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Effect of confinement on phase-separation processes in a polymer blend observed by laser scanning confocal microscopy

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Structure self-assembling in the late stage spinodal decomposition of a polymer blend at its critical composition has been explored by laser-scanning confocal microscopy with particular emphasis on the effects of confinement (dimensionality) and preferential wetting of solid surface by one of the constituent polymers. A mixture of deuterated polybutadiene and polybutadiene (PB) with relatively narrow thickness ($D\cong 55\ \mu$m) was observed in three dimensions over the entire thickness. Formation of a wetting layer was clearly observed near the glass surface, while a bicontinuous structure evolved in the middle of the specimen. Global as well as local features of the phase-separating structures were quantified by several structural parameters, e.g., characteristic length $\Lambda_m(t)$, structure factor $S(q)$, interfacial area per unit volume $\Sigma(t)$, probability densities of interfacial curvatures $P(H,K;t)$, etc. (t is a phase-separation time). From the time evolution of these structural parameters, a deviation from the self-similar growth of a bicontinuous structure was found to occur at a transition time, t_{tr}, at which a scaled thickness, D/Λ_m, approached unity. The breakdown of the self-similar growth was most sensitively observed by the local characteristics, i.e., $\Sigma(t)$ and $P(H,K;t)$. On the other hand, the global characteristic, $\Lambda_m(t)$, did not provide useful insight into the effects of dimensionality. It turned out that the bicontinuous structure, initially growing with dynamical self-similarity, eventually transformed into a ‘‘columnlike’’ structure (at $t\cong t_{tr}$) in which cylindrical PB-rich domains bridge the upper and lower PB wetting layers.

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I. INTRODUCTION

Phase-separation phenomena have been extensively studied in the past three decades from both fundamental and industrial points of view. As a fundamental problem, the phase separation, especially the one called spinodal decomposition (SD), attracted researchers' attention as a typical example of nonlinear and nonequilibrium phenomena [1]. It is known that the transient structure developed in the course of SD shows interpenetrating network morphology exhibiting bicontinuity (‘‘bicontinuous structure’’) [2]. Most studies to date have concentrated on morphological and temporal features of such morphology in the bulk SD.

Influences of confinement and spatial dimensionality on the kinetics of the phase separation present interesting problems. In the late stage of fluid phase separation, theoretical and experimental investigations have shown that the power law behavior, $l\sim t^n$, realizes in the three-dimensional (3D) case ($d=3$; d is dimensionality). Here, l and t are a characteristic length of domains and time, respectively. The Rayleigh-Tomotika liquid thread instability plays an important role in the coarsening process: development of capillary waves on the locally cylinderlike bicontinuous phase causes breakup in the late stage SD. On the other hand, such instability does not exist in $d=2$ and the corresponding breakup of domains occurs by a diffusive process, leading to $n=1/2$ [3]. Sung *et al.* [4] studied the dimensional crossover in thin films of deuterated polystyrene (PSD) and polybutadiene (PB) blend. According to their observation, 1000-Å-thick and 200-Å-thick films showed $n=1$ and 0.44, respectively. Based on this experimental result, Sung *et al.* concluded that the dimensional crossover from three- to two-dimensional SD occurred somewhere between 1000 Å and 200 Å sample thickness. Although not mentioned in Sung's paper, what is intriguing is that the coarsening rate of the PSD-PB blend was significantly slower in the 1000-Å film than in the 200-μm-thick film. Thus, even though the exponent of the power law agrees with the theoretical prediction of the 3D SD ($n=1$), the kinetics of the 1000-Å film of PSD-PB blend may *not* be the phase separation in the bulk (as observed in the 200-μm film).

Thus, spatial dimensionality could strongly affect the kinetics of SD. It is well known that the preferential wetting of the surface by one component of a mixture affects the phase-separation kinetics [5]. For the complete understanding of these effects, it is essential to investigate how the phase-separating domains grow both in parallel and perpendicular to the surface. In reality, however, it is often difficult to perform 3D real-space observations because the depth of focus of objectives is normally thicker than the phase-separating structures, leading to heavy overlap of them in the depth direction. This problem could be even more crucial as they become complex, e.g., bicontinuous, structures. An effective and easy way to get around this experimental problem is to reduce the sample thickness to a couple of micrometers. Doing so, in turn, makes the phase-separation kinetics two-dimensional (2D) or, at least, quasi-3D. What is misleading is that the experimental results obtained from such 2D or quasi-3D studies are sometimes treated as if they were 3D ones, although the obtained structural parameters essentially reflect 2D nature. Therefore, fundamental knowledge about

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the effects of dimensionality on the phase-separation processes and morphology is not at all obvious and thus further studies are needed to examine the effects.

