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ORIGINAL CONTRIBUTION

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Effects of miscible diluent of poly(ether imide) on ring-banded morphology of poly (trimethylene terephthalate)

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Abstract The melting, crystallization, and self-packed ring patterns in the spherulites of miscible blends comprising poly(trimethylene terephthalate) (PTT) and poly(ether imide) (PEI) were revealed by optical, scanning electron microscopies (PLM and SEM) and differential scanning calorimetry (DSC). Morphology and melting behavior of the miscible PTT/PEI blends were compared with the neat PTT. Ringed spherulites appeared in the miscible PTT/PEI blends at all crystallization temperatures up to 220 °C, whereas at this high temperature no rings were seen in the neat PTT. A postulation was proposed, and interrelations between rings in spherulites and the multiple lamellae distributions were investigated. The specific interactions and the segregation of amorphous PEI were discussed for interpreting the morphological changes of 220 °C-melt-crystallized PTT/PEI samples. Interlamellar segregation of PEI might be associated with multiple lamellae in the spherulites of PTT/PEI blends; therefore, rings were more easily formed in the PTT/PEI blends at all crystallization temperatures. A postulated model of uneven lamellar growth, coupled with periodical spiraling, more properly describes the possible origin of ring bands from combined effects of both interactions and segregation between the amorphous PEI and PTT in blends.

Keywords Poly(trimethylene terephthalate) (PTT) · Poly(ether imide) (PEI) · Ring bands · Segregation · Blends · Spherulites

Introduction

There have been numerous investigations of morphological changes in compatible blend. Some of these earlier literatures focused on morphological changes, including the occurrence of ringed extinction patterns and/or the effect of inducing "bands" in spherulites of host polymers, such as poly(ϵ-caprolactone) (PCL)/poly(benzyl methacrylate) (PBzMA) and PCL/poly (phenyl methacrylate) (PPhMA) systems [1], PCL/poly(vinyl chloride) (PVC) system [2–5], PCL/poly (styrene-co-acrylonitrile) (SAN) [6, 7] and poly(vinylidene fluoride) (PVF_2)/ploy(methyl methacrylate) (PMMA) systems [8] etc. Neat PCL is known to exhibit ring bands at a high temperature (50 °C for 24 h); however, no ring bands are found at lower temperatures (45 °C or below) [1, 3]. In addition, ringed spherulites were observed in PCL miscible systems in the same temperature range (45 °C or below) where no ring bands formed in neat PCL. Distinct rings were shown in spherulites even when small amount of amorphous polymer (1%) added to neat PCL [1, 7]. The addition of non-crystallizable polymeric diluents to a crystallizable host polymer can induce to form ring bands in miscible blends. Moreover, the extinction rings are more populated with increasing amorphous component in the PCL/acrylic polymer blends. This fact suggests that a greater fraction of the amorphous polymer can be trapped between the spherulites to form the interference rings at higher volume fractions of the amorphous polymer [1].

Interestingly, neat poly(trimethylene terephthalate) (PTT) is also known to show ringed spherulites upon melt-crystallization at most temperatures [9–11]. And more recently, we have explored the correlation between thermal multiple melting and ring patterns of PTT [12]. As PTT was melt-crystallized at low to medium temperatures (150–215 °C), distinct rings were present in the spherulites; in the meanwhile, two or three melting peaks were shown during differential scanning calorimetry (DSC) scanning. Furthermore, as PTT was melt-crystallized at a temperature (i.e. 220 °C) near the melting temperature, only a single type of lamella could develop, then no rings were discovered in the spherulites. At the same time, DSC results showed only one peak upon heating. Therefore, it can be concluded that there should be no rings in PTT if a crystallization temperature is selected so that there is only one type of lamella in the spherulites. The cut-off temperature was 220 °C for PTT [12].

Additionally, we have demonstrated earlier that PTT forms a miscible blend with poly(ether imide) (PEI) of all compositions [13]. Thus, it will be interesting to extend discussions into possible influence of PEI on morphological changes in crystallizing PTT as a component in a miscible blend. In continuation with the earlier finding in the neat PTT, ring bands in miscible blend such as PTT/PEI may also be influenced by formation of multiple lamellae in the spherulites, which will be examined more thoroughly using thermal analysis. In addition, interlamellar segregation of PEI from PTT during crystallization or interactions between PEI and PTT in the amorphous state might influence the pattern of ring bands. A plausible model was examined and proposed to explain the procedure.

Experimental

Materials and procedures

Semicrystalline PTT was obtained as a courtesy sample material from Industrial Technology Research Institute (ITRI, Taiwan) with inherent viscosity $\eta = 0.724$ dL/g (measured in *m*-Cresol). PEI was obtained from research-grade polymer suppliers (Polysciences, Inc., $M_w = 30{,}000$ g/mol). Blending of PTT and PEI was carried out by solution mixing and co-precipitation. For brevity, two miscible blend compositions were prepared: weight ratios of PTT/PEI blends are 9/1 and 8/2, respectively). PTT and PEI (with weight ratio = 9/1, 8/2) were co-dissolved with sufficient stirring in dichloroacetic acid at room temperature, followed by co-precipitating in 20-fold excess volume of water. The precipitated blend was washed with a large amount of water and then dried under vacuum at 80 °C for 5 days to remove possible traces of solvent.

