Morphological Study on Binary Blends of Poly(ϵ -caprolactone)-*block*-Polybutadiene and Poly(ϵ -caprolactone)

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ABSTRACT: The morphology and melting behavior of binary blends of poly(ϵ -caprolactone)-*block*-polybutadiene (PCL-*b*-PB) and poly(ϵ -caprolactone) homopolymer (PCL) were investigated by small-angle X-ray scattering (SAXS) and differential scanning calorimetry (DSC) as a function of the homopolymer fraction ϕ_{homo} in the system. Three sets of the blends were prepared considering the degree of miscibility between PCL-*b*-PB and PCL in the melt. The morphology after crystallization of PCL and the PCL block in PCL-*b*-PB depended strongly on the miscibility in the melt; when PCL was uniformly dissolved with the PCL block in the microdomain structure of PCL-*b*-PB, an alternating structure of lamellae and amorphous layers (lamellar morphology) was formed in which the PCL block and PCL together made a lamellar crystal, suggesting the formation of a *mixed crystal* composed of the PCL block and PCL. When PCL was localized in the microdomain structure or macroscopically segregated in the melt, two separate crystalline regions were observed over a wide range of ϕ_{homo} , each consisting of PCL and PCL + PCL-*b*-PB. The lamellar morphology is qualitatively discussed as a function of ϕ_{homo} from the viewpoint of the chain conformation of the PB block.

KEY WORDS Diblock Copolymer–Homopolymer Blend / Crystallization / Morphology / Small-Angle X-Ray Scattering / Differential Scanning Calorimetry /

Crystalline–amorphous diblock copolymers have a potential to form complicated morphologies by an interplay between microphase separation and crystallization of the constituent blocks. There are several theoretical and experimental studies on the morphology and morphology formation of such block copolymers.^{1–15} It has been found from these studies that the final morphology is intimately dependent on the nature of the block copolymers. That is, when each block has a low glass transition temperature and the total molecular weight of the copolymer is not large, the crystallization destroys the microdomain structure in the melt to yield an alternating structure of lamellae and amorphous layers (lamellar morphology).^{7,10,11} When the glass transition temperature of the amorphous block is higher than the melting temperature of the crystallizable block or the copolymer is long enough, the microdomain structure remains unchanged to result in the extreme reduction of the subsequent crystallization.^{5,12}

When the crystalline–amorphous diblock copolymer is blended with the constituent crystalline homopolymer, the morphology formation seems to be more complicated than that of pure copolymers. That is, macrophase separation between the components may intervene in the morphology formation in addition to microphase separation and crystallization. As a result, the final morphology will be strongly dependent on the phase structure in the melt; whether the added homopolymer is macroscopically segregated, localized within the microdomain structure, or uniformly mixed in the microdomain structure. The phase behavior of such blends above the melting temperature of the crystallizable block is considered to be the same as the binary blends of amorphous–amorphous diblock copolymer and homopolymer, so that the details of the phase structure are well known on the basis of the miscibility

between the copolymer and homopolymer.^{16–18}

There are several experimental studies on the morphology formed in binary blends of crystalline–amorphous diblock copolymer and crystalline (or amorphous) homopolymer.^{5,19–27} Cohen *et al.*,⁵ for example, investigated the morphology of a nylon 6-*block*-poly(dimethyl siloxane)/nylon 6 blend and observed path-dependent morphologies which could be qualitatively explained by the phase diagram of this system. Liu *et al.*^{21,23} observed the morphology of a poly(tetrahydrofuran)-*block*-poly(methyl methacrylate) (PTHF-*b*-PMMA)/PTHF blend and showed that the final morphology was strongly dependent on the microdomain structure in the melt.

