

# Coalescence-Induced Coalescence and Dimensional Crossover during the Phase Separation in Ternary Surfactant/Polymer/Water Mixtures

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We studied the separation process in the ternary mixtures of nonionic surfactant (C<sub>12</sub>E<sub>6</sub>, hexaethylene glycol monododecyl ether), polymer (PEG = poly(ethylene glycol)), and water. The separation process of PEG/water rich domains from the surfactant rich matrix was observed by the optical microscopy. From the morphological analysis, we determined the size of the domains as a function of time. On this basis we identified a dominating mechanisms of domains growth, that is the coalescence-induced coalescence mechanism. The coalescence (collision) event of two droplets induces a flow or a change of concentration distribution around droplets which pushes other droplets together inducing further growth. We also observed the evaporation–condensation (Lifshitz–Slyozov) mechanism of growth, but it did not affect the growth of large domains appreciably. We determined two regimes of the coalescence-induced coalescence associated with the dimensionality of the system. When the domains were smaller or comparable in size to the sample thickness we observe a three-dimensional growth. When the domains became larger than the sample thickness, a two-dimensional growth was observed. In the first regime, the size of the domains,  $L(t)$ , grew linearly with  $t$ , while in the second regime,  $L(t) \sim t^{0.3}$ . In the binary, surfactant/water system, water domains grew by the geometrical coalescence-induced coalescence as  $L(t) \sim t$  in three dimensions.

## 1. Introduction

The separation/demixing process is used for the formation of the complex self-assembled materials.<sup>1–7</sup> Consequently, the detailed analysis of the process in complex multicomponent fluids is of prime importance for many technological applications. The pathway of the transformation from the initial homogeneous mixture to the equilibrium two-phase coexistence has been a subject of many theoretical investigations.<sup>8–11</sup> One of key issues in the separation process is the kinetics and mechanisms of growth of domains of one phase in the matrix of the other phase.

When a homogeneous AB mixture below its lower critical point (or above its upper critical point) is suddenly heated (cooled) above/below its critical temperature, it ceases to be in the thermodynamical equilibrium stage and starts to demix. The homogeneous state can be now either a metastable or unstable state. In the case of the metastable state the process of demixing requires, in the first place, nucleation of droplets of the minority phase, e.g., an A-rich phase. Then, the droplets start to grow. At first they grow independently and their size,  $L(t)$ , changes with time,  $t$ , according to the rule  $L(t) \sim t^{1/2}$ . The exponent  $1/2$  reflects the fact that matter flows to the droplet via diffusion. This behavior has been observed in binary polymer blends.<sup>12</sup> At the later stage significant fraction of A molecules disappear from the homogeneous mixture (most of them form droplets), and competitive growth starts. Small droplets decrease in size, and the A molecules from these droplets diffuse toward large droplets which grow. This mechanism is known as the “evapo-

ration–condensation” mechanism and is described by the Lifshitz–Slyozov–Wagner (LSW) law<sup>8</sup> for the growth rate of large droplets  $L(t) \sim t^{1/3}$ . For this mechanism to work efficiently, one requires that the minority phase occupies a vanishingly small volume fraction of the system. When the system is quenched into the thermodynamically unstable region the demixing proceeds via the spinodal decomposition mechanism. Early stages of this process are described by the Cahn–Hilliard theory. According to this theory, the system becomes unstable with respect to small fluctuations of wave vector  $q$  smaller than some value  $q_0$ . The key prediction of the theory is the exponential growth of the scattering intensity in time with a well-defined maximum at  $q_{\max} = q_0/\sqrt{2}$ . Interpenetrating A-rich and B-rich domains of the size of  $L \sim 1/q_{\max}$  are formed. Afterwards, the process of the separation at short experimental times is often divided into three conventional regimes corresponding to the major dynamic mechanism that governs the evolution of the system. The diffusion transport dominates at the early and middle stages of the separation providing that sizes of domains grow time as  $t^\alpha$ , where  $\alpha$  is between  $1/3$  and  $1/4$  depending on whether the transport is likely perpendicular<sup>13</sup> or parallel<sup>14</sup> to the interface. At the later stages, the diffusive growth is dominated by the mechanisms that involve long-range hydrodynamic interactions.<sup>15,16</sup> The crossover time between these two regimes depends on the relative importance of the streaming effect in comparison to the diffusion process, i.e., on the diffusion constant and viscosity of the mixture.<sup>17</sup> The hydrodynamic regime is characterized by  $L(t) \sim t$ .

