical volume $u = (u_{PS}u_{PI})^{1/2} \approx 144$ Å^3. Additionally, the T_{ODT} was obtained by three independent dynamic mechanical experiments, (i) isochronal temperature scans ($\omega = 1$ rad/s), (ii) isothermal frequency scans, and (iii) isochronal/isothermal time scans, but the most accurate determination was from (iii); the value of T_{ODT} (=359 K) is in good agreement with SAXS data.

The light-scattering setup with the incident and scattered beams polarized vertically (V) and horizontally (H) with respect to the scattering plane, respectively, is described elsewhere.[14] Measurements were made at a scattering angle θ of 135°. Under heterodyne conditions, the measured depolarized light-scattering intensity autocorrelation function, $G_{VH}(Q,t)$, is directly related to the desired normalized field correlation function $g_{VH}(Q,t)$, i.e., $bg_{VH}(Q,t) = G_{VH}(Q,t) - 1$, where b is the amplitude of $G_{VH}(Q,t)$ at short times and $Q = (4\pi n/\lambda)\sin(\theta/2)$ is the amplitude of the scattering wave vector with λ (=488 nm) being the wavelength of the laser and n the refractive index in the medium. The dust-free sample was prepared by filtration of an SI/toluene solution through a 0.22 μm Millipore filter into the dust-free light-scattering cell and subsequent evaporation of the solvent under vacuum for 1 week.

We have made three DLS experiments. In the first experiment, we monitored the intensity trace by following a temperature jump from the disordered phase ($T_i = 363$ K) to different final temperatures (T_f): 343, 351, 352, 353, 355, and 356 K near but below the ODT. All temperature jumps were made with the sample in the heating stage and the time

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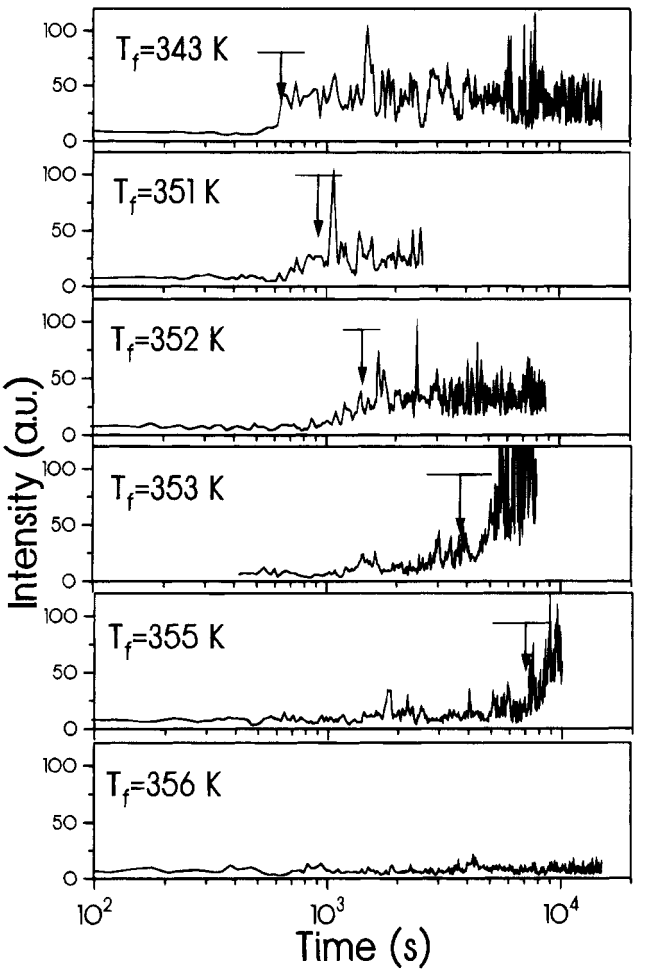

Figure 1. Depolarized intensity traces vs time following a quench from the disordered phase (T_i = 363 K) to different final temperatures, as indicated. Arrows separate the undercooled disordered from the ordered phases. Horizontal lines give the uncertainty in the characteristic time for the ordering

required to reach a constant T_f was ~600 s, which poses the lower time limit for the kinetic studies. In a second experiment, we monitored the intensity trace after a temperature jump from the ordered to the disordered phase. Additionally, for temperature jumps in the ordered phase we have measured $G_{VH}(t)$ for some temperatures at carefully chosen times.

