

A transition from shearinduced order to shearinduced disorder in block copolymers

N. P. Balsara and H. J. Dai

Citation: *The Journal of Chemical Physics* **105**, 2942 (1996); doi: 10.1063/1.472162

View online: <http://dx.doi.org/10.1063/1.472162>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/105/7?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

[Experimental measurement of shearinduced diffusion in suspensions using long time data](#)

Phys. Fluids **8**, 2011 (1996); 10.1063/1.869004

[The influence of shear on the ordering temperature of a triblock copolymer melt](#)

J. Chem. Phys. **104**, 1589 (1996); 10.1063/1.470747

[BINGHAM AWARD LECTURE—1994 Shearinduced particle diffusion in concentrated suspensions of noncolloidal particles](#)

J. Rheol. **39**, 813 (1995); 10.1122/1.550619

[Shearinduced particle migration in suspensions of rods](#)

J. Rheol. **38**, 444 (1994); 10.1122/1.550522

[A constitutive equation for concentrated suspensions that accounts for shearinduced particle migration](#)

Phys. Fluids A **4**, 30 (1992); 10.1063/1.858498



A transition from shear-induced order to shear-induced disorder in block copolymers

N. P. Balsara and H. J. Dai

Department of Chemical Engineering, Polytechnic University, Six Metrotech Center, Brooklyn, New York 11201

(Received 29 March 1996; accepted 6 June 1996)

The effect of steady shear flow on a weakly ordered block copolymer material was examined by *in situ* small angle neutron scattering. We demonstrate this material undergoes a transition from shear-induced ordering to shear-induced disordering at a fixed temperature above the quiescent disordering temperature. Current theories, which assume that the primary effect of shear flow on block copolymers is to suppress disordered concentration fluctuations, can only predict shear-induced ordering. Our results indicate that the coupling between flow and microstructure is not unique and that it can change qualitatively with shear rate. © 1996 American Institute of Physics. [S0021-9606(96)51431-5]

The imposition of shear flow can have profound effects on phase transitions in weakly ordered systems.¹ Current theories and experiments suggest that diametrically opposite results can be obtained, depending on the coupling between the applied shear field and the internal microstructure. For example, in ordered colloidal suspensions, plane-over-plane sliding becomes more difficult with increasing shear rate, eventually leading to a disordering transition.^{2,3} On the other hand, by suppressing fluctuations in the isotropic or disordered phase, shear flow causes an ordering transition in surfactant solutions and block copolymers.^{4–8}

In this paper we report on the shear-induced phase behavior of a concentrated block copolymer solution. We have identified a temperature at which this material exhibits both shear-induced ordering and shear-induced disordering. This implies that the coupling between shear and block copolymer microstructure is not unique, and that it can change qualitatively with shear rate.

A polystyrene–polyisoprene diblock copolymer was synthesized by anionic polymerization under high vacuum. The weight average molecular weights of the polystyrene and polyisoprene blocks were determined to be 8 and 22 kg/mol, respectively, polydispersity index of the copolymer

=1.07, 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). No deuterium labeling was necessary due to the natural neutron contrast between polystyrene and polyisoprene. The solution was placed in a shear cell consisting of two concentric quartz cylinders, an outer rotor, and an inner stator. The shear rate, $\dot{\gamma}$, is the ratio of the velocity of the outer rotor surface to the gap size (0.5 mm). Neutrons with a wavelength of 0.5 nm were directed through the shear cell in two directions—radial and tangential (see Ref. 6 for details). Small angle neutron scattering (SANS) intensity profiles were measured in two planes, one containing the flow and neutral directions, and the other containing the velocity gradient and neutral directions; the neutral direction is defined to be the one perpendicular to both flow and gradient directions. The SANS intensity, normalized to 10^8 monitor counts, were corrected for background scattering and are reported as a function of \mathbf{q} , the scattering vector, $|\mathbf{q}| = 4\pi \sin(\theta/2)/\lambda$, where θ is the scattering angle and λ is the wavelength of incident beam ($\lambda = 0.5$ nm).

