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Phase behavior and crystallization in blends of a low molecular weight polyethylene-*block*-poly(ethylene oxide) diblock copolymer and poly(hydroxyether of bisphenol A)

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Abstract

The phase behavior, morphology and crystallization in blends of a low-molecular-weight ($M_n = 1400$) double-crystalline polyethylene-*block*-poly(ethylene oxide) (PE-PEO) diblock copolymer with poly(hydroxyether of bisphenol A) (PH) were investigated by differential scanning calorimetry, transmission electron microscopy and small-angle X-ray scattering. The symmetric PE-PEO diblock copolymer consists of a PH-miscible PEO block and a PH-immiscible PE block. However, PH only exhibits partial miscibility with the PEO block of the copolymer in the PH/PE-PEO blends; both macrophase and microphase separations took place. There existed two macrophases in the PH/PE-PEO blends, i.e., a PH-rich phase and a PE-PEO copolymer-rich phase. The PE block of the copolymer in the blends exhibited fractionated crystallization behavior by homogeneous nucleation. There appeared three crystallization exotherms related to the crystallization of the PE block within three different microenvironments in the PH/PE-PEO blends.

Keywords: Polymer blends; Phase behavior; Crystallization; Poly(hydroxyether of bisphenol A); Polyethylene-*block*-poly(ethylene oxide)

1. Introduction

In blends comprising a block copolymer and a homopolymer, the phase separation of the blend components can be coupled with the microphase separation of the block copolymer [1,2]. The macrophase separation may take place between the block copolymer and the homopolymer while the block copolymer alone can undergo microphase separation and form microdomains. There is interplay between the macrophase separation and the microphase separation, which therefore brings about a variety of morphologies. Furthermore, in block copolymer/homopolymer blends where the block copolymer is crystallizable, phase behavior and crystallization are very complicated, especially in the regime where both macrophase and microphase separations can take place. Coupling and competition between macrophase separation, microphase separation, and crystallization process would result in the richness and complex changes in morphology. However, this would enable us to create self-assembled structures over a variety of length scales and hold the key to the development of new structures and advanced devices [3,4].

We report here blends of a double-crystalline polyethylene-*block*-poly(ethylene oxide) (PE-PEO) diblock copolymer and a homopolymer, poly(hydroxyether of bisphenol A) (PH). The PE-PEO is a low-molecular-weight amphiphilic diblock copolymer with an average $M_n = 1400$ and 50 wt.% ethylene oxide content. It has been known that PEO homopolymer is miscible with PH [5] and there is a favorable hydrogen-bonding interaction between PEO and PH [6]. The symmetric PE-PEO diblock copolymer consists of a PH-miscible PEO block and a PH-immiscible PE block. Thus, the PH would selectively mix to some extent with the PEO block in the PE-PEO diblock copolymer without dissolving the PE block. The crystallizable PE block that is immiscible with both PH and the PEO block would form separate microdomains in the PH/PE-PEO blends.

This work presents an example of block copolymer/homopolymer blend systems containing a double-crystalline diblock copolymer where the homopolymer is miscible with one block but immiscible with the other. The phase behavior, thermal properties and crystallization in these block

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copolymer/homopolymer blends are investigated by differential scanning calorimetry (DSC). The morphology of the blends is examined by transmission electron microscopy (TEM) and small-angle X-ray scattering (SAXS).

2. Experimental

2.1. Materials and preparation of samples

The PE-PEO diblock copolymer, namely, polyethylene-*block*-poly(ethylene glycol), was purchased from Aldrich Chemical Co., Inc. It had an average $M_n = 1400$ and 50 wt.% ethylene oxide content. The PH sample with an average $M_w = 40{,}000$ was also a product of Aldrich Chemical Co., Inc. The PE-PEO and PH, totally 1.0 g, were dissolved in 20 ml chloroform at room temperature to form a 5% (w/v) solution. The blend samples were cast from the solutions at room temperature. The residual solvent was removed in vacuum at room temperature for 2 weeks.

