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ORIGINAL ARTICLE

Analysis of the degree of crystallinity in interpenetrating spherulites of poly(ethylene succinate) and poly(ethylene oxide) blends using pulsed NMR

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The degree of crystallinity (ϕ) in interpenetrating spherulites, whereby spherulites of one component continue to grow inside those of the other component, was examined for the blends of poly(ethylene succinate) (PES) and poly(ethylene oxide) (PEO) using pulsed nuclear magnetic resonance. The value of ϕ for PES increased with PEO blending and was slightly dependent on the blend composition when crystallized below ~ 65 °C. However, ϕ for PEO monotonically decreased with the PES content in the blends and was dependent on the blend composition. The composition dependence of ϕ is discussed based on the change in temperature at which the molecular transport is frozen with the blend composition. The effect of secondary crystallization, which is only relevant for PEO, was taken into account when determining ϕ. The amount of crystals of both constituents in the blends primarily depended on the blend composition.

INTRODUCTION

Miscible blends composed of two crystalline polymers often exhibit interpenetrating spherulites, whereby a spherulite of one component grows inside that of the other component.[1–21] In the formation process of interpenetrating spherulites, one component crystallizes inside the amorphous regions of the spherulites of the other component maintaining the spherulitic shape. When one component with a higher melting point (T_m) crystallizes and develops spherulites in a homogeneous melt, the other component with a lower T_m is expelled out of the crystalline lattice and remains in the interlamellar and interfibrillar regions, the characteristic sizes of which are typically of the order of 10 and 100 nm–1 µm, respectively. There is a possibility that the crystallization of the component with the lower T_m is suppressed in these regions.

Although the morphology and growth rate of interpenetrating spherulites have been reported,[1–23] investigations of the degree of crystallinity are still insufficient. To the best of our knowledge, no studies have provided a detailed characterization of the change in the degree of crystallinity with the crystallization temperature and blend composition for interpenetrating spherulites.

Although differential scanning calorimetry has been widely used for evaluating the degree of crystallinity, pulsed nuclear magnetic resonance (NMR) is another powerful method for this purpose.[24,25] The absolute value of the degree of crystallinity can be obtained using pulsed NMR by decomposing the spin–spin relaxation decay into the immobile crystalline and mobile amorphous components when the temperature is sufficiently above the glass transition temperature (T_g).

For some polymers, pulsed NMR also detects an additional intermediate component that has often been assigned to the interfacial regions between the crystalline and amorphous regions.[24–30]

When the crystallization process is sufficiently slow and the degree of crystallinity is assumed to only slightly change during the acquisition time of the spin–spin relaxation data, one can obtain the change in the degree of crystallinity with the crystallization time, including slow processes such as secondary crystallization. Applying differential scanning calorimetry to such a slow process is very difficult owing to the small heat flow.

The blends of poly(ethylene succinate) (PES) and poly(ethylene oxide) (PEO) are a few of the systems that exhibit interpenetrating spherulites.[6,9,19–21] For this blend, PES and PEO are the higher and lower T_m components, respectively. When the PES/PEO blends are crystallized in a homogeneous melt, both components simultaneously nucleate and form interpenetrating spherulites below ~ 50 °C. However, PES crystals fill the entire volume, and then PEO nucleates and develops spherulites inside the PES spherulites at higher temperatures. Other investigations of the properties and morphology of PES/PEO blends and block copolymers have been previously reported.[22,23]

The aim of this article is to investigate the degree of crystallinity of PES and PEO by pulsed NMR under the conditions at which interpenetrating spherulites are formed. After examining the crystallization process of the homopolymers, the change in the degree of crystallinity with the crystallization time is evaluated for the blends. The degree of crystallinity after the primary crystallization is evaluated by taking the influence of the secondary crystallization into account.

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The influences of the composition and the crystallization temperature on the degree of crystallinity of the constituents and the fractional amount of crystals in the samples are discussed.

