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Formation of lamellar structure by competition in crystallization of both components for crystalline−crystalline block copolymers

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Abstract

Crystallization and structure formation of poly(ethylene oxide)−poly(ε-caprolactone) block copolymers (PEG−PCL) in which the melting temperatures of the components are close to each other were elucidated using differential scanning calorimetry (DSC), small-angle X-ray scattering (SAXS) and wide-angle X-ray diffraction (WAXD) techniques. The diblock copolymers with 33, 46 and 59 wt% of PEG composition formed ordinary *single* spherulites similar to those of PCL homopolymers, while concentric double-circled spherulites appeared for the PCL−PEG−PCL triblock copolymer with 66 wt% PEG composition as observed previously. For the diblock copolymers, despite of the ordinary appearance of the *single* spherulites, the DSC thermograms and the WAXD patterns indicated the crystallization of PEG as well as PCL. The time-resolved SAXS profiles for the diblock copolymers showed that long spacings of the crystal lamellae decreased stepwise in the crystallization process. Synthesizing these results for the *single* spherulites, it was concluded that PCL crystallized first followed by the crystallization of PEG with preservation of the PCL crystal lamellar structure. This means that PEG must crystallize within confined space between the formerly formed PCL crystal lamellae. Such confined crystallization of PEG caused the suppressed melting temperature, crystallinity and crystallization rate especially in the smaller PEG compositions. In the melting process of the diblock copolymers, it was observed that the PEG component first melted with a stepwise increase in the long spacing.

Keywords: Block copolymer; Crystallization; SAXS

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1. Introduction

Crystallization and formation of higher-order structure of crystalline block copolymers have been studied extensively in recent years [1−17]. The structure formation in crystallization can be classified into two patterns, that is, whether the melt microphase separation structure is destroyed or maintained. In the crystallization by quenching from the disordered to ordered state, the resulting structure is determined by complex interplay between microphase separation and crystallization [2,3]. On the other hand, in the crystallization from microphase-separated melts, whether a constituent amorphous block is rubbery or glassy at crystallization temperatures is an important factor in the structure formation of crystalline−amorphous block copolymers. For the block copolymers having a rubbery amorphous component, whether or not crystallization destroys the microphase separation structure depends on the morphology and segregation strength in the melt as well as molecular weight and crystallization temperature [4,5,7,14]. In contrast, for block copolymers having a glassy amorphous component, the microphase separation structure is maintained completely [6,9,13,15,17].

Crystallization behavior of block copolymers having two or more crystalline components has not been investigated so extensively. In the crystallization of such block copolymers, competition of crystallization among the crystalline components as well as the interplay between microphase separation

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Table 1
Characteristics of polymers

Sample	$\overline{M}_{n,PEG} \times 10^{-3}$[a]	$\overline{M}_{n,PCL} \times 10^{-3}$[b]	$\overline{M}_w/\overline{M}_n$[c]	Composition[d] (wt%)	
				PEG	PCL
AB-33	5.0	10.0	1.35	33	67
AB-46	5.0	5.8	1.32	46	54
AB-59	5.0	3.5	1.28	59	41
ABA-66	8.0	2.0×2	1.22	66	34
PEG	5.0	–	–	100	–
PCL	–	80.0	–	–	100

[a] Nominal value.
[b] Determined by ^{1}H NMR.
[c] Determined by GPC.
[d] Calculated from $\overline{M}_{n,PEG}$ and $\overline{M}_{n,PCL}$.

and crystallization should be important. Crystallization of the leading component should destroy the microphase separation structure in the same way as weakly segregated crystalline–amorphous block copolymers because the glass transition temperature of crystalline polymers is generally low. Therefore, the other components which crystallize latterly are left within the confined space determined by the crystal lamellae of the firstly crystallizing component. Consequently priority of crystallization becomes a major factor that determines the crystallization behavior and the resulting higher-order structure. Therefore, the relation between the melting temperatures T_m values of the crystalline components should be important. For the block copolymers in which T_m of one component is sufficiently higher than those of the others, the high-T_m component must crystallize first, followed by the others. This means that the components that crystallize latterly must crystallize within the crystal lamellar structure of the component that crystallized first. Nojima et al. investigated the crystallization and structure formation of poly(ε-caprolactone)–*block*–poly(ethylene) (PCL–PE) in which T_m of PE is much higher than that of PCL ($T_{m,PE} \sim 100\,°C$, $T_{m,PCL} \sim 55\,°C$), and found that the crystallization of PCL chains was greatly affected by the crystal lamellae of the firstly crystallized PE [18]. Hamley et al. reported confined crystallization of PCL within poly(L-lactide) (PLLA) crystal lamellae for PCL–PLLA block copolymers, in which T_m of PLLA is much higher ($T_{m,PLLA} \sim 170\,°C$) than that of PCL [19]. Albuerne et al. explored the crystallization of poly(*p*-dioxanone)(PPDX)–PCL block copolymers ($T_{m,PPDX} \sim 100\,°C$), and found that, as well as being confined between the crystal lamellae of PPDX, the crystallization of PCL was accelerated because of the PPDX crystal lamellae acting as nucleating agents for PCL [20]. In the case that T_m values of the components are close to each other, on the other hand, almost the same supercooling degrees may cause competition in crystallization between different components. Such competition should affect the crystallization behavior and the resulting higher-order structure such as crystal lamellae and spherulites. In the present study, we focus on formation of crystal lamellar structure in block copolymers, poly(ethylene oxide)–*block*–poly(ε-caprolactone) (PEG–PCL), having two crystalline blocks whose melting temperatures are close (within 10 °C) to each other. Small-angle X-ray scattering and wide-angle X-ray diffraction (SAXS and WAXD), polarizing optical microscopy (POM) and differential scanning calorimetry (DSC) measurements were performed in order to clarify the formation of

