Macromolecules **1993,** *26,* 6681-6683

Phase Separation Morphology in the Critical to Off-Critical Crossover Region

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Received February 19, 1993

Revised Manuscript Received July 8, 1993

Introduction. In the late stage of phase separation, the concentration of each domain reaches the coexisting value and phase separation proceeds to minimize the interfacial energy.[1] Mechanisms of this coarsening process depend on morphological structures of the domains.[2,3] The presence of continuity among the domains plays an essential role in fluid mixtures. When the volumes of two separated phases are close (critical), the domains are connected with each other and form a cocontinuous structure. According to Siggia,[2] in the cylindrical part of such a cocontinuous structure, the gradient of interfacial tension along an axis of the cylinder causes a flow of inner fluid from a narrow to a wide region, which results in coarsening of the domains. When the phase volume fraction of a minority phase is small (off-critical), the minority phase cannot form a continuous domain and forms droplets, for which coalescence and the Ostwald ripening[4] have been proposed as mechanisms of coarsening. For the crossover region between critical and off-critical regions, direct observation of phase separation morphology was not reported yet, though a few experimental studies using scattering techniques have been made over wide concentration and temperature ranges covering the crossover region.[5-8]

The present study aims to elucidate the crossover behavior from a cocontinuous structure to a droplet structure by observing domain structures in real space. We used polystyrene (PS)/poly(2-chlorostyrene) (P2ClS) blends, whose coexistence curve was already determined,[9] as a sample and observed domain structures by an electron microscope under various phase separation conditions. The present system had the great advantage of giving a large contrast in the electron micrograph. However, since the temperature dependence of the χ parameter of this system was very weak, it was difficult to fit the phase diagram into an appropriate temperature range by controlling the molecular weights of the components. We added a small amount of plasticizer to adjust the location of the phase diagram, and thus the present system is not a two-component system in the strict sense.

Experimental Section. Materials and Sample Preparation. Polystyrene with nominal weight-average molecular weight $M_w = 5 \times 10^4$ and molecular weight distribution index $M_w/M_n < 1.06$ was purchased from Pressure Chemical Co. Poly(2-chlorostyrene) was radically polymerized in toluene at 60 °C and fractionated by the precipitation method and gel permeation chromatography. M_w and M_w/M_n of P2ClS were 9.03×10^4 and 1.10, respectively. Plasticizer di-*n*-butyl phthalate (DBP) was a product of Tokyo Kasei Kogyo and was used without further purification. Blend films of 0.2-mm thickness were prepared by solvent casting. Details of the film preparation were given in a previous paper.[9] All measurements were made for samples with a fixed DBP content of 6.9 wt %.

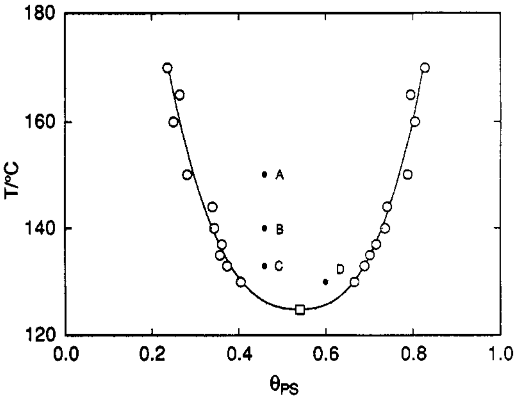

Figure 1. Quasi-binary representation of the coexistence curve of polystyrene/poly(2-chlorostyrene) containing 6.9 wt % di-*n*-butyl phthalate. θ_{PS} denotes the volume fraction of PS in the total polymer volume. The square indicates the critical point.

Observation of Morphology. A temperature jump from the one-phase region to the spinodal region was carried out by transferring a sample film to a thermostat made of aluminum block controlled at a desired temperature to ±0.03 °C. After a certain phase separation time, the sample film was taken out of the thermostat and quenched to room temperature, which was well below the glass transition temperature of the blend. We neglected the change during the quench, because the rate of phase separation already was very slow when we took out the sample film. Instead of following the time evolution of the domain structure of a single piece of sample film, a different piece prepared from the same cast film was used for observation at each stage of phase separation. Phase separation morphology at the fractured surface of the sample was observed by an electron microscope JEOL JSM-T220 operated at 10-15 kV. The surface of a sample was coated with carbon, and the composition image was observed by detecting backscattered electrons. Since one component contains chlorine atoms, a large contrast was obtained in the electron micrograph without staining. The topographical contribution to the image was negligible.

