Formation of phase structure and crystallization behavior from disordered melt for ethylene-isoprene block copolymers and their blends

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ABSTRACT

The structure formation and crystallization kinetics in crystallization from a disordered melt were investigated for a polyethylene-polyisoprene block copolymer (LEI) having $M_n = 3.2 \times 10^4$ and 53 wt% of polyethylene content and for its blends with the corresponding homopolymers, polyethylene (PE) and polyisoprene (PIp), using synchrotron small-angle X-ray scattering techniques (SAXS) and differential scanning calorimetry (DSC). For LEI copolymer and the blends, no microphase separation structure was observed in the molten state. In the crystalline state of the neat LEI, the first and higher order scattering peaks were clearly observed, in which the intensity of the higher order peaks was considerably strong. This unusual behavior of the higher order peaks was explained by the lamellar insertion model of Hama and Tashiro. From the analyses based on this model and one-dimensional electron density correlation function with a three phase model, the phase structure in the crystalline state of the neat LEI was concluded to be a regular lamellar structure consisting of crystalline lamella of PE block and amorphous layers of PE and PIp blocks. This phase structure was quite different from that reported previously for a polyethylene-polyisoprene block copolymer (HEI) with a higher molecular weight in which HEI crystallized with keeping the microphase separation structure in the melt. For the blends of LEI with PIp homopolymer, the phase structure is affected by the blend composition, while for the blends with PE homopolymer, the phase structure depended on the crystallization temperature as well as the molecular weight and composition of the added PE. The Avrami index was 2–3 for neat LEI, all blends and PE homopolymers.

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1. Introduction

Structure formation and crystallization behavior of crystalline block copolymers continue to be of considerable interest [1–27]. In contrast to purely amorphous block copolymers, microphase structure in crystalline-amorphous block copolymers can result from two competing mechanisms: incompatibility of the two blocks, i.e., microphase separation, and the crystallization of the crystalline block. Previous studies have demonstrated that the resulting morphology in crystallization depends on whether block copolymers crystallize from a microphase-separated melt or from a disordered melt [2–6,9–14].

In crystallization of crystalline-amorphous block copolymers from microphase-separated melts, there are two possibilities for the resulting morphology: either the preexisting microphase structure is destroyed in crystallization or crystallization is confined within the preexisting microdomain. It has been well accepted that such structure development mainly depends on the state (glassy or rubbery) of amorphous blocks in crystallization and on the segregation strength (χN_t). In our previous papers [24–27], we have found that some other factors will affect the resulting morphology in crystallization, which are melt morphology, crystallization temperature and degree of crystallinity.

The crystallization with keeping the melt morphology is restricted by the microdomain. In the crystallization from disordered melts, on the other hand, structure development is not restricted by the microphase separation structure in the melt. Consequently, a lamellar morphology consisting of crystalline lamella and amorphous layer is formed regardless of the copolymer composition [6,9–12,14]. Register et al. and Ryan et al. have investigated the final morphology for polyethylene-poly(ethylene-*alt*-propylene) (PE-PEP), polyethylene-

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poly(3-methyl-1-butene) (PE-PMB) and polyethylene-poly(ethyl-ethylene) (PE-PEE) block copolymers in crystallization from disordered or weakly segregated melts, and an alternating lamellar morphology has been obtained at all copolymer compositions [9–12,14]. Such lamellar structure of crystalline-amorphous block copolymers may be different from that of crystalline homopolymers. In the block copolymers, the amorphous domain contains two kinds of chains: the chain belonging to the amorphous block and the non-crystalline part of the crystalline chain. Even though these two chains are miscible, the amorphous region containing only the former chains is expected to exist in the amorphous domain, because the latter is anchored to the crystalline lamella to be localized in the vicinity of the crystalline region. Thus, if semi-microphase separation structure is formed in the amorphous domain, the total alternating structure consisting of amorphous and crystalline layers may be more regular than that of the homopolymer. However, if some crystalline lamellae are formed to be dispersed heterogeneously within the domain, regularity of such a total structure may be disturbed. We reported previously the structure formation in crystallization of polyethylene-polyisoprene block copolymer (PE-PIp) with a *high* molecular weight (HEI) from microphase-separated melts [27]. In the crystallization with keeping the melt microphase separation structure, we observed scattering profiles that a broad peak from the correlation between crystalline lamellae was superimposed on the scattering peak due to the microphase separation structure, while only one broad peak was observed in the case that the melt structure was destroyed by crystallization. These results show that some crystalline lamellae were formed within the PE domain regardless of keeping or destroying the melt structure. If only one crystalline lamella is formed within the PE domain, the alternating structure consisting of crystalline lamella and amorphous layer is more regular, which may be realized for a low-molecular-weight block copolymer.

In this article, we will present the phase structure of PE-PIp block copolymers with a relatively low molecular weight (LEI), in which crystallization occurs from the disordered melt. The results obtained for the LEI system will be compared with those for the HEI system as well as for polyethylene homopolymers. The blends of such LEI block copolymer with polyethylene (PE) and polyisoprene (PIp) homopolymers were also studied to reveal the influence of blending homopolymers on the structure formation and crystallization behavior.