The properties of the SI/DOP solution used in this study under quiescent conditions were reported in a previous publication.⁹ At low temperatures the solution consists of

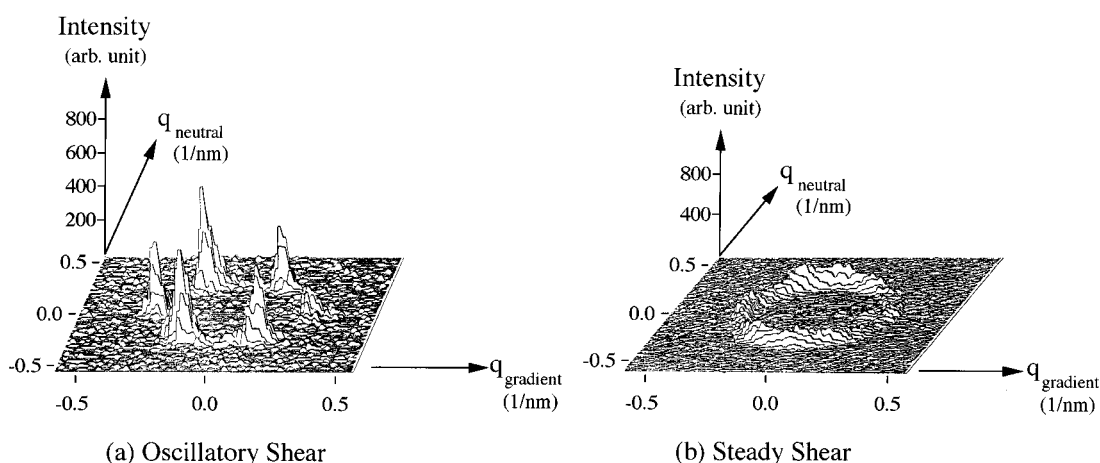


FIG. 1. Scattering profiles in the gradient-neutral plane at 46 °C under (a) oscillatory shear (0.2 Hz, 200% strain) and (b) steady shear ($\dot{\gamma}=0.38$ s⁻¹).

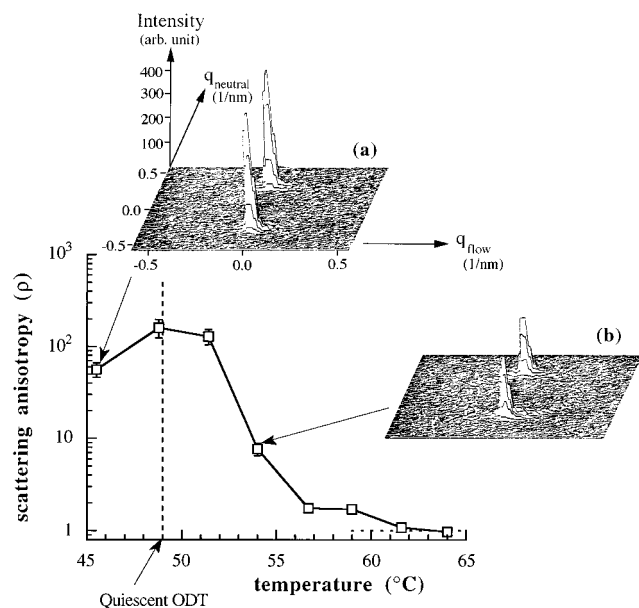


FIG. 2. The temperature dependence of scattering anisotropy, ρ , under a steady shear rate of 0.38 s^{-1} . The two-dimensional SANS profiles in the flow-neutral plane, which were used to obtain ρ , are shown at selected temperatures of (a) 46°C and (b) 54°C . The scales for (a) and (b) are identical.

ordered polystyrene cylinders embedded in a polyisoprene matrix and the DOP is more or less uniformly distributed throughout the sample. The average spacing between cylinders is 20 nm and the cylinder radius is estimated to be 5 nm. At high temperatures this solution is liquidlike or disordered. Under quiescent conditions, the order-to-disorder transition (ODT) occurs at $49 \pm 1^\circ\text{C}$.

The application of shear on the ordered phase causes alignment of the cylinders. In Fig. 1(a) we show SANS pattern obtained in the gradient-neutral plane under low frequency (0.2 Hz) and large amplitude (200%) oscillatory shear at 46°C . The sixfold symmetry in the scattering profile implies that the cylinders pack on a hexagonal lattice in the gradient-neutral plane with axes aligned in the flow direction. The prismatic planes of the hexagonal lattice are par-