The late stage configuration of the separating mixture depends on the initial volume fractions and size of the system but not

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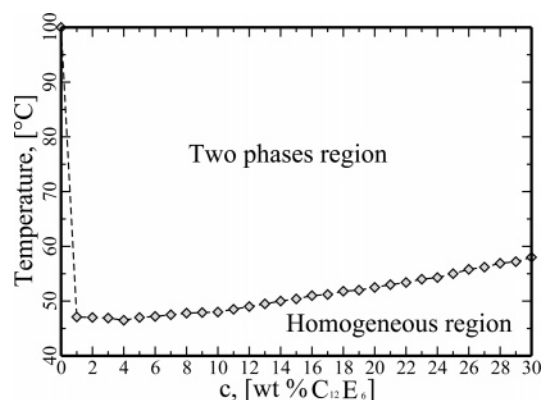
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on the early stage mechanism of demixing. In the late stage we have either a dilute gas of droplets of the minority phase in the sea of the majority phase, a dense system of droplets in the matrix of majority phase, or the interpenetrating network of A-rich and B-rich domains which coarsen in time. One observe crossover between the interpenetrating network and the dense system of droplets which occurs<sup>18,19</sup> at the volume fraction 0.3 of the minority phase. The growth rate and the growth mechanism for the first case is described by the LSW law. In the second case a Binder–Stauffer mechanism of collisions and coalescence of droplets is valid. It gives  $L(t) \sim t^{1/3}$ , similar to in the first case. Finally, in the last case of interpenetrating network, if the coarsening proceeds via the flow induced by the surface tension of interfaces, the scaling law  $L(t) \sim t$  holds. However this network may also break into droplets when a typical size in the network reaches the boundaries of the system, especially when the walls of the container are wetted by one of the phases. As we have mentioned earlier, most of the aforementioned mechanisms of growth are valid for small droplet sizes. Usually when we observe the growth of domains of one phase in another under the optical microscope, we encounter a situation which is not captured by these mechanisms. Usually the system consists of large droplets and their diffusion is not the primary mechanism of growth. Also because we have droplets in the system, the hydrodynamic flow along the interfaces induced purely by the curvature effects and surface tension cannot be a valid mechanism of transport of matter and growth.

When the system consists of very large droplets of one phase in the continuous matrix of another phase a new mechanism of domain growth was postulated and observed recently, i.e., the coalescence-induced coalescence.<sup>18,20–23</sup> In short the coalescence between two droplets induces a hydrodynamic flow which generates the second coalescence. Tanaka<sup>22</sup> made another observation that in the dense system of droplets the concentration field of one of the component around the droplets might overlap and thus might be responsible for the long-range attractive interactions between droplets which accelerate the collisions. He also stated that during the coalescence process the concentration field around the droplets changes rapidly and might induce further collisions. Finally, when two droplets experience coalescence, their shape changes and, in the process touch another droplet. This is a purely geometrical effect in the coalescence-induced coalescence mechanism. Therefore, Tanaka gives three submechanisms of the coalescence induced coalescence: “coalescence-induced coalescence via diffusion”, “coalescence-induced coalescence via flow”, and “geometrical coalescence-induced coalescence”. The direct computer simulations of coalescence induced coalescence via flow<sup>21</sup> predicts the growth  $L(t) \sim t$ , while the coalescence induced coalescence via diffusion<sup>22</sup> predicts  $L(t) \sim t^{1/3}$ .

In this paper we study the kinetics of the phase separation process in the ternary mixture of surfactant, polymer and water. This system is characterized by the lower consolute temperature,  $T_c$ , i.e., two components mix at temperature  $T < T_c$ , and separate at  $T > T_c$ . The system is studied for different surfactant and polymer concentrations. It is the purpose of this paper to establish the growth mechanism in the mixture and the kinetics of this growth.

The main questions posed here is: *which mechanism of the domains growth dominates during the separation in polymer/surfactant/water system and how does the system size (dimensionality of the system) influence the growth mechanism of the domains?*



**Figure 1.** Phase diagram of  $C_{12}E_6/H_2O$ . Ordered phases are not shown. The shape of the diagram shows that in the mixture of 10% of surfactant the minority phase is almost pure water after the phase separation.

