

## Double Phase Separation in a Confined, Symmetric Binary Mixture: Interface Quench Effect Unique to Bicontinuous Phase Separation

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It is found that for a geometrically confined, symmetric binary mixture the secondary phase separation is spontaneously induced by the extremely quick reduction of the interface area caused by the hydrodynamics unique to bicontinuous phase separation. This hydrodynamic coarsening is likely too quick for the concentration diffusion to establish the local equilibrium. This phenomenon is generally observed for nearly symmetric binary mixtures confined both in one-dimensional and in two-dimensional capillaries, under deep quench conditions. This *interface quench* effect and the resulting double phase separation could exist even for bicontinuous phase separation in bulk.

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Phase separation phenomena have been extensively studied in the past two decades from both the experimental and the theoretical viewpoints [1]. Since the finding of critical wetting phenomena [2], wetting phenomena [3] have also been widely studied mainly in the stable region. Because both phase separation and wetting occur near the criticality, these two nonequilibrium phenomena can be coupled with each other. From this standpoint, much attention has recently been paid to the interplay between phase separation and wetting in a confined geometry [4–13]. However, wetting dynamics is coupled with phase separation in a complicated manner, and thus the coarsening dynamics under the influence of wetting has not been clarified yet. Recently Wiltzius and Cumming *et al.* [8,9] have demonstrated the existence of the fast and slow growth modes for phase separation under an influence of wetting. However, the mechanism to cause these modes, or double phase separation (DPS), remains unknown. In this Letter, we demonstrate that the slow growth mode could be spontaneously induced by bicontinuous phase separation itself.

First we show the experimental evidences of DPS. The samples used were the mixtures of oligomers of  $\epsilon$ -caprolactone (OCL) and styrene (OS). The weight-average molecular weights of OCL and OS were 2000 and 1000, respectively. In OCL/OS mixtures, an OCL-rich phase is more wettable to glass than an OS-rich phase [12]. A sample mixture was set in a two-dimensional (2D) capillary composed of two parallel plates (cover glasses having a thickness of 120  $\mu\text{m}$ ) with a gap of  $d$ . The temperature of the sample was changed with a rate of  $-2^\circ\text{C}/\text{s}$  by using a hot stage (Linkam TH-600RMS). It was confirmed by a direct temperature measurement using a thin thermocouple with a thickness of  $\sim 12 \mu\text{m}$  (Omega Engineering, Inc.) that for the quench of  $\Delta T = 1$  K the sample temperature was settled within 1 s to the final one ( $\pm 0.1$  K) for a sample with a thickness of 20  $\mu\text{m}$  and its temporal change during the quench was step-like. The phase-separation time  $t$  was measured from the time when the temperature becomes the final one, which

roughly corresponds to the time when the sample starts to look cloudy.

Figure 1 shows the pattern evolution of the OCL/OS (31/69) mixture confined in a 2D capillary ( $d \sim 8 \mu\text{m}$ ) at  $134.2^\circ\text{C}$ . This mixture has almost the critical, symmetric composition (31 wt% OCL). The quench depth  $\Delta T$  measured from the binodal line was 0.8 K. Since this composition was symmetric, bicontinuous phase separation was observed in the initial stage. Then the macroscopic wetting layer of the OCL-rich phase was rapidly formed by the tube hydrodynamic instability unique to bicontinuous phase separation [11,12]. Then only large domains (the radius  $r > d/2$ ) bridging both glass walls grew, while small domains ( $r \lesssim d/2$ ) were absorbed into the wetting layers and disappeared [12]. Further, the retarded, secondary phase separation was observed inside the macroscopically separated phases. This can be noticed around 40–50 s after the quench from the fact that the two phases look cloudy. Then droplets caused by

