Miscibility and Transesterification in Ternary Blends of Poly(ethylene naphthalate)/Poly(pentamethylene terephthalate)/Poly(ether imide)

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ABSTRACT: Miscibility and morphology of poly(ethylene 2,6-naphthalate)/poly(pentamethylene terephthalate)/poly-(ether imide) (PEN/PPT/PEI) blends were studied by differential scanning calorimetry (DSC), optical microscopy (OM), proton nuclear magnetic resonance imaging (^{1}H-NMR), and wide-angle X-ray diffraction (WAXD). OM and DSC results from ternary blends revealed the immiscibility of PEN/PPT/PEI blends, but ternary blends of all compositions were phase-homogeneous following heat treatment at 300°C for over 60 min. Annealing samples at 300°C yielded an amorphous blend with a clear and single T_g at the final state. Experimental data from ^{1}H-NMR revealed that PEN/PPT copolymers (ENPT) were formed by the so-called transesterification. The effect of transesterification on glass transition and crystallization was discussed in detail. The sequence structures of the copolyester were identified by triad analysis, which showed that the mean sequence lengths became shorter and the randomness increased with heating time. The results reveal that a random copolymer improved the miscibility of the ternary blends, in which, the length of the homo segments in the polymer chain decreased and the crystal formation was disturbed because of the irregularity of the structure, as the exchange reaction proceeded. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 3840–3849, 2006

Key words: miscibility; morphology; differential scanning calorimetry (DSC); immiscibility; annealing

INTRODUCTION

Multicomponent blends that comprised various polymers with different characteristics provide a unique means of developing a new material with variable combination constituents. In ternary blends, a third component (as a compatibilizer) is typically added to an immiscible pair to ensure miscibility in cases in which the third component is miscible with each of the other two polymers because of hydrogen bonding or van der Waals forces.[1,2] Additionally, chemical interactions in the ternary blends enhance their miscibility and phase homogeneity.

Aryl polyesters, including poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT), have valuable characteristics, such as strength, toughness, insolubility, and thermal resistance. Their favorable characteristics have caused PET and PBT to have been extensively studied over several decades.[3,4] Although poly(pentamethylene terephthalate) (PPT) is one of a series of thermoplastic aromatic polyesters,

including PET and PBT, PPT has a low glass-transition temperature (T_g = 8.1°C), which limits the application of this semicrystalline polymer. Naphthalene groups in the repeated structure of poly(ethylene 2,6-naphthalate) (PEN) make the polymer backbone rigid; increase the glass-transition temperature, and improve its mechanical properties. In contrast, poly(ether imide) (PEI) is amorphous and is used as a high-performance engineering thermoplastic polymer known for its thermal stability, toughness, high T_g, and other favorable mechanical properties; one of the disadvantages is that PEI has weakness against organic solvents. In the literature,[5–12] binary blends that comprise semicrystalline polymer and an amorphous polymer have been extensively investigated and potentially provide synergistic balance of polymer properties. The PEN/PEI blends have been reported to be completely miscible over the whole range of compositions. In the UCST phase diagram, PEN/PEI blends exhibited simultaneous liquid–liquid phase separation and crystallization.[5,6] With regard to polyester/PEI blends, PET/PEI,[7,8] poly(trimethylene terephthalate) (PTT)/PEI,[9,10] and PBT/PEI[11] blends have been reported over recent years. These studies have improved our understanding of the morphology, crystallization, processing, and characteristics of miscible blend systems. Additionally, both PPT/PEI and poly(hexa-
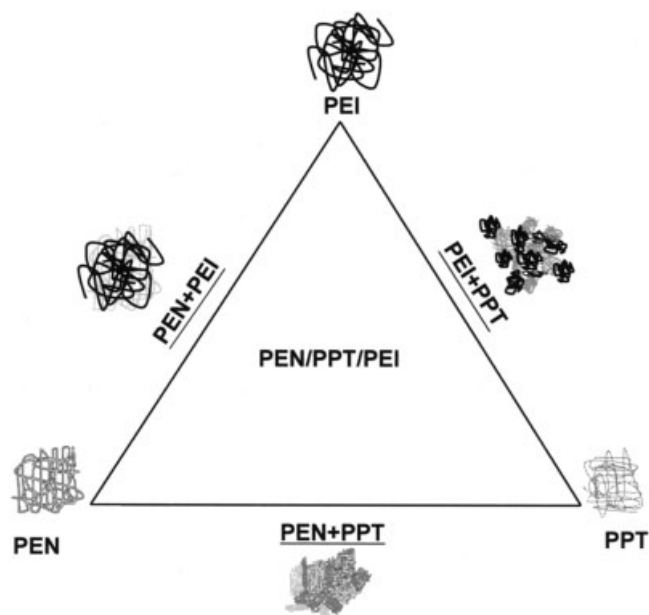
Scheme 1 Miscibility of binary blends in a ternary polymer blend.

methylene terephthalate) (PHT)/PEI blends exhibit phase heterogeneity. Notably, PET, PTT, PBT, PPT and PHT, which have 2, 3, 4, 5, and 6 methylene moieties, respectively, in their repeating units, are linear aromatic polyesters with similar chemical structures. The polymer–polymer interaction parameter (χ_{12}) between the aryl polyester and PEI in aryl polyester/PEI blends, increases with the number of methylene moieties in the repeating unit of the aryl polyester, changing the morphology from a homogeneous phase to a heterogeneous phase, indicating that more methylene moieties in the repeating unit of the aryl polyester weaken the interaction between the aryl polyester and PEI.[12] Blends of aryl polyester and PEN obtained by solvent precipitation are immiscible and, when the extent of transesterification reaches 50% of the completely randomized state independent of blend composition, the blends show a single glass-transition temperature between those of the starting polymers.[13–18] Given that the process is not completely understood, previous literature suggests three possible mechanisms: alcoholysis, acidolysis, or direct ester exchange.[15–17] Whatever be the mechanism at work, it is generally agreed that the interchange reactions first lead to the formation of block copolymers, and then random copolymers that promote the miscibility of the blend.[15] Studies of miscibility and transesterification in blends of polycarbonate (PC) and aryl polyester,[19,20] as well as PC and tetraglycidyl-4,4'-diaminodiphenylmethane (TGDDM) identified that transesterification plays an important role in these systems.[21]

Scheme 1 presents the miscibility of the three binary

pairs associated with three polymers. In the blends, PEN/PEI is miscible in any ratio and both PEN/PPT and PPT/PEI binary blends exhibit heterogeneous phases. Notably, although the blends of PPT with PEN were initially immiscible, annealing at a high temperature for a sufficiently long period caused the original two phases to merge into a single phase. This study investigates how the ternary polymer and binary blends differ in miscibility. As expected, transesterification reactions also occur between PEN and PPT in the ternary PEN/PPT/PEI blends that comprise two polyesters with different repeating structures. In this study, the effects of transesterification on the miscibility of ternary systems are studied by differential scanning calorimetry (DSC) and optical microscopy (OM). The relationship between crystallization and transesterification was also studied by wide angle X-ray diffraction (WAXD). The sequence distribution and degree of randomness of the copolyesters (ENPT), which are transesterification products of PEN/PPT, were studied using high-resolution nuclear magnetic resonance imaging (^{1}H-NMR).

