

Apparent phase dissolution at the two-phase region in polymer-polymer mixtures

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A binary blend of poly(methyl methacrylate) and poly(styrene-co-acrylonitrile) with 32.2 wt% acrylonitrile was found to exhibit lower critical solution temperature (LCST) type phase behaviour. In this binary system, a strange phenomenon was observed: the phase dissolution at the two-phase region above LCST, i.e., when the solution cast film with two-phase structure was annealed at the two-phase region, light scattering intensity decreased and the microscopic image contrast of the two-phase structure became weaker with a longer time of annealing. A computer simulation on the concentration fluctuation by the Cahn-Hilliard type of nonlinear diffusion equation suggested that the phase dissolution is an apparent one caused by the decrease in the composition difference between the coexisting phases along binodal curves attaining the new equilibrium compositions at the annealing temperature.

(Keywords: polymer blend; phase dissolution; lower critical solution temperature (LCST); nonlinear diffusion equation; poly(methyl methacrylate); poly(styrene-co-acrylonitrile); poly(styrene-co-maleic anhydride))

INTRODUCTION

Recently we became interested in the phase behaviour of binary polymer blends of poly(methyl methacrylate) (PMMA) and poly(styrene-co-acrylonitrile) (SAN), especially the effect of the acrylonitrile content of SAN on the miscibility of PMMA and SAN. During these studies, we found a very strange phenomenon: the phase dissolution at the two-phase region above the lower critical solution temperature (LCST) in the phase diagram. This is difficult to understand from a thermodynamic point of view.

In this paper, we describe this strange phenomenon and interpret it with the aid of computer simulation of the concentration fluctuation using the nonlinear diffusion equation presented in our previous paper¹. We also discuss the related problems on the structure change in polymer-polymer mixtures with annealing at two-phase region.

PHASE DISSOLUTION PHENOMENON

PMMA used in this study was a commercial polymer, Acrypet M001, Mitsubishi Rayon Co. Ltd., ($M_n = 50\,000$, $M_w = 110\,000$). SAN was from the Mitsubishi Monsanto Chemical Co. Ltd., (AN content = 32.3 wt%, $M_w = 63\,000$). PMMA and SAN were dissolved at 7 wt% of total polymer in tetrahydrofuran. The solution was cast onto a cover glass (for microscopy). After the solvent was evaporated at 15°C, the cast film was further dried under vacuum of 10^{-4} mmHg at 100°C for 24 h.

The phase diagram was determined by the cloud point method employing very long isothermal annealing (up to 48 h)². Results are shown in Figure 1. They indicate LCST-type phase behaviour.

The solution casting yielded a phase-separated film. Even if dissimilar polymers are miscible, the casting from the solution in a common solvent sometimes results in the two-phase film, typically observed on poly(ether sulphone)/poly(ethylene oxide)/cyclohexanone³ and the polystyrene/poly(vinylmethyl ether)/chloroform system⁴. This behaviour has been interpreted by the presence of the two-phase region in the triangle phase diagram of the ternary system⁴. The phase-separated structure was observed under a light microscope. A typical result is shown in Figure 2a. A highly interconnected two-phase morphology with uniform domain size is seen in the micrograph. For convenience we refer to it as a modulated structure in order to describe the morphological features of unique periodicity and high level of phase connectivity⁵. Figure 2b shows a light scattering pattern from the cast film of Figure 2a. The ring pattern indicates some degree of regularity of the phase-separated structure in Figure 2a. The Bragg spacing from the peak of the goniometer trace (see Figure 3) corresponds to the periodic distance in Figure 2a.

