Annealing Effects and Signatures of the Order–Disorder Transition in Block Copolymer Cylinders

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ABSTRACT: Significant effects on annealing on the signatures of the order–disorder transition in quiescent block copolymers were observed. We find that the disordering transition in cylindrically ordered block copolymers is accompanied by discontinuous changes in the small-angle X-ray scattering profiles, due to broadening of the structure factor. The sharpness of the observed transition is strongly affected by the size of the coherently ordered regions (grains), which, in turn, is determined by annealing history. The temperature of the transition was confirmed by optical birefringence measurements, which show a discontinuous decrease to zero at the same temperature.

Introduction

The formation of ordered block copolymer microstructures in the bulk and in solution is a subject of continuing interest. Recent investigations have focused on the transition from an isotropic disordered state to an ordered state. A systematic understanding of this transition was initiated by the pioneering work of Leibler, who proposed a mean-field theory for the thermodynamics of diblock copolymers.[1] For asymmetric block copolymers ($\phi < 0.5$, where ϕ is the volume fraction of the minor component), a sequence of transitions from a disordered state to ordered spheres, cylinders, and lamellae, are predicted upon cooling. This theory was extended by Fredrickson and Helfand,[2] who used a formalism due to Brazovskii,[3] to include the effects of concentration fluctuations. These effects tend to stabilize the disordered phase. For low molecular weight block copolymers, the spherical morphology is unstable in the presence of fluctuations. In these systems, the disordered phase is predicted to form either a cylindrical or a lamellar phase on cooling, depending on ϕ and N, the total number of repeat units per chain.[2] In this paper we present a study of diblock copolymer materials with $\phi = 0.23$, exhibiting a disordered-to-cylindrical phase transition.

A wide variety of experimental tools have been used to locate the order–disorder transition (ODT). The first and most widely used technique is rheology, wherein the formation of the ordered phase is inferred from an anomalous frequency dependence of the shear modulus. Discontinuous changes in the low-frequency modulus are often,[4] though not always,[5] observed at the ODT. In contrast, traditional scattering methods for structure determination, such as small-angle X-ray and neutron scattering (SAXS and SANS), show only gradual changes at the ODT.[6] In particular, no discontinuity in either I_{max}, the intensity at the peak of the scattering profile, or q_{max}, the scattering vector at the peak has been observed.[6–8] Concentration fluctuations in the disordered state give rise to a maximum in the scattering porfile which is qualitatively similar to that obtained from the ordered state. However, if the microstructure is aligned by an external field, then qualitative changes in the small-angle scattering are observed at the ODT. Transitions from disordered to lamellar,[9] cylindrical,[10] and spherical[11] morphologies have been reported by Bates and co-workers in shear-oriented block copolymers. Like the rheological technique, this method for determining ODTs requires perturbing the sample.

In this paper we study the disordering of unperturbed, cylindrically ordered block copolymer materials. We demonstrate that the signatures of the ODT depend crucially on the coherence of the ordered structures, which, in turn, is governed by annealing history. We observe discontinuous changes in both low-resolution and high-resolution SAXS profiles if the samples have been sufficiently annealed. The low-resolution signatures reported here were first observed by Bates et al.[12] We also demonstrate that the disordering of the cylindrical phase results in a discontinuous decrease of the optical birefringence of the sample to zero. Previous studies have demonstrated that the ODT in lamellar samples can be identified by discontinuous changes in optical birefringence.[13,14] The ODTs obtained from SAXS and birefringence were found to be in good agreement.

Experimental Section

Two nearly monodisperse (polydispersity index = 1.07) polystyrene–polyisoprene block copolymers were synthesized by anionic polymerization under high vacuum. The characteristics of the materials were determined by methods described in ref 15. The molecular weights (M_W) of the polystyrene and polyisoprene blocks were 4.2×10^3 and 12.6×10^3, respectively for the smaller diblock, SI(4–13), and 7.9×10^3 and 22.3×10^3 for the larger one, SI(8–22). The volume fraction of the polystyrene in both polymers is 0.23. Dioctyl phthalate (DOP) was purchased from Aldrich, purified using Na_2CO_3 and $CaCl_2$, and distilled under vacuum (10^{-4} torr) at 200 °C. Experiments were performed on SI(4–13) melts and on a 75 wt % solution of SI(8–22) in DOP.