Direct visualization of phase-separating structures has become possible by using laser-scanning confocal microscopy (LSCM) [6,7]. It has far better depth resolution, dz, than the conventional microscope ($dz \sim 1\ \mu$m for LSCM) and thus enables 3D observation [8]. Time evolution of the phase-separating structure in SD has been extensively studied using LSCM [2,6,7]. The obtained results were observed in the intermediate region of the sample where no confinement and surface effects play substantial roles (''bulk''). In the present paper, we examine SD processes of a polymer mixture in a confined space. The thickness of the specimen is close to the periodicity of the phase-separating morphology. LSCM will be used to obtain not only lateral but also depth profiles of the concentration fluctuations of the phase-separating structure to clarify the influence of the limited space on the structure evolution. Symmetry breakdown of the phase-separating structure near the surface will be discussed.

II. EXPERIMENT

A binary mixture of deuterated polybutadiene (DPB) and PB was used. The weight-average molecular weight (M_w) and polydispersity (M_w/M_n) of DPB were, respectively, 14.3×10^3 and 1.12 (M_n denotes the number-average molecular weight). M_w and M_w/M_n for PB were 9.5×10^3 and 1.07, respectively. In order to enhance contrast in microscopy, a small amount of anthracene was attached to PB. The mixtures of DPB and PB having the critical composition (46 vol % DPB) were dissolved in benzene to form ca. 7 wt % solution and then lyophilized. The mixture after lyophilization was homogenized by mechanical mixing and placed between glass plates. A ring spacer made of aluminum foil was used to adjust thickness of the mixture, D, to be ca. 50–55 μm. The glass plates were cleaned by the UV-ozone cleaner (UV-1, SAMCO Intl. Inc., Japan), and their surfaces were hydrophilic.

The blend specimen was heated at 40 °C for different phase-separation times, t. In the present study, t spans from 2846 to 21508 min, corresponding to the reduced time, τ, from 198 to 1500 [9]. The phase-separating structures of the DPB-PB blend were observed at room temperature by LSCM (Carl Zeiss, LSM 410). A UV laser (wavelength λ, 364 nm) was used to excite anthracene. Intensity of fluorescence from a particular point in a focal plane (x-y or lateral plane) at a given depth z, $I(x,y,z)$, was recorded by the detector behind the band-pass filter (395–440 nm). Experimental details can be found elsewhere [2].

III. RESULTS AND DISCUSSION

A. General features of three-dimensional phase-separating structure in confined space

Figure 1 shows 2D optical slices of the DPB-PB mixture undergoing SD at 40 °C for 2846 min at three different depths, z, from the glass surface.

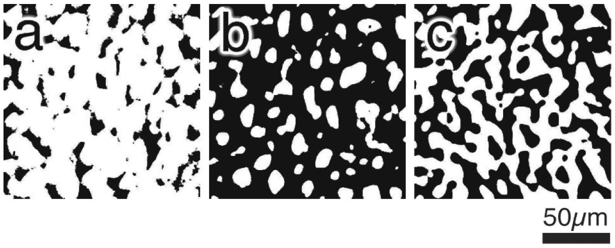

FIG. 1. Two-dimensional (2D) optical slices of the DPB-PB mixture undergoing SD at 40 °C for 2846 min. Binarized images at three different depths from the glass surface, z, are presented: (a) $z=0$ (at glass surface), (b) $z\sim4\ \mu$m, and (c) $z=25\ \mu$m. White and black regions of the 2D images correspond, respectively, to PB-rich and DPB-rich phases. Bar corresponds to 50 μm.

The volume fraction of the PB-rich phase, $\phi_{\rm PB}$, was found to be nearly 0.8 at the glass surface [see Fig. 1(a)], while $\phi_{\rm PB}$ at $z\sim4\ \mu$m was only 0.2 [see Fig. 1(b)]. 2D optical slices of the phase-separating structure at this depth looked much like an ''island-in-sea'' structure (PB-rich phases are islands), being different from that of the conventional bicontinuous structure deeper inside the specimen ($z \cong 25\ \mu$m) [see Fig. 1(c)]. Such drastic variation of $\phi_{\rm PB}$ is demonstrated in Fig. 2, in which $\phi_{\rm PB}$ is plotted against z for the DPB-PB mixture ($t=2846$ min).

