Introduction

Structure formation in block copolymers has been extensively studied from both theoretical and experimental viewpoints1–17. In block copolymers composed of only amorphous components, the driving force for structure formation is the incompatibility between the block chains, characterized by \( cN_t \), where \( c \) is the Flory interaction parameter and \( N_t \) is the total number of segments in the copolymer. When \( cN_t \) exceeds a critical value, block copolymers form segregation structure with a size of several to several ten nanometers, called microphase separation1,18. On the other hand, when a block copolymer has one or more crystalline components, crystallization plays an important role in structure formation. For such block copolymers, crystallization occurs from disordered or microphase-separated melt depending on the segregation.

When crystallization occurs from disordered melt, competition between crystallization and formation of microphase separation is highlighted. In some cases, crystallization might induce microphase separation structure. On the other hand, in the case that crystallization occurs from a microphase-separated melt, it is of main interest whether crystalline blocks crystallize within microdomains with preserving the preexisting microphase structure, or microphase separation structure in the melt is destroyed and reorganized by crystallization to be alternating structure consisting of the crystal lamella and amorphous layer as seen in usual crystalline polymers.

The structure formation of such kinds of block copolymers has been investigated extensively for the last decade. It has been elucidated that such structure change firstly depends on the glass transition temperature of the

Abstract

Time-resolved simultaneous synchrotron small-angle X-ray scattering and differential scanning calorimetry experiments have been performed on crystallization of polyethylene-polyisoprene diblock copolymers (HEI or LEI) and their blends with corresponding homopolymers, polyethylene (PE) and polyisoprene (PIp). For the neat block copolymer having a 50 wt% of the crystalline component, preexisting microphase separation structure in the melt was kept at high and low crystallization temperatures \( T_c \) (\( T_c=94^\circ C \) and \( T_c<60^\circ C \)), while disrupted at intermediate \( T_c \) (\( 60^\circ C \leq T_c <94^\circ C \)). This complex behavior was interpreted by combination of two mechanisms. The behavior in the crystallization below 94°C was attributed to the competition between the crystallization and chain diffusion rates, that is, the fast crystallization rate at lower \( T_c \) makes it difficult to rearrange the phase structure in the melt. On the other hand, at a higher \( T_c \) (\( 94^\circ C \)), the preservation of the microphase separation structure was explained by a small degree of crystallinity due to the ethyl branch of polyethylene (hydrogenated poly(butadiene)). For HEI/PE blends, crystallization behavior was the simple superposition of those for HEI and PE, while, for HEI/PIp with a small composition of PE, suppression of crystallinity was observed. Crystallization kinetics in the neat block copolymer and all the blends was not so different from that in the PE homopolymer.

Keywords

Microphase separation, Structure formation, Crystallization, Polyethylene-polyisoprene block copolymer.
amorphous component \( T_{c}^{A} \). When crystallization temperature \( T_{c} \) is lower than \( T_{c}^{A} \), that is, the amorphous component is in glassy state at \( T_{c} \), microphase separation structure in the melt is usually maintained in crystallization, because the microphase separation structure is frozen by the glassy domains \( T_{c}^{A} \).

On the other hand, when \( T_{c} \) is higher than \( T_{c}^{A} \), it has been reported that structural change in crystallization depends on the segregation strength between components \( (\gamma N) \). Quiram et al. explored the crystallization of a high molecular weight polyethylene-poly(3-methyl-1-butene) block copolymer (strongly segregated system) with a polyethylene weight fraction \( f_{p} \) of 0.27, and found that polyethylene crystallized within preexisting cylindrical microdomains \( T_{c}^{A} \). Nojima et al. \( T_{c}^{A} \) also investigated a crystallization process of crystalline-rubbery amorphous block copolymers for poly(\( \varepsilon \)-caprolactone)-polybutadiene (weakly segregated system) through a time-resolved small-angle X-ray scattering (SAXS) technique using synchrotron radiation as a light source, and observed that a preexisting SAXS peak from the microphase separation disappeared with development of a new peak originating from the long period of crystal lamellae. Furthermore, we have reported that a high molecular weight poly(ethylene glycol)-poly(butadiene) block copolymer (PEG-PBD), which is relatively strongly segregated system, with \( f_{p} = 0.58 \) crystallizes within the preexisting lamellar microdomain, but for a low molecular weight PEG-PBD with \( f_{p} = 0.58 \), the lamellar microdomain is destroyed in crystallization.