The birefringence of the samples was measured as a function of temperature using procedures and an apparatus that are described in ref 16. SAXS measurements were made

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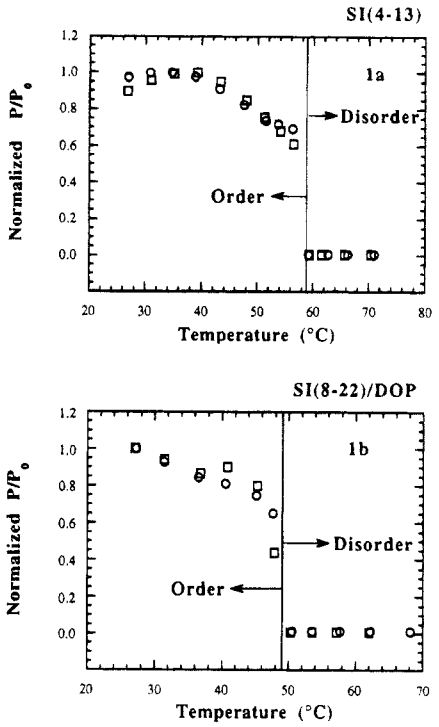

Figure 1. Normalized fraction of transmitted power P/P_0 versus temperature of (a) SI(4−13) melt (circles correspond to 8.5 h of annealing and a normalization factor of 0.03, and the squares correspond to 20.5 h of annealing and a normalization factor of 0.07) and (b) 75 wt % SI(8−22)/DOP solution (circles correspond to 4.6 h of annealing and a normalization factor of 0.012, and the squares correspond to 20.0 h of annealing and a normalization factor of 0.122). [Actual P/P_0 = (normalized P/P_0) × (normalizing factor).]

on two different instruments. Low-resolution measurements were carried out on an 18 kW rotating-anode X-ray generator (Rigaku RU300) at Exxon Research and Engineering Co. A vertically bent perolite graphite monochromator (002) crystal was used for focusing the beam. A combination of horizontal and vertical slits was used to define the resolution and to cut the tail of the direct beam (slit geometry). The full width at half-maximum (fwhm) of the main beam was 0.21°, corresponding to Δq of 3×10^{-2} Å^{-1}. This configuration allowed us to probe scattering vectors $q = (4\pi/\lambda)\sin(\theta/2)$ as low as 3×10^{-2} Å^{-1}, where λ is the X-ray wavelength and θ is the scattering angle. High-resolution SAXS measurements were carried out at the X10A beamline at the Brookhaven National Synchrotron Light Source at 8 keV (λ = 1.54 Å) in point geometry, obtained with slits. A triple-bounce silicon monochromator was used to collimate the beam into the detector. The fwhm of the main beam was 0.005°, corresponding to a Δq of 7×10^{-4} Å^{-1}. In this geometry we could probe q values as small as 5×10^{-3} Å^{-1}. X-ray measurements were made on ca. 0.3−0.5 mm samples held between Kapton windows.

In all the experiments—birefringence and SAXS—the samples were studied as a function of increasing temperature. The temperature was increased in steps, and data were recorded after the signal had reached a steady value. In the vicinity of the ODT this process took about 2 h.

Results and Discussion

The ODT of SI(4−13) and the 75 wt % SI(8−22)/DOP solution were determined by birefringence. The fraction of light transmitted through the sample, held between crossed polarizers, was measured as a function of temperature. The temperature dependence of P/P_0, where P_0 and P are the incident and the transmitted power, respectively, is shown in Figure 1. Both samples were subjected to similar thermal histories. The SI(4−13) sample was heated well above the ODT, cooled to 55 °C, and annealed at this temperature for a given period of time. The sample was then cooled to 28 °C and studied as a function of increasing temperature. Regardless of annealing history, a discontinuity in P/P_0, corresponding to a singularity in the optical birefringence, was observed when the sample was heated from 58 to 60 °C. Results obtained from SI(4−13) with annealing times of 8.5 and 20.5 h are typical and are shown in Figure 1. The ODT of SI(4−13) thus occurs at 59 ± 1 °C. Similar measurements were made on the SI(8−22)/DOP solution. We find that the disordering of solvated block copolymer cylinders is also accompanied by a discontinuous decrease of optical birefringence, as shown in Figure 1b. The ODT of the SI(8−22)/DOP solution occurs at 49 ± 1 °C and is also independent of annealing history.

