Universality of Viscoelastic Phase Separation in Dynamically Asymmetric Fluid Mixtures

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We demonstrate here the possibility that strong dynamic asymmetry between two components of a fluid mixture *generally* leads to unusual phase separation ("viscoelastic phase separation"), which does not belong to the conventional classification of phase separation. In addition to polymer solutions, a mixture, one of whose components is close to its glass transition, transiently exhibits a morphology peculiar to viscoelastic phase separation, namely, a spongelike continuous pattern of the minority phase. This pattern is likely the morphology universal to elastic and viscoelastic phase separation in a *dynamically asymmetric mixture containing a fluid as at least one of its components*.

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Phase-separation phenomena are commonly observed in various kinds of condensed matter, including liquids, polymers, metals, and semiconductors. It has been widely believed that phase separation of such systems with a conserved order parameter (composition) can be classified into only two types, namely, *a fluid and a solid model* [1,2]. In conventional theories of phase separation, it has been implicitly assumed that the two components of a mixture behave dynamically in the same way [1,2]. However, this assumption can be severely violated in a binary mixture having intrinsic dynamic asymmetry, especially for a deep quench, which leads to a large difference in the viscoelastic property between the two phases. One such example is a polymer solution, where the polymer has a large number of internal degrees of freedom while solvent does not. Recently we have found [3] that for a deep quench a polymer solution exhibits a new type of phase-separation behavior essentially different from either a fluid or a solid model [1,2], in contrast to the conventional understanding of polymer phase separation. A phase-separation pattern of such a mixture near its critical composition is characterized by a spongelike continuous structure of the more viscoelastic phase.

In this Letter, we demonstrate that unusual phase-separation behavior very similar to that in polymer solutions is observed for a binary mixture in which only one of its components is close to its glass-transition temperature T_g, which suggests the *generality* of this phenomenon. Effects of elasticity on phase separation have so far been considered only for solids, and not for fluids, simply because the latter have no static elasticity. Hidden dynamic elasticity, or viscoelasticity, however, can come into play for a dynamic process of phase separation when a mixture has strong *dynamic asymmetry* between the components.

The system studied here is a mixture of polystyrene (PS) and poly(vinylmethylether) (PVME), whose phase diagram is shown schematically in Fig. 1. The weight-averaged molecular weights of PS and PVME were 1.01×10^5 and 9.4×10^4, respectively. The polydispersity ratios M_w/M_n were 1.01 and 1.5 for PS and PVME, respectively. The critical composition was 30 wt % PS, and the critical temperature was 122 °C. This mixture is one of the most well-studied polymer mixtures on phase separation. Phase separation of this mixture has so far been believed to be typical of the usual phase separation of binary liquid mixtures and is classified as a fluid model ("model H" in the Hohenberg-Halperin notation [2]). This is supported by many previous experiments [4]. It is likely true for a shallow quench for which the difference in the rheological property between the two phases is small because of the small difference in concentration between them. It should be noted that the difference in the degree of polymerization N itself is too small to cause *dynamic asymmetry stemming from N-dependent molecular dynamics* [3] between the two coexisting phases. However, this polymer mixture can have strong *dynamic asymmetry stemming from slow dynamics associated with glass-transition phenomena* especially for a deep quench for the following reasons. (1) The characteristic rheological time τ_t of

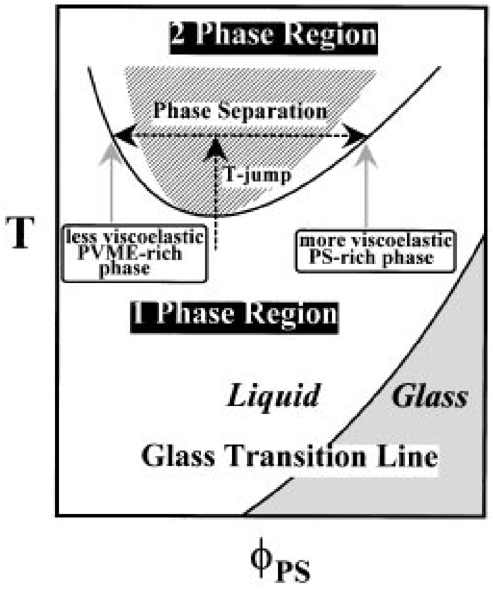

FIG. 1. Schematic phase diagram of a mixture of PS and PVME. T is the temperature and ϕ_{PS} is the PS composition.

a phase with the composition of ϕ_{PS} is proportional to $\exp\{-A/[T - T_g(\phi_{\mathrm{PS}})]\}$ (A is a constant, ϕ_{PS} is the PS composition). (2) $T_g(\phi_{\mathrm{PS}})$ is strongly dependent upon ϕ_{PS} since T_g of PS [$T_g(1) \sim 100$ °C] is very different from that of PVME [$T_g(0) \sim -26$ °C]. Thus τ_t of the PS-rich phase can be much longer than that of the PVME-rich phase (see Fig. 1) *for a deep quench*. This dynamic asymmetry can play a dominant role in the phase separation. We demonstrate such evidence below.

