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Morphology formed in binary blends of poly(ε-caprolactone) and ε-caprolactone–butadiene diblock copolymer

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The morphology formed in binary blends of poly(ε-caprolactone) (PCL) and ε-caprolactone–butadiene diblock copolymer (PCL-*b*-PB) has been investigated by small-angle X-ray scattering (SAXS). The difference in the microdomain structure in the melt yielded different morphologies after crystallization: when PCL dispersed uniformly in the PCL domain in the melt, the morphology was an alternating structure composed of lamellae and amorphous layers (lamellar morphology). When PCL was localized within the PCL domain, a mosaic structure of two lamellar morphologies, each consisting of a PCL region and a PCL-*b*-PB-rich region, was formed over a limited composition range.

(Keywords: homopolymer/copolymer blend; microdomain structure; crystallization)

Introduction

In a recent study[1], we examined regularly banded spherulites observed in a binary blend of poly(ε-caprolactone) (PCL) and ε-caprolactone–butadiene diblock copolymer (PCL-*b*-PB). The repeating distance of the extinction ring was significantly dependent on the volume fraction of PCL chains in the system, ϕ_{PCL}, i.e. sum of the volume fractions of PCL and the PCL block. We speculated that the amorphous PB block, covalently bonded with the PCL block to exist between the PCL lamellae, played an important role in the formation of the spherulites, because pure PCL did not show such regularly banded spherulites.

There are several studies on the morphology of crystalline–amorphous diblock copolymers[2–5], where the systems have various microdomain structures (lamellar, cylindrical or spherical) in the melt, the details of which depend intimately on the molecular characteristics of the constituent copolymers. In the case of binary blends of homopolymer and copolymer, segregation of the homopolymer will make the microdomain structure more complicated[6,7]. In the blends of PCL and PCL-*b*-PB, for example, PCL may be uniformly dissolved in the microdomain structures formed by PCL-*b*-PB, or segregated microscopically or macroscopically. This difference will affect the subsequent crystallization behaviour and eventually the final morphology and spherulitic superstructure[8,9].

In this study, we examine the morphology formed in two binary blends of PCL and PCL-*b*-PB by small-angle X-ray scattering (SAXS), where PCL exists in different forms within the microdomain structure in the melt: in one system, PCL is uniformly dissolved with the PCL block in the microdomain structure, and in the other, PCL is localized within the PCL domain.

Experimental

Materials and sample preparation. The samples used in this study were synthesized by successive anionic polymerizations under vacuum. Details of this synthesis were described elsewhere[10]. The samples were characterized by gel permeation chromatography (g.p.c.), and the PCL content in the copolymer was evaluated by ^{1}H n.m.r. (Varian Gemini-200). The melting temperature, T_m, was measured by differential scanning calorimetry (d.s.c.) (MAC Science model 3100) at a heating rate of 5°C min^{-1}. The results of molecular characterization are summarized in *Table 1*.

Two binary blends, B7/PCL1 and B16/PCL2, were used, which had different microdomain structures in the melt: in B7/PCL1, PCL was uniformly dissolved with the PCL block in the microdomain structure in the melt, while in B16/PCL2, PCL was localized within the PCL domain. Each blend was prepared by the solvent-casting method: B7 (or B16) and PCL1 (or PCL2) were dissolved in a common solvent (benzene) and the solution was cast on a glass plate. The solvent was evaporated under vacuum at 70°C over 24 h.

Small-angle X-ray scattering (SAXS) measurements. Two SAXS techniques were used according to the structural spacing in the samples: conventional SAXS (C-SAXS) for samples with shorter spacing (up to 20 nm) and synchrotron SAXS (SR-SAXS) for samples with longer spacing. Details of C-SAXS and SR-SAXS measurements are described elsewhere[11,12]. After the SAXS intensity was corrected for the background and Lorentz factor, relative scattered intensity $I(s)$ was obtained as a function of wavenumber $s (= 2\sin\theta/\lambda$, where 2θ is the

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Table 1 Characterization of polymers used in this study