Apparatus

Polarized-light microscope (Nikon Optiphot-2) was used for observation of lamellar changes and growth of spherulites. The samples were pressed between two glass slides and first melted on the hot stage at 250 °C for 5 min. It was rapidly quenched to designated temperatures on the microscopic heating stage (Linkam THMS-600 with TP-92 temperature programmer). Furthermore, the spherulitic/lamellar morphology of PTT/PEI samples subjected to different thermal histories was examined using a scanning electron microscope (SEM, Philips XL-40FEG). Etching by 2% potassium permanganate in H_3PO_4 + H_2SO_4 (1:1) solution (24 h at ambient temperature) was performed to enhance the crystalline/amorphous contrast. The washed/dried samples were then coated with gold by vapor deposition using vacuum sputter-coating prior to SEM characterization.

A differential scanning calorimeter (DSC-7, Perkin-Elmer) equipped with a mechanical intracooler was used for analyzing thermal behavior. Heating rates of 5, 10, 20, up to 30 °C/min were used wherever needed. The instrument was calibrated with indium and zinc standards on the temperature and heat of transitions. Melt-crystallization of all samples was performed by melting at 250 °C (in DSC cells) for 5 min, and then quenched quickly to a desired isothermal temperature for a specified period of time. The DSC cell (temperature chamber) was also used for thermal treatments of the samples in preparation for other experimental characterizations such as PLM or SEM analysis.

Results and discussion

Spherulitic morphology

Figure 1 shows the spherulitic structure of the melt-crystallized PTT/PEI (9/1) at various temperatures. It can be found that the spherulites of PTT/PEI (9/1) exhibit not only a Maltese-cross pattern but also distinct ring bands at all crystallization temperatures. Generally, the ringed pattern is indicative of lamellar twisting in the direction of radial growth, but the origin of lamellar twisting is still debated [14–16]. The growth rate starts to decrease above 210 °C (i.e. 220 °C), resulting in fewer and smaller spherulites. Apparently, the spherulites are coarser at higher crystallization temperatures, where the crystallization rate is slower. It is seen that at lower temperatures, the ring bands are less concentric, whereas at higher temperatures, the ring bands are more concentric and uniform. The observations of the ring patterns in the PTT/PEI (9/1) at lower crystallization temperatures (190, 205, and 210 °C) are similar to those in neat PTT, but the ring patterns become more

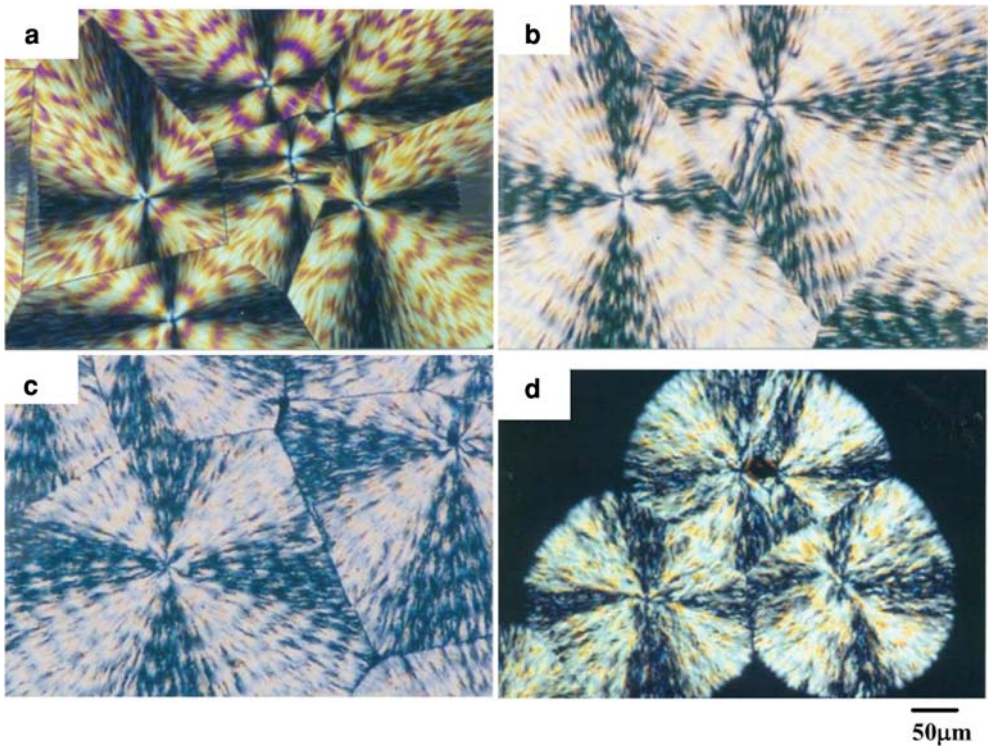

Fig. 1 Ring patterns as shown in PLM photos for PTT/PEI (9/1) crystallized at **a** 190 °C, 30 min; **b** 205 °C, 30 min; **c** 210 °C, 30 min; and **d** 220 °C, 240 min