In our earlier paper,¹⁹ we studied the spherulite structure of poly(ϵ -caprolactone)-*block*-polybutadiene (PCL-*b*-PB)/poly(ϵ -caprolactone) (PCL) blends and suggested the possibility to form a *mixed crystal*, *i.e.*, a crystal composed of the PCL block and PCL. In this study, we further study the PCL-*b*-PB/PCL blends to elucidate the relationship between the phase structure in the melt and the final morphology after crystallization of the PCL chains (*i.e.*, PCL block + PCL) in the system.

EXPERIMENTAL

Materials

The poly(ϵ -caprolactone)-*block*-polybutadiene (PCL-*b*-PB) diblock copolymers used in this study were synthesized by successive anionic polymerizations under vacuum with *n*-butyllithium as an initiator. Details of the synthesis were described elsewhere.^{7,10} The molecular characterization of the copolymers was carried out by gel permeation chromatography (GPC), nuclear magnetic resonance (¹H NMR), and differential scanning calorimetry (DSC). The results are shown in Table I.

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Table I. Characterization of polymers

Notation	Polymer	M_w^a	M_w/M_n^a	PCL:PB ^b	$T_m/^\circ\text{C}^c$
B7	PCL- <i>b</i> -PB	12400	1.10	61:39	55
B16	PCL- <i>b</i> -PB	11400	1.18	47:53	51
PCL1	PCL	8300	1.40	—	55
PCL2	PCL	8400	1.27	—	55
PCL3	PCL	21600	1.61	—	57

^a Values relative to polystyrene standards determined by GPC.^b Volume ratio determined by ¹H NMR. ^c Determined by DSC at a heating rate of 5°C min⁻¹.**Table II.** Systems used in the present study

Notation	System	Behavior of PCL in the melt
A1	B7 + PCL1	Uniformly dissolved in the PCL domain
A2	B16 + PCL2	Localized in the PCL domain
A3	B7 + PCL3	Macroscopically phase-separated

The following specific volumes were used for the volumetric consideration of the phase structure in the melt and the morphology after crystallization, as described later. For polybutadiene,²⁸

$$v_{sp} = 1.1138 + (8.24 \times 10^{-4}) \times T \quad (1)$$

and for amorphous poly(ϵ -caprolactone),²⁹

$$v_{sp} = 0.9106 + (6.013 \times 10^{-4}) \times T \quad (2)$$

where v_{sp} is in cm³ g⁻¹ and T is in °C. For the perfect crystal of poly(ϵ -caprolactone),³⁰ $v_{sp} = 0.833$ cm³ g⁻¹ was used irrespective of temperature.

Blend Preparation

Three binary blends, A1, A2, and A3, were prepared for the morphological study considering the degree of miscibility between PCL-*b*-PB and PCL in the melt (Table II); in A1, PCL is uniformly dissolved with the PCL block in the microdomain structure, in A2, PCL is localized microscopically within the PCL domain, and in A3, PCL is macroscopically segregated. The addition of a large amount of PCL may bring the system into a disordered state rather than the microdomain structure in the melt. It was, however, quite difficult to distinguish between two states from the SAXS results since even in the disordered state the scattering peak could be observed at a finite angle due to the *correlation hole effect* of the block copolymer. This indicates that the system is in close proximity to the order-disorder transition of the microphase separation.³¹

The solution-casting method was employed to prepare blends with various compositions. First, PCL-*b*-PB and PCL were dissolved homogeneously in a common solvent (benzene) and the solution was cast on a glass plate. The solvent was then evaporated under vacuum at *ca.* 70°C for more than 24 h.

