Growth Rate of Microdomains during Phase Separation by a Two-Step Temperature Jump

Kyu Dae Kwak,[†] Mamoru Okada,[*,†] Tsuneo Chiba,[‡] and Takuhei Nose[†]

Departments of Polymer Chemistry and of Organic and Polymeric Materials, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152, Japan

Received September 21, 1992
Revised Manuscript Received December 17, 1992

Introduction

In phase-separation kinetics studies, the 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. The behavior observed when the temperature is suddenly changed during the phase-separation process so as to increase the driving force in the phase separation is more complicated but is quite an interesting subject of both industrial and theoretical studies. The two-step temperature jump (the first-step jump is made to start the phase separation) can give new morphological structures that have not been obtained by the usual single-step jump, for example, as shown in Figure 1. It is observed in Figure 1 that there are small droplets in co-continuous domains, indicating that more than one characteristic domain size can coexist in the case of a two-step temperature jump. To elucidate the mechanism of time evolution of these characteristic lengths is an interesting theoretical problem.

The two-step jump was first studied by Ohnaga and Inoue,[1] who calculated the concentration profile in a one-dimensional system numerically based on the Cahn–Hilliard nonlinear diffusion equation that neglected hydrodynamic interactions. Recently we performed the two-step temperature jump for a polymer blend and observed a new morphological structure using an electron microscope.[2] Independently, Tanaka[3] also studied experimentally the morphological structures formed by the two-step temperature jump with a phase-contrast microscope. Our observation was summarized as follows: By the second temperature jump, small droplets were emerged inside large co-continuous domains that were already formed by the first temperature jump (see Figure 1). Inner small droplets grew in size first, but after a certain period the average sizes of droplets did not change appreciably and the number of droplets started to decrease. Small droplets eventually disappeared and the large domains continued to grow. In the present paper, quantitative study of the growth rate of the larger co-continuous domains has been made by image analysis of electron micrographs.

Experimental Section

Sample Preparation. The sample used in this study was a blend of polystyrene (PS) and poly(2-chlorostyrene) (P2CS) containing a small amount of di-*n*-butyl phthalate (DBP). DBP was added so that the phase diagram was located in an appropriate temperature range. PS with a nominal 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. P2CS was radically polymerized in toluene and fractionated with a preparative gel permeation chromatography apparatus. M_w and M_w/M_n of P2CS were determined by light scattering and analytical gel permeation chromatography to be 9.6×10^4 and 1.10, respectively. Blend films were cast from about 3 wt % benzene solution. The cast film was air-dried at 60 °C overnight, followed by vacuum drying first at 80 °C for 4 days and then at 120 °C for 1 day. Small pieces cut from the cast film were annealed to obtain 0.2-mm-thick sample films. All measurements were made for samples with a fixed weight composition of PS:P2CS:DBP = 46.6:46.5:6.9.

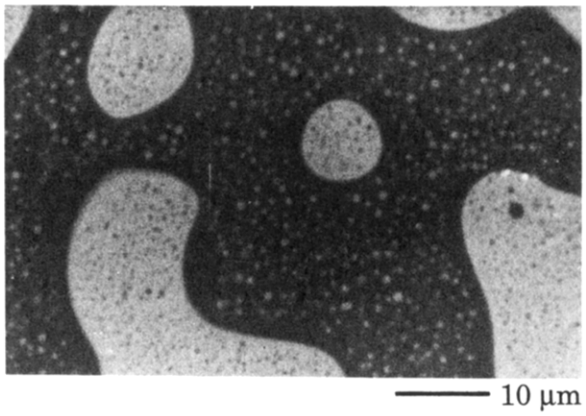

Figure 1. Backscattered electron image of the phase-separation structure formed in the two-step temperature jump of a polystyrene/poly(2-chlorostyrene)/*n*-butyl phthalate blend (1.35×10^4 s after the second temperature jump). White regions correspond to the poly(2-chlorostyrene)-rich phase. The first jump was mde to 140 °C, at which the sample was kept for 70 h, and then the second jump was made to 165 °C.