In addition to segregation strength of melt, we have elucidated that the structure change in crystallization from a microphase-separated melt also depends on some other factors \( T_{c}^{A} \). For the PEG-PBD block copolymers, the microphase separation structure as well as the molecular weight \( (\varepsilon) \), segregation strength \( (\gamma N) \), and crystallization temperature \( T_{c} \), influence the crystallization behavior itself is also interesting. In the block copolymers having a glassy component as an amorphous block, the dimension of the crystalline-rubbery amorphous block copolymers, structure formation or change in crystallization was also investigated mainly in the kinetic aspect.

**Experimental**

**Materials**

Polyethylene-polyisoprene block copolymers (EI) and polyethylene homopolymers (PE) were synthesized by selective hydrogenation of polybutadiene-polyisoprene block copolymers (BI) and polybutadiene homopolymers (PBd), respectively. PBd and polyisoprene (Plp) homopolymers were purchased from Polymer Source, Inc. The BI block copolymers were prepared via successive anionic polymerization of butadiene and isoprene. Polymerization of butadiene was carried out by using sec-butyl lithium (BuLi) as an initiator, followed by polymerization of isoprene. Catalytic hydrogenation for the block copolymers and the homopolymers was carried out in toluene solution with a Wilkinson catalyst \((\text{Ph}, \text{P}, \text{Rh})_{2} \text{Cl}\) under 6 atm hydrogen gas for 24 h at 90°C. The resulting polymers were purified by repeated precipitation with toluene/methanol system followed by freeze-drying from benzene solution.

All of the hydrogenated samples showed a narrow peak of size exclusion chromatography (SEC) as shown in an example of LEI (low molecular weight EI, see Table 1) in Figure 1. The molecular weight and \( M_{w}/M_{n} \) of the hydrogenated samples were almost the same as those of the precursors. PBd homopolymers and B blocks of the block copolymers were hydrogenated completely. An
example of the $^1$H NMR spectra before and after hydrogenation (i.e., for LBI and LEI, respectively) is shown in Figure 2, where the signals (designated by a and c before hydrogenation) due to the double bonds in B blocks vanished after hydrogenation. For I blocks, the double bonds in 1,2-structure were hydrogenated completely (Signal d before hydrogenation vanished after hydrogenation.), but those in 1,4-structure were partially hydrogenated (Signal b before hydrogenation changed to h after hydrogenation). The hydrogenation ratio of the 1,4-structure in I blocks was estimated to be about 20% from the area ratio of the signals m and h. The characteristics of the block copolymers are listed in Table 1 together with those of PE and Plp homopolymers. The obtained polyethylene has the traces of the 1,2-structure of the polybutadiene as ethyl branches.

**Sample preparation and measurements**

The block copolymers and blends were cast from 2.5 wt% solutions in toluene at 60°C to form films, followed by removing the solvent completely in a vacuum oven for 1 day. The cast films were packed in DSC sample pans and in sample cells for SAXS measurements. The SAXS cells had a path length of 1 mm and were sealed.