EXPERIMENTAL PROCEDURE

PES ($M_w = 10\,000$, $T_g = -20\,°C$, $T_m = 98\,°C$) and PEO ($M_v = 100\,000$, $T_g = -67\,°C$, $T_m = 65\,°C$) were purchased from Scientific Polymer Products (Ontario, NY, USA) and the Sigma-Aldrich (St Louis, MO, USA), respectively. The blends were prepared using the solution-cast method with chloroform as a mutual solvent. The solutions were dried in a fume hood at room temperature for 1 day and then in vacuum for at least 3 days. The temperature ranges for crystallization of PES and PEO are below $\sim 75\,°C$ and $55\,°C$, respectively. The crystallization rate above these temperatures was too slow to result in crystallization. The blend compositions were PES/PEO = 5/5, 4/6, 3/7 and 2/8 (weight/weight). The samples contain smaller amounts of the higher T_m component (PES) and larger amounts of the lower T_m component (PEO) to allow for the formation of interpenetrating spherulites.

The blend in the NMR sample tube was melted at $130\,°C$ for at least 5 min, and then the blend was quickly transferred into the NMR probe, the temperature of which was maintained at the crystallization temperature. The spin–spin relaxation signals of ^1H were repeatedly obtained at a resonant frequency of 25 MHz using a solid-echo pulse sequence[31] on a JNM-25MU, Jeol (Tokyo, Japan). Four or eight signals were averaged to reduce noise in acquiring the spin–spin relaxation decay data. The relaxation data were fitted to an exponential function before the onset of crystallization. After the onset of crystallization, the relaxation data were decomposed into two components that correspond to the immobile crystalline and mobile amorphous regions. An example of the fitted relaxation data is shown in Figure 1. The fractional amount of the crystals (f), which is derived from the intensity of the fast-decaying Gaussian function with the spin–spin relaxation time (T_2) of the order of 10^{-5} s, denotes the degree of crystallinity on the basis of the number of protons for the homopolymers. For blends, f denotes the sum of the fractional quantities of the crystals of both components. The slowly decaying exponential function with the T_2 of the order of 10^{-3}–10^{-4} s can be assigned to the amorphous regions. Further details of the pulsed NMR measurement can be found elsewhere.[24,25]

The spherulitic growth process was observed using a polarizing optical microscope (BX51, Olympus, Tokyo, Japan) equipped with a temperature stage and controller (THMS 600 and 10002, Linkam, Surrey, UK). The micrographs were obtained with a charge-coupled device camera (Micro Publisher RTV5.0, QImaging, Surrey, BC, Canada). A sample film was placed between two optical glass plates, melted at $\sim 120\,°C$ for ~ 1 min and quenched to T_c for observation.
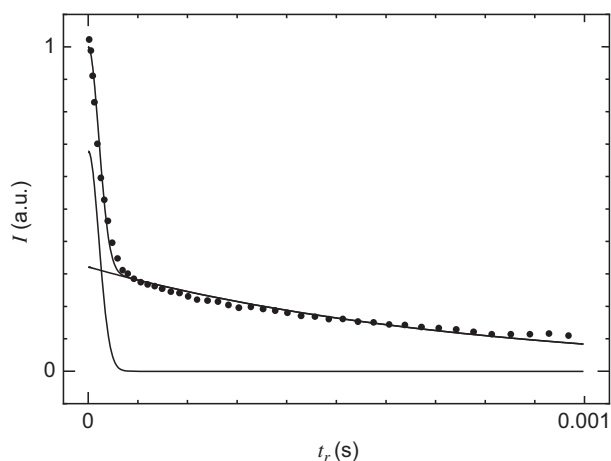

Figure 1 Normalized intensity (I) of the spin–spin relaxation data as a function of the relaxation time (t_r) for poly(ethylene succinate)/poly(ethylene oxide) = 3/7, $T_c = 50\,°C$, and a crystallization time of 5.23×10^3 s.

RESULTS AND DISCUSSION

Figure 2 shows the change in f as a function of the crystallization time (t) for the PES and PEO homopolymers crystallized at $50\,°C$. After the induction periods (that is, on the order of 10^2 s), f increased with t for both polymers. Here, the increase in f is owing to the primary crystallization (that is, the spherulitic growth of the crystalline polymers). The primary crystallization lasted for ~ 500 s for PES and 2500 s for PEO. After the primary crystallization, the value of f for PES was nearly constant, whereas that for PEO exhibited a slight increase, as indicated by the solid lines in Figure 2. These results indicate that PES and PEO undergo negligible and slight secondary crystallization, respectively. The degree of crystallinity of PES is represented by the value of the solid line. However, the degree of crystallinity of PEO just after the primary crystallization can be obtained from the intersection of the solid and dashed lines in Figure 2.

