polymer

Thermal and NMR characterization on trans-esterification-induced phase changes in blends of poly(ethylene-2,6-naphthalate) with poly(pentylene terephthalate)

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Abstract

By using thermal and NMR analyses with supporting evidence from X-ray and scanning electron and optical microscopy, this study has attempted to clarify confusing issues of physical miscibility vs. chemical trans-reaction in blends of aryl polyesters upon heating. The study demonstrated that the blends of poly(pentylene terephthalate) (PPT) with poly(ethylene naphthalate) (PEN) were initially immiscible; however, with heating/annealing at high temperatures (300 °C) for long enough times, the original two phases merged into one single phase composed of two polyesters and some minor fractions of copolyesters. Upon extended heating, however, two original polyesters disappeared, and a random copolyester, coded as EN-*co*-PT, of various sequence lengths was produced as a result of extensive trans-reactions between PEN and PPT. The trans-reacted products from heated PEN/PPT (50/50) blend were characterized using ^{1}H NMR. The sequence structures of the produced co-polyesters and intermediate products were determined by a triad analysis, which showed that the mean sequence lengths became shorter and the randomness increased with time of heating. X-ray analysis confirmed that the PEN/PPT (50/50) blend completely lost its crystallizability only when heated at 300 °C for time of 60 min or longer, indicating formation of fully random copolyesters.
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1. Introduction

Chemical exchange reactions and physical blend miscibility in mixtures of polyesters above melt temperature can be quite confusing and must be dealt with carefully, especially in temperature ranges, where possible exchange reactions may be involved. Blends of aryl polyesters have been extensively studied [1–13], such as poly(ethylene naphthalate)/poly(ethylene terephthalate) (PEN/PET) [4–8], poly(ethylene naphthalate)/poly(butylene terephthalate) (PEN/PBT) [9], or poly(ethylene terephthalate)/poly(butylene terephthalate) (PET/PBT), etc. [10] The PEN/PET blends have been extensively studied, and it has been found that an originally immiscible PEN/PET blend can turn into a homogeneous single-phase blend with a negative value of interaction parameter χ [14]. Similar behavior has also been reported for blends of polyesters with polycarbonates [15]. Porter et al. [11,16] have extensively studied on blends of polyesters and carefully examined whether or not trans-reaction is a pre-requisite for forming a single phase system for polyester blends. It is generally agreed in the literature that trans-esterification can lead to miscibility or enhance the compatibility between phases in many blends of polyesters. Of the many blend systems, the PEN/PET blend seems to offer the most commercial interests; however, blends of PEN with other aryl polyesters, though less studied, may offer additional advantages of property balances.

More recently, however, Guo et al. [17] have argued and questioned on correctness of the statements that trans-reaction is a pre-requisite for forming a single phase system for polyester blends. Indeed, some blends of polyesters or copolyesters, such as PET/PHB-*co*-PEN and PEN/PET-*co*-PHB [poly(β-hydroxybutyrate)] are miscible without any

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trans-reactions, while in other blends, trans-reactions may be necessary to bring in a single-phase mixture. Depending on the chemical structures, some blends of polyesters can indeed be miscible without any trans-reactions. For examples, we have recently reported that three aryl polyesters of a homologous series, i.e. PET, PTT, and PBT, may form miscible ternary blends without any trans-reactions [18]. However, for some polyester blends processed at high temperatures, exchange reactions may be inevitable and the reactions may induce phase changes. Kenwright et al. [19,20] have studied the effects of end groups on trans-reaction kinetics and have claimed that alcoholysis and acidolysis are two key mechanisms. Montaudo et al. [21] have used NMR in characterizing trans-reaction mechanisms, while Devaux et al. [22] have proposed a terminology of block lengths of sequence, from which the randomness in the copolymers may be calculated. However, it is cautioned here that if the chemical constituents in a blend have changed, interactions per se for a physically blended system vs. chemically-reacted one should be interpreted differently. This is so because the interactions and phases may not longer be between polyester A and B; rather the phase and morphology may involve two polyesters as well as a new copolymerized species yet to be determined. In addition, the observed single phase may no longer be referred to physical miscibility in a blend because trans-reactions may have occurred between aryl polyesters. Blends of polyamides can exhibit similar behavior. For examples, poly(m-xylene adipamide) (MXD6) has been found to be physically immiscible with several aliphatic nylon-x,y; however, owing to interchange reactions during melt mixing at 290 °C, the mixtures of polyamides eventually can become one-phase [23].

Regardless of ongoing arguments on the mechanisms which lead to phase changes in polyester blends, it is more uniformly agreed that trans-reactions lead to first block copolymers, then random copolymers, which may be responsible for the final uniform phase upon heating. It may be straightforward in interpretation if a blend of two originally immiscible crystalline polyesters undergoes extensive exchange reactions to form a series of random copolyesters exhibiting a homogeneous phase. However, it may be quite confusing in interpreting the transitions, phases, and mechanisms involved during the intermediate stages when the blend system contains two crystalline polyesters and various fractions of a partially exchanged copolyester species.

The objectives were to use the thermal analysis and NMR techniques to investigate the phase, morphology, and thermal behavior of blends of a naphthalate polyester (PEN) and an aryl polyester with a longer olefin segment (five methylenes) in the repeat unit, i.e., poly(pentylene terephthalate) (PPT). Blends were prepared in co-precipitated state, and then subjected to various post annealing conditions that simulated melting blending at high temperatures for various times. For more meaningful comparisons with results from co-precipitated blends, another series of blends were also prepared by melt-blending at 300 °C for similar analyses. Note that the selection of the blend system of PEN and PPT offers an easier and less ambiguous way for more positive identification of the exchange blocks in the trans-reacted products of copolyesters since, one block involves two methylense (in PEN) while another block involves five methylenes (in PPT).

2. Experimental

2.1. Materials and methods

Poly(ethylene 2,6-naphthalene-dicarboxylate) (PEN) was supplied by Aldrich Chemical Company Inc. PEN has a T_g of 116 °C and a T_m of 268 °C. Poly(pentylene terephthalate) (PPT) was synthesized (from 1,5-pantanediol and dimethyl terephthalate) in house with a molecular weight $M_w = 16,600$ g/mol (determined by GPC) [24]. Owing to the long olefin segment (five methylenes) in the repeat unit, PPT possesses a relatively low T_g of 8.2 °C and T_m of 130 °C. The chemical structure of the repeating units of PEN and PPT are shown as following:

PEN

PPT
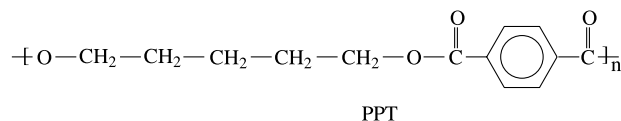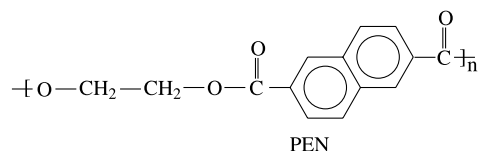
Co-precipitation was used in blend sample preparation. Blends were obtained by dissolving both polymers in dichloroacetic acid (4 wt%) by continuous stirring, then were co-precipitated in large quantity of methanol. The precipitates were dried in vacuum at 80 °C for 1 week. The 'as-prepared' blends are designated for those co-precipitated from the solution without any heating, while various extents of trans-esterification were imposed on the as-prepared blends by heating at 300 °C for various times.

