Ringed Spherulite in Binary Blends of Poly(ϵ -caprolactone) and ϵ -Caprolactone–Butadiene Diblock Copolymer

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ABSTRACT: Ringed spherulites were found in binary blends of poly(ϵ -caprolactone) (PCL) and ϵ -caprolactone–butadiene diblock copolymer (PCL-*b*-PB), while the regularly banded structure could not be observed in an oligomeric blend of PCL and polybutadiene (PB). The repeating distance of the ring and its distribution (irregularity) were evaluated as a function of PCL homopolymer (host polymer) fraction, total PCL fraction in the blend, and crystallization temperature. The morphology and melting behavior of the PCL/PCL-*b*-PB blends were also investigated by small-angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC). These results suggest that the PCL block of the copolymer takes part in the crystallization of the host polymer and is incorporated into the PCL lamellar crystal. The PB block is, as a result, forced to remain in the amorphous layer between PCL lamellae to lengthen the long spacing (alternating period of the lamella and amorphous layer). This existence of the PB block in the amorphous layer may play an important role in the lamellar twist during the course of crystallization.

KEY WORDS Ringed Spherulite / Homopolymer–Copolymer Blend / Polarized Microscopy / Small-Angle X-Ray Scattering / Differential Scanning Calorimetry /

It has been well known that when synthetic polymers crystallize from the melt, beautiful spherulites sometimes appear with regular extinction rings.¹ This regularity of the ring is promoted when the crystalline polymer (host polymer) is blended with a small amount of second polymer (diluent).^{2–9} Especially, in the case of compatible blends with a crystalline polymer and a chemically dissimilar amorphous polymer, such as poly(ϵ -caprolactone) (PCL)/poly(vinyl chloride) (PVC) system^{3–6} and poly(vinylidene fluoride) (PVF₂)/poly(methyl methacrylate) (PMMA) system,⁷ extremely periodical rings were found, which were never observed in pure crystalline polymers. It is also reported that the repeating distance of the ring changes significantly with changing the diluent fraction and crystalliza-

tion temperature.^{3,4}

Though there are extensive discussions about the spherulite formation in crystalline polymers^{10–12} and in polymer blends,^{6,13,14} the mechanism to yield such rings is still open question. One reason may be an insufficiency of method to measure the structure between sizes of the lamella and spherulite. The other reason is that only few combinations of polymers which show the ringed spherulite have been reported so far. Following two conditions are, however, at least necessary to meet with the ringed spherulite from a number of examples reported in the literature. (1) The blend system is thermodynamically compatible. Keith *et al.*,⁶ for example, did not observe the ringed spherulite in phase-separated systems, such as PCL/poly(ethyl acrylate) and

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PCL/PVF₂. (2) The amorphous component has a specific polar group to interact with the crystalline polymer during the process of spherulite formation. These facts make us expect that in order to yield the ringed spherulite, large-scale segregation of the amorphous component is necessary to be suppressed by an attraction between constituent polymers when the host polymer crystallizes in the lamellar texture. The amorphous component consequently remains between lamellae, and eventually plays an important role in the periodical twisting of the lamella during crystallization.

In this study, we introduce a new pair of polymers, a binary blend of poly(ϵ -caprolactone) (PCL) and ϵ -caprolactone-butadiene diblock copolymer (PCL-*b*-PB), that shows the spherulite with regular rings when PCL crystallizes. A specific interaction is not expected between the PCL and PB blocks from the fact that corresponding binary blends of PCL and PB do not show the compatibility over a large interval of composition. An oligomeric blend of PCL and PB, on the other hand, does not show any evidence of the regularly ringed spherulite even if they are thermodynamically compatible at a crystallization temperature. This system is also interested in the viewpoint of compatibilizer-added polymer systems, which have an important

practical use in polymeric materials. The morphology and the melting behavior of the PCL/PCL-*b*-PB systems were examined by small-angle X-ray scattering (SAXS), polarized microscopy (PM), and differential scanning calorimetry (DSC). The spherulite of a binary oligomeric blend of PCL and PB was also observed by PM to be compared with that of the PCL/PCL-*b*-PB systems. The change in the repeating distance of the extinction ring is evaluated as a function of PCL homopolymer fraction, total PCL fraction in the blend, and crystallization temperature. From above results, we finally discuss the morphology after the crystallization of PCL chain in the present homopolymer/copolymer blend system.

