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Attenuation of concentration fluctuations after a quench to a temperature in the single-phase region

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Abstract

Attenuation of concentration fluctuations in a polystyrene/poly(2-chlorostyrene) blend after a quench from a temperature in the spinodal region to one in the single-phase region was studied by using the time-resolved light scattering technique and a scanning electron microscope. The characteristic wave number q_m, where the maximum of the scattered light intensity was located, move towards smaller values during the attenuation process. The corresponding growth of the wave length of the dominant concentration fluctuation was clearly observed by the electron microscope. The scattered light intensities at small wave numbers were found to increase before they attenuated. In the later period the power-law behavior $q_m \sim t^{-0.3}$ was observed. The exponent was smaller than the value (0.5) obtained on the basis of the non-linear theory by Akcasu and collaborators. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Attenuation of fluctuation; Phase dissolution; Phase separation dynamics

1. Introduction

Being driven by the thermal noises, local concentration in a polymer blend fluctuates incessantly. When temperature is changed, distribution of wave length of concentration fluctuations changes until it reaches new equilibrium. If a temperature change is made beyond a certain limit, concentration fluctuations grow enormously and the blend undergoes phase separation through spinodal decomposition mechanism. Dynamics of fluctuation growth during spinodal decomposition has been extensively investigated in the last decades because of its theoretical as well as practical importance [1–3]. When the temperature of a blend undergoing spinodal decomposition is changed to a value in the single-phase region, concentration fluctuations that were grown once in the spinodal region gradually attenuate. Dynamics of such attenuation of concentration fluctuations follows the same mechanisms as the growth of fluctuations during spinodal decomposition, and study of dynamics of attenuation of concentration fluctuations is helpful in acquiring better understanding of phase separation dynamics. However, only a few experiments have been made to investigate the dynamics of attenuation of concentration fluctuations [4–7], which makes a marked contrast with experimental studies made to clarify the dynamics of fluctuation growth during phase separation.

Investigation of dynamics of fluctuation attenuation is also important in understanding the mechanisms of some interesting phenomena. Phase separation under time-dependent thermodynamic conditions, such as periodical phase separation [8–12], has been studied recently, and phase separation under periodic thermodynamic conditions involves the process of attenuation of concentration fluctuations in a cycle. Beside, phase separation of a blend of polyesters is usually accompanied by ester-interchange reactions, which increase the misciblity of the blend leading to attenuation of concentration fluctuations [13–15].

In this work, dynamics of attenuation of concentration fluctuations was experimentally investigated by employing time-resolved light scattering (TRLS) technique and electron microscopy. The initial concentration fluctuations were prepared by phase separation in the spinodal region, and their attenuation after a quench to a temperature in the single-phase region was studied. Amplitudes and wave lengths of initial concentration fluctuations were varied by systematically changing the phase separation time. The phase separation time was set to be shorter than the time required to reach the late stage. Results of dissolution of large concentration inhomogeneity prepared by phase separation for a longer period will be published in a separate paper.

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2. Experimental

2.1. Materials

Blend of polystyrene (PS) and poly(2-chlorostyrene) (P2CLS) containing 12.0 wt% di-*n*-butyl phthalate (DBP) was used as the sample. DBP was added so that the phase diagram of the blend was located in an appropriate temperature range. PS of weight-average molecular weight $M_w = 5.0 \times 10^4$ and molecular weight distribution $M_w/M_n < 1.06$ was purchased from Pressure Chemical Co. P2CLS was radically polymerized and fractionated with a preparative size exclusion chromatography apparatus. Its molecular weight and molecular weight distribution were determined by analytical size exclusion chromatography to be $M_w = 6.7 \times 10^4$ and $M_w/M_n = 1.13$, respectively. DBP of reagent grade (purity > 99%) was a product of Tokyo Kasei Kogyo Co. and used as supplied. The blend composition was fixed at PS/P2CLS/DBP = 41.4/46.6/12.0 by weight. 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 and then dried in a vacuum oven with increasing heating temperature stepwise; at 60°C for 1 day, at 80°C for 1 day, and finally at 135°C for 2 days. The sample film was sandwiched by glass plates of 8 mm diameter with a 0.2 mm thick Teflon spacer.

