Spinodal decomposition of a symmetric binary fluid mixture in quasi two dimensions: Local orientational ordering of fluid tubes

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We demonstrate here the experimental evidence that a stripe pattern having a local orientational order appears for a phase-separating symmetric fluid mixture confined in quasi two dimensions. This local parallel arrangement of bicontinuous tubes is probably induced by (i) the spatial symmetry breaking of a bicontinuous pattern due to the geometrical confinement and (ii) the interface tension that favors tubes with a straight rodlike shape. *Confinement into quasi two dimensions* is likely prerequisite for this unusual ordering phenomenon. This could be the rare example of phase separation with a stripe pattern for simple binary mixtures having no long-range repulsive interaction. We also show the discrete nature of the elementary coarsening process of bicontinuous phase separation.

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I. INTRODUCTION

Spatial patterns of isotropic two-phase systems having no bulk energy associated with geometry [1] can be classified into two types for the symmetric composition: (i) a "stripe pattern," which is an interconnected pattern with a local orientational order where domains are arranged locally in parallel (see, e.g., Refs. [2] and [3]), and (ii) a "bicontinuous pattern," which is an interconnected pattern without such a local orientational order (see, e.g., Fig. 32 in Ref. [4]). A stripe pattern has so far been found only in the phase separation of systems with a nonlocal, long-range repulsive interaction such as magnetostatic and electrostatic interactions [2,3]. Isotropic phase separation of simple binary fluids having no such interaction, on the other hand, is known to exhibit a bicontinuous pattern with a randomly interconnected structure, at the symmetric composition [5].

For any system with a scalar conserved order parameter, an increase in the composition symmetry increases the interdomain spatial correlation. Furthermore, in binary fluid mixtures, spinodal decomposition is strongly affected by the long-range hydrodynamic interaction unique to fluid systems [5,6] and the coupling strength between concentration and velocity fields is critically dependent on whether the phase-separated pattern is bicontinuous or not. Siggia [7] studied the hydrodynamic coarsening dynamics of bicontinuous phase separation in a rather intuitive way and found the growth law of $R \sim t$, where R is the characteristic domain size. Much experimental research [8,9] has also indicated that phase-separation dynamics in symmetric fluid mixtures can be well described by this mechanism. Since it is rather difficult to attack the late-stage coarsening dynamics on the basis of analytical theories [10], this problem has recently been intensively studied by computer simulations [4,11–16]. Because of the lack of information on the local structure, however, the coarsening process and the interdomain interaction in a bicontinuous pattern are largely unknown, although the coarsening of a single tube has been studied theoretically based on capillary instability [7,17].

In this paper, we demonstrate the experimental evidence that the local orientational order of a bicontinuous pattern in phase-separating symmetric fluid mixtures is largely enhanced by the geometrical confinement into quasi two dimensions. It has so far been believed that a stripe pattern can be observed only in systems having a competition between a nonlocal, long-range repulsive interaction and a short-range attractive interaction; however, our study indicates that such a pattern could be observed even for simple fluid mixtures under a suitable geometrical confinement.

II. EXPERIMENT

The sample used was a mixture of oligomers of ϵ-caprolactone (OCL) and styrene (OS). The number averaged molecular weights of OCL and OS were 2000 and 1000, respectively. Polydispersity ratios of OCL and OS were 1.2 and 1.04, respectively. This mixture has the upper-critical-solution-temperature-type phase diagram. The critical composition was OCL:OS(33:67) and the critical temperature was 135.5 °C. In this mixture OCL is more wettable to glass walls than OS. In bulk phase separation of a fluid mixture at the symmetric composition, we have a bicontinuous pattern. Under a geometrical confinement, however, the more-wettable phase often wets the solid surface by a rapid hydrodynamic process [18–22]. Accordingly, a bicontinuous pattern is quickly destroyed and the macroscopic wetting layers are formed on the solid surface. For studying a coarsening process of a bicontinuous pattern in quasi two dimensions, therefore, we need to avoid such a drastic wetting effect. We have realized naive experimental conditions that allows us to avoid the effect in the following way: We carefully chose the quench depth and the composition to realize the situation that the minority phase is

