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Morphology Control of Binary Polymer Mixtures by Spinodal Decomposition and Crystallization. 2. Further Studies on Polypropylene and Ethylene–Propylene Random Copolymer[†]

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Received April 21, 1987; Revised Manuscript Received August 17, 1987

ABSTRACT: Morphology control of binary polymer mixtures through spinodal decomposition and crystallization was studied by using polypropylene and ethylene–propylene random copolymer as a model system. The solid texture consisted of dual morphological units, (i) the modulated network structure resulting from spinodal decomposition and its coarsening processes in the isothermal demixing of the mixture in the molten liquid state and (ii) the spherulite structure resulting from crystallization by subsequent cooling of the demixing liquid. Interrelations of the two morphological units in the solid texture were closely investigated by polarized and phase-contrast optical microscopy and light scattering by changing isothermal demixing conditions and crystallization conditions. A criterion for conservation of the modulated structure developed in the demixing liquid during and after the crystallization is discussed, and the locking-in phenomenon of the demixing processes by crystallization is clearly presented in some certain cases and was found to be responsible for the conservation of the structure existing in the liquid. Some unique morphologies are presented schematically in the text.

I. Introduction

In a previous paper[1] we proposed a particular method of morphology control for polymer mixtures such as isotactic polypropylene (PP) and ethylene–propylene random copolymer (EPR), which can be immiscible in the molten liquid state and contain a crystallizable component, at least as one component. The method involves liquid–liquid (L–L) phase separation to a certain demixed state by spinodal decomposition, subsequent coarsening processes in the molten liquid state, and then crystallization by cooling the demixing liquid mixture. It was found[1] that a unique demixed structure in the molten liquid state, i.e., the *modulated*, bincontinous, and periodic structure,[2] is conserved during the rapid crystallization process, resulting in space-filling PP spherulites of average radius R within which the L–L demixing structure of the spacing Λ_m ($\Lambda_m < R$) is conserved, as a particular example (this phenomenon being designated as "memory conservation").

In this paper we further investigate the interrelation between the two morphological units, i.e., the *modulated structure* and the *spherulites*, in the solid texture by changing further demixing and crystallization conditions. The interrelation will be fully investigated by polarized and phase-contrast light microscopy and by light scattering. We explore the cases where $R < \Lambda_m$ as well as $R > \Lambda_m$ as in the previous case[1] by changing the time spent for demixing in the molten liquid state before crystallization.

We will explore slow isothermal crystallization as compared with a rapid crystallization involved in athermal quenching (one of the "diffusion-limited" crystallization[1] conditions) as in the previous case in order to investigate criteria in which the "structure memory" of the L–L demixing is conserved during the crystallization process. The criterion will be studied both by optical microscopy and by studying crystallization kinetics. The rapid crystallization which is found to meet the criterion involves "the diffusion-limited crystallization",[1] i.e., the crystallization occurring in and through PP-rich domains and by finding and following PP-rich domains without invoking long-range rearrangement of PP molecules such as segregation of the EPR component from crystallization front of PP and destruction of the modulated structure developed before crystallization. It will be shown also that the crystallization is very effective to *lock-in* further growth of the L–L demixing.

II. Experimental Methods

The details of the experimental methods were described in the previous paper.[1] Here we briefly describe only the essential part.

[†] Presented in part at the 34th Polymer Symposium, the Society of Polymer Science, Japan, Sept 26–28, 1985. Inaba, N.; Sato, K.; Suzuki, S.; Hashimoto, T. *Polym. Prepr. Jpn., Soc. Polym. Sci., Jpn.* **1985**, *34*, 2809.

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The PP has a weight-average molecular weight M_w of 2.35 × 10^5 and a heterogeneity index M_w/M_n = 4.1. The EPR contains 73 mol % ethylene and has M_w = 1.49 × 10^5 and M_w/M_n = 2.5. A mixture of PP and EPR of 50/50 w/w % designated as EP-50 was dissolved to a dilute solution in hot xylene. The solution was precipitated by pouring it into a large amount of methanol cooled with ice. The precipitate was then dried and cold-pressed into thin films and used as starting film specimens (designated Q).

Structure evolution in the mixture both above and below T_m of PP was observed in real time or after quenching by polarized (V_V) and depolarized (H_V) light scattering and by polarized and phase-contrast light microscopy. The sample was placed on a Mettler hot stage mounted on a horizontal XY stage. The scattered light was recorded on a photographic film or by a CCD videocamera connected to a dynamic image analyzer (DIA).[1]

The starting film specimens Q were rapidly heated to a temperature T_x above melting temperature T_m of PP in the mixture for various length of time ($t - t_s$). For a particular mixture with a particular composition, the temperature T_x is normally well below the spinodal temperature, and at this temperature the mixture is thermodynamically unstable and hence undergoes demixing through spinodal decomposition.[1,2] The specimens subjected to demixing at T_x for the time period t − t_s were then subjected to crystallization either by rapid quenching below T_m (athermal crystallization) or by rapid quenching to a given temperature T_c for the isothermal crystallization for a certain period of time. The isothermally crystallized samples were then quenched to a dry-ice–methanol bath, and the solidified samples were further studied by light scattering and optical microscopy. For the investigations under optical microscopy, the specimens were cut into thin films 5–20 μm thick, depending on the size of the internal structures, at −140 °C by ultramicrotome (LKB 2088 ULTROTOME V), equipped with a cooling attachment (14800 CRYO KIT) in order to avoid complications associated with an overlap of the internal structures along the thickness direction of the specimens.

The rapid temperature rise to T_x was attained by inserting the specimens Q into the hot stage precontrolled to T_x. The time t_s required for the specimen to achieve T_x was measured to be about 20–30 s. Consequently one may neglect the thermal history occurring during the time period t_s for the time scale $t - t_s > 100$ s.

III. Experimental Results and Discussion

In our previous paper, we reported the morphology of PP/EPR mixtures developed by a rapid crystallization from the demixing liquids (see, for example, Figure 8 of ref 1) and found space-filling PP spherulites of average radius R with a modulated periodic structure of average spacing Λ_m as their internal structures (as proposed schematically in Figure 5 in this paper). The modulated structure is a structure memory which resulted from the L–L demixing process and which was conserved during the rapid crystallization, i.e., under the crystallization specified as diffusion-limited crystallization.

