Semicrystalline Morphology of Poly(aryl ether ether ketone)/Poly(ether imide) Blends

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ABSTRACT: A variety of semicrystalline morphologies in poly(aryl ether ether ketone)/poly(ether imide) (or PEEK/PEI) blends are revealed by electron and optical microscopy. Although the two polymeric components are compatible in the melt, phase separation occurs during crystallization of the PEEK component. At high temperatures (~320 °C), compact PEEK spherulites are observed even for dilute blends containing only 25% PEEK, and the accumulation of rejected PEI is primarily interspherulitic. At intermediate temperatures, PEI segregates primarily to pockets between bundles of lamellae within a spherulite. The length scale of segregation is progressively smaller at lower temperatures. At the lowest temperatures, approximately 35 °C above the glass transition temperature, a new and unexpected single-crystal-like dendritic morphology results. This morphology appears unique to the blends and consists of short, crystallographically faceted lamellae, uncharacteristic of typical PEEK lamellae. At all temperatures, the same unit–cell dimensions for PEEK are found.

Introduction

Poly(aryl ether ether ketone) (or PEEK) is a high-performance engineering thermoplastic which is increasingly being used in commercial applications requiring its high-temperature and high-strength properties. It serves as an excellent melt-processable matrix material for composites, and it holds promise for use in precision-molding applications.[1] The highly aromatic chemical structure of PEEK gives it good chemical resistance and high use temperature. Poly(ether imide) (or PEI) is another high-performance/high-temperature engineering thermoplastic which is also miscible with PEEK in all concentrations.[2] By blending, the favorable properties of each polymer may be optimized. PEEK is semicrystalline whereas PEI is amorphous and glassy. Blends are shown to have an increased toughness over either of the individual components.

Not only are these two polymers commercially important, but the unique aspects of the crystallization behavior of PEEK are the subject of considerable recent investigation. The preceding paper has reviewed and investigated in particular the crystallization of PEEK at high temperatures.[3] Other studies have investigated the peculiar double-melting behavior of PEEK. A lower temperature (and usually comparatively weaker) endotherm occurs approximately 15 °C above the crystallization temperature; the other, final melting endotherm is typically at 345 °C. Double melting, when observed in more flexible polymers, is due to the presence of small imperfect crystals which have grown at large undercoolings. During heating these crystals melt and recrystallize, forming larger, more perfect, entities. These lamellae then melt at a higher temperature, producing a second melting peak as observed by differential scanning calorimetry. For PEEK, however, two melting peaks are observed even at heating rates sufficiently rapid to preclude recrystallization.[4] Bassett et al.[5] postulated that the two peaks must be derived from two different populations of crystals—primary crystals which grow first in an unhindered melt, followed by more imperfect crystals which fill in the remaining more constrained environments. Although the concept of two crystal populations can explain the thermal data from PEEK, these distinct populations have not been assigned. There is no polymorphism, since X-ray measurements indicate the existence of only one crystal form. The unit cell is orthorhombic, with the chains adopting a planar zigzag conformation in the *bc* plane.[6,7] The crystallinity of PEEK is quite low, typically about 30%.[8] A study of the glass transition behavior by Cheng et al.[4] indicates that crystallization causes some fraction of the amorphous phase to have an increased rigidity. Because PEEK chains are relatively stiff, pinning of the chain during crystallization from the melt more easily forms constrained (higher rigidity) environments and hinders further crystal growth.

Morphological investigations have not clarified completely our understanding of the double-melting behavior but demonstrate nonetheless that PEEK crystals are unique compared to those of more flexible polymers. When crystallized either from the melt[5,9] or from solution,[10] lamellae are narrow and fibrillar instead of the more typical sheet-like shape. Even the individual lamellae grown from solution are highly disordered, being composed of tiny microcrystallites, contrary to the usual regular morphologies of most solution-grown polymer single crystals. Electron-diffraction patterns from single crystals show arcing, and bright-field observations reveal profuse microfragmentation.

At higher temperatures, the lamellae are progressively more sheet-like in shape. Nevertheless, the crystal structure remains the same, and the evidence for considerable disorder within these crystals is similar.[10] The primary difference observed at high crystallization temperatures is that spherulites or regions of spherulites may be more compact and birefringent.[11] We have demonstrated in the previous paper that these regions consist of lamellar bundles 100–200 nm wide which are packed parallel to one another.[3] Because bundles are stiffer than individual lamellae, splaying of lamellae is much reduced. Questions remain, however, regarding the relationship between morphology and melting behavior.

We are interested in investigating the semicrystalline morphology of PEEK in blends with PEI. Poly(ether imide) also has favorable high-temperature/high-performance properties,[12,13] having especially good environmental stress cracking resistance.[14] PEI has also been blended with other high-performance polymers to form miscible blends or composites with improved processability.[15,16]

Blends of PEEK and PEI are found to be molecularly miscible at all compositions.[2] Blending allows optimiza-

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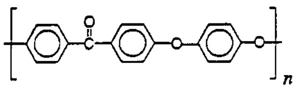
tion of various properties such as glass transition temperature, solvent resistance, crystallization rate, and toughness. The PEEK component is crystallizable even at very low concentrations, while the PEI remains amorphous. Crevecoeur and Groeninckx[17] have recently studied the crystallization behavior of PEEK in its blends with PEI using thermal analysis and SAXS. In general, PEI only weakly influences the crystallization of PEEK. The melting temperature of PEEK is only slightly depressed by addition of PEI. The heat of fusion varies linearly with composition, indicating that the crystallinity of PEEK is constant. The growth rate is depressed in the blends. For amorphous samples, the glass transition varies nearly as predicted by the Gordon–Taylor equation.[18] In semicrystalline samples, however, the amorphous phase is enriched in PEI, so the glass transition temperature increases. Therefore the PEEK component crystallizes much as in pure PEEK, with the PEI segregating to the amorphous phase. During crystallization of the PEEK component, PEI may be rejected in any of three distinct modes: interspherulitic, inter(lamellar bundle), or interlamellar. On the basis of SAXS measurements which show that the long period is rather independent of blend composition, Crevecoeur and Groeninckx[17] conclude that, within the spherulites, PEI is primarily rejected between bundles of lamellae.

