Real Space Observation of Dynamic Scaling in a Critical Polymer Mixture

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We have studied the growth of the wetting layer formed at the surface of a critical mixture of poly(ethylene propylene) and perdeuterated poly(ethylene propylene) during spinodal decomposition. The wavelength of the surface spinodal wave is found to grow as $t^{1/3}$ over the entire range of times accessible in the experiment. The composition profiles exhibit universal scaling behavior in the near-surface region. These results are in excellent agreement with a recent numerical study on surface-directed spinodal decomposition.

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When a binary mixture is quenched from a single homogeneous phase to a point inside the spinodal curve, spontaneous phase separation takes place. For bulk systems, this process has been extensively studied in the past both by theory and experiment [1–6]. Several distinguishable time regimes during the evolution of bulk spinodal decomposition are now well established. The initial stage is described by the linear theory of Cahn, Hillard, and Cook, while at later times nonlinear effects become dominant and a scaling description is applicable, where the average size of the domains $R(t)$ is the only relevant length scale in the system. In this regime, $R(t)$ is found to grow like $R(t) \sim t^{1/3}$. For fluid mixtures, however, hydrodynamic effects become important at later times and the growth law is found to change to $R(t) \sim t$ in the so-called final stage of spinodal decomposition.

Only recently, it has been recognized that in the vicinity of a symmetry breaking surface the process of spinodal decomposition may be severely altered as compared to the bulk behavior [7]. If one of the two components of the mixture is preferentially attracted to the surface, a quite anisotropic evolution of the phase separation is expected to occur in the near-surface region. This was first observed experimentally by Jones *et al.* [8] who found an oscillatory composition profile near the surface of an isotopic polymer mixture after a quench into the two-phase region. Meanwhile, different theoretical studies have focused on this effect [9–11], aiming toward a detailed understanding of the time dependence of the spinodal decomposition close to an attractive wall. For sufficiently deep quenches, both simple scaling arguments [10] and coarse-grained order parameter simulations [10,11] predict a $t^{1/3}$ growth of the wetting layer thickness at later times, closely resembling the bulk behavior. In addition, the composition profiles perpendicular to the wall are expected to show scaling behavior; i.e., they should collapse onto a unique master curve when rescaled with the actual wetting layer thickness. In contrast to these clear and unanimous theoretical results, the experimental data on surface-directed spinodal decomposition are still rare and an unambiguous analysis of the time dependence of the "surface spinodal wave" is still lacking. In this Letter, we present the first experimental evidence for both a power law growth of the wetting layer thickness $l(t)$ during spinodal decomposition and a scaling behavior of the respective composition profiles. We find that the thickness $l(t)$ grows as $l(t) = a + bt^{1/3}$ for all times accessible in our experiments. Furthermore, the composition profiles fall onto a unique master curve when rescaled with respect to $l(t)$. These results are in excellent agreement with the theoretical predictions of surface-directed spinodal decomposition quoted above.

The system under consideration is a symmetric binary mixture of poly(ethylene propylene) (PEP) and its deuterated analog (dPEP) with nearly equal index of polymerization ($N_{\mathrm{PEP}} = N_{\mathrm{dPEP}} = 2286$). The polymers were synthesized and characterized following standard procedures [12]. The substitution of hydrogen by deuterium results in a small positive interaction parameter χ, reflecting the differences in bond length and polarizability between the C-H and the C-D bonds, respectively [13,14]. For sufficiently long chains, this leads to a miscibility gap in the phase diagram, characterized by an upper critical solution temperature $T_c = 365(2)$ K, below which phase separation may occur. The deuteration as well leads to a small difference in surface energy between the two isotopic species; the deuterated component therefore tends to segregate to the polymer/vacuum interface [15].

Thin PEP/dPEP films with nearly critical composition ($\Phi = \Phi_c \approx 0.5$) were prepared by spin casting from toluene solution. The thickness of the films was kept well above 2000 nm. The samples were annealed under vacuum for various times at 296(1) K and 321(1) K, respectively. These annealing temperatures correspond to reduced quench depths of $0.81 T_c$ and $0.87 T_c$. The volume fractions of the two components were determined as a function of depth perpendicular to the film surface by

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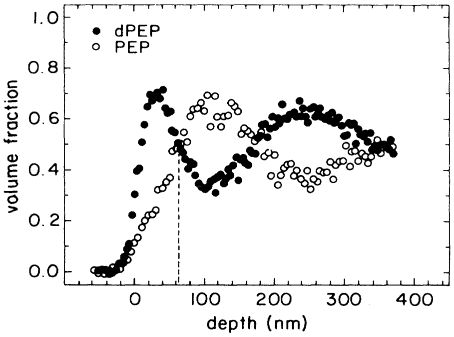

