Miscibility and Cocrystallization in Homopolymer–Segmented Block Copolymer Blends

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ABSTRACT: The amorphous phase behavior of blends of poly(butylene terephthalate) (PBT) and poly(ester–ether) segmented block copolymers (PEE) was found to vary from completely immiscible to miscible, depending on the copolymer composition. The predictions of the Flory–Huggins relationship are in general agreement with the observed behavior when the interaction parameters are estimated from solubility parameters. The results of thermal analysis and small-angle X-ray scattering experiments strongly suggest that the PBT and PEE copolymers are capable of cocrystallization in the miscible blends under all crystallization conditions. The cocrystalline microstructure results from the complete miscibility and the blocky nature of the copolymer (i.e., the identical chemical and crystalline structures of the PEE hard segments and PBT). The crystallization rate of the copolymer in the miscible blends was found to be significantly enhanced due to the presence of PBT, and the resulting crystal thickness was found to be the same as that observed for PBT. Partially miscible blends of PBT with copolymers containing intermediate hard-segment concentrations formed distinguishable crystal populations, but the crystallization rate of the copolymer in these blends was also strongly influenced by the presence of PBT.

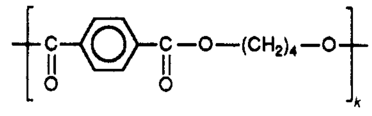
1. Introduction

Early in the development of poly(ester–ether) segmented block copolymers (PEE) it became apparent that the mechanical properties of blends of the copolymers with poly(butylene terephthalate) (PBT) were, in general, grossly different from those of the pure copolymers containing the same overall hard-segment concentration.[1] For example, two blends each having a total weight fraction of 76% tetramethylene terephthalate units were found to be stiffer and have a higher yield strength at room temperature that an unblended copolymer of the same overall composition. In addition, at subambient temperatures, the blends were found to have greater flexibility and improved impact strength compared to the copolymer.

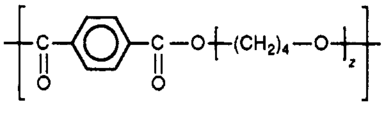
Since PBT is the homopolymer analog of the crystallizing copolymer segments and preliminary experiments suggest that some PBT/PEE blends are miscible, we postulated previously that PBT and certain PEE copolymers are capable of cocrystallization, i.e., crystallization into the same lamellar crystal.[2] Cocrystallization is extremely rare in polymer blends: only a few cases have been reported in the literature, and even in these, it is only observed under certain crystallization conditions.[3-10] In addition to their novelty, such cocrystals may act as labile intermolecular cross-links which could have an important effect on mechanical properties. The focus of this paper is to characterize the crystalline- and amorphous-phase behavior of PBT/PEE mixtures and, in particular, to determine if a cocrystalline microstructure does indeed develop.

2. Experimental Section

2.1. Materials and Preparation. The poly(butylene terephthalate) used in these experiments (Celanex 2000, provided by Hoechst-Celanese) has a number-average molecular weight ($\bar{M}_n$) of ~20 500.[11] The poly(ester–ether) segmented block copolymers have chemical repeat units as follows:



hard segment



soft segment

A series of copolymers with hard-segment concentrations ranging from 40 to 90 wt % (76–98 mol %) were synthesized using established procedures. As an example, the synthesis of a copolymer containing 43 wt % hard segment and a soft segment of $\bar{M}_n$ ~2100 is reported here: 53 g of dimethyl terephthalate, 67 g of poly(tetramethylene glycol), 33 g of 1,4-butanediol, 0.35 g of tetrabutyltitanate, 0.08 g of trimethyltrimellitic ester, and 0.35 g of Irganox 1019/1098 (50/50 mixture by weight) were heated at 200 °C for 75 min in a typical polycondensation reactor equipped with a mechanical stirrer, a nitrogen purge, and a distillation outlet. Methanol and butanediol (15.8 g) were collected. The temperature was increased to 250 °C and held there for 30 min. Partial vacuum (15 min at 175 mmHg, 30-min gradual decrease to 1.8 mmHg) was applied for 1 h and full vacuum (i.e., 1.7 mmHg) for 75 min. $\bar{M}_n$ for the copolymers was estimated to be 25000–30000 based on melt index measurements. It is important to note that all of the copolymers used in the present study had a soft-segment molecular weight of ~1100 (i.e., z ~ 14).

It is well known that these copolymers are semicrystalline, and the prevailing morphological view is one of chain-folded lamellae (ca. 30–100 Å) comprised only of hard segments within an amorphous matrix composed of a miscible mixture of the soft and any uncrystallized hard segments (i.e., they will exhibit a

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single T_g).[12-17] On a larger scale, the crystalline lamellae are generally organized into spherulites.[12,18] In this paper the copolymers will be identified as PEE, followed by a number which designates the weight percent hard segment in the copolymer. Blends will be referred to by the blend composition followed by the blended components in parentheses. For example, 75/25 (PBT/PEE-80) refers to a blend composed of 75 wt % PBT and 25 wt % of the PEE-80 copolymer.

Interchain chemical reactions in polyester blends are favored by high temperatures. To minimize these, the blends (and pure polymers) were cast from 1,1,1,3,3,3-hexafluoro-2-propanol into aluminum pans, allowed to air-dry, and then dried under vacuum at 100 °C (above the T_g of all materials) for 24 h. To obtain uniform films, the samples were initially melted on a hot press between two sheets of Teflon-coated aluminum foil at 250 °C for 1 min and then compressed at 250 °C and 10 000 psi for 1 min. The resulting foil–polymer sandwich was then quickly removed from the press and quenched to ambient temperature. The resulting films were typically about 70 μm thick.

2.2. Characterization. A 7 series Perkin-Elmer differential scanning calorimeter (DSC) was used extensively in this investigation, both as a means to characterize the degree of crystallinity and melting behavior of each material and as a technique to probe for cocrystallization. The instrument was calibrated using two standards, indium and lead. Baselines were adjusted to have a maximum fluctuation of less than 0.1 mW over the temperature range of interest. All scans were carried out under flowing argon. The perfect crystal heat of fusion ($\Delta H_f°$) of PBT (142 J/g) was used to calculate the degree of crystallinity for both PBT and the copolymers.[19] The volume fraction crystallinity (ϕ_c) was estimated from the DSC weight fraction crystallinity by assuming a mixture rule of additive volumes. When examining the melting behavior, small samples of 0.2–0.4 mg were used to minimize the influence of low polymer thermal conductivity. A minimum of two runs were used to determine melting temperatures, and a maximum variation of ±0.5 °C was normally observed. A heating rate of 20 °C/min was frequently used, but rates ranging from 2.5 to 40 °C/min were utilized in certain cases to investigate the origin of the multiple melting endotherms in the PBT, PEE, and blend samples.