2.2. Differential scanning calorimetry

The calorimetric measurements were made on a Perkin-Elmer Pyris 1 differential scanning calorimeter in a dry nitrogen atmosphere. Indium and tin standards were used for calibration for low and high-temperature regions, respectively. Samples of about 8 mg were placed in the DSC pan. All samples were first heated to 150 °C at a rate of 20 °C/min (first heating scan) and kept at that temperature for 2 min; subsequently they were cooled at a rate of −20 °C/min to detect crystallization (cooling scan). Following the cooling scan, a second scan was conducted at 20 °C/min. The midpoint of the slope change of the heat capacity plot of the second heating scan was taken as the glass transition temperature (T_g). The crystallization temperature (T_c) was taken as the minimum of the exothermic peak, whereas the melting temperature (T_m) was taken as the maximum of the endothermic peak. The heat of fusion (ΔH_f) and the heat of crystallization (ΔH_c) were evaluated from the areas of the melting and crystallization peaks, respectively. The degree of crystallinity, X_c, was calculated by the following equations:

$$X_c(\text{blend}) = \frac{\Delta H_f}{\Delta H_f^0} \tag{1}$$

$$X_c(\text{copolymer}) = \frac{X_c(\text{blend})}{W(\text{copolymer})} \tag{2}$$

where ΔH_f^0 is the heat of fusion of 100% crystalline polymer, W is the weight fraction, ΔH_f is the heat of fusion of the blend during the heating scan. The ΔH_f^0 values used for PE and PEO are 286 J/g [7] and 205 J/g [8], respectively.

2.3. Transmission electron microscopy

For the TEM observation, the as-cast samples of PH/PE-PEO blends were first melted at 150 °C for 2 min and then microtomed at −80 °C with a Leica EMFCS instrument equipped with a diamond knife. The resulting ultrathin sections of 80 nm thickness were picked up on copper grids and stained in the vapor of an aqueous solution of RuO_4. Stained samples were imaged in a JEOL 1010 transmission electron microscope with an accelerating voltage of 120 kV.

2.4. Small-angle X-ray scattering

The SAXS measurements were obtained with a Bruker NanoSTAR instrument using a HR-PHK high resolution pinhole chamber with high brilliance Cu Kα X-rays from Göbel mirrors. Prior to the measurement, the as-cast samples of PH/PE-PEO blends were first melted at 150 °C for 2 min. Two-dimensional diffraction patterns were collected on a HI-STAR high resolution multiwire detector at room temperature, corrected for response characteristics, and converted into a one-dimensional format (intensity versus q) by azimuthal averaging of the data [$q = (4\pi/\lambda)\sin(\theta/2)$ is the scattering wavevector].

3. Results and discussion

3.1. Phase behavior and thermal properties

All the PH/PE-PEO blends were subjected to DSC measurement. Fig. 1 shows DSC thermogams of the second scan of the PH/PE-PEO blends. The PE-PEO diblock copolymer exhibits two obvious melting points, $T_{m1(PEO)} = 30\,^\circ C$ and $T_{m(PE)} = 106\,^\circ C$, attributable to the crystalline PEO block and the crystalline PE block, respectively. The $T_{m1(PEO)}$ substantially shifts down to lower temperatures with increasing PH content up to 40 wt.% in the blends. It has been known that PH is miscible

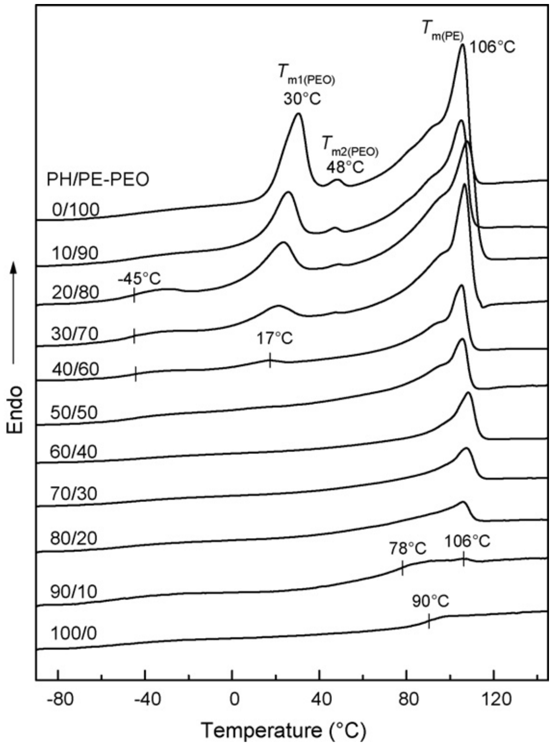

Fig. 1. DSC thermograms of the second scan of PH/PE-PEO blends after the cooling scan. The heating rate is 20 °C/min.