Figure 3 shows the change in f as a function of t for the PES/PEO = 3/7 blend. In Figure 3, the data at 42 and $50\,°C$ were shifted
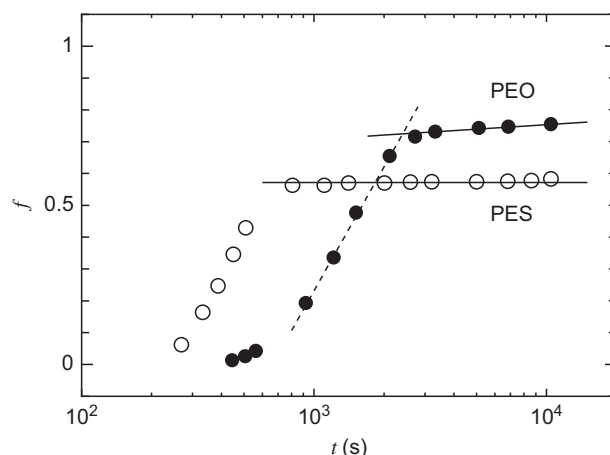

Figure 2 Change in the fractional amount of crystals (f) as a function of the crystallization time (t) for the poly(ethylene succinate) (PES) and poly(ethylene oxide) (PEO) homopolymers crystallized at $50\,°C$.
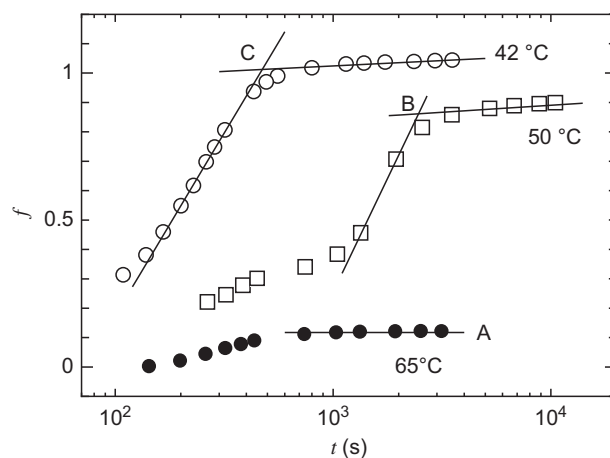

Figure 3 Change in the fractional amount of the crystals (f) as a function of the crystallization time (t) in the poly(ethylene succinate)/poly(ethylene oxide) (PES/PEO) = 3/7 blend. The data at 42 and $50\,°C$ were shifted upward by 0.3 and 0.2, respectively. Line A represents f after the primary crystallization of PES. The intersection points B and C represent f after the primary crystallization of PES and PEO.

upward by 0.3 and 0.2, respectively, for better visualization. After induction periods on the order of 10^2 s, f increased with t, and the crystallization temperature (T_c) influenced the change in f. At 65 °C, at which only PES crystallizes, the increase in f represents the crystallization of only PES. As shown by line A, the value of f was nearly constant after the primary crystallization, indicating that the PES in the blend exhibits little secondary crystallization, which is consistent with that observed for the homopolymer. The degree of crystallinity of PES can be determined from the value of line A and the blend composition.

At a T_c of 50 °C, at which both PES and PEO crystallize, f increased twice before and after ~10^3 s. The first increase, the amount of which is comparable to that at 65 °C, was less than the second increase. The first and second increases must correspond to the primary crystallization of PES and PEO, respectively, because the PES content in the blend is less than that of the PEO. At this temperature, the larger degree of supercooling for PES may have resulted in PES nucleating earlier than PEO.

In contrast to the data at 65 °C, f exhibited a slight increase after the primary crystallizations of PES and PEO at 50 °C. The slow increase at approximately $t = 5$–8×10^2 s may be owing to the overlap of the crystallizations of PES and PEO because PES exhibited little secondary crystallization. The slight increase after approximately $t = 3 \times 10^3$ s originates from the secondary crystallization of PEO, which is consistent with that observed for the homopolymer. The value of f determined from intersection point B contains the contributions from both the PES and PEO crystals. The degree of crystallinity of PES cannot be accurately determined using this intersection method owing to the overlap of the crystallization of the two constituents.

At 42 °C, PES and PEO crystallized nearly simultaneously because f increased only once. The value of f indicated by intersection point C also contains contributions for the PES and PEO crystals, which is similar to the data obtained at 50 °C. Again, the slight increase in f

after the primary crystallization may be owing to the secondary crystallization of PEO.

