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Dimensional Crossover in the Phase Separation Kinetics of Thin Polymer Blend Films

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The kinetics of phase separation in thin polymer blend films of polystyrene and polybutadiene on a silicon substrate is examined by optical microscopy of the free film boundary. Our observations on 1000 and 200 Å films are consistent with a crossover from three- to two-dimensional spinodal decomposition kinetics in the (off-critical) viscous hydrodynamic regime. In this stage of phase separation the exponent n, characterizing the scale $R(t) \sim t^n$ of the coarsening pattern, is predicted to change from 1 to a value near 0.46 upon lowering the dimensionality. [S0031-9007(96)00326-2]

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Many previous studies have considered the influence of confinement on the equilibrium phase separation temperature of thin films [1,2] and of spatial dimensionality on the kinetics of spinodal decomposition [3]. The present study involves a combination of these factors. We examine the effect of finite film thickness on the kinetics of spinodal decomposition in a film thickness range where a transition from three-dimensional bulk-like to near two-dimensional kinetics is anticipated.

Recent measurements on phase separating polymer blend films have shown that interfaces can induce the development of composition waves (normal to interfaces) whose scale coarsens with time [4,5]. However, Krausch *et al.* [4] have shown that this "surface directed spinodal decomposition" is *suppressed* in sufficiently thin blend films [5(a)–5(c)] and, accordingly, we constrain our films to a thickness range which avoids this type of phase separation. Oscillatory composition waves are suppressed in films thinner than a characteristic thickness L_c on the order of the "spinodal wavelength" $L_c \sim O(1000\ \text{Å})$ in the measurements of Krausch *et al.*, and we expect a similar order of magnitude L_c in our measurements. We also choose a binary mixture for which one component has an affinity for both film interfaces [5(b),5(c)]. Having one component attracted weakly to both boundaries inhibits phase separation into layers. These special circumstances should allow for a study of "quasi-two-dimensional" spinodal decomposition.

Theoretical and numerical investigations of the early stages of phase separation in idealized fluid mixtures in $d = 2$ and $d = 3$ dimensions exhibit little sensitivity to dimensionality, apart from a dependence of the phase separation temperature and fluid transport properties on dimensionality effects which influence the coarsening rate. At an intermediate stage of phase separation, the critical binary mixture coarsens by diffusive (surface or bulk) growth processes $R(t) \sim t^{1/3}$, and a bicontinuous spinodal structure gradually evolves in the fluid mixture in a fashion similar to solid alloy mixtures [6]. Dimensionality effects become apparent in the later stages of fluid phase separation where the pattern coarsening is driven by surface tension counterbalanced by viscous forces. Siggia and McMaster have shown that this late stage coarsening leads to a growth of the pattern scale $R(t)$ with time as $R(t) \sim t^n$ where $n = 1$ in $d = 3$ [7]. They offer an intuitive picture of this coarsening process in terms of the development of capillary waves on the locally cylinder-like bicontinuous spinodal phase separation pattern [7]. The peculiarities of fluid hydrodynamics in $d = 2$ can be expected to significantly alter the late stage coarsening in $d = 2$, however. The Rayleigh-Tomotika [7(c)–7(e)] liquid thread instability *does not exist* in $d = 2$ and San Miguel *et al.* [3(b)] suggest that the corresponding fluid "ribbons" obtained in two-dimensional spinodal decomposition break up by a diffusive process, leading to $n = 1/2$. There have been no previous experiments in near-two-dimensional systems which have confirmed this scaling in the viscous hydrodynamic regime.

It is difficult to study late stage coarsening by molecular dynamics simulation [8], but recent Langevin model calculations by Wu *et al.* [3(a)] have shown that the late stage coarsening exponent n in two-dimensional mixtures equals $n = 0.46 \pm 0.02$ in off-critical quenches of fluids having sufficiently strong hydrodynamic interactions. These off-critical observations are relevant to the present investigation since the preferential attraction of one of the blend components for the boundaries tends to push the composition of the film interior somewhat off-critical from its original near-bulk critical composition. Here we investigate whether a crossover in the late stage kinetics (i.e., the n exponent) from the familiar pattern exhibited in $d = 3$ to the form predicted numerically for $d = 2$ by recent simulation [3(a)] is found in thin blend films.