with PEO homopolymer [5,6]. The addition of PH may dilate the PEO microdomains of the PE-PEO diblock copolymer; the amorphous PH chains can be mixed with the PH-miscible PEO block to some extent. Thus, the microphase separated PE-PEO diblock copolymer can be swollen with PH. When the dissolution of PH in the PEO microdomains has reached its limit, a PH-rich macrophase can be separated from the microphase-separated PE-PEO diblock copolymer that is swollen with PH. For the PH/PE-PEO blends with 50 wt.% or more PH, no melting peak for the PEO block appears. DSC thermogams of the first scan (not presented here for brevity) of the as-prepared PH/PE-PEO blends with 50 wt.% or more PH also does not display melting peak for the PEO block. This implies that the PEO block of the PE-PEO copolymer was completely dissolved in a PH-rich phase in these blends.

It can also be seen from Fig. 1 that melting point of the PE block, $T_{m(PE)}$, remains little affected in the blends even with PE-PEO content down to 10 wt.%, consistent with the immiscibility between the PE block and PH. The PE block, which is immiscible with both PH and the PEO block, forms a separate microphase in the blends. It is interesting to notice that there is a small melting peak at 48 °C responsible for the PEO block in the pure PE-PEO copolymer and in the blends with PH content up to 30 wt.%. The appearance of this small peak is attributable to recrystallization of the PEO block and the subsequent melting.

The pure PH exhibits a glass transition, $T_{g(PH)} = 90\,^{\circ}C$, which becomes broad and shifts down to a lower temperature (78 °C) in the blend containing 10 wt.% PE-PEO. This glass transition disappears in the blends when the content of PE-PEO copolymer reaches 20 wt.%. This result indicates the dissolution of the PEO block of PE-PEO copolymer in the PH-rich phase. The glass transition for the plain PE-PEO and the blend with 90 wt.% PE-PEO was not detectable under the experimental condition. However, the PH/PE-PEO blends containing 20, 30 and 40 wt.% PH clearly display a glass transition in the proximity of −45 °C, substantially higher than that of the PEO block which ranges from −70 to −60 °C [9]. This result implies that some amount of PH was dissolved in the PEO microphase.

Fig. 2 summarizes all the thermal transition temperatures from the second scans as a function of the blend composition. It clearly displays that the $T_{m(PE)}$, remains almost unchanged in the blends with PE-PEO content down to 10 wt.%. Fig. 2 also illustrates that the melting point of the PEO block, $T_{m1(PEO)}$, substantially decreases in the blends with increasing PH content, suggesting that considerable amount of PH was dissolved in the PEO microphase and that PH and the PEO block are partially miscible. The melting point depression is a common phenomenon for miscible blends containing one crystallizable component [10,11]. Morphological factors can also influence on the melting point of the PEO block.

The values of $X_{c(PE)}$ and $X_{c(PEO)}$ for the PH/PE-PEO blends are plotted as a function of blend composition in Fig. 3. The value of $X_{c(PE)}$, i.e., crystallinity of the PE block in the blends does not decrease even with the copolymer content down to 20 wt.%. The crystallinity of the PE block is not significantly influenced in the blends. This phenomenon is due to the immiscibility between PH and the PE block. However, $X_{c(PEO)}$ decreases drastically with decreasing PE-PEO content, and the PEO block no longer crystallizes under the experimental condition when the PE-PEO copolymer is less than 60 wt.% in the blends. The crystallization process of the PEO block is remarkably hindered in the blends. This is due to the partial miscibility of the PEO block with PH and the much higher T_g of PH (90 °C) than that of PEO block (−70 to −60 °C).