EXPERIMENTAL

Materials and Sample Preparation

The molecular characteristics of the host polymer (PCL) and diluents (PCL-*b*-PB and PB) used in this experiment are listed in Table I.

The PCL-*b*-PB diblock copolymers were synthesized by an anionic polymerization under vacuum.^{15,16} The butadiene monomer in toluene was first polymerized at 25°C for 2 days with *n*-buthyllithium as initiator, and followed by adding caprolactone monomer to synthesize the block copolymer at -20°C for 5–15 min. The butadiene monomer/initiator

Table I. Materials

Notation	Polymer	Source	Total M_w^c	M_w/M_n^c	PCL:PB ^d	mp ^e /°C
B1	PCL- <i>b</i> -PB	a	14,300	1.14	18:82	~40 ^f
B2	PCL- <i>b</i> -PB	a	15,100	1.31	39:61	~45 ^f
B3	PCL- <i>b</i> -PB	a	8,600	1.26	65:35	~42 ^f
PCL1	PCL	SPP ^b	16,100	1.71		58.1
PCL2	PCL	SPP ^b	7,000	1.80		57.4
PB1	PB	a	7,200	1.04		

^a Synthesized in our laboratory.

^b Obtained from Scientific Polymer Products Inc. and fractionated with a benzene/*n*-heptane system.

^c Determined by GPC.

^d Determined by elementary analysis.

^e Determined by DSC.

^f Crystallized at room temperature. The endothermic peak is small and diffuse.

ratio and the reaction time of the caprolactone monomer were adjusted to obtain copolymers with various compositions and molecular weights. The PB homopolymer was also synthesized by an anionic polymerization with *n*-butyllithium as initiator. The PCL homopolymer was obtained from Scientific Polymer Products Inc., and was fractionated with a benzene/*n*-heptane system at 25°C.¹⁷ All samples were characterized by gel permeation chromatography (GPC), and PCL content in the copolymer was also evaluated by elementary analysis. The small-angle X-ray scattering (SAXS) measurement indicates that B1 and B3 copolymers are homogeneous above the melting temperature T_m of the PCL block ($\sim 40^\circ\text{C}$) as judged from the fact that a diffuse SAXS peak due to the *correlation hole effect* of copolymers can be observed,¹⁸ which decreases in intensity with increasing temperature. The B2 copolymer is, on the other hand, micro-phase separated at above T_m from a sharp SAXS peak.

Four binary blends, PCL1/B1, PCL1/B2, PCL1/B3, and PCL2/PB1 are used in the present experiment. Each blend was prepared by solvent-casting method from tetrahydrofuran (THF) onto a glass plate. The THF was subsequently evaporated at a temperature above T_m ($\sim 60^\circ\text{C}$) for 10 h, and then the sample was used for the experiment. No indication of macro-phase separation could be observed in every blend studied.

Small-Angle X-ray Scattering (SAXS) Measurement

SAXS intensity curves were obtained with a pin-hole collimation system by a one-dimensional position sensitive proportional counter (PSPC) made by Rigaku Co.¹⁹ The X-ray from a rotating anode X-ray generator (Rigaku RU-300) operating at 50 kV and 100 mA was filtered by Ni ($\lambda = 1.542 \text{ \AA}$). The distance between the sample and the PSPC was about 40 cm. After the SAXS intensity was corrected for the linearity and sensitivity of the PSPC

and Lorentz factor, relative scattered intensity was obtained as a function of wave number s ($= 2/\lambda \sin \theta$, 2θ : scattering angle). The X-ray intensity scattered from each blend was measured after the blend was quenched from the melt ($\sim 80^\circ\text{C}$) into the crystallization temperature T_c ($= 40^\circ\text{C}$) and completely crystallized in the sample cell of the SAXS apparatus. The time necessary for each measurement was about 2000 s, during which the sample was kept at T_c within the fluctuation of 0.1°C .

Microscopic Observation

The spherulite of PCL in the blend was observed by a polarized microscope with a hot stage.⁵ The temperature of this hot stage was controlled by circulating water of constant temperature, and crystallization was started by dropping the water temperature from 65°C to a crystallization temperature T_c ranging from 30°C to 42°C . The sample thickness prepared for the microscopic observation was about 0.02 mm. It took less than one minute that the sample reached to the final T_c . The spherulite was photographed between crossed polarizers for further investigations of the spherulite structure.

