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Phase separation induced by a two-step temperature jump in polystyrene/poly(2-chlorostyrene) blends: dependence on duration and temperature of the first step

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Phase separation induced by a two-step temperature jump was studied by time-resolved light scattering and scanning electron microscopy for polystyrene/poly(2-chlorostyrene) blends. A co-continuous domain structure was formed by the first-step jump, with small droplets being formed in these co-continuous domains by the second-step jump made in the intermediate stage, as well as in the late stage, of phase separation at the first-step temperature. When the duration of the first step was long enough, the growth of co-continuous domains formed after the second jump was well described by the same power function as that found for the corresponding single-step jump if the phase-separation time was shifted; this feature was confirmed for different first-step temperatures.

(Keywords: polymer blends; phase-separation dynamics; two-step temperature jump)

INTRODUCTION

The dynamics of phase separation under a time-dependent thermodynamic condition has been attracting increasing attention in recent years[1–9]. In the study of such phase separation, temperature or pressure is usually chosen as the time-dependent variable because of their ease in controlling. Composition can be a time-dependent variable if chemical reactions are used, but it is extremely difficult to control the conversion of a reaction as a function of time. Various patterns of time variation of a thermodynamic condition, which are periodic or non-periodic and continuous or stepwise, have been attempted. Of these patterns, the two-step jump[5–8] (or double quench) is the simplest. In the two-step jump procedure, the thermodynamic condition is changed stepwise during the phase separation which has been initiated by the first jump. Since any continuous change may be approximated by a set of small-step changes, the two-step jump is regarded as an elementary process of various patterns of the time-dependent condition. Therefore, the study of phase separation induced by a two-step jump is expected to give us a basis for understanding phase separation behaviour under various conditions which depend on time in more complicated ways.

In previous studies[6,7] of phase separation induced by a two-step jump process, we adopted temperature as the time-dependent thermodynamic variable and chose the direction of the second temperature jump so as to increase the thermodynamic driving force of phase separation. We made the second temperature jumps in the late stage of phase separation induced by the first jumps for samples of composition close to the critical composition, and found that small droplets appeared in the co-continuous microdomains after the second jump. In the late stage of phase separation, the microdomains (or clusters) generated as a result of phase separation are bounded by sharp interfaces, with the concentration in each domain having already reached its equilibrium value[10,11]. This indicates that the observed microdomain structure was formed simply by phase separation of each microdomain having a homogeneous concentration. On the other hand, if the second jump is made immediately after the first jump, the phase separation behaviour must be identical to that found for a single-step jump to the same final temperature. Therefore, the phase separation behaviour should be changed by decreasing the time interval between the first and second jumps, and so it is interesting to study the phase separation behaviour after the second jump that was made when phase separation did not reach the late stage of the first step.

In our previous work[7], we also found that, for a certain period after the second jump, the growth of the

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characteristic length of the co-continuous domain structure was described by the same function as that used for the single-step jump to the same final temperature if the phase separation time was shifted by a certain amount. As mentioned above, the second jump was made during the late stage of phase separation at the first-step temperature, and the result suggests that coarsening of the co-continuous domains in the late stage was proceeding independently of their internal structures, at least over a certain period of time. The question is whether the growth of the characteristic length of the co-continuous structure is also described by the same function when the second jump is made before a sharp interface is formed. In addition, it is not clear either whether the presence of internal droplets will not affect the growth of the co-continuous domains, even when the volume ratio of the droplets in the co-continuous domain is increased.

In order to elucidate these points, in this paper we have studied the phase separation induced by a two-step temperature jump with a varying duration and temperature of the first step. We have employed a time-resolved light-scattering (TRLS) technique and scanning electron microscopy (SEM) on samples of polystyrene (PS)/poly(2-chlorostyrene) (P2CLS) blends, these blends having a lower critical solution temperature (*LCST*)-type phase diagram[12,13]. The interaction parameter (χ) between PS and P2CLS shows a very weak temperature dependence, and a small change in molecular weight results in a large shift in the phase diagram[14]. The experimental temperature range is restricted at the high end by sample degradation and at the low end by the glass transition, and it is difficult to adjust the spinodal temperature to this temperature range by only changing the molecular weight. To get around this difficulty, we added a plasticizer, i.e. di-n-butyl phthalate (DBP) to adjust the spinodal temperature and to extend the experimental temperature range by decreasing the glass transition temperature. Consequently, the present system is not a binary system in the strictest sense.

EXPERIMENTAL

Materials

Polystyrene (PS) with a weight-average molecular weight M_w of 5.0×10^4 and a narrow molecular-weight distribution, i.e. $M_w/M_n < 1.06$, was purchased from the Pressure Chemical Company. Poly(2-chlorostyrene) (P2CLS) was produced by a radical polymerization of the monomer in toluene at 60°C and then fractionated in a preparative gel permeation chromatography apparatus equipped with two columns (Toso G5000H) of 6 cm diameter and 60 cm length. Its molecular weight and molecular-weight distribution were determined by analytical gel permeation chromatography, giving values of $M_w = 1.18 \times 10^5$ and $M_w/M_n = 1.11$, respectively. The plasticizer (DBP) was a product of Tokyo Kasei Kogyo Company and was used without further purification. Two samples that had almost the same PS/P2CLS composition, but different DBP contents, namely PS/P2CLS/DBP = 50.3/40.0/9.7 and 46.2/36.8/17.0 by weight, were used in this work. The blend films were prepared by casting from about 3.0 wt% benzene solution. The cast film was air dried at 60°C for 1 day, followed by vacuum drying with increasing temperatures, i.e. at 60°C for 1 day, at 80°C for 2 days, and finally at 100°C (sample with 9.7 wt% DBP content) or 105°C (17.0 wt% DBP) for 2 days. Small pieces cut from the cast film were sandwiched between glass plates using a 0.2 mm thick spacer and then annealed at either 100 or 105°C for 24 h to produce samples suitable for both the time-resolved light-scattering measurements and morphology observations.

