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Thermal-History Dependence of Phase Separation Induced by Radical Polymerization of 2-Chlorostyrene in the Presence of Polystyrene

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ABSTRACT: Thermal-history dependence of phase separation induced by radical polymerization of 2-chlorostyrene in the presence of polystyrene was studied by making a stepwise temperature change (jump) to a higher temperature T_2 during the phase separation. Morphological structure of poly(2-chlorostyrene)-rich domains changed from droplets to continuous domains after the temperature change if the duration at the first phase-separation temperature T_1 was longer than a certain value t_1*. The morphological change to the continuous domains was accompanied by an increase of the volume of poly(2-chlorostyrene)-rich phase. The increase of the volume was observed even when temperature was jumped after the polymerization reaction finished. The minimum duration t_1* at T_1 required for the morphological change to occur after the temperature jump increased with T_1 but scarcely depended on T_2. An explanation for the experimental results was proposed on the basis of the difference in the viscosity dependence between the phase-separation rate and the reaction rate.

Phase separation induced by polymerization reaction attracts considerable attention in recent years.[1−12] However, the understanding of its dynamics and mechanism remains at a relatively primitive stage, because of the inherent complexity arisen from the interplay between phase separation and reaction. Generally nonequilibrium phenomenon such as phase separation depends on the past history of the conditions imposed on the system under consideration.[13] Study of such history dependence of a nonequilibrium phenomenon sometimes gives information that is useful in understanding the phenomenon. In this study, the thermal-history dependence of polymerization-induced phase separation was investigated in expectation of acquiring a better understanding of its dynamics.[14]

The system investigated here was a 2-chlorostyrene (2ClS)/polystyrene (PS) (= 50/50 by weight) mixture. Phase separation was induced by radical (thermal) polymerization of 2-chlorostyrene monomer, and its phase-separation dynamics at fixed temperatures was studied in a previous work.[2] It is known that in radical polymerization the concentration of the product poly(2-chlorostyrene) (P2ClS) increases with the reaction conversion while the average molecular weight remains constant. Quite different morphological structure developments were observed during the phase separation depending on temperature. At lower temperatures, the P2ClS-rich phase initially formed droplets, and these droplets coagulated into continuous domains as phase separation proceeded, while at higher temperatures droplets continued to coarsen without the morphological change. From such large difference between the morphological developments at high and low temperatures, it is expected that the phase-separation dynamics will exhibit a strong thermal-history dependence.

In this work, the thermal-history dependence was studied by changing temperature stepwise during phase separation. Duration at the first phase-separation temperature was varied, and its effects on the phase-separation dynamics, especially on the morphological development of phase-separated domains, after the stepwise temperature change (temperature jump) were investigated. On the basis of the experimental results thus obtained, we discussed the mechanisms of the phase separation.

Experimental Section

Materials. 2-Chlorostyrene (2ClS) was purchased from Tokyo Kasei Co. and purified by distillation under reduced pressure after removing inhibitor by a conventional method. Purified monomer was sealed in a container against access of moisture and kept in a refrigerator until use. The monomer was used within 1 week after purification. Polystyrene (PS) was a product of Pressure Chemical Co., whose weight-average molecular weight and polydispersity index were $M_w = 5 \times 10^4$ and $M_w/M_n < 1.06$, respectively. Dibutyl phthalate (DBP) was added to 2ClS/PS mixtures to reduce the viscosity at high monomer conversions. DBP of reagent grade (purity > 98%) was purchased from Tokyo Kasei Co. and used without further purification. Composition of the mixture was fixed at 2ClS/PS/DBP = 45/45/10 by weight. The mixture was stirred overnight at room temperature to accomplish homogeneous mixing. The sample was sandwiched by two glass plates with a Teflon spacer of 0.2 mm thickness. Polymerization was initiated by raising temperature without an aid of initiator.