For comparisons, a second series of blend samples were prepared by direct melt-blending (without any solvents) at above the melting temperatures of the polyesters (~ 300 °C). The neat polymers were first pulverized (ground) into fine powder. This manipulation was made in order to ensure that thorough melt-mixing could be completed within the shortest time possible, with least thermal degradation. An aluminum mold with a miniature-mixing chamber (ca. 2-g capacity) was laboratory-made and it was designed in such way that thorough blending could be completed with sufficient manual stirring. This set-up was especially ideal for handling small quantities of polymer samples (1–2 g or

less per batch). Heating and temperature control was provided by a hot stage with a temperature controller set at ∼300 °C. The exposure time at the melt-blending was kept short and was usually no longer than 10 min. During blending, dry nitrogen was maintained by continuously purging into the mixing chamber to ensure minimum thermal degradation.

The ^{1}H NMR spectra were recorded on a Bruker AVANCE-400 spectrometer operating at 400 MHz. Tetra-methylsilane was used as an internal standard for chemical shift reference. The 2D ^{1}H COSY (correlated spectroscopy) experiment was performed to correlate of pairs of protons through their spin–spin coupling. Co-precipitated PEN/PPT blend (50/50 by weight) was heated to 300 °C, and then held for various times. The heated blends were dissolved in $CF_3COOD/CDCl_3 = 10/90$ (v/v) for NMR experiments. The ^{1}H NMR measurement was also performed on the neat PET to obtain the chemical shift value of ethylene unit between two terephthalates.

Additional characterizations were performed using thermal analysis and microscopy techniques. The glass transition (T_g) temperatures, crystallization, and melting temperatures of the thermal analyses were performed with a differential scanning calorimeter (Perkin–Elmer DSC-7) equipped with an intracooler. Measurements of T_g, cold-crystallization, and melting transitions were made at a scan rate of 20 °C/min in the range of −60–300 °C. The reported T_g values were taken as the onset of the glass transition (i.e. step change in the specific heat capacity) in the DSC thermograms. A polarized-light optical microscope (Nikon Optiphot-2 POL) with UFX-DX automatic exposure was used to examine and confirm the phase structure of the polymer mixtures. Samples for microscopy were placed between micro glass slides, then heated and gently pressed by hands to thin films on the microscope heating stage (Linkam THMS-600 with TP-92 temperature programmer). Additionally, to further confirm the phase homogeneity, some selected blend samples (compression-molded to films) were also examined using a scanning electron microscope (SEM) (JEOL, Model JXA-840). Thicker blend films (0.3 mm in thickness) for SEM were prepared by compression molding. They were then fractured across the thickness after dipping into liquid nitrogen; subsequently, the fractured surfaces were sputter-coated with gold for SEM characterization.

Wide-angle X-ray instrument (WAXD) was Shimadzu XRD-6000 with copper K_α radiation (40 kV and 45 mA) and a wavelength of 1.542 Å. The scanning angle ranged $2\theta = 5$–$35°$, with a step scanning of $0.02°$ (parameter equivalent to a scanning speed of 2 °/min). Thermal treatments of blend samples for both X-ray diffraction and SEM characterization were performed in the DSC cells for precise temperature control of intended thermal treatments.

3. Results and discussion

3.1. Co-precipitated blends vs. melt-blended systems

Note that the co-precipitated blend samples were in powdery form and contact between samples and DSC pan might not be ideal. Secondly, the T_g signals from fully crystalline samples were found to be weak and difficult for interpretation. As a result, the blend samples were heated to 300 °C briefly for a half minute (30 s), and then rapidly quenched before a new scan was started. The extents of trans-reaction upon brief exposure at 300 °C, if any, would be minimal and could be ignored. Fig. 1 shows the DSC thermograms (second run, heating rate = 20 °C/min) for the PEN/PPT blends (prepared by co-precipitation) and two neat polymers (PEN and PPT), respectively. The DSC traces show that two T_g's (marked on onset positions indicated with arrows) are seen in the blends. These two T_g's indicate two phases in the blend and the first T_g at ∼5 °C is apparently associated with the PPT-rich phase, while the second one at ∼100 °C is associated with the PEN-rich phase. Two separate T_g's are apparent for the blends, indicating clearly two phases. Note that the second T_g is located at position that is not masked or overlapped with the cold-crystallization peaks of PPT; thus it is clearly resolved. Note that these two separate T_g's for the blends are slightly shifted to each other in comparison to those for the neat polymers (PPT and PEN). The lower T_g (for PPT rich-phase) is up-shifted about 5 °C, while the upper one (for PEN-rich phase) is down-shifted about 10 °C. This information indicates that although there are two separated phases, these two phases to some extents contain 'partially miscible' constituents of both.

Furthermore, the cold-crystallization in the blends is analyzed to infer the phase behavior. As mentioned, the data
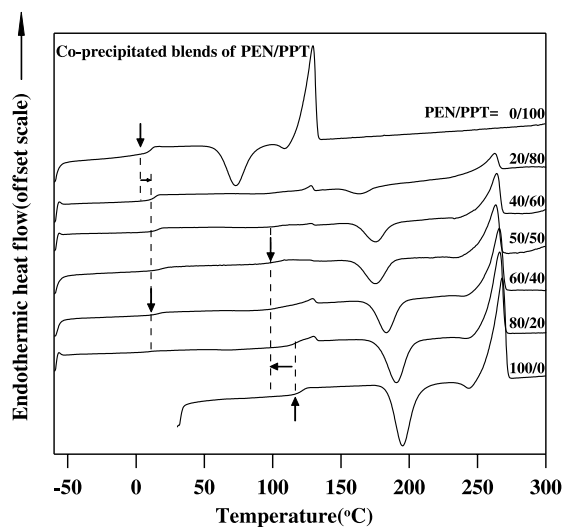