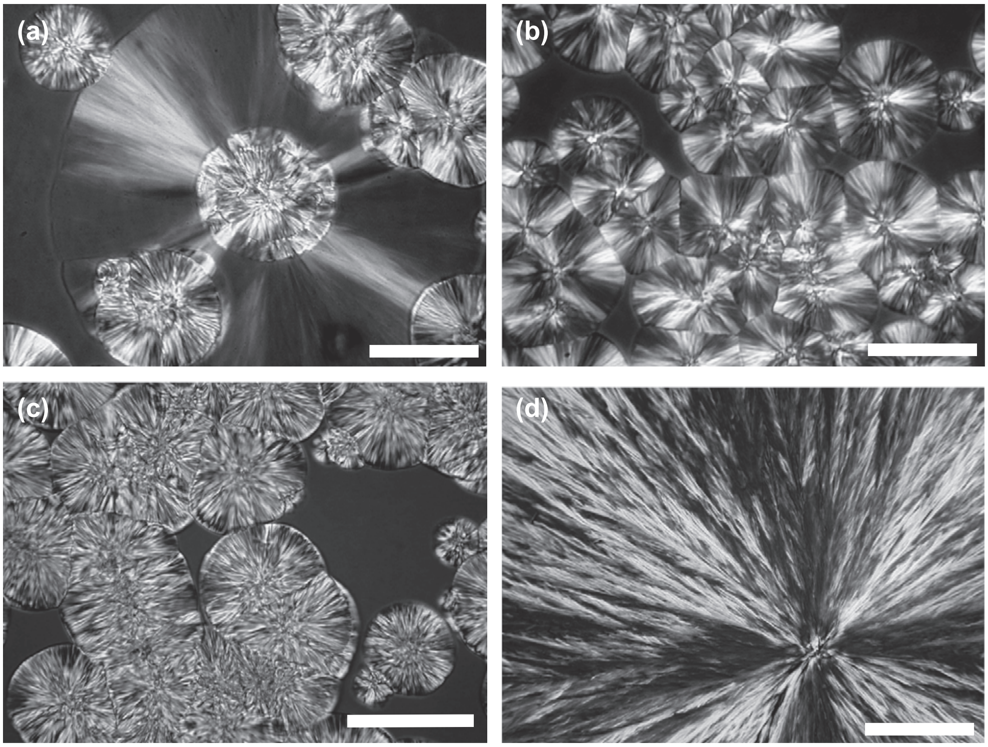

Fig. 1. Polarizing optical micrographs of (a) ABA-66, (b) AB-46, (c) PCL homopolymer and (d) PEG homopolymers. The scale bar is 100 μm.

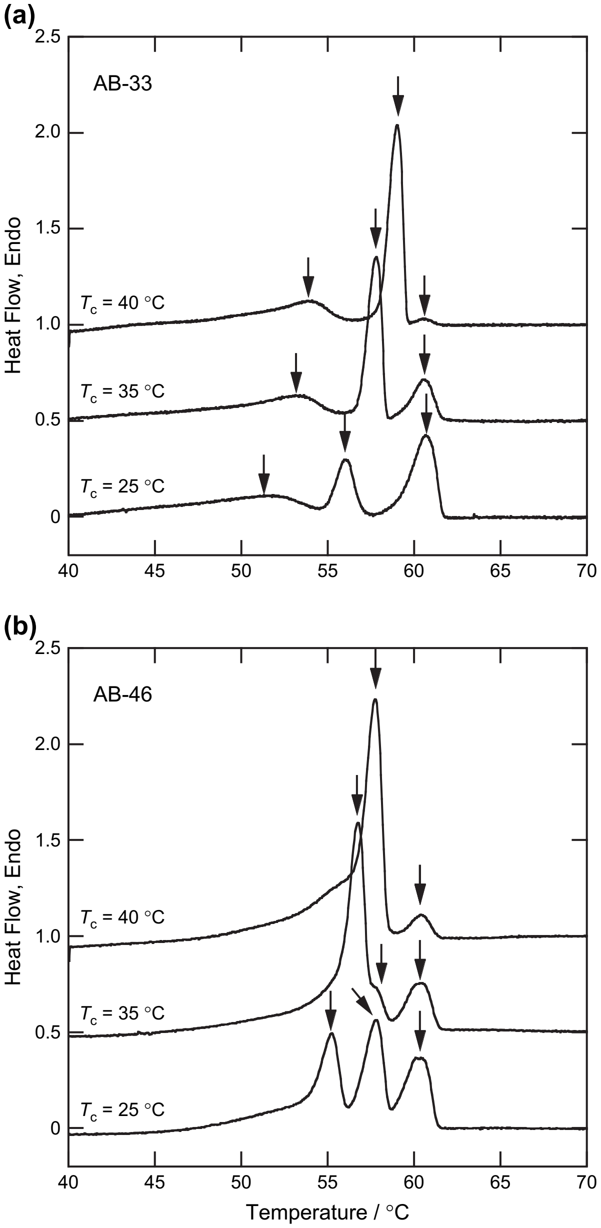

Fig. 2. DSC thermograms for the melting of AB-33 and AB-46 crystallized at the indicated temperatures.