The PB-rich phase preferentially wets the glass surface. Within ca. 10 μm from the glass surface ($z<10\ \mu$m), there is a wetting layer of the PB-rich phase that is followed by a ''depletion layer'' where the PB-rich phase became a minor phase. Similar composition variation can be observed at the other side of the specimen (43 $\mu{\rm m}<z<55\ \mu$m).

These wetting and depletion layers are similar to those observed in poly(ethylenepropylene) (PEP) and perdueterated poly(ethylenepropyrene) (d-PEP) blend having much lesser thickness, $D\sim9000$ Å [10]. They concluded that these layers were induced by van der Waals interaction from the surface. Namely, breaking translational and rotational symmetry by the preferential wetting of one of the components to the surface caused the spinodal waves to grow normal to

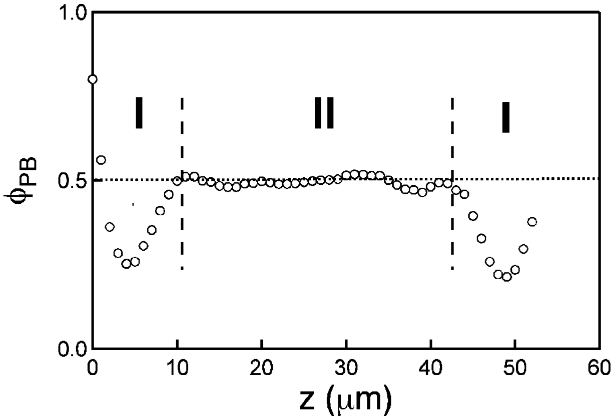

FIG. 2. Depth dependence of volume fraction of PB-rich phase, $\phi_{\rm PB}$. Phase-separation time is 2846 min. The wetting and bulk regions (labeled as I and II, respectively) were observed.

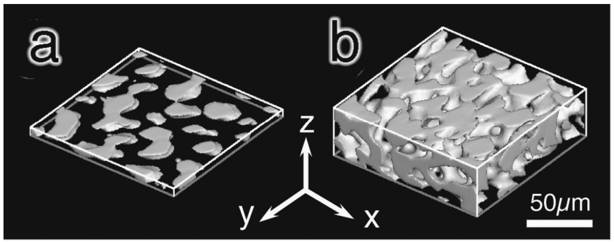

FIG. 3. 3D representations of phase-separating structures (a) in the wetting region, (b) and in the bulk region. The DPB-PB mixture was annealed for 2846 min at 40 °C. Images show only PB-rich phase labeled with anthracene and DPB-rich phase is left empty. Bar shows 50 μm.

the surface in the early stage of SD (“surface-directed spinodal decomposition”) [11]. Note that the thicknesses of the wetting layers were of the order of the radius of gyration of polymers, R_g. In the present study, we emphasize that the wetting and depletion layers in the DPB-PB mixture extended for as long as 10 μm, much longer than R_g. The existence of the thick wetting and depletion layers cannot be explained by the short-range interaction, e.g., the van der Waals interaction from surfaces alone. Possible explanation may be the following.

The DPB-PB phase-separating structure corresponding to the depletion layer consisted of highly anisotropic “tubes” (as shown later in Fig. 3): most of the tubes are perpendicular to the surface and very few domains lie parallel to the surface. The wetting layer initially formed due to the van der Waals interaction, which was followed by the rapid formation of the macroscopic wetting layer due to the hydrodynamic “pumping” of fluid into the layers through the fluid “tubes” connected to it [5]. The bicontinuous structure allows the more wettable phase, i.e., PB-rich phase, to be transported into the wetting layer in a very efficient way. The strong variation of ϕ_{PB} observed in the DPB-PB mixture near the glass surfaces may be attributed to the peculiar tube-like phase-separating morphology. Hereafter we call the region consisting of the wetting and depletion layers a “wetting region.” We note that the phase-separating structure in the wetting region was found to be a bit *larger* in size than that in the bulk region [12].

Wiltzius and Cumming [13] and Shi *et al.* [14] found that two distinct coarsening mechanisms exist in the SD processes under the influence of the preferential wetting. One corresponds to standard bulk hydrodynamic growth whose growth rate can be well described by the power law $l \sim t^n$ $(n=1)$. Besides this well-known mechanism, a substantially fast growing phase separation in the direction parallel to the surface, characterized by $n=3/2$ (“fast mode”) was found. Note that this first mode kinetics was observed in a simple fluid mixture of guaiacol and glycerol-water [14] as well as in a polymer blend of polyisoprene and poly(ethylene-propyrene) [13], demonstrating that the observation is as generic to phase-separating fluid, in general. Although the polymer mixture used in the present study was similar to that of Wiltzius and Cumming [13], the growth rate of the phase-separating structure near the glass surface was not considerably different from that of the bulk structure. The time-evolution of phase-separating structure near the surface will be reported in the subsequent paper of this series [12].