Measurements

The first temperature jumps to initiate phase separation were made by transferring the sample films to an aluminium block which was controlled at the desired temperature to ±0.03°C. This block was placed in an atmosphere of nitrogen to suppress sample degradation at high temperatures. Before the second-temperature jump, samples that had been kept at the first-step temperature were taken out from the block and then quickly quenched by contacting both sides of the sample glass plate with two brass blocks that had been cooled to −15°C in a refrigerator. These samples were kept at room temperature, which was well below the glass transition temperature, until they were returned back to the block after the temperature of the latter had been set and stabilized at the second-step temperature. To observe the morphological structures during phase separation, the sample films were taken out of the block and quenched immediately.

The morphological structure was observed by using an electron microscope (JEOL JSM-T220). The composition image was taken by detecting electrons that had been back scattered from a fractured surface of a sample. Two separated phases, being rich and low in P2CLS content, respectively, showed large contrasts in their electron micrographs, without the need for staining with a dye, because a heavy chlorine atom was contained in the P2CLS molecule. The characteristic length of the continuous microdomains was determined from the electron micrographs by using a PIAS LA525 image analysis system. The characteristic length was evaluated as the average length of the segments, sectioned by interfaces between the two phases, of a straight line arbitrarily drawn on the electron micrograph. Fuller details of the evaluation of this characteristic length are given in ref. 7.

The time-resolved light-scattering (TRLS) measurements were carried out with an instrument constructed in our laboratory[15]. The angular dependence of the scattered light intensity was measured by scanning a photomultiplier tube with a stepping motor. The temperature control of the instrument was better than ±0.03°C.

RESULTS AND DISCUSSION

Dependence on the duration of the first step

We carried out the two-step temperature jump experiment for the sample with PS/P2CLS/DBP = 50.3/40.0/9.7 (wt%) by varying the duration of the first step in order to examine its influence on the phase-separation behaviour at the second step. The temperatures of the first and the second step were $T_1 = 135$ and $T_2 = 155$°C, respectively. We also carried out experiments with ordinary single-step jumps to 135 and 155°C for comparison. *Figure 1* shows the morphological structures

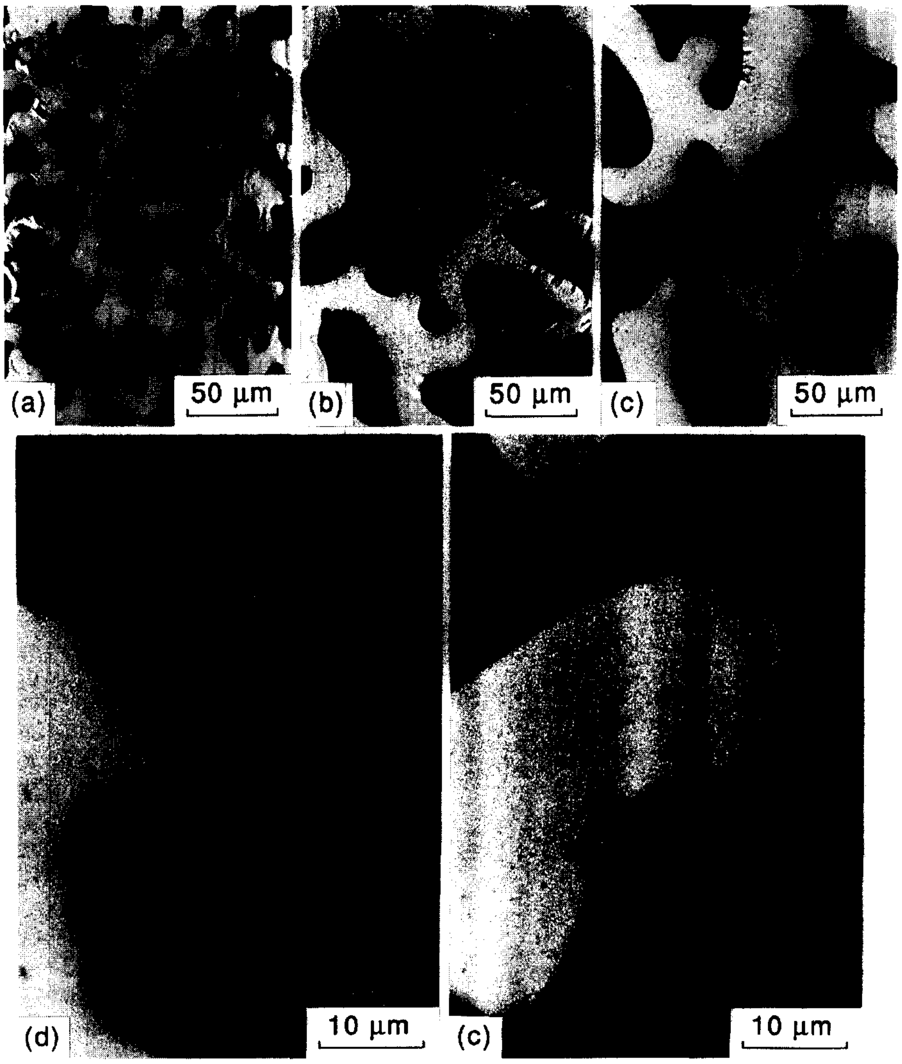

Figure 1 Electron micrographs of a fractured surface of a sample with PS/P2CLS/DBP = 50.3/40.0/9.7 (wt%), phase separated by a single-step jump to 155°C. The phase-separation times are: (a) 3.0 h; (b) 6.5 h; (c) 11.0 h; (d) 4.5 h; (e) 6.5 h

observed after a single-step jump to 155°C. A co-continuous domain structure typical of phase separation in the critical composition range was observed after the jump. Surprisingly, small droplets appeared inside the co-continuous domains at a very late stage of the phase separation (6.5 h after the jump), as shown in *Figure 1e*. This domain structure resembles the structures formed by two-step jumps, which will be shown later, although the number density of the droplets was relatively small when compared with the density given by a typical two-step jump. Formation of this structure was reproducible: all samples for which we made single-step jumps to 155°C showed the same kind of structure when they were kept at this temperature for more than 6.5 h. We confirmed that the structure was not a result of incomplete sample preparation, such as phase separation during the process of sample drying or the presence of any residual casting solvent (benzene) in these films. No indication of phase separation was detected in the profile of the light intensity scattered from the sample films as prepared. The sample films that were dried at 100°C under reduced pressure for as long as one week also produced the same result. In addition, we carried out single-step temperature jumps to 156 and 160°C for blend films containing as much as 17 wt% DBP, for which it was much easier to remove the casting solvent than the sample with 9.7 wt% DBP content at 100°C because of the lower glass transition temperature of higher-DBP-content samples. However, similar internal droplets were likewise observed during the very late period of phase separation. Evaporation of the plasticizer DBP during phase separation can be neglected because the boiling temperature of DBP is very high (340°C at 1 atm) compared with the phase-separation temperature of 155°C.

