Influence of Imperfections on the Disordering of Block Copolymer Cylinders

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ABSTRACT: Small-angle neutron scattering and optical birefringence were used to study the disordering transition of a cylindrically ordered block copolymer material. It was found that the disordering temperature of shear-oriented "single crystals" was 62 °C, while that of imperfect, granular samples formed under quiescent conditions was 49 °C. In sheared samples where the imperfections were partially removed, coexistence of ordered and disordered regions was observed at temperatures between 49 and 62 °C.

Introduction

The transition from an ordered phase to an isotropic (liquid-like), disordered phase in block copolymers has been the subject of several investigations. In a seminal publication, Leibler obtained a phase diagram for block copolymers by comparing the free energy of ordered phases with several different symmetries and the disordered phase.[1] This theory was extended by Fredrickson and Helfand[2] to account for fluctuation effects which tend to stabilize the disordered phase and cause the order–disorder transition to be weakly first order. In this respect block copolymers belong to a more general class of materials that includes smectic liquid crystals. A comprehensive analysis of the thermodynamics of such materials was published by Brazovskii.[3]

Current thermodynamic theories on ordered block copolymers are limited to single crystals. An infinite periodic structure is assumed to propagate coherently with no change in amplitude, phase, or direction. However, it is well known that ordered block copolymer materials formed under quiescent conditions are only ordered on a local scale and thus contain *imperfections*. Regions within which coherent order prevails are often referred to as "grains". The term grain is perhaps an oversimplification because electron micrographs on quiescently ordered materials show continuous variation in structure orientation in addition to line and surface imperfections—defects and grain boundaries, respectively.[4] This granular texture arises due to the highly viscous (nearly sold-like) nature of the ordered phase and the lack of a preferential orientation within the sample during the ordering process. Micron-sized grains are usually observed,[4,5] indicating that a large number of imperfections are expected in typical experimental samples with dimensions of a few millimeters. The question of whether the disordering of granular block copolymer materials into an isotropic, liquid-like state is affected by the nature of the imperfections has not been addressed, either experimentally or theoretically. The implicit assumption has been that the presence of imperfections does not affect the disordering transition.

In this paper, we present evidence for imperfection-mediated disordering of a granular block copolymer material.

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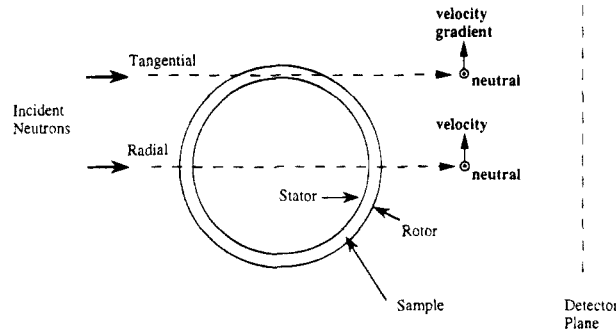

Figure 1. Schematic of the shear cell (top view).

Experimental Results

A nearly monodisperse polystyrene–polyisoprene diblock copolymer was synthesized by anionic polymerization under high vacuum (polydispersity index = 1.07). The molecular weights (M_w) of the polystyrene and polyisoprene blocks were determined to be 8×10^3 and 22×10^3 g/mol, respectively, and we refer to this polymer as SI(8–22). Experiments were conducted on a 75 wt % solution of SI(8–22) in dioctyl phthalate (DOP)—a nonvolatile solvent for polystyrene and polyisoprene. It is believed that the solvent acts like a plasticizer and is uniformly distributed throughout the sample.[6]

The properties of this sample were studied by small-angle neutron scattering and optical birefringence as a function of increasing temperature. Because of natural neutron and optical contrast between polystyrene and polyisoprene, no deuterium labeling was necessary. Data were recorded at each temperature after the signal had reached a steady value. In some cases this took up to 2 h. Before starting a new series of measurements, the shear and thermal history of the sample was erased by heating it to the disordered state (65 °C).