Here we extended our studies by changing further the L–L demixing and crystallization conditions. As for crystallization conditions, we will explore a rapid athermal crystallization (sections III-1 and -2) as well as "rapid" and "slow" isothermal crystallizations (sections III-3 and -4). Here again as a rapid crystallization, we refer to the diffusion-limited crystallization and, as a slow crystallization, to the crystallization that invovles segregation of EPR from the crystallizing front of PP and destruction of the modulated structure.

1. Morphology Developed under a Rapid Crystallization from Demixing Liquids. Case of $D > \Lambda_m$. Figure 1 shows the spacing Λ_m (μm) of the modulated structure as determined from what is called the "spinodal ring" in a V_V scattering pattern[1] and the average spherulite diameter D (μm) determined from the H_V light scattering pattern[4] for mixtures demixed at 170, 200, and 250 °C, for the time interval $t - t_s$ (s) as specified in the abscissa, and subsequently crystallized by quenching the demixing mixtures in an ice-water bath. Both Λ_m and D were determined by finding scattering angles θ_{max} and $\theta_{max,s}$ at which the corresponding scattering intensity reaches a maximum value and by applying eq 1 and 9 of ref 1. The angles were determined from the scattering profiles measured by a TV camera and DIA systems.[1] The value Λ_m increased as $t - t_s$ increased, reflecting the coarsening of the modulated structure during the isothermal demixing process.[3] However, average spherulite size was independent of the time $t - t_s$ spent for the demixing for a given crystallization condition (i.e., the rapid athermal quenching).

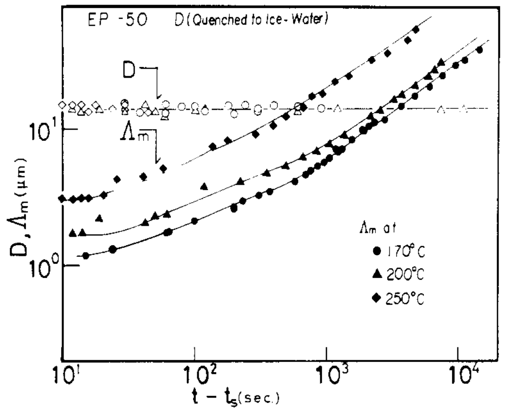


Figure 1. Characteristic wavelength Λ_m of the modulated structure developed by the L–L demixing process and average spherulite diameter D for EP-50 (PP/EPR mixtures of 50/50 w/w %) demixed isothermally at 170, 200, and 250 °C for the time period of $t - t_s$ and subsequently crystallized by quenching the demixing liquid in an ice-water bath.

The increase of Λ_m with $t - t_s$ in the solidified texture was clearly observed also under phase-contrast microscopy, as shown in Figure 2 for the mixtures demixed at 170 °C for 5 (a), 20 (b), and 30 min (c) and subsequently crystallized by quenching in an ice-water bath. The micrographs obtained on the thin sections cut by the Ultrotome V clearly show an increase of the characteristic distance Λ_m with increasing time $t - t_s$ spent for the isothermal demixing process. The black and white pattern in the micrograph corresponds to the modulated structure. One of the regions (e.g., black region) reflects either the PP- or the EPR-rich region, and the other reflects the region rich in the other component. A similar modulated pattern was also reported by Kresge[5] and Lohse[6] for PP/EPR mixtures.

According to the results shown in Figure 1, in certain cases Λ_m can be equal to D. Figure 3 shows the H_V and V_V light scattering patterns corresponding to such a particular case observed for the mixture demixed at 200 °C for 30 min and subsequently quenched in an ice-water bath. The scattering angle $\theta_{max,s}$ at which the H_V spherulitic scattering intensity becomes maximum was observed to be about equal to $\theta_{max,r}$ at which the V_V "spinodal ring" intensity becomes maximum. The peculiar scattering patterns can be interpreted only on the basis of the interplay of the two morphological entities resulting from the two kinds of phase transitions.

Figure 4 shows H_V (upper row) and V_V scattering patterns (lower row) for the as-solidified mixture (a and e) and the mixtures subsequently annealed at 150 °C for 15 (b and f), 30 (c and g), and 90 min (d and h). As usual, the as-solidified mixture was prepared by demixing at 170 °C for 5 min and a subsequent crystallization by quenching in an ice-water bath. The H_V spherulitic scattering pattern was unchanged upon further annealing of the as-soldified

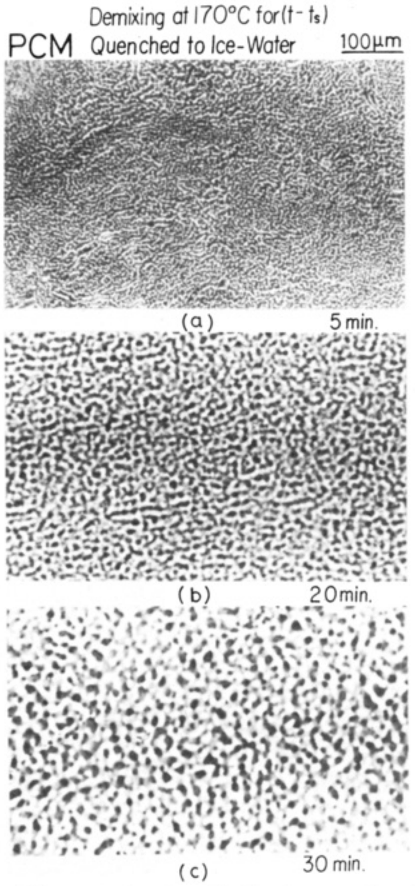
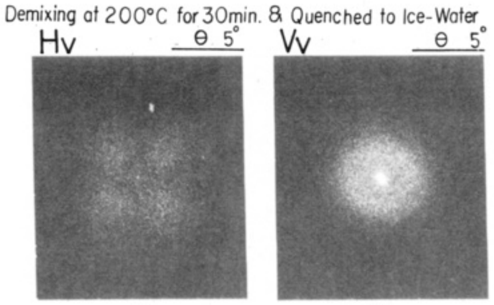


Figure 2. Phase-contrast optical micrographs showing the coarsening of the modulated pattern for EP-50 demixed isothermally at 170 °C for $t - t_s = 5$ (a), 20 (b), and 30 min (c) and subsequently crystallized by quenching the demixing liquid into an ice-water bath.



