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Phase Behavior and Rhythmically Grown Ring-Banded Spherulites in Blends of Liquid Crystalline Poly(aryl ether ketone) and Poly(aryl ether ether ketone)

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ABSTRACT: Phase behavior and rhythmically grown ring-banded spherulites in thin films of liquid crystalline poly(aryl ether ketone) (LC-PAEK) and poly(aryl ether ether ketone) (PEEK) blends have been investigated by differential scanning calorimetry (DSC), polarized light microscopy (PLM), atomic force microscopy (AFM), transmission electron microscopy (TEM), and electron diffraction (ED) techniques. The results show that the composition of the blends has great effect on the phase behavior and structure. Thin films of pure LC-PAEK and PEEK crystallized from the melts exhibit typical mosaic and spherulitic structures, respectively. For the blends with higher LC-PAEK contents (>50%), the two components are miscible at the molecular level in the melting state, and a phase separation takes place during the cooling process, as a result of the competition between the phase separation and the LC-PAEK phase transition, resulting in an unusual ring-banded spherulite. The bright core and rings of the ring-banded spherulites under PLM are composed of the LC-PAEK phase, while the dark rings consist of a coexisting phase of PEEK with part of LC-PAEK. The formation of the ring-banded spherulites is attributable to structural discontinuity caused by a rhythmic radial growth. For the 50:50 LC-PAEK/PEEK blend, the ring-banded spherulites and individual PEEK spherulites coexist, which implies that a partial phase separation between the two components takes place in the melting state. In PEEK-rich blends, LC-PAEK is rejected into the boundary of PEEK spherulites. In addition, the effect of cooling rate and crystallization temperature on the phase behavior, especially the ring-banded spherulite formation in the blends, is discussed.

Introduction

Poly(aryl ether ketone)s (PAEKs) are semicrystalline aromatic thermoplastics with an unusual combination of properties, such as high melting points, good mechanical properties, excellent chemical resistance, and thermal stability. In this family, poly(aryl ether ether ketone) (PEEK) is the most typical and widely applied member due to its excellent physical and mechanical properties. A great deal of studies on morphology, chain conformation, and packing of PEEK crystals have been reported in recent years.[1−10] The unit cell is orthorhombic with dimensions of $a = 0.783$ nm, $b = 0.594$ nm, and $c = 0.986$ nm.[3] The structure and the morphology of PEEK thin films crystallized from the melts were reported.[5−8] Generally, spherulitic morphology is observed, with the crystallographic b axis as the lamellar growth direction. However, the lamellae in PEEK thin films are not necessarily on edge but may have a variety of orientations, including flat-on and other intermediate orientations, especially in the vicinity of the spherulitic nuclei.[6]

To obtain different properties of PAEK for various applications, structural modifications, such as introduction of lateral groups or biphenyl units onto the main chains, have been attempted.[11,12] Recently, we have investigated a series of thermotropic liquid crystalline poly(aryl ether ketone)s (LC-PAEKs),[13−15] which were synthesized by introduction of substituted side groups (such as chloro, *p*-phenyl, *tert*-butyl, methoxy, 3-trifluoromethylbenzene, etc.) and biphenyl mesogenic units to the PAEK backbones. The main-chain LC-PAEKs were found to exhibit complicated phase behavior, including nematic, smectic, smectic crystalline, and crystalline phases, and abundant LC textures, such as schlieren, fan-shaped, shear-induced focal conic, and spiral textures, as well as highly ordered smectic structures (S_E phase), including monodomain, mosaic, and single-crystal-like banded textures.[16−20] The single faceted crystals of the copolymer containing a chloro side group are also obtained, which possess orthorhombic packing and very good crystallographic orientation with the c axes perpendicular to the film plane. The unit cell parameters calculated from electron diffraction pattern are $a = 0.766$ nm and $b = 0.612$ nm.[21]

Although LC-PAEKs and PAEKs have similar chain structure and some similar properties, remarkable dissimilarities also exist between the two polymers, especially in the morphology, phase, and crystallization behavior. If PAEKs are blended with LC-PAEKs, the addition of LC-PAEKs can improve the processability of the PAEKs by reducing their melt viscosity. On the other hand, the introduction of PAEKs into LC-PAEKs will certainly affect the liquid crystalline textures and phase behavior of the latter. Therefore, it is of interest to study the phase behavior and morphology of LC-PAEK/PAEK blends.

Ring-banded spherulites are often observed under polarized optical microscope in some semicrystalline homopolymers[22−25] and polymer blends.[26−30] It is generally believed that the extinction bands in spherulites are due to periodic twisting of lamellae along the radial growth direction of the spherulites.[31−40] However, in the 1950s, on the basis of the fact that the same concentric rings in polyethylene spherulites were observed under

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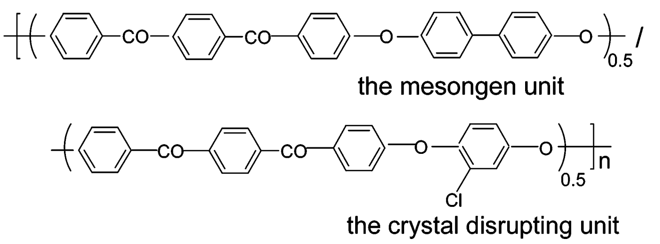
an unpolarized configuration,[41−43] Keith and Padden proposed that the lamellar twisting cannot be the only cause for the observed concentric ringed patterns in polymer spherulites, and the concentric ringed pattern is a consequence of structural discontinuities caused by rhythmic crystal growth as well.[44,45] Recently, rhythmic crystal growth of ring-banded spherulites in some blends of crystalline and amorphous polymers has been observed experimentally[46,47] and explained by simulation.[48] Very recently, Schultz et al. reported a depletion-induced nonbirefringent banding in isotactic polystyrene thin films, which is similar to the rhythmic crystallization processes.[49]

In a previous short communication,[50] we reported the concentric ringed structures in thin films of LC-PAEK/PEEK blends, which actually are crystalline/crystalline polymer blends. In this work, phase behavior, morphology, miscibility, and phase separation of the blends with various compositions have been studied, with particular emphasis on the generation and development of the ring-banded spherulites and factors affecting them, and a structural discontinuity model is proposed to explain the concentric ring development.

