Communications to the Editor

Explanation of “Dark-Streak” Light Scattering Patterns and Shear-Induced Structure Development of Phase-Separated Polymer Blends

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Introduction. The miscibility of flowing polymer blends has attracted much attention over the last decade (ref 1 and references therein). Several different techniques have been employed in this research area, including rheological measurements,[2] turbidity,[3] fluorescence,[4] and neutron[5] and light scattering.[6−8] It has been reported that the phase boundary of polymer blends can be shifted by applying shear flow, and both shear-induced phase mixing and demixing have been observed. An understanding of shear-induced behavior of polymer blends is far from complete due to the complexity of the phenomena. For example, it is not clear whether the observed phase changes are due to thermodynamic effects or hydrodynamic effects or whether the shear stress or shear rate is the dominant controlling factor.

Neutron and light scattering techniques enable one to study flow-modified concentration fluctuations and changes of phase sizes and shapes. Changes in the scattering patterns of a flowing polymer blend can distinguish between thermodynamic and nonthermodynamic effects. Because the phase size in polymer blends is usually on the order of several microns, small-angle light scattering is an appropriate method for this type of research. Rheo-SALS instruments have been constructed in several laboratories for studying the phase behavior of polymer blends under shear flow.[7,9,10]

Research has shown that light scattering patterns characterized by a bright streak normal to the flow direction develop when shear flow is applied to a phase-separated polymer mixture.[6,7,11] The streak may disappear at certain shear conditions, which has been taken as evidence for shear-induced phase mixing.[6,7,11] Transient SALS results have recently been reported for polymer blends under simple shear flow.[6,12] It was observed that an H-shaped scattering pattern (or dark-streak pattern) developed initially, and the two wings of the H-shaped pattern eventually merged to a bright-streak image after a finite time during steady shearing of the sample. In this paper, the origin of the streak and H-shaped light scattering patterns and the corresponding morphological changes in real space are discussed for a polystyrene/poly(vinyl methyl ether) blend.

Experiments and Results. The weight-average molecular weights of PS and PVME were 135 000 and 99 000, respectively, and their polydispersity indices, M_w/M_n, were 1.13 and 2.13, respectively. The phase diagram for PS/PVME blends constructed from turbidity measurements indicated that the critical composition of the lower critical solution temperature (LCST) system was about 75 wt % of PVME and the critical temperature was about 123 °C.

A blend of 25% PS/75% PVME (w/w) was prepared by dissolving both polymers in toluene and casting the solution onto a Teflon dish. The sample was dried in a vacuum oven at 50 °C for about 2 weeks before use. A small quantity of blend was formed into a 0.05-mm film between two glass microscope slides.

The phase structure was directly observed under an optical microscope with a hot stage, using a magnification of 600×.

Light scattering patterns were obtained using a He−Ne laser (λ = 632.8 nm) and a Polaroid camera. The scattered light was imaged on a white screen. The distance between the sample and the screen was 965 mm, which gave a scattering vector range of 0−8.4 μm^{-1}.

The blend sample was first heated on the microscope hot stage to about 3 °C above the cloud point. Bicontinuous phases typical of spinodal decomposition were observed with the microscope. The initial phase sizes were very small at the early stage of phase separation but grew larger after several minutes, characteristic of late-stage spinodal decomposition. Figure 1a shows the bicontinuous phase structure at about 30 min after the phase separation started. The domain size was about 4 μm. The corresponding light scattering for this structure (Figure 1d) showed a spinodal ring at a scattering vector of about 1.5 μm^{-1}. Both microscopy and light scattering indicated that the spinodal decomposition was in an intermediate stage.[13]

A shear strain of 4 was then applied to the sample. The sample was immediately removed from the microscope stage and rapidly quenched to room temperature. The relaxation of the sample was very slow, so that no significant change in the phase structure of the blend occurred after quenching the sample. This allowed us to measure light scattering on the same morphology observed with the microscope. Figure 1b shows the photomicrograph and Figure 1e shows the corresponding light scattering image after the shear strain of 4.

Next, the sample was returned to the microscope hot stage, and an additional strain of 26 was applied to the upper glass slide before the sample was quenched to room temperature. The bicontinuous phase became distorted into an aligned fibrillar structure, as shown in Figure 1c. The corresponding light scattering image is shown in Figure 1f.

The same blend sample was also studied using a custom-designed rheo-SALS system that is described elsewhere.[9] The sample with a thickness of 0.3 mm was loaded between parallel plates and the temperature was increased to about 2 °C above the cloud point temperature. After the phase separation had proceeded for about 40 min, a shear rate of 0.5 s^{-1} was applied. Figure 2 shows the light scattering pattern taken at about 1 min after shear was started.