In this Letter we report optical microscopy (OM) measurements on phase separating blend films of deuterated polystyrene (PSD, $M_w = 1000$ g/mol, $M_w/M_n = 1.13$) and polybutadiene (PB, $M_w = 5300$ g/mol, $M_w/M_n = 1.07$). Thin film blend samples were cast on a 5 cm dia × 5 mm thick polished silicon substrate by spin coating from toluene solutions of the blend. Prior to spin coating, the silicon substrate was cleaned in a bath of 70% H_2SO_4/30% H_2O_2 for one hour at 80 °C, rinsed in deionized water, and subjected to a 2% HF solution for 2 min, and then rinsed again [9]. For this investigation, PSD/PB blend films having bulk critical composition (75% PSD/25% PB by weight, volume fraction of PSD ≈ 0.7) were studied [10]. Phase separation kinetics of films of three different thicknesses were investigated. An approximately 1000 Å film was prepared by spin coating from a 2 wt% blend solution at 2000 rpm, while a film of thickness ≈2000 Å film was cast from 2.4 wt% solution spun at 1500 rpm. In order to minimize sampling error between the different films due to variations in substrate characteristics the *same* silicon substrate (appropriately cleaned and etched) was used for each freshly prepared film. (As cast all films appeared homogeneous under the optical microscope and the film thicknesses cited above were determined by x-ray reflectivity measurements on the freshly cast films.) Each film was placed under quiescent conditions at ambient (25 °C) temperature, and their temporal pattern evolution at the free boundary observed and imaged by OM using a Nikon Photo Opt reflection camera equipped with automatic exposure settings [11]. Subsequently, these OM micrographs were digitized by a scanner and 2D fast Fourier transforms (FFT) were taken for a square area whose dimensions were kept constant. A radial average of the FFT transformed data exhibited a maximum intensity at a characteristic wave vector $q^*(t)$.

The kinetics of phase separation in bulk (≈200 μm thick) blend samples of PSD/PB was previously examined by temperature-jump light scattering [10] and the binodal and spinodal curves obtained from these measurements are given in Fig. 1. The bulk critical temperature was estimated to be 51 °C at the critical polystyrene composition $\phi_{\mathrm{PSD}} = 0.7$. Since the critical temperature can be expected to shift for such thin films [1,2], we performed cloud point measurements on the blend films by monitoring the intensity of light scattered from the blend film surface [12]. The cloud point was higher than 45 °C for both films, so the shifts involved must be modest for the present measurements [12]. The bulk glass transition temperature (T_g) was obtained using differential scanning calorimetry (DSC) measurements [10] and T_g as a function of PS composition is indicated in Fig. 1. Previous studies of finite size effects on the glass transition of polystyrene on differently prepared silicon surfaces have indicated both a decrease as well as an increase of T_g in thin films having a free polymer-air interface [13]. While these effects complicate a comparison between the rates of phase separation in the bulk and thin film blends, they should not alter the general kinetic pattern of phase separation [14], which is the subject of the present paper. Note that the temperature of the experiment corresponds to a temperature well within the unstable regime for all the blend film samples.

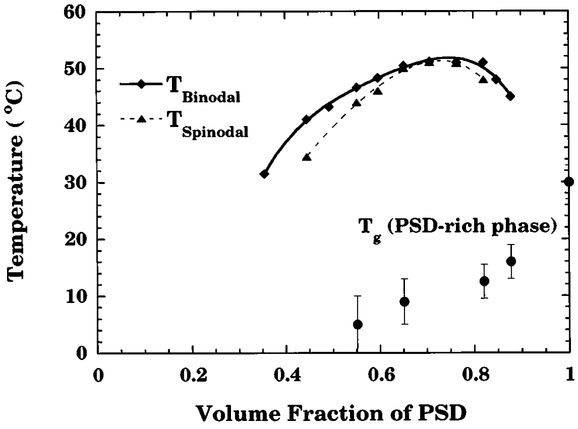

FIG. 1. The upper curves correspond to the bulk binodal (—) and spinodal (----) curves for PSD/PB samples. The variation of the bulk glass transition temperature with ϕ_{PSD} is also shown. Data in this figure are taken from Sung and Han [10].

Figure 2 shows the time development optical micrographs of the surface pattern formation associated with the phase separation within the 200 Å film where the scales of observation are indicated by reference bars. The phase separation of the 1000 Å film is morphologically similar.