2.2. Measurements

The TRLS measurements were carried out with an instrument constructed in this laboratory. Details of the instrument were given in Ref. [16] and only an outline was described here. A He–Ne laser operated at 632.8 nm was used as a light source, and a photo-multiplier tube was used as a detector. Angular dependence of scattered light intensity was measured by scanning a photo-multiplier tube with a stepping motor driven by a microcomputer. Temperature control of the heating block in which a sample holder was kept was better than ±0.03°C.

TRLS experiments were carried out in two steps. In the first step, large concentration fluctuations were generated by phase separation. Phase separation was stopped by quenching the sample to room temperature, which was well below the glass transition temperatures of PS (100°C) and P2ClS (130°C) [17]. Rapid quench was achieved by contacting both sides of the sample glass plates with brass blocks that were cooled to −15°C in a refrigerator. In the second step, the sample was transferred in the heating block controlled at a temperature in the single-phase region, and attenuation of concentration fluctuations was measured.

Concentration inhomogeneity was observed with an electron microscope JEOL JSM-T220. Composition image of a sample quenched to room temperature was obtained by detecting electrons back-scattered from the microtomed surface. The sample was not stained with dye because heavy chlorine atoms contained in one of the components provided a sufficient contrast in an electron micrograph.

3. Results and discussion

A boundary between the single-phase region and the two-phase region was determined from temperature dependence of phase separation rate. Phase separation rate was determined by the TRLS experiments. Intensity of the light scattered from a blend undergoing spinodal decomposition had a peak in its angular dependence, and the peak was shifting toward lower angles as the phase separation proceeded. Reciprocal of the time $t(\theta_m = 3)$ required for the peak to reach an apparent angle of 3° was used as a measure of the phase separation rate. In Fig. 1, the rate $[t(\theta_m = 3)]^{-1}$ was plotted as a function of temperature. The blend has a lower critical mixing temperature [17], and the phase separation rate was increasing with temperature. Data points at three lower temperatures were fitted with a straight line, and the phase boundary was evaluated to be 158.5°C by extrapolating the line to $[t(\theta_m = 3)]^{-1} = 0$. The temperature thus determined corresponds to the spinodal temperature rather than the true phase boundary, i.e. the binodal temperature. However, the composition of the sample was chosen to be the critical composition calculated on the basis of the Flory–Huggins theory with the quasi-binary approximation [18] and was expected to be very close to the true critical composition, where the spinodal and the binodal temperatures agreed.

Experiments of the attenuation of concentration fluctuations were made at 155°C, i.e. 3.5°C below the estimated phase boundary. To confirm that the temperature lay in the single-phase region, concentration fluctuation change at this temperature was followed by the TRLS measurements. Two

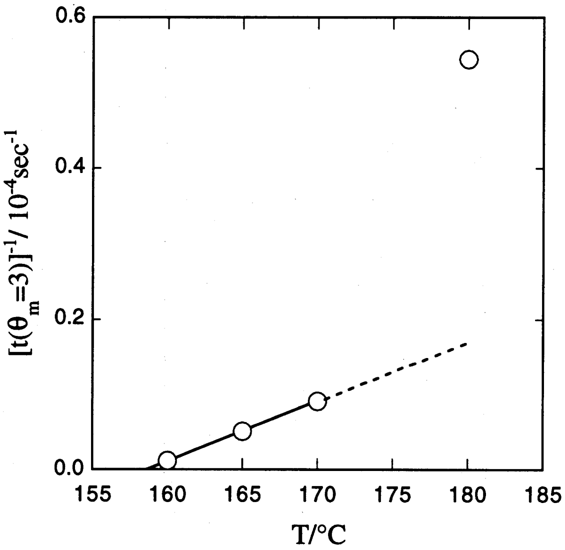

Fig. 1. Plots of rate $[t(\theta_m = 3)]^{-1}$ against temperature T. $t(\theta_m = 3)$ is the time required for the peak in the scattered light intensity profile to move to an apparent scattering angle of 3°.

independent measurements were made over different ranges of wave number q. Fig. 2 shows double-logarithmic plots of scattered light intensity $I(q,t)$ against the duration of time t at 155°C for different q. No appreciable growth of scattered intensity was observed at any wave number for the duration of 2.59×10^6 s (30 days), showing that the blend was stable at this temperature.