Although the ODT temperature is not affected by the annealing history, the average size of a coherently ordered region (i.e., average grain size) increases significantly with annealing time. The fraction of transmitted light through a collection of randomly oriented, optically uniaxial grains held between crossed polarizers, P/P_0, depends on the difference in the refractive index for light polarized parallel and perpendicular to the optical axis of the grain, Δn, the wavelength of the incident beam, λ, the sample thickness, t, and the average grain size, l_{av}:[16,17]

$$P/P_0 = 4\pi^2(\Delta n)^2 t l_{av}/15\lambda^2 \quad (1)$$

In the ordered state Δn depends on the inherent order within a grain. Since the order parameter vanishes at the ODT,[1] both Δn and l_{av} tend to zero. The disordering of quiescently ordered materials thus results in no transmitted light through crossed polarizers ($P/P_0 = 0$). Since P/P_0 at a given temperature in the ordered phase is proportional to the grain size, l_{av}, the normalization factors in Figure 1a,b (see caption) are also proportional to l_{av}. We find that the SAXS profiles from these systems also depend on inherent order and l_{av}.

Low-resolution SAXS measurements were performed on SI(4−13) after it had been heated well above the ODT to erase the sample history and allowed to cool slowly (in ca. 8 h) to room temperature. The SAXS profiles were then measured in steps of ca. 2 °C. The results are shown in Figure 2, where the scattered intensity, I, is plotted as a function of the scattering vector, q. A broad peak is observed on the shoulder of the main beam at $q = 0.04$ Å^{-1}, corresponding to a period of 157 Å in real space. There are no discontinuous changes in either the intensity or the position of the main peak as the sample crosses the ODT temperature (59 °C). While q_{max} remains constant, I_{max} decreases continuously with increasing temperature. The peak width is within instrumental resolution. There is, however, an interesting change in the scattering profiles at $q > q_{max}$ ($q \sim 0.055$ Å^{-1}). The scattering curves obtained above and below the ODT form separate "bunches"; the scattering intensity obtained below 59 °C decays more rapidly than that obtained above 59 °C. In the inset in Figure 2 we plot the scattered intensity at $q = 0.056$ Å^{-1} (i.e., $q \approx 1.4q_{max}$) as a function of temperature. A discontinuous increase in the intensity is observed when the sample is heated from 58 to 60 °C, as expected from a system undergoing a weakly first-order phase transition. This is in very good agreement with the ODT temperature determined by birefringence. This signature is similar to those reported by Bates et al.[12] and Winey et al.[18] Bates et al. found that the ODT determined from the

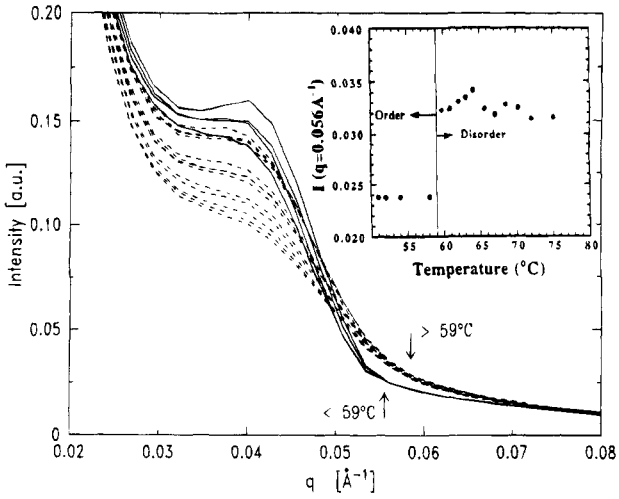

Figure 2. Scattering intensity of SI(4−13) melt, obtained on the low-resolution SAXS instrument, plotted as a function of scattering vector, q, at different temperatures. Note that the intensity is presented as measured without any vertical shifts. The dashed lines correspond to $T > 59$ °C, and the solid lines correspond to $T < 59$ °C. Inset shows the temperature dependence of I at $q = 0.056$ Å^{-1}. A discontinuity is evident at the ODT.