In light of the limited morphological evidence of these blends, we wanted to investigate how PEI influences the crystallization of the PEEK component. In particular, we were interested in determining the mode and scale of PEI segregation and how the unique high-temperature crystallization behavior of PEEK is affected. In the course of this investigation, we also found an unexpected single-crystal textured morphology at low crystallization temperatures, which we discuss in this report.

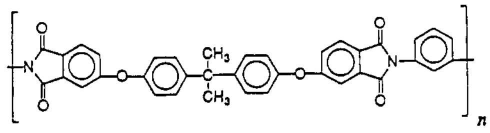
Method

We used commercially available PEEK (from ICI Ltd., $M_n \sim 14\,000$, $M_w \sim 39\,000$, $T_g = 143$ °C, $T_m = 345$ °C, which is the same material used for our previous studies) and PEI (from GE, Ultem 1000, $M_n \sim 12\,000$, $M_w \sim 30\,000$, $T_g = 218$ °C). The molecular weights are estimates from the manufacturers. The chemical structures are shown below.

PEEK :



PEI :



Our DSC results for the glass transition temperature, the melting temperature, and the enthalpy of fusion as a function of composition are in agreement with previously published results of Crevecoeur and Groeninckx[17] and are therefore not shown here. Pure PEEK and blends of various compositions were dissolved in 0.2 wt % solutions of benzophenone. Ultrathin films (≤50 nm) were cast near the boiling point of benzophenone onto freshly cleaved mica substrates and quenched to room temperature. The films were subsequently melted at 370 °C for 30 s before isothermal crystallization in a nitrogen atmosphere. When crystallizing at the lowest temperatures, the films were first rapidly quenched (>100 °C/s) to room temperature to form a glass. In either case, the crystallization was arrested after a specified time during a rapid quench to room temperature. To enhance contrast in the TEM, films were then Pt-shadowed at 26°; they were also coated with amorphous carbon to promote mechanical stability. To calibrate the diffraction patterns some films were also coated with thalium chloride. Samples were examined using a JEOL 100-CX TEM operating at 100 keV.

Table I
Interplanar Spacings of PEEK from Electron-Diffraction Patterns of PEEK/PEI Blends Having the Indicated Compositions

hkl reflection	d_{measd}, nm	$d_{\text{lit.}}$,[a] nm
020	0.298,[b] 0.299[c]	0.298
200	0.392[e]	0.394
110	0.472,[b] 0.473,[c] 0.474,[d] 0.473,[e] 0.476[f]	0.473
111	0.428,[b] 0.427,[c] 0.429,[d] 0.428[f]	0.428
211	0.311,[c] 0.310,[d] 0.310,[e] 0.313[f]	0.310

[a] From ref 7. [b] $\phi = 75\%$ PEEK; $T = 320$ °C. [c] $\phi = 75\%$ PEEK; $T = 270$ °C. [d] $\phi = 25\%$ PEEK; $T = 270$ °C. [e] $\phi = 75\%$ PEEK; $T = 195$ °C. [f] $\phi = 25\%$ PEEK; $T = 230$ °C.

Results and Discussion

Diffraction. Electron diffraction helps determine whether crystallization temperature or PEI content influences the crystal structure of PEEK. There is precedence for such a change in another blend system: poly(vinylidene fluoride) crystallizes preferentially into its piezoelectric β-phase when blended with amorphous poly(methyl methacrylate) instead of in the dominant α-phase.[19] However, at all temperatures from 320 to 195 °C and all blend compositions from 25 to 100% PEEK, the unit-cell parameters agree to better than 1% with previously published values.[7] Individual measurements are presented in Table I. Only two measurements are given for the 200 reflection, because in most samples this reflection is unobservable. As previously reported for pure PEEK samples,[9] the a-axis is typically normal to the film plane. (This alignment may be caused by a specific orientational interaction with the substrate. It is also presumably enhanced by the molecular stiffness of PEEK. The orientation is not caused by surface tension requiring chain alignment parallel to the film surface.[3]) Since at high and intermediate temperatures the a-axis is normal to the film plane, a sample tilt of 90°, which is physically impossible in the TEM, would be required to observe the 200 reflection. In the samples crystallized at the lowest temperatures, however, the a-axis tends to lie in the plane of the film, so that the 200 reflection may be observed. Although the crystal structure remains constant, three different morphological forms occur at the temperatures reported in Table I. All morphological forms that we discuss, therefore, contain the same constituent PEEK crystals, and PEI does not appear to distort or alter the crystal structure of PEEK.