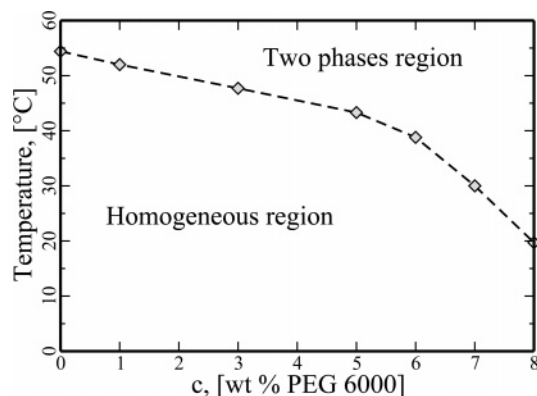
## 2. Experimental Section

We have used the nonionic surfactant  $C_{12}E_6$  (hexaethylene glycol monododecyl ether) purchased from Fluka Chemical Co. of purity better than 98% (checked on the thin-layer chromatography (TLC)). The melting temperature given by Fluka Chemical Co. for pure  $C_{12}E_6$  is between 27 and 28 °C and our measurement using differential scanning calorimetry gave 27.11 °C. The molecular weight of the surfactant was 450.66. The polymer PEG (poly(ethylene glycol)) was purchased from Merck for gas chromatography. The molecular mass of PEG was 6000. Water was distilled, filtered with the Millipore filters and degassed. We have found that it is good to ultracentrifuge samples before measurements, since in this way we can remove even tiny gas bubbles from solutions.

The mixtures were prepared at room temperature in a humid atmosphere in order to avoid evaporation of water. From the prepared mixtures, we have made thin samples in the following way. First, a drop of solution was placed on a glass plate (cleaned in ultrasound cleaner). Next, it was covered by the second glass plate. To control the thickness of the sample, the copper wire spacer of known thickness was placed between two glass plates. Finally, the samples were sealed with the glue “Poxipol” in order to avoid the evaporation of water during the measurements. We made samples of two thicknesses: 12 and 16  $\mu\text{m}$ . These samples were used for the optical microscopy measurements. It was impossible to use thicker samples because of the multilayer location of the domains. Optical microscopy measurements were performed using the Nikon Eclipse E 400 microscope with crossed polarizers, equipped with the heating/cooling stage LINKAM THMS 600. The samples were heated at 3 °C up to 1 °C above the coexistence curve with a velocity of 1 °C/min. The temperature was controlled up to 0.01 °C. The images were taken every 15 s. during the demixing process. The kinetics of phase separation was determined by the quantitative study of sizes and shapes of the domains with the help of the commercially available software LUCIA (which we purchased together with the Nikon Eclipse E 400 microscope) for the optical image analysis. The binary images were obtained by LUCIA program and analyzed quantitatively. The domains appear to be black and white after the binary analysis.

## 3. Results and Discussion

The phase diagrams of PEG/water and surfactant/water binary mixtures are well-known. PEG and water mix in all proportions<sup>24,25</sup> for temperatures between 0 and 100 °C. The phase diagram of  $C_{12}E_6$  and water is shown<sup>26–28</sup> in Figure 1. The pre-



**Figure 2.** Phase diagram of PEG 6000/H<sub>2</sub>O/C<sub>12</sub>E<sub>6</sub> at a fixed concentration of C<sub>12</sub>E<sub>6</sub> (10% C<sub>12</sub>E<sub>6</sub> at respect to H<sub>2</sub>O).