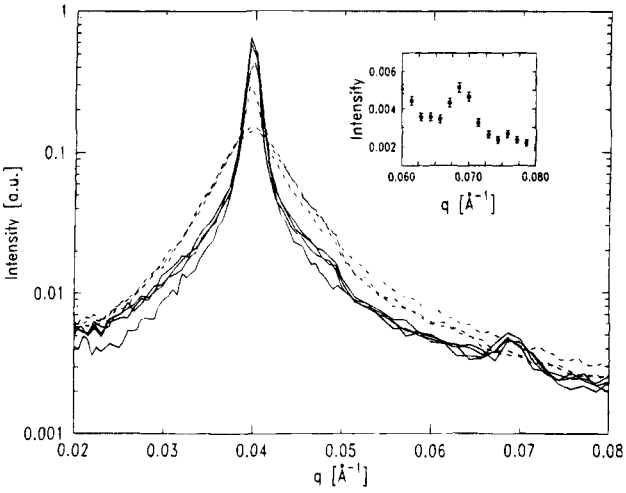

Figure 3. Scattering intensity of SI(4−13) melt, obtained on the high-resolution SAXS instrument, plotted as a function of scattering vector, q, at different temperatures. The sample was annealed at room temperature for 3 months. The dashed lines correspond to $T > 59$ °C, and the solid lines correspond to $T < 59$ °C. The inset shows scattering intensity obtained in the vicinity of the higher order peak ($q = 0.07$ Å^{-1}) in the ordered state.

discontinuity in SAXS line shape was in good agreement with their rheology measurements. Similar observations were made by Winey et al. on cylindrical polystyrene−polyisoprene diblock copolymers.

The reason for the increased scattered intensity at $q \approx 1.4q_{max}$ upon disordering becomes obvious when one examines the high-resolution SAXS data from SI(4−13). The sample was cooled slowly from well above the ODT to room temperature and kept at room temperature for 3 months. The sample was then heated in the SAXS machine in steps of about 2 °C. The temperature dependence of the SAXS profiles is shown in Figure 3. In contrast to the patterns shown in Figure 2, these data show fully resolved peaks. At temperatures well below 59 °C a sharp maximum at $q = 0.04$ Å^{-1} and a second-order peak at $q = 0.07$ Å^{-1} are observed. These two peaks correspond to a Bragg spacing ratio of $1:1/\sqrt{3}$, which is consistent with an array of hexagonally packed

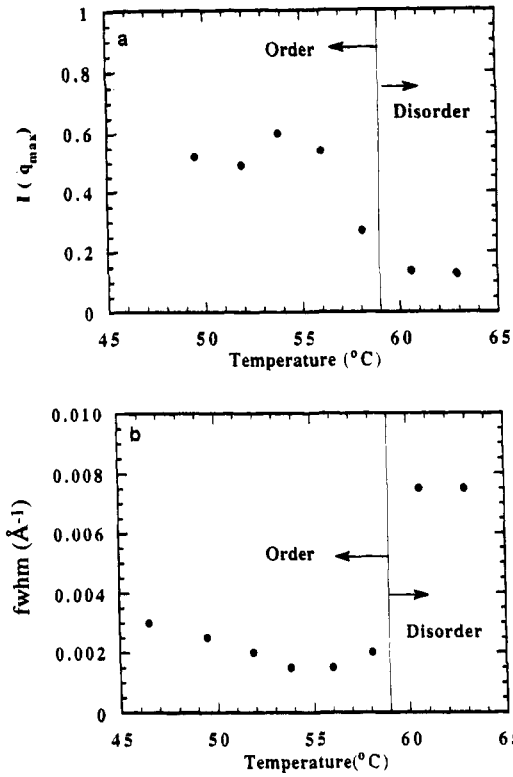

Figure 4. Temperature dependence of (a) I_{max} and (b) full width at half-maximum (fwhm) of the first-order peak, as derived from the data presented in Figure 3.

cylinders with intercylinder spacing of 157 Å. The radius of the cylinders is estimated to be 40 Å, based on the composition of SI(4−13). Upon heating from 59 to 61 °C, the line shape changes abruptly to that of a diffuse scattering peak. It is obvious that plotting the scattered intensity at any q between 0.035 and 0.06 Å^{-1} would reveal a discontinuity at 59 °C. Note that the second-order peak also vanishes abruptly at the ODT. In Figure 4, I_{max} and the fwhm of the first-order peak are plotted as a function of temperature. The plot of fwhm of the first-order peak versus temperature shows an obvious discontinuity at the ODT, while the change in I_{max} is not as abrupt. The discontinuous increase in the low-resolution scattered intensity at $q \approx 1.4q_{max}$ is thus simply due to a broadening of the structure factor upon disordering. This broadening is not evident in low-resolution data because of interference from the main beam and instrumental smearing effects, which are most prominent at low q values.