Small-Angle X-Ray Scattering (SAXS) Measurements

Two SAXS techniques were used in this study: conventional SAXS (C-SAXS)³² and synchrotron SAXS (SR-SAXS).^{7,33} The C-SAXS measurement was performed with a point focusing optics and a one-dimensional position sensitive proportional counter (PSPC)

with an effective length of 10 cm. The SAXS optics had a toroidal mirror and a crystal monochromator to focus the scattered intensity on the PSPC. The Cu-*K_α* radiation supplied by a MAC Science M18X generator operating at 40 kV and 30 mA was used throughout. The distance between the sample and PSPC was about 40 cm. The SR-SAXS experiment was carried out at National Laboratory for High Energy Physics, Tsukuba, Japan (Photon Factory), with small-angle X-ray equipment for solution (SAXES) installed on a beam line BL-10C. Details of the optics and instrumentation are described elsewhere.³³ The geometry for both C-SAXS and SR-SAXS apparatuses was further checked by a chicken tendon collagen, which gives a set of sharp diffractions corresponding to 65.3 nm.

After the SAXS intensity was corrected for the background and transmission factor, relative scattered intensity $I(s)$ was obtained as a function of wave number s defined by,

$$s = 2 \sin \theta / \lambda \quad (3)$$

where 2θ is the scattering angle and λ is 0.1542 nm for C-SAXS and 0.1488 nm for SR-SAXS. Since C-SAXS and SR-SAXS apparatuses had point focusing optics, the scattered intensity was not corrected for the smearing effect from the finite cross section of the primary beam. There was no discrepancy detected between the results obtained by C-SAXS and SR-SAXS.

For the SAXS measurement at the melt, the sample was first annealed for more than 30 min at a measuring temperature T_a ($> T_m$) by circulating temperature-controlled water to the sample holder. The annealing time was long enough to yield the reproducible SAXS results. The sample was then quenched to the crystallization temperature T_c ranging from 30–45°C and kept at T_c for a long time (depending on T_c) before SAXS measurements. For SR-SAXS, the change of the integrated intensity was also monitored to ensure the end of crystallization. The fluctuation of T_a was less than 1°C throughout. The accumulation time for C-SAXS and SR-SAXS was 3000–5000 s and 10–300 s, respectively.

Differential Scanning Calorimetry (DSC) Measurements

A Perkin-Elmer Model 7 DSC was used to determine the melting temperature T_m of the PCL chains (*i.e.*, PCL block and PCL), PCL crystallinity (*i.e.*, wt% of the crystallized PCL chains against the existing PCL chains in the system), and system crystallinity (*i.e.*, wt% of the crystallized PCL chains against the whole sample). The sample, first annealed at 65°C for 1 h, was quenched by a maximum quenching rate ($= 500^\circ\text{C min}^{-1}$) to the crystallization temperature T_c ranging from 25°C to 45°C, followed by heating at a rate of 5°C min⁻¹. T_m was evaluated from the endothermic peak position and PCL crystallinity (and also system crystallinity) was calculated from the peak area assuming that the heat of fusion for the perfect PCL crystal is 135.44 Jg⁻¹.²⁹

RESULTS

Phase Structure in the Melt

In a binary blend of copolymer and homopolymer,

Figure 1. SAXS intensity curves measured at *ca.* 65°C ($> T_m$) for A1 with various compositions indicated. The SAXS curves are shifted upward successively for legibility.

various phase structures, such as microdomain structure, macroscopically phase-separated morphology, or homogeneous state, are expected in the melt depending on the molecular characteristics of the constituent polymers, and it might affect the final morphology after crystallization. In order to investigate quantitatively the phase structure of three systems (A1, A2, and A3) in the melt, small-angle X-ray scattering (SAXS) measurements were carried out at around 65°C, which is above the melting temperatures of the PCL block and PCL.

The SAXS curves obtained for A1 with various volume fractions of the homopolymer, ϕ_{homo} , in the system are shown in Figure 1, where the ordinate is the logarithm of the relative scattered intensity and the abscissa is the wave number s defined by eq 3. The SAXS curves for A2 and A3 change similarly with changing ϕ_{homo} on the whole, though there are minor differences for each system as mentioned later. Each SAXS curve has an intensity maximum and this maximum becomes diffuse with increasing ϕ_{homo} . For B7 (and also B16), the second intensity maximum (indicated by an arrow in Figure 1) can be observed, which corresponds exactly to twice the angular position of the first, suggesting that B7 and B16 have a lamellar microdomain structure in the melt. This fact is consistent with our previous observations by transmission electron microscopy (TEM) showing that the microdomain structure of B16 was certainly lamellar.¹⁵