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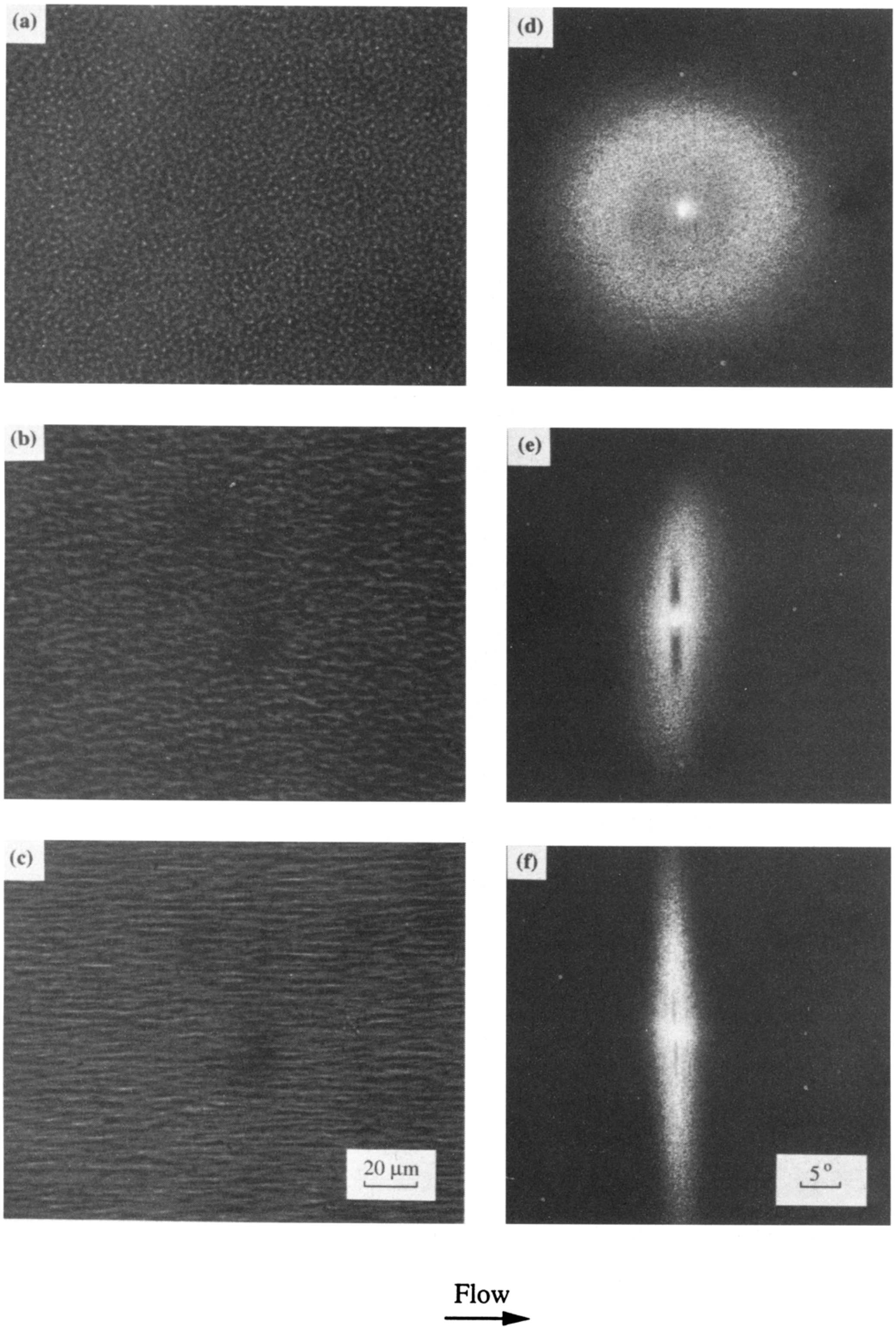

Figure 1. Phase structures of a near-critical PS/PVME blend seen under the microscope (a–c), along with the corresponding light scattering images (d–f): (a and d) after phase separation for about 30 min with no shear; (b and e) after a shear strain of about 4; (c and f) after a shear strain of about 30.

Discussion and Conclusions. In ref 6 it was shown that an H-shaped light scattering pattern developed upon shear and changed to a bright-streak pattern after longer shearing. The present study, however, demonstrated that the H-shaped (or dark-streak) pattern and the bright-streak pattern actually were parts of the same scattering image (Figure 1e,f). That is, at low scattering angles, two bright wings are separated by a dark region (the dark streak) and at higher angles only the bright streak in the vorticity direction is observed.

From Figure 1b, it is clear that the bicontinuous phases were stretched, upon shear, in the flow direction, while the size scale remained almost unchanged in the vorticity direction. The larger size in the flow directionyields maximum scattering at lower angle in that direction, and the spinodal scattering ring is squashed in Figure 1e.

