

## New Types of Phase Separation Behavior during the Crystallization Process in Polymer Blends with Phase Diagram

Hajime Tanaka and Toshio Nishi

Department of Applied Physics, Faculty of Engineering, University of Tokyo, Bunkyo-ku, Tokyo 113, Japan

(Received 29 April 1985)

There is a possibility that the phase separation process is coupled with other ordering processes such as crystallization. New types of phase separation behavior during the crystallization process in polymer blends with phase diagram are presented probably for the first time. Two different types of nonequilibrium phenomena take place simultaneously and new structures and new dynamics of pattern formation are observed as the result of the competition between these two phenomena.

PACS numbers: 61.40.Km, 61.50.Cj, 64.30.+t, 81.30.-t

Recently, many studies have been carried out on the dynamics of the phase separation behavior<sup>1</sup> in various systems such as polymer alloys, liquid mixtures, and metallic alloys. In general, there is a possibility that the phase separation process is coupled with other ordering processes such as crystallization. These new types of coupling between nonequilibrium phenomena have been studied from neither the theoretical nor the experimental viewpoint. This type of study is very interesting because two nonequilibrium phenomena occur simultaneously. The competition between these two phenomena might produce new structures, which may be important from both scientific and industrial points of view, and new dynamic behavior might be disclosed.

These phenomena may be common in polymer, liquid, and metal systems. Among them, polymer systems are most suitable for experimental studies since both phase separation and the crystallization process take place very slowly. The diffusion of a polymer molecule is limited by the reptation process on account of its large molecular weight.

We consider here a polymer blend with phase diagram, whose components are a crystalline and an amorphous polymer. The phase diagrams are grouped into several types by the relation between melting curve and binodal line and further by the types of phase diagram, that is, the upper critical solution temperature type or the lower critical solution temperature type. In actual systems, the location of the glass-transition-temperature curve has a strong effect on the kinetics of both phase separation and crystallization behavior.

Here we consider a polymer blend with the phase diagram shown in Fig. 1. The nucleation and growth (NG)-type phase separation takes place in the metastable region between the binodal and spinodal lines, and the spinodal decomposition (SD)-type one in the unstable region within the spinodal line. The crystallization of crystalline polymer due to primary droplet nucleation and the successive growth by secondary nucleation takes place below the melting curve and a spherulite is formed in the usual way. During the cry-

stallization process, the amorphous polymer is preferentially removed from the crystal.

Strictly, a binodal line cannot be defined below the melting curve in an equilibrium phase diagram. However, various phase structures are formed in reality by the competition between two nonequilibrium phenomena. We indicate the melting curve and the binodal and spinodal lines independently in Fig. 1. When two or more nonequilibrium phenomena take place simultaneously, the final phases strongly depend on their dynamics and cannot be determined by an equilibrium phase diagram. The details will be presented in another paper. In cases A and B, the crystallization and phase-separation processes take

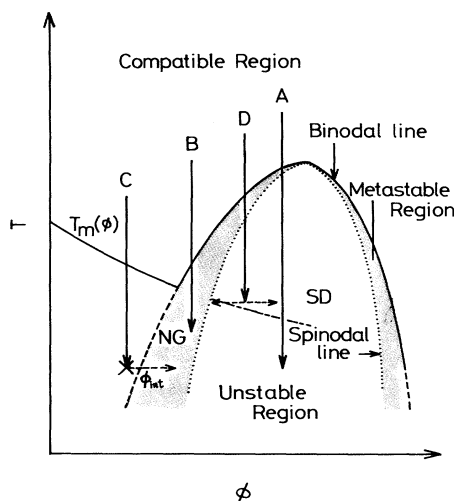


FIG. 1. Schematic phase diagram of a polymer blend of PCL and PS.  $\phi$  is the concentration of PS in the blend and  $T$  is the temperature.  $T_m(\phi)$  represents the melting curve. The melting curve below the binodal line, which is obtained by considering only crystallization, is represented by the dot-dashed line. Strictly, the binodal line below the melting curve cannot be defined in an equilibrium phase diagram and it is represented by the dashed line. Arrows A, B, C, and D indicate the quenching conditions.

place simultaneously and their structures will be strongly affected by the crystallization temperature  $T_c$ . In case A, the SD-type phase separation takes place and a periodically modulated structure will appear especially in the initial stage of phase separation. There is no induction time in this phase-separation process in contrast to NG-type phase separation and crystallization. In case B, the NG-type phase separation takes place and a dropletlike structure will appear. In case C, the crystallization can induce phase separation because the amorphous polymer is removed by crystallization and regions whose composition is within the binodal line are formed. In case D, the phase separation at  $T > T_m$  can induce crystallization because it forms a crystalline-polymer-rich region where the melting point at the composition is higher than  $T$ .