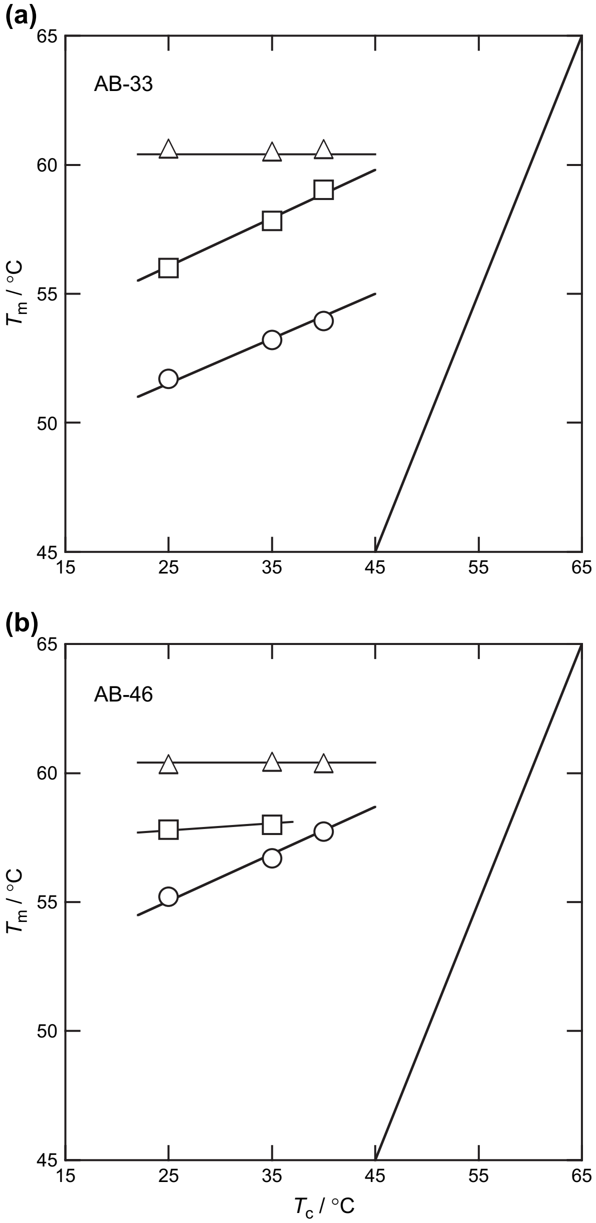

Fig. 3. Hoffman-Week's type plots for the melting temperatures (peak top) estimated from the DSC thermograms in Fig. 2.

complex structure composed of crystal lamellae of PEG and PCL.

2. Experimental section

2.1. Materials

PEG–PCL diblock and PCL–PEG–PCL triblock copolymers were prepared by bulk polymerization of ε-caprolactone initiated with hydroxy groups at chain ends of PEG. Poly(ethylene glycol) monomethyl ether supplied kindly by NOF Co. and common PEG purchased from Aldrich Co. were used for the syntheses of the di- and triblock copolymers, respectively. Diol contained in *monomethyl ether* PEG used here is virtually undetectable according to the description in the catalog. Details of the synthesis of the block copolymers are described elsewhere [21]. The characteristics of the block copolymers together with those of PEG and PCL homopolymers are listed in Table 1. The diblock copolymers have a PEG chain with a molecular weight of 5.0 (kg/mol) and a PCL with a molecular weight ranging from 3.5 to 10.0 (kg/mol), resulting in the PEG contents varying from 33 wt% to 59 wt%.

2.2. Sample preparation and measurements

The polymers were dissolved in THF and then casted from 5 wt% solution to form films. The films were dried for three

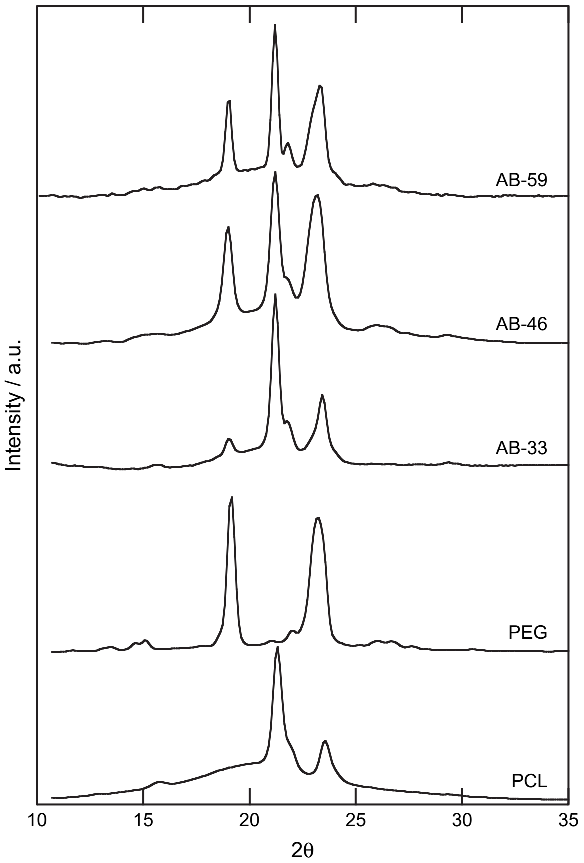

Fig. 4. WAXD profiles at each temperature in the melting process of the diblock copolymers and the homopolymers. $T_c = 35$ °C.

days at room temperature and were then dried under a vacuum overnight. The casted films were packed in DSC sample pans and sample cells for SAXS and WAXD measurements. The sample cells had a path length of 1 mm and were sealed with polyimide films.

For all the measurements, the sample was first annealed at 90 °C, which is higher than T_m of both PCL and PEG, for 30 min. After that, the sample was quenched rapidly to a desired crystallization temperature T_c in the temperature controlled sample holder and then isothermally crystallized. After the crystallization was completed, the sample was subsequently heated in order to observe the melting behavior. The heating rate was 1.5 °C/min except for DSC measurements.

The morphology of the spherulites was observed by POM under crossed polarizers using an OLYMPUS BH-2 equipped with a digital camera system and a calibrated hot stage. The melting behavior was analyzed at a heating rate of 10 °C/min with a Perkin–Elmer Pyris1 DSC calorimeter calibrated with indium and tin. The WAXD measurements were performed using CuKα radiation ($\lambda = 0.154$ nm) with a pinhole collimated camera (Rigaku Nano Viewer) and an imaging plate as a detector. Time-resolved SAXS experiments were performed using synchrotron radiation at beam line BL-10C of the Photon Factory at the Institute of Materials Structure Science of the High Energy Accelerator Research Organization in Tsukuba, Japan [22]. The SAXS data were collected in 15-s frames separated by a waiting-time of 5 s using a position sensitive proportional counter (PSPC).