The initial large concentration fluctuations were generated by phase separation at 180°C with varying the phase-separation time. Fig. 3 shows time evolution of the maximum value I_m in the scattered light intensity profile and the characteristic wave number q_m where the maximum was located. In the period of $t > 3600$ s, I_m and q_m followed power laws

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

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

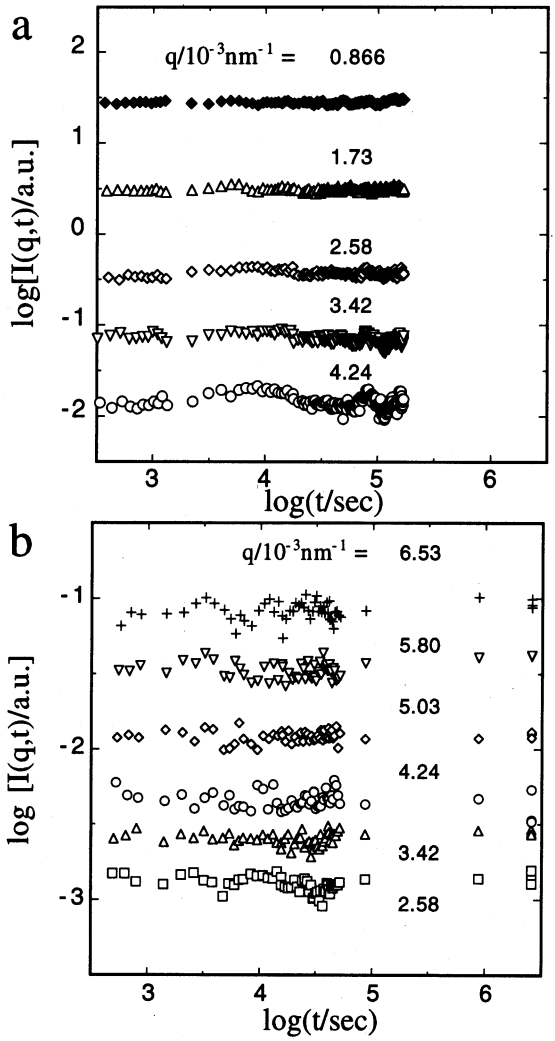

Fig. 2. Double-logarithmic plots of the scattered light intensity $I(q,t)$ against duration of time t at 155°C for two independent measurements of *a* and *b*.

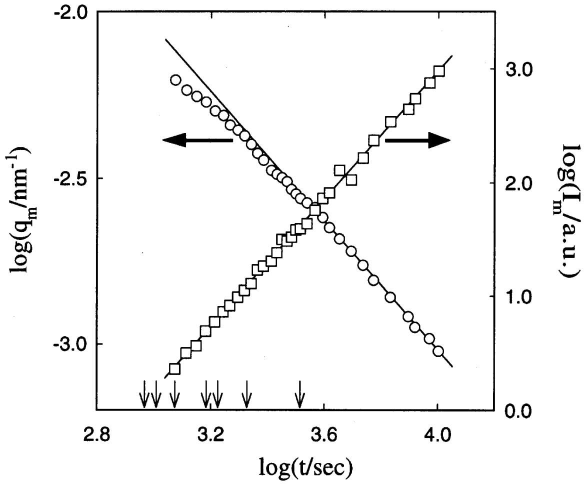

Fig. 3. Double-logarithmic plots of maximum scattered light intensity I_m (□) and characteristic wave number q_m (○) against phase separation time t at 180°C. Arrows on the abscissa indicate phase separation times to prepare the initial concentration fluctuations.

The evaluated exponents satisfied the relation $\beta/\alpha = 3$, which is indicative of the late stage of the phase separation [1,2]. The phase separation time t_{ps} for preparing the initial fluctuations was varied in the range $t_{ps} < 3600$ s, i.e. before the late stage set in. The values of t_{ps} used in this study were indicated by the arrows on the abscissa.