Fig. 1. DSC thermograms (2nd runs, heating rate = 20 °C/min) of PEN/PPT blends (prepared by co-precipitation), and two neat polymers (PEN and PPT).

in Fig. 1 are actually the second DSC runs (after quenching from 300 °C) on the as-prepared co-precipitated samples. Thus, in addition to two distinct T_gs, cold crystallization peaks were observed in the DSC traces for the blends. Co-precipitated and as-prepared blends would involve crystallinity and there should be no 'cold-crystallization' seen in DSC scans. By comparison, the cold crystallization peak for the PPT phase is much more suppressed than that for the PEN phase, indicating that crystallization of PPT in blend seems to be disrupted more than that that of PEN. It is worthy to elaborate on this difference. The partial miscibility between PEN and PPT is sufficient to cause some disruption of chain packing of PPT and/or PEN. PPT (with five methylenes between the terephthalate groups) by nature is less crystallizable; furthermore, its weak crystallizing tendency is hindered by the partial miscibility between PEN and PPT, as revealed by the DSC traces. Selectively, the hindrance for undergoing cold-crystallization upon heat scan is more for PPT than for PEN. The reason is clear. In the temperature window, where PPT is heated to undergo cold-crystallization (75–100 °C), the PPT chains are partially entangled with the PEN chains in the blend, which are still of a rigid glassy chain conformation (below the PEN T_g). Oppositely, in the temperature window, where PEN is heated to undergo cold-crystallization (nearly 200 °C), the PEN chains are partially entangled with the PPT chains in the blend, which are of a liquid/rubbery conformation (well above PPT T_g).

Additionally, the morphology of the co-precipitated blends (after briefly hot-pressed into thin films at 300 °C) was grossly phase-separate, as revealed in the actual POM images for the co-precipitated PEN/PPT blends (which were heated briefly above melting to press into uniform films for OM characterization). Except for the two neat polymers that are naturally homogeneous, quite apparent phase domains were observed in the co-precipitated PEN/PPT blends, indicating apparent phase immiscibility. The POM study concludes a phase-separated morphology in the co-precipitated PEN/PPT blends (prior to extended annealing at high temperatures), which is in line with the DSC thermal analysis evidence shown and discussed earlier.

Blends prepared by melt-blending, however, led to different results. Fig. 2 shows the DSC traces of melt-blended PEN/PPT (for five compositions and two neat polymers) samples in comparison to the two neat polymers. All blends show a single, composition-dependent T_g, suggesting that the melt-blended PEN/PPT may be superficially or seemingly 'miscible' according to the blend's T_g criterion. Both POM and SEM (for brevity, not shown) were performed and both also revealed a homogeneous morphology with no observable domains. However, it is known that high temperature melt-blending might have induced some types of chemical reactions (i.e. exchange reactions) between PEN and PPT leading to the observed single phase. Thus, care must be exercised to discern between two
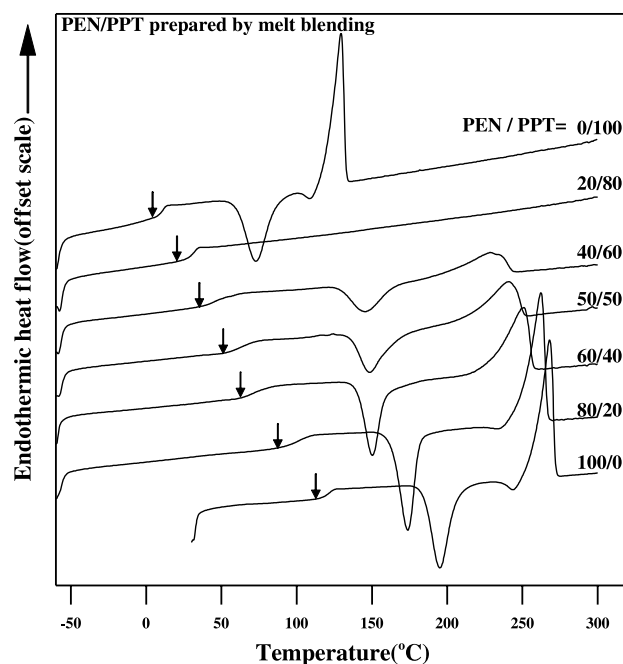

Fig. 2. DSC traces of melt-blended PEN/PPT samples (for five blend compositions and two neat polymers).

possible facts of physical miscibility or chemical-induced phase homogeneity in this blend system.

3.2. Is the phase homogenization at 300 °C physically reversible?

First of all, one wondered whether or not the homogeneous phase in the melt-blended system was permanently changed and not reversed back to a two-phase system if the blends were re-dissolved and re-cast from solutions. Irreversibility in the phase would suggest probable reactions had taken place during melt-blending. A melt-blended PEN/PPT (50/50) mixture was re-dissolved into dichloroacetic acid and cast into films. Preliminary OM characterization revealed that the blend film was clear and transparent. Further, DSC was performed. Fig. 3 shows a direct comparison of (a) melt-blended PEN/PPT (50/50) that had been re-dissolved/re-cast, vs. (b) original melt-blended PEN/PPT (50/50) blend. There is a single T_g in sample-a as well as sample-b. The T_g and other thermal transitions are almost identical, suggesting that solvent dissolution and re-casting did not alter the homogeneous morphology in the melt-blended PEN/PPT. It gives evidence that the melt blending at 300 °C (for 10 min) possibly induced some extents of reactions between PPT and PEN, which helped gradually transform the phase-separated blend into a homogeneous phase. By comparison, one should note here a PEN/PPT blend (without any prior heating or melt-blending) directly prepared and cast from the same solvent (dichloroacetic acid) would have exhibited a phase-separated morphology with two T_g's.
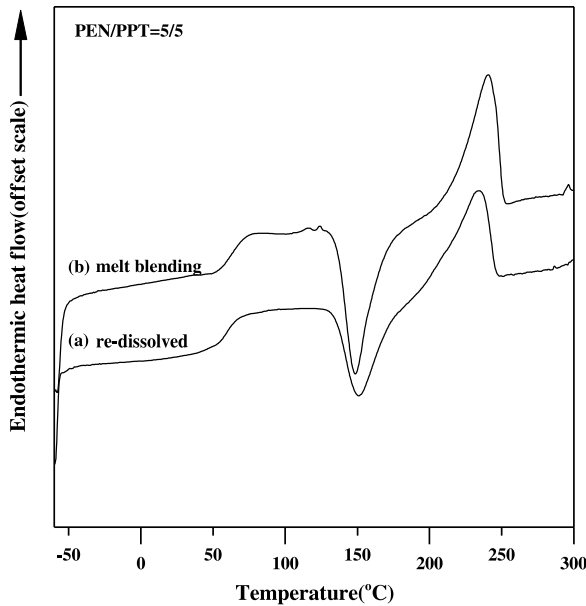
Fig. 4 shows DSC traces of co-precipitated PEN/PPT (of