pronounced as the PEI content increases. A comparison of spherulitic morphology in ring patterns of the PTT/PEI (8/2) under the same thermal treatment is illustrated in Fig. 2. The crystallization rate becomes slower while relatively larger non-crystallizable PEI content adds to PTT polymeric system. The ring shape including the white-ringed area and the yellow-ringed area is less zigzag (more regular) with increasing crystallization temperature as well as PEI content. The appearance of more regular and distinct ring bands in the PTT blends as compared to neat PTT seems to be a general feature since it has been observed for other blend systems [1–8]. The ring width may have some relationship with the crystallization temperature and non-crystallizable diluents [1–8]; however, the dependence of the ring width on crystallization temperatures and PEI content seems indistinct in the PTT blends.

Scanning electron microscope characterization was performed on the melt-crystallized PTT/PEI blend systems, and shown in Figs. 3 and 4. The SEM results clearly show that a bright/fibrous band and a dark/smooth grainy band exist in spherulites. We have earlier reported characteristic features of ring bands in the neat PTT that the bright region in SEM corresponds to the yellow-ringed area in PLM while the white-ringed area in PLM corresponds to the dark region in SEM [12]. Furthermore, heating of the ringed blend samples on a PLM heating stage caused melting of white-ringed area first, and then the yellow-ringed area. The high melting point of bright region appears to be of a fiber-like nature, with an edge-on pattern. On the other hand, the low melting point of dark region appears to be of an amorphous nature. The graphs in Figs. 1, 2, 3 and 4 have clearly shown that ringed spherulites are apparent in the PTT/PEI blends at all crystallization temperatures. However, it has been demonstrated earlier that no ring bands exist in the neat PTT melt crystallized at 220 °C or above [12], a situation quite different from the miscible PTT/PEI blends. Causes for the different morphology in the neat PTT versus its blend with PEI at 220 °C will be expounded in later sections.

Multiple melting peaks

According to our previous results for neat PTT [12], the melting behavior seemed to relate with the formation of ringed spherulites. If a crystallization temperature is selected so that there is only one lamellar type in the spherulites, then there should be no rings. Thus, it is helpful to discuss the melting behavior of PTT/PEI blend first. Thus, interestingly, ringed spherulites are present in the PTT/PEI blends even at a high crystallization temperature (i.e. 220 °C), where no rings appear in the neat PTT. For the neat PTT, it has been suggested that no ring bands are seen if there is only one uniform type of lamellae in the spherulites [12]. Hence, the melting endotherm for PTT/PEI blends crystallized at 220 °C was measured. Figure 5 shows the DSC thermograms (all scanned at 10 °C/min) for two blend

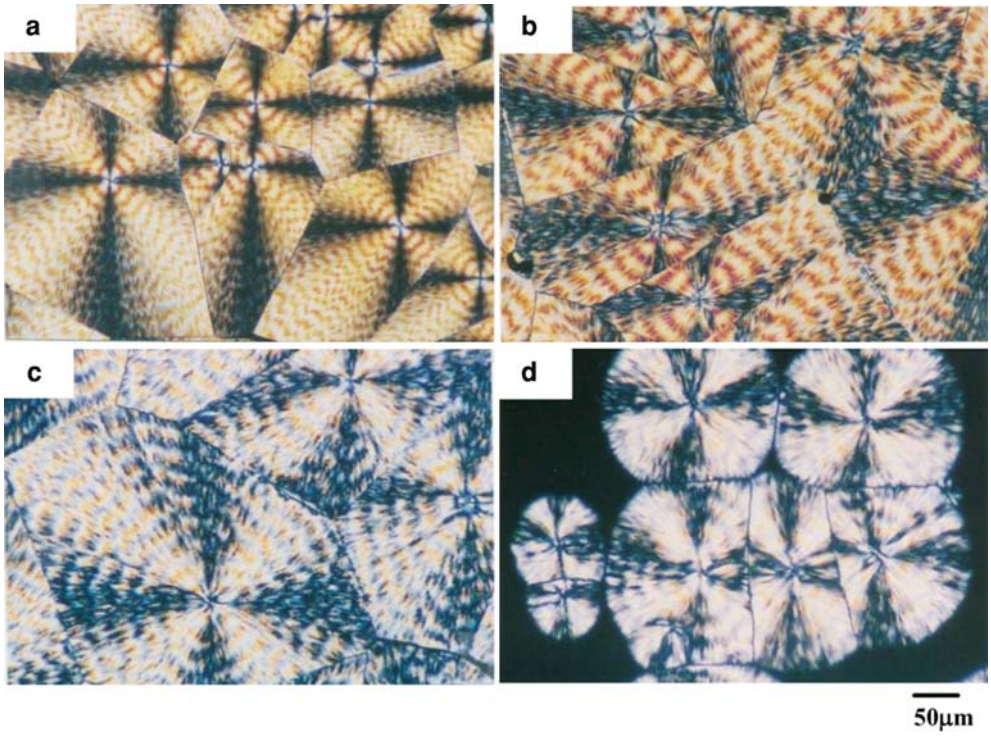

Fig. 2 Ring patterns as shown in PLM photos for PTT/PEI (8/2) crystallized at **a** 190 °C, 30 min; **b** 205 °C, 30 min; **c** 210 °C, 30 min; and **d** 220 °C, 240 min

