

# Reactive Blending of Aromatic Polyesters: Thermal and X-ray Analysis of Melt-Blended Poly(ethylene terephthalate)/Poly(trimethylene terephthalate)

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**ABSTRACT:** We investigated the reactive melt blending of poly(ethylene terephthalate) (PET) and poly(trimethylene terephthalate) (PTT) in terms of the thermal properties and structural features of the resultant materials. Our main objectives were (1) to investigate the effects of the processing conditions on the nonisothermal melt crystallization and subsequent melting behavior of the blends and (2) to assess the effects of the blending time on the structural characteristics of the transreaction products with a fixed composition. The melting parameters (e.g., the melting temperature, melting enthalpy, and crystallization temperature) decreased with the mixing time; the crystallization behavior was strongly affected by the composition and blending time. Moreover, a significant role was played by the final temperature of the heating treatment; this meant

that interchange reactions occurred during blending and continued during thermal analysis. The wide-angle X-ray diffraction patterns obtained under moderate blending conditions showed the presence of crystalline peaks of PET and PTT; however, the profiles became flatter after blending. This effect was more and more evident as the mixing time increased. Transesterification reactions between the polyesters due to longer blending times with an intermediate composition led to a new copolymer material characterized by its own diffraction profile and a reduced melting temperature. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 122: 698–705, 2011

**Key words:** polyesters; polymer blends; thermal properties; X-ray

## INTRODUCTION

With the development of a new low-cost method for synthesizing the monomer 1,3-propanediol,<sup>1</sup> poly(trimethylene terephthalate) (PTT) was introduced into the market for fiber, film, and thermoplastic engineering applications. The odd number of methylene groups of its repeating unit induces different and peculiar properties in comparison with those of poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT). Indeed, because of its different chain structure, the molecular flexibility and rate of crystallization of PTT are intermediate between those of PET and PBT.<sup>2,3</sup> This fact reflects the differences in the work of chain folding for nucleation between the three polyesters: 5 kcal/mol for PBT,<sup>4</sup> 6–7 kcal/mol for PTT,<sup>5</sup> and 10 kcal/mol for PET.<sup>6</sup> Like PET,<sup>7</sup> PTT crystallizes in a triclinic crystal structure, with the periodicity along the *c* axis containing two repeating units and the methylene groups being arranged in a highly contracted gauche–gauche con-

formation.<sup>2,8,9</sup> Several articles have appeared recently in the literature concerning the physical properties of PTT,<sup>10–15</sup> such as its outstanding resilience, ability to rapidly crystallize, morphological structure, and fiber properties.

To produce new low-cost polymeric materials that retain some of the advantageous properties of PTT, we find it interesting to explore the possibility of applying this polyester in blends with other conventional polymers and particularly with PET. Binary blends of both crystallizable polymers are usually believed to be immiscible; however, partial miscibility can arise if the chemical structures of the components are very similar.<sup>16–18</sup> Ester-interchange reactions often take place during the melt processing of polyester–polyester blends and play an important role in miscibility or compatibility.<sup>19–23</sup>

Numerous published articles concerning binary blends of polyesters are available in the literature; some of these, for example, deal with blends of PET and poly(ethylene naphthalate)<sup>22,24–26</sup> or PET and PBT.<sup>27–30</sup> Some articles concerning blends of PET and PTT have also been published in recent years.<sup>11,31–38</sup>

Evidence for miscibility restricted to amorphous regions is provided in all these articles, and the crystallization behavior and wide-angle X-ray diffraction (WAXD) patterns suggest that the pure PET

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and PTT components crystallize simultaneously to form their own crystalline entities; this means that the unit cells remain individually different even if they coexist in the same bundles or spherulites.<sup>31,32,34</sup> If the blends are kept in the melt for a prolonged period of time, some transesterification, evidenced by modification of the melting behavior, takes place.<sup>11,33</sup> New signals have not been observed in the WAXD patterns; only overlapping of the crystalline peaks of the two polyesters has been found, and this suggests the formation of block copolymers.<sup>33,34</sup> In a certain composition range, fibers with outstanding properties can be achieved from blends of PTT and PET. Fibers containing 10% PTT exhibit a marked improvement in their elastic recovery without significant drops in their tenacity and modulus in comparison with neat PET; with a PTT content close to 30%, the dyeing properties are far superior to those of PET and even better than those of pure PTT.<sup>11</sup>

In a previous article,<sup>36</sup> we considered fundamental aspects of the reactive blending of PET and PTT by performing thermal and kinetic analyses of mechanical mixtures of various compositions; transesterification was evidenced by the isothermal melt crystallization behavior of the mixtures in terms of the variation of the degree of crystallinity and the crystallization rate with the composition and permanence time in the molten state. The aim of this work was to investigate the reactive melt blending of PET and PTT in terms of the thermal properties and structural features of the resultant materials as a part of more extensive research focused on the control of ester interchange to obtain new materials combining the peculiar properties of PTT with the economy of PET. Our main objectives were (1) to investigate the effects of the processing conditions on the nonisothermal melt crystallization and subsequent melting behavior of the blends and (2) to assess the effects of the blending time on the structural characteristics of the transreaction products with a fixed composition.

