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Appearance of double spherulites like concentric circles for poly(ϵ-caprolactone)-*block*-poly(ethylene glycol)-*block*-poly(ϵ-caprolactone)

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Abstract

A unique morphology of spherulites, namely double spherulites like concentric circles, was observed for poly(ϵ-caprolactone)-*block*-poly(ethylene glycol)-*block*-poly(ϵ-caprolactone) (PCL-*b*-PEG-*b*-PCL) triblock copolymers, ABA-2 and ABA-3, with PCL compositions of 66 and 60 wt%, respectively. The central and outer sections in the concentric spherulites were those of PCL and PEG, respectively. In formation of the concentric spherulites, the spherulites of the PCL component always appeared first and grew, and then the PEG spherulite developed from the growth front of the PCL spherulite. Any nucleation of the PEG spherulite prior to that of PCL was not observed. In the triblock copolymers, ABA-1 and ABA-4, with PCL compositions of 83 and 34 wt%, respectively, no concentric spherulites were observed but usual single-circle spherulites were formed; only PCL spherulites were formed for ABA-1 while for ABA-4 only PEG spherulites were observed. For ABA-2 and ABA-3 having the concentric spherulites, two melting peaks appeared and the WAXD patterns were a superposition of those for the PEG and PCL homopolymers. The SAXS curves for ABA-2 and ABA-3 also had two kinds of peaks due to the long spacings relative to the PCL and PEG crystal lamellae, respectively. The values of the long spacing estimated from the peak positions suggested that the PEG (or PCL) segments located between the crystal lamellae of PCL (or PEG) existed as amorphous segments. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Concentric spherulites; Crystalline block copolymer; Poly(ϵ-caprolactone)-*block*-poly(ethylene glycol)-*block*-poly(ϵ-caprolactone)

1. Introduction

Recently crystallization of block copolymers and resulting higher order structure containing crystal lamellae have been investigated [1–15]. These are classified into two kinds of block copolymers. One is crystalline–amorphous block copolymers and the other is crystalline–crystalline block copolymers. In the former block copolymers the most interesting point is a relation between crystallization and microphase separation in melt. Some investigations on this relation have been conducted [1–9]. In consequence, it has been clarified that microphase separation structure is destroyed by crystallization in the case of weakly segregated phase-separation [1–3] while in the strongly segregated case [4–8], the microphase separation structure is maintained even after crystallization. In the block copolymers containing only crystalline components, on the other hand, a competition in crystallization between different component chains rather than the effect of microphase separation is an important factor. However, basic studies on this aspect are not so many [10–15].

The competition in crystallization may be remarkable for the components having a melting temperature close to each other because their supercooling degrees are not so different in isothermal crystallization. Such competition may affect crystallization itself and the resulting higher order structure of crystals. In this study we have found the formation of double spherulites, like concentric circles, for poly(ϵ-caprolactone)-*block*-poly(ethylene glycol)-*block*-poly(ϵ-caprolactone) (PCL-*b*-PEG-*b*-PCL) triblock copolymers. The difference in the melting temperature between the PCL and PEG homopolymers is within 10°C. In this paper, we report such a unique morphology of the spherulite together with melting behavior and the long spacing due to the alternating structure of the crystal lamella and amorphous layer.

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Table 1
Molecular weights, compositions, and melting temperatures

Sample[a]	MW × 10^{-3}		PCL composition[b] (wt%)	M_w/M_n[c]	T_m (°C)	
	PEG[d]	PCL[b]			PEG	PCL
PEG1	8.0		0		62	
PEG2	5.0		0		59	
PCL		5.1	100	1.13		52
ABA-1	2.2	5.3 × 2	83	1.30		51
ABA-2	4.6	4.5 × 2	66	1.28	44	51
ABA-3	8.0	6.0 × 2	60	1.29	58	(53)
ABA-4	20.0	5.2 × 2	34	1.33	59	
Blend	8.0	5.1	50		61	53

[a] ABA: PCL-*b*-PEG-*b*-PCL.
[b] Determined by NMR.
[c] Determined by GPC, relative to polystyrene standards.
[d] Nominal value.