3. Results and discussion

3.1. Spherulite morphology

Fig. 1 shows POM micrographs of typical spherulites of AB-46 and ABA-66 crystallized at 35 °C together with those of PEG and PCL homopolymers. As we reported previously [21], unique concentric *double spherulites* are observed for the triblock copolymer. Based on the spherulite growth rate and the temperature dependence of the WAXD and SAXS profiles in melting, we concluded that the different texture between the inner and the outer part of the *double spherulites* comes from the difference in the dominant component in crystallization. In the crystallization of the triblock copolymers, PCL crystallizes first to form the inner part of the *double spherulite*, followed by the formation of the outer part in which PEG crystallizes predominantly. This means that the dominant component changes from PCL to PEG during the formation of the spherulites. On the other hand, the spherulites for the diblock copolymer AB-46 shown in Fig. 1 are not *double* but ordinary *single spherulites.* All the diblock copolymers studied here showed only *single spherulites*, while *double spherulites* were reported to appear for the triblock copolymers with PEG contents corresponding to those of the present diblock copolymers [21]. The size and the textures of the *single spherulites* for the diblock copolymers are similar to those for the PCL homopolymers and for the inner parts of the *double spherulites* formed in the triblock copolymers. The appearance of the spherulites observed for the diblock copolymers may suggest that, as in the case of the inner part of the *double spherulites*, PCL is a dominant component in the crystallization and the crystal lamellae structure of PCL is preserved over the crystallization process. Supposing that PCL is a dominant component in the crystallization of the diblock copolymers, then do PEG chains remain amorphous or not?

3.2. Behavior of crystallization and melting

Fig. 2 shows DSC thermograms in melting for AB-33 and AB-46 crystallized at the indicated temperatures. Despite the ordinary appearance of the spherulites, the thermograms are somewhat complicated. Two or three melting peaks are observed depending on the crystallization temperature as well as the PEG content, which may imply the crystallization of the both components. The melting temperatures are plotted against the crystallization temperatures T_c as Hoffman-Week's type plots in Fig. 3. Since the highest T_m is almost independent of T_c and the endotherm becomes smaller with increasing T_c for both AB-46 and AB-33, these are assigned to the melting of the recrystallized chains (PCL or PEG). The lower two peaks, one of which for AB-46 at $T_c = 40$ °C may be hidden behind the largest peak, can be attributed to melting of the crystal lamellae formed at each T_c indicated, because they depend on T_c. The area of these lower two peaks depends on the

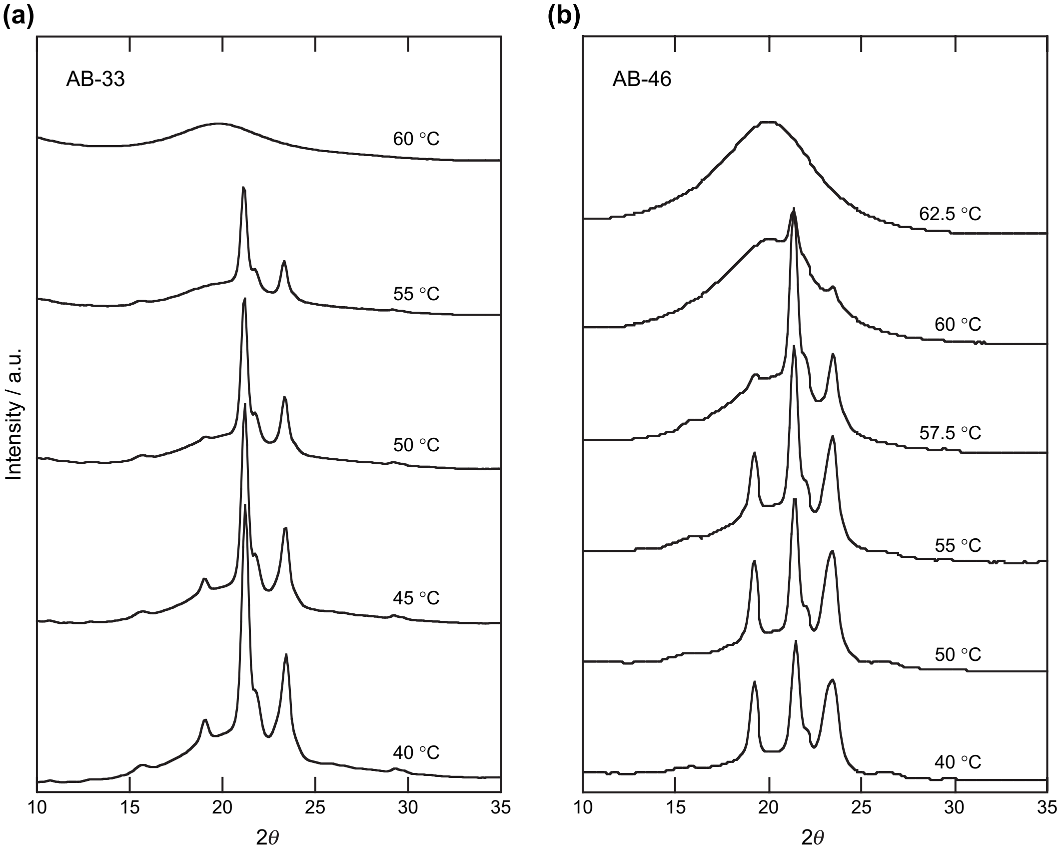

Fig. 5. The WAXD profiles for the melting of AB-33 and AB-46. $T_c = 35$ °C.

copolymer composition. In particular, the lowest melting peaks for AB-33 are very small and broad compared with those for AB-46.

WAXD patterns of AB-33, AB-46 and AB-59 crystallized at 35 °C are shown in Fig. 4, compared with those of PEG and PCL homopolymers. For all the block copolymers, the diffraction patterns indicate the crystallization of PEG as well as PCL, which is contrary to the appearance of the ordinary *single spherulites*. Fig. 5 shows the WAXD profiles in the melting process for AB-46 and AB-33 crystallized at 35 °C. For both the block copolymers, the PEG crystal melts at lower temperatures than PCL. The diffraction peaks from PEG in AB-33 and AB-46 disappear at approximately 50 °C and 57.5 °C, respectively, whereas the PCL crystal remains up to approximately 60 °C. These WAXD results can explain the multiple melting peaks in the DSC thermograms shown in Fig. 2. The lowest T_m in the DSC thermograms can be assigned to the melting of PEG, and the higher two T_m values can be attributed to the melting of PCL. The small and broad endotherms at the lowest T_m (Fig. 2a) coincide with the small WAXD peaks from PEG in AB-33. Since the highest T_m values are independent of T_c and are almost the same between AB-46 and AB-33, they can be attributed to the melting of the recrystallized crystal lamellae of PCL.

