Effects of Blend Composition and Crystallization Temperature on Unique Crystalline Morphologies of Miscible Poly(ethylene succinate)/Poly(ethylene oxide) Blends

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ABSTRACT: In a previous short communication (Macromolecules 2002, 35, 8251-8254), we reported a unique morphology in binary miscible crystalline poly(ethylene succinate) (PES)/poly(ethylene oxide) (PEO) polymer blends, in which two kinds of spherulites, corresponding to each component, respectively, grew simultaneously and PEO spherulites continued to crystallize inside PES spherulites on contact, forming interpenetrated spherulites. In the present work the effects of blend composition and crystallization temperature on the crystalline morphologies of PES/PEO blends were studied by optical microscopy in detail. The unique morphology of PES spherulites penetrated by PEO spherulites was observed for the blends with PEO content ranging from 50 to 90% in a wide crystallization temperature range. Furthermore, three novel and interesting crystalline morphologies were found depending on blend composition and crystallization temperature. First, new boundaries were formed by the growth of a single PEO spherulite itself after penetrating into PES spherulites because of the change in the growth direction. Second, both components penetrated each other and formed interpenetrated spherulites. Third, PES and PEO formed a special kind of blended spherulite that nucleated from the same site and showed two growth fronts with PEO growing faster than PES. The growth rates of both components were studied; furthermore, much more attention has been directed to the study of the observed growth rates of both types of spherulites when they developed freely in the undercooled melt and when they were forced to penetrate each other. The blend composition and crystallization temperature effects on the various crystalline morphologies were summarized in PES/PEO polymer blends, which should be of great interest and importance for a better understanding of the crystallization and morphology in miscible crystalline/crystalline polymer blends.

Introduction

Binary crystalline blends have received much less attention than fully amorphous or amorphous/crystalline systems; however, it is of great interest and importance to study crystalline/ crystalline polymer blends from both academic and technological points of view because both components are able to crystallize, providing various conditions to investigate the crystalline morphology in polymer blends.^{1–19} The investigation of crystalline morphology in these blend systems is not only concerned with the effects of blend composition and crystallization temperature but also related to the question of how the crystallinity of the one component affects the crystallization behavior of the other. Only a small number of works are reported on miscible polymer blends of two crystalline polymers with different chemical structures until now. The melting points $T_{\rm m}$ s of the two components in these studies are usually about 100 $^{\circ}$ C apart, and the high- $T_{\rm m}$ component crystallizes first. The low- $T_{\rm m}$ component crystallizes in the constrained space in the spherulites or on the interspherulitic boarders on lowering the crystallization temperature, indicating that the two components crystallize sequentially not simultaneously. 1-8,16 It is interesting to investigate whether the two components can crystallize simultaneously, and which kind of morphology will arise from the simultaneous crystallization since both of them are crystallizable. Interpenetrated spherulites are occasionally formed in a few miscible pairs of two crystalline polymers. 9,12-14,16-19 Spherulites of one component continue to grow in the spherulites of the other component after they make contact with each other.

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Poly(ethylene succinate) (PES)/poly(ethylene oxide) (PEO) blends are typical crystalline/crystalline polymer blends. Wang et al. studied the miscibility, crystallization kinetics, and semicrystalline morphology of PES/PEO blends by differential scanning calorimeter (DSC), optical microscopy, and smallangle X-ray scattering (SAXS). 11 The miscibility of PES/PEO blends was evidenced by the single composition dependent glass transition temperature over the entire blend composition.¹¹ In a previous short communication, we reported the spherulitic morphologies of PES/PEO blends crystallized at 50 °C by optical microscope.¹³ It was found that PES crystallized first and filled the whole space before PEO could nucleate down to PES/PEO = 40/60 blend composition. However, for PES/PEO= 20/80 PES and PEO crystallized simultaneously and the formation of interpenetrated spherulites of PES by PEO was observed. Moreover, it was found that the growth rate of the PEO fibrils inside the PES spherulite was fast than that developed in the bulk. Such increase in the growth rate may be related to the fact that the PEO content in the amorphous regions of the PES spherulite was higher than the nominal melt concentration due to rejection of PEO from PES crystals.¹³ It was proposed that the density of lamellae in PES spherulites was lower than that in PEO spherulites, and PEO spherulites continued to penetrate into PES spherulites on contact. It is expected that such interesting crystalline morphologies must be related to blend composition and crystallization conditions. In the present work the crystalline morphologies of PES/PEO blends observed in ref 13 are further investigated by changing blend composition and crystallization temperature. Effects of blend composition and crystallization temperature on the crystalline morphologies of PES/PEO blends were studied in detail. Compared with the qualitative result regarding growth velocities of PEO in the bulk and within PES spherulites in the previous communication, much more attention has been directed to the study of the observed growth rates of both types of spherulites quantitatively when they freely develop in the undercooled melt and when they are forced to penetrate each other. The growth rates of both components were studied by following the development of the spherulites as a function of crystallization time. Furthermore, some novel and interesting crystalline morphologies are also found. The blend composition and crystallization temperature effects on the various crystalline morphologies were summarized in miscible crystalline/crystalline polymer blends, which should be of great interest for a better understanding of the crystallization in polymer blends.