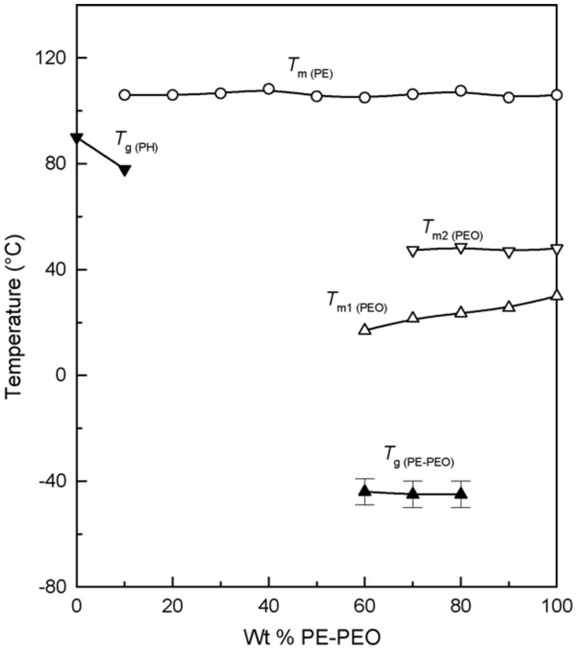

Fig. 2. Thermal transitions of the second scan of PH/PE-PEO blends.

The PH/PE-PEO blends were characterized by TEM. Fig. 4 shows TEM micrographs for the PH/PE-PEO blends containing 30, 50, and 60 wt.% PH. It can be seen that these blends are macrophase-separated, exhibiting characteristics of a bicon-

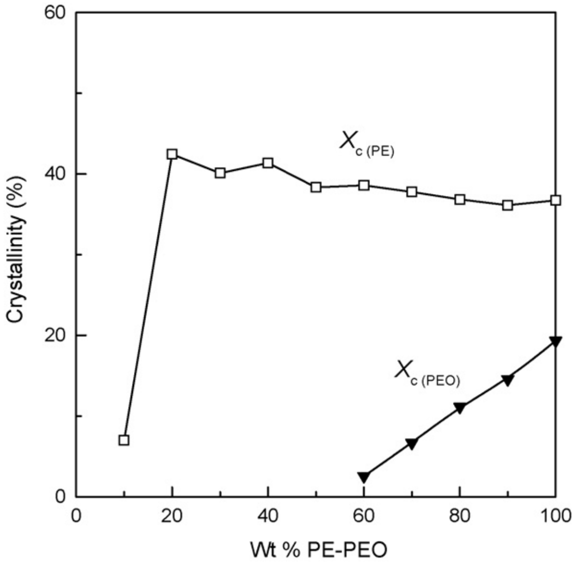

Fig. 3. $X_{c(PE)}$ (□) and $X_{c(PEO)}$ (▼) vs. PE-PEO weight fraction of PH/PE-PEO blends.

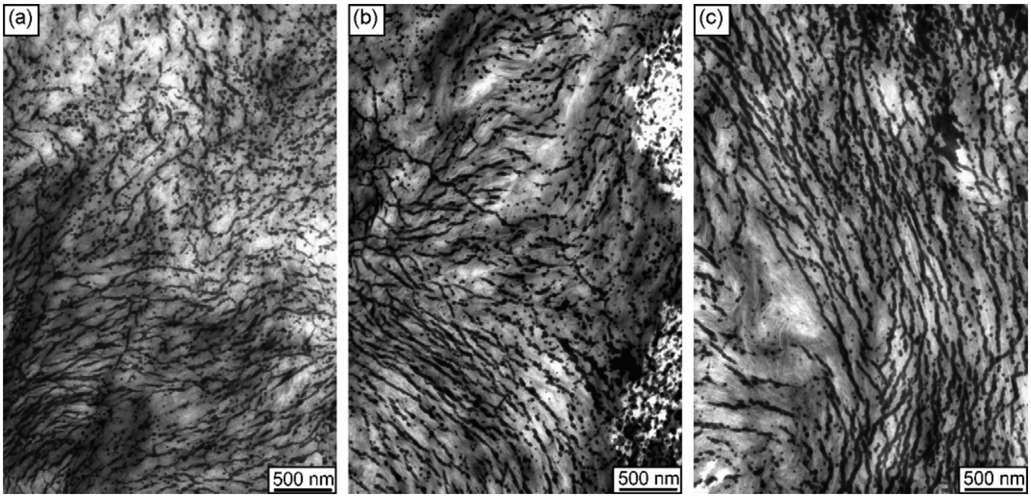

Fig. 4. TEM micrographs of (a) 30/70, (b) 50/50, and (c) 60/40 PH/PE-PEO blends. The specimens for TEM observation were stained with RuO_4 vapor.

tinuous phase structure. There exist two macrophases, i.e., a PH-rich phase and a PE-PEO copolymer-rich phase. The phase which looks black can be considered as the PH-rich phase, i.e., mainly composed of PH, which is preferentially stained with RuO_4 due to the aromatic moieties in the main chain [12,13].