Experimental Section

Materials and Sample Preparation. The PEEK used in this work was a commercial product, with a number-average molecular weight of 22 000 and a polydispersity index (M_w/M_n) of 2.8. The LC-PAEK with a lateral chloro group was synthesized from 4,4′-biphenol and chlorohydroquinone with 1,4-bis(p-fluorobenzoyl)benzene by a nucleophilic substitution reaction.[13] The number-average molecular weight was about 5000, and the polydispersity index was 1.4. The chemical structure of the polymer chain is



Thin films of the LC-PAEK/PEEK blends were prepared by casting 0.5−2 wt % solutions in pentafluorophenol on glass slides for PLM and AFM observations and on carbon-coated mica for TEM observation. After being heated at 380 °C for 2 min to eliminate previous thermal history, the films were cooled to room temperature at different cooling rates for nonisothermal crystallization experiments or rapidly transferred to another hot stage controlled at a preset temperature for isothermal crystallization experiments. The ultrathin films for TEM observation were subsequently stripped, floated on the surface of water, and then collected on copper grids. Solvent washing experiment of the thin films was also carried out to identify the phase composition of the ring-banded structures, where thin films of the blends supported by glass slides were etched for several minutes in a 40/60 (w/w) mixed solvent consisting of p-chlorophenol and 1,1,2,2-tetrachloroethane, which can only dissolve the LC-PAEK in the blends.

Equipment and Characterizations. DSC measurements were carried out using a Perkin-Elmer calorimeter (model DSC-7), under a protective nitrogen atmosphere, at a cooling and heating rate of 10 °C/min. To determine the glass transition temperature (T_g), the samples were first heated at 380 °C for 2 min and subsequently quenched into liquid nitrogen prior to DSC runs.

The PLM observations of the thin films were performed on a Leica DMLP microscope equipped with a Linkam TM600 hot stage and a CCD camera.

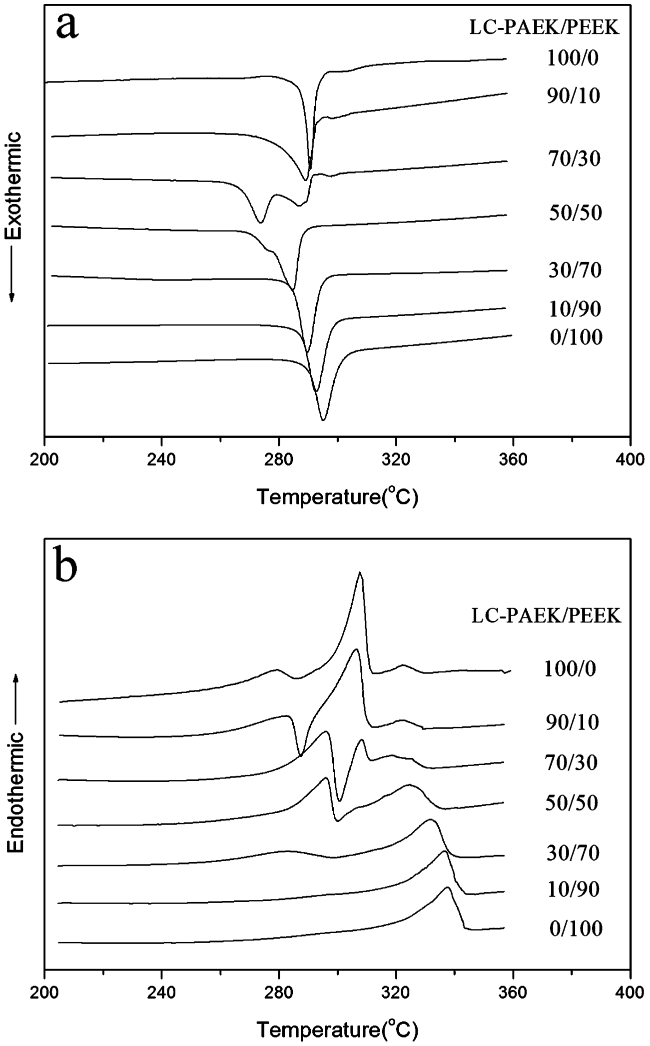


Figure 1. DSC cooling (a) and reheating (b) curves of the LC-PAEK/PEEK blends with various compositions at scanning rates of 10 °C/min.

AFM images were obtained with a SPA-HV300 with a SPI 3800N controller (Seiko Instruments Industry Co., Ltd.). Probes with a resonant frequency of 250−300 kHz and a spring constant of 42 N/m were used. A 150 μm scanner was selected, and tapping mode was used to obtain height images.

TEM bright field (BF) images and ED patterns were obtained with a JEOL 2010 TEM using an accelerating voltage of 200 kV. Calibration of the camera length was carried out using Au as the standard.

Results and Discussion

Thermal Behavior and Miscibility of the Blends. The miscibility of the LC-PAEK/PEEK blends was studied by measuring the T_g of the melt-quenched samples. The T_gs of neat LC-PAEK and PEEK are ca. 103 and 142 °C, respectively. Each of the LC-PAEK/PEEK blends only exhibits a single composition-dependent T_g intermediate between the T_gs of the two pure components, which indicates that LC-PAEK and PEEK are miscible.

The LC-PAEK/PEEK blends exhibit complicated thermal behavior. Figure 1 shows the DSC cooling and reheating curves of the blends with various compositions. For pure LC-PAEK, the cooling curve exhibits two thermodynamic first-order transitions (Figure 1a), i.e., the isotropic-to-liquid crystalline transition with an onset temperature of 309 °C and the liquid crystalline-