2. Experimental section

2.1. Materials

LEI and PE homopolymers were synthesized by selective hydrogenation of the corresponding polybutadiene-polyisoprene (BI) block copolymer and polybutadiene (PBd) homopolymer, respectively. PBd and PIp homopolymers were purchased from Polymer Source,

Inc. The BI block copolymers were prepared via successive anionic polymerization of butadiene and isoprene. Details of the polymerization and hydrogenation methods were same as those for preparing HEI as described in our previous paper [27].

All of the hydrogenated samples had a narrow peak of size exclusion chromatography; M_w/M_n was almost the same as those of the precursors. From the ^{1}H NMR spectra, the PBd homopolymers and the PBd block of the block copolymer were hydrogenated completely. For the PIp block, on the other hand, the double bonds in 1,2-structure were hydrogenated completely, while those in 1,4-structure were partially hydrogenated. The hydrogenation ratio of the isoprene was estimated to be about 20%. SEC curves and [1]H
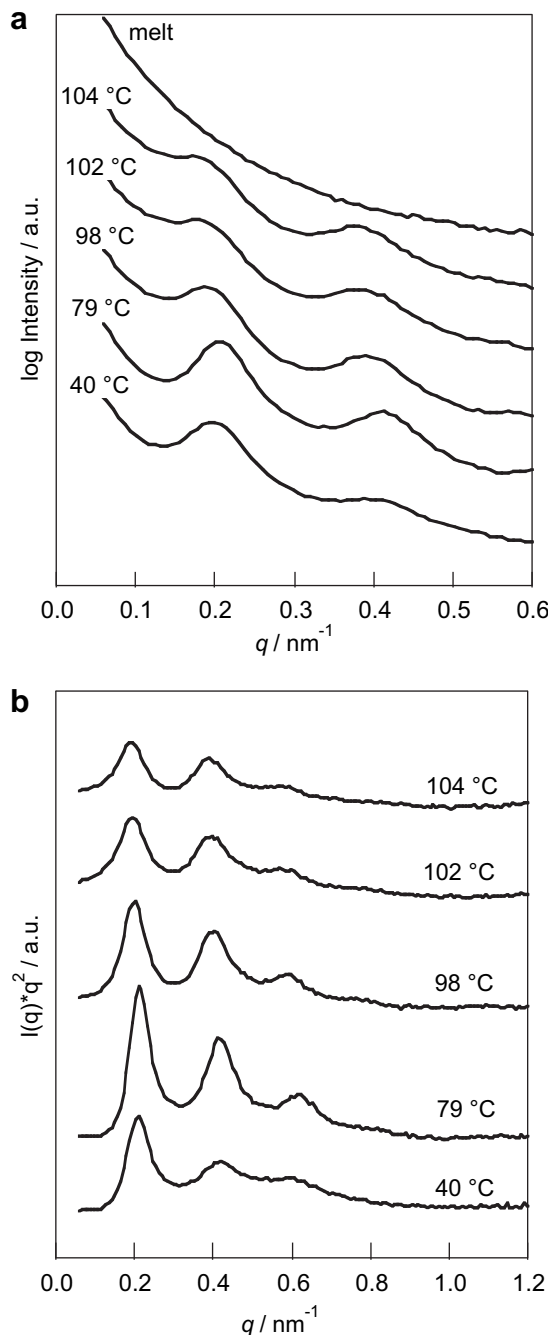

Table 1
Characteristics of block copolymer and homopolymers.

| Sample | Sample code | M_w/M_n[a] | M_n (kg/mol)[a] | | f_{PE} (wt) | Branch (mol%)[b] | |
			PE	PIp		PE	PIp
EI	LEI	1.05	17.0	15.1[c]	0.53	5.9	6.3
PIp	LPIp	1.04	–	12.0	0	–	5
	HPIp	1.04	–	25.0	0	–	6
PE	LPE	1.04	6.0	–	1	6	–
	HPE	1.06	12.0	–	1	5	–

[a] Determined by SEC in toluene calibrated against PS standards.
[b] Determined by ^{1}H NMR spectroscopy in C_6D_6 before hydrogenation.
[c] Determined by ^{1}H NMR spectroscopy using the molecular weight of the PBd precursor obtained by a.

Fig. 1. SAXS profiles of LEI in the molten and crystalline states. The temperature in the molten state is 140 °C. The samples were crystallized isothermally at the indicated temperatures after being rapidly quenched from 140 °C.

a T_c=40 °C

6min

0.3min

intensity / a.u.