The addition of PCL to B7 or B16 may change the lamellar microdomain structure into a cylinder and finally into a sphere, or it may bring the system directly into a disordered state because the blend is not in a strong segregation owing to the low molecular weight of PCL-*b*-PB. The type of this microdomain structure including disordered state, however, may not affect significantly the crystallization behavior and eventually final morphology, since our recent studies on crystalliza-

Figure 2. ϕ_{homo} dependence of the spacing (a) and normalized distance between chemical junctions of the PCL and PB blocks a/a_0 (b) for A1 (●), A2 (○), and A3 (□).

tion behavior of various PCL-*b*-PBs revealed that the microdomain structure was completely destroyed by the subsequent crystallization without any significant effect from the different microdomain structures.^{7,10}

Figure 2a shows the ϕ_{homo} dependence of the spacing D for A1, A2, and A3 evaluated from the angular position of the SAXS intensity peak. The value of D for A2 increases abruptly with increasing ϕ_{homo} , while D for A1 and A3 increases slightly with increasing ϕ_{homo} . In particular, D for A3 remains substantially unchanged at $\phi_{\text{homo}} \geq 40\%$, suggesting that the system is macroscopically phase-separated in this composition range. The phase separation was also confirmed from the turbidity of A3 in the melt, and this fact is supported by the large molecular weight of PCL3 compared with that of PCL1 and PCL2 (Table I). We consider and discuss mainly the results of A1 and A2 hereafter.

Tanaka *et al.*¹⁷ derived a relation to check the details of the microdomain structure from a simple volumetric consideration:

$$a/a_0 = [(D/D_0)(1 - \phi_{\text{homo}})]^{-1/2} \quad (4)$$

where a is the average distance between the chemical junctions of the PCL and PB blocks in the binary blend, a_0 is that in pure copolymer, and D_0 is the spacing of pure copolymer. It is therefore possible to evaluate the degree of miscibility of PCL with the PCL block in the microdomain structure by plotting a/a_0 against ϕ_{homo} ; when PCL is miscible uniformly with the PCL block, then a/a_0 increases with increasing ϕ_{homo} , while PCL segregates microscopically from the PCL block within the microdomain structure, then a/a_0 is constant irrespective of ϕ_{homo} .

The plots of a/a_0 against ϕ_{homo} for A1 and A2 are shown in Figure 2b. a/a_0 for A1 increases monotonously

Figure 3. SAXS intensity curves for A1 with various compositions crystallized at 35°C.

with increasing ϕ_{homo} to show the swelling of the PCL blocks by the added PCL homopolymer (uniform solubilization). In A2, on the other hand, a/a_0 is almost constant irrespective of ϕ_{homo} , indicating that the PCL block is not swollen by PCL (localized solubilization). This difference in the microdomain structure probably arises from the minor differences in the block ratio and molecular weight of the constituent polymers, and affects significantly the final morphology after crystallization as mentioned later. Table II summarizes the above observations, that is, the behavior of PCL in the melt for three systems employed.

Morphology after Crystallization

Figure 3 shows the SAXS curves scattered from A1 crystallized at 35°C. The angular position of the primary intensity peak shifts toward the higher angle with increasing ϕ_{homo} . The SAXS curves for A1 at B7/PCL1 = 80/20 and 60/40 clearly show the second peak (indicated by arrows in Figure 3) which corresponds exactly to twice the angular position of the primary peak, indicating that the morphology after crystallization of the PCL chain is also lamellar as demonstrated in many crystalline-amorphous diblock copolymers. This lamellar morphology is also detected in the SAXS curves shown in Figure 4 for A2 at B16/PCL2 = 100/0, 80/20, and 60/40 (indicated by arrows on the curve). Another characteristic feature of Figure 4 is the second intensity peak (indicated by dashed arrows) at a limiting range of ϕ_{homo} (i.e., B16/PCL2 = 30/70, 20/80, and 10/90). The angular position of the higher angle peak corresponds exactly to that of PCL irrespective of ϕ_{homo} . The bimodal SAXS curve suggests that there are two morphologies in the system in which the long spacings are different each other.