Dielectric measurements were conducted on two different instruments. Measurement of the dielectric constant and loss from −150 to +150 °C and 1–100 kHz for all of the polymers and blends used in this investigation was accomplished using a Hewlett-Packard Model 4274A multifrequency LCR meter. It was occasionally desired to determine the dielectric properties at frequencies down to 0.1 Hz, and a TA Instruments dielectric analyzer (DEA 2970) was used for this purpose. A heating rate of 2 °C/min was used in all experiments.

Small-angle X-ray scattering (SAXS) experiments were conducted at Oak Ridge National Laboratory (ORNL) on the ORNL 10-m SAXS camera. The X-rays were produced by a 6-kW Rigaku-Denki rotating-anode X-ray generator, and a pyrolytic graphite monochromator was used to select Cu K_α radiation. The collimation system consisted primarily of two square pinholes (1 × 1 mm) separated by 3.1 m, encased in a 15-cm-diameter vacuum pipe. The instrument was equipped with a two-dimensional position-sensitive proportional counter (20 × 20 cm active area and electronic spatial resolution of 1 mm). A more complete description of the ORNL 10-m SAXS camera has been presented by Hendricks.[20]

SAXS samples were prepared by stacking 1.5 × 1.5 cm squares of the as-prepared materials to a height of 1–1.5 mm. This stack was then tightly wrapped in Teflon-coated aluminum foil and placed in Mettler hot stage under a nitrogen purge where it received the desired thermal history.

Correction of the scattering data was required to account for parasitic scattering and the detector sensitivity. Dark current and background measurements were made and subtracted from the scattering observed from each sample. The transmission was also calculated for each sample and was utilized in the background correction. A glassy carbon sample was used as a standard to facilitate the calculation of the transmission. In addition, the detector sensitivity was calibrated by placing radioactive ^{55}Fe, which emits uniform radiation in all directions, into the sample chamber. With the ^{55}Fe information, corrections could be made for the nonuniformity in the detector as well as the shadowing effects from an aluminum grid that supports the beryllium window. In addition to the above corrections, absolute intensities were obtained by normalizing the intensity with a polyethylene calibration standard (designated as PES-3). The X-ray generator was operated at 100 mA and 40 kV, and the scattering data were collected over a period of 20–30 min as a two-dimensional intensity profile. Azimuthal averaging of those isotropic data was performed to give a one-dimensional plot of scattered intensity ($I(q)$), and the resulting data were Lorentz corrected and plotted as a function of the scattering vector (q), where $q = (4\pi \sin \theta)/\lambda$ (θ is half of the Bragg angle and λ is the X-ray wavelength). Additionally, the SAXS data were also analyzed by calculating the correlation function, $G(r)$:[21,22]

$$G(r) = \int_0^\infty q^2 I(q) \cos(qr)\, dq \qquad (1)$$

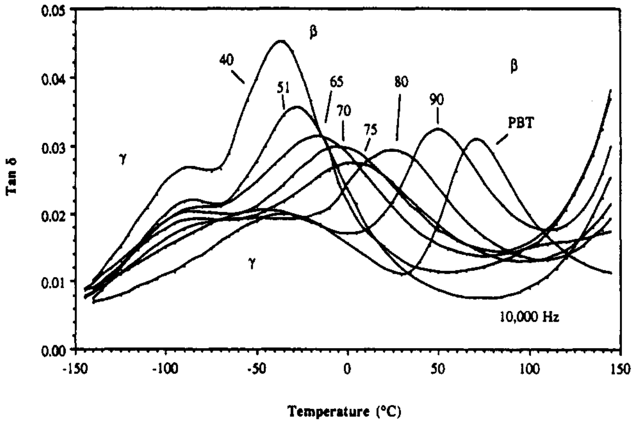

Figure 1. Dielectric relaxation behavior of PBT and various PEE copolymers at 10 kHz.

Finally, transmission optical microscopy was used to examine the phase behavior of blend melts at 250 °C as well as the room temperature supermolecular structure of the PBT/PEE blends. An Olympus BHSP-300 optical microscope equipped with a PM-10AD photomicrographic system and a Mettler FP80 hot stage was used in all experiments.

3. Results and Discussion

3.1. Amorphous Phase Behavior. Since both PBT and the copolymers are relatively polar, dielectric spectroscopy was employed to gain insight into the amorphous phase behavior of both the pure materials and blends. The dielectric loss (tan δ) at 10 kHz for the PEE copolymers and PBT is shown in Figure 1. The dielectric spectrum of each of these polymers contains two relaxations in the temperature range of interest: a low-temperature transition, γ, which is associated with local motions and a high-temperature relaxation, β, which is associated with cooperative (T_g-like) motion in the amorphous phase. For PBT, the γ relaxation has been attributed to the local mode motions of the ester group in noncrystalline regions, while the γ transition of the copolymers is believed to be a combination of the local motions of the tetramethylene oxide units of the soft segment and the γ relaxation of the uncrystallized hard segments.[13] As the hard-segment concentration in the copolymer increases, there is a smooth transition of the β relaxation to higher temperatures, and the experimental values are consistent with the predictions of the Fox–Flory expression if the fraction of crystalline material is accounted for. For the β relaxation, activation energies (derived from Arrhenius plots) were found to vary from ≈67 to 32 kcal/mol with decreasing hard-segment concentration (from PBT to PEE-45) and from ≈13 to 10 kcal/mol for the γ transition. These values are consistent with those derived previously.[2,13]

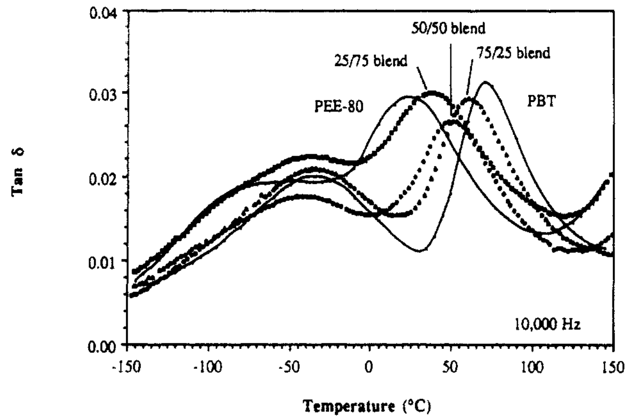

Figure 2. Tan δ vs temperature for PBT, PEE-80, and three PBT/PEE-80 blends at 10 kHz.