(a) D=14.2μm

(b) Λ_m=7.7μm

Figure 3. H_V (a) and V_V (b) light scattering patterns for EP-50 demixed isothermally at 200 °C for 30 min and subsequently crystallized by quenching the demixing liquid in an ice-water bath. Note that the average spherulite radius $R = D/2$ (=7.1 μm) is nearly equal to Λ_m (=7.7 μm). The scattering angle $\theta_{max,s}$ at which the H_V spherulitic scattering intensity becomes maximum is nearly equal to $\theta_{max,r}$ at which the V_V "spinodal-ring" intensity becomes maximum.

films at 150 °C, indicating that the average size of the PP spherulites was unchanged upon annealing. This phenomenon is best interpreted as a consequence of the as-solidified mixture being composed of volume-filling PP spherulities as discussed in detail in the previous paper. Upon annealing, the spinodal ring in the V_V pattern also did not change in terms of $\theta_{max,r}$, indicating that the *crystallization locks in further growth and coarsening of the fluctuations* in the demixing process and the once-locked-in structure was essentially maintained during the particular annealing process well below the melting temperature of PP crystals. The spherulitic V_V scattering pattern which existed inside the spinodal ring and near the center of the pattern lost its intensity upon annealing, indicating that the annealing suppressed the density fluctuations between the spherulites.

Figure 5 respresents schematically the morphology obtained by isothermal demixing of the mixtures in the molten liquid state at a certain temperature and for a certain period of time and by a subsequent crystallization by quenching in an ice-water bath, the particular solidification condition which gives rise to the case of $D > \Lambda_m$. The upper half of the figure indicates the modulated structure with Λ_m resulting from L–L demixing. The rapid crystallization from the demixing liquids involves the *diffusion-limited crystallization*, i.e., the crystallization in and through continuously connected PP-rich domains without invoking long-range rearrangements of PP molecules such as segregation of the EPR component from crystallizing fronts of PP. The nucleation starts to develop the PP-rich domain,[9] which is followed by lamellar crystallization and branching of lamellae. The crystallization fronts move by following and finding PP-rich domains whose spatial arrangements were a priori set up by the L–L demixing process, resulting in the volume-filled spherulites with the unique structure memory inside as shown in the bottom half of the figure (Figure 5b).

2. Morphology Developed under a Rapid Crystallization from Demixing Liquids. Case of $D < \Lambda_m$. From Figure 1 it is obvious that one obtains the morphology in which the values of Λ_m can be larger the values of D, if the time spent in the molten liquid state is long enough. Figure 6 shows the H_V (a) and V_V (b) light scattering patterns corresponding to this situation. The specimes were obtained by demixing at 200 °C for 20 min and crystallization by quenching in an ice-water bath. Note that the angular marks are different for the large pictures and for the small inserted pictures (which are the enlarged pictures of the small-angle scattering). The H_V pattern shows a clover-leaf spherulitic pattern[4] at $\theta_{max,s} \simeq 5°$ (in air), and the V_V pattern shows a spinodal ring at very small angle, $\theta_{max,r} \simeq 0.6°$ (in air). The inserted small picture shows the spinodal ring better. It should be worth noting that the H_V pattern also shows the spinodal ring at very small angles. The spherulitic V_V pattern was very weak compared with the V_V spinodal pattern. Hence the spherulitic V_V pattern cannot be seen in the pattern taken with an exposure time appropriate for the spinodal ring (as seen in Figure 6b). If the pattern was taken with an exposure time appropriate for the spherulitic pattern, the spinodal ring will be overexposed and hence will not be resolved. A peculiar phenomenon, that the spinodal ring appeared even in the H_V scattering, will be discussed later (section III-5). The estimated sizes were $D = 10.4$ μm and $\Lambda_m = 60$ μm. Figure 7 shows an optical micrograph taken under crossed polarizers (set in vertical and horizontal directions of the pictures) for the sample whose scattering patterns are shown in Figure 6. It is clearly seen that a group of impinged spherulites (which we call hereafter the "spherulitic domain") and a spherulite-poor domain (which is, more or less, isotropic) form a periodic and bicontinuous modulated structure with periodicity Λ_m.

Figure 8 represents schematically the structure model obtained from the results shown in Figures 1, 6, and 7. As the time spent for demixing increases, the coarsening of the modulated structure further advances and Λ_m becomes so large that a number of nucleation centers of the spherulites can be developed within a given PP-rich do-

