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VISCOELASTIC PHASE SEPARATION IN DYNAMICALLY ASYMMETRIC FLUID MIXTURES

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In conventional theories of phase separation, it has been implicitly assumed that the two components of a mixture behaves dynamically in the same way[1,2]. However, this assumption is severely violated in a binary mixture which has intrinsic dynamic asymmetry, especially for a deep quench which leads to a large difference in the viscoelastic property between the two phases. One of such examples is a polymer solution, where only the polymer has a large number of internal degrees of freedom while the solvent does not: Recently we have found [3] that for a deep quench polymer solution exhibits a new type of phase-separation behavior essentially different from either a fluid or a solid model, in contrast to the conventional understanding of phase separation. A phase-separation pattern of such a mixture is characterized by a spongelike morphology of the more viscoelastic phase. In this paper, we demonstrate that unusual phase-separation behavior completely similar to that in polymer solutions is observed for a binary polymer mixture only one of whose component is close to the glass-transition temperature Tg, which indicates the generality of this phenomenon (see Fig.1). Effects of elasticity on phase separation have so far been considered only for solids [4], and not for fluids, simply because the latter has 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.

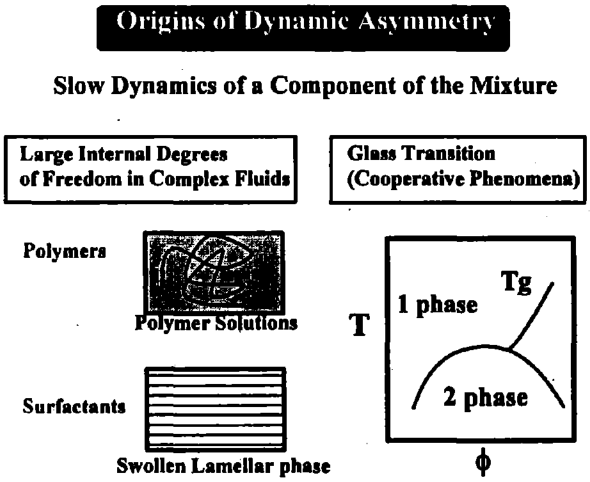

Fig.1 Possible candidates of dynamic asymmetry

First we show the phase separation process of a mixture of polystyrene (PS) and poly(vinyl methyl ether) (PVME). This mixture is one of the most well-studied polymer mixtures on phase separation[5]. It should be noted that phase separation of this mixture has so far been believed to be typical of usual phase separation of binary liquid mixtures which is classified into a fluid model [1,2]. This is supported by many previous experiments [5]. It is likely true for a shallow quench for which a difference in the rheological property between the two phases is small because of a small difference in the concentration between them. However, this polymer mixture can have strong dynamic asymmetry especially for a deep quench since its critical temperature Tc is close to Tg of PS .

Figure 2 show the morphological evolution during phase separation of the two mixtures. The time shown in the figure is that after the temperature jump. In the initial stage, the system phase separates as a fluid mixture, and the behavior looks usual. However, the system starts to behave as an elastic body after the initial regime, since the enhancement of the concentration fluctuation makes the PS-rich phase more viscoelastic than the PVME-rich phase. This causes the transition from a fluid regime to an elastic regime, reflecting an increase in the coupling strength between the velocity and stress fields. In the time regime before this crossover (t<700 s) which we call a "frozen period", there is no formation of macroscopic domains. In an elastic regime (800 s<t<2000 s), the elastic energy dominates phase separation and the PS-rich phase behaves like a gel. After a long initial frozen period, holes of a PVME-rich phase appear and grow in their size. Then, the volume of the PS-rich phase starts to decrease with time and the PS-rich phase transforms into a spongelike pattern. In this elastic regime, a domain shape is determined by the mechanical balance of elastic forces and the interfacial tension plays almost no roles in determining the domain shape. In the late stage of phase separation (t>2000 s), the deformation rate of domains slows down since the volume fraction approaches to that determined by the thermodynamic phase diagram (the counter-balance law). Thus, the PS-rich phase behave as a fluid again, and the domain shape transforms into the shape of the lowest interfacial energy (sphere) as in usual phase separation. The spongelike phase becomes unstable and the interconnectivity breaks (tube hydrodynamic instability). The overall feature of the viscoelastic phase separation near a symmetric composition is schematically drawn in Fig.3. We also study the temporal change in the structure factor S(q) calculated from a real-space image[6]. The details of the analysis will be shown elsewhere. Depending upon the composition symmetry, viscoelastic spinodal decomposition in the intermediate stage can be grouped into three types in terms of the morphology [3]: (i) moving droplet phase, (ii)networklike phase, and (iii) spongelike phase. Here we focus our attention only on the case (ii). Cases (i) and (iii) will be intensively discussed in the future publication.