Fig. 3. DSC traces for (a) melt-blended PEN/PPT (50/50) that had been re-dissolved/re-cast, and (b) original melt-blended PEN/PPT (50/50) blend.

five compositions) blends having been heated at 300 °C, all for 30 min. All blends exhibit a single, composition-dependent T_g. Blends after heating for 30 min were still crystallizable, which could be seen in the still discernible $T_{c,c}$ and T_m peaks in the DSC traces for the PPT-rich blends. However, for longer heating times of 60 min or longer, the crystallinity and crystallization tendency of the blend rapidly diminished or finally disappeared from the DSC and X-ray analyses (for brevity, data graphs not shown here). Heating, apparently, induced some chemical
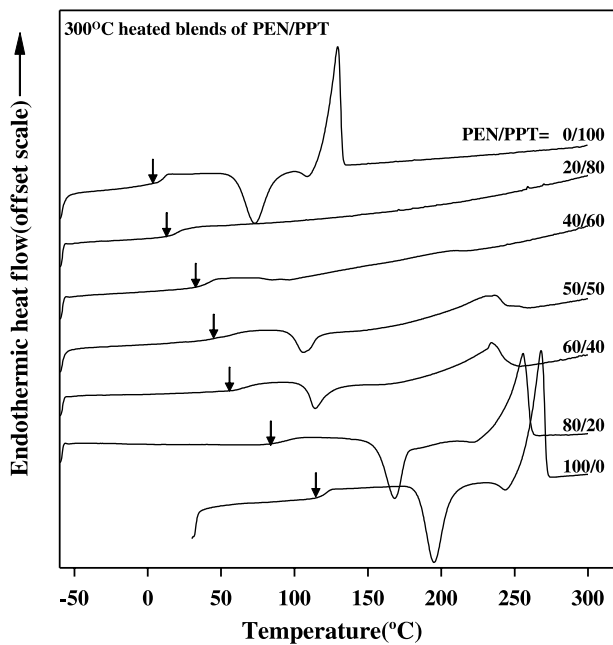

Fig. 4. DSC traces of co-precipitated PEN/PPT (for five compositions) having been heated at 300 °C for 30 min.

reactions between PPT and PEN. The imposed heating at 300 °C for a specified period of time on solution-blended system might have induced homogenization of structure on the blend. Two interesting features are noted in the heated blends. One is that all blends exhibit a depressed crystallization tendency, and the second feature is that all heated blends now exhibit a single T_g of narrow T_g breadth. Both features together indicate that heating at 300 °C for 30 min might have induced a certain extent of phase/morphology homogenization, as evidenced by the T_g behavior and POM or SEM characterization (for brevity, not shown).

Fig. 5 shows the T_g vs. composition plots for (A) melt-blended samples in comparison with the co-precipitated PEN/PPT blends, and (B) co-precipitated PEN/PPT blends further annealed/heated at 300 °C for 30 and 240 min, respectively. Apparently, Fig. 5(a) shows that two T_g's are
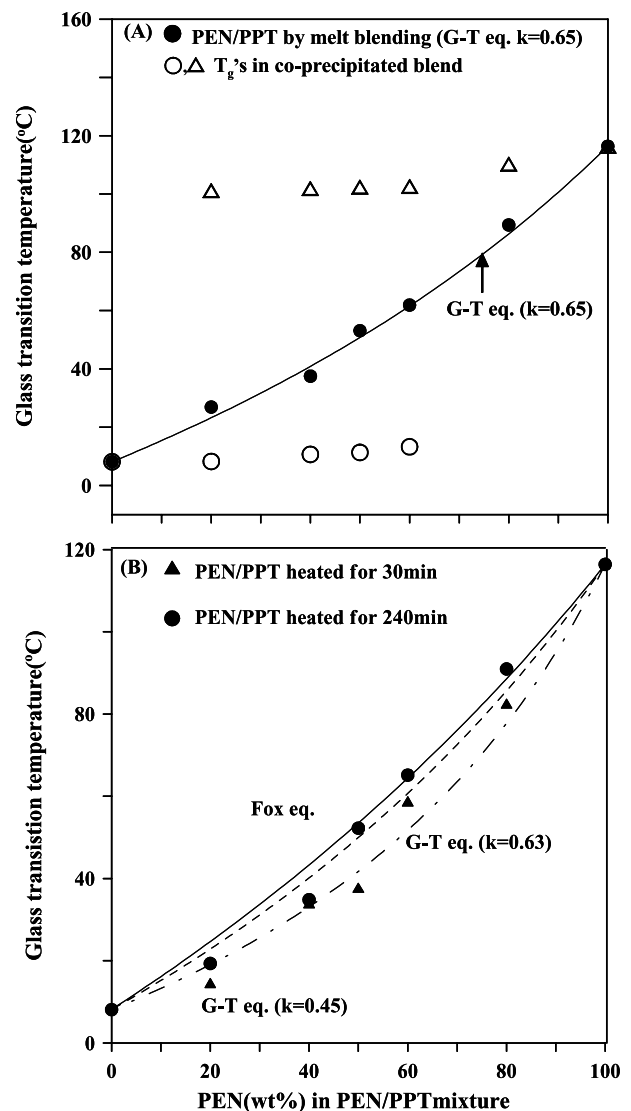

Fig. 5. T_g vs. composition relationship plots for: (a) melt-blended blends (filled symbol) in comparison with co-precipitated PEN/PPT blends (open symbols), and (b) co-precipitated PEN/PPT blends further heated at 300 °C for 30 and 240 min.

present in the co-precipitated blend system, while the melt-blended system possesses a single T_g dependent on compositions. The as-prepared co-precipitated PEN/PPT blends are phase separated and they expectedly exhibit two T_gs corresponding to the PPT-rich (lower T_g) and PEN-rich (upper T_g) phases, respectively. By comparison, the melt-blended PEN/PPT system (melt blending performed at 300 °C for 10 min) is one phase showing a composition-dependent T_g, roughly in agreement with the Gordon–Taylor model prediction. For reference, the T_g data fitting with the Gordon–Taylor equation was performed for the melt-blended system, leading to a parameter $k = 0.65$. Fig. 5(b) shows the parameters from the fitting between data and the classic Fox [25] or Gordon–Taylor equation [26] for the heated blends. As discussed earlier, the co-precipitated PEN/PPT blends that were post-annealed at 300 °C quickly were transformed into a single-phase mixture. Upon post-heating at 300 °C for various times, the co-precipitated blends had been homogenized into one amorphous phase, or in the other words, turned into single-T_g blends. It was observed that the blends after 10–30 min heating at 300 °C readily turned into a homogeneous phase. The blends' T_g, however, was changing with the time of heating until it leveled off at long time (4 h). For the co-precipitated blend heated for 30 min, $k = 0.45$, while for blends heated for 4 h, the parameter for the G–T equation became larger at $k = 0.63$.