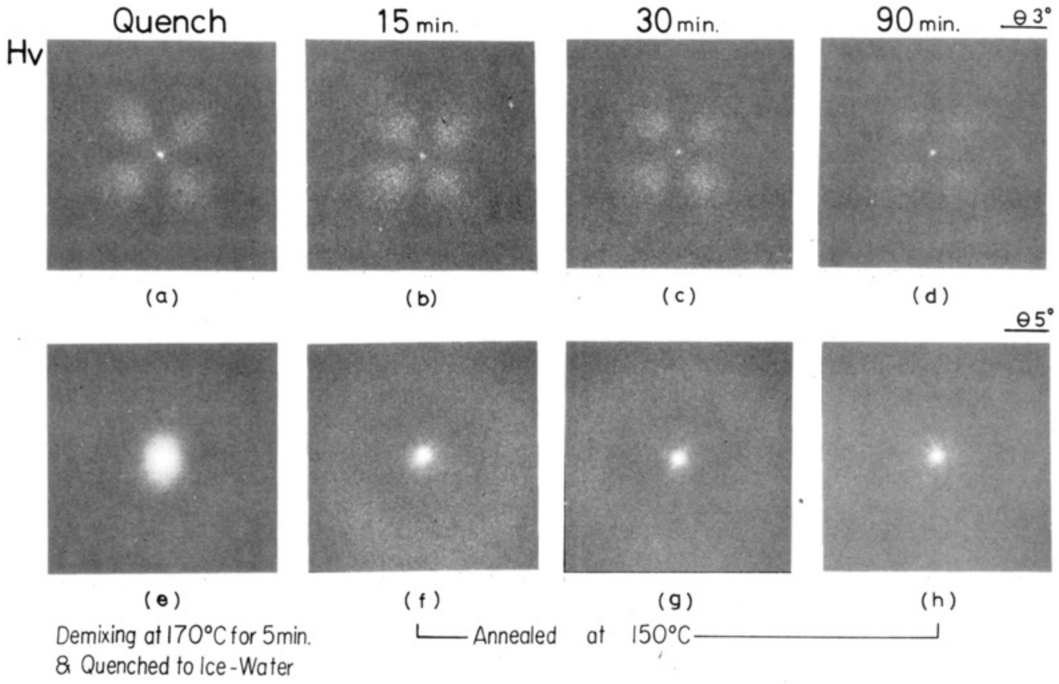


Figure 4. H_V (upper half) and V_V (lower half) scattering patterns from as-quenched EP-50 mixtures (a and e) and subsequently annealed isothermally at 150 °C for 15 (b and f), 30 (c and g), and 90 min (d and h). The as-quenched specimens were prepared by demixing isothermally at 170 °C for 5 min and subsequently crystallized by quenching the mixture in an ice-water bath.

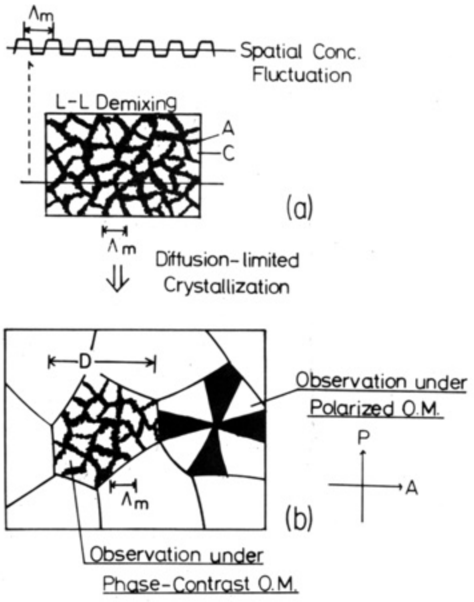


Figure 5. Schematic representations of (a) the modulated structure with periodicity Λ_m developed by the isothermal L–L demixing at temperatures above melting point of PP and (b) the volume-filling spherulites with the modulated structure memory as their internal structures developed by the diffusion-limited crystallization of the demixing liquid. Case of $\Lambda_m < D$ (average size of the spherulite).

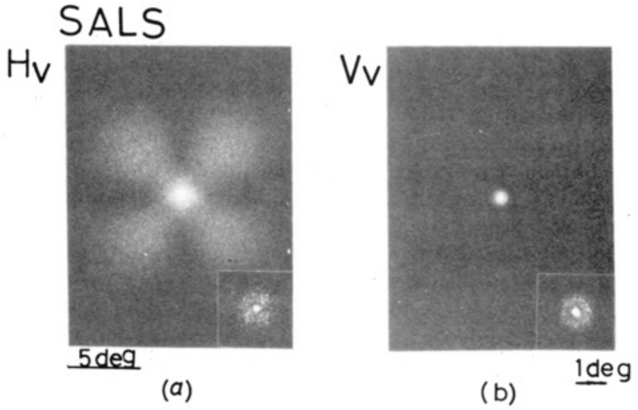


Figure 6. H_V (a) and V_V (b) light scattering patterns for EP-50 isothermally demixed at 200 °C for 20 min and subsequently crystallized by quenching the mixture in an ice-water bath. Note that $\theta_{max,s}$ (the scattering angle which gives rise to maximum intensity) for spherulitic scattering is much larger than $\theta_{max,r}$ for the ring scattering, the ring scattering being observed near the center of H_V and V_V patterns. The ring scattering patterns under H_V and V_V polarizations are better seen in the enlarged patterns shown in the lower right corner of each pattern. The angular mark for the inserted patterns (1°) is different from that for the large patterns (5°). The values $\theta_{max,s}$ and $\theta_{max,r}$ in air are 4.9° and 0.65° for the spherulitic and ring scattering, respectively, corresponding to $D = 10.4$ μm and $\Lambda_m = 60$ μm.

main when the demixing mixture is put below the melting temperature. Thus the diffusion-limited crystallization develops the volume-filled spherulites within the PP-rich domain, i.e., "spherulitic domain". The spherulitic domains and less-crystallized EPR-rich regions form the modulated structure with periodicity Λ_m resulting from the conservation of the memory of the L-L demixing structure.

There is an interesting feature of crystallization related to a dual nature: (i) Overall, the crystallization has characteristics relevant to the crystallization from demixing liquids, but (ii) locally within each domain, the crystallization has characteristics relevant to the crystallization from a homogeneous mixture.

3. Isothermal Crystallization of Demixing Melts. Linear versus Nonlinear Spherulite Growth. In the preceeding sections (sections III-1 and III-2) we dealt with only a special crystallization condition, i.e., athermal rapid crystallization induced by quenching the mixtures in an ice-water bath. In the following two sections (sections III-3 and III-4) we will be concerned with the conservation of the L–L demixing structure memory during the isothermal crystallization process.

