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Dynamics of Phase Separation Induced by Radical Polymerization

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SUMMARY: Isomeric chlorostyrene monomer exhibited different phase separation behavior when it was radically polymerized in a mixture with polystyrene. In the2-chlorostyrene system, domain structure changed from droplets to continuous domains depending on temperature, and the strong thermal-history dependence was observed. In the 4-chlorostyrene system, size of droplets showed bimodal distribution. Results of computer simulation suggested that drastic decrease in mobility with the increase in conversion played an important role in the formation of bimodal size distribution.

Introduction

Interplay of phase separation and chemical reaction generates a variety of morphological structures, and phase separation induced by chemical reaction forms an important field of pattern formation. Phase separation induced by polymerization reaction has an advantage over phase separation induced by chemical reaction of low molecular-weight molecules in that the morphological structure at high conversion can be directly observed by an electron microscope, which gives valuable information necessary to understand fundamental aspects of reaction-induced phase separation.

In this study, we investigated mixtures of chlorostyrene monomer and polystyrene were investigated. Radical polymerization of chlorostyrene monomer was initiated by raising temperature. In radical polymerization, the average molecular weight of product remains unchanged, whereas the reaction yield increases with the reaction time. Consequently the mixture was destabilized by an increase in concentration of polychlorostyrene and underwent phase separation. Since isomeric polychlorostyrenes, poly(2-chlorostyrene) and poly(4-chlorostyrene), have different segregation strength with polystyrene, mixtures of polystyrene with 2-chlorostyrene exhibited different phase separation behavior from those with 4-chlorostyrene when the monomer was polymerized.

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Morphological Change from Droplets to Continuous Domains [1)]

Intensity profile of the light scattered from a mixture of 2-chlorostyrene (2ClS) and polystyrene (PS) undergoing phase separation was not largely different from those observed in spinodal decomposition of polymer blends: A single peak appeared and moved toward smaller wavenumbers with a lapse of time. However, evolution of the scattered light intensity was quite different. Scattered intensity increased rapidly after an induction period and then reduced its growth rate. Re-acceleration of intensity growth was observed under certain conditions.

The phase being rich in the polymerization product initially formed droplets. These droplets coagulated and non-spherical domains were formed. At higher temperatures these domains eventually became spherical again, and coarsened in a way similar to that observed in phase separation of ordinary polymer blend with an off-critical composition, though the total volume of the droplet phase was not small. At lower temperatures, coagulation of droplets occurred frequently, which led to the change from the disperse domain structure into continuous domains. Comparison with the scattering data revealed that this morphological change of phase-separated domains caused the re-acceleration of growth of scattered intensity. In a fluid, bi-continuous domains are known to be growing much faster than droplets owing to the hydrodynamic effects [2)]. The morphological change occurred later as temperature was decreased: 8 h at 140 °C, 48 ~72 h at 130°C in the case of 2ClS/PS = 50/50 by weight. Polymerization of 2-chlorostyrene initially proceeded very rapidly and gradually decelerated. At 130°C and 2ClS/PS = 50/50, polymerization finished in 10 h.

Morphological change from droplets to continuous domains does not occur in ordinary phase separation of non-reactive polymer blends, where change in the opposite direction occurs in the late stage so as to decrease the interface. Since the morphological change occurred after polymerization finished, poly(2-chlorostyrene) (P2ClS) necessary to increase the volume of 2ClS-rich phase must have been supplied from the sea phase. This indicates that accumulation of P2ClS preceded the morphological change to continuous domains. From these arguments, the following explanation can be proposed for the mechanisms of the observed morphological change. In polymerization-induced phase separation, the time evolution of domain structures is determined by competition between chemical reaction and phase separation. Because polymerization and phase separation rates have different dependence on viscosity, the relation between these two rates is expected to be changing with time. In an early period of phase separation, viscosity of the mixture is low because a considerable amount of monomer still remains unreacted, and phase separation is fast compared with the reaction. Thus phase separation rapidly proceeds as soon as the system enters the two-phase region. Since phase separation occurs near the phase boundary, volumes of two phases are asymmetrical and droplets of the minor phase are formed. As viscosity increases with the reaction conversion, phase separation slows down more quickly than the reaction and the polymerization rate exceeds the phase separation rate in later periods, leading to the accumulation of the polymerizing product in the sea phase. Phase separation is going on after monomers are consumed, and accumulated polymers are supplied to the droplet phase. Since viscosity decreases with temperature, the amount of accumulation also decreases with temperature and becomes insufficient for the morphological change to occur at high temperatures.