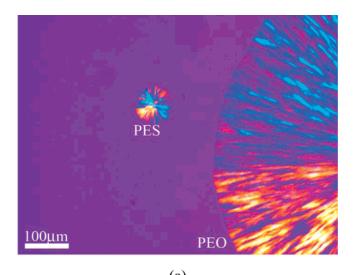
Experimental Section

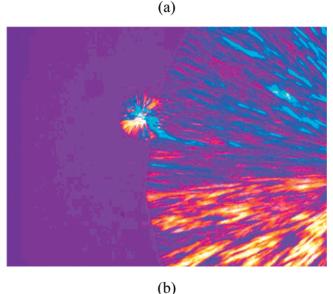
Both PES ($M_{\rm w}=10\,000$, $T_{\rm g}=-11\,^{\circ}{\rm C}$, $T_{\rm m}=103\,^{\circ}{\rm C}$) and PEO ($M_{\rm w}=100\,000$, $T_{\rm g}=-55\,^{\circ}{\rm C}$, $T_{\rm m}=67\,^{\circ}{\rm C}$) samples were purchased from Scientific Polymer Products, Inc. and used as received. PES/PEO blends were prepared with mutual solvent chloroform. The solution of both polymers (0.0125 g/mL) was cast on glass plate at room temperature. The solvent was allowed to evaporate in a controlled air stream for 1 day and the resulting films were further dried in vacuum at 50 °C for 3 days. In this way, blends were prepared with various compositions ranging from 100/0, 80/20, 60/40, 50/50, 40/60, 30/70, 20/80, and 10/90 to 0/100 in weight ratio, the first number referring to PES.

Crystalline morphologies of PES/PEO blends were observed under crossed polarizers with an optical microscope (Olympus BX51) equipped with a first-order retardation plate and a temperature controller (Linkam THMS 600). The samples were first annealed at 130 °C for 3 min to erase any thermal history and then quenched to the crystallization temperature (T_c) at a cooling rate of 100 °C/min. The spherulitic growth rate G was studied by following the development of the radius R of spherulite with crystallization time t, namely, G = dR/dt.

Results and Discussion

Effect of Blend Composition on the Formation of Penetrated Spherulites of PES/PEO Blends. PES/PEO blends are miscible crystalline/crystalline polymer blends. Both PES and PEO crystallize in their neat states according to spherulitic growth with negative birefringence under crossed polarizers with a first-order retardation plate. In previous work, it was found that for a 20/80 blend PES and PEO crystallized simultaneously at 50 °C and the formation of interpenetrated spherulites of PES by PEO was observed.¹³ It is expected that such interesting crystalline morphologies must be related to blend composition and crystallization conditions. In the present work, we extend our investigation on the formation of interpenetrated spherulites to other blend composition and crystallization temperature. Figure 1 shows the crystalline morphology in a 30/70 blend crystallized at 47.5 °C. Similar to the morphology in the 20/80 blend, the simultaneous growth of both PES and PEO spherulites was observed. Two different types of spherulites were observed during the crystallization of this blend sample with the large and compact spherulite being PEO type spherulite and the small and open one being PES type spherulite. As shown in Figure 1a, both PES and PEO crystallized simultaneously, with PEO spherulite generally growing faster than PES spherulite. The growth rates of PEO and PES were determined to be around 3.9×10^2 and $38 \,\mu\text{m/min}$, respectively, when they developed freely in the undercooled melt. With further prolonging crystallization time, both types of spherulites contacted each other. Figure 1b shows that the PEO spherulite continued to crystallize inside the PES spherulite and the growth front of the PEO type





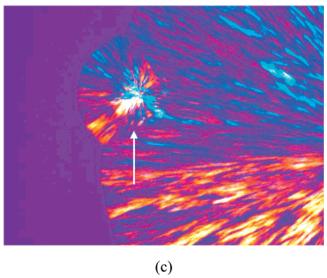
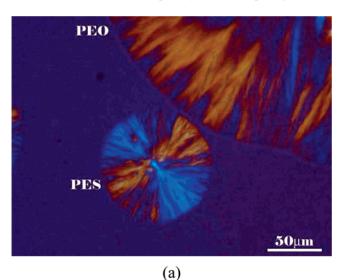