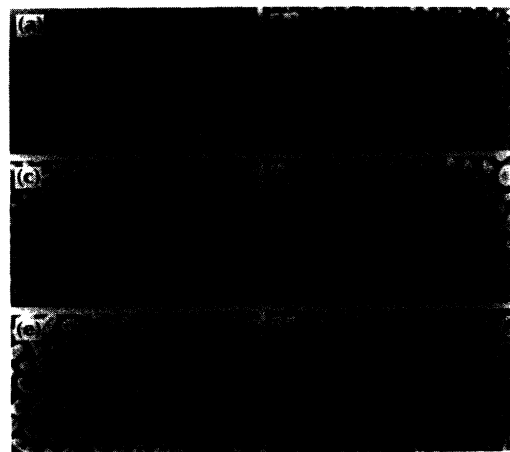


FIG. 1. Phase separation in a 2D capillary ( $d \sim 8 \mu\text{m}$ ) for OCL/OS (31/69) at  $134.2^\circ\text{C}$  ( $\Delta T = 0.8$  K). (a) 2.5 s, (b) 10.0 s, (c) 30.0 s, (d) 50.0 s, (e) 80.0 s, and (f) 180.0 s. The bar corresponds to 40  $\mu\text{m}$ .

the secondary phase separation grew to become visible around 70 s after the quench. This unusual phenomenon (DPS) was not observed for a shallow quench ( $\Delta T \leq 0.3$  K).

Figures 2(a1)–2(a3) show a pattern evolution of the same mixture in a 2D capillary ( $d \sim 8 \mu\text{m}$ ) for  $\Delta T = 3$  K. The only difference in the experimental conditions between Fig. 1 and Figs. 2(a1)–2(a3) is the quench depth. The essential behavior is the same as that in Fig. 1, but DPS is more clearly observed for a deeper quench and the secondary phase separation occurs in the earlier stage: It becomes visible as cloudy texture around  $\sim 4$  s for  $\Delta T = 3$  K, while around 40–50 s for  $\Delta T = 0.8$  K.

Figures 2(b1)–2(b3) show the DPS for the same mixture confined in a thinner 2D capillary ( $d \sim 2 \mu\text{m}$ ). The quench depth is the same as in Figs. 2(a1)–2(a3) [ $\Delta T = 3$  K]. It is found that DPS is significantly suppressed by the strong spatial confinement: For a thick sample ( $d \geq 3 \mu\text{m}$ ) DPS was clearly observed as in Figs. 2(a1)–2(a3), while for a thin sample ( $d < 3 \mu\text{m}$ ) it was not observed even though the other experimental conditions were the same. The deeper quench is required to cause DPS for a thinner sample. This fact indicates the importance of bicontinuous phase separation in bulk.

The completely similar phenomena were also observed in other mixtures like poly(vinyl methyl ether) (PVME)/water in both 2D and 1D capillaries [12], and thus the above phenomena are quite universal.

Before discussing the mechanism, we should consider a possibility that a secondary phase separation is caused by a nonideal temperature quench, namely, a slow continuous quench or a double quench [14]. In Fig. 1 DPS becomes noticeable as cloudy texture at  $t > 30$  s, which is much longer than the temperature stabilization time ( $\sim 1$  s). This clearly indicates that the quench itself cannot cause double phase separation. This conclusion is also strongly supported by the experimental results of Cumming *et al.* [9] that the secondary phase separation starts to be observable by light scattering around  $3 \times 10^3$  s for their shallowest quench of  $\Delta T = 0.15$  K (see Fig. 13 in Ref. [9]), sufficiently after the complete stabilization of the temperature which takes  $\sim 50$  s (see Fig. 4 in Ref. [9]) in their case. Further we have found the quite general phenomena denying the effects of thermal history: *Even for the samples having the same thermal history*, DPS was observed only for nearly symmetric mixtures showing hydrodynamic coarsening driven by capillary instability and never observed for off-symmetric mixtures having droplet morphology. This can be easily confirmed by comparing Figs. 2(a1)–2(a3) with Figs. 2(c1)–2(c3). In light of the current understanding of the thermal history effect, thus, it could be said that DPS is free from a noninstantaneous quench effect and is likely intrinsic.