Fig. 4 shows time variation of the scattered light intensity $I(q,t)$ after the temperature was quenched from 180 to 155°C for the blend that had undergone phase separation at 180°C for 1680 s. The peak in the scattered light intensity reduced its height and shifted to lower wave numbers with

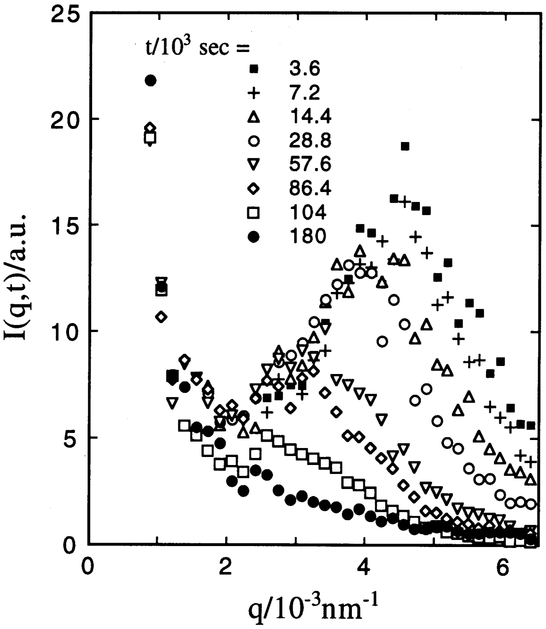

Fig. 4. Temporal variation of scattered light intensity profile $I(q,t)$ after quench to 155°C. Phase separation time at 180°C is $t_{ps} = 1680$ s.

time. Attenuation of fluctuations was extremely slow. It took two days for the peak to disappear.

For the samples of different phase separation times t_{ps}, similarly the peak shifted to smaller wave numbers during the attenuation of concentration fluctuations. When t_{ps} was short, no peak was initially observed in the measured q range but a peak appeared at the largest side of q and shifted to smaller wave numbers in a later period as shown in Fig. 5.

The decrease of q_{m} during the attenuation of concentration fluctuations has been observed experimentally by Akcasu et al. [7] for PS/poly(vinyl methyl ether) blend. However, Inoue et al. has reported that the peak location remained almost unchanged in the attenuation process for *cis*-1,4-polybutadiene/poly(styrene-*co*-butadiene) blend [4] and polycarbonate of bisphenol A/poly(styrene-*co*-acrylonitrile) blend [6]. The decrease of q_{m} during the attenuation of fluctuations has been predicted by the theoretical calculation based on the non-linear Langevin equation [7,19] and is considered to result from that concentration fluctuations of shorter wavelengths more rapidly attenuated. It is not clear at present why q_{m} does not change in the *cis*-1,4-polybutadiene/poly(styrene-*co*-butadiene) blend and the polycarbonate of bisphenol A/poly(styrene-*co*-acrylonitrile) blend.

The decrease of q_{m} means that the wavelength of the dominant concentration fluctuation increased in the attenuation process. This was confirmed by observation in real space with using an electron microscope. Fig. 6 shows scanning electron micrographs of microtomed surfaces of the blends quenched to 155°C after phase-separation at 180°C for 1680 s. The brighter parts in the micrograph correspond to the regions of higher P2CLS content. Immediately after the quench, an undulate structure typical to spinodal decomposition was observed as shown in micrograph (a). At 29 h after the quench (micrograph (b)), the characteristic size of the undulate structures obviously increased from the initial size, and the contrast in the micrograph became less distinct. To the best of our knowledge, this is the first observation in real space of the increase in the wavelength of the dominant fluctuation during the attenuation.

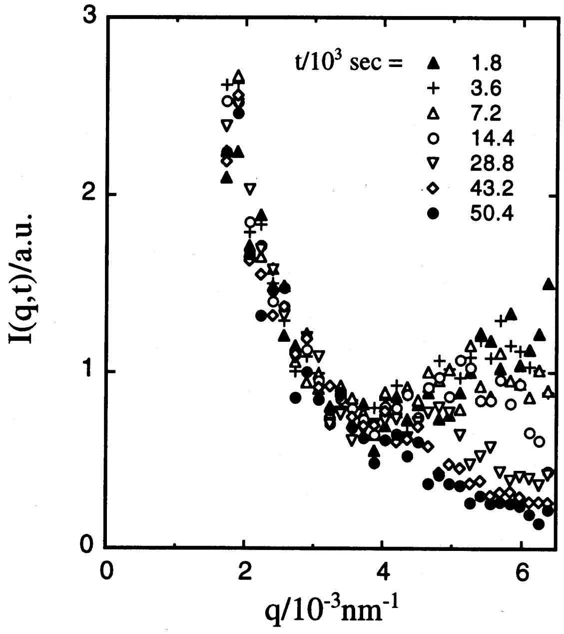

Fig. 5. Temporal variation of scattered light intensity profile $I(q,t)$ after quench to 155°C. Phase separation time at 180°C is $t_{\mathrm{ps}} = 1020$ s.