In the strict sense, the present system was not a binary blend. It is not clear at present whether formation of this sort of morphological structure is a general phenomenon which occurs in a very late stage of the phase separation process, or is only characteristic of a ternary system containing a low-molecular-weight component. Experimental checks on binary blends could not be made by using these present polymer samples, because the lower bound of the immiscible region became lower than the glass transition temperature for the system when no plasticizer was added.

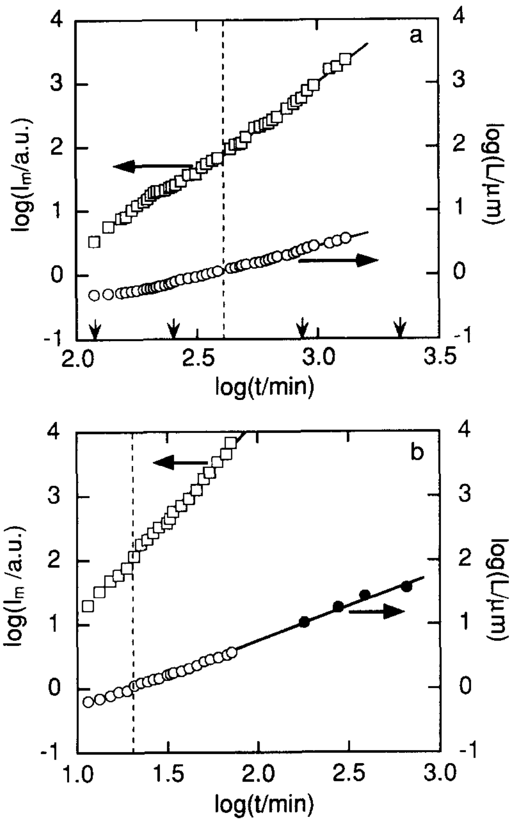

Figure 2 Double-logarithmic plots of the characteristic length L (○, ●) of co-continuous domains, and the maximum intensity I_m (□) in scattered light intensity profiles, *versus* phase-separation time t after the single-step jumps (a) from 100 to 135°C and (b) from 100 to 155°C for the blend where PS/P2CLS/DBP = 50.3/40.0/9.7 (wt%). The filled circles denote the results obtained by image analysis, while the vertical broken lines indicate the boundary between the intermediate and late stages of phase separation

In the scattered intensity profile measured by the time-resolved light-scattering technique, a peak was observed at a non-zero angle. The wavenumber q_m where the peak was located was related to the characteristic length L of the co-continuous domain by $L = \pi/q_m$. *Figure 2* shows double-logarithmic plots of the peak intensity I_m and the characteristic length L calculated from q_m *versus* phase-separation time t for the single-step jumps to 135 and 155°C. For the jump to 135°C, as seen in *Figure 2a*, both I_m and L could be expressed by power relationships, as follows:

$$L \sim t^{\alpha} \tag{1}$$

$$I_m \sim t^{\beta} \tag{2}$$

for the range where $t > 400$ min. In the late stage of phase separation[11,16], where the concentration of each domain (cluster) attains to the co-existing value and domains are coarsening so as to reduce the total area of the interface, the exponents α and β are related by $\beta = 3\alpha$. The coarsening mechanism of the co-continuous domains in a fluid system was discussed theoretically by Siggia[16]. He pointed out that hydrodynamics play a central role in the coarsening and predicted that the exponent became $\alpha = 1$. The least-squares fitting of the experimental data in the range where $t > 400$ min gave $\alpha = 0.97$ and $\beta = 2.92$, which agreed very well with the theoretical predictions. This means that at 135° the late stage of phase separation began after about 400 min.

The characteristic length L in the later period could be evaluated by image analysis of the electron micrographs, and the results thus determined for the temperature jump to 155°C are shown in *Figure 2b* (solid circles), together with the characteristic length L evaluated from the TRLS measurements. The data points obtained from these two measurements can be connected smoothly, which indicates a consistency of the two different methods for evaluating the characteristic length L. Again, both L and I_m could be expressed by power relationships during the later periods. The exponents were evaluated in the range where $t > 20$ min as $\alpha = 1.07$ and $\beta = 3.12$, which again agrees well with theoretical predictions. It is noted that the two data points at the longest phase-separation times were already in the region where small droplets appeared in the co-continuous domains. In other words, the growth rate of the co-continuous domain was not appreciably changed by the appearance of small droplets inside it.

In the two-step jump experiments, the second temperature jumps were made at $t_0 = 2.0$, 4.0, 14.5 and 37.0 h after the first jump. These times are indicated by arrows in *Figure 2a*. For the last two (14.5 and 37.0 h), phase separation initiated by the first jump had already reached its late stage, while for the earlier two times phase separation was still in its intermediate stage. (The approximate location of the boundary between the two stages, namely 400 min, is indicated by a vertical broken line in *Figure 2a*.) After the second temperature jump, the co-continuous domains formed by the first jump continued to grow in all cases. *Figure 3* shows the morphological structures inside these continuous domains at various phase-separation times after the second jump, which was made at $t_0 = 37.0$ h. The dark and the bright areas in the micrographs are PS-rich and P2CLS-rich phases, respectively. Many small droplets appeared inside the continuous domains after the second jump. As mentioned in the introductory section, it is considered that this morphological structure was formed in the following way: since phase separation was already in its late stage at $t_0 = 37.0$ h and the concentration of each microdomain had attained the coexisting value $\phi_{\mathrm{coex}}(T_1)$ at the first-step temperature T_1, each microdomain was separated into new equilibrium phases by the second temperature jump to T_2 in the same way as a single homogeneous phase of concentration $\phi_{\mathrm{coex}}(T_1)$ was itself separated by a corresponding temperature jump to T_2.