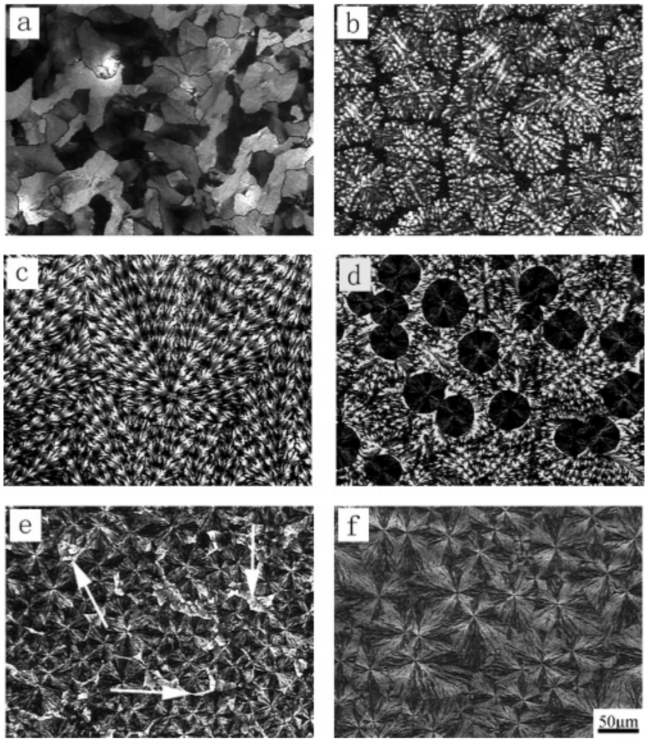


Figure 2. PLM images of thin films of the LC-PAEK/PEEK blends with various compositions heat-treated at 380 °C for 2 min and then cooled to room temperature at a cooling rate of 10 °C/min: (a) LC-PAEK, (b) 90:10 LC-PAEK/PEEK, (c) 70:30 LC-PAEK/PEEK, (d) 50:50 LC-PAEK/PEEK, (e) 30:70 LC-PAEK/PEEK, and (f) PEEK.

to-crystalline transition (ca. 295 °C). It should be pointed out that the LC transition is usually a thermodynamic equilibrium transition, and there should not be significant undercooling involved. With the addition of the PEEK, the two transitions shift slightly to lower temperatures. Meanwhile, the liquid crystalline-to-crystalline transition peak becomes broader at low-temperature side (see the blend with 10% PEEK), and even new crystallization peaks at lower temperatures are observed for the blends with 30% and 50% PEEK. This is attributed to the presence of the second component PEEK, which retards the isotropic-to-liquid crystalline transition of LC-PAEK. As a result, the nontransited LC-PAEK crystallizes directly at lower temperatures, forming incomplete and small crystals. For the blends with PEEK as the predominant component, the cooling curves exhibit only a single crystalline peak, and the peak temperature decreases with the increase of the LC-PAEK content.

The phase transitions of LC-PAEK are reversible. In DSC reheating curves (Figure 1b), there exist two corresponding transitions, i.e., the crystalline-to-liquid crystalline transition and the liquid crystalline-to-isotropic transition. For LC-PAEK-rich blends, in addition to the two thermodynamic first-order transitions, strong melting and recrystallization peaks at lower temperatures are observed, which are attributable to the small size crystals of LC-PAEK formed during cooling, as mentioned above. For PEEK-rich blends, the melting temperature of the PEEK shifts to lower temperatures with the increase of LC-PAEK content, indicating again the miscibility between the two components.

Phase Behavior of the Blends. Figure 2 shows the PLM images of the thin films of the LC-PAEK/PEEK blends in the whole composition range, heat-treated at 380 °C for 2 min and then cooled to room temperature at a cooling rate of 10 °C/min. The neat LC-PAEK and PEEK display a typical mosaic texture,[18] a highly ordered smectic phase S_E, and a spherulite morphology[9] (Figure 2a,f). For the LC-PAEK/PEEK blends with higher content (>50 wt %) of LC-PAEK, an unusual type of ring-banded spherulites is formed (Figure 2b,c), which has never been found in pure LC-PAEK and PEEK. Especially in the 70:30 LC-PAEK/PEEK blend, well-developed spherulites with concentric extinction rings are observed under PLM. The size of perfect ring-banded spherulites is even greater than 500 μm, and the mean band spacing is about 20 μm. It should be noted that in the 90:10 LC-PAEK/PEEK blend the absence of the spherulitic impingement may imply that phase separation is occurred at which the growth of LC-PAEK excludes out the PEEK. In the blends with intermediate compositions, e.g. 50:50 LC-PAEK/PEEK, in addition to the ring-banded spherulites, individual PEEK spherulites are also observed (Figure 2d), which disperse in the incomplete ring-banded spherulites. For the PEEK-rich blends, e.g., 70:30 PEEK/LC-PAEK, typical PEEK spherulites are produced, while the LC-PAEK phase is mainly located at the boundary between the spherulites, as marked by the arrows in Figure 2e. When the content of PEEK in the blends is high enough (90%), no LC-PAEK phase is observed under PLM, exhibiting the same morphology as that of pure PEEK.

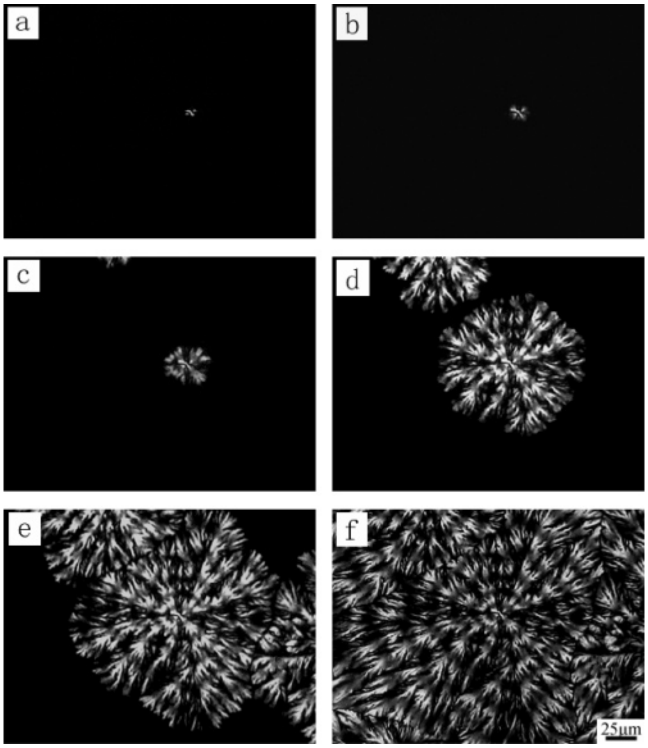


Figure 3. PLM images depicting the evolution of the ring-banded spherulites in the 70:30 LC-PAEK/PEEK blend heat-treated at 380 °C for 2 min and then cooled at a cooling rate of 10 °C/min: (a) 297.5, (b) 294, (c) 288.1, (d) 283.1, (e) 280, and (f) 272.5 °C.