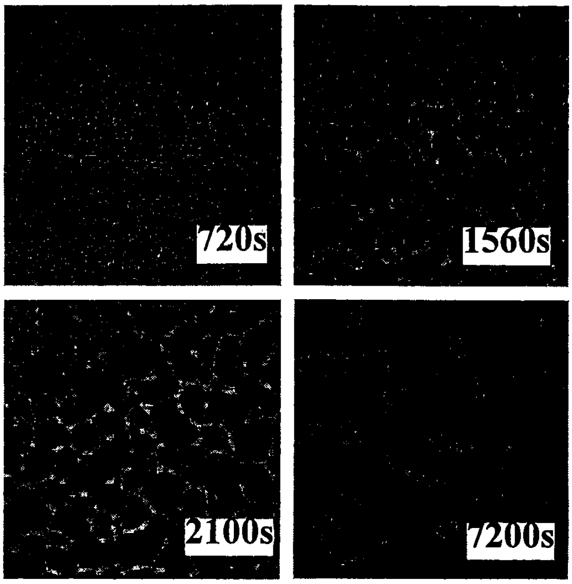

Fig.2 Phase separation process in PS/PVME

The behavior observed here suggests that strong dynamic asymmetry between the two components of a fluid mixture generally leads to unusual phase separation ("viscoelastic phase separation"), which does not belong to the above conventional classification (fluid and solid models): In addition to polymer solutions, a polymer mixture one of whose components is close to its glass transition is found to transiently exhibit a morphology peculiar to viscoelastic phase separation, namely a spongelike continuous pattern of the minority phase. We probably need a new model of phase separation in addition to conventional fluid and solid models. We think [3] that this type of phase separation (viscoelastic model) is likely described by the generalized diffusion and kinetic equations including viscoelastic effects, which has recently been derived by Doi and Onuki [7].

Next, we discuss the similarity of viscoelastic phase separation to gel phase separation[8,9]. The elastic regime of viscoelastic phase separation is essentially the same as bulk volume phase transition of gel. Volume phase transition of gel in bulk is likely a special case of viscoelastic phase separation [3]. In gel phase separation, however, the system is likely trapped in the local minimum in the phase space because the reorganization of the structure has to overcome the high elastic energy barrier. In this sense, the structure of the steady-state solution could be very much different between viscoelastic and elastic phase separation. In other words, the relaxational nature of viscoelastic phase separation causes a significant difference in the late stage behavior from elastic phase separation in gel. Two-level structure is characteristic of viscoelastic phase separation. Although the similarity between volume phase transition in gel and the liquid-gas phase transition has been pointed out, we believe that there is an essential difference between them since gel has intrinsic topological and elastic asymmetry. Recently Sekimoto et al. [10] pointed out the importance of geometrical factors on gel phase transition. We would like to stress that the dynamics including critical phenomena and phase separation kinetics in gel and polymer solutions [3] should be essentially different from liquid-gas phase transition and phase transition in binary fluids, although there are experimental results supporting that gels belong to the same universality class as binary fluid mixtures. Tese results likely correspond to cases of a limit of weak elastisity. Because of the constraint of network connectivity, any concentration fluctuation inevitably produces elastic deformation of the network, which should cost the elastic energy. This difference originates from the dynamic asymmetry as in the case of polymer solutions. The understanding of the physics of bulk phase transition in gel is likely prerequisite to the understanding of phase transition in dynamically asymmetric binary fluids, since the former is a special case of the latter.

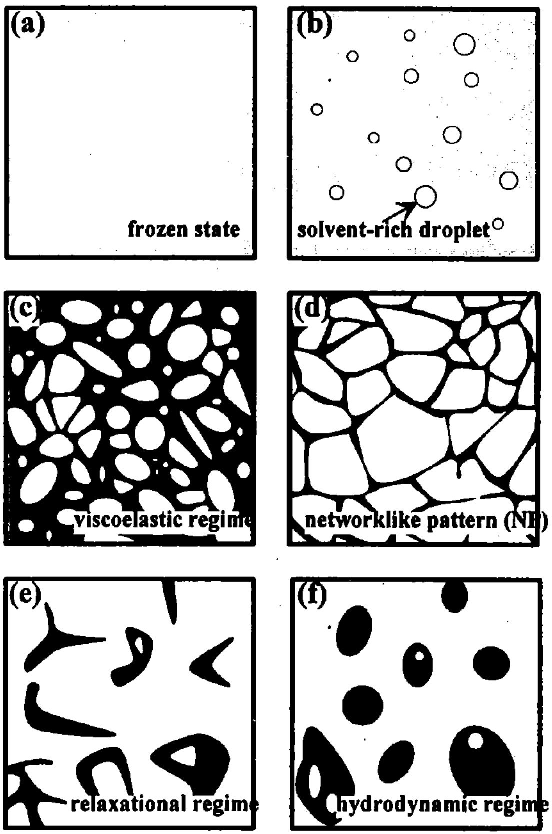

Fig.3 Schematic figure showing the coarsening behavior of viscoelastic phase separation near a symmetric composition.

Finally, we discuss the universal nature of the foamlike morphology and its physical origin. It is known that gel undergoing volume shrinking phase transition forms the bubble-like structure [8,10]. The physical origin of the appearance of the honeycomb structure in polymer foams (e.g.polystyrene foam and urethane foam) is also likely similar to ours. All these processes have a common feature that the holes of a less viscoelastic phase (gas in foam, water in gels, a 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, the more viscoelastic phase decreases its volume. This volume shrinking process is dominated by the transfer (diffusion or flow) of the less viscoelastic component in the more viscoelastic phase to satisfy the total mass conservation. Thus, the limiting process of pattern evolution is commonly the diffusion or flow process of the fluid component under stress. Among these examples, a polymer foam is unique in the point that the total volume is not conserved since it accompanies the liquid-gas phase transition. In addition to patterns in mixtures of condensed matters, we also point out the similarity of these patterns to the foamlike structure of the universe [11], where the gravitational attractive interaction likely plays a role similar to elasticity in producing the structure. The foamlike structure is probably the universal morphology for the phase separation of a system in which only one component asymmetrically has elasticity stemming from either topological connectivity or attractive interaction. The common feature of these systems originates from the volume phase transition, or more strictly elastic phase separation of dynamically asymmetric mixtures including fluid (liquids and gasses) at least as a component. This differs from the elastic phase separation of dynamically symmetric solid mixtures (e.g. metal alloys) which does not accompany the volume change of each phase [4]: In this case, a softer phase always form a continuous phase to minimize the total elastic energy, in contrary to our case.

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