The film specimens with modulated structure underwent a rapid temperature jump from room temperature to higher temperatures set isothermally above the LCST. The goniometer trace of the intensity of the scattered light from the film was given by a light scattering apparatus⁶. A typical example of the change of light scattering profile during the isothermal annealing is shown in Figure 3. The scattered intensity decreases with time of annealing, keeping the peak angle almost constant. The intensity decay in Figure 3 seems to correspond to the phase dissolution, keeping the periodic distance of modulated structure constant. This was confirmed by microscopy, i.e., the image contrast of modulated structure gradually became weaker over longer annealing times. The dissolution phenomenon was observed at various

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temperatures up to 155°C. These results suggest that the phase dissolution takes place at the two-phase region above LCST. This is a very strange phenomenon.

COMPUTER SIMULATION

Why does the phase dissolution take place in two-phase region? In order to answer this question, we carried out a computer simulation using the nonlinear diffusion equation. The detail of the simulation procedure was presented previously¹. This simulation is a one-dimensional analysis. A more sophisticated two-dimensional version has been given by Petschek and Metiu⁷. However, because of the difficulty in mathematical treatment of the diffusion equation, the two-dimensional analysis inevitably involves certain assumptions, which mean that the simulation is valid only under restricted conditions. We prefer the one-dimensional version because it is more generally applicable for studies of structure development in the demixing processes under various quench conditions.

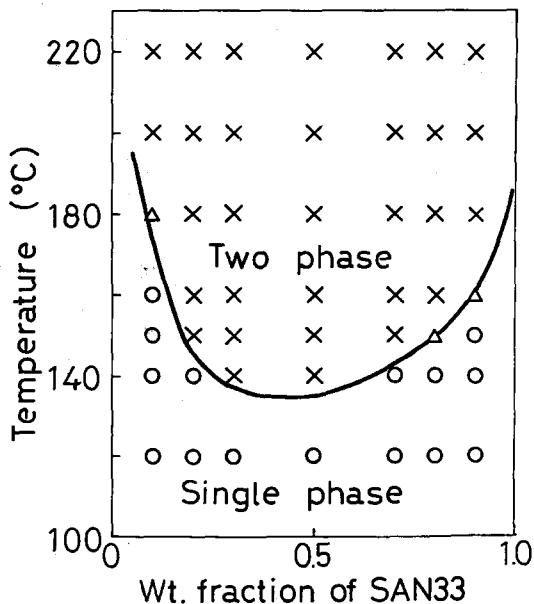


Figure 1 Phase diagram of PMMA/SAN system. x, the film was cloudy and an irregular two-phase morphology was observed under light microscope; O, clear film; Δ, the x judgment after 10 h annealing changed to the O judgment after a further 38 h annealing

Diffusion equation

The concentration fluctuation on the basis of nonlinear diffusion equation is described below. The concentration fluctuation $q(q=c-c_a, c_a$ being the average concentration) at time t and position x is expressed by a sum of Fourier series:

$$q(x, t) = \sum q_n \exp[2\pi xi/(L/h)] \tag{1}$$

where l is the longest wavelength that exists in the demixing system, Q_n is the amplitude of the Fourier wave with wavelength l/h . The nonlinear diffusion equation for spinodal decomposition is approximated by

$$\partial c/\partial t = \partial(D\partial c/\partial x)/\partial x - 2K(\partial^4 c/\partial x^4) \tag{2}$$

where K is the gradient energy coefficient and D is the interdiffusion coefficient, defined by

$$D = M(\partial^2 f/\partial c^2) \tag{3}$$

where M is the mobility and f is the free energy of mixing⁸. Any type of the free energy curve $f(c)$ of a binary mixture can be expressed in the polynomial form:

$$f(c) = a_6 c^6 + a_5 c^5 + \dots + a_1 c + a_0 \tag{4}$$

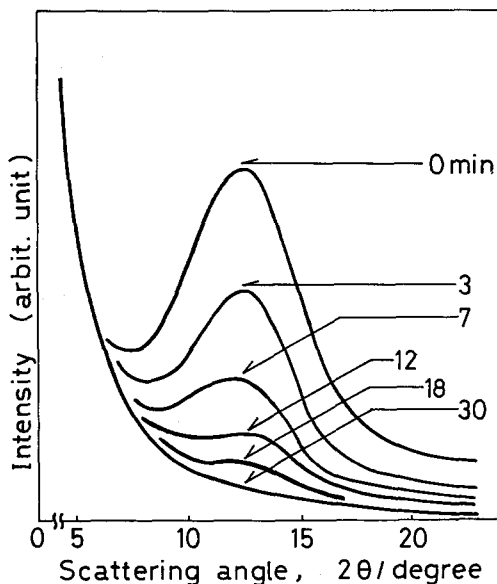


Figure 3 Change of light scattering profile of 50/50 PMMA/SAN film during annealing at 150°C. Figures are times after temperature jump

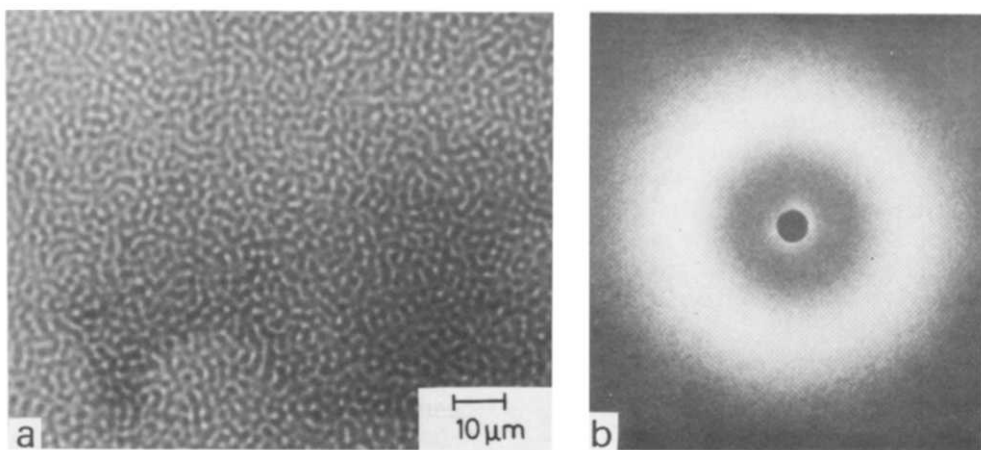


Figure 2 (a), Light micrograph of 50/50 PMMA/SAN film, scale bar 10 μm; (b), light scattering pattern (V) from the film in (a). A He-Ne laser of 632.8 nm wavelength was used

Substituting equation (4) into equation (3) and then into equation (2), we have

$$\partial Q_h / \partial t = -(hb)^2 [(D_0 + 2h^2 b^2 \mathbf{K}) Q_h + (1/2) D_1 R_h + (1/3) D_2 S_h + (1/4) D_3 T_h + (1/5) D_4 U_h] \quad (5)$$

where $b = 2\pi/L$, $R_h = \int_{-\infty}^{+\infty} Q_k Q_{h-k} dk$, $S_h = \int_{-\infty}^{+\infty} R_k Q_{h-k} dk$, $T_h = \int_{-\infty}^{+\infty} S_k Q_{h-k} dk$, $U_h = \int_{-\infty}^{+\infty} T_k Q_{h-k} dk$, and

$$D_0 = 30M [a_6 c_a^4 + (2/3) a_5 c_a^3 + (2/5) a_4 c_a^2 + (1/5) a_3 c_a + (1/15) a_2]$$

$$D_1 = 30M [4a_6 c_a^3 + 2a_5 c_a^2 + (4/5) a_4 c_a + (1/5) a_3]$$

$$D_2 = 30M [6a_6 c_a^2 + 2a_5 c_a + (2/5) a_4]$$

$$D_3 = 30M [4a_6 c_a + (2/3) a_5]$$

$$D_4 = 30M a_6$$

Thus, we can calculate the time evolution of the Fourier component by

$$Q_h(t + \Delta t) = Q_h(t) + (\partial Q_h / \partial t) \Delta t \quad (6)$$

Inserting all values of Q_h into equation (1), we can calculate time evolution of the concentration fluctuation.