EXPERIMENTAL

Materials

Poly(ethylene naphthalate) (PEN) was purchased from Aldrich (USA), with $M_w = 10,000$. Poly(pentamethylene terephthalate) (PPT) was synthesized in our laboratory ($M_w = 16,600$ and polydispersity index (M_w/M_n) = 1.54). Poly(ether imide) (PEI) was obtained from Polysciences (USA), with $M_w = 30,000$. The chemical structures of the repeating units of PEN, PTT, and PEI are as follows:
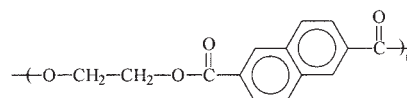
PEN
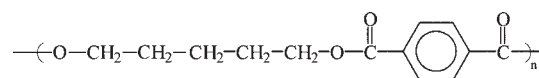
PPT
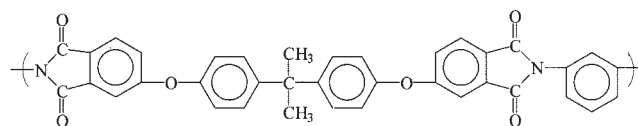
PEI

Coprecipitation was applied to produce ternary PEN/PPT/PEI blends. Polymers of various fractions were codissolved in dichloroacetic acid at 120°C to

yield a 4% (w/w) solution and then precipitated in an excess volume of methanol. The blends were washed with a large amount of hot water, and left to dry at 60°C for several days. Residual solvent was then removed from the blends after being left in a vacuum oven at 80°C for about 1 week.

Apparatus

The ^{1}H-NMR analysis of the blend was performed at room temperature by applying a Bruker AMX-400 NMR spectrometer operating at 400.13 MHz. The blend was dissolved in a 1/9 (v/v) mixture of deuterated trifluoroacetic acid (CF$_3$COOD)/deuterated chloroform (CDCl$_3$) solution. The central peak of CDCl$_3$ was assigned as 7.27 ppm with respect to tetramethylsilane (TMS) as the internal standard.

The thermal behaviors of blend samples were measured with a differential scanning calorimeter (Perkin–Elmer DSC-7) equipped with an intracooler. The experiments were performed in two consecutive scans under ambient environment of nitrogen gas at a flow rate of 20 mL/min. The glass-transition temperature (T_g), cold-crystallization temperature (T_c), and melting temperature (T_m) were each measured at 20°C/min after heat treatment at 300°C for a desired period of time. The obtained T_g values were taken as the onset of the glass transition (i.e., change in the specific heat) in the DSC thermograms.

A polarized-light optical microscope (POM) (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 two microglass slides, and then heated and gently pressed by hand to reduce film thickness for the microscopic heating stage (Linkam THMS-600 with a TP-92 temperature programmer).

The WAXD experiments were performed with a Shimadzu XRD-6000 X-ray diffractometer with Cu Kα X-rays at 40 kV and 30 mA current in the 2θ range of 5–35° with a step scanning of 2°/min. The blends encapsulated in the DSC cells were heat treated at 300°C for different time periods, then quickly transferred to the microscopic heating stage, and preheated to 200°C for 8 h to attain maximum crystallinity. The DSC cells were then opened and the crystallized blends were subjected to WAXD measurements.

RESULTS AND DISCUSSION

Phase behavior

In ternary PEN/PPT/PEI systems, blends were obtained by applying solution precipitation at room temperature to prevent transesterification during blend preparations. In the ternary blend, PEI is an amorphous polymer (T_g = 215.6°C), whereas PPT (T_m

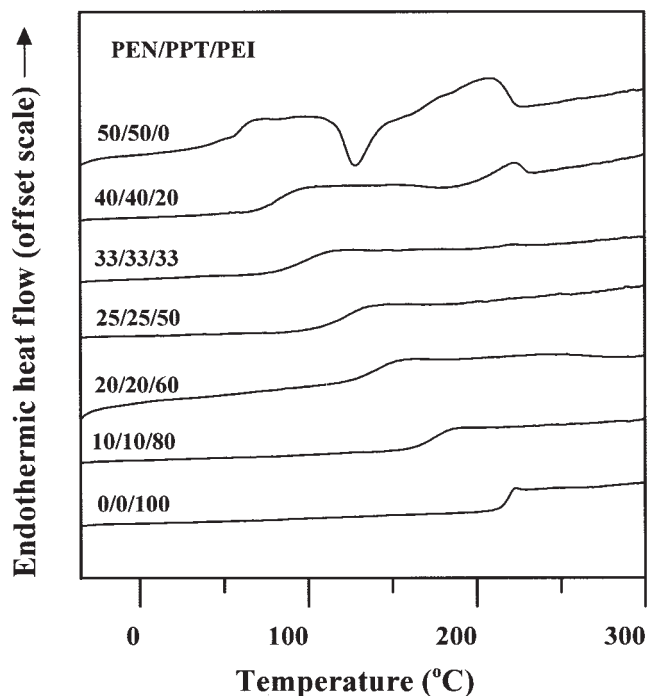**Figure 1** DSC traces for different compositions (weight ratio) of PEN/PPT/PEI blends heated at 300°C for 60 min.

