Surface-Directed Spinodal Decomposition

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The spinodal decomposition of mixtures of poly(ethylenepropylene) (PEP) and perdeuterated poly(ethylenepropylene) (d-PEP) has been studied near the surface using forward-recoil spectrometry. Instead of the composition waves with randomly oriented wave vectors (and random phases) found in the bulk, we observe composition waves with wave vectors normal to, and which propagate inwards from, the surface, maintaining coherence for several wavelengths. We argue that these surface-directed spinodal decomposition waves are caused by the preferential attraction of the d-PEP to the surface.

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The spinodal decomposition of a binary mixture following a rapid quench to an unstable state from a homogeneous solution has been extensively investigated.[1-5] In the bulk fluids, of which polymer melt blends are a particularly convenient special case,[6-10] the unstable state decays by the growth of long-wavelength fluctuations with randomly directed wave vectors leading to a characteristic interconnected phase morphology and a structure factor which is isotropic with a broad peak at a wave number q_m. As time proceeds after the quench, the magnitude of this peak grows and q_m shifts toward zero as the structure coarsens, but the structure factor remains isotropic.

The presence of a surface, however, may alter the course of this spinodal decomposition, by breaking the translational and rotational symmetry. Within a certain coherence length of the surface, such broken symmetry may cause the spinodal waves to grow with a dominant wave vector directed normal to the surface and a definite phase relative to it. Recent theoretical work[11] predicts such surface-directed spinodal decomposition when the symmetry is broken by the attraction of one of the components to the surface. In this paper we give the first experimental evidence for such surface-directed spinodal decomposition.

We investigate a mixture of the isotopic polymers poly(ethylenepropylene) (PEP) and perdeuterated poly(ethylenepropylene) (d-PEP). These polymers have essentially identical polymerization indices $N_H \approx N_D = N = 2286$, and were synthesized and characterized by standard methods.[12] Mixtures of deuterated and protonated polymers are not ideal,[13] but have a small posi-

tive segment-segment interaction parameter χ, which is almost entirely enthalpic in origin, due to the C-D bond having a smaller length and polarizability than the C-H bond; e.g., for symmetric isotopic polymer mixtures, $\chi \approx AT^{-1}$, where A is a constant.[14] For large enough N's therefore the mixture will separate into two phases on cooling below a critical temperature T_c, that was determined to be 92.4 °C (±1.5 °C) for these d-PEP/PEP mixtures. Over all but a narrow temperature range around the critical point polymer-polymer thermodynamics can be described by mean-field theory[15] so that the mean-field critical value of $\chi_{c,MF}$ is the appropriate parameter for defining quench depth.[16] The same difference in bond length and polarizability that leads to phase separation also causes the surface energy of the deuterated hydrocarbon to be slightly less than its protonated counterpart, thus providing a driving force for preferential segregation of the deuterated polymer to the surface.[17-19]

Uniform, 9000-Å-thick films with d-PEP volume fraction $\varphi = 0.5$ (the critical composition) were spun cast from toluene on silicon wafers. These films were then annealed in vacuum at temperatures between room temperature and T_c for various times t to initiate spinodal decomposition. A major advantage of the polymer mixture for these experiments is that the diffusion coefficient is small enough ($\ll 10^{-13}$ cm^2/s) that the spinodal decomposition is very sluggish and the film does not begin to decompose until the annealing temperature has been reached.

We measure the volume fraction versus depth profile of the mixture using forward-recoil spectrometry