OS rich and nonwettable to glass by introducing a slight asymmetry that does not break the bicontinuous nature of the phase-separation pattern. This enables us to keep having a bicontinuous pattern for phase separation even in the confined geometry. The sample thickness d is controlled by using monodisperse glass beads as spacers to be about 2 μm. The temperature quench is performed by using a hot stage (Linkam TH-600RMS) with a rate of 1.5 °C/s. The phase-separation kinetics is studied by video phase-contrast microscopy and analyzed by digital image analysis (DIA) [23].

III. RESULTS

Figure 1 shows the typical coarsening process of bicontinuous phase separation in OCL:OS(32:68) at $T = 131.0$ °C [24]. We can see the elementary process of coarsening, namely, the breakup of tubes, which was more clearly confirmed by the slow playback of the video tape recording the phase-separation process. This elementary process is likely the same in the coarsening of a bulk bicontinuous structure. It can be noticed especially in Figs. 1(b) and 1(c) that tubes have a local orientational order. Comparing the observed patterns with bulk bicontinuous patterns reported in the literature (see, e.g., Fig. 18 in [9] and Fig. 32 in Ref. [4]), we notice that our patterns have more local orientational order than the bulk bicontinuous patterns and further that the ratio between the length (L) and the thickness (D) of a tube, which could be correlated to the persistent length of a tube, is much larger in our case ($L/D \geq 3$) than in the bulk case ($L/D \sim 1$). In the final stage [see Figs. 1(e) and 1(f)], we also observe the morphological transformation from the bicontinuous to droplet pattern.

Figure 2 shows the size dependence of the two-dimensional power spectrum $S(\vec{q})$, which is calculated from the real-space images by using DIA [23]. The digitized two-dimensional image was numerically Fourier transformed with a Hamming window after a zero-filling operation and the power spectrum $S(\vec{q})$ was calculated. $S(\vec{q})$ for a "small" region [see Figs. 2(a) and 2(b)] has a clear anisotropy, reflecting the "local" orientational order. The local orientational order can also be directly confirmed by observation of Figs. 1(b) and 1(c) from the fact that tubes are locally in parallel. $S(\vec{q})$ becomes more isotropic with an increase in the size of the original image. $S(\vec{q})$ for a large region of more than 50× 50 μm^2 is almost perfectly isotropic [see Fig. 2(c)].

Since $S(\vec{q})$ is isotropic for a large image (see Fig. 2), we obtain the radial distribution function in q space, $S(q)$, by circularly averaging $S(\vec{q})$ for an image with the size of 400 × 400 points ($\sim 60 \times 60$ μm^2). Figure 3 indicates the temporal change in the structure factor $S(q)$ in the three-dimensional plot, while Figs. 4(a) and 4(b) show the change in the two-dimensional plots. The multiple peaks (at least four peaks) are clearly observed in $S(q)$. This feature of $S(\vec{q})$ stemming from the local parallel arrangement of tubes is clearly observed for 1 s $\leq t \leq$ 4 s. It should be noted that these peaks are not due to the artifact of the analysis since the analysis gives a usual single-peaked $S(q)$ for any droplet patterns of spinodal decomposition in several mixtures including OCL-OS mixtures and further the validity of the analysis has been carefully checked for various simulated patterns. The ratios of the three higher peak wave numbers to the lowest peak wave number are about 2, 3, and 4, respectively. We made a fitting of the summation of four Gaussian functions to the observed $S(q)$, as shown in Figs. 4(a) and 4(b).