2. Experimental

2.1. Synthesis and characterization

PCL-*b*-PEG-*b*-PCL triblock copolymers were prepared by bulk polymerization of ϵ-caprolactone initiated with hydroxy groups at both chain ends of PEG without any catalyst according to the method of Cerrai et al. [12]. Four kinds of PEGs with molecular weights of 2200, 4600, 8000 and 20 000, purchased from Scientific Polymer Products, were used as prepolymers. These were purified by repeated precipitation into *n*-hexane from chloroform solution, followed by freeze-drying from benzene solution. ϵ-Caprolactone monomers were distilled in the presence of 3% 2,4-diisocyanato-1-methylbenzene. After drying over calcium hydride it was redistilled under vacuum. Mixtures of ϵ-caprolactone and PEG thus purified were degassed under nitrogen atmosphere and then polymerized for 50 h at 200°C. Polymerization was terminated by cooling rapidly to ice-water temperature, and molecular weights of PCL segment were controlled to be ca. 5000 by polymerization time. The products were dissolved in chloroform and precipitated into *n*-hexane. Purification was performed by reprecipitation in the chloroform/methanol system. Furthermore, the copolymers except the sample with PEG of MW = 20 000 were washed with water to remove unreactive homopolymer PEG, though no PEG was detected in the wash water. PCL-*b*-PEG-*b*-PCL copolymers thus obtained have hydroxy groups at both chain ends. To avoid an effect of hydrogen bonds on crystallization, the end groups were acetylized with acetic acid in the presence of pyridine. The final products of the copolymers were purified by reprecipitation, followed by freeze-drying from benzene solution.

PCL homopolymers were prepared by anionic polymerization in tetrahydrofuran (THF) for 15 min at −15°C using *n*-butyllithium as an initiator and acetic acid as a terminator. The products were purified by repeated precipitation in the THF/methanol system. The end groups of the homopolymer were also acetylized by the same method as that for the copolymers.

Molecular weights of the PCL homopolymers and the polydispersity M_w/M_n of the homopolymers and copolymers were determined by GPC (a Tohso HLC-8020 apparatus with a set of G3000HXL and G4000HXL columns) with THF as an eluent at 40°C, relative to polystyrene standards. GPC traces indicated a single peak for a series of triblock copolymers as well as the homopolymer. Copolymer compositions were evaluated by ^{1}H NMR (JEOL-GX270) in $CDCl_3$ at 40°C. Molecular weights of the PCL components in the copolymers were determined from the copolymer compositions on the basis of PEG's molecular weight.

2.2. Sample preparation

The samples used for crystallization were prepared by casting from a 3 wt% toluene solution on a Teflon® plate; drying for three days at room temperature and then under vacuum for two days.

2.3. Measurements

Morphology of spherulites was observed under crossed polarizers using an optical polarizing microscope (OLYMPUS BHS-705-P) equipped with a calibrated hot stage.

Melting behavior was analyzed at a heating rate of 10°C min^{-1} with a SEIKO I & E DSC20 differential scanning calorimeter.

Small-angle X-ray scattering (SAXS) measurements were carried out with a modified Kratky U-slit camera and a one-dimensional position sensitive proportional counter (PSPC) made by Rigaku Co. Ltd. CuK$_\alpha$ radiation (λ = 0.154 nm) nickel-filtered to eliminate CuK$_\beta$ was supplied by a Rigaku X-ray generator operated at 40 kV and 50 mA. The distance between the sample and PSPC was