Spherulitic Texture. The spherulitic texture is a function of both the composition and the crystallization temperature. From diffraction, we know that the noncrystalline PEI component is rejected from pure PEEK crystals. There are three modes of rejection that are possible, as is shown in Figure 1. The occurrence of these modes may depend upon the relative rates of PEI diffusion and PEEK growth. PEI may be rejected completely ahead of the growing front between spherulites as shown in Figure 1a. Alternatively, it may be trapped in pockets between lamellar bundles within the spherulite as shown in Figure 1b. PEI may also be rejected between individual lamellae as shown in Figure 1c.

If intraspherulitic rejection occurs (as in Figure 1b,c), the texture of a spherulite may be characterized by its compactness and coarseness.[20] The compactness of a spherulite is the fraction of crystalline (or semicrystalline) material within the spherulite. This is obviously related to, but not predetermined by, the composition of

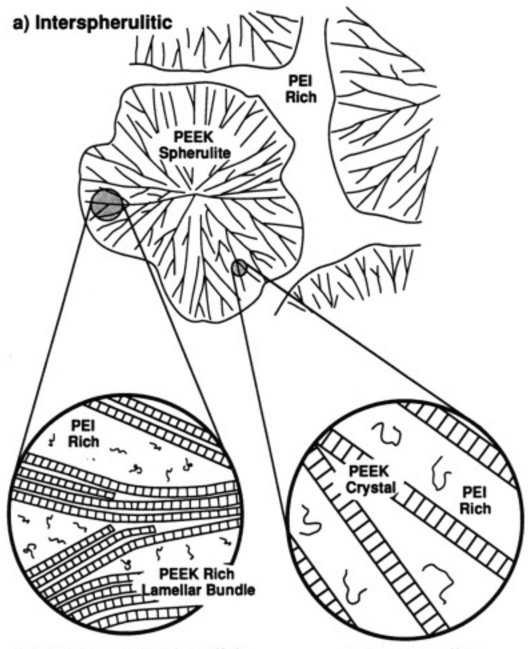


Figure 1. Schematic diagram of possible PEI segregation modes during crystallization of a compatible PEEK/PEI blend.

the blend. Coarseness, on the other hand, is a measure of the size of lamellar aggregates within the spherulite. A coarse structure is characterized by inter(lamellar bundle) rejection of noncrystallizable material, whereas the finest structure occurs when the rejection is between individual lamellae. These characteristics depend not only upon temperature and composition but also upon the affinity of the two polymers as well as specific morphological characteristics of the crystallizable polymer. Typically spherulites are more open and more coarse at higher temperatures but more compact and fine at lower temperatures. PEEK follows this rule at intermediate temperatures, but different behavior is observed at both high and low temperatures. The principal tool used to characterize the spherulitic texture is bright-field TEM, but in a later section, phase-contrast optical micrographs are presented to reveal structure at spherulitic impingement.

In a broad range of intermediate temperatures (from (T_g + 50) to 310 °C), the predominant mode of PEI rejection is between stacks of PEEK lamellae. Figures 2 and 3 show the internal and peripheral spherulitic structure, respectively, as a function of blend composition and crystallization temperature. Electron diffraction reveals that the lamellae are edge-on and the *b*-axis is radial; arced 020 and 002 reflections are observed. In bright field, the lamellae appear arranged in electron-dense bundles, with amorphous pockets rich in PEI included between. The scale of segregation, defined as the sum of the average lamellar-bundle and amorphous-pocket widths, quantifies the coarseness. For a blend composition of 75% and a crystallization temperature of 300 °C (Figure 2a), the scale of segregation is approximately 1.2 μm. Lamellar bundles are thick and compact and average approximately 800 nm in width. Amorphous pockets between bundles are typically 400 nm in width and 1–2 μm in length. Individual lamellae or fibrous groupings of lamellae are observed at the edges of an amorphous pocket or sometimes extending through it. The lamellar bundles in PEEK/PEI blends appear to form a network which includes pockets of amorphous material rather than the more isolated branches of semicrystalline material found on occasion in Keith and Padden's work.[20]

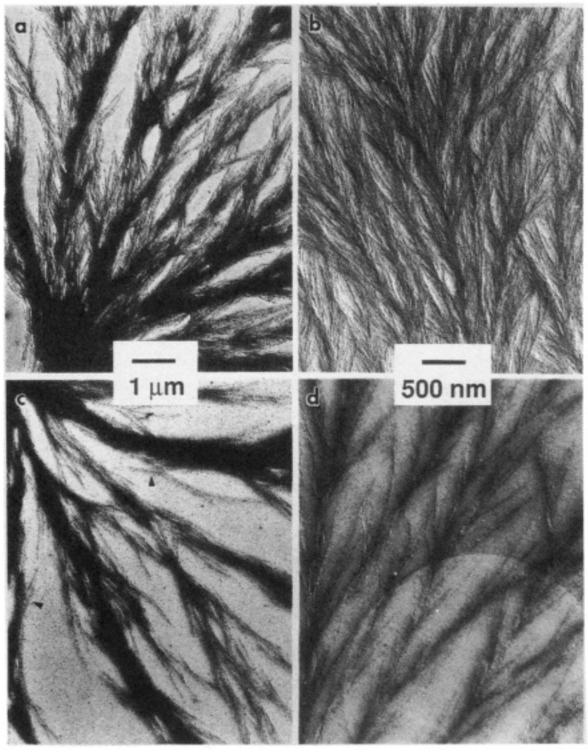


Figure 2. Transmission electron micrographs of PEEK/PEI blends at the indicated compositions and crystallization temperatures, demonstrating the characteristic inter(lamellar bundle) mode of segregation at intermediate temperatures: (a) ϕ = 75% PEEK, T_c = 300 °C; (b) ϕ = 75% PEEK, T_c = 270 °C; (c) ϕ = 25% PEEK, T_c = 300 °C; (d) ϕ = 25% PEEK, T_c = 270 °C. The scale of segregation at 300 °C is approximately 1.2 μm; at 270 °C it is 0.6 μm.

