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Dissolution of phase-separated domains after a jump to a temperature in the single-phase region

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Abstract

Phase-separated domains prepared in the two-phase region were dissolved at a temperature in the single-phase region, and their dissolution dynamics was studied by using the time-resolved light scattering (TRLS) technique and a scanning electron microscope (SEM). The time t_{ps} of preparation of domains was chosen to be long enough for phase separation to proceed into the late stage. The scattered light intensity at small wavenumbers increased before it attenuated. As t_{ps} increased, the increase at smaller wavenumbers became more significant and the peak intensity decreased only slightly with dissolution time. The characteristic wavenumber q_m evaluated from TRLS and SEM followed the power-law relation $q_m \sim t^{-0.3}$. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Phase dissolution; Micro-domains; Hydrodynamic interactions

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1. Introduction

With advance of understanding of phase separation dynamics, phase separation under a more complicated condition than a simple temperature or pressure quench has attracted a great deal of attention in recent years. Under some complicated conditions, systems undergo a process of phase dissolution in addition to phase separation. For example, periodic phase separation [1–5], where the thermodynamic condition is varied periodically between the single-phase region and the two-phase region, involves a phase-dissolution process in a cycle. Another example is the phase separation of a polyester blend concurring with trans-esterification reaction, where the thermodynamic driving force of phase separation changes with advance of the reaction [6–8]. Thus for understanding the mechanism of these phenomena, it is indispensable to study the dynamics and mechanism of phase dissolution. However, compared with the study of phase separation dynamics, an extremely smaller number of experiments have been made to investigate the phase dissolution dynamics so far [9–13].

In a previous work [13], we investigated dynamics of attenuation of concentration fluctuations after a quench to a temperature in the single-phase region. Initial concentration fluctuations prepared by phase separation were limited to have relatively short wavelengths, i.e. phase separation was stopped before it reached the late stage. In the present study, we extended phase separation time so that phase separation proceeded into the late stage, and studied dissolution of phase separated domains with well-defined boundaries.

2. Experimental

Materials and experimental methods are the same as those used in the previous work. Details are given in Ref. [13] and only an outline is described here.

2.1. Materials

Blend of polystyrene (PS) and poly(2-chlorostyrene) (P2CLS) containing di-*n*-butyl phthalate (DBP) as plasticizer were used as the sample. The blend composition was fixed at PS/P2CLS/DBP = 41.4/46.6/12.0 by weight. PS was purchased from Pressure Chemical Co. and P2CLS was radically polymerized and fractionated with a preparative size exclusion chromatography apparatus. DBP of reagent

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grade (purity > 99%) was a product of Tokyo Kasei Kogyo Co. and used as supplied. Weight-average molecular weight M_w and polydispersity indices M_w/M_n of the polymer samples were as follows: PS, $M_w = 5.0 \times 10^4$, $M_w/M_n < 1.06$, and P2CLS $M_w = 6.7 \times 10^4$ and $M_w/M_n = 1.13$. The blend films were prepared by casting from about 3.0 wt% benzene solution.

2.2. Measurements

The instrument used for time-resolved light scattering (TRLS) measurements was specially constructed [14]. A He–Ne laser operated at 632.8 nm was used as a light source. A photo-multiplier tube was used as a detector, and angular dependence of scattered light intensity was measured by scanning a photo-multiplier tube with a stepping motor. Temperature control of the heating block, where a sample holder was kept was better than ±0.03 °C.

Phase-separated domains were prepared by phase separation at 180 °C with varying phase separation time. Samples undergoing phase separation were rapidly quenched to room temperature, which was well below the glass transition temperature, so that their phase-separated domain structures were fixed. These samples were kept at room temperature until using for dissolution experiments. Temporal variation in the scattered light intensity profile was measured after transferring a phase-separated sample into the heating block that was controlled at a temperature in the single-phase region.

Concentration inhomogeneity was observed with an electron microscope JEOL JSM-T220. After the sample was kept at a dissolution temperature for a desired period, it was quenched to room temperature and a composition image of its microtomed surface was obtained by detecting electrons back scattered from it. The characteristic domain size was evaluated from electron micrographs by averaging over intervals between two adjacent intersections of an arbitrarily drawn line with boundaries of domains [15].

