

Solvent dependence of self-assembled structures formed by solvent evaporation from polymer solutions

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We have studied solvent dependence of self-assembled structures of ternary mixtures of a polymer, an organic compound and water during solvent evaporation by means of optical microscopy. We used two kinds of organic solvents, 2-butanone partially miscible with water at 25 °C and tetrahydrofuran (THF) miscible with it over a whole range of concentration. In both systems, as the solvent is evaporated, some droplets appeared by nucleation from the homogeneous solution and afterwards they grew with time. As solvent evaporation proceeded further, both systems showed different behaviors. In the polymer/water/2-butanone system, it was found that the droplets with almost the same size were arranged with a nearly constant spacing, while such regular arrangement of the droplets was not observed for the polymer/water/THF system. On the basis of these results, effect of solvent quality is discussed on the self-assembled structures and processes.

Key words: self-assembled structure, polymer solution, solvent evaporation, adsorption

1. INTRODUCTION

Numerous researchers have investigated self-assembled structures caused by evaporation of solvents from multicomponent systems such as polymer solutions or colloidal dispersions containing nanoparticles [e.g., 1-3]. In many of these studies, the self-assembled structures have been formed due to phase separation of the system. As a consequence, such self-assembly can generate various morphologies such as network pattern [1], honeycomb pattern [2], or concentric ring pattern [3] on the length scale of micrometers. The material with such micropatterning can be used in optical applications, e.g., microlens array or lithography [4,5]. Recently, we showed that water-rich droplets were hexagonally arranged in the course of the self-assembling process induced by solvent evaporation from polymer solutions in mixed solvents of 2-butanone and a small amount of water [6,7]. In this case, we utilized phase separation in the mixture of 2-butanone and water for fabrication of the self-assembled structures [6,7]. Namely, the phase separation can be induced by the concentration change due to a large difference between volatilities of the two components. Moreover, it has been shown that certain kinds of

polymers such as poly (vinyl methyl ether) (PVME) or poly (methyl methacrylate) (PMMA), which are soluble in 2-butanone and have polar groups in the chemical structure, play an important role on the formation of regular arrangement of the droplets. These polymers prevented the droplets from coalescing with others for a while. On the other hand, polystyrene (PS) without any polar groups had no effect on such stabilization of the droplets. Thus, stabilization of the droplets depends upon quality of polymers. Similarly, it may be affected by quality of solvents as well as polymers.

In this study, we have investigated solvent dependence of self-assembled structures formed by solvent evaporation from polymer solutions in mixed solvents of water and an organic compound. We used two kinds of organic solvents, 2-butanone and tetrahydrofuran (THF). The mixture of 2-butanone and water is partially miscible at 25 °C, i.e., it phase-separates in an intermediate range of concentration, while that of THF and water is miscible over a whole range of concentration. In this paper we shall discuss the

self-assembled structures and processes of the polymer solutions in both systems.

2. EXPERIMENT

In this study we used poly (vinyl acetate) (PVAc) as the polymer sample, which was purchased from Aldrich Co. PVAc was dissolved in an organic solvent (2-butanone or THF) and then a small amount of water (8.2 wt% of water for the PVAc/water/2-butanone mixture and 6.9 wt% of water for the PVAc/water/THF mixture) was added into the solution to make a homogeneous solution. After the polymer solution prepared thus was poured into a petri dish with a diameter of 30 mm, we observed time-evolution of self-assembling structures formed during solvent evaporation using optical microscopy at 25 °C.

3. RESULTS AND DISCUSSION

In Figure 1, we show optical micrographs of a self-assembling process for a PVAc/water/2-butanone mixture. For a while after the onset of solvent evaporation, no structures were observed in sight of optical microscopy. At 488 sec, droplets suddenly appeared and afterwards grew, as evaporation of solvents proceeded. The droplets are considered to be water-rich phase, since volume fraction of water is expected to be small at the early stage of the self-assembling process. As the volume fraction of water got larger with time due to a volatility difference between 2-butanone and water, interdroplet distance became short as shown in Figure 1(b). Afterwards, coalescence of the droplets did not take place for a while. As a result, the distribution of the droplet size became small and the regular array of the droplets was formed. However, after that the droplets coalesced with others in order to reduce the interfacial free energy as usually observed at the late stage of phase separation in fluid mixtures [8] and finally the droplets became small and disappeared, because the solution with high concentration of water became homogeneous again. The result is essentially the same as those for solutions of PVME and PMMA in mixed solvents of 2-butanone and water as reported in previous papers [6,7].