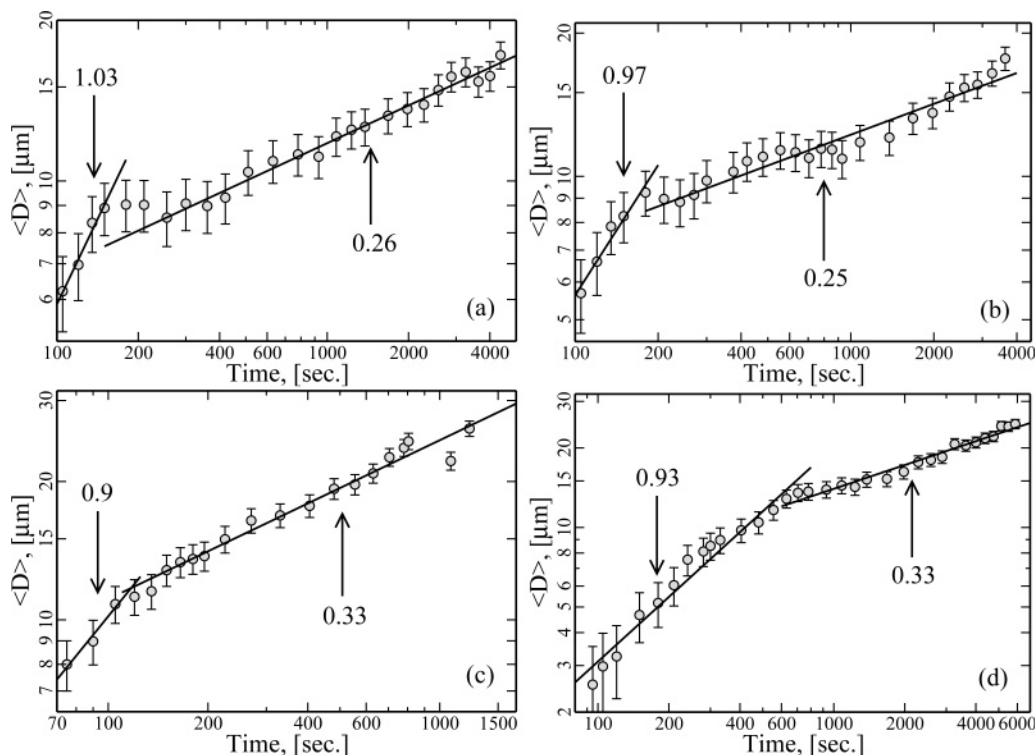
cise calorimetric study of the diagram has been done recently.<sup>29</sup> The surfactant is miscible with water in the whole range of concentrations of C<sub>12</sub>E<sub>6</sub> and for temperatures between 0 and 50 °C. In the liquid state, PEG and surfactant mix in all proportions.

The binary surfactant/water mixture phase separates at temperatures higher than 50 °C (Figure 1), and the separation temperature depends weakly on the surfactant concentration in a wide range of concentrations. The origin of this phase transition is due to the dehydration of the surfactant heads and the progressive increase of the influence of the van der Waals attraction between surfactant micelles. Adding PEG to the binary mixture induces the depletion interactions and thus changes the mechanism of phase separation. The idea of such nonspecific, geometrical interactions was introduced by Asakura and Oosawa<sup>30</sup> and Vrij.<sup>31</sup> There is a zone around each colloidal

particles (micelles) which cannot be penetrated by the center of mass of a polymer molecule. The size of the zone is proportional to the radius of gyration of a polymer. The polymer cannot penetrate the zone because if it did it would result in a great loss of its conformational entropy. If two zones overlap, there is an imbalance of osmotic pressures which pushes the colloids together and finally results in the phase separation into the colloid-rich phase and polymer-rich phase.<sup>32</sup> PEG reduces the transition temperature as is shown in Figure 2. PEG also influences the kinetics of phase separation process as will be evident from our studies.

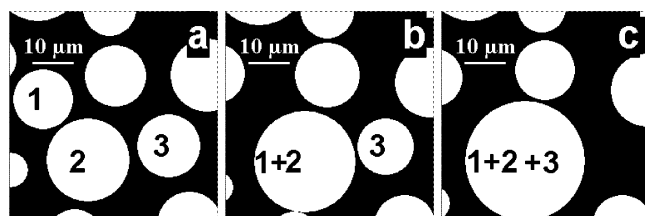
Figure 3 shows the time evolution of the mean domains diameter ( $\langle D \rangle$ ) during the phase separation in the surfactant-(10%)/PEG/water mixtures for the following: (a) PEG 1%; (b) PEG 3%; (c) PEG 5%; (d) PEG 7%. The samples of thickness 12  $\mu\text{m}$  (see Figure 3. parts a–c) and 16  $\mu\text{m}$  (see Figure 3d) were heated to 1 °C above the coexistence curve. When the size of the domains is smaller than the size of the system, three-dimensional growth is observed. In this case, the domains grow linearly in time  $\langle D \rangle \sim t^\alpha$ ,  $\alpha \approx 1$ . When the droplet size (average diameter of the domains  $\langle D \rangle$ ) becomes larger than the thickness of the sample, the dimensional crossover from three-dimensional system to two-dimensional system occurs and the change in the droplet growth is observed. After the dimensional crossover occurs, the growth of the domains slows down and the exponent becomes  $\alpha \approx 1/4 - 1/3$ .