Thermal History Dependence

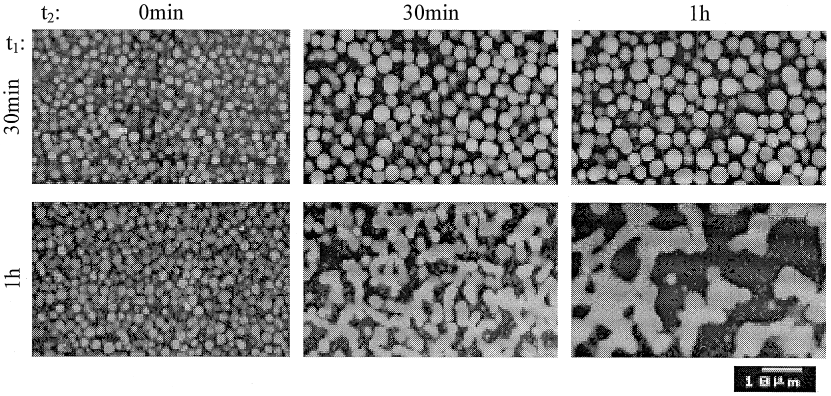


Fig.1. Domain structures after the second temperature jump of the two-step jump (room temperature → 130 °C → 160 °C) experiments. t_1 is the duration at 130 °C and t_2 is the time after the second jump. The brighter parts corresponds to the P2ClS-rich phase.

Non-equilibrium phenomena generally depend on the history of thermodynamic conditions. The strong temperature dependence of the morphological development during phase separation of 2ClS/PS mixture suggests that phase separation dynamics is appreciably affected by the thermal history. To elucidate the effect of the thermal history, dynamics of polymerization-induced phase separation was studied by making a stepwise temperature change in the course of phase separation. Namely, after being kept at T_1 for a duration of time

t_l temperature was changed stepwise to a higher value T_2. In the case of a single step jump (i.e., $t_l = 0$) to $T_2 = 160$ °C, P2ClS-rich phase formed droplets, which were coarsening without changing into continuous domains (at composition of 2ClS/PS = 50/50). However, if temperature was kept at $T_l = 130$ °C before jumping to $T_2 = 160$ °C, droplets of P2ClS-rich phase formed by phase separation at T_l coagulated into continuous domains after the jump to T_2 as shown Fig. 1 3). For such a morphological change to occur, the duration t_l at T_l was required to be longer than a certain value t_l^*. t_l^* was found to strongly depend on T_l 4). Thermal-history dependence of phase separation dynamics was clearly detected by scattering experiments as well. The time evolution of the peak intensity of scattered light I_m exhibited different growth behavior after the second jump depending on whether the duration at the first step temperature was longer than t_l^* or not. In the case of $t_l \geq t_l^*$, after the second jump I_m approached the I_m-t curve obtained for the single-step jump to 160 °C, while in the case of $t_l \leq t_l^*$ I_m increased rapidly beyond the I_m-t curve for the single-step jump to 160 °C.

The strong dependence on thermal history observed in these experiments strongly supports the mechanism proposed in the previous section for the morphological change from droplets to continuous domains at a constant temperature. The lower the temperature is, the more accumulation of the polymerizing product in the sea phase occurs. Once a sufficient amount is accumulated the morphological change occurs irrespective of the subsequent temperature change. Study of thermal history dependence proved to be very useful for understanding the mechanisms of polymerization-induced phase separation.

Bimodal Distribution of Droplet Size

Phase separation dynamics of 4ClS/PS mixture is significantly different from that of 2ClS/PS mixture 5). Fig. 2a shows the time evolution of the scattered light intensity profile. A single peak appeared and its intensity increased with time. However, location of the peak scarcely changed with time. In addition, the intensity at small wavenumbers was simultaneously increased. Electron microscope observation revealed that P4ClS-rich phase formed droplets with bimodal distribution of size as shown in Fig. 2b. Distribution of smaller droplets were relatively regular and the distance between these smaller droplets agreed with the characteristic length calculated from the peak position in the scattered light intensity profile.

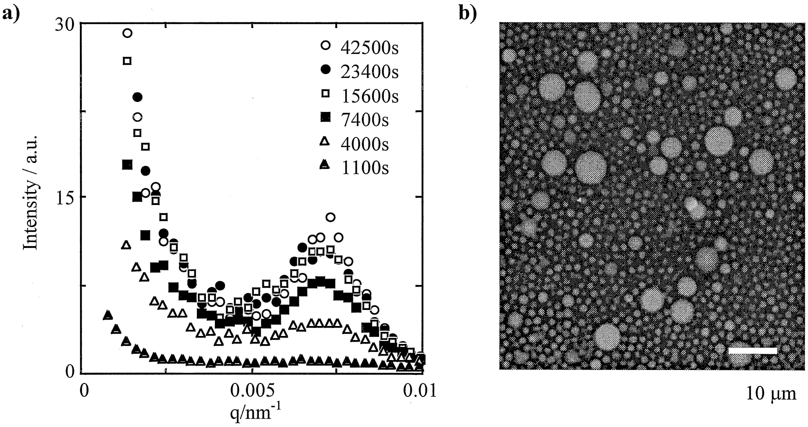


Fig.2. a) Time evolution of the intensity profile of light scattered from a 4ClS/PS (= 50/50) mixture phase-separated at 130 °C. b) Domain structure of a 4ClS/PS (= 50/50) mixture at 130 °C and 72 h. The brighter parts corresponds to the P4ClS-rich phase.