To clearly understand the evolution process of the phase structure of the LC-PAEK/PEEK blends during nonisothermal crystallization process, in situ observation of selected typical blends was carried out under PLM. Figure 3 shows the evolution of a ring-banded spherulite in a thin film of the 70:30 LC-PAEK/PEEK blend. The formation temperature of the nucleus is

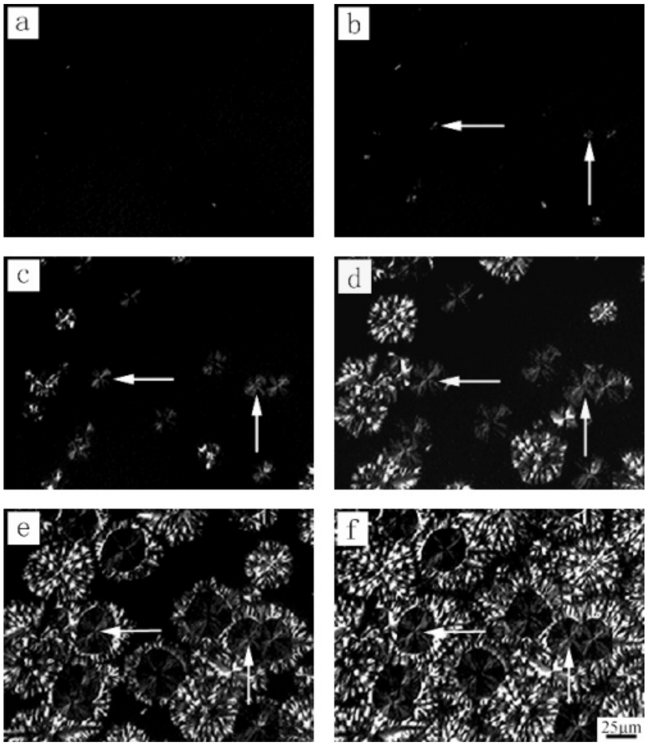


Figure 4. PLM images showing the morphological evolution of the 50:50 LC-PAEK/PEEK blend heat-treated at 380 °C for 2 min and then cooled at a cooling rate of 10 °C/min: (a) 297.1, (b) 295.5, (c) 288, (d) 284, (e) 280.1, and (f) 270 °C.

about 297.5 °C, which is significantly lower than the isotropic-to-liquid crystalline transition temperature (309 °C) of pure LC-PAEK. Although the spherulitic growth front is nearly circular in the early stage of growth, the spherulitic boundary becomes wavy (the formation mechanism of the ring-banded spherulites will be discussed below). It should be pointed out that the whole phase transition process is much slower than that of pure LC-PAEK, which implies that the addition of PEEK may retard the isotropic-to-liquid crystalline transition of the LC-PAEK. Figure 4 depicts the morphological evolution of a 50:50 LC-PAEK/PEEK blend film during the nonisothermal crystallization process. At about 297.1 °C, a small number of LC-PAEK nuclei appear in the system at first (Figure 4a). Subsequently, several PEEK nuclei are also observed at about 295.5 °C, as marked by the arrows in Figure 4b. Starting from these two kinds of nuclei, ring-banded structures and individual PEEK spherulites grow simultaneously with the decrease of the temperature. For the nonisothermal crystallization of the 30:70 LC-PAEK/PEEK blend, the morphological development is shown in Figure 5. In the initial stage, only PEEK nucleates and develops into spherulites (Figure 5a−c). The individual phase regions of LC-PAEK can be found in the boundary of PEEK spherulites at about 270 °C (as marked by the arrows in Figure 5d), which is far lower than the phase transition temperature of pure LC-PAEK (309 °C).

The above results indicate that the complicated phase behavior of the LC-PAEK/PEEK blends is strongly dependent on the composition of the blends. In both the LC-PAEK-rich and PEEK-rich blends, a common feature is that the two components should be molecular miscible in the melting state, while during the cooling process a phase separation takes place. The predominant difference between the phase behavior of the LC-PAEK-rich and PEEK-rich blends lies in that in the former the high molecular weight PEEK is liable to segregate from the low molecular weight LC-PAEK matrix, which is one of the causes for the formation of the ring-banded spherulites (the phase composition of the ring-banded structure will be discussed below), while in the latter the low molecular weight LC-PAEK is difficult to separate from the high molecular weight PEEK matrix, which results in a much lower formation temperature (270 °C) of individual LC-PAEK phase regions. For the 50:50 LC-PAEK/PEEK blend, the two components are not completely miscible and a partial liquid−liquid phase separation occurs in the melt; i.e., a small amount of PEEK segregates to form individual phases, which leads to almost simultaneous occurrence of two kinds of nuclei during the cooling process, followed by simultaneous development of the ring-banded structures and PEEK spherulites.

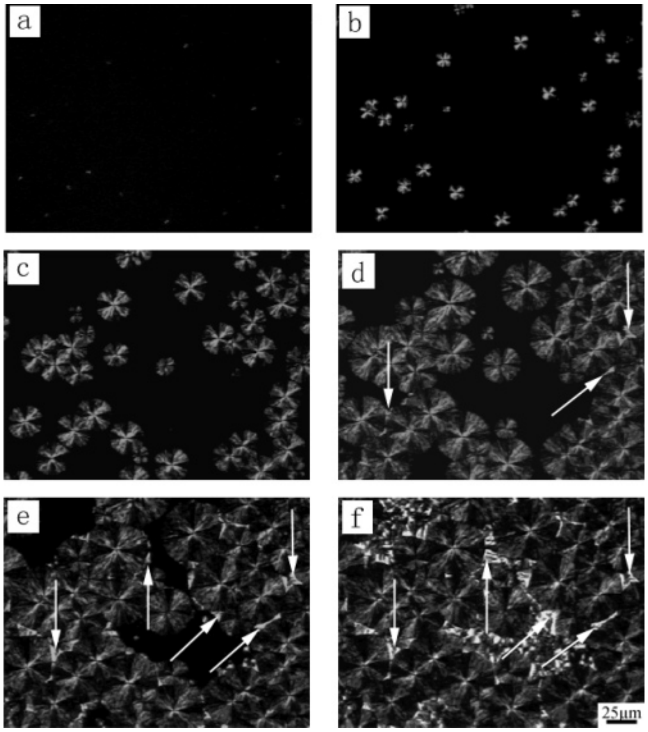
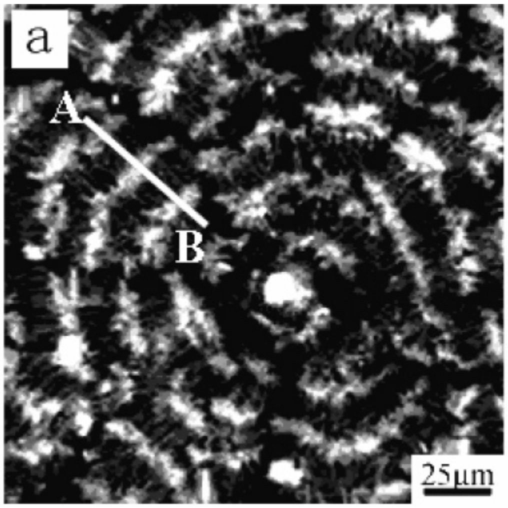