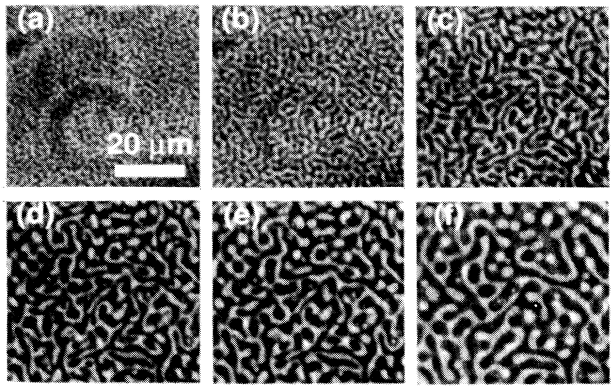


FIG. 1. Coarsening process of bicontinuous spinodal decomposition of the nearly symmetric mixture [OCL:OS(32:68)] in the quasi-two-dimensional configuration for $T = 131.0$ °C. (a) 1 s, (b) 2 s, (c) 4 s, (d) 6 s, (e) 8 s, and (f) 19 s. In (b) and (c), we can clearly see the local parallel ordering of fluid tubes. In the late stage [(e) and (f)], we see the indication of the gradual morphological transition from a bicontinuous to a droplet pattern.

Figures 5(a) and 5(b) show the temporal changes of the peak wave number q_p and the peak intensity $S(q_p)$ of each Gaussian component, respectively. The peak of the lowest wave number becomes more and more dominant with phase-separation time t, while the peak of the higher wave number decays faster. The q_p of the lowest wave number peak is almost constant, but finally starts to decrease for $t \geq 4$ s.

To understand the average coarsening behavior, $S(q)$ is smoothed to obtain a single peak by filtering the original $S(q)$ with a Gaussian window function (low-pass filter) of $\exp[-f/(sf_{\max})^2]$ with $s = 0.06$ (s is the smoothing factor and $f_{\max}$ is the highest frequency in the Fourier

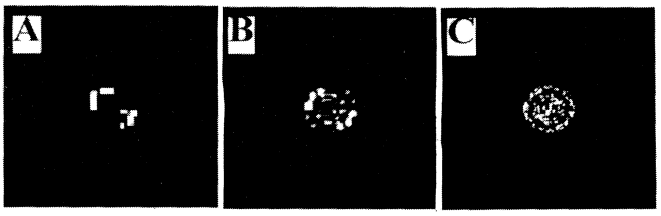


FIG. 2. Two-dimensional images of the power spectra $S(\vec{q})$'s, at 3 s for three real-space images with different sizes: (a) 15×15 μm^2, (b) 25×25 μm^2, and (c) 50×50 μm^2. The anisotropic scattering patterns in (a) and (b) clearly indicate the existence of the local orientational order of tubes. In the image in (c), on the other hand, we cannot see any anisotropy. This result shows the existence of the local orientational order with a finite correlation length.

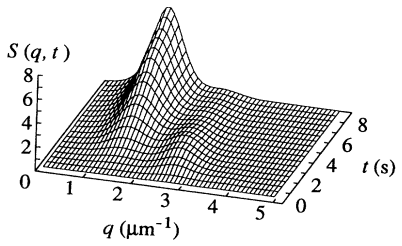
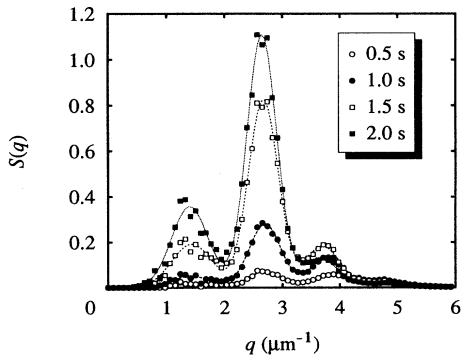


FIG. 3. Three-dimensional plot of the temporal change in $S(q)$. The multiple-peak structure in $S(q)$ is observed in the early stage, while it disappears in the late stage.

space). The temporal change in the filtered $S(q)$ is shown in Fig. 6. The temporal change in the peak wave number of the filtered $S(q)$ shown in Fig. 6 is plotted against time in Fig. 7. As expected from Fig. 5, the averaged peak position shifts to the lower wave number with time, reflecting the overall coarsening. We see sequentially the initial slow coarsening regime, the relation $q_p \propto t^{-1}$ characteristic of the late stage of bulk bicontinuous phase separation, the relation of $q_p \propto t^{-1/3}$ unique to bicontinuous phase separation in quasi two dimensions, and finally the slower coarsening. The final slowing down of the coarsening likely reflects the morphological transformation from the bicontinuous to the droplet pattern due to the slight composition asymmetry (see Fig. 1).



