String Phase in Phase-Separating Fluids under Shear Flow

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Transmission light micrographs show that domains in spinodal decomposition are elongated into extremely long strings in steady states of a polymer solution under strong shear flow. The shear flow stabilizes the string against their intrinsic surface tension instabilities. The string diameter decreases with increase in the shear rate and ultimately becomes of the order of the interface thickness, resulting in shear-induced homogenization.

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The effects of shear flow have recently been attracting growing attention in various fluid systems. In particular, when a fluid mixture phase separates in the presence of shear, a number of intriguing dynamical effects are observed [1–6]. In this situation domains grow due to the thermodynamic instability or metastability, but they are deformed by the flow field, however small the shear rate is, as their size increases [7]. The fluid eventually tends to a nearly stationary two-phase state, in which a dynamical balance is attained between the two mechanisms of growth and deformation. The aim of this Letter is to report direct observation of a strikingly elongated domain structure in this case.

Dating back to Taylor [8], many authors have studied the interplay of viscosity, surface tension, and flow, which causes the break up of small droplets in shear or extentional flow [9]. It is known that, when the viscosity inside a droplet and that outside it are of the same order, the droplet takes an approximately ellipsoidal shape with $R_\parallel/R_\perp = 2$–3 and $R_\perp \sim \sigma/\eta S$ at the breakup, where $R_\parallel$ is the longest radius, $R_\perp$ is the shortest radius, and S is the shear rate. Light scattering experiments have detected nearly monodisperse distributions of droplets with sizes of the order of the break-up size, when the composition is far from the critical value and the break-up size is larger than the critical droplet size [2,10]. On the other hand, when the two phases are both percolated near the critical composition, the light scattering pattern exhibits very strong anisotropy, indicating highly elongated domains, as observed in the course of domain growth [1] and in steady states [4,6,11]. Computer simulations have also shown very anisotropic deformations immediately after quenching even in very weak shear [12–14]. However, no unambiguous information has yet been gained on the detailed morphology in the bicontinuous steady states. To clarify this aspect we conducted an *in situ* real space analysis of the domain structure by optical microscopy, simultaneously with a reciprocal space analysis by light scattering. We shall report for the first time direct evidence of a string phase of phase-separating fluids in steady states under strong shear.

As in our previous experiments [3–6] we use a ternary polymer solution of polybutadiene (PB) and polystyrene (PS) with dioctylphthalate (DOP) as a common solvent. The PB has a weight-averaged molecular weight of $M_B = 3.13 \times 10^5$ and PS has $M_S = 2.14 \times 10^5$. In the solution the polymer weight fraction is at 3.3%. The composition PS/PB is 50/50 wt%/wt% (46/54 vol%/vol%), nearly equal to the critical value (equal to the maximum of the cloud point curve) or 80/20 wt%/wt% (77/23 vol%/vol%), an off-critical value [5]. The polymer concentration c is of the order of the overlap concentration c^*, being $c/c^* \sim 2$, at which the entanglement effect is not yet severe. The binary solutions of PS/DOP and PB/DOP at the same polymer concentration are Newtonian for shear rates used in our experiment. The system may be regarded as a pseudobinary mixture of PB blobs and PS blobs with sizes of the order of the gyration radii [15]. Their segmental interaction is weakened by the solvent, but they phase separate into PB-rich regions and PS-rich regions as the temperature T is lowered. We will discuss, first, our results in the critical composition case. There, the final temperature is 66 °C, which is lower than the critical temperature ($T_c = 74$ °C) by $\Delta T = 8$ °C.

Polymer systems are unique in that the blob size is relatively large (~100 Å) and the viscosity is considerably high (~2 P) [16], so that the spatial and temporal scales which can be observed in phase separation are dramatically enlarged even for large quench depth. In fact, from the experiments of Ref. [16] one can calculate the characteristic time τ of the thermal composition fluctuations to be $\tau \sim 6$ s. τ is evaluated by the growth rate of the intensity at the peak wave number $q_m(0)$ in an early stage spinodal decomposition after cessation of a strong shear. Therefore the strong shear regime $S\tau > 1$ can be easily realized in our system.