## EXPERIMENTAL

### Materials

PET and PTT were obtained as courtesy research materials from Shell Chemical Co Amsterdam (The Netherlands). The PET sample was Cleartuf P82 resin with a density of 1.40 g/cm<sup>3</sup>, a melting temperature ( $T_m$ ) of 250°C, and an intrinsic viscosity of 0.63 dL/g [measured in a 60/40 w/w phenol/1,1,2,2-tetrachloroethane (Ph/TCE) mixture at 30°C], which corresponded to a viscosity-average molecular weight of 53,000 Da.<sup>39</sup> The PTT sample was Corterra 509200 with a density of 1.35 g/cm<sup>3</sup>, a  $T_m$  value of 228°C,

and an intrinsic viscosity of 0.92 dL/g (determined in a 60/40 w/w Ph/TCE mixture at 30°C); the viscosity-average molecular weight was 54,000 Da.<sup>40</sup>

### Preparation of the mixtures

Blends of PET and PTT (50/50 or 75/25 w/w) were prepared by melt processing in the 55-mL mixing room of a Brabender plasticorder at 30–80 rpm and 270–280°C for 5–30 min. To prevent the hydrolytic degradation induced at high temperatures by the water content of the original materials, both polyesters were carefully dried *in vacuo* before processing (48 h at 130°C). During processing, dry nitrogen was continuously purged into the mixing chamber to ensure minimum thermooxidative degradation. Neat PET and PTT were processed under similar conditions and were investigated as reference materials.

All the samples were obtained after uncontrolled cooling from the Brabender processing temperatures to room temperature.

### Characterization techniques

The blends were characterized with various techniques to investigate their chemical and physical properties, morphology, and structure.

Some samples of the blends and neat polyesters were analyzed in terms of thermogravimetric stability with a PerkinElmer TGS 2 analyzer Waltham Massachusetts (USA) with heating from 50 to 270°C at 10°C/min and, after an isothermal treatment of 30 min at 270°C, with heating from 270 to 700°C at 20°C/min. Calorimetric analysis was performed up to 310°C at heating and cooling rates of 20°C/min for samples (5–10 mg) dried *in vacuo* at 130°C for 48 h with a DSC 2920 (TA Instruments; New Castle DE, USA).

Viscometric analysis of dilute solutions was carried out with an Ubbelohde viscometer (Schott Instruments, Mainz-Germany) at 30°C in Ph/TCE (60/40 w/w).

The morphology of the samples was investigated with a Leica Stereoscan 440 Wetzlar (Germany) scanning electron microscope at a 20-kV accelerating voltage; the analyses were carried out on samples fractured in liquid nitrogen and coated with gold in an Agar Aid PS 3 Stansted (UK) sputtering unit.

WAXD measurements were obtained at room temperature with a Siemens D-500 Munchen (Germany) diffractometer equipped with a Siemens FK 60-10 2000-W copper tube (Cu K $\alpha$  radiation with a wavelength of 0.154 nm). The degree of crystallinity by weight was calculated with diffracted intensity data in the scattering angle ( $2\theta$ ) range of 5–35° by using the area integration method.<sup>41</sup>

## RESULTS AND DISCUSSION

As already discussed in our previous article,<sup>36</sup> ester-interchange reactions often take place during the melt processing of polyester–polyester blends and promote miscibility or compatibility.

Hence, we suppose that during melt processing in a Brabender plasticorder, compatibilization between PET and PTT takes place.

Preliminarily, blends (50/50 w/w) were prepared to test the roles of the processing temperature (270 or 280°C), the Brabender rotor speed (30 or 80 rpm), and the blending time (30–45 min). Viscometric analysis of the blends in dilute solutions (60/40 w/w Ph/TCE) showed intrinsic viscosity values independent of the processing conditions and confirmed the stability of the samples.

