

A Study on Reaction-Induced Miscibility of Poly(trimethylene terephthalate)/Polycarbonate Blends

Indose Aravind,[†] Klaus-Jochen Eichhorn,[‡] Hartmut Komber,[‡] Dieter Jehnichen,[‡] N. E. Zafeiropoulos,[‡] Kyung Hyun Ahn,[§] Yves Grohens,^{||} Manfred Stamm,[‡] and Sabu Thomas^{*,†}

School of Chemical Sciences, Mahatma Gandhi University, Priyadarshini Hills P.O., Kottayam, Kerala, India 686 560; Leibniz Institute of Polymer Research Dresden, Germany; School of Chemical and Biological Engineering, Seoul National University, Seoul 151-744, Korea; and University of De-Bretagne Sud, Lorient, France

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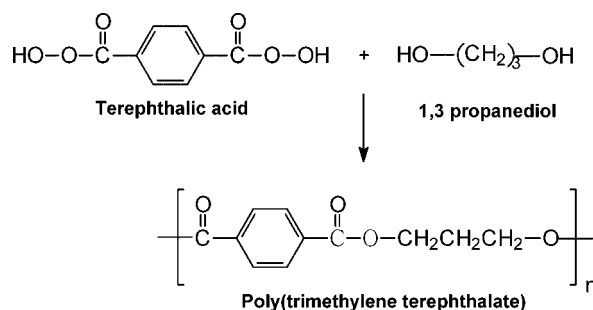
The effect of annealing on the miscibility and phase behavior of Sorona {poly(trimethylene terephthalate), PTT} and bisphenol A polycarbonate (PC) blends was examined. These blends exhibited heterogeneous phase-separated morphology and two well-spaced glass transition temperatures (T_g s) indicating immiscibility. The Sorona/PC blends were thermally annealed at 260 °C for different times to induce various extents of transreactions between the two polymers. After annealing at high temperature the original two T_g s of blends were found to merge into one single T_g , exhibiting a homogeneous morphology. It is interesting to note that upon extended annealing the original semicrystalline morphology transformed into an amorphous nature. This is attributed to chemical transreactions between the PTT and PC chain segments as evidenced with FTIR, DSC, DMA, ¹H NMR, and WAXS measurements. A new characteristic aryl C—O—C vibration band present at 1070 cm⁻¹ in the FTIR spectra of the annealed blends indicated the formation of an aromatic polyester structure due to the transreactions between PTT and PC. The sequence structures of the produced copolyesters were determined by a NMR triad analysis, which showed that the randomness increased with time of heating. WAXS analysis confirmed that the PTT/PC blends completely lost their crystallinity when annealed at 260 °C for a period of 120 min or longer, indicating the formation of fully random copolyesters. A random copolymer formed as a result of the transreactions between PTT and PC serves as a compatibilizer at the beginning, and upon extended annealing this became the main species of the system which is finally transformed to a homogeneous and amorphous phase.

1. Introduction

Because of their potential to exhibit tailor-made properties, polymer blends continue to attract much attention in academia and industry. Blends of two different polymers are not always miscible or compatible. Among the blends studied, aromatic polyesters represent a major class of engineering plastics having excellent properties with a large variety of applications and the possible transesterification reactions that they can possibly undergo in certain environments. As a consequence, it can strongly enhance the applications of homopolyesters. It is known that temperature can have a thermodynamic effect on phase behavior of blends owing to the variation of free energy of mixing. For polyesters blends (or some polyamides), temperature effects on phase behavior can be more complex than just variation of free energy. Transreactions can induce variation in chemical structures of the polymer constituents in blends. If one is capable of controlling the extent of the interchange reactions, miscible blends as well as tailored block and/or random copolyesters can be formed with desirable properties. The phase behavior and miscibility in poly(ethylene terephthalate) (PET)/polycarbonate (PC) and poly(butylene terephthalate) (PBT)/PC blends have been reported. Several examples of such transreactions in polyester blends have been reported, including, e.g., poly(trimethylene terephthalate) (PTT),^{1,2} poly(butylene terephthalate) (PBT),^{3,4} poly(ethylene terephthalate) (PET), polycarbonate (PC), polyarylate (PAR), and poly(ethylene 2,6-naphthalate) (PEN).^{5–14} Devaux et al.¹⁵ have pointed out that transesterification could take place in the temperature range used for melt blending, and the observed T_g changes could be accounted for by copolymer formation rather than purely thermodynamics modifications.

There is a growing urgency to develop bio-based materials as replacements/substitutes of fossil fuel-based materials. A new

SCHEME 1: Preparation of Poly(trimethylene terephthalate)



* Corresponding author. E-mail: sabuchathukulam@yahoo.co.uk or sabut552001@yahoo.com.

[†] Mahatma Gandhi University.

[‡] Leibniz Institute of Polymer Research.

[§] Seoul National University.

^{||} University of De-Bretagne Sud.