PES and PEO simultaneously exhibited primary crystallization at ~46 °C or below. However, PES crystallized before the onset of crystallization of PEO at ~48 °C or above, even though a portion of the crystallization time for the two components overlapped with each other.

A decrease in T_c from 65 to 50 °C resulted in a longer induction period for PES, which further reduced T_c to 42 °C, leading to a longer induction period. This variation is because of the crystalline polymers crystallizing in the temperature range between the melting point and the glass transition point. The relatively low crystallinity of PES makes it crystallize in a wide temperature range, and the maximum crystallization rate was observed at ~55–60 °C. The crystallinity of PES may decrease when T_c decreases to ~50 °C.

In addition, the induction period in the pulsed NMR data depends on the crystalline growth rate. The onset of crystallization can be detected by pulsed NMR when f has increased to a sufficient amount, which is typically ~3–5%, after the primary nucleation. The time until the primary nucleation and the growth rate of the crystals influence the crystallization onset detected by pulsed NMR. Therefore, the decreased crystallinity and reduced growth rate of PES may retard the detection of the crystallization onset when T_c decreases to ~50 °C.

However, the crystallization process of PEO can only be observed around the melting point owing to its high crystallinity. At a T_c of 50 °C, at which T_c is close to the melting point of PEO (~65 °C), the induction period of PEO is longer than that of PES. When T_c is decreased to 42 °C, at which PES and PEO nucleate nearly simultaneously, the enhanced crystallinity and fast crystallization rate of PEO contribute to the early detection of crystals in the current study.

The crystallization process described above can be confirmed by polarizing optical microscopy. The micrographs of the spherulites in the 3/7 blend are shown in Figure 4. As shown in Figure 4a, where T_c
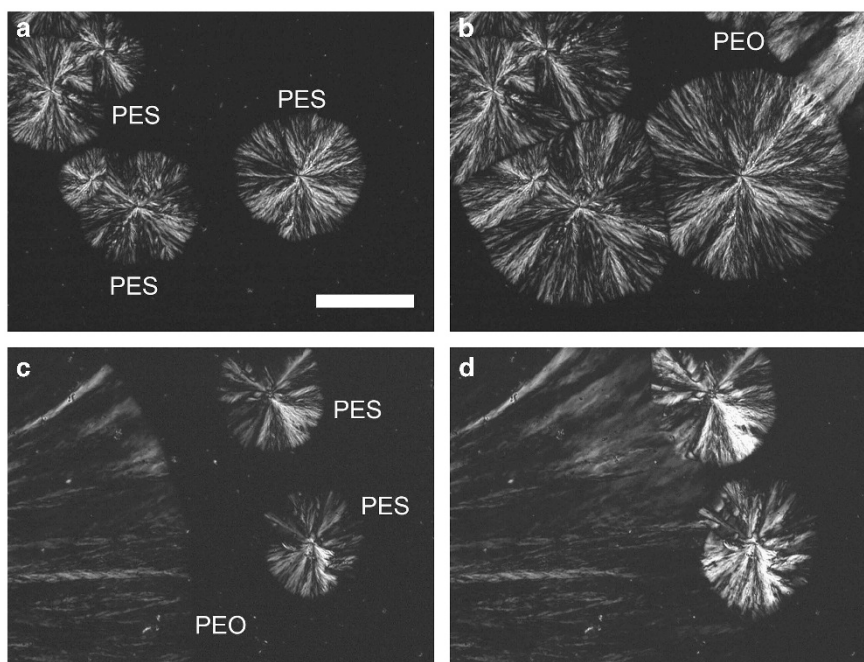

Figure 4 Spherulitic growth process in the poly(ethylene succinate)/poly(ethylene oxide) (PES/PEO) = 3/7 blend observed by polarizing optical microscopy. (a) Spherulites of PES growing at 50 °C. (b) PEO spherulite growing into a PES spherulite from the upper right corner 235 s after (a). (c) PES and PEO spherulites growing at 42 °C. (d) Continuous growth of the PEO spherulite inside the PES spherulites 25 s after (c). The scale bar in (a), which is common to all of the micrographs, represents 100 μm.

is 50 °C, only PES spherulites nucleated first. After ~ 235 s, at which the size of the PES spherulites was larger than that shown in panel (a), a PEO spherulite was observed in the upper right corner of the micrograph and grew in the lower left direction, as shown in Figure 4b. The PEO spherulite continued to grow inside the PES spherulite, as indicated by the bright area in the PES spherulite. At a T_c of 42 °C, PES and PEO nucleated nearly simultaneously, as shown in Figure 4c. The larger PEO spherulite continued to grow inside the smaller PES spherulites as shown in panel (d). This growth made the PES spherulites brighter than those shown in panel (c). The spherulitic growth rate of PEO was much faster than that of PES at 42 and 50 °C. This result can be confirmed by the growth distance of the PES and PEO spherulites between (a) and (b) and between (c) and (d).