These droplets inside the continuous domains show coarsening with time. The P2CLS-rich droplets in the PS-rich background grow faster than the PS-rich droplets in the P2CLS-rich background. This is explained by the difference in mobility between the respective phases. The P2CLS-rich phase had a higher glass transition temperature[14] and consequently had a lower mobility. In a previous study[6], we observed that the droplets in the co-continuous domains were decreasing in number with time during the very late period until they eventually disappeared. However, we did not observe such a decrease in number density of the droplets in the time range investigated here.

When the interval between the two jumps t_0 was decreased to 14.5 h, the phase-separation behaviour inside the co-continuous domains was scarcely changed from the behaviour observed in the case of $t_0 = 37.0$ h for

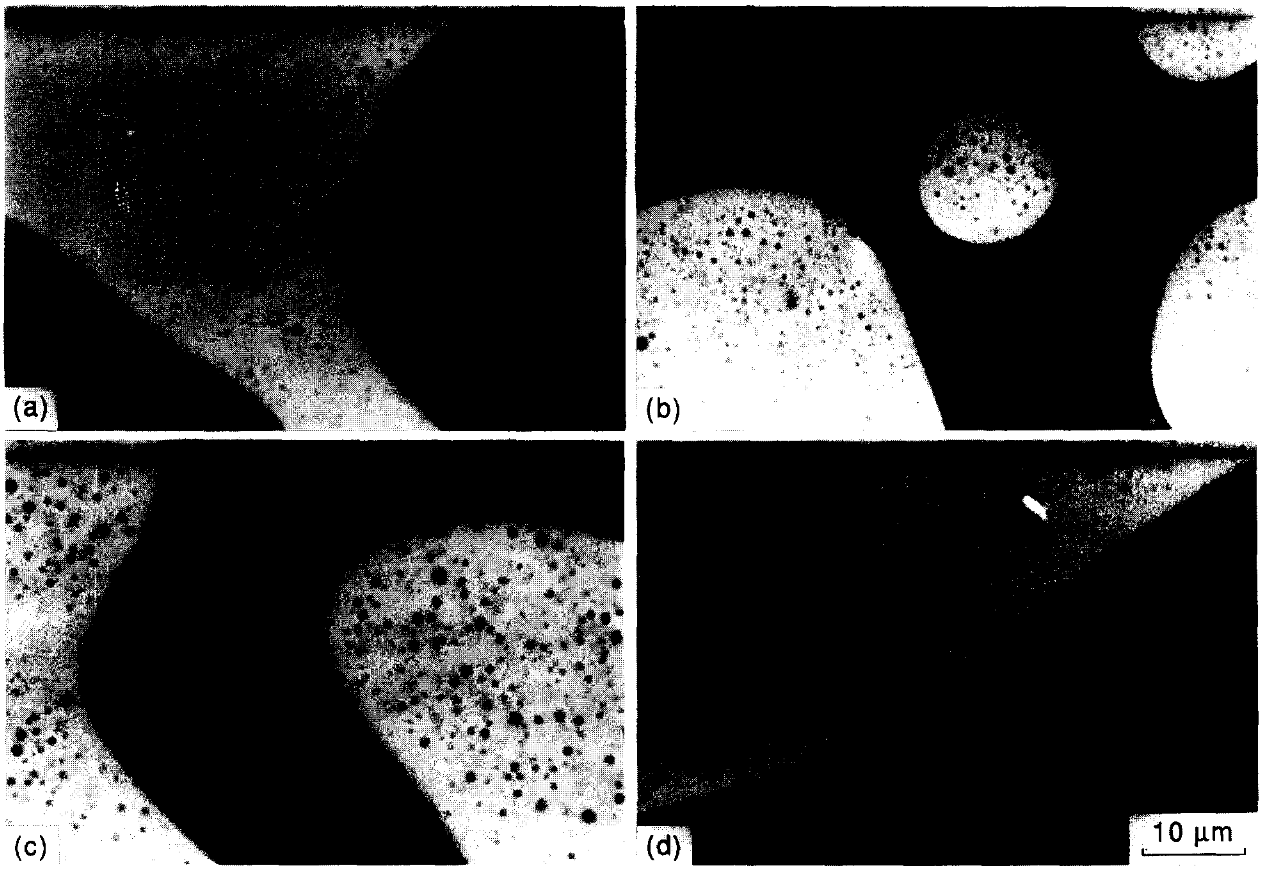

Figure 3 Electron micrographs of the microdomain structures after the second jump from 135 to 155°C for the blend where PS/P2CLS/DBP = 50.3/40.0/9.7 (wt%). The duration t_0 of the first step is 37.0 h, and the phase-separation times after the second jump ($t - t_0$) are: (a) 5.8 h; (b) 11 h; (c) 22 h; (d) 43 h

the investigated time range. This seems quite reasonable because phase separation was already in its late stage at $t_0 = 14.5$ h and consequently the concentrations of continuous domains at $t_0 = 14.5$ h were the same as those at $t_0 = 37.0$ h.