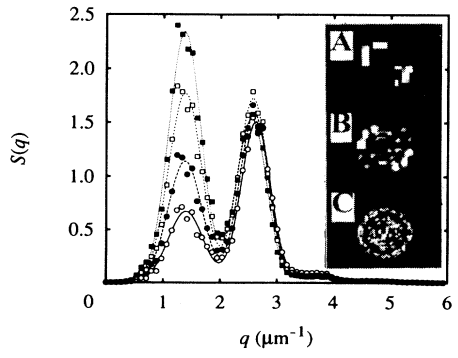


FIG. 4. Temporal change in $S(q)$. The lines are those obtained by the fitting of Gaussian functions at (a) early stage and (b) late stage. Multiple-peak structures can be evidently seen in the figures.

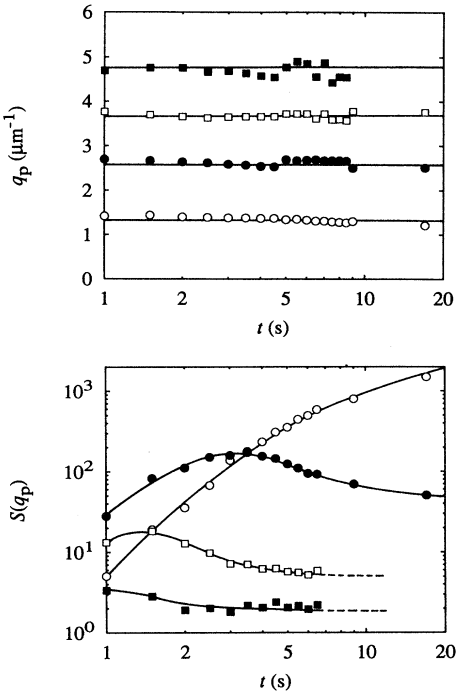


FIG. 5. Temporal change in the (a) peak wave numbers and (b) intensities of the fitted four Gaussian functions for bicontinuous phase separation. The lines are a guide for the eye.

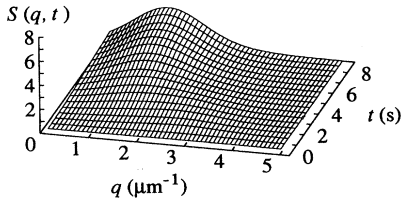


FIG. 6. Three-dimensional plot of the temporal change in the smoothed structure factor $S(q)$ obtained from that shown in Fig. 3. This shows the overall coarsening dynamics.

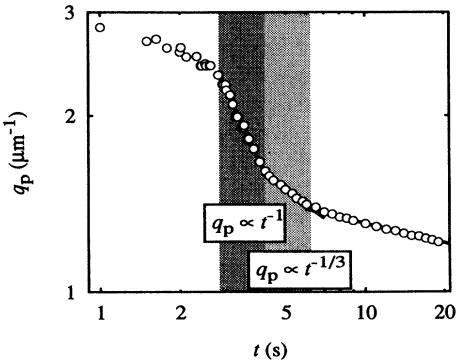


FIG. 7. Temporal change in the average peak wave number q_p of the smoothed $S(q)$. The line in the heavily shaded area has a slope of -1 and that in the lightly shaded area has a slope of $-1/3$.

IV. DISCUSSION

A. Possible physical origins of multiple scattering peaks

The most striking feature of the phase-separation behavior in quasi two dimensions is the existence of multiple peaks in $S(q)$. The multiple peaks are likely caused by (i) the discrete nature of the elementary coarsening behavior and (ii) the local orientational order of tubes.