We use the Flory-Huggins equation for the free energy function $f(c)$. The temperature dependence of the interaction parameter is described by the equation of state theory:

$$\chi(T) = \frac{P_1^* V_1^*}{RT_1^*} \left[\frac{V_1^{1/3}}{V_1^{1/3} - 1} \left(\frac{X_{12}}{P_1^*} \right) + \frac{V_1^{1/3}}{2(4/3 - V_1^{1/3})} \tau^2 \right] \quad (7)$$

$$\tau = 1 - (T_1^*/T_2^*) \quad (8)$$

$$V_1 = V_1/V_1^* \quad (9)$$

The asterisked parameters are the characteristic temperature (T^*), volume (V^*) and pressure (P^*). X_{12} is the exchange energy. When these variables are known, we can formulate $f(c)$. Then the $f(c)$ obtained is approximated in the form of equation (4) by the least-squares method, to obtain the values of a_0, a_1, \dots, a_6 .

Simulation procedure

We assumed that the phase-separated structure in solution cast film is identical to the structure which develops by the thermally induced phase separation at a certain temperature above the LCST (T_1 in Figure 4). (This supposition will be shown to be reasonable later.)

We performed the computer simulation on the demixing caused by a temperature jump and drop manipulation shown in Figure 4. That is, a homogeneous mixture underwent the temperature jump from T_4 to T_1 , the system was allowed to demix at T_1 for a while, then the demixed system underwent the temperature drop from T_1 to T_2 (or T_3). The drop corresponds to a change from deep quench to shallow one.

Results

As described above, we need the free energy function $f(c)$ in order to perform the computer simulation. Unfortunately, the equation of state parameters are not available for our PMMA/SAN system. So, instead of PMMA/SAN, we chose polystyrene(PS)/poly(vinyl methyl ether) (PVME)⁹. The binodal and spinodal curves in Figure 4 were calculated from the $f(c)$ of the PS/PVME system. The values of kinetic variables are also available for this system¹⁰. First, a single-phase mixture with

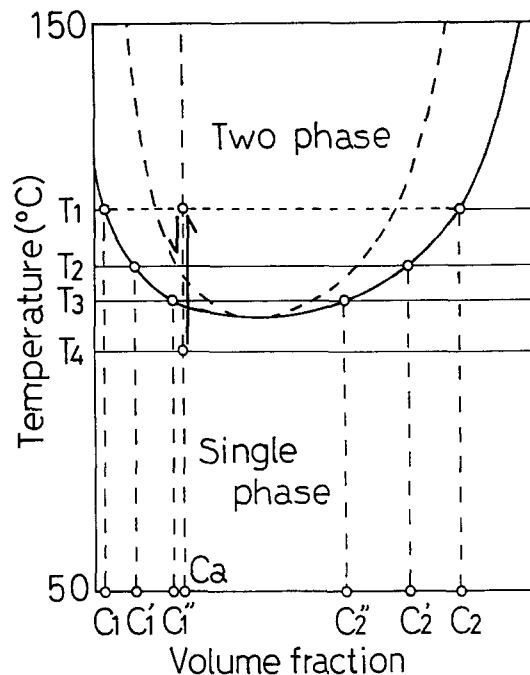


Figure 4 LCST-type phase diagram calculated and temperature jump ($T_4 \rightarrow T_1$) and drop ($T_1 \rightarrow T_2$ or T_3) manipulation. $V_1^* = 151\,000 \text{ cm}^3/\text{mol}$; $V_2^* = 46\,000 \text{ cm}^3/\text{mol}$; $T_1^* = 8\,191\,000$, $T_2^* = 7\,201\,000$; $P_1^* = 500 \text{ J/cm}^3$, $X_{12} = -0.922$ (from ref. 9)