The mechanism of crystallization with phase separation (cases A and B in Fig. 1) is understood qualitatively as follows. In a mixture of a crystalline and an amorphous polymer, crystallization becomes more difficult as the content of the crystalline polymer becomes lower. Crystallization usually does not take place in the region where the content of the crystalline polymer is less than 50%. In the case of a polymer blend with phase diagram as shown in Fig. 1, however, crystallization takes place because the phase separation produces a region where the content of the crystalline polymer is high enough for primary nucleation of the crystal. Since the rate of primary nucleation of the crystal is a function of the content of crystalline polymer, the distribution of the crystalline nuclei is roughly determined in this stage. The type of phase separation, namely SD or NG, has a strong influence on the final structure. After this stage, continual phase separation and secondary nucleation of crystallization take place simultaneously. As the crystallization process proceeds, phase separation is inhibited by the small diffusion constant in the crystalline region. In the late stage of this process, crystallization becomes the main process.

The final structures under this process are grouped into several types by the relationship between the degree of undercooling for crystallization  $\Delta T_m (= T_m - T_c)$  and the depth of the quench into the ordered two-phase state  $\Delta T_p (= T_p - T_c; T_p$  is the phase separation temperature). When the crystallization process is faster than the phase-separation process, the scale of the crystal formed as a spherulite is larger than the wavelength of the concentration modulation which is equal to the Cahn wavelength for SD. This structure is possible because the barrier for secondary nucleation is low enough and it takes place even in a region where the content of crystalline polymer is rather low. In the opposite case, the scale of the macroscopic phase separation is larger than the radius of the spherulite. In both cases, the type of phase separation, that is

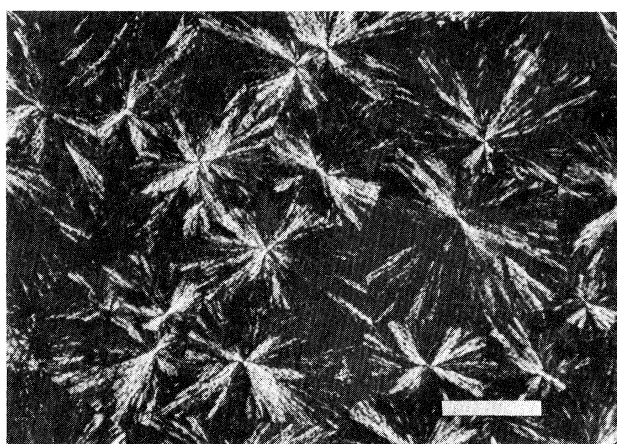
whether it is SD or NG, affects the final structures strongly in the initial stage of the phase separation.

Here we present experimental results corresponding to type A in Fig. 1. Samples used were poly( $\epsilon$ -caprolactone) (PCL) (the weight-average molecular weight  $\overline{M}_w \sim 33\,000$  and the number-average molecular weight  $\overline{M}_n \sim 10\,700$ ) and polystyrene (PS) ( $\overline{M}_w \sim 950$  and  $\overline{M}_n \sim 840$ ). The phase diagram of the mixture of PCL and PS is schematically the same as in Fig. 1.