Figure 1. Formation processes of interpenetrated spherulites in a 30/70 blend at 47.5 °C at different crystallization times: (a) 264, (b) 284, and (c) 300 s. The white arrow indicates the new boundary.

spherulite became distorted when it contacted the PES type spherulite. Moreover, as shown in Figure 1b, the brightness increased in the part of PES spherulite where the crystallization of PEO has occurred, and does not change where the crystallization

lization of PEO has not occurred, indicating that PES spherulite is penetrated by PEO spherulite. Figure 1c shows that the growth front of PEO finally passed through the PES spherulite and continued to grow in the left melt. In this case, the birefringence of the growth front of PEO was almost the same as that in the region of the PEO spherulite where the interpenetration process did not occur, unlike the increase in the birefringence of the region where the interpenetration occurred as shown in Figure 1b. The interpenetration of PES spherulite by PEO spherulite can be verified by the same discussions as in previous works.¹² However, two experimental aspects should be noted during the formation process of interpenetrated spherulites. On one hand, the outline of the brighter area is not consistent with the shape of the rest of the PEO spherulite, and the brighter area seems too large. Such result may be related to the fact that the PEO fibrils grew faster inside the PES spherulite because the PEO content in the amorphous regions of the PES spherulite was higher than the nominal melt concentration due to rejection of PEO from PES crystals. By following the development of the spherulite with crystallization time, the growth rate of the PEO fibrils inside the PES spherulite was estimated to be around $8.6 \times 10^2 \,\mu\text{m/min}$, which was significantly greater than that of PEO developing freely in the melt. It should also be noted that the growth rate of PEO fibrils decreased to be around 3.9 \times $10^2 \, \mu \text{m/min}$ after finishing penetration of the PES spherulite as shown in Figure 1c, indicating that the melt concentration recovered to be almost the same as those in the undercooled melt. On the other hand, the PEO fibrils (stacks of lamellae) cannot keep their original growth direction during the penetration process into the PES spherulite, which must change their growth direction and continue to grow along the PES fibrils. As a result the fibrils of the PEO spherulite developed in the PES spherulite should have new growth direction and stop growing when they meet the growth fronts of the fibrils of other part of the PEO spherulite with original growth direction, resulting in a new boundary as indicated by the arrow in Figure 1c. The aforementioned results indicate that the PES spherulite becomes a new growth site for the PEO spherulite after the formation process of penetrated spherulites and leads to the change of the original growth direction. Thus, a new boundary can be formed by the growth of one PEO spherulite after the penetration into the PES spherulite. As is well-known, the boundary can only appear when neighboring spherulites contact each other. Therefore, it is of great interest that new boundaries are found for a single PEO spherulite after penetrating the PES spherulite. To the best of our knowledge, such novel morphological aspect has never been noticed before in the literature.

By adjusting blend composition and crystallization temperature, the penetration of PES type spherulites by PEO type spherulites can be found in a wide crystallization temperature range for a variety of blend compositions. Furthermore, a novel morphological pattern that the PEO type and PES type spherulites can interpenetrate each in some special cases depending on blend composition and crystallization temperature. Figure 2 presents the crystallization process of a 50/50 blend at 47.5 °C. As shown in Figure 2a both PES and PEO spherulites grew simultaneously with the growth rate of PEO being higher than that of PES. When the two types of spherulites developed freely in the undercooled melt, the growth rate of PES type spherulite was around 36 μm/min, while that of PEO type spherulite was around $1.9 \times 10^2 \,\mu\text{m/min}$. The growth rate of the PEO type spherulite decreased significantly from around $3.9 \times 10^2 \,\mu\text{m}$ min in Figure 1 to $1.9 \times 10^2 \,\mu\text{m/min}$ in Figure 2 by decreasing the low- $T_{\rm m}$ component from 30/70 to 50/50, if we ignored the



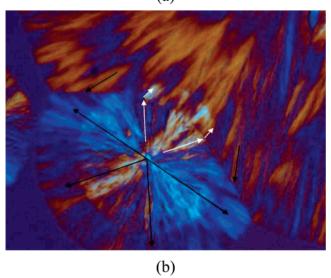


Figure 2. Simultaneous crystallization and formation process of interpenetrated spherulites in a 50/50 blend at $T_c = 47.5$ °C at different crystallization time: (a) 221 and (b) 245 s. The black arrow indicates the growth direction of PEO spherulite, and the white arrow indicates the growth direction of PES spherulite.