Here we consider the mechanism of DPS. The same phenomena had been interpreted by usual bulk phase separation [8,9] or by the disconnection of some domains during the growth of the percolated pattern [15]. How-

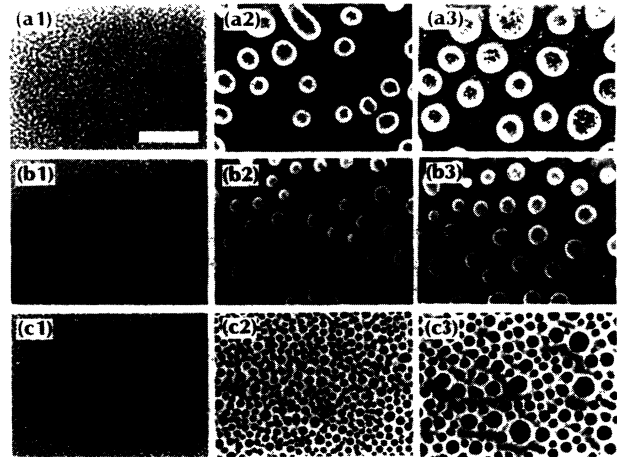


FIG. 2. (a) Phase separation in a 2D capillary ( $d \sim 8 \mu\text{m}$ ) for OCL/OS (31/69) at  $132.0^\circ\text{C}$  ( $\Delta T = 3.0$  K). (a1) 2.5 s, (a2) 10.0 s, (a3) 20.0 s. (b) Phase separation in a 2D capillary ( $d \sim 2 \mu\text{m}$ ) for OCL/OS (31/69) at  $132.0^\circ\text{C}$  ( $\Delta T = 3.0$  K). (b1) 2.0 s, (b2) 60.0 s, (b3) 300 s. (c) Droplet phase separation in a 2D capillary ( $d \sim 8 \mu\text{m}$ ) for OCL/OS (38/62) at  $131.2^\circ\text{C}$  ( $\Delta T = 3.0$  K). (c1) 3.0 s, (c2) 20.0 s, (c3) 240.0 s. The bar corresponds to  $40 \mu\text{m}$ .

ever, neither of the mechanisms can explain (i) the fact that DPS is not observed for a small  $\Delta T$  [11,12] and (ii) the fact that the secondary phase separation occurs independently in each phase after the disappearance of the initial bicontinuous structure.

Another possibility is the solid surface effect: The quick reduction of the solid-liquid interface energy caused by the wetting layer formation might lead to the quick change in the total free energy. However, this should not be the case because of the following reasons: (i) The effect should be more important near the critical point, which is inconsistent with the fact that DPS is observed only for a deep quench. (ii) DPS is suppressed by a strong spatial confinement [see Figs. 2(b1)–2(b3)] for a thin sample, where the solid surface energy should play a more important role than for a thick sample. This clearly indicates the importance of the bulk hydrodynamic process for DPS.

Here we show a possible scenario for DPS. DPS is observed only for bicontinuous phase separation unique to symmetric compositions (see the first photographs in Figs. 1 and 2). In bicontinuous phase separation, the total interface area of the system is drastically reduced within a short time by the hydrodynamic coarsening originating from the coupling between the concentration and the velocity fields. According to Siggia's mechanism [16], the interface area per unit volume  $s$  is estimated to decrease as  $s \propto [(\sigma/\eta)t]^{-1}$ , where  $\sigma$  is the interface tension and  $\eta$  is the viscosity. Since the hydrodynamic interface motion is much faster than the concentration diffusion, *the hydrodynamic flow due to the capillary instability causes only the geometrical coarsening and does not accompany the concentration change*. Namely, the hy-

drodynamic coarsening is likely too quick for the concentration diffusion to establish the local equilibrium. This probably causes a kind of double quench effect, which we call *interface quench*. This leaves the system with macroscopic domains which have concentrations near the coexisting ones, but lying within the coexisting curve. These domains are thus metastable or unstable, and the secondary phase separation could be induced. In all the previous studies [1] the local equilibrium has been assumed in the hydrodynamic regime, but it is probably not true in the exact sense.

Before checking this possibility, it is worth mentioning the difference in hydrodynamic coarsening between the phase separation in a confined geometry and bulk phase separation. For both cases the coarsening dynamics is dominated by capillary instability [1,6,11–13,16]. The only difference is likely the prefactor  $k$  in the relation  $R = k(\sigma/\eta)t$  [1,6,16,17]. Here  $k = k_b$  or  $k_w$  for bulk and wetting phase separation, respectively. For wetting phase separation, the pressure difference  $\Delta P$  between the bicontinuous tube in bulk and its wetting part is  $\sim \sigma/R$  over the distance  $R$ . Thus  $k_w$  is estimated as  $\sim 0.1$  from Poiseuille's formula [16]. For bulk phase separation, on the other hand, the tube flow is essentially caused by the fluctuation. San Miguel *et al.* [18] theoretically estimated  $k_b$  as 0.04 for the two phase fluids having similar viscosity. The recent experiments [15,19] supported this evaluation ( $k_b \sim 0.04$ ). If we employ  $k_b \sim 0.04$ , the difference between  $k_b$  and  $k_w$  is likely within 1 order of magnitude. However, it should be noted that the anisotropic ordering for wetting phase separation might further accelerate the reduction of the interface area.