compositions: (a) PTT/PEI (9/1) and (b) PTT/PEI (8/2), respectively, crystallized at various isothermal temperatures (180–220 °C). Triple-melting behavior is evident for these two blend compositions, which is similar to that in the neat PTT [12]. The first and second endotherms (P1, P2) are strongly dependent on the crystallization temperature, and the third one (P3) remains the same regardless of the crystallization temperature. A re-crystallization exotherm (arrow-marked) is seen apparently in PTT/PEI blends crystallized at relatively

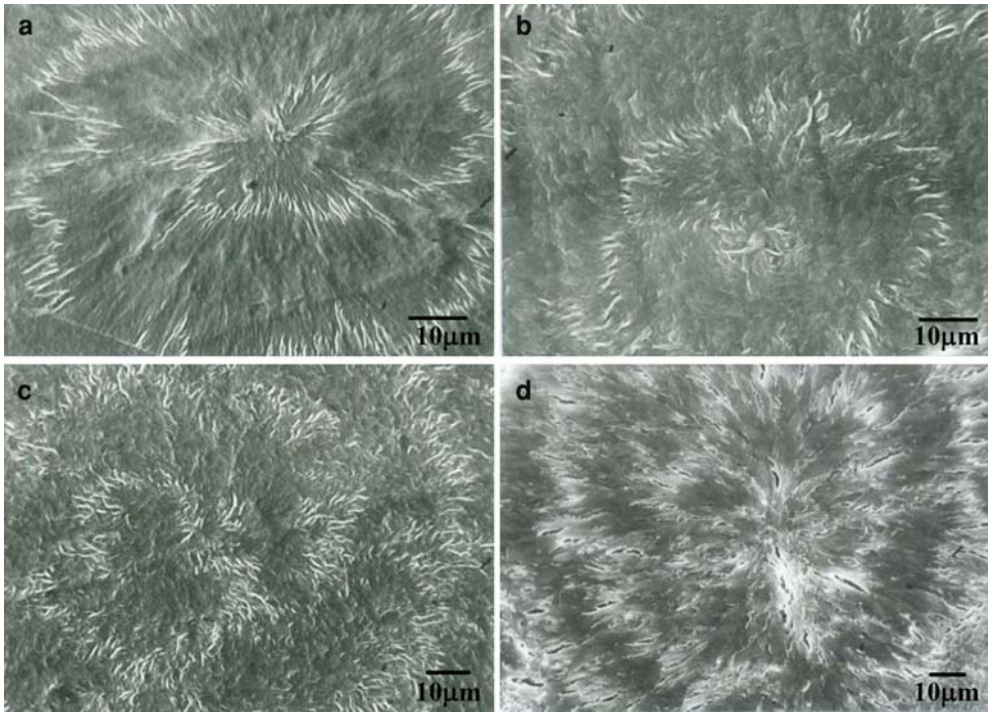

Fig. 3 SEM graphs of PTT/PEI (9/1) blend crystallized at **a** 190 °C, 30 min; **b** 205 °C, 30 min; **c** 210 °C, 20 min; and **d** 220 °C, 240 min

