Spinodal Decomposition in Thin Films of a Polymer Blend

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Spinodal decomposition in thin films of a blend of deuterated polystyrene and poly(styrene-co-4-bromostyrene) was studied with time-of-flight–elastic-recoil detection and light microscopy. We found different demixing behavior, depending on whether the films were prepared on the oxide layer of a silicon wafer or on a chromium-plated one. On the latter surface a bilayer of the two bulk phases is formed, whereas on the oxide layer a domain structure remains. The formation of the bilayer is ascribed to the complete wetting of each surface by the corresponding, preferentially adsorbed component.

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Spinodal decomposition of a polymer blend has been the scope of much recent research work [1-3]. The development of the demixing structure with time has been monitored with light and neutron scattering techniques [4-7]. In the very early stage, fluctuations with a characteristic time-independent wave number q_m grow exponentially with time. This behavior is well understood by linearization of the equation of motion of the dynamic variable. In the intermediate stage the onset of nonlinear effects shifts the wave number q_m to lower values, mimicking the coarsening of the structure with time. When the fluctuations have reached their maximum amplitudes (i.e., the compositions on the binodal) in the transition stage the structure is characterized by two length scales, the mean distance between domains of the same composition $L_m \propto 1/q_m$ and the interfacial width of the domains. This width decreases until it reaches its equilibrium value. The final stage is characterized by the mean distance between domains L_m which grows by hydrodynamic flow, driven by the decrease of the interfacial tension, which means by flattening of the still rippled interfaces of the domains.

In thin films the translational and rotational symmetries are broken due to the presence of the two surfaces. This leads to an anisotropic structure factor, or in real space to a marked dependence of the related composition profile on the coordinate z normal to the surface. This fact shows up in the one-phase region of polymer blends or other fluid mixtures by an enrichment of one of the components at the surface [8-12]. There is presently much effort applied to studying these processes in isotopic mixtures of a homopolymer and its deuterated counterpart [13-15]. The preferential adsorption of the deuterated component can also lead to a damped oscillating concentration profile emerging from the surface, when the initially homogeneous mixture is quenched into the unstable region of the bulk phase diagram. Ball and Essery [16] have shown this theoretically for the early stage of spinodal decomposition. In a recent study Jones *et al.* [17] verified this prediction in an isotopic polymer blend where they observed an oscillating structure in the mean concentration profile $\Phi(z)$ with a mean wavelength increasing with time.

In this study we focus on more than just the early stages of demixing of polymer blends in thin films. We give the first experimental results of how surface interactions can influence and alter spinodal decomposition in thin films up to the final state.

We used blends of deuterated polystyrene (dPS) and poly(styrene-co-4-bromostyrene) (PBr$_x$S). In this blend the Flory-Huggins interaction parameter χ is positive and can be controlled by the degree of bromination x of the copolymer [18]. The blend was nearly symmetric, with degrees of polymerization of $N_{\mathrm{dPS}} = 1098$ and $N_{\mathrm{PBr}_x\mathrm{S}} = 1285$ and a degree of bromination $x = 0.119$. This blend shows an upper critical solution temperature. The phase diagram was measured by interdiffusion [19] in the temperature region of 160 °C up to 210 °C. The compositions of the coexisting phases on the binodal curve are $\Phi_B^{\mathrm{I}} = 0.15$ and $\Phi_B^{\mathrm{II}} = 0.87$ at a temperature of 180 °C. Φ is the volume fraction of the deuterated styrene segments in this blend. The χ parameter was calculated from these binodal compositions as 2.12×10^{-3}. According to the Flory-Huggins theory the critical parameter χ_C and critical composition Φ_C are 1.69×10^{-3} and 0.52. This gives a quench depth of $\epsilon = (\chi - \chi_C)/\chi_C = 0.254$. In the one-phase region of this blend ($\Phi < \Phi_B^{\mathrm{I}}$) we found an enrichment of the dPS at the vacuum surface. Its divergence at the binodal shows the complete wetting of this surface by the dPS-rich bulk phase.