Instruments. The temperature jumps were carried out by transfering the sample films to an aluminum block controlled at a desired temperature to ±0.03 °C. To observe the morphological structure, sample films were taken out of the block and quenched to room temperature, which was well below the glass transition temperature of the blend. We have neglected the structural change which may occur during the quench since the phase separation was very slow when compared with the quench speed. We followed the time evolution of the phase-separation structure by observing different sample pieces quenched at various stages of phase separation.

Morphological structures of the fractured surface of the sample were observed by using an electron microscope JEOL JSM-T220. A backscattered electron image of the carbon-coated surface was observed at 10 or 15 kV. Since one component contained chlorine atoms, a large contrast between the two separated phases was obtained in the backscattered electron image without staining. A typical morphological structure observed after the second jump is shown in Figure 1. Characteristic lengths of large domains were evaluated from such electron micrographs with an image analysis system PIAS LA 525 by the following procedure. Images of small droplets inside the large domains were first smeared out to analyze only co-continuous patterns of the large domains. Then we drew a straight line arbitrarily, which crossed both domains several times. The length of each segment of the line sectioned by the boundaries between the two phases was measured. The characteristic length was determined by averaging these segment lengths over many segments on various arbitrarily-drawn lines.

The time-resolved light-scattering measurements were carried out with an instrument similar to those described in ref 4. The angular dependence of the scattered light was detected by scanning a photomultiplier tube with a stepping motor driven by a microcomputer.

Results and Discussion

Figure 2 shows the quasi-binary representation of the coexistence curve of the present system.[5] The lower critical point is located at a volume fraction of PS in total polymers $\phi_c \cong 0.54$ and a temperature $T_c = 124.8$ °C. The process of temperature jumps is indicated in Figure 2. The first temperature jump was made from 120 to 140 °C, at which the temperature was kept for 70 or 209h, and then the

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[†] Department of Polymer Chemistry.
[‡] Department of Organic and Polymeric Materials.

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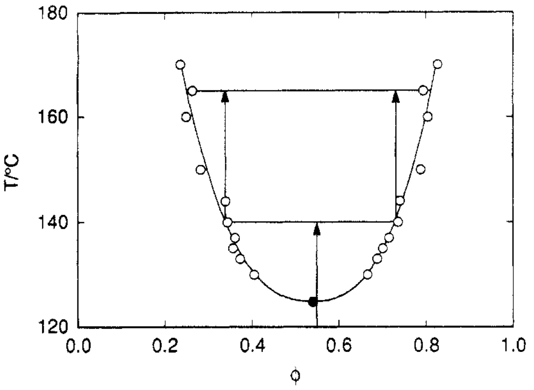

Figure 2. Quasi-binary representation of the coexistence curve of a blend of polystyrene/poly(2-chlorostyrene) containing 6.9 wt % di-*n*-butyl phthalate as a plasticizer. The critical point is indicated by a filled circle. The process of temperature jumps is indicated by arrows.

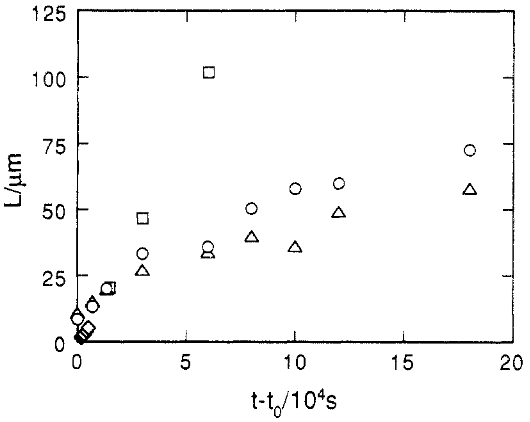

Figure 3. Time evolution characteristic domain size *L* after the temperature was jumped to 165 °C. The second temperature jump to 165 °C was made at t_0 = 70 h (○) and 209 h (△). Data of the single-step jump determined by image analysis (□) and time-resolved light scattering (◇) are also shown for comparison purposes.