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### Table 1. Characteristics of the Block Copolymers and the Homopolymers

| Sample | Sample code | $M_w/M_n$ | $M_w$ (kg/mol)$^{a}$ | Composition (wt%) | Branch comp. (wt%)$^{b}$ |
|--------|-------------|-----------|---------------------|-------------------|------------------------|
| EI     | HEI         | 1.02      | 65                  | 50                | 6.2                    |
|        | LEI         | 1.05      | 17                  | 47                | 5.9                    |
| Plp    | LPlp        | 1.04      | 12                  | 100               | 5.0                    |
| Plp    | HPlp        | 1.04      | 25                  | 100               | 6.0                    |
| PE     | PE58k       | 1.05      | 58                  | 100               | 6.4                    |
| LPE    | LPE         | 1.04      | 6                   | 100               | 6.0                    |
| HPE    | HPE         | 1.06      | 12                  | 100               | 6.0                    |

$^a$ Determined by SEC in toluene, calibrated using PS standards.

$^b$ Determined by $^1$H NMR in C$_6$D$_6$.

$^c$ Determined by $^1$H NMR using the molecular weight of the PBd precursor obtained by $a$.

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**Figure 1.** SEC curves of LBI (before hydrogenation) and LEI (after hydrogenation).

**Figure 2.** $^1$H NMR spectra of LBI (top) and LEI (bottom) in C$_6$D$_6$. 
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\(^2\). The SAXS data were collected in 15-s 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 

\[ q = \frac{4\pi \lambda}{\sin(\theta/2)} \]

where \( \theta \) and \( \lambda \) are the scattering angle and the wavelength of the incident X-ray, respectively. The measurement range of \( q \) was about 0.07–1.00 nm\(^{-1}\).

DSC measurements were also performed for the crystallization and the successive melting process at a heating rate of 10°C/min, with a Perkin-Elmer Pyris 1. The crystallization kinetics, the melting temperatures and the crystallinity were analyzed.

Results and Discussion

Segregation strength of microphase separation

Figures 3a and 3b indicate the temperature dependence of the SAXS profiles of EI block copolymers having high and low molecular weights, HEI and LEI, respectively. As shown in Figure 3a, HEI has a first-order peak due to the microphase separation structure around \( q = 0.09 \) nm\(^{-1}\) in the molten state (above about 110°C by DSC) of E blocks. Although no higher-order peak is observed, the morphology of the microphase separation is expected to be lamellar, taking into account the copolymer composition. Neither peak intensity nor peak position is changed even at high temperatures up to 200°C. This means that the order-disorder transition temperature \( T_{\text{ODT}} \) of HEI is higher than 200°C which is enough higher than the melting temperature \( T_m \) of the E block. Therefore, HEI may crystallize from the microphase-separated melt.

As shown in Figure 3b, on the other hand, LEI has no SAXS peak above 110°C. This means that \( T_{\text{ODT}} \) of LEI may be lower than \( T_m \) of PE. Although we could not determine the exact \( T_{\text{ODT}} \) for HEI and LEI, it is suggested that the segregation degree of the microphase separation in HEI is not so strong judging from the behavior of LEI. Consequently, it follows that crystallization of HEI occurs from weekly segregated microphase-separated melt, although Flory-Huggins \( \chi \) parameter for PE/PIp has not been measured directly as far as we know.

Structure formation in crystallization of the neat copolymer

Figure 4 shows SAXS profiles of HEI in the molten and crystalline states crystallized by quenching to the temperatures indicated. In the melt, as described above, the SAXS profile has a scattering peak from microphase separation structure around \( q = 0.09 \) nm\(^{-1}\), which gives 70 nm of the spacing in the lamellar structure and the PE domain thickness of about 35 nm. The scattering profiles in the crystalline state depend on \( T_c \). The change in the SAXS profiles can be classified into three groups: \( T_c \geq 94°C \), \( 60°C < T_c < 94°C \) and \( T_c < 60°C \).
In both ranges of $T_c \geq 94°C$ and $T_c < 60°C$, the scattering peak around $q = 0.09$ nm$^{-1}$ remains even after enough crystallization time. The conservation of the peak indicates that the microphase separation structure in the melt is preserved even in crystallization of the E block. On the other hand, when crystallized at the intermediate crystallization temperatures ($60 \leq T_c < 94°C$), the peak from the microphase separation structure in the melt disappears completely, indicating that the microphase separation structure was disrupted in crystallization of the E block.