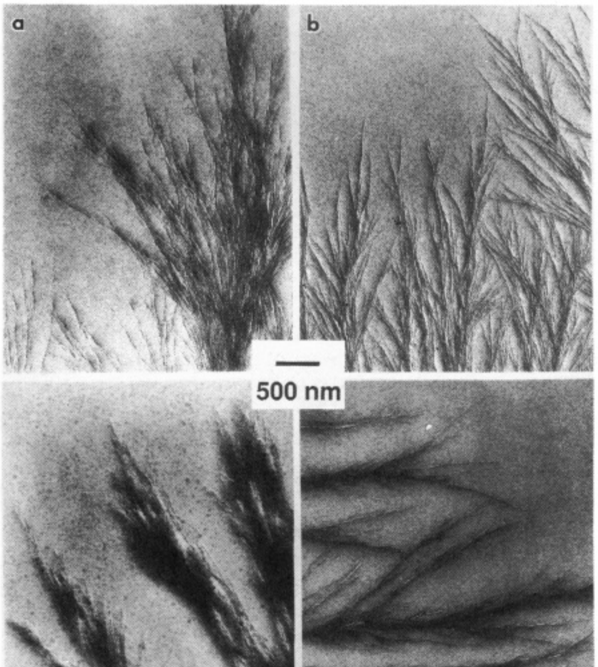


Figure 3. Transmission electron micrographs showing the growth tips of PEEK spherulites in PEEK/PEI blends of the indicated compositions and growth temperatures: (a) ϕ = 75% PEEK, T_c = 300 °C; (b) ϕ = 75% PEEK, T_c = 270 °C; (c) ϕ = 25% PEEK, T_c = 300 °C; (d) ϕ = 25% PEEK, T_c = 270 °C.

The spherulitic texture is finer when the same composition is crystallized at 270 °C (Figure 3b). The scale of segregation is reduced by a factor of 2 (600 nm), and

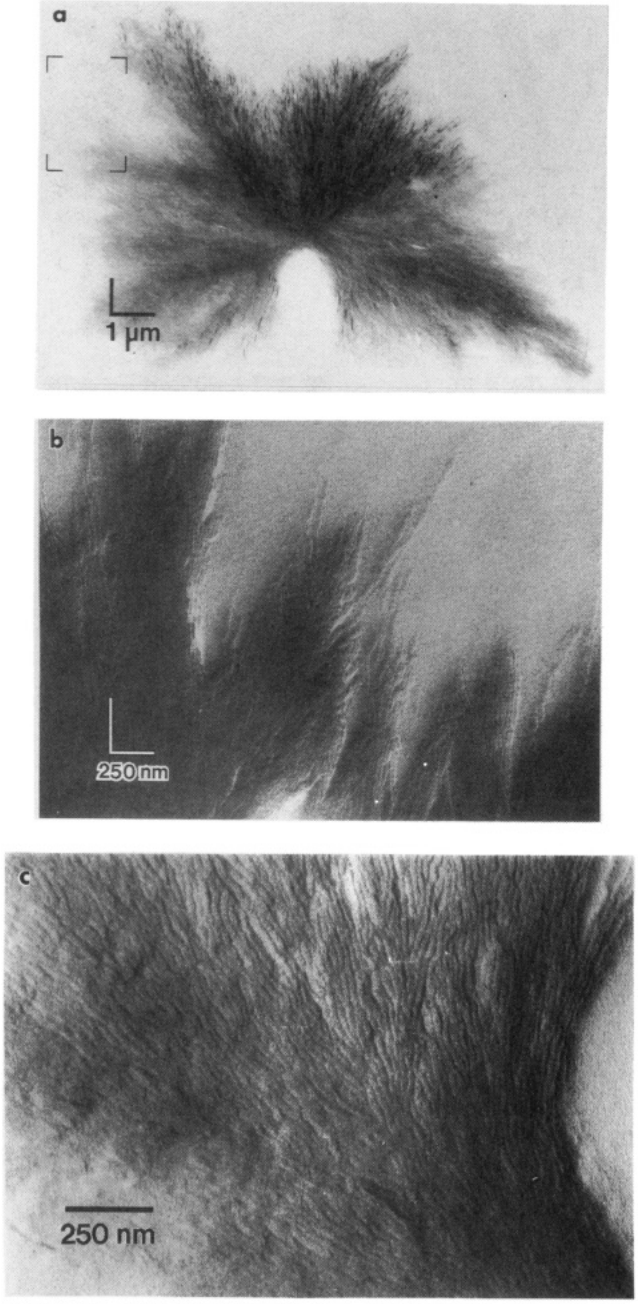


Figure 4. Transmission electron micrographs showing the compact structure of spherulites crystallized at 320 °C in PEEK/PEI blends: (a) ϕ = 75% PEEK, t_c = 25 h; (b) growth tips of spherulite shown in (a); (c) ϕ = 25% PEEK, t_c = 68 h.