We have observed the phase-separation process of a mixture having the composition of 20 wt % PS, which is sandwiched between two cover glasses to form a thin film of a few μm thickness [5]. Figure 2 shows the morphological evolution observed at 143 °C. The system phase separates as the usual fluid mixture in the initial stage. We call this stage ($t < \sim 800$ s) where no macroscopic domains are formed a "frozen period" [3]. After this frozen period, macroscopic holes (PVME-rich domains) appear and grow in size. This process is characteristic of a metastable state and can be interpreted as the nucleation of holes overcoming the elastic energy barrier. Then, the PS-rich phase starts to shrink with time and the PS-rich phase transforms into a spongelike pattern. The transition in the phase-separation behavior around 800 s can be explained as follows. The enhancement of the concentration fluctuation makes the PS-rich phase much more viscoelastic than the PVME-rich one, and this increase in dynamic asymmetry strengthens the coupling between the velocity and stress fields. In the elastic regime (~ 800 s $< t < \sim 2000$ s), a domain shape is determined by the mechanical balance of elastic forces, and the interfacial tension plays little role in determining the domain shape. Namely, the elastic energy dominates phase separation and the system behaves like an *elastic gel*. In the late stage of phase separation ($t > \sim 2000$ s), the system approaches its final equilibrium state; accordingly, the deformation rate of domains slows down, which leads to the weakening of the resulting stress fields. Thus the PS-rich phase eventually behaves as a fluid, and the domain shape transforms into the shape of the lowest interfacial energy (sphere) as in usual phase separation. The spongelike structure becomes unstable in the absence of stress fields and, thus, the interconnectivity breaks (tube hydrodynamic instability) [1]. A thickness difference along a tube of the PS-rich phase causes an internal pressure difference and produces a hydrodynamic flow. Thus a thin part becomes thinner and eventually breaks, while a thick junction part becomes thicker and finally forms an isolated droplet. The shape relaxation from a thin thread to a sphere is characterized by a time of $\eta R/\sigma$ (R is the domain size, η the viscosity, and σ the interface tension). The disruption of the network structure leads to a significant decrease in the coarsening rate, because only slow growth mechanisms such as evaporation-condensation and Brownian-coagulation mechanisms [1] can work for this isolated-domain morphology.

Figure 3 shows the temporal change in the structure factor $S(q)$, which is numerically calculated from a real-space image by two-dimensional Fourier transformation as described earlier [6]. The scattering intensity grows with time in the early stage [see (a)], while it decreases in the late stage [see (b)]. This unusual feature is likely caused by the volume shrinking of the PS-rich domains (see the following discussion on the volume shrinking dynamics). For viscoelastic phase separation, there are two competing factors affecting the scattering intensity oppositely: (i) the increase in the amplitude of concentration fluctuation and (ii) the decrease in the volume fraction of domains. Further, the scattering function has a multiple-peak structure, which likely stems from the geometrical characteristics of the spongelike structure. The wave number q_p of the main peak rapidly decreases with time as $q_p \sim t^{-3/2}$ ($t < 1500$ s) [7] in the elastic regime [see Fig. 3(a)], reflecting the fast growth of the PVME-rich holes. In the hydrodynamic regime, on the other hand, it almost becomes constant with time [see Fig. 3(b)] ($t > 2000$ s), reflecting the very slow coarsening after the disruption of a network-like structure.

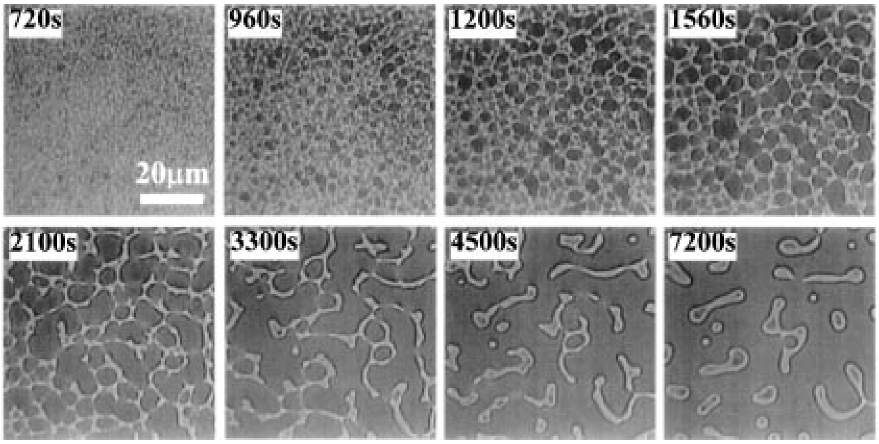

FIG. 2. Pattern-evolution process in phase separation of the PS/PVME mixture observed by video phase-contrast microscopy. The time shown in the figure is an elapsed time after the temperature jump.