Next we estimate the *interface quench* effect. The free energy of the system can be described by the Ginzburg-Landau-type free energy as

$$F = \int dr \left[ -\frac{r}{2}\phi^2 + \frac{u}{4}\phi^4 + \frac{K}{2}(\nabla\phi)^2 \right]. \quad (1)$$

Here  $\phi$  is the concentration. Provided that the concentration profile can be approximated by the trapezoidal shape with an interface width of  $\xi$  [20],

$$F \sim \left[ -\frac{r}{2}(\Delta\phi)^2 + \frac{u}{4}(\Delta\phi)^4 \right] R(t) + \frac{K}{2} \left( \frac{\Delta\phi}{\xi} \right)^2 \xi, \quad (2)$$

where  $\Delta\phi$  is the concentration of the phase measured from the average one. From the local energy minimum condition for the above free energy,

$$\Delta\phi(t) = \Delta\phi_b \left( 1 - \frac{K}{\xi r R(t)} \right)^{1/2} = \Delta\phi_b \left( 1 - \frac{2\xi}{R(t)} \right)^{1/2}, \quad (3)$$

where  $\Delta\phi_b = (r/u)^{1/2}$  is the equilibrium concentration for an infinite domain size. Here the relation  $\xi^2 = K/2r$  is used. Reflecting the change in the domain size [ $R(t) = k(\sigma/\eta)t$ ],  $\Delta\phi(t)$  changes with time. However, the diffusion is not fast enough for the real concentration to follow this change in the local equilibrium concentration.

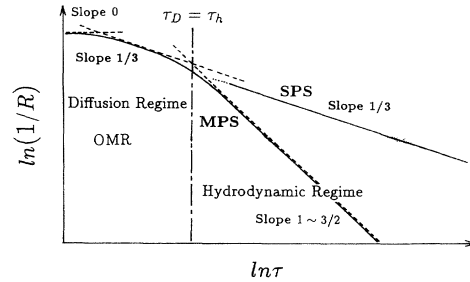


FIG. 3. Schematic figure for the coarsening process of DPS. MPS and SPS stand for main and secondary phase separation, respectively. Around  $\tau_D = \tau_h$  there is a gradual transition from the diffusion regime to the hydrodynamic regime, which leads to secondary phase separation. OMR stands for optical microscope resolution.

Thus there could be a significant *interface quench* effect.

To check the above possibility, we have to study whether the concentration diffusion can follow this quick change in the local equilibrium concentration or not. The time required to hydrodynamically form a domain with a size of  $R$  is estimated as  $\tau_h \sim R\eta/k\sigma$ . On the other hand, the characteristic diffusion time for the domain size  $R$  is given by  $\tau_D \sim R^2/D$ , where  $D$  is the diffusion constant and  $D = k_B T / 5\pi\eta\xi$  ( $k_B$  is Boltzmann's constant). Thus the ratio between  $\tau_h$  and  $\tau_D$  is given by  $\tau_h/\tau_D = D\eta/k\sigma R$ . From the 2-scale-factor universality,  $\sigma = A_\sigma k_B T / \xi^2$ , where  $A_\sigma$  is the universal constant and  $A_\sigma \sim 0.2$  in 3D [21]. Using this relation and the expression for  $D$ , we obtain the relation  $\tau_h/\tau_D \sim \xi/5\pi A_\sigma kR \sim \xi/3kR$ . For  $\tau_h < \tau_D$  the hydrodynamic coarsening is likely too quick for the concentration diffusion to establish the local equilibrium. Thus the *interface quench* is likely initiated around  $\tau_h/\tau_D \sim 1$ . For wetting phase separation ( $k_w \sim 0.1$ ),  $R_t \sim 3\xi$  ( $R_t$  is the transient domain size when the *interface quench* is initiated). For bulk phase separation ( $k_b \sim 0.04$ ), on the other hand, we obtain  $R_t \sim 10\xi$  or  $\tau \sim 100$  ( $\tau = t/\tau_\xi$ , where  $\tau_\xi = \xi^2/D$ ) from the condition  $\tau_h/\tau_D \sim 1$ . The beginning of the *interface quench* characterized by these values of  $R_t/\xi$  and  $\tau$  is consistent with the crossover from the slow, diffusion growth to the fast, hydrodynamic growth in the scaled plots of  $2\pi R/\xi$  against  $\tau$  [15,19,22,23]. The *interface quench* probably brings the system into a new nonequilibrium (unstable or metastable) state and thus causes the retarded, secondary phase separation. The situation is schematically shown in Fig. 3. The difference between the fast hydrodynamic coarsening ( $R \sim t$  or  $t^{3/2}$  [8,9,12]) and the slow droplet coarsening ( $R \sim t^{1/3}$ ) is the main reason why the secondary phase separation apparently looks retarded from the main phase separation for microscopic observation (see Fig. 3).