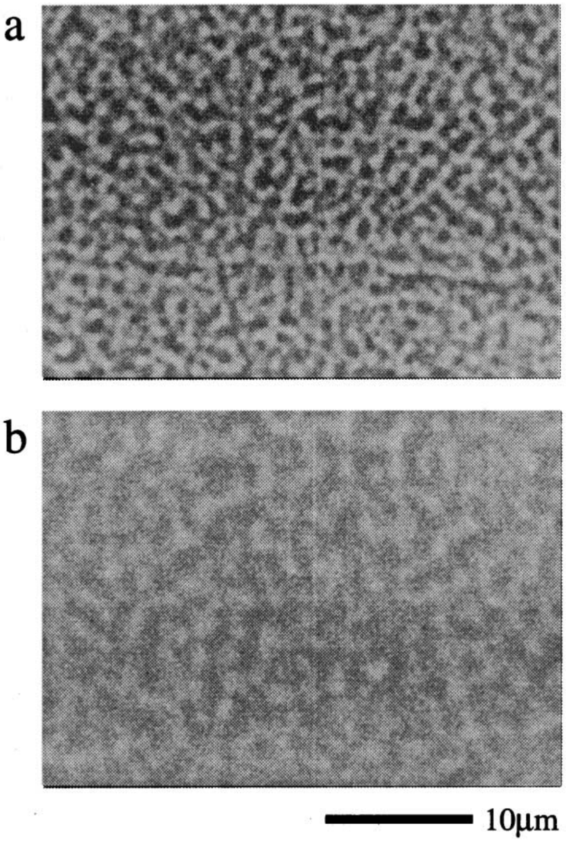

Fig. 6. Electron micrographs of microtomed surface of the blend at t after quench from 180 to 155°C: (a) $t = 0$ h, (b) 29 h. Phase separation time at 180°C is 1680 s.

Dynamics of the attenuation of concentration fluctuations in the single-phase region should be described by the same theoretical formulation as that given for dynamics of the growth of concentration fluctuations in spinodal decomposition. The early stage of spinodal decomposition of a polymer blend has often been analyzed by the Cahn–Hilliard–Cook (CHC) theory [20,21]. We attempted analyzing an early period of the attenuation of concentration fluctuations by the CHC theory. According to the CHC theory, the scattered light intensity $I(q,t)$ after a temperature change made at time $t = 0$ is expressed as a function of wave number q and t to be

$$I(q,t) = I(q,\infty) + [I(q,0) - I(q,\infty)]\mathrm{e}^{-2R(q)t} \tag{3}$$

The rate $R(q)$ is given by

$$-R(q) = -Mq^2[(\partial^2 f/\partial\phi^2)_0 + 2Kq^2] \tag{4}$$

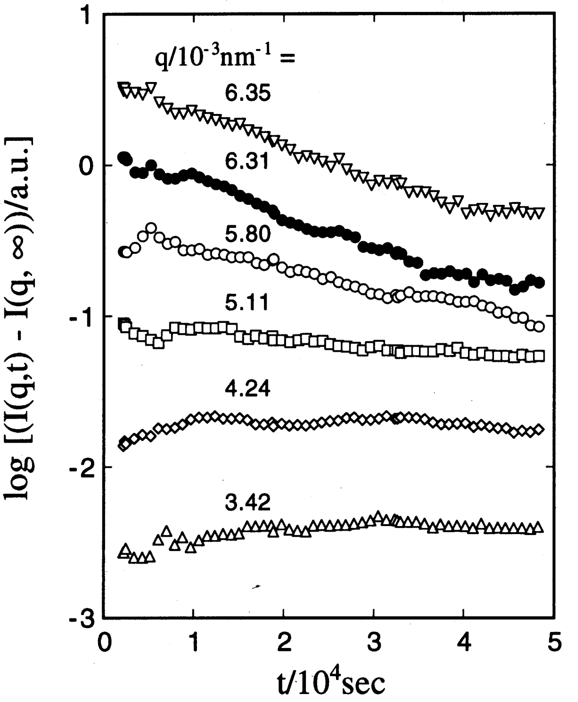

Fig. 7. Semi-logarithmic plot of $[I(q,t) - I(q,\infty)]$ against time t at several wave numbers q. $t_{ps} = 1200$ s.