q / nm^{-1}

b T_c=98 °C

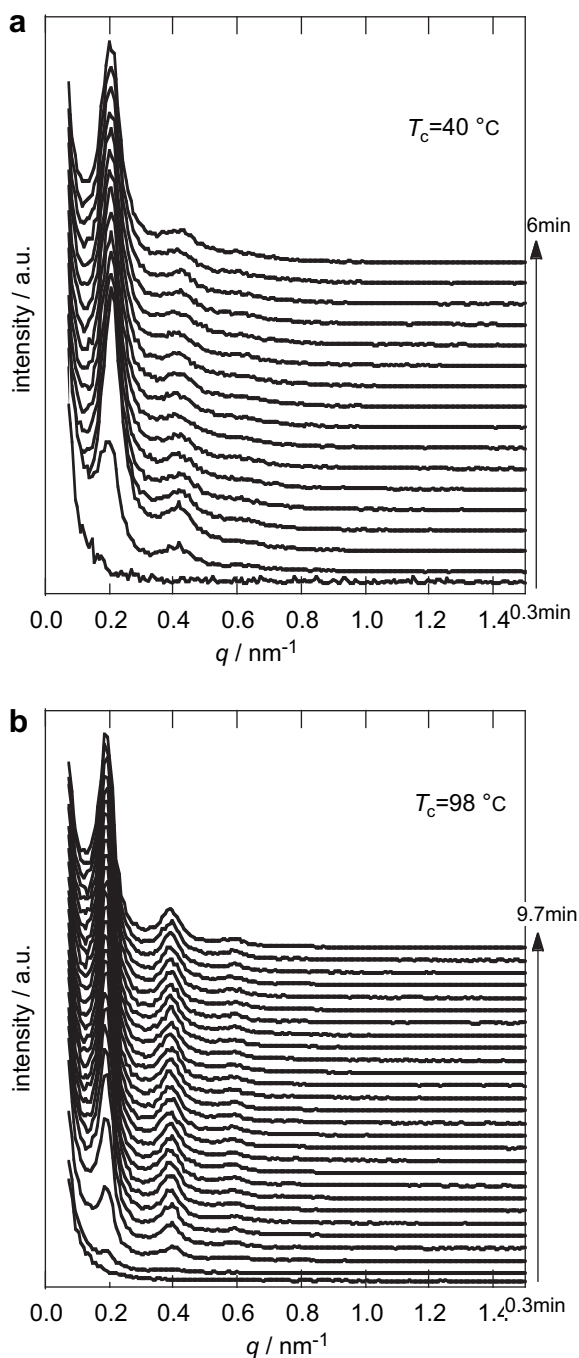9.7min

0.3min

intensity / a.u.

q / nm^{-1}

Fig. 2. Time development of SAXS profiles for LEI in isothermal crystallization at indicate T_c.

NMR spectra for the block copolymer before and after hydrogenation have shown elsewhere [27].

The characteristics of the block copolymer LEI are listed in Table 1 together with those of PE and PIp homopolymers. As described above, as the polyethylene used in this study was prepared by hydrogenation of PBd, the obtained PE has the traces of the 1,2-structure of PBd as ethyl branches.

2.2. Sample preparation and measurements

The block copolymer and blends were cast at 60 °C from 2.5 wt% solutions in toluene to form films, followed by removing
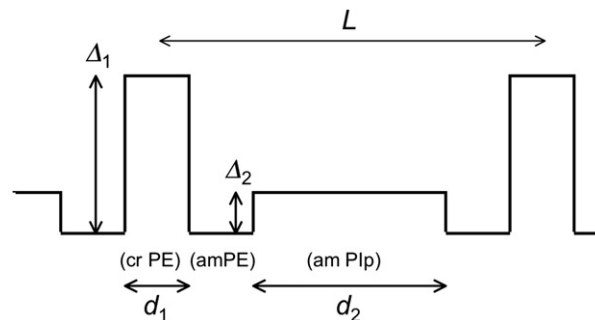

Fig. 3. Three phase model. In the calculation of the SAXS profile based on the insertion lamellar model, the following values of the parameters were used: $L = 36$ nm, $d_1 = 6$ nm, $d_2 = 18$ nm, $\Delta_1 = 0.164$ g cm^{-3}, $\Delta_2 = 0.0331$ g cm^{-3} and $\sigma_L = 5$.

the solvent completely in a vacuum oven for 1 day. The cast films were packed in sample pans and sample cells for DSC and small-angle X-ray scattering (SAXS) measurements, respectively. The SAXS cells had a path length of 1 mm and were sealed with polyimide films.

Isothermal crystallization was conducted by quenching to a desired crystallization temperature after annealing the sample at 140 °C for 30 min to erase the thermal history. The structural change due to the crystallization was monitored by time-resolved SAXS. The time-resolved SAXS experiments were conducted using synchrotron radiation at beamline BL-10C of the Photon Factory at the Institute of Materials Structure Science of the High Energy Accelerator Research Organization in Tsukuba, Japan. Details of the optics and the instrumentation were described elsewhere [28]. The SAXS data were collected in 15-sec frames separated by a waiting-time of 5 s using a position sensitive proportional counter (PSPC). The scattering angle was calibrated by using a chicken tendon having periodical structure of 65.3 nm. The scattering vector was defined as $q = (4\pi/\lambda) \sin(\theta/2)$, where θ and λ are the scattering angle and the wavelength of the incident X-ray, respectively.

DSC measurements were also performed with a Perkin–Elmer Pyris 1 for analyses of crystallization kinetics in the isothermal crystallization.