We first describe results obtained from in-situ small-angle neutron scattering (SANS) under shear. The shear cell[7] and its orientation relative to the incident neutron beam are shown in Figure 1. The SI(8–22)/DOP solution was placed in a 0.5 mm gap between two concentric quartz cylinders—an inner stator and an outer rotor with an inner diameter of 6 cm. Collimated neutrons with a wavelength (λ) of 5 Å ($\Delta\lambda/\lambda = 0.15$) were directed radially and tangentially through the shear cell to give the scattering profiles in two planes, one containing the velocity and neutral directions and the

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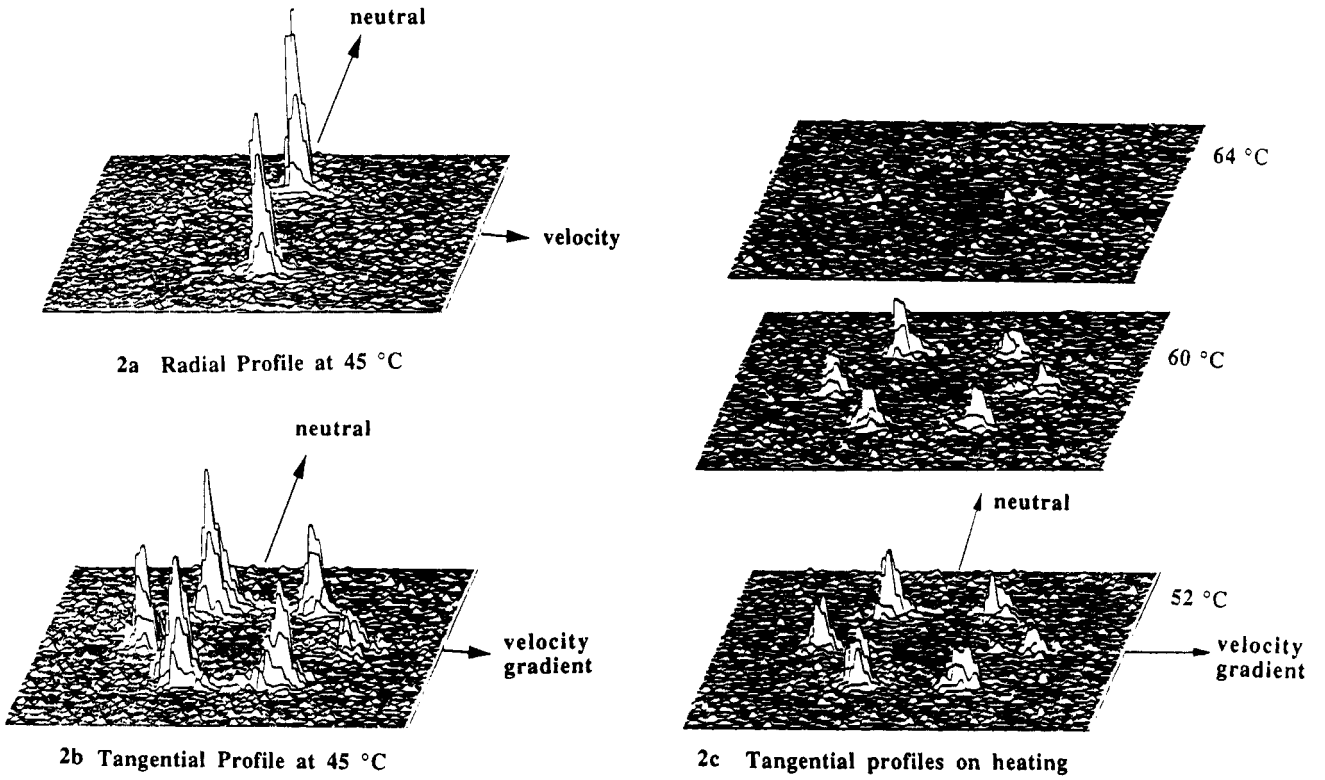

Figure 2. (a and b) Two-dimensional radial and tangential SANS profiles obtained from the SI(8–22)/DOP after oscillatory shear at 45 °C. (c) Tangential profiles as a function of temperature. The disordering of the single crystal of hexagonally packed cylinders occurs between 60 and 64 °C. The scattering maxima are located at a scattering vector of 0.031 Å^{-1}.