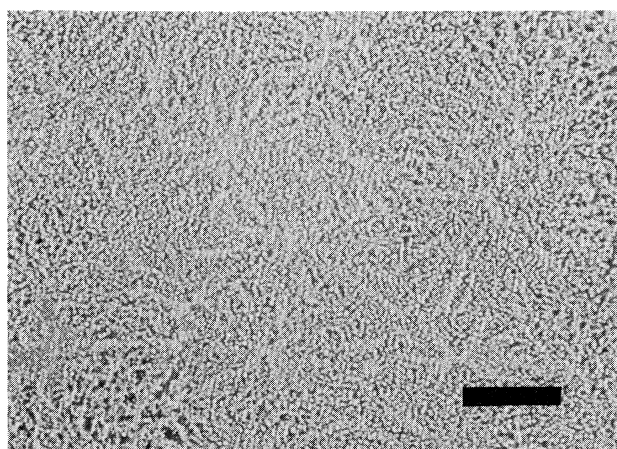
Since PCL is a semicrystalline polymer, crystallization behavior is observed below the melting point  $T_m$ . Because of the low molecular weight of PS, a large melting-point depression of PCL occurs. A polymer blend with 40 wt. % PCL was used in this experiment. The sample was quenched very rapidly from 220 °C to 25 °C. After the quench, a SD-type separation occurred in the system and crystallization also took place. Since  $\Delta T_p$  was so large, the phase separation occurred rapidly and the system entered the late stage of SD within a very short time after the quench. Figures 2(a) and 2(b) show the final structure observed at the same place by a polarizing microscope under crossed Nicols and by a phase contrast one, respectively. In Fig. 2(a) birefringent spherulites of PCL are clearly seen, while droplets of PS-rich region are seen in Fig. 2(b). The size of the droplets is much smaller than that of the spherulites. From actual observation, it becomes clear that phase separation starts first and then crystallization follows. In this process, fibrils grow in the radial direction of the spherulite, avoiding the droplets of PS. In the droplets of PS-rich region, no crystal has been observed because there is too little crystalline polymer for the secondary nucleations. From these figures we find that the distribution of droplets of PS is not uniform and it is affected by the crystallization process. The number density of droplets is lower at the boundary of the spherulite than at its center. Before growth of the spherulite, the distribution of droplets is uniform. The nonuniform distribution of the droplets is clearly ascribed to crystallization and the phase-separation process is not independent of the crystallization. After crystallization, the growth of droplets stops because of the low diffusion constant of PS in the spherulite. The PS molecules in the PCL-rich phase may be trapped in the interlamellar region of the spherulite of PCL.

These features are strongly influenced by the quench condition, i.e., the quench speed and the values of  $\Delta T_m$  and  $\Delta T_p$ , etc. The details of the relation between morphology and quench condition and the dynamics of these phenomena will be presented elsewhere.

In case C, we find that phase separation occurs at the growth front of the spherulite during crystallization at a certain condition when the initial composition of



(a)



(b)

FIG. 2. (a) Photograph of a spherulite of PCL/PS (40/60) system crystallized at 25°C. This is observed under the polarizing microscope under crossed Nicols. The bar corresponds to 200  $\mu\text{m}$ . (b) Photograph of a spherulite of the same system observed by the phase-contrast microscope. The droplets of PS-rich region are mainly observed. The scale is the same as in (a).

blends is sufficiently near the binodal line. Samples used in this experiment are a mixture with 70 wt. % PCL.

Figure 3 shows a photograph of a spherulite of PCL at 50°C after 6000 min from the quench. At this temperature, the degree of undercooling is very small and the spherulite grows very slowly. This was observed under a polarizing microscope and the angle between the polarizer and the analyzer was set equal to 45° in order to observe both the droplets and spherulite clearly. The small spheres at the growth front are droplets of the PS-rich phase, which appear when the spherulite grows to a certain size and become larger as the spherulite grows. The outside of the spherulite is in the melt state. This is probably the first observation of

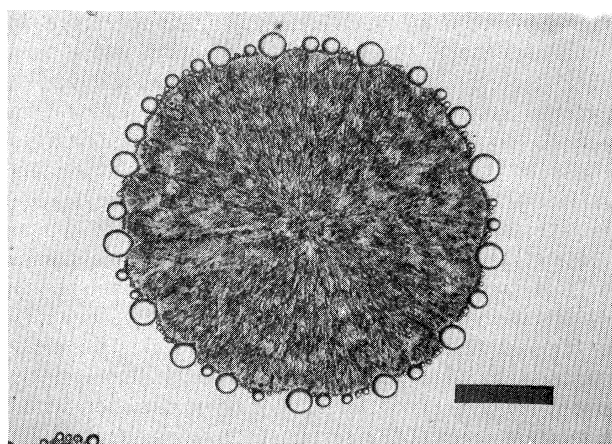


FIG. 3. The phase separation behavior at the growth front of the spherulite of PCL during the crystallization process in the system PCL/PS (70/30) at  $T_c = 50.0^\circ\text{C}$ . The black bar corresponds to 100  $\mu\text{m}$ .

this type of phase separation behavior at the growing interface during crystallization.

The phase separation at the growth front is understood as follows. The characteristic feature of this system is that the melting curve crosses the binodal line (see Fig. 1). The initial composition of this blend is indicated by the cross. We quench the blend from above  $T_m$  to below the  $T_m$  line. Since the initial composition of the blend is in the compatible region, ordinary primary nucleation of crystal in a polymer blend occurs.