The spherulite structure was analyzed by evaluating the blackness of the film (Figure 3-(F)), and two kinds of the average radial width were evaluated for the repeating distance of the black and white rings: (1) number-average width L , which is defined by $\sum n_i l_i / \sum n_i$, where n_i is the number of the width l_i , and (2) weight-average width L' defined by $\sum n_i l_i^2 / \sum n_i l_i$. The distribution or irregularity of the ring width σ was also evaluated as $\sigma = L'/L$.

Differential Scanning Calorimetry (DSC) Measurement

MAC Science Inc. Model 3100 DSC was used to determine the melting temperature and crystallinity of PCL in the blend. The sample, first annealed at 80°C for 1 h, was crystallized by quenching at the maximum rate to a

crystallization temperature T_c , followed by heating at a rate of 5°C min^{-1} . The quench process was completely finished before the PCL started to crystallize. The crystallinity and melting temperature were evaluated from the peak area and peak position of the DSC endothermic curve. The exothermic heat flow during crystallization was also monitored to ensure the end of crystallization.

RESULTS

SAXS Curve

Figure 1 shows the Lorentz-corrected X-ray intensity scattered from PCL1/B3 crystallized at 40°C . Each scattering curve has an intensity peak arising from the alternating period of the lamella and amorphous layer. This peak disappears when the sample temperature is raised above the melting temperature T_m ($\sim 60^\circ\text{C}$) of pure PCL, and a monotonically decreasing intensity with s , which is characteristic of the scattered intensity from a homogeneous blend, can be observed. The angular position of the peak shifts gradually toward smaller s with decreasing the homopolymer (PCL) fraction ϕ_{homo} in the system. The other characteristic of the SAXS intensity is a large increase of the integrated intensity or invariant Q ($= \int_0^\infty s^2 I(s) ds$) with decreasing ϕ_{homo} . This increase comes from the increase of the peak intensity and of the diffuse scattering at Porod's region. The SAXS curve from the *pure* block copolymers (B1, B2, or B3), on the other hand, has an intensity peak at above T_m of PCL, which is sharp for B2 and diffuse for B1 and B3. The sharp peak for B2 will be attributed to the micro-phase separated structure of block copolymers and the diffuse peak for B1 and B3 comes from the *correlation hole effect* of copolymers at a homogeneous state.²⁰ The micro-structure and order-disorder transition of the pure copolymers are not discussed in this paper.

The long spacing D in PCL1/B3, the sum of the lamellar and amorphous layer thick-

Figure 1. Lorentz-corrected X-ray intensities, scattered from the blends crystallized at 40°C containing 100, 80, 60, and 50% poly(ϵ -caprolactone) homopolymer. The scattering angle is expressed in s ($= 2 \sin \theta / \lambda$). The plots for data with PCL1/B3 = 80/20, 60/40, and 50/50 are shifted upward successively for legibility.

Figure 2. Long spacing D , evaluated from the peak position of SAXS intensity, plotted against PCL homopolymer fraction ϕ_{homo} in the system.

nesses, was evaluated from the angular position of the peak and is shown in Figure 2. The long spacing increases linearly with decreasing ϕ_{homo} , which can be observed in many compatible crystalline/amorphous polymer blend systems, such as PCL/poly(vinyl chloride) system^{3,5} and poly(vinylidene fluoride)/poly(methyl methacrylate) system,⁴ when the host polymer crystallizes. This increase is attributed to the fact that an amorphous

component expelled out from the lamellar crystal during crystallization is accommodated in the amorphous layer between lamellae. An attractive interaction between crystalline and amorphous polymers will prevent large-scale phase separation of the amorphous component. The existence of the amorphous polymer between lamellae is expected to play a key role for the lamellar twisting during crystallization through the specific interaction.⁶ In the present system, PCL-*b*-PB or a part of PCL-*b*-PB acts as an amorphous component and the copolymer expelled out from the lamella remains in the amorphous layer between PCL lamellae. The existence of PCL-*b*-PB in the amorphous layer is also expected from a large increase of the SAXS peak intensity with decreasing ϕ_{homo} , which is proportional to the square of electron density

difference between the lamella and amorphous layer. The electron density of PB is much smaller (293.2 e nm^{-3} at 40°C)²¹ compared to those of PCL crystal (392.9 e nm^{-3})²² and amorphous PCL (359.3 e nm^{-3} at 40°C)²³ so that the intrusion of the PB chain into the amorphous layer makes the electron density of this layer further smaller, yielding the electron density difference (and eventually SAXS intensity peak) larger. It is not certain from the SAXS measurement whether or not the PCL block of the copolymer is incorporated into the lamellar crystal, that is, the PCL crystal is made up of the PCL homopolymer and the PCL block of the copolymer. This will be discussed in the next section.