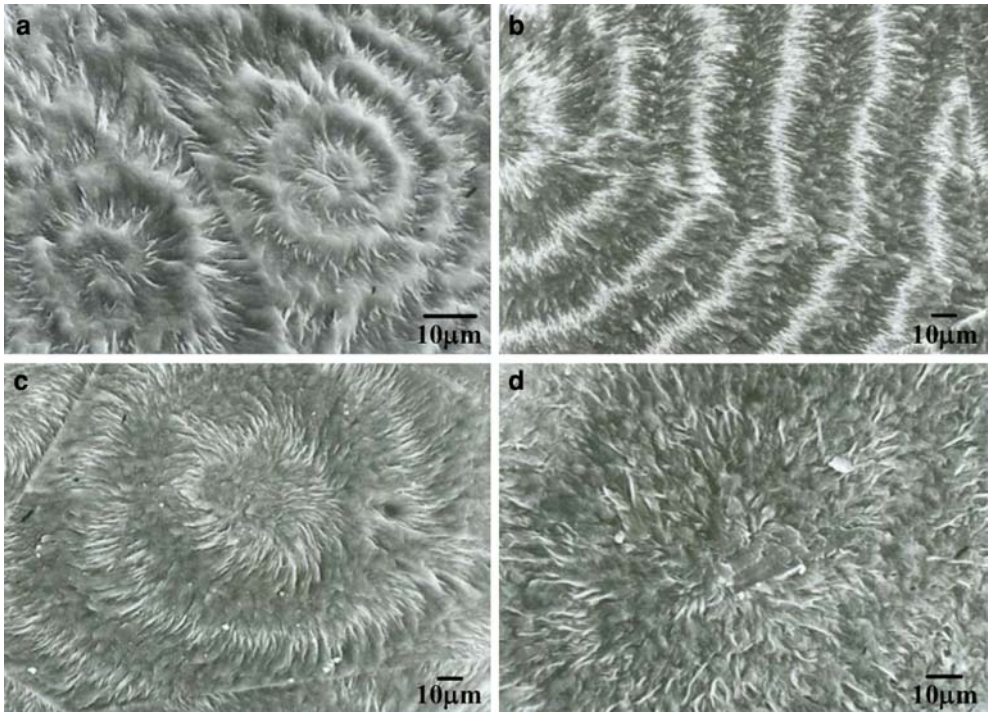

Fig. 4 SEM morphologies for PTT/PEI (8/2) blend crystallized at: **a** 190 °C, 30 min; **b** 205 °C, 30 min; **c** 210 °C, 30 min; and **d** 220 °C, 240 min

lower temperatures (i.e., 180 or 190 °C). Apparently, the melting/re-crystallization process is more extensive and it immediately follows the melting of the P1 crystal during DSC scanning in the blends crystallized lower

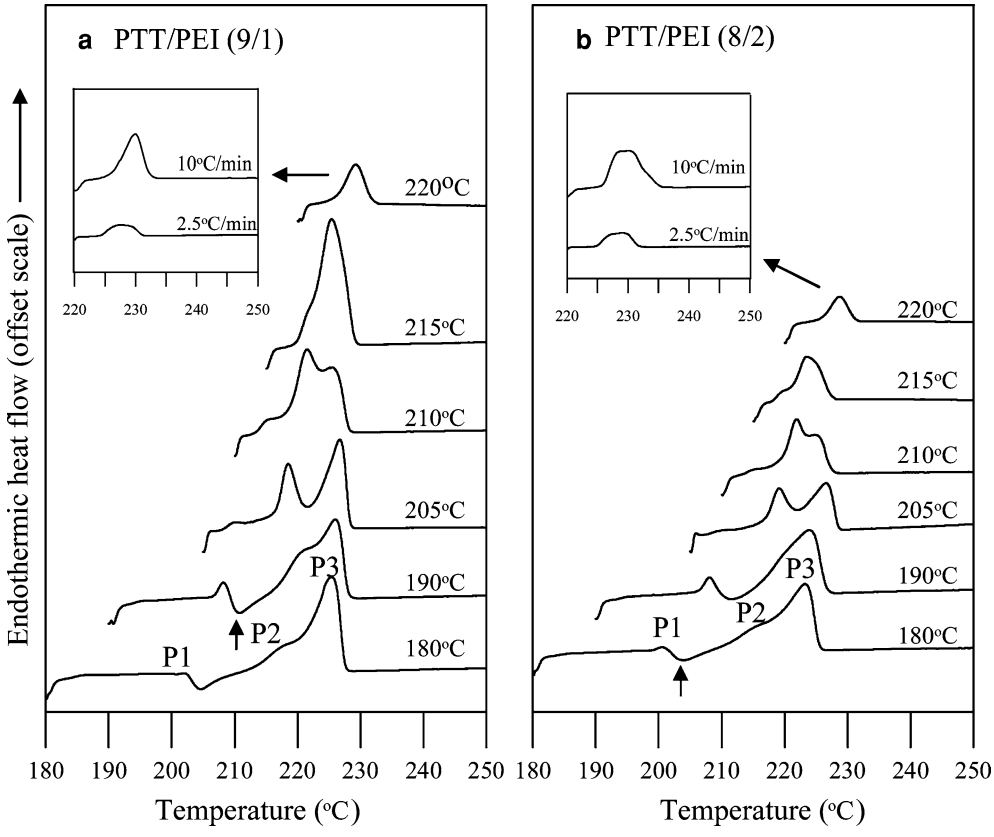

Fig. 5 DSC traces (all scanned at 10 °C/min) in **a** PTT/PEI (9/1), and **b** PTT/PEI (8/2) melt-crystallized at various temperatures. *Insets* show blends annealed at 220 °C for 24 h, and then scanned at two low rates

temperatures; on the other hand, the melting/re-crystallization of the P1 crystal is less evident in the blends if crystallized at higher temperatures (205–220 °C).

The inset of Fig. 5a shows the DSC traces of the PTT/PEI (9/1), annealed at 220 °C for 24 h and then scanned at different scanning rates. Apparently, a broad melting endotherm is seen at a lower scanning rate (i.e. 2.5 °C/min). A similar observation is shown in the PTT/PEI (8/2) blend from the inset of Fig. 5b. The broad melting peak consists of multiple heterogeneous lamellae with different proportions. The co-existence of different lamellar types (i.e. P1, P2, P3) leads to a broader melting peak during DSC scanning, and also forms distinct ring patterns in spherulites. The melting behavior thus is related to the formation of ringed spherulites in both neat PTT and PTT/PEI blends. The results show that multiple-melting endotherms are evident in the miscible PTT/PEI blends crystallized at all temperatures ranging from 190 to 220 °C, whereas only one melting peak is present in the neat PTT crystallized at 220 °C.