The fwhm of the scattering peaks obtained from ordered materials depends on instrumental resolution and on properties of the sample such as the degree of order and the coherence length of the ordered structure. For good enough instrumental resolution, the X-ray line width can be described in a siplified way in terms of the inherent order and average grain size, l_{av}:[19,20]

$$\text{fwhm} \sim \{\pi^2\delta^2/2d^3 + (1/l_{av})^2\}^{1/2} \qquad (2)$$

where δ is the half-width of a Gaussian distribution of intercylinder distances around a given d spacing; i.e., δ is inversely proportional to the degree of order within a grain. In our case, due to the polycrystalline nature of the samples, both δ and l_{av} contribute to fwhm. It is expected that δ and l_{av} will change discontinuously at the ODT. As was demonstrated in the birefringence experiments, l_{av} is strongly affected by the annealing history of the sample.

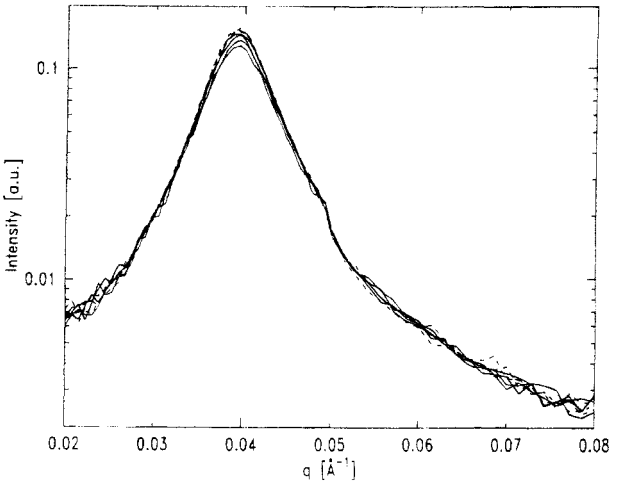

Figure 5. Scattering intensity of SI(4−13) melt, obtained on the high-resolution SAXS instrument, plotted as a function of scattering vector, q, at different temperatures. The sample was annealed at room temperature for 1 h. The dashed lines correspond to $T > 59$ °C, and the solid lines correspond to $T < 59$ °C.

Immediately after obtaining the data shown in Figure 3, the sample was cooled to room temperature where it was annealed for 1 h and then reheated in steps of 2 °C. The resulting scattering profiles are shown in Figure 5. The only difference between the data shown in Figures 3 and 5 is the vast difference in annealing times, ~2000 versus 1 h, respectively. The scattering peaks obtained from the ordered sample (below 59 °C) which was annealed for only 1 h are quite broad and are qualitatively similar to those obtained in the disordered state (above 59 °C). It is evident that the signature of the ODT in SI(4−13) at $q \approx 1.4q_m$ is not evident after 1 h of annealing at room temperature, even when a high-resolution SAXS instrument is used.

Annealing effects are important in quiescently ordered block copolymer materials due to the presence of imperfections[21]—defects and grain boundaries. These imperfections are bound to have higher free energy than the material within the coherently ordered grains and may therefore undergo rearrangements upon annealing at temperatures below the ODT. Since the time required for the rearrangements must depend on the mobility of the matrix phase, it is expected that clear signatures of the ODT would be observed with smaller annealing times if the mobility of the matrix phase were increased. The 75 wt % SI(8−22)/DOP solution was used to confirm this effect. DOP is a well-known plasticizer, and thus its presence will result in increased mobility of the polyisoprene matrix. This solution also exhibits a cylindrical microstructure at temperatures below 49 °C.[22]

A significant difference between the SI block copolymers with and without solvent is manifested in the rate of growth of birefringence after quenching from the disordered state. The time dependence of the growth of the P/P_0 of the two samples—SI(4−13) melt and SI(8−22)/DOP solution—is shown in Figure 6. Both samples were quenched from well above the ODT to 4 °C below the ODT, and the fraction of light transmitted through crossed polarizers was measured as a function of time. For the SI(4−13) melt, nonzero values of P/P_0, indicating the formation of coherently ordered grains, were obtained after 4.5 h of annealing. In contrast, only 2.5 h of annealing time was required for detecting the first signs of coherent order in the SI(8−22)/DOP