Results and Discussion

The thermal treatment of the sample was as follows: The sample was first heated to 398 K—to erase any memory effects related to T_g and T_{ODT}—and then set to 363 K, which is a convenient starting temperature for the kinetic studies; it is located near but above the T_{ODT} as measured by SAXS and rheology. The sample was then quenched to different temperatures below the T_{ODT}, and the intensity traces vs time, $I_{VH}(t)$, for the different quenches are shown in Figure 1. The $I_{VH}(t)$ shown in Figure 1 is an average value over t_{av} = 20–30 s. In all traces but the last (T_f = 356 K) there is a "low" initial depolarized intensity of ~8 kHz with fluctuations of ±3 kHz (36%) followed by an increasing average intensity (typically 5–8 times higher) with higher fluctuations (typically 46%). The intensity profiles for the two time regimes which are separated in Figure 1 by arrows, correspond to the undercooled disordered and ordered phases, respectively. The characteristic time required for the ordering process is clearly temperature dependent. For shallow quenches (i.e., to T_f = 355 K) the formation of anisotropic grains requires a long time, but for deeper quenches (T_f = 343 K) the ordering process is very fast. For a quench to T_f = 356 K there was no change in the average intensity, and this was monitored for a period about 4 times longer than that shown in Figure 1. The effective T_{ODT} in the light-scattering experiment ($T_{ODT} \approx$ 356 K) is about 3 K below the one obtained by rheology (T_{ODT} = 359 K). It is worth noticing with respect to Figure 1 that the intensity fluctuations at $T \geq T_{ODT}$ are of the same magnitude as in the undercooled disordered phase but the fluctuations in the ordered phase are always higher than in the disordered phase. This finding suggests the presence of a slow relaxation process with characteristic time longer than t_{av}.

The short- and long-time plateaus (Figure 1) provide a way of evaluating the average grain size. Alternatively, we can use the SAXS length scale to predict the change in the depolarized intensity in going from the undercooled disordered to the ordered phase. The depolarized scattered intensity from a block copolymer melt in the disordered phase is due to the segmental anisotropies of the two blocks, but in the ordered phase there are contributions from both intrinsic and form anisotropies. The intensity ratio can be expressed as

$$\frac{I_{VH}^{ord}}{I_{VH}^{dis}} = \frac{\varrho_c \beta^2_{intr,c} + \varrho_g \beta^2_{form,g} F(x)}{\varrho^*_{PS} \beta^2_{PS} + \varrho^*_{PI} \beta^2_{PI}} \quad (1)$$

In the numerator, ϱ_c is the chain number density (=4.76 × 10^{-5} c/Å), $\beta^2_{intr,c}$ is the intrinsic optical anisotropy per chain (=2.1 Å^6/c), ϱ_g is the grain number density, $\beta^2_{form,g}$ is the form optical anisotropy per grain, and $F(x)$ is[15] a function of $x = (L/2)Q$, derived for a collection of anisotropic disks of diameter L. In the denominator of eq 1, ϱ^*_{PS} and ϱ^*_{PI} are the monomer number densities and β^2_{PS} (=38 Å^6)[16] and β^2_{PI} (=10.2 Å^6)[17] are the measured effective monomer optical anisotropies for PS and PI chains, respectively. The form anisotropy, β^2_{form}, entering eq 1 is calculated from the form birefringence, Δn_f, of a regular assembly of thin parallel plates:[18]

$$\Delta n_f = \frac{n_{PS} n_{PI}}{\sqrt{f_{PS} n^2_{PI} + f_{PI} n^2_{PS}}} - \sqrt{f_{PS} n^2_{PS} + f_{PI} n^2_{PI}} \quad (2)$$

where n_i and f_i are the refractive index and volume fraction of the ith (i = PS, PI) phases. In the limit of strong segregation, eq 2 leads to $\Delta n_f = -1.575 \times 10^{-3}$. The contribution from the intrinsic birefringence, Δn_{intr}, of block copolymer lamellae due to the effective monomer polarizability anisotropies, $\Delta\alpha$, and the stretching of the two blocks perpendicular to the interphase has recently been derived.[19] Assuming equal stretching for both blocks and using the values of -1.027×10^{-23} and 0.577×10^{-23} cm^3 for $\Delta\alpha$ of PS and PI, respectively, we obtain $\Delta n_{intr} = -3 \times 10^{-4}$. Then, β^2_{intr} and β^2_{form} of eq 1 are calculated from the corresponding Δn values using:

$$\beta^2_{intr,form} = (9/25)(\Delta\gamma_{intr,form})^2$$
$$\Delta\gamma_{intr,form} = (9/2\pi)(n/(n^2+2)^2)\Delta n_{intr,form} \quad (3)$$

with n being the average of the refractive indices n_{PI} and n_{PS}. Notwithstanding the similar values of Δn_{form} and Δn_{intr} the contribution of the second term in the numerator of eq 1 is the dominant one ($\varrho_c = L^{-3}$). In principle, the depolarized intensity originating from the form anisotropy (eq 1) depends on Q through $F(x)$ and