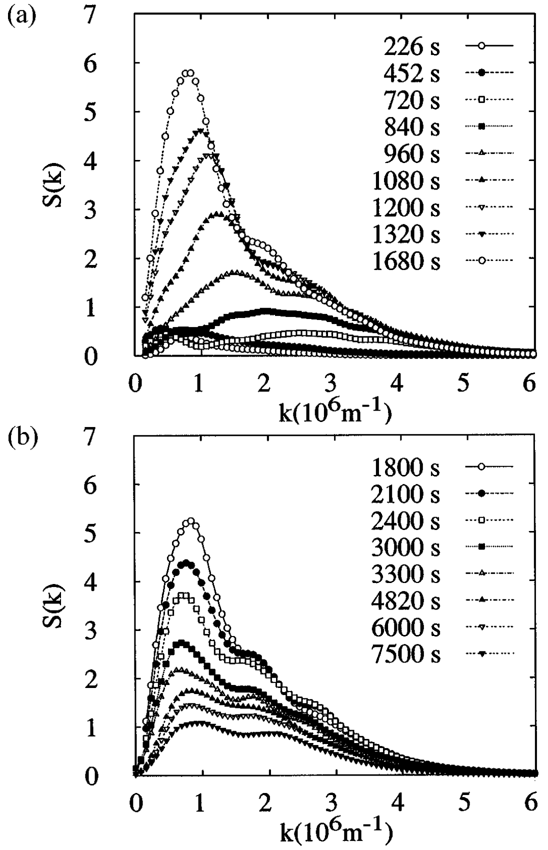

FIG. 3. Temporal change in the scattering function $S(q)$ (q: wave number). (a) Early stage and (b) late stage.

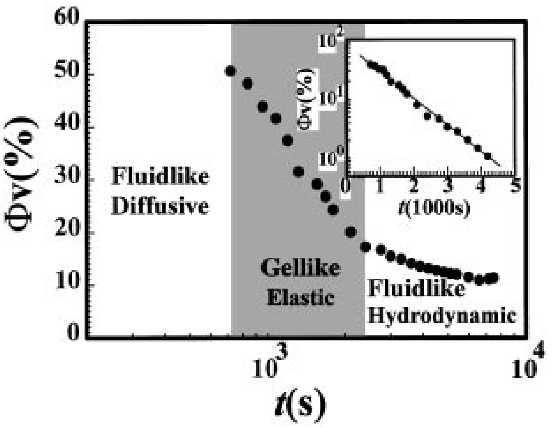

FIG. 4. Temporal change in the volume fraction Φ_V of the PS-rich phase (the phase having bright contrast in Fig. 2). The shaded region corresponds to the elastic gel-like regime, where the volume fraction of the PS-rich phase steeply decreases with time. The small inset shows that Φ_V decreases exponentially with time in the elastic regime.

Figure 4 shows a decrease in the volume fraction Φ_V of the more viscoelastic (PS-rich) phase with time, which is obtained by a black and white operation of a digital image analysis [6]. Since the phase-separation pattern is essentially two dimensional, especially after 1200 s, we can obtain the volume fraction from the area fraction. This unusual phenomenon is one of the most striking characteristics of *viscoelastic phase separation* [3]. The phase-separation process can be divided into three regimes (see Fig. 4): the initial diffusive regime, the intermediate elastic regime, and the final hydrodynamic regime. Only in the elastic regime does the volume fraction steeply decrease with time. The temporal change of Φ_V can be roughly given by $\Phi_V \sim \Phi_V^{\rm eq} + (1 - \Phi_V^{\rm eq})\exp(-t/\tau)$ with $\Phi_V^{\rm eq} \sim 0.12$ and $\tau \sim 10^3$ s (see the small inset in Fig. 4). Here $\Phi_V^{\rm eq}$ is the final equilibrium value of Φ_V, and τ is the characteristic time of volume shrinking. This exponential decrease in the volume reminds us of the late-stage volume shrinking kinetics of gels [8,9]. As discussed before, this volume shrinking is likely responsible for the decrease in the peak intensity of the structure factor in the late stage, which is supported by the fact that both processes have nearly the same characteristic time τ. Since the concentration must be conserved, this volume change tells us that the concentration of each phase changes with time by the transport (diffusion or flow) of PVME from the PS-rich phase to the PVME-rich one through the phase boundary. This violates the well-accepted view of the late-stage phase separation that after the formation of a sharp interface the two phases are almost in equilibrium and the volume fraction is almost constant [1]. Since the absence of concentration change after the formation of a sharp interface is a prerequisite to self-similar growth, our experimental result indicates that *there is no self-similarity in pattern evolution for viscoelastic phase separation*. This volume-shrinking process of the PS-rich phase should be very similar to a bulk phase-separation process in a gel, which itself has also been largely unexplored so far [10,11].