Instruments. Electron microscopy and time-resolved light scattering techniques were employed to follow the phase separation dynamics, and size exclusion chromatography (SEC) was used to determine the reaction conversion of 2-chlorostyrene.

The time-resolved light-scattering (TRLS) measurements were performed with an instrument constructed in our laboratory.[2] Angular dependence of the scattered light intensity was measured by scanning a photomultiplier tube with a stepping motor. The transmitted light intensity was monitored by a

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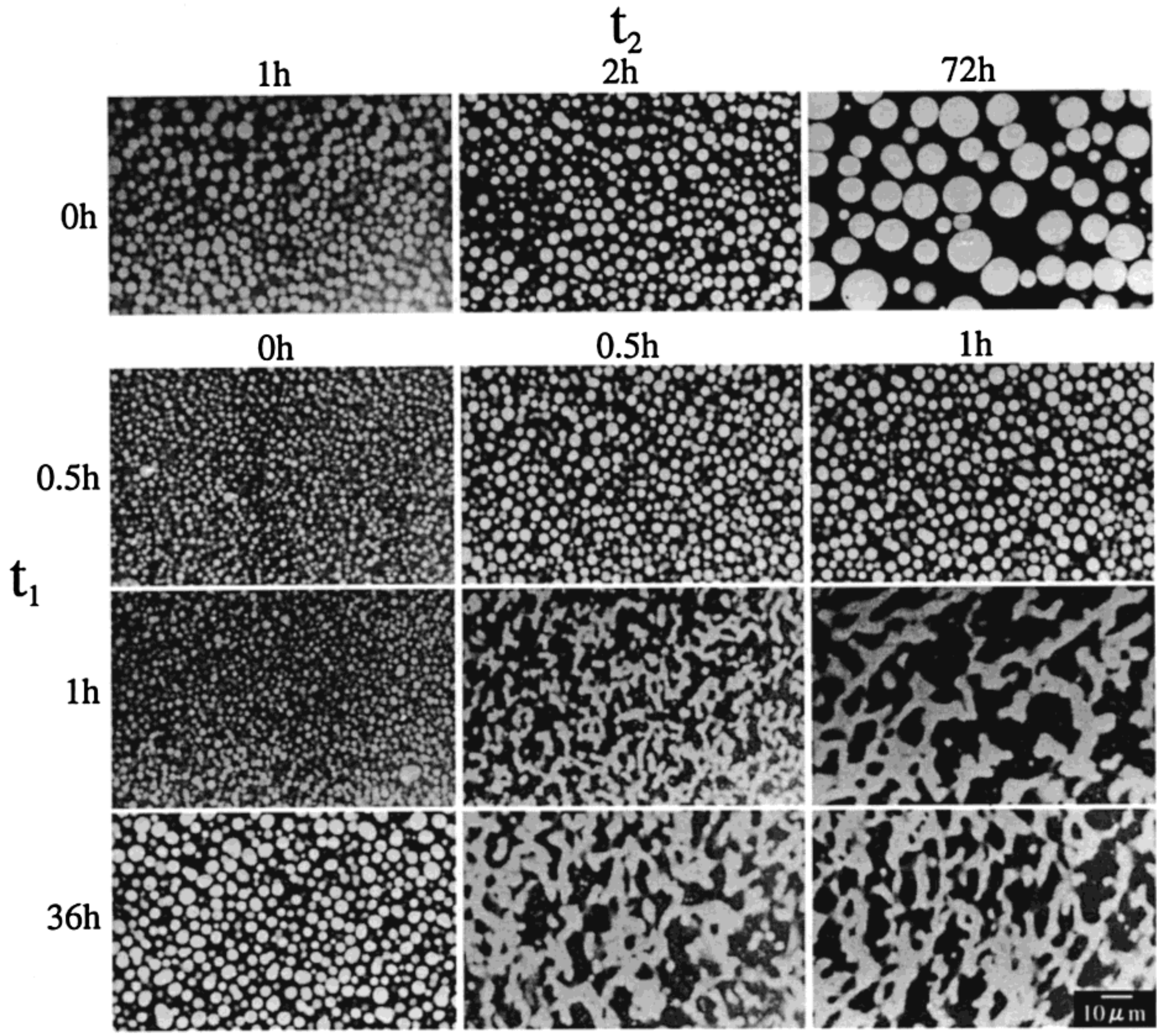