For crystalline-rubbery amorphous block copolymers, we reported the crystallization of PEG-PBD diblock copolymers, in which PBd is rubbery in crystallization of PEG$^{(26)}$. In the crystallization of PEG-PBD, reorganization of the phase structure depended on the crystallization temperature as well as the microphase separation structure, i.e., the melt structure tends to be preserved at lower $T_c$, while it is reorganized to the alternating structure of crystalline and amorphous layers at higher $T_c$. This behavior can be explained based on the competition between the crystallization and diffusion rates of the polymer chains. At the lower $T_c$, the crystallization proceeds too fast to reorganize the preexisting microphase separation structure, while the slow crystallization at the higher $T_c$ provides enough time for structural change.

Applying the above consideration for PEG-PBD to the block copolymers studied here, the behavior of the structure change at $T_c < 94°C$ can be explained. Below 60°C, the crystallization rate is so high that the microphase separation structure cannot be reorganized, which leads to the fact that the SAXS peak from microphase separation structure remains even after the crystallization. On the other hand, when $T_c$ is higher than 60°C (but lower than 94°C), crystallization rate is relatively low so that the melt structure can be reorganized to the alternating structure of the crystalline and amorphous layers.

Thus the crystallization behavior below 90°C can be explained by the competition between the crystallization and chain diffusion rates, just like other crystalline-rubber amorphous block copolymers such as PEG-PBD. However, the analogy cannot explain the crystallization behavior at $T_c$ above 90°C, in which the microphase separation structure is maintained in the crystalline state despite that the crystallization rate should be low compared to that at lower $T_c$. Why is the microphase separation structure in the melt still kept at crystallization temperatures higher than 90°C?

Figure 5 shows the $T_c$ dependence of DC estimated by DSC for HEI and the homopolymer PE58k. DC of both PE58k and HEI strongly depends on the crystallization temperature, that is, decreases drastically at $T_c$ above 90°C. This low DC at higher $T_c$ is considered to preserve the melt microphase structure even though the crystallization rate is low. Such a $T_c$ dependence of DC has been found and discussed for polyethylene random copolymers containing a small amount of comonomers such as vinyl acetate, 1-hexene, and 1-butene$^{(28–30)}$. In these systems, it has been pointed out that the comonomers act as impurities for the crystallization of polyethylene and make the distribution of melting temperature broad. Because the polyethylene part in our block copolymers is actually a hydrogenated polybutadiene, it is essentially a random copolymer of ethylene with a small amount of 1-butene, which is incorporated in the copolymer as an ethyl branch.
Therefore, when crystallized at higher temperatures, some polyethylene parts with relatively more branched segments are excluded from the crystalline lamellae. As $T_c$ decreases, such polyethylene chains become able to crystallize and therefore DC increases. These effects make DC of the E block low at higher $T_c$.

The difference in the structure formation among $T_c<60°C$, $60≤T_c<94°C$ and $T_c≥94°C$ is reflected in the spacing of the crystalline lamellar structure of E. In Figure 4, we can find a broad peak at a higher $q$, which is attributed to the crystalline lamellar structure of the E block. At $T_c≥94°C$, the intensity of the broad peak is so weak that the peak range cannot be detected clearly, reflecting the low DC. On the other hand, we can observe the broad peak around $q=0.15–0.4\,\text{nm}^{-1}$ at $60≤T_c<94°C$ and around $q=0.22–0.5\,\text{nm}^{-1}$ at $T_c≤50°C$. These broad peaks suggest that the spacings of the E crystalline lamellar structure are broadly distributed in the size of 16–40 nm and 13–28 nm at $60≤T_c<94°C$ and $T_c≤50°C$, respectively. Here, it is noted that the spacing is longer in the former $T_c$ range than in the latter. Taking account of the E domain size (about 35 nm thickness) in the melt, this suggests that at $60≤T_c<94°C$ the crystalline lamellae develop well by disrupting the microphase structure in the melt, while that the crystallization occurs keeping the melt structure at $T_c≤50°C$.