(FRES), which gives a lateral average over several square millimeters of the surface.[20,21] If the spinodal decomposition near the surface were to proceed with an isotropic wave vector q, because of this lateral averaging FRES should reveal φ to be constant with depth, except for a surface layer that would be enriched in d-PEP because of its lower surface energy. To the contrary, at annealing temperatures of 35 and 76 °C, which correspond to reduced quench depths $\varepsilon = (\chi - \chi_{c,\mathrm{MF}})/\chi_{c,\mathrm{MF}}$ of 0.200 and 0.059, respectively, we observe wavelike composition profiles; some of those at 35 °C are shown in Fig. 1. The
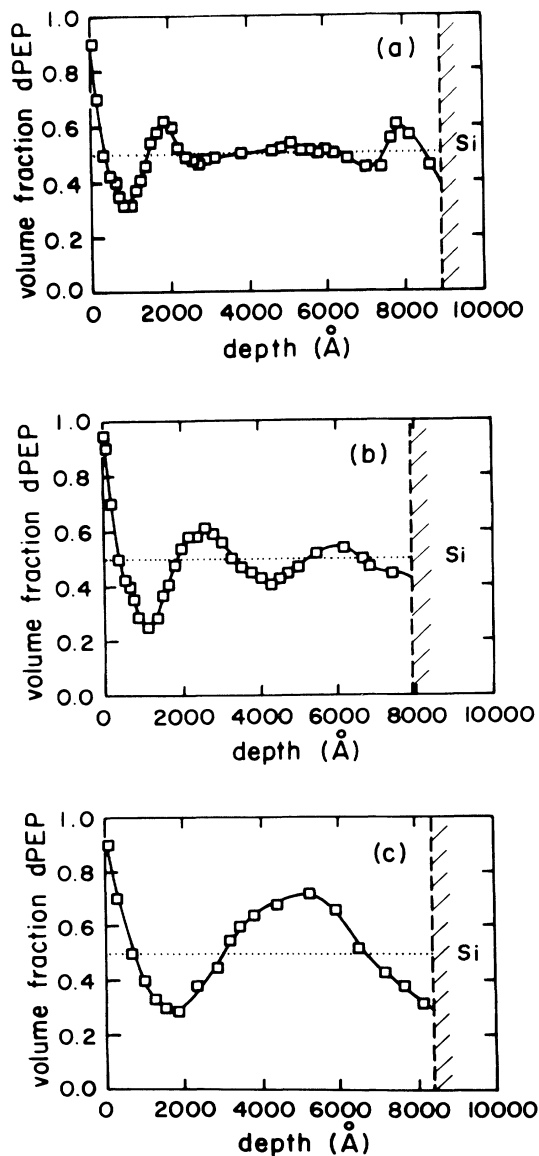

FIG. 1. Volume fraction vs depth profiles of d-PEP in an initially uniform mixture with a d-PEP volume fraction of 0.5 after aging at 35 °C for (a) 19 200 s, (b) 64 440 s, and (c) 172 800 s.

surface of the polymer melt is indeed enriched in d-PEP but $\varphi(z)$ shows a damped oscillation with depth z from the surface which grows with time and whose wavelength increases with time.[22] We believe this damped oscillation is the result of surface-directed spinodal decomposition.

To test this hypothesis we have computed the Fourier transforms of the $\varphi(z)$ profiles,[22] that should be the analog for the film of the structure factors measured by light or x-ray scattering for bulk specimens. Each of these also shows a broad maximum at a wave number q_m ($= 2\pi/\lambda$, where λ is the wavelength along z), similar to the maximum observed in the isotropic scattering pattern from the bulk samples.

The value of q_m decreases with annealing time, as shown in Fig. 2, corresponding to the coarsening of the structure noted qualitatively above. These values can be compared directly with measurements of q_m on bulk samples of the same blend of d-PEP/PEP derived from light-scattering data at the same temperatures.[23] The dotted lines represent the values q_m [$= q_m(t=0)$] extrapolated to zero time after the quench. At short times the values of q_m of the oscillation approach those of the (isotropic) spinodal decomposition in the bulk; at short times the q_m for the more shallow quench (76 °C) is less than that for the deeper quench (35 °C) and the ratio of the short-time q_m's at the two temperatures is ~ 1.6, approximately the same ratio as that for the bulk (1.85). This correspondence is predicted by the analytical modeling and numerical simulations of Ball and Essery and is thus strong evidence that the volume-fraction oscillations in Fig. 1 are caused by surface-directed spinodal decomposition. However, as is clear from the direct
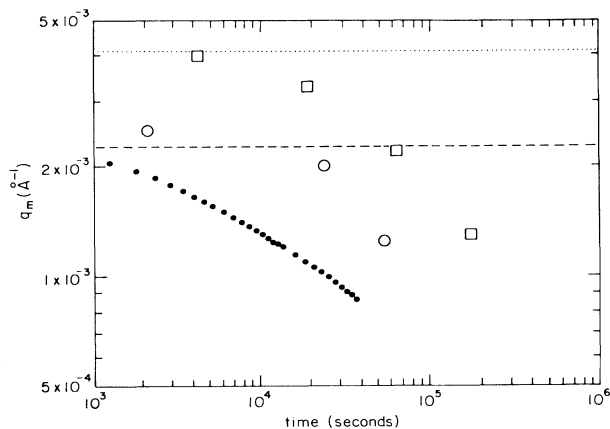

FIG. 2. Wave number of the peak in the Fourier transform of profiles like those in Fig. 1 after various aging times at 35 °C (squares) and 76 °C (open circles). The dashed and dotted lines correspond to the values of q_m at these temperatures from light-scattering measurements on bulk samples extrapolated to $t = 0$. The solid circles show the time-dependent value of q_m at 76 °C from the light-scattering measurements on bulk samples.

comparison between the bulk and surface data in Fig. 2, the composition waves of the bulk mixture seem to coarsen more rapidly with time. At any given q_m there appears to be a shift to longer times for the surface values by about a factor of 4.