Figure 1. Electron micrographs of phase-separated domains at t_2 after temperature jump from 130 to 160 °C for different durations t_1 at 130 °C. The darker parts correspond to the polystyrene-rich phase.

photodiode and used for the turbidity correction. The temperature jump was made by pushing a sample holder manually into a heating block controlled at a desired temperature to ±0.03 °C. Temperature of the holder was stabilized within 5 min after the jump.

Domain structures during the phase separation were studied by electron microscopy. After being kept in a thermostat controlled to ±0.03 °C for a desired period, a sample cell was taken out and rapidly quenched to room temperature to fix the phase-separated domain structure of the sample. A back-scattered electron image of a microtomed surface of the quenched sample was observed with an electron microscope JEOL JSM-T220 operated at 10−15 kV. The ratio of the volume of each phase to the total volume was evaluated from electron micrographs by using an image analysis system PIAS LA525.

The size exclusion chromatography measurements were made by an apparatus Toso HLC8 with a UV detector Toso UV8011. Details of the method of evaluating the reaction conversion from a SEC chart were given in a previous paper.[2]

Results and Discussion

As mentioned above, thermal-history dependence was studied by changing temperature stepwise during phase separation: Temperature was initially kept at T_1 for a duration of time t_1 and then jumped to a higher temperature T_2. Figure 1 shows development of domain structures after the temperature jump from $T_1 = 130$ °C to $T_2 = 160$ °C for various durations t_1 at T_1. Here t_2 is the time passing since temperature was jumped to T_2. Darker parts in these scanning electron micrographs correspond to the polystyrene-rich phases. When phase separation was made at the constant temperature of 160 °C (i.e., $t_1 = 0$ h), the phase being rich in the reaction product, poly(2-chlorostyrene) (P2ClS), formed droplets, and these domains continued to coarsen with preserving their spherical figure, as seen in the first row of Figure 1. However, when temperature was kept at 130 °C for 1 h or over before being jumped to 160 °C, droplets of the P2ClS-rich phase formed at 130 °C rapidly changed into continuous (percolated) domains after the jump. As expected, it was found that development of the morphological structure during the phase separation induced by polymerization reaction depended significantly on the past thermal history.[15]

It was observed in the previous study that the morphological change from droplets to continuous domains occurred at a fixed temperature if the temperature was 140 °C or below.[2] However, it took more than 48 h for droplets to change into continuous domains when the temperature was fixed at 130 °C. In the case of the stepwise temperature change, the domain struc-