The coarsening behavior described above is essentially the same as that of polymer solutions [3] which have intrinsic dynamic asymmetry originating from the topological difference between the component molecules. This suggests the possibility that *viscoelastic spinodal decomposition is commonly observed in any dynamically asymmetric fluid mixture, irrespective of the origin of slow dynamics of the component*. In such a system, the order parameter is no longer the only slow variable of the system. We tentatively call this type of phase separation a “viscoelastic model.” The basic equations of this model are given in literature [3,12,13]. We find that viscoelastic phase separation is characterized by *switching of a relevant coarsening mode*; namely, it switches from an initial diffusive mode to an elastic mode at a certain time, and eventually switches again to a hydrodynamic mode (see Fig. 4). This switching behavior between the hydrodynamic and elastic mode can be interpreted as *viscoelastic relaxation* induced by the change in the coupling strength between the stress and velocity fields. This behavior can also be easily understood from the fact that a viscoelastic model includes a fluid and a gel model [14] as its extreme cases (see the equations in Refs. [3,12]).

Next we discuss the universal nature of a spongelike morphology and its physical origin. It is known that a gel undergoing a volume-shrinking phase transition forms a bubblelike structure [8,10,11,15]. The competition between phase separation and gelation also causes spongelike morphology [16]. The physical origin of the appearance of a honeycomb structure in plastic foams (e.g., polystyrene foam and urethane foam) is also likely similar to ours. All these processes have a common feature that holes of a less viscoelastic fluid phase (gas in plastic foam, water in gel, solvent in polymer solution, and so on) are nucleated to minimize the elastic energy associated with the formation of a heterogeneous structure in an elastic medium. Then, a more viscoelastic phase decreases its volume with time (see Fig. 4). This volume-shrinking process is dominated by the transfer (diffusion or flow) of a more mobile component under stress fields, from a more viscoelastic phase to a less viscoelastic phase. The above picture suggests the possibility that a spongelike structure is the *universal morphology* for phase separation in systems in which only one component asymmetrically has elasticity stemming from either topological connectivity or long-range attractive interaction [17]. The common feature of phase-separation patterns in these systems originates from volume phase transition, or more strictly elastic phase separation of a *dynamically asymmetric mixture which is composed of a network-forming component and a fluid (such as a liquid and a gas)*. The elastic network can be a real one as in gels (permanent network) and polymer solutions (transient network), or a virtual one due to a long-range attractive interaction. This differs from phase separation of elastic solid mixtures (e.g., metal alloys), which does not accompany a drastic volume change of each phase; in this case, further, a softer phase always forms a continuous phase to minimize the total elastic energy [18], in contrast with our case.

Finally, we briefly discuss the application of the spongelike morphology observed in viscoelastic phase separation. Although a spongelike structure appears only transiently in viscoelastic phase separation, this structure can be frozen by suitable methods: (i) simultaneous evaporation of a solvent for a polymer solution during phase separation, (ii) a further quench of a system below T_g, and (iii) combination of other processes such as crosslinking reactions. We think that spongelike structures reported in the literature [19,20] are likely induced primarily by the mechanism described here [21]. In the common sense view of conventional phase separation, a minority phase never forms a continuous phase and forms only an isolated phase [1]. However, our present study indicates the possibility that we can intentionally form a spongelike continuous structure of the minority phase of a more viscoelastic phase for any dynamically asymmetric mixture.

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[17] We also point out the similarity of these patterns in condensed matter to the spongelike structure of the universe (the large-scale galaxy distribution) [see, e.g., M.J. Geller and J.P. Huchra, Science **246**, 897 (1989)]. We speculate that the gravitational attractive interaction, which is stronger between heavier matter, may play a role similar to elastic network in producing the spongelike large-scale structure. This explanation seems to be consistent with a standard picture of the universe evolution (a gravitational-instability model) that such a heterogeneous structure develops by gravitational amplification of density fluctuations.

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