SAXS measurements have been performed for the plain PE-PEO and the PH/PE-PEO blends to characterize their microphase structures. For the plain PE-PEO, the SAXS scattering peak is centered at a value of the scattering vector q corresponding to a long spacing of 12.7 nm (Fig. 5), which represents the average spacing between the neighboring PE and PEO microdomains. Previous studies have shown that the symmetric low-molecular-weight ($M_n = 1400$ and 2100) PE-PEO diblock copolymers are microphase-separated at room temperature [14–17]. It can be seen from Fig. 5 that the long spacing increases with PH content up to 30 wt.% in the PH/PE-PEO blends, indicating that the microphase-separated PE-PEO diblock copolymer was swollen with PH. The addition of PH dilated the PEO microdomains of the PE-PEO diblock copolymer, presumably through the incorporation of PH within the polar PEO microdomains. The long spacing reaches a maximum at 17.9 nm for the 30/70 PH/PE-PEO blend, implying that the dissolution of PH in the PEO microdomains had reached its limit and that there could have appeared a PH-rich macrophase aside from the swollen microphase-separated PE-PEO. This result is in agreement with the TEM observation that the 30/70 PH/PE-PEO blend was macrophase-separated and composed of a PH-rich phase and a PE-PEO copolymer-rich phase. The scattering peaks for the blends with 60–30 wt.% PE-PEO remain less affected, corresponding to a long spacing ranging from 17.2 to 18.1 nm ascribed to the microphase-separated PE-PEO-rich phase swollen with PH. The SAXS patterns for the blends with 20 and 10 wt.% PE-PEO are featureless.

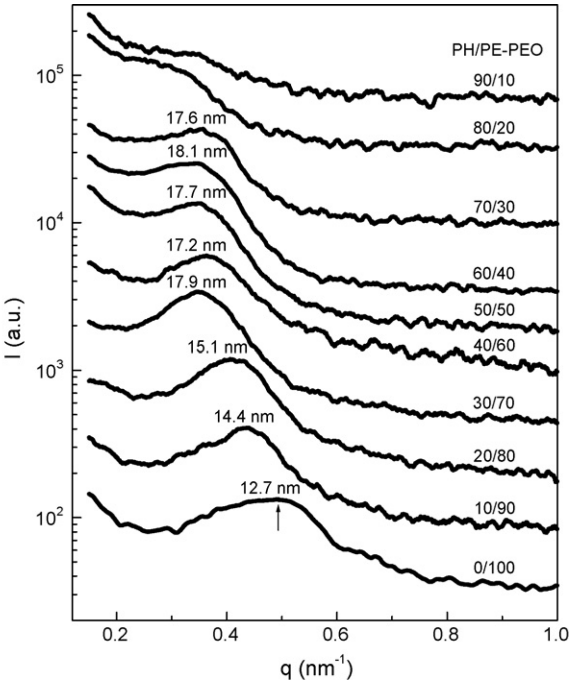

Fig. 5. SAXS patterns of PH/PE-PEO blends as a function of composition. The scattering vector $q = (4\pi/\lambda)\sin(\theta/2)$, where $\lambda = 0.154$ nm is the wavelength and θ the scattering angle.

From the DSC, TEM and SAXS results, it is clear that PH exhibits partial miscibility with the PEO block of the copolymer in the blends. The PH/PE-PEO blends exhibit a two-macrophase structure, i.e., a PE-PEO copolymer-rich phase composed of microphase-separated PE-PEO copolymer swollen with PH and a PH-rich phase composed of PH matrix dispersed with PE-PEO copolymer. It is noted that the present results are different from our earlier findings in diblock copolymer/thermoset blends of PE-PEO and bisphenol-A-type epoxy resin [14]. The latter has a chemical structure similar to that of PH; PH is actually the corresponding linear high-molecular-weight homopolymer of the bisphenol A-type epoxy resin. The cured epoxy resin/PE-PEO blends were nanostructured and macrophase separation did not occur. It has been shown that the crosslinking of the epoxy resin plays a significant role in preventing macroscopic phase separation in the cured epoxy resin/PE-PEO blends [14] and in the cured epoxy resin blends with other PEO-based block copolymer [18,19].