= 128.0°C and T_g = 8.1°C) and PEN (T_m = 337.0°C and T_g = 117.0°C) are crystalline polymers. Figure 1 shows the DSC thermograms of PEN/PTT/PEI blends obtained by heating the quenched samples after melting at 300°C for 60 min. The increased annealing time virtually eliminated cold crystallization and melting. The thermal behavior revealed that the disruption of the chain periodicity inhibited the crystallization of PEN and PPT; a consequence of transesterification in PEN and PPT. In ternary blends, a single glass transition was observed; the glass transition range narrowed as the reaction time increased, suggesting that transesterification promoted miscibility. The transesterification caused morphological change from a heterogeneous phase to a homogeneous one.

Figure 2 shows the optical micrographs (A–F) of the coprecipitated PEN/PPT/PEI samples with five compositions, after being heated at 300°C for 1 min and 60 min. When the blends were heated at 300°C for 1 min, the PEN/PPT/PEI blends exhibited phase separation. For immiscible compositions, the phase domain sizes depended on the composition and decreased as the PEI weight fractions in the micrographs increased. Both PEN/PPT and PPT/PEI blends are immiscible for all compositions,[12] but PEN/PEI blends are miscible in all of the compositions.[5,6] Before transesterification, the ternary blends exhibited a heterogeneous phase. After the compositions had been heated to 300°C for 60 min, their morphologies were homogeneous, indicating that transesterification in PEN and
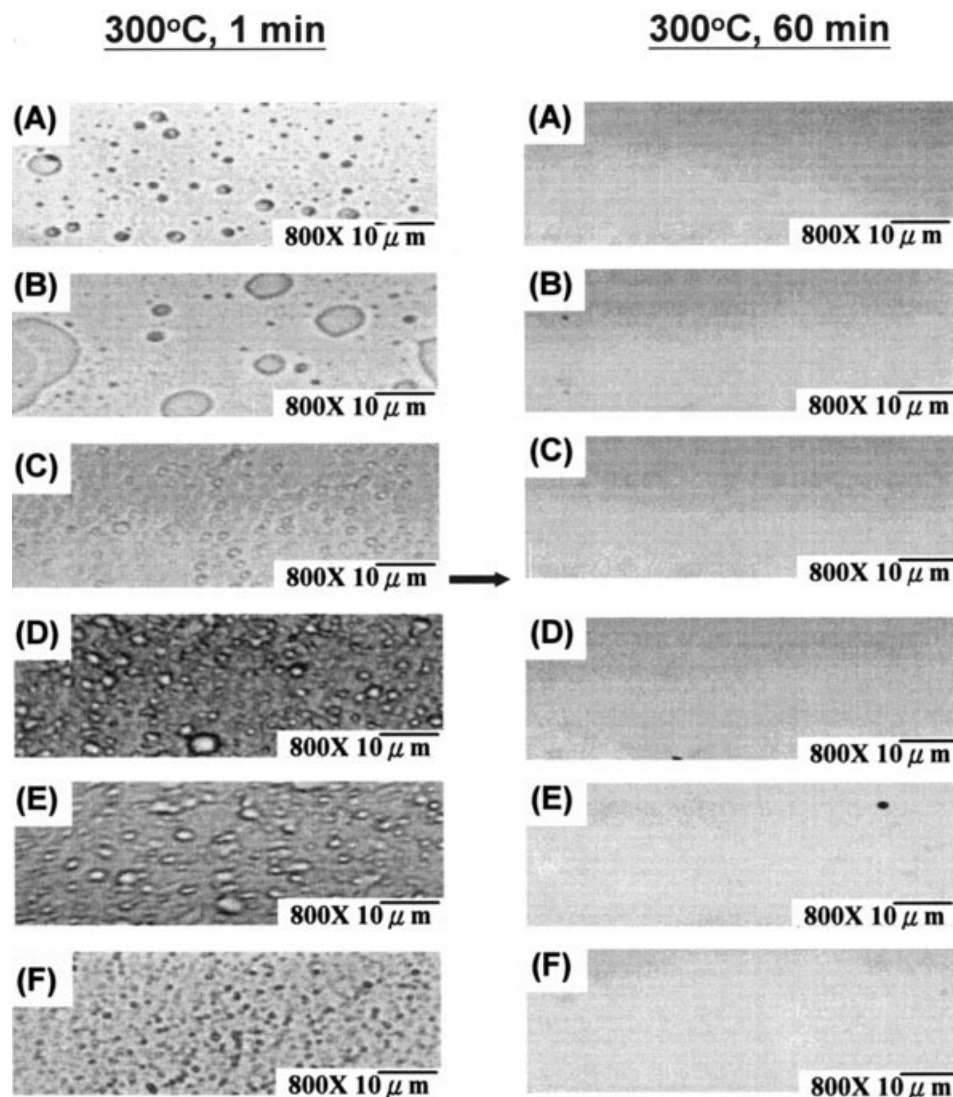
300°C, 1 min

300°C, 60 min

Figure 2 OM graphs for PEN/PPT/PEI blends of different compositions: (A) 50/50/0, (B) 40/40/20, (C) 33/33/33, (D) 25/25/50, (E) 20/20/60, (F) 10/10/80 (weight ratio).

PPT improved the miscibility of the PEN/PPT/PEI blends.

NMR characterization

The interchange reaction in the carbonyl group of PEN and PPT in the PEN/PPT/PEI blends changed the chemical shift, intensity of the methylene moieties, and naphthalate proton resonances in the copolyesters. The extent of the interchange of the blends was determined from the methylene moieties of the ^{1}H-NMR spectrum. Figure 3 shows the proton NMR spectra of the PEN/PPT/PEI blends following annealing for different periods at 300°C. The PEN peaked at around 4.86 ppm, whereas the peak for PPT was at ~4.44 ppm. In Figure 3, (a) shows the region of the NMR spectrum for a mixture of two homopolymers prepared in solution (no interchange reaction). At the