Films with nearly critical composition $\Phi = 0.50$ were prepared by spin casting. A solution of the polymers in toluene was spread on an untreated silicon wafer and on a silicon wafer covered by a chromium layer of 50 μg/cm^2 thickness. The film thicknesses were 550 nm. Always two samples, one on a silicon backing and one on a chromium backing, were heated simultaneously in vacuum at a temperature of 180 °C for various times. After quenching to ambient temperatures with a rate of 60 K/min, the laterally averaged volume fraction versus depth profile was measured with time-of-flight–elastic-recoil detection (TOF-ERD) for each film [20].

Figure 1 shows a series of dPS profiles at increasing annealing times for the untreated silicon backing. The

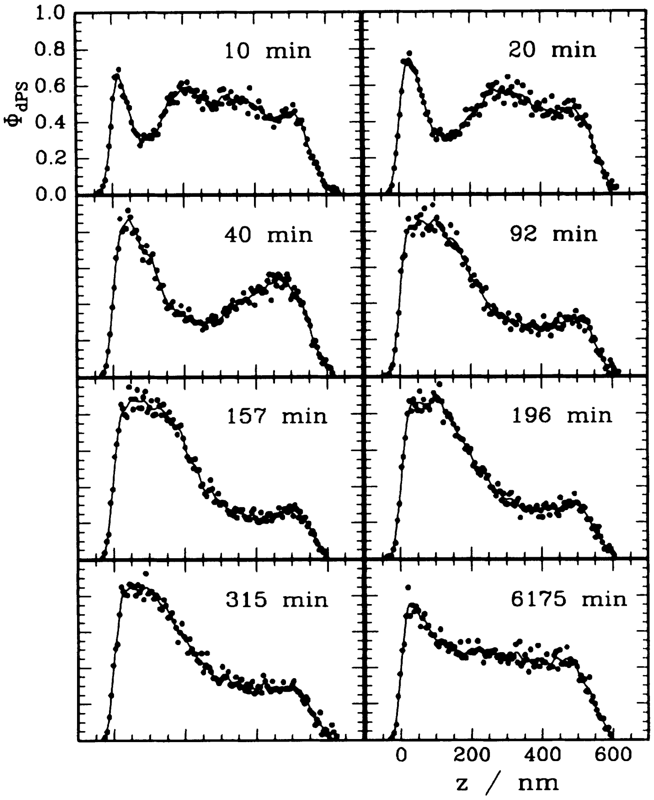

FIG. 1. Volume fraction vs depth profiles of dPS normal to the film surface after various times of annealing at 180 °C. The backing is a silicon wafer covered with a native oxide layer. The lines are cubic splines to guide the eye only.

initial profile is flat within the depth resolution of TOF-ERD of ≈ 31 nm. After 10 min a dPS-rich surface layer has established on the vacuum side, followed by oscillations as expected for spinodal decomposition [17]. With increasing annealing time this structure coarsens. After 157 min a macroscopic surface layer can be clearly identified with a maximum extension of ≈ 220 nm and a plateau composition of Φ_B^{II}. The layer near the silicon surface has a mean composition Φ of 0.23, much larger than $\Phi_B^{I}=0.15$, indicating that there is no homogeneous layer of the PBr_xS-rich bulk phase at the silicon surface, but a laterally demixed one. Also the decay width is much broader than expected for a flat interface between the two bulk phases. For larger times (157–6175 min) we observe that this structure is not stable, but decays continuously. At very large times the composition profile $\Phi(z)$ does not change any more. It shows an enrichment of the dPS at the vacuum surface that decays to a plateau value of $\Phi=0.43$, close to the average composition of 0.50.

