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Communications to the Editor

Phase Separation in Bilayer Films

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Introduction. Phase separation in the vicinity of a surface is different from that in the bulk because one of the separated phases wets a substrate in contact with the surface. Such surface effects on the kinetics of phase separation of polymer blends and solutions have been attracting wide attention in recent years.[1−6] In contrast to the widening interest in the phase separation near a surface, the phase separation near a boundary between two layers that are different in component, composition, or morphological structure has not attracted due attention, and only a few computer simulation studies[7,8] have been made so far concerning this subject. The boundary is analogous to the surface in that the wetting phenomenon is expected to influence phase-separation behavior in its vicinity. At the same time, the boundary is different from the surface in that the boundary allows materials to transfer across it. As a consequence, some interesting behavior may be expected near the boundary.

In this paper, we studied morphological structures produced by the phase separation of bilayer films employing electron microscopy. The bilayer films that we studied here consisted of layers identical in component but different in composition. The composition of one layer was chosen to be one of the coexisting compositions at the experimental temperature. In such a bilayer film, microdomains formed in one layer by phase separation are in contact with a homogeneous layer of the same composition as one of the two compositions of these domains. Since two macroscopic domains must be formed finally at the thermodynamic equilibrium, the boundary between these homogeneous and phase-separating layers is expected to change its location and shape as phase separation proceeds. It is very interesting to study how phase-separation behavior near a boundary leads to the change of the boundary.

Experimental Section. Blends of polystyrene and poly(2-chlorostyrene) containing a plasticizer di-*n*-butyl phthalate (DBP) by an amount of 6.8 wt % of the total polymer weight were used as the sample. Polystyrene (PS) was a product of Pressure Chemical Co. with a nominal weight-average molecular weight $M_w = 5.0 \times 10^4$ and polydispersity index $M_w/M_n < 1.06$. Poly(2-chlorostyrene) (P2CS) of $M_w = 9.0 \times 10^4$ and $M_w/M_n = 1.13$ was prepared by radical polymerization in toluene and subsequent fractionation by using preparative gel permeation chromatography. The bilayer films were prepared by welding two precursory monolayer films. Preparation of the monolayer films was made by solvent casting from a benzene solution in the similar manner as described in a previous paper.[9] Welding of the two monolayer films was made as follows: The two precursory films of 0.11_5 mm thickness were sandwiched with a 0.20 mm thick spacer between two round glass plates and annealed at 120 °C for 2 h with a weight placed on the top.

The present system had a lower critical solution temperature, and phase separation was initiated by transferring a sample film to a thermostat controlled at a temperature in the two-phase region to ±0.03 °C. The sample film was placed horizontally in the thermostat, with the layer of the lower density being always on the upper side to prevent a flow by gravity. After a desired phase-separation time, we took out the sample film and rapidly quenched below the glass transition temperature by contacting with cooled metal blocks. Morphology of the phase-separated domains was observed with a JEOL JSM T220 electron microscope by detecting back-scattered electrons from the fractured surface of the quenched sample.

The coexisting compositions were estimated, with the aid of the lever rule, from a set of phase-volume fractions of the two coexisting phases obtained by varying the initial compositions. We assumed the uniform distribution of the plasticizer DBP between the two coexisting phases, which was reasonable because DBP was a good solvent for both polymers and its content was relatively small. Since macroscopic domains were not formed within an experimentally accessible time scale, the phase-volume fractions were evaluated by the image analysis of electron micrographs of the microscopic domains obtained at the late stage of phase separation.[9] The image analysis was performed with a PIAS LA525 image analysis system.

Results and Discussion. Figure 1 shows microdomain structures during phase separation at 165 °C of the sample consisting of the layers of polymer compositions $\theta \equiv$ (volume of PS)/[(volume of PS) + (volume of P2CS)] = 0.54 and $\theta = 0.82$. The composition $\theta = 0.82$ corresponded to one of the coexisting compositions at 165 °C estimated by the image analysis of the electron micrographs. The lighter portion of the image corresponds to the P2CS-rich phase and the darker portion corresponds to the PS-rich phase. The cocontinuous domain structure typical of the phase separation at a composition in the critical range was produced in the lower layer where the initial composition was $\theta = 0.54$. Because of the inaccuracy of the estimation of the coexisting composition, phase separation occurred in the upper layer and small droplets were produced. However, the volume ratio of the droplet phase in the layer was very small, which allowed us to approximately regard the layer as a single homogeneous domain.