Figure 4 shows the morphological structures inside the co-continuous domains at various phase-separation times after the second jump was made at $t_0 = 4.0$ h. In the present case, the second temperature jump was made before the concentrations of the microdomains (clusters) reached their coexisting values at the first-step temperature and the interface became sharp. We could clearly observe that small droplets had appeared inside the co-continuous domains. Compared with the droplets formed by the jumps in the late stage, the small droplets formed by the jump in the intermediate stage were growing more slowly (see *Figures 3* and *4*). The domain structure which consisted of continuous domains and internal small droplets was formed even by a single-step jump, as seen above. However, such structures appeared only during the fairly late stages of phase separation in the case of the single-step jump. The characteristic length L of the continuous domains increased to a value of 28 μm when small droplets appeared in the continuous domains. Therefore, when the droplet structures were observed in the two-step jump before the characteristic length increased to 28 μm, it is reasonable to consider that these droplet structures were produced by the second temperature jump. Since small droplets were clearly observed in the continuous domains with $L = 18\,\mu$m (see *Figure 4a*) in the case of the two-step jump with $t_0 = 4.0$ h, it is concluded that the small droplets were produced in the continuous domains by the second jump that was made even before phase separation reached the late stage.

When we further decreased the interval between the two jumps to $t_0 = 2.0$ h, droplets were not observed until the size of the co-continuous domains became comparable to the size of the continuous domains in which small droplets appeared as a result of the single-step jump. Therefore, when t_0 became small, the influence of the first step did not extend over the late period of phase separation at the second step. This is consistent with the requirement that at the limit of the vanishing t_0 a two-step jump should reduce to a single-step jump to a temperature of T_2.

Figure 5 shows double-logarithmic plots of the evolution with time of the characteristic length L of the continuous domains after the second temperature jump from $T_1 = 135$ to $T_2 = 155$°C, together with the results for the single-step jumps to T_1 and T_2. Here, the phase separation time t was measured from the moment that the first temperature jump was made. The growth rate of the characteristic length L of the continuous domains was accelerated by increasing the temperature further into the two-phase region, with L approaching the line representing the single-step jump to T_2.

Since the final equilibrium state is determined by the second-step temperature T_2 and is independent of

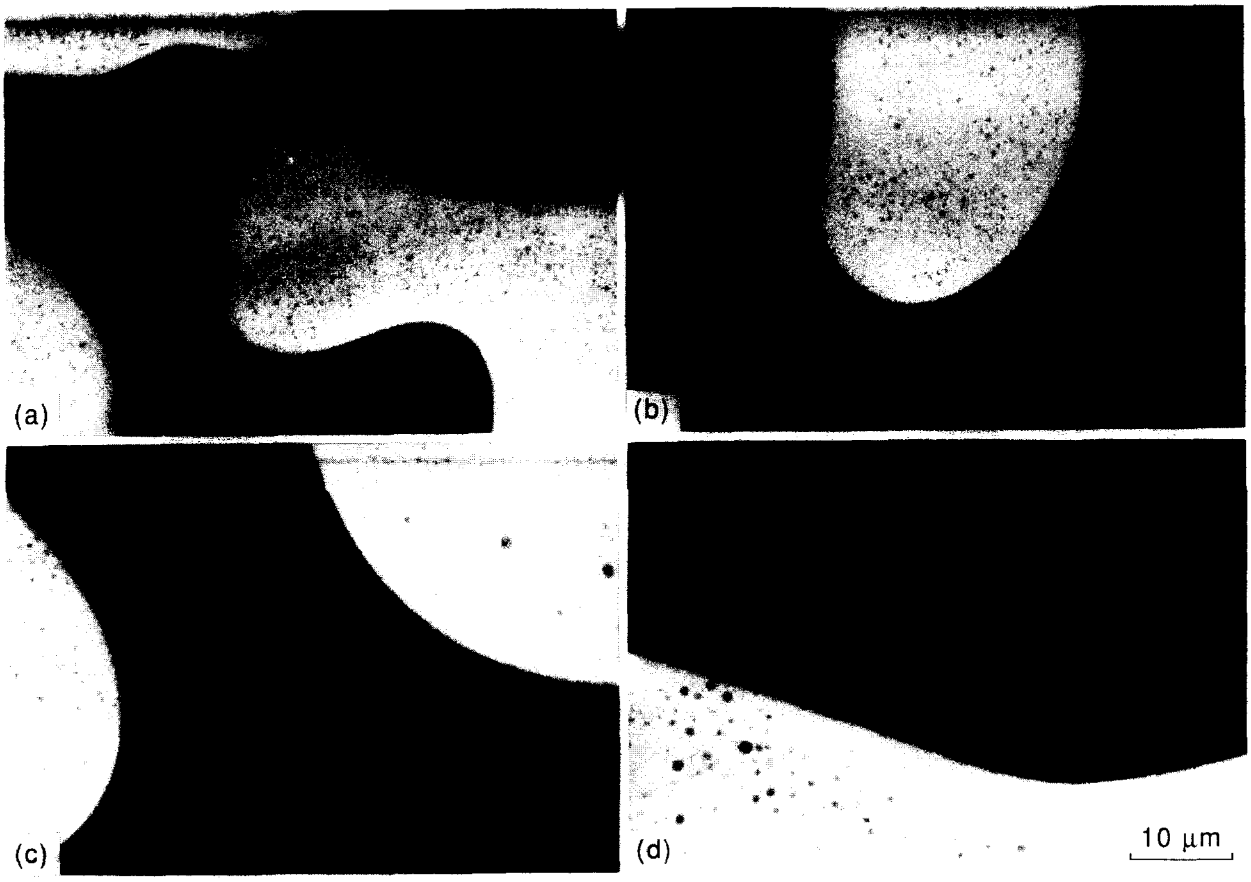

Figure 4 Electron micrographs of the microdomain structures after the second jump from 135 to 155°C for the blend where PS/P2CLS/DBP = 50.3/40.0/9.7 (wt%). The duration t_0 of the first step is 4.0 h, and the phase-separation times after the second jump $(t - t_0)$ are: (a) 5.8 h; (b) 11 h; (c) 22 h; (d) 43 h

the first-step temperature T_1, the phase separation behaviour after the second jump is expected to become indistinguishable, in time, from that induced by the single-step jump to the same temperature. If this is the case, the characteristic length L of the co-continuous domains can be expressed by the same function as that used for the single-step jump:

$$L = f_2(t') \tag{3}$$

by using an appropriate effective phase-separation time t' instead of a real phase-separation time t:

$$t' = t - t_r \tag{4}$$

In the late stage of phase separation, the growth of the characteristic length obeys a power law, as follows:

$$L = f_2(x) \equiv K_2 x^{\alpha} \tag{5}$$

as seen in *Figure 2*.