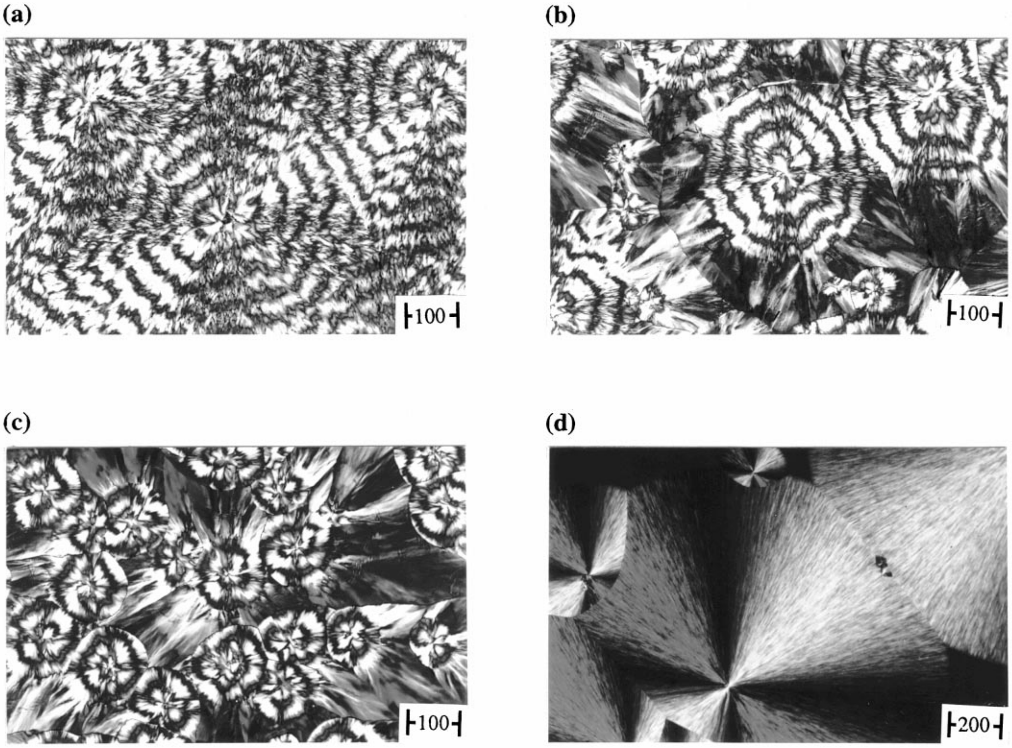

Fig. 1. Polarizing micrographs of spherulites of (a) ABA-1; (b) ABA-2; (c) ABA-3; and (d) ABA-4 crystallized at 45°C. The unit in the scale bar is micrometer.