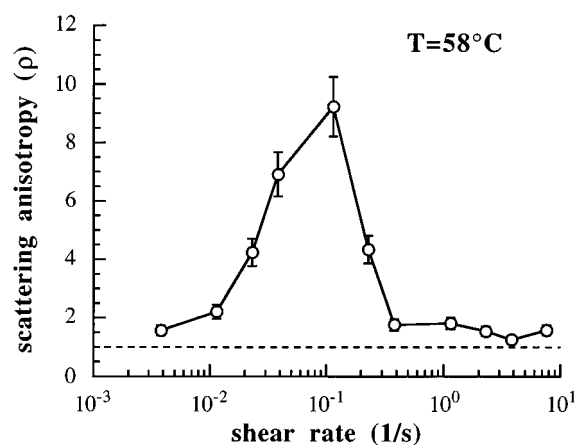


FIG. 3. The effect of shear rate on ρ under steady shear flow at 58°C .

allel to the shearing surfaces. The effect of imposing steady shear ($\dot{\gamma} = 0.38 \text{ s}^{-1}$) at the same temperature (46°C) is shown in Fig. 1(b). The scattering profile in the gradient-neutral plane is devoid of well-defined scattering peaks. The structure under steady shear thus consists of locally ordered, hexagonal “crystallites” with a mosaic spread.

In Fig. 2 we show scattering profiles obtained in the flow-neutral plane. At 46°C and $\dot{\gamma} = 0.38 \text{ s}^{-1}$ [same conditions as that for Fig. 1(b)] we see well defined peaks in the neutral direction and negligible scattering in all other directions [Fig. 2(a)]. This indicates good alignment of the cylinders in the flow direction. Increasing temperature to 54°C at constant shear rate results in a decrease in the peak intensity in the neutral direction and the development of a scattering ring at $|\mathbf{q}| = 0.31 \text{ nm}^{-1}$ [Fig. 2(b)]. These observations indicate a weakening of cylinder alignment and/or increased disorder. Increasing temperature further to 64°C results in an isotropic scattering pattern, characteristic of concentration fluctuations in disordered systems.¹⁰ The order in the system at a given shear rate and temperature can be gauged by a parameter, ρ , which quantifies the anisotropy of the scattering pattern in the flow-neutral plane.

$$\rho = \frac{\text{peak intensity in the neutral direction in the flow-neutral plane}}{\text{peak intensity in the flow direction in the flow-neutral plane}}.$$

Values of ρ that are significantly greater than 1 indicate that the system is ordered. It is evident that ordered phase under a shear rate of 0.38 s^{-1} persists at temperatures well above the quiescent disordering temperature (49°C). This observation of shear-induced ordering is consistent with previous experiments and theories on weakly ordered block copolymers.

The effect of changing shear rate at a constant temperature of 58°C leads to a surprising result, as shown in Fig. 3, where ρ is plotted versus $\dot{\gamma}$. At shear rates between 0.004 s^{-1}

and 0.1 s^{-1} we find that increasing shear rate leads to increased order (ρ), as expected. In contrast, at shear rates between 0.1 s^{-1} and 10 s^{-1} we find that *increasing shear rate leads a decrease in ρ , i.e., increased disorder*. The observed changes in ρ could be due to changes in the order within the crystallites caused by a shear-induced shift in the order to disorder transition temperature, or due to changes in the fraction of aligned crystallites.

Kinetic experiments, in which the shear rate was switched from one value to another, were conducted at

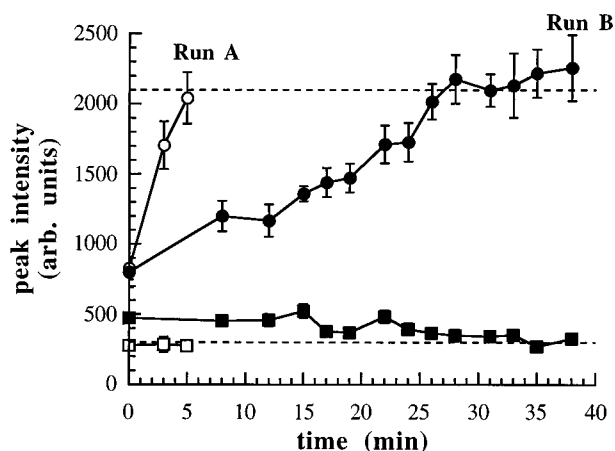


FIG. 4. Evolution of scattering in the neutral-flow plane after switching from one shear rate to another at 58 °C. Unfilled symbols: from $\dot{\gamma}=0.038$ to 0.077 s^{-1} (Run A). Filled symbols: from $\dot{\gamma}=0.575$ to 0.077 s^{-1} (Run B). Circles and squares: peak intensity in the neutral and flow directions, respectively.