beginning of transesterification, all of the methylene moieties proton resonances (4.36–4.90 ppm) of the PEN/PPT copolyesters were split into multiplets because ethylene and pentamethylene units had six possible environments—A_1-B_1-A_1, A_2-B_1-A_1, A_2-B_1-A_2, A_1-B_2-A_1, A_1-B_2-A_2, and A_2-B_2-A_2, where A_1 and A_2 represent naphthalate and terephthalate units, respectively, and B_1 and B_2 represent ethylene units and pentamethylene units, respectively, as shown in Figure 3. In this figure, new ethylene proton signals, including A_2-B_1-A_1 and A_2-B_1-A_2, were generated by the substitution of a terephthalate unit for a naphthalate unit. Additionally, new pentamethylene proton signals, such as A_1-B_2-A_1 and A_1-B_2-A_2, were also identified. These were caused by the substitution of a naphthalate unit for a terephthalate unit. As PEN and PPT reacted, an increasing number of terephthalate-ethylene-naphthalate (A_2-B_1-A_1), terephthalate-ethylene-terephthalate
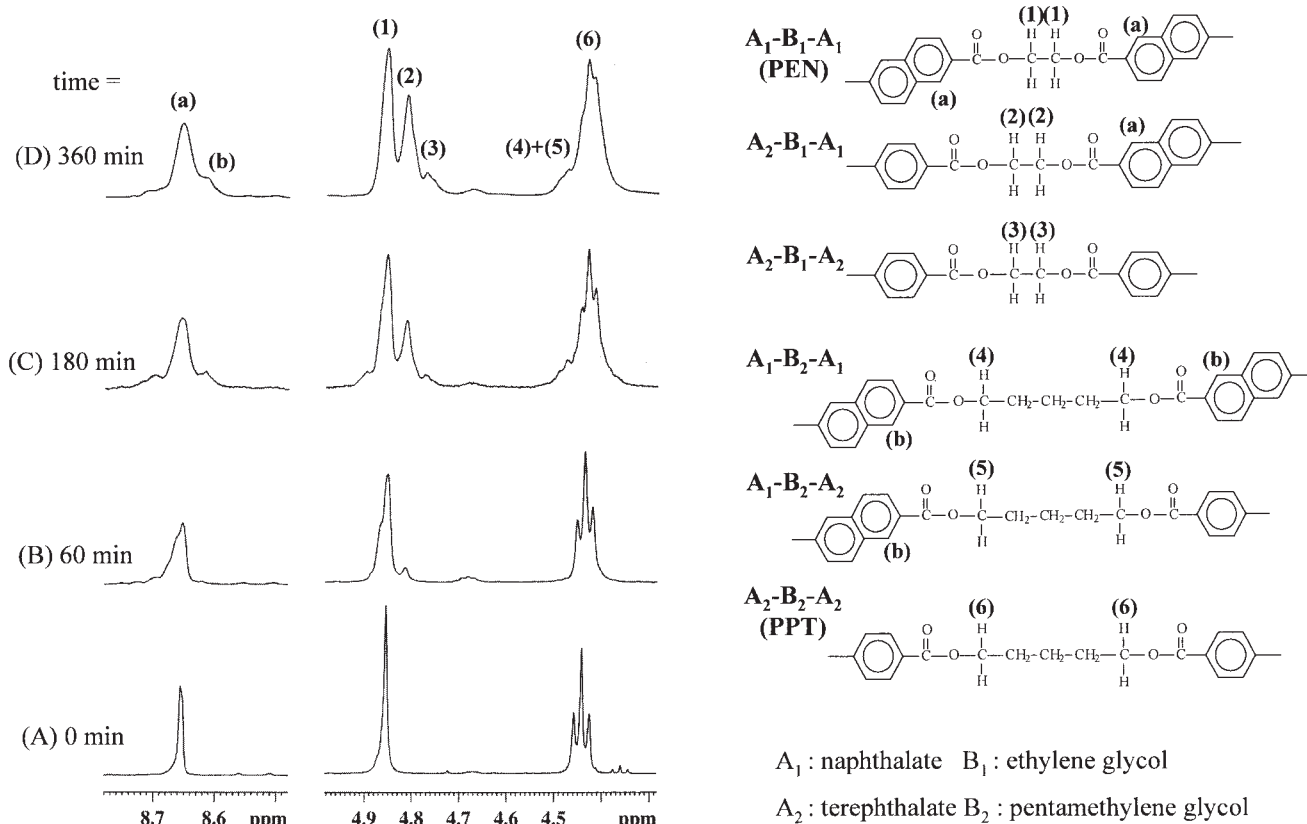
Figure 3 ^{1}H-NMR of PEN/PPT/PEI = 1/1/1 with assignment of the main peaks after different reaction times at 300°C.

(A_2-B_1-A_2), naphthalate-pentamethylene-naphthalate (A_1-B_2-A_1) and naphthalate-pentamethylene-terephthalate (A_1-B_2-A_2) residues were present in the blend; the concentration of PEN and PPT decreased with the reaction time. The ^{1}H-NMR signals from these units were at 4.81, 4.76, 4.49, and 4.47 ppm. They were easily differentiated from the resonance of the A_1-B_1-A_1 (4.67 ppm) and A_2-B_2-A_2 (4.44 ppm) sequences. Furthermore, altering the methylene moieties generated new proton resonance (8.61 ppm) signals for naphthalate units, including A_1-B_2-A_1 and A_1-B_2-A_2. Experimental results concerning the copolyesters revealed that the number of hetero units in the copolyesters had increased.

Analyzing sequence distribution

Transesterification in the PEN/PPT/PEI blends significantly involved in the formation of block or random copolyesters between PEN and PPT. The NMR data were used to determine the randomness factors and mean sequence lengths, as transesterification proceeds, of the terephthalate and naphthalate sequences in the copolymers.[17] The amplitude of these A_i-B_j-A_k signals was directly proportional to the mole fractions for triad sequences in the polymer. In this study, the chain ends are ignored in the calculation because only

copolycondensates produced in an exchange reaction between two linear polycondensates PEN and PTT exhibit such a high degree of polymerization. The mole fractions for naphthalate (F_N) and terephthalate (F_T) groups were given as the concentration ratios

$$F_N = A_{8.67}/(A_{1.93} + A_{8.67}) \quad (1)$$

$$F_T = A_{1.93}/(A_{1.93} + A_{8.67}) \quad (2)$$

where $A_{8.67}$ and $A_{1.93}$ represent the area under the characteristic peaks for naphthalate and pentamethylene glycol, respectively. The mole fraction of $F_{A_iB_jA_k}$ was calculated from the area of the characteristic peak between 4.3 and 4.9 ppm, respectively, and is defined as

$$F_{A_iB_jA_k} = [A_iB_jA_k]/\sum_{i,j,k=1}^{2} [A_iB_jA_k] \quad (3)$$

The probability of finding an A_2-B_1-A_k sequence in the copolyester can be expressed as

$$P_{A_2B_1A_k} = F_{A_2B_1A_k}/F_N \quad (4)$$

TABLE I
Sequence-Distribution Analysis of PEN/PPT/PEI=1/1/1 Heated at 300°C for Different Times

