Communications to the Editor

Thermal-History Dependence of Polymerization-Induced Phase Separation

Mamoru Okada* and Toshiki Sakaguchi

Department of Polymer Chemistry, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152-8552, Japan

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The dynamics of polymerization-induced phase separation is dominated by the ratio between phase separation rate and reaction rate.[1,2] One of the characteristics of polymerization-induced phase separation is a drastic change of viscosity with progress of polymerization reaction. In the case of chain polymerization, the phase separation rate and reaction rate exhibit a different dependence on the viscosity, and the dynamics of phase separation induced by chain polymerization can be explained qualitatively by the change of the ratio of these two rates caused by this drastic increase of viscosity. Since viscosity is a function of temperature, the change of the ratio also depends on temperature. In fact, in a 2-chlorostyrene/polystyrene mixture quite different domain structures were observed depending on temperature.[1] Hence, it is expected that a temperature change over the course of phase separation has an appreciable influence on the subsequent phase separation behavior. In other words, different domain structures will be produced at the same final temperature depending on the previous thermal history.

The purpose of this short communication is to show in a definite fashion that the dynamics of phase separation induced by radical polymerization strongly depends on thermal history.[3] A stepwise temperature change over the course of phase separation was adopted as a simplest form of thermal history. To examine the effects of thermal history, we varied the duration at the first phase-separation temperature and observed phase separation behavior after the stepwise temperature change.

A mixture of 2-chlorostyrene, polystyrene, and dibutyl phthalate was used as a sample. The weight-average molecular weight and polydispersity index of polystyrene were $M_w = 5 \times 10^4$ and $M_w/M_n = 1.06$, respectively. Dibutyl phthalate was added to reduce the viscosity at high monomer conversions. The composition of the mixture was fixed at 45/45/10 by weight. No initiator was used, and radical polymerization of 2-chlorostyrene was initiated by raising the temperature. In radical polymerization the average molecular weight and molecular weight distribution of the product remain unchanged with reaction time (conversion), while the concentration of the product is increasing. Electron microscopy and time-resolved light scattering techniques were used to follow the development of phase-separation domain structures, and size exclusion chromatography was used to determine the conversion of 2-chlorostyrene. The sample and instruments were the same as those used in a previous work, and details of the sample preparation and instrumentation were given in ref 1.

The first and second phase-separation temperatures were set to be 130 and 160 °C, respectively. Thus, the entire thermal history employed in this work was as follows: the temperature was jumped from room temperature to 130 °C (the first jump) and kept at this value for the duration of t_1, and then the temperature was further jumped to 160 °C (the second jump) and fixed.

Figure 1 shows the development of domain structures of polymerization-induced phase separation after a single-step jump ($t_1 = 0$) to 160 °C. Darker parts in these scanning electron micrographs correspond to the polystyrene (PS)-rich phase. The phase rich in the polymerization product, namely poly(2-chlorostyrene) (P2ClS), formed droplets. Over the entire period of our investigation, only droplet-type domain structure was observed. (Morphological structure in a very early period, which could not be observed with the electron microscope because of low glass transition temperature, was left out of the present discussion.) Development of morphological structure was similar to that observed in phase separation at an off-critical composition of nonreactive polymer blend.[4]

Figure 2 shows domain structures after the second jump in the two-step temperature jump (room temperature → 130 °C → 160 °C) experiments for various duration t_1 at the first-step temperature, together with structures immediately before the second jump. It must be noted that at the instance of the second jump the P2ClS-rich phase had a droplet structure. In case of short duration $t_1 = 30$ min, droplets that had formed at the first step continued to grow after the second jump. However, in the case of longer duration t_1, namely $t_1 =$ 1, 3, and 36 h, the continuous domain of the P2ClS-rich phase formed within 30 min after the second jump although a single-step jump to the same temperature did not produce continuous domains.[5]

As far as the total volume of each phase is conserved, only a morphological change from the bicontinuous domain to droplet occurs as observed in the late stage of phase separation of a nonreactive system.[6] In other words, the total volume of the P2ClS-rich phase should be increasing during the morphological change from droplets to continuous domains. Image analysis of electron micrographs showed, in fact, that the phase-volume fraction increased from 0.23 at $t_2 = 0$ to 0.35 at $t_2 = 0.5$ h in the case of $t_1 = 1$ h and from 0.37 at $t_2 = 0$ to 0.48 at $t_2 = 0.5$ h in the case of $t_1 = 36$ h. Time evolutions of conversion of 2-chlorostyrene at 130 and 160 °C were not largely different. At both temperatures conversion reached about 96% in 6 h and did not change after that. Thus, at least in the case of $t_1 = 36$ h the

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* Corresponding author. E-mail mokada@polymer.titech.ac.jp; FAX 81-3-5734-2888.