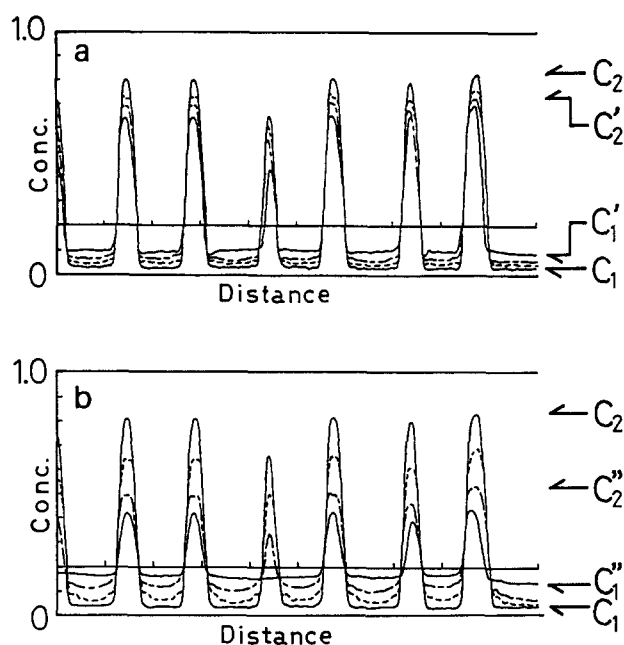


Figure 5 Decay of concentration fluctuation after temperature drop from (a), T_1 to T_2 (116.85–106.85°C) and (b), T_1 to T_3 (116.85°C–101.0°C), estimated by computer simulation: $L = 50 \mu\text{m}$, $h = 256$

composition C_a ($=20 \text{ vol}\%$) was transferred to T_1 ($=116.85^\circ\text{C}$). Concentration fluctuation grew to generate a periodic nature in the concentration profile, as demonstrated previously¹. This isothermal demixing was continued until the peak of the concentration profile reached the equilibrium compositions C_1 and C_2 in Figure 4. The concentration profile of the demixed system at this moment is shown by the wave (denoted by a solid line) with the largest amplitude in Figure 5a.

Then the demixed system was transferred to T_2

(= 106.85°C; in the unstable region of phase diagram). The amplitude of the wave gradually decreased with time after the temperature drop, eventually attained the equilibrium compositions C_1' and C_2'' , as shown in *Figure 5a*. A similar decay of the amplitude was simulated for a temperature drop to T_3 (= 101.0°C in the metastable region of phase diagram) as shown in *Figure 5b*. Note that, in both cases, the peak positions of waves hardly change during the amplitude decay; in other words, average wavelength is kept constant.

When the calculation was further continued at T_2 , the coarsening was simulated, as described previously¹. That is, the small peak, such as the third peak in *Figure 5a*, was absorbed into neighbouring peaks, resulting in an increase of average wavelength. It was, however, a very slow process.

DISCUSSION

From the results of computer simulation, we are able to interpret the experimental results. As noted before assume that the solution cast film is composed of two phases with the coexisting compositions, C_1 and C_2 in *Figure 4*. When the film undergoes a temperature jump from room temperature to T_2 and is annealed at T_2 , the compositions of the two phases are expected to shift to C_1' and C_2' , keeping the periodic distance constant, as demonstrated in *Figure 5*.

Because the intensity of the scattered light from the two-phase system is proportional to the square of the composition difference of two phases; i.e., $I \propto |C_1 - C_2|^2$, a small change in composition to $|C_1' - C_2'|$ is expected to cause a dramatic change in the scattered light. Hence, the intensity decay in *Figure 3* is to be expected. In fact, the result in *Figure 3* does not necessarily correspond to the phase dissolution into a homogeneous mixture, but to a decrease in the composition difference with annealing, maintaining the modulated structure. This 'dissolution' ceases on the way to homogeneous solution. In other words, although the result in *Figure 3* looks like complete dissolution, it is not; even after the longest annealing in *Figure 3*, the system is still expected to be a two-phase system.