second jump was made to 165 °C. Since the composition (in total polymers) of the sample 0.54$_7$ in volume fraction, was very close to the critical composition, the co-continuous phase-separation structure was observed after the first jump. The characteristic domain size grew to 8.6 μm in 70 h after the first jump and 10.9 μm in 209 h. The growth rate of the size in the period from 70 to 209 h seemed to be too small when compared with those predicted for various coarsening mechanism.[6,7]

Figure 3 shows the characteristic size *L* of the large domain determined by the image analysis of electron micrographs as a function of time $t - t_0$ after the second jump, where t_0 is the time when the second jump was made. As mentioned above, we used different samples to obtain respective data points in the figure. The plot shows a relatively small scatter, and it appears that the difference among individual samples is not large. For comparison, the characteristic length for the usual single-step temperature jump to 165 °C (i.e., $t_0 = 0$), which was determined by the image analysis and the time-resolved light scattering measurement, is also shown in Figure 3. In the light scattering experiment, the characteristic length *L* was calculated from the wavenumber q_m giving the maximum light intensity by using an equation $L = \pi/q_m$. In Figure 3, the large domains continued to grow in size after the second jump. However, its growth rate was appreciably slower than that of the single-step jump when compared at the same domain size. The growth rate decreased slightly with increasing t_0.

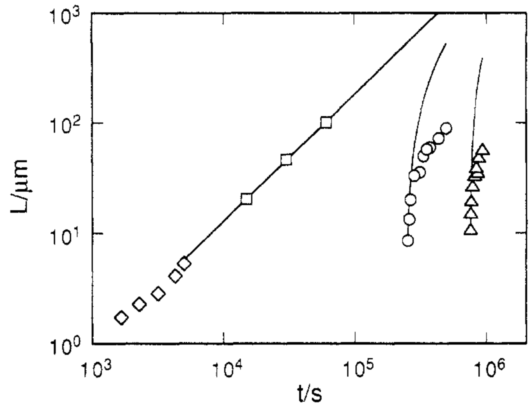

Figure 4. Double-logarithmic plot of characteristic domain size *L* versus time *t* after the first jump. Symbols are the same as in Figure 3. Curves were calculated by eq 4.

Figure 4 shows a double-logarithmic plot of the large domain size against the period over which the samples were kept in the two-phase region, that is, time *t* after the first jump. The results of light scattering for the earlier period of the phase separation could be connected smoothly to the results calculated with the image analysis for the later period, thus supporting the validity of our evaluation method of the characteristic length by the image analysis. In the late stage of phase separation by the single-step jump, the domain size could be well described by a power relation:

$$L = Kt^{\alpha} \equiv L_1(t) \qquad (1)$$

The exponent $\alpha = 1.1_6$ evaluated by the least-squares fitting was consistent with the prediction by Siggia[6] for the coarsening mechanism of the co-continuous phase-separation structure of a fluid mixture. The size *L* was very small at the moment of the second jump $t = t_0$ when compared with *L* of the single-step jump to 165 °C because of the smaller thermodynamic driving force at the shallower quench, and the size *L* gradually approached the line of the single-step jump to 165 °C (eq 1) after the second jump. This is quite reasonable because, in principle, the mechanism of phase separation must finally become identical irrespective of the history of the temperature change during the phase separation if the final temperature is the same. Therefore, after the second jump, the characteristic length *L* will be expressed sooner or later by the equation

$$L = K(t - t_r)^{\alpha} \equiv L_2(t) \qquad (2)$$

with the same exponent α and prefactor *K* as those of the single-step jump. The difference lies only in the time shift factor t_r. As an extreme case, we assume here that the phase-separation kinetics starts to obey eq 2 immediately after the second jump. Then the shift factor t_r is easily calculated to be $t_0 - t_x$, where t_x is the time necessary for the domain to grow to the size L_0 when the sample is jumped directly to 165 °C:

$$L_2(t_0) = L_0 = L_1(t_x) \qquad (3)$$

From these equations, one can obtain

$$L = K[t - t_0 + (L_0/K)^{1/\alpha}]^{\alpha} \qquad (4)$$

By using the experimental values of α and *K* determined from the single-step jump, eq 4 is plotted in Figure 4. Agreement with experimental data is good in the early period of the second jump but deteriorates in later periods.