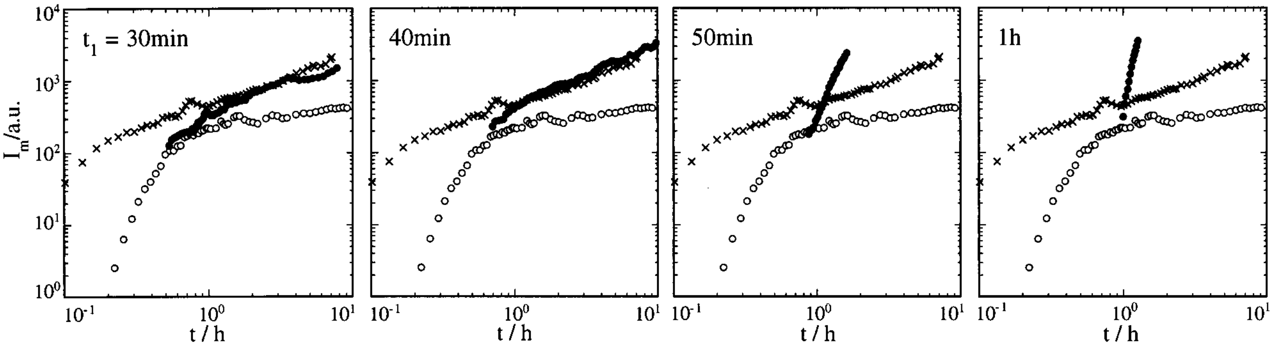

Figure 2. Time evolution of the peak intensity I_m after temperature jump from 130 to 160 °C (●) for various durations t_1 at 130 °C and I_m at fixed temperatures (○) 130 °C and (×) 160 °C.

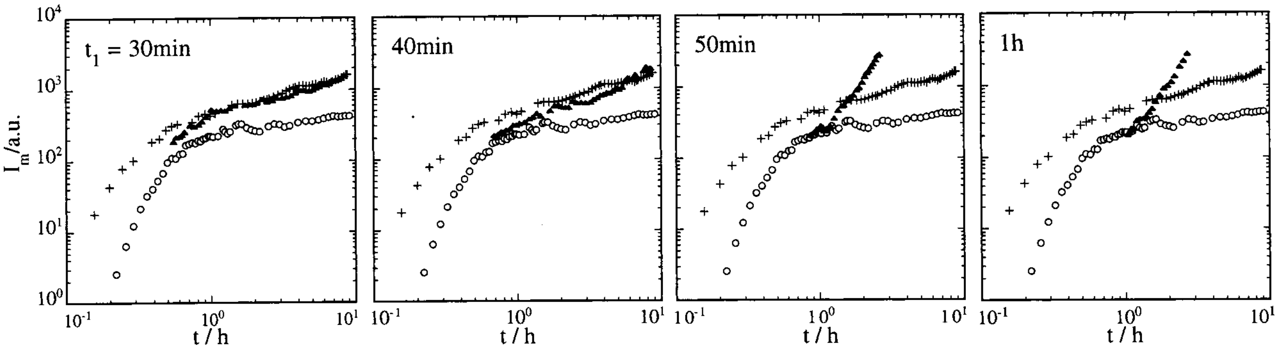

Figure 3. Time evolution of the peak intensity I_m after temperature jump from 130 to 150 °C (▲) for various durations t_1 at 130 °C and I_m at fixed temperatures (○) 130 °C and (+) 150 °C.

ture changed within 30 min after the jump to 160 °C only if the duration at 130 °C was longer than 1 h. The temperature change during phase separation significantly shortened the time necessary for the morphological change.

The thermal-history dependence was also found in the time evolution of scattered light intensity. Like in the spinodal decomposition of a mixture of nonreactive components,[16] a maximum appeared in the scattered light intensity profile $I(q)$ and its intensity increased with time. Figure 2 shows the time evolution of the maximum intensity I_m after the temperature jump from $T_1 = 130$ °C to $T_2 = 160$ °C for various t_1, together with the evolution of I_m observed when the temperature was fixed at 130 or 160 °C. Here, t is the total duration at the first and second phase-separation temperatures, i.e., $t = t_1 + t_2$. In the case of $t_1 = 30$ min, where droplets coarsened without changing into continuous domains after the jump to T_2 as already seen in Figure 1, I_m approached the curve obtained for the phase separation at the fixed temperature of 160 °C. On the other hand, in the case of $t_1 = 1$ h, where the droplets changed into the continuous domains after the jump, I_m increased rapidly across the $I_m - t$ curve of 160 °C. We also made electron microscope observations and TRLS measurements for $t_1 = 3$ h and confirmed that such large and rapid increase of I_m concurred with the structure change to continuous domains. It is known that bicontinuous domains grow much faster than droplets in the phase separation of a fluid mixture owing to the hydrodynamic interactions.[17,18] Therefore, the acceleration of the I_m growth is explained by the change in the coarsening mechanism accompanying the morphological change of the phase-separated domains.