The structural change after the apparent dissolution, that is, what happens if the film is annealed for much longer time, is discussed below. The computer simulation has suggested that coarsening would take place, resulting in the two-phase morphology of dispersed droplets of non-uniform size. When we observed very carefully under light microscope, such image with very weak contrast was observed in the well-annealed film, (for example, film annealed for 24 h at 150°C).

Another problem is what happens when the solution cast film is annealed at the higher temperatures than T_1 . On the basis of the results in *Figures 3-5* and the above discussion, it is expected that the phase separation proceeds to attain a larger difference in composition along the binodal curve in *Figure 4*. This would result in the increase in the scattered intensity with annealing. This situation does occur, as described in Appendix 1.

The apparent phase dissolution takes place at low temperatures (above LCST) and the phase separation proceeds at the higher temperatures. Where is the borderline between these two phenomena? In order to answer this question, we carried out the light scattering experiments for the 50/50 PMMA/SAN blend at various

temperatures. From these results, the borderline was found to be around 170°C. In other words, the solution cast film of the 50/50 PMMA/SAN is supposed to be composed of two phases with the compositions on the binodal line in *Figure 1* at 170°C.

CONCLUSIONS

The apparent phase dissolution of the solution cast film of PMMA/SAN at the two-phase region has been interpreted by the change in compositions of the two phases along the binodal curve in phase diagram. This is quite a natural result from the theoretical point of view and is not at all surprising. However, from the experimental point of view, it presents an important caution, demonstrated by the short tale below.

Let us suppose that a smart man intended to determine the phase diagram of PMMA/SAN mixture by light scattering. He obtained similar results to those in *Figure 3*. As the scattered light intensity decreased, he judged that it was due to the phase dissolution and hence it was at single phase region. He obtained similar results for the temperature jump and isothermal annealing experiments at various temperatures below 170°C. Above 170°C, when the scattered light intensity increased with time of annealing, he judged that it was at the two-phase region. On the basis of these results, he concluded that the LCST was at 170°C. This is an incorrect conclusion which results from a trick of 'apparent phase dissolution at the two-phase region'.

In order to reach the correct conclusion, it is necessary to carry out the very long isothermal annealing². The judgment from the observation based on a short time scale is quite dangerous when one uses the solution-cast film with a two-phase structure. In order to stress this aspect, we note another example of 'apparent phase dissolution' in Appendix 2.

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APPENDIX 1

The solution cast film of 50/50 PMMA/SAN having the modulated structure underwent a rapid temperature jump to 187°C and the change of light scattering profile was observed. The results are shown in *Figure 6*.

As shown in *Figure 6a*, the scattered intensity increased with time of annealing, keeping the peak angle