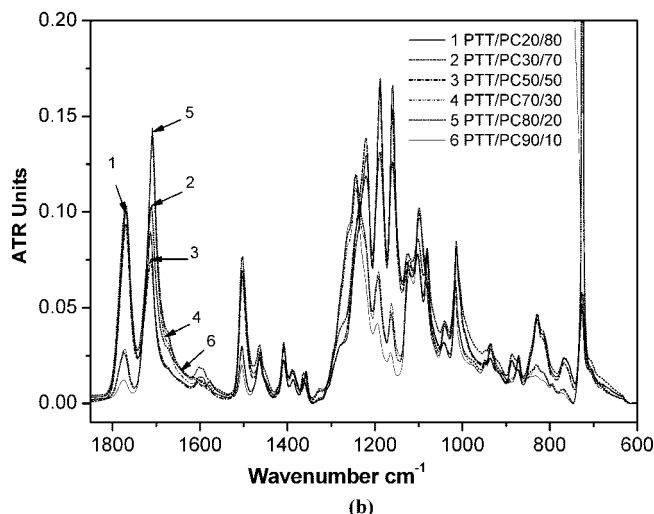
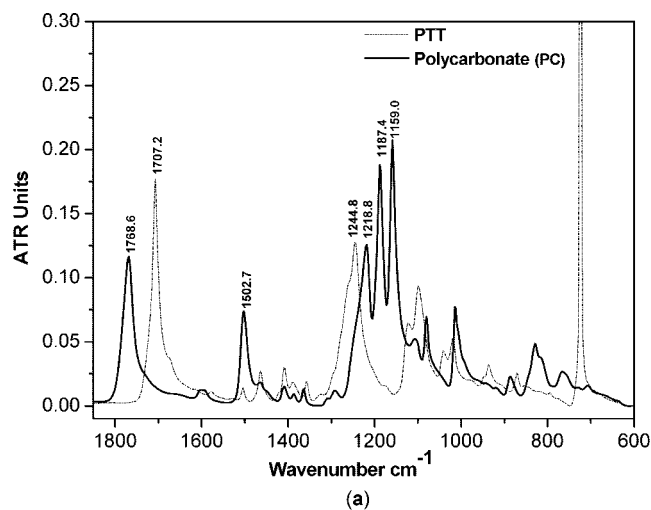


Figure 1. (a) Complete mid-IR spectra of neat PTT and PC. (b) Complete mid-IR spectra of PTT/PC blends of different composition.

aromatic polyester, poly(trimethylene terephthalate) (PTT), has been commercialized by DuPont under the trade name Sorona which is prepared by the melt condensation polymerization of 1,3-propanediol (derived from renewable corn sugar) with either terephthalic acid or dimethyl terephthalate, as shown in Scheme 1. Its mechanical properties are comparable to those of PET and PBT; its crystal structure and thermal properties have been studied, and some studies on PTT-based blends were conducted.^{16–22} Poly(ether imide) (PEI) and poly(ethylene-*co*-cyclohexane 1,4-dimethanol terephthalate) (PETG) are miscible counterparts reported for PTT.^{23–25} The blends of PTT with immiscible counterparts such as polystyrene (PS) and polyamide-12 (PA12) were investigated.^{26,27} More recently, miscibility and phase behavior of blends of PTT with bisphenol A polycarbonate (PC) were studied. The solution-cast PTT/PC blends are inherently immiscible,²⁸ and after annealing at 260 °C, the blends could become miscible thanks to the transesterification reaction. According to Yavari et al.,²⁹ PTT/PC blends are partially miscible, and after annealing at 300 °C for 10 min the blends changed to a miscible state through a transesterification reaction. From these investigations, it can be concluded that transesterification plays an important role in controlling the properties of PTT/PC blends. Therefore, the effect of annealing on the transesterification and various properties of PTT/PC blends are of paramount importance and should be investigated. In the present

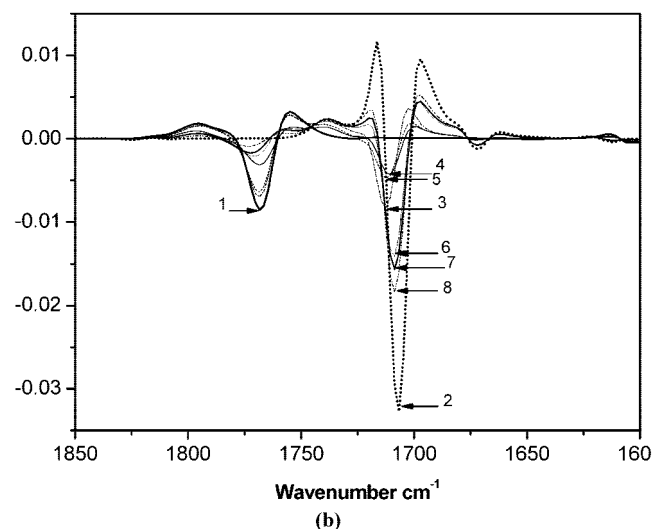
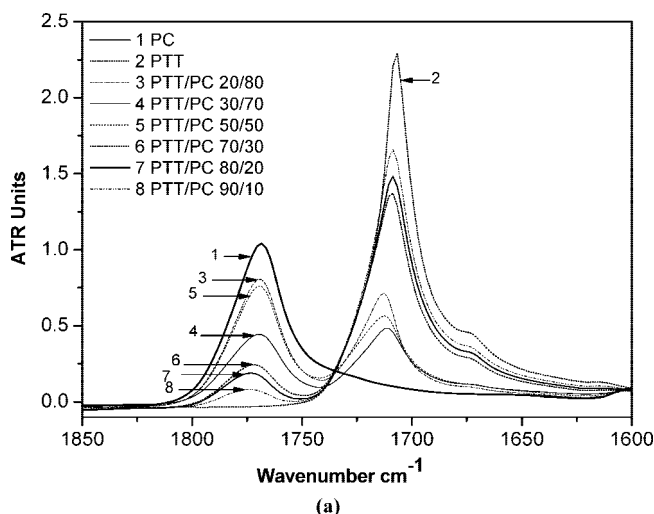


Figure 2. (a) Evaluation of the normalized carbonyl region (1850–1600 cm^{-1}) of PTT/PC blend. (b) Second derivative of carbonyl region which indicate the dependence of PTT content on the position of PC carbonyl ($\text{C}=\text{O}$) stretch.

study, melt-mixed Sorona/PC blends with different compositions were prepared through the melt mixing technique, and the effect of annealing on the extents of transesterification and the apparent changes in miscibility, phase morphology, and thermal properties of the blends were evaluated. For this purpose, the PTT/PC blends were annealed at 260 °C for different times (0–180 min) to induce various extents of reactions between the two polymers.