When the duration t_1 at 130 °C was varied in the range of 30 min to 1 h, the growth behavior of I_m after the jump altered between $t_1 = 40$ and 50 min as seen in Figure 2. As discussed above, the change in the growth behavior of I_m is considered to be a manifestation of the change in the morphological structure of phase-separated domains. Consequently, the shortest duration t_1* at $T_1 = 130$ °C required for the morphological change to occur after the jump to 160 °C lies between 40 and 50 min.

To evaluate the thermal-history dependence further, we changed either the first phase-separation temperature or the second temperature with leaving the other one unchanged and studied the phase separation behavior after the temperature jump. Figure 3 shows time evolution of I_m after the jump from 130 to 150 °C. Figure 3, together with Figure 2, illustrates the effects of T_2. Similarly to the preceding case, when t_1 was short I_m approached the curve obtained for the phase separation at the fixed temperature of T_2, and when t_1 was long I_m increased rapidly across the curve. The change in the growth behavior of I_m occurred between $t_1 = 40$ and 50 min, which is the same as in the case of $T_2 = 160$ °C, indicating that the decrease in the second temperature T_2 did not have an appreciable influence on the minimum duration t_1* required for the morphological change to occur after the jump.

Though T_2 had little influence on t_1*, it had an appreciable influence on the growth rate of I_m after the jump. Comparison between Figures 1 and 3 (especially at $t_1 = 50$ min and 1 h) shows that I_m increased more slowly as T_2 decreased. The slower domain growth after the jump to $T_2 = 150$ °C was confirmed by observation with an electron microscope. Figure 4 shows the morphological development after the jump to 150 °C for $t_1 = 1$ h. At $t_2 = 30$ min, the P2ClS-rich phase still maintained a clear droplet structure, though continuous domains had appeared within the same span of time in

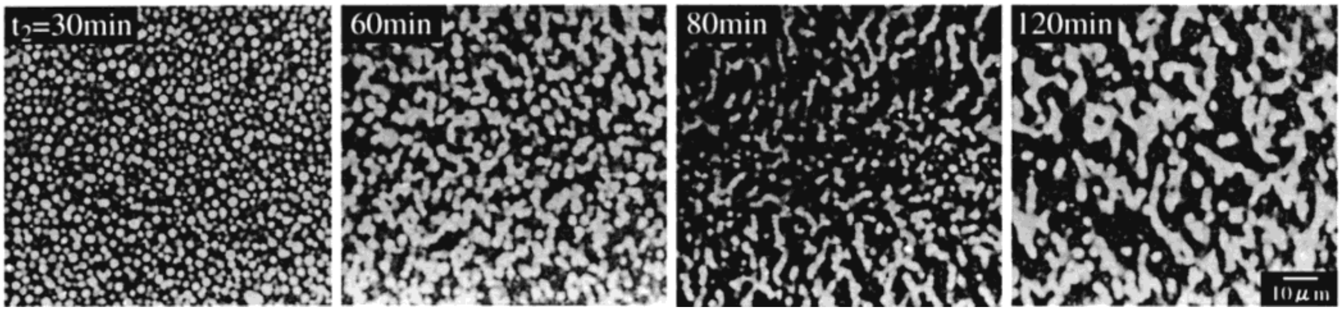

Figure 4. Electron micrographs of phase-separated domains at t_2 after temperature jump from 130 to 160 °C for t_1 = 1 h.