1. Discrete nature of the elementary process of coarsening

First we discuss the discrete nature of the hydrodynamic coarsening process of a bicontinuous pattern. The coarsening is composed of two elementary processes [25]: (i) continuous thickening and thinning of tubes due to capillary instability unique to a tube configuration of two-phase fluids and (ii) the resulting breakup of tubes and the shape relaxation driven by the interface tension. *This coarsening process partly preserves the memory of the initial bicontinuous structure* since it is essentially dominated by the breakup of the existing tubes and the shape relaxation of the broken tubes into the part of the original structure. The disappearance of a tube increases the local intertube distance between the two neighboring tubes. This would result in the coexistence of a few characteristic wavelength in the pattern. The discrete process is thus likely responsible for the formation of the multiple peaks. It should be noted that the local ordering of tubes is necessary for this mechanism to produce the multiple peaks. The tube network density decreases with time by the breakup of tubes; this coarsening process is not completely continuous and is dominated by both the discrete and the continuous processes as long as the percolated nature of domains is preserved.

2. Local orientational ordering of fluid tubes

Next we consider the local ordering of tubes. This ordering is likely enhanced by the confinement of tubes into quasi two dimensions. This phenomenon can be understood if we consider the situation that many rods of the diameter of D are confined into a quasi-two-dimensional capillary having the thickness d slightly larger than D. This picture is supported by the above observation that the persistent length of a tube is longer in our case than in the usual bulk bicontinuous pattern. This ordering requires a repulsive interaction between rods. In symmetric binary mixtures, an apparent repulsive interaction may come from the conserved nature of the order parameter, which produces the periodical change in concentration. In our case, the initial tube diameter is rather close to the film thickness and thus only a single tube can exist between the walls. Further, the tube configuration is stabilized since a tube of the nonwettable, slightly minority phase has a repulsive interaction with the walls [21]. In relation to the local ordering and the resulting higher-order peaks, it should be mentioned that there is a shoulder in $S(q)$ around $2q_p$ [9,26] or $3q_p$ [4,13,27] even for bulk hydrodynamic phase separation in the late stage. This was observed in both experiments [9,27] and simulations [4,13]. The shoulder was interpreted as an indication of the local orientational order by Bates and Wiltzius [9] and Ohta and Nozaki [26]. Our present study is consistent with their interpretation, although the local orientational order is much more enhanced for quasi two dimensions than for three dimensions.

Here we consider why the persistent length of a tube is significantly increased in quasi two dimensions compared to three dimensions. This can be explained as follows. The phase-separated structure of the two phases are largely dominated by the interface energy in the late stage since there the concentration in each phase is almost in its local equilibrium. Suppose $1/R_1$ and $1/R_2$ are the local principal curvatures. The local mean curvature is given by $H = (1/2)(1/R_1 + 1/R_2)$. Since in simple binary mixtures we need not consider the Gaussian curvature, the interface, which is saddlelike everywhere, satisfies requirements for nonplanar minimum area ($H = 0$). This is consistent with the observation of $L/D \sim 1$ for bulk bicontinuous patterns. In three dimensions, therefore, the spongelike pattern made of a saddlelike interface (see, e.g., Fig. 32 in Ref. [4]) is favored and commonly observed for isometric bulk partitions [1]. In quasi two dimensions, on the other hand, the spatial symmetry is broken by the geometrical confinement and we cannot construct a spongelike pattern as in bulk. The elementary pattern is changed from a pattern with a saddlelike interface to a pattern with a cylindrical interface by the geometrical restriction along the thickness direction. The nonwettability of the slightly minority domain to the walls favors tubes of a cylindrical shape. The local mean curvature H is given by $H = (1/2)(1/L + 1/R)$ for $2R < d$, where $1/L$ is the curvature parallel to the walls. It should be noted that there is no freedom of tube deformation along the direction perpendicular to the walls. To lower the interface energy, the straight configuration of a tube with small $1/L$ is favored in quasi two dimensions. This is likely the origin of the long persistent length of a tube. The persistent length of a tube and the resulting orientational order are probably increased with an increase in the interface tension σ. Thus there might exist two length scales (R and L) characterizing this pattern. In the late stage, the local orientational order is gradually decreased by (i) the decrease in the local curvature due to the domain coarsening, (ii) the transition of the cross-sectional shape of a tube from circle to ellipse (the dimensional crossover from three to two dimensions), and, more significantly, (iii) the morphological transformation from a tube to a droplet due to the slight composition asymmetry. This is consistent with the observation that for $R \geq d$ ($t \geq 4$ s) the local orientational order starts to disappear: The multiple-peak structure of $S(q)$ almost disappears for $t \geq 7$ s.