In crystallization in polymer blends, in general, a noncrystalline polymer behaves as an impurity for the crystallization of a crystalline polymer. Ordinarily, a noncrystalline polymer is thought to be trapped in the interlamellar region, which is confirmed by the fact that the interlamellar spacing measured by small-angle x-ray scattering becomes larger as the content of the amorphous polymer increases.<sup>2</sup>

So far, the study of crystallization in polymer blends has been restricted to fully compatible systems without phase separation. In our case, however, the composition is near the binodal line. In the process of growth of the lamellae, the noncrystalline polymer (PS) is rejected from the crystal because of the stabilizing force of the crystal and piled up in the interlamellar region. In this stage, the concentration of the amorphous polymer in the interlamellar region becomes much higher than its initial value and the amorphous polymer is then rejected by the force of incompatibility. In our case, the diffusion constant of the noncrystalline polymer PS is very large because of its low molecular weight. For this reason, the PS molecules are effectively rejected on a macroscopic scale beyond the scale

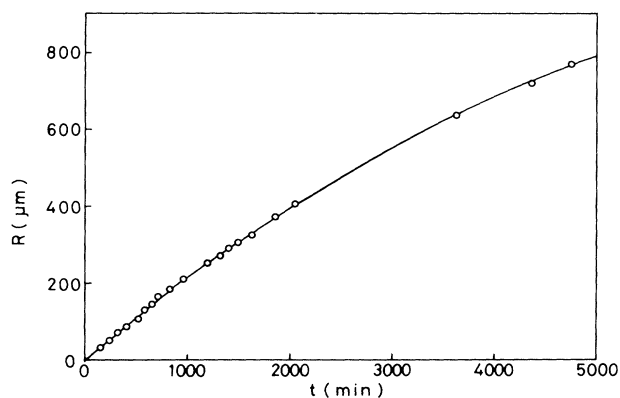


FIG. 4. The diameter of the spherulite,  $2R(t)$ , plotted against time  $t$  for a blend with 70 wt. % PCL at the crystallization temperature  $50^\circ\text{C}$ .

of the interlamellar spacing. The impurities, PS molecules, are rejected to the outside of the spherulite and piled up at the growing interface of the spherulite. This feature depends on the relation between the diffusivity and the growth rate of the crystal.

The concentration of PS at the growing interface,  $\phi_{\text{int}}$ , becomes larger with the growth of the spherulite. If we roughly assume that the PS molecules are completely rejected to the outside of the spherulite and ignore the interaction among the spherulites which is not important in the initial stage, the concentration profile of PS at the interface,  $\phi(r,t)$ , is expressed by

$$\phi(r,t) = [R(t)/\delta] \exp(-r/\delta),$$

where  $t$  is the time after the quench,  $R(t)$  is the radius of the spherulite,  $r$  is the distance from the growth front, and  $\delta = D/G$  [ $D$  is the diffusion constant of the PS molecule and  $G$  is the growth rate of the spherulite,  $G = dR(t)/dt$ ].  $\phi_{\text{int}}$  becomes larger as the spherulite grows and at last it exceeds the value at the binodal line (see Fig. 1). Then NG-type phase separation occurs at the growth front and droplets of PS-rich material are formed. These initial small droplets grow with the growth of the spherulite and combine with one another to form larger droplets to minimize the surface energy. This observation gives direct evidence of the presence of the impurity-rich layer at the growth front.

In this system, we also study the dynamics of the spherulite growth. Figure 4 shows the radius of the

spherulite measured as a function of time. We find nonlinear growth behavior in this polymer blend when the degree of undercooling is not too large. Usually, the radius of the spherulite is linear in time in various systems containing metals, etc., which is understood as the limiting process being secondary nucleation at the crystalline surface.

This nonlinear growth is understood qualitatively as follows. As the crystal grows, the PS concentration at the growing interface increases. This causes two effects: (1) The concentration of the semicrystalline polymer becomes lower at the interface and (2) the degree of undercooling  $\Delta T$  becomes smaller at the interface because the low-molecular-weight PS causes a large melting-point depression.

The profile of  $\Delta T$  at the interface region leads to the instability of the crystal form because the degree of undercooling becomes larger as the distance from the growing interface increases. If a fluctuation in the growth of crystal exists, the fluctuation does not decay but grows because of the unusual  $\Delta T$  profile. This is the well-known Mullins-Sekerka-type instability.<sup>3</sup> The scale of this instability is given roughly by  $\delta$ .<sup>4</sup>

In our case,  $\delta$  is extraordinarily larger than the usual case on account of the large diffusion constant of PS molecules and the very small growth rate. In usual polymer systems,  $\delta$  is on the order of the scale of the fibril (about  $1 \mu\text{m}$ ). In this system, the scale of the instability exceeds  $100 \mu\text{m}$  (see Fig. 3). For these reasons, this system is very suitable to the study of interface instability and the pattern formation problem. Precise arguments on the nonlinear growth and the interface instability will be presented in a future paper.