Figure 5. PLM images depicting the morphological evolution of the 30:70 LC-PAEK/PEEK blend heat-treated at 380 °C for 2 min and then cooled at a cooling rate of 10 °C/min: (a) 297.5, (b) 288, (c) 275, (d) 270, (e) 266, and (f) 256.8 °C.

Ring-Banded Spherulites in the Blends. As mentioned above, for LC-PAEK-rich blends an unusual type of ring-banded spherulites are formed during the cooling process of the melt films. The ring-banded structures can also be examined with AFM. Figure 6a shows the AFM height image of a nonisothermally crystallized film of the 70:30 LC-PAEK/PEEK blend. The concentric dark and bright bands alternating around the bright core are also observed. The brightness contrast of the alternating bright and dark bands, which represent the depth profiles of the ridges and valleys, respectively, is attributed to height contrast. The AFM height trace (Figure 6b) shows that the vertical distance between the lowest and the highest points on the sample surface (band height amplitude) ranges from 50 to 90 nm. The ridges and the valleys correspond respectively to the bright and dark regions of the extinction rings seen under the PLM.



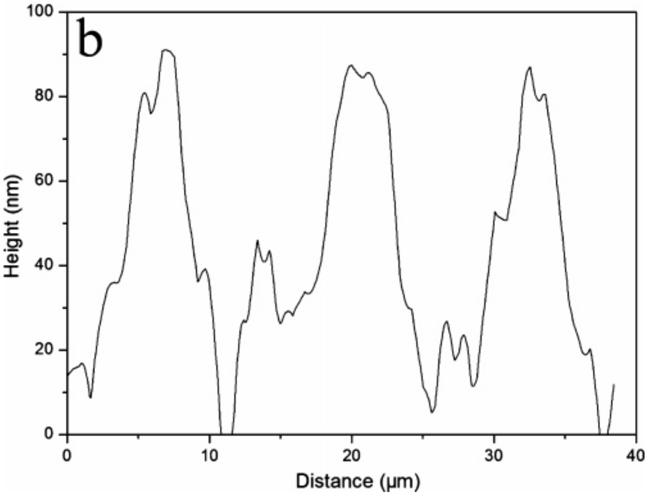


Figure 6. (a) AFM height image of ring-banded spherulites in thin films of the 70:30 LC-PAEK/PEEK blend and (b) a through A−B height trace.

To identify the material composition in both the light (ridge) and dark (valley) regions of the ring-banded spherulites, a solvent washing experiment was carried out, using a 40/60 (w/w) mixture of *p*-chlorophenol and 1,1,2,2-tetrachloroethane as the washing solvent, which can only dissolve LC-PAEK in the blends. The etching experiment has been described in a previous short communication.[50] For the convenience of the readers, some of the results are present here. Figure 7 shows the PLM image of the etched ring-banded spherulites in the 70:30 LC-PAEK/PEEK blend. By carefully comparing Figure 7 with Figure 2c (or Figure 3), it is found that the contrast is just inversed; i.e., the dark and bright regions in Figure 7 correspond respectively to the bright and dark regions in Figure 2c. Clearly, this result indicates that in Figure 2c the bright rings and core are the LC-PAEK phase (which could be washed out by the solvent, resulting in the dark rings and core in Figure 7), while the dark rings are mainly the PEEK phase (which could not be washed out, resulting in the bright rings in Figure 7). AFM characterization of the etched films of the blends yields a quite similar result to that of PLM (comparing Figure 8a with Figure 6a); i.e., inversed contrast occurs, which indicates that the ridges in Figure 6a represent the LC-PAEK phase, while the valleys correspond to the PEEK phase. Figure 8b shows a magnified image of Figure 8a in the location shown by the circle to identify more detailed phase composition. After etching, almost no LC-PAEK can be found in the dark band (the middle in Figure 8b), most of which is washed out. In the bright bands (the upper right and lower left in Figure 8b), however, there are some dark regions among the unwashed PEEK crystals, as marked by the arrows, which are no doubt etched LC-PAEK. This implies that the valleys in Figure 6a are actually a coexisting phase of PEEK with part of LC-PAEK.

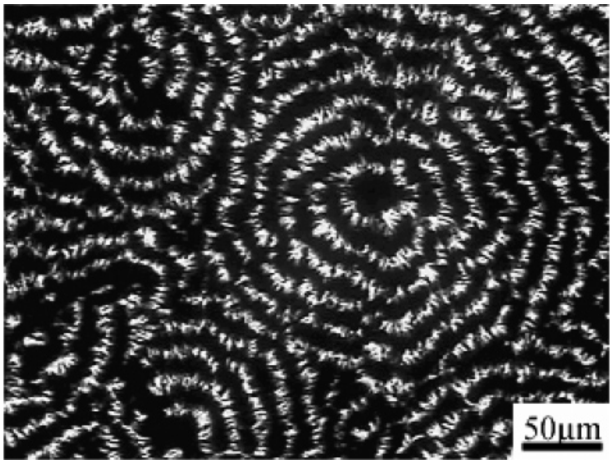


Figure 7. PLM image of the etched ring-banded spherulites in the 70:30 LC-PAEK/PEEK blend.