Calorimetric tests indicated double-melting peaks centered at approximately 206 and 220°C; these temperatures were substantially lower than the melting points of the component polyesters. This means that a transesterification reaction occurred, took place quite quickly, and was notably enhanced with the blending time increasing; this seems to be the fundamental parameter for the system under investigation. In fact, small variations occurred when the blending temperature or rotor speed was increased: the two melting peaks shifted to slightly lower temperatures (temperature change  $\sim 5^\circ\text{C}$ ), and the total melting enthalpy moderately decreased ( $\sim 10\%$ ), whereas a significant effect was observed as a function of the blending time.

In line with the aforementioned preliminary tests, we decided to work under less drastic conditions. Therefore, the role played by the mixing time (5–30 min) was studied at a fixed temperature (270°C) and at a fixed rotor speed (30 rpm) for two compositions (50/50 and 75/25 w/w PET/PTT).

Neat polyesters were also processed under the same conditions and for even longer mixing times (up to 60 min).

To verify the thermal stability, thermogravimetric analysis of the neat polyester and blends at the times and temperatures used for the Brabender plasticorder was performed. The isothermal treatment of 30 min at 270°C led to a very slight weight loss ( $<0.5\%$ ) for all samples.

The processed polyesters and their blends were characterized by viscosity measurements in dilute solutions. Intrinsic viscosity values of the order of 0.63 and 0.80 dL/g were found for PET and PTT, respectively, and they were independent of the mixing time. These values, compared with those of the polyesters as received (0.63 and 0.92 dL/g) and measured in the same solvent, showed a certain reduction of the molecular weight for PTT. The reduction could be correlated to the processing temperature, as previously reported in the literature.<sup>42</sup>

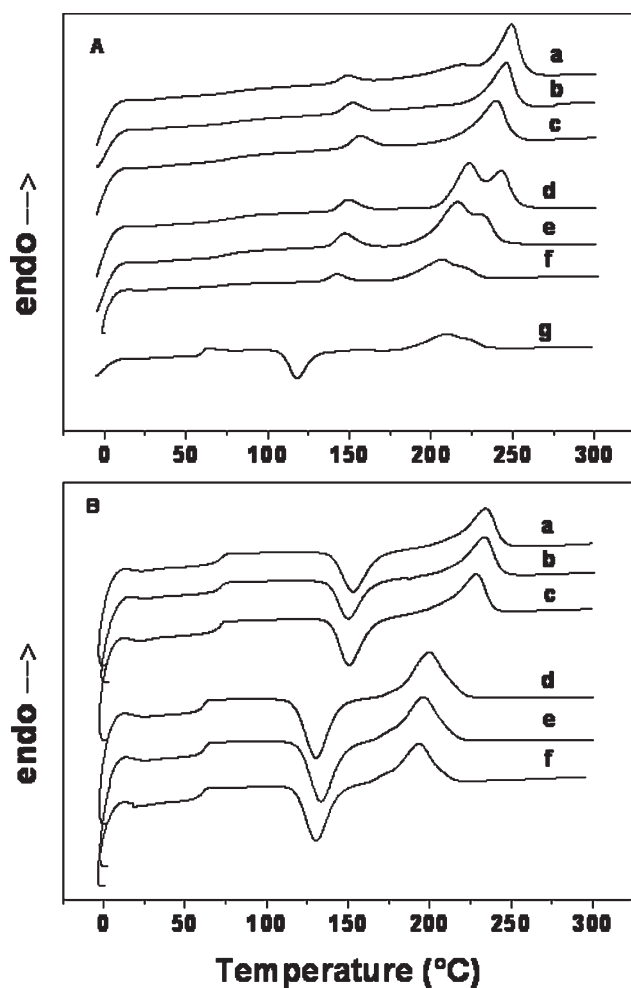
The viscosity values of the blends were intermediate between those of the pure materials (0.70 and 0.65 dL/g for the 50/50 and 75/25 PET/PTT blends, respectively). No significant variation of the intrinsic viscosity with the mixing time was observed. Both thermogravimetric analysis and viscosity analysis confirmed the good stability of the samples under our processing conditions.

Calorimetric analyses of PET and PTT, after they were dried *in vacuo* at 130°C for 48 h, did not indicate significant variations of the related parameters as a function of the processing time. Calorimetric analysis, which used the thermal profile of heating to 310°C, a 3-min isotherm at 310°C, and cooling to 0°C, indicated that substantial crystallization on cooling took place for both polyesters. Indeed, a cold crystallization of very low enthalpy (ca. 1 J/g) occurred during the second heating of PET, whereas in the PTT second-heating profiles (0–310°C) an exotherm of approximately 13 J/g always appeared just before the melting peak.