When PBT is mixed with copolymers containing from 40 to 51 wt % hard segment, the blends are found to exhibit two β transitions that correspond to those of the component polymers, indicating complete amorphous-phase immiscibility. One β transition intermediate between those of the pure polymers is observed for blends with copolymers containing 80 wt % or more hard segment (see Figure 2). The indicates amorphous miscibility, at least at the level which is probed with the dielectric technique. In blends of PBT with copolymers containing 58–75 wt % hard segment, two β relaxations are observed, with the high-temperature relaxation shifting to lower temperatures with increasing copolymer concentration. For example, in the spectrum of the 50/50(PBT/PEE-65) blend, T_β of the high-temperature relaxing phase (i.e., PBT-rich) is depressed by ≈10 °C. Assuming that the Fox–Flory relationship applies, this PBT-rich amorphous phase is estimated to contain as much as 8% PEE-65. Due to the overlap of the β relaxation of PEE-65 and the γ relaxation of PBT at higher, more conventional measurement frequencies, it is difficult to evaluate if there is any mixing of PBT in the low-temperature relaxing phase. However, because of their different activation energies, improved separation was obtained at lower frequencies. The relaxation behavior of PBT/PEE-65, PBT/PEE-70, and PBT/PEE-75 blends were analyzed at frequencies down to as low as 0.1 Hz; the low-temperature β process was clearly resolved and was found at the same temperature in the blends as the pure copolymer. In these "partially miscible" blends then, the amorphous region consists of two phases, an essentially pure copolymer phase and a PBT-rich phase.

In addition to the dielectric analysis, the gross amorphous phase behavior of the blends was characterized in the melt at 250 °C. PBT as well as all of the copolymers used in this investigation exhibited no structure in the optical microscope (100× magnification) at 250 °C. However, molten blends of PBT with PEE-45, PEE-51, PEE-65, PEE-70, and PEE-75 were all found to be cloudy at 250 °C, and a definite structure could be seen when viewing with optical microscopy. As the hard-segment concentration of the copolymer component of the blend increased, a noticeable decrease in both the phase size and degree of opacity was observed. Blends of PBT/PEE-80 and PBT/PEE-90 showed no such structure. These results are consistent with those observed in the solid state by transitional analysis.

Typically, theoretical modeling of polymer mixtures begins with the well-known Flory–Huggins relationship:[23]

$$\Delta G_{\mathrm{m}}/RT = (\phi_{\mathrm{A}}/N_{\mathrm{A}}) \ln \phi_{\mathrm{A}} + (\phi_{\mathrm{B}}/N_{\mathrm{B}}) \ln \phi_{\mathrm{B}} + \chi_{\mathrm{AB}}\phi_{\mathrm{A}}\phi_{\mathrm{B}} \tag{2}$$

where ΔG_{m} is the free energy of mixing, χ_{AB} is the Flory interaction parameter, and N_{A} and N_{B} and ϕ_{A} and ϕ_{B} represent the degrees of polymerization and volume fractions of components A and B, respectively. In the case of PBT/PEE blends, the intermolecular interactions are expected to be dispersive or weak polar interactions. Therefore, treatment of the miscibility with a Flory–Huggins approach and estimating χ_{AB} from solubility parameters appear to be appropriate.[24] χ_{AB} can be estimated from the solubility parameters of the blend components using the relationship[25,26]

$$\chi_{\mathrm{AB}} = (V_{\mathrm{r}}/RT)(\delta_{\mathrm{A}} - \delta_{\mathrm{B}})^2 \tag{3}$$

where V_{r} is an arbitrarily chosen reference volume and δ_{A} and δ_{B} are the solubility parameters of polymers A and B, respectively. Solubility parameters for PBT and the copolymers were calculated by the group contribution method using molar attraction constants and corresponding molar volumes recently reported by Coleman et al.[27] The solubility parameters of the copolymers were determined by the volume fraction average of the solubility parameters of the constituents.[28] δ_{PBT} was calculated to be 10.8 (cal/cm^3)$^{1/2}$ and the δ_{PEE}'s were determined to vary from 9.1 to 10.8 (cal/cm^3)$^{1/2}$ as the concentration of hard segment in the copolymer increased from 0 to 100 wt %. χ_{AB} was estimated from eq 3 by using a reference temperature of 25 °C and a reference volume of 164 cm^3/mol (calculated by the group contribution method) which corresponds to the molar volume of the PBT repeat unit. However, since the solubility parameters obtained by the group contribution technique are expected to only be accurate to ±0.4 (cal/cm^3)$^{1/2}$, the corresponding variance in χ_{AB} is significant.[27]

From the Flory–Huggins expression, a critical value of the interaction parameter (χ^*_{AB}) can be determined where there is a balance between the favorable contribution to mixing from combinatorial entropy and the unfavorable contribution from dispersive forces. χ^*_{AB} for the entire range of blend compositions can be determined by setting $\partial^2[\Delta G_{\mathrm{M}}/RT]/\partial\phi_{\mathrm{A}}^2$ and $\partial^3[\Delta G_{\mathrm{M}}/RT]/\partial\phi_{\mathrm{A}}^3$ equal to zero and solving for χ_{AB} in terms of N_{A} and N_{B}:

$$\chi^*_{\mathrm{AB}} = (1/2)[(1/N_{\mathrm{A}}^{1/2}) + (1/N_{\mathrm{B}}^{1/2})]^2 \tag{4}$$

Assuming a lattice size equal to the repeat unit of PBT and using 20 000 and 25 000 for the average molecular weights of PBT and PEE, respectively, $\chi^*_{\mathrm{AB}} = 0.02$ is estimated from eq 4. In Figure 3, the calculated χ_{AB} values for the PBT/PEE blends are plotted vs the hard-segment concentration of the copolymer in each blend. The experimentally determined phase behavior is also indicated on this curve, with the open circles representing the miscible blends. The uncertainty resulting from the estimation of the solubility parameters is shown by the two dotted curves. Comparing the estimated value of χ^*_{AB} to χ_{AB} of the blends, a miscibility window is predicted when the copolymer contains a high weight percent of hard segment. By considering the uncertainty in the calculated χ_{AB}, the critical copolymer hard-segment concentration, above which the PBT/PEE blends are predicted to be miscible, is found to be between 75 and 91 wt %. This is consistent with the experimentally observed critical copolymer hard-segment concentration (between 75 and 80 wt %), and it appears that the miscibility in these blends is a result of a favorable contribution to the free energy of mixing from the combinatorial entropy which

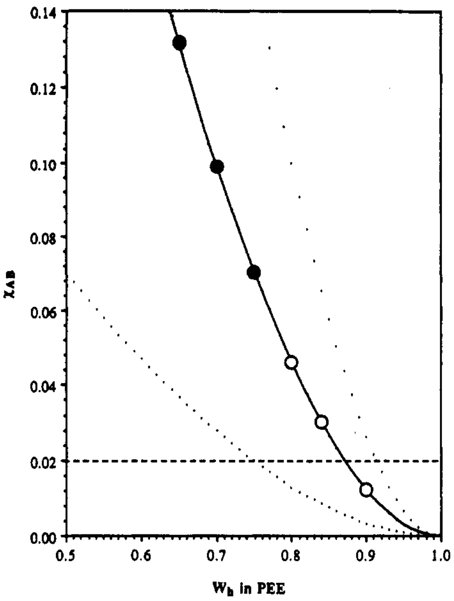

Figure 3. Comparison of the estimated χ^*_{AB} (dashed line) to the calculated χ_{AB} (solid curve) for PBT/PEE blends. Also indicated are the experimentally determined miscible blends (open circles) and multiphased blends (solid circles).

overcomes a small unfavorable contribution from χ_{AB}.