where M is the mobility, K is a coefficient of the excess energy arisen from concentration gradient, $(\partial^2 f/\partial\phi^2)_0$ is the second derivative of the local free energy f at the initial concentration ϕ_0, and $I(q,0)$ is the initial intensity. It is noted that in the case of phase dissolution $I(q,\infty)$ is an experimentally accessible quantity corresponding to the equilibrium scattered intensity at the quenched temperature though it is not in the case of phase separation.

By using the equilibrium scattered intensity at 155°C for $I(q,\infty)$, $\ln[I(q,t) - I(q,\infty)]$ is plotted against time t for the sample of $t_{ps} = 1200$ s in Fig. 7, where each set of data at a single wave number q was vertically shifted for viewing clarity. A linear relationship between $\ln[I(q,t) - I(q,\infty)]$ and t was observed in an early period of the attenuation as predicted by Eq. (3). Similar linear relationship was observed when t_{ps} was changed. The attenuation rate $-R(q)$ was evaluated from the initial slope for each wave number q, and $-R(q)/q^2$ is plotted against q^2 for various t_{ps} in Fig. 8. The $-R(q)/q^2$ vs q^2 relation displayed no systematic dependence on t_{ps}, indicating that $R(q)$ was independent of the initial intensity $I(q,0)$. At larger wave numbers, $-R(q)/q^2$ linearly changed with q^2. Extrapolation of this linear portion to $q^2 = 0$ gave a negative intercept. If the intercept thus obtained corresponds to $-M(\partial^2 f/\partial\phi^2)_0$ as indicated by Eq. (4), the negative value is reasonable because the diffusion constant $M(\partial^2 f/\partial\phi^2)_0$ should be positive in the single-phase region.

Eq. (3) is led by linearizing the time-dependent Langevin equation and the CHC theory inherently holds only in the case where amplitudes of concentration fluctuations are sufficiently small [1]. In preparation of the initial concentration fluctuations at 180°C, the characteristic wave number q_m shifted with time, indicating that the CHC theory did not hold in the phase separation. This suggests that concentration fluctuations at the beginning of the attenuation process were too large in amplitude for the subsequent process to be described by the CHC theory. However, unexpectedly data points at large wave numbers appeared to be consistent with the theory.

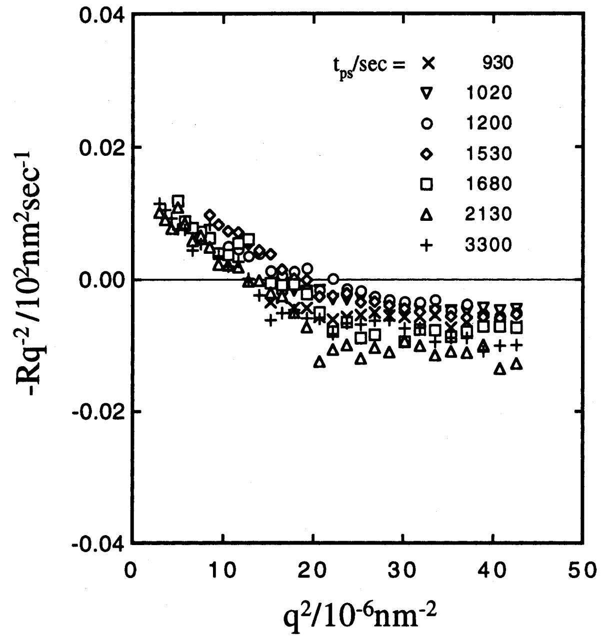

Fig. 8. Plot of $-R(q)/q^2$ against q^2 for various phase separation time t_{ps} at 180°C.