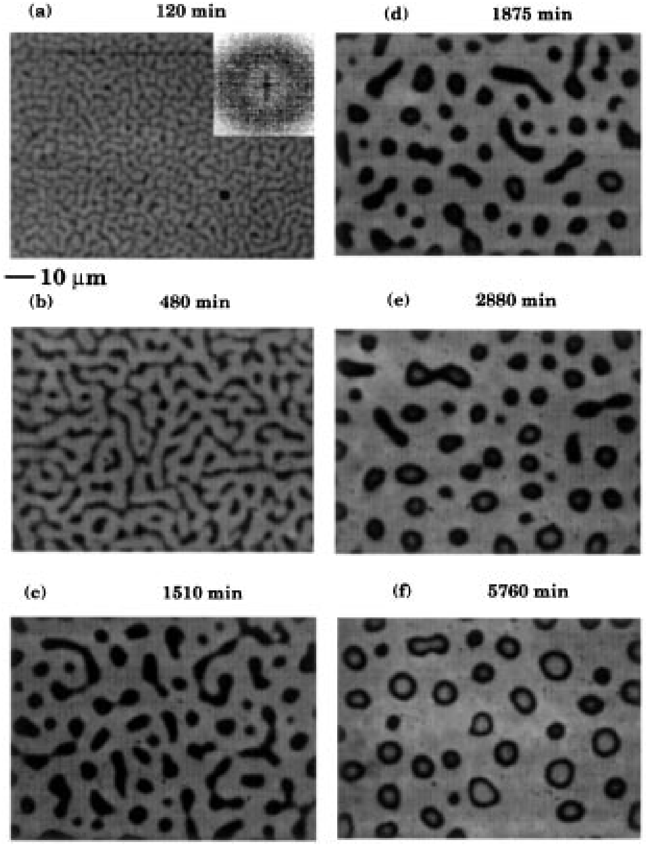

FIG. 2. Time development optical micrographs of the surface pattern development associated with the phase separation of a PSD/PB blend film. The film thickness after spin casting on a silicon substrate at 25 °C is about 200 Å. A bar indicates the scale for each micrograph. Inset in (a) shows a numerical FFT image (spinodal ring) corresponding to the optical image at 120 min.

For the 1000 Å film it was also possible to image the early stage of phase separation where the clusters of the incipient bicontinuous spinodal decomposition structure first form. This "spinodal structure" coarsens in the intermediate stage and in the late stage the bicontinuous structure breaks up [7] and the fragments rearrange to form an array of regularly spaced and sized surface features. The intermediate and late stage regimes are evident for the representative 200 Å images shown in Fig. 2. These images of the phase separating film certainly have the appearance of spinodal decomposition with a late stage "pinning" process associated with the finite film thickness.

We next examine the surface pattern formation as if it corresponded to spinodal decomposition and compare the results obtained to bulk observations and two-dimensional spinodal decomposition calculations. The inset of Fig. 2(a) shows a typical FFT for the 200 Å film image after 120 min. The peak maximum q^* from the radially averaged FFT pattern (intensity plots not shown) for the 1000 and 200 Å films is shown in Fig. 3. A distinctive pattern of behavior is observed. The thicker 1000 Å film exhibits a diffusive (bulk) pattern growth [6], followed by a slope near unity appropriate for the surface tension driven viscous flow coarsening regime [7] and finally the pattern becomes "pinned" at a scale near 20 μm (see Ref. [15]). It is likely that this pinned state is a long lived metastable state as found in recent simulations of phase separation in capillaries [16], but it is difficult to confirm this possibility given the slow structural evolution in this late stage regime. The insert in Fig. 3(a) indicates the coarsening for bulk samples at 40 °C by temperature-jump light scattering [10]. This comparison shows that the pinning has its origin in the finite film thickness. Note also that the occurrence of pinning makes the inertial stage of phase separation inaccessible.

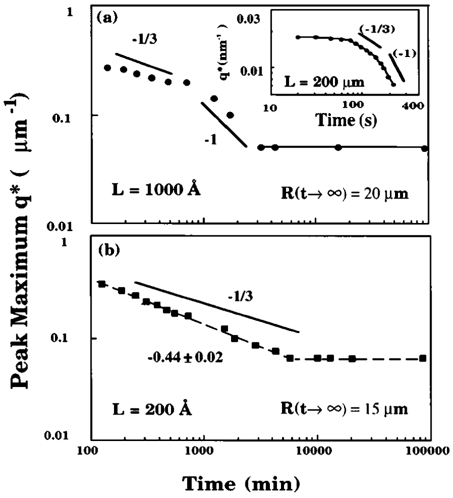

FIG. 3. Kinetics of surface pattern coarsening. (a), (b) The variation of the intensity peak maximum q^* from the radially averaged FFT for the 1000 and 200 Å films, respectively. q^* characterizes the inverse scale of the coarsening surface pattern as a function of time t for the 1000 Å film $[R(t) = (q^*/2\pi)^{-1}]$. The time dependence of q^* in the "bulk" (200 μm film) is shown in the insert. Error estimate of exponent is obtained from a least-squares fit and does not reflect systematic errors. The thickness of the films has been chosen to be $\leq$ the characteristic scale L_c below which surface-directed spinodal decomposition becomes suppressed [4]. The effective dimensionality of the film phase separation process should be defined in relation to the initial film thickness relative to L_c rather than the final "pinned" film pattern size.