3.2. Crystalline Phase Behavior. The stringent conditions necessary for the development of a cocrystalline microstructure are met by certain PBT/PEE blends. First, it is well known that only the hard segments in the PEE copolymers crystallize, and these hard segments are identical in chemical structure to PBT. Second, the unit cell parameters of PBT and the PEE copolymers are identical.[29] These two conditions, which arise from that blocky nature of the copolymer, make it possible for both polymers to be accommodated into the same lamellar crystal. Another essential condition for cocrystallization is that both polymers must be present at the crystal growth front at the same time. This condition would be met in a miscible blend since miscibility implies that the chains of the component polymers are intimately mixed at the molecular level. The primary goal of this part of our research was to evaluate the microstructure of selected PBT/PEE blends and to determine if cocrystallization does indeed occur in these systems.

3.2.1. Miscible and Immiscible Blends. 3.2.1.1. Crystallization. For a completely immiscible blend, such as 50/50(PBT/PEE-51), crystallization is expected to occur separately for each of the melt phases. The DSC cooling scan of 50/50(PBT/PEE-51) does reveal two crystallization exotherms at the same temperature as those of the component polymers. However, when crystallization of the miscible PBT/PEE-80 blends is examined under the same conditions, dramatically different behavior is observed. Figure 4 shows the crystallization of three PBT/PEE-80 blends as well as the component polymers at a cooling rate of 40 °C/min. Only one exotherm is observed for all of the blends. Additionally, the heats of crystallization are intermediate between those of the unblended polymers and are much greater than would be expected if only PBT had crystallized. This strongly suggests, to the limit that individual exotherms can be resolved with DSC, that both PBT and PEE-80 crystallize simultaneously. Additionally, for each of the blends the endotherm width at half peak height is about 7 °C and is equal to that of both pure components. Additional controlled cooling experiments were conducted at various rates, down to as slow as 2.5 °C/min, and in all cases only one exotherm was observed. Another important observation is that the temperature range over which crystallization occurs in the blends is much more like that of PBT than PEE-80. In fact, the crystallization of 50/50(PBT/PEE-80) appears to be nearly complete at a temperature above the onset of crystallization in pure PEE-80.

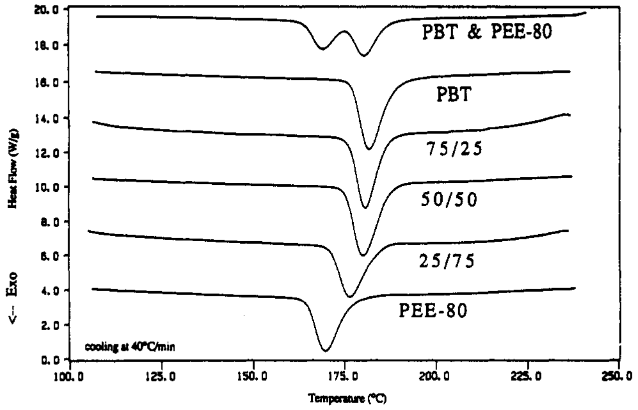

Figure 4. Crystallization of PBT/PEE-80 blends, PBT, PEE-80, and PBT & PEE-80 upon cooling from the melt at 40 °C/min. "PBT & PEE-80" refers to a sample in which equal weights of PBT and PEE-80 are placed in a DSC pan and the resulting behavior is used to model the crystallization of a mixture that crystallizes separately.

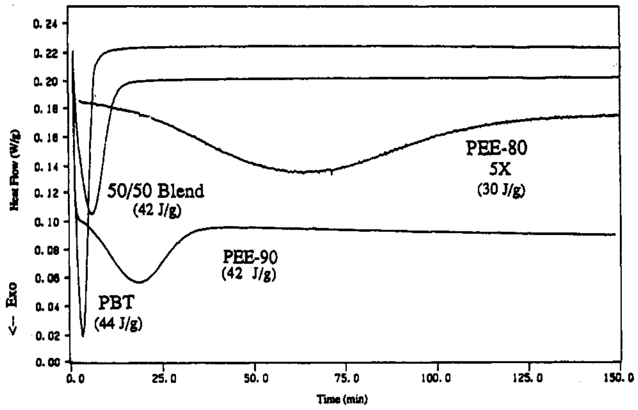

Figure 5. Isothermal crystallization of 50/50(PBT/PEE-80), PBT, PEE-90, and PEE-80 at 205 °C (PEE-80 curve is magnified 5×).

The results of controlled cooling experiments for PBT/PEE-90 blends are similar to those of PBT/PEE-80. One crystallization exotherm is observed and the width at half peak height is the same as that of the components for all blend compositions. However, since the crystallization temperatures of PEE-90 and PBT are closer than those of PEE-80 and PBT, the influence of PBT on the crystallization behavior is less pronounced than for blends of PBT and PEE-80.

In addition to controlled cooling experiments, the crystallization of various blends was also examined under isothermal conditions. Figure 5 shows the crystallization of three unblended polymers (PBT, PEE-90, and PEE-80) and a 50/50(PBT/PEE-80) blend, all of which have been isothermally crystallized at 205 °C. Only a single crystallization exotherm is observed for the blend, and its crystallization rate is only slightly slower than that of PBT. In addition, the heat of crystallization for the blend was found to be between those of PBT and PEE-80, further supporting the idea that both polymers crystallize within the same time interval. Since this is a miscible blend, the crystallization rate of both polymers might be expected to be reduced due to diluent effects and a reduction in the equilibrium melting temperature of each component. Yet,

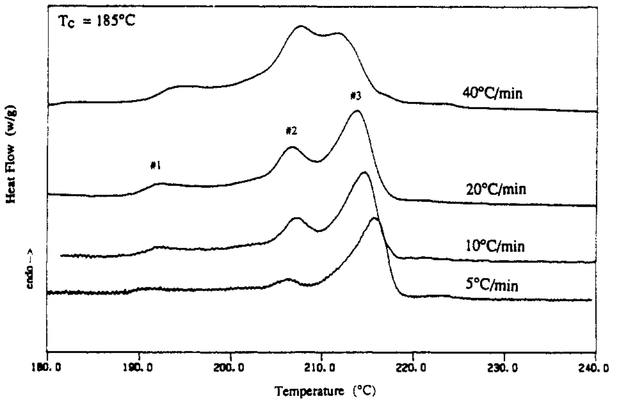

Figure 6. Melting behavior of PEE-80 isothermally crystallized at 185 °C for 1 hour at various heating rates.

the crystallization rate of the copolymer in the blend increases dramatically relative to pure PEE-80.