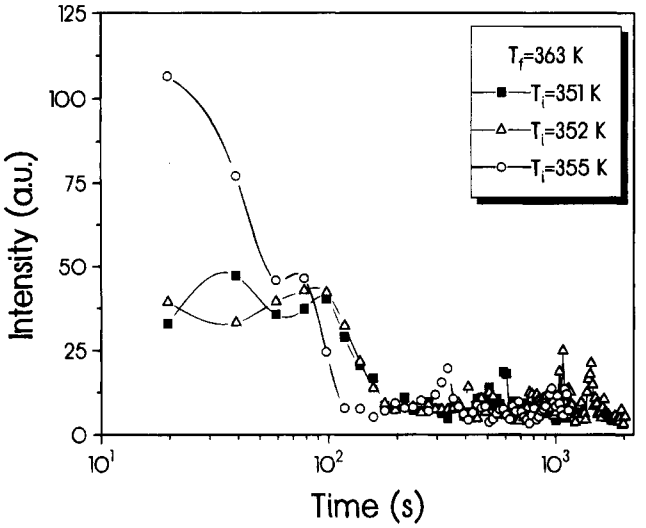

Figure 2. Depolarized intensity traces vs time taken while heating the sample from the ordered to the disordered phase (T_f = 363 K).

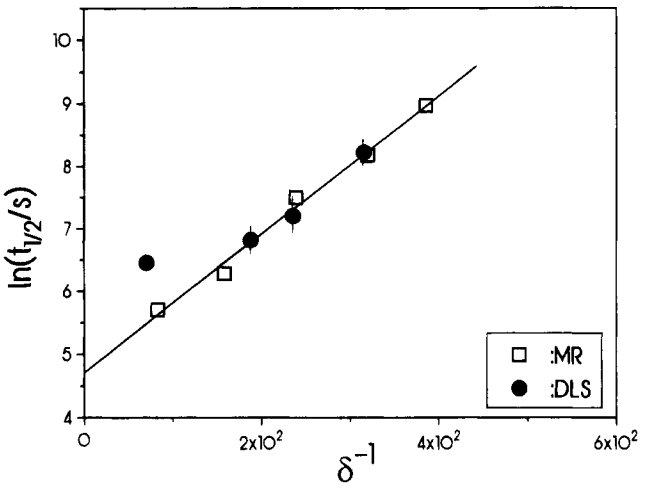

Figure 3. Ordering times as obtained from depolarized light scattering (DLS) (●) and rheology (MR: mechanical relaxation) (□), plotted vs δ^{-1}. The solid line is a linear fit to the former set of data. Vertical lines through the DLS times correspond to the horizontal lines (error bars) in Figure 1.

the curves of I_{VH}/β^2_{form} vs (sin θ)/2 show considerable dispersion. In our case, the size of the grains is small compared with the wavelength of light ($L/2\lambda \approx 0.07$) resulting in $F(x) \approx 1$ for light-scattering Q's. From the above, the intensity ratio in eq 1 is calculated to be equal to 10, which is only moderately higher than the experimentally obtained ratio. Inversely, a grain size of ~500 Å can account for the experimental intensity ratio of ~5.

In the second light-scattering experiment, we monitored the depolarized intensity while heating the sample from $T_i < T_{ODT}$ to 363 K. The intensity traces for some T jumps are shown in Figure 2. In Figure 2, the intensity at $t = 0$ corresponds to the long-time intensity plateau in Figure 1, and the long-time intensity in Figure 2 is the same (~8 kHz) for all T jumps notwithstanding the different starting intensities. Clearly, the dissolution (Figure 2) of the initially ordered structure is much faster than the ordering process: it takes about 10^2 s to dissolve the structure, but it needs a much longer time for the structure to grow following a T jump from the disordered phase. This is why in many experiments the T_{ODT} is observed much more clearly by heating the specimen: when a block copolymer is heated through the ODT, the kinetic effects are largely decoupled. Hysteresis effects have also been reported in measurements of the birefringence[10,11] in diblock copolymers which are related to the kinetic effects (Figure 1 vs Figure 2) above.