T_c = 98 °C

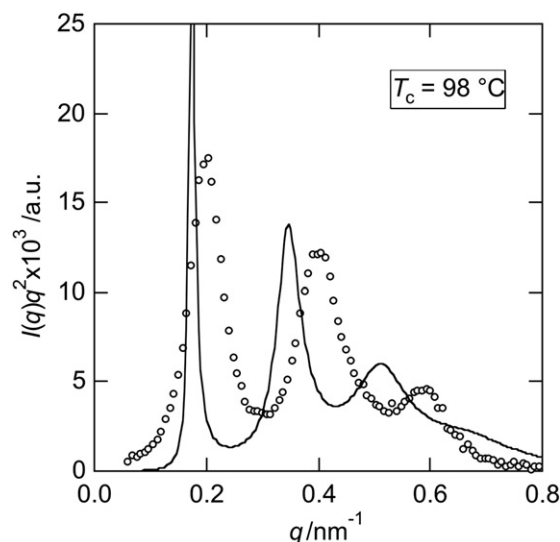$I(q)q^2 \times 10^3$ /a.u.

q /nm^{-1}

Fig. 4. The SAXS profiles calculated (line) by the lamellar insertion model eq (1) using the parameters shown in Fig. 3, and observed (circles) at 98 °C.
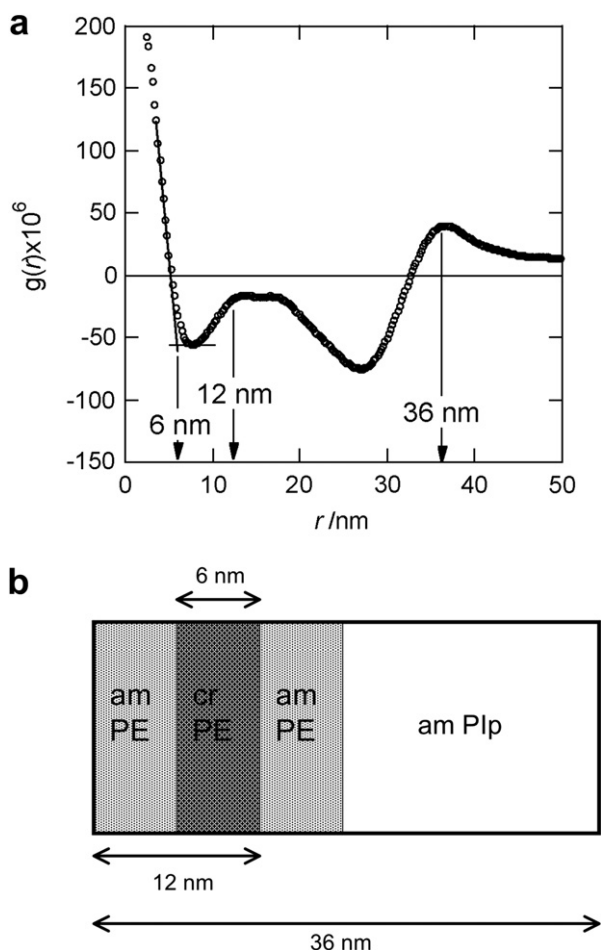
Fig. 5. (a) One-dimensional electron density correlation function for LEI crystallized at 98 °C. (b) Schematic phase structure deduced from (a) and three phase model.

3. Result and discussion

3.1. Structure formation in crystallization of the neat LEI block copolymer

Fig. 1a shows SAXS profiles of the LEI block copolymer in the molten state at 140 °C and in the state crystallized isothermally at

As shown in Fig. 1a, the position of the peaks can be observed clearly at the ratio of whole number, which means lamellar structure. The first-order peak shifts to a larger q as T_c decreases, reflecting that the crystalline stem becomes shorter. The Bragg spacing estimated from the peak position is 34 nm at $T_c = 104$ °C and 30 nm at $T_c = 40$ °C.

The higher order peaks observed clearly for LEI are contrastive to the SAXS profiles of PE homopolymers (LPE and HPE in Fig. 7, discussed later) in which very broad peaks or only one broad peak is observed. Lorentz-corrected SAXS profiles for LEI are also presented in Fig. 1b. The intensity of the higher order peaks is considerably strong, compared with that of the first-order peak. Similar SAXS profiles have been observed in crystallization from disordered melts or weakly segregated melts for polyethylene-poly(ethylethylene) (PE-PEE) [10], polyethylene-poly(head-to-head propylene) (PE-PhhP) [11] and polyethylene-poly(3-methyl-1-butene) (PE-PBM) [14] with relatively small molecular weights. For the same kinds of block copolymers with high molecular weights, on the other hand, common SAXS profiles were observed in the crystallization from strongly segregated melts [13–15].

The relatively strong higher order peaks in the above systems were attributed to the sum of a broad peak from the correlation between crystalline lamellae within the PE domain plus the multiple Bragg peaks from a total lamellar structure composed of PE and amorphous component phases [10,11,14]. Also, Ryan et al. [10] proposed a three phase model composed of PE-crystalline and PE- and PEE-amorphous domains, like the model shown in Fig. 5b described later, for PE-PEE systems. However, from the aspect of the relation between interlamellar distance of crystalline PE and the total lamellar period, the above two assumptions seem inconsistent with each other, because the interlamellar distance of crystalline PE should be equal to the total lamellar period in the three phase model.