Figure 9 shows spherulite size D (μm) measured under a polarized optical microscope as a function of crystallization time t_c (min) during the isothermal crystallization at 140 °C for homopolypropylene (J-700 M) and mixtures

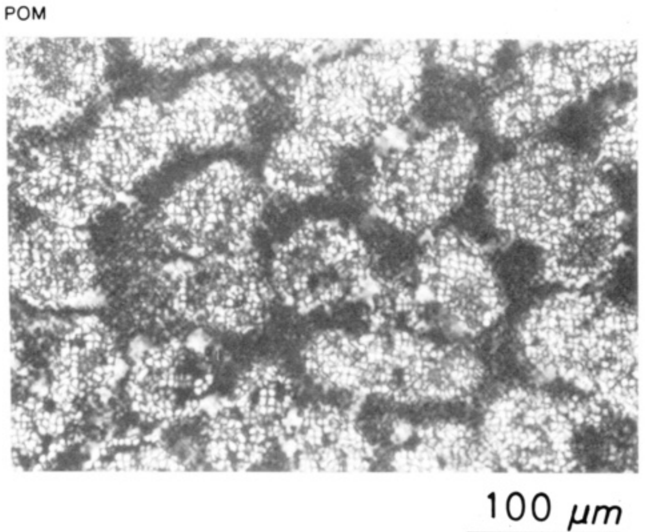


Figure 7. Modulated structure observed under polarized light microscopy (polarizer and analyzer being set in vertical and horizontal directions) for the specimens which give rise to scattering pattern shown in Figure 6. Note that the modulated pattern consists of a bicontinuous network structure of PP-rich domains which contain volume-filling spherulites and which have high optical anisotropy and of EPR-rich domains which have small or no optical anisotropy.

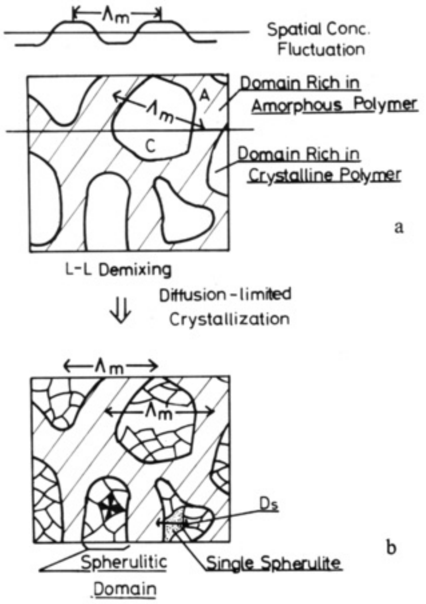


Figure 8. Schematic representation of (a) the modulated structure with periodicity Λ_m developed by the isothermal L–L demixing at temperatures above melting point of PP and (b) the corresponding structure obtained after the diffusion-limited crystallization. The case of $\Lambda_m \gg D$. The PP-rich domain is large enough to have many spherulite nuclei within its domain, and hence it contains the volume-filling spherulites after the crystallization ("Spherulitic Domain"). Even after the crystallization, the bicontinuous and periodic structure existed in the molten state is essentially conserved.

of PP and EPR of 50/50 w/w % (EP-50) and 70/30 w/w % (EP-30). The spherulite size was measured only in the time domain where the spherulites do not impinge on each other. The mixtures were demixed at 200 °C for 5 min, and homopolypropylene was melted at 200 °C for 5 min prior to isothermal crystallization. The mixtures show a linear growth of spherulites as in the case of homopolypropylene. The mixtures have a growth rate of spherulite slightly slower than that of homopolymer, which may be due to melting point depression of the PP domain and hence to a smaller degree of supercooling compared with that of the homopolymer.[10] The melting-point depression results from the EPR component dissolved in the PP-rich domain. The fact that the growth rates for the two mixtures are identical suggests that each domain (PP-rich and EPR-rich domains) in the demixing mixtures already has an equilibrium concentration determined by the binodal points at 200 °C and the modulated structure is coarsening self-similarly, the coarsening behavior being scaled by a single length parameter.[3a]

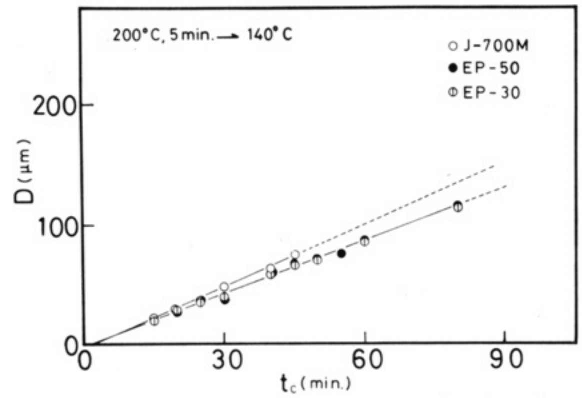


Figure 9. Growth of the average spherulite diameter *D* with time during the isothermal crystallization at 140 °C for pure isotactic PP (J-700) and for a EP-50 mixture and a EP-30 mixture (PP/EPR mixture containing 70/30 w/w %). The pure isotactic PP specimens was melted at 200 °C for 5 min and then subjected to the isothermal crystallization. Similarly EP-50 and -30 were first demixed at 200 °C for 5 min and subsequently crystallized isothermally at 140 °C.

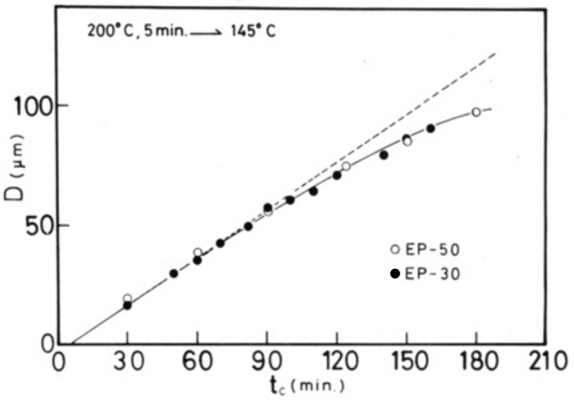


Figure 10. Growth of the spherulite size with time during the isothermal crystallization at 145 °C for the EP-50 and -30 mixtures first subjected to demixing at 200 °C for 5 min.

The most important and striking experimental evidence is seen in that the spherulite growth at 140 °C is linear with time even for the mixtures. This strongly suggests that the diffusion-limited crystallization takes place even for the isothermal crystallization at 140 °C. In other words the crystallization front advances by finding and following the PP-rich domains in the modulated structure. Since this process does not involve long-range structure rearrangements and segregation of EPR from the crystallization front, the crystallization front always finds the same fraction of EPR and hence the same degree of supercooling, resulting in the linear spherulite growth. The *segregation of the EPR* component from the crystallization front would occur only *on a local scale* and hence the memory of the modulated structure can be conserved during the crystallization as will be shown in Figures 11 and 12.

