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ORIGINAL CONTRIBUTION

Self-assembling process of zirconium oxide suspension induced by vaporization of volatile solvents

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Abstract We investigated the self-assembling processes of solutions of poly(vinyl methyl ether) in mixed solvents of 2-butanone and water with and without zirconium oxide (ZrO_2) particles with average size of 75 nm during vaporization of the solvents by means of optical microscopy. The self-assembling processes can be classified into three regimes: (1) early stage (nucleation and growth regime), (2) intermediate stage (regularly arranged regime), and (3) late stage (aggregation and coalescence regime). In the intermediate stage, the water droplets, including the ZrO_2 particles, were regularly arranged with an almost constant spacing. The mechanism of the self-assembling processes is discussed on the basis of experimental results.

Keywords Self-assembling process · Nanoparticles · Hexagonally ordered array · Optical microscopy · Nucleation

Introduction

In recent years, a considerable number of studies have been made on the self-assembly of water droplets condensed on the surface of a polymer solution by evaporating a volatile solvent under a flow of moist air [1–7]. The self-assembly generates a regular pattern of pores with honeycomb morphology on the length scale of a micrometer. Stabilization of droplets in the self-assembly is indispensable for the fabrication of the regular pattern. For the stabilization, many of these studies have used special polymers, such as block copolymers, star polymers, or amphiphilic polyion complexes. On the other hand, interestingly, Srinivasaro et al. [5] showed that hexagonally ordered arrays of air holes can be formed even in solutions of a simple flexible polymer. In their experiments, the water droplets condensed on the surface of the solution did not coalesce during formation of the hexagonal packing. They speculated that no coalescence of the droplets was attributed to either thermocapillary convection arising from a temperature gradient induced by evaporating the volatile solvent or elastic interactions between the droplets induced by the vapor of the evaporating solvents. However, the experimental proof concerning the key factors remained ambiguous. More importantly, their speculation is not clear about the role of the simple flexible polymers on the regular pattern. Thus, at the present stage, essential factors for production of the regular pattern do not seem to be sufficiently understood.

On the other hand, it is very important to fabricate the regular pattern of colloidal particles with specific characteristics for technological applications. For example, such regular pattern of the colloidal particles has been utilized as optical devices such as photonic crystals [8]. In this study, we try to utilize self-assembled structures formed for mixture of water, organic solvents, and a polymer for fabrication of regular pattern of colloidal particles (zirconium oxide [ZrO_2] particles). ZrO_2 have characteristics of high refractive index, high strength, and refractory. The colloidal additives have the potential to newly produce materials with better performance in refractive or mechanical properties.

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We investigated the time evolution of the self-assembling process induced by evaporation of volatile solvents for suspensions of ZrO_2 particles with dimensions of tens of nanometers. For comparison, we also observed the self-assembling process for simple coil-like polymer solutions without adding the colloidal nanoparticles. In doing so, we did not use any flow of moist air but used a mixture of volatile organic solvent and a small amount of water as a source of supply of droplets unlike other researchers, because the nanoparticles are insoluble in usual organic solvents immiscible with water. In this paper, we shall discuss the effects of the nanoparticles and polymers on the self-assembling processes.

Experiments

Samples and sample preparation

Hydrous ZrO_2 particles (Sumice Fine® TK010, Sumitomo Osaka Cement) were used in this study. The ZrO_2 particles (0.2 $\mathrm{mol{\cdot}dm^{-3}}$) were prepared according to the method reported by Clearfield [9] with slight modification. Briefly, aqueous solution of $ZrOCl_2$ containing ammonia (pH value between 1 and 2) was boiled at 100 °C for 72 h in a flask with a reflux condenser. Dialysis was carried out for aqueous colloidal suspensions of the ZrO_2 particles with a seamless cellulose tubing with 28.8 mmϕ (UC-36-32, Sanko Junyaku, Japan) to remove excess ions. After dialysis, the conductivity measured by applying 500-V potential according to ASTM D257 protocol using a resistivity meter (Mitsubishi Chemical, HIRESTA-IP with a concentric ring URS probe) was 180 μs/cm for 1 wt% colloidal suspension. Poly(vinyl methyl ether) (PVME) purchased from Aldrich Chemical was used. The PVME was roughly fractionated with using toluene as a good solvent and hexane as a poor solvent. The fractionated PVME has the number-averaged molecular weight M_n of 2.3×10^4 and the polydispersity indices for the molecular weight distribution M_w/M_n of 1.82, where M_w represents the weight-averaged molecular weight. These values were obtained by using size exclusion chromatography. We prepared the mixture used in this study as follows. First, the PVME was dissolved in 2-butanone at desired concentration. A small amount of distilled water was added into the polymer solution so that the mixture does not phase-separate. A very small amount of the ZrO_2 aqueous suspension with a concentration of 10 wt% was further added into the polymer solution. Although the ZrO_2 particles are dispersed in water, they precipitate in pure 2-butanone. When the mixture prepared in the above manner precipitated, a small amount of acetone was added into it to homogeneously disperse the ZrO_2 particles.