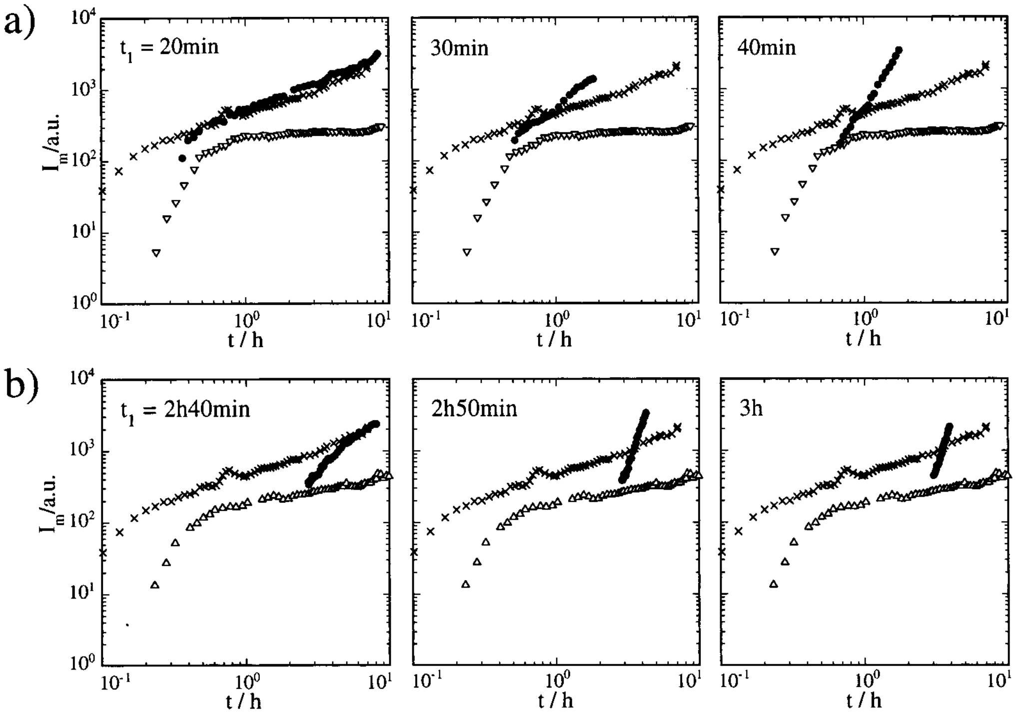

Figure 5. Time evolution of the peak intensity I_m after temperature jump from T_1 to 160 °C (●) for various durations t_1 at T_1 and I_m at fixed temperatures (▽, △) T_1 and (×) 160 °C. (a) T_1 = 125 °C, (b) T_1 = 135 °C.

the case of T_2 = 160 °C (see Figure 1). In the case of T_2 = 150 °C, continuous domains appeared around 60 min after the jump.

Figure 5 shows time evolutions of I_m after the jumps from different temperatures (125 and 135 °C) to the same final temperature (160 °C). Again we could distinguish two kinds of growth behavior of I_m depending on the length of t_1. It was found from comparison with Figure 2 that when T_1 was increased the longer duration t_1 at T_1 was required for the rapid increase of I_m across the curve for 160 °C to occur after the jump. The threshold value t_1* increased from 30 to 170 min as T_1 increased by 10 deg from 125 to 135 °C. This large dependence of t_1* on the first phase-separation temperature T_1 makes a marked contrast with its little dependence on T_2.

The results of the time-resolved light scattering measurements and the electron microscopy observations are summarized as follows: At the temperature T_2 where spherical domains were coarsening without changing to continuous domains, the morphological change occurred if the system was kept at a lower temperature T_1 for a certain period in advance. The minimum duration t_1* at the lower temperature required for the morphological change to occur after the jump increased with increasing the lower temperature but did not appreciably depend on T_2 at least in the investigated range of T_2. This result suggests that whether the morphological change would occur at T_2 or not was determined before the temperature jump was made.

