Crystallization behaviour of a microphase-separated diblock copolymer

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(Received 11 May 1993; revised 24 May 1993)

The crystallization behaviour of a microphase-separated diblock copolymer, ε-caprolactone-*block*-butadiene (PCL-*b*-PB), was observed by small-angle X-ray scattering employing synchrotron radiation. The Avrami analysis at the early stage of crystallization did not show any significant difference between PCL-*b*-PB and a poly(ε-caprolactone) homopolymer (PCL), suggesting that the initially existing microphase structure does not affect the early stage of crystallization. In the late stage, the crystallization of PCL-*b*-PB was significantly retarded compared to the case of PCL, and the rate was dependent on the microphase structure and/or molecular characteristics of the copolymer.

Introduction

The crystallization of block copolymers is complicated by the existing microphase structure (sphere, cylinder or lamella) when they are cast from a good solvent or quenched from high temperature[1-9]. When the molecular weight of block copolymers is high enough, they show a path-dependent morphology due to competition between the crystallization and microphase separation[2-4]. Morphological control is therefore possible by adjusting the spinodal temperature of microphase separation T_s by changing the molecular weight and/or block ratio of the copolymer.

In a recent study[8], we investigated such a process in a crystalline–amorphous diblock copolymer, ε-caprolactone-*block*-butadiene (PCL-*b*-PB), by small-angle X-ray scattering employing synchrotron radiation (SR-SAXS). This system had T_s close to T_m (melting temperature of the PCL block), so that the morphology formation, induced by quenching from a homogeneous state to a crystallization temperature T_c, was characterized by the appearance of microphase structure during a short period until crystallization of the PCL block started. It is the first time this type of phase transformation has been observed; this is due to the strong X-ray source of synchrotron radiation recently available[10]. In this study, we analyse quantitatively the early and late stages of crystallization of PCL-*b*-PB which presents a microphase structure (lamella or sphere) at high temperature ($> T_m$).

Experimental

Materials. Two PCL-*b*-PBs, designated B7 and B8, were synthesized by successive anionic polymerization under vacuum. Details of the synthesis are described elsewhere[8]. The copolymers were characterized by gel permeation chromatography (g.p.c.), and the PCL content (volume fraction) in the copolymer was evaluated by ^{1}H n.m.r. (Varian Gemini-200). The melting temperature of the PCL block T_m was also measured by d.s.c. The results of characterization are as follows: B7 ($M_w = 12\,400$, $M_w/M_n = 1.10$, PCL:PB = 61:39, $T_m = 55°C$); B8 ($M_w = 15\,900$, $M_w/M_n = 1.08$, PCL:PB = 20:80, $T_m = 42°C$). B7 and B8 have a spinodal temperature of microphase separation T_s far above T_m, and the SAXS curve at $60°C$ ($> T_m$) indicates that B7 has a lamellar microphase structure and B8 a spherical structure with the PCL block inside. Therefore, the crystallization starts from the existing microphase structure of the diblock copolymer.

SR-SAXS measurements. The SR-SAXS experiment was carried out at the 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 equipment and the experimental procedures are described elsewhere[8,11]. The SAXS intensity was corrected for the decrease of the ring current and background scattering. Since SAXES has point focusing optics, the scattered intensity was not corrected for the smearing effect by the finite cross section of the primary beam.

Results and discussion

Time-resolved SAXS curves. In our previous paper[8], we showed time-resolved SAXS curves for PCL-*b*-PB with $T_s \simeq T_m$, and diffraction due to the microphase structure appeared during a short period until crystallization of the PCL block started. *Figure 1* shows the time-resolved SAXS curves for B8, where the copolymer already had a spherical microphase structure at $60°C$ and crystallization of the PCL block started from this structure. The SAXS curve just after quenching was similar in shape to that at $60°C$, i.e. there was a sharp diffraction arising from the regular microphase structure. At time $t = 110$ s another scattering maximum appeared at a lower angle. This second maximum grew with t and simultaneously the diffracted intensity gradually decreased. Finally ($t = 1330$ s) the diffraction almost disappeared, although a shoulder remained at the angular position of