58 °C. In run A the shear rate was increased from 0.038 s^{-1} to 0.077 s^{-1} (on the shear-ordering side), while in run B the shear rate was decreased from 0.575 s^{-1} to 0.077 s^{-1} (on the shear-disordering side). In Fig. 4 we show the evolution of the scattering anisotropy after switching by plotting the time dependence of the peak intensity in the flow and neutral directions. In both runs, the peak intensity in the neutral direction rises from about 800 to 2100 units. In run A this change occurs in 5 min while in run B it occurs in 30 min. If the shear-induced changes in ρ at 58 °C were due only to reorientation of crystallites, then the time scale in runs A and B would be similar. The fact that they are different by a factor of 6 indicates that the applied shear field affects the internal order within the crystallites.

To further clarify the characteristics of the solution at 58 °C we performed experiments where the shear field was turned off after the solution was sheared at a given $\dot{\gamma}$. As shown in Fig. 5(a), when $\dot{\gamma}=0.077 \text{ s}^{-1}$ was imposed, the anisotropic scattering profile obtained under shear persisted after the shear field was turned off. The data obtained at shear rates less than 0.57 s^{-1} were qualitatively similar to those shown in Fig. 5(a). On the other hand, when $\dot{\gamma}=7.66 \text{ s}^{-1}$ was imposed, the scattering anisotropy obtained under shear was lost when the shear field was turned off. These data are shown in Fig. 5(b). This is consistent with the notion that the imposition of a steady shear of 7.66 s^{-1} leads to a disordered phase and that the shear-induced disordering transition at 58 °C occurs at a shear rate of about 1 s^{-1} (between 0.57 and 7.66 s^{-1}).

Our criteria for distinguishing between ordered and disordered block copolymer phases is based on the work of Bates and co-workers.¹¹ In the mean-field theory, which becomes increasingly applicable with increasing molecular weight, the scattering peak from the disordered phase is predicted to diverge as the ordering transition is approached.¹⁰ Consequently, for high polymers it is difficult to distinguish between order and disorder on the basis of peak width, as is

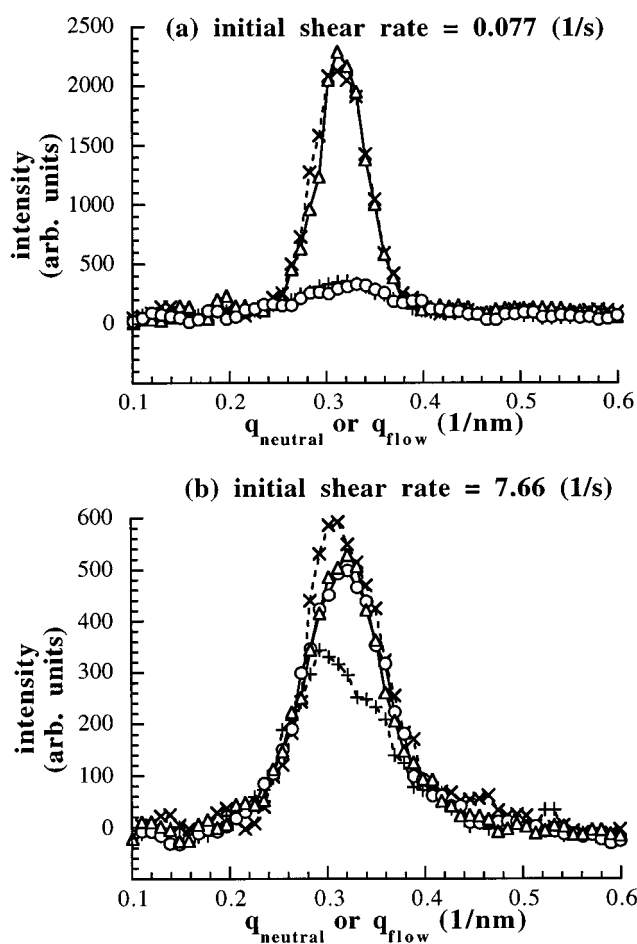


FIG. 5. Scattering in the neutral-flow plane before and after stopping shear at 58 °C. (a) Initial $\dot{\gamma}=0.077 \text{ s}^{-1}$. (b) Initial $\dot{\gamma}=7.66 \text{ s}^{-1}$. (\times) and ($+$): Scattering profiles in the neutral and flow directions, respectively, while the initial shear rate was imposed. (Δ) and (\circ): Scattering profiles in the neutral and flow directions, respectively, after stopping shear.

done in small molecule systems. Previous experiments^{6,11} indicate that ordered block copolymer phases that have been aligned do not spontaneously lose alignment when the shear field is turned off. Anisotropic scattering patterns obtained after the application of shear, are thus reliable indicators of an ordered phase.