Fig. 6 depicts the time evolution of WAXD patterns in the crystallization of AB-33 and AB-46. PCL crystallizes first, followed by PEG. The predominance of PCL in the crystallization is considered to be a result of the lower surface free energy, which results in a large nucleation rate, as shown in the early stage of formation of concentric *double spherulite* of the triblock copolymers [18]. In AB-33, as shown in Fig. 6a, crystallization of PEG is very slow and is barely detected after three days. The difficulty with the crystallization of PEG in AB-33 may come from the small PEG composition or small space confined by PCL crystal lamellae as discussed later.

3.3. Crystal lamellar structure

From the above results of DSC and WAXD, the presence of PEG crystallites is confirmed even in the *single spherulites* formed for the diblock copolymers. SAXS experiments were carried out in order to obtain information about the crystal lamellar structure. Fig. 7 shows the time and temperature dependences of the SAXS profiles for the crystallization and melting processes, respectively, of AB-46. The vertical and horizontal axes show the Lorentz-corrected scattering intensity and the magnitude of scattering vector q ($=(4\pi/\lambda)\sin(\theta/2)$), respectively, where λ and θ are the wavelength of the incident beam and the scattering angle, respectively. In the melt, no scattering peak can be observed because of the very small difference in electron density between PCL and PEG (341.6 and 354.3 e/nm^3 at 80 °C for amorphous PCL and PEG,

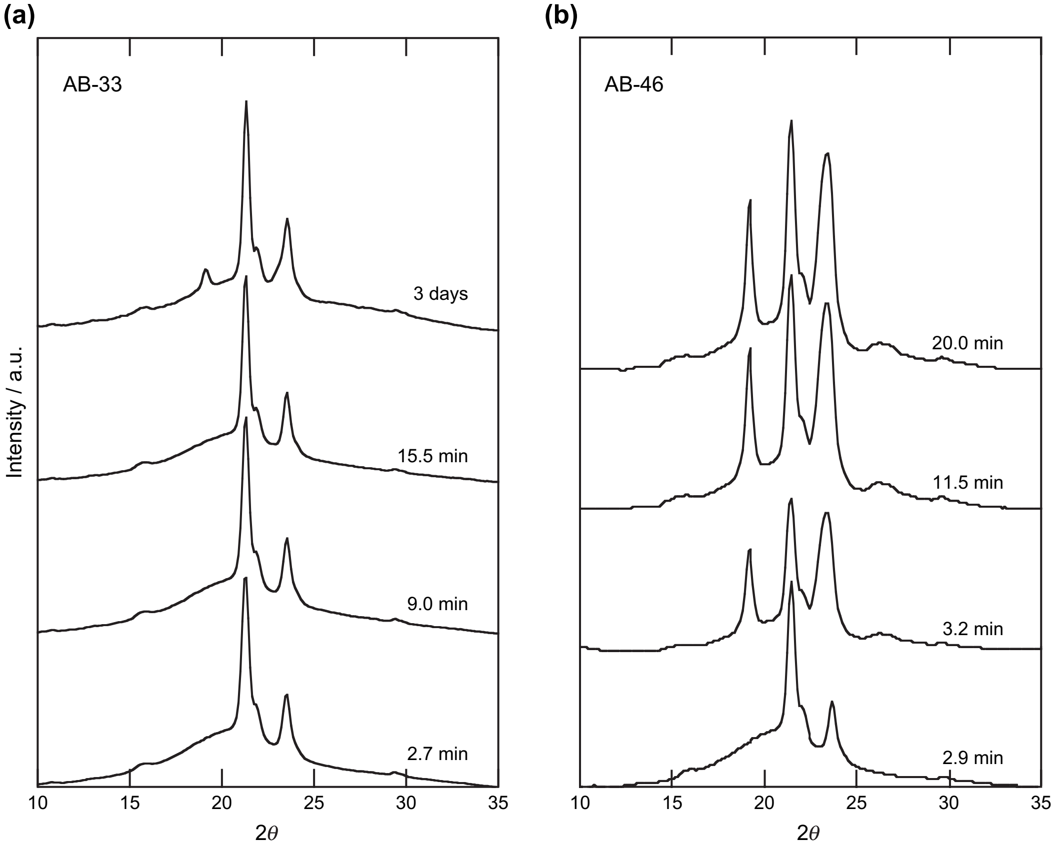

Fig. 6. Time evolution of the WAXD profiles for the crystallization of AB-33 and AB-46. $T_c = 35$ °C.