Figure 10 shows experimental results similar to Figure 9 but the experiments here were carried out at 145 °C. For

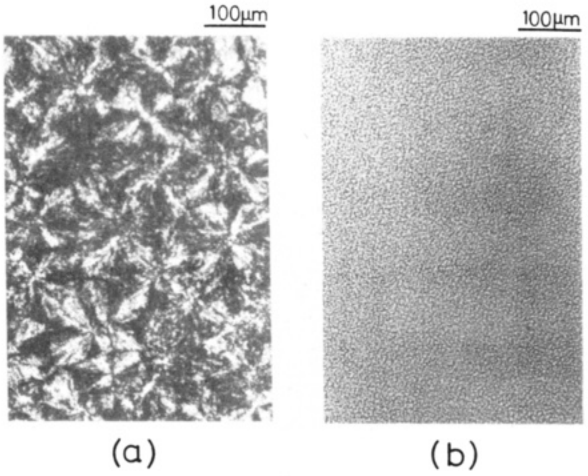


Figure 11. (a) Polarized light micrograph (POM) and (b) phase-contrast light micrograph (PCM) for the EP-50 mixture demixed at 200 °C for 5 min and subsequently crystallized at 125 °C for 5 min. The POM which was obtained by setting polarizer and analyzer in vertical and horizontal directions clearly shows the volume-filling spherulites, while the PCM clearly shows the modulated structure resulted from the L–L demixing. Note that corresponding H_V and V_V light scattering patterns are shown in parts b and d of Figure 15, respectively, and that the two pictures were obtained on the same field on the same sample.

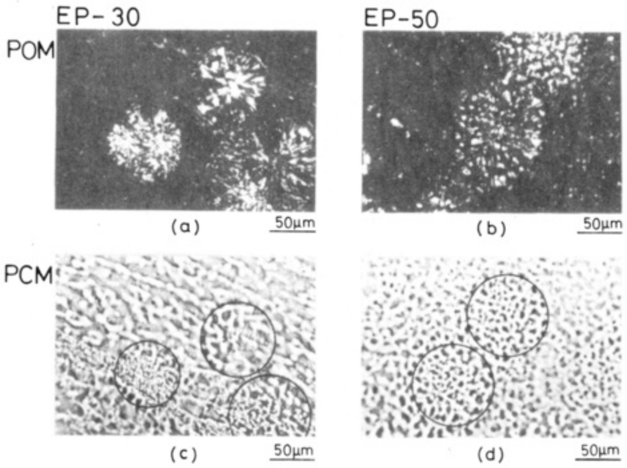


Figure 12. POM (upper half) and PCM (lower half) for the EP-30 (a and c) and EP-50 mixtures (b and d) prepared by demixing at 200 °C for 5 min and subsequent crystallization at 140 °C for 81 min. The POM and PCM were taken on the same field, and the circles in the PCM correspond to the spherulites observed under POM (the bright region). The polarizer and analyzer were set in vertical and horizontal directions in POM. Note that $\Lambda_{m,o}$ for the modulated structure outside the spherulite is larger than that $\Lambda_{m,i}$ inside the spherulite, indicating that the crystallization suppresses or locks in further growth of the demixing processes.

the isothermal crystallization at 145 °C, the spherulite growth is much slower than that at 140 °C and becomes *nonlinear* with time. This is best interpreted as a consequences of the long-range rearrangement of the modulated structure and segregation of EPR from the crystallization front. Owing to the long-range segregation of EPR, the fraction of EPR component at the crystallizing front increases with time, resulting in suppression of the rate of spherulite growth.

4. Spherulite Morphology Obtained by Isothermal Crystallization of Demixing Liquids. Criterion of Memory Conservation. From the discussions in the previous section, a criterion for the conservation of the L–L demixing structure during the isothermal crystallization was found to exist in the temperature range between 140 and 145 °C. In this section, we closely investigate the criterion by optical microscopy.

Figure 11 shows the optical micrograph under crossed polarizers (a), polarizer and analyzer being set vertically and horizontally in the picture, and by phase-contrast microscopy (b) for the mixture first demixed at 200 °C for 5 min and subsequently crystallized at 125 °C for 5 min. The polarized photomicrograph clearly shows the volume-filled spherulites with some internal structure. The phase-contrast micrograph clearly shows the modulated structure as the internal structure of the spherulites. It should be noted that the corresponding H_V and V_V scattering patterns are shown in parts b and d of Figure 15, respectively. It is obvious that the patterns show the spherulitic scattering at very small angles ($R \simeq 69$ μm) and the ring scattering due to the modulated structure with $\Lambda_m \simeq 4.4$ μm at a larger angle. The average spherulite size is much bigger than that for the quenched samples, due to the slow crystallization, but yet the structure memory of L–L demixing is conserved within the spherulite.

Figure 12 shows the polarized light micrographs (POM) (upper half, polarizer and analyzer being in vertical and horizontal directions of the picture) and phase-contrast micrographs (PCM) (bottom half) for the mixtures of the EP-30 (the left half) and the EP-50 (the right half), first demixed at 200 °C for 5 min and subsequently crystallized isothermally at 140 °C for 81 min. The POM and PCM were taken on the same field, the circled regions in the PCM corresponding to the spherulite with optical anisotropy in the POM. Again, the micrographs were obtained on thin sections of ca. 10 μm thich cut at −140 °C by the ultratome. The experimental results give a number of important pieces of information: (i) the spherulites contain the memory of the modulated structure in the L–L demixing as their internal structures; (ii) the characteristic length $\Lambda_{m,i}$ of the modulated structure inside the spherulites is smaller than that $\Lambda_{m,o}$ outside the spherulites, indicating that the *crystallization locks in further evolution of the demixing processes*, while a further evolution of demixing takes place in the amorphous region outside the spherulites at 140 °C (even there a small crystallinity may slow down the coarsening); (iii) the large $\Lambda_{m,i}$ causes the Maltese cross of the spherulites observed under POM and boundaries between the neighboring spherulites to be less clear.