Time (min)	Composition molar fraction[a]		Fraction of dyads centered in the glycol unit[b]				Probability		Average sequence length		Degree of randomness (B)
	F_N	F_T	$F_{A_1B_1A_1}$	$F_{A_2B_1A_k}$	$F_{A_1B_3A_k}$	$F_{A_2B_2A_2}$	$P_{A_2B_1A_k}$	$P_{A_1B_2A_k}$	$L_{A_1B_1A_1}$	$L_{A_2B_2A_2}$	
0	0.461	0.539	0.461	0.000	0.000	0.539	0.000	0.000	—	—	0.000
60	0.462	0.538	0.423	0.043	0.012	0.522	0.093	0.022	10.764	45.249	0.115
180	0.472	0.528	0.283	0.185	0.063	0.469	0.392	0.120	2.548	8.326	0.513
360	0.499	0.501	0.278	0.238	0.055	0.429	0.477	0.110	2.100	9.132	0.587

[a] The molar fraction of PEI is not included.
[b] $F_{A_2B_1A_k} = F_{A_2B_1A_1} + F_{A_2B_1A_2} = F_{A_1B_2A_1} = F_{A_1B_2A_1} + F_{A_1B_1A_1}$
[c] F_N: mole fraction of naphthalate; F_T:T mole fraction of terephthalate.

and the probability of finding an A_1-B_2-A_k sequence in the copolyester is given by

$$P_{A_1B_2A_k} = F_{A_1B_2A_k}/F_T \qquad (5)$$

The degree of randomness, B, of a copolymer is defined as the sum of two probabilities.[22]

$$B = P_{A_2B_1A_k} + P_{A_1B_2A_k} \qquad (6)$$

$B = 0$ refers to a mixture of two homopolymers in the sample. Additionally, values for $B < 1$ indicate that the units tend to cluster in the blocks of each unit. For random copolyesters, B is unity; and B values between 1 and 2 represent the tendency of A_1 and A_2 to alternate around B_j. If $B = 2$, then the distribution of units alternate in the copolymers. The degree of randomness was interpreted as the content of the hetero sequence in the PEN/PPT blends divided by the corresponding content of the random copolymer with the same compositions of PEN and PTT. In this study, the degree of randomness was used as a parameter that indicates the extent of transesterification.[13,22] Moreover, the mean length of PEN sequence ($L_{A_1B_1A_2}$) in copolyester, is defined as[18,22]

$$L_{A_1B_1A_1} = 1/P_{A_2B_1A_k} \qquad (7)$$

The mean length of the PTT sequence ($L_{A_2B_2A_2}$) in copolyester, is defined as

$$L_{A_2B_2A_2} = 1/P_{A_1B_2A_k} \qquad (8)$$

Table I lists the molar fractions in the compositions, the fraction of triad sequences, the probability that the A_2-B_1-A_k and A_1-B_2-A_k sequences form in a copolyester, the mean sequence length of A_1-B_1-A_1 and A_2-B_2-A_2, and the degree of randomness of PEN/PTT/PEI = 1/1/1 heated at 300°C for various periods. The results for the copolyesters show that both the content of the hetero sequences ($F_{A_2B_1A_k}$) and ($F_{A_1B_2A_k}$), and the

probability of obtaining the A_2-B_1-A_k ($P_{A_2B_1A_k}$) and A_1-B_2-A_k sequences ($P_{A_1B_2A_k}$) rose with annealing time. The degree of transesterification increased with the annealing time. The mean sequence lengths of both PEN ($L_{A_1B_1A_1}$) and PPT ($L_{A_2B_2A_2}$) decreased sharply until the reaction had continued for 180 min. The randomness of samples also increased with the annealing time, finally reaching a value close to 0.59, which specifies the block distribution,[13,22] which is the tendency of A_1-B_1-A_1 and A_2-B_2-A_2 to dominate A_1-B_2-A_k and A_2-B_1-A_k units in the copolyesters. In Table I, the block lengths of the PEN/PPT block copolyesters revealed that although ($L_{A_1B_1A_1}$) and ($L_{A_2B_2A_2}$) decreased with the onset of heating, both ($L_{A_1B_1A_1}$) and ($L_{A_2B_2A_2}$) decreased slightly during the final period of annealing. The variations in block lengths in each unit were closely related to the change in the chemical structure, particularly those caused by intermolecular chain reactions that are associated with the transesterification reactions of PEN and PPT.

Transesterification analysis

Figure 4 shows how annealing time influences the glass-transition behavior of the blend with compositions PEN/PPT/PEI = 1/1/1. Initially, the thermograms showed that the PPT-rich region had a low crystallization temperature ($T_{c,PPT}$) and a low melting temperature ($T_{m,PPT}$), and the PEN-rich region had a relatively high crystallization temperature ($T_{c,PEN}$) and a high melting temperature ($T_{m,PEN}$). Additionally, the blends exhibited two T_g's, which were denoted $T_{g,PPT\text{-rich region}}$ and $T_{g,PEN\text{-rich region}}$ for PPT and PEN, respectively. During transesterification, T_g of the PPT-rich regions increased with reaction time, and that of the PEN-rich regions decreased with the reaction time. At time of $t = 60$ min, the two T_g's of the blend converged into a single T_g, because transesterification occurred between PEN and PPT. After 60 min, T_g of the blends remained constant and independent of the annealing time. During the later stages of the
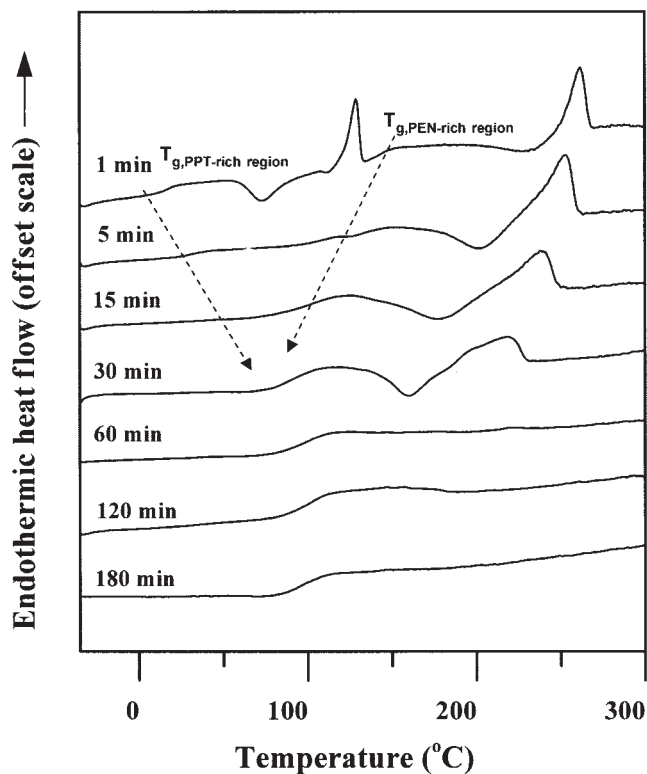
Figure 4 DSC traces of PEN/PPT/PEI = 1/1/1 after heated at 300°C for different times.