The long spacing L evaluated from the angular position of the SAXS intensity peak is plotted in Figure 5 against volume fraction of the PCL chains (i.e., PCL + PCL block), $\phi_{\text{V,PCL}}$, in the system, where L decreases linearly

Figure 4. SAXS intensity curves for A2 with various compositions crystallized at 35°C.

Figure 5. $\phi_{\text{V,PCL}}$ dependence of the long spacing evaluated from the angular position of the SAXS peaks for A1 (○) and A2 (●, ■) crystallized at 35°C.

with increasing $\phi_{\text{V,PCL}}$ for A1. In our previous study of the spherulite observation for the miscible binary blends of PCL-*b*-PB and PCL,¹⁹ we suggested the possibility to make a *mixed crystal*, a crystal composed of the PCL block and PCL, from the change in the banded structure of the spherulite. The monotonous decrease of L for A1 shown in Figure 5, which is in contrast with the case of A2, also suggests strongly the possibility to make the mixed crystal in the miscible blend of B7 and PCL1.

At $1 > \phi_{\text{V,PCL}} \geq 0.8$ for A2, there is another long spacing which reflects the bimodal character in SAXS curves shown in Figure 4. The shorter spacing appearing at a limited range of $\phi_{\text{V,PCL}}$ corresponds exactly to the long spacing observed in PCL, suggesting that this phase mainly consists of PCL. That is, the final morphology formed in A2 over a limited range of $\phi_{\text{V,PCL}}$ is a mosaic structure consisting of a PCL region and a PCL + PCL-

Figure 6. Temperature dependence of the spacing for B7 (○) and B16 (●). T_m and T_m' represent the melting temperature of B7 and B16, respectively.

Figure 7. $\phi_{V,PCL}$ dependence of PCL crystallinity (circles) and system crystallinity (squares) for A1 (○, □) and A2 (●, ■).

b-PB region. The SAXS curves for A3 also show the bimodal character over a wide range of $\phi_{V,PCL}$ to indicate a mosaic structure, which will be caused by the phase-separated morphology in the melt.

The characteristic features shown in Figure 5 did not change significantly with changing the crystallization temperature T_c . In Figure 6, for example, T_c dependence of L is shown for B7 and B16, together with the temperature dependence of D in the melt. The value of D never changes at all with changing temperature, while L increases slightly with increasing T_c toward T_m . This increase in L is usually observed in crystalline homopolymers and was reported previously for various PCL-*b*-PBs.⁷

Melting Behavior

The DSC curves for A1, A2, and A3 showed a single endothermic peak at any compositions and we could not observe the bimodal melting curves arising from the mosaic structure mentioned above at a limited range of $\phi_{V,PCL}$ for A2 and A3.

Figure 7 shows the $\phi_{V,PCL}$ dependence of PCL crystallinity (circles), the crystallinity based on the weight of the PCL chains in the system, and system crystallinity (squares), the crystallinity based on the total weight of the sample. Though the system crystallinity increases linearly with increasing $\phi_{V,PCL}$, the PCL crystallinity is almost constant irrespective of $\phi_{V,PCL}$. This suggests that there is no difference in the crystallization behavior

Figure 8. $\phi_{V,PCL}$ dependence of the average lamellar thickness l_c (circles) and average amorphous layer thickness l_a (squares) for A1 (○, □) and A2 (●, ■).

between PCL and the PCL block to lead the same crystallinity, and therefore the blend has a same PCL crystallinity even if it consists of two crystalline regions as the case of A2 and A3.