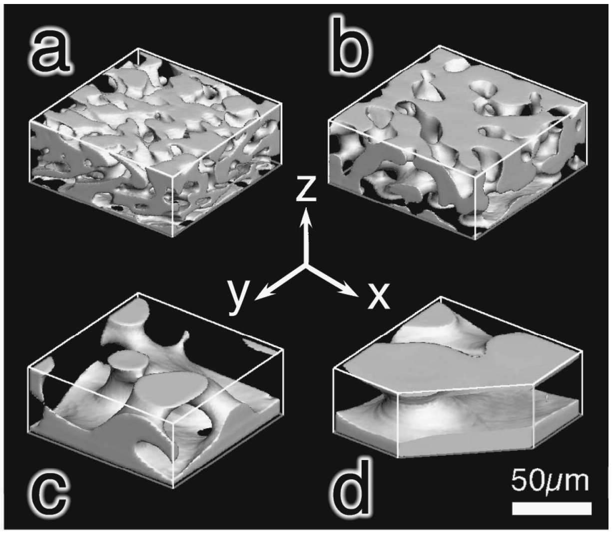

FIG. 4. Time evolution of phase-separating structure at (a) $t=2846$ min, (b) $t=4310$ min, (c) $t=9823$ min, and (d) $t=21\,508$ min. Solid part of each figure represents PB-rich phase. Bottom plane of each 3D image as shown by gray edges represents glass surface. A part of the phase-separating structure in (d) was removed to show a cross section of 3D structure, demonstrating the formation of thick wetting layer and “columnar structure.” Bar corresponds to 50 μm.

In the middle of the sample deeper than the wetting regions, there exists a region where ϕ_{PB} stayed constant at around 0.5. This composition is consistent with the bulk composition previously obtained in the thicker specimens consisting of the same DPB-PB blend ($D=200$ μm) [2]. In this region, the phase-separating structure is free from surface effects and thus exhibits isotropic bulk phase separation (“bulk region”).

Figure 3 displays 3D phase-separating structures corresponding to the wetting region [$z=3\sim6$ μm, part (a)] and the bulk region [$z=14\sim44$ μm, part (b)] for the DPB-PB mixture at $t=2846$ min. Reconstruction of 2D binarized images into a 3D image is described elsewhere [2]. Note that the phase-separating structures near the upper and lower coverslips were essentially the same at each phase-separation time. The effects of gravity on the phase-separating structures are negligible in our experiments. The phase-separating structure in the wetting region becomes anisotropic network structure as mentioned above. In the bulk region, the phase-separating structure is an “isotropic” bicontinuous network structure as expected for the polymer mixture with the critical composition.

Demonstrated in Fig. 4 is the time evolution of the phase-separating structure of DPB-PB mixture [reconstructed from the glass surface $(z=0)$ to the bulk region]. Up to $t=4310$ min, bicontinuous network structure was dominant except for the wetting region, while it transformed into the “columnar structure” in which cylindrical domains consisting of PB-rich phase bridge the upper and lower PB wetting layers [see Fig. 4(d)]. As shown below, the occurrence of the topological transition was characterized by the various structural parameters.

B. Time evolution of characteristic length of the phase-separating structure in confined DPB-PB blend

Characteristic length of the phase-separated structure, $\Lambda_m(t)$, is a first-choice structural parameter in morphological studies, especially in (light) scattering experiments. $\Lambda_m(t)$ can be directly calculated from the LSCM 3D volume data [2]. In the scattering experiments, the incident laser is sent from the film normal (z axis) and the scattering intensity is measured in x-y plane. The scattering intensity in the q_x-q_y plane, $I(q_x,q_y;t)$, was first obtained from the 3D image by taking the square of the magnitude of its 3D Fourier transformation, which was then orientationally averaged in the q_x-q_y plane to calculate $I(q,t)$. Here, q_i ($i=x$ and y) denotes x and y axes in Fourier space. The characteristic wave number, $q_m(t)$, is related to $\Lambda_m(t)$ in the form of $\Lambda_m(t)=2\pi/q_m(t)$, where $q_m(t)$ corresponds to the wave number at the maximum intensity in the scattering function, $I(q,t)$.