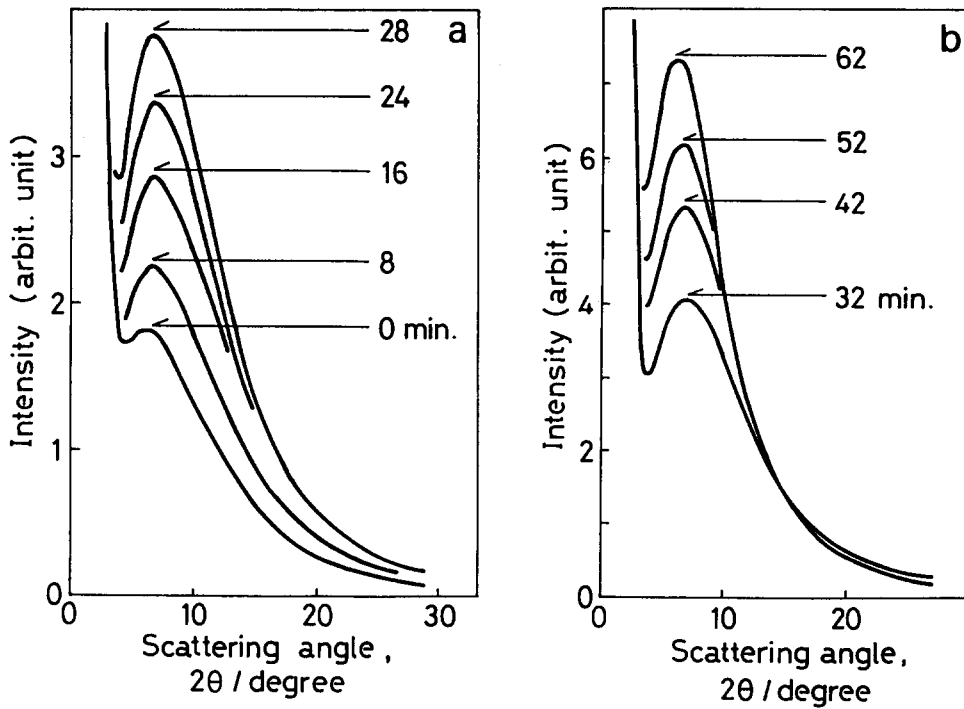


Figure 6 Change of light scattering profile with annealing at 187°C at (a) early and (b) late stages. 50/50 PMMA/SAN

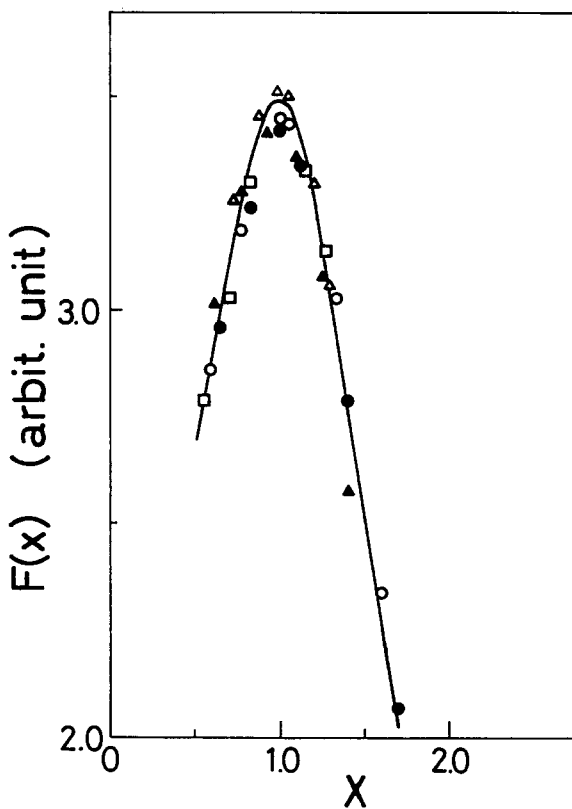


Figure 7 Scaling plot from Figure 6(b) at times: ○, 52 min; ●, 62 min; □, 72 min; △, 82 min; ▲, 92 min

constant. This indicates that the phase separation keeps the periodic distance constant. Later, the peak position shifted toward smaller scattering angle as shown in Figure 6b. It looks like the late stage of spinodal decomposition. We analysed the scattering data using the dynamic scaling on the late stage of SD proposed by Furukawa¹¹. In the context of the dynamic scaling, the