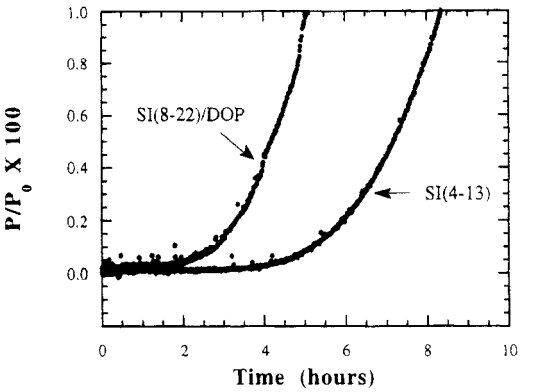

Figure 6. Time dependence of P/P_0 of SI(4−13) melt and a 75 wt % SI(8−22)/DOP solution. At $t = 0$ both samples were quenched from the disordered state to a temperature that was 4 °C below the ODT temperature.

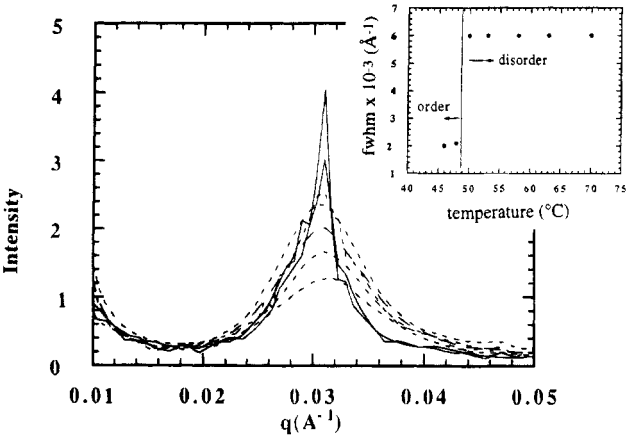

Figure 7. Scattering intensity of the 75 wt % SI(8−22) solution, obtained on the high-resolution SAXS instrument, plotted as a function of scattering vector, q, at different temperatures. The sample was annealed at room temperature for 1 h. The dashed lines correspond to $T > 49$ °C, and the solid lines correspond to $T < 49$ °C. Inset: Temperature dependence of full width at half-maximum of the first-order peak.

solution. The rate of growth of grains, as judged by the slope of the P/P_0 versus time curves, of the SI(8−22)/DOP solution is also significantly faster than that of pure SI(4−13).

High-resolution X-ray measurements on the SI/DOP solution confirm this fast growth of grains. SAXS patterns obtained after annealing for 1 h at room temperature are shown in Figure 7. As was the case with the high-resolution SAXS experiments on SI(4−13), the thermal history of the solution was erased by quenching from well above the ODT temperature. A sharp peak is observed at low temperatures at $q = 0.031$ Å^{-1}, which corresponds to an intercylinder spacing of 203 Å. The peak width increases discontinuously in the vicinity of 49 °C, which is the ODT determined by birefringence (see Figure 1b). It is thus evident that an unambigous signature of the ODT can be observed in plasticized SI(8−22) polymer after only 1 h of annealing. Careful examination of the SAXS profile at $q \approx 1.4q_{max}$ reveals a discontinuous increase in the intensity at the ODT, similar to that observed in SI(4−13) melts.

Conclusions

Signatures of the disordering transition in cylindrically ordered block copolymer melts and solutions were found to depend crucially on the annealing history of

the sample. We found that the disordering transition is accompanied by a discontinuous *increase* of the SAXS intensity at $q > q_{max}$. High-resolution SAXS data showed a discontinuity in the peak width due to broadening of the structure factor at the ODT. This discontinuity was observed in a quiescently quenched materials without applying any orienting field such as shear. The ODT inferred from the SAXS data was consistent with that obtained from optical birefringence measurements.

Our experiments demonstrate that the order–disorder transition of a sample with randomly oriented grains can only be detected from small-angle scattering, if the coherently scattering domains are large enough to allow the inherent order to contribute significantly to the peak width. The ability to detect the transition thus depends not only on annealing history of the sample but also on instrumental details such as incident flux and instrumental resolution.

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