Notation	Total M_w [a]	M_w/M_n [a]	PCL:PB (vol%) [b]	Microstructure of the PB block [b]			T_m [c] (°C)
				cis-1,4	*trans*-1,4	1,2-linkage	
B7	12400	1.10	61:39	36	52	12	55
B16	11400	1.18	47:53	37	51	12	51
PCL1	8300	1.40					55
PCL2	8400	1.27					55

[a] Values relative to PS standards determined by g.p.c.
[b] Determined by ^{1}H n.m.r
[c] Determined by d.s.c. at a heating rate of 5 °C min^{-1}

scattering angle). Since both C-SAXS and SR-SAXS have point focusing optics, the scattered intensity was not corrected for the smearing effect from the finite cross-section of the primary beam[13].

Results and discussion

In a previous paper[1], we showed micrographs of regularly banded spherulites formed in a PCL-*b*-PB/PCL system. In the present B7/PCL1 and B16/PCL2 systems, we could observe similar extinction rings over a wide range of ϕ_{PCL}. It is therefore interesting to examine structures smaller than the spherulite in order to understand the influence of the existing microdomain structure on the final morphology after crystallization.

Microdomain structure in the melt. In copolymer/homopolymer blends, a microdomain structure, which might affect the subsequent crystallization behaviour and eventually the final morphology, appears in the melt[6,7]. In order to qualitatively investigate such microdomain structures, SAXS measurements were carried out at 65°C. Each SAXS curve had an intensity maximum, and this maximum became diffuse with increasing the volume fraction of homopolymer in the system, ϕ_{homo}: for B7 and B16, the second intensity maximum corresponded exactly to twice the angular position of the first, while for the blends with a large ϕ_{homo}, a diffuse intensity maximum could be observed.

The microdomain structure of B16 was previously found to be lamellar by transmission electron microscopy (TEM)[14]. It is therefore reasonable to assume that the microdomain structure for B7 is also lamellar, by considering the first and second peak positions together with the block ratio in the copolymer. The addition of PCL may change the lamellar microdomain structure into a cylinder and finally into a sphere. It is, however, uncertain whether the type of microdomain structure significantly affects the crystallization behaviour and final morphology[15].

The repeating distance of the microdomain structure, D, evaluated from the angular position of the intensity maximum, is plotted against ϕ_{homo} in *Figure 1a*. The value of D for B16/PCL2 increases abruptly with increasing ϕ_{homo}, while for B7/PCL1, D increases slightly with ϕ_{homo}. Tanaka *et al.*[6] derived a relation to check the details of the lamellar microdomain structure from a simple volumetric consideration:

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

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 domain spacing of pure copolymer. It is therefore possible to know the miscibility of PCL with the PCL block by plotting a/a_0 against ϕ_{homo}; when PCL solubilizes uniformly in the PCL domain, then a increases with increasing ϕ_{homo}, but when PCL segregates from the PCL block within the PCL domain, a is constant irrespective of ϕ_{homo}.

Figure 1b shows the plot of a/a_0 against ϕ_{homo} for B7/PCL1 and B16/PCL2. For B7/PCL1, a/a_0 increases with increasing ϕ_{homo}, suggesting the swelling of the PCL domain by the added PCL homopolymer (uniform solubilization). For B16/PCL2, 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 the final morphology after crystallization, as described in the next section.

Morphology after crystallization. *Figure 2* shows the X-ray intensities scattered from B7/PCL1 and B16/PCL2 crystallized at $T_c = 35$°C, where the abscissa is the wavenumber $s = 2\sin\theta/\lambda$, with 2θ being the scattering angle. The angular position of the intensity peak shifts