Characterization of ZrO_2 particles

The ZrO_2 particles were observed by the use of a transmission electron microscopy (H-800, Hitachi) operated at 200 kV for the sample dried on a grid. The particles have anisotropic shape and the size in the range of 50 to 100 nm as shown in Fig. 1. The average size of the particles was 75 nm.

Optical microscopy

We poured 0.5 ml of the mixture prepared in the above method into a petri dish with a diameter of 30 mm and then, observed time-evolution of the self-assembling process during vaporization of volatile solvents such as 2-butanone and acetone by means of optical microscopy (OM). The observation was performed at room temperature (at about 21 °C for PVME solution containing colloidal ZrO_2 and at about 26 °C for PVME solution without it; the temperature difference does not essentially affect the self-assembling behavior). The humidity in the measurements is less than

Fig. 1 Transmission electron microscopy image for a sample dried from a ZrO_2 aqueous suspension

60%. We estimated the average diameter of droplets from OM images as detailed later. The number of droplets measured to obtain the average was from several tens to five hundreds, mostly from one hundred to three hundreds.

Results and discussion

Typical self-assembling pattern

Before we show the result of the self-assembling process, we shall show a typical example of time variation of solvent, PVME, ZrO_2 composition accompanying with evaporation of solvents for help to elucidate the self-assembling process (Fig. 2). The fraction was estimated from weight loss measurement of a sample with the composition comparable to those used in this study. As shown in Fig. 2, solvent composition gradually decreases with time until a certain time, whereas composition of PVME or ZrO_2 gradually increases. At the late stage of evaporation, the composition abruptly changes. However, the result should not be quantitatively compared with other samples, because we did not control the evaporating rate of solvents in this study and the time-variation of composition has large difference depending on the experimental conditions.

Next, let us show a typical self-assembling process induced by vaporization of volatile solvents for PVME solutions containing colloidal ZrO_2. Figure 3 presents a time evolution of the self-assembling pattern observed for the colloidal suspension with a concentration of 0.12 wt% ZrO_2 and 2.0 wt% PVME. In the initial stage, no structures are observed in the spatial scale of OM. This stage corresponds to the incubation period before nucleation. At about 25 min after the onset of evaporation of the solvents, some droplets suddenly appear in the course of the

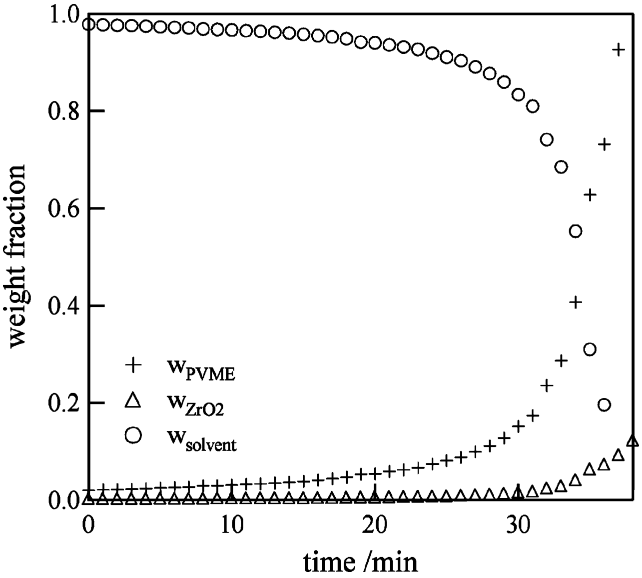

Fig. 2 Time variation of concentration of solvent, PVME, ZrO_2 accompanying with solvent evaporation estimated from weight loss measurement of a sample. The measurement was carried out for a sample with composition of 2.0 wt% PVME and 0.2 wt% ZrO_2