3. Results and discussion

The critical composition (PS/P2CLS/DBP = 41.4/46.6/12.0), at which all measurements were made, was estimated on the basis of the Flory–Huggins theory with the quasi-binary approximation [16]. The blend has a lower critical solution temperature. The thermodynamic boundary between the single-phase region and the two-phase region was determined as a temperature, where phase separation rate was reduced to zero. Dissolution experiments were carried out at 155 °C, i.e. 3.5 °C below the phase boundary thus estimated. Thermodynamic stability of a homogeneous blend at this dissolution temperature was confirmed by using TRLS: No appreciable growth in intensity of light scattered from the blend was observed at any wavenumbers for a duration of 2.59×10^6 s (30 days).

Phase separation reached the late stage in 3600 s at 180 °C. We used $\beta/\alpha = 3$ as a criterion for the late stage [17], where α and β are the exponents for time dependence of the characteristic wavenumber q_m, where the maximum in the scattered light intensity profile was located, and the maximum intensity I_m

$$q_m \sim t^{-\alpha} \tag{1}$$

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

respectively. Phase-separated domains were generated by phase separation at 180 °C with varying phase separation time t_{ps} within the late stage ($t_{ps} > 3600$ s).

Fig. 1 shows the temporal variation of the scattered light intensity profile $I(q,t)$ during phase dissolution at 155 °C of two different t_{ps} samples. In the case of $t_{ps} = 4320$ s, the peak of the scattered light intensity reduced its height and shifted to lower wavenumbers q with dissolution time t. It is

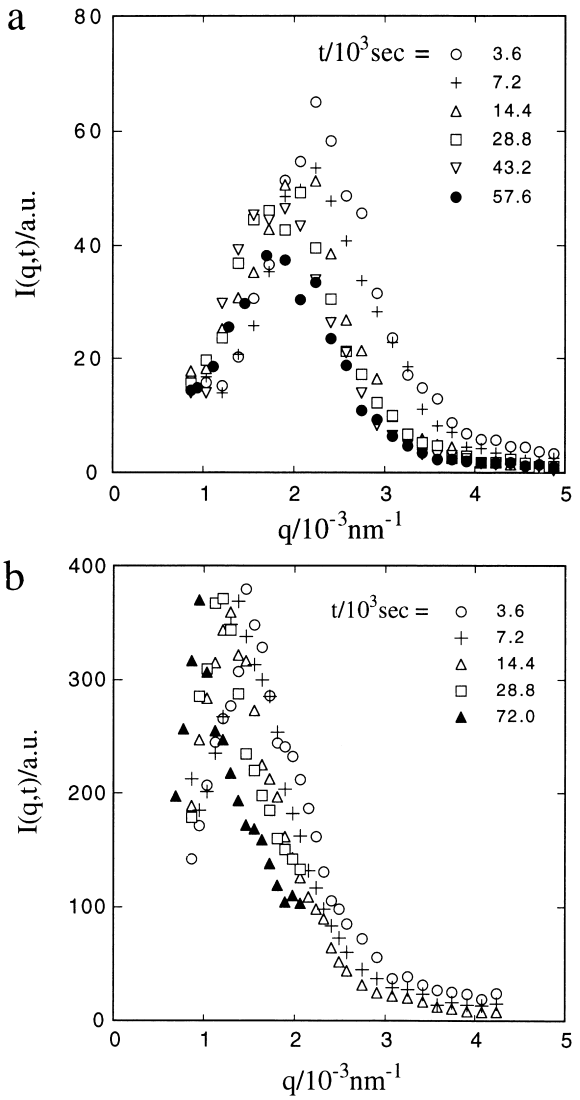

Fig. 1. Temporal variation of scattered light intensity profile $I(q,t)$ during phase dissolution at 155 °C. Phase separation time at 180 °C t_{ps} are (a) 4320 s and (b) 6480 s.