Next we estimate the rate of the *interface quench*, which should likely be large enough to cause the secondary phase separation. Here we consider the equivalent temperature quench instead of the composition quench since the former is easier to understand than the lat-

ter. Since  $r$  is proportional to the quench depth  $\Delta T$ , the change in  $R(t)^{-1}$  has the same meaning as the change in  $\Delta T(t)$ , according to Eq. (3). Using the universal relation  $\Delta\phi_b = m\Delta T^\beta$  ( $\beta \sim 0.33$ ;  $m$  is a constant),  $\Delta T(t)$  satisfying  $\Delta\phi_b(\Delta T(t)) = \Delta\phi(\Delta T, R(t))$  is estimated as

$$\Delta T(t) = \Delta T[1 - 2\xi/R(t)]^{1/2\beta}. \quad (4)$$

For example, the *interface quench* caused by the hydrodynamic coarsening from small domains ( $R = 10\xi$ ) to large domains ( $R = 100\xi$ ) is equivalent to the temperature double quench [14] composed of a first quench ( $\Delta T_i = 0.88\Delta T$ ) and a second deeper quench ( $\delta T = \Delta T - \Delta T_i = 0.12\Delta T$ ) around the time of  $\tau_D = \tau_h$ . Thus the average quench rate from  $R = 10\xi$  to  $R = 100\xi$  can be estimated as

$$\delta T/\delta t = (0.3\Delta T/90\xi)k\sigma/\eta = 4 \times 10^{-4}\Delta T/\tau_\xi. \quad (5)$$

For an isobutyric acid/water mixture, for example, the average quench rate is 0.07 mK/s for  $\Delta T = 0.01$  K and 40 K/s for  $\Delta T = 1$  K. Here we use the relation  $\tau_\xi \sim 2 \times 10^{-10}(\Delta T/T_c)^{-3\nu}$  [24]. The former rate is probably too slow to cause DPS and the latter rate is probably fast enough. The steep increase of the quench rate with an increase in  $\Delta T$  is consistent with our experimental results that DPS was observed only for large  $\Delta T$ .

Finally, we discuss the validity of our mechanism on the basis of the experimental results. (1) DPS was never observed for droplet phase separation under any quench conditions [see, e.g., Figs. 2(c1)–2(c3)]. This strongly supports our mechanism and indicates that *the quick hydrodynamic coarsening is a prerequisite for DPS*. (2) The fact that the secondary phase separation is suppressed for a very thin sample [see Figs. 2(b1)–2(b3)] is also consistent with our mechanism. For a very thin film, the dimensional crossover from 3D to 2D slows down the coarsening dynamics in the very early stage and the *interface quench* effect is not enough to cause DPS. (3) The fact that the secondary phase separation always has a droplet morphology can be explained by our mechanism since both compositions of the two original phases just before the *interface quench* ( $\sim \pm\Delta\phi_b$ ) are off symmetric. (4) Our mechanism is also consistent with the light scattering data by Wiltzius and Cumming [8], which indicate that (i) the secondary phase separation (in our notation) has the growth law of  $R \sim t^{1/3}$  unique to droplet pattern and (ii) it starts to appear around  $\tau_h = \tau_D$ , namely, just after the hydrodynamic process (the fast mode in their notation [8,9,25]) is initiated (see our Fig. 3 and also Fig. 13 in Ref. [9]).