The effect of crystallization on the locking in of the L–L demixing structure is further demonstrated in Figure 13 where the H_V (upper row) and V_V (lower row) patterns are shown for the EP-50 mixtures first demixed at 200 °C for 3 min and subsequently crystallized by quenching into an ice-water bath (a and e) and by isothermal crystallization at 120 °C for 4 min (b and f), at 125 °C for 7 min (c and g), and at 130 °C for 25 min (d and h). The spherulites developed are found to impinge to each other and to fill the whole sample space as shown in Figures 5 and 11. It is obvious that the isothermal crystallization give rise to much bigger spherulites than those developed by the quenching process, due to the slower nucleation rate. The nucleation rate of the spherulite centers is slower at higher temperature of crystallization, and hence the average spherulite size increases with increasing crystallization temperature as shown in the value R (in μm unit) beneath each pattern. In the quenched samples, it was shown before that the periodicity of the modulated patterns are the same before and after the quenching, indicative of the L–L demixing structure being locked in by the rapid crystallization. However, in the case of isothermal crystallization, the crystallization rate is much slower than in the case of quenching, so that the structure developed by

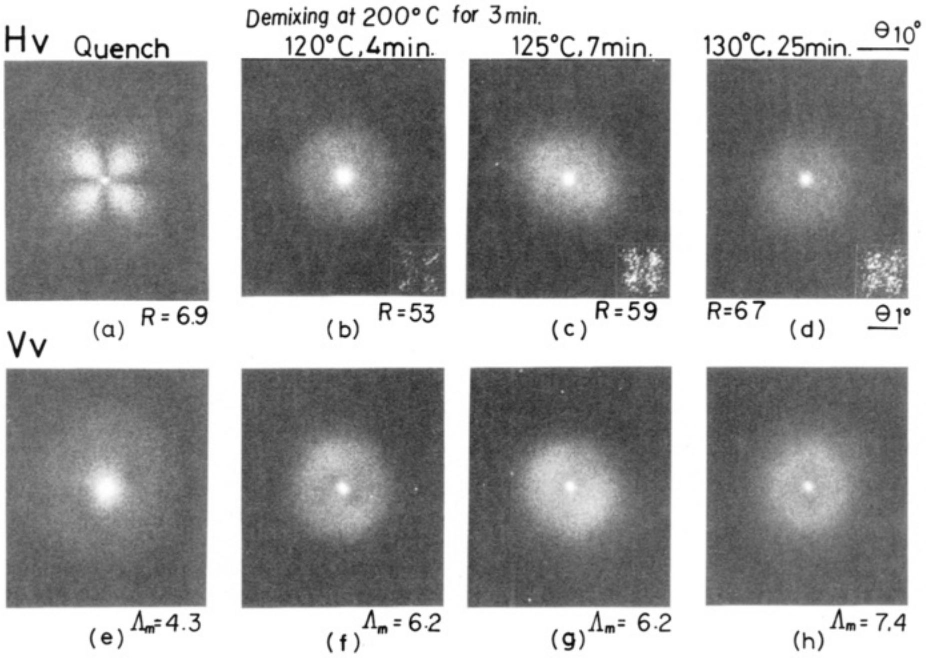


Figure 13. H_V (upper half) and V_V (lower half) light-scattering patterns for the EP-50 mixtures first demixed at 200 °C for 3 min and subsequently crystallized by quenching in an ice-water bath (a and e) or by isothermal crystallization at 120 °C for 4 min (b and f), at 125 °C for 7 min (c and g), and at 130 °C for 25 min (d and h). The values R and Λ_m indicated beneath each pattern correspond to the average radius of spherulite and the periodicity of the modulated patterns in μm. The spherulite sizes are very big for the specimens isothermally crystallized, and hence the H_V spherulitic pattern exists near the center of each pattern. The H_V spherulitic pattern may be better resolved in the enlarged patterns inserted in the lower right corner of patterns b–d. Note that the H_V spinodal ring can be seen outside the spherulitic pattern in patterns b–d.

the L–L demixing 200 °C can grow further at the crystallization temperatures in the regions not yet crystallized. Hence the values $\Lambda_m = 6.2–7.4$ μm for the samples isothermally crystallized are larger than the value $\Lambda_m = 4.3$ μm for the samples crystallized by quenching. However, a further advance of crystallization would certainly pin down a further growth of the demixing.

Figure 14 shows POM (a) and PCM (b) micrographs for the mixture first demixed at 250 °C for 5 min and subsequently crystallized at 145 °C for 360 min. Again POM and PCM were taken on the same field, and the circles marked on PCM corresponding to the spherulites under POM (bright regions with optical anisotropy). It is clearly observed that the modulated structure is significantly perturbed during the crystallization, though the memory of the L–L demixing has not been completely destroyed.

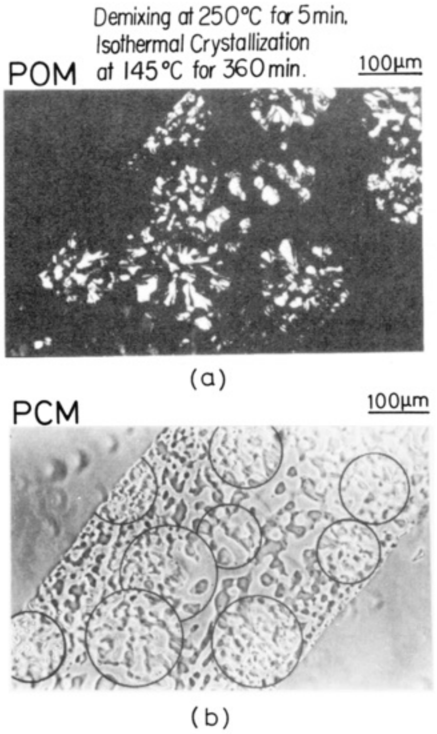


Figure 14. POM (a) and PCM (b) for the EP-50 specimen prepared by demixing at 250 °C for 5 min and subsequently crystallized at 145 °C for 360 min. The POM and PCM were taken on the same field, and the circles in the PCM correspond to the spherulites observed under POM. The polarizer and analyzer were set in vertical and horizontal directions in POM.