B. Overall coarsening dynamics

Here we discuss the overall coarsening dynamics shown in Fig. 7 to clarify the relation between the spatial char-

acteristics of patterns and the overall coarsening dynamics. First, we briefly consider the initial and the intermediate stages of bicontinuous phase separation. The initial stage of phase separation is likely dominated by the enhancement of thermal concentration fluctuation via concentration diffusion. Nonlinearity causes the coarsening after the initial linear regime and the hydrodynamic interaction starts to play some roles in coarsening. This process is seen in Fig. 7 as the initial slow coarsening regime. This early stage coarsening, which is often characterized by $t^{1/3}$ or $t^{1/4}$, is probably largely dominated by diffusion process [5,6]. There should also be a transient process from diffusional coarsening to hydrodynamic coarsening [10], reflecting the formation of the sharp interface. A sufficiently sharp interface is likely prerequisite to the strong coupling between concentration and velocity fields, namely, the hydrodynamic interaction. It is a future problem to clarify how sharp the interface should be to cause hydrodynamic coarsening and how the transition from the diffusion to the hydrodynamic regime proceeds.

In the late stage, we need to consider the effect of the dimensionality on bicontinuous phase separation under the influence of the hydrodynamic interaction since the domain size becomes comparable to the characteristic spatial scale of the system. The coarsening dynamics of a bicontinuous structure after the formation of a sharp interface was first studied by Siggia [7] for three dimensions. He obtained the coarsening law $q_p \propto t^{-1}$ on the basis that the coarsening is dominated by the tube hydrodynamic instability [7]: Fluctuation in a tube diameter is enhanced by the capillary pressure difference along the tube axis. This is essentially the same mechanism as the Rayleigh instability of a one-dimensional fluid tube. This coarsening law was confirmed in many systems by experiments [8,9] and also by computer simulations [11,4,13–16]. For purely two-dimensional fluid systems [6,15,16], the coarsening of bicontinuous phase separation is described by the initial diffusive growth of $q_p \sim t^{1/2}$ and the late-stage hydrodynamic growth of $q_p \sim t^{2/3}$ [6].

For quasi-two-dimensional fluid systems, on the other hand, the problem is very complicated because of the dimensional crossover and further due to the wetting effect on the solid walls. When the minority phase is more wettable to the glass, the wetting of the more wettable phase to the solid walls significantly affects phase-separation dynamics [18–22]. When the minority phase is less wettable to the glass, on the other hand, there is no drastic wetting effect and the tubes of the nonwettable phase likely sit between the two substrates [28]. Our experiments correspond to this latter situation. For this case, we have the dimensional crossover of a tube from three to two dimensions with its coarsening. The behavior can be explained on the basis of the Navier-Stokes equation [28]

