Shear Effects on Solvated Block Copolymer Lamellae: Polystyrene-Polyisoprene in Dioctyl Phthalate

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Small-angle neutron scattering experiments were performed on a polystyrene-polyisoprene diblock copolymer in concentrated dioctyl phthalate solution under Couette shear. Lamellar orientations were monitored below and above the order-disorder transition temperature with the neutron beam incident either radially or tangentially on the cylindrical shear cell. It was found that lamellae are oriented mostly parallel to the plane of the shear cell walls. Oscillatory shear helps improve the lamellar alignment. Above the quiescent order-disorder transition, the shear-induced alignment (observed as an anisotropy of the scattering ring) follows a master curve for all temperatures.

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The rheology of a concentrated polystyrene-polyisoprene (PS-PI) diblock copolymer solution in dioctyl phthalate (DOP) has been investigated using small-angle neutron scattering (SANS) and a Couette shear cell. Other scattering experiments on copolymers under shear have been reported. Reciprocating shear has been used [1,2] in order to study shear-induced structural changes in diblock copolymer lamellae both below and above the order-disorder transition (ODT). Lamellar orientation with normals in the neutral direction (which is perpendicular to the velocity and velocity gradient directions) was reported along with shear-induced order above the quiescent ODT. Couette shear has been used [3] on a triblock copolymer and a high degree of orientation of cylindrical structures along stream lines was observed. Because this shear-induced cylindrical alignment was almost perfect, bright "diffraction" spots were observed along with well resolved higher order peaks. Moreover, a number of shear investigations have been performed on smectic fluids (liquid crystals, wormlike micelles, disklike micelles, vesicles, etc.) [4–6]. The purpose of our experiments was to carefully monitor shear-induced changes in a PS-PI lamellar diblock copolymer solution in all three directions (both in the plane of the lamellae and perpendicular to them). This was done using a neutron beam that was incident either radially or tangentially to the Couette shear cell. Both simple shear and oscillatory shear were used and the solution was measured at temperatures both above and below the quiescent ODT.

SANS data were taken at the National Institute of Standards and Technology [7] at the following instrument configuration: wavelength of 5 Å, wavelength spread of 15%, source-to-sample distance of 11 m, and sample-to-detector distance of 6.5 m. Two sample apertures were used: rectangular aperture of 2 mm × 1.27 cm for the tangential geometry and circular aperture of 1.27 cm diameter for the radial geometry. This configuration yielded well defined peaks and/or a ring at a scattering wave number of 0.032 $Å^{-1}$. Because the purpose of our experiments was to monitor lamellar orientations, and because of nonuniformity of the sample thickness in the tangential beam configuration, the scattered data were not scaled to an absolute cross section. The NIST-Boulder shear cell [8] used in these experiments consists of two concentric quartz cylinders (an inner stator and an outer rotor whose inner diameter is 6 cm) with a 0.5 mm gap for the sample. Both the simple shear and oscillatory shear modes were computer controlled. Sample heating was controlled through circulating water in the stator and the sample temperature was monitored at all times. In order to avoid sample degradation (of polyisoprene mainly), a nitrogen gas sample environment was set up during measurements. The sample consisted of a PS-PI diblock copolymer (molecular weights of the PS and PI blocks were 1.1×10^4 and 1.7×10^4, respectively, and polydispersity was less than 1.07) dissolved in dioctyl phthalate, DOP, with 65% polymer weight fraction (which corresponds to the lamellar phase). DOP is a nonvolatile good solvent for both PS and PI especially within the temperature range of our measurements. The quiescent ODT has a strong dependence on polymer weight fraction; it is believed, however, that solvent acts mainly as a "plasticizer" and is uniformly distributed throughout the sample [9]. Because of the natural contrast between PS and PI, no deuteration was necessary. When loaded into the shear cell, the sample showed a clear and uniform texture above the quiescent ODT and developed small elongated bubbles when sheared below the ODT. The data were obtained in two separate runs during which several of our observations were reproduced. Each time a new series of measurements were made, the sample shear and thermal histories were "erased" by heating the sample to a temperature above the ODT.