The solid symbols in Figure 5 show the T_c dependence of the fractional amount of the PES crystals, f_{PES}, in the blends determined from line A in Figure 3 in the T_c range where only PES crystallizes. The value of f_{PES} decreased with increasing T_c, which is owing to the polydispersity of the samples.[32] The fraction with a higher molecular mass has a higher melting point and a smaller degree of supercooling, which results in a lower degree of crystallinity for that fraction. The f_{PES} data exhibited a linear dependence on T_c, as indicated by the lines in Figure 5. The value of f_{PES} increased as the PES content increased in the blends.

The open symbols in Figure 5 indicate the degree of crystallinity of PES (ϕ_{PES}), which was derived from the relationship below using the weight fraction (w_i), the molar mass of the repeating units (M_i) and the number of protons in the repeating units (N_i) of component i (1 for PES and 2 for PEO).

$$\phi_{PES} = f_{PES}(F_1 + F_2)/F_1,$$

where $F_i = w_i N_i / M_i$ and $F_1/(F_1 + F_2)$ is the fractional amount of the PES protons in the sample. The value of ϕ_{PES} exhibited a smaller dependence on the blend composition than f_{PES}, and this value was nearly independent of the blend composition below 65 °C.

Figure 6 shows the fractional amount of PEO crystals (f_{PEO}) in the samples and the degree of crystallinity of PEO (ϕ_{PEO}). Here f_{PEO} was derived by subtracting f_{PES} from the value of f at the intersection points (that is, B and C in Figure 3). Because the simultaneous crystallization of PES and PEO makes the precise evaluation of f_{PES} difficult, in this temperature range, f_{PES} was determined based on the assumption that the linear relationship in Figure 5 is valid down
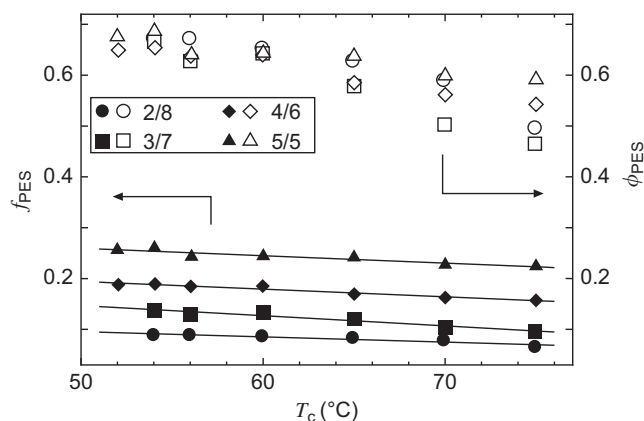
to ~ 40 °C. This assumption is discussed in the Supplementary Information. Once f_{PEO} is obtained, ϕ_{PEO} can be obtained in the same manner as that obtained for PES.

As observed for PES, the values of f_{PEO} and ϕ_{PEO} slightly decreased with T_c, as shown in Figure 6. Although ϕ_{PEO} exhibited a smaller dependence on the blend composition than f_{PEO} below 45 °C, the difference was not very large. These results are different from the T_c dependence of ϕ_{PES} below 65 °C in Figure 5, at which the dependence of ϕ_{PES} on the blend composition was very small.