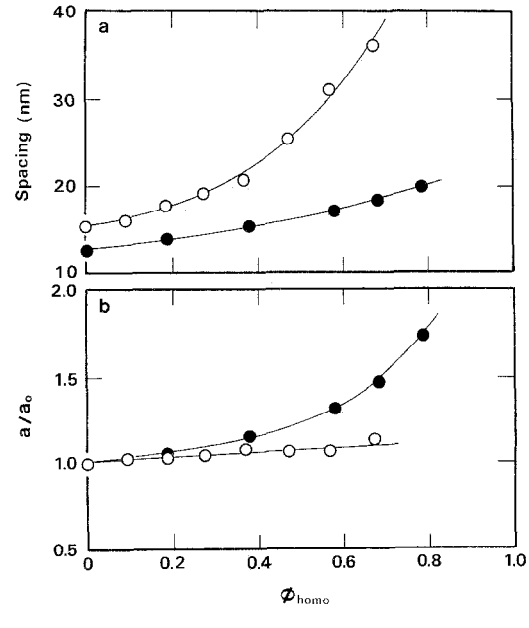

Figure 1 Lamellar domain spacing (a) and normalized distance between chemical junctions a/a_0 (b) plotted against ϕ_{homo} for B7/PCL1 (●) and B16/PCL2 (○)

towards larger s with increasing ϕ_{homo}, and two intensity peaks can be observed at a limited range of ϕ_{homo}, $1 > \phi_{homo} > 0.7$, for B16/PCL2 (indicated by arrows). The long spacing, L, evaluated from each intensity peak is shown in *Figure 3*. The value of L decreases linearly with increasing ϕ_{homo} for B7/PCL1 and B16/PCL2, in contrast with the case of ϕ_{homo} dependence of the domain spacing in the melt (*Figure 1a*). At $1 > \phi_{homo} > 0.7$ for B16/PCL2, two long spacings can be evaluated, reflecting two intensity peaks on the SAXS curve: one spacing corresponds exactly to that for PCL and the other to that for the blend. The characteristic features appearing in *Figure 3* changed slightly with increasing crystallization temperature T_c: the long spacing increased slightly with increasing T_c, as usually observed in the morphology of crystalline homopolymers, but two spacings were always detected at $1 > \phi_{homo} > 0.7$ for B16/PCL2. These results indicate that the final morphology formed in B16/PCL2 at $1 > \phi_{homo} > 0.7$ is a mosaic structure consisting of a PCL2 region and a B16-rich region.

In a previous paper[1], we pointed out that the crystallization behaviour of the PCL block was the same as that of PCL; there was no difference in crystallinity between PCL and the PCL block of the copolymer, and a mixed crystal composed of PCL and the PCL block was formed, suggesting the same crystallization rate for PCL and the PCL block. The present results, together with the previous results mentioned above, led us to speculate on the morphology formation in the present systems as follows. In B7/PCL1, crystallization starts from the uniformly mixed state of PCL and the PCL block in the melt, and there is no difference in the crystallization behaviour between PCL and the PCL block. Consequently the resultant lamellae are mixed crystals. In the case of B16/PCL2, on the other hand, PCL2 is localized within the PCL domain in the melt. Crystallization of the PCL chains starts simultaneously and independently at the regions of PCL2 and the PCL block with the same crystallization rate. Consequently the morphology is a mosaic structure consisting of the PCL2 region and B16-rich region. This segregation of the PCL2 region may also occur at $\phi_{homo} < 0.7$, but will not be detected by the SAXS technique. This is because the scattering from the lamellar morphology formed mainly by B16 (which is large enough owing to a large electron density difference between the PB layers and PCL lamellae) overlapped the scattering from the lamellar morphology formed by PCL2.

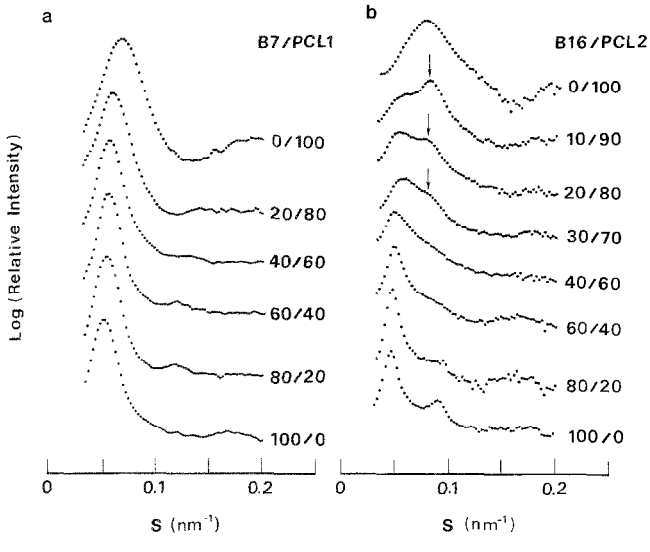

Figure 2 Lorentz-corrected X-ray intensities plotted against s for B7/PCL1 (a) and B16/PCL2 (b). The crystallization temperature is 35°C