First, the ODT of the sample was determined by moni-

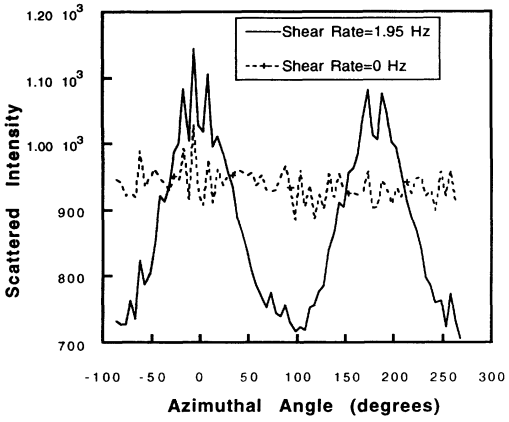

FIG. 1. Scattered intensity for the radial profile averaged over a narrow scattering wave number range containing the observed ring (0.028–0.037 $Å^{-1}$) for increasing azimuthal angle in the detector plane obtained at a temperature of 43 °C and shear rate of 1.95 s^{-1}. The curve for the zero shear case is also shown. The origin in angles is taken to be vertical axis (vertical spots appear at 0° and 180°).

toring whether sample alignment persists after shearing is stopped. This was done by comparing the heights of the vertical and horizontal cuts of the scattering ring (in the detector plane) at various temperatures. Deviation of the ratio of these peak heights from unity is the signature of an ordered phase (Fig. 1). The ODT was estimated to be 36 ± 2 °C which is in good agreement with the value obtained using optical birefringence (38 ± 1 °C) [9].

Starting from a temperature above the ODT (42 °C), the sample was cooled down to 25 °C under quiescent conditions. Upon starting simple shear at a shear rate of 0.2 s^{-1}, both the radial and tangential profiles changed rapidly over the first 20 min before settling down to the spectra that are shown in Figs. 2(a) and 2(b); the radial geometry shows peaks along the neutral direction (vertical spots) while the tangential geometry shows both a residual ring and peaks along the velocity gradient direction (horizontal spots). These observations are consistent with the following physical model. Quenching from the disordered to the ordered state results in randomly oriented lamellae which locally could be described as "crumpled sheets." Simple shear results in stretching these sheets in the shear velocity direction thus smoothing the crumples (or ripples or wrinkles) that run perpendicular to that direction (and leaving only crumples that run parallel to that direction). The peaks observed in Fig. 2(a) are due to the aligned ripples while the peaks observed in Fig. 2(b) characterize lamellar alignment parallel to the shear cell walls. Repeating these experiments with oscillatory shear (200% strain, 0.2 s^{-1} shear rate) gives qualitatively similar results with much sharper peaks and no residual ring in the tangential geometry [see spectra shown in Figs. 2(c) and 2(d)]. Changing the oscillatory shear