If the values of the k parameters obtained from the fittings were taken as semi-qualitative indication for the process going from a phase separated blend system to homogeneous system by heating at 300 °C, there is an interesting trend. For comparison of the trend, note that for the melt-blended system, $k = 0.65$ (Fig. 5(a)). The fact suggests that melting blending at 300 °C would bring the PEN/PPT blend system to a homogeneous phase more quickly than static heating at the same temperature of 300 °C, owing to an apparent reason that blends under continuous stirring and mechanical shear approached the final equilibrium state in faster time frames. However, one cannot yet conclude a physical miscibility by just judging this figure, as a random copolyester comprising these two units (or a copolyester of short blocks) may also exhibit such a relationship.

Transformation of the morphology of the initially co-precipitated PEN/PPT blends during heating was visually recorded and monitored using OM. Fig. 6 shows the OM graphs taken illustrating the homogenization process of the initially co-precipitated PEN/PPT blends (five compositions, as indicated on graphs) upon further heating at 300 °C for 30 min. The result demonstrates that brief heating (30 min, static heating—no stirring) is sufficient to bring the blends of initially phase separated co-precipitated PEN/PPT blends from an apparent phase-separation to a homogeneous morphology. Note that preparation of PEN/PPT blend by direct melt blending (no solvent used) was usually performed at 300 °C (with shear stirring for about

10 min or less). In addition, for comparison with the co-precipitated blends further heated at 300 °C, melt-blended PEN/PPT samples of five different compositions were also similarly examined using OM. The OM result also demonstrated melt-blended PEN/PPT blends exhibited a homogeneous morphology similar to the OM graphs on the right-hand side of Fig. 6. However, for brevity, they are not shown. The fact that one usually can obtain a single-phase system by melt-blending PEN/PPT is quite clearly supported by the OM evidence given and discussed in this figure showing the evolution and transformation of phase morphology of the initially co-precipitated PEN/PPT blends.

3.3. Interaction strength between blend components

For blends heated for 10 min, the system apparently turned into a single-phase morphology with a single T_g. At this state, although there might be some reactions taking place between the constituent polymers (PEN and PPT), the blends were still crystallizable. Consequently, interactions and their strength might be estimated. An assumption must be specified, though. The parameter may not be for two neat polymers; instead, one must realize that some types of trans-reaction product might have been in the blend system. Nevertheless, for simplicity, we treated the system as a binary blend between PEN and PPT. For PEN, apparent $T_m = 268$ °C, but for PPT, apparent $T_m = 130$ °C. The difference between these two melting points is 138 °C, and within the crystallization range of PEN, PPT is at molten state. Thus, χ_{12} for PEN and the amorphous component may be obtained by using the Flory–Huggins equation. The blends of PEN/PPT were brought to a miscible mixture by heating. They then were quickly quenched to $T_c = 225$–240 °C for 8 h. The crystallized samples were then scan in DSC at 10 °C/min, and the melting temperature T_m was recorded.

From the Flory–Huggins equation:

$$\frac{1}{T_{mb}} - \frac{1}{T_m^0} = -\frac{RV_{2u}}{\Delta H_{2u} V_{1u}} \chi (1 - \phi_2)^2$$

$$= -\frac{RV_{2u}}{\Delta H_{2u} V_{1u}} \chi \varphi_1^2 \tag{1}$$

where T_{mb} is the equilibrium melting point for the blend, T_m^0 is equilibrium melting point for neat PEN, R is the universal gas constant, V_{iu} is the molar volume of repeating unit-I, ϕ_1 is the volume fraction of PPT, $\Delta H_{2u} = $ molar enthalpy for the PEN repeat unit. Extrapolation was performed according to the Hoffman–Weeks methods, and the equilibrium melting, T_m^0, for the blends and neat PEN could be obtained. Note that prior to measuring the melting temperatures, the initially co-precipitated PEN/PPT blends were heated at 300 °C for 30 min to induce blend phase homogenization. The blend samples so treated were homogeneous in the amorphous phase but the PEN constituent in the blends was
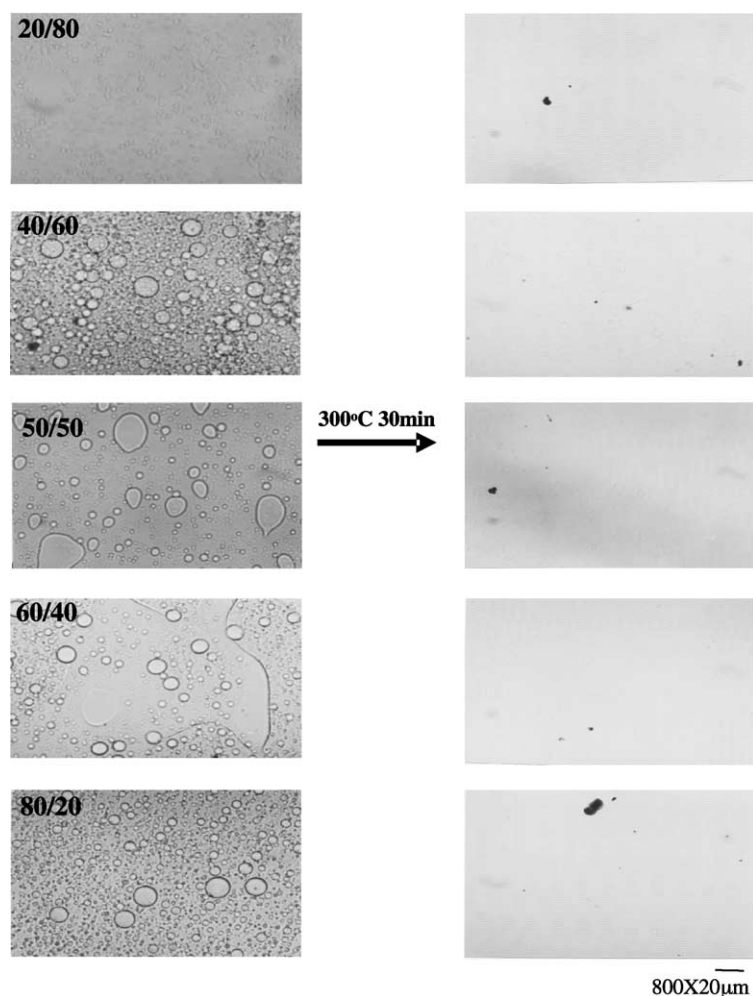
Fig. 6. POM graphs illustrating the homogenization process of the initially co-precipitated PEN/PPT blends (five compositions, as indicated on graphs) upon further heating at 300 °C for 30 min.