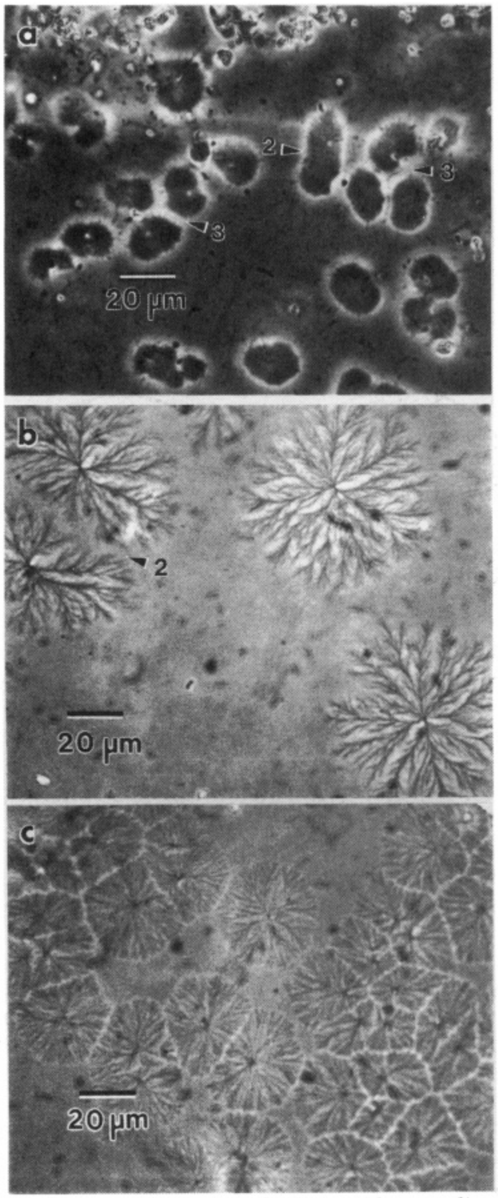


Figure 5. Phase contrast optical micrographs revealing the interspherulitic segregation of PEI as a function of crystallization temperature in 50% PEEK blends. (a) T_c = 320 °C. Arrows highlight where two or three isolated spherulites have impinged. (b) T_c = 300 °C. (c) T_c = 270 °C. At this temperature, no interspherulitic segregation is observed.

individual lamellae now often fill the PEI-rich pockets. At crystallization temperatures of 250 °C, the scale of segregation is still finer at 400 nm. Finer texture is expected at lower temperatures, since the segregation scale should decrease with the ratio of spherulite growth rate to PEI diffusion. Taking the reasonable assumption that a spherulite nucleates at the beginning of the quench to the crystallization temperature, the radial growth rate in 75% blends at 300 °C is 0.4 μm/min. At 270 °C, the PEI diffusional rate is expected to be somewhat reduced and the spherulitic growth rate is measured to be 8 μm/min, or 20 times faster.

In addition to crystallization temperature, the segregation scale is further controlled by the structure at the spherulitic periphery, which is more fine and open (Figure 3a) than observed in the interior of the spherulite. Individual lamellae grow into the uncrystallized melt. These branch and splay are characteristically at each temperature and composition, defining the subsequent segregation dimensions and morphology. Within 2 μm from the local spherulitic periphery, the structure appears nearly as in the interior of the spherulite.

The scale of segregation is not, however, greatly influenced by blend composition. The internal spherulitic texture for more dilute blends (ϕ = 25%) is shown in Figure 2c,d. Again the bundles of lamellae are compact, with some smaller branches consisting of individual (or pairs of) lamellae extending into the PEI-rich pockets. The ratio of lamellar-bundle to amorphous-pocket width reflects the composition. Although the growth rate, at the same crystallization temperature, for the more dilute blend is a factor of 8 less than for the 75% blend, the scale of segregation is nearly independent of composition. At 300 °C, perhaps due to the slower growth rate in the more dilute blends, the peripheral structure (Figure 3c) is coarser. Even at the periphery, lamellae grow together in bundles. Bundles are inherently stiffer than individual lamellae; therefore the internal branches are more straight