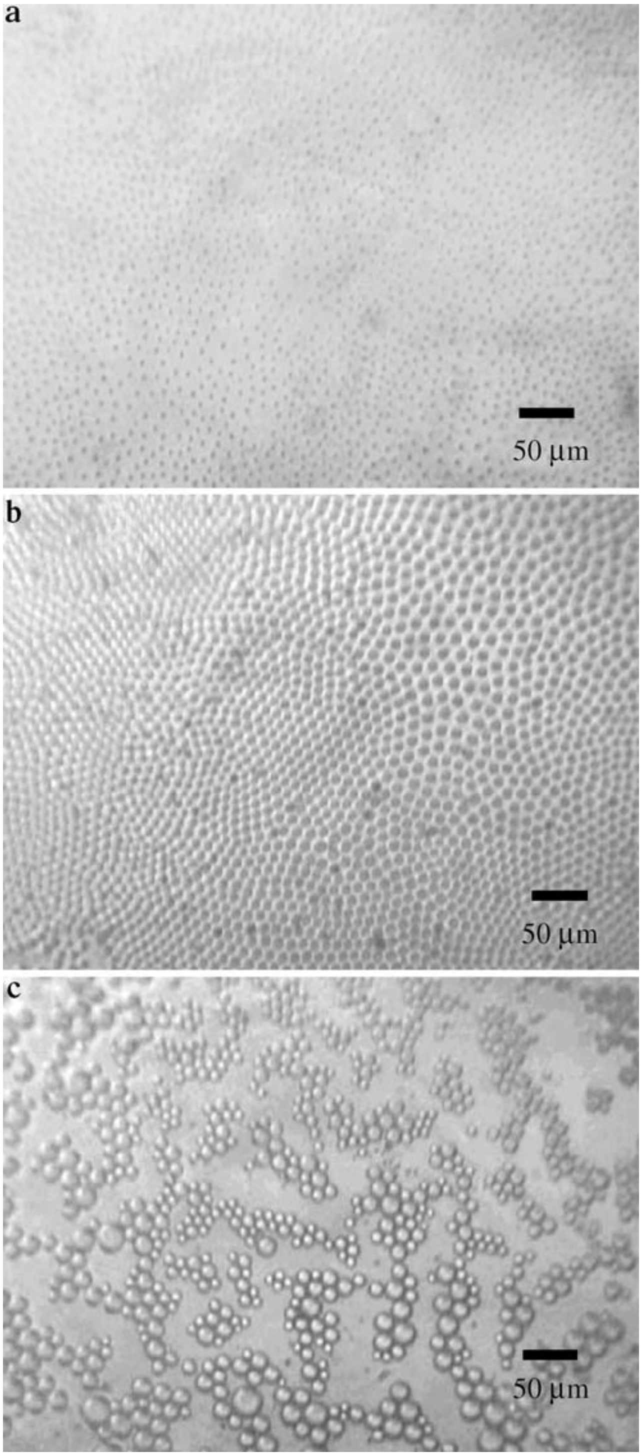

Fig. 3 Optical microscopy images of the self-assembling pattern for the colloidal suspension with a concentration of 0.12 wt% ZrO_2 and 2.0 wt% PVME at **a** 1,466, **b** 1,858, and **c** 2,046 s

evaporation process. Afterward, the droplets grow, and the interdroplet distance decreases with evaporation of volatile organic solvents (Fig. 3a). As time elapses, the distribution of the interdroplet distance becomes narrow, and the droplets are regularly arranged with an almost constant spacing (Fig. 3b). The regular array appears to be hexagonal type. Furthermore, as the solvents evaporate more and more, the droplets begin to come into contact, so that the regular array collapses and the droplets start to aggregate and coalesce with others (Fig. 3c). Finally, when most of the organic solvents are evaporated, the aggregated droplets disappear; that is, the residual aqueous colloidal suspension becomes homogeneous again, and therefore, any structures become invisible on the scale of OM.

In some cases, during evaporation of organic solvents, multiple steps of nucleation take place. For the colloidal suspension with a concentration of 1.0 wt% PVME and 0.12 wt% ZrO_2, the droplets have a comparatively large spacing until a certain time. However, at t=1,260 s, newly formed small droplets appear between the large droplets (Fig. 4). This result suggests that the matrix phase became unstable (or metastable) with evaporation of the volatile solvents, and therefore, further nucleation was induced.

Effects of ZrO_2 particles and polymers on the self-assembling pattern

To understand the effects of ZrO_2 particles on the self-assembling process, we observed the process for the samples without adding ZrO_2 particles, i.e., PVME solutions. Figure 5 shows time evolution of the self-assembling pattern for a polymer solution with a concentration of 2.3 wt% PVME. Similar to the case of the PVME solution containing ZrO_2 particles, nucleated droplets grow with time, and the interdroplet distance decreases (Fig. 5a). Moreover, as time passes, the size distribution of the droplets becomes narrow, and the array of droplets becomes hexagonally ordered (Fig. 5b). At the late stage, droplets coalesce with each other, and the hexagonal array collapses (Fig. 5c). Thus, addition of PVME has effects to inhibit

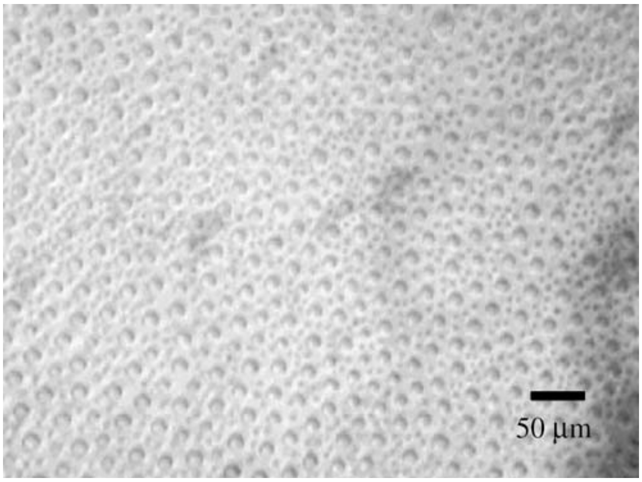

Fig. 4 Optical microscopy image for the colloidal suspension with a concentration of 0.12 wt% ZrO_2 and 1.0 wt% PVME at 1,258 s