Figure 5(a) shows the time evolution of $q_m(t)$ [and thus $\Lambda_m(t)^{-1}$] in the DPB-PB mixture ($D=55$ μm). For comparison, the time dependence of $q_m(t)$ in a thick DPB-PB blend ($D=200$ μm) is also presented. Hereafter, the DPB-PB blends whose thicknesses were 55 and 200 μm are referred to as "thin (or confined)" and "thick (or nonconfined)" blends, respectively. The filled circles correspond to $q_m(t)$ estimated for the thin DPB-PB mixture. In Fig. 5(b), the ratio of the sample thickness to the characteristic length (scaled thickness), D/Λ_m, is plotted against t in a double-logarithmical way for the two DPB-PB mixtures having different thicknesses. The thickness of the thin DPB-PB mixture became smaller than $\Lambda_m(t)$ at $t\sim9000$ min, while that of the thick DPB-PB mixture stayed always more than, at least, three times the characteristic length of the structure over the entire experimental time. It is intriguing that the time evolution of $q_m(t)$ in the thin blend traced a similar path as that of the thick DPB-PB mixture. In the late time region, $q_m(t)$ showed power law behavior, i.e., $q_m(t)\sim t^{-1}$ regardless of the thicknesses, being consistent with the experimental observations in liquid mixtures free from the viscoelastic effects [15]. We here note that the last point of the thin DPB-PB blend, i.e., $q_m(t=21508\,\text{min})$, may deviate from the power law behavior. The time evolution of $q_m(t)$ indicates that the growth of the bicontinuous structure in lateral plane is *not significantly affected* by the confinement in the depth direction.

C. Time evolution of scaled structure factor

A scaled structure factor, $F(x,t)$, is often used to statistically characterize the form of the phase-separating structure that can be estimated from the following equation:

$$F(x,t)\equiv I(x,t)q_m(t)^3=C\langle\eta(t)^2\rangle S(x,t), \tag{1}$$

with $x\equiv q/q_m(t)$. C is a proportionality constant. $\langle\eta(t)^2\rangle$ is the mean squared amplitude of concentration fluctuations, and $S(x,t)$ is the structure factor at a given t during SD which characterizes the form of the phase-separating structure.

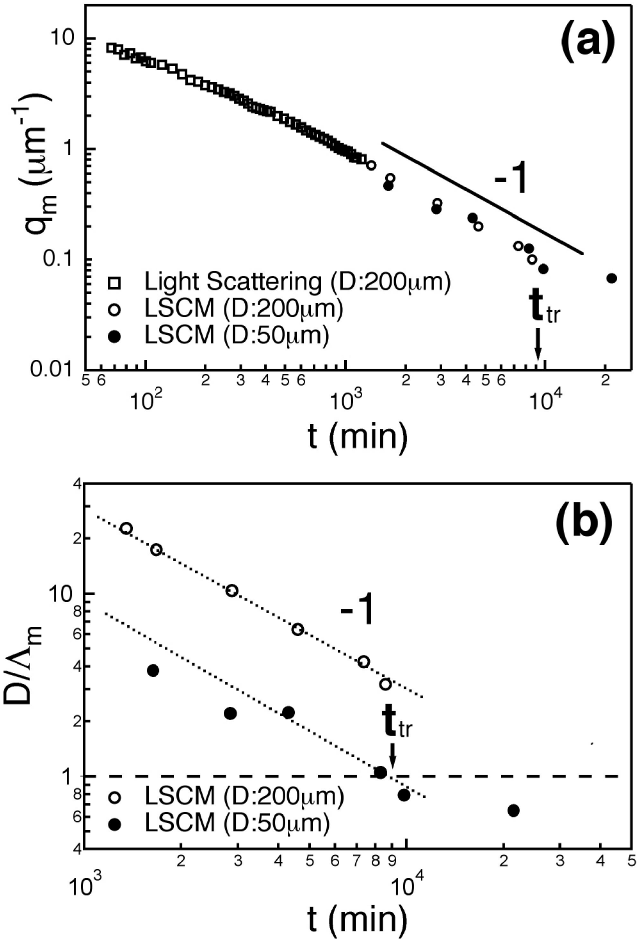

FIG. 5. (a) Time evolution of characteristic wave number, $q_m(t)$, in a double-logarithmic plot. $q_m(t)$ was determined from peak position of scattering intensity. Open symbols represent $q_m(t)$ for the DPB-PB "thick" sample ($D=200$ μm), while filled circles show $q_m(t)$ for the DPB-PB "thin" sample ($D=55$ μm). Circular and square symbols correspond to the data obtained from light scattering and LSCM, respectively. (b) Time evolution of scaled thickness, D/Λ_m, is plotted. Open and filled circles show results for thick and thin DPB-PB mixtures, respectively.