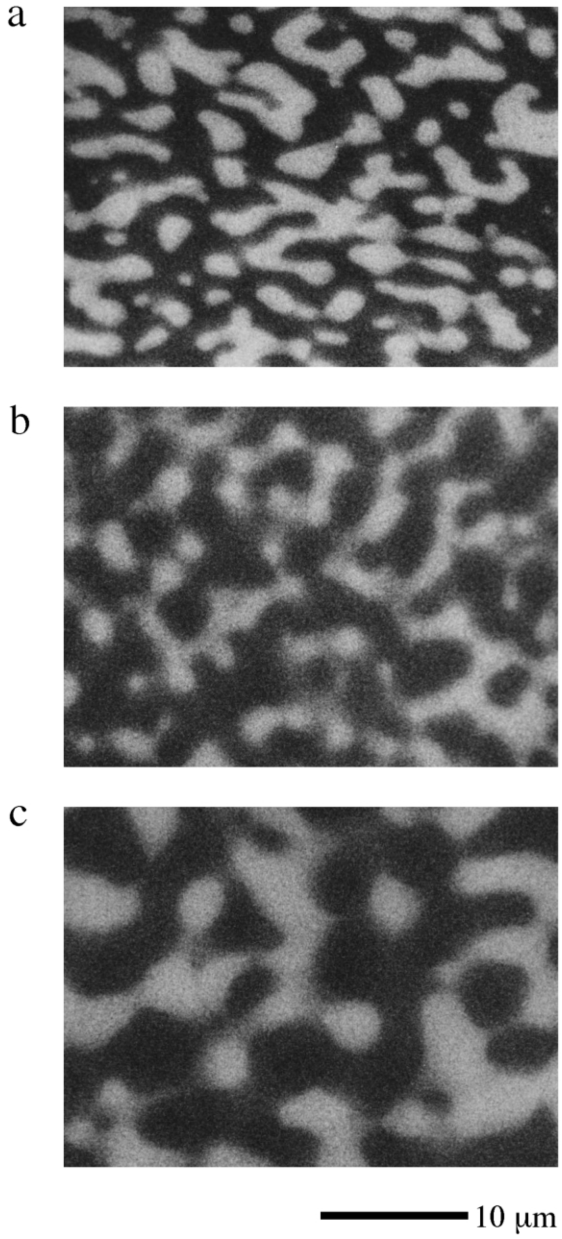

Fig. 2. Electron micrographs of microtomed surface of the blend undergoing phase dissolution at 155 °C for duration t. (a) $t = 0$ s; (b) 8.64×10^4 s; (c) 3.456×10^5 s. Phase separation time at 180 °C t_{ps} is 6480 s.

noted that the intensity at the smaller wavenumbers around $q = 1.5 \times 10^{-3}$ nm^{-1} increased initially. Such initial intensity growth was observed for t_{ps} at less than 3600 s, but it was not so large as observed here [13]. When t_{ps} increased to 6480 s, initial intensity growth at smaller qs became quite large and the peak scarcely decreased its intensity I_m while it shifted to smaller wavenumbers.

The increase of characteristic domain size indicated by the shift of q_m could be observed in real space. Fig. 2 shows scanning electron micrographs of microtomed surfaces of the blends undergoing phase dissolution for different durations of t after they were phase-separated at 180 °C for 6480 s. The brighter parts in these micrographs correspond to the regions of higher P2CLS content. It is clearly seen that domains formed by phase separation at 180 °C increased their characteristic size with time t. The contrast between PS-rich regions and P2ClS-rich regions were fading quite slowly, being in accord with the fact that I_m scarcely decreased with time (Fig. 1(b)).