**Structural change in crystallization of the blends**

PE and Plp homopolymers having a lower molecular weight than the corresponding blocks in HEI were blended with the block copolymer in order to control the microdomain structure in the molten state. The compositions of the blends are listed in Table 2. The number in the sample code denotes the total weight fraction of polyethylene (sum of PE homopolymer and E block in the copolymer) in the blend.

Because the molecular weights of Plp and PE homopolymers are smaller than those of corresponding blocks in HEI, the added homopolymers are expected to be miscible in the microdomains of HEI, and to alter the microphase separation structure in the melt. Figure 6 shows the SAXS profiles of the blends and the neat block copolymer in the melt. The SAXS peak observed in the neat block copolymer has disappeared for all of the blends. If the homopolymers are dissolved in the corresponding blocks of the copolymer, the microphase separation structure is enlarged because the blends contain at least 20 wt% of the homopolymer. Then, the SAXS peak observed in the neat block copolymer might be shifted toward lower $q$, and therefore be hidden by the beam stopper. Alternatively, there is another possibility that blending low molecular weight homopolymers weakened the segregation strength of the system, which leads to resulting in dissolution or disarrangement of the melt microphase separation structure. However, because the melting temperature of the polyethylene was not lowered in the blends, it is natural to consider that polyethylene and polyisoprene are phase-separated even in the blends.

Figure 7 depicts SAXS profiles for the HEI/Plp and HEI/PE blends crystallized at 80°C, at which the microphase structure in the melt is destroyed for the neat block copolymer. As for the blend samples, we cannot declare from the SAXS results whether or not the preexisting microphase structure is changed by the crystallization, because the scattering peak from the microphase separation is not observed in the melt for the blends. As shown in Figure 7, however, obvious dependence on the blend composition can be observed in the scattering profiles around $q=0.15–0.4\,\text{nm}^{-1}$, which reflects the crystalline lamellar structure of the E block. For the HEI/PE blends, although the scattering profiles are very similar to that for the PE homopolymer in all the blend compositions, the peak becomes broader with decreasing PE composition. On the other hand, HEI/Plp blends show more strong dependence on the composition. The scattering peak from the crystal lamellae becomes weaker with increasing the blended Plp. Especially, it is hard to observe the peak in HEI/Plp-17 having only 17 wt% of polyethylene part. This behavior will be discussed with DSC results in the following section.

**Crystallization behavior of HEI/PE and HEI/Plp blends**

In Tables 3 and 4, DC of the blends measured by DSC are summarized (where the condition of hydrogenation of HEI used in the blends with Plp is somewhat different from that in the PE blends). Figure 8 shows melting...
Figure 6. SAXS profiles for HEI, HEI/Plp and HEI/PE in the molten state at 140°C.

Figure 7. SAXS profiles for HEI, HEI/Plp and HEI/PE in crystalline states. The crystallization temperature is 80°C.
behavior for HEI, HPE, LPE and the HEI/PE blends crystallized at 85°C. For the HPE and LPE homopolymers, as shown in Figure 8, multiple melting endotherms were observed. The origin of the multiple melting peaks is considered to be the chain heterogeneity originating from the ethyl branches described before. For both HEI/HPE and HEI/LPE blends, the crystallization behavior seems just to move toward that of the PE homopolymer with increasing the blended PE. As the PE composition increases, as shown in Figure 8, the DSC curves become to present multiple melting peaks and DC is close to that for the blended PE homopolymer (Table 3). Since the microphase separation structure of the neat HEI is lamellar, the interconnectivity of the polyethylene phase in the melt is not essentially changed by blending PE. Therefore, the crystallization behavior in HEI/HPE and HEI/LPE blends can be explained as just the superposition of that in HEI and PE. With increasing PE composition, the behavior tends to become that of PE homopolymers. The same tendency can be seen on the SAXS profiles shown in Figure 7-c.d. For HEI/PIp-17 blends, on the other hand, DC is suppressed at higher $T_c$ as shown in Table 4. This means that crystallization of the E block is disturbed by blending PIp. Unlike the HEI/PE blends, for the HEI/PIp-17 blends, the lamellar microphase separation structure should tend to be changed with increasing PIp to be isolated domains of the E block in the melt. Thus, the disturbance of crystallization may come from the change in the melt microphase structure. The crystallization kinetics has been analyzed based on the Avrami expression. The Avrami formulation is given by