In Fig. 6, $F(x,t)$ is plotted double logarithmically against the reduced wave number, x. The intensity scale of $F(x,t)$ has been scaled by the maximum intensity in order to compare the forms of the phase-separating structure at different phase-separating times and hence it is essentially equivalent to $S(x,t)$. Note that $F(x,t)$ depends both on $\langle\eta(t)^2\rangle$ and $S(x,t)$, the former may be constant in the late stage of SD. In the present study, we are interested in the latter alone. $F(x,t)$ obtained from the LSCM 3D image at different t nicely falls onto a single master curve up to $t=4310$ min. Although not shown, $F(x,t)$ was found to be in good agreement with that estimated by a computer simulation based on the time-dependent Ginzburg-Landau theory [15]. $F(x,t)$ at t

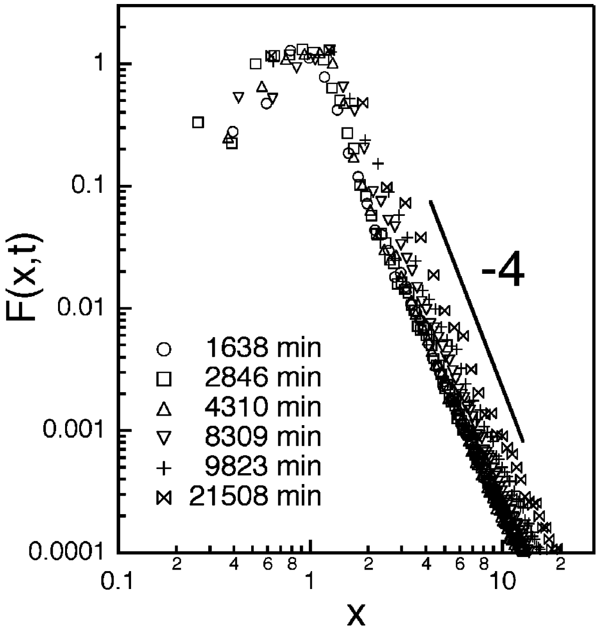

FIG. 6. Time evolution of scaled structure factor, $F(x,t)$, shown in double-logarithmical way. $F(x,t)$ at several t are plotted.

$=8309$ min got broader than the master curve around the scattering peak and thus deviated from it, indicating occurrence of some sort of morphological transition. The scaled thickness, D/Λ_m, corresponding to the transition is roughly unity, i.e., $D/\Lambda_m \sim 1$ at $t \equiv t_{tr} \simeq 9000$ min [see Fig. 5(b)]. Here t_{tr} denotes a characteristic time when the morphological transition took place. Note that the reduced time, τ, corresponding to t_{tr} turned out to be approximately 630.

D. Temporal change of interfacial area of the confined blend

Interfacial area per unit volume (Σ) is an essential structural measure since the reduction of the interfacial area is one of the main driving forces of the phase separation.

Depicted in Fig. 7 is the time evolution of $\Sigma(t)$ for the thin and thick DPB-PB mixtures. $\Sigma(t)$ was measured from the 3D reconstructed images. As reported before [2], a power law behavior, $\Sigma(t) \sim t^{-1}$, was observed for the thick blend, while the thin blend showed same exponent until t_{tr}, and stayed constant afterwards. This experimental observation indicates that the phase-separation kinetics was changed when the periodicity of the bicontinuous structure approached the thickness of the sample, i.e., $D/\Lambda_m \simeq 1$ [see Fig. 5(b)]. After the morphological transition, the reduction of interfacial area will no longer be a major driving force of the phase separation, but the pressure difference between the tubes and the wetting layer will play a significant role in inducing hydrodynamic flow from and into the tubes, depending upon the lateral size of the tubes [5,12].

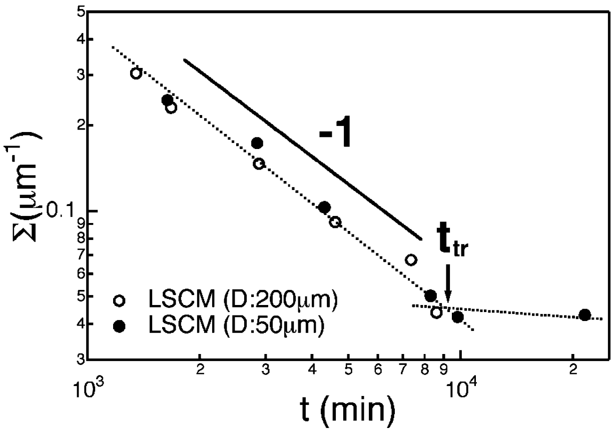

FIG. 7. A double-logarithmic plot of interfacial area per unit volume, $\Sigma(t)$, as a function of t. Open and filled circles represent data from thick and thin DPB-PB mixtures, respectively.