Optical microscopy observations have also shown that there are two mechanisms of growth in our system: coalescence-induced coalescence and the Lifshitz–Slyozov mechanism. The coalescence-induced coalescence is found to be the dominating mechanism of domain coarsening.

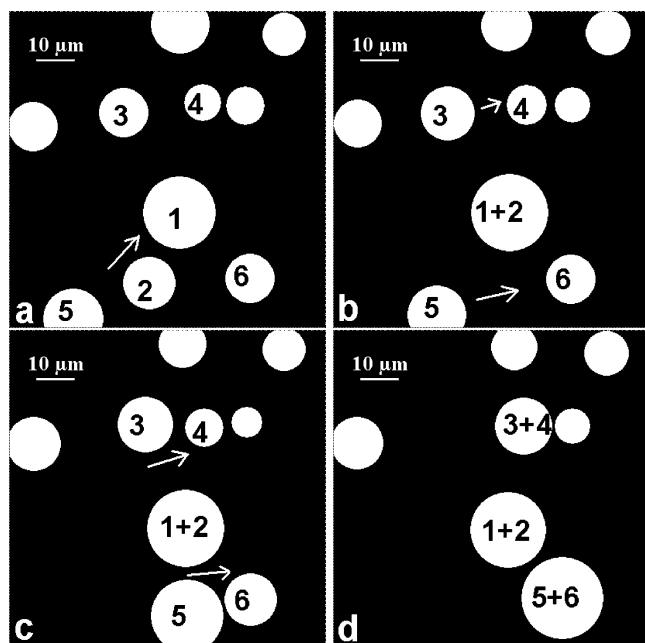


**Figure 3.** Time evolution of the mean domains diameter  $\langle D \rangle$  in the surfactant(10%)/PEG/water mixtures: (a) PEG 1%; (b) PEG 3%; (c) PEG 5%; (d) PEG 7%. The samples of thickness: Samples a–c, 12  $\mu\text{m}$ , and sample d, 16  $\mu\text{m}$ , were heated to 3 °C, up to 1 °C above the coexistence curve (see Figure 2). The three-dimensional growth of the domains is possible when their average diameters are smaller than the system size ( $\langle D \rangle \leq 12 \mu\text{m}$  for parts a–c;  $\langle D \rangle \leq 16 \mu\text{m}$  for part d). We found the growth rule to be  $\langle D \rangle \sim t^\alpha$ ,  $\alpha \approx 1$ . When the domains become larger than the sample thickness a two-dimensional growth with the exponent  $\alpha \approx 0.3$  is observed. The dominating mechanisms of the droplets growth is the coalescence-induced coalescence via flow and geometrical coalescence-induced coalescence (see Figures 4 and 5). The Lifshitz–Slyozov mechanism is also observed (see Figure 6).





**Figure 4.** Geometrical coalescence-induced coalescence in the mixture of PEG(5%)/surfactant(10%)/water after (a) 150, (b) 165, and (c) 180 s. The coalescence between domains 1 and 2 (a) induces the change of shape of the resulting domain 1 + 2 (b), which induces coalescence with droplet 3 (c).

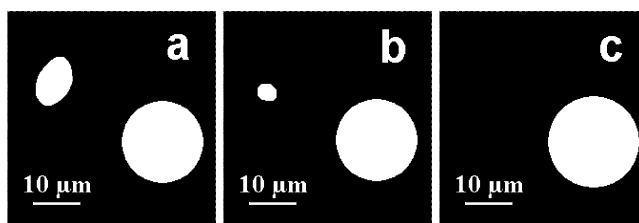


**Figure 5.** Coalescence-induced coalescence via flow in the PEG(3%)/C<sub>12</sub>E<sub>6</sub>/H<sub>2</sub>O mixture (wt 10% of C<sub>12</sub>E<sub>6</sub>) after (a) 630, (b) 705, (c) 780, and (d) 855 s. The coalescence between 1 and 2 (a) induces hydrodynamic flows (b and c), and, as a result, generates the next coalescences (d).