Results and Discussion. Figure 1 shows a quasi-binary representation of the coexistence curve of the blend polystyrene/poly(2-chlorostyrene) containing 6.9 wt % di-*n*-butyl phthalate.[9] The abscissa θ_{PS} is the volume fraction of PS in the total polymer volume that is related to volume fractions ϕ_i (i = PS, P2ClS) in the total blend volume by $\theta_{PS} = \phi_{PS}/(\phi_{PS} + \phi_{P2ClS})$. The lower critical point was located at composition $\theta_c = 0.54$ and temperature T_c = 124.8 °C, and the coexistence curve was almost symmetrical about the critical volume fraction.

Figure 2 shows domain structures of blends of the same initial composition $\theta_{PS} = 0.46$ observed at different phase separation temperatures T = 150, 140, and 133 °C (points A-C, respectively, in Figure 1). The lighter portion of the image corresponds to the P2ClS-rich (chlorine-rich) phase. As the phase separation temperature was decreased at a fixed initial PS composition θ_{PS} off critical, the phase volume fraction v of the minority phase was decreasing. Phase volume fraction v was 0.35 at 150 °C (point A) and a cocontinuous structure typical of critical quench was observed, while at 133 °C (point C) the fraction v was 0.27 and a droplet structure typical of off-critical quench was observed.

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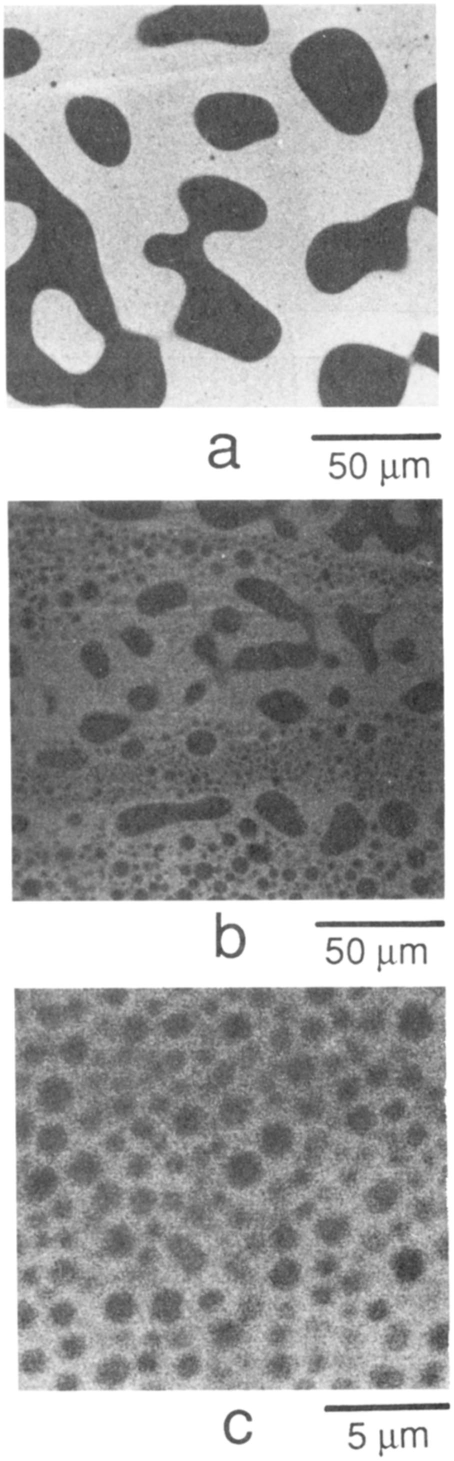

Figure 2. Electron micrographs (backscattered image) of the domain structures of the blend $\theta_{PS} = 0.46$ at different phase separation temperatures and times: (a) 150 °C, 72 h; (b) 140 °C, 230 h; (c) 133 °C, 265 h. The lighter portion corresponds to the P2ClS-rich (chlorine-rich) phase.