Hama and Tashiro [29] proposed a lamellar insertion model for interpretation of the SAXS profiles of polyoxymethylene and polyethylene homopolymers [29,30]. For these polymers, the two stage crystallization was assumed: the first stage is an appearance of lamellar stacking structure and the second stage is an insertion of a new lamella into the already-existing lamellae. Consequently, in their model, the lamellar stacking structure consists of three phases, that is, an amorphous phase and two kinds of crystalline phases. Combining the lamellar insertion model with the second-kind of paracrystalline disorder concerning the lamellar stacking regularity, the scattering function was concretely derived as [29]

$$I(q) = N_t \frac{4\left[\Delta_1^2 \sin^2(d_1 q/2) + 2\Delta_1\Delta_2 \cos(Lq/2)\sin(d_1 q/2)\sin(d_2 q/2) + \Delta_2^2 \sin^2(d_2 q/2)\right]\sinh(q^2\sigma_0^2/2)}{q^2\left[\cosh(q^2\sigma_L^2/2) - \cos(Lq)\right]} \tag{1}$$

the indicated temperatures T_c after quenching it rapidly from the molten state. As seen in the SAXS curve of the melt, no scattering peak is observed, which suggests that the microphase separation does not occur in the molten state. Fig. 2a and b show the time development of SAXS profiles in the isothermal crystallization after quenching LEI rapidly to 40 and 98 °C, respectively, from 140 °C. At both temperatures, the peaks appear at 0.6–0.7 min and develop. No peak exists before those peaks appear. In addition, the position of the first-order peak is around $q = 0.2$ nm^{-1} which is the same as that shown in Fig. 1a. Namely the peaks at both temperatures are not attributed to the microphase separation structure in the molten state but to the structure containing crystalline lamellae. Therefore, it is concluded that the crystallization is regarded as that from the disordered melt at T_c's investigated here.

where Δ_1 and Δ_2 are the difference of electron density between the respective crystalline phases and the amorphous phase. d_1 and d_2 are the thickness of the main and the inserted lamella, respectively, L is the total lamellar period, and σ_L is a standard error of Gaussian distribution of L. The scattering function indicated that, in the three phase model, the second peak could be relatively strong without taking account of any other superimposed structure. They also showed that the intensity of the second-order peak can even exceed that of the first-order peak, depending on the conditions [29].

We attempt to apply the model of Hama and Tashiro to the present LEI system, where three phases consist of PE-crystalline and PE- and PIp amorphous domains, different from the case of Hama and Tashiro. In Fig. 3 are shown the three phase model and the parameters used for the calculation of the scattering intensity at

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Table 2
Composition of the blends.

Sample code	Comp. of blends (wt%)		PE comp. (wt%)
	Block	Homo	
LEI/LPIp-17	33	67	17
LEI/LPIp-32	60	40	32
LEI/HPIp-19	36	64	19
LEI/HPIp-35	66	34	35
LEI/LPE-60	85	15	60
LEI/LPE-70	65	35	70
LEI/LPE-80	42	58	80
LEI/HPE-60	85	15	60
LEI/HPE-70	65	35	70
LEI/HPE-80	42	58	80

98 °C. Δ_1 and Δ_2 are the difference of the density between PE crystalline and PE amorphous phases and between PE amorphous and PIp amorphous phases, respectively, in which the densities of crystalline and amorphous PE were evaluated from crystallographic

data extrapolated to 98 °C [31] and by the extrapolation of PVT data in the molten state for a PE random copolymer containing 10% 1-butene [32], respectively, and the density of PIp was taken from that for cis-1,4 rich PIp [33], where the two polymers nearly correspond to the present PE and PIp blocks, respectively. Fig. 4 shows the SAXS profile at 98 °C, where the values of L, d_1 and d_2 used in calculation are the same as those estimated from the analysis by the one-dimensional correlation function described below. As shown in Fig. 4, the relatively high intensity of the second-order peak in Fig. 1b is reproduced well by the three phase model.

In order to elucidate the lamellar structure in more detail, the one-dimensional electron density correlation function $g(r)$ was computed from the Lorents-corrected SAXS profiles (Fig. 1b) using the following equation:

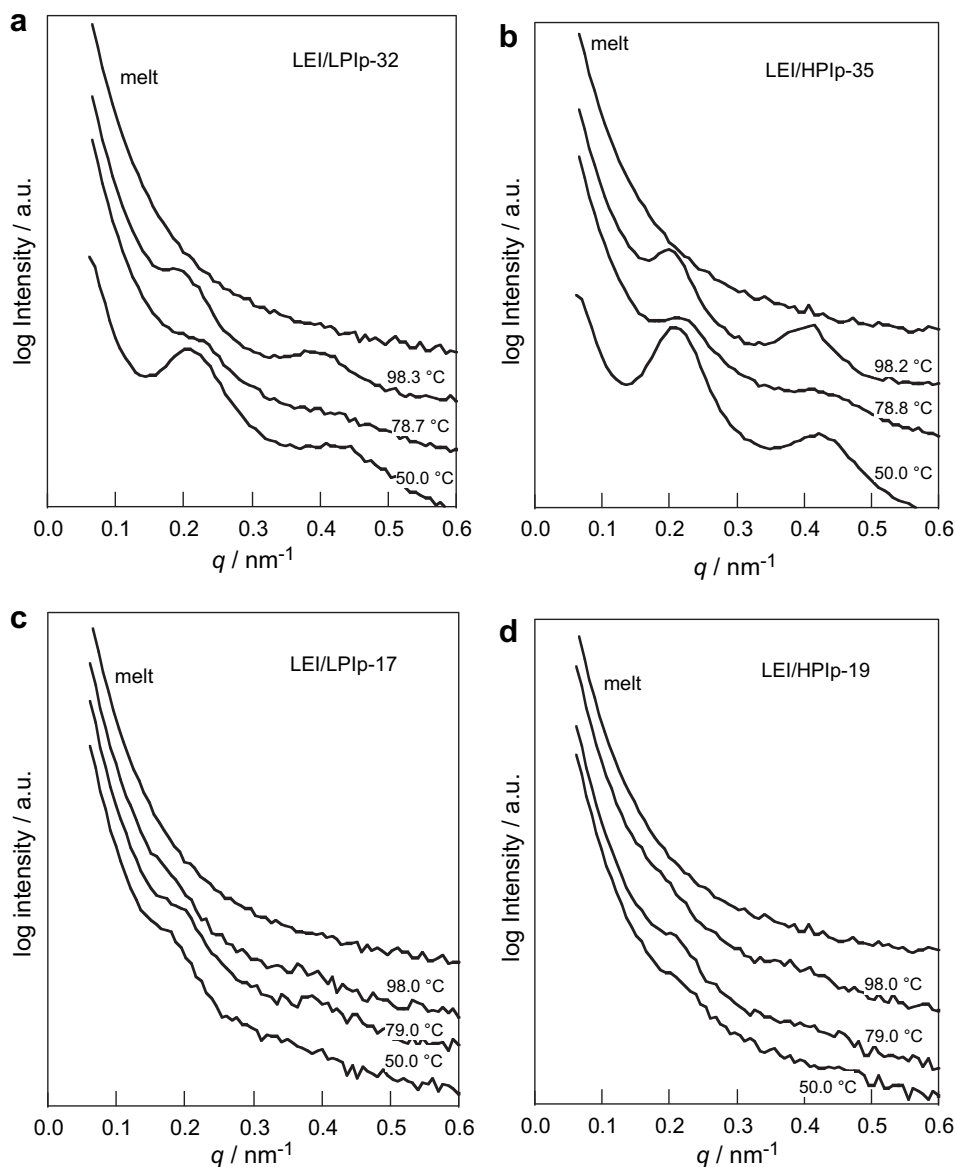$$g(r) = \int_0^\infty I(q) \cdot q^2 \exp(i \cdot q \cdot r) dq \qquad (2)$$

Fig. 6. The SAXS profiles for (a) LEI/LPIp-32; (b) LEI/HPIp-35; (c) LEI/LPIp-17; (d) LEI/HPIp-19 in the molten and crystalline states. The temperature in the molten state is 140 °C. The samples were crystallized isothermally at the indicated temperatures after being rapidly quenched from 140 °C.

As shown in Fig. 5a, there exists a plateau starting from about 12 nm as well as a peak around 36 nm in $g(r)$. This behavior may be explained on the assumption of a three phase model like drawn in Fig. 3. On the basis of the model, as shown in Fig. 5a, the peak around 36 nm corresponds to the total lamellar period, and 12 nm of the onset of the plateau is the length of the PE region. The crystalline thickness can be determined from the extrapolation of the first linear region of $g(r)$, as shown in Fig. 5a, to be about 6 nm. From the above consideration, a schematic picture of the phase structure in the crystalline state can be drawn as shown in Fig. 5b. The PE amorphous domain may be caused by the localization of the noncrystalline part of PE chain anchored to the crystalline lamella.

The phase structure for LEI shown in Fig. 5b is very contrastive to that for HEI. We previously reported the crystallization of HEI from microphase-separated melts, where HEI has a higher molecular weight of $M_n = 130,000$ and 0.5 wt. fraction of PE content [27]. When HEI crystallized keeping the melt microphase structure, the SAXS profile had a peak at $q = 0.09$ nm^{-1} and a broad peak ranging $q = 0.22$–0.5 nm^{-1}, which means that the crystalline lamellar structure with a broadly distributed size of 12–28 nm is dispersed within the PE domain with 35 nm thickness. Also, only a broad peak appeared when the crystallization destroyed the melt microphase structure. In HEI, the molecular weight of PE block is high enough to form a few crystalline lamellae within the PE domain between the domains of PIp. On the other hand, LEI may be hard to form even a few crystalline lamellae but almost one lamella, because its molecular weight is low. This is a different point between the phase structures of LEI and HEI. In addition, such a PE domain is sandwiched by the PIp amorphous domains like a microphase separation structure, which may explain why the structure for LEI is more regular than that for PE homopolymers.