In Fig. 1 transmission light micrographs are shown in steady states at various shear rates, together with

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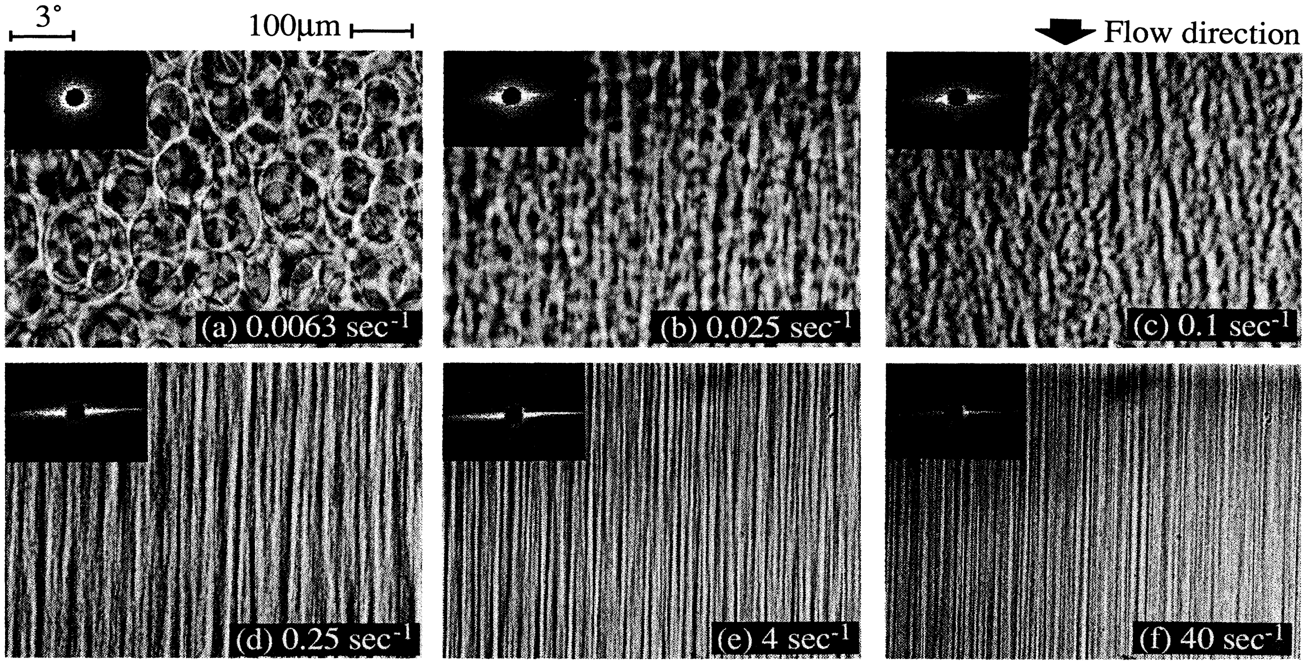

FIG. 1. Transmission light micrographs and corresponding light scattering patterns (shown in the insets), obtained *in situ* in steady states of PS/PB (50:50)/DOP 3.3 wt% at $\Delta T = 8\,^\circ\mathrm{C}$. The flow direction is vertical, and the bar in the inset of (a) indicates the scattering angle in air for all the patterns. The bar attached to (a) is common for all the pictures.

corresponding light scattering patterns in the insets of the micrographs. They are taken simultaneously from the same solution on planes perpendicular to the velocity-gradient direction as described elsewhere [17]. The sample thickness is 0.5 mm at the position where the observation has been made. The microscopy and scattering experiment were conducted as follows. A specimen was first brought into a single phase state at 79 °C and was then filled inside a shear cell kept at 66 °C. This was then immediately sheared at $S = 0.0063\ \mathrm{s}^{-1}$. The resultant domain growth was extremely slow and a steady state in which the data were taken was reached after at least 4 h. The shear rate was then increased to $0.025\ \mathrm{s}^{-1}$, where the relaxation time to a steady state was about 20 min. We repeated these procedures to obtain the data in Fig. 1. The micrographs represent the structures existing over a depth of focus of about 10 μm and are taken at a shutter speed of 10^{-4} s. Fourier transformations of the micrographs produced patterns are essentially identical to the real light scattering patterns shown in the insets. This confirms that the micrographs reflect the structural entities occurring in shear flow. The same argument is applied also to Fig. 2 to be discussed later. Characteristic features observed in Fig. 1 are explained in the following.

(i) At the smallest shear, $S = 0.0063\ \mathrm{s}^{-1}$, the scattering is nearly isotropic and the picture of Fig. 1(a) shows slightly elongated ellipsoidal PS-rich domains enclosed by a continuously connected PB-rich region. This was confirmed in a separate experiment in which a small amount of the solution containing droplets after shearing at the same shear rate was quickly put on a slide glass, followed by staining with osmium tetraoxide vapor. The vapor selectively stains the PB-rich domains but not the PS-rich domains, giving rise to a strong contrast under transmission optical microscopy. In our deep quench condition, the solution undergoes a phase separation into the PS-rich solution phase and PB-rich solution phase, with a relative volume of the former phase being smaller than the latter. As a result the PS-rich phase forms a droplet phase in our case. The domain size here is confirmed to be of the order of the Taylor breakup size $R \sim \sigma/\eta S$ in steady states [4], where σ is the surface tension of order $10^{-4}\ \mathrm{erg\,cm}^{-2}$.