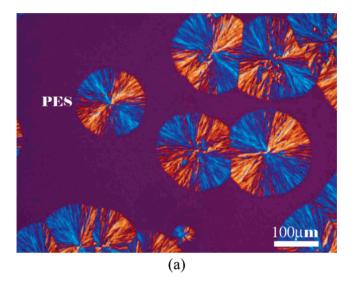
crystallization temperature influence. On the other hand, the growth rates of the high- $T_{\rm m}$ component PES shown in Figures 1 and 2 were almost unchanged, indicating that the blend composition showed a very profound effect on the growth rate of PEO type spherulite than that of PES type spherulite. When the two spherulites contacted, they continued to crystallize inside the spherulite of the other component each other, forming interpenetrated spherulites as shown in Figure 2b. During this penetration process, the PEO fibrils inside the PES spherulite traveled at a growth rate of around $6.6 \times 10^2 \,\mu\text{m/min}$. However, the growth rate value was estimated to be around 1.9×10^2 μm/min for the same PEO spherulite developing along other directions in the undercooled melt. Such growth rates difference resulted in the distortion phenomenon of the PEO spherulite growth front observed in Figure 2b. After passing through the PES spherulite, the growth rate of PEO recovered to be around $1.9 \times 10^2 \, \mu \text{m/min}$ again. As also indicated by the arrows in Figure 2b, the PES spherulite became a new growth site for the PEO component, indicative of the penetration of PES spherulite by PEO spherulite. PEO must continue to grow along the fibrils of PES spherulites, resulting that the growth direction of PEO changed and formed new boundaries with original PEO spherulite. Furthermore, unlike the crystalline morphology

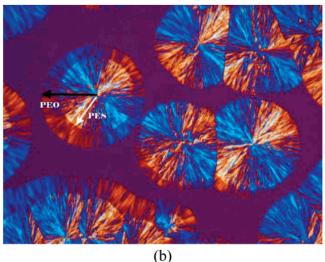
pattern that PES stopped growing inside the PEO spherulite in the 20/80 and 30/70 samples, PES continued to crystallize inside the PEO spherulite in a 50/50 blend as indicated by the increase of brightness and the growth front shown in Figure 2b. Such result indicated that PES spherulite also penetrated into PEO spherulite. Thus, PES and PEO formed interpenetrated spherulites. The growth rates was estimated to be around 50 $\mu m/min$ for the PES fibrils, which continued to develop inside the PEO spherulite as indicated by the white arrow in Figure 2b. Such increase in the growth rate of PES fibrils can also be attributed to the melt concentration change during the formation of penetrated spherulites.

It is apparent that blend composition plays a dominant role on the development of PES spherulite inside PEO spherulite. For $\phi_{\text{PEO}} \geq 70\%$, the advancement of PES spherulites terminated inside PEO spherulites. For $50\% \leq \phi_{\text{PEO}} < 70\%$, PES continued to grow inside PEO spherulite during the interpenetration. Such results may be explained as follows. For $\phi_{\text{PEO}} \geq 80\%$, the structure of PEO spherulite is so compact that there is no enough space for PES to continue to crystallize inside. For $50\% \leq \phi_{\text{PEO}} < 70\%$, the compactness of the structure of PEO spherulite reduced, thus providing the space for PES to continue to crystallize inside further. The model of the spherulites structures that are open or compact with crystalline lamellae has been described in more detail elsewhere. 12

From the previous studies, we propose that the important factors in realizing penetrated spherulites are the difference in the lamella population density in the different types of spherulites of the two components and the sufficient amount of the melt of one component inside the spherulites of the other component. It should be noted whether simultaneous spherulitic growth of two components is not a requirement for interpenetrating spherulites. In the miscible poly(vinylidene fluoride) (PVDF)/ poly(butylene succinate-co-butylene adipate) (PBSA) blends, the low- $T_{\rm m}$ component PBSA spherulites nucleated and continued to grow and penetrate into the high- $T_{\rm m}$ component PVDF spherulites, which developed at high crystallization temperature and ceased growth, forming interpenetrated spherulites. 18 As a result, it was found that penetrated spherulites appeared for a wide crystallization temperature range and blend composition in PES/PEO blends. The blends with the PEO content ϕ_{PEO} between 50 and 90% exhibited penetrated spherulites morphology in a wide crystallization temperature range of 37.5 to 57.5 °C. The effects of blend composition and crystallization temperature on the crystalline morphology of PES/PEO blends will be shown in detail in the following section.