FIG. 1. Volume fraction vs depth profiles for both dPEP (●) and hPEP (○) as determined by TOF-FRES. The film was annealed for 4 h at 321 K. The dashed line corresponds to the thickness $l(t)$ (see text). The data are cut at about 370 nm in order to avoid any overlap of the deuterium and hydrogen signals in the energy spectra.

time-of-flight forward recoil spectrometry (TOF-FRES). TOF-FRES is based on conventional forward elastic scattering, where hydrogen and deuterium nuclei are elastically scattered from an incident ^{4}He beam impinging on the sample at a small angle. The energy of the scattered particles is recorded and readily converted into a depth scale using tabulated values for the specific energy loss of the particles on their path through the sample. In addition to the energy we determine the flight time of the scattered particles; this enables us to distinguish between the different hydrogen isotopes and the large flux of elastically scattered ^{4}He and circumvents the need for a stopper foil conventionally used in FRES experiments [16]. Since straggling in the stopper foil is avoided, the depth resolution of TOF-FRES is limited only by the finite energy resolution of the solid state detector; with the present setup, we achieve a depth resolution of about 23 nm (full width at half maximum) at the film surface. In addition, we use the flight time information to gate the data acquisition system such that any overlap between the energy spectra of deuterium and hydrogen is avoided. While this arrangement restricts the accessible depth range of the technique to some 400 nm, it enables us to monitor unambiguously both hydrogen and deuterium in the near-surface region even in very thick samples. This feature shall be crucial for the present study.

In Fig. 1 we show composition vs depth profiles for both dPEP and PEP near the surface of a sample quenched for 5 h at 321 K. A dPEP-rich layer is formed at the surface followed by a damped oscillatory composition profile extending into the film. For both quench depths investigated in the present study, the evolution of the composition waves has been monitored as a function of time after the quench. While the amplitude of the oscillation is found to saturate quite rapidly, the wavelength of the oscillations continuously increases with time, reflecting a coarsening of the phase morphology similar to the bulk behavior. In order to quantify this effect, we

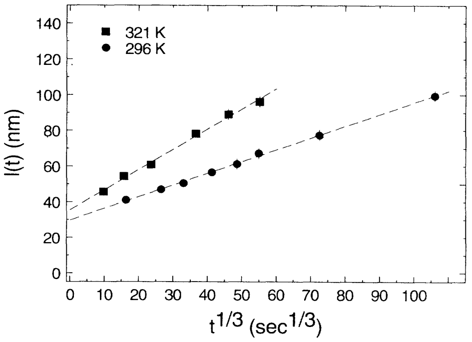

FIG. 2. Thickness of the wetting layer as determined from the point where both Φ_{dPEP} and Φ_{PEP} are equal to the average composition for the first time (see Fig. 1). The dashed lines are least-squares fits to the data assuming $l(t) = a(T) + b(T)t^{1/3}$.

determine the thickness $l(t)$ of the dPEP-rich surface layer as a function of time. We define $l(t)$ as the depth where the volume fractions of the two species are equal for the first time, i.e., $\Phi_{\mathrm{dPEP}} = \Phi_{\mathrm{PEP}} = 0.5$. The additional requirement that at $l(t)$ both Φ_{PEP} and Φ_{dPEP} match the average composition of the sample serves as an independent test of the proper correction for differences in cross section and detection efficiency between hydrogen and deuterium, thereby minimizing possible ambiguities in the determination of $l(t)$ [17]. In Fig. 2 the results of this analysis are shown. For both quench depths studied, the data are well represented by $l(t) = a(T) + b(T) \cdot t^{\alpha}$ over the whole time range accessible in the experiment. From least-squares fits we find exponents $\alpha = 0.32(1)$ ($T = 296$ K) and $\alpha = 0.30(2)$ ($T = 321$ K), respectively. These values strongly indicate a $t^{1/3}$ growth law for the wetting layer thickness. The dashed lines in Fig. 2 correspond to linear least-squares fits assuming a fixed value of $\alpha = 1/3$.