Figure 5 Soluble fraction of PEN/PPT/PEI = 1/1/1 as a function of reaction time at 300°C (solvent: chloroform).

reaction, the breadth of the glass-transition range remained constant and independent of the reaction time. These results reveal that transesterification increased the miscibility of the ternary blends. Restated, the miscibility of the ternary blends increased with the concentration of the product, ENPT copolymer, which was formed by the copolymerization of PEN and PPT. Therefore, T_g remained constant and the glass-transition range was narrow when the blends were heated at 300°C for over 60 min. In the copolyester generated by transesterification, the single T_g was related to the degree of randomness, 0.12, and the mean sequence lengths of PEN and PPT repeating units, which were 10.76 and 45.25, respectively. Furthermore, sequences of PEN and PPT became shorter as concentration of the ENPT copolymer increased, suppressing the crystallization of PEN and PPT in the ternary blends.

In the solubility test, chloroform was an effective solvent for both PPT and PEI but not for PEN. The mixtures of various blending compositions were exposed to a constant temperature, 300°C, for various intervals. The reacted samples were extracted using chloroform, and the residual solids and the extracted solution were both separately maintained for thermal analysis. Figure 5 shows the solubility of PEN/PPT/PEI = 1/1/1 blends as a function of reaction time when they were heated to 300°C for various periods. Initially, the solubility of the annealing samples de-
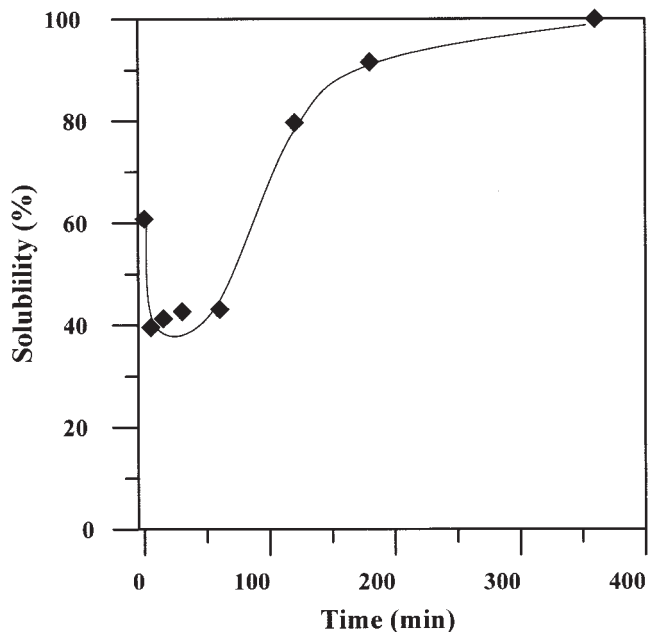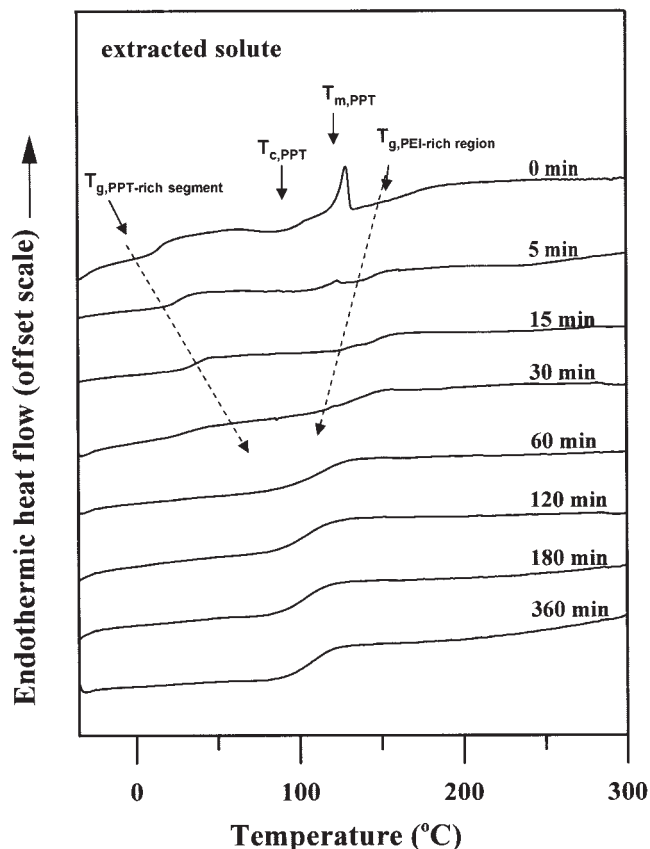

Figure 6 DSC traces for the soluble portion of PEN/PPT/PEI = 1/1/1 extracted with chloroform, heated at 300°C for different times.

creased until the reaction time reached 15 min. After 60 min, the solubility of the blends increased quickly with annealing time. The NMR analysis revealed that the mean sequence length of PEN ($L_{A_1B_1A_1}$) and PPT ($L_{A_2B_2A_2}$) declined at the beginning of heating, and the variation of the block length in each unit was strongly related to the change in the chemical structure. In Figure 5, although the solubility of the blends decreased with an increasing PEN sequence length in the copolyester, the copolyester with an extremely random unit and the increase in the PPT sequence length increased the solubility. This finding suggests that the transesterification yielded a block copolymer with homo segments, and then, formed a random copolymer with hetero segments in the ternary blends. Such behaviors reveal not only that the transesterification of PEN and PPT occurred at 300°C, but also that the blend system became randomized as the transesterification progressed.