It is well known that crystalline homopolymers have a lamellar morphology, an alternating structure of lamellar crystals and amorphous layers, after crystallization. The crystalline-amorphous diblock copolymers are theoretically predicted to have a lamellar morphology after crystallization,^{1,2} which is supported by several experimental results. In fact, we observed the lamellar morphology of B16 crystallized at 25°C by TEM observations.¹⁵ These facts mean that the crystalline morphology of A1, A2, and A3 is intrinsically lamellar, apart from the result whether the system has a single lamellar morphology or a mosaic structure composed of two lamellar morphologies. Therefore it is reasonable to estimate the average lamellar thickness (l_c) and average amorphous layer thickness (l_a) from the combination of L obtained by SAXS and system (or PCL) crystallinity by DSC when the system has a single lamellar morphology. When the mosaic structure consisting of two lamellar morphologies prevails in the blend, we need further information about the morphological details in order to estimate each l_c and l_a .

Figure 8 shows the $\phi_{V,PCL}$ dependence of l_c and l_a for A1 and A2 with a single lamellar morphology. The value of l_c is almost constant irrespective of $\phi_{V,PCL}$, though a small decrease can be observed at a limited range of small $\phi_{V,PCL}$. l_c is, however, strongly dependent on T_c as usually observed in crystalline homopolymers. The value of l_a , on the other hand, increases linearly with decreasing $\phi_{V,PCL}$, reflecting the intervention of the PB block between PCL lamellae. Figure 8 indicates that the details of the lamellar morphology are determined only by the volume fraction of the PCL chain in the system, and it is no matter whether the PCL chain belongs to PCL or the PCL block in PCL-*b*-PB. This is ascribed to the same crystallization rate between PCL and the PCL block.

DISCUSSION

Analysis of the Morphology after Crystallization

The A1 and A2 were found to have a single lamellar morphology over a wide range of ϕ_{homo} after crystallization of the PCL chains, and the lamellar thickness and amorphous layer thickness were evaluated from the combination of SAXS and DSC results (Figure 8). Here, we discuss qualitatively this lamellar morphology from the viewpoint of the chain conformation of the PB block confined within the amorphous layers between PCL lamellae.

First, we consider the single lamellar morphology consisting of PCL-*b*-PB and PCL and assume that the morphology is schematically illustrated in Figure 9, where the PB block segregates completely from the amorphous PCL chains within the amorphous layer because of a repulsive force between the PCL and PB chains. This assumption is reasonable when PCL-*b*-PB is rich in the system. That is, since the PB block in pure PCL-*b*-PB is intrinsically extended to the direction perpendicular to the lamellar surface as theoretically predicted^{1,2} and experimentally obtained in our previous study,¹⁵ the addition of small amount PCL will make the PB block closer to the random coil conformation. Consequently, there is no force working to change the essential picture of the morphology. When PCL is rich in the system, however, the model represented in Figure 9 will not hold since the average distance between the chemical junctions of the PCL and PB blocks increases to yield too much room for the accommodation of the PB block, and hence the PB block has to be flattened resulting in the increase of the conformational free energy. Therefore, we treat the copolymer-rich system in this discussion.

The above assumption leads simply to the following equation,

$$L = l_c + l_a = l_c + l_{a,\text{PCL}} + l_{a,\text{PB}} \quad (5)$$

where $l_{a,\text{PCL}}$ and $l_{a,\text{PB}}$ are the average thicknesses of amorphous PCL and PB layers, respectively. The normalized average distance between the chemical junctions of the PCL and PB blocks, a/a_0 , in the lamellar morphology shown in Figure 9 can be expressed from the volumetric consideration similar to eq 4:

$$a/a_0 = (l_{a,\text{PB}}/l_{a,\text{PB}_0})^{-1/2} \quad (6)$$

Figure 9. The model used for the analysis of the lamellar morphology formed by the crystallization of the PCL chains. Thick and thin lines represent the PCL chains and the PB blocks, respectively. The small filled circles represent the junctions between the PCL and PB blocks.

where a_0 and l_{a,PB_0} represent the corresponding values for the pure copolymer, respectively. Equation 6 is simply derived from the incompressibility principle of the PB block in the lamellar morphology. The values of $l_{a,\text{PB}}$ and l_{a,PB_0} are easily estimated from l_a and the system crystallinity on the basis of eq 5.