Similarly, Fig. 6 shows the DSC thermograms at various heating rates (5–30 °C/min) for two blend compositions: (a) PTT/PEI (9/1) and (b) PTT/PEI (8/2), which had been melt-crystallized at 190 °C for 30 min. For the PTT/PEI (9/1) composition, P1 and P2 increase in peak temperature and magnitude as the heating rate increases, while P3 diminishes in magnitude, and finally overlaps with the gradually elevating P2. On the other hand, a similar trend is observed in the PTT/PEI (8/2). The re-crystallization exotherm appears just next to the low-temperature endotherm (P1) for all scanning rates. Nevertheless, the re-crystallization enthalpy decreases with increase in the scanning rate and/or the amorphous content. It suggests that the P1 crystals melt and then can re-crystallize/repack to P3 crystals upon scanning. On the other hand, the P2 crystals cannot re-pack quick enough to the P3 crystals under a normal scanning rate (e.g., 10 °C/min). Partial melting of less perfect crystals, followed by re-crystallization, and then final melting could occur in the PTT/PEI blends.

Intermolecular interactions between PTT and PEI

Keith et al. [3, 17] have investigated the morphological changes in polyesters induced by blending with small concentrations of polymer diluents, and have indicated that there is likely an interaction between host and diluent polymers strong enough to cause significant modification of the crystal growth process on a molecular scale. The morphological changes in the PTT/PEI blends (i.e. ringed spherulites are shown at 220 °C) can be similarly examined from the intermolecular interactions between PTT and PEI. The Nishi-Wang equation [18] was carried out to estimate the interaction between PTT and PEI according to the following relationship:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{RV_1}{\Delta H_{f1} V_2} x_{12} \phi_2^2, \quad (1)$$

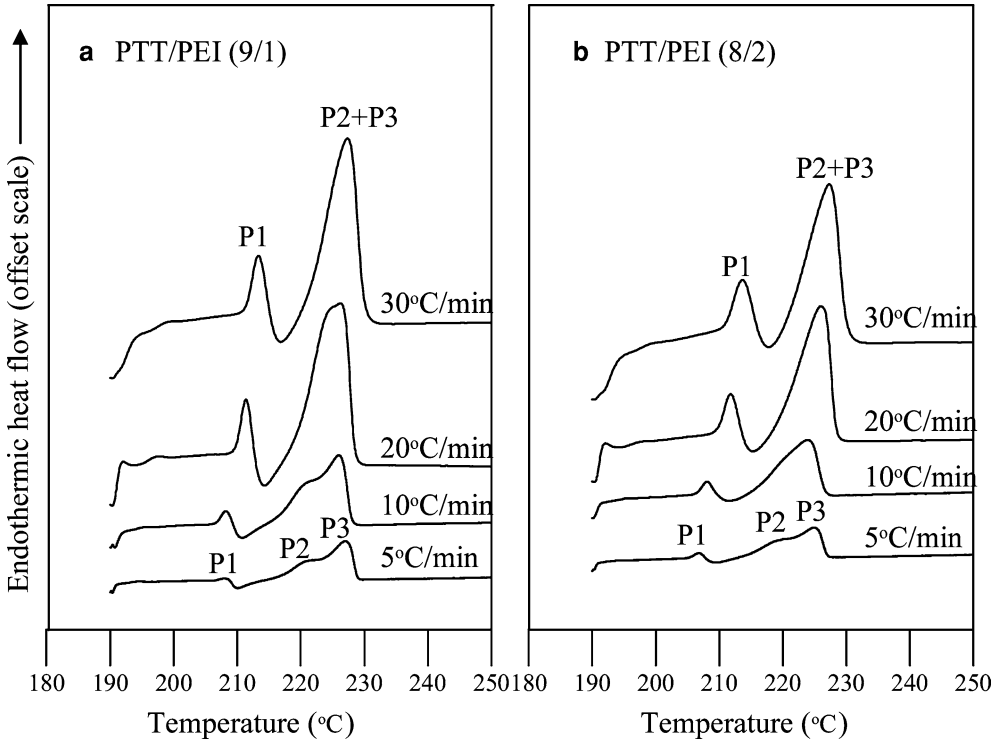

Fig. 6 DSC thermograms for **a** PTT/PEI (9/1), and **b** PTT/PEI (8/2) melt-crystallized at 190 °C for 30 min, then scanned at different heating rates (5–30 °C/min, as indicated on the respective traces)