2. Experimental Section

2.1. Materials and Blends Preparation. Sorona (PTT) in pellet form was supplied by DuPont, USA. The polycarbonate (PC) used was a product from LG Dow Chemical Co. with a melt flow rate of 30 g/10 min (ASTM D1238, 300 °C/1.2 kg). Blends were prepared in a Haake mixer at 260 °C for 5 min with a rotor speed of 60 rpm. Before melt mixing, PTT and PC were dried under vacuum at 105 °C for at least 16 h to minimize the possibility of hydrolysis during the mixing.

All the annealing experiments were done inside the vacuum oven at 260 °C in which the sample is placed between two metallic parallel plates which are also the same temperature as the oven. Therefore, the sample attains the annealing temperature very fast from the surface of the metal plates. Also, the

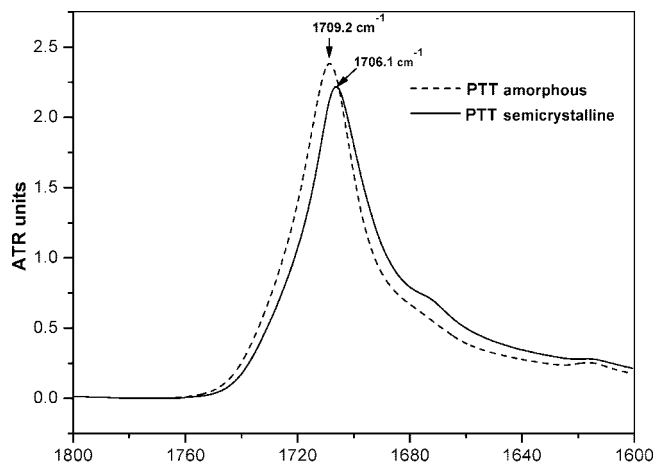


Figure 3. Evaluation of the normalized carbonyl region (1800–1600 cm^{-1}) of semicrystalline and highly amorphous PTT samples.

measurements started only after giving an incubation period of ~ 1 min for each sample to attain the temperature.

2.2. Characterizations. The phase morphology of the samples was investigated by a scanning electron microscope (JEOL JSM-5410). Fractured surfaces of the blended samples were prepared, and the PC phase was etched out with dichloromethane to clearly observe the phase morphology.

FTIR investigations were carried out by the ATR FTIR technique with a “Golden Gate” unit (diamond internal reflection element), Bruker IFS 66v/S spectrometer; mid-IR spectra were measured (4000–600 cm^{-1}).

^1H NMR measurements were carried out on a Bruker DRX 500 spectrometer operating at 500.13 MHz for ^1H . The samples were completely dissolved in CDCl_3 /trifluoroacetic acid- d_1 (TFA- d) and measured immediately at 30 $^\circ\text{C}$. The spectra were referenced on residual CHCl_3 ($\delta(^1\text{H}) = 7.26$ ppm). The signal intensities of the terephthalate-centered triads were evaluated to characterize the copolyester structure.

The melting and crystallization behaviors of the blends were determined using a Mettler 820 DSC thermal analyzer. The first heating was done from room temperature to 270 $^\circ\text{C}$ at a rate of 10 K/min followed by isothermal heating for 5 min, and first cooling and second heating were performed at 10 K/min in a nitrogen atmosphere.

The WAXS instrument was a Bruker AXS (Karlsruhe) with copper K α radiation (40 kV and 30 mA) and a wavelength of 1.542 \AA in transmission by area detection system HiStar/GADDS and accumulation time of 600 s. The scanning angle ranged from $2\theta = 1.5^\circ$ to 40° as $I(2\theta)$ plots by sectoral integration with steps of $\Delta 2\theta = 0.1^\circ$.

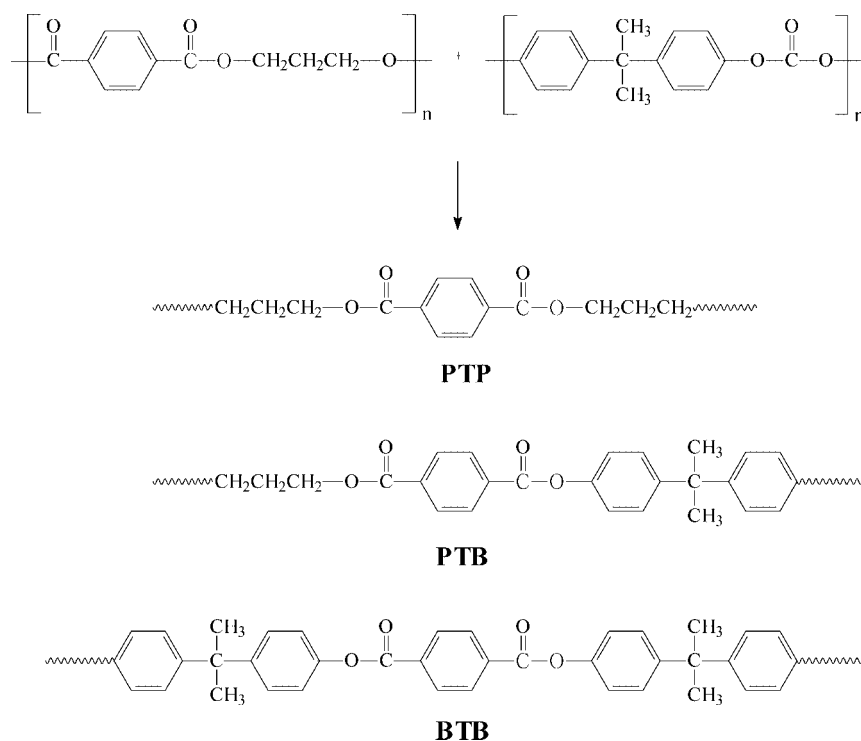
Dynamic mechanical analysis of the annealed blends was performed on a DMA 2980 analyzer from TA Instruments from 30 to 180 $^\circ\text{C}$ at a heating rate of 1 K/min in tension film mode with 1 Hz frequency.