In Figure 6, the fraction of the volume of P2ClS-rich domains to the total volume, V_{P2ClS}, is plotted against the time after the jump from 130 to 160 °C for different durations t_1 at 130 °C. The domain structure of the P2ClS-rich phase at each point was indicated by its symbol: The open symbol denotes the spherical domains, and the filled symbol denotes continuous domains. The fraction V_{P2ClS} always rapidly increased in the first 30 min after the jump and changed only slightly thereafter. The morphological change to the continuous domains occurred in the same period where V_{P2ClS} rapidly increased. This is reasonable because the morphological change occurs only in the opposite direction, i.e., from the bicontinuous to spherical domains, if the total volume of each phase is conserved, as is the case with the late stage of phase separation of a nonreactive system at a fixed temperature.[19]

Although the morphological change to the continuous domains was accompanied by the increase of the phase-volume fraction V_{P2ClS}, it must be noted that the domain

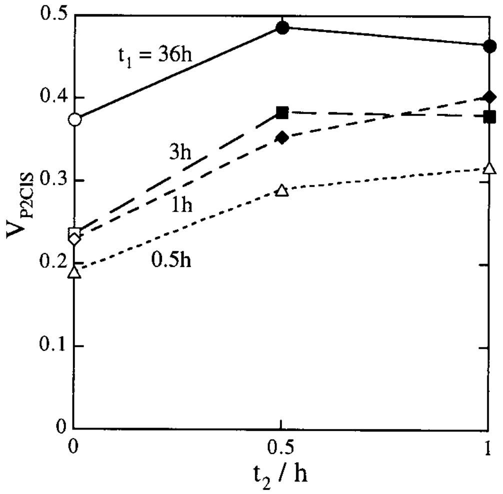

Figure 6. Phase-volume fraction V_{P2ClS} of P2ClS-rich phase at t_2 after temperature jump from 130 to 160 °C for various durations t_1 at 130 °C. Open symbols indicate spherical P2ClS-rich domains, and closed symbols indicate continuous domains.

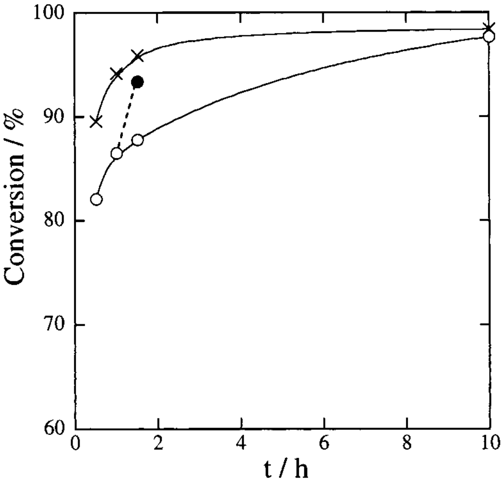

Figure 7. Time evolution of conversion of 2ClS reacted at (○) 130 °C and (×) 160 °C. A point (●) denotes conversion of 2ClS reacted at 130 °C for 1 h and then at 160 °C for 30 min.

structure was not determined only by the absolute value of the fraction V_{P2ClS}. The fraction V_{P2ClS} at $t_2 = 0$ h for $t_1 = 36$ h was roughly identical to the value at $t_2 = 0.5$ h for $t_1 = 3$ h, but their morphological structures were largely different as indicated by their symbols. In addition, continuous domains formed at $t_2 = 0.5$ h after the jump made at $t_1 = 1$ h, but V_{P2ClS} at this moment was slightly smaller than the value at the $t_2 = 0$ h for $t_1 = 36$ h when domain structure still remained to be spherical.

Reaction conversions of 2-chlorostyrene were evaluated from the size exclusion chromatographs, and the time evolution of the conversion during polymerization at 130 and 160 °C is shown in Figure 7. The conversion reached 96%, and the polymerization was almost completed in 6 h at both 130 and 160 °C. The reaction proceeded more rapidly at 160 °C than 130 °C. Consequently, a temperature jump made during progress of the reaction accelerated the reaction as seen in the case of the reaction at 130 °C for 1 h and then at 160 °C for 0.5 h shown in the figure (filled circle). Such acceleration of the reaction is expected to cause a rapid increase of the total volume of the P2ClS-rich domains observed in Figure 6. However, the progress of the reaction could not be a principal origin of the increase of V_{P2ClS} immediately after the temperature jump, because V_{P2ClS} obviously increased even after the temperature jump made at $t_1 = 36$ h, when the reaction had already finished.