Next let us show the result for polymer/water/THF systems. Figure 2 presents optical micrographs of the self-assembled structures for 5.4 wt% PVAc in mixed solvents of water and THF. At a certain time phase separation took place and afterwards size of droplets became larger and they became denser, as evaporation of solvents proceeded. Until this stage, the behavior is similar to that of the PVAc/water/2-butanone mixture. However, in the case of the PVAc/water/THF system, coalescence of the droplets easily occurred, immediately after they contacted with others, so that they grew at a large rate with time. Thus, no stabilization of droplets was observed in this

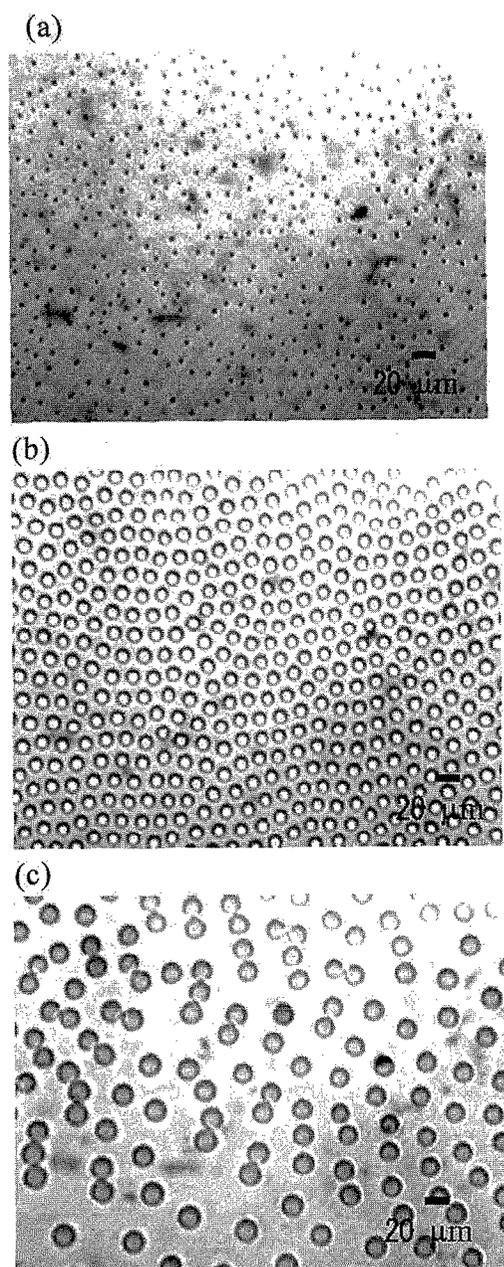


Figure 1 Optical micrograph of self-assembled structures for 2.0 wt% PVAc in mixed solvents of water and 2-butanone at 488 sec (a), 744 sec (b) and 1128 sec (c).

system. Therefore, size distribution of the droplets was larger and regularity of arrangement of the droplets was worse in comparison with that of the polymer/water/2-butanone system.

We estimated average diameter of the droplets D from the optical micrographs in order to pursue time-evolution of the droplet growth. Figure 3 shows double logarithmic plots of diameter against time after the onset of evaporation of solvents. As shown in Figure 3(a), the self-assembling process can be divided into three

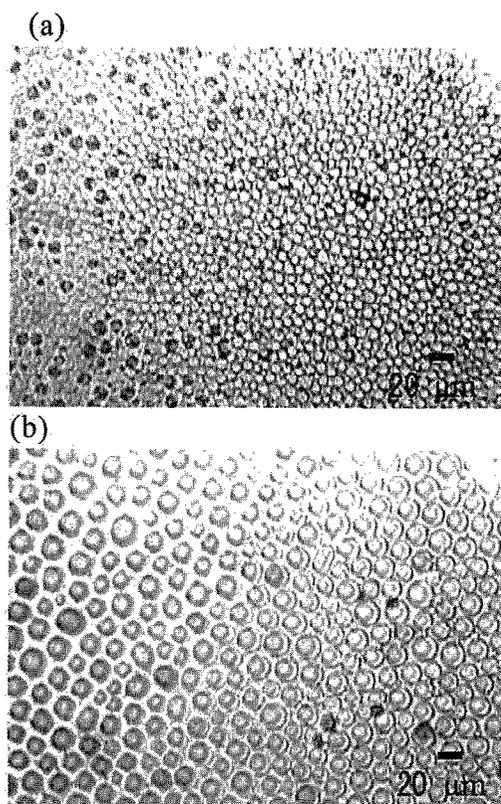


Figure 2 Optical micrograph of self-assembled structures for 5.4 wt% PVAc in mixed solvents of water and THF at 688 sec (a) and 884 sec (b).