The heating profiles of the blends processed for 5–30 min are presented as curves a–g of Figure 1(A). In Table I, thermodynamic data determined for dried samples in the first heating run and in the second scan are reported. Only a single composition-dependent glass-transition temperature ( $T_g$ ) was identified for each blend, and it was intermediate between the values of 50 and 75°C measured for PTT and PET, respectively.  $T_g$  of 75/25 PET/PTT increased by  $5^\circ$  when the mixing time was increased from 5 to 30 min; in the case of 50/50 blends,  $T_g$  was instead independent of the mixing times. The different behaviors of the two blends could be ascribed to kinetic effects of the mixing process on the amorphous phases of the polyesters due to the different compositions. However, as already discussed,<sup>31–38</sup> these results suggest miscibility of the polyesters in the amorphous regions, which was probably also enhanced by the synthesis *in situ* of PET/PTT copolymer chains.<sup>36</sup>

The first differential scanning calorimetry (DSC) run conducted on dried blends showed some crystallinity [curves a–f in Fig. 1(A)]. Moreover, the drying treatment induced the appearance of an endotherm of approximately 10 J/g close to 150°C; this arose from the melting of some small and imperfect crystals formed during the drying procedure of both components, as discussed in our previous work.<sup>36</sup>

As the blending time in the Brabender plasticorder increased, the  $T_m$  and melting enthalpy ( $\Delta H_m$ ) values decreased; with longer times,  $T_m$  mainly continued to decrease. The shift of the double-melting temperatures for the 50/50 blend with an increasing processing time could be attributed to the formation of block copolymers by interchain reactions, with the block length decreasing as the treatment time increased.



**Figure 1** (A) First-heating and (B) second-heating DSC profiles of the PET/PTT blends processed for different times without the drying treatment: (a) 75/25 PET/PTT blend for 5 min, (b) 75/25 PET/PTT blend for 15 min, (c) 75/25 PET/PTT blend for 30 min, (d) 50/50 PET/PTT blend for 5 min, (e) 50/50 PET/PTT blend for 15 min, (f) 50/50 PET/PTT blend for 30 min, and (g) 50/50 PET/PTT blend for 30 min.

The melting of the 75/25 blend appeared to be less affected by the same blending times. At short times, the profile exhibited peaks for both components

[curve a in Fig. 1 (A)]; with increasing time, a broader single peak appeared with a lower  $T_m$  value that was ascribable to the interchain reactions.

When the drying treatment was suppressed, the 50/50 blend exhibited in the first heating a sharp glass transition at 60°C followed by cold crystallization around 120°C [curve g in Fig. 1(A)]; no difference was observed in the  $T_m$  and  $\Delta H_m$  values. This suggests that the drying step at 130°C affected only the crystallinity degree and not the transesterification reactions.

Crystallization did not take place with cooling at a rate of  $-20^\circ/\text{min}$ . The amorphous character of the blends was clearly shown during the second heating run by sharp glass transitions around 60 and 68°C for the 50/50 and 75/25 blends, respectively. Moreover, a single cold-crystallization signal was observed; the cold-crystallization temperature ( $T_{cc}$ ) and the cold-crystallization enthalpy ( $\Delta H_{cc}$ ) were composition-dependent and were substantially insensitive to the blending time [curves a–f in Fig. 1(B) and Table I]. Furthermore, a single melting endotherm was substantially evident and was associated with a further reduction of  $T_m$  in comparison with the corresponding value observed in the first run. The strong decrease in  $T_m$  and the appearance of a cold-crystallization signal suggested an important extension of the transesterification reactions. To deepen the effect of the DSC final scan temperature, new experiments were carried out with blends prepared under the same conditions (Brabender plastimeter at 270°C for 15 or 30 min) with a lower DSC final scan temperature (280–290–300°C) and with the same isothermal-treatment time (3 min). The profiles of the second heating show a considerable effect of the final temperature on the melting characteristics of the blends (Fig. 2). When we took into account the 75/25 PET/PTT mixture,  $T_m$  appeared to be progressively reduced from 239.9 to 231.9°C as the final