$$1 - \frac{X_t}{X_i} = \exp\left(-Kt^n\right)$$  \hspace{1cm} (1)

where $X_t$ is the degree of crystallinity at crystallization time $t$, $K$ is the overall rate constant of crystallization, and $n$ is the Avrami index which expresses the dimensionality of the crystal growth. At a small degree of crystallinity, Eq. 1 can be reduced as

$$X_t = K t^n$$  \hspace{1cm} (2)

Table 3. Degree of Crystallinity and Avrami Indices in the Indicated Range of $T_c$ for HEI, PE Homopolymer and HEI/PE Blends

| Sample code | $T_c$ (°C) | DC (%) $^a$ | Avrami index $^b$ |
|-------------|------------|-------------|------------------|
| HEI         | 80.0–100.0 | 53.1–26.7   | 2.0              |
| HPE         | 80.0–100.0 | 67.0–41.8   | 2.2              |
| LPE         | 80.0–100.0 | 49.2–2.1    | 2.1              |
| HEI/LPE-60  | 80.0–100.0 | 38.3–18.6   | 2.3              |
| HEI/LPE-70  | 80.0–100.0 | 47.2–25.0   | 2.3              |
| HEI/LPE-80  | 80.0–100.0 | 43.8–5.8    | 2.0              |
| HEI/HPE-60  | 80.0–100.0 | 35.5–23.1   | 2.2              |
| HEI/HPE-70  | 80.0–100.0 | 68.2–43.2   | 2.2              |
| HEI/HPE-80  | 80.0–100.0 | 61.2–37.3   | 2.5              |

$^a$ Normalized to polyethylene content. $\Delta H_m^{c=4.051}$ kJ/mol was used.

$^b$ For $T_c = 96°C$.

Table 4. Degree of Crystallinity and Avrami Indices in the Indicated Range of $T_c$ for HEI and HEI/PIp Blends

| Sample code | $T_c$ (°C) | DC (%) $^a$ | Avrami index $^b$ |
|-------------|------------|-------------|------------------|
| HEI         | 80.0–96.0  | 53.7–43.4   | 2.3              |
| HEI/LPIp-17 | 80.0–96.0  | 53.4–1.4    | 2.0              |
| HEI/LPIp-34 | 80.0–96.0  | 55.3–45.9   | 2.6              |
| HEI/HPIp-17 | 80.0–96.0  | 52.1–25.0   | 2.7              |
| HEI/HPIp-34 | 80.0–96.0  | 57.3–42.7   | 2.3              |

$^a$ Normalized to polyethylene content. $\Delta H_m^{c=4.051}$ kJ/mol was used.

$^b$ For $T_c = 94°C$.

$^c$ The hydrogenation condition of HEI is somewhat different from that in Table 3.