Figure 9 shows TEM BF electron micrographs and ED patterns of the ring-banded spherulites in nonisothermally crystallized thin films of the 70:30 LC-PAEK/PEEK blend. For a large scale structure, the contrast in BF image is generally attributed to amplitude contrast, including diffraction contrast and mass thickness contrast. Because the band height amplitude ranges from 50 to 90 nm, the contrast of the bright and dark regions should mainly come from the mass thickness contrast. Therefore, the alternating bright and dark bands in Figure 9a correspond to the valleys and ridges of AFM height image (Figure 6a), respectively. Figure 9b shows the ED pattern of the dark band in Figure 9a in the location shown by the white circle. All of the reflections can be indexed based on orthorhombic packing of the LC-PAEK crystal. The strong (*hk*0) reflections indicate that the LC-PAEK molecular chains (*c*-axes) are perpendicular to the film plane, while the *a*- and *b*-axes are in the film plane. It should be pointed out that the ED patterns have been taken in various regions within the dark bands. All of the diffraction patterns observed indicate the same orientation of the *c*-axes and indefinite directions of the *a*- and *b*-axes. As for the light band regions, it seems that there exist bright and dark strips with definite orientation along the radial direction of the ring-banded spherulites. Figure 9c shows a magnified BF image of the bright band of Figure 9a in the location shown by the black circle to identify the phase structure in detail. At least two kinds of phase regions in Figure 9c are observed. One is a relatively bright region (the lower left in Figure 9c), consisting of short and thin lamellae. This region should be the PEEK phase. The other is a relatively dark region (the upper right in Figure 9c) containing crystallites, which should be the LC-PAEK phase. It should be pointed out that within the LC-PAEK region a number of PEEK long lamellae along the radial direction of the ring-banded spherulite are observed dispersing in it. It is these two kinds of phase structures

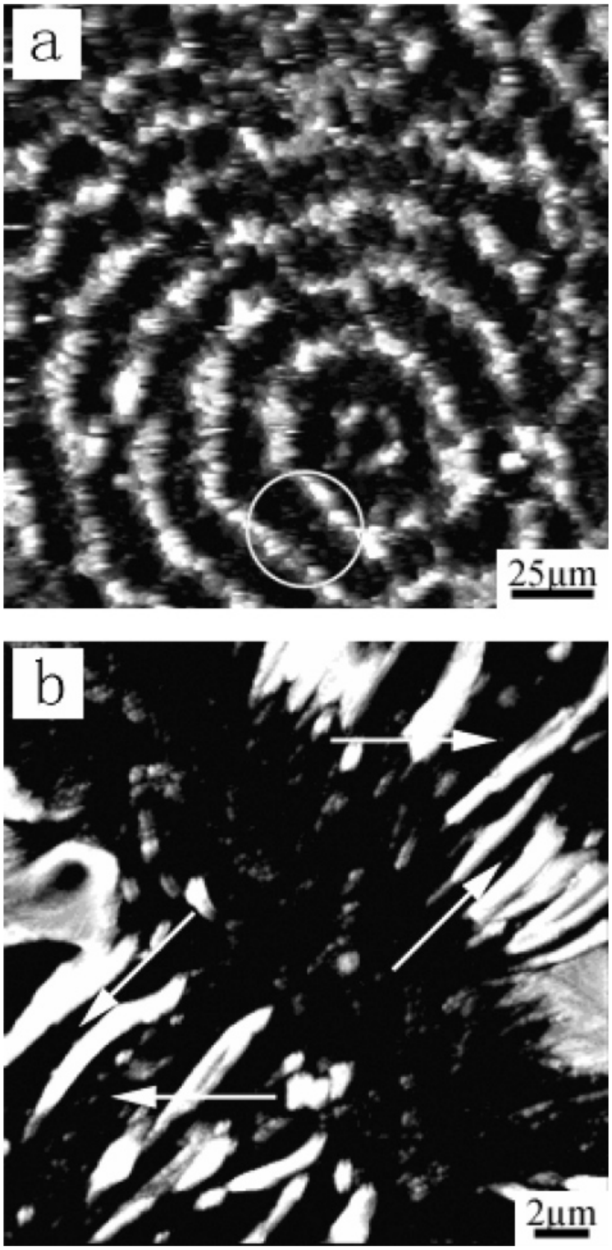


Figure 8. (a) AFM height image of the etched ring-banded spherulites of the 70:30 LC-PAEK/PEEK blend and (b) a magnified image of (a) in the location shown by a circle.

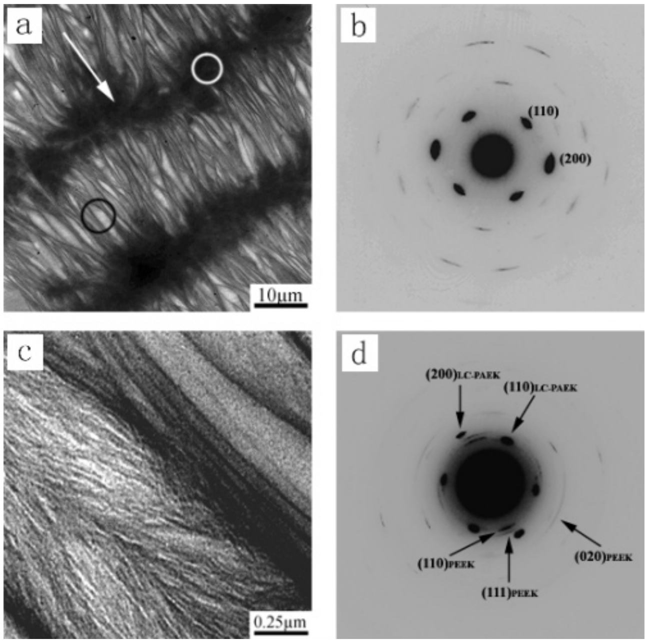


Figure 9. (a) BF image of ring-banded spherulites in thin films of the 70:30 LC-PAEK/PEEK blend, with the radial growing direction shown by the arrow, (b) ED pattern of the dark band in (a) in the location shown by the white circle, (c) a magnified image of the bright band in (a) in the location shown by the black circle, and (d) its corresponding electron diffraction pattern. The sample was annealed at 380 °C for 2 min and then cooled to room temperature at a cooling rate of 10 °C/min.