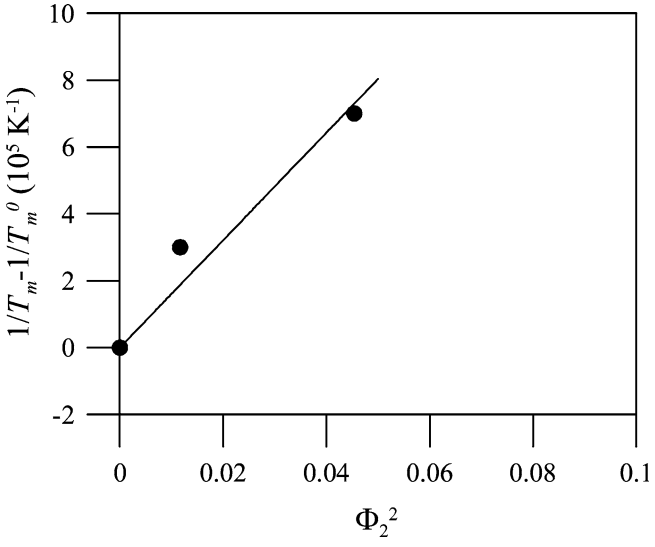

Fig. 7 Determination of interaction parameter using the Flory-Huggins equation for PTT/PEI blends

where T_m and T_m^0 are the equilibrium melting points of PTT in the blends and PTT homopolymer, respectively. R is the gas constant, ΔH_{f1} is the heat of fusion of the fully crystalline PTT (30 KJ/mol), V_1 (149.6 cm^3/mol) and V_2 (399.5 cm^3/mol) are the molar volumes of the repeat units of the crystallizing and amorphous polymers, and ϕ_2 is the volume fraction of the amorphous polymer [20, 21]. x_{12} is the polymer/polymer interaction parameter, and it is an indication of intermolecular interactions between components. x_{12} can be obtained by plotting the left hand side of Eq. 1 versus the square of PEI volume fraction in the blends (ϕ_2^2). From the slope of the regression line in Fig. 7, x_{12} is then determined to be –0.1. The negative value of x_{12} confirms that the polymer pairs of PTT and PEI can form a thermodynamically stable compatible mixture in the melt, consisting with our earlier results [13]. However, the interaction is very weak in the PTT/PEI blend due to the small x_{12} value. Therefore, it can be concluded that the specific interaction is not the main reason for the

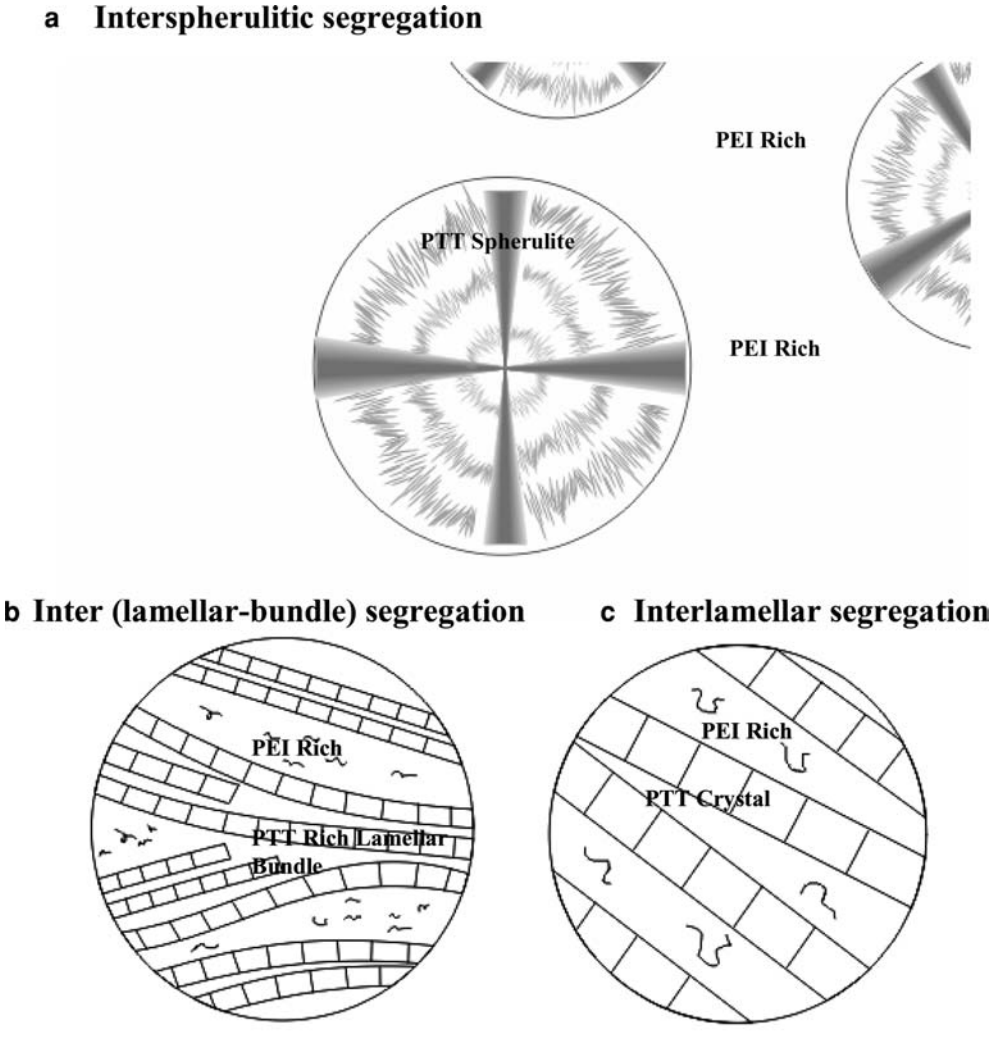

Fig. 8 Schematic diagram of possible PEI segregation modes during crystallization of PTT/PEI blend

formation of intense ring in the PTT/PEI blend. On the one hand, there are interactions between the amorphous and crystalline polymers; but on the other hand, the segregation of PEI during crystallization of PTT may also affect the morphology of the blends. This is discussed in the following scheme.