respectively, as well as 392.9 and 403.2 e/nm^3 for crystalline PCL and PEG, respectively [23]). As we reported previously [21], the SAXS profiles of the ABA triblock copolymers that form concentric *double spherulites* have two scattering peaks, which disappear at different temperatures as the temperature increases. Based on POM observation of the melting behavior of the *double spherulite*, we concluded that the two long spacings were due to the different crystal lamellae structure in the inner and outer parts of the *double spherulites*. For the diblock copolymers, on the other hand, as shown in Fig. 7, only one long spacing is observed. This coincides with the ordinary appearance of the *single spherulite*, in contrast to the triblock copolymers. The scattering peak shifts toward a higher q in the process of crystallization (Fig. 7a). This means that the long spacing decreases as the crystallization proceeds. Conversely, the peak shifts toward a lower q in the melting process (Fig. 7b), suggesting an increasing long spacing. This behavior of the SAXS profile observed for the diblock copolymers is quite similar to that reported for some homopolymers [24,25]. Hama and Tashiro [24] studied the isothermal crystallization of poly(oxymethylene) by time-resolved infrared spectra, DSC, SAXS and WAXD. They concluded that the long spacings of the initially formed stacked lamellae decrease because of the insertion of newly formed lamellae between the original lamellae. For the system studied here, because SAXS cannot distinguish between PEG and PCL because of the small difference in electron density, the shifting of the peak toward a higher q just indicates the insertion of new lamellae between the crystal lamellae of PCL. Considering with the DSC and WAXD results, it is suggested that PCL crystallizes first, followed by crystallization of PEG remaining between the PCL crystal lamellae. The crystallization of PEG between the PCL crystal lamellae shortens the long spacings, resulting in the peak shift toward a higher q. In Fig. 8, time evolution of the long spacing d estimated from the peak position q_m ($d = 2\pi/q_m$) is shown against logarithm of time. The initially observed d, which is from the long spacing of the formerly formed PCL crystal lamellae, changes stepwise to a smaller value. The stepwise change in d should be due to the crystallization of PEG. Fig. 9 depicts the time dependence of invariant Q calculated by integration of the Lorentz-corrected scattering profiles:

$$Q = \int_0^\infty I q^2 \, \mathrm{d}q,$$

which is proportional to the product of the crystallized and the amorphous phases, indicating time evolution of the degree of crystallinity. Q values, which increase monotonically with time, also show steps at the same time as d values. The stepwise changes in Q and d correspond to the insertion of PEG

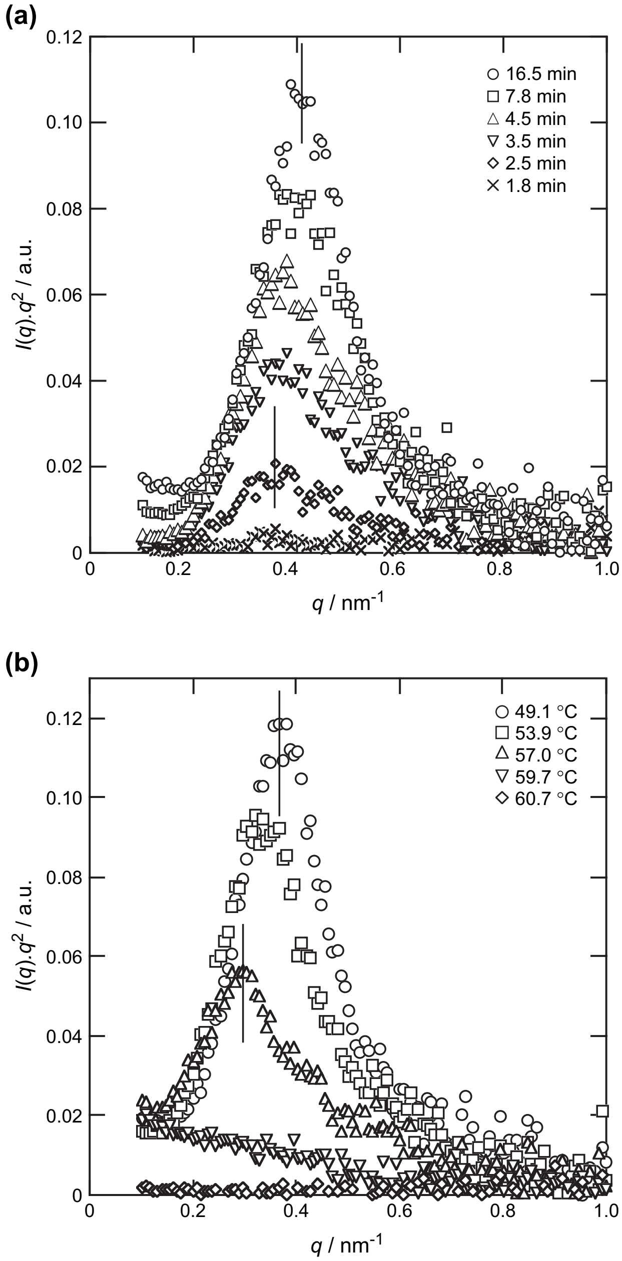

Fig. 7. Evolution of Lorentz-corrected SAXS profiles in (a) crystallization and (b) melting processes of AB-46. $T_c = 35$ °C.

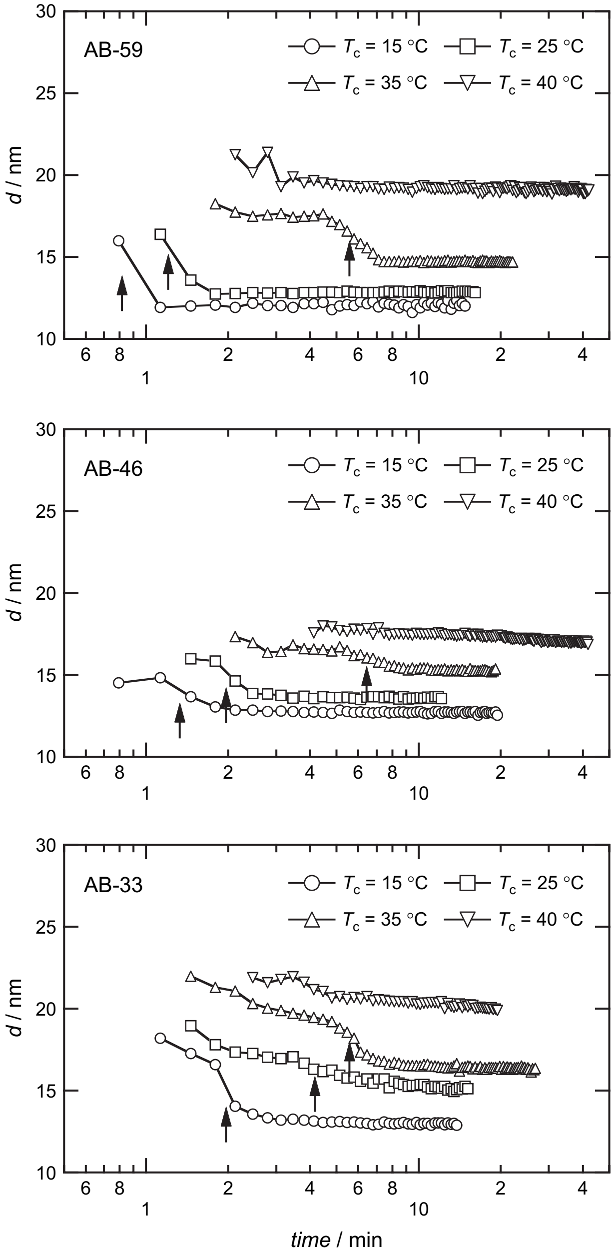

Fig. 8. Time dependence of the long spacing d in the crystallization of the diblock copolymers at the indicated temperatures.