Figure 10 shows the plot of a/a_0 against $\phi_{\text{V,PCL}}$ for A1 and A2, where a/a_0 increases smoothly with increasing $\phi_{\text{V,PCL}}$. In each case, the system is expected to have a specific a/a_0 , $(a/a_0)^*$, at which the PB block has a random coil conformation in the amorphous layer. This $(a/a_0)^*$ can be evaluated in principle from the absolute molecular weights of the constituent blocks and their compositions as demonstrated in our previous paper.¹⁵ Since the PB blocks have to be flattened beyond $(a/a_0)^*$, the schematic model represented in Figure 9 has to be modified at a large ϕ_{homo} . In this region, the PB block is, for example, miscible with the amorphous PCL chain to make a unified amorphous layer.

The difference in $(a/a_0)^*$ might lead to the two lamellar morphologies after crystallization of the PCL chains. That is, the addition of PCL imposes the deformation of the PB block in a different fashion depending on $(a/a_0)^*$, so that PCL-*b*-PB with a smaller $(a/a_0)^*$ is difficult to keep a single lamellar morphology shown in Figure 9 at PCL-rich regions to yield two lamellar morphologies, one is rich in PCL and another rich in PCL-*b*-PB. The above explanation is, however, not consistent with the results of A1, where (a/a_0) changes smoothly through $(a/a_0)^*$ with increasing $\phi_{\text{V,PCL}}$ and we do not observe the two lamellar morphologies at a large ϕ_{homo} (Figures 3 and 5). Therefore, it is concluded that the dominant factor to control the morphological outline is not the conformational restriction of the amorphous block but the phase structure in the melt as explained in the next section.

Relation between Phase Structure in the Melt and Morphology after Crystallization

In this study, we obtained a phenomenological relationship between the phase structure in the melt and the morphology after crystallization of the PCL chains. This relation is schematically summarized in Figure 11. When PCL solubilizes uniformly within the microdomain structure in the melt, a single lamellar morphology (with

Figure 10. $\phi_{\text{V,PCL}}$ dependence of normalized distance between chemical junctions of the PCL and PB blocks, a/a_0 , in the lamellar morphology for A1 (○) and A2 (□).

Figure 11. Schematic illustration to indicate the relationship obtained in this study between the phase structure in the melt (left) and the morphology after crystallization (right).

the long spacing L) appears in the system. This fact is attributed to the same crystallization rate between PCL and the PCL block, and suggests the possibility to make a mixed crystal composed of PCL and the PCL block. The formation of the mixed crystal means the coexistence of PCL with the PCL block within a lamellar crystal, which should influence the PB block to result in the favorable conformation as mentioned above.

When PCL localizes within the microdomain structure or segregates macroscopically in the melt, two lamellar morphologies (with the long spacings L_1 and L_2) appear in the system after crystallization of the PCL chains. It is simply speculated that the spatial separation of the PCL block and PCL in the melt yields the separate lamellae each consisting of the PCL block or PCL. Thus, the interrelation between the phase structure in the melt and morphology after crystallization seems to be simple in this system. However, the crystalline morphology formed in many binary blends of block copolymer and homopolymer may be determined cooperatively by many factors, such as the phase structure in the melt, crystallization behavior, or the conformational restriction of the amorphous block in the lamellar morphology, and it is necessary to study the morphology of many other binary blends of copolymer and homopolymer on the basis of molecular characteristics of the constituent polymers.

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