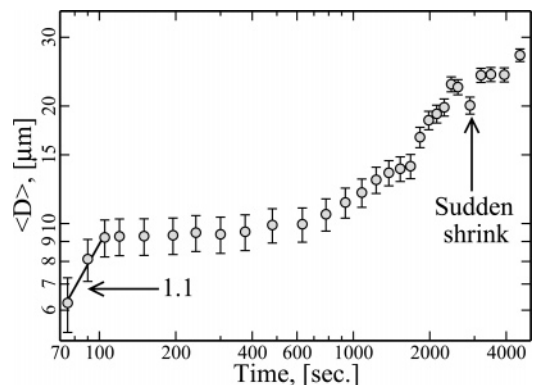
Figure 4 shows the geometrical coalescence-induced coalescence in the mixture of PEG(5%)/surfactant(10%)/water at (a) 150, (b) 165, and (c) 180 s following the temperature jump. After the domains 1 and 2 coalesce, the domain 1 + 2 (see Figure 4, parts a and b) changes its shape, and gets closer to the domain 3, and the second coalescence (see Figure 4c) occurs. Such a process was observed for different PEG concentrations during phase separation.

The coalescence-induced coalescence via flow was also observed for the PEG(1, 3, 5, 7%)/surfactant/water mixtures for different domain sizes. Figure 5 illustrates the coalescence-induced coalescence process at (a) 630, (b) 705, (c) 780, and (d) 855 s following the phase separation with the PEG(3%)/surfactant(10%)/water system. The coalescence of the domains 1 and 2 generates flows (see Figure 5, parts b and c) which move the droplets 3 toward 5 and 5 toward 6. As a result, the next coalescences occur (see Figure 5d).

The third mechanism of the growth observed by us at later times of separation, when the domains are far from each other, is the evaporation–condensation (Lifshitz–Slyozov) mechanism. As an example, we show this process for the mixture of PEG(1%)/surfactant(10%)/water in Figure 6. At the beginning there are two domains (see Figure 6a), and the smaller one slowly dissolves. The larger domain grows at the expense of the smaller droplet (see Figure 6, parts a–c), because the



**Figure 6.** Evaporation–condensation (Lifshitz–Slyozov) mechanism of the droplets growth in the mixture of PEG(1%)/surfactant(10%)/water after (a) 1980, (b) 2280, and (c) 2580 s. The small droplet decrease in time because of their size falls below the critical size due to the depletion of the matrix from one of the components. As a result, the smaller domain disappears and the growth of the larger domain is observed.

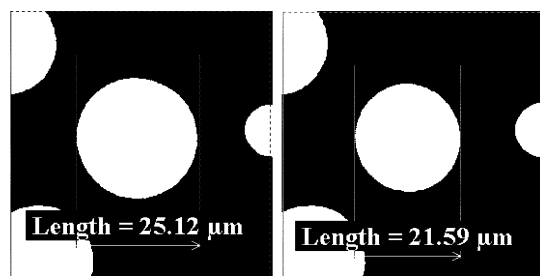


**Figure 7.** Time evolution of the mean domains diameter  $\langle D \rangle$  for the binary surfactant(10%)/water mixture. The initial growth is fast and linear  $\langle D \rangle \sim t$  when the domains are smaller than the system size. After the dimensional crossover occurs and the mean diameter of droplets is larger than the sample thickness the domains stop to grow for a long time. Next, they grow slowly and stop again in later times. It is observed that some of domains decrease their size by 20% in the horizontal direction, when they suddenly move toward the boundaries (see Figure 8).

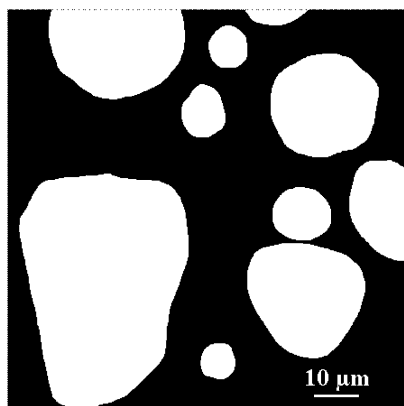
dissolution increases locally the concentration of one compound and molecules from the dissolved droplet diffuse toward larger domains which grow.

In the case of the ternary (polymer/surfactant/water) system, the domains are circular during the phase separation process because of a sufficiently large surface tension of the interface between the domains.