In an early period (Figure 1, panels a and b) of the phase separation, the apparent boundary between the two layers remained flat and smooth. A more magnified view of the morphological structures near the apparent boundary is shown in Figure 2. No variation with the

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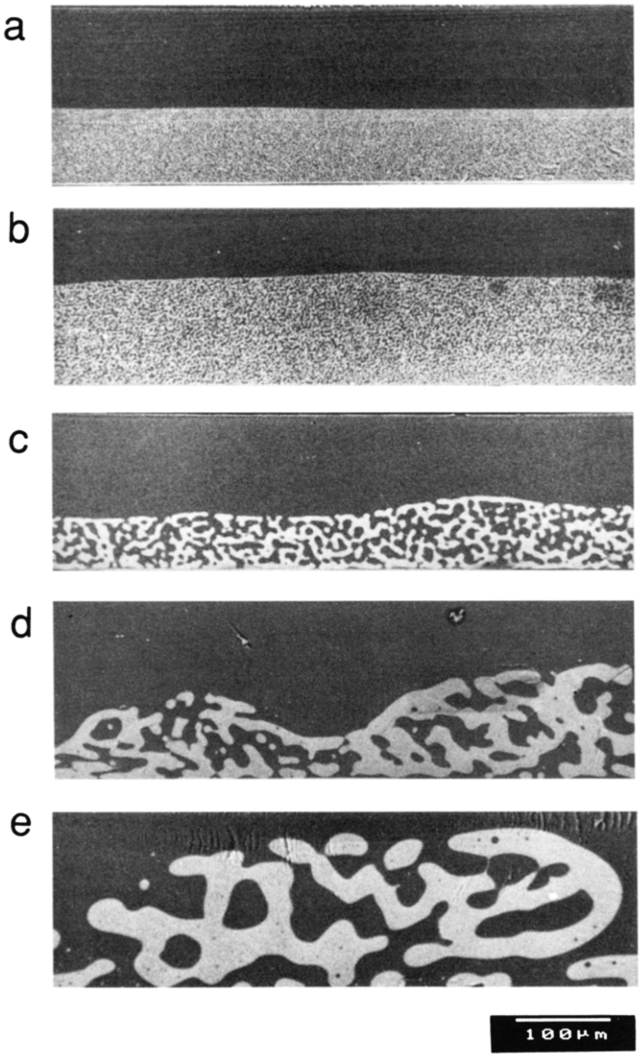

Figure 1. Electron micrographs (backscattered image) of domain structures of the film consisting of two layers of the initial compositions $\theta = 0.54$ and 0.82 at different phase-separation times after the temperature jump to 165 °C: (a) 33, (b) 72, (c) 243, (d) 423, (e) 908 min. Film thickness is 200 μm. Lighter portions correspond to the P2CS-rich (chlorine-rich) phase.

distance from the boundary was observed in the morphological structure, except the existence of a narrow region adjacent to the boundary, where the P2CS-rich phase (lighter portion) spread in a belt (a sheet in three dimensions) along the boundary. In other words, the influence of the upper layer ($\theta = 0.82$) on the phase-separation morphology of the lower layer was limited in a distance comparable to the characteristic length of the cocontinuous domains. Similar results have been obtained for the phase separation near a surface.[4,6] This similarity indicates that in the phase separation near the boundary the upper layer plays the role of a substrate in the phase separation near the surface. Since the upper layer was made of the same material as the PS-rich phase in the lower layer, it had a stronger affinity with the PS-rich phase than the P2CS-rich phase. Therefore, a large sheetlike PS-rich domain must have formed between the initial boundary and the sheetlike P2CS-rich domain, though it was not distinguished from the upper layer.

Around 4 h after the phase separation started, the boundary began to be disturbed, and the degree of the disturbance was amplified with time as shown in Figure 1, panels c–e. At a very late period (Figure 1e), the P2CS-rich continuous domains extended over the whole system and the boundary between two layers was no longer clearly distinguished. This suggests that the phase separation behavior in the very late period becomes indistinguishable from that of the monolayer film of the same total composition. We repeated the experiment for the same bilayer film ($\theta = 0.54/\theta = 0.82$) to confirm the reproducibility of this interesting phenomenon. Further, we performed the experiment twice for the bilayer film consisting of the two compositions $\theta = 0.54$ and $\theta = 0.84$, because the upper-layer composition $\theta = 0.82$ of the previous sample turned out to be in the two-phase region. In all these experiments, the disturbance of the boundary in the later period of the phase separation was reproduced. The time of the beginning of the disturbance was dependent on samples and varied in a range from 4 to 6 h.