The dependence of f_{PES} and ϕ_{PES} on the weight fraction of PES (w_{PES}) in the blends and the homopolymer is shown in Figure 7. The value of f_{PES} for the blend samples exhibited a monotonic dependence on w_{PES} because f_{PES} is dominated by the PES content in the blends. The blends contain a larger amount of the PES crystals for a larger PES content. However, ϕ_{PES} is less dependent on w_{PES} than f_{PES}, and ϕ_{PES} is more dependent on the crystallization temperature. This dependence is consistent with the data shown in Figure 5, where ϕ_{PES} exhibited little dependence on the blend composition, especially below 65 °C. The value of ϕ_{PES} for the blends was larger than that for the homopolymer under most of the conditions.
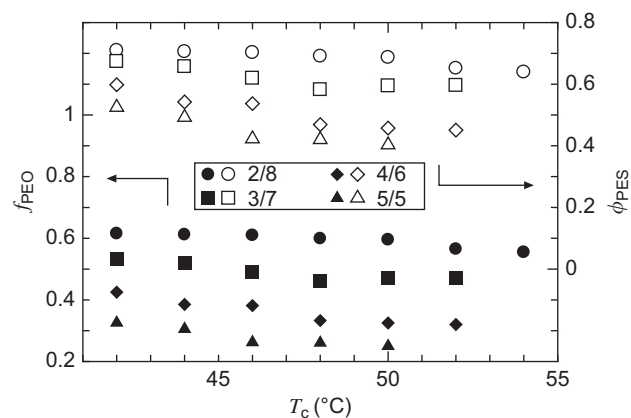

Figure 6 Fractional amount of poly(ethylene oxide) (PEO) crystals (f_{PEO}) (solid symbols) and the degree of crystallinity of PEO (ϕ_{PEO}) (open symbols) as a function of the crystallization temperature (T_c). The compositions of the PES/PEO blends are indicated in the inset. PES, poly(ethylene succinate).

Figure 5 Fractional amount of poly(ethylene succinate) (PES) crystals (f_{PES}) (solid symbols) and the degree of crystallinity of PES (ϕ_{PES}) (open symbols) as a function of the crystallization temperature (T_c). The compositions of the PES/PEO blends are indicated in the inset. PEO, poly(ethylene oxide).
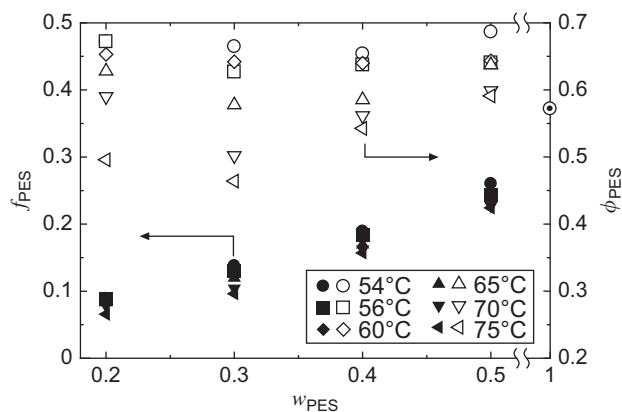

Figure 7 Fractional amount of poly(ethylene succinate) (PES) crystals (f_{PES}) (solid symbols) and the degree of crystallinity of PES (ϕ_{PES}) (open symbols) as a function of the weight fraction of PES (w_{PES}). The data point at $w_{PES} = 1$ is ϕ_{PES} for the homopolymer determined from Figure 2.

Figure 8 shows the dependence of f_{PEO} and ϕ_{PEO} on the weight fraction of PEO (w_{PEO}) in the blends and the homopolymer. In contrast to the results for PES in Figure 7, both f_{PEO} and ϕ_{PEO} increased with w_{PEO}, and the value of ϕ_{PEO} exhibited a nearly monotonic dependence on the PEO content.

Figures 7 and 8 indicate that blending PES and PEO resulted in different effects on the degree of crystallinity for the two polymers. As shown in Figure 7, ϕ_{PES} for the blends was larger than that for the PES homopolymer under most of the studied conditions. However, ϕ_{PEO} for the blends was smaller than that for the PEO homopolymer, as shown in Figure 8.

The dependence of the degree of crystallinity on the blend composition was classified into several types based on the data for nonisothermal crystallization.[33] Although some blends exhibit monotonic dependence on the composition, a few of the blends exhibit a maximum degree of crystallinity at a certain composition (that is, blending another component enhances the crystallinity in a certain composition range). PES and PEO can be categorized into the latter and the former dependence, respectively. Although the discussion in the literature[33] is based on the results of nonisothermal crystallization, it can be used as a basis for discussion of the studied isothermal behavior.

The difference in T_g must be one of the potential factors that results in different blending effects. PEO has a lower T_g value than PES, and the PEO segments are more mobile than the PES segments in the homopolymers at the same temperature. When the two components are blended with each other, the blended system has a single T_g between the T_gs of the original homopolymers.[22] The PES and PEO segments are more mobile and less mobile, respectively, in the blends than in the corresponding homopolymers, which enhances the crystallinity of PES and reduces that of PEO.