In a previous publication[7], by assuming that equation (3) holds immediately after the second jump, we have derived the time shift factor t_r as follows:

$$t_r = t_0 - t_x \tag{6}$$

where t_0 is the time when the second temperature jump is made, t_x is the time required for the characteristic length L to reach the value L_0 when the single-step jump is made to T_2, and L_0 is the characteristic length at the moment $(t = t_0)$ of the second jump. If $f_1(t)$ denotes the function describing the growth of L at the temperature T_1, then it follows that:

$$f_1(t_0) = L_0 = f_2(t_x) \tag{7}$$

From equations (3)–(6), we obtain the following:

$$L = K_2(t - t_0 + t_x)^{\alpha} \tag{8}$$

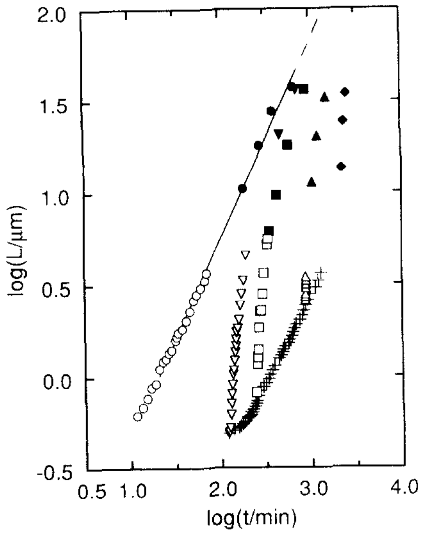

Figure 5 Double-logarithmic plots of the characteristic length L of the co-continuous domains obtained from TRLS (open symbols) and image analysis (filled symbols) *versus* phase-separation time t after the first jump for the blend where PS/P2CLS/DBP = 50.3/40.9/9.7 (wt%): single-step jumps to (○, ●) 155 and (+) 135°C; two-step jumps from 135 to 155°C in which the second jump was made at t_0 = (▽, ▼) 2.0 h, (□, ■) 4.0 h, (△, ▲) 14.5 h and (◆) 37.0 h

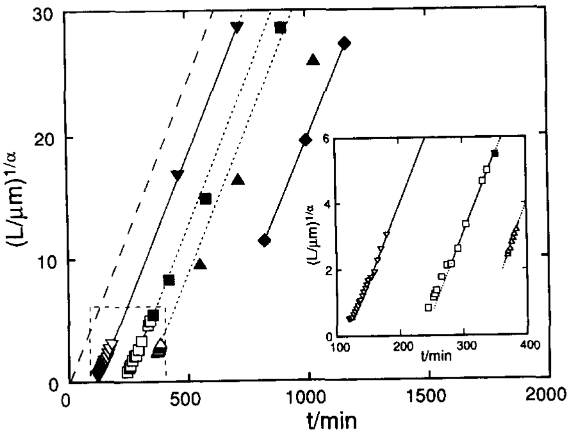

Figure 6 Plots of $L^{1/\alpha}$ ($\alpha = 1.07$) *versus* phase-separation time t for the blend where PS/P2CLS/DBP = 50.3/40.0/9.7 (wt%). The dashed line represents the power relationship obtained by the best fit to the data of the single-step jump to 155°C. The symbols used are the same as those in *Figure 5* and the data for $t_0 = 14.5$ and 37.0 h are shifted horizontally by −500 and −1400 min, respectively, for clarity. Inset shows magnification of the area surrounded by broken lines; solid lines are parallel to the dashed line

However, the assumption introduced to derive equation (6) imposes a strong restriction on the applicability of this equation. In addition, the values of L_0 at $t_0 = 2.0$ and 4.0 h are located outside the range where the power law (equation (5)) holds. To relax the restriction, here we regard t_r as an adjustable parameter and instead of equation (8) we use the following:

$$L^{1/\alpha} = K_2^{1/\alpha}(t - t_r) \qquad (9)$$

By using a value of α of 1.07, determined from the data in the late stage of phase separation by the single-step jump to 155°C, we obtained the plots of $L^{1/\alpha}$ against t which are shown in *Figure 6*. For the period where equation (6) holds, the data points fall on a line with the same slope as that of the single-step jump, i.e. $K_2^{1/\alpha}$. All points for $t_0 = 37.0$ h fell on the straight line parallel to the line of the single-step jump. The data points obtained for $t_0 = 14.5$ h fell on a straight line with a slope of $K_2^{1/\alpha}$ in the relatively early period after the second jump but obviously deviated from the line during the later period. Similar trends were also observed in the data for $t_0 = 4.0$ h, but deviations from the line in the early period were also seen in this case. The data points obtained for $t_0 = 2.0$ h lay on this line over a long period, with the exception of a short period immediately after the second jump.

Since equation (9) does not hold for L being smaller than the value which satisfies equation (5) in the case of the single-step jump, the deviation at small values of $t - t_0$ in the $L^{1/\alpha}$ *versus* t plot does not necessarily mean a failure of equation (3). To examine the validity of equation (3) at small L values, we plotted L against $(t - t_r)$ in *Figure 7*. The time shift factor t_r was determined as the intersection with the abscissa of the straight line given by extrapolating the data points on the line with the slope of $K_2^{1/\alpha}$. It appeared that the data points where $L < 2\,\mu$m for $t_0 = 2.0$ h showed a slight deviation from the data of the single-step jump. This indicates that the phase-separation behaviour was initially influenced by concentration fluctuations at the first step, although it soon became identical to that of the single-step jump when the interval between the two jumps was small.