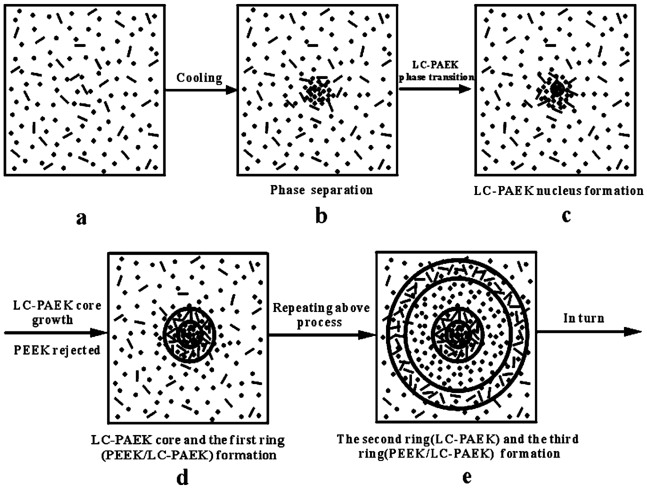


Figure 10. Schematic diagram of the developing process of the ring-banded spherulites in the LC-PAEK/PEEK blends. Dots and short rods represent LC-PAEK and PEEK molecules, respectively.

that constitute the bright and dark strips in the bright band regions of the spherulites. This result evidences that the bright bands in Figure 9a are coexisting phase of PEEK with LC-PAEK. The conclusion can be further confirmed by the corresponding ED pattern, as shown in Figure 9d. The ED pattern contains two sets of reflections. One results from the LC-PAEK crystals. The strong (*hk*0) reflections indicate that the LC-PAEK molecular chains in the bright band regions have the same orientation as that in the dark band regions; i.e., the *c*-axes are perpendicular to the film plane. The other comes from the PEEK crystals. Indexing result of the reflections based on the orthorhombic packing of the crystals indicates that besides the (110) and (020) reflections there exists a weak (111) reflection. The simultaneous appearance and disposition of the (110) and (111) reflections of PEEK implies that there is an intermediate lamellar orientation; i.e., the PEEK lamellae are inclined about their *b*-axis (growth direction) by an average of 52° from their usual edge-on orientation.[6]

Thus, it is clear that the above electron microscopy and electron diffraction results not only further confirm the phase composition of the ring-banded structure as determined by the solvent etching technique but also reveal the structural particulars.

Unambiguously, this kind of concentric ring (target) structure is different from classical banded spherulites, and a rhythmic growth process is suggested. Figure 10 shows schematically the development process of the ring-banded spherulites. For the LC-PAEK-rich blends, the two components in the melting state should be molecular miscible (Figure 10a). During the cooling

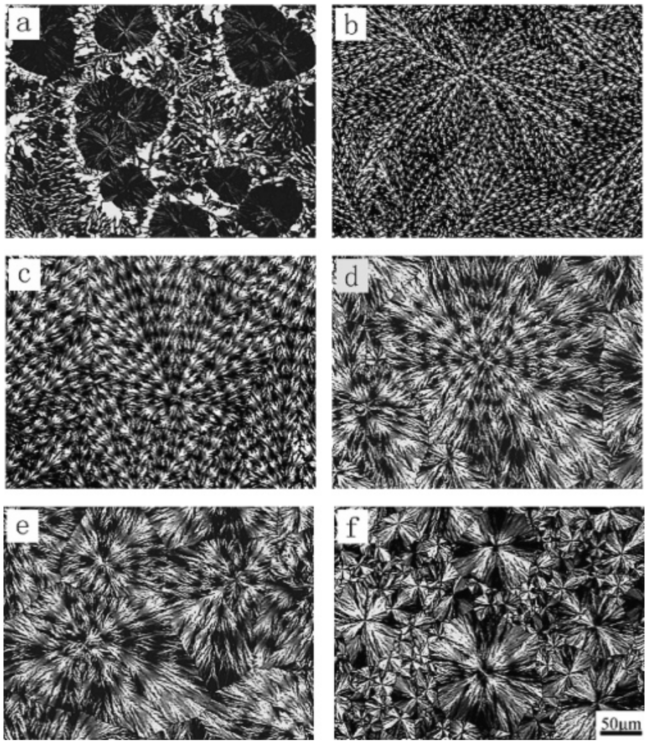


Figure 11. PLM images of thin films of the 70:30 LC-PAEK/PEEK blend nonisothermally crystallized at different cooling rates from the melt: (a) 1 °C/min, (b) 3 °C/min, (c) 10 °C/min, (d) 80 °C/min, (e) 120 °C/min, and (f) 200 °C/min.

process, a phase separation takes place, resulting in small LC-PAEK phase regions (Figure 10b). Subsequently, a highly ordered liquid crystalline phase (S_E) with small dimension forms first in the LC-PAEK region (Figure 10c) since the isotropic-to-liquid crystalline transition temperature (about 309 °C) of LC-PAEK is higher than the crystallization temperature (about 295 °C) of PEEK. It should be pointed out that the S_E phase actually is in solid state, which can act as a nucleus of the ring-banded spherulites. (Note: during the cooling process the S_E phase of the LC-PAEK will transform to a crystalline phase very quickly since the transition is almost a thermodynamic equilibrium.) At the same time, the PEEK molecular chains are rejected from the core, forming the PEEK-rich regions around the LC-PAEK core, i.e., the first dark or valley region (Figure 10d). Repeating the above rhythmic growth process, i.e., LC-PAEK phase transitions (including both the isotropic-to-liquid crystalline and subsequent liquid crystalline-to-crystalline transitions) and PEEK being rejected simultaneously, the concentric ring or target spherulites are produced in the blends (Figure 10e).

It should be noted that, as a result of the rhythmic growth, the amorphous phase of both the PEEK and LC-PAEK should be mainly accumulated in the valley regions of the ring-banded spherulites, which is one of the reasons that leads to the relatively weak contrast of the valley regions under PLM. The other reason is due to the mass thickness difference. The lower mass thickness of the valleys must produce weak contrast compared with the ridges.

It is noteworthy that the rhythmically grown ring-banded spherulites with structural discontinuity reported here possess similarity to the development of Liesegang rings, which have been well-known for a long time in small molecule systems,[51,52] where the generation of these phenomena are dependent on an interplay of diffusion and precipitation or crystallization, analogous to the composition variation of LC-PAEK and PEEK/LC-PAEK phases in the present case.