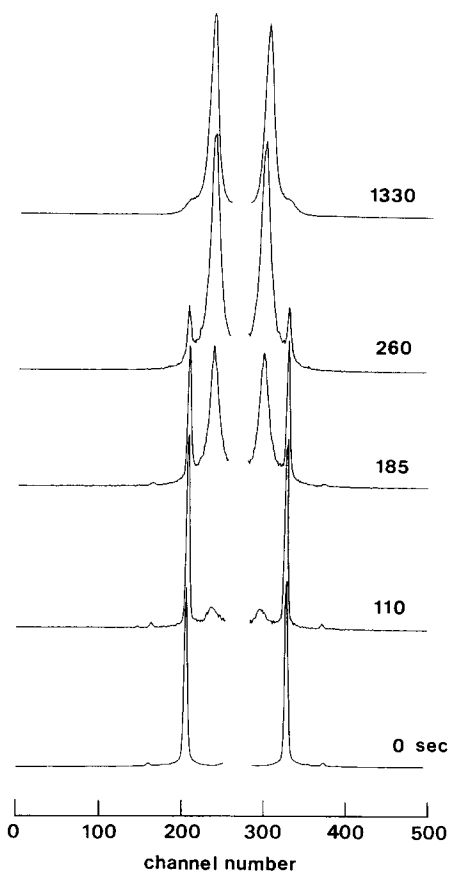**Figure 1** Time-resolved SAXS curves plotted against channel number for B8 quenched from ~60°C to $T_c = 28.4°C$. Channel number 266 corresponds to zero angle, and each SAXS curve is symmetrical against this channel. The number on each curve represents the time (in s) elapsed since the sample was quenched. The SAXS curve of 0 s is the accumulation during a period of 300 s, and the others are those of 10 s. The SAXS curve for 1330 s is reduced in magnitude by a factor of four for clarity

the diffraction. A conventional SAXS measurement revealed that the diffraction shoulder finally disappeared at a large t. *Figure 1* indicates that the regular microphase structure, with a characteristic size of 13.1 nm, was steadily replaced by the crystalline morphology with a long spacing of 22.2 nm during phase transformation.

It is interesting to investigate the molecular weight dependence of the rate of morphology formation. The enhanced entanglement of higher molecular weight copolymers is expected to play an important role in determining the rate of morphology formation. Veith *et al.*[2], for example, observed a significant path-dependent morphology for a nylon 6-poly(dimethyl siloxane) diblock copolymer with a sufficiently high molecular weight and discussed the molecular weight dependence of the final morphology. The molecular weight and block ratio dependences of the final morphology in the present PCL-*b*-PB systems will be described in a forthcoming publication[12].

Early stage of crystallization. The early stage of polymer crystallization is usually analysed by the Avrami equation[13–15]. The volume fraction of the crystal at time t, $X(t)$, is given by:

$$X(t) = 1 - \exp(-Kt^n) \tag{1}$$

where K is a rate constant and n is the Avrami exponent expressing the mode of crystallization. The volume

change evaluated from a dilatometric measurement is usually used for $X(t)$. The intensity maximum $I_{max}(t)$ at t scattered from the crystalline morphology, an alternate structure of the lamellae and amorphous layers, was previously used instead of $X(t)$ after normalizing it by the final intensity $I_{max}(\infty)$[11], as:

$$X(t) = I_{max}(t)/I_{max}(\infty) \tag{2}$$

Generally speaking, the scattered intensity (and also volume fraction of the crystal) is small at the early stage of crystallization and is difficult to extract from a comparable background scattering. It is therefore difficult to evaluate n with acceptable accuracy. This is the most ambiguous point in the Avrami analysis since the evaluation of n needs to take a double logarithm of $X(t)$. If the diffracted intensity $I'_{max}(t)$ from the microphase structure may be used as $X(t)$, then the analysis will be more reliable because $I'_{max}(t)$ is strong enough at the early stage of crystallization. In our previous paper[8] we found that the phase transformation occurred directly from the microphase structure into the crystalline morphology, and no third phase (for example, a disordered phase) appeared during the transition. That is, the system is a mosaic structure consisting of the microphase structure and crystalline structure at every t, and we can state:

$$X(t) = 1 - I'_{max}(t)/I'_{max}(0) \tag{3}$$

where $I'_{max}(0)$ is the diffracted intensity just before crystallization. Inserting equation (3) into equation (1), we can obtain n from the plot of $\log\{-\log I'_{max}(t)/I'_{max}(0)\}$ against $\log t$.

Figure 2 shows an example of the Avrami plot evaluated from the t dependence of the scattered intensity (equation (2)) and diffracted intensity (equation (3)) for B7 at $T_c = 40.4°C$. Here, data from the first 25% in intensity were used because the Avrami analysis is valid only for the early stage of crystallization. The plot obtained from the diffracted intensity has more data points than that from the scattered intensity at the beginning of crystallization, and seems to make the Avrami analysis more reliable. The Avrami exponent n evaluated for B7 and B8 ranged between 2 and 3, irrespective of T_c; this is indistinguishable from n evaluated for the PCL homopolymer and also the value
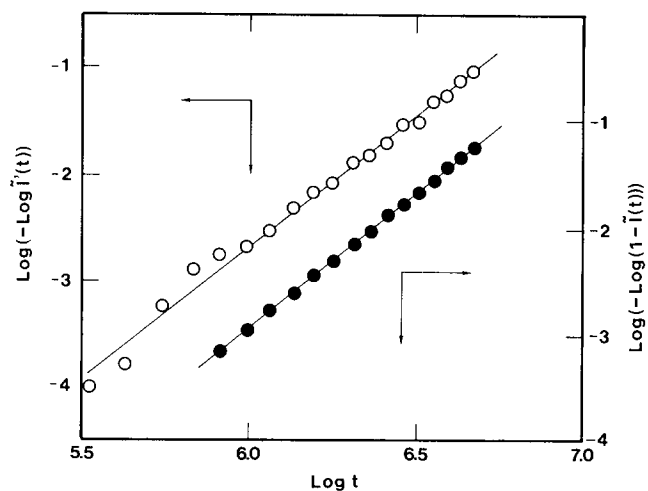