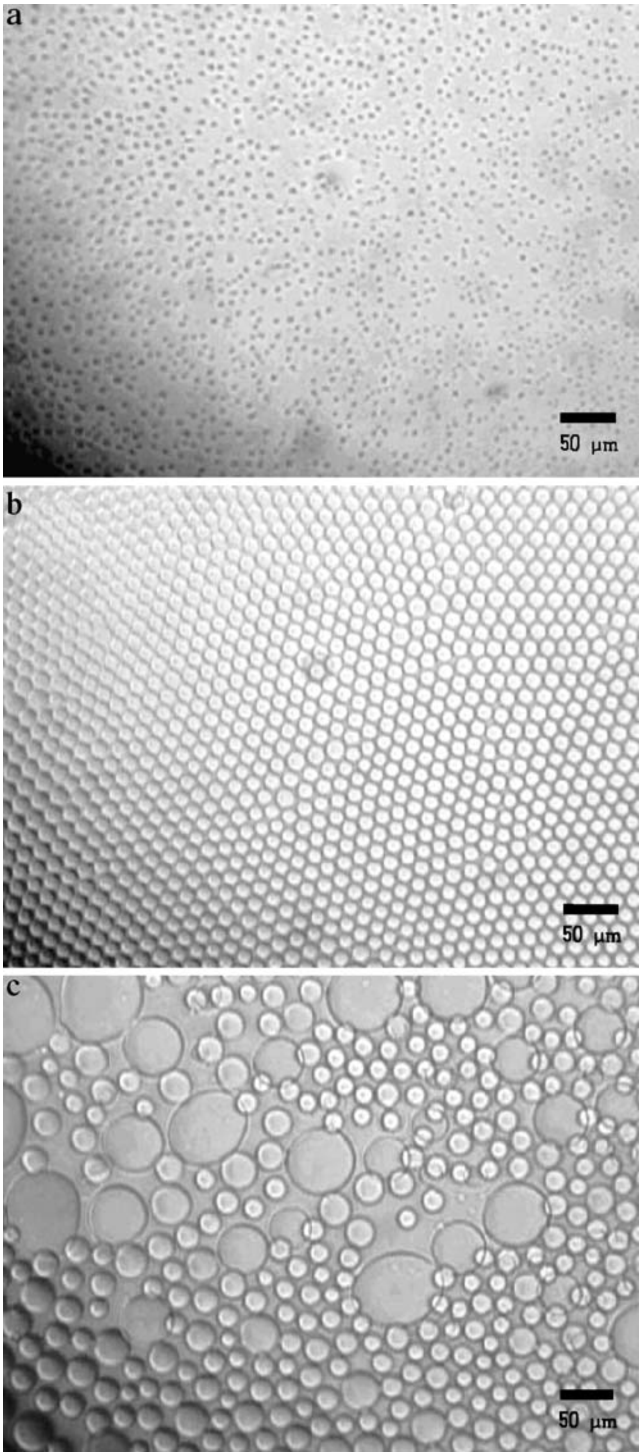

Fig. 5 Optical microscopy images of the self-assembling pattern for a polymer solution with a concentration of 2.3 wt% PVME (without adding ZrO_2 particles) at **a** 350, **b** 622, and **c** 856 s