The influence of the segment mobility on nucleation can be discussed as follows. The nucleation rate I_n is expressed by[34]

$$I_n = I_0 \exp\left(-\frac{U}{k(T - T_\infty)}\right) \exp\left(-\frac{C}{kT}\right), \qquad (1)$$

where I_0 is a constant, U and C are the activation energies of molecular transport and nucleation, respectively, T_∞ is the temperature at which the motion in the main chain is frozen, k is the Boltzmann constant and T is the absolute temperature. The mobility of the polymers is expressed by the exponential factor containing U. Because T_∞ is $\sim 30\,K$ below the T_g for crystallization,[35] the change in T_g influences I_n, an increase in which should enhance the crystallinity. The value of U is typically considered to be independent of the polymer species. The T_g values for the PES and PEO homopolymers are $-20\,°C$ and $-67\,°C$, respectively, and the T_gs of the blends are located in this range.[22] Equation 1 indicates that the higher T_∞, namely the higher T_g, results in a smaller I_n. Blending the two polymers reduces T_g for PES and increases T_g for PEO. On the basis of Equation 1, these changes lead to an enhancement in the crystallinity of PES and a suppression in the crystallinity of PEO, as shown in Figures 7 and 8.

The existence of PES crystals may be an additional factor that reduces the crystallinity of PEO. PES crystallizes in the melt, whereas PEO crystallizes inside the PES spherulites, in most cases, when the interpenetrating spherulites are formed. Although the PES crystals may suppress the crystallization of PEO, the influence of this factor is not sufficiently clear and must be examined further for the following reasons. The existence of crystals of poly(butylene succinate) (PBS) has been reported to exhibit little influence on the spherulitic growth rate of PEO in the formation of interpenetrating spherulites.[16] Therefore, PEO primarily crystallized in the interfibrillar regions of the PBS spherulites. Because the characteristic size of the interfibrillar regions is larger than that of the interlamellar regions, the mobility of the PEO chains was not substantially suppressed. If the discussion on the PBS/PEO blends is applicable to the present PES/PEO system, the PES crystals may also have little influence on the crystallinity of PEO.

CONCLUSION

The amount of the crystals and the degree of crystallinity in the blends of PES and PEO, which form interpenetrating spherulites, were examined by pulsed NMR. The blend composition had a dominant influence on the amount of crystals in the blends. For example, the fractional amount of PES crystals increased with the PES content in the blends. However, the degree of crystallinity of the two components exhibited a different dependence on the blend composition. The value of ϕ_{PES} was not substantially dependent on the blend composition, especially for $T_c < 65\,°C$, whereas ϕ_{PEO} was dependent on the composition. The degree of crystallinity of PES in the blends was larger than that in the homopolymer under most of the studied conditions, whereas that of PEO in the blends was smaller than that of the homopolymer. The change in molecular mobility due to blending the two polymers with different T_g values is a possible factor that can explain the different dependences of the degree of crystallinity.

CONFLICT OF INTEREST
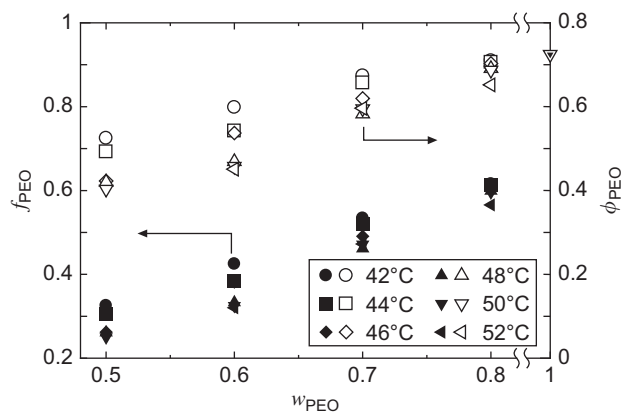
The authors declare no conflict of interest.

Figure 8 Fractional amount of poly(ethylene oxide) (PEO) crystals (f_{PEO}) (solid symbols) and the degree of crystallinity of PEO (ϕ_{PEO}) (open symbols) as a function of the weight fraction of PEO (w_{PEO}). The data point at $w_{PEO} = 1$ is ϕ_{PEO} of the homopolymer determined from Figure 2.

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