still crystallizable; thus, the equilibrium melting points of PEN in various blend compositions could then be measured. Fig. 7 (with an inset graph) shows the Hoffman–Weeks extrapolation plots for three PEN/PPT blend compositions and the neat PEN. The inset in this figure shows the slope from which the interaction strength was estimated. From the literature [27], it may be estimated: $V_{1u} = 193.39$ cm^3/mol, $V_{2u} = 182.23$ cm^3/mol, $\Delta H_{2u} = 25$ kJ/mol. By plotting $(1/T_{mb} - 1/T_m^0)$ vs. $(1 - \phi_2^2)$, it was obtained that Slope $= -RV_{2u}/\Delta H_{2u}T_{mb}\chi_{12} = 6.2 - 10^{-5}$. From this plot, one obtained the interaction strength between the two constituents in the blend: $\chi_{12} = -0.20$.

3.4. ^1H NMR characterization on sequence structures of copolyesters

In order to clarify the relationship between the thermal behavior and the evolution of the chemical and sequence structures of copolyesters, ^{1}H NMR has been used to study the products from trans-esterification. Fig. 8 shows the one-dimensional ^{1}H NMR spectra in the range from 4.3 to 5.0 ppm, of the PEN/PPT blend (50/50, w/w) heated at 300 °C for (a) 0 min (unheated), (b) 60 min, (c) 120 min, and (d) 480 min. In spectrum-a (unheated blend), the singlet at 4.86 ppm represents the ethylene protons (**1**) in PEN and the triplet at 4.45 ppm is from methylene protons (**6**) adjacent to oxygen in PPT (refer to schematic illustration to be shown in following figure).

With increase of heating times (up to 480 min) imposed on the PEN/PPT blend, spectra (b)–(d) show that new peaks appear. The new peaks, assigned as (**2**) through (**5**) are to be identified. Fig. 9 summarizes the schematic representations of several sequence structures of various blocks in PEN/PPT blends upon heating. In this scheme, A1 represents the naphthalate unit, A$_2$ the terephthalate, B$_1$ the ethylene glycol unit, and B$_2$ the pentylene glycol unit. For examples, A$_1$B$_1$A$_1$ block is the original ethylene naphthalate unit, while A$_1$B$_1$A$_2$ represents one of the exchanged blocks, where the terephthalate of PPT has been exchanged with PEN.

The new singlet appears at 4.82 ppm in the sample that was heated for 60 min, indicating that trans-esterification
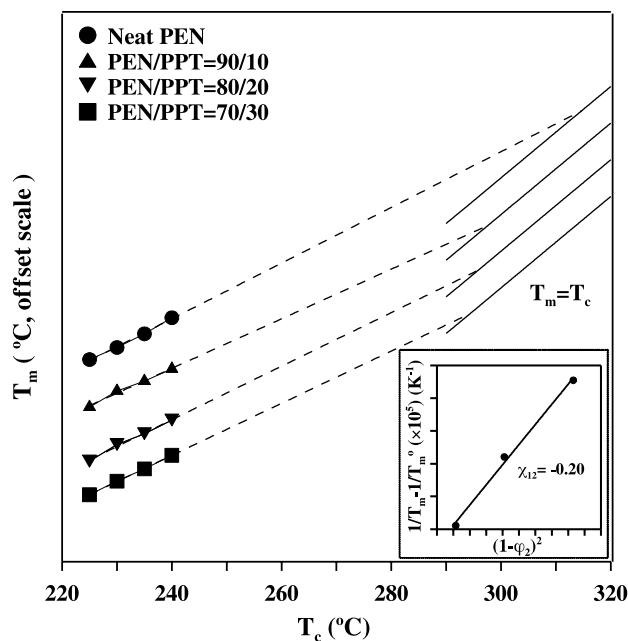
Fig. 7. Hoffman–Weeks extrapolation plot and determination of the interaction parameter in PEN/PPT blends after heat-induced phase homogenization (300 °C, 30 min). The inset in figure shows the slope for determining the interaction strength (χ).

might have occurred between PEN and PPT. This peak is assigned to protons of the ethylene group (**2**) between 2,6-naphthalate and terephthalate (see schemes in Fig. 9). With increase of reaction times, the intensity of this peak increases. After 120 min, another singlet at 4.78 ppm shows up, and this peak becomes distinct after 480 min. By comparing to the chemical shift of ethylene protons (4.77 ppm) of neat PET, the singlet at 4.78 ppm corresponds to the protons of ethylene group (**3**) bonded between two terephthalate. On the other hand, after 60 min of heating a shoulder peak at 4.51 ppm has grown in. This indicates that the chemical environment of pentylene protons changes by trans-esterification between PEN and PPT, which relative to the appearance of the singlet at 4.82 ppm. The proton signals in the range of 4.45–4.51 ppm split into three sets of peaks (**4**), (**5**), and (**6**), after 480 min of heating.

To further conform the assignments based on one-dimensional ^{1}H NMR, ^{1}H COSY (H–H correlation spectroscopy) experiment was performed. The off-diagonal peaks (cross peaks) in a COSY spectrum show the correlations of pairs of protons by means of their spin–spin coupling. Fig. 10 shows the COSY spectrum of the PEN/PPT blend (50/50) heated at 300 °C for 480 min. It shows that the protons at 1.92 ppm, the methylene protons (**7**) of B_2 (shown earlier schemes in Fig. 9), correlate with the protons (**4**)–(**6**), which have been assigned to the methylene protons of the pentylene unit adjacent to oxygen. Additionally, no correlation between the protons (**7**) and the protons (**1**)–(**3**) was found, suggesting that these protons are not coupled to the methylene protons (**7**). Therefore, we concluded that the protons (**1**)–(**3**) are the ethylene protons
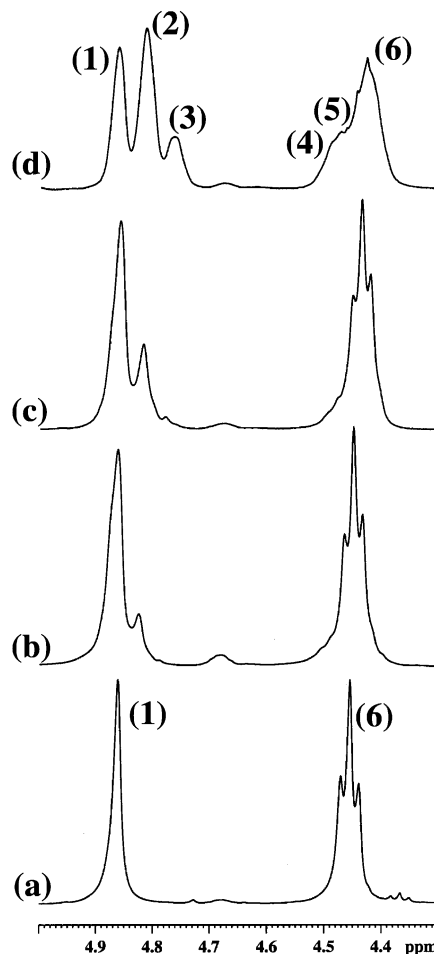