It is interesting to compare the present system with the type A-B/A systems where A-B is a diblock copolymer with one block consisting of monomers of type A and the other block of type B and where A is a homopolymer with monomers of type A, i.e., the repeat unit of the homopolymer is the same as that of the A block in the A-B diblock copolymer. For an A-B/A diblock copolymer/homopolymers blend, interaction parameter χ between one block and its homopolymer is 0 from the viewpoint of the wet-brush/dry-brush behavior [20]. In general, the type A-B/A blends have been shown to have different behavior depending on the relative molecular weight of the homopolymer A compared to the molecular weight of the block A of the diblock copolymer. It has been shown that when the homopolymer A is longer than the block A of the diblock, dry brush behavior is observed, and when it is shorter, wet-brush behavior is observed. In the present system, PH is 57 times larger than the PEO block in its molecular weight (and molecular size), i.e., the PH chain is much longer than the PEO block of the PE-PEO, seemingly suggesting an extremely dry-brush behavior. However, there is a favorable hydrogen-bonding interaction between the PEO and the PH which makes $\chi_{\mathrm{PEO,PH}} < 0$; the determination of the interaction parameter $\chi_{\mathrm{PEO,PH}}$ yielded the rather large negative value of −0.94 [21] or −0.74 [22]. This then allows a wet-brush and limited solubility of the PH in the PEO block. The favorable hydrogen-bonding interaction imparts the partial miscibility between the PH and the PEO block, which changes the behavior of the corona PEO chains from that of dry-brush to wet-brush behavior against the PH.

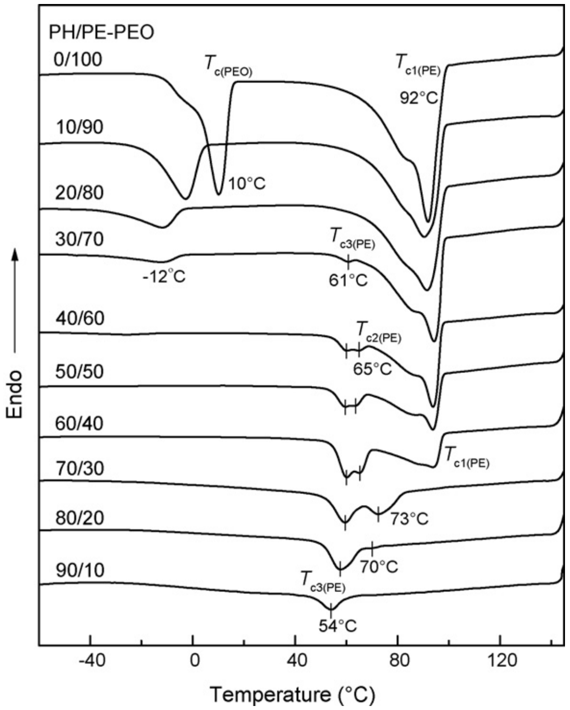

Fig. 6. Crystallization curves of PH/PE-PEO blends during the cooling at −20 °C/min. All samples were first heated to 150 °C and kept at that temperature for 2 min to remove the thermal history.

3.2. Crystallization during the cooling

Fig. 6 shows DSC thermograms of the cooling scan for the PH/PE-PEO blends at a cooling rate of −20 °C/min from 150 °C. All the samples were molten at 150 °C for 2 min to remove the thermal history prior to the cooling scan. The pure PE-PEO copolymer displays a crystallization peak, $T_{\mathrm{c(PEO)}}$, at 10 °C, attributable to the crystallization of the PEO block. This crystallization peak, $T_{\mathrm{c(PEO)}}$, shifts to lower temperatures in the blends with increasing PH content. For the 30/70 PH/PE-PEO blend, this crystallization peak becomes very small and shifts down to −12 °C, indicating a reduced crystallization rate. There is no crystallization exotherm of the PEO block during the cooling scan for the blends containing 60 wt.% or less PE-PEO copolymer. The overall crystallization rate of PEO block of PE-PEO copolymer in the blends decreases substantially with increasing PH content, which can be ascribed to the dissolution of the PEO block in PH and the much higher T_g of PH (90 °C) compared to that of PEO (−70 to −60 °C). The crystallization behavior of the PH-miscible PEO block in the blends is as expected for crystallizable/miscible blends.