**TABLE I**  
DSC Analysis of the PET/PTT Mixtures

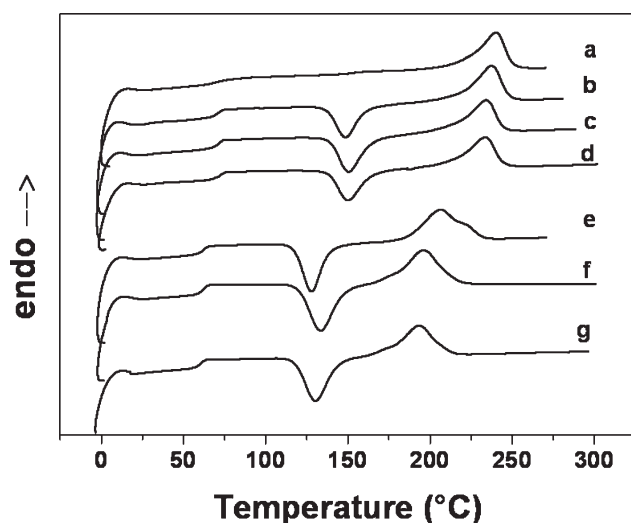
PET/PTT blend composition (w/w)	Blending time (min)	First heating <sup>a</sup>			Second heating <sup>b</sup>			
		$T_g$ (°C)	$T_m$ (°C)	$\Delta H_m$ (J/g)	$T_{cc}$ (°C)	$\Delta H_{cc}$ (J/g)	$T_m$ (°C)	$\Delta H_m$ (J/g)
75/25	5	70	249.1 <sup>c</sup>	41.9	149.1	23.3	233.5	29.0
75/25	15	68	246.3 <sup>c</sup>	25.2	147.4	19.1	231.9	23.9
75/25	30	65	239.4 <sup>c</sup>	27.2	146.2	23.0	227.0	25.4
50/50	5	60	224.0–244.0	44.8	131.6	30.9	197.2	32.6
50/50	15	60	216.0–230.1	36.6	132.0	30.8	196.1	29.9
50/50	30	61	209.2–225.0	34.6	130.3	31.0	193.4	28.8

<sup>a</sup> The samples were dried *in vacuo* at 130°C for 48 h.

<sup>b</sup> After a 3-min isotherm at 310°C and cooling at  $-20^\circ/\text{min}$  to 0°C.

<sup>c</sup> Main peak.

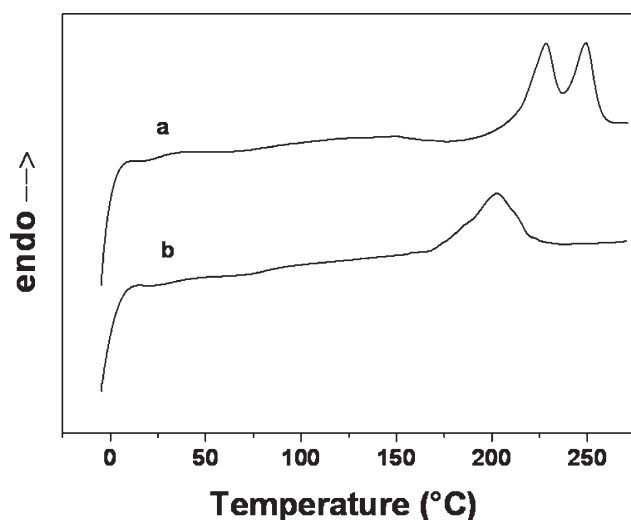




**Figure 2** Role of the final temperature of the first DSC heating run in the second-heating profiles of the PET/PTT mixtures processed in the Brabender plasticorder at 270°C for 15 or 30 min: (a) 280, (b) 290, (c) 300, and (d) 310°C for the 75/25 blend for 15 min; (e) 280 and (f) 310°C for the 50/50 blend for 15 min; and (g) 310°C for the 50/50 blend for 30 min.

temperature increased in comparison with the value of the first run (246.3°C, Table I). Moreover, a significant influence on crystallization emerged because this phenomenon occurred on cooling only for samples heated to a final temperature of 280°C [Fig. 2(a)] and on heating after a first run to temperatures higher than 290°C [Fig. 2(b–d)];  $\Delta H_m$  decreased as the temperature rose from 280 to 290°C (32 and 26 J/g, respectively) and then leveled off.

Mixtures with a 50/50 composition were unable to crystallize on cooling; this was independent of the



**Figure 3** DSC first-heating profile of the 50/50 PET/PTT mixtures after solubilization and precipitation: (a) the mechanical mixture and (b) the mixture processed in the Brabender plasticorder at 270°C for 30 min.