3. Results and Discussion

3.1. FTIR Spectroscopy. Blends of different composition mixed in a Haake mixer, unannealed and annealed at 260 $^\circ\text{C}$ for different times (0–180 min), were analyzed, and spectral regions of interest were chosen, zoomed, and evaluated.

Unannealed Blends. Figure 1a shows the complete mid-IR spectra of neat polymers, PTT (Sorona) and PC, and Figure 1b shows the spectra of Sorona/PC blends of different composition. As expected, new bands indicating copolymer structures of transesterification products were not found in the spectra of unannealed blends. But an influence of both polymer components on phase behavior of the blends could be detected using special spectral data treatment: Since PTT itself is semicrystalline, carbonyl groups exist in the well-ordered crystalline as well as in the disordered amorphous phase. They absorb at slightly different wavenumbers due to the influence of the supermolecular interactions on $\text{C}=\text{O}$ stretching vibrations. In the crystalline phase strong interactions lead to absorption at lower wavenumbers; in the amorphous phase there are more “free” or less interacting carbonyls, which absorb at higher

SCHEME 2: Expected Chemical Structures of the Transesterification Products of PTT and PC



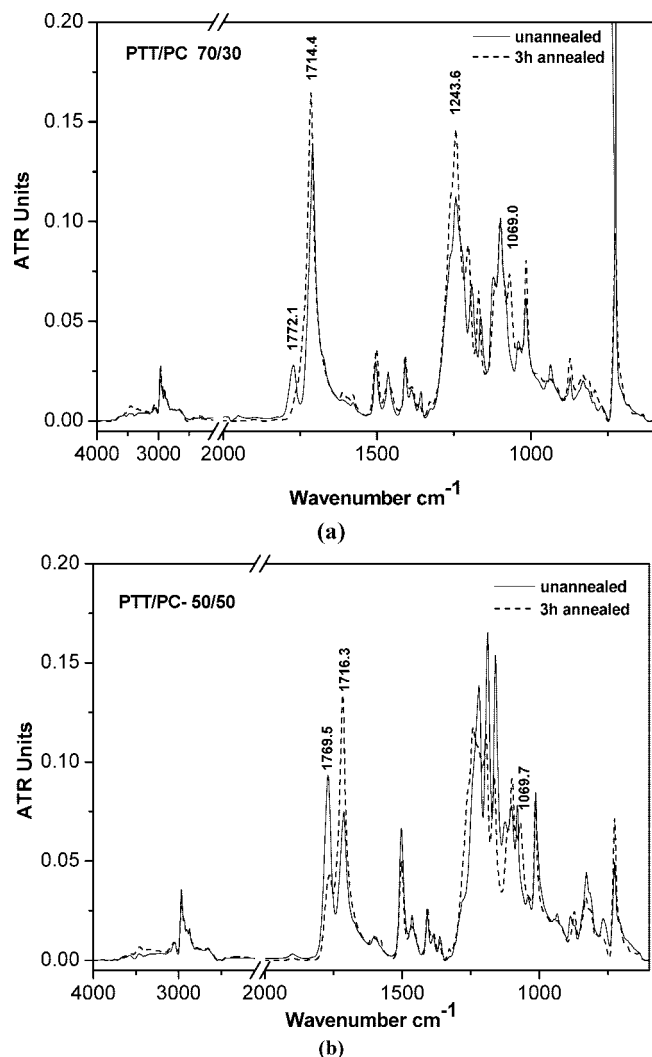


Figure 4. (a) Complete mid-IR spectra of unannealed and 3 h annealed PTT/PC 70/30 blends. (b) 50/50 blends.

wavenumbers. The polymer chains of the added amorphous PC can disturb especially the ordered crystalline PTT in the blend; that means that some of the ordered polyester chains were transformed into more disordered ones which can be followed by detailed analysis of the carbonyl spectral region. Evaluation of the normalized carbonyl region $1850\text{--}1600\text{ cm}^{-1}$ is represented in Figure 2a and its second derivative in Figure 2b.