3.2. Structural change in crystallization of the blends

As shown in Table 1, PIp homopolymers with molecular weights of 12,000(LPIp) and 25,000 (HPIp) and PE homopolymers with molecular weights of 6000 (LPE) and 12,000 (HPE) were employed to make blends with LEI. The molecular weights of LPIp and HPIp are comparable and high, respectively, compared to those of PIp block in LEI, while those of LPE and HPE are small and comparable, respectively, compared to PE block in LEI. The blend compositions employed are listed in Table 2. The number in the sample code denotes the total weight fraction of PE (sum of PE homopolymer and PE block in the copolymer) in the blend.

Fig. 6 shows SAXS profiles for the blends of LEI with PIp homopolymer in the molten state at 140 °C and in the state crystallized isothermally at the indicated temperatures. In the molten state of all the LEI/PIp blends, no peak can be observed in the SAXS profiles, suggesting that the melt is disordered. In the crystalline state of LEI/LPIp-32 and LEI/HPIp-35 containing 40–34% of the PIp homopolymer, as shown in Fig. 6a and b, clear scattering peaks at 1:2 position can be observed at all crystallization temperatures. On the other hand, in the crystalline state of LEI/LPIp-17 and LEI/HPIp-19 containing more than 60% of PIp homopolymer, as shown in Fig. 6c and d, the scattering peaks are not so clear in particular for the HPIp blend. These results suggest that addition of PIp homopolymer up to about 40 wt% maintains a regular phase structure in the same way as the neat LEI, while that it is disrupted for the blends with a content more than 60% of PIp homopolymer.

Fig. 7 shows SAXS profiles for the LEI/PE blends in the crystalline state at indicated T_c's. The SAXS results for LEI neat copolymer and PE homopolymers are also shown in Fig. 7 for comparison. At a lower crystallization temperature, $T_c = 79$ °C, the SAXS profiles for the blends change in proportion to the blend composition for both

blends with LPE and HPE, namely the phase structure of neat LEI is disrupted with the addition of the homopolymer. This tendency is enhanced for the blends with HPE and at a higher T_c, 98 °C. In particular, the SAXS profile of the blends with HPE at 98 °C is similar to that of HPE homoplymer even in LEI/HPE-60. It is noted here that the phase structure for neat LEI is not affected so much by T_c, as shown in Fig. 1. Such T_c dependence of the phase structure for the blends suggests that the phase structure for the blends with PE homopolymer is governed by crystallization itself as well as the composition and molecular weight of the added homopolymer, which is different from the case of the PIp blends.
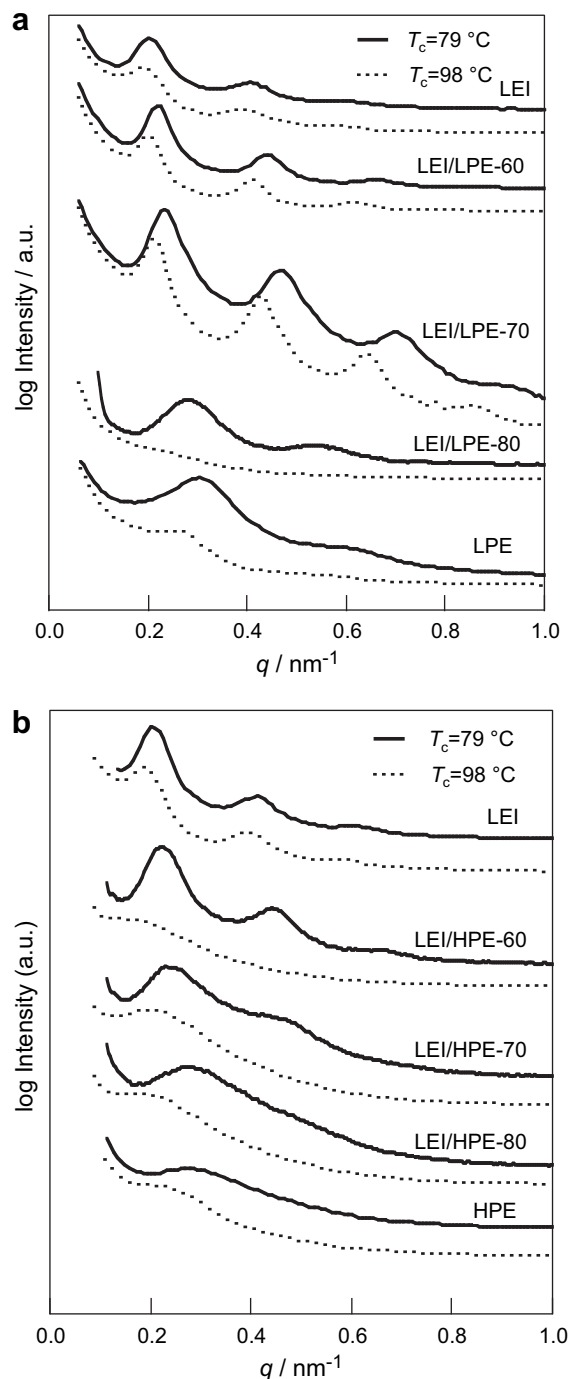
Fig. 7. SAXS profiles for LEI/PE blends, neat LEI block copolymer and LPE and HPE homopolymers crystallized isothermally at indicated T_c.
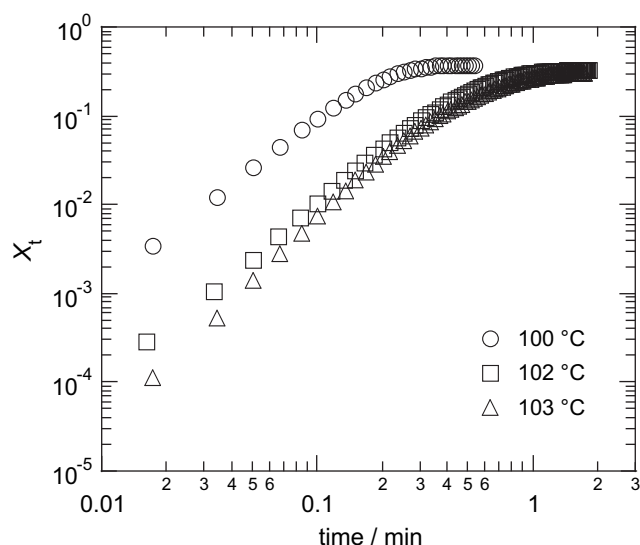
Fig. 8. Avrami plots of LEI/HPIp-35 at the indicated temperatures.