**TABLE II**  
Degree of Crystallinity by Weight as a Function of the Processing Time for the Polyesters and Blends

Sample	Degree of Crystallinity by Weight <sup>a</sup>		
	5 min	15 min	30 min
PET	—	0.30	0.29
PTT	—	0.39	0.34
75/25 PET/PTT	0.32	0.25	0.23
50/50 PET/PTT	0.28	0.27	0

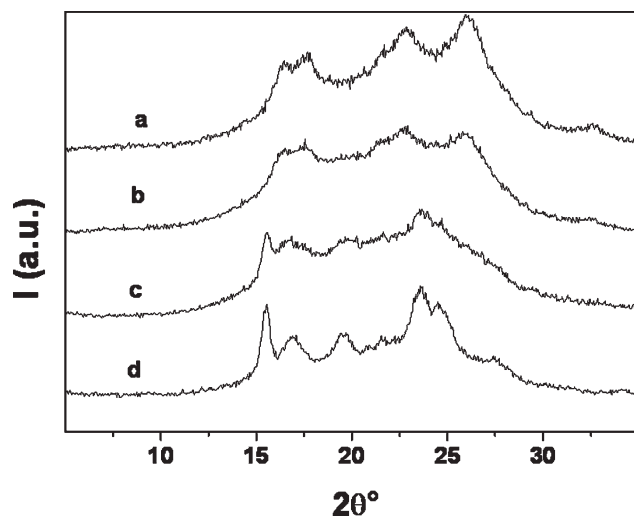
<sup>a</sup> Derived from WAXD measurements.

final scan temperature of the first cycle [Fig. 2(e,f)]. When this temperature was increased from 280 to 310°C, the two melting peaks merged together and shifted to a lower temperature.

To further confirm the occurrence of transesterification reactions during melt blending, the 50/50 PET/PTT sample processed in the Brabender plasticorder for 30 min was solubilized in  $\text{CHCl}_3/\text{CF}_3\text{COOH}$  (80/20 v/v) and precipitated with methanol. Its first DSC heating profile after drying at 130°C was compared to the profile shown by a mechanical mixture with an identical composition after solubilization, precipitation, and drying (Fig. 3). The DSC profile of the mechanical mixture [Fig. 3(a)] showed two melting peaks ascribable to the neat polyesters; the blend prepared in the Brabender plasticorder [Fig. 3(b)] showed mainly a single endotherm with a strong decrease in  $T_m$  greater than 30°C. This result strongly suggests the formation of PET–PTT copolymers.

A morphological analysis performed with scanning electron microscopy showed similar homogeneous fracture surfaces lacking any discernible, separated domains for all the samples; this was independent of the composition and mixing time.

The WAXD profiles of pure PET and PTT processed for 15 min were sharper and better defined than those of 30-min specimens. The degrees of crystallinity by weight, deduced from WAXD, are reported in Table II. The values for PTT showed a clear difference between samples treated for different times and were higher than those determined for PET; as expected, this indicated a greater inclination of PTT to crystallize. The effect of the composition on the WAXD profiles is presented in Figure 4, in which the patterns of the mixtures and neat polyesters processed for 15 min are compared. The crystal unit cells of both polyesters are triclinic, and PET diffraction peaks can be observed at  $2\theta$  values of approximately 16.3, 16.8, 21.8, 22.9, 26.2, and 28.1° [Fig. 4(a)]. For PTT, the diffraction peaks can be observed at  $2\theta$  values of approximately 15.6, 17.2, 19.5, 21.8, 23.7, and 24.9° [Fig. 4(d)]. The profiles in Figure 4(b,c) are different from those for the neat polyesters. In particular, the diffraction pattern of



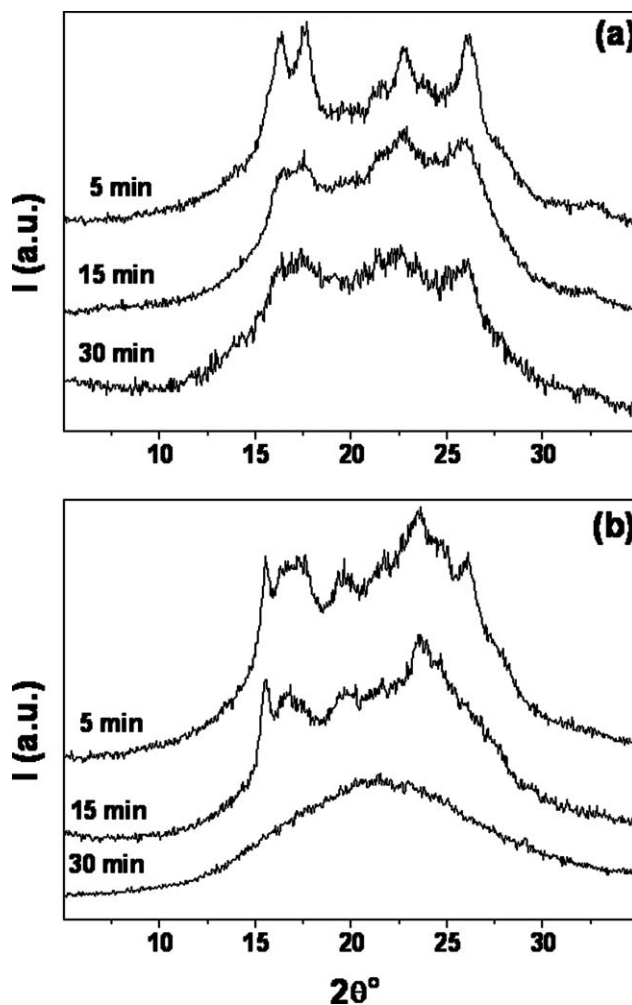
**Figure 4** WAXD diffraction profiles as a function of the composition with a processing time of 15 min: (a) PET, (b) 75/25 PET/PTT, (c) 50/50 PET/PTT, and (d) PTT ( $I$  = intensity).