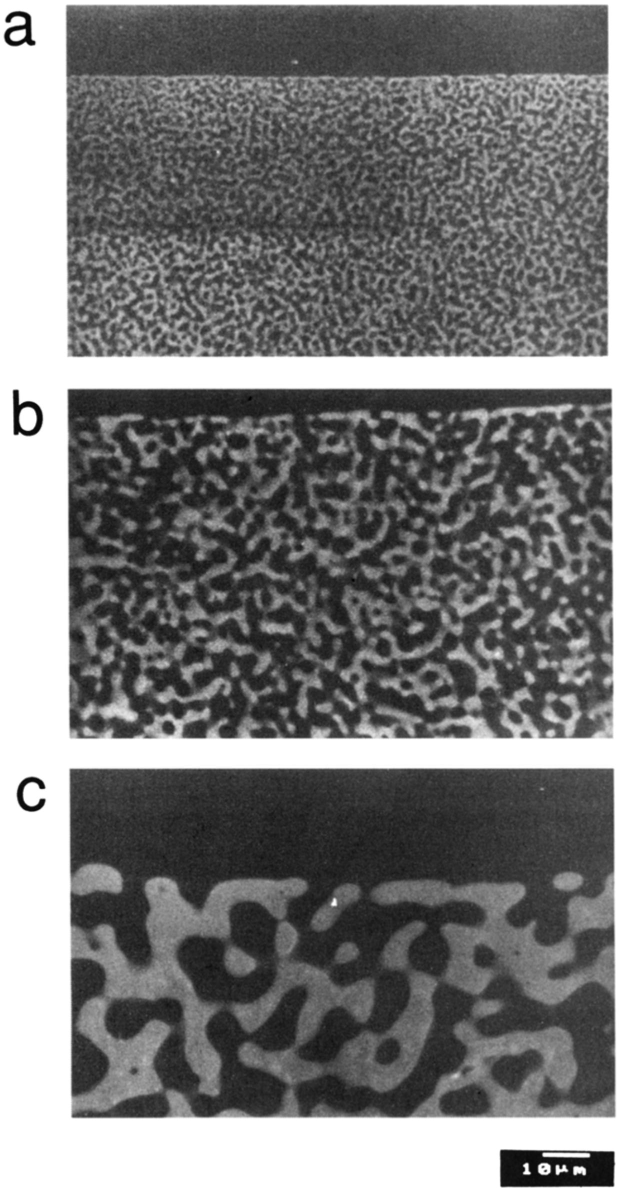

Figure 2. Enlargement of morphology in the vicinity of the boundary of the same sample as shown in Figure 1. Phase separation times are (a) 33, (b) 72, and (c) 243 min.

In order to clarify that the disturbance of the boundary is a phenomenon related to the phase-separation dynamics, a bilayer film consisting of compositions very close to the two coexisting compositions at 165 °C, namely, $\theta = 0.25$ and $\theta = 0.84$, was kept at that

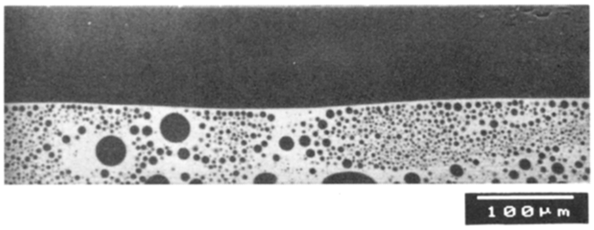

Figure 3. Electron micrographs of domain structures of the film consisting of two layers of the initial compositions $\theta = 0.42$ and 0.84. The phase-separation time at 165 °C is 192 h.

temperature for 192 h. Although gentle undulation of the boundary was observed, such a large disturbance was not found to occur. Therefore, the disturbance of the boundary was not caused by the simple convection driven by a temperature gradient that might be produced in the sample.

The dependence on the composition of the demixing layer was studied by varying the composition of the lower layer with the composition of the upper layer fixed at $\theta = 0.84$. In the cases of the composition of the lower layer $\theta = 0.48$ and 0.60, the cocontinuous domain structures were produced in the demixing layers and no appreciable difference from the case of $\theta = 0.54$ was observed in the process of the boundary disturbance. In the case of $\theta = 0.42$, an inhomogeneous droplet structure was produced by the phase separation as shown in Figure 3. It is known that a similar inhomogeneity of the structure is produced in the phase separation in the crossover region from the critical to the off-critical compositions.[10] At the phase-separation time 192 h, the boundary undulated only gently and the disturbance of the boundary was not observed. The typical size of the droplets at 192 h was comparable to the characteristic size of the cocontinuous domain (approximately 5 μm) at the beginning of the disturbance of the boundary between the layers of $\theta = 0.54$ and 0.84. Therefore, even taking into account the difference in the coarsening rate between the droplets and the cocontinuous domains,[11] we can conclude that the disturbance of the boundary will not occur in the case where the demixing layer producing the droplet domain structure is in contact with the homogeneous layer.

The dependence on the domain structure of the demixing layer suggests that the channel running through the sheetlike P2CS-rich domain plays an important role in the disturbance of the boundary. It was observed that the number of such channels was decreasing with the coarsening of the cocontinuous domains. As a result, the most surface area of the upper layer was covered with the sheetlike P2CS-rich domain in a later period, and the coarsening of this huge PS-rich domain, namely, the upper layer, could proceed only through a few remaining channels. Probably these channels are the source of the disturbance.

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