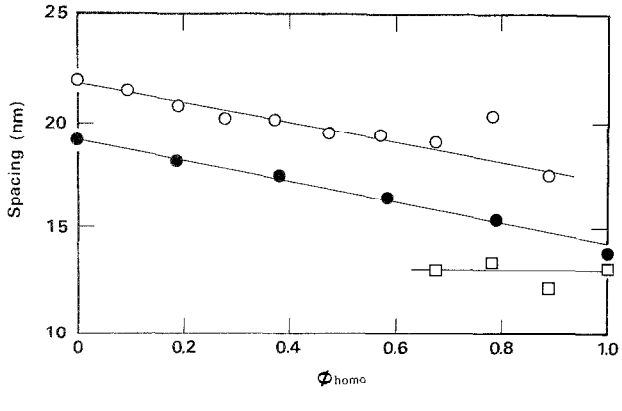

Figure 3 Long spacings, evaluated from the angular position of the intensity maximum, plotted against ϕ_{homo} for B7/PCL1 (●) and B16/PCL2 (○, □)

The morphological difference between B7/PCL1 and B16/PCL2 may bring about changes in the features of the ringed spherulite. Therefore, the quantitative investigation of ϕ_{homo} dependence of the spherulite, such as the repeating distance of the ring and distribution of this distance, may be a clue to knowing the difference in morphological structures smaller than the spherulite. The quantitative analysis of the crystallization process may also give information about the morphological difference between these systems. By these approaches we hope to derive the relationships between the lamellar morphology and the spherulite, and to elucidate the crystallization mechanism in block copolymer/homopolymer systems. Complete results will be published later.

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References

1 Nojima, S., Wang, D. and Ashida, T. *Polym. J.* 1991, **23**, 1473
2 Douzinas, K. C., Cohen, R. E. and Halasa, A. F. *Macromolecules* 1991, **24**, 4457
3 Unger, R., Beyer, D. and Donth, E. *Polymer* 1991, **32**, 3305
4 Ishikawa, S., Ishizu, K. and Fukutomi, T. *Polym. Commun.* 1991, **32**, 374
5 Cohen, R. E., Cheng, P. L., Douzinas, K., Kofinas, P. and Berney, C. V. *Macromolecules* 1990, **23**, 324
6 Tanaka, H., Hasegawa, H. and Hashimoto, T. *Macromolecules* 1991, **24**, 240
7 Hashimoto, T., Tanaka, H. and Hasegawa, H. *Macromolecules* 1990, **23**, 4378
8 Sakurai, K., Macknight, W. J., Lohse, D. J., Schulz, D. N. and Sissano, J. A. *Macromolecules* 1994, **27**, 4941
9 Liu, L., Li, H., Jiang, B. and Zhou, E. *Polymer* 1994, **25**, 5511

10 Nojima, S., Kato, K., Yamamoto, S. and Ashida, T. *Macromolecules* 1992, **25,** 2237
11 Nojima, S., Satoh, K. and Ashida, T. *Macromolecules* 1991, **24,** 942
12 Nojima, S., Kato, K., Ono, M. and Ashida, T. *Macromolecules* 1992, **25,** 1922
13 Ueki, T., Kataoka, M., Inoko, Y. Amemiya, Y., Izumi, Y., Tagawa, H. and Muroga, Y. *Biophys. Chem.* 1985, **23,** 115
14 Nojima, S., Yamamoto, S. and Ashida, T. *Polym. J.* in press
15 Nojima, S., Nakano, H., Takahashi, Y. and Ashida, T. *Polymer* 1994, **35,** 3479