other containing the velocity gradient and neutral directions.[8,9] The radial profiles were obtained using a 12.7 mm diameter circular sample aperture while the tangential profiles were obtained using a 2 mm × 12.7 mm rectangular aperture. Other instrument configuration details are described in refs 8 and 9. The SANS experiments were carried out on the NG3 beamline at the National Institute of Standards and Technology.[10]

The sample was first disordered by heating to 65 °C and then cooled to 45 °C. This process was carried out in the absence of shear. The sample was then subjected to *oscillatory* shear (200% strain, frequency = 0.2 Hz) in which the time dependence of the deformation had a triangular wave form. The radial and tangential scattering profiles obtained after shearing are shown in Figure 2. The sixfold symmetry of the tangential profile and the scattering peaks in the neutral direction of the radial profile indicate the presence of polystyrene-rich cylinders arranged on a hexagonal lattice with cylinder axes pointing in the velocity direction. The average spacing between cylinders is 200 Å and the cylinder radius is estimated to be 50 Å, based on the composition of SI(8–22) and assuming that the DOP is uniformly distributed throughout the sample. The full widths at half-maximum of the peaks (0.008 Å^{-1}) are larger than instrumental resolution (ca. 0.003 Å^{-1}).[11] Some imperfections thus remain after shear alignment to give a "mosaic spread", and we thus refer to this material as a "textured single crystal". Shear orientation of cylindrical block copolymers was first demonstrated by Keller and co-workers.[12] Our "single crystal" was heated under *quiescent* conditions. Tangential SANS profiles at selected temperatures are shown in Figure 2c. The hexagonal scattering pattern is lost between 60 and 64 °C. The "single crystal" disordering temperature, $T_{ODT}^{crystal}$, is thus 62 ± 2 °C.

Previous studies have demonstrated that the disordering of granular block copolymer materials is accompanied by a sharp decrease in the sample birefringence.[6,13] The optical birefringence of the SI(8–22)/DOP solution was measured using an apparatus and procedures described in ref 14. The solution was placed in a heat-sealed, cylindrical, glass cuvette (0.74 cm inner diameter), and the birefringence of the encased sample was measured as a function of increasing temperature. The experiment was repeated several times, starting with different grain sizes, which were obtained by annealing the sample at 45 °C for variable amounts of time. Longer annealing times led to larger grains, which in turn produced a larger birefringence signal.[14] In Figure 3, the fraction of incident light transmitted through the sample held between crossed polarizers, P/P_0 (P is the transmitted power, and P_0 is the incident power of a He–Ne laser), is shown as a function of temperature. Note that P/P_0 at 27 °C increases by an

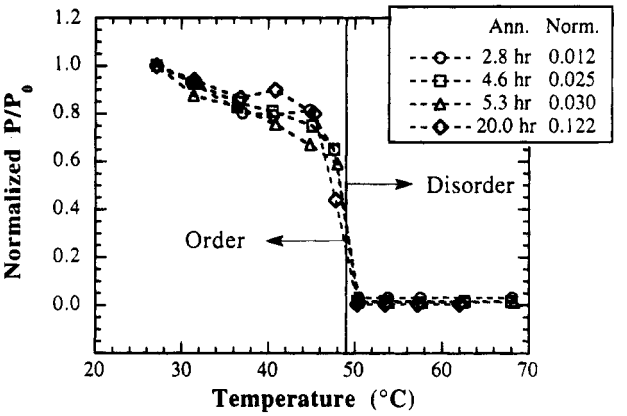

Figure 3. Fraction of transmitted power P/P_0 versus temperature of quiescently prepared samples. Samples were annealed at 45 °C for different amounts of time, as indicated in the legend (Ann.). The data obtained from different samples are normalized so that all the data can be presented on one graph. The normalizing constants corresponding to each data set are shown [actual P/P_0 = normalized P/P_0 × (Norm)]. The disordering of the granular material occurs at 49 ± 1 °C, regardless of annealing history.