In the smaller q^2 range, $-R(q)/q^2$ seriously deviated upwards from the linear relationship and surprisingly it became positive at the smallest side of q^2. The positive rate $-R(q)$ means that concentration fluctuation of the wave number q was growing instead of attenuating. In fact, inspection of Fig. 5 revealed slight increase in intensity around the minimum of its q-dependence. This unexpected result posed a question whether the experimental temperature was indeed in the single-phase region. However, the increase of the intensity occurred only in a limited range of time and wave number, and the peak intensity never increased as already seen in Figs. 4 and 5. It was also confirmed by using an electron microscope that no detectable inhomogeneity existed in the sample after the peak disappeared in the measured q-range. In addition, if the increase in the intensity was assumed to be caused by phase separation, the phase separation rate calculated from the data in Fig. 9 based on the CHC theory was not consistent with the results shown in Fig. 2. The intensity at $q_{m0} = (1/\sqrt{2})q_c = 2.8 \times 10^{-3}\ \mathrm{nm}^{-1}$, where q_c was defined by $R(q_c) = 0$, was evaluated to increase to twice as much as the initial value after 17 h, which should be detected with the present experimental accuracy, but in

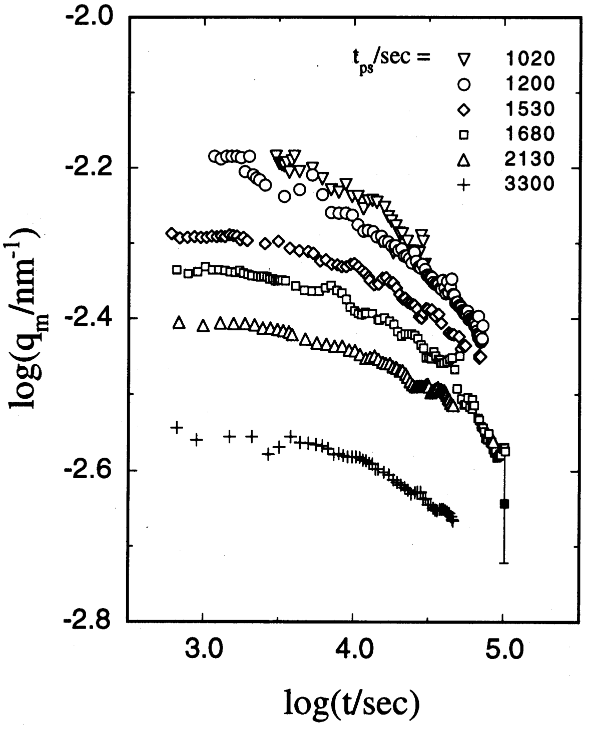

Fig. 9. Double-logarithmic plot of q_m against time t for various phase separation time t_{ps} at 180°C. Filled symbol (■) indicates q_m evaluated from image analysis of electron micrographs.

the TRLS experiment at 155°C no appreciable increase in the scattered light intensity was detected at this wave number for 1.73×10^5 s as shown in Fig. 2. Therefore, the observed positive $-R(q)$ was not attributable to phase separation.

Physical origin of the slight increase in $I(q, t)$ at higher q before the attenuation is not clear at present. We speculate that the hydrodynamic interaction is a possible origin rather than the non-linear terms in the generalized Langevin equation neglected in the CHC treatment, because no increase in intensity was observed in the results of the attenuation process calculated by Akcasu et al. on the basis of their non-linear theory [7,19].

Fig. 9 shows the plots of the characteristic wave number q_m against time t for various t_{ps}. The characteristic wave number evaluated from an electron micrograph by using the relation

$$q_m = \pi/L \tag{5}$$

was also shown in the figure. Here, L is the characteristic length of phase-separated domains determined by image analysis [22]. The characteristic wave number thus obtained was consistent with q_m obtained by the TRLS measurements. Except for the case of $t_{ps} = 1020$ s, there was a period where q_m scarcely changed with time before a period where q_m decreased rapidly. In the case of $t_{ps} = 1020$ s, the period of scarce change in q_m was not observed because q_m was initially located outside of the measured range (see Fig. 5). The period where q_m scarcely changed became longer as the phase separation time t_{ps} at 180°C was increased. As already mentioned, concentration fluctuations of shorter wave lengths more rapidly attenuated, which causes the shift of q_m to smaller wave numbers in the attenuation process. Thus as the wave length of the dominant fluctuation at the initial state is increased, longer time is required for the dominant fluctuation to begin to attenuate appreciably.