These results are in good agreement with a recent numerical study of the growth of the wetting layer during the process of spinodal decomposition. In a two-dimensional model, Brown and Chakrabarti [11] determined the order parameter profile parallel and perpendicular to the surface of an incompatible binary mixture after a quench into the two-phase region. Assuming that one of the components is preferentially attracted to the surface, they find characteristic oscillations of the order parameter, which eventually decay as one moves from the surface into the bulk. Taking the first zero of the order parameter as a characteristic measure of the wetting layer thickness, the authors find a $t^{1/3}$ growth law for both deep and shallow quenches. The lateral growth of the surface domains follows the same power law, yet with a different prefactor. Quench depths of $0.85T_c$ and $0.5T_c$ were studied, the former being quite close to the situation realized in the present experiments. Based on their finding that all relevant lengths in their study grow as $t^{1/3}$, Brown and Chakrabarti could show that the density

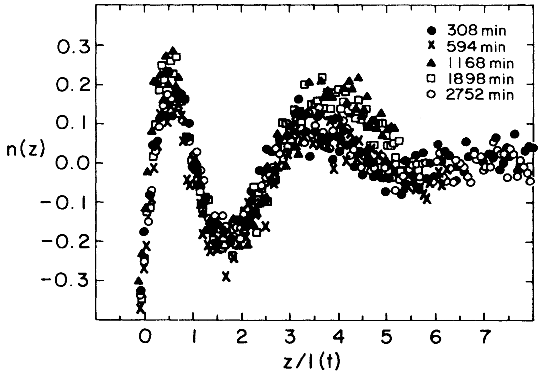

FIG. 3. Deviation of the dPEP volume fraction from its average value, rescaled by the wetting layer thickness $l(t)$ according to Eq. (2) for quenches at 296 K at different times: 308 min (●), 594 min (×), 1168 min (▲), 1898 min (□), 2752 min (○).

profiles exhibit scaling behavior and fall on a single master curve when rescaled by the actual thickness of the wetting layer at a given time t, i.e.,

$$n(z)=n[z/l(t)]\,, \tag{1}$$

where n is the order parameter and z is the distance perpendicular to the surface. In order to test this hypothesis with the present experimental data, we may plot the deviation of the dPEP volume fraction from its average value and rescale the depth by the values for $l(t)$ obtained above (Fig. 2); i.e., we determine an experimental order parameter

$$n(z)=\Phi[z/l(t)]-0.5\,. \tag{2}$$

The result of this procedure is shown in Fig. 3. For either quench depth, the data fall nicely onto a universal curve in the near-surface region; however, deviations are observed farther away in the bulk. This behavior again is in agreement with the results of Ref. [11], where scaling was found to work less well at depths farther than about one wavelength away from the surface. As one proceeds into the bulk, the growth of bulk domains becomes increasingly important, and $l(t)$ may no longer be regarded as the dominant length scale of the system. This finding is corroborated by the fact that, given the particular strength of the surface fields and the respective temperatures, the oscillatory composition profiles decay over about one wavelength.

We may compare the above findings to earlier investigations of surface-directed spinodal decomposition. The first experimental evidence for the occurrence of a "surface wave" during the process of spinodal decomposition in thin films was given by Jones *et al.* [8], who investigated the identical polymer mixture with conventional forward recoil scattering. However, the poor spatial resolution of this technique together with the fact that rather thin films were studied did not allow an unambiguous investigation of the surface layer growth. As a matter of fact, in a recent study on the thickness dependence of the spinodal decomposition in thin films we were able to observe interference effects of the two spinodal waves originating from the film surface and the film/substrate interface [18]. As a result of this interference, the phase morphology of the entire film is found to be severely influenced by the presence of the substrate surface. Bruder and Brenn [19] reported a study on surface-directed spinodal decomposition in blends of poly(styrene) and partially brominated poly(styrene); their study, however, aimed at understanding the equilibrium structure after sufficiently long annealing times and no detailed investigation of the time dependence was carried out. Finally, we shall mention a recent study by Cumming *et al.* [20], who investigated the spinodal decomposition in critical mixtures of low molecular weight poly(isoprene) and poly(ethylene propylene) by both light scattering and optical microscopy. Besides the $t^{1/3}$ growth of bulk domains the authors observed a "fast mode" with a characteristic length following a $t^{3/2}$ behavior, which was attributed to the lateral growth of surface domains. However, only very shallow quenches were studied and the final temperature was always well within the fluctuation regime. In contrast, both in our experiments and in the theoretical study mentioned above, much deeper quenches were investigated where mean field behavior can be expected.

In summary, we have investigated the growth of the wetting layer during the process of spinodal decomposition of a binary polymer mixture. The use of rather thick films together with the particular advantages of the TOF-FRES technique enabled us to unambiguously establish a power law dependence; i.e., the thickness of the wetting layer was found to grow as $t^{1/3}$ for all times and temperatures studied. Furthermore, the growth of the surface layer exhibits dynamic scaling behavior with the composition profiles collapsing onto a single master curve when rescaled with respect to the actual wetting layer thickness. This finding can be attributed to the existence of a unique length scale characterizing the process of surface-directed spinodal decomposition. The experimental findings are in excellent agreement with recent theoretical predictions.

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