In summary, DPS has been found in confined, symmetric binary mixtures. This phenomenon is likely universal for any confined, symmetric binary mixtures, and we actually observed the same phenomena in other mixtures such as PVME/water. It is demonstrated that this unusual phenomenon is likely caused by the *interface quench* effect unique to bicontinuous phase separation. Our simple theory predicts that DPS could be observed *even for bulk phase separation* under a deep quench con-

dition if the anisotropic ordering for wetting phase separation does not play a crucial role in the interface reduction. Further theoretical and experimental studies are highly desirable for a deep understanding of this new phenomenon.

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*Note added.*—(i) The fact that the concentration does not necessarily reach the final equilibrium value even after the formation of a sharp interface is supported by a recent computer simulation of phase-separating binary fluid by Shinozaki and Oono [Phys. Rev. E **48**, 2622 (1993)]. Further, their numerical instability could correspond to the double phase separation caused by the *hydrodynamic interface quench effect*. (ii) Shi *et al.* [Phys. Rev. Lett. **70**, 206 (1993)] have recently reported the universality of the fast and slow growth modes.

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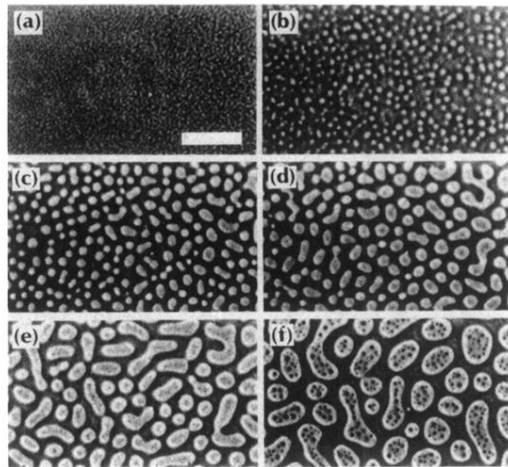


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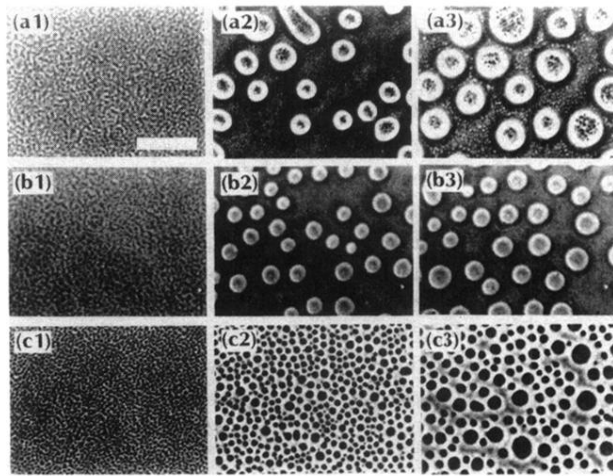


FIG. 2. (a) Phase separation in a 2D capillary ( $d \sim 8 \mu\text{m}$ ) for OCL/OS (31/69) at  $132.0^\circ\text{C}$  ( $\Delta T = 3.0 \text{ K}$ ). (a1) 2.5 s, (a2) 10.0 s, (a3) 20.0 s. (b) Phase separation in a 2D capillary ( $d \sim 2 \mu\text{m}$ ) for OCL/OS (31/69) at  $132.0^\circ\text{C}$  ( $\Delta T = 3.0 \text{ K}$ ). (b1) 2.0 s, (b2) 60.0 s, (b3) 300 s. (c) Droplet phase separation in a 2D capillary ( $d \sim 8 \mu\text{m}$ ) for OCL/OS (38/62) at  $131.2^\circ\text{C}$  ( $\Delta T = 3.0 \text{ K}$ ). (c1) 3.0 s, (c2) 20.0 s, (c3) 240.0 s. The bar corresponds to  $40 \mu\text{m}$ .