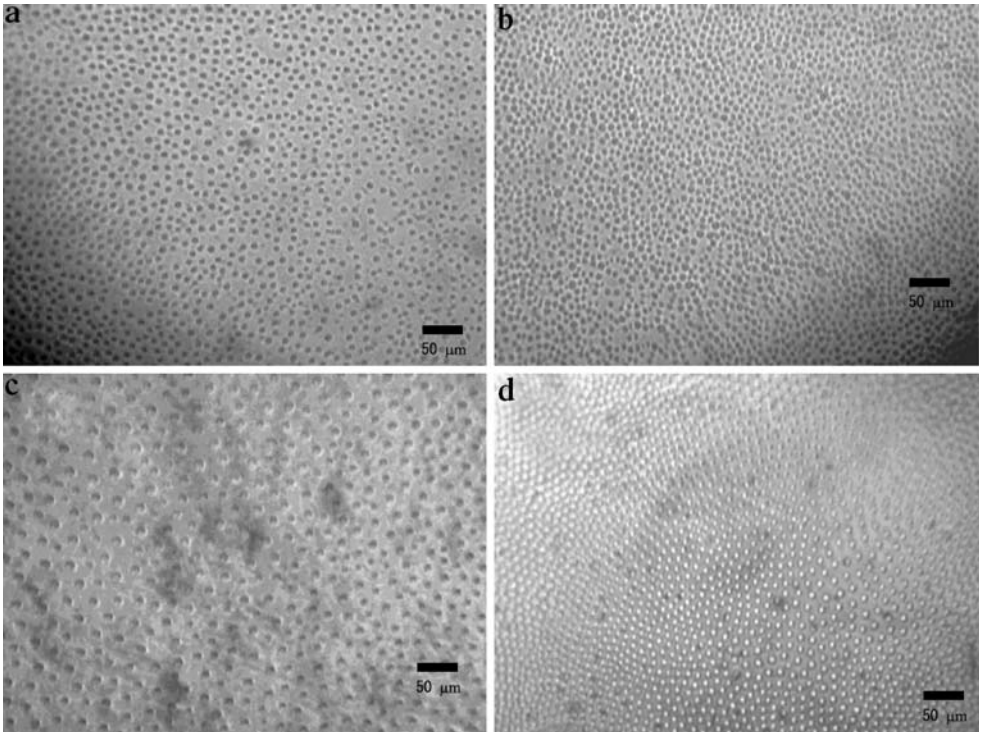

Fig. 6 Comparison of optical microscopy images of the self-assembling pattern for **a** 0 wt% ZrO_2 and 2.3 wt% PVME (t= 376 s), **b** 0 wt% ZrO_2 and 1.5 wt % PVME (t=712 s), **c** 0.12 wt% ZrO_2 and 2.3 wt% PVME (t= 2076 s), **d** 0.12 wt% ZrO_2 and 2.0 wt% PVME (t=1638 s)

coalescence of droplets and helps in forming the regular pattern of droplets.[1] Note that we did not add any stabilizer except for PVME in the experiment. Srinivasaro et al. [5] showed that three-dimensional ordered array of droplets are formed during solvent casting in the presence of a moist airflow for organic solutions of a simple flexible polymer, when the solvent is less dense than water. In our experiments, three-dimensionally ordered structures could not be observed, although some droplets sank on the bottom of the solution at the late stage. To examine the effect of polymers, we carried out the similar measurements using other kinds of simple flexible polymers. We observed a regular array of droplets for solutions of poly(vinyl acetate) (PVAc) with M_w of about 1.7×10^5 (although the period keeping the regular pattern was shorter in comparison with that for PVME), whereas we did not succeed in its fabrication for solutions of polystyrene (PS; purchased from Aldrich Chemical), where arrangement of the droplets once formed was largely disturbed by an intense convective flow in the solution. In the work of Srinivasaro et al., they used PS with one end terminated by a carboxylic acid group and fabricated the three-dimensonally ordered array of droplets. Introduction of the polar group at the end of the polymer may play an important role on the formation of the regular array of droplets. As a matter of fact, both PVME and PVAc have polar side groups. Especially, PVME is dissolved in both solvents of 2-butanone and water at room temperatures.

The ZrO_2 suspensions without adding PVME have no ability to form the regular array of the droplets. The formed droplets precipitated quickly with a short period. The array of the droplets before the precipitation was also largely influenced by an intense flow in the solution, and regular arrangement of the droplets was not observed at least under the experimental conditions covered in our study. On the whole, any intense flows in the solution and precipitations of droplets disturbed the formation of the regular array of the droplets.

Although the hexagonally ordered array of droplets were formed for PVME solutions both with and without ZrO_2 particles, the behavior of the stabilized droplets appears to be a little different depending on the systems. In the former case, from the beginning of the self-assembling process, i.e, when the droplets are modestly apart, they keep equal distance to some degree (see Fig. 6c,d). Furthermore, the motions of many droplets observed under OM measurements appear to be collective; that is, the droplets move in the same direction as surrounding droplets. On the other hand, for the PVME solutions without ZrO_2 particles, the interdroplet distance in the beginning of the process has some distribution (see Fig. 6a,b), and many droplets move independently, until the interdroplet distance becomes small. Thus, the ZrO_2 particles are suggested to significantly influence the interactions between the droplets.

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[1] The regular pattern of droplets was not observed for mixtures of 2-butanone and water without adding polymers.

Time evolution of droplet size

Next, let us investigate the time evolution of droplet size. Figure 7 shows the time change of average droplet diameter estimated from the OM image D for various samples. The error bars in the figure represent the standard deviation values of the measurement. The behavior can be divided into three regimes. In the early stage, the nucleated droplets grow with time at a large rate (regime I). Afterward, in the intermediate stage, the growth of droplets slows down, as the interdroplet distance gets close with evaporation of the volatile solvents (regime II). This regime corresponds to the stage where the droplets are regularly arranged with a constant spacing, as shown in Figs. 3b or 5b. In the late stage of the self-assembling process, the growth rate of the droplet size becomes large again due to aggregation and coalescence of the droplets (regime III).

The growth of droplets in phase separation dynamics of fluid mixtures has been often described by a power law of time $(D \sim t^{\alpha})$, e.g., [10–12], where α is the scaling exponent that characterizes the time evolution of droplets. In this paper, we estimate the exponent α in each regime. For PVME solution containing ZrO_2 particles, the values of the exponent α in regime I, α_I, are much larger than unity for all the samples (α_I=3.5–5; Fig. 6a–d). These values are very large in comparison with those expected from usual phase separation dynamics for fluid mixtures; for example, α=1/3 in droplet growth [13–15], or α=1 in the phase separation dynamics where hydrodynamic interactions are effective [16]. The extraordinarily large values of α_I may be caused mainly by the following reason. In our experiments, the phase separation is induced by evaporation of volatile organic solvents, and therefore, the composition in the mixture continuously changes with time. Especially because the composition of butanone in the matrix phase,