5. On Anisotropy Fluctuations of H_V Scattering from Spherulites. The modulated structure-memory conserved in the solidified material would produce fluctuations of the optical anisotropy as well as those of refractive index or density. The two types of fluctuations originate commonly from the concentration fluctuations of PP and EPR in the L–L demixing process and hence should have the same characteristic length Λ_m. The PP-rich regions have higher crystallinity and hence higher optical anisotropy and density than EPR-rich regions.

The density fluctuations give rise to V_V scattering,[4] and the particular modulated pattern on the spatial distribution of the density fluctuations gives rise to the "spinodal ring" as discussed earlier.[1] The anisotropy fluctuations[7,8] give rise to H_V scattering as well as V_V scattering, and the particular pattern of the spatial distribution of the anisotropy fluctuations should give rise to an "*H_V spinodal ring*" at the same scattering angle as the *V_V spinodal ring*. In fact, one can clearly observe the H_V spinodal ring in Figure 6a for the case of $\Lambda_m \gg D$, corresponding to the model shown in Figure 8, and also in Figures 13b–d and 15a,b for the case of $\Lambda_m \ll D$, corresponding to the model shown in Figure 5. Figure 15 shows H_V and V_V scattering patterns for the specimens demixed at 170 °C for 7 min and subsequently crystallized by quenching in an ice-water bath ((a) and (c)) and those for the specimens demixed at 200 °C for 5 min and subsequently crystallized isother-

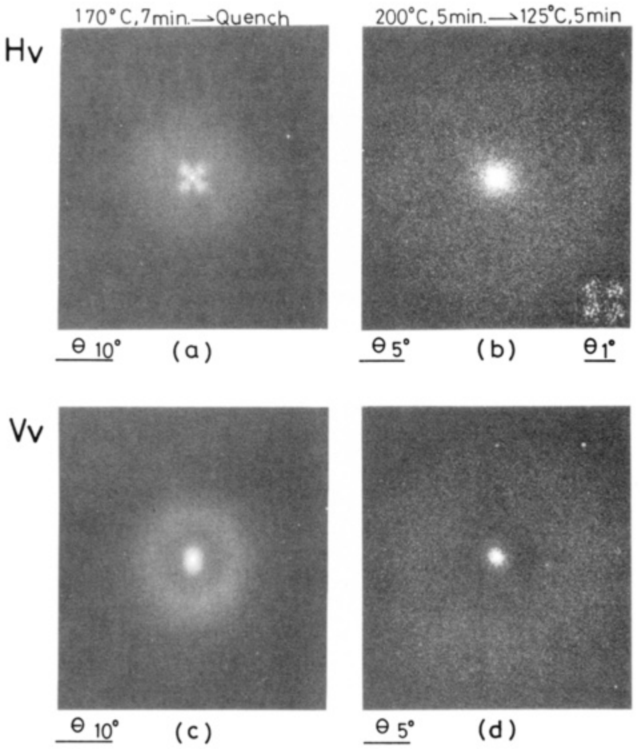


Figure 15. H_V and V_V patterns for the EP-50 mixture prepared by demixing at 170 °C for 7 min and subsequently crystallized by quenching the demixing liquid into an ice-water bath (a and c) and by demixing at 200 °C for 5 min and subsequently crystallized at 125 °C for 5 min (b and d). Note that the spinodal ring can be observed even for H_V scattering at the same scattering angle as that for the spinodal ring for V_V scattering. The modulated structure conserved during the crystallization gives rise to the anisotropy fluctuations responsible for the H_V spinodal ring as well as the density fluctuations.

mally at 125 °C for 5 min ((b) and (d)).

It should be noted that the particular anisotropy fluctuations give rise to the nonzero H_V intensity along the polarizer and analyzer axes (vertical and horizontal directions, respectively), in contrast to the H_V spherulitic scattering for which the intensity is usually minimum along these two directions. In the case when $\Lambda_m \gg D$, the H_V intensity along these two directions should be equal to that at any other azimuthal angle direction, giving rise to the H_V ring scattering with intensity independent of the azimuthal angle.

IV. Concluding Remarks

The role of L–L demixing on the morphology developed by subsequent crystallization was further discussed in this paper. It was found that the modulated structure developed above the melting point of PP by the L–L demixing is conserved during and after crystallization if the crystallization rate is much faster than the rate of mutual diffusion of the constituent polymer molecules but is not conserved if the crystallization rate is sufficiently slow compared with the rate of mutual diffusion. In the former case, where crystallization rate is much faster than the mutual diffusion rate, the crystallization has characteristics as specified by the "diffusion-limited crystallization" in the text. For the particular systems studied here, the diffusion-limited crystallization was found in the cases of rapid athermal quenching in the ice-water temperature as well as isothermal crystallization at temperatures below about 140 °C. In this region the modulated structure is controlled by controlling the time and temperature of the mixture in the molten liquid state, and the size of the spherulite is controlled by crystallization conditions. The typical morphologies observed are schematically summarized in Figures 5b and 8b. The diffusion-limited crystallization was found to lock in further growth of the modulated structure in the molten liquid and hence conserve the structure memory in the liquid. The criterion for the diffusion-limited crystallization was found to be clearly manifested in the linear versus nonlinear growth of spherulite size with time.

Registry No. PP, 25085-53-4; EPR, 9010-79-1.

References and Notes

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(9) The domain is not large enough to develop many nuclei for the spherulite centers within its domain.

(10) The initial growth rates of the spherulites $G = [\mathrm{d}R/\mathrm{d}t]_{t=0}$ were measured as a function of temperature T for PP and the mixtures in the temperature range 125–145 °C. The results show that log G linearly increases with $1/T$ for all the systems studied, indicating that the crystallization studied here is in the nucleation-control regime rather than in the diffusion-control regime. The growth rates for the mixtures were only slightly smaller than that of PP at all temperatures. All the systems had nearly equal d log $G/\mathrm{d}(1/T)$.