To study the lateral structure we investigated the films with light microscopy in a reflecting geometry. There we benefit from the fact that after the irradiation of the samples with the ion beam in the TOF-ERD method, the PBr_xS-rich structures appear darker than those rich in dPS, giving an excellent contrast. Outside the ion beam spot on the target the structures can be observed in principle by interference contrast microscopy. As a result of the small film thicknesses and the small difference in the index of refraction between the components, sufficient contrast was only reached for the most demixed structures, where we observed equivalent structures inside and outside the beam spot. The lateral structure can also be seen in a scanning electron microscope where the difference in Z between dPS and PBr_xS gives rise to contrast in the backscatter mode [21]. Unfortunately this contrast bleaches out very quickly, due to radiation damage. Figure 2 shows a series of photographs which belong to the profiles in Fig. 1. The base side of a picture is equivalent to 35 μm. Lateral structures could be first resolved after 40 min of annealing. At this time a typical structure for spinodal demixing can be seen. For later times small droplets rich in dPS appear. They must be located in the layer near the silicon substrate and not in the layer near the vacuum surface since the latter shows the composition Φ_B^{II} of the dPS-rich bulk phase (Fig. 1). Note that for intermediate times (profiles for 157–315 min in Fig. 1) the mean dPS composition near the silicon backing is $\leq \Phi_s^{I}=0.29$, the respective spinodal composition of this blend. So this layer is in the metastable region of the bulk phase diagram, and further demixing can occur only by nucleation or by droplet growth due to interdiffusion, which are much slower processes than spinodal decomposition. The relatively fast buildup of the homogeneous dPS-rich surface layer slows down the lateral demixing in the inhomogeneous layer, because the depletion in dPS shifts it from the unstable to the metastable region of the bulk phase diagram. This will stabilize the homogeneous surface layer for some time. When

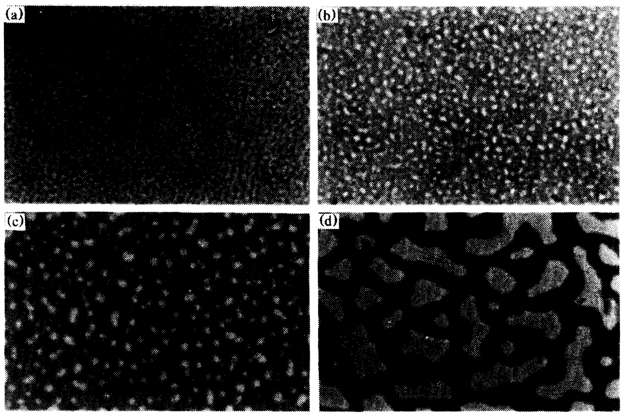

FIG. 2. Microscopy pictures for some profiles from Fig. 1. They show the concentration fluctuations in the film plane. The bright regions are those rich in dPS; the dark regions are those rich in PBr_xS. The base side of the photographs is equivalent to 35 μm. (a) 40 min, (b) 157 min, (c) 315 min, and (d) 6175 min of annealing time.

it decays the droplets grow in size. The $t=315$ min picture shows that their mean diameter has reached the film thickness. For larger times the domain growth takes place in an effective two-dimensional geometry. As mentioned before, the profiles do not change any more for the longest annealing times. Also the domain size increases only very slowly. This can be understood if the domains have already reached their equilibrium composition and further growth can only occur by the colliding of two domains and the subsequent formation of one domain, which tends to flatten its still rippled surface.

Finally we can formulate our suggestion for the three-dimensional structure of the blend in the late stage of spinodal decomposition on a silicon backing. It is a thin homogeneous layer of the dPS-rich phase at the vacuum that reflects the complete wetting by dPS. This layer gradually evolves to a domain structure where dPS-rich domains with a composition of Φ_B^{II} emerge like columns into a matrix of composition Φ_B^{I} of the dPS-poor phase. Therefore we conclude that neither the dPS component nor the PBr$_x$S component wets the native oxide layer on the silicon surface completely.