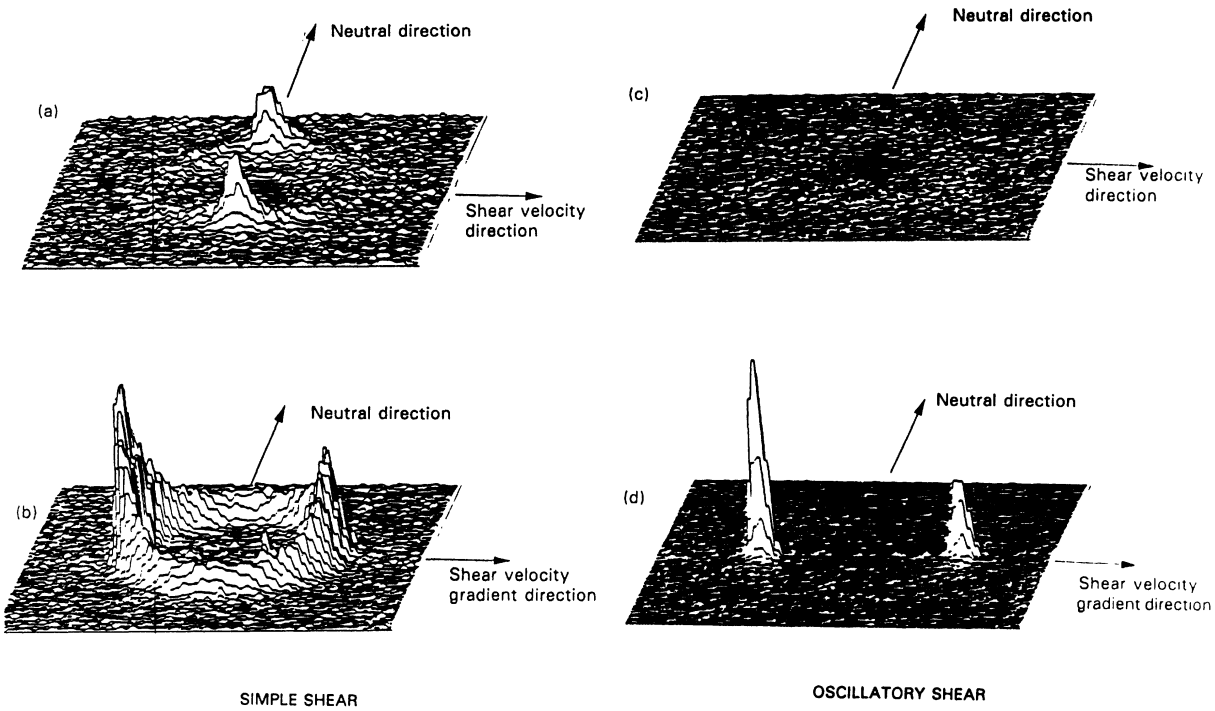

FIG. 2. SANS profiles obtained at a temperature of 25 °C and shear rate of 0.2 s^{-1}: (a) simple shear, radial configuration; (b) simple shear, tangential configuration; (c) oscillatory shear, radial configuration; and (d) oscillatory shear, tangential configuration.

strain amplitude (to 100%) does not seem to change our qualitative observations. Simple shear and oscillatory shear were applied sequentially and seen to have reversible effects on the sample. Simple shear on a well oriented sample (i.e., following oscillatory shear) seems to reintroduce the local ripples that run along the shear velocity direction. Simple shear seems to be a way of "ironing out" the wrinkles along the shear direction (only). It should be noted that the tangential profile was no longer observable when the neutron beam was translated by as little as 2 mm away from the aligned tangential configuration; in which case an almost pure radial profile was observed. This fact and the very high tangential profile peaks (despite the fact that the sampled scattering volume is smaller) confirm our conclusion that lamellae are oriented mainly parallel to the shear cell walls.

Above the quiescent ODT, shearing induces order in the copolymer sample. For each sample temperature, there is a characteristic shear rate γ_c above which structure formation is observed. This is manifested as an anisotropy of the scattering ring (vertical and horizontal sector cuts of the data have different peak heights) and is reminiscent of what was observed below the quiescent ODT. This could be seen as a shear-induced shift of the spinodal line to higher ODT temperatures [1,2,10]. At the measured shear rates (below 40 s^{-1}) and temperatures (42 °C to 60 °C), the observed shear-induced structure was characterized by two vertical peaks in the radial profile (see Fig. 1) and an isotropic ring in the tangential profile (not shown here, see Ref. [11]). The fact that no peaks were observed in the tangential profile excludes the possibility of lamellar layers with normals oriented mainly along the neutral direction or the velocity gradient direction. It is not clear what structure was formed; rough conjectures include cylindrical morphology with cylinders oriented along stream lines or "rolled" lamellae with isotropic cross sections. The "structure" formed under shear seems to be poorly defined, maybe because it has not reached the final stages of spinodal decomposition. The shear-induced upward "shift" of the ODT temperature has been explained theoretically [10] in terms of nonlinear fluctuations.