3.2.1.2. Melting Behavior of Component Polymers and Blends. The interpretation of the DSC melting behavior of semicrystalline polymers can often be difficult due to the formation of multiple crystal populations and reorganization of crystals during the heating scan; thus, an understanding of the melting behavior of PBT and the copolymers is essential in order to properly interpret the melting behavior of mixtures of these materials. Previously, we have reported on the melting behavior of isothermally crystallized PBT, including the evaluation of the equilibrium melting temperature using a Hoffman–Weeks approach.[30,31] The melting behavior of selected PEE copolymers has also been examined in detail, and the origin of the endotherms could be confirmed through comparison with PBT samples prepared under similar conditions. As for PBT, as many as three endotherms were identified in the thermograms of the copolymers. One of these is generally small and located ca. 5–10 °C above the crystallization temperature. Similar endotherms have previously been noted as a result of annealing PBT and other semicrystalline polymers.[32] The origin of these endotherms is not well established, but the best explanation to date appears to be that they are associated with the melting of crystals formed in the interlamellar regions that are constrained by the preexisting lamellae.[33] Melting, recrystallization, and remelting are frequently observed when heating a crystalline polymer in the DSC.[34,35] At faster heating rates, less time is available for crystal reorganization; therefore, a simple test to establish if recrystallization is responsible for double melting is to scan samples prepared in the same manner at different heating rates and examine changes in the position and relative sizes of the endotherms. Figure 6 shows the melting behavior of PEE-80 samples that were crystallized at 185 °C for 1 h and were scanned at four different heating rates. In addition to the lowest temperature endotherm (#1 in Figure 6), two endotherms are observed at higher temperatures (labeled #2 and #3). As the heating rate increases, endotherm #3 shifts to lower temperatures and becomes smaller relative to endotherm #2. These results indicate that endotherm #3 represents the melting of crystals formed during the DSC experiment and is not representative of the melting of the "original" crystals. Further, the recrystallization endotherm (#3) decreases in magnitude as T_c increases. In fact, for PEE-80 crystallized at a T_c of 195 °C or higher, endotherm #3 is no longer observed. This is consistent with the idea that the thicker crystals formed at higher crystallization temperatures are more stable and less likely to reorganize. These and other experiments indicate that endotherm #2 is most closely associated with the melting of the crystals formed during the crystallization process (especially at higher heating rates) and to a first approximation, the peak temperature can be considered as the melting temperature of the as-formed crystals.

With the relatively careful determination of "true" melting points (obtained at a rate of 20 °C/min), it was possible to estimate the equilibrium melting temperatures of selected PEE copolymers. Considering that there is excellent wide-angle X-ray scattering evidence that the soft segments are completely excluded from the hard-segment crystals,[29] a relationship directly analogous to the Gibbs–Thomson expression can be derived from the expressions developed by Sanchez and Eby[36] for the copolymers under consideration here:

$$T_m' = T_m^{\circ\prime}(1 - [2\sigma_e/\Delta H_f^{\circ} l_c]) \qquad (5)$$

where T_m' and $T_m^{\circ\prime}$ represent the experimental and equilibrium melting temperatures of the copolymer, respectively, and σ_e is the fold surface free energy. From this relationship, it is possible to rederive the Hoffman–Weeks expression for such copolymers:

$$T_m' = (1 - 1/B)T_m^{\circ\prime} + T_c/B \qquad (6)$$

where B is the thickening factor. Since this equation is analogous in form to that for homopolymers, equilibrium melting temperatures can be evaluated for the PEE copolymers in the same manner as for PBT.

The determination of the equilibrium melting temperature of PBT was complicated by the unexpected crystallization time dependence of T_m.[30,31] However, the melting temperatures of the copolymers were found not to be time dependent, and a single crystallization time of 10 h was chosen to evaluate $T_m^{\circ\prime}$ for the copolymers of interest. The derived $T_m^{\circ\prime}$ values for PEE-80, PEE-65, and PEE-51 were 233, 229, and 224 °C, respectively. [The error associated with this extrapolation is estimated to be ±5 °C.]

Flory[23] and others[36] have shown that the equilibrium melting point of a random copolymer consisting of A units which crystallize and B units which do not and are excluded from the A crystals can be written as:

$$1/T_m^{\circ\prime} - 1/T_m^{\circ} = -(R/\Delta H_f^{\circ}) \ln (N_A) \qquad (7)$$

where N_A and ΔH_f° are the mole fraction and the equilibrium heat of fusion of the crystallizable units and R is the gas constant. Since $T_m^{\circ\prime}$ values for the copolymers were derived from the melting temperatures of samples crystallized for 10 h at T_c, T_m° = 236 °C (also obtained from crystallizing at T_c for 10 h) was chosen as the reference value for PBT.[30,31] The predicted $T_m^{\circ\prime}$ values were 232, 228, and 223 °C for PEE-80, PEE-65, and PEE-51, respectively, in excellent agreement with the experimentally-derived values.