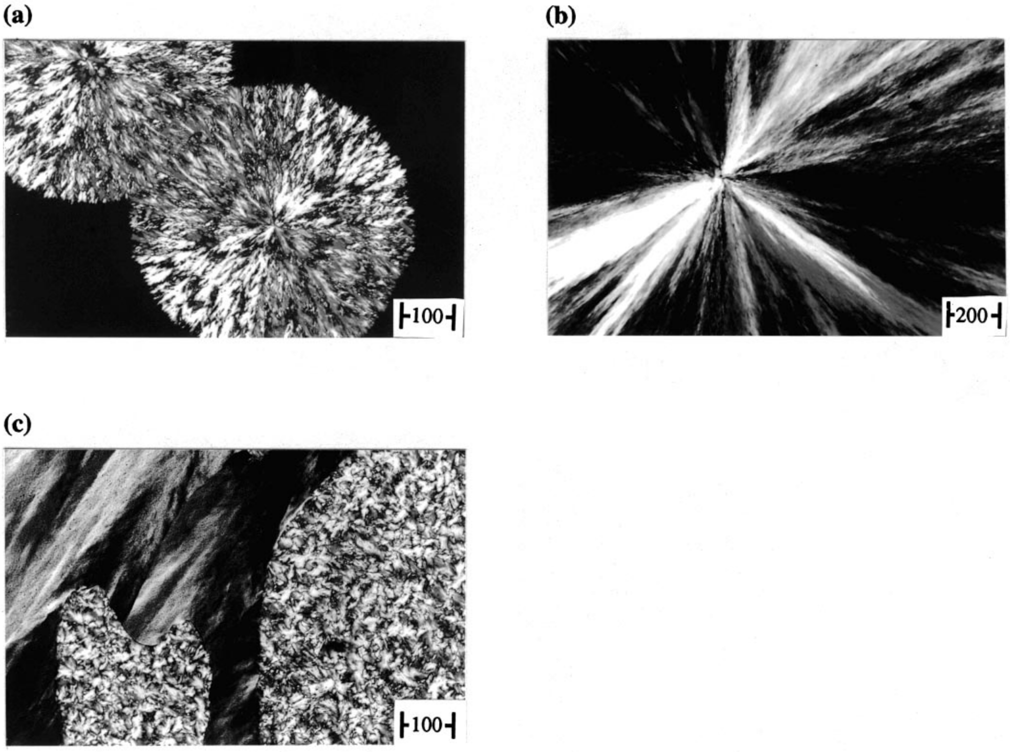

Fig. 2. Polarizing micrographs of spherulites of (a) PCL; (b)PEG homopolymers; and (c) their blends crystallized at 45°C. The unit in the scale bar is micrometer.

53.7 cm. The measured intensity was desmeared according to the method of Glatter.

Wide-angle X-ray diffraction (WAXD) measurements were performed using CuK$_\alpha$ radiation generated at 60 kV and 80 mA.

3. Results and discussion

The molecular weight and composition of the component chains of PCL-*b*-PEG-*b*-PCL triblock copolymers (ABA) used for crystallization are listed in Table 1 together with those of PEG and PCL homopolymers and their blends. All the samples were kept for 30 min at 100°C which was higher than the melting temperatures of both PCL and PEG, and then cooled rapidly to a crystallization temperature, 45°C, and isothermally crystallized completely at that temperature.

Fig. 1 shows the optical micrographs of spherulites of ABA-1–ABA-4 observed under crossed polarizers. Concentric spherulites can be seen for ABA-2 and ABA-3 in which the molecular weights of the PEG and PCL components are close to each other. A similar spherulitic structure has been observed for poly(dioxolane) [16] but it is due to a phase change, namely two phases. On the other hand, only single-circle spherulites were observed for ABA-1 and ABA-4.

In the concentric spherulites, the morphology of the central ring is quite different from that of the outer one; the former is similar to that of the PCL homopolymer shown in Fig. 2a while that of the latter to that of PEG homopolymer in Fig. 2b. The central spherulites of ABA-2 and ABA-3 have extinction rings, which have been observed for PCL in polymer blends [17,18]. The growth rate of the central spherulite was as slow as that of the PCL homopolymer, while that of the outer one was rapid and close to that of the PEG homopolymer. From both observations of morphology and growth rates, the central and outer spherulites can be assigned to the PCL and PEG components, respectively. By the same reason, the spherulites in ABA-1 and ABA-4 can be concluded to be those of the PCL and PEG components, respectively.

For the blends of PCL and PEG homopolymers, as shown in Fig. 2c, the spherulites of each homopolymer exist in the respective macrophase-separated domains.

In the formation of the concentric spherulites of ABA-2 and ABA-3, the spherulites of the PCL component always occurred first and grew exclusively, and then the spherulite of PEG developed from the growth front of the PCL spherulite. Any nucleation of PEG spherulites prior to that of PCL was not observed over the whole sample film and throughout crystallization time. Thus, the central and outer parts of the concentric spherulites were necessarily PCL and PEG ones, respectively, and no single-circle spherulites of only PEG were formed. For ABA-1 and ABA-4 in which no concentric spherulites were observed, no spherulites of the counter component were found.