In the aforementioned studies, we found that both components crystallized as separate spherulites and formed penetrated spherulites when they contacted each other in most cases. However, a novel crystalline morphology pattern was also found in some cases for the samples with $50 \le \phi_{PEO} \le 70\%$ at 37.5 $\leq T_{\rm c} \leq$ 50 °C. Under such conditions, PES and PEO usually appeared as separate spherulites and they formed penetrated spherulites in some area of the sample. However, in some area of the sample different crystalline morphology was found. Figure 3 shows the crystallization process of a 50/50 blend at 42.5 °C. Figure 3a shows the spherulitic morphology of PES component with the growth rate being around 22 μ m/min. With prolonging crystallization time, it was found that low- $T_{\rm m}$ component PEO nucleated at the center part of high- $T_{\rm m}$ component PES spherulites as shown in Figure 3b, which further grew through a spherulitic shape inside the PES spherulites and surpassed the growth front of original PES spherulites. Finally PEO spherulites stopped growing and formed straight boundaries





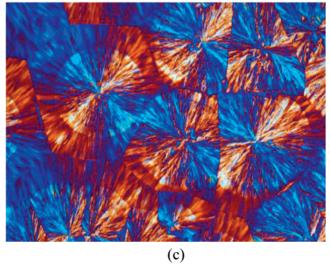


Figure 3. Formation of blended spherulites showing two growth fronts in a 50/50 blend at $T_c = 42.5$ °C with the nucleation of PEO spherulite inside PES spherulite at different crystallization time: (a) 310, (b) 335, and (c) 390 s. The black arrow indicates the growth front of PEO spherulite, and the white arrow indicates the growth front of PES spherulite.

when they contacted each other as shown in Figure 3c. From Figure 3, it was seen that PEO spherulite started to crystallize inside PES spherulite, showing two growth fronts, corresponding

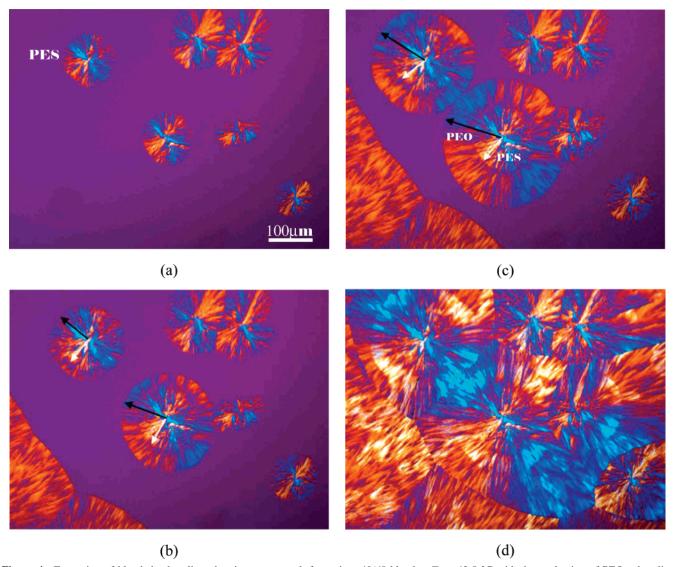


Figure 4. Formation of blended spherulites showing two growth fronts in a 40/60 blend at $T_c = 42.5$ °C with the nucleation of PEO spherulite inside PES spherulite at different crystallization time: (a) 261, (b) 291, (c) 297, and (d) 411 s. The black arrow indicates the growth front of PEO spherulite, and the white arrow indicates the growth front of PES spherulite.

to the growth of PES and PEO components, respectively, in one spherulite. The inner front was still ascribed to the growth front of PES as indicated by the white arrow in the center of Figure 3b. The growth rate of PES corresponding to the inner growth front was determined to be around 28 μ m/min, which was higher than that developed freely in the undercooled melt at the same crystallization temperature. Such increase in the growth rate may be related to the melt concentration change during the crystallization process of PES surpassed by PEO. The outer front was ascribed to the growth front of PEO component as indicated by the black arrow. The growth rate corresponding to the growth front of PEO was determined to be $1.9 \times 10^2 \,\mu\text{m/min}$. It is clear that the growth rate of PEO spherulite was obviously faster than that of PES spherulite. We named such crystalline morphology as blended spherulites showing two growth fronts. One easy experiment was performed to verify that the inner and outer fronts of the blended spherulite were from PES and PEO, respectively by heating the sample to a temperature between $T_{\rm m}$ s of two components. It was found that the outer front part disappeared while the inner part still