(ii) In Figs. 1(b) and 1(c), S is larger but is still in the regime $S\tau < 1$. Here the PS-rich domains also become percolated, giving rise to elongated bicontinuous structures. They contain a number of random irregularities undergoing frequent breakup, interconnection, and branching, although the overall structure is stationary.

(iii) In Figs. 1(d)–1(f) the strong shear condition $S\tau > 1$ holds. Remarkably, stringlike domains extend along the flow direction. In addition to this extreme elongation, the string as observed under microscopy appears to have the following unique characteristic which is difficult to be reduced from the scattering pattern: A high uniformity and continuity along flow such that the random irregularities as observed above (ii) are strongly suppressed. The spatial continuity of the domains along

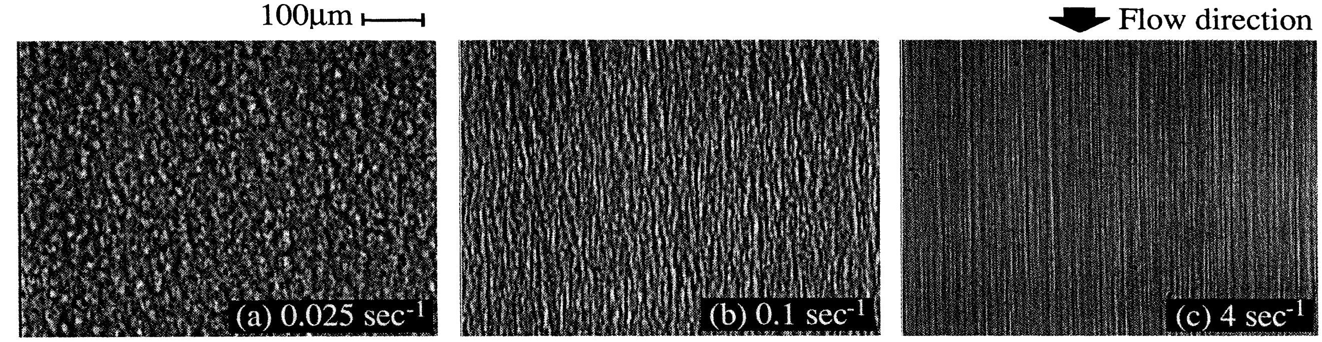

FIG. 2. Transmission light micrographs obtained *in situ* in steady states of PS/PB (80:20)/DOP 3.3 wt% at $\Delta T = 14\,^\circ$C. The flow direction is vertical. The bar attached to (a) is common for all the pictures.

the flow direction increases with S, i.e., roughly about 300 μm at $S = 0.25$ s^{-1} and extending from the top to the bottom of the pictures at 40 s^{-1}. They scatter light to produce the streak patterns of Figs. 1(d)–1(f). In our previous work [4,6] the scattering intensity perpendicular to the string in this regime was fitted to the squared Lorentzian form proportional to $1/(1 + q_y^2 \xi_\perp^2)^2$, which has the Porod tail at large q_y, where q_y is the component of the scattering vector perpendicular to both the flow direction and the velocity gradient direction. The length $\xi_\perp$ represents the diameter of the string and behaves in the strong shear regime as

$$\xi_\perp \cong [A_\perp / q_m(0)] (S\tau)^{-\alpha}, \qquad (1)$$

where $A_\perp \cong 10$ and α is in the range between $\frac{1}{4}$ and $\frac{1}{3}$ [6]. The contrast between the two phases becomes weak with further increasing S, because $\xi_\perp$ approaches to the interface thickness (~5 000 Å), and PS and PB are forced to be mixed progressively. It is really surprising that these stringlike domains can be macroscopically long even when their diameter is about 5 000 Å. They can be stable only when undulations of the surfaces of the strings are strongly prohibited by shear. Note that the literature has treated deformations and breakup of an isolated domain only [8,9]. As a classic result, in the absence of shear, a long cylinder is unstable against long wavelength undulations [18]. However, it is suggestive that in shear flow a droplet can be extended more transiently than it is in a stationary state [19], in which the flow suppresses the growth of undulations. The breakup of the strings upon cessation of shear was confirmed by the light scattering [20] and shear microscopy experiments [21].