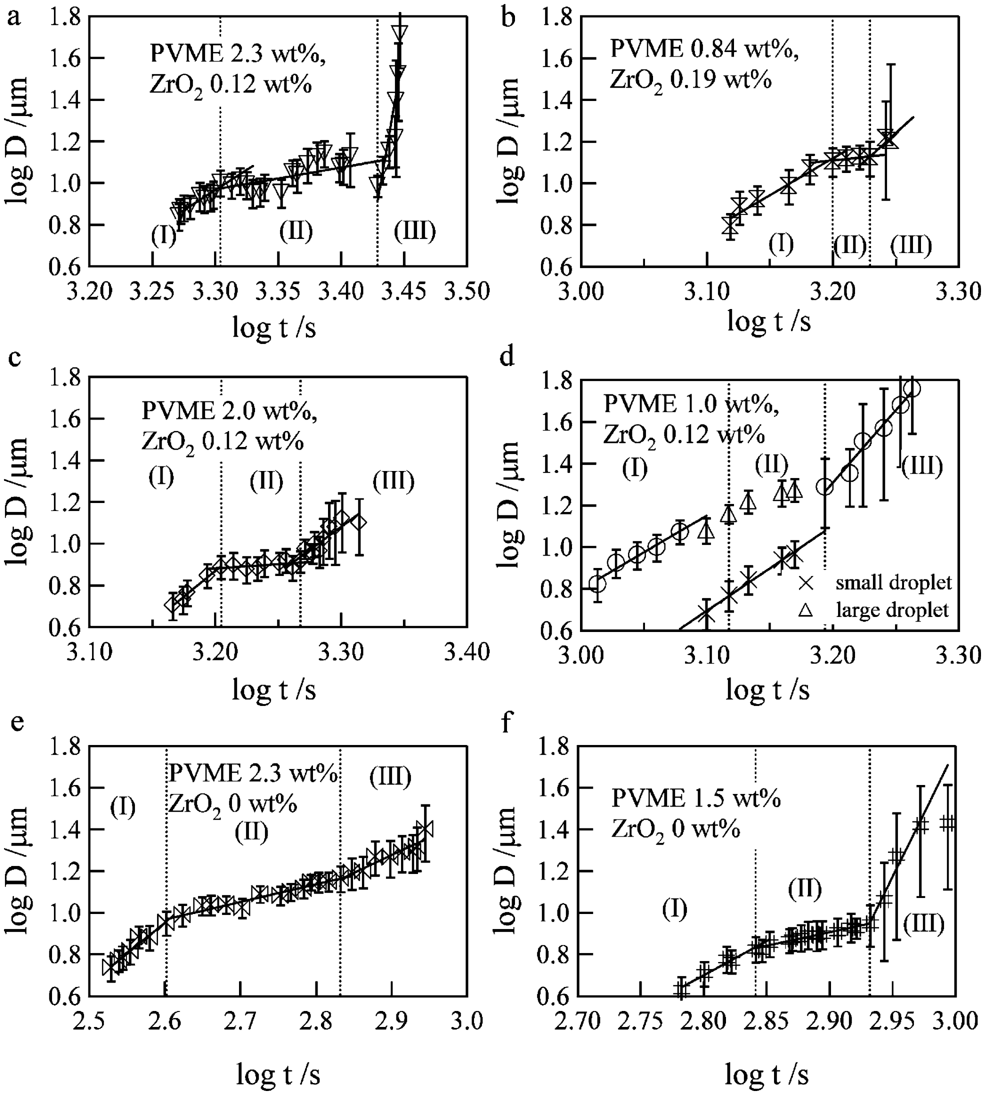

Fig. 7 Time change in the droplet size for various samples: **a** 0.12 wt% ZrO_2 and 2.3 wt% PVME, **b** 0.19 wt% ZrO_2 and 0.84 wt% PVME, **c** 0.12 wt% ZrO_2 and 2.0 wt% PVME, **d** 0.12 wt% ZrO_2 and 1.0 wt% PVME, **e** 0 wt% ZrO_2 and 2.3 wt% PVME, **f** 0 wt% ZrO_2 and 1.5 wt% PVME