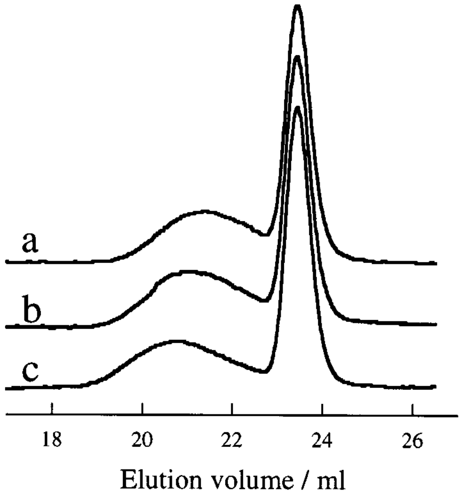

Figure 8. Size exclusion chromatographs for mixtures reacted under different thermal conditions: (a) 160 °C for 1.5 h, (b) 130 °C for 1 h and then 160 °C for 0.5 h, (c) 130 °C for 1.5 h.

Because of the conservation of materials, P2ClS molecules necessary to increase the volume of P2ClS-rich domains must be supplied from the PS-rich domains after the polymerization reaction finished. Then, from the fact that the minimum duration $t_1{}^*$ at T_1 was the same for $T_2 = 150$ and 160 °C, it is suggested that whether the morphological change would occur at T_2 was determined by the amount of P2ClS accumulated in a PS-rich phase for a duration of t_1 at T_1.[20] In other words, once a sufficient amount is accumulated, the morphological change occurs irrespective of the subsequent temperature change.

It is of principal importance to know the relation between phase separation rate and reaction rate in order to understand the dynamics of phase separation induced by a chemical reaction.[2,4] The accumulation of the reaction product in the phase being poor in it means that the phase separation was slow compared with the reaction. In the phase separation induced by radical polymerization, the phase separation rate is more sensitive to the viscosity of the system than the reaction rate is, because diffusion of long polymer chains is necessary for the phase separation to proceed while diffusion of small monomer molecules is sufficient for radical polymerization to proceed. Therefore, the higher the viscosity at high conversions is, the more the product tends to be accumulated. Since the temperature range investigated in this study was located near the glass transition temperatures of polystyrene and poly(2-chlorostyrene),[21] the decrease in temperature results in a considerable increase in the viscosity at high reaction conversions. Consequently, the product tends to be accumulated more at lower temperatures. This accounts for the experimental result that the minimum duration $t_1{}^*$ increased with T_1.

In the above discussion, we neglected the difference in the molecular weight of P2ClS caused by the difference in the reaction temperature. Figure 8 shows size exclusion chromatographs of the samples reacted for 1.5 h under different thermal conditions. A sharp peak of the UV absorption located at the elution volume of 23.5

mL corresponds to polystyrene and a broad peak at a smaller elution volume corresponds to P2ClS produced by the polymerization reaction. Molecular weight of P2ClS was evaluated from the elution volume at the peak absorption: P2ClS produced at 130 °C had a molecular weight of 3.1×10^5, and P2ClS produced at 160 °C had a molecular weight of 2.4×10^5. It was found that the molecular weight of P2ClS scarcely changed with the reaction time at a constant temperature. (The experimental results are not shown here.) The molecular weight decreased with the reaction temperature, but the difference in the molecular weight between poly(2-chlorostyrene)s produced at 130 and 160 °C was considerably small compared with the difference between P2ClS and polystyrene ($M_w = 5.0 \times 10^4$). The increase in the molecular weight causes an increase in the viscosity and a shift of the coexistence curve, which influence the phase separation dynamics. However, such an influence is conceived to be small in this case, because the viscosity and the mixing free energy (entropy) more strongly depend on the molecular weight of the lower molecular weight component.

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