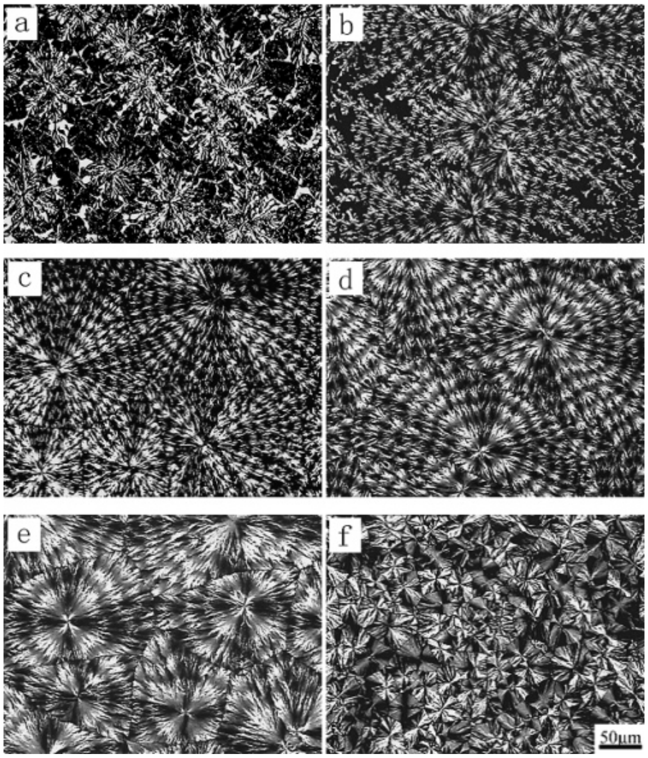


Figure 12. PLM images of thin films of the 70:30 LC-PAEK/PEEK blend isothermally crystallized at different crystallization temperatures from the melt: (a) 288, (b) 280, (c) 275, (d) 273, (e) 271, and (f) 260 °C.

Effect of Crystallization Conditions on Ring-Banded Spherulite Formation. The cooling rate in nonisothermal crystallization and the isothermal crystallization temperature have significant effect on the ring-banded spherulite formation of the LC-PAEK/PEEK blends. Taking the 70:30 LC-PAEK/PEEK blend as an example, Figure 11 shows a series of PLM images of phase morphologies formed at different cooling rates. At a low cooling rate (≤1 °C/min), both the individual LC-PAEK phase (the bright regions) and typical PEEK spherulites (dark regions), instead of the concentric ring structures, are observed simultaneously (Figure 11a), which implies that the phase separation of the two components takes place in the system before the phase transition. If the cooling rate is high (about 200 °C/min), a volume-filled spherulite can be found (Figure 11f). Only at appropriate cooling rates (3−120 °C/min), the concentric ring spherulites are produced (Figure 11b−e). Figure 12 shows a series of PLM images of the phase morphology of the 70:30 LC-PAEK/PEEK blend formed at different isothermal crystallization temperatures (T_c). At higher T_c (≥288 °C), individual LC-PAEK phase and typical PEEK spherulites are clearly observed (Figure 12a), which indicates that there is a phase separation for both components before the phase transition. When the T_c is low enough (260 °C), the system exhibits a volume-filled spherulite (Figure 12f). The temperature range suitable for forming the ring-banded spherulites is from 280 to 271 °C.

The above results indicate that the occurrence of the ring-banded spherulites is strongly dependent on the cooling rate and the crystallization temperature. For the

LC-PAEK-rich blends, as mentioned above, the two components should be molecular miscible in the melting state. During cooling both the phase separation and the phase transition (or crystallization) processes take place, competing with etch other. At low cooling rate or high T_c, the phase separation rate is much higher than that of the phase transition. In this aspect, individual LC-PAEK and PEEK phases produce simultaneously, as shown in Figures 11a and 12a. If the cooling rate is very high or the T_c is quite low, the phase transition (or crystallization) rate of LC-PAEK is much higher than that of the phase separation, resulting in volume-filled spherulites (Figures 11f and 12f). Only at appropriate cooling rates or T_c, the phase transition (or crystallization) and phase separation rates are comparable or the former is slightly higher than the latter. In this case, well-developed ring-banded spherulites of the LC-PAEK/PEEK blend could be formed.

Conclusions

The complicated phase behavior of the LC-PAEK/PEEK blends is strongly dependent on the composition of the blends. In both LC-PAEK-rich and PEEK-rich blends, the two components are molecular miscible in the melting state, while during cooling a phase separation takes place. The essential difference of the phase behavior of the two systems lies in that for the former rhythmically grown ring-banded spherulites with structural discontinuity have been formed, while for the latter the LC-PAEK phase is rejected into the boundary of the PEEK spherulites. For the 50:50 LC-PAEK/PEEK blend, the two components are not completely miscible and a partial liquid−liquid phase separation occurs in the melt, which leads to simultaneous formation of the ring-banded structures and PEEK spherulites.

There are two completely different phase compositions and structures for both the bright and dark regions in the ring-banded spherulites. The bright core and rings are mainly composed of LC-PAEK phase with the crystallographic orientation of the *c*-axes (the chain direction) perpendicular to the film plane and the *a*- and *b*-axes in the film plane with indefinite directions. The dark rings consist of a coexisting phase of PEEK and part of LC-PAEK, in which the LC-PAEK molecular chains in the crystals are also perpendicular to the film plane, while the PEEK lamellae exhibit intermediate crystallographic orientations. The development of the ring-banded spherulites in the LC-PAEK/PEEK blends is a rhythmic growth process, and thus it is consistent with the structural discontinuity model proposed by Padden and Keith based on polyethylene spherulites.

In addition to the composition of the blends, the cooling rate and crystallization temperature have a significant effect on the formation of the ring-banded spherulites. As for the 70:30 LC-PAEK/PEEK blend, low cooling rates (≤1 °C/min) or high T_cs (≥288 °C) result in individual LC-PAEK and PEEK phases formation, while very high cooling rates (≥200 °C/min) or quite low T_cs (≤260 °C) will lead to volume-filled spherulites. Only at appropriate cooling rates (3−120 °C/min) or T_cs (280−271 °C), well-developed ring-banded spherulites of the LC-PAEK/PEEK blend are produced.

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