Similar results were also found in other blend composition. Figure 4 shows the similar crystalline morphology in a 40/60 blend at 42.5 °C. As shown in parts b and c of Figure 4, the white arrows indicated the growth fronts of PES with the growth rate of 27 μ m/min, while the black arrows indicated the growth fronts of PEO with the growth rate of $3.2 \times 10^2 \,\mu\text{m/min}$. PEO would form separate spherulites and form penetrated spherulites when they contact PES spherulites if PEO nucleated from the homogeneous melt. However, PEO would form blended spherulites with two growth fronts if PEO nucleated inside the preexisting PES spherulites. Where PEO started to nucleate is the key factor influencing the crystalline morphologies. Whether the formation of PES spherulites penetrated by PEO spherulites or the blended spherulites with two growth fronts occurred mainly depended on the nucleation sites of PEO in binary miscible crystalline/crystalline polymer blends. The fact that blended spherulites showing two growth fronts were only observed with $50 \le \phi_{PEO} \le 70\%$ may be explained as follows. In the case of the PEO content above 70%, the PES content is low. Therefore, PES spherulites grow slowly with open spherulitic structure and leave sufficient undercooled melt in the blends. In this case, it will be easier for PEO to nucleate in the undercooled melt rather than inside the PES spherulites. Thus, it will be difficult to form blended spherulite showing two growth fronts.

(a)

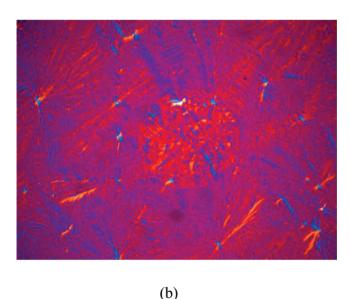


Figure 5. Crystalline morphology in a 20/80 blend at 57.5 °C: spherulitic morphology and growth of PEO spherulites after the PES spherulites filled the whole space sample at (a) 150 min and (b) 202 min

Effect of Crystallization Temperature on the Crystalline Morphologies of PES/PEO Blends. It is clear that blend composition and crystallization temperature play a significant role on the crystalline morphology of miscible crystalline/ crystalline polymer blends. In the above section effect of blend composition on the crystalline morphology of PES/PEO blends were studied in detail. In this section much more attention has been directed to the effect of crystallization temperature on the crystalline morphology of PES/PEO blends. We chose a 20/80 blend as a model blend, which can present various crystalline morphologies depending on crystallization temperature. When T_c is not lower than 60 °C, only PES can crystallize through spherulitic growth; however, PEO is still in the melt due to the different supercooling required by the two components. For brevity, the POM micrograph of PES spherulites is not shown here. On further lowering T_c , both components can crystallize. Figure 5 shows the crystalline morphology of a 20/80 blend at 57.5 °C. At this high T_c , PES crystallized first through spherulitic growth with growth rate being around 6.1 μ m/min and filled the whole sample. In this case, PEO is still in the melt due to the low supercooling. The crystallization of PES corresponds to the phase transition from amorphous/amorphous to crystalline/ amorphous state. By prolonging crystallization time, PEO also crystallized in the matrix of PES spherulites. The crystallization of PEO corresponds to the phase transition from crystalline/ amorphous to crystalline/crystalline state. Figure 5 show the growth process of PEO component. One PEO spherulite with strong birefringence was found to nucleate and continue to grow within the pre-existing PES spherulites. The growth of the PEO spherulites proceeded with keeping almost the spherulitic shape until they impinged on other PEO spherulites, which has also been found in several binary miscible crystalline polymer blends. 8,12,14,16-19 The growth rate of PEO nucleating and growing inside the preexisting PES spherulites was determined to be around 2.7 μ m/min because of the small supercooling at such a high crystallization temperature. It is usually difficult for the low- $T_{\rm m}$ component to crystallize through the spherulitic growth in crystalline/crystalline polymer blends because it must crystallize in the matrix of the pre-existing crystals of the high- $T_{\rm m}$ component. Only tiny crystals of the low- $T_{\rm m}$ component are found to grow within the spherulites or at the boundaries of the spherulites of the high- $T_{\rm m}$ component for most crystalline/ crystalline polymer blends.^{6,8} The possibility of the observation of the nucleation and spherulitic growth of the low- $T_{\rm m}$ component within the matrix of the pre-existing crystals of the high- $T_{\rm m}$ component may be related to the following two factors. One is the nucleation ability of the low- $T_{\rm m}$ component, and the other is the amount of its melt in the matrix of the pre-existing crystals of the high- $T_{\rm m}$ component. The lower nucleation ability and the higher amount of the melt of the low- $T_{\rm m}$ component favor the observation of its nucleation and spherulitic growth. On the basis of the aforementioned factors, PEO nucleated and grew within the pre-existing PES spherulites for the blend with high PEO content at high crystallization temperatures.