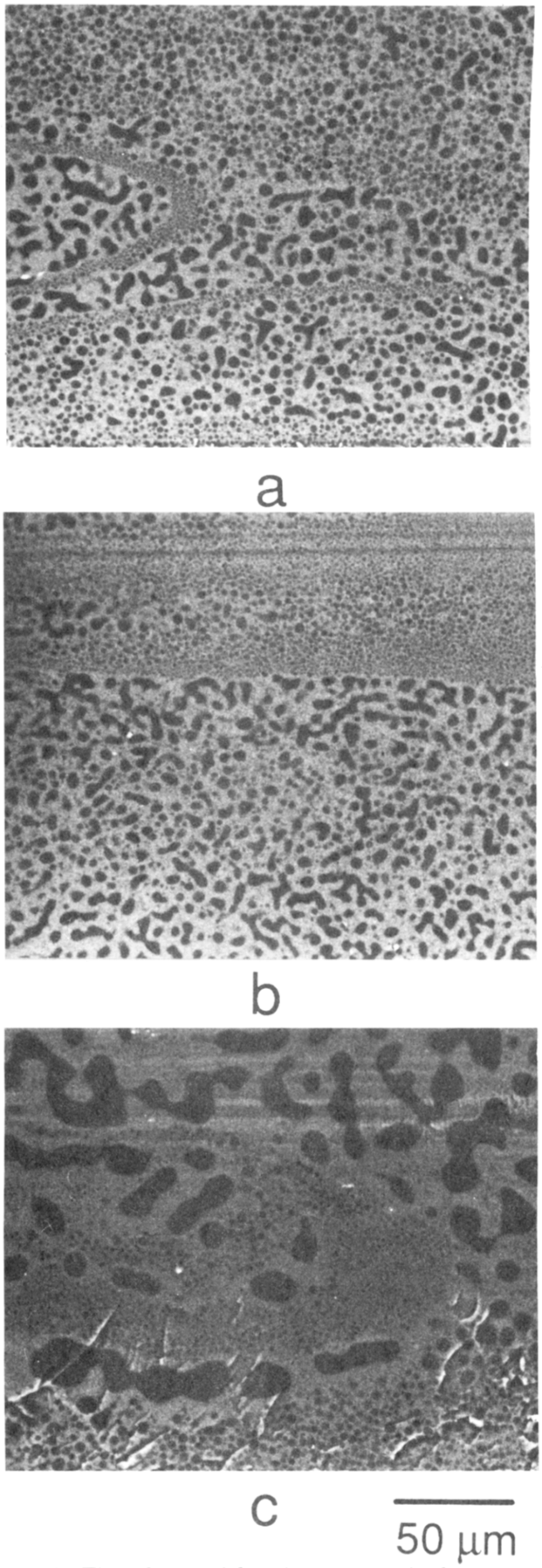

Figure 3. Time change of domain structures in the crossover region, $\theta_{PS} = 0.46$ and $T = 140$ °C. Phase separation times are (a) 63 h, (b) 73 h, and (c) 230 h.

Parts a and c of Figure 2 showed only well-known phase separation morphology in the critical and off-critical regions. However, the morphology observed at an intermediate phase volume fraction $v = 0.29$ (140 °C, point B) as shown in Figure 2b is obviously different from these known morphological structures: Droplets and cocontinuous domains coexisted in the system and these two types of domains were not mingled homogeneously with each other, but droplets gathered in certain regions. The characteristic size of the droplets is quite smaller than the characteristic length of the cocontinuous domains. The time change of this domain structure was shown in Figure 3. A heterogeneous phase separation structure could be observed in earlier periods as well. However, the difference in the characteristic size between the droplets and the