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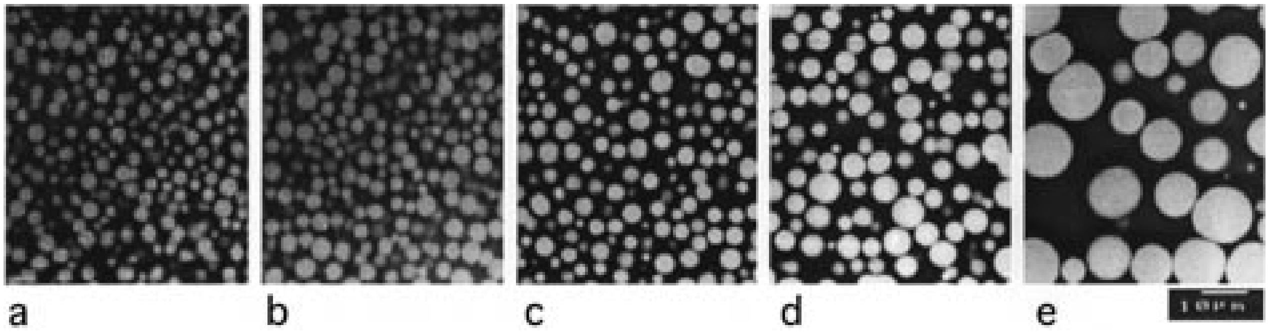

Figure 1. Electron micrographs of a microtomed surface of the sample under phase separation induced by polymerization at 160 °C. The dark parts correspond to the PS-rich phase. Time after the jump from room temperature to 160 °C: (a) 30 min, (b) 1 h, (c) 2 h, (d) 6 h, and (e) 72 h.

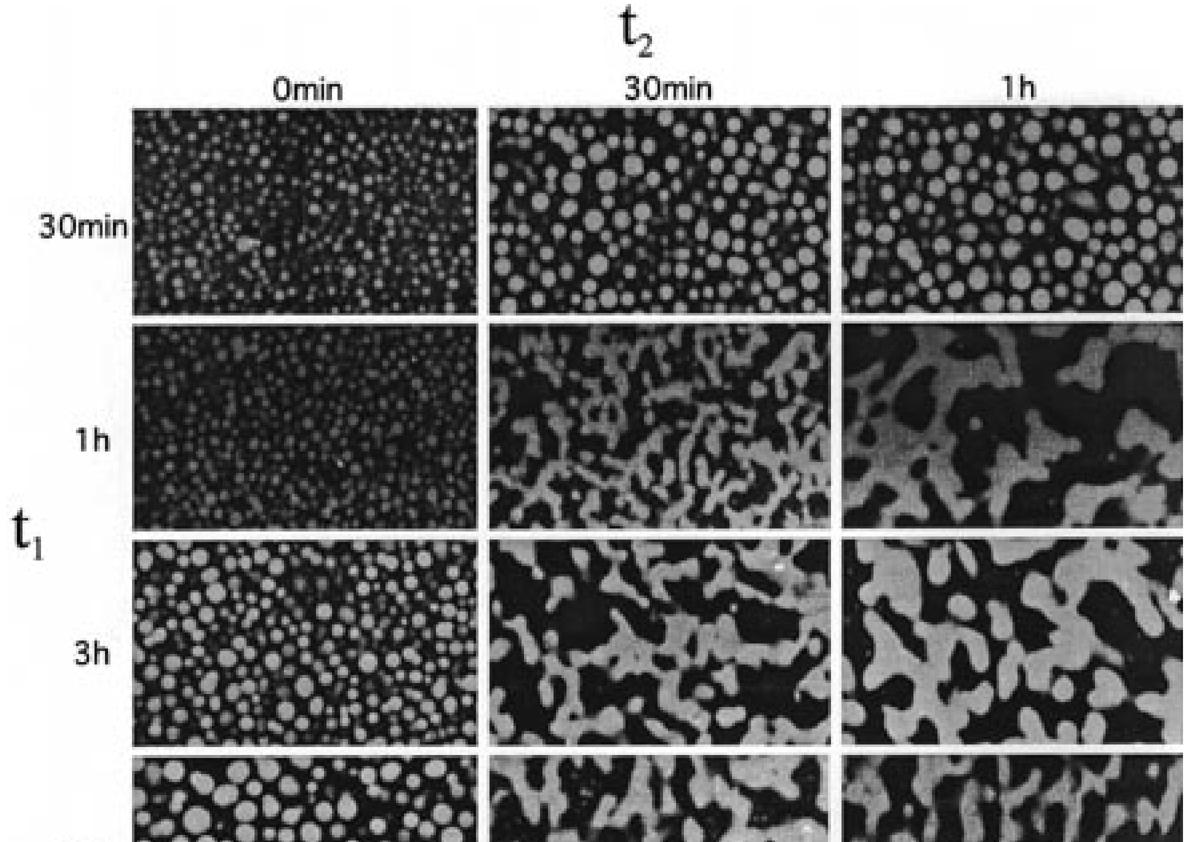

Figure 2. Domain structures after the second temperature jump of the two-step jump (room temperature → 130 °C → 160 °C) experiments. t_1 is the duration at 130 °C and t_2 is the time after the second jump.

progress of the reaction was not an origin of the increase in the total volume of P2ClS-rich domains. Since the total amount of P2ClS molecules was conserved in the process of the morphological change, P2ClS molecules necessary to increase the volume of P2ClS-rich domains must have been supplied from the PS-rich sea phase. Therefore, these experimental results confirm our conjecture given in the previous paper for the mechanisms of polymerization-induced phase separation:[1] At a low temperature, phase separation becomes much slower than reaction does when the conversion is high, and a fair amount of the reaction product is accumulated in the background sea phase.