On further lowering $T_{\rm c}$ to 55 °C and below, the nucleation ability of low- $T_{\rm m}$ component was improved because of relatively high supercooling. In this case PEO can also nucleate and grow through spherulitic growth before the high- $T_{\rm m}$ component fill the whole sample. In this case two types of spherulites, corresponding to PES and PEO spherulites, respectively, can grow simultaneously. Furthermore, the penetration of PES spherulites with slow growth rate by PEO spherulites with fast growth rate can be found in the 20/80 blend. The detailed crystallization process has been described in the short communication previously. 13

Upon further lowering T_c to 45 °C and below, the crystallizability of PEO was improved significantly. As a result PEO nucleated first and continued to fill the whole sample before the nucleation of PES. When a 20/80 blend was quenched to 45 °C and below, PEO spherulites contacted each other and showed clear boundaries between neighboring spherulites first. The nucleation of PES component was impossibly able to be observed before PEO type spherulites filled the whole sample. However, the brightness of PEO spherulites increased apparently with further prolonging crystallization time, indicative of the occurrence of crystallization of PES inside the PEO spherulites. Unlike the crystalline morphology that PEO could crystallize through the so-called spherulitic growth, PES spherulites cannot be observed when they crystallized inside the PEO spherulites in the interlamellar and interfibrillar regions. The different crystalline morphologies may arise from the difference in the nucleation ability of the two components and the supercooling. At T_c as high as 57.5 °C the nucleation ability of PES was stronger than that of PEO; therefore, PES crystallized first and

filled the whole sample followed by the nucleation and growth of PEO spherulites inside the pre-existing PES spherulites. At $T_{\rm c}$ as low as 40 °C the nucleation ability of PEO was stronger than that of PES; therefore, PEO crystallized first and filled the whole sample followed by the crystallization of PES crystals inside the pre-existing PEO spherulites.

On the basis of the above study, it can be found that crystallization temperature plays a dominant role on the crystalline morphology for a given blend composition sample in miscible crystalline/crystalline polymer blends. Various crystalline morphologies can be obtained by just controlling crystallization temperature.

From the aforementioned studies, it is clear that crystalline morphologies of miscible crystalline/crystalline polymer blends are dependent on not only blend composition but also crystallization temperature. In this section, we summarize the crystalline morphologies dependence of blend composition and crystallization temperature in PES/PEO blends. The difference in the crystallization rates (or spherulitic growth rates) of both components is a key factor influencing the crystalline morphology patterns. All morphological features discussed above could be forecast at least on qualitative terms on the basis of wellestablished rules governing the crystal growth rate dependence on crystallization temperature and blend composition in crystalline polymer blends. By adjusting crystallization temperature and blend composition, three different kinds of crystalline morphologies could be formed. The first is that the growth rate of PEO is significantly greater than that of PES. In this case the low-T_m component PEO crystallized first with compact structure and filled the whole space, while the high- $T_{\rm m}$ component PES crystallized subsequently as microcrystals inside the preexisting PEO spherulites with prolonging crystallization time. The second is that the growth rates of both components are comparable. Both components can crystallize simultaneously. Depending on the nucleation site of the low- $T_{\rm m}$ component PEO, both components can form interpenetrated spherulites or blended spherulite containing two growth fronts from the same growth site with PEO growing faster than PES. The third is that the growth rate of PES is significantly greater than that of PEO. In this case, the high- $T_{\rm m}$ component PES crystallized first with very open structure, while the low- $T_{\rm m}$ component PEO nucleated and continued to grow subsequently in the preexisting PES spherulites with prolonging crystallization time. Although such summary is obtained on the basis of PES/PEO blends, it is expected that it will be also useful for the better understanding and prediction of morphological patterns for other miscible crystalline/crystalline polymer blends.

