SHORT COMMUNICATIONS

Phase Separation Induced by Two Step Temperature Jump

Mamoru OKADA, Kyu Dae KWAK, and Takuhei NOSE

*Department of Polymer Chemistry, Tokyo Institute of Technology,
Ookayama, Meguro-ku, Tokyo 152, Japan*

Phase separation kinetics has been extensively investigated for polymer blends,[1,2] as well as for low molecular weight substances,[3] as a fascinating problem of non-equilibrium statistical thermodynamics. The study on phase separation kinetics has also a great practical importance, since it gives us basic information necessary to establish a method of controlling microscopic domain structure of polymer blends. In studies on phase separation kinetics, temperature of a sample is generally fixed at a constant value in the two-phase region after it was jumped from a value in the miscible one-phase region, with a few exceptions such as the periodic spinodal decomposition.[4,5] Although simplified condition such as the single temperature jump makes analysis of phase separation kinetics easier, it gives a rather limited variety of micro-domain structure and is not considered to be an effective method of controlling the morphological structure. When temperature is changed in the course of phase separation, a different structure from that observed in a single temperature jump experiment is expected to be observed.

In the present study, we intended to obtain a new morphological structure that many small droplets exist in large highly-connected domains. This will be achieved by the following procedure: Temperature of a polymer blend which is already in the late stage of phase separation initiated by a temperature jump is jumped further in the direction to increase the quench depth. The second temperature jump will accelerate the coarse-graining of the domains already formed by the first jump, and at the same time it will induce phase separation inside each domain. When the composition of the polymer blend is close to the critical one, highly-connected domain structure will be obtained by the first jump, and the second jump will produce discrete droplets inside the large domains, since the second jump generally becomes off-critical quench for the coexistence phases formed by the first jump, unless the first jump is very shallow. In this two step temperature jump experiment, more than one characteristic length is expected to exist in the system at least in a certain period after the second temperature jump, and it is very interesting to study how these characteristic lengths are growing or diminishing in competition with each other.

Blend of polystyrene (PS) and poly(2-chlorostyrene) (P2CS) was used as a sample. Since one of the components contains chlorine atoms, a relatively large contrast is obtained in scanning electron micrographs which are used to observe morphological structure of the blend. A small amount of the plasticizer di-n-butylphthalate (DBP) was added to the blend so that the spinodal temperature is

located in an appropriate range above the glass transition temperature. PS was a product of Pressure Chemical and its nominal molecular weight M_w and molecular weight distribution index M_w/M_n were $M_w = 5 \times 10^4$ and $M_w/M_n < 1.06$, respectively. P2CS was radically polymerized in toluene and fractionated with a preparative gel permeation chromatography (GPC) apparatus (Tosoh, HLC-837). PS equivalent M_w and M_w/M_n of P2CS were determined with an analytical GPC apparatus to be $M_w = 6.6 \times 10^4$ and $M_W/M_n = 1.10$. Blend film with a composition of PS : P2CS : DBP = 46.6 : 46.5 : 6.9 in weight % was cast from about 3 wt% benzene solution. This composition is close to the critical one, since degrees of polymerization of both polymers are roughly the same. The cast film was air-dried at 60°C overnight, followed by vacuum drying at 80°C for 4 days and at 120°C for 1 day. The film was cut into small pieces, which were placed between circular microscope slide glasses with a 0.2 mm thick spacer.

The temperature jump was carried out by transferring the sample films to an aluminum block whose temperature was controlled to an accuracy of ± 0.03°C. For the second temperature jump, the samples were taken out from the block and quenched to a room temperature, which is well below the glass transition temperature. After the temperature of the block was stabilized at a set value of the second jump, the samples were transferred to the block again. After the lapse of a certain period, one sample was taken out from the block and quenched to a room temperature. Morphological structure of the fractured surface of the quenched sample film was observed by a scanning electron microscope JEOL JSM-T220.

The prsent system has a lower critical temperature.[6] The spinodal temperature T_S was estimated to be 137°C from the initial rates of phase separation at several different temperatures. The first jump was made to 140.0°C, at
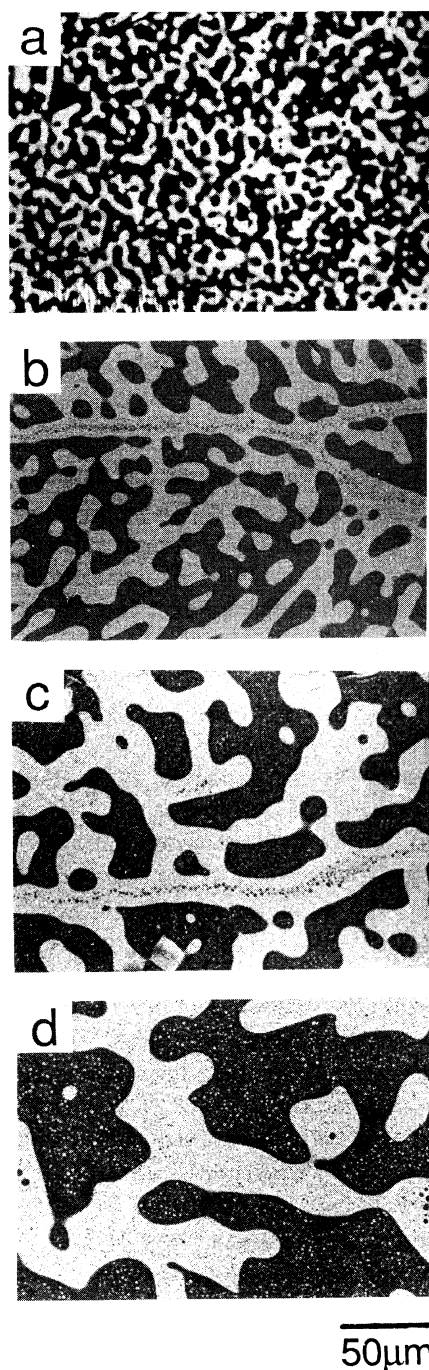