E. Time evolution of interfacial curvature distributions

In addition to the interfacial area, shape of the interface is another important aspect of the phase-separating structure. Two kinds of curvatures, the mean, H, and Gaussian, K, curvatures, were measured at many points on the interface in order to evaluate the probability density of the interfacial curvatures, $P(H,K;t)$ [2,16]. Here, $H \equiv (\kappa_1+\kappa_2)/2$ and $K \equiv \kappa_1\kappa_2$ (κ_1 and κ_2 denote the principal curvatures at a given point on the interface). From $P(H,K;t)$, the probability densities of the mean and Gaussian curvatures, $P_H(H)$ and $P_K(K)$, respectively, can be elucidated. In order to facilitate comparison, $P_H(H)$ and $P_K(K)$ have been scaled with respect to the interfacial area per unit volume, Σ, in the following fashion:

$$\tilde{P}_H(\tilde{H}) \equiv P_H(H)\Sigma, \tag{2a}$$

$$\tilde{P}_K(\tilde{K}) \equiv P_K(K)\Sigma^2. \tag{2b}$$

Here $\tilde{H} \equiv H\Sigma^{-1}$ and $\tilde{K} \equiv K\Sigma^{-2}$.

Figure 8 shows the time evolution of $\tilde{P}_H(\tilde{H})$ [part (a)] and $\tilde{P}_K(\tilde{K})$ [part (b)]. Note that both $\tilde{P}_H(\tilde{H})$ and $\tilde{P}_K(\tilde{K})$ were measured in the "bulk" region. Up to $t=4310$ min, $\tilde{P}_H(\tilde{H})$ and $\tilde{P}_K(\tilde{K})$ fall onto master curves, indicating that the local interfacial structure evolved in a self-similar fashion. These results are in consistence with our previous observation on the thick DPB-PB blend [2]. $\tilde{P}_H(\tilde{H})$ exhibits a broad maximum at $H \cong 0$; the interface is equally concave and convex. Most data points of $\tilde{P}_K(\tilde{K})$ shown in Fig. 8(b) resides at $\tilde{K} < 0$, demonstrating that the interface is mainly hyperbolic. At a later time than 8309 min, both $\tilde{P}_H(\tilde{H})$ and $\tilde{P}_K(\tilde{K})$ deviated from the master curves, just as the results observed in $F(x,t)$ and $\Sigma(t)$. The maximum of $\tilde{P}_H(\tilde{H})$ gradually shifted from zero to a positive value and got broader with time, while the change of $\tilde{P}_K(\tilde{K})$ was rather subtle except for the sudden change at $t=9823$ min, which is in good agreement with t_{tr} obtained in the analyses described in Secs. III C and III D. This change is considered to be the collapse of bicontinuous structure into the "columnar structure" in which the columnar domains have $H>0$ and slightly negative K. This result was also supported by the 3D reconstructed images