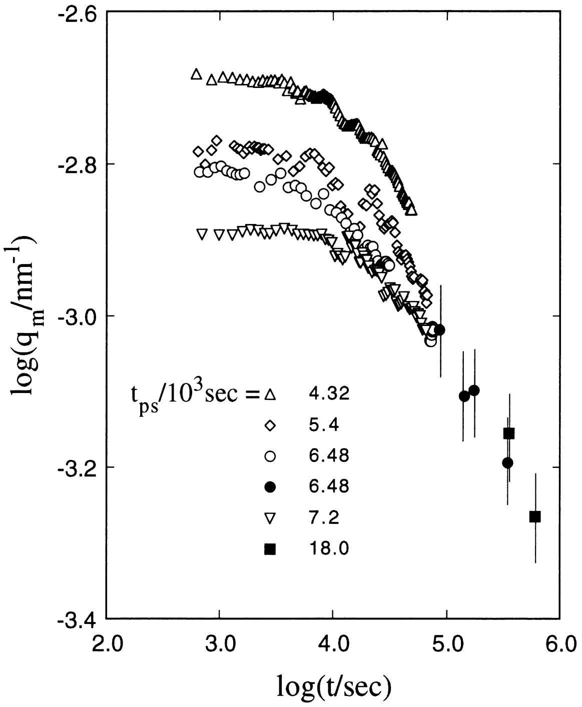

Fig. 3. Double-logarithmic plots of q_m against time t for various phase separation times t_{ps} at 180 °C. Filled symbols (●,■) indicate q_m evaluated from image analysis of electron micrographs.

The decrease of q_m during phase dissolution is generally considered to result from the fact that concentration fluctuations of shorter wavelengths attenuate more rapidly. However, this cannot explain the intensity increase at smaller wavenumbers observed in Fig. 1. The theoretical calculation by Akcasu et al. [12,18] based on the non-linear Langevin equation has demonstrated the shift of q_m towards lower values, but it appears to give no increase in intensity at any wavelengths. The interaction neglected by their theoretical calculation and that known to have a significant effect on phase separation dynamics is the hydrodynamic interaction [19,20]. The mechanism similar to the accelerating domain growth in phase separation of a fluid mixture might work in increasing the intensity at smaller wavenumbers. Computer simulations will give valuable information about the role of the hydrodynamic interaction played in a phase dissolution process.

Fig. 3 shows the plots of characteristic wavenumber q_m against dissolution time t for various phase separation times t_{ps}. Filled symbols denote q_m evaluated from electron micrographs by using the relation

$$q_m = \pi/L \quad (3)$$

where L is the characteristic domain size of one phase (corresponding to a half wavelength of concentration fluctuations) determined by image analysis. At longer dissolution times, q_m follows the power-law relation as has been predicted by Akcasu et al. [12,18]. The exponent was evaluated to be about -0.3 for all t_{ps} except $t_{ps} = 1.8 \times 10^4$ s, for which a sufficient number of data points were not available. The same value of the exponent was obtained for $t_{ps} < 3600$ s in the previous study [13].

Numerical integration of the non-linear Langevin equation made by Akcasu et al. [12,18] gave -0.5 to the exponent. According to them, the exponent is determined by the asymptotic slope of the initial intensity profile $I(q,0)$ in the small q region. This can be understood as follows. As pointed above, concentration fluctuations of shorter wavelengths attenuate more rapidly, and the scattering intensity profile is gradually eroded away from the large q side. Consequently, the peak of the profile will move along the slope on the small q side of the initial intensity profile. The q-dependence of $I(q,0)$ evaluated in the region of $q < q_m$ was weaker than $I(q,0) \sim q^2$, which they assumed. Since our measured q-range was not wide enough to evaluate asymptotic q-dependence in the small q region reliably, it is not clear whether the deviation from the theoretical value was caused by the difference in the initial intensity profile $I(q,0)$ or had another origin. The discrepancy might have a correlation with the intensity increase at smaller wavenumbers observed in Fig. 1. As mentioned above, the shift of q_m is principally brought by more rapid attenuation of concentration fluctuations of shorter wavelengths. The intensity increase at smaller wavenumbers changes the functional form of the attenuation rate, which can lead to retardation of the shift of q_m.

Finding of the increase at small wavenumbers shows that the mechanism of phase dissolution is not so simple and indicates the necessity of further experimental study of its dynamics. Since phase dissolution and phase separation should be described on a single physical basis, investigations of phase dissolution are expected to supply useful information to increase our understanding on phase separation dynamics as well.

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