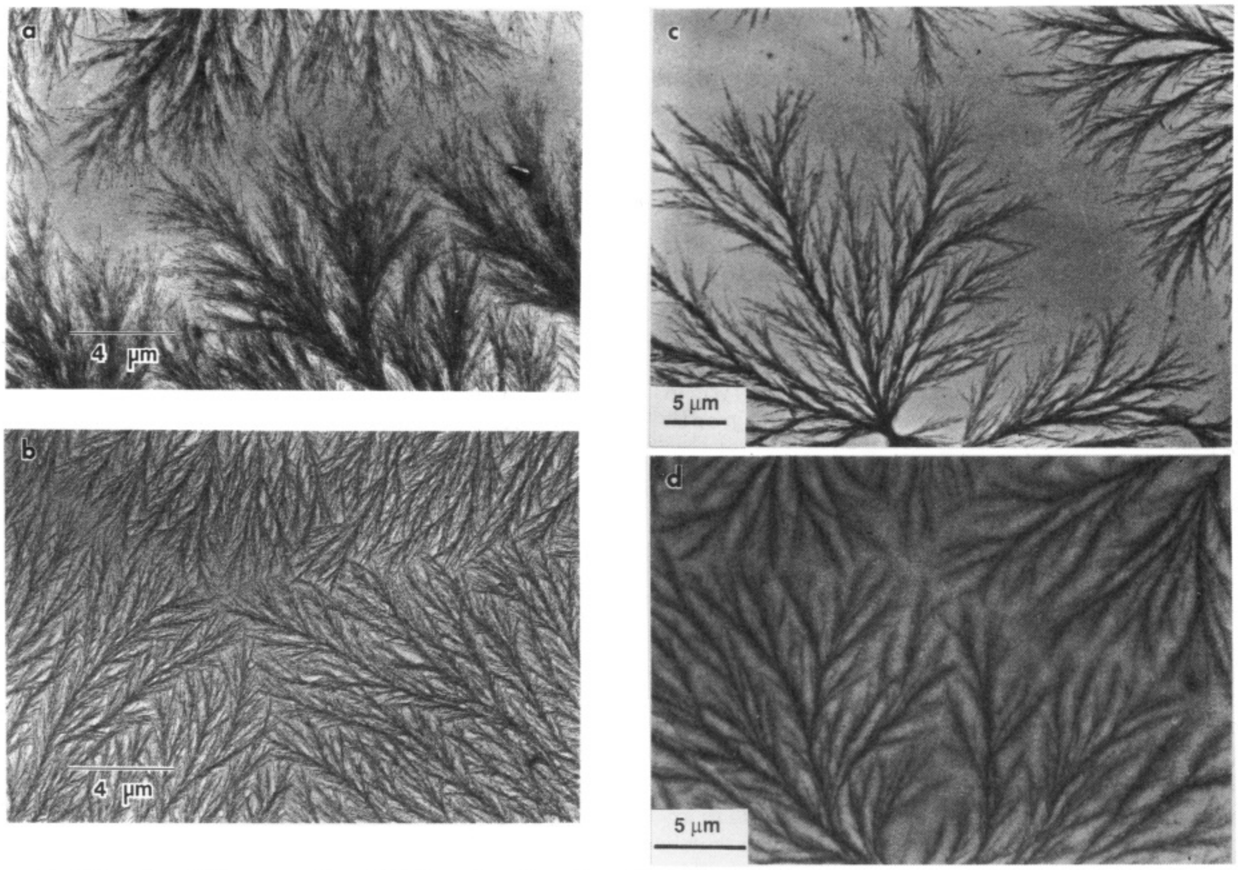


Figure 6. Interspherulitic segregation of PEI as a function of crystallization temperature and composition: (a) ϕ = 75% PEEK, T_c = 300 °C; (b) ϕ = 75% PEEK, T_c = 270 °C; (c) ϕ = 25% PEEK, T_c = 300 °C; (d) ϕ = 75% PEEK, T_c = 270 °C.

and parallel (Figure 2c). Also visible in Figure 2c is the tendency of lamellae to branch backward (arrowed) as well as forward. It is unclear whether this arises from crystallographic branching or from spawning[21] of lamellae.

When the 25% blend is crystallized at 270 °C (Figures 2d and 3d), the structure is very fine. Many individual lamellae grow within the amorphous pockets between narrow stacks of lamellae. The lamellae are also very narrow, with many being narrower than the film thickness, casting no shadow (from Pt). In agreement with Crevecoeur and Groeninckx,[17] lamellae still form bundles. Measurements from various higher-magnification images show that the lamellar period, within a bundle, in independent of composition.

At temperatures above ca. 300 °C, the spherulitic texture does not continuously become more open. Instead the much more compact morphology characteristic of pure PEEK is adopted.[3] Lamellae grow together as bundles, 100–200 nm wide, which are packed tightly together. In blends, PEI is rejected outside of the spherulite (Figure 4). The bundle growth mechanism and the slow growth rate of spherulites at this temperature contribute to the segregation of PEI ahead of the growing front. The growth rate for the 75% blend is approximately 5×10^{-3} μm/min, and for the 25% blend an order of magnitude less. The lamellae are again edge-on, and the *bc* crystallographic plane lies in the plane of the film. Lamellae are revealed in Figure 4a by 110 diffraction contrast; the specimen is tilted by 37° about the horizontal axis. This tilt angle maximizes the intensity of the 110 diffracted beam, consistent with the unit-cell structure of PEEK. Much as in pure PEEK, spherulites have a very uneven growth front (Figure 4a and, at higher magnification, Figure 4b) with, in addition, some individual lamellae. This difference is sensible since at the growth tips the amorphous material must be highly enriched in PEI. Figure 4c shows that even in dilute blends where the PEEK concentration is only 25%, the spherulites are very compact, having the same morphology.

Interspherulitic Structure. Interspherulitic structure may be examined by continuing crystallization to completion. If PEI is rejected ahead of the growing front, a layer of amorphous material lies between spherulites. Phase-contrast optical microscopy is used to examine the impingement of spherulites for a range of temperatures and a 50% concentration only, because this concentration is optimal for observing both the spherulites and the segregation at impingement (Figure 5). Higher-resolution information available from TEM is also presented for the 75% and 25% concentrations (Figure 6).

At 320 °C, the spherulites are very compact (Figure 5a). The major amount of PEI, approximately 3 μm in width, lies between spherulites. Although the crystallization is not yet complete, the growth fronts of the spherulites are mutually flattened, indicating that PEI trapped between spherulites has inhibited their growth. The width of this PEI layer is expected to be nonuniform, being less when two isolated spherulites impinge, where the PEI may be rejected to the sides (indicated by the arrow labeled 2). This phenomenon requires that the diffusion of PEI be extremely fast compared to the growth rate of PEEK. The growth rate is indeed very slow (2×10^{-3} μm/min) and decreases with time, as rejection of PEI appears to impede further growth. When the spherulites are more crowded, wider layers of PEI are expected, as observed in regions labeled 3.