which is butanone rich, decreases with time, diffusion of water in the matrix phase into the droplet phase is expected to take place. Such diffusion accelerates the growth of the droplets, so that the α_I values become large. In the regime II, where the droplet growth slows down, the values of the exponent α are sufficiently small in comparison with those in regime I (α_{II}=0.4–1). In this regime, as the interdroplet distance becomes small, it is predicted that droplet growth is significantly restricted by the interactions between other droplets in the surroundings. In this paper, it is important to notice that the exponent α_{II} has large values even in this regime because of acceleration of the phase separation dynamics arising from evaporation of the solvents. Furthermore, as the organic solvents evaporate with time, the droplets are forced to come into contact with others. Thus, in the late stage (regime III), the regular array of the droplets collapses, and the droplets begin to coalesce, so that α has very large values (α_{III}=4–34). Especially, in this regime, the behavior largely fluctuated with samples under the visual field. In many cases, droplets aggregated heterogeneously, and therefore, the droplet size has a large distribution as shown by large error bars. Sometimes after aggregation, a strong flow takes place, and accordingly, the droplets observed under OM go outside the visual field, and other droplets come into it. Therefore, the α values have a very large scatter. Finally, we shall comment about the fact that the α values even in regimes I and II are different to some degree by the samples. The self-assembling dynamics seem to be very sensitive to the experimental conditions, such as the evaporation rate, moisture in the atmosphere, a flow in the solution, or decrease in temperature arising from evaporation of solvents. The subtle difference in the experimental condition may cause some difference in the α values of various samples. However, apart from the absolute values of α, the relative trend of the dynamics in each regime is reproducible, and therefore, it can be concluded that the self-assembling process is classified into three regimes. On the other hand, the self-assembling dynamics for PVME solutions without adding ZrO_2 particles are similar to those for the solution containing ZrO_2 particles; that is, we can divide it into three regimes (Fig. 7e,f). The α values estimated for 2.3 wt% PVME and 1.5 wt% PVME solutions are 3.0 and 3.3 in regime I, 0.84 and 1.3 in regime II, and 1.7 and 12.2 in regime III, respectively. These values are fairly close to those for the solution containing ZrO_2 particles, except for the value in regime III for 2.3 wt% PVME solution. For the 2.3 wt% PVME solution, the regular pattern of droplets was kept for a very long period compared to other samples. As a matter of fact, although some of the droplets for the solution coalesced with others even in the regime II, the regular pattern did not easily collapse. Therefore, the boundary between regimes II and III becomes ambiguous for the solution.

A possible mechanism for the self-assembling process

From the above results, we present our speculation about the mechanism for self-assembling process of the PVME solutions containing ZrO_2 particles during evaporation of volatile solvents as follows (Fig. 8). In the beginning of the self-assembling process, water droplets are nucleated.

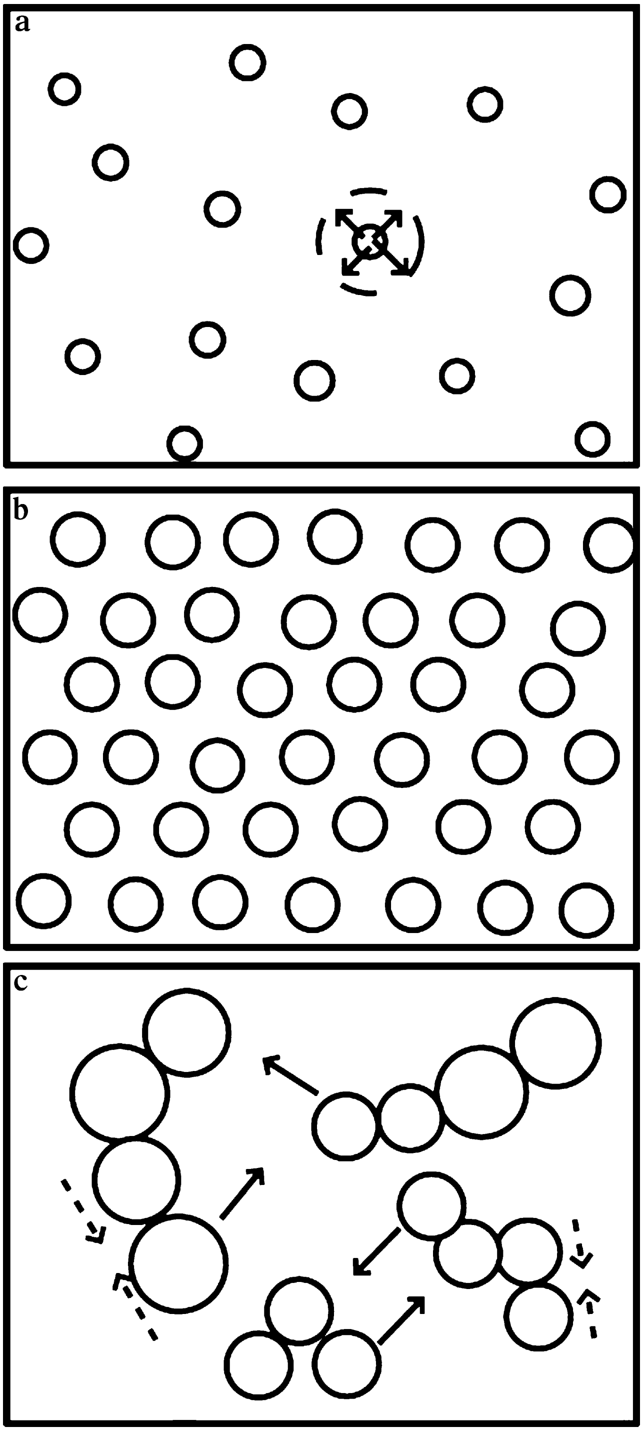

Fig. 8 A schematic representation for the self-assembling process of PVME solution with ZrO_2 particles