Spherulite Structure

Figure 3-(A)–(E) shows the spherulite

Figure 3. Spherulite structure observed in pure PCL (A) and PCL/B1 blends containing 90, 80, 70, and 60% PCL homopolymer (B–E). The crystallization temperature is 40°C (F): Computer output of the spherulite structure (C).

observed in each blend crystallized at 40°C, and Figure 3-(F) is the computer output after processing Figure 3-(C). Every spherulite except pure PCL has a ringed structure and the alternating distance, the sum of black and white ring widths, decreases with decreasing ϕ_{homo} . If PCL-*b*-PB is assumed as an impurity for the PCL crystallization, the decrease of the ring width with increasing the impurity fraction is qualitatively similar to that previously observed in a PCL/PVC system,⁵ though the ringed structure in the present case is less regular at the same ϕ_{homo} . The pure PCL, which never has an extinction ring at 40°C, has a crude banding with large radial separations in the range of 50–100 μm at above $T_c = 45^\circ\text{C}$.⁶ The spherulite observed in the compatible blend of PCL2/PB1 crystallized at 40°C also has a crude banding similar to that observed in pure PCL crystallized at above 45°C. The spherulite structure is, however, significantly different from that observed in the PCL/PVC and PCL/PCL-*b*-PB systems in that small segments of the ring are dispersed in the spherulite without making perfect rings. The ring observed in pure PCL and PCL2/PB1 is too irregular to process it by the computer.

The repeating distance L evaluated with the aid of computer is plotted in Figure 4 for three PCL/PCL-*b*-PB systems, where the abscissa represents the content of PCL homopolymer ϕ_{homo} in the system. Each blend makes three different curves with a steep increase as $\phi_{\text{homo}} \rightarrow 1$. In the Figure, the change in L of the PCL/PVC system previously studied⁵ is also shown to be compared with the present data. The result of the PCL/PVC system is in qualitative agreement with the present PCL/PCL-*b*-PB systems, though the data points are shifted along the abscissa. Figure 5 shows the same plot of Figure 4 but the abscissa is replaced by the PCL content ϕ_{PCL} in the system, that is, the sum of fractions of the PCL homopolymer and the PCL block in the copolymer. The three curves in Figure 4 now coincide with one another and make

Figure 4. The alternating distance $L (= \Sigma n_i l_i / \Sigma n_i)$ of the extinction ring against ϕ_{homo} . $\circ$, PCL1/B1 system; $\square$, PCL1/B2 system; $\diamond$, PCL1/B3 system; $\triangle$, PCL/PVC system previously obtained in our laboratory.⁵

Figure 5. The alternating period $L (= \Sigma n_i l_i / \Sigma n_i)$ and $L' (= \Sigma n_i l_i^2 / \Sigma n_i l_i)$ of the extinction ring against the total PCL fraction ϕ_{PCL} (i.e., sum of fractions of the PCL homopolymer and PCL block in the copolymer). For the symbols, see Figure 4.

one master curve irrespective of the copolymer (B1, B2, or B3) included. The SAXS results (Figure 2) have revealed that the long spacing increases with decreasing ϕ_{homo} and PCL-*b*-PB is accommodated in the amorphous layer between PCL lamellae without making new domains mainly consisting of the copolymer. Figure 5 means that the spherulite structure formed by the crystallization is determined only by ϕ_{PCL} . Therefore, Figures 2 and 5 indicate that the PCL block in the copolymer also takes part in the crystallization of PCL chain, and eventually is in-

Figure 6. The distribution of the alternating period of the extinction ring L'/L against ϕ_{PCL} . For the symbols, see Figure 4.

incorporated in the lamellar crystals to yield a *mixed crystal* composed of the PCL homopolymer and the PCL block of the copolymer. It is also manifested from the melting behavior of the blends (Figure 8) that the PCL homopolymer and the PCL block of the copolymer do not make separate lamellae in the system. The block copolymer, therefore, can not go out from the crystalline region for making a new domain. As a result, the PB block in the copolymer is ejected from the PCL lamella and is forced to remain as an impurity in the amorphous layer due to the chemical bond between the PCL and PB blocks. It is expected that this existence of the PB block may strongly influence the lamellar twisting during crystallization.