Our observation of shear-induced disordering is inconsistent with recent theories^{7,8} and all other previous experiments on weakly ordered block copolymers.^{5,6} The currently held view, that the primary role of shear in these block copolymers is to suppress disordered concentration fluctuations,^{1,7,8} can only lead to shear-ordering. From our experiments thus far, we cannot tell if the mechanism for shear-disordering is related to the properties of individual cylinders or due to collective effects. Other processes (e.g., chain deformation) that occur during shear-mixing and shear-demixing of polymer blends and solutions,¹² may also play a role. A possible mechanism for shear-disordering is depicted in Fig. 6. Fluctuations in cylinder orientation are evident in this material [e.g., Fig. 2(b)]. The relative motion of adjacent, fluctuating cylinders under shear will result in an

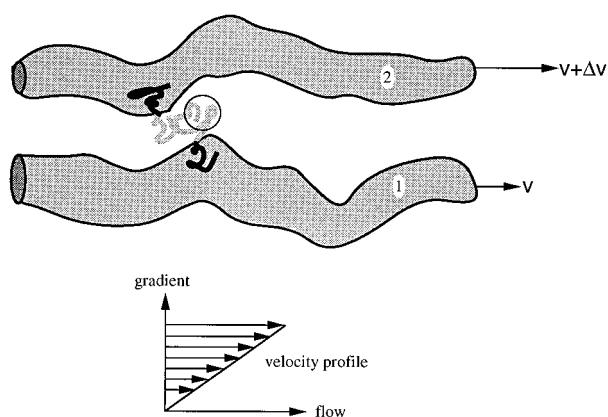


FIG. 6. Schematic representation of the effect of steady shear on fluctuating block copolymer cylinders. The motion of cylinder 2 past cylinder 1 causes an unfavorable increase in polymer concentration in some locations (e.g., inside the circle) unless the local cylinder orientation changes. This can lead to disordering at high shear rates.

unfavorable increase in local polymer concentration. If the relaxation time for cylinder fluctuations, τ , is much larger than $1/\dot{\gamma}$, then the cylinders cannot respond to the resulting osmotic forces, and this would lead to shear-disordering at $\dot{\gamma}\tau > 1$. This interpretation suggests that in our system τ is about 1 s.

In summary, we have discovered a temperature at which a hexagonal block copolymer phase exhibits shear-ordering at low shear rates and shear-disordering at high shear rates. The low shear rate result is consistent with the shear-induced suppression of disordered fluctuations.^{1,7,8} We propose that the high shear rate result is caused by fluctuations of the ordered microstructure.

Financial support was provided by grants from the National Science Foundation: DMR-9457950 to Polytechnic University and DMR-9122444 to NIST. We thank the NIST for providing access to the SANS instrument, Boualem Hammouda for his help with the experiments, and Mohan Srinivasarao for helpful suggestions.

¹A. Onuki and K. Kawasaki, *Ann. Phys. (NY)* **121**, 456 (1979).

²B. J. Ackerson and N. A. Clark, *Physica* **118A**, 221 (1981).

³M. J. Stevens, M. O. Robbins, and J. F. Belak, *Phys. Rev. Lett.* **66**, 3004 (1991).

⁴C. R. Safinya *et al.*, *Science* **261**, 588 (1993).

⁵K. A. Koppi, M. Tirrell, and F. S. Bates, *Phys. Rev. Lett.* **70**, 1449 (1993).

⁶N. P. Balsara and B. Hammouda, *Phys. Rev. Lett.* **72**, 360 (1994).

⁷M. E. Cates and S. T. Milner, *Phys. Rev. Lett.* **62**, 1856 (1989).

⁸C. M. Marques and M. E. Cates, *J. Phys. (France)* **51**, 1733 (1990).

⁹N. P. Balsara *et al.*, *Macromolecules* **27**, 7406 (1994).

¹⁰L. Leibler, *Macromolecules* **13**, 1602 (1980).

¹¹F. S. Bates, J. H. Rosedale, and G. H. Fredrickson, *J. Chem. Phys.* **92**, 6255 (1990).

¹²*Rheo-Physics of Multiphase Polymer Systems*, edited by K. Sondergaard and J. Lyngaae-Jorgensen (Technomic, Lancaster, PA, 1995).