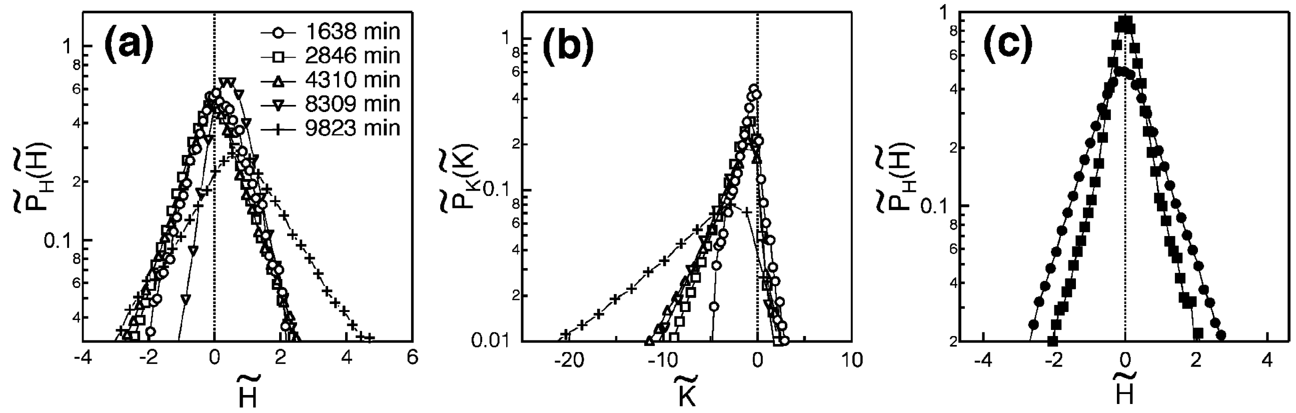

FIG. 8. Scaled probability densities (a) $\tilde{P}_H(\tilde{H})$ and (b) $\tilde{P}_K(\tilde{K})$ for the thin DPB-PB mixture. In part (c), comparison of master curves of $\tilde{P}_H(\tilde{H})$ obtained from thick (filled squares) and thin (filled circles) DPB-PB mixtures is made. Data before morphological transition ($t < 4310$ min) are used to construct the master curve in the thin DPB-PB mixture.

where the anisotropic columns are bridging the wetting layers at $t \gtrsim 9823$ min.

It is intriguing that $\tilde{P}_H(\tilde{H})$ has thickness dependence even in the time regions where the master curves were obtained [see Fig. 8(c)]. $\tilde{P}_H(\tilde{H})$ of the thin DPB-PB blend is noticeably broader than that of the thick blend. The thickness dependence of $\tilde{P}_K(\tilde{K})$ was negligibly small (not shown). Even though the local structure evolved with dynamical self-similarity ($t < 4310$ min), the interfacial shape was somewhat affected by the confinement and thus the phase-separating structure ‘‘felt’’ the limited space of the container.

IV. SUMMARY

The structure evolution in the late stage of SD with particular emphasis on the effect of confinement (dimensionality) was investigated by LSCM. A binary polymeric mixture of DPB and PB with a relatively narrow thickness ($D \cong 55$ μm) was heated to induce SD. The phase-separating morphology over the entire thickness was observed in 3D as a function of time *t*. The morphological change was observed over the extended period of time, as long as 21 508 min, corresponding to the reduced time, τ, of ca. 1500. A wetting layer consisting of a PB-rich phase formed in the vicinity of the glass wall (within a couple of micrometers), while the bicontinuous structure was formed in the middle of the specimen. Between the wetting layer and the bicontinuous structure, a region was found where the volume fraction of the PB, ϕ_{PB}, became considerably smaller (ca. 0.2) than the bulk ϕ_{PB} (0.5) (‘‘depletion region’’). In the depletion region, the phase-separating structure was anisotropic; cylindrical domains perpendicular to the glass surface were dominant.

Overall dynamics and morphology were governed by the bicontinuous nature, which was confirmed by analyzing the time evolution of characteristic length of the morphology, $\Lambda_m(t)$, and structure factor, $S(x,t)$. Time evolution of $\Lambda_m(t)$ in the DPB-PB blend ($D \cong 55$ μm) was found to be *almost identical* to that of the DPB-PB blend made of the same constituent polymers but having different thickness ($D \cong 200$ μm). $S(x,t)$ fell nicely onto a single master curve until $t \cong 9000$ min.

After $t \cong 9000$ min, $S(x,t)$ of the DPB-PB mixture ($D = 55$ μm) started deviating from the master curve. Interfacial area per unit volume, $\Sigma(t)$, and interfacial curvature distributions, $P(H,K;t)$, both characterizing the local features of the phase-separating structure, exhibited this structural change dramatically. The power law behavior of $\Sigma(t)$ changed from $\Sigma(t) \sim t^{-1}$ to $\Sigma(t) \sim t^{0}$ and $P(H,K;t)$ deviated from the master curve. Thus, from the time evolution of various structural parameters, we conclude that the self-similar growth of the bicontinuous structure broke down and the occurrence of this event was ca. 9000 min ($\tau \cong 630$). We call this phase-separation time t_{tr}. It is quite intriguing that a scaled thickness, D/Λ_m, approached unity at t_{tr} [see Fig. 5(b)]. In other words, the DPB-PB blend began ‘‘feeling’’ the container wall and kinetics of the phase separation changed when the characteristic length of the bicontinuous structure reached the thickness of the sample. Together with the LSCM 3D images, at $t \cong t_{tr}$, it was found that the phase-separating structure transformed from the bicontinuous structure to the columnar structure, i.e., tubes bridging the wetting layers.

Note that the local characteristics such as $\Sigma(t)$ and $P(H,K;t)$ were more sensitive measures of the effect of confinement than the global characteristics, $\Lambda_m(t)$ and $S(x,t)$. Therefore, in most of the existing studies that used the global structural parameters alone to characterize the kinetics of SD, the effects had not been evident.

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