Plots of the peak anisotropy ratio ρ in the radial profile (ratio of the peak heights for sector cuts along the vertical and horizontal directions) with shear rate γ at various temperatures T [Fig. 3(a)] show the following scaling law: $\rho \sim (\gamma/\gamma_c)^{0.19 \pm 0.03}$ for ratios $\rho < 0.95$. Note that the scaling exponent is independent of temperature, which could be interpreted as a nonweakening of the driving force behind the shear-induced order (at least over an 18 °C temperature range). Extrapolation of this $\log(\rho)$ vs $\log(\gamma)$ linear behavior to $\rho = 1$ (disordered sample) yields an estimate for the characteristic shear rate γ_c which is the onset of shear-induced ordering. γ_c increases exponentially with sample temperature as evidenced by the linearity of a $\log(\gamma_c)$ vs T plot [Fig. 3(b)]. If the shear rate is rescaled so that the anisotropy ratio ρ is plotted for increasing γ/γ_c, curves corresponding to the various temperatures fall on a "master" curve [Fig. 3(c)]. This is reminiscent of the time-temperature superposition principle for polymer melts in the rubbery region.

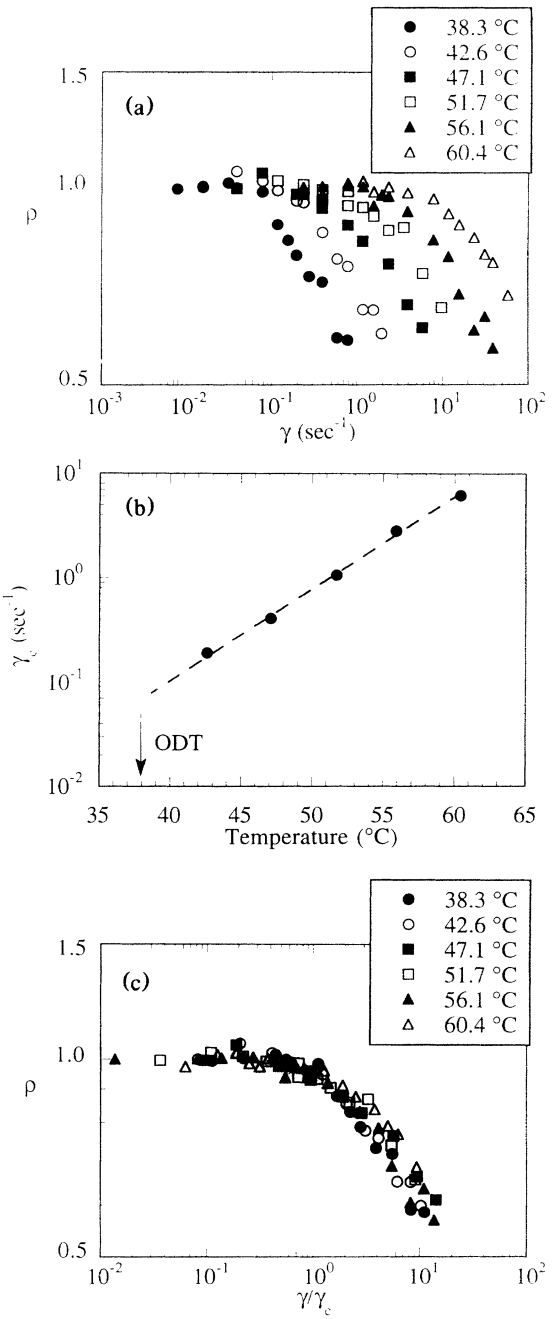

FIG. 3. (a) Variation of the peak anisotropy ratio ρ (ratio of the peak heights for sector cuts along the vertical and horizontal directions) in the radial profile with shear rate γ at various temperatures T (above the quiescent ODT). (b) Variation of the characteristic shear rate γ_c (onset for shear-induced order) with sample temperature. (c) Master curve for the variation of the peak anisotropy ratio ρ with rescaled shear rate γ/γ_c for all temperatures.