At 300 °C (Figure 5b), the spherulites are open and coarse as previously revealed by TEM (Figure 2). An amorphous interface of PEI occurs between two isolated spherulites. This is consistent with Keith and Padden's observation for isotactic polypropylene.[20] Although isolated spherulites are generally circular, the growth front is irregular. Greater detail of the impingement regions is revealed by TEM. Figures 6a and 6c demonstrate that an amorphous band does occur at the impingement of two spherulites crystallized at 300 °C. The width of this band is clearly larger than that of the pockets within a spherulite. The growth tips of the sperulites are fibrous and open. For the 25% blend, this is in contrast to that observed at the peripheries of isolated spherulites.

At lower temperatures, 270 °C (Figure 5c), the spherulites are finer and more circular. The impinged edges are fairly straight, forming polygonal spherulites typical of undiluted semicrystalline polymers. Here the growth rate of PEEK is very rapid (4 μm/min), so PEI is not able to diffuse significantly ahead of the growing front. Segregation at the point of spherulitic impingement is minimal. This is confirmed by TEM (Figure 6b,d). The scale of segregation at the impingement is identical to that within the spherulite: at these temperatures, no segregation of PEI occurs ahead of the growth front. Therefore it is possible to control the length scale of PEI segregation during crystallization and, in particular, to maintain it sufficiently low for the two polymeric components to remain in close contact.

Low-Temperature Dendritic Morphology. Crystallization from the quenched amorphous phase at temperatures slightly above the glass transition results in an unexpected new morphology unique to the blends in which lamellae are uncharacteristically short and crystallographically faceted. This is in marked contrast with the narrow, fibrillar lamellae obtained in all previous studies of PEEK.[5,9,10] In thin films, the lamellar aggregates lie generally in the plane of the film as shown in Figure 7. For various blend compositions, crystallization at a similar elevation above the glass transition is required. For 25% PEEK blends, this new morphology has been obtained at a crystallization temperature of 230 °C, or approximately 35 °C above the glass transition temperature. When 75% PEEK blends are crystallized at this same temperature, the morphology characteristic of intermediate temperatures results as previously discussed. For the higher-concentration blends it is necessary to crystallize at lower temperatures, i.e., at 195 °C, again 35 °C above the glass transition. The lamellae are larger in the more dilute blends where crystallization temperature is higher; the lateral dimension of the lamellae ranges from 50 to 500 nm when grown at 230 °C in 25% blends and from 30 to 150 nm when grown at 195 °C in 75% blends. This morphology has not been obtained so far in pure PEEK.[9]

Within the aggregate, some PEI may be rejected between lamellar branches, radiating out from a common nucleation point. In channels between branches the material remains amorphous. The branches and channels are easily observed in 25% blends as shown in Figure 7b. Much narrower amorphous channels are also present in 75% PEEK blends; they are not visible in Figure 7a (which is chosen to show the centers of such aggregates): in the more concentrated blends they appear only beyond approximate radial distances of 1 μm.

A bright-field image/diffraction pair (Figure 8) reveals the single-crystal texture of the dendrite. The crystallographic orientation of the dendrites varies from one to another, yet the b-axis is within a few degrees from the film surface whereas the a-axis is within 30°. The occurrence of the dendritic structure therefore is not due to a specific interaction with the substrate. The three-dimensional structure of these dendrites in the bulk is not known. It is unlikely that it would continue to be single-crystal-like but may be broadly cylindrulitic, as a result of splaying and space-filling from precursor crystals of the type found here. Local misorientation between crystals within the dendritic structure is perhaps 10–20°. Regular crystal faceting on the 200, 020, and 110 planes is observed. These facets display a common orientation not only over a long range but also in that the crystallographic orientation remains the same independent of position about the nucleation point of the dendrite. Single-crystal-like dendrites are quite rare in melt-crystallized polymers, particularly at such large undercoolings. For poly(trifluoroethylene), somewhat similar dendritic structures are obtained, which are single crystals as evidenced by electron

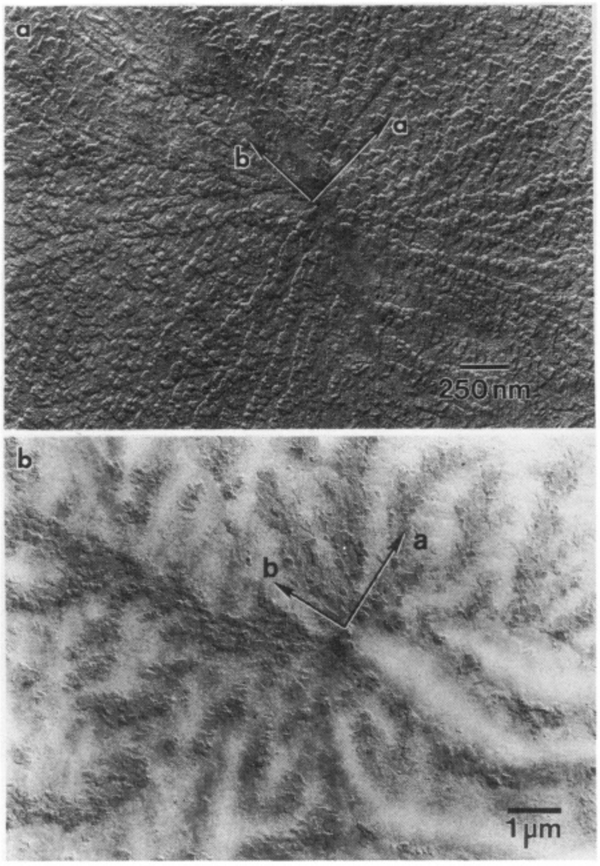


Figure 7. Transmission electron micrographs of single-crystal textured dendrites grown upon heating from the quenched glass for the following compositions and temperatures: (a) ϕ = 75% PEEK, T = 195 °C; (b) ϕ = 25% PEEK, T = 230 °C.