DSC was used to determine the thermal transition temperatures and further elucidate the physical difference between the extracted solute and the solid residue. Figure 6 shows thermograms of the extracted solute of PEN/PPT/PEI = 1/1/1 heated at 300°C for various periods. The extracted solute comprises a mixture of PEI, which is the product of transesterification (ENPT) with a short PEN segment in the molecular backbone, and possibly some unreacted PPT. At time of $t = 0$ min, the extracted solute exhibited two glass-transition temperatures ($T_{g,\text{PPT-rich segment}}$ and $T_{g,\text{PEI}}$), cold-crystallization exotherms, and melting endotherms. In the early stages of transesterification, T_g of the PPT-rich regions increased with the reaction time, and T_g of the PEI-rich regions decreased with the reaction time. In the extracted solute, the amount of the ENPT copolymer with a short PPT segment in the molecular backbone increased, and the amount of unreacted PPT decreased, as the degree of transesterification increased with the annealing time. Finally, the two T_g's of the blends converged into a single value because the produced PEN/PPT copolymers (ENPT) were miscible with PEI at time of $t = 60$ min. Beyond 60 min, T_g of the extracted solute remained constant and independent of annealing time. These findings reveal that transesterification shortened the sequence lengths of both PEN and PPT, and increased the miscibility of the ternary blends. Restated, the miscibility of the extracted solute increased with the concentration of the product, ENPT copolymer, which was produced by the copolymerization of PEN and PPT. Accordingly, a consistent T_g and a narrow glass-transition range appeared when the blends were heated at 300°C for over 60 min. Additionally, the sequence length of PPT was shortened as the concentration of the ENPT copolymer increased, inhibiting the crystallization of PPT in the extracted solute.
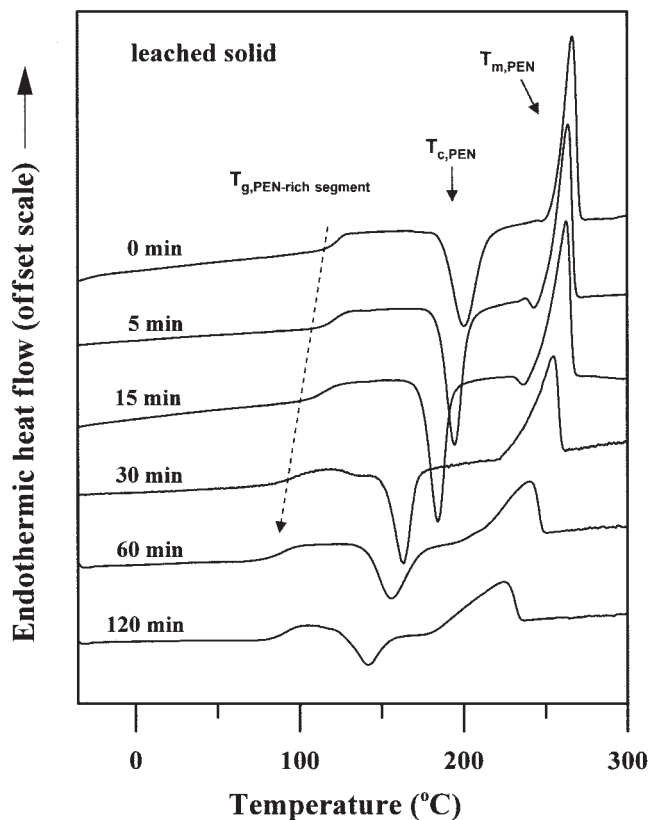

Figure 7 DSC traces for the insoluble portion of PEN/PPT/PEI = 1/1/1 extracted with chloroform, heated at 300°C for different times.

Figure 7 plots the thermograms of the leached solid when PEN/PPT/PEI = 1/1/1 blend was heated at 300°C for various periods. Theoretically, the insoluble portion of the blends comprises a mixture of the product of transesterification (ENPT), with a long PEN segment in the molecular backbone, and possibly some unreacted PEN. The leached solid exhibited a single glass-transition temperature ($T_{g,\text{PEN-rich segment}}$), cold-crystallization exotherms ($T_{c,\text{PEN}}$), and melting endotherms ($T_{m,\text{PEN}}$). In the thermograms, all of the thermal transition temperatures decreased as the reaction proceeded, indicating that transesterification shortened the sequence lengths of PEN, which also inhibited the crystallization of PEN in the copolyester.

Crystallization behavior

Figure 8 shows the WAXD diffractograms of annealed samples (PEN/PPT/PEI = 1/1/1), which were heat-treated at 300°C for various periods, and then crystallized at 200°C for 8 h to maximize the crystallization. The peak from the PEN homopolymer at a diffraction angle of 15.5° was assigned to the (010) plane, while peaks at diffraction angles of 23.4° and 26.8° corresponded to (100) and (110) planes, respectively.[23] Additionally, the WAXD patterns of crystals for PEN
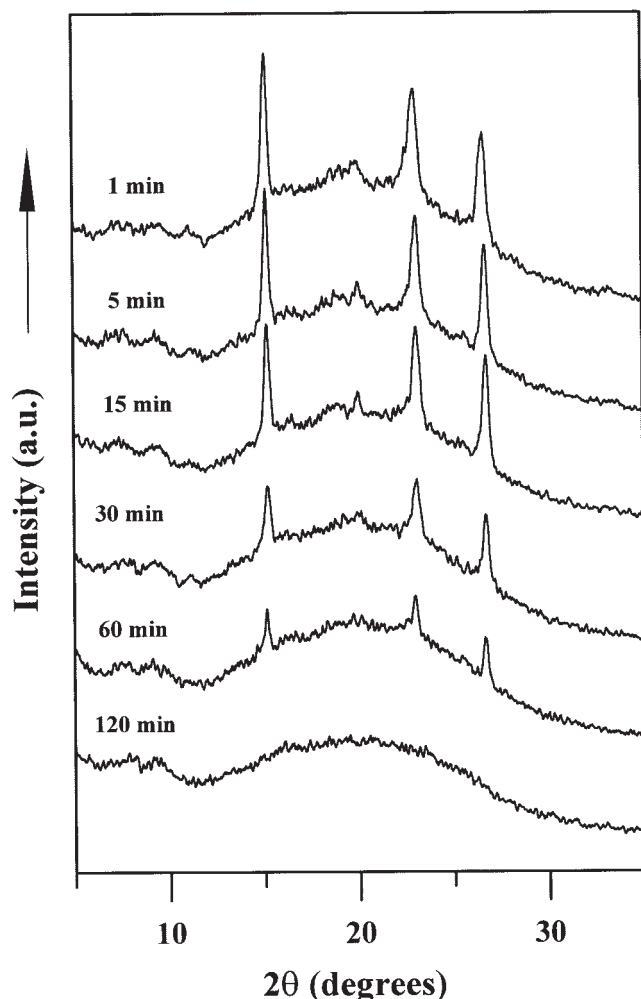
Figure 8 WAXD diffractograms for the PEN/PTT/PEI = 1/1/1 blends heated at 300°C for different times (isothermal crystallization at 200°C for 8 h).