(iv) Finally, for $S > S_C$ (equal to 127 s^{-1}, the critical shear rate for the single-phase formation), the microscope image shows no structure and the domain scattering vanishes. Thus the fluid is brought into a disordered phase. Here the scattering intensity as a function of q_y is fitted to the Ornstein-Zernike form [6,16]. This phenomenon is called shear-induced homogenization. The critical temperature thus shifts downward as $(\Delta T)_c / T_c \cong 1.3 \times 10^{-3} S^{1/2}$ with S in s^{-1}. A similar downward shift of T_c was predicted and detected in near-critical fluids [22,23], but its magnitude is much smaller than in our system by 3 orders of magnitude for the same S.

Next we discuss formation of the string phase in the case of off-critical compositions such as PS/PB, 90/10, 80/20, 20/80, and 10/90 wt%/wt%. We found that in the weak shear regime $S\tau < 1$ the minority phase forms droplets, regardless of the viscosity difference, which are elongated into ellipsoids of revolution with aspect ratio of about 2 and are fragmented into smaller ellipsoidal domains [8,9]. However, in the strong shear regime $S\tau > 1$, they are interconnected and percolated along the flow and are eventually transformed into the string phase. At even higher shear rates $S > S_c$, the shear-induced single-phase is obtained [5]. Figure 2 shows typical experimental results for the off-critical system with PS/PB 80/20 wt%/wt% (77/23 vol%/vol%) at 3.3 wt% total polymer concentration in DOP at 44 °C or $\Delta T = 10\,^\circ$C. In this experiment the solution was first homogenized by shearing at $S = 800$ s^{-1}, which is higher than the critical shear rate $S_c = 639$ s^{-1} and then subjected to a shear drop at $S = 0.0063$ s^{-1}. The domain structure in a steady state was attained at about 4 h after the shear drop. Thereafter the experiment was conducted in the same way as that for the critical composition. The micrograph, Fig. 2(a), shows PB-rich droplets dispersed in a PS-rich matrix, while Figs. 2(b) and 2(c) show a string structure oriented parallel to the flow direction. The longitudinal continuity increases and the diameter decreases with increase of S, as in the case of the critical composition. Thus the string-phase formation under strong shear appears to be a general phenomenon in our systems. It should also be noted that the droplets formed for the off-critical composition in weak shear are much smaller than those for the critical composition in weak shear [Fig. 1(a)]. Furthermore, because the PB-rich droplets in Fig. 2(a) have a higher viscosity than the PS-rich matrix, the droplets are subjected to less elongation than those in complementary compositions in which PS-rich droplets are dispersed in a PB-rich matrix. We confirmed that the string phase is more easily obtained in the PB-rich case than in the PS-rich case.

We also comment on the rheological behavior in two-phase states under shear [24]. It is well known that the surface tension contribution to the stress tensor is written as $\Pi_{ij} = \sigma \int da\,(n_i n_j - \delta_{ij})$, where da is the surface element, the integration is over the surfaces in a unit volume, and $\mathbf{n}$ is the normal unit vector. In particular, this is the sole contribution to the excess stress if the viscosities of the two phases are the same. It is valid only when the domain size is much longer than the interface thickness. When the minority phase forms droplets near the breakup size, we readily find an excess viscosity $\Delta\eta \sim \phi\eta$ and a normal stress difference $N_1 = \Pi_{yy} - \Pi_{xx} \sim \phi\eta|S|$ as the surface contributions [24], where ϕ is the volume fraction of the droplet phase. These two predictions on $\Delta\eta$ and N_1 have been confirmed [25,26]. In our string phase, however, the normal $\mathbf{n}$ is perpendicular to the flow almost everywhere on the surfaces and the surface contribution to $\Delta\eta$ vanishes.

In summary, we have shown extremely high elongation of domains in our polymer solution under even rather weak shear where the two phases are both percolated. We believe that similar elongation should also occur in usual near-critical fluids. To support this, Hamano *et al.* have recently observed that the viscosity increase $\Delta\eta(t)$ in a near-critical fluid slowly decays to zero as a function of time after quenching at the critical composition under stationary shear [27]. This relaxation should arise from the reorganization of domains from random to highly elongated shapes.