$$\eta \nabla^2 v = \frac{dP}{dx}, \tag{1}$$

where η is the viscosity, P is the pressure, v is the velocity, and x is the coordinate along a tube. When the characteristic size of a tube is less than the thickness of film, a tube has a cross section of a circular shape. For a tube of radius R, we obtain $v \sim \partial R/\partial t \sim \sigma/\eta$, following Siggia's discussion [7]. Thus we get the coarsening law of $R \sim (\sigma/\eta)t$. When the characteristic size exceeds the film thickness d, on the other hand, a tube has a cross section of an ellipsoidal shape. For a tube of short radius d and long radius R, $\eta v/d^2 \sim \sigma/R^2$ according to Eq. (1). Thus the coarsening dynamics is described by $R^3 \sim (\sigma d^2/\eta)t$ [28]. We expect the crossover of the coarsening dynamics from $q_p \sim t^{-1}$ [7] to $q_p \sim t^{-1/3}$ [12,28], reflecting the dimensional crossover from three to two dimensions. According to Fig. 7, the slowing down of the coarsening rate occurs around t =4 s. Direct observation (see Fig. 1) tells us that the tube size is equal to the thickness d ($\sim$ 2 μm) around 4 s. This is quite consistent with the above picture that the temporal change in the growth exponent α from -1 to $-1/3$, which occurs around $t = 4$ s, is caused by the crossover between the tube diameter and the film thickness. In the final stage of phase separation ($t \geq 7$ s), the domain coarsening further slows down (apparently $\alpha \sim 1/9$, which is a transient exponent having little physical meaning) and at the same time the multiple-peak structure of $S(q)$ disappears (see Fig. 3). This can qualitatively be explained by the morphological transformation from a bicontinuous to a droplet pattern induced by the slight composition asymmetry (see Fig. 1). This morphological transition destroys the local orientational order and leads to the disappearance of the multiple-peak structure of $S(q)$ (see Fig. 3). We can never avoid this effect of composition symmetry in any actual experiments and a complete symmetric situation can be realized only by simulations. Although $R \sim t^{1/3}$ [6,12,28] for both bicontinuous and droplet phase separation in quasi two dimensions, the prefactor for the diffusive growth of droplets is much smaller than that for the hydrodynamic coarsening of bicontinuous tubes in quasi two dimensions: $R^3 \sim (k_B T/\pi\eta)t$ for the former, while $R^3 \sim (\sigma d^2/\eta)t$ for the latter. From the two-scale-factor universality [29], $\sigma \sim 0.2 k_B T/\xi^2$, where ξ is the correlation length or the interface thickness. The ratio of the prefactor of the hydrodynamic growth to that of the diffusive growth is proportional to $(d/\xi)^2$ ($\gg 1$). This drastic decrease in the prefactor caused by the morphological transition is likely responsible for the slowing down of the coarsening. The system is likely in the gradual transitional regime even in the late stage of our observation: This is confirmed by the coexistence of bicontinuous and droplet structures [see Figs. 1(e) and 1(f)]. Since the time span of each power-law behavior in Fig. 7 is very narrow, further careful studies are necessary to confirm the above picture on the different coarsening stages.

V. CONCLUSION

In summary, we have demonstrated the local orientational order of the phase-separated pattern and the discrete nature of the elementary coarsening process for bicontinuous phase separation of a symmetric fluid mixture confined in the two-dimensional capillary. The discrete

nature of the coarsening process is *intrinsic* to bicontinuous spinodal decomposition of fluid mixtures, irrespective of whether the system is confined or not, since the tube hydrodynamic instability eventually leads to the breakup of tubes without exception. On the other hand, the enhancement of the local orientational order can be explained by the spatial symmetry breaking of the bicontinuous pattern induced by the geometrical confinement. In this quasi-two-dimensional configuration the interface energy likely favors a stripe pattern with a local orientational order, while in bulk a spongelike pattern with a zero-mean curvature is favored. The pattern observed here is likely a rare example of a transient, nonequilibrium stripelike pattern that is caused only by the interface energy and the conserved nature of the order parameter. It should be stressed that our binary polymer mixture does not have any long-range repulsive interaction between the components and thus it can be regarded as a simple fluid mixture. This study gives us important information on the elementary process of the hydrodynamic coarsening of a bicontinuous pattern, which has so far been largely unexplored. We think that the basic idea described in this paper can be applied even to the coarsening process of bicontinuous spinodal decomposition of fluid mixtures in bulk. Further experimental and theoretical studies are highly desirable for the quantitative understanding of the phenomenon.