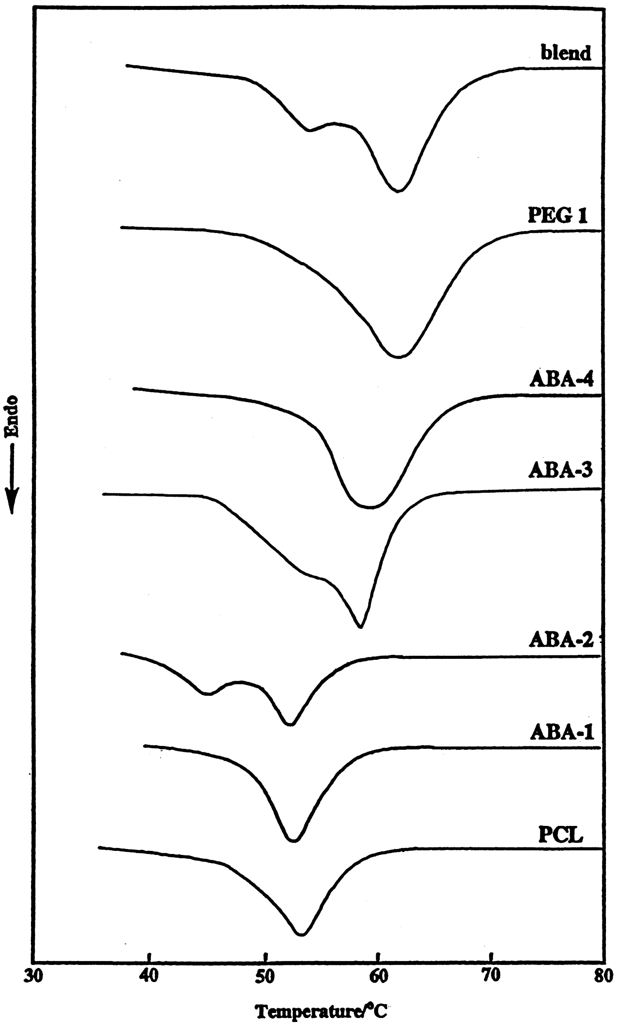

Fig. 3. Melting curves detected by DSC for block copolymers, homopolymers, and homopolymer blends crystallized at 40°C.

Fig. 3 shows the melting curves for the samples crystallized at 40°C, and the melting temperatures T_m are listed in Table 1. Two melting peaks were observed for ABA-2 and ABA-3 having the concentric spherulites. Cerrai et al. [12] and Nojima et al. [13] also found double melting peaks for the PCL-*b*-PEG-*b*-PCL triblock copolymers as did Gan et al. [14,15] for the diblock copolymers, though they did not confirm existence of any concentric spherulites. Assignment of the two melting peaks was performed by observation of morphology with increasing temperature. As a result, the ring of PEG melted at a lower temperature than that of PCL for ABA-2, while the PCL ring melted at a lower temperature than that of PEG for ABA-3. Namely, the lower and higher peaks for ABA-2 are due to the crystals of PEG and PCL, respectively, while the melting peaks for ABA-3 are in reverse order. The much depression in T_m of PEG in ABA-2 may be caused by the comparably small molecular weight of PEG as well as the copolymer composition. The melting temperatures of PCL whose molecular weights are almost the same among all the samples are not