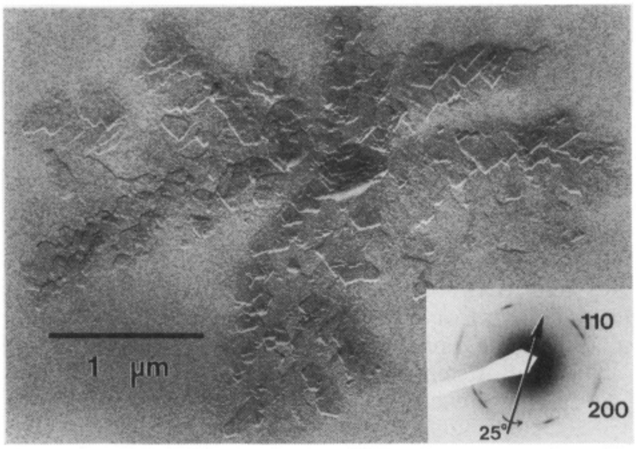


Figure 8. Selected-area electron-diffraction pattern from the entire dendrite shown, revealing overall single-crystal-like texture.

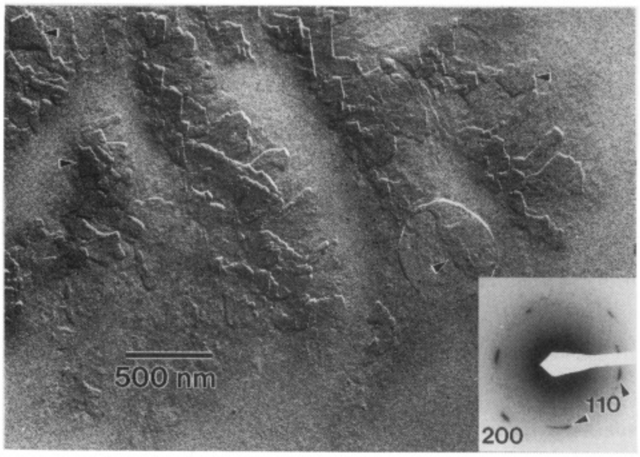


Figure 9. Selected-area electron-diffraction pattern at the growth tips of a dendrite grown at 230 °C from a 25% PEEK blend. The lamellae are parallel to the film, and the chain axis is perpendicular to the lamellae. 200, 110, and 020 crystal facets are observed.

diffraction.[22] The irregular, branched morphology is the result of channeling as impurity is rejected.

To reveal the details of the inclination of the chain stem[3] with respect to the lamellar normal, it is necessary to examine an area where the lamellae happen to be parallel to the film surface. This is confirmed in Figure 9 where the entire perimeter of growth edges of several lamellae may be observed about the periphery of the crystals. A few of these are arrowed. There are also lamellae which show neither distinct shadows nor edges and lie within the thin film. Diffraction from the lamellae delineated by the selector aperture is shown in the inset. The principal reflections in the diffraction pattern which accompanies this figure are the strong 200 and 110 reflections. The weak 020 reflection is also observed in the original negative (but is not sufficiently intense to be printed), so that both *a* and *b*-axes are in fact within the film plane and the *c*-axis (or chain axis) is normal to both the film and the lamellae. The lamellae are typical of PEEK in this respect. The orientation of the lamellar facets elsewhere in this figure shows that the surrounding lamellae have crystallographically the same mutual alignment as the field inside the aperture. Within a lamellar crystal, as shown in this figure, there is no evidence for microfragmentation of the type observed in pure PEEK.[10]

Conclusions

We have investigated the morphology of molecularly compatible blends of two technologically important high-temperature polymers, i.e., a crystallizable one (PEEK) and an amorphous diluent (PEI). Pure PEEK crystals are obtained from the blends upon isothermal crystallization. At all crystallization temperatures and blend compositions, the unit-cell dimensions are constant. PEI, acting as a diluent, is rejected from growing PEEK crystals. At intermediate temperatures, where the growth rate is most rapid, the rejection is primarily between lamellar bundles, and the length scale of PEI segregation decreases with decreasing temperature. At higher temperatures, interspherulitic segregation occurs to various degrees, but at temperatures 270 °C and below, interspherulitic segregation can be completely eliminated. Increasing the PEI content slows the growth rate and causes the spherulites to become more open. At high temperatures (~320 °C), the very compact spherulitic morphology characteristic of pure PEEK occurs in even very dilute blends. The lamellae grow together in the form of bundles, forming a very compact spherulite and expelling the PEI. At temperatures near the glass transition of the blend, however, we discovered a novel single-crystal-like morphology in thin films that differs markedly from the typical fibrillar crystalline morphology seen up to now in PEEK samples.

References and Notes

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Registry No. PEEK, 31694-16-3; Ultem 1000 (SRU), 61128-24-3; Ultem 1000 (copolymer), 71148-53-3.