It is of interest to see if reducing the wave numbers $[q_m/q_m(t=0)]$ and time $(\tau = t|D|[q_m(t=0)]^2)$ to scaling variables[9,10] results in superposition of the data since we can determine the mutual diffusion coefficient D from our measurements of the tracer diffusion coefficient D^* and the quench depth ε of the blends. (Inside the spinodal D is negative corresponding to diffusion against the concentration gradient and its magnitude at $\varphi = 0.5$ is given by $D = D^*\varepsilon$. FRES was used to measure D^* at several different temperatures from concentration versus depth profiles of thin films of partially deuterated PEP diffused for various times into PEP; the values were consistent with the time-temperature superposition shift factor a_T of PEP, measured by dynamic mechanical spectrometry.[24]) Figure 3 shows that a plot of these scaling variables fails to quantitatively collapse these data onto a master curve, mimicking the corresponding lack of bulk superposeability, also documented for another symmetric isotopic mixture.[9,10]

Finally, we can give a simple physical picture for how the surface-directed spinodal decomposition waves develop. It has been observed[25] that at compositions outside the coexistence curve, the growth of a surface enrichment layer is diffusion limited with the layer near the surface staying in local equilibrium with a region further below the surface that is depleted in the segregating component (in this case d-PEP). The kinetics of the
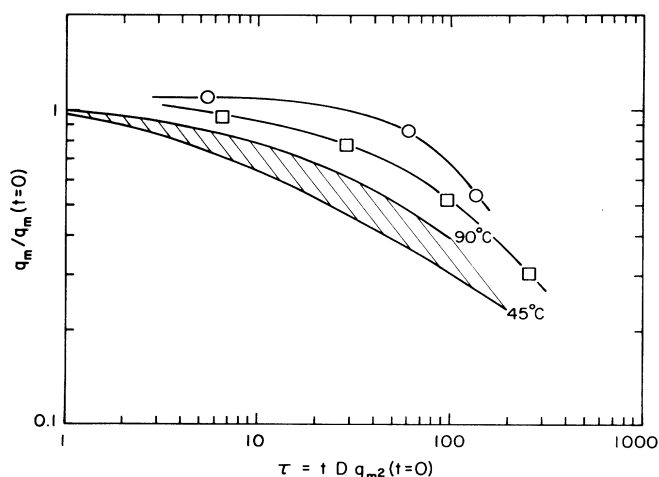
segregation are controlled by diffusion of the d-polymer down the diffusion gradient from the bulk composition to that in the depleted layer. As the enriched layer nears equilibrium, the diffusion gradient becomes smaller and smaller as the composition in the depleted layer approaches the bulk composition.

Now imagine what happens inside the spinodal. The initial results are rather similar as the enrichment of d-PEP at the surface inevitably leads to a layer below the surface depleted in d-PEP and a gradient from the bulk composition ($\varphi = 0.5$) into this depleted layer. However, inside the spinodal the mutual diffusion coefficient is negative, so that rather than gradually being erased as time proceeds, this gradient is consistent with recent optical observations of the layering of wetting and nonwetting phases of a small molecule fluid mixture at much later reduced times τ.[26]

In summary, we have shown for the first time that the preferential attraction of the surface for one of the components in a binary polymer mixture can lead to spinodal decomposition waves with a preferred wave vector normal to the surface and a phase such that the composition of the mixture is enriched in the preferred component at the surface. While many questions remain to be answered (e.g., How far do these coherent waves extend into the bulk before they break up into an isotropic structure?), the range of these waves is certainly large enough that they will affect many surface and near-surface properties. Nor does there seem to be any reason why surface-directed spinodal decomposition waves should be confined to polymer blends. One can imagine that similar waves should exist as well at the surface of metallic alloy crystals and inorganic glasses that undergo spinodal decomposition. The presence of such waves in solid systems may lead to interesting mechanical properties.

FIG. 3. Reduced plot of the peak position vs time at 76 °C (circles) and 35 °C (squares). The scaling variables $q_m(t=0)$ and D were determined from light-scattering measurements on bulk samples and FRES measurements of diffusion, respectively. The shaded area represents the behavior of the bulk mixture from light scattering with the extreme lines showing the data at 90 and 45 °C.

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[22] The silicon interface attracts the more polarizable PEP so that waves also originate from that interface. Here we focus on the structure near the vacuum interface as it can be more easily determined using FRES. To ensure this, the measured profile is damped by a factor $\exp\{-[z/(4000 \text{ Å})]^2\}$ before Fourier transformation. The q_m thus computed compare well with those estimated from the z values of the maxima and minima of the wave near the surface.

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