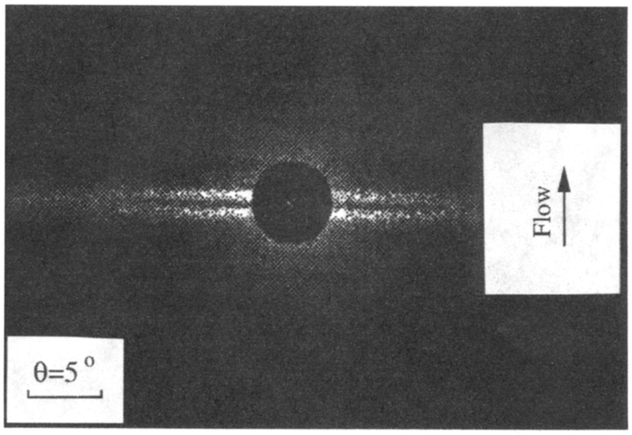

Figure 2. Two-dimensional light scattering pattern of the PS/PVME blend when it was sheared at 0.5 s^{-1} for about 60 s.

At larger shear strain, domains align along the flow direction, as shown in the Figure 1c. While this structure resembles that reported in ref 14, the explanation is different. By changing the microscope focus, we established that the fibrillar structure due to elongated domains was the same in near-surface and off-surface planes and not strictly a surface phenomenon.

From parts e and f of Figure 1, the spacing of the two wings of the H-shaped pattern (i.e., thickness of the dark streak) decreased with increasing shear strain. Notice that these two wings were actually parts of the squashed spinodal ring, and this spacing should be about twice the scattering vector of the maximum intensity in the flow direction. Thus we are able to relate this spacing of the scale of concentration fluctuations in the flow direction. This is useful because the length of this periodicity is large and the corresponding intensity maximum in the flow direction is at too low an angle to detect, being obscured by the main beam (or the beam stop, as in Figure 2).

It appears from Figure 1c and from the figures in ref 14 that there is a periodicity in the flow direction even when the domains are highly elongated. The length of this periodicity may depend on the viscosity ratio of the two phases, the interfacial energy, and the applied shear rate. More research is necessary for the characterization of the concentration fluctuations in the flow direction.

The streak pattern was also obtained using the rheo-SALS instrument for the same blend sample, and the result is shown in Figure 2. The black spot in the center is a beam stop. The scattering image has a bright streak which consists of two bright wings and a dark region between them. The center of the wings are blocked by the beam stop, and the position of maximum scattering in the flow direction cannot be obtained by plotting the intensity profile along the flow direction. The spacing of the two wings is about twice the scattering vector of the position of maximum intensity in the flow direction. From the scattering result in Figure 2, the position of the maximum scattering in the flow direction is found at a scattering vector of 0.11 μm^{-1} (scattering angle of 0.65°), which corresponds to a periodicity in real space of 57 μm.

In most studies of shear-induced phase mixing phenomena for polymer mixtures, it has been reported that a bright streak develops before it disappears at longer shear times or higher shear rates.[6,7,9] This report shows that the bright streak arises from distortion of a spinodal structure and orientation of phase-separated domains. Although shear-induced mixing was not observed in this study (i.e., disappearance of the bright streak), it appears that that process is preceded by high elongation of one of the phases in the flow direction. This suggests that there may be a critical shear strain required for mixing.

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References and Notes

(1) Larson, R. G. *Rheol. Acta* **1992**, *31*, 497.
(2) Rector, L. P.; Mazich, K. A.; Carr, S. H. *J. Macromol. Sci., Phys.* **1988**, *B27*, 421.
(3) Wu, R.; Shaw, M. T.; Weiss, R. A. *J. Rheol.* **1992**, *36*, 1605.
(4) Mani, S.; Malone, M. F.; Winter, H. H. *Macromolecules* **1992**, *25*, 5671.
(5) Nakatani, A. I.; Kim, H.; Takahashi, Y.; Matsushita, Y.; Takano, A.; Bauer, B.; Han, C. C. *J. Chem. Phys.* **1990**, *93*, 795.
(6) Chen, Z. J.; Wu, R.-J.; Shaw, M. T.; Weiss, R. A.; Fernandez, M. L.; Higgins, J. S. *Polym. Eng. Sci.*, in press.
(7) van Egmond, J. W.; Fuller, G. G.; Frank, C. W. *Theor. Appl. Rheol. Proc. XIth Int. Congr. Rheol.* **1992**, 498.
(8) Hindawi, I. A.; Higgins, J. S.; Weiss, R. A. *Polymer* **1992**, *33*, 2522.
(9) Wu, R.-J.; Ph.D. Dissertation, University of Connecticut, Storrs, CT, 1993.
(10) Nakatani, A. I.; Waldow, D. A.; Han, C. C. *Rev. Sci. Instrum.* **1992**, *63*, 3590.
(11) Takebe, T.; Fujioka, K.; Sawaoka, R.; Hashimoto, T. *J. Chem. Phys.* **1990**, *93*, 5271.
(12) Chen, Z. J.; Shaw, M. T.; Weiss, R. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1993**, *34* (2), 838.
(13) Hashimoto, T. *Phase Transitions* **1988**, *12*, 47.
(14) Fernandez, M. L.; Higgins, J. S.; Richardson, S. M. *Int. Chem. Eng. Res. Event* **1994**, in press.

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