Figure 6 summarizes the crystallization temperature and blend composition dependence of morphological patterns of PES/PEO blends in detail. Only PES component crystallized for $\Phi_{PEO} \leq$ 40% in the blends. Both components crystallized at the same crystallization temperature and formed interpenetrated spherulites for the samples with $50 \le \phi_{PEO} \le 90\%$ at $37.5 \le T_c \le$ 57.5 °C. Furthermore, a new crystalline morphology pattern of blended spherulite with two growth fronts could be observed for the samples with $50 \le \phi_{PEO} \le 70\%$ at $37.5 \le T_c \le 50$ °C. For the samples with high ϕ_{PEO} at high T_c , PES crystallized first and filled the whole space followed by the crystallization of PEO inside the pre-existing spherulites through spherulitic growth. For the samples with $80 \le \phi_{PEO} \le 90\%$ at $T_c \le 45$ °C, PEO crystallized first and filled the whole space followed by the crystallization of PES inside the pre-existing PEO spherulites as microcrystals. In brief, various morphologies can be formed

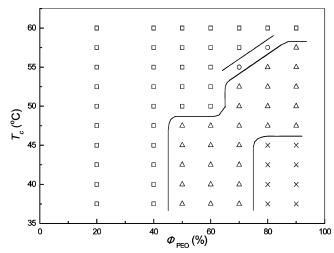


Figure 6. Dependence of the spherulitic morphologies in PES/PEO blends on the crystallization temperature T_c and the PEO content ϕ_{PEO} (%): square, only PES crystallized; circle, PES first filled the whole space while PEO crystallized in the matrix of PES spherulites later; triangle, simultaneous crystallization and penetration of spherulites took place; cross, PEO first filled the whole space while PES crystallized inside the PEO spherulites later.

in binary miscible crystalline/crystalline polymer blends by changing blend composition and crystallization temperature.

Conclusions

The unique morphology of PES spherulites penetrated by PEO spherulites was investigated in detail depending on blend composition and crystallization temperature. It was found that such morphology occurred for the blends with PEO content ranging from 50 to 90% in a wide crystallization temperature range. Some novel and interesting crystalline morphologies were observed, including the formation of new boundaries by the growth of a single PEO spherulite itself after penetrating into PES spherulites, the formation of interpenetrated spherulites by both components on contact, and the formation of blended spherulites with two growth fronts from the same growth site with PEO growing faster than PES. The growth rates of both components were studied when they developed freely in the undercooled melt and when they were forced to penetrate each other. The blend composition and crystallization temperature effects on the various crystalline morphologies were summarized in PES/PEO polymer blends, which should be of great interest and importance for the better understanding and prediction of morphological patterns for other miscible crystalline/crystalline polymer blends.

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References and Notes

- (1) Avella, M.; Martuscelli, E. Polymer 1988, 29, 1731.
- (2) Edie, S. L.; Marand, H. Polym. Prepr. 1991, 32, 329.
- (3) Cheung, Y. W.; Stein, R. S. Macromolecules 1994, 27, 2512.
- (4) Blümm, E.; Owen, A. J. Polymer 1995, 36, 4077.

- (5) Penning, J. P.; Manley, R. St. J. Macromolecules 1996, 29, 77.
- (6) Penning, J. P.; Manley, R. St. J. Macromolecules 1996, 29, 84.
- (7) Liu, L.; Chu, B.; Penning, J. P.; Manley, R. St. J Macromolecules **1997**, 30, 4398.
- (8) Lee, J.; Tazawa, H.; Ikehara, T.; Nishi, T. *Polym. J.* **1998**, *30*, 327. (9) Lee, J.; Tazawa, H.; Ikehara, T.; Nishi, T. *Polym. J.* **1998**, *30*, 780.
- (10) Liu, A.; Liau, W.; Chiu, W. Macromolecules 1998, 31, 6593.
- (11) Chen, H.; Wang, S. Polymer 2000, 41, 5157.
- (12) Hirano, S.; Nishikawa, Y.; Terada, Y.; Ikehara, T.; Nishi, T. Polym. J. 2002, 34, 85.
- (13) Qiu, Z.; Ikehara, T.; Nishi, T. Macromolecules 2002, 35, 8251.

- (14) Qiu, Z.; Ikehara, T.; Nishi, T. Polymer 2003, 44, 2799.
- (15) Kuo, Y.; Woo, E. Polym. J. 2003, 35, 236.
- (16) Qiu, Z.; Fujinami, S.; Komura, M.; Nakajima, K.; Ikehara, T.; Nishi, T. Polymer 2004, 45, 4355.
- (17) Ikehara, T.; Kimura, H.; Qiu, Z. Macromolecules 2005, 38, 5104.
- (18) Qiu, Z.; Yan, C.; Lu, J.; Yang, W.; Ikehara, T.; Nishi, T. J. Phys. Chem. B. 2007, 111, 2783.
- (19) Qiu, Z.; Yan, C.; Lu, J.; Yang, W. Macromolecules 2007, 40, 5047. MA7020997