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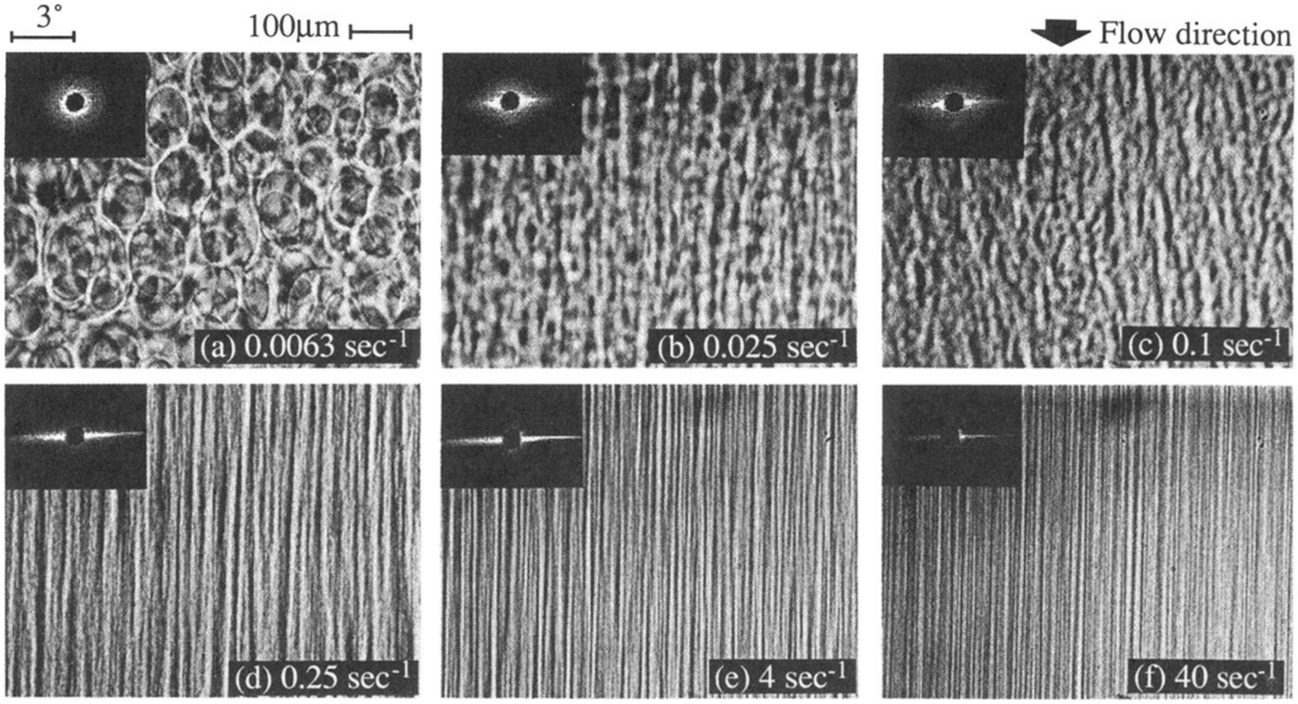

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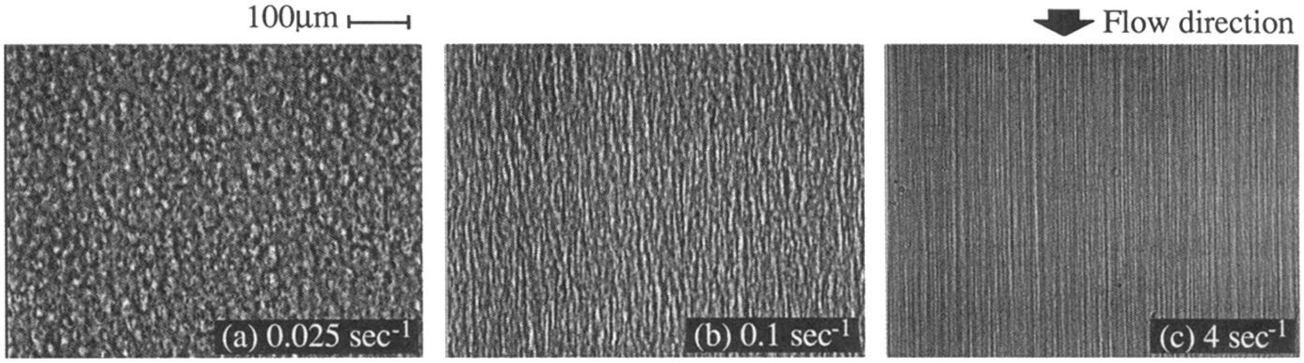

FIG. 2. Transmission light micrographs obtained *in situ* in steady states of PS/PB (80:20)/DOP 3.3 wt% at $\Delta T = 14\,^{\circ}\mathrm{C}$. The flow direction is vertical. The bar attached to (a) is common for all the pictures.