The demixing process in binary surfactant(10%)/water system was also studied by optical microscopy observations quantitatively. The shape of the diagram (see Figure 1) shows that the minority phase in the mixture (10% of surfactant) is almost pure water. Therefore, we observe the growth of water droplets in the surfactant-rich matrix. This growth is different from polymer/surfactant/water systems. Figure 7 shows the change in the mean diameter  $\langle D \rangle$  of droplets in time during phase separation for binary surfactant(10%)/water mixture. The initial growth is found to be fast with the exponent  $\langle D \rangle \sim t^\alpha$ ,  $\alpha \approx 1$ . During this fast period, the droplets grow via coalescence-induced coalescence mechanism. In fact, after reaching the boundaries of the system (dimensional crossover occurs), the domains suddenly stop growing for a long time (see Figure 7). Following the theoretical prediction of Tanaka<sup>22,23</sup> the coalescence-induced coalescence process via flow or via diffusion is not effective in such system because of the velocity of the droplets depends on their surface tension  $\gamma$  and the viscosity of surrounding fluid  $\eta$  as  $v \sim \gamma/\eta$ . Thus, in our case of the water domains in the surfactant/water matrix, the surface tension is very low, and as a consequence, the velocities of the domains are small. It is



**Figure 8.** We observe that water domains decrease their size by 20% in horizontal direction when the domains suddenly move toward the boundaries in the case of surfactant(10%)/water mixture. Time interval between the snapshots was 15 s.



**Figure 9.** Water domains in the surfactant matrix. They have shapes different from circular, because of a very low surface tension.

also possible that the water domains easily deform and slide to the walls. It is evident that low surface tension causes easy deformations of domains (see Figure 9). The “sudden shrink” effect of domains was detected in the later times of demixing process. It means that the nearly circular domains with the horizontal sizes larger than vertical sizes (thickness of the sample) have to move toward the boundaries and as a result their shapes are changing, and we observed a sudden decrease of the horizontal size of some water domains by about 20% (see Figure 7 and Figure 8).

#### 4. Conclusions

The separation process in the ternary mixture of water/PEG/ $C_{12}E_6$  has been studied by the optical microscopy. We have observed that the domains growth proceeds via the coalescence-induced coalescence mechanism. For small domains the domains size growth is linear in time. It is consistent with the theoretical predictions of Nikolayev et al.<sup>21</sup> and the growth in polymers studied recently by the laser scanning confocal microscope.<sup>33</sup> Most probably the submechanism of this growth is the geometrical coalescence-induced coalescence and coalescence-induced coalescence via flow. On the other hand, when the domains reach the size of the thickness of the sample the growth character changes: the domains grow as  $t^{1/3}$ . The same exponent for the two-dimensional system was also observed by Tanaka<sup>20</sup> in a different systems. Thus, we observe a dimensional crossover in the coalescence induced coalescence via flow. The growth of the domains in the pure water/surfactant system is different. The initial growth is fast with the exponent 1 as in the previous case, however after reaching the boundaries of the system the domains stop to grow for a long time in contrast with the separation in ternary mixture. Moreover the water domains in the surfactant matrix have shapes different from circular

indicating a very low surface tension (see Figure 9). It means following the theoretical analysis of Tanaka,<sup>22,23</sup> that the coalescence induced coalescence via flow might not be effective for such a system. Most probably the initial fast growth of water domains in surfactant-rich matrix is due to geometrical coalescence-induced coalescence. The large changes of shape of the water domains are also observed under the microscope, i.e., a seemingly circular domain of horizontal size larger than the vertical size of the system can suddenly decrease its horizontal size by 20% indicating large shape changes in the vertical direction (see Figure 7).

We hope that the results presented here for the phase separation in surfactant systems will stimulate further investigation of the problem especially that the new mechanisms proposed recently have not been studied experimentally in detail. We note that the mechanism of coalescence induced coalescence is very general and not restricted to the system studied here. The same mechanism of growth, as in the mixture of water—surfactant—polymer system described in this paper, was observed in the mixtures of  $\epsilon$ -caprolactone oligomer and styrene oligomer,<sup>20</sup> polystyrene with a liquid crystal 4-cyano-4'-n-octylbiphenyl (8CB) (recently observed by us) and mixture of isotactic polypropylene and diphenyl ether.<sup>34</sup> All these different systems behave similarly in the late stage of phase separation and therefore we may conjecture that the mechanism of coalescence-induced coalescence is rather general.

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