The pure PE-PEO copolymer displays a major crystallization peak for the PE block, $T_{\mathrm{c1(PE)}}$, at 92 °C, which does not shift to lower temperatures in the blends with PE-PEO content down to 40 wt.%, then drops abruptly to much lower temperatures (73 and 70 °C) at 30 and 20 wt.% PE-PEO compositions. The relative intensity of this crystallization peak substantially decreases with decreasing PE-PEO content. Finally, this major crystallization peak disappears when the PE-PEO content is further down to 10 wt.%. It is also noted that a small crystallization peak, $T_{\mathrm{c3(PE)}}$, appears on the low temperature side (61 °C) for the blend with 70 wt.% PE-PEO, indicating that the crystallization of a small amount of the PE block was performed at a greatly reduced rate in the blends. This crystallization peak does not significantly shift to lower temperatures in the blends even with PE-PEO content down to 10 wt.%; its value only slightly varies between 54 and 61 °C. The relative intensity of this crystallization peak however gradually increases with decreasing PE-PEO content and finally becomes the dominated one at the lowest PE-PEO concentrations. For the blends at the mid-compositions of 40/60, 50/50 and 60/40 PH/PE-PEO, there appears another small crystallization peak, $T_{\mathrm{c2(PE)}}$, at about 65 °C intermediate between the crystallization peaks $T_{\mathrm{c1(PE)}}$ and $T_{\mathrm{c3(PE)}}$.

The existence of more than one crystallization exotherm is known as fractionated crystallization [23,24]. It has been observed that fractionated crystallization can occur in droplets or dispersed domains of crystallizable polymers in low molecular weight media [23–25], in block copolymers [26–28], and in polymer blends [23–25,29–33]. For fractionated crystallization to take place, the polymer melt must be dispersed finely enough that the number of dispersed domains is significantly greater than the number of heterogeneities that are active at low supercoolings [23]. As a result, most of the dispersed domains contain either less efficient heterogeneities or no heterogeneities at all. Dispersed domains or droplets for homogeneously nucleation are usually very small; crystallization of dispersed domains by homogeneous nucleation will occur if the number of dispersed domains is greater than the number of active heterogeneities originally present in the bulk polymer [34,35]. It has been shown that the lowest crystallization exotherm with the largest supercooling is usually associated with homogeneous nucleation [23–25].

For PE homopolymer, the lowest crystallization exotherms reported for homogeneous nucleation are in the temperature range between 67 and 70 °C [32]. In the present case, the appearance of fractionated crystallization, i.e. the presence of three crystallization exotherms can be ascribed to the crystallization of the PE block in three different microenvironments in the PH/PE-PEO blends. $T_{c1(PE)}$, the major crystallization peak at about 106 °C, is due to heterogeneous nucleation of the PE block of the PE-PEO copolymer. The crystallization is highly cooperative among the PE microdomains. $T_{c2(PE)}$, the crystallization peak in the proximity of 65 °C, represents another crystallization process of the PE block in the blends. This crystallization process can be ascribed to the PE microdomains in the PE-PEO copolymer-rich phase where the crystallization of the PE block is hindered but not highly restricted in the PE microdomains. $T_{c3(PE)}$, the lowest one intermediate between 54 and 61 °C is related to homogeneous nucleation, which is attributable to the individual microdomains of the PE block. The PE block is immiscible with both PH and the PEO block and thus may form separate microdomains individually dispersed in the PH-rich phase. The crystallization of the PE block is largely confined within these individual PE microdomains. However, only a single melting endotherm was observed in the subsequent heating thermogram (see Fig. 1) regardless of whether the PE block crystallized by homogeneous or heterogeneous nucleation, which is as expected for fractionated crystallization.

4. Conclusions

From the results presented above, it can be concluded that PH has partial miscibility with the PEO block of PE-PEO copolymer in the PH/PE-PEO blends. Both macrophase and microphase separations took place. There existed two macrophases in the PH/PE-PEO blends, i.e., a PH-rich phase and a PE-PEO copolymer-rich phase. Fractionated crystallization behavior by homogeneous nucleation was observed for the PE block of the copolymer in the blends. The appearance of three crystallization exotherms is attributable to the crystallization of the PE block in three different microenvironments in the PH/PE-PEO blends.

Acknowledgements

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