crystallites between the initially formed PCL crystal lamellae. In the melting process, although such stepwise changes are not so clear compared with those in the crystallization, steps in Q and d can be observed in some conditions (Figs. 10 and 11), which suggest that the firstly melting PEG makes the long spacing even longer, followed by the melting of the PCL crystal lamellae.

3.4. Confinement of crystallization between crystal lamellae

As described thus far, in the crystallization of PEG–PCL block copolymers, PCL crystallizes first, followed by the crystallization of PEG chains with the preservation of the PCL lamellar structure. This means that PEG must crystallize within the space confined by the PCL crystal lamellae. Crystallization behavior within the confined space has been studied in recent years for crystalline block copolymers having glassy amorphous components [6,9,13,15,17]. In crystallization of such block copolymers from microphase-separated melt, crystallinity, crystallization rate and T_m are lowered depending on the size and morphology of the microphase separation structure: crystallization is suppressed within smaller and isolated (spherical or cylindrical) microdomains because such microdomains are surrounded by a rigid matrix [13,17]. The present study also showed a reduction in both T_m and crystallinity of

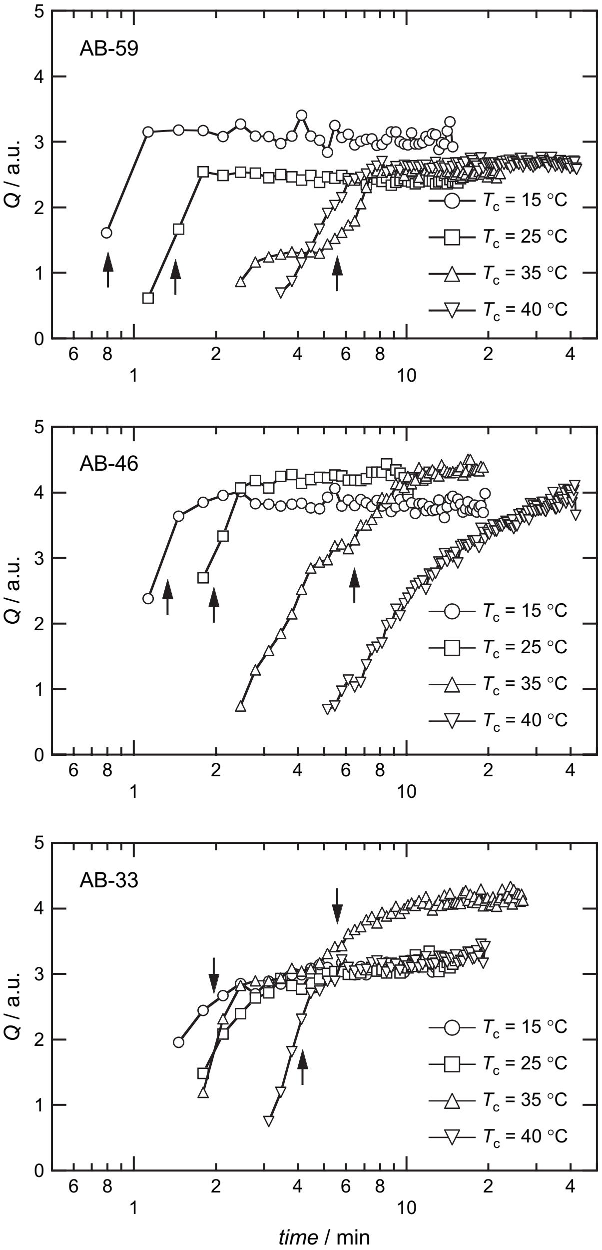

Fig. 9. Time dependence of the invariant Q in the crystallization of the diblock copolymers at the indicated temperatures.

PEG. Despite of the higher equilibrium melting temperature of PEG than that of PCL for their homopolymers, the PEG component melts first at lower temperatures for all diblock copolymers. The reduction of T_m is more remarkable in AB-33 than in AB-46. The crystallization rate of the PEG component is also much suppressed in AB-33. These phenomena may come from the fact that the PEG component must crystallize within microspace confined by the rigid PCL crystalline lamellae.

Nojima et al. [18] reported the crystallization behavior of PE–PCL block copolymers, in which PE crystallizes first, followed by the crystallization of PCL because the T_m of PE is sufficiently higher than that of PCL. They found that, in the crystallization of PE–PCL, the firstly formed crystal lamellar structure of PE was destroyed by the crystallization of PCL at relatively high crystallization temperatures, whereas PCL crystallizes between the PE lamellae with preserving the lamellae structure at lower temperatures. On the other hand, confined crystallization of a low-T_m component between the crystal lamellae of the firstly crystallized component has been reported by some other researchers for double crystalline block copolymers, such as PCL–PPDX and PCL–PLLA [19,20]. In the crystallization of PEG–PCL studied here, the crystal lamellae structure of PCL was preserved even after the crystallization of PEG. The factor that governs whether the latterly crystallizing component destroys the formerly formed lamellae structure remains unclear. More systematic experimental data are desired for clarification of lamellar formation in crystalline–crystalline block copolymers.