In conclusion, the reported experiments show that a monitoring of both the radial and tangential profiles yield a reliable picture of lamellar alignment. Observation of the radial profile alone would lead to erroneous conclusions. We suggest that the peaks observed on the radial profiles under simple shear below the ODT are due to local wrinkles and do not characterize the dominant lamellar alignment which can be seen in the pure tangential configuration only. Oscillatory shear yields a much better lamellar alignment than simple shear. Simple shear was found to iron out the lamellar wrinkles along the shear direction but also to introduce such wrinkles on a perfectly oriented sample (i.e., following oscillatory shear) that run parallel to the shear direction. Lamellar morphology of copolymers could be characterized [12] by smooth continuous meandering of the direction of the normal vectors rather than in terms of well defined domains that are highly ordered and breaks (defects) between these domains. More details about the above described experiments will be published elsewhere [11].

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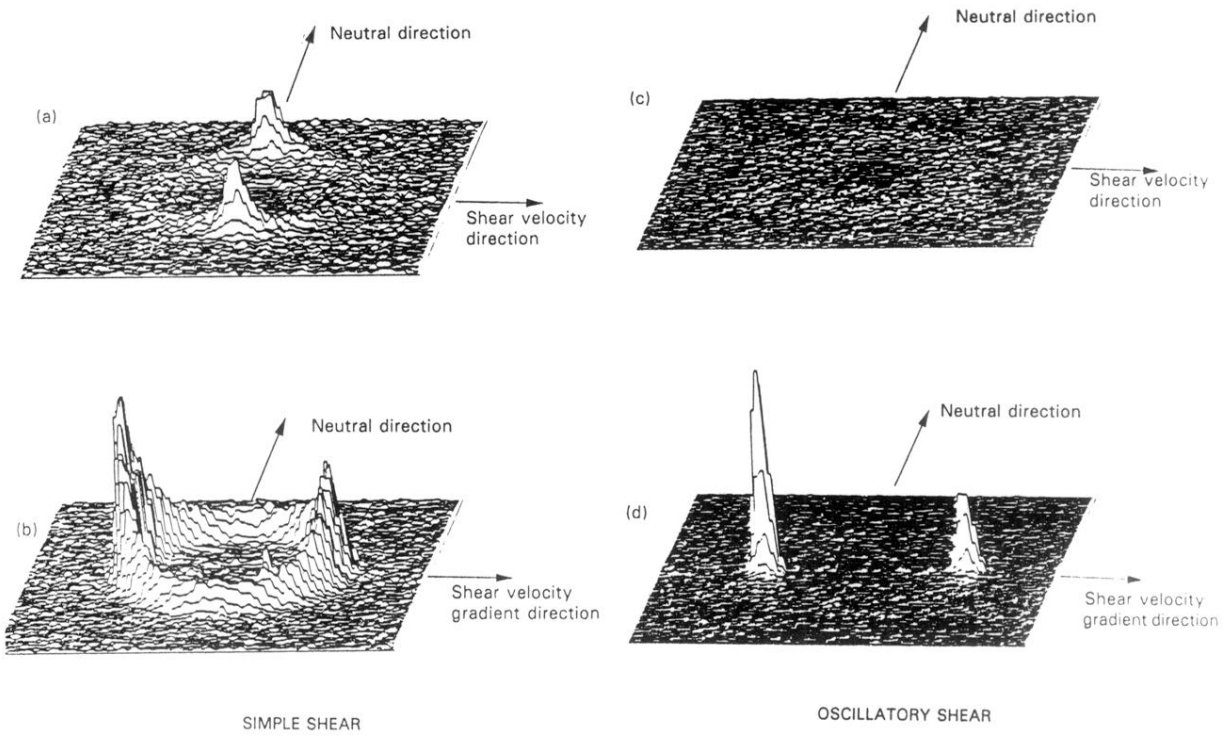
[13] Certain equipment and instruments or materials are identified in this paper in order to adequately specify the experimental conditions. Such identification does not imply recommendation by the National Institute of Standards and Technology nor does it imply that the materials are necessarily the best available for the purpose.



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