Fig. 8. ^{1}H NMR spectra of co-precipitated PEN/PPT = 50/50 blend after heating at 300 °C for different times: (a) 0, (b) 60, (c) 120 and (d) 480 min.

in $A_1B_1A_1$, $A_1B_1A_2$, and $A_2B_1A_2$, respectively; and that (**4**)–(**6**) are the methylene protons next to oxygen in $A_1B_2A_1$, $A_1B_2A_2$, and $A_2B_2A_2$, respectively.

Using the results from NMR analyses, the sequence structures of copolyesters from trans-esterification may be determined by application of the statistical methods described by Devaux et al. [22] The exchange reaction between PEN and PPT will generate a four-component copolyester, which can be represented as following:

$$[(A_1 - B_1)_x - (A_2 - B_1)_y]_m - [(A_1 - B_2)_z - (A_2 - B_2)_w]_n$$
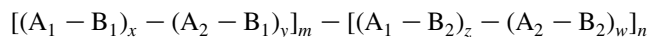
In this formula, A_1, A_2, B_1, and B_2 are the monomer units of different chemical structure (shown earlier schemes in Fig. 9) but of the same functionality; x, y, z, and w represent the average length of the various sequences; m and n are the mean lengths of blocks having in common the same B_1 or B_2 unit.

In the present work, the distribution of the copolyester sequence was calculated based on an analysis of triads centered on the ethylene unit (B_1). Table 1 shows summary results of the triad analysis for the PEN/PPT (50/50) blend upon heating at 300 °C (for theoretical details, see
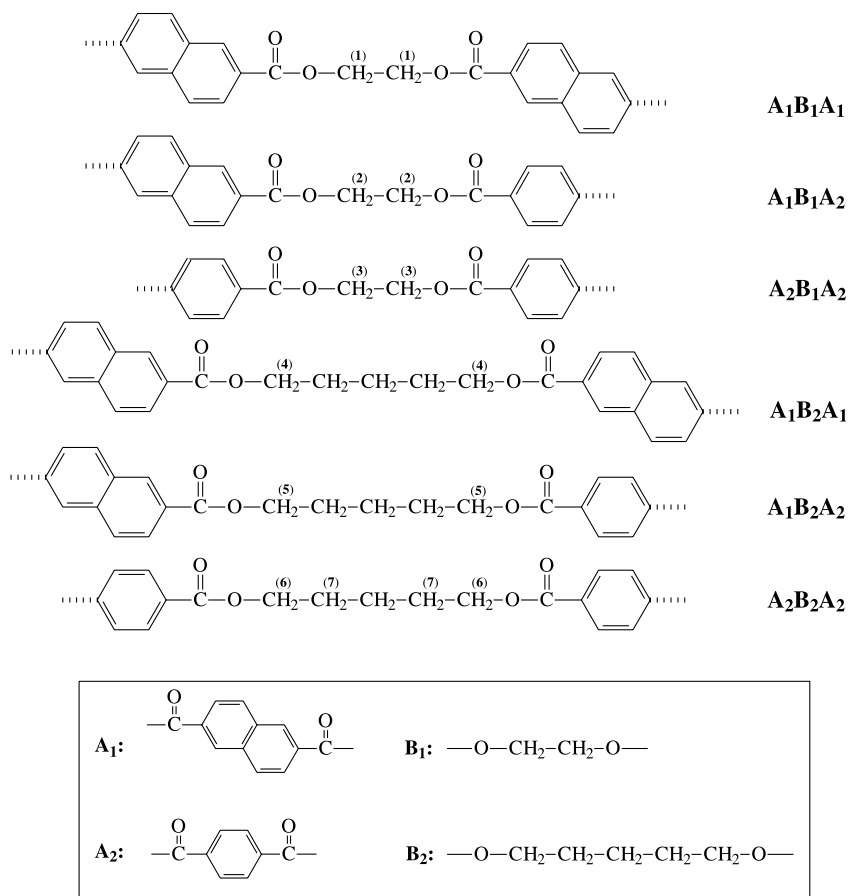
Fig. 9. Sequence structures of the copolyester on the glycol unit of co-precipitated PEN/PPT=50/50 blend after heating at 300 °C for a period of time.

Ref. [22]). The theoretical values for a statistical copolyester of the same composition are also included in Table 1. The triad fractions $f_{A_iB_1A_k}$ around the ethylene unit (B_1) is defined by the concentration ratio and can be determined from previous ^1H NMR assignments.

$$f_{A_iB_1A_k} = \frac{[A_iB_1A_k]}{[B_1]} \qquad (2)$$

Note that $f_{A_1B_1A_2} = f_{A_2B_1A_1}$, the degree of randomness (BB_1)

around B_1 is given by

$$BB_1 = f_{A_1B_1A_2}\left(\frac{1}{F_{EN}} + \frac{1}{F_{PT}}\right) \qquad (3)$$

where F_{EN} and F_{PT} are the mole fraction of 2,6-naphthalate and terephthalate group, respectively. The degree of randomness is related to the distribution of monomer units in the copolyester formed by exchange reaction. In a mixture of polyesters or in a copolyester with long homogeneous sequences, BB_1 equals to 0. Value of $BB_1 = 1$ indicates a copolyester with a random distribution of A_1 and A_2 units around B_1; whereas BB_1 between 1 and 2 denotes a

Table 1
Sequence structure for PEN/PPT copolyesters determined by ^1H NMR and triad analysis