As for PBT and the copolymers, the origin of the individual melting endotherms in the blends could be identified by comparing samples that were crystallized under different conditioins or scanned at different heating rates. The melting behavior of completely immiscible blends such as PBT/PEE-51 was found to be consistent with the melting of two separate crystal populations, with the melting behavior of both polymers relatively unaffected by the presence of the other. For PBT/PEE-80 blends, however, only one orignal crystal population could be identified, regardless of the crystallization conditions or heating rate. One example of this is illustrated in Figure 7, where the melting behavior of a 50/50(PBT/PEE-80) blend as well as the component polymers (crystallized at

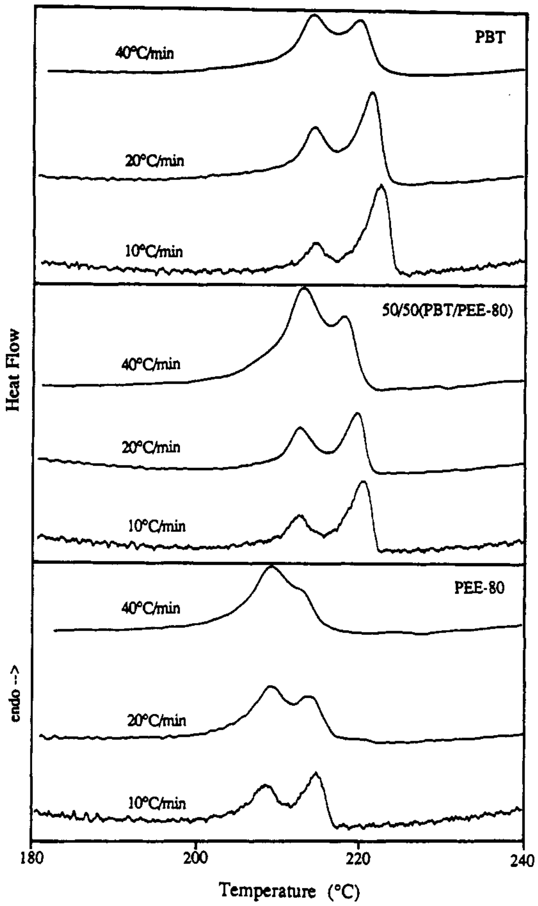

Figure 7. Melting behavior of PBT, PEE-80, and a 50/50(PBT/PEE-80) blend that were crystallized by cooling from the melt at 2.5 °C/min at various heating rates.

2.5 °C/min) is shown. Each thermogram exhibits two melting endotherms, and in order to identify their origin, a heating rate study was conducted on each material. From the behavior in Figure 7 as well as the results of other similar experiments, the higher temperature endotherm for each of these materials appears to result from recrystallization during the DSC scan while the lower temperature endotherm more closely represents the melting of crystals that exist prior to heating. This leads to the conclusion that the 50/50(PBT/PEE-80) blend crystallized at 2.5 °C/min contains only one original crystal population. The melting behavior of PBT/PEE-80 blends crystallized at other cooling rates and under isothermal conditions was investigated as well and in no case was there evidence for separate crystal populations. However, for isothermal crystallization, the PBT and PEE-80 melting temperatures are nearly the same and it is doubtful that even if separate crystals did form, the individual melting endotherms would be resolvable.

The most likely explanation for the observed melting and crystallized behavior of the miscible PBT/PEE blends is the existence of a cocrystalline microstructure. Since PBT/PEE-80 blends are miscible, it is anticipated that even at the initial stages of crystal growth, PEE-80 chains will encounter the growth front. During the crystallization process, one would expect a certain percentage of the copolymer chains (or portions thereof) at the crystal growth front to be rejected due to the probability that the noncrystallizing soft segments encounter the growing crystal. However, there is no known thermodynamic or kinetic reason for rejection of sufficiently long copolymer hard segments since they are identical to PBT in chemical and crystalline structure.

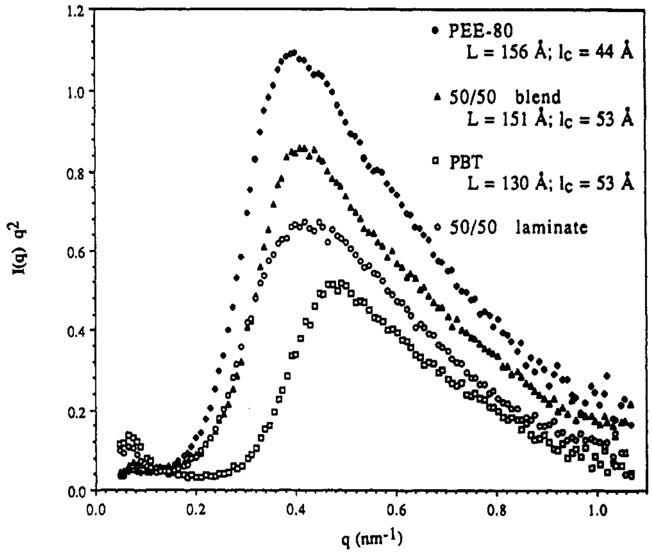

Figure 8. Lorentz-corrected SAXS intensities vs scattering vector for a 50/50(PBT/PEE-80) blend, the component polymers, and a laminate of PBT and PEE-80 that were crystallized by cooling from the melt at 25 °C/min.

Because PBT is more readily crystallizable than PEE-80, it is envisioned that a portion of the PBT chains in the blend nucleate and begin to crystallize prior to the copolymer. In this veiw, the necessity for the copolymer to form its own nuclei would be eliminated. Since the overall crystallization rate is well known to be directly proportional to the nucleation rate,[37] nucleation by PBT can explain both the observed increase in crystallization temperature upon cooling from the melt and the increase in isothermal crystallization rate of the blended PEE-80 over that of the pure copolymer.

In the blend systems that have been previously reported to cocrystallize, cocrystallization has been found to be strongly dependent on crystallization rate.[3,5-7,9] In contrast, cocrystallization in PBT/PEE-80 mixtures is independent of crystallization conditions. This is consistent with the fact that these blends are miscible at the crystallization temperature and that the crystal structures of PBT and PEE-80 are identical.

An alternative explanation for the observed behavior is the possibility that PEE-80 crystallizes onto completed PBT crystals. [We will use the term "epitaxial crystallization" to describe this situation, although it is used here in a different context than used classically.] If the copolymer crystallization rate approaches that of PBT, the crystallization exotherms might overlap sufficiently so that a single exotherm results. Consequently, it is not possible in this case to distinguish between epitaxial crystallization and cocrystallization from an examination of the crystallization exotherms alone. However, the former process would result in the formation of essentially separate lamellae and two melting temperatures would be anticipated. The identification of only one melting endotherm corresponding to the original crystal population for PBT/PEE-80 blends under all crystallization conditions reconfirms the notion that cocrystallization occurs in these blends.