The thermal-history dependence was found in the time evolution of scattered light intensity as well. A peak appeared in the scattered light intensity profile $I(q)$, where q is wavenumber, and its intensity was increased with time. Figure 3 shows the peak intensity I_m as a function of the total time $t = t_1 + t_2$, where t_2 is time after the second jump. In case of a single-step jump ($t_1 = 0$) I_m increased rapidly in an early period and was gradually reducing its rate. In the case of two-step jump, I_m exhibited different growth behavior after the second jump depending on the length of duration t_1 at the first step. In the case of $t_1 = 30$ min (Figure 3a), after the second jump I_m approached the curve for the single-step

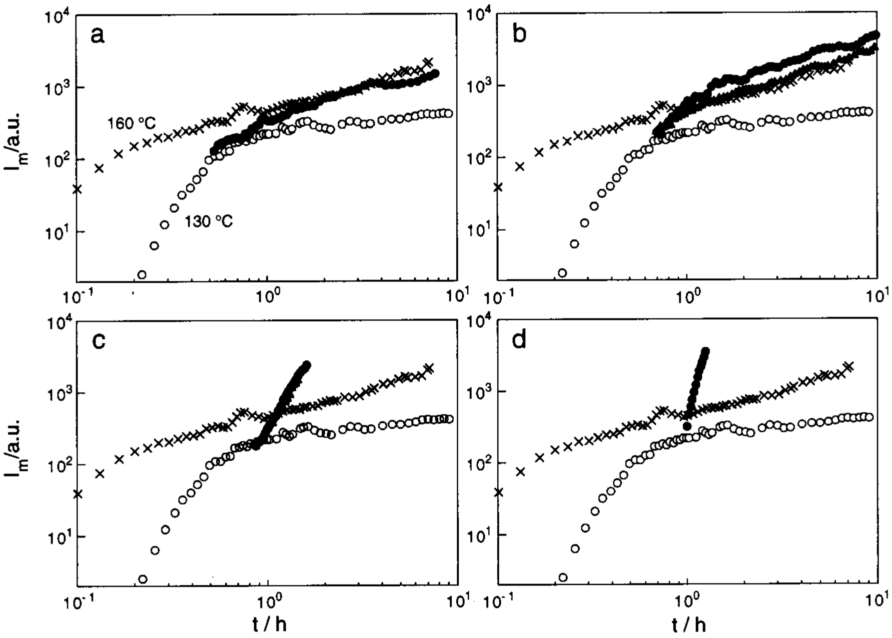

Figure 3. Time dependence of the peak intensity I_m after single-step jump to (×) 160 and (○) 130 °C and (●, ▲) second jump of the two-step jump (room temperature → 130 °C → 160 °C) experiments. Duration at the first-step temperature (130 °C) is (a) 30 min, (b) 40 min, (c) 50 min, and (d) 1 h.

jump to 160 °C, while in the case of $t_1 = 1$ h (Figure 3d) I_m increased rapidly beyond the curve for the single step to 160 °C. As was seen in Figure 2, domain structures after the second jump were quite different between these two cases. It is known that in a fluid mixture bicontinuous domains are growing much faster than droplets because of the hydrodynamic effects.[7] Thus, the large acceleration of I_m observed in the case of $t_1 = 1$ h was attributed to a change in the coarsening mechanism associated with the domain-structure change.

Along with $t_1 = 30$ min and 1 h, for which electron microscope observations were made, we performed time-resolved light scattering measurements for $t_1 = 40$ and 50 min. To confirm the reproducibility, measurements were made twice for each t_1. Two independent runs could not be distinguished from each other in the case of 50 min. In the case of $t_1 = 40$ min I_m approached the curve for the single-step jump to 160 °C, while in the case of $t_1 = 50$ min I_m increased rapidly beyond the curve. The result suggests that after the second jump the morphological change occurred in the case of $t_1 = 50$ min but not in the case of $t_1 = 40$ min.

In this communication, we showed that polymerization-induced phase separation has a large thermal-history dependence. Examination of thermal-history dependence gives valuable information about polymerization-induced phase separation and is expected to be a very useful method for elucidating the mechanisms of this very complicated phenomenon.

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References and Notes

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(5) Recently Yang et al. (Yang, Y.; Fujiwara, H.; Chiba, T.; Inoue, T. *Polymer* **1998**, *39*, 2745) found that in the curing of diallyl phthalate/poly(2,6-dimethyl-1,4-phenyl ether) mixture with a cure agent α,α-bis(*tert*-butylperoxy-*m*-isopropylbenzene) continuous domains formed when it was cured at 120 °C for 12 h and then at 150 °C for 5 h although droplets formed when it was cured at 150 °C for 8 h. However, it was not known whether the continuous domains formed before the temperature was increased to 150 °C or after.

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