In Fig. 3 a time series of profiles for a chromium backing is shown. Again in the first stages a dPS-rich layer at the vacuum surface is formed followed by oscillations normal to the surface. But contrary to the silicon case a strong depletion of dPS at the chromium surface can be seen already after 20 min. After 157 min a bilayer exists which is stable with time. The compositions of the layers are 0.14 and 0.87, in very good agreement with the binodal values for the coexisting bulk phases [19]. The interface width w also remains stable with time. Correcting for the depth resolution of TOF-ERD, a value of 31_{-15}^{+9} nm was estimated for w from the profile. The theoretical width can be calculated from Ref. [3] via $w=(2a^2/9\chi_C\epsilon)^{0.5}$ to be about 15 nm using a segment length a of 6.7 Å. This is in reasonable agreement with the experimental value, so that we can assume a plane surface between the two phases. Only after 40 min of annealing could we identify a lateral structure in the light microscope, similar to that in the untreated silicon case (Fig. 2). But contrary to that case, these structures decay and no lateral structure can be seen for larger times. Therefore we conclude that the PBr$_x$S component wets the chromium surface completely, so that anisotropic demixing is triggered by both surfaces and the macroscopic bilayer of the two coexisting bulk phases is stabilized for all times. The wetting of the chromium surface by the PBr$_x$S is assumed to originate from the permanent dipole moment of the brominated benzene ring in the copolymer, which will induce image charges in the metallic layer, leading to an attractive interaction.

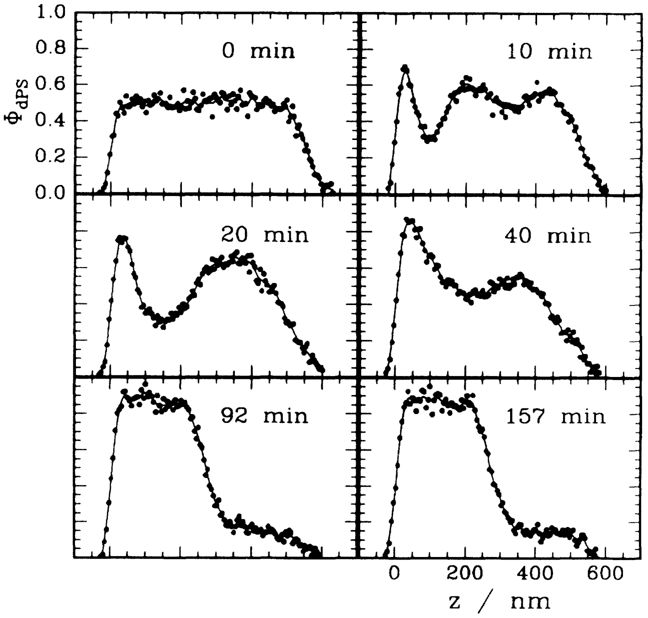

FIG. 3. Volume fraction vs depth profiles of dPS normal to the film surface after various times of annealing at 180 °C. The backing is a silicon wafer covered with a layer of chromium. The lines are cubic splines to guide the eye only.

In summary, we have shown for the first time that spinodal decomposition in thin films of a polymer blend can lead to a macroscopic bilayer of the two coexisting bulk phases. This is the case if each of the components wets one of the two film surfaces completely. If just one of the surfaces is wet and the other shows finite contact angles with both bulk phases, the structure of the demixed film is a homogeneous surface layer at the wet surface that changes gradually into a column structure of the two bulk phases extending to the other surface. This structure was made visible in a quasi-three-dimensional profiling, i.e., by recording a mean concentration versus depth profile $\Phi(z)$ normal to the film surfaces, in combination with an analysis of the laterally demixed structure by light microscopy. The formation of a plane bilayer by spinodal demixing opens a new way to create well-defined inner interfaces in a polymer blend. Also the formation of U-shaped profiles should be possible if the same component wets both surfaces completely.