Nucleation appears to take place homogeneously in space when the solution contains ZrO_2 particles compared to that without the particles. As is well known, there are two types of nucleation mechanism: (1) homogeneous nucleation and (2) heterogeneous nucleation. In the latter case, dust particles or other solid impurities often become nuclei. In our case, ZrO_2 particles may be a candidate for the nuclei of water droplets. In fact, the ZrO_2 particles before nucleation should be dispersed homogeneously in the solution (the number density of the ZrO_2 particles added before evaporation corresponds to about 1 particle per μm^3, roughly calculated from average size and density of ZrO_2 particles). In regime I, the nucleated water droplets grow by diffusion of water and ZrO_2 particles in the matrix phase into the droplet phase as noted in the previous section (see the growth of the representative droplet drawn by a solid line into that by a broken line in Fig. 8a). It is reasonable to predict that some ZrO_2 particles are dispersed in the water droplet. In this regime, the number of the droplets essentially does not change after the nucleation finished. The volume fraction of the water droplet phase increases with evaporation of 2-butanone, whereas that of the matrix phase decreases, so that the interdroplet distance decreases. In the next stage (regime II), as the interdroplet distance becomes short, the diffusion of water containing ZrO_2 particles into the droplet phase is restricted due to repulsive interactions between droplets. As cause of the repulsive interactions, two factors may be considered. One is due to the polymers adsorbed at the water–butanone interface. It is important to remember that PVME is dissolved in both solvents of butanone and water. Namely, droplets are stabilized by steric repulsions of polymers. Or the droplets may elastically interact with others like viscoelastic phase separation effects proposed by Tanaka [17–19]. The other is due to repulsions of electrical double layers around the droplets arising from ZrO_2 particles. These repulsive interactions give rise to a minimum concerning the potential energy between the droplets, which plays a crucial role on the formation of the regular pattern of the droplets. As noted in the previous section, it is possible to form regular structures with some spacing for PVME solution with ZrO_2 particles. Therefore, the potential energy may have a minimum at larger interdroplet distance compared to PVME solution without ZrO_2. On the other hand, the self-assembled structure for polymer solutions without ZrO_2 appears to have somewhat better regularity than that for the mixture with ZrO_2. An addition of ZrO_2 particles tends to make stability of droplets worse because of strong segregation between ZrO_2 particles and 2-butanone. Hence, the period of regime II is shorter than that for PVME solutions without ZrO_2. The longer the period of regime II, the better the regularity of the structures, because the denser droplets with equal size usually form hexagonal closed packing.

However, as volatile solvents in the matrix phase are further evaporated, the droplets are forced to touch each other. At last, the regular array of droplets collapses, and droplets begin to coalesce to lower interfacial energy (regime III), so that the droplets become larger with time at very large rate (see the illustration of coalescence of aggregated droplets as shown by the broken arrows or diffusion coalescence of droplets as shown by the solid arrows in Fig. 8c). The driving force of the aggregation of the droplets is very large, as the system overcomes the (meta) stability of the arrangement of droplets. Hence, the growth rate in this regime is very large. In the final stage, as the most of the organic solvents evaporate, the droplets disappear, and we obtain a homogeneous colloidal suspension again.

Summary

We studied the self-assembling process induced by evaporation of volatile organic solvents for PVME solutions with and without ZrO_2 particles by means of OM. The self-assembling processes were found to have a unique regime, where the water droplets are hexagonally ordered on the scale of micrometers. Steric repulsion of polymers adsorbed at the water–butanone interface and/or electrostatic repulsion arising from the ZrO_2 particles is suggested to play a crucial role on formation of the regular pattern.

References

1. Widawaski G, Rawiso B, François B (1994) Nature 369:387
2. Pitois O, Francois B (1999) Colloid Polym Sci 277:574
3. Pitois O, Francois B (1999) Eur Phys J B 8:225
4. Jenekhe SA, Chen XL (1999) Science 283:372
5. Srinivasarao M, Collings D, Phillips A, Patel S (2001) Science 292:79
6. Karthaus O, Maruyama N, Cieren X, Shimomura M, Hasegawa H, Hashimoto T (2000) Langmuir 16:6071
7. Hayakawa T, Yokoyama H (2005) Langmuir 21:10288
8. Bowden CM, Dowling JP, Everitt HO (1993) J Opt Soc Am B 10:280
9. Clearfield A (1964) Inorg Chem 3:146
10. Hashimoto T (1988) Phase Transitions 12:47
11. Takeno H, Hashimoto T (1997) J Chem Phys 107:1634
12. Takeno H, Hashimoto T (1998) J Chem Phys 108:1225
13. Lifshitz IM, Slyozov VV (1961) J Phys Chem Solids 19:35
14. Wagner CZ (1961) Electrochemie 65:581
15. Binder K, Stauffer D (1974) Phys Rev Lett 33:1006
16. Siggia ED (1979) Phys Rev A 20:595
17. Tanaka H (1992) Macromolecules 25:6377
18. Tanaka H (1994) J Chem Phys 100:5323
19. Tanaka H (1997) Phys Rev E 56:4451