regimes for the polymer/water/2-butanone system: (i) nucleation and growth regime, (ii) regularly arranged regime, (iii) aggregation and coalescence regime, corresponding to the result for PVME solution in mixed solvents of 2-butanone and water [6]. Thus, the self-assembling dynamics became slow in the regime where the droplets were regularly arranged. On the other hand, the similar plot for the polymer/water/THF system showed a linear relation, i.e., time-evolution of the droplet size obeyed a power law of time ($D \sim t^\alpha$), as usually observed in phase separation dynamics of fluid mixture [9], where α is the scaling exponent which characterizes the droplet growth. For this system, the droplet size in the nucleation and growth regime was too small to estimate it from the optical micrographs. However, we can see that there is no regime corresponding to regime II. We evaluated the α value of 3.2 from the best fit to the data. The extraordinarily large value of α in comparison with that of usual phase separation dynamics of fluid mixtures ($\alpha = 0.3 - 1$ [10 - 13]) may be caused by the following reason as discussed elsewhere [6]: in this experiment the composition of THF (or 2-butanone) continuously decreases with time because of solvent evaporation. Therefore,

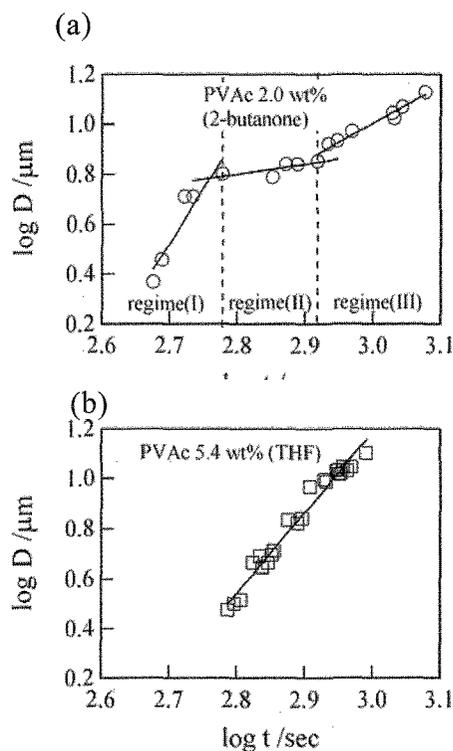


Figure 3 Time-evolution of droplet diameter during solvent evaporation for the polymer/water/2-butanone mixture (a) and the polymer/water/THF mixture (b).

water molecules in the matrix phase, i.e., THF-rich phase diffuse into the droplet phase in order to keep the equilibrium composition of each phase determined by the coexistence curve, so that the droplet growth is accelerated. Thus, slowing down of the self-assembling dynamics was not observed for this system. Similar trend was observed for solutions of other polymers such as poly (vinyl ethyl ether) or poly {methyl methacrylate (MMA)-*co*-methacrylic acid(MA)} with a MA fraction of 0.016 (not shown).

Here we would like to discuss the result of the self-assembling process for both systems. It was shown by both this study and previous one that quality of solvents and polymers was important for formation of regular arrangement of droplets. The regular arrangement can be formed by stabilization of the droplets, i.e., no coalescence of the droplets. The stabilization may be caused by adsorption of polymers at the interface of the droplets. As a matter of fact, adsorption of polymers at interfaces of water droplets has been reported by other researchers [14,15]. For example, Ptois and François experimentally proved that a block copolymer was adsorbed at the interface of water droplets with hexagonal array and no coalescence of the droplets occurred due to decrease of the surface

tension [14]. Similar situation may take place in the polymer/water/2-butanone system. As mentioned in Introduction, PS had no effect on stabilization of the droplets even in the polymer/water/2-butanone system. The reason is probably due to the fact that PS without any polar groups tends to avoid water molecules, i.e., the interface of the droplets. In the polymer/water/THF system, addition of polymers induces phase separation rather than moderate it, because mixtures of water and THF without adding polymers does not phase-separate during solvent evaporation. Therefore, the polymers are not likely to stay at the droplet interface. Thus, it is predicted that quality of solvents or polymers affects the phase separation dynamics and the structure through change in the interface.

4. CONCLUSION

Self-assembling process cast on a petri dish has been studied for polymer solutions in mixed solvents of an organic compound (2-butanone or THF) and water. It has been suggested that solvent quality affects adsorption of polymers at the interface of the droplet, so that the self-assembling dynamics and the morphology changes.

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