ACKNOWLEDGMENTS

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[25] Both processes that cause the local coarsening of a tube diameter can be described by the well-known coarsening law $q_p^{-1} \propto (\sigma/\eta)t$, although there is a difference in the prefactor between the two processes. This is likely the reason why the overall coarsening process can be described by $q_p^{-1} \propto (\sigma/\eta)t$. We believe that deeper consideration on the above two elementary processes and their relative weights is necessary to quantitatively estimate the prefactor of this scaling relation.
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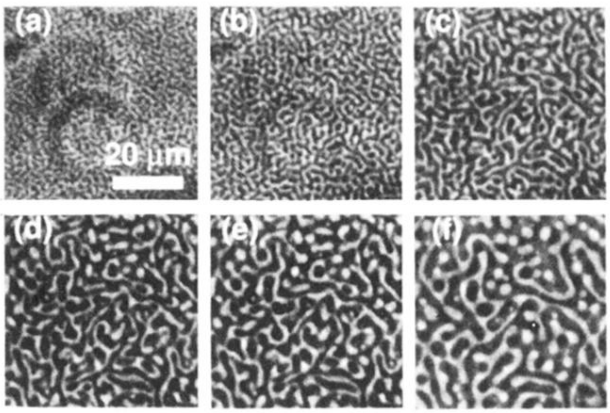

FIG. 1. Coarsening process of bicontinuous spinodal decomposition of the nearly symmetric mixture [OCL:OS(32:68)] in the quasi-two-dimensional configuration for $T = 131.0\,^{\circ}\mathrm{C}$. (a) 1 s, (b) 2 s, (c) 4 s, (d) 6 s, (e) 8 s, and (f) 19 s. In (b) and (c), we can clearly see the local parallel ordering of fluid tubes. In the late stage [(e) and (f)], we see the indication of the gradual morphological transition from a bicontinuous to a droplet pattern.

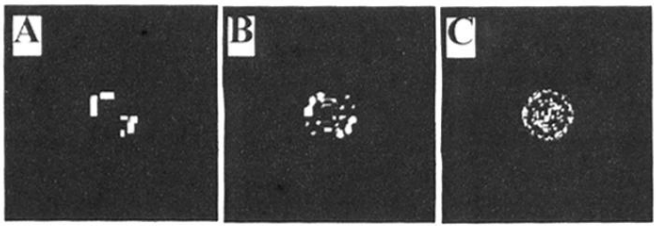

FIG. 2. Two-dimensional images of the power spectra $S(\vec{q})$'s, at 3 s for three real-space images with different sizes: (a) 15×15 μm^2, (b) 25×25 μm^2, and (c) 50×50 μm^2. The anisotropic scattering patterns in (a) and (b) clearly indicate the existence of the local orientational order of tubes. In the image in (c), on the other hand, we cannot see any anisotropy. This result shows the existence of the local orientational order with a finite correlation length.

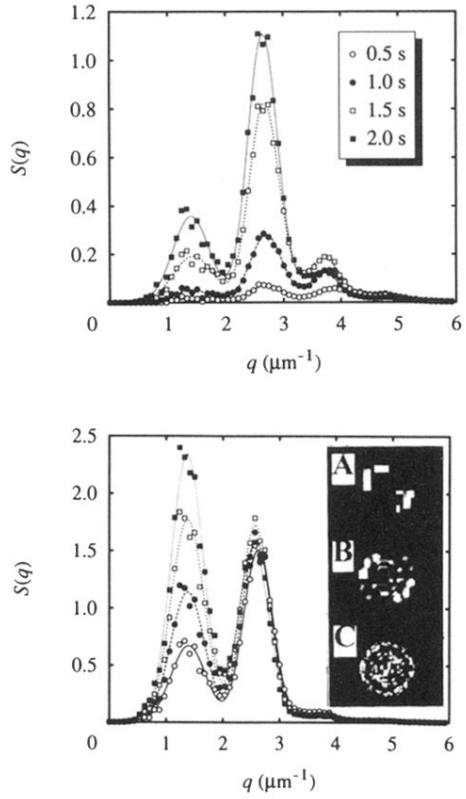

FIG. 4. Temporal change in $S(q)$. The lines are those obtained by the fitting of Gaussian functions at (a) early stage and (b) late stage. Multiple-peak structures can be evidently seen in the figures.