Figure 8. Melting behavior for HEI, LPE and HEI/LPE blends (a), and HEI, HPE and HEI/HPE blends (b), crystallized at 85°C.
Avrami plots are depicted for HEI, HEI/PIp, HEI/PE and PE homopolymers in Figure 9. The Avrami indices estimated from the initial slope of the double logarithmic plots are also listed in Table 3 and Table 4. The Avrami indices obtained here range from 2 to 3 and no systematic tendency can be observed. In our previous papers, it was found that the Avrami indices were reduced for block copolymers having a glassy amorphous component, because crystallization occurs within confined rigid microdomains\(^{19,20}\). On the other hand, for PEG-PBD, in which the amorphous component is rubbery in crystallization, we reported that the Avrami index is not reduced even when crystalline PEG is in cylindrical microdomains\(^{26}\). In the system studied here, the reduction of \(n\) was not found even in the blends with the small amount of the crystalline component (HEI/LPip-17 and HEI/HPip-17). This means that, even though the crystallization is suppressed, the growth dimensionality in crystallization is not lowered. This may result from the flexibility of the rubbery amorphous chains.

The inverse of the crystallization time \(\tau\) at a certain degree of crystallinity \(X_c\) corresponds to the overall crystallization rate \(\nu\), that is,

\[
\nu \sim 1/\tau
\]  

Here, \(\tau\) was taken to be the time at \(X_c=0.015\), which lies on the straight line of the \(\log t\)-\(\log X_c\) relation for all the samples. Figure 10 shows Arrhenius-type plots of \(1/\tau\), that is, \(1/t_{0.015}\) versus the inverse of the supercooling degree \(\Delta T=T_m^o-T_c\) for the PE homopolymers (HPE, PE58k) and HEI block copolymer, where the equilibrium melting temperature \(T_m^o\) was assumed to be 145°C\(^{31}\) which is for the linear PE homopolymer. The result of SE54 (polystyrene-polyethylene block copolymer, weight fraction of E, \(f_E^{0.54}\))\(^{32}\) is also presented in Figure 10 for comparing with HEI.

As seen in Figure 10, the slope of the plots, which corresponds to the apparent activation energy of crystallization, is almost the same among the HEI block copolymer and the two kinds of PE homopolymers. This means that the crystallization of the E block in HEI is not restricted by the rubbery I block. On the other hand, the

\[
\log X_c = n \log t + \log K
\]  

Figure 9. Avrami plots for HEI and HEI/PIp at 94°C (a), for HEI, LPE and HEI/LPE at 96°C (b), and for HEI, HPE and HEI/HPE at 96°C (c).
slope of the plots is gentle for HEI compared with that of SE54. Also, the crystallization rate of HEI is much faster than that of SE54 when compared with each other at the same ΔT. This tendency can be attributed to the fact that the glassy component S in SE54 restricts the crystallization of the SE54 block copolymer, but that the crystallization of HEI is not restricted because the I block is rubbery.

Conclusion

Structure formation in crystallization from microphase-separated melts was studied for polyethylene-polyisoprene block copolymers and their blends with corresponding homopolymers. Results of SAXS show that, for HEI, preexisting microphase separation morphology in the melt was kept at high and low T_c (T_c≥94°C and T_c<60°C), while disrupted at intermediate T_c (60°C≤T_c<94°C). This complicated behavior was attributed to two factors. One is the competition between the crystallization and chain diffusion rates, which explains the behavior in the temperature range of T_c<94°C in the same way as previously reported for crystalline-rubbery amorphous block copolymers. The other is the small DC in the higher temperature range of T_c≥94°C. The reduction of DC is caused by the chain heterogeneity acting as impurities in crystallization. The melt structure is maintained owing to a small DC at T_c≥94°C.

For HEI/PE blends, crystallization behavior was explained by the simple superposition of those for HEI and PE. On the other hand, DC of HEI/Pip blends having a smaller polyethylene composition is suppressed at higher T_c. This behavior was attributed to that the interconnectivity of the polyethylene phase was partially broken down to form isolated polyethylene domains in the melt. However, the Avrami index was not reduced as reported for other crystalline-rubbery amorphous block copolymers. Also, the apparent activation energy of crystallization was not so different from that for the PE homopolymer. This may be because the amorphous polyisoprene chains are flexible.

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