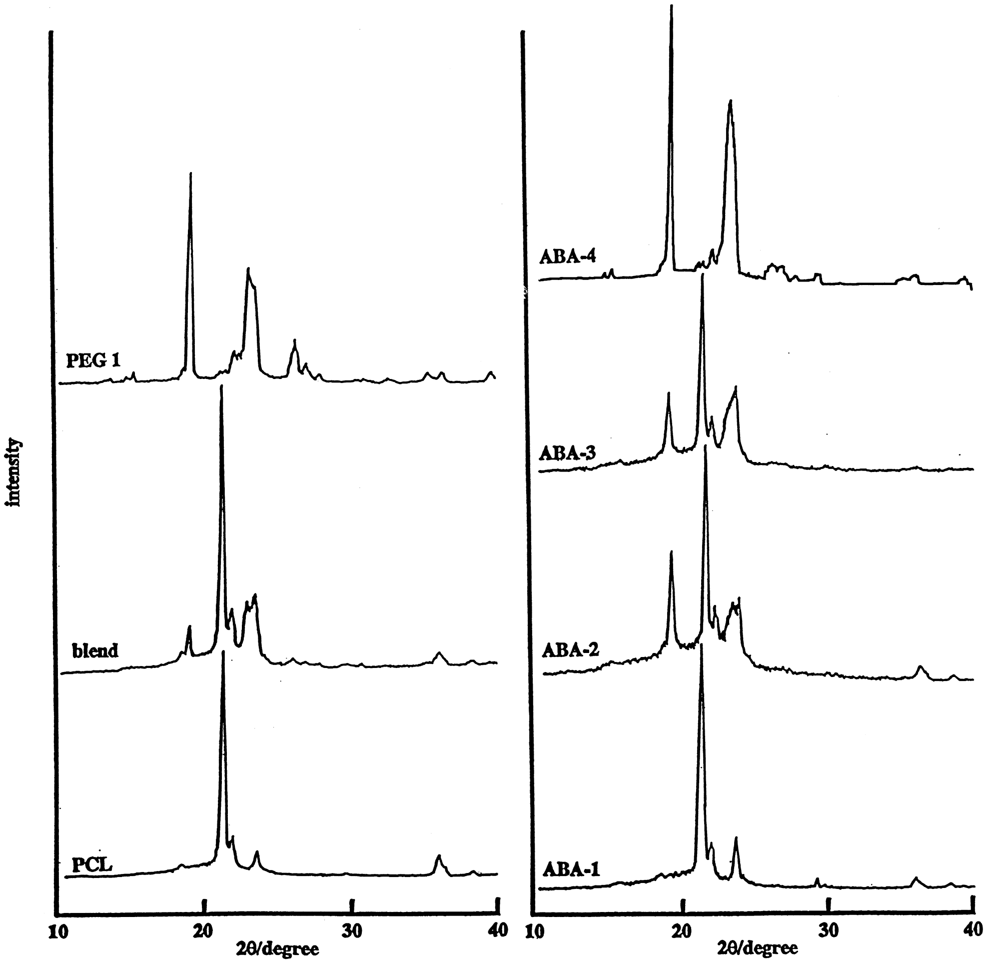

Fig. 4. WAXD patterns of homopolymers, homopolymer blends, and block copolymers.

so different from one another irrespective of the copolymer composition. On the other hand, T_m of the PEG component appears to depend on the molecular weights. This suggests that the molecular weight as well as the copolymer composition may affect the crystallization of PEG in the copolymers including ABA-1; the effect of the molecular weight may be enhanced by the situation of PEG as a middle chain in the copolymer.

Fig. 4 shows the WAXD results for the copolymers, homopolymers and the homopolymer blends. The WAXD patterns of ABA-2 and ABA-3 as well as the blend are superposition of those for the PEG and PCL homopolymers. For ABA-1 and ABA-2 where only single-circle spherulites were observed, on the other hand, there are no major peaks due to the crystal of the counter-component. Thus, the WAXD results correspond to the spherulite morphology of the respective copolymers.

Fig. 5 shows the SAXS curves measured at 25°C for the copolymers and homopolymers. Two peaks were observed for ABA-2 and ABA-3. The appearance of these two peaks suggests that there exist two kinds of alternating structure consisting of the crystal lamella and amorphous layer, relative to the PEG and PCL components. Additional SAXS measurements were carried out for ABA-2 and ABA-3 at higher temperatures to determine which peak was due to the alternating structure containing PEG or PCL crystal lamella. For ABA-2, as a result, the peak at larger scattering vector s disappeared at 40–50°C as shown in Fig. 5 and the other peak remained even at 50°C. As described above, the melting temperature of the PEG component in ABA-2 is lower than that of PCL. From both results of the melting and additional SAXS measurements, the peaks at smaller and larger scattering vector s (($= 4\pi/\lambda$)sin θ) at 25°C for ABA-2 can be assigned to the PCL and PEG crystal lamellae, respectively. For ABA-3, on the other hand, the peak at the larger s disappeared in the measurement at 48.5°C but that at the smaller s did not. Therefore, the peaks at smaller and larger s for ABA-3 are due to PEG and PCL, respectively, because the melting temperature of the PCL component is lower than that of PEG for ABA-3.