Figure 6 shows the distribution (or irregularity) of the ring width ($=L'/L$) against ϕ_{PCL} . The result of the PCL/PVC system is also added in the Figure. Again three curves are scaled by ϕ_{PCL} and coincide to one curve, together with the data of the PCL/PVC system. The irregularity of the ring increases linearly with decreasing ϕ_{PCL} , though there is scattering of the data points at smaller ϕ_{PCL} . Figure 6 suggests that with decreasing ϕ_{PCL} , the irregularity of the ring width becomes larger and finally makes the ringed structure indistinguishable. At the limit of $\phi_{\text{PCL}} \rightarrow 1$, on the other hand, the separation between rings

Figure 7. The alternating period L ($\circ$) and L' ($\bullet$) against crystallization temperature T_c for the system with PCL1/B1 = 90/10.

increases steeply and this makes the observation of the ringed structure difficult. This result is also found in the PCL/PVC system previously studied,⁷ where the observation of the ringed spherulite was restricted to a narrower ϕ_{PCL} range.

Figure 7 shows the T_c dependence of the ring width for the system with PCL1/B1 = 90/10. The width increases with increasing T_c , and this change is observed in a number of blend systems which show the ringed spherulite such as PCL/PVC³ and poly(ethylene sebacate) (PESEB)/PVC.⁶ The distribution of the ring width ($=L'/L$) is almost constant within the temperature range investigated. At $T_c \rightarrow T_m$, larger separations of the ring make the observation of the ringed structure difficult, while with decreasing T_c the number of spherulites increases and a large spherulite suitable for the observation of the extinction ring is difficult to find.

DSC Thermogram

Figure 8 shows the DSC thermograms at a heating rate of 5°C min^{-1} for the blends first annealed at 80°C for 1 h, crystallized at 40°C for 2 h, and quenched to room temperature. The pure copolymers (B1, B2, and B3) do not crystallize at 40°C , so that the melting behavior

Figure 8. Typical DSC thermogram for B3 copolymer, PCL1 homopolymer, and PCL1/B3 blends containing 80, 50, 30% PCL1 crystallized at 40°C for 2 h. The heating rate is 5°C min⁻¹.

of B3 in Figure 8 was observed with the sample crystallized at room temperature for about 2 h, though a slight increase of the melting temperature and crystallinity could be observed when the copolymer was annealed at room temperature for a longer time. The melting curve of all pure copolymers (B1, B2, and B3) has an endothermic peak at around 40°C which is diffuse and small in magnitude, indicating a low crystallinity of the sample. The extremely low crystallinity of the crystalline block is reported in a number of crystalline-amorphous block copolymers.^{24,25} The melting temperature of pure PCL is about 58°C and slightly decreases with ϕ_{homo} . For the sample with PCL1/B3 = 30/70, there is another endothermic peak at about 47°C. This second peak is unique for this sample and could not be observed for other blends measured. The sample includes a long PCL block in the copolymer. The two peaks in the DSC thermogram can be interpreted as a result of segregation effect of the PCL chains (PCL homopolymer and PCL block in the copolymer), that is, there are two kinds of lamellae, one is rich in PCL homopolymer and therefore has a high melting temperature, the other is rich in PCL block and

Figure 9. The PCL crystallinity against ϕ_{PCL} . The heat of fusion for the perfect crystal of PCL was assumed to be 32.37 cal g⁻¹.²³

a low melting temperature.

Figure 9 shows the crystallinity of the blend plotted against ϕ_{PCL} . The crystallinity of the PCL chain was evaluated from the peak area assuming that the heat of fusion for pure PCL crystal is 32.37 cal g⁻¹.²³ The crystallinity, which makes three different curves when plotted against ϕ_{homo} , forms a straight line irrespective of the copolymer included when it is plotted against ϕ_{PCL} . Figure 9 indicates that (a) the PCL chain, whether it belongs to the PCL homopolymer or PCL block of the copolymer, participates in the crystallization, and (b) a small amount of PCL block, which melts at about 40°C in the pure copolymer, melts in a higher temperature range similar to the PCL homopolymer. These facts suggest that there is no lamellar crystal consisting of only PCL block of the copolymer and the lamellar crystal is a *mixed crystal* composed of the PCL homopolymer and the PCL block of the copolymer. The melting behavior in Figures 8 and 9, together with the results of the SAXS measurement and the spherulite observation, strongly supports the fact that the PB block is forced to remain in the amorphous layer between the PCL lamellae and eventually plays a key role for the formation of the ringed spherulite.