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[1] P. G. de Gennes, J. Chem. Phys. **72**, 4756 (1980).
[2] P. Pincus, J. Chem. Phys. **75**, 1996 (1981).
[3] K. Binder, J. Chem. Phys. **79**, 6387 (1983).
[4] L. Snyder and P. Meakin, J. Chem. Phys. **79**, 5588 (1983).

[5] T. Hashimoto, M. Itakura, and H. Hasegawa, J. Chem. Phys. **85**, 6118 (1985); T. Hashimoto, M. Itakura, and N. Shimidzu, J. Chem. Phys. **85**, 6773 (1985).

[6] F. S. Bates, P. Wiltzius, and W. R. Heffner, Phys. Rev. Lett. **60**, 1538 (1988); F. S. Bates and P. Wiltzius, J. Chem. Phys. **91**, 3258 (1989).

[7] D. Schwahn, T. Springer, S. Janssen, and E. Hädicke, J. Appl. Cryst. **24**, 685 (1990).

[8] J. W. Cahn, J. Chem. Phys. **66**, 3667 (1977).

[9] H. Nakanishi and P. Pincus, J. Chem. Phys. **79**, 997 (1983).

[10] I. Schmidt and K. Binder, J. Phys. (Paris) **46**, 1631 (1985).

[11] I. Carmesin and J. Noolandi, Macromolecules **22**, 1689 (1989).

[12] S. M. Cohen and M. Muthukumar, J. Chem. Phys. **90**, 5749 (1989).

[13] R. A. L. Jones, E. J. Kramer, M. H. Rafailovich, J. Sokolov, and S. A. Schwarz, Phys. Rev. Lett. **62**, 280 (1989); R. A. L. Jones *et al.*, Europhys. Lett. **12**, 41 (1990); R. A. L. Jones and E. J. Kramer, Philos. Mag. B **62**, 129 (1990).

[14] S. K. Kumar and T. P. Russell, Macromolecules **24**, 3816 (1991).

[15] X. Zhao, W. Zhao, J. Sokolov, M. H. Rafailovich, S. A. Schwarz, B. J. Wilkens, R. A. L. Jones, and E. J. Kramer, Macromolecules **24**, 5991 (1991).

[16] R. C. Ball and R. L. H. Essery, J. Phys. Condens. Matter **2**, 10303 (1990).

[17] R. A. L. Jones, L. J. Norton, E. J. Kramer, F. S. Bates, and P. Wiltzius, Phys. Rev. Lett. **66**, 1326 (1991).

[18] G. R. Strobl, J. T. Bendler, R. P. Kambour, and A. R. Schultz, Macromolecules **19**, 2683 (1986); R. P. Kambour and J. T. Bendler, Macromolecules **19**, 2679 (1986).

[19] F. Bruder and R. Brenn, Macromolecules **24**, 5552 (1991).

[20] J. Sokolov, M. H. Rafailovich, R. A. L. Jones, and E. J. Kramer, Appl. Phys. Lett. **54**, 590 (1989).

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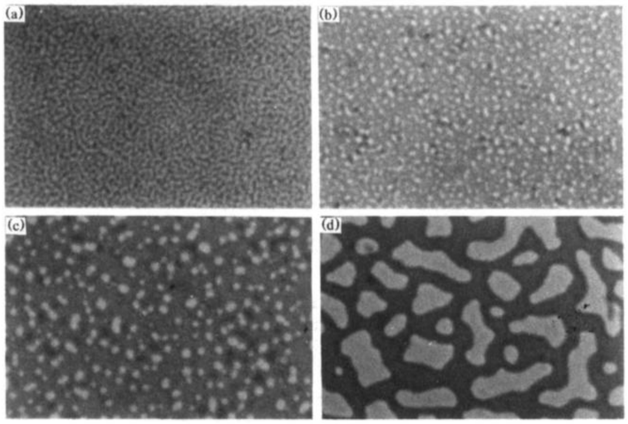

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