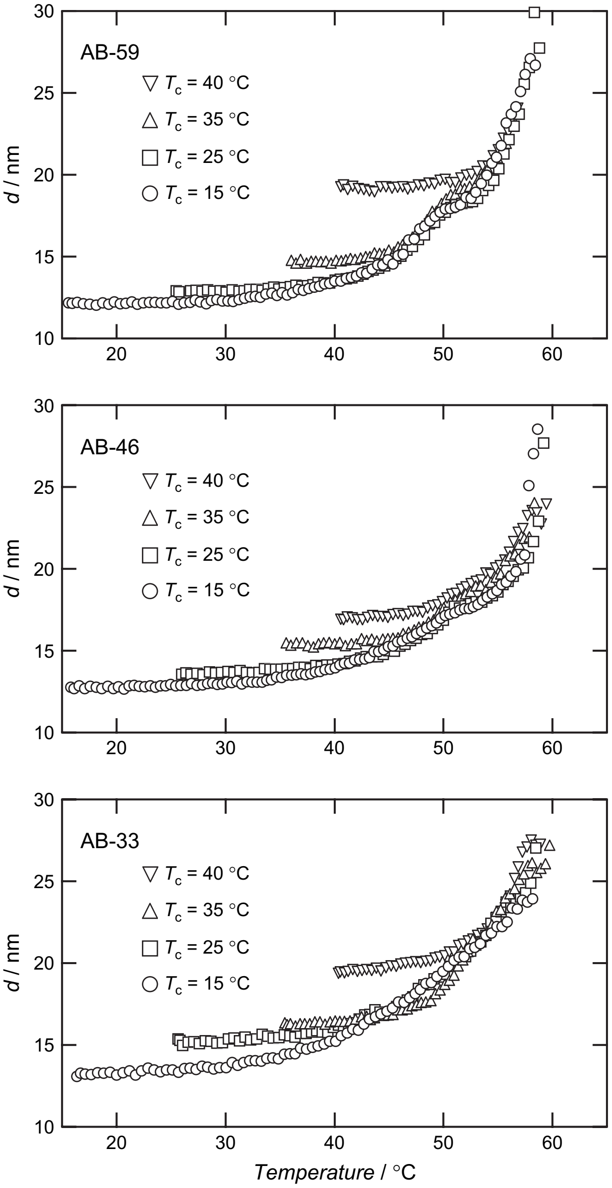

Fig. 10. Temperature dependence of the long spacing d in the melting of the diblock copolymers crystallized at the indicated temperatures.

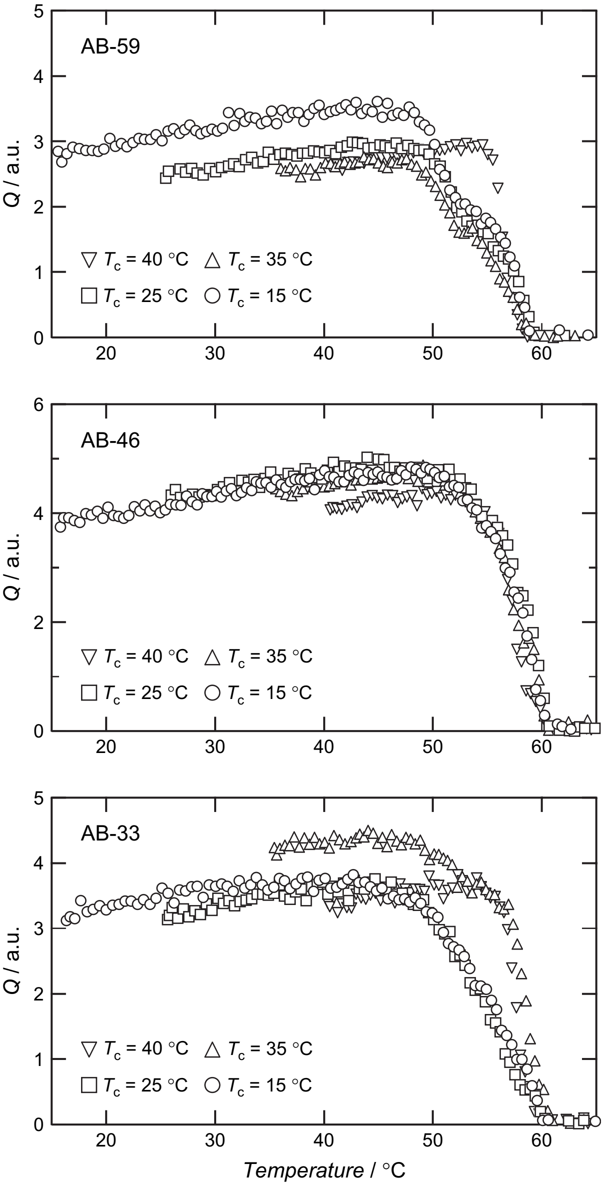

Fig. 11. Temperature dependence of the invariant Q in the melting of the diblock copolymers crystallized at the indicated temperatures.

4. Conclusion

Crystallization of PEG–PCL diblock copolymers was investigated by using POM, DSC, WAXD and SAXS. In the POM observation, a series of diblock copolymers studied here showed ordinary *single spherulites* contrary to the PCL–PEG–PCL triblock copolymers which showed unique concentric *double spherulites*. For the diblock copolymers, in spite of the formation of the *single spherulites* like PCL, it was observed through the WAXD and DSC measurements that both PCL and PEG crystallize in that order. From the time-resolved SAXS measurements employing synchrotron radiation as an incident beam, we conclude that, in the crystallization of PCL–PEG diblock copolymers, PCL crystallize first, followed by the crystallization of PEG chains between the formerly formed PCL crystal lamellae, resulting in the formation of ordinary single-circled spherulite having alternating crystal lamellae structure of PEG and PCL. Since PEG crystallizes within a confined space that is regulated by the formerly crystallized PCL crystal lamellae, the T_m and the crystallinity of PEG in the diblock copolymers are lowered especially for the block copolymers with a smaller PEG composition, whereas the T_m of PCL was approximately constant for all block copolymers.

Acknowledgements

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