From the intensity traces in Figure 1 we have assigned a characteristic time (arrows in Figure 1) which separates the low- from the high-intensity plateaus. This assignment becomes difficult at some temperatures, and we use the horizontal lines as the limiting kinetic times. The characteristic times are then plotted in Figure 3 vs δ^{-1}, where δ ($=\chi - \chi_{ODT}/\chi_{ODT}$) is a dimensionless undercooling parameter. To obtain δ, we have extrapolated the χ parameter to the final temperatures at $T \leq T_{ODT}$ using the known $\chi(T)$ from the disordered phase. In Figure 3, the light-scattering kinetic times are compared with the kinetic times from rheology using 359 K as T_{ODT}. The data points near the ODT are excluded since a small error in temperature can greatly affect the picture. With the exception of the slowest light-scattering time, the agreement between the two sets of data is good when the difference in the

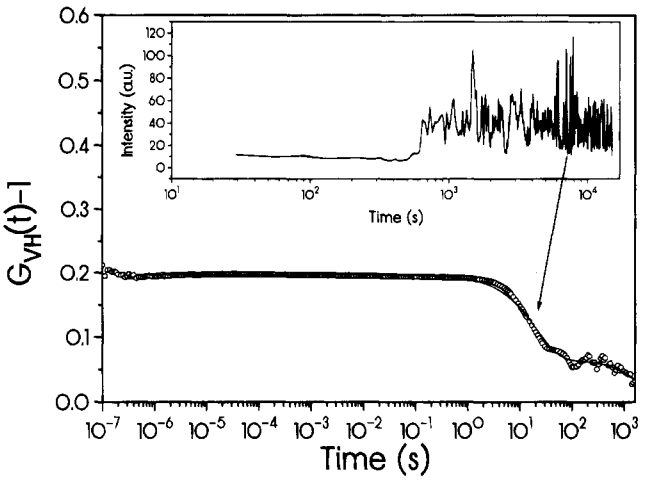

Figure 4. Depolarized intensity autocorrelation function taken after a quench to 343 K with an average intensity of ~38 kHz. The depolarized intensity trace is shown in the inset. The arrow indicates the intensity and the corresponding fluctuations under which the correlogram was recorded. The solid line denotes a double exponential fit to the experimental relaxation function accounting for the "fast" and "slow" fluctuations in the depolarized intensity.

T_{ODT} is taken into account. The reason for the first light-scattering time being too slow is probably associated with the limited experimental time resolution at this temperature. Moreover, both sets of data yield a linear relationship when plotted vs δ^{-1}, which is in agreement with the notion of heterogeneous nucleation.[5,6]

In the last experiment we have measured the depolarized intensity correlation function $G_{VH}(t)$ at some temperatures after structure formation, as indicated by the stabilized long-time intensity. Figure 4 shows the intensity trace at 343 K and the corresponding correlation function taken with an average intensity of ~38 kHz in the ordered phase. Long-time fluctuations are present in the baseline of $G_{VH}(t)$ as a result of very slow ($\tau > 10^3$ s) fluctuations in the I_{VH} intensity profile, and the experiment is practically made under heterodyne conditions which is also evident from the low value of $G_{VH}(t)$ at short times. The major fraction of the relaxation function decays exponentially (solid line in Figure 4) with a characteristic time of ~30 s, in accord with

the "fast" fluctuations in the I_{VH} profile shown in the inset of Figure 4. To account for the underlying mechanism, we first assume a translational diffusion mechanism and calculate the self-diffusion coefficient D_s ($=k_BT/N\zeta_0$, where $N = 144$ and ζ_0 is the local friction coefficient for Rouse dynamics[20]). Using the measured $\eta(T)$ we find good agreement with published self-diffusion measurements[21] at $T > T_{ODT}$ but at 343 K the calculated D_s ($=3.9 \times 10^{-19}$ m^2/s) is 2 orders of magnitude smaller than the measured value ($D = (\tau Q^2)^{-1}$) of 2.6×10^{-17} m^2/s at the same temperature. The large difference excludes a translational diffusion mechanism for the depolarized data in Figure 4. The situation here is similar to the one found for an asymmetric SI diblock melt[22] in the ordered phase with a Q-independent relaxation time.

Alternatively, we assume a rotational diffusion mechanism for the grain relaxation and we estimate the characteristic length scale $\xi_R(\sim(\tau k_BT/\eta)^{1/3})$. Substitution of $\tau = 30$ s and the measured viscosity ($=1.4 \times 10^5$ Pa s) leads to $\xi_R \sim 100$ Å at 343 K. ξ_R is smaller than the SAXS length of ~700 Å, and an effective viscosity of 4.7×10^2 Pa s should be used to reproduce the SAXS grain size. Anisotropic grains probably relax by slow rotational motions which apparently are sensing a liquid-like viscosity.

Conclusion

We have shown that depolarized light scattering can be used to study the ordering kinetics in diblock copolymers. Such kinetic experiments provide excellent identification of the order–disorder transition temperature. Furthermore, the metastable states below T_{ODT} and the fluctuations associated with the undercooled disordered and ordered phases can be studied by monitoring the changes in the depolarized intensity following a quench from the disordered phase. The intensity change as a function of time resulting from the phase transformation is consistent with the SAXS grain size. Anisotropic grains are relaxing through slow rotational motions in a mobile environment. Finally, the metastability gap is similar to the one obtained in rheology.

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