3.3. Crystallization behavior

The feature in the crystallization kinetics has been discussed on the basis of the Avrami expression. According to the Avrami equation, the fraction of crystallinity X_t at a crystallization time t is expressed as

$$X_t = 1 - \exp(-Kt^n) \tag{3}$$

where K is the overall crystallization rate constant and n is the Avrami index. Since Eq. (3) can be rewritten as

$$\log[-\ln(1 - X_t)] = \log K + n\log t \tag{4}$$

n can be evaluated from the initial slope of the plots of log $[-\ln(1-X_t)]$ vs log t. At a small degree of crystallinity, Eq. (3) can be rewritten as

$$\log X_t = \log K + n\log t \tag{5}$$

Fig. 8 shows an example of double logarithm plots of X_t against t. The Avrami indices n obtained from the initial slope of the plots are summarized in Table 3. As shown in Table 3, the values of n thus obtained are almost the same, i.e., $n = 2$–3, among the LEI block copolymer and all the blends, and are not different from those of the PE homopolymers. This result suggests that the growth dimension of crystals is not restricted. The same tendency has been

Table 3
Avrami index n at indicated T_c.

Sample	T_c (°C)	n
LEI	96	2.5
HPE	96	2.2
LPE	96	2.1
LEI/LPIp-32	102	2.4
LEI/LPIp-17	100	2.1
LEI/HPIp-35	102	2.2
LEI/HPIp-19	100	2.2
LEI/LPE-60	96	2.4
LEI/LPE-70	96	2.4
LEI/LPE-80	96	2.5
LEI/HPE-60	96	2.8
LEI/HPE-70	96	2.7
LEI/HPE-80	96	2.6

obtained in crystallization for miscible homopolymer blends such as poly(ethylene oxide)/poly(methyl methacrylate) blends [34] and for crystalline-rubbery amorphous block copolymers such as HEI and poly(ethylene glycol)-PBd copolymers [27,24]. A considerable reduction of n has been observed for the crystalline-glassy amorphous block copolymers such as polyethylene-polystyrene block copolymers [25,26].

4. Conclusion

The formation of the phase structure in crystallization and the behavior of the crystallization were investigated for polyethylene-polyisoprene (LEI) block copolymer having a relatively small molecular weight and 53% of PE and for its blends with the corresponding homopolymers PIp and PE. No microphase separation structure was observed for the neat LEI and the blends in the molten state, that is, the crystallization was that from the disordered melt.

The SAXS profiles for the neat LEI had clear scattering peaks at 1:2:3 q positions in the crystalline state at all crystallization temperatures studied here. The intensity of the second-order peak in the SAXS profile was considerably strong. Such unusual SAXS profiles were reproduced qualitatively by the lamellar insertion model of Hama and Tashiro. In addition to that, from the analysis based on the one-dimensional electron density correlation function $g(r)$, the phase structure in the crystalline state for the neat LEI was concluded to be a regular lamellar structure consisting of three phases: crystal lamella of PE block and amorphous layers of PE and PIp blocks. This is very contrastive to that for the system of HEI with a higher molecular weight reported in the previous paper [27]. In HEI, the crystal lamellar structure with broadly distributed sizes was dispersed within the microdomain. Also, the SAXS profile of the neat LEI was contrastive to that of PE homopolymers in which the scattering peaks were very broad and the higher order peaks were not clear.

For the blends with PIp homopolymer, the phase structure in the crystalline state was affected by the blend composition. In the blend composition up to 40%, the phase structure was not different from that of the neat LEI, while it was destroyed in the blend with more than 60% of PIp. On the other hand, for the blends with PE, the phase structure was changed to that of PE homopolymers depending on the blend composition. It was enhanced for the high molecular weigh of PE and at high T_c.

The Avrami index for both neat LEI and blends was 2–3 which was the same as that for PE homopolymers. This result was the same as that in crystallization for miscible homopolymer blends [34].

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