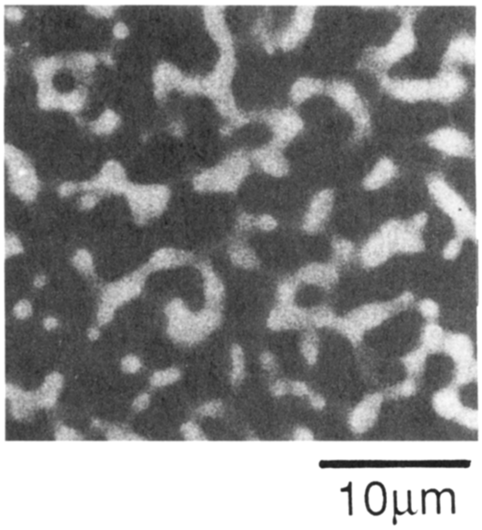

Figure 4. Electron micrograph (backscattered image) of domain structures of the blend $\theta_{PS} = 0.60$ at phase separation temperature $T = 130$ °C and time $t = 295$ h.

cocontinuous domains was not so large and the difference was enhanced with a lapse of time. The droplets appeared to be growing very slowly with phase separation time.

We saw that the crossover from the cocontinuous to the droplet structure was located in a range between $\upsilon = 0.35$ and 0.27 on the P2ClS-rich side of the phase diagram. If the domain structure is determined only by the phase volume fraction, the crossover on the PS-rich side is expected to be located at the symmetrical point on the phase diagram. However, as shown in Figure 4, the cocontinuous structure was observed at the phase volume fraction of PS $\upsilon = 0.74$ ($\theta_{PS} = 0.60$ and $T = 130$ °C, point D in Figure 1), i.e., 0.26 in the phase volume fraction of the minority phase, although droplets were observed at approximately the same phase volume fraction of the minority phase $\upsilon = 0.27$ on the other side of the phase diagram. Thus the crossover on the PS-rich side seemed to be located at a smaller volume fraction of the minority phase.

The heterogeneous phase separation morphology observed in the crossover region was considered to be formed in the following way. In an early stage of phase separation, the concentration fluctuation is symmetrical about the initial concentration and the modulated phase separation structure produced by the spinodal decomposition extends uniformly over the whole system. However, in the process of fluctuation growth from the intermediate to the late stage of phase separation, the modulated structure of the minority phase breaks into droplets and continuous domains of finite sizes, since the phase volume fraction υ of the minority phase is not large enough to form a continuous domain extending over the whole system. It is well-known that, in a fluid mixture, the growth rate of the droplets is much slower than that of cocontinuous domains: Characteristic size L of cocontinuous domains is proportional to phase separation time t, while the characteristic size of droplets is proportional to $t^{1/3}$.[2,10] Furthermore, in a blend of long polymer chains, Kotnis and Muthukumar[11] theoretically predicted that droplets did not grow because a large entropic barrier in transporting a long chain across a sharp interface obstructed the coarsening of the droplets. Therefore, the difference in the average size between droplets and continuous domains is enhanced with time. It is reasonable to consider that the droplets were distributed uniformly in the system at the beginning. This means that the droplets are scattered among the continuous domains and the average distance between the two adjacent cylinders constituting the continuous structure of the minority phase is larger than the characteristic diameter of the cylinder at the beginning: In other words, the continuous structure of the minority phase is swelled by the majority phase comprising droplets of the minority phase. Coarsening of the continuous domain proceeds by Siggia's mechanism in a fluid system, and such an expanded finite-sized continuous domain will decrease its dimension (the volume of space that the domain extends over) in the process of coarsening, while leaving space at the boundary with another continuous domain. Some droplets surrounded by a continuous domain will be absorbed by the domain during the coarsening, but the rate of such a process is very slow and of the same order as the growth rate of the droplets. Consequently, most droplets are flowing out to the exterior of the continuous domains without being absorbed and accumulate in boundary space between continuous domains, which leads to the heterogeneous structure we observed.

References and Notes

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(10) We observed that the L–t relation held for the growth of the cocontinuous domain in the present system by carrying out the time-resolved light scattering and the image analysis of the electron micrograph, which indicates that the coarsening of the continuous domain proceeds by Siggia's mechanism.

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