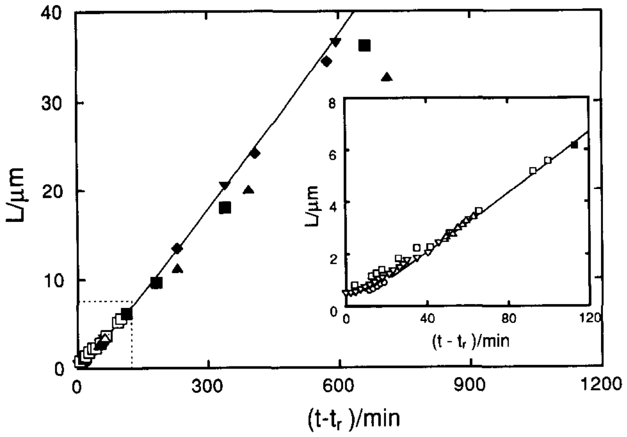

Figure 7 Plot of L *versus* $(t - t_r)$ for the blend where PS/P2CLS/DBP = 50.3/40.0/9.7 (wt%); symbols used are the same as those in *Figure 5*. The solid curve represents the power relationship obtained by the best fit to the data of the single-step jump; inset shows magnification of the area surrounded by broken lines

Dependence on the temperature at the first step

We carried out the two-step temperature jump experiment for the sample PS/P2CLS/DBP = 46.2/36.8/17.0 (wt%) by varying the temperature at the first step to elucidate its influence on the phase-separation behaviour after the second jump. The first jump was made to three different temperatures, namely 136, 131 and 128°C, and then the second jump was made to the same temperature, i.e. 156°C. The duration of the first step was set to be 38 h at 136°C, 68 h at 131°C, and 117.4 h at 128°C so that the characteristic length L_0 of the continuous domains became roughly identical (~ 8 μm) at the moment of the second jump.

Figure 8 shows the morphological structures inside the continuous domains at approximately the same phase-separation times $(t - t_0)$ after the second jump from different first-step temperatures. Comparison of the morphological structures at $(t - t_0) = 2$ h reveals that droplets were formed more rapidly at lower first-step temperatures T_1. This was explained by the difference in the driving force of phase separation as follows. When the characteristic length became as large as 8 μm, phase separation at the first-step temperature was considered to have already reached the late stage. Thus, with lowering the temperature of the first step, the compositions of the microdomains formed at that temperature were approaching the critical composition. Hence, the driving force of phase separation, which was proportional to the distance of the phase-separation temperature from the spinodal line, was increased by decreasing the first-step temperature. The difference in composition of the microdomains formed at the first step also resulted in a difference in the fraction of the total volume of droplets in the continuous domain. In fact, the fraction of the total volume of the droplets in a continuous domain was decreased by increasing the first-step temperature, as seen in the electron micrographs at $(t - t_0) = 12$ and 13 h.

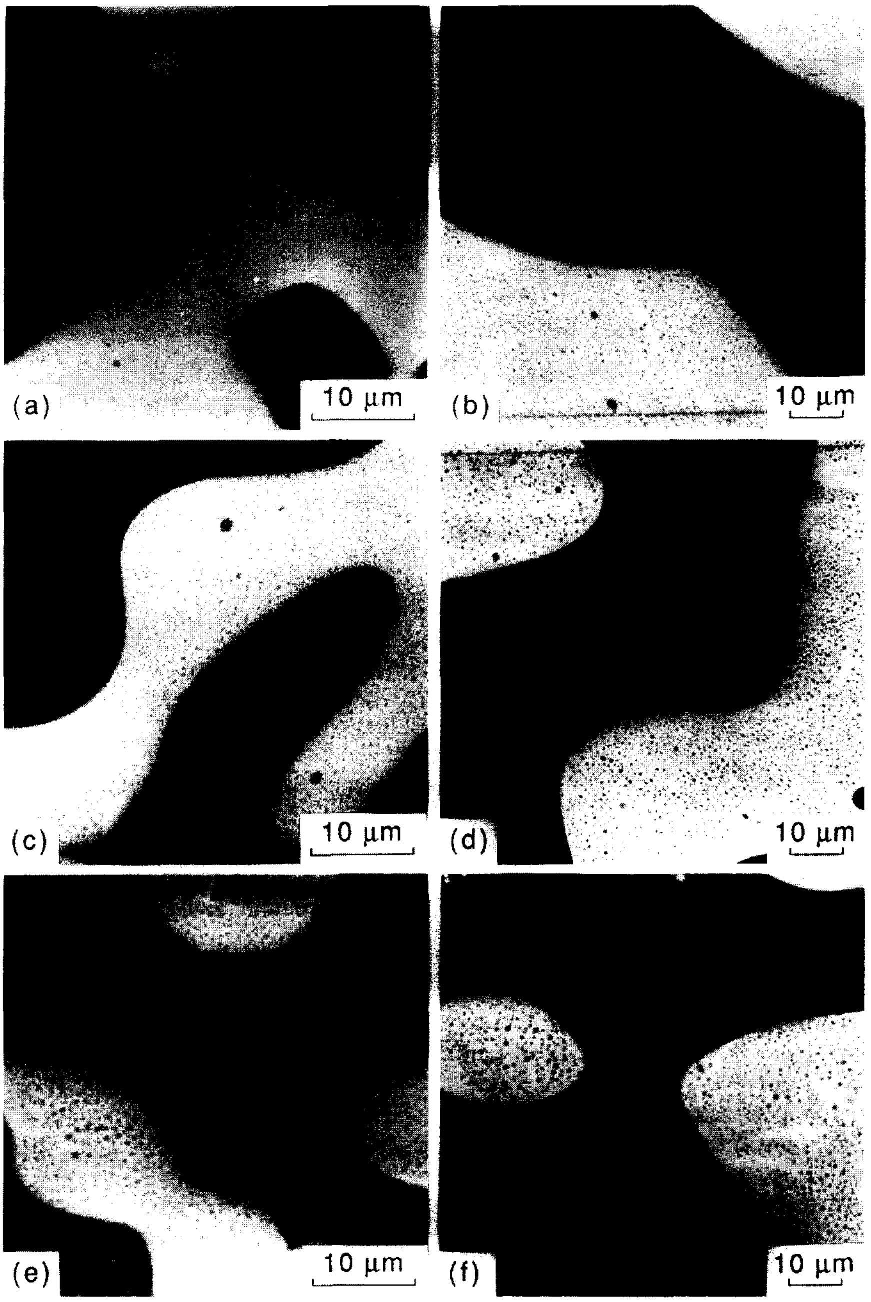

Figure 8 Electron micrographs of the microdomain structures after the second jump from (a, b) 136°C, (c, d) 131°C and (e, f) 128°C to 156°C for the blend where PS/P2CLS/DBP = 46.2/36.8/17.0 (wt%). The duration after the second jump $(t - t_0)$ is: (a, c, e) 2 h; (d, f) 12 h; (b) 13 h