Reaction time	$f_{A_1B_1A_1}$[a]	$f_{A_1B_1A_2} + f_{A_2B_1A_1}$	$f_{A_2B_1A_2}$	x[b]	y[b]	BB_1[c]
0	1.00	0	0	–	–	0
60 min	0.81	0.19	0	9.53	1.00	0.38
120 min	0.69	0.27	0.04	6.11	1.29	0.54
480 min	0.37	0.46	0.17	2.61	1.73	0.92
Theoretical values for a statistical copolyester	0.23	0.50	0.27	1.92	2.08	1

Temperature of reaction 300 °C; PEN/PPT mole ratio=47.6/52.4.
  [a] $f_{A_iB_1A_k}$ represents the fraction of triads centered on B_1 (ethylene unit).
  [b] x, the average length of A_1B_1 sequences; y, the average length of A_2B_1 sequences.
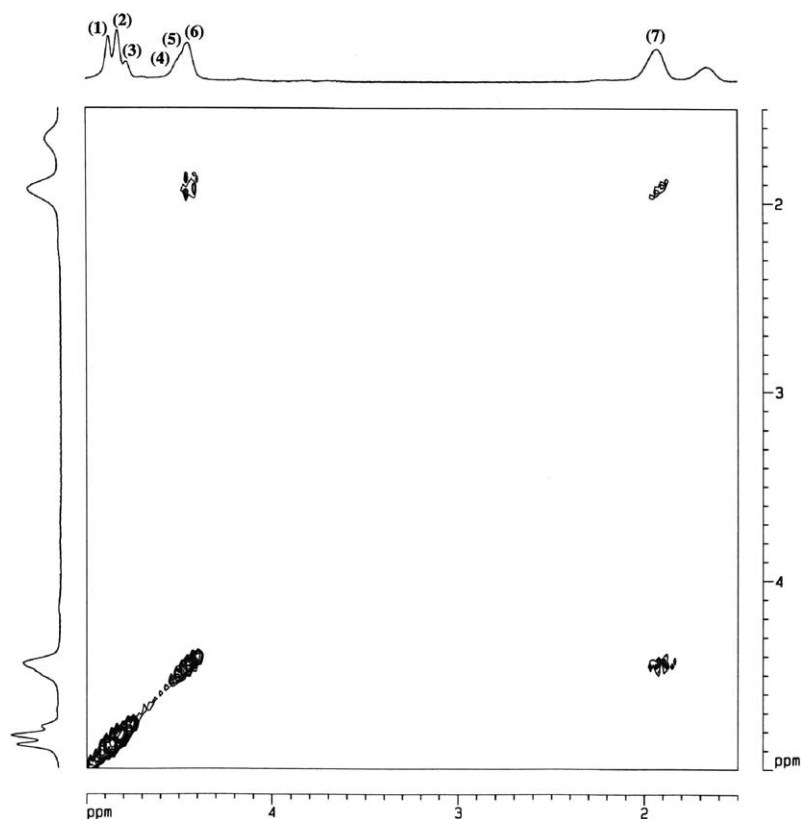 [c] BB_1 represents the degree of randomness around B_1 (ethylene unit).

Fig. 10. ^{1}H COSY spectra of the co-precipitate PEN/PPT (50/50) blend after heating at 300 °C for 8 h.

tendency of A_1 and A_2 to alternate around B_1 [22]. Because the resolution of ^{1}H NMR is not enough to deconvolute the proton peaks (**4**)–(**6**), we only calculated the evolution of the mean lengths of the ethylene 2,6-naphthalate (x) and ethylene terephthalate (y) sequences. The average lengths of A_1B_1 (x) and A_2B_1 (y) sequences can be deduced from the fraction of $A_iB_1A_k$ triads and is given by

$$x = \frac{f_{A_1B_1A_1} + f_{A_1B_1A_2}}{f_{A_1B_1A_2}} \qquad (4)$$

$$y = \frac{f_{A_2B_1A_1} + f_{A_2B_1A_2}}{f_{A_2B_1A_1}} \qquad (5)$$

As shown in Table 1, as the degree of randomness increases, the average sequence lengths decrease with time of heating imposed on PEN/PPT blend. DSC and X-ray analyses have shown that PEN/PPT (50/50) blend lost its crystallizability completely for heating of 60 min or longer. Up to 120 min of reaction, the mean sequence length of PEN (x) is ∼6; therefore, the length of six repeat units (ethylene-2,6-naphthalte) is not long enough to fold, and to exhibit the crystalline behavior. The degree of randomness BB_1 is 0.54 after 120 min of heating, indicating that the sequence structures of the copolyester at this point is not completely random.

Apparently, by combining the DSC results shown earlier in Figs. 4 and 5 (the blend heated at 300 °C for 30 min), it

can be concluded that a statistically random copolyester is not necessarily an agent or a pre-requisite for forming a homogenous morphology (i.e. a single-T_g blend) in the melt-blended PEN/PPT (50/50) system. After 480 min of heating, a random copolyester was formed, with a large value of $BB_1 = 0.92$. However, the copolyester is still not a truly statistical copolyester ($BB_1 = 1$). But this random copolyester exhibits a large parameter k (0.63) in the T_g-composition relationship for the G–T equation, suggesting that the random sequence structures can either enhance the interactions among copolyester chains, or alternatively, by nature, they themselves help to bring a single-phase morphology. The statistical analysis also reveals a fact that the exchange reaction rate is slow, as comparison to PEN/PET (50/50) system at reaction temperature of 280 °C [8]. The degree of randomness of such a blend reaches ∼0.8 in 120 min; whereas in PEN/PPT (50/50) system, to form a random copolyester takes a longer reaction time (480 min), which may be due to the longer pentylene group (five-carbon segment) hindering the exchange reaction with PEN upon heating.

4. Conclusion

A random copolyester, coded as EN-*co*-PT, of various sequence lengths was produced as a result of the exchange

reactions between PEN and PPT. X-ray analyses confirmed that the PEN/PPT (50/50) blend completely lost its crystallizability when heated at 300 °C for time of 60 min or longer, indicating formation of random copolyesters. DSC characterization on re-dissolved/re-cast a melt-blended PEN/PPT mixture demonstrated that trans-reactions between PEN and PPT at 300 °C were irreversible if heated for sufficient times (10 min or longer). The trans-reacted amorphous products, random copolyesters code-named as EN-*co*-PT, could form partially miscible blends with either PEN or PPT. Through ^{1}H NMR and statistical analysis, the chemical and sequence structures of PEN/PPT heated-blend can be determined. It shows that the degree of randomness increases and the average sequence lengths decrease with time of heating imposed on PEN/PPT blend, and the exchange rate is slow in comparison with the PEN/PET system. The re-distribution of the repeat units of PEN and PPT results in the loss of crystallinity and a homogeneous morphology.

Acknowledgements

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