In similarity to schemes that have been commonly proposed for amorphous/crystalline polymer blend systems [21], Fig. 8 depicts that there are three types of segregations in PTT/PEI blends: (a) interspherulitic segregation, (b) interlamellar-bundle segregation, and (c) interlamellar segregation upon crystallization in miscible blends containing a crystallizable and an amorphous diluent polymer. Schemes (b) or (c) are more likely the type of amorphous/crystalline segregation that influences ring-band patterns.

Figure 9 depicts a possible model for effects of the amorphous miscible diluent (PEI) on the ring bands in PTT. It is primarily based on a mode of less coordinated twisting (spiraling) of the lamellar bundles that radiate out from the nuclei. The spiraling mode has been more widely proposed and accepted by many earlier investigators [3–5, 17], which is thought to more closely resemble the periodical changes from the edge-on to flat-on lamellae. The less coordinated growth of the lamellae bundles, coupled with spiraling, may account for the more pronounced zigzag rims in the ring bands.

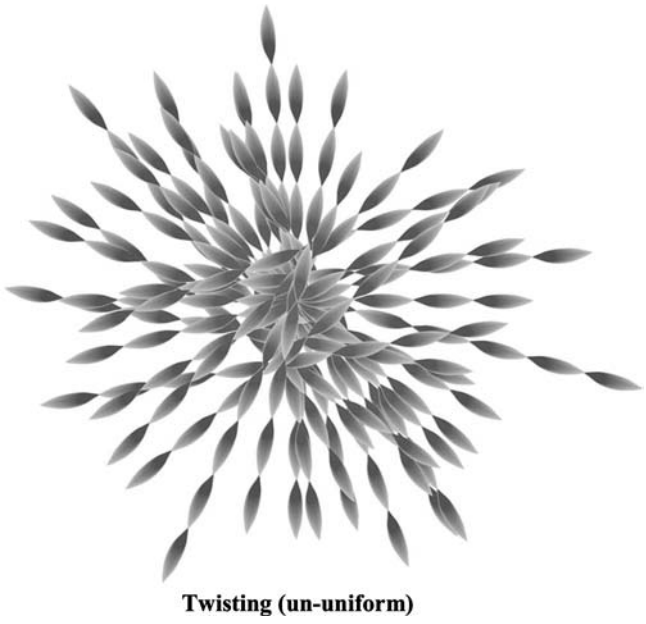

Fig. 9 Model depicting the zigzag rims of the ring bands in miscible

Conclusion

The ring-bands in spherulites and mechanism in the miscible PTT/PEI blends have been compared with the neat PTT. While ringed spherulites are seen in either the neat PTT or PTT/PEI blend system, there are some differences between them. First of all, the ring patterns are more intense for the blends. Secondly, at a high temperature of 220 (C, no rings are present in the neat PTT, while rings are apparent in the PTT/PEI blend system when crystallized at this same temperature. The DSC evidently verified that dual peaks implying mixed lamellae co-existing in the PTT/PEI blends crystallized at 220 (C, which led to ringed spherulites. On the other hand, the single melting peak in the neat PTT suggests that the lamellae are uniformized to a singular type at 220 (C, leading to no ring pattern in the spherulites of PTT crystallized at this same temperature.

An additional factor is also at work that leads to differences in the ring bands in the miscible PTT/PEI blends versus neat PTT. For the miscible PTT/PEI blends, addition of the amorphous PEI miscible diluent causes a larger population of multiple lamellae in the PTT spherulites owing to easier interlamellar segregation of PEI between the lamellae upon annealing or crystallization. Upon crystallization of the PTT/PEI blends, the amorphous PEI chains are gradually rejected from the PTT crystallizing fronts into the interlamellar, interlamellar bundle, and interspherulitic regions of the growing spherulites. Of these three, the interlamellar segregation is responsible for the easier formation of ringed-patterns in PTT/PEI blends. Therefore, rings are seen in 220 °C melt-crystallized blends, but not in neat PTT. In addition, the specific interaction between PTT and PEI is not particularly strong and it should not be the main reason for morphological ring patterns. Of particular interest was the observation of the ringed patterns of PTT spherulites in the blends isothermally crystallized at 220 °C. The addition of amorphous PEI can induce ''banding'' in 220 °C-melt-crystallized samples. Thus, the ringed spherulites growth behavior is apparently influenced by multiple factors, including multiple types of lamellae, specific interactions between the amorphous and crystalline components, and the segregation of the amorphous PEI during crystallization. A postulated model of uneven lamellar growth, coupled with periodical spiraling, more properly describes the possible origin of the ring bands from combined effects interactions on the one hand, and segregation on the other hand between the amorphous PEI and crystallizing PTT.

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