In Table 2 are listed the values of the long spacing, L, estimated from the peak position of the SAXS curve at 25°C. The long spacing of the alternating structure containing

Table 2
Long spacing, L, evaluated from SAXS

Sample	PCL composition (wt%)	PEG		PCL	
		s^a (nm^{-1})	L (nm)	s^a (nm^{-1})	L (nm)
PEG1	0	0.35	18		
PCL	100			0.56	11
ABA-1	83			0.40	16
ABA-2	66	0.43	15	0.35	18
ABA-3	60	0.20	31	0.38	17
ABA-4	34	0.29–0.40	22–16		

[a] $s = (4\pi/\lambda)\sin\theta$.

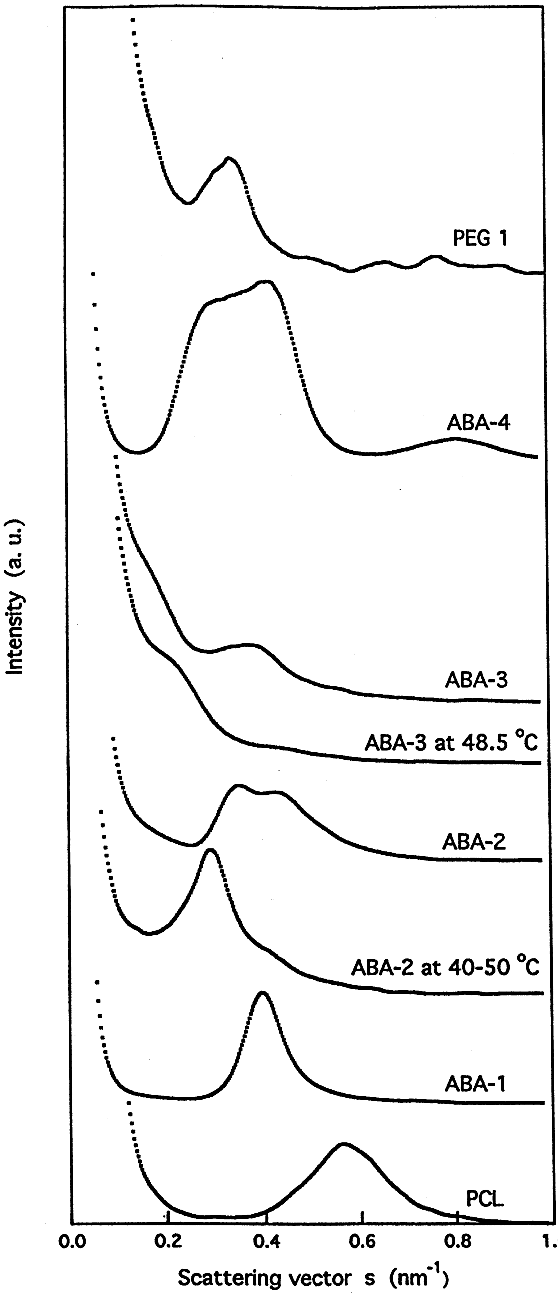

Fig. 5. SAXS intensities plotted against the scattering vector $s = (4\pi/\lambda)\sin\theta$. The measurement temperature is 25°C except for the indicated ones.

the crystal lamella of PCL for ABA-1, ABA-2 and ABA-3 are larger by 5–7 nm than that for the PCL homopolymer. The difference in L between the copolymer and homopolymer corresponds to the end-to-end distance, ca. 3.7–7.1 nm, of the unperturbed chains of PEG [19] with the molecular weight of 2000–8000. This suggests that the PEG segments located between the crystal lamellae of PCL exist as amorphous entities. On the other hand, although the L value concerning the PEG crystal lamella is not compared directly with one another because of the difference in the molecular weight of PEG, the small L for ABA-2 may come from a shorter thickness of the PEG crystal lamella, as suggested from the much depression of the melting temperature shown in Table 1.

In this study a unique morphology of spherulites, concentric spherulites, was observed. Here we have two problems: why only one component crystallizes in the first step and why a crystallizing component is changed from PCL to PEG in the process of crystallization. Now we are conducting further investigation to clarify these phenomena.

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