DISCUSSION

The small-angle X-ray scattering (SAXS) measurement reveals that the PCL-*b*-PB copolymer remains in the amorphous layer between PCL lamellae from the fact that the long spacing increases with increasing impurity (PCL-*b*-PB) fraction in the system. This is also confirmed from a large increase of the peak intensity with increasing copolymer fraction. The results of the spherulite observation and DSC indicate that the PCL block in the copolymer participates in the crystallization of PCL chain to make the *mixed crystal* composed of the PCL homopolymer and the PCL block of the copolymer. The PB block is, therefore, forced to remain in the amorphous layer between PCL lamellae owing to the chemical bond between the PCL and PB blocks, as schematically illustrated in Figure 10. There are a number of systems where an amorphous component remains between lamellar crystals owing to an attractive interaction between components.^{2-4,6} In the present system, on the other hand, the amorphous component remains by the quite different reason, and this will be the first example of such kind of polymer blends.

It is interesting to investigate the micro-

Figure 10. Schematic illustration of the morphology in the present PCL/PCL-*b*-PB system when PCL crystallizes in the lamellar structure. The PCL block is incorporated in the PCL lamella, and therefore the PB block remains in the amorphous layer between lamellae. (a) The PB block is compatible with the PCL chain to make a homogeneous and amorphous layer. (b) The PB block makes a domain structure in the amorphous layer due to the repulsion with the PCL chain.

structure of the PB chain in the amorphous layer because it will have an important role for the lamellar twisting during crystallization. The above results by SAXS, DSC, and optical microscopy, however, do not present any clue to clarify the conformation of the PB block. That is, it is impossible to manifest that whether the PB chain is compatible with the amorphous PCL chain to result in a *homogeneous* amorphous layer (Figure 10-(A)), or the PB block gathers together by the repulsion force with the PCL chain to make a PB domain in the amorphous layer (Figure 10-(B)). The compatibility of the PCL and PB homopolymers is not high from the fact that there is no intimate interaction between the two polymers. In addition, the entropic freedom of the PCL and PB chains in the amorphous layer is reduced by the restriction that a part of the polymer is fixed by the PCL lamellar crystal. These facts suggest to us that the homogeneous amorphous layer is not stable thermodynamically, that is, the domain structure schematically shown in Figure 10-(B) is favorable. It is necessary to find the structural details from another kind of experiments.

According to a number of examples reported in the literature,²⁻⁶ the combination of polymers which shows a beautifully ringed spherulite is thermodynamically compatible with a specific interaction between components. Keith *et al.*,⁶ for example, observed regularly banded spherulites in compatible combinations of aliphatic polyesters and polar polymers, and discussed that an attractive interaction between the crystalline and amorphous polymers are essential to yield the ring during the process of crystallization. That is, the specific interaction works intimately at the interface between polymer segments in the lamella and amorphous layer during crystallization, and makes the lamella twisted. In the present study, the PCL/PCL-*b*-PB system shows the beautifully ringed spherulite, while the binary oligomeric blend of PCL and PB homopolymers does not show any *regularly*

banded structure. The PB component is expected to be rejected from PCL lamellae and makes another domain mainly consisting of the PB chain outside the crystalline region. The above results lead the fact that for the formation of ringed spherulites, the impurity is necessary to exist in the amorphous layer between lamellae to influence the lamellar twisting during crystallization, whether the amorphous component is thermodynamically favorable to stay in or is forced to stay by a specific reason such as the present case. This fact suggests that the specific interaction between components may not be an essential factor for the formation of the ringed spherulite, and the existence of the impurity itself has a key role for the lamellar twisting during crystallization through a specific factor such as a modification in rate of the chain attachment on the growth front of the lamella or in mode of the chain folding on the lamellar surface.

The validity of the above speculative discussions should be confirmed by further experimental results. Especially, the mechanism to form the regular ring during crystallization should be elucidated from the studies of many combinations of polymer pairs which show the regular extinction ring.

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