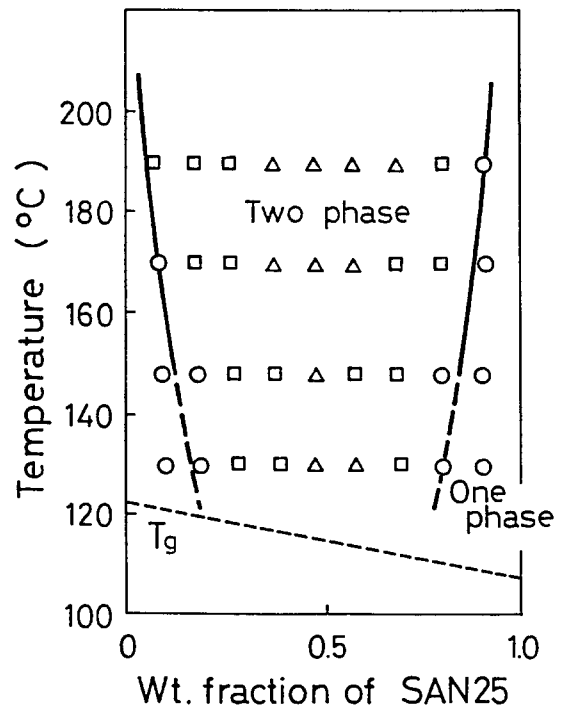


Figure 8 Phase diagram of SAN-25/SMA (ref. 2)

scattering function $I(k, t)$ or the structure function $S(k, t)$ of the decomposition systems at time t can be scaled with the wave number $k_m(t)$ of the dominant Fourier component of concentration fluctuation

$$I(k, t) \sim k_m^{-3}(t) S[k/k_m(t)] \quad (A1)$$

where S is the universal scaling function (or the scaled structure function). According to the theory, S is time-independent in the late stage of SD where the concentration fluctuation has reached the equilibrium composition and the structure in the system grows

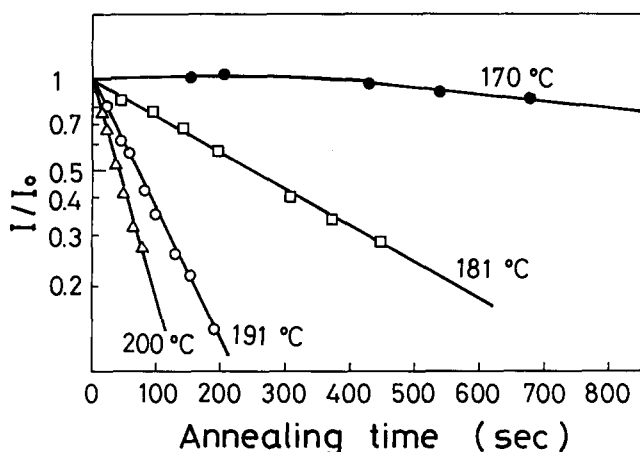


Figure 9 Change of scattered light intensity at peak angle ($2\theta=7^\circ$) with time of annealing at various temperatures. 50/50 SAN-25/SMA

self-similarly with time. According to equation (A1) the experimental scaled structure function $F(x)$ is given by

$$S(x) \sim I(k, t)k_m^3 \equiv F(x) \quad (\text{A2})$$

where x is $k/k_m(t)$.

The plots of $F(x)$ versus x are shown in Figure 7. Values of $F(x)$ obtained at different times (after 52 min) fall onto a single master curve. This implies that the process of phase separation after 52 min can be described by the ordinary decomposition process.

APPENDIX 2

Here we note another example of the apparent phase dissolution. It is on the SAN-25/SMA system. SAN-25 is a poly(styrene-co-acrylonitrile) supplied from Mitsubishi Monsanto Co. Ltd., SAN-C, (acrylonitrile content 25 wt%, $M_w = 194\,000$). SMA is poly(styrene-co-maleic anhydride) supplied from Arco Polymers Inc., Dylark 332 (maleic anhydride content 15.3 wt%, $M_w = 132\,000$). The phase diagram of this binary system is reproduced from ref. 2 in Figure 8. We obtained the similar results to those shown in Figure 3; i.e., the intensity decay of the scattered light during annealing the solution cast film of 50/50 SAN-25/SMA at various temperatures at the two phase region above LCST. The intensity of scattered light at peak angle is plotted as a function of annealing time in Figure 9.