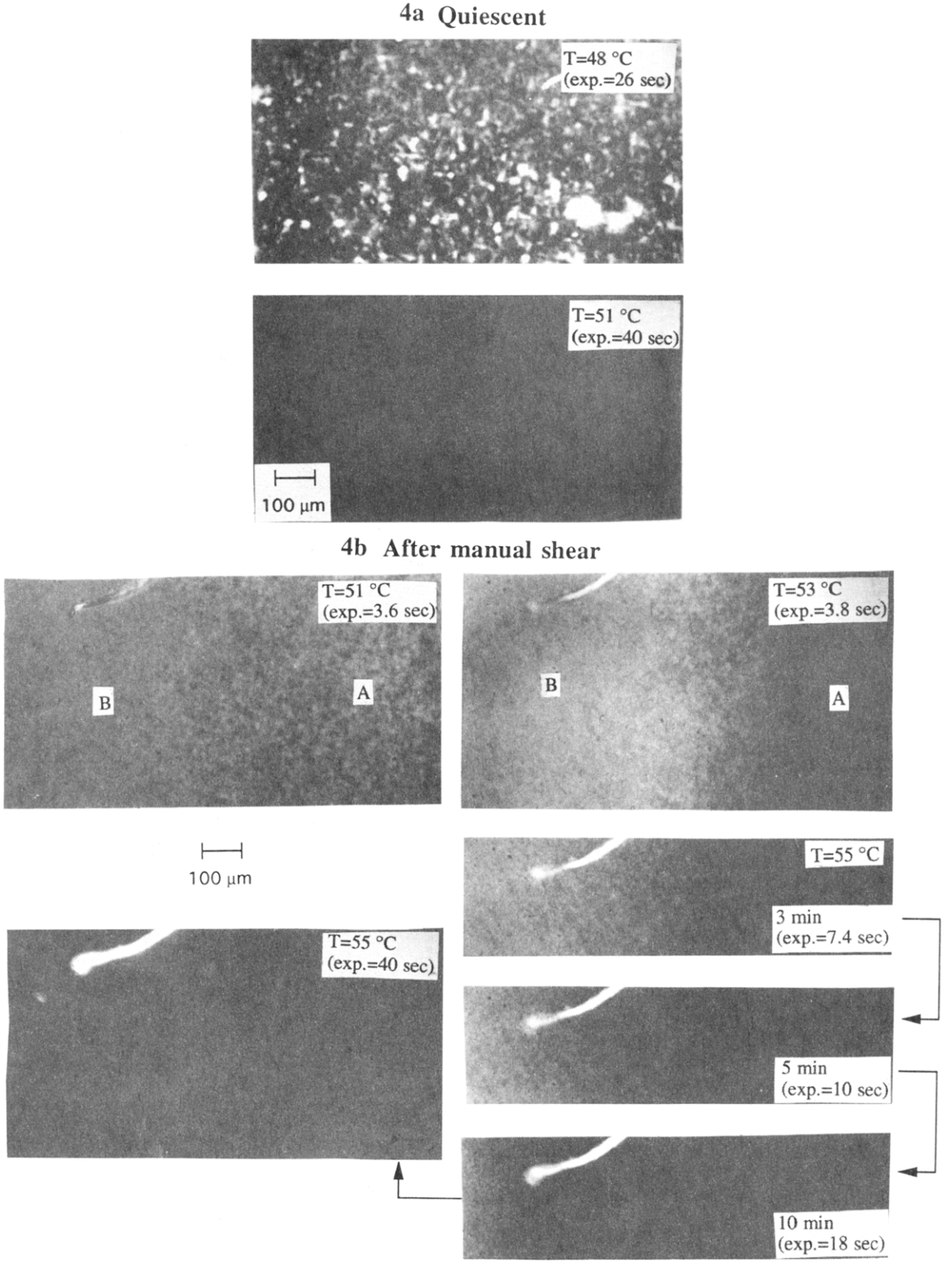

Figure 4. Optical micrographs of the SI(8−22)/DOP solution obtained (a) under quiescent conditions wherein the granular material, evident at 48 °C, disorders when heated to 51 °C and (b) after imposing manual shear deformation. At 51 °C we see evidence of order; region B has a more uniform texture than region A. At 53 °C region A disorders, while region B remains ordered. Upon heating to 55 °C, we see the disordering of region B. The kinetics of the disordering process was captured on micrographs; the time in minutes refers to the time after heating from 53 to 55 °C. The scratch on the cell wall at the top of the micrographs serves as a convenient reference. The exposure time (exp) used to obtain the micrographs are indicated to facilitate intercomparisons (the incident light intensity was kept constant).

order of magnitude when the annealing time is increased from 2.8 to 20 h. However, regardless of annealing history, we find a sharp transition in the birefringence signal between 48 and 50 °C, indicating that the disordering temperature of the granular material, T_{ODT}^{grains}, is 49 ± 1 °C. This is 13 °C lower than $T_{ODT}^{crystal}$, indicating that the presence of imperfections affects the disordering of granular material.