75/25 PET/PTT mirrors the pattern of neat PET, and this suggests an influence of the diffraction of the PET unit, as previously reported by others.<sup>43</sup> The WAXD diffraction profile of 50/50 PET/PTT is quite different from all the others.

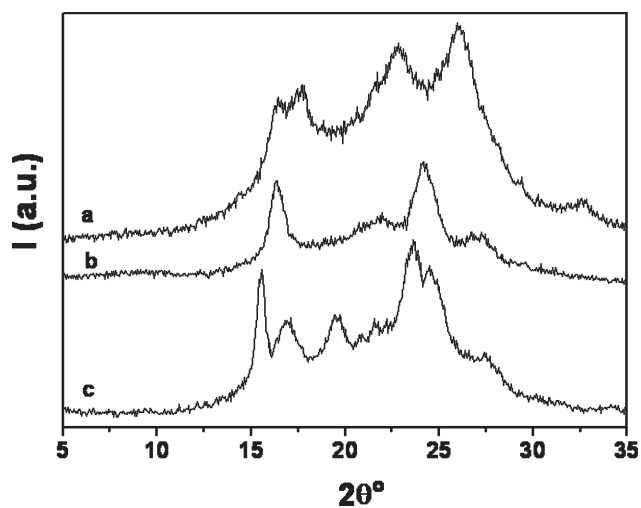
Variations induced by the blending time are shown in WAXD profiles of the 75/25 and 50/50 PET/PTT blends obtained with uncontrolled cooling from the Brabender plasticorder (Fig. 5). Figure 5(a) exhibits a reduction of the crystallinity for the 75/25 blend with an increase in the mixing time (see also Table II). An analogous trend can be observed for the 50/50 blend in Figure 5(b): the profile of the 30-min sample does not show any evidence of crystallinity. This result is in agreement with the findings from DSC analysis [curve g in Fig. 1(A)], which showed in the first heating cold crystallization (30.6 J/g at 118.1°C) and a double-melting endotherm (34.6 J/g at 208.9–224.8°C). This behavior suggests significant interactions between PET and PTT in the melt state and/or the synthesis of new molecular features based on PET/PTT block copolymers.

To gain more insight into this aspect, the 50/50 blend was annealed for 20 h at 130°C and was analyzed with WAXD. In Figure 6, the diffraction pattern of this blend is compared to the patterns of neat PET and PTT. The WAXD profile of the 50/50 blend shows two main peaks centered at  $2\theta$  values of 16.3 and 24.1° [Fig. 6(b)] and less pronounced peaks at  $2\theta$  values of 21.9 and 27.2°.

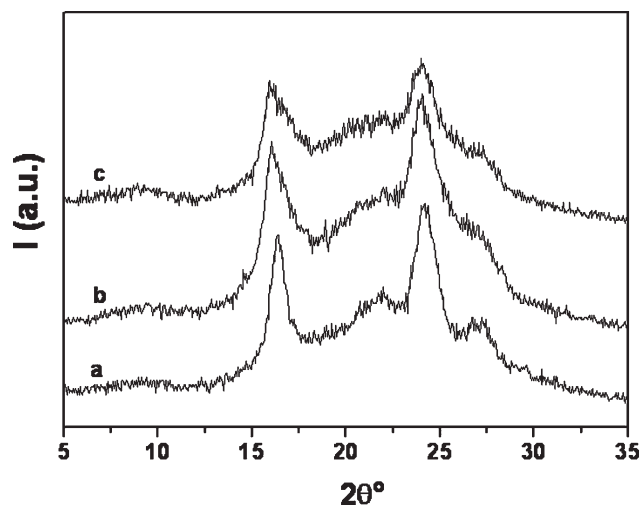
For the 50/50 PET/PTT copolymer synthesized by a polycondensation reaction and characterized by a randomness parameter of approximately 1, the WAXD pattern is the same as that reported in the literature.<sup>43</sup> In other words, the pattern of the 50/50



**Figure 5** WAXD diffraction profiles of the blends processed in the Brabender plasticorder at 270°C for 5–30 min: (a) 75/25 PET/PTT and (b) PET/PTT 50/50 ( $I$  = intensity).