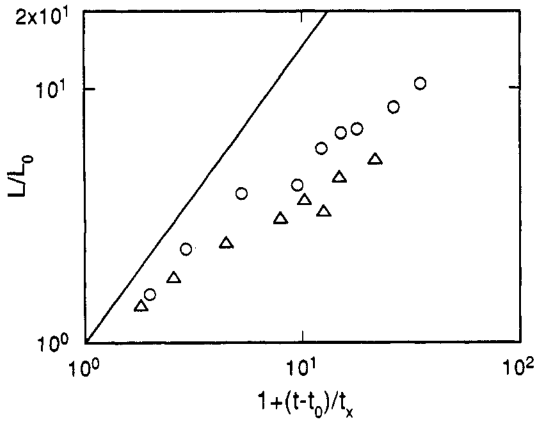

Figure 5. Double-logarithmic plot of L/L_0 against $1 + (t - t_0)/t_x$. The solid line was calculated by eq 4a, and symbols are the same as in Figure 3.

Equation 4 can be rewritten with the aid of eq 3 as

$$L/L_0 = [1 + (t - t_0)/t_x]^{\alpha} \tag{4a}$$

which indicates that all data points fall on a single curve when L/L_0 is plotted against $(t - t_0)/t_x$. In Figure 5, L/L_0 is plotted against $1 + (t - t_0)/t_x$ in a double-logarithmic scale and thus the single straight line with a slope of $\alpha = 1.16$ is expected from eq 4a. It seems that a few data points in the early period of the second jump are consistent with the prediction. However, two different jumps give slightly different lines especially at later periods, and the slopes of the respective lines are about 0.5 which is appreciably smaller than 1.16.

We assume in the above discussion that the time t^* when the phase-separation kinetics starts to be described by eq 2 is equal to t_0. For the case $t^* > t_0$, the time shift t_r differs from the present value of $t_0 - t_x$ and is expected to become larger than that value. Thus the plot given in Figure 5 should have a slope larger than or equal to α in the period of $t > t^*$. However, the slope is obviously smaller than α in the experimentally investigated range of t except for the short period after the second jump. Although the phase-separation kinetics is expected to be eventually described by eq 2 again, this result indicates that it will take a very long time for phase separation to reach such a stage after the second jump.

References and Notes

(1) Ohnaga, T.; Inoue, T. *J. Polym. Sci., Polym. Phys. Ed.* **1989**, *27*, 1675.

(2) Okada, M.; Kwak, K. D.; Nose, T. *Polym. Prep., Jpn.* **1991**, *40*, 767. Okada, M.; Kwak, K. D.; Nose, T. *Polym. J.* **1992**, *24*, 215.

(3) Tanaka, H. *Polym. Prepr., Jpn.* **1991**, *40*, 766. Tanaka, H.; Sigefuji, T. *Polym. Prepr., Jpn.* **1992**, *41*. 925.

(4) Okada, M.; Han, C. C. *J. Chem. Phys.* **1986**, *85*, 5317.

(5) Kwak, K. D.; Okada, M.; Chiba, T.; Nose, T. *Macromolecules*, in press.

(6) Siggia, E. D. *Phys. Rev. A* **1979**, *20*, 595.

(7) Kawasaki, K.; Ohta, T. *Progr. Theor. Phys.* **1978**, *59*, 362, 1406. Onuki, A. *J. Chem. Phys.* **1986**, *85*, 1122.