Optical microscopy was used to confirm the phenomenon of imperfection-mediated disordering. The SI(8−22)/DOP solution was confined between two quartz disks separated by a 1 mm aluminum spacer. The texture of

the sample was examined on a microscope equipped with crossed polarizers and a hot stage. In Figure 4a we show the results obtained under quiescent conditions. The granular texture evident at 48 °C is due to the presence of local order. However, heating the sample to 51 °C results in disordering as evidenced by the dark, featureless micrograph that was obtained. This is consistent with the birefringence measurements described in the previous paragraph.

The sample was then heated well above $T_{ODT}^{crystal}$, cooled to 45 °C, and subjected to shear by translating the top quartz disk manually. The resulting texture was much smoother, indicating that some imperfections had been eliminated. The alignment of microstructure in the sample was confirmed by rotating the sample on the microscope stage and observing the periodic increase and decrease of the transmitted light intensity. However, different regions of the sample exhibited different textures, indicating that some regions were better aligned than others. Upon heating this sample, it was found that the order in many regions persisted at temperatures well above 49 °C (T_{ODT}^{grains}). In Figure 4b we show one such region at 51 °C. Note that the amount of light transmitted through the sample after shear is significantly larger than that transmitted through the unperturbed sample (Figure 4a), as is evident from the large difference in exposure times used to obtain the micrographs. In Figure 4b the region marked A appears "grainy" or "speckled" while the region marked B appears to have a more uniform texture. When the sample was heated to 53 °C, we found that region A disordered while region B (the one with a smoother texture) remained ordered. Upon heating to 55 °C, we observed that the boundary between the ordered and disordered regions moved across rapidly from right to left, resulting in the disordering of the entire region under observation. It is thus evident that the imperfections found at the edge of region B, which were stable at 53 °C, became unstable at 55 °C and caused the disordering of region B. We repeated such experiments several times and observed the disordering of several different regions at temperatures ranging from 51 to 57 °C. Thus the disordering temperature measured by optical methods is seen to approach that obtained by SANS on a single crystal (62 °C) if the sample is shear-oriented. We also performed SANS on an imperfectly aligned sample (there was considerable overlap of the peaks in the hexagonal scattering pattern obtained in the tangential configuration) and found that it disordered at 56 ± 2 °C (i.e., lower than $T_{ODT}^{crystal}$).

Concluding Remarks

In summary, we find that the disordering temperature of a granular block copolymer material depends on the nature of the imperfections. Imperfections may thus be used to tune the properties of block copolymers, as is done routinely in crystalline solids and semiconductors. One might expect imperfections to undergo transformations at temperatures lower than the disordering temperature of a single crystal since the material trapped in the imperfections is bound to have higher free energy than material within a grain. However, the fact that these transformations can result in the disordering of the coherently ordered grains was unexpected. Defect-mediated phase transitions in related materials such as smectic liquid crystals have been studied.[15] However, which of the imperfections are important in the disordering of block copolymers remains to be established.

From the limited experiments that we have performed, it appears that imperfections play a bigger role in determining the ODT of cylindrically ordered materials than that of lamellar samples. In previous publications we had reported on similar experiments performed on a lamellar SI(11−17)/DOP solution with 65 wt % polymer.[8,9] In those experiments we found that SANS-determined ODT from shear-oriented samples (using steady shear) was in reasonable agreement with the birefringence determined ODT from quiescently ordered material. While we cannot rule out a small difference between $T_{ODT}^{crystal}$ and T_{ODT}^{grains} in the SI(11−17)/DOP solution, or data indicate that this difference—if it exists—is less than 4 °C.[16]

Pioneering experiments of Koppi et al. established that the disordering transition in the presence of shear fields is different from that obtained under quiescent conditions.[17] Our results indicate that the disordering transition depends not only on instantaneous shear rate but on shear history, due to the relationship between shear and imperfections.

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