To understand the mechanism which controls generation of droplets with two distinct sizes, computer simulation was performed. Main characteristic which distinguishes phase separation induced by chemical reaction from ordinary phase separation induced by temperature quench is that the quench depth increases with time. In addition, polymerization reaction is accompanied by a drastic decrease of mobility in the mixture with time. Instead of introducing reaction term explicitly, we incorporated these two characteristics in the simulation model for phase separation induced by polymerization reaction.

The Cahn-Hilliard equation

$$\frac{\partial\psi}{\partial t} = M\nabla^2\left(-b\psi + u\psi^3 - K\nabla^2\psi\right) \qquad (1)$$

was used to describe the time evolution of the local concentration ψ ($\boldsymbol{r}$, t) at position $\boldsymbol{r}$ and time t. Time dependence is introduced into the mobility M and the coefficient b corresponding to the quench depth. Eq. (1) can be written in a more simple form

$$\frac{\partial\phi}{\partial t} = m(\tau)\nabla^2\left(-a(\tau)\phi + \phi^3 - \nabla^2\phi\right) \qquad (2)$$

by using the reduced variables $\boldsymbol{x}$, t, and ϕ for coordinate, time, and local concentration [6]. $m(\tau)$ and $a(\tau)$ are dimensionless quantities given by dividing M and b by a certain time-independent reference mobility M_r and a coefficient b_r, respectively. The reduced variables are given by

$$\mathbf{r} = \left(\sqrt{K/b_r}\right)\mathbf{x}$$
$$t = \left(K/M_r b_r^2\right)\tau \qquad (3)$$
$$\psi = \left(\sqrt{b_r/u}\right)\phi$$

The following functional forms were assumed for the time-dependence of dimensionless quench depth and mobility.

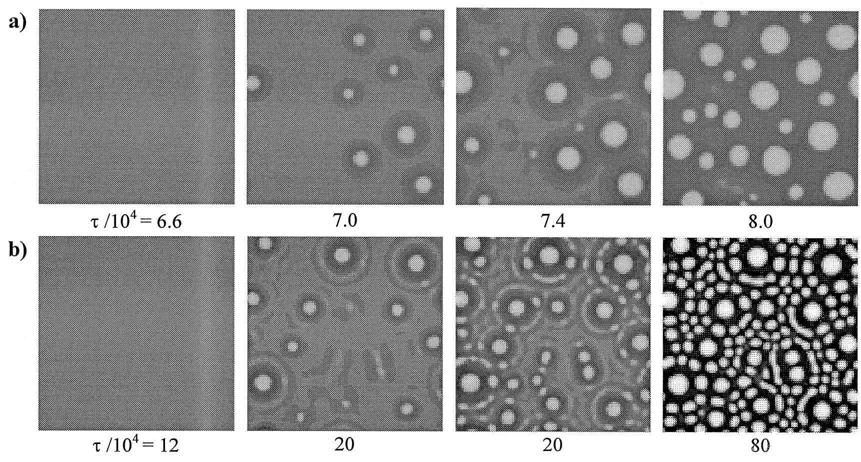
$$a(\tau) = \begin{cases} a(0) + \dfrac{[1 - a(0)]}{\tau_a}\tau & \tau \le \tau_e \\ 1 & \tau > \tau_e \end{cases} \qquad (4)$$

$$m(\tau) = [m(0) - m(\infty)]\left(1 + \frac{\tau}{\tau_b}\right)^{-a} + m(\infty) \qquad (5)$$

In this study, the initial composition was set at an off-critical value $\phi(0) = -0.3$, and the quench was started from the spinodal point $a(0) = 0.27$. We solved Eq. (3) numerically on a two-dimensional 256×256 square lattice with periodic boundary conditions. An Euler discretization was used with mesh size $\Delta x = 1$. Random concentration fluctuation with Gaussian distribution was given as an initial condition.

Figure 3 shows domain structures at various phase separation times for different exponents α with the remaining quantities in Eqs. (4) and (5) being fixed at

$$\tau_a = 1\times10^6, \tau_e = 1\times10^6, \tau_b = 2\times10^5, m(0) = 1, m(\infty) = 1\times10^{-4}$$



Local concentration was displayed by the difference in brightness, which was divided into 32 levels. The brightest and the darkest levels correspond to $\varphi = -1$ and 1, respectively. In the case of $\alpha = 5.0$, the minor phase ($\phi > -0.3$) formed droplets, which was growing with time. Distribution of droplet size was wide but appeared unimodal. In the case where the mobility decreased more rapidly, namely $\alpha = 8.2$, new droplets were generated during the growth of droplets that appeared initially, and the size distribution became bimodal. These results strongly suggests that the decrease in mobility with time, which is characteristic to polymerization reaction, plays an important role in generating droplets with bimodal size distribution.

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