Figure 2 Avrami plot based on the scattered intensity maximum (●) and the diffracted intensity maximum (○) for B7 crystallized at 40.4°C

$\tilde{I}'(t) = I'_{max}(t)/I'_{max}(0)$ and $\tilde{I}(t) = I_{max}(t)/I_{max}(\infty)$
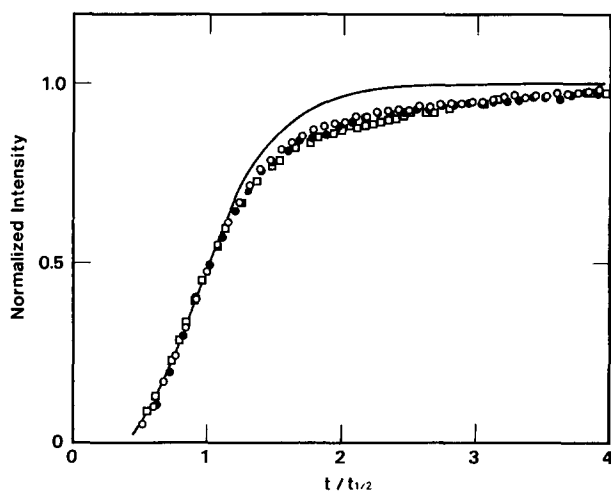
Figure 3 Normalized intensity maximum plotted against reduced time, $t/t_{1/2}$, for B8 at 26.0 (O), 26.7 (●) and 28.4°C (□). The solid curve represents the result of the PCL homopolymer at various crystallization temperatures[11]

of n widely reported for crystalline homopolymers. For example, a value of n ranging from 2 to 3 is reported for a high density polyethylene[16], poly(ethylene oxide)[17] and a compatible blend of poly(ε-caprolactone) and poly(vinyl chloride)[18,19]. In these studies, the crystallization process was assigned to be two-dimensional with a heterogeneous nucleation on the basis of the Avrami analysis and the spherulite observation. The agreement of n mentioned above suggests that the mode of nucleation is the same in PCL-b-PB and general crystalline homopolymers, so that, whatever the initially existing microphase structure, it does not affect the early stage of crystallization.

Late stage of crystallization. There is no practical theory available to evaluate quantitatively the late stage of polymer crystallization. In our previous study of a binary blend of PCL and polystyrene oligomer (PCL/PSO)[11], we found that the driving force for the whole crystallization process was the same in PCL and PCL/PSO, by plotting the normalized intensity maximum (equation (2)) against the reduced time. *Figure 3* shows such a plot of $I_{max}(t)/I_{max}(\infty)$ against $t/t_{1/2}$ for B8 at each T_c, where $t_{1/2}$ represents the half-time of crystallization, i.e. the time necessary to reach the half-value at the angular position of the maximum intensity. The solid curve in the figure represents a master curve obtained for the PCL homopolymer[11]. Although the t dependence of the intensity maximum shows different curves according to T_c, they coincide with each other and make one master curve in *Figure 3*. This suggests that the overall feature of crystallization is the same irrespective of T_c[11]. The data points agree well with the solid curve until $t/t_{1/2}$ reaches 1, which is consistent with the conclusion of the Avrami analysis at the early stage of crystallization. The master curve at $t/t_{1/2} > 1$ is, on the other hand, significantly different from the solid curve; the copolymer crystallization is retarded when it is compared with the PCL crystallization. In particular, the normalized intensity for PCL-b-PB

gradually increases at $t/t_{1/2} > 2$ towards the completion of crystallization. This asymptotic behaviour is also dependent on the initially existing microphase structure and/or molecular characteristics of the copolymer; the master curve for B7 is located between those of PCL and B8 in the figure. *Figure 3* indicates that the crystallization behaviour of PCL-b-PB is not the same as that of PCL at the late stage of crystallization. Another factor, for example, competition between crystallization and decay of the microphase structure, has to be taken into account to understand the morphology formation of such copolymers at the late stage of crystallization.

Conclusions

We found that the crystallization behaviour of PCL-b-PB was significantly different from that of PCL at the late stage of crystallization, although the behaviour at the early stage is quite similar in both. The SAXS results show no specific morphology appearing during phase transformations in this diblock copolymer. It is therefore useful to study the morphologies during crystallization by visual techniques such as electron microscopy as well as those before and after crystallization. This will give additional information about the crystallization of microphase-separated copolymers, and in particular about the cooperation between crystallization and decay of the microphase structure. This study is currently being carried out and will be published soon[12].

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