3.2.1.3. Small-Angle X-ray Scattering. The small-angle X-ray scattering data from PBT/PEE-80 blends that were cooled from the melt at 2.5 °C/min revealed only a single scattering maximum (see Figure 8). To determine if separate crystal populations could be resolved in these blends with SAXS, a laminate of PBT and PEE-80 (crystallized under the same conditions as the blend) was used to model a 50/50(PBT/PEE-80) blend containing

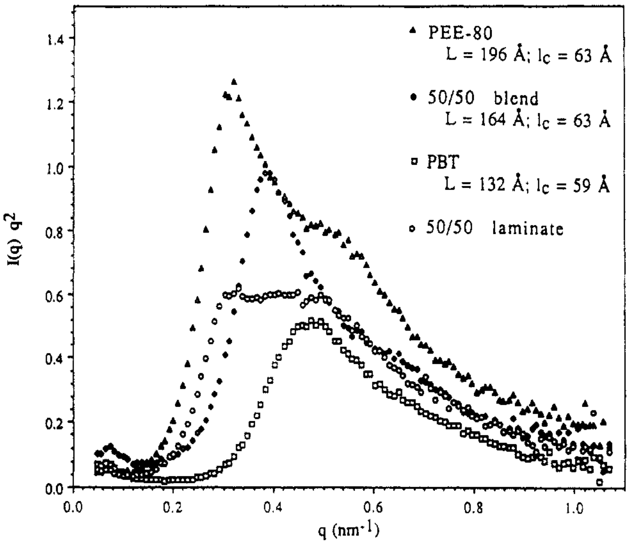

Figure 9. Lorentz-corrected SAXS intensities vs scattering vector for a 50/50(PBT/PEE-80) blend, the component polymers, and a laminate of PBT and PEE-80 that were isothermally crystallized at 205 °C for 5 h.

two completely separate crystal populations. However, as seen in Figure 8, the scattering curve of the laminate also contains only one scattering maximum and the resolution is, in this case, insufficient to distinguish between a single crystal population and overlapping scattering from two crystal populations. This is apparently a result of the close proximity of the scattering peaks and the relatively broad distribution of long periods. Further, the scattering data from a 50/50(PBT/PEE-51) laminate cooled at 2.5 °C/min were also found to yield insufficient resolution of the PBT and PEE-51 long periods.

As expected, the scattering data revealed that the long-period distributions were narrower for isothermally crystallized samples and the resolution of separate scattering maxima improved. In particular, the scattering curve of the 50/50(PBT/PEE-80) laminate that was isothermally crystallized at 205 °C exhibits the expected bimodal scattering behavior (see Figure 9). However, the scattering from the 50/50(PBT/PEE-80) blend still shows only one relatively sharp scattering maximum. This type of scattering would be expected either from a cocrystalline microstructure or from a stack of separate PBT and PEE-80 lamellae, and these two possibilities cannot be readily distinguished from SAXS alone. However, the latter structure should result in separate melting temperatures but, as shown earlier, this was not observed. The SAXS results for the PBT/PEE-80 blends are therefore, consistent with a cocrystalline microstructure. It should also be noted that the scattering from PEE-80 crystallized at 205 °C shows a second maximum at an angular position approximately twice that of the first. This higher angle maximum is apparently a second-order reflection that develops as a consequence of the improved crystal packing efficiency that results from the relatively slow crystallization of this sample.

The average long period (L) for each sample was calculated by applying Bragg's law to the position of the Lorentz-corrected scattering maximum and from the position of the first maximum of the correlation function. The values obtained from both methods were found to be in general agreement with L derived from the scattering maxima tending to be 0.5–1.5 nm larger than that obtained from the correlation function. The values reported in Table I are those derived from the scattering maximum of the Lorentz-corrected scattering data. The crystal thickness (l_c) can be determined from the long period and volume percent crystallinity (which was measured for the SAXS samples directly) from the relation $l_c = L\phi_c$. Experimental results for PBT, PEE-80, PEE-51, and PBT/PEE-80 blends prepared under a variety of conditions are listed in Table I.

Table I
Summary of the Long Period, Lamellar Thickness, and Volume Fraction Crystallinity for PBT, PEE-80, PEE-51, and Various Blends Crystallized under Different Conditions

samples	L (nm)	ϕ_c	l_c (nm)
T_c = 205 °C for 5 h			
PBT	13.2	0.45	5.9
50/50(PBT/PEE-80)	16.4	0.39	6.4
PEE-80	19.6	0.32	6.3
T_c = 195 °C for 5 h			
PBT	12.3	0.42	5.1
50/50(PBT/PEE-80)	14.9	0.36	5.4
PEE-80	17.6	0.31	5.4
cooled at 2.5 °C/min			
PBT	13.0	0.41	5.3
75/25(PBT/PEE-80)	13.8	0.37	5.1
50/50(PBT/PEE-80)	15.1	0.35	5.3
PEE-80	15.6	0.28	4.4
PEE-51	15.6	0.14	2.2
cooled at 20 °C/min			
PBT	11.8	0.38	4.5
50/50(PBT/PEE-80)	13.2	0.33	4.4
PEE-80	13.2	0.27	3.5

An intriguing result is seen by comparing the average lamellar thickness of the PBT/PEE-80 blends to those of the pure components. When cooling at 2.5 or 20 °C/min (see Table I), PEE-80 was found to have a smaller crystal thickness than PBT. The equilibrium melting temperatures for PBT and PEE-80 prepared under the same conditions were found to be 236 and 233 °C, respectively, but when cooled from the melt, the depression of the temperature of maximum crystallization of the copolymer was found to be greater than the corresponding decrease in the equilibrium melting temperature. These differences in crystal thickness therefore appear to be of kinetic origin, with the copolymer soft segment acting as a diluent to slow crystallization to a higher average degree of supercooling. The lamellar thicknesses of the PBT/PEE-80 blends were found to be essentially the same as that of PBT prepared under the same conditions. This behavior is consistent with a cocrystalline microstructure and the conclusion that PBT nucleates the crystallization in these blends. In this scenario, the initial lamellar thickness is established by PBT, and additional PBT and copolymer chains add to the crystal in a random fashion. Since the equilibrium melting temperature of the copolymer is lower than that of PBT, the PEE-80 could potentially crystallize to a somewhat greater thickness than PBT. However, the additional surface free energy associated with the formation of random stem lengths would result in a significant energy penalty. Therefore, in addition to strongly influencing the crystallization rate, PBT nuclei are envisioned as establishing the crystal thickness of the blend.

3.2.2. Partially Miscible Blends. The crystallization of PBT/PEE-65 blends and component polymers (at a cooling rate of 40 °C/min) are illustrated in Figure 10. Unlike PBT/PEE-80 blends, these blends were found to contain two melt phases, and consequently, crystallization was expected to occur independently in each phase, resulting in separate crystallization exotherms. The thermogram of the 50/50(PBT/PEE-65) blend does show two exotherms; however, the position of the one at lower temperature is shifted to a temperature higher than that

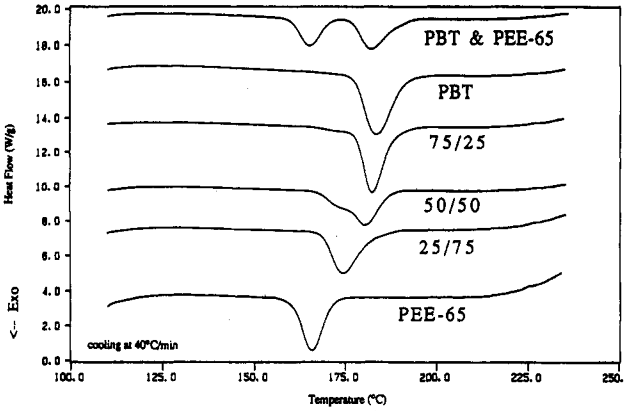

Figure 10. Crystallization of PBT/PEE-65 blends, PBT, PEE-65, and PBT & PEE-65 upon cooling from the melt at 40 °C/min. "PBT & PEE-65" refers to a sample in which equal weights of PBT and PEE-65 are placed in a DSC pan and the resulting behavior is used to model the crystallization of a mixture that crystallizes separately.