50µm

Figure 1. Scanning electron micrographs of fractured surface of the blend (positive image). The elapsed time after the second jump t: a) 0 s; b) 7×10^3 s; c) 1.4×10^4 s; d) 3.0×10^4 s.
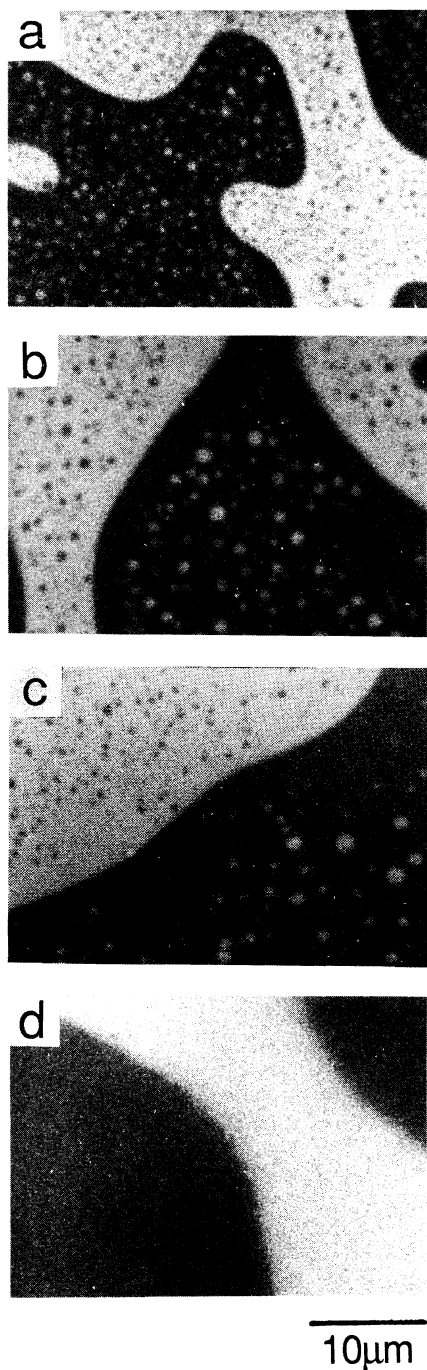
10μm

Figure 2. Scanning electron micrographs of fractured surface of the blend with a higher magnification. a) $t = 7 \times 10^3$ s; b) 3.0×10^4 s; c) 6.0×10^4 s; d) 1.2×10^5 s.

which the temperature was kept for 70h, and then the second jump was made to 165°C. Figure 1(a) shows a scanning electron micrograph of the blend immediately before the second temperature jump. White part corresponds to chlorine rich (*i.e.*, P2CS rich) phase. It is observed that highly-connected domains were formed by the first jump. Figure 1 also shows morphological structures at various elapsed times t after the second temperature jump. In Figure 2, micrographs with higher magnification are shown. It is clearly seen, especially in Figure 2, that many small droplets emerged inside the larger connected domains, just as we expected. Such microscopic domain structure was not observed in a conventional single step temperature jump experiment. The larger connected domain structure continue to grow steadily in size after the second jump (See Figure 1). The small droplets inside the connected domains are growing in size in a relatively early period from $t = 0.7 \times 10^4$ s to 3.0×10^4 s as seen in Figures 2(a) and 2(b). However, in the succeeding period, the growth rate of the typical size of small droplets is much reduced. In this period, the number density of small droplets is apparently decreasing with time as seen Figures 2(b) and 2(c). Eventually these small droplets disappear around $t = 1.2 \times 10^5$ s. Interface of the larger domain seems to become diffuse in the very late period after the small droplets disappear. It is not clear at present whether this is a reflection of real physical behavior or is caused merely by a technical problem in electron microscopy.

The smaller droplets were observed to decrease its number, until they finally disappeared, and which can be explained by the evaporation-condensation mechanism.[7] Since excess free energy is necessary to create surface, a large droplet is more stable than a small droplet. As a consequence, component molecules evaporate from smaller droplets and condense to the surface of large connected domains. Aggregation by collision of

droplets can also explain the decrease in number of the samll droplets. In that case, the typical size of small droplets inside a large domain should increase with time, but the observed growth rate of the typical size was not so large. Therefore aggregation is not a dominant mechanism of the disappearance of the small droplets though it is partially responsible.

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