**Figure 6** WAXD diffraction profiles of (a) PET, (b) a 50/50 PET/PTT sample treated in the Brabender plasticorder for 30 min and annealed at 130°C for 20 h, and (c) PTT ( $I$  = intensity).



**Figure 7** WAXD diffraction profiles of a 50/50 sample treated in the Brabender plasticorder for 30 min: (a) annealing at 130°C for 20 h, (b) DSC heating for 3 min at 310°C and annealing at 130°C for 20 h, and (c) DSC heating for 3 min at 310°C and annealing at 130°C for 2 h ( $I$  = intensity).

PET/PTT blend, which was mixed at 270°C for 30 min, indicates that the same copolyesters obtained by synthesis from the monomers can be obtained by melt blending.

A 30-min 50/50 PET/PTT sample was also investigated to ascertain whether the mixing time of 30 min in the Brabender plasticorder was enough to obtain equilibrium molecular structures without effects induced by subsequent thermal treatments, such as a DSC run up to 310°C, a 3-min isothermal treatment for the removal of the thermal history, and cooling to room temperature. In Figure 7(a–c), the WAXD patterns of this blend, which was annealed at 130°C for 20 h, treated with DSC, and then annealed at 130°C for 20 and 2 h, are shown.

Figure 7(b,c) shows the main peaks centered at  $2\theta$  values of 16.1 and 24.1°, and this agrees with the characteristic profile of 50/50 PET/PTT copolymers.<sup>43</sup> However, the peaks at  $2\theta$  values of 21.9 and 27.2° are less pronounced in Figure 7(b,c) versus Figure 7(a). These profile changes indicate that the transesterification reactions continued during DSC scanning at temperatures higher than 150°C but not during annealing at 130°C.

Finally, the higher intensities of the main peaks in Figure 7(b) versus Figure 7(c) indicate, as expected, an annealing time effect at 130°C with an increase in the degree of crystallinity.

## CONCLUSIONS

The results on the whole suggest the occurrence of substantial transesterification during the melt blending of PET and PTT. DSC and X-ray results indicate

that moderate blending conditions (mixing time = 5–15 min, temperature = 270°C) lead to the formation of block copolymers. In this case, homopolymer sequences of the components are still able to segregate and crystallize; as a result, the melting points of PET and PTT are depressed. The ability of the system to form crystals is affected by the length of the blocks and by the distributions of crystallizable segments of different lengths; as a result, crystallization does not occur at the cooling rate of  $-20^\circ\text{C}/\text{min}$  used in the experiments but takes place with heating over  $T_g$ . Blends show single exotherms because double peaks, if they occur, cannot be resolved on account of their overlap. The blend composition seems to play a fundamental role; with high PET contents (the 75/25 PET/PTT blend), PET sequences dominate the crystallization process, and the crystallization of PTT seems to be considerably hindered.

A further increase in the transesterification level (or randomness level) arises with longer residence times (30 min) in the Brabender plasticorder and leads to a reduced ability to form crystals. However, also in this case, the crystallization behavior is strongly affected by the relative contents of the two polyesters. With high PET contents (the 75/25 PET/PTT blend), only PET sequences are long enough to undergo crystallization; enhanced crystal imperfections due to less regular molecular structures further lower the heat of fusion and  $T_m$ . With a 50/50 composition, interchange reactions lead to the formation of nearly alternating copolymer chains. The new species exhibits its own diffraction profile and a  $T_m$  value close to 200°C. The amorphization after melt blending and the excellent crystallinity after annealing at 130°C must be related to effects of crystallization kinetics. The possibility that the 50/50 blend, like other polyester–polyester blends, undergoes restoration of blocks by crystallization-induced sequential reordering,<sup>44</sup> which is favored by miscibility in the amorphous state, can be excluded by the invariance of both the WAXD profile and the  $T_m$  value with the annealing time. Moreover, the transesterification reactions continue during DSC scanning at temperatures higher than 150°C.

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