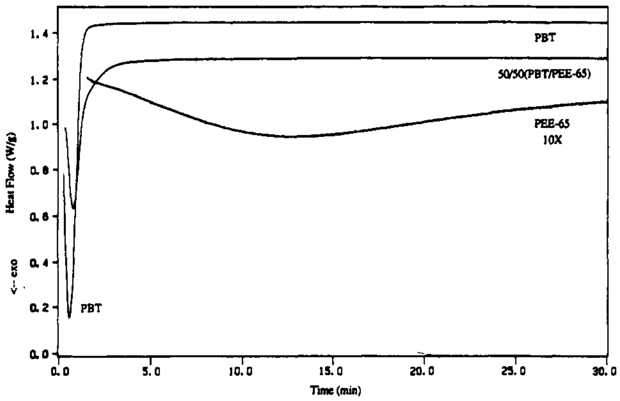

Figure 11. Isothermal crystallization of a 50/50(PBT/PEE-65) blend, PBT, and PEE-65 at 195 °C (PEE-65 curve is magnified 10×).

of the unblended PEE-65 copolymer. Further, only one resolvable exotherm is noted for the 75/25(PBT/PEE-65) and 25/75(PBT/PEE-65) blends, with only the 25/75 material showing a slight increase in the width at half peak height (≈2 °C) over that of the component polymers. Thus, the presence of PBT dramatically influences the crystallization of the copolymer, even in these phase-separated blends.

This effect of increasing the crystallization temperature of the slower crystallizing component is not limited to blends containing PBT. In a 50/50(PBT/PEE-51) blend, as noted earlier, the crystallization temperature of the copolymer is largely unaffected by the presence of PBT. However, when PBT is replaced by PEE-90, the crystallization exotherm of PEE-51 shifts to a higher temperature. Based on the difference in solubility parameters, χ_{AB} values for the PEE-90/PEE-51 and PBT/PEE-65 blends are essentially equal and PEE-90/PEE-51 blends are also expected to be "partially miscible".

The isothermal crystallization behavior of 50/50(PBT/PEE-65) blends was examined in a similar fashion to the PBT/PEE-80 blends. Since PEE-65 crystallizes more slowly than PEE-80, it was necessary to choose a lower crystallization temperature to allow for crystallization in a reasonable time period. At T_c = 195 °C, the crystallization of PEE-65 was found to be complete in about 40 min while PBT crystallized in about 2 min. Only a single exotherm was observed for the 50/50(PBT/PEE-65) blend, and the crystallization rate was found to be very much like that of PBT (see Figure 11). Further, the heats of crystallization suggest that at this crystallization temperature both PEE-65 and PBT crystallize within the first 5 min in the blend. However, the accuracy of these measurements is compromised by the inability of the DSC to stabilize at T_c at short times. Still, as in the controlled cooling experiments, the crystallization rate of PEE-65 in the blend is greatly enhanced as a result of the presence of PBT.

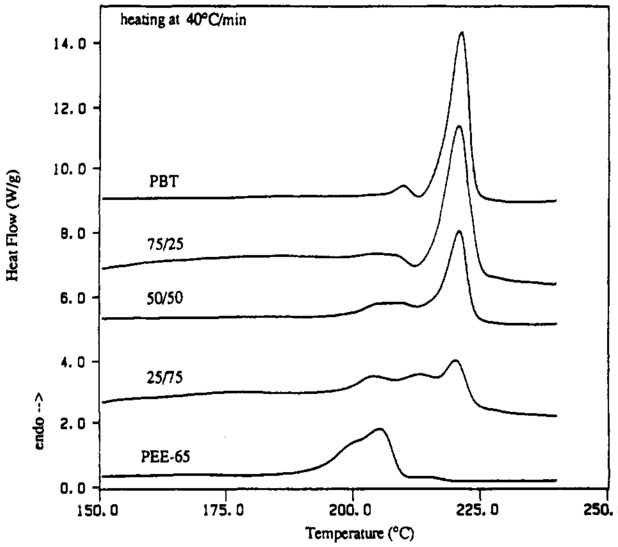

Figure 12. Melting behavior of PBT/PEE-65 blends and the component polymers that were crystallized by cooling from the melt at 40 °C/min.

The melting behavior of the PBT/PEE-65 blends, however, is consistent with the existence of two crystal populations. The thermograms of PBT/PEE-65 blends crystallized at 40 °C/min exhibit three melting endotherms while the components polymers only show two each (see Figure 12). In contrast, thermograms of PBT/PEE-80 blends prepared under the same conditions exhibit only two endotherms. Additionally, the melting behavior of a series of isothermally crystallized PBT/PEE-65 blends (from which both pure materials were found to crystallize completely) exhibited a complex combination of endotherms, compared to just two for PBT/PEE-80 blends crystallized under similar conditions. Therefore, although only a single crystallization exotherm could be discerned under isothermal crystallization conditions, examination of the melting behavior suggests that separate crystal populations do in fact develop.

Recalling that there is apparently little or no PBT in the low-temperature (copolymer) relaxing phase, the most plausible explanation for the observed behavior at this time is that PBT crystals at the phase boundaries serve as nucleation sites for the copolymer chains in the adjacent phase. However, since some copolymer resides in the PBT-rich phase, limited cocrystallization cannot be ruled out. As noted earlier, the crystallization and melting temperatures of the PEE-51 copolymer in PBT/PEE-51 blends were not significantly influenced by the presence of PBT. Also recall that the apparent size of the phases in the melt were found to decrease as copolymers with an increasing weight fraction of hard segment were blended with PBT. As the phase size decreases, the surface areas at the phase boundaries increases and the opportunity for surface nucleation should increase. It is proposed that in the PBT/PEE-65 blends, for example, the phases are sufficiently small so that PBT crystals at the phase boundaries can significantly influence the crystallization of the copolymer phase.

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