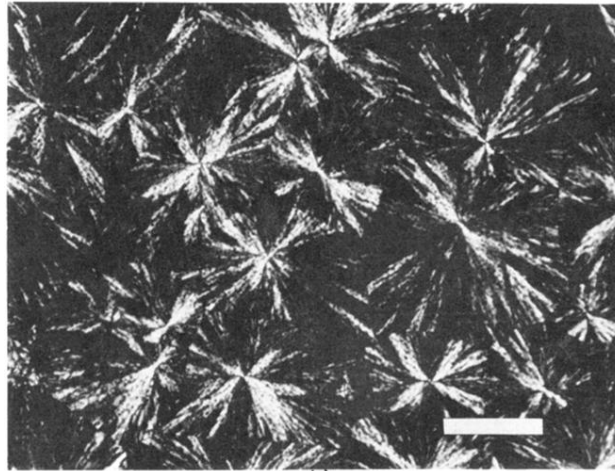
This work was partly supported by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan.

<sup>1</sup>See for a review J. D. Gunton, M. San Miguel, and P. Sahni, in *Phase Transition and Critical Phenomena*, edited by C. Domb and J. H. Lebowitz (Academic, London, 1983), Vol. 8.

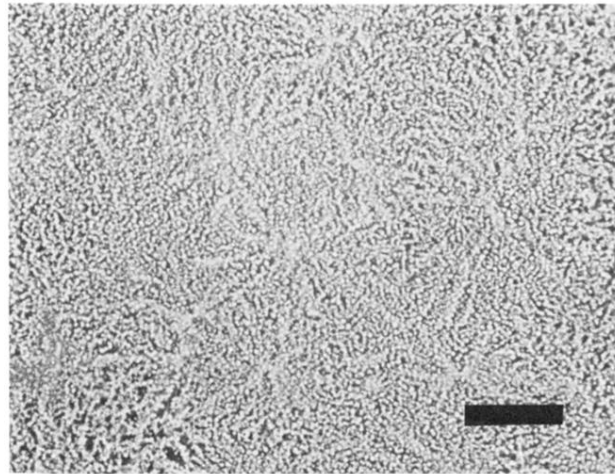
<sup>2</sup>T. P. Russell and R. S. Stein, *J. Macromol. Sci. Phys. B* **17**, 617 (1980).

<sup>3</sup>W. W. Mullins and R. F. Sekerka, *J. Appl. Phys.* **34**, 323 (1963).

<sup>4</sup>H. D. Keith and F. J. Padden, Jr., *J. Appl. Phys.* **34**, 2409 (1963).



(a)



(b)

FIG. 2. (a) Photograph of a spherulite of PCL/PS (40/60) system crystallized at 25 °C. This is observed under the polarizing microscope under crossed Nicols. The bar corresponds to 200  $\mu\text{m}$ . (b) Photograph of a spherulite of the same system observed by the phase-contrast microscope. The droplets of PS-rich region are mainly observed. The scale is the same as in (a).

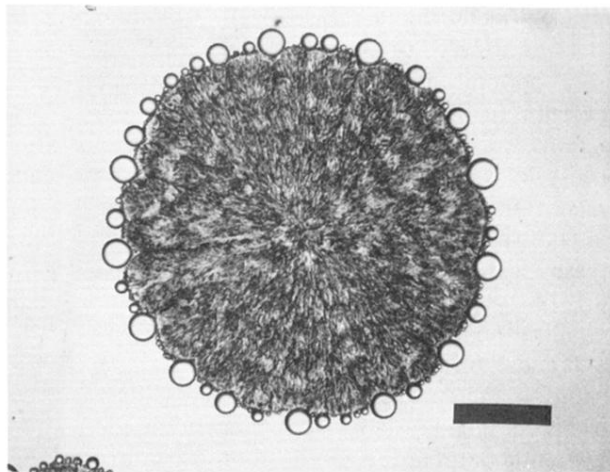


FIG. 3. The phase separation behavior at the growth front of the spherulite of PCL during the crystallization process in the system PCL/PS (70/30) at  $T_c = 50.0^\circ\text{C}$ . The black bar corresponds to  $100\ \mu\text{m}$ .