depended on the melting temperature.[24] In this study, melting the blends at 300°C yielded the α form of PEN crystallized at 280°C. The scattering patterns of the PEN/PPT/PEI = 1/1/1 blends exhibited characteristics of both PEN and PPT when the peak positions of the two polymers were mixed.[25,26] No shift in the peak position was observed from blends crystallized at 280°C. The arrangement of the unit cells remained the same as that in the original PEN and PPT sequences, and cocrystallization did not occur in the PEN/PPT/PEI blends. The peaks in the diffractograms for PEN were clearly identifiable from the ternary blends, until the annealing time reached 120 min. The experimental results in Table I reveal not only that the sequence lengths of PEN and PPT were short, but also that the sequence distribution of PEN/PPT copolymer became more random as the reaction progressed, reducing the crystallization of PEN and PPT in the PEN/PPT/PEI = 1/1/1 blend. The numerical analysis showed that the critical degree of randomness for crystallization

was ~0.46 at a reaction time of $t = 120$ min. However, crystallization was inhibited when the transesterification reaction progressed to such an extent that the sequence length of both PEN and PPT were too short. This result reveals that the length of homo segments in the polymer chains decreased and the structural irregularity disturbed the crystal formation as the exchange reaction progressed.

CONCLUSIONS

Two polyesters, PEN and PPT in the PEN/PPT/PEI blends, formed copolymers via transesterification when the samples were annealed at 300°C. Before heat treatment, PEN and PPT were immiscible. Additionally, transesterification of PEN and PPT increased the miscibility of the PEN/PPT/PEI blends that were annealed at 300°C for over 60 min. The extent of transesterification of PEN and PPT seemed to be related to a threshold value of miscibility for PEN/PPT/PEI blends in the exchange reaction. The degrees of randomness and mean sequence lengths were determined from the ^{1}H-NMR data. These results revealed that the final product was a random copolymer of the two polyesters. In the ternary blends, partial compositions of the ternary blends were immiscible; but following a sufficient reaction time, a single T_g was obtained, indicating the homogeneous phase in the ternary systems. The initially immiscible blends became miscible after a critical amount of transesterification occurred; specifically, this homogenization occurred when the randomness factor was 0.12. This value did not completely correspond to random copolymer formation, but suggested that the mean sequence lengths of the PEN and PPT repeating units in the copolyester were 10.76 and 45.25, respectively. In the PEN/PPT/PEI blends, the miscibility of the ternary systems was improved not only by the interaction of van der Waals forces among the three components, but also by the transesterification in PEN and PPT.

References

1. Su, C. C.; Lin, J. H.; Woo, E. M. Polym Int 2003, 52, 1209.
2. Kwei, T. K.; Frisch, H. L.; Radigan, V. V. S. Macromolecules 1977, 10, 157.
3. Yokouchi, M.; Sakakibara, Y.; Chatani, Y.; Tadokoro, H.; Tanaka, T.; Yoda, K. Macromolecules 1976, 9, 266.
4. Wang, Z. G.; Hsiao, B. S.; Sauer, B. B.; Kampert, W. G. Polymer 1999, 40, 4615.
5. Chen, H. L.; Hwang, J. C.; Wang, R. C. Polymer 1998, 39, 6067.
6. Cakmak, M.; Kim, J. C. J Appl Polym Sci 1997, 65, 2059.
7. Martinez, J. M.; Eguiazabal, J. I.; Nazabal, J. J Appl Polym Sci 1993, 48, 935.
8. Chen, H. L. Macromolecules 1995, 28, 2845.
9. Harris, J. E.; Robeson, L. M. J Appl Polym Sci 1988, 35, 1877.
10. Wu, P. L.; Woo, E. M. J Polym Sci Polym Phys Ed 2002, 40, 1571.
11. Woo, E. M.; Yau, S. N. Macromolecules 1997, 30, 3626.

12. Su, C. C.; Lin, J. H. Colloid Polym Sci 2004, 283, 182.
13. Mackintosh, A. R.; Liggat, J. J. J Appl Polym Sci 2004, 92, 2791.
14. Pilati, F.; Marianucci, E.; Berti, J. J Appl Polym Sci 1985, 30, 1267.
15. Stewart, M. E.; Cox, A. J.; Naylor, D. M. Polymer 1993, 34, 4060.
16. Collins, S.; Kenwright, A. M.; Pawson, C.; Peace, S. K.; Richards, R. W.; MacDonald, W. A.; Mills, P. Macromolecules 2000, 33, 2974.
17. Devaux, J.; Godard, P.; Mercier, J. P. J Polym Sci Polym Phys Ed 1982, 20, 1875.
18. Jun, H. W.; Chae, S. H.; Park, S. S.; Myung, H. S.; Im, S. S. Polymer 1999, 40, 1473.
19. Wahrmund, D. C.; Paul, D. R.; Barlow T. W. J Appl Polym Sci 1978, 22, 2155.
20. Karavia, V. K.; Koulouri, E. G.; Kallitsis, J. K. J Macromol Sci Pure Appl Chem 2002, 39, 527.
21. Su, C. C.; Woo, E. M. Macromolecules 1995, 28, 6779.
22. Yamadera, R.; Murano, N. J Polym Sci 1967, 5, 2259.
23. Park, S. S.; Kim, I. K.; Im, S. S. Polymer 1996, 37, 2165.
24. Buchner, S.; Wiswe, D.; Zachmann, H. G. Polymer 1989, 30, 480.
25. Su, C. C.; Shih, C. K. Colloid Polym Sci 2005, 283, 1278.
26. Su, C. C.; Woo, E. M.; Shih, C. K. Colloid Polym Sci 2005, 284, 66.