The coarsening kinetics shown in Fig. 3(b), corresponding to the 200 Å film, is strikingly different from the 1000 Å film. Although the early stage development is difficult to detect due to poor optical contrast, we observed a scaling of pattern size $R(t) \sim t^n$ over nearly 2 orders of magnitude in time for the viscous coarsening regime with an exponent $n = 0.44 \pm 0.02$. This regime is followed by pinning at a scale near 15 μm which is similar, but somewhat smaller than the scale found in Fig. 3(a). The observed exponent n for our thin blend film coincides within numerical uncertainty with recent numerical estimates of n for this coarsening regime obtained by Wu *et al.* [3(a)]. The data of Fig. 3 are consistent with a crossover from bulk-like three-dimensional type phase separation to near two-dimensional hydrodynamic coarsening.

A different pattern of phase separation can be anticipated in blend films having an initial thickness L larger than a scale for which surface-directed spinodal decomposition becomes suppressed, $L_c \sim O(1000\ \text{Å})$. [It is presently unclear to us whether L_c depends on the bulk spinodal wavelength alone [4] [see inset in Fig. 3(a)] or a surface correlation length reflecting the boundary interaction.] Recent theory [5(a)] and experiments on thicker films [4,5(b)] (typically $L \geq 1/2\ \mu$m) show the development of layers parallel to the solid interface, at least in the earlier stages of the phase separation process. This rather different type of phase separation within the blend film can be expected to influence surface pattern formation. We made a preliminary examination of this effect by preparing a relatively thick 2000 Å film (compared to L_c) and monitoring the surface pattern kinetics. The surface of the 2000 Å film at room temperature was observed to be almost featureless over an extended period of time ($\approx$2 days). Evidently, the large scale coarsening within the 2000 Å thick film does not reflect itself in the optical micrographs which revealed predominantly the surface features of the film. Further study of this interesting phenomenon is required (especially neutron reflection) to determine if they very different observations for the thicker film are a consequence of layering due to surface-directed spinodal decomposition or simply a diminished surface pattern formation in thicker films.

The optical microscopy study of PSD/PB blend phase separation does not allow us to infer the nature of the phase separation normal to the solid interface. Some information about this process can be obtained from a recent complementary study of phase separation within PS/PVME films

($L \leq 1000$ Å) by neutron reflection and atomic force microscopy (AFM) [17]. The AFM micrographs were qualitatively similar to the present study of PSD/PB blend films, but a time resolved study of phase separation in the plane of the solid interface not yet been performed due to measurement difficulties at high temperatures. The neutron reflectivity measurements [17] on phase separation transverse to the solid interface showed a relatively rapid phase separation normal to the silicon interface leading to a buildup of PVME at both the silicon and air interfaces, but no oscillatory composition waved developed within these thin films (see also Krausch *et al.* [4]). Optical microscopy and AFM measurements showed that phase separation within the plane of the film occurred over much longer time scales. We expect that neutron reflection and AFM studies of PSD/PB blend will lead to a very similar picture for the 2000 Å film where surface directed composition waves are expected, as in previous studies of phase separation in relatively thick films [4]. Studies of the late stage coarsening within these films should be especially interesting to determine if there is a relation between "fast mode" phase separation kinetics, observed previously [18] in relatively thick films [$L \sim O(1\ \mu\text{m})$], and surface-directed spinodal decomposition [5]. Perhaps the "fast mode" is associated with the breakup of the layer-like rather than tube-like structure arising in this type of phase separation?

In summary, we have prepared blend films sufficiently thin to suppress the development of composition waves away from the surface. The 1000 Å films is found to be sufficiently thick to exhibit phase separation kinetics similar to bulk blends, albeit with a modified time constant for coarsening associated with a small shift of the phase boundary and presumably the glass transition temperature due to finite size effects. The thinner film ($L \approx 200$ Å) exhibited a different phase separation kinetics, however. Although the structures observed on the surface of these films resemble one another and also structures found in simulations of bulk phase separation [10], the coarsening exponent n in the surface tension driven hydrodynamic regime for the thin film ($L \approx 200$ Å) is found to equal $n = 0.44 \pm 0.02$, which accords with recent numerical estimates of n for this regime (off-critical) in two dimensions [3(a)]. At present it is not clear whether the n exponent in the thin blend film and the numerical simulations is a true exponent or an effective exponent reflecting a crossover between intermediate and late stage regimes, but the resemblance between the numerical simulations and our measurements is striking. It is notable that the scaling of $R(t)$ with t is obtained for about two decades in time which suggests to us that n is a true exponent.

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