In the period of rapid q_m decrease, the power-law behavior was observed. The exponents evaluated for different t_{ps} were around -0.3, which was obviously different from the value -0.5 obtained by numerical integration of the non-linear equation given by Akascu et al. [7,19]. The $t^{-0.5}$ dependence arose from the initial intensity profile $I(q, 0)$ in the small q region, for which they assumed

$$I(q,0) \sim q_m(0)^{-3} y^2/(2 + y^6); \quad y = q/q_m(0) \tag{6}$$

The scaled form of Eq. (6) holds after the system undergoes spinodal decomposition for sufficiently long time, but in this study the initial intensity was prepared by allowing the system to undergo spinodal decomposition for relatively short time before the late stage set in. This might account for the observed discrepancy. However we could not observe any tendency that the exponent approached 0.5 with increasing the phase separation time at 180°C.

4. Conclusions

Attenuation of concentration fluctuations in a PS/P2CLS blend after quench from a temperature in the two-phase region to one in the single-phase region was studied by using the TRLS technique and scanning electron microscopy. The initial concentration fluctuations were prepared by allowing the blend to undergo spinodal decomposition for a predetermined period. The period of the spinodal decomposition t_{ps} was set to be shorter than the time required for the late stage to begin. In the attenuation process, the wave number q_m where the maximum in the scattered light intensity profile was located moved towards smaller wave numbers. Growth in the wave length of the dominant concentration fluctuation corresponding to the decrease of q_m was clearly observed by an electron microscope.

The early period of attenuation of concentration fluctuations was analyzed by using the CHC theory. The rate $-R(q)$ evaluated from the initial slope of the $\ln I(q, t)$–t plot satisfied the linear relation between $-R(q)/q^2$ and q^2 only in a large q region. As q^2 decreased, $-R(q)/q^2$ seriously deviated upwards from the linear relationship and it became positive at small wave numbers, indicating that concentration fluctuations of certain wave lengths continued to grow for a short period even after the system was returned to the single-phase region. In a later period the power-law behavior $q_m \sim t^{-0.3}$ was observed. The exponent was obviously smaller than the value 0.5 that was obtained based on the non-linear theory by Akcasu and collaborators. It is not clear whether the observed discrepancy was caused by the difference in the profile of the initial intensity.

References

[1] Gunton JD, Miguel MS, Sahni PS. Phase transitions and critical phenomena, vol. 8. New York: Academic Press, 1983. p. 267.

[2] Hashimoto T. Phase Transitions 1988;12:47.

[3] Binder K. Adv Polym Sci 1994;112:181.

[4] Takagi Y, Ougizawa T, Inoue T. Polymer 1987;28:103.

[5] Sato T, Han CC. J Chem Phys 1988;88:2057.

[6] Okamoto M, Shiomi K, Inoue T. Polymer 1995;36:87.

[7] Akcasu AZ, Bahar I, Erman B, Feng Y, Han CC. J Chem Phys 1992;97:5782.

[8] Onuki A. Phys Rev Lett 1982;48:753.

[9] Onuki A. Prog Theor Phys 1982;67:1740.

[10] Joshua M, Maher JV, Goldberg WI. Phys Rev Lett 1983;51:196.

[11] Joshua M, Goldberg WI, Onuki A. Phys Rev Lett 1985;54:1175.

[12] Tanaka H, Sigehuzi T. Phys Rev Lett 1995;75:874.

[13] Tanaka H, Suzuki T, Hayashi T, Nishi T. Macromolecules 1992;25:4453.

[14] Okamoto M, Kotaka T. Polymer 1997;38:1357.

[15] Lee SC, Yoon KH, Park IH, Kim HC, Son TW. Polymer 1997;38:4831.

[16] Okada M, Fujimoto K, Nose T. Macromolecules 1995;28:1795.

[17] Kwak KD, Okada M, Nose T. Polymer 1991;32:864.

[18] Scott R. J Chem Phys 1949;17:279.

[19] Akcasu AZ, Klein R. Macromolecules 1993;26:1429.

[20] Cahn KW, Hilliard JE. J Chem Phys 1958;28:258.

[21] Cook HE. Acta Metall 1970;18:297.

[22] Okada M, Kwak KD, Chiba T, Nose T. Macromolecules 1993;26:4047.