In *Figure 9*, the time evolution of the characteristic length L of the co-continuous domains after the second temperature jump was plotted on double-logarithmic scales, together with the results of the single-step jump to the corresponding temperature. In the single-step jump, the characteristic length L was expressed by a power relationship (equation (5)) in the range with $t > 15\,\text{min}$, and the prefactor K_2 and the exponent α were evaluated to be 0.059 and 1.01, respectively, by a least-squares fitting. Following the procedure described in the previous section, we analysed the time dependence of the characteristic length L after the second jump, based on equation (9), with t_r being an adjustable parameter. The plots of $L^{1/\alpha}$ (with $\alpha = 1.01$) against t showed a good linear relationship in all cases, as shown in the inset of *Figure 10*. By using the time shift factor t_r, determined as the intersection with the abscissa in the $L^{1/\alpha}$ *versus* t plot, we plotted L against $(t - t_r)$ in *Figure 10*. All data points for the different first-step temperatures fell on the single line of the corresponding single-step jump. As mentioned above, the fraction of the total volume of the droplets in a continuous domain is increased by lowering the first-step temperature, but any increase in the fraction of the droplets appeared to exert no obvious influence on the growth rate of the continuous domains. These results, together with the results for $t_0 = 37.0\,\text{h}$ in the preceding section, suggest that, in coarsening of the continuous domains that are bounded with sharp interfaces, Siggia's mechanism[16] works well regardless of their internal structures.

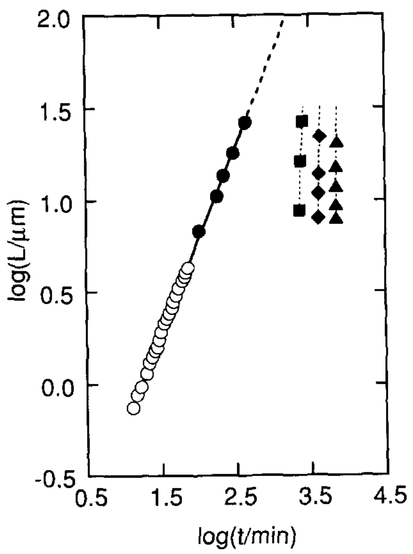

Figure 9 Double-logarithmic plots of the characteristic length L of the co-continuous domains obtained from TRLS (open symbols) and image analysis (filled symbols) *versus* phase-separation time t after the first jump for the blend where PS/P2CLS/DBP = 46.2/36.8/17.0 (wt%): (○, ●) single-step jump to 156°C; two-step jumps from T_1 = (■) 136°C, (◆) 131°C and (▲) 128°C to T_2 = 156°C

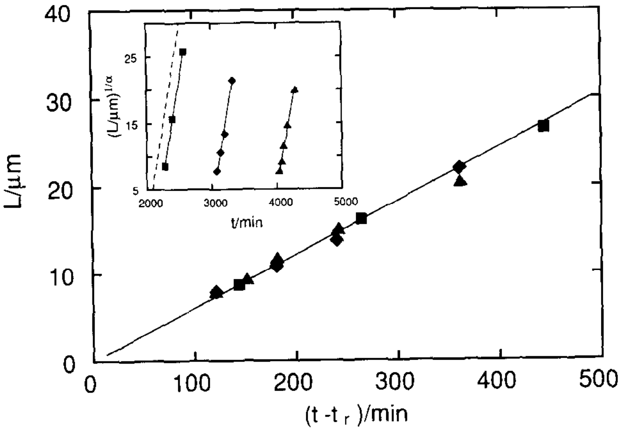

Figure 10 Plots of L *versus* $(t - t_r)$ for the blend where PS/P2CLS/DBP = 46.2/36.8/17.0 (wt%): symbols used are the same as those in *Figure 9*. The solid curve represents the power relationship obtained by the best fit to the data of the single-step jump to 156°C. Inset shows plots of $L^{1/\alpha}$ ($\alpha = 1.01$) *versus* t, where the dashed line represents the power relationship for the single-step jump; the data for $T_1 = 131$ and 128°C are shifted horizontally by −1000 and −3000 min, respectively, for clarity

In the preceding section, we observed that when the second jump was made at $t_0 = 14.5$ h, agreement with equation (9) deteriorated in the later period, although it was good initially. The time $t_0 = 14.5$ h was already in the region where the exponents α and β for L and I_m satisfied the relationship $\beta = 3\alpha$, and consequently phase separation is considered to have reached the late stage at the moment of the second jump, as in the case of $t_0 = 37.0$ h. It is not clear whether the case where $t_0 = 37.0$ h and those presented in this section will show a similar deviation from equation (9) if we investigate much longer periods than we have done in this study. In our previous work[7], we carried out the second jumps in a similar fashion, i.e. in the very late stage of the first-step phase separation, and observed deviations from equation (8) at fairly late periods after the second jumps. However, these experiments were performed in the presence of air, and consequently there was a strong possibility that sample degradation as a result of oxidation by air could not be regarded as being negligible after such long-time exposures to high temperatures.

The mechanism giving rise to the deviation from equation (9) observed in the case of $t_0 = 14.5$ h is obscure. Since the decrease in the interfacial tension results in a decrease in the growth rate of the co-continuous domains, one may consider that the sharp interfaces between the continuous domains become diffuse again while the internal small droplets were absorbed by the surrounding and much larger continuous domains. However, this is not likely to occur because none of the coarsening mechanisms[10,16,17] reported so far can account for such a process.

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