The dependence of the position of PC carbonyl ($\text{C}=\text{O}$) stretch on PTT content is shown in Figure 2b. It can be seen that there is a shift from 1768 cm^{-1} (pure PC) to 1773 cm^{-1} (90% PTT), indicating an increasing interruption of the PC–PC interaction of the PC chains in the blends due to the added PTT chains (dilution effect), and as a result more and more “free” PC carbonyls were formed. Also, the position of PTT carbonyl ($\text{C}=\text{O}$) stretch shows a shift in dependence on PC content from 1707 cm^{-1} (pure PTT) to 1712 cm^{-1} (80% PC), indicating an increasing interruption of the PTT–PTT interaction due to the PC chains. Detailed analysis of the structured asymmetric shape of the PTT carbonyl stretching band ($1745\text{--}1650\text{ cm}^{-1}$) to assign carbonyls in well-ordered (e.g., in crystalline phase) and less ordered state (e.g., in amorphous phase or “free” carbonyl groups) was done using the OPUS curve fit program by peak-fitting with Lorentz–Gauss curves. As a result, three PTT individual band components could be separated: (1) $\text{C}=\text{O}$ stretch around 1674 cm^{-1} (ester groups with strong molecular interac-

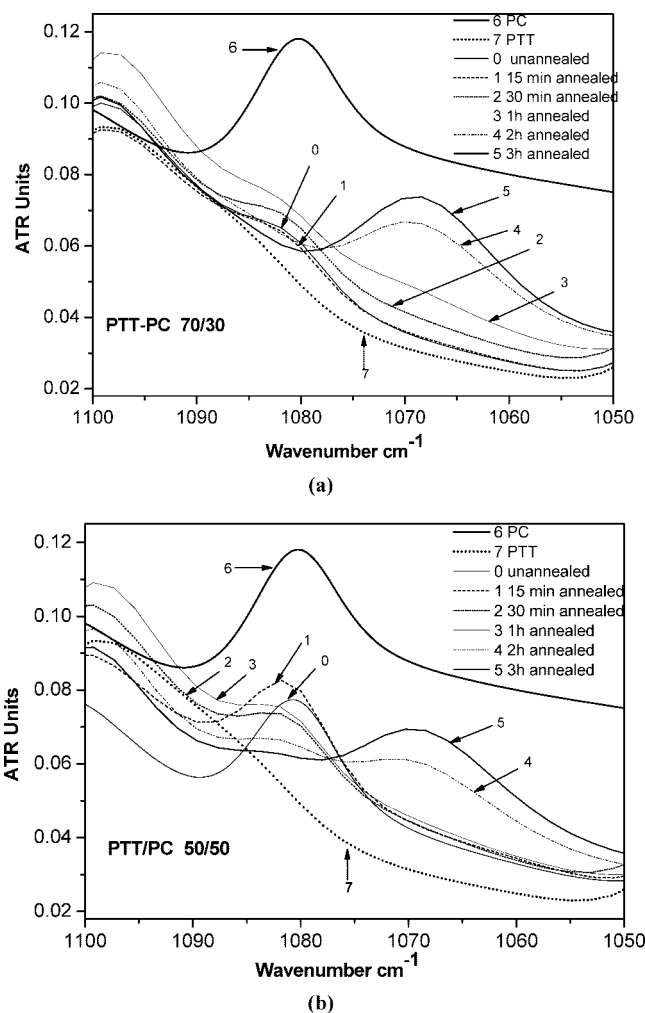


Figure 5. (a) Formation of new band at $\sim 1070\text{ cm}^{-1}$ ($\text{C}=\text{O}$ stretching vibration) with increasing annealing time for 70/30 blends indicates the presence of fully aromatic ester structure of the transesterification product. (b) Formation of new band at $\sim 1070\text{ cm}^{-1}$ ($\text{C}=\text{O}$ stretching vibration) with increasing annealing time for 50/50 blends.

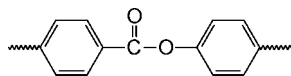
tion in ordered regions of PTT-rich blends); (2) $\text{C}=\text{O}$ stretch around 1710 cm^{-1} (ester groups with lower (medium) molecular interaction in PC-rich blends); (3) $\text{C}=\text{O}$ stretch around 1725 cm^{-1} (ester groups with low molecular interaction in unordered regions).

In order to understand whether the band shift in the carbonyl region is really the only contribution of a change in crystallinity, we prepared a highly amorphous sample by melting of a dry pure PTT sample (thin foil, heated for 30 s at $260\text{ }^{\circ}\text{C}$, which means above $T_m \sim 230\text{ }^{\circ}\text{C}$) and quenching the melt in liquid nitrogen. The FTIR-ATR spectrum of the quenched sample was reordered immediately and compared with that of the semicrystalline PTT material as shown in Figure 3. Indeed, we found the $\text{C}=\text{O}$ stretching vibration of the less ordered/less interacting groups in the spectrum of the quenched, highly amorphous PTT sample at higher wavenumbers (only one band maximum at 1709 cm^{-1}) in comparison to the initial semicrystalline PTT (band maximum at 1706 cm^{-1} with a shoulder near 1674 cm^{-1}). That means changes in crystallinity or, more generally, changes in intermolecular interactions are responsible for the band shift and change in band shape; i.e., the band shifts observed in the spectra of unannealed blends are only ascribed to modification in the level of the intermolecular interactions in dependence on

composition, and it will be seen that annealing yield more complex spectral effects.

Annealed Blends. The PTT/PC 70/30 and 50/50 blends were annealed for different times after processing to initiate remarkable transesterification. Scheme 2 shows the expected chemical structures of the transesterification products of PTT and PC. This mechanism shows that the carbonyl groups of PTT are exchanged with the carbonate groups in PC upon annealing at high temperatures, and the exchange leads to formation of possibly a new copolymer that is comprised of randomly spaced segments detached from the PC and PTT chains. ATR spectra of samples at all annealing times were measured. An annealing time of 5 min gives no detectable transesterification which means no spectral changes when compared to the spectra of unannealed blend samples. So, these spectra serve as initial ones for the evaluation of the subsequent annealing steps. The most significant spectral changes can be seen at annealing time of 3 h. The complete mid-IR spectra of annealed (3 h) and unannealed PTT/PC 70/30 and 50/50 blends are shown in Figure 4a,b.

The new band present at 1070 cm^{-1} (C–O–C stretching vibration) for the annealed blends beside the PTT and PC bands indicates the formation of the fully aromatic ester structure of the transesterification product, i.e., COO linked to two phenyl groups on each side as shown below (see also PTB and BTB in Scheme 2). Figure 5a,b shows the formation of this band with increasing annealing time.



At the same time the intensity of the PC band at 1080 cm^{-1} decrease because of the consumption of aromatic carbonate groups. It seems that there is no remarkable transesterification up to 60 min annealing time. Such an “induction period” was also found by NMR (see section 3.2).

Again, the important carbonyl spectral range was evaluated in more detail. For that, difference spectra were calculated as follows: Difference spectrum = (spectrum of blend sample annealed for 3 h) – (spectrum of blend sample annealed for 5 min).

In Figures 6a (70/30 blend) and 6b (50/50 blend) these difference spectra are shown together with the two blend spectra used for subtraction procedure. The annealing effects (transesterifications) are discussed for both blend compositions, but they are more pronounced in the 70/30 blend.

There is a shift of the ester carbonyl band (C=O stretch) from 1709 to 1714 cm^{-1} (in 70/30 blend) or 1712 to 1716 cm^{-1} (in 50/50 blend) connected with an intensity increase; the small band at 1674 cm^{-1} disappeared. That generates a positive band in the difference spectra at 1718 cm^{-1} and negative ones at 1705 and 1674 cm^{-1} . These features demonstrate a strong increase of the number of less ordered ester segments in the annealed sample (1718 cm^{-1}) which is related to a corresponding dramatic decrease of ordered ester segments (1705 and 1674 cm^{-1}). A new high-frequency shoulder at 1739 cm^{-1} band of the annealed samples is better seen in the difference spectrum, which indicates the formation of the new C=O stretch in the ester linkage of the produced fully aromatic ester structure of transesterification product. The shoulder at 1760 cm^{-1} in the difference spectra is coming from the C=O stretch of the carbonyl groups in the carbonate linkage of aliphatic carbonate structures of transesterification product. Nevertheless, the decrease of the carbonyl

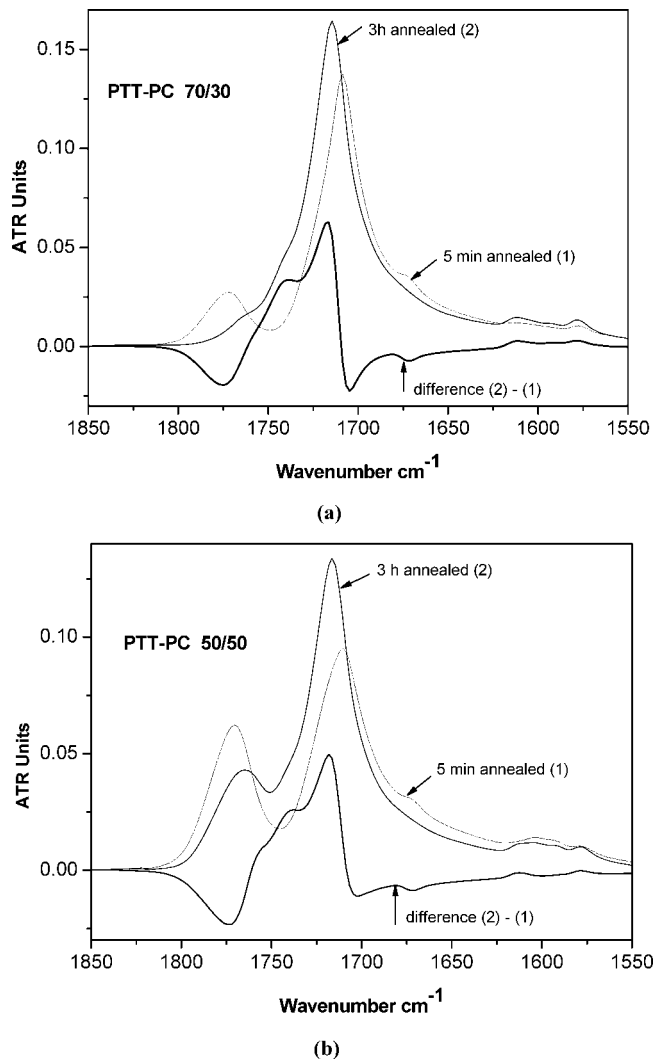
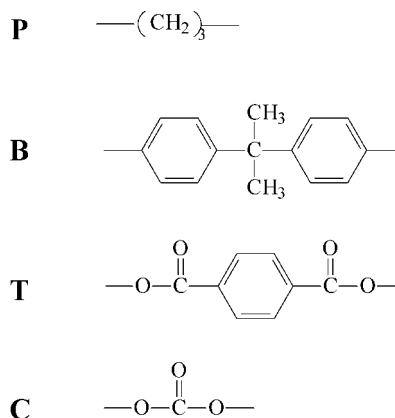


Figure 6. (a) Difference spectra indicating the annealing effects on carbonyl spectral range of PTT/PC 70/30 blend. (b) Difference spectra of PTT/PC 50/50 blend.

SCHEME 3: Components in the Exchange Reaction between PTT and PC



band at 1775 cm^{-1} of the carbonate unit of the PC component in the 3 h annealed blends (gives negative band in the difference spectra) demonstrates the consumption of initial PC aromatic carbonate groups due to the transesterification.

3.2. ^1H NMR Analysis. The progress of transesterification reactions can be well followed and quantified by NMR spectroscopy. In principle, the exchange reactions in Sorona/

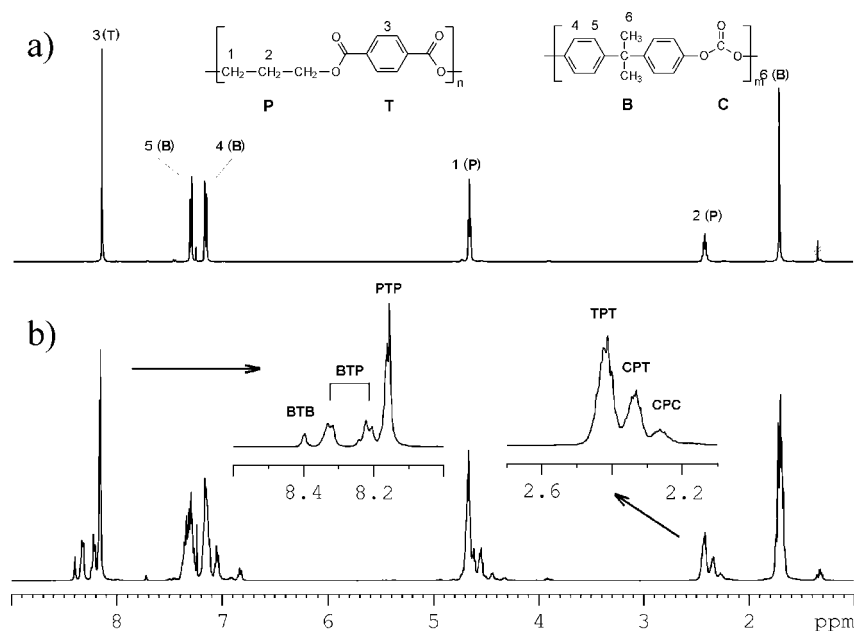


Figure 7. ^1H NMR spectra of a PTT/PC 50/50 blend after 5 min (a) and 180 min (b) annealing at 260 $^{\circ}\text{C}$ (solvent: $\text{CDCl}_3/\text{TFA-d}$ 1:1 v/v).

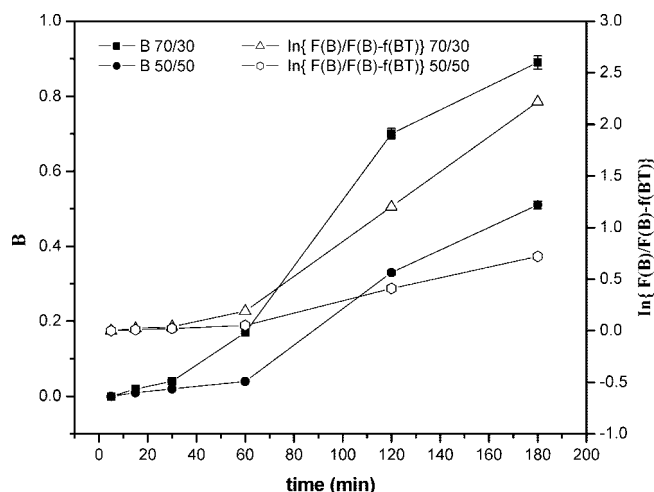


Figure 8. Time dependence randomization of 70/30 and 50/50 blends.

PC blends are the same like in PBT/PC blends intensively studied by Devaux et al.,¹⁵ except that the aliphatic component is propylene instead of butylene. Starting from PTT with the components propylene (P) and terephthalate (T) in a (PT)_n chain and PC with the components bisphenol A (B) and carbonate (C) in a (BC)_m chain, the exchange reactions will generate a four-component polycondensate containing the components in a polymer structure with a certain degree of randomness (Scheme 3).

This process results in characteristic changes in the ^1H NMR spectra²⁹ (Figure 7a,b) because, e.g., terephthalate originally bonded to two propylene units in a PTP triad appears after transesterification with PC under exchange of one propylene unit by a bisphenol A unit in a BTP triad and after a second exchange in a BTB triad. These three triads can be well distinguished in the ^1H NMR spectrum (Figure 7b), and the progress of transesterification is reflected in their ratio. The second inset in Figure 7b shows the signals of the central methylene group of the P unit which can be located in TPT, CPT, or CPC triads after transesterification. Because of higher accuracy, the integral values of terephthalate signals were used

TABLE 1: Relative Triads and Dyads Contents f Determined from the ^1H NMR Spectra of Two PTT/PC Blends after Different Annealing Times at 260 $^{\circ}\text{C}$ and Calculated Degrees of Randomness B and Number-Average Length of PT Sequences L_{PT}

time [min]	f_{PTP}^a [%]	f_{BTP}^a [%]	f_{BTB}^a [%]	$f_{\text{PT}}^{a,b}$ [%]	$f_{\text{BT}}^{a,b}$ [%]	B^a	L_{PT}
PTT/PC 50/50: $F_{\text{P}} = F_{\text{T}} = 0.552$ and $F_{\text{B}} = F_{\text{C}} = 0.448$							
5	100	0.0	0.0	100	0.0	0.0	
15	99.0	1.0	0.0	99.5	0.5	0.01	200
30	98.0	2.0	0.0	99.0	1.0	0.02	100
60	95.5	4.5	0.0	98.0	2.0	0.04	50
120	72.5	25.0	2.5	85.0	15.0	0.33	6.7
180	58.5	36.5	5.0	77.0	23.0	0.51	4.3
c	30.47	49.46	20.07	55.2	44.8	1.0	2.23
PTT/PC 70/30: $F_{\text{P}} = F_{\text{T}} = 0.742$ and $F_{\text{B}} = F_{\text{C}} = 0.258$							
5	100	0.0	0.0	100	0.0	0.0	
15	99.0	1.0	0.0	99.5	0.5	0.02	200
30	98.0	2.0	0.0	99.0	1.0	0.04	100
60	91.5	8.0	0.5	95.5	4.5	0.17	22.2
120	66.5	30.5	3.0	82.0	18.0	0.70	5.60
180	58.5	36.5	5.0	77.0	23.0	0.89	4.30
c	55.06	38.28	6.66	74.2	25.8	1.0	3.88

^a Estimated absolute errors: $\Delta f = \pm 1\%$; $\Delta B = \pm 0.02$. ^b $f_{\text{PT}} = f_{\text{PTP}} + 0.5f_{\text{BTP}}$; $f_{\text{BT}} = f_{\text{BTB}} + 0.5f_{\text{BTP}}$. ^c Theoretical values for the statistical four-component polyester.

to describe the segmental sequence structures of the copolyesters produced by transesterification applying the statistical model developed by Devaux et al.^{15a} Table 1 summarizes the relative contents f of the terephthalate centered units and T-containing dyads for the PTT/PC 70/30 and 50/50 blends upon annealing at 260 $^{\circ}\text{C}$ for various times from 5 to 180 min. The theoretical values for the statistical copolyester of the same composition are also included in the table. Comparing the compositions at 180 min annealing time with the calculated composition of the corresponding random four-component condensates, it is obvious that the progress in transesterification is higher for the PTT/PC 70/30 blend due to the higher molar excess of PTT. This is in agreement with the IR results (see Figures 5 and 6). Devaux et al. have used a degree of randomness B which is associated with the distribution of monomer units in the copolyester. A

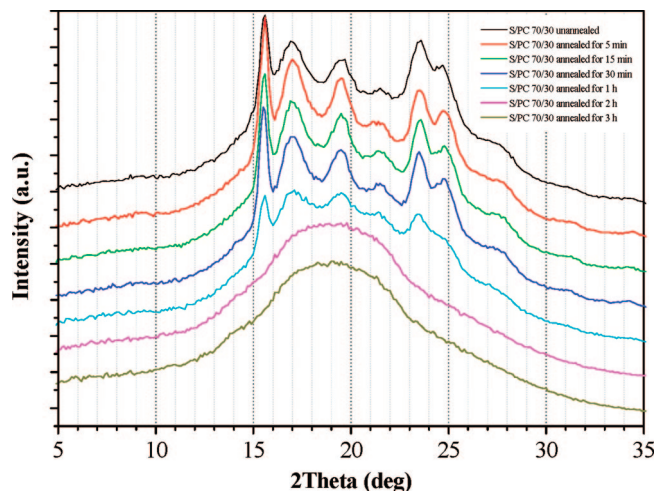


Figure 9. WAXS patterns for the PTT/PC 70/30 blends annealed at 260 °C for different times (0–180 min).

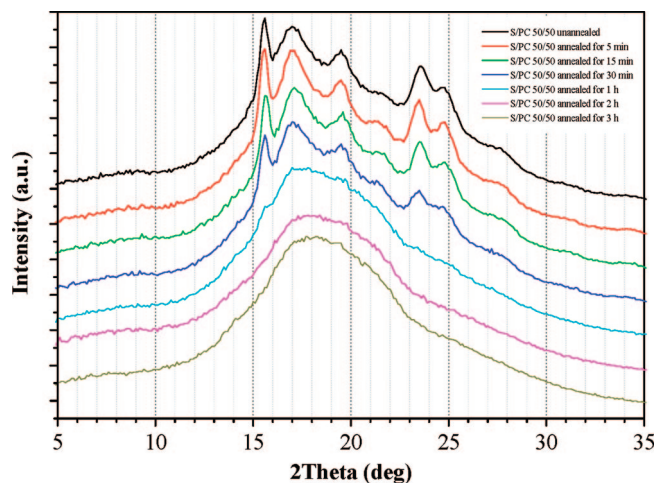


Figure 10. WAXS patterns for the PTT/PC 50/50 blends annealed at 260 °C for different times (0–180 min).

value of $B = 0$ corresponds to the mixture of the two polycondensates, whereas $B = 1$ is characteristic of a random polymer. Here, values between both limits indicate increasing transesterification. B can be calculated from the dyad mole fraction, e.g., $F_{BT} = f_{BT}F_T$, according to the equation

$$B = F_{BT}/(F_P F_B) \quad (1)$$

with $F_P (= F_T)$ and $F_B (= F_C)$ are the mole fractions of propylene and bisphenol A units ($F_P + F_B = 1$).

A further parameter, the number-average sequence length X , gives an impression about the shortening of the initial homopolymer chains, $(PT)_n$ and $(BC)_m$, by the random transesterifications with the second one. From the 1H NMR spectra, only the shortening of $(PT)_n$ can be calculated according to the equation

$$L_{PT} = F_{PT}/F_{BT} + 1 \quad (2)$$

Both B and L_{PT} are given in Table 1 for the annealing series. Additionally, Table 2 and Figure 8 illustrates the time-dependence randomization. It is obvious that the transesterification starts after an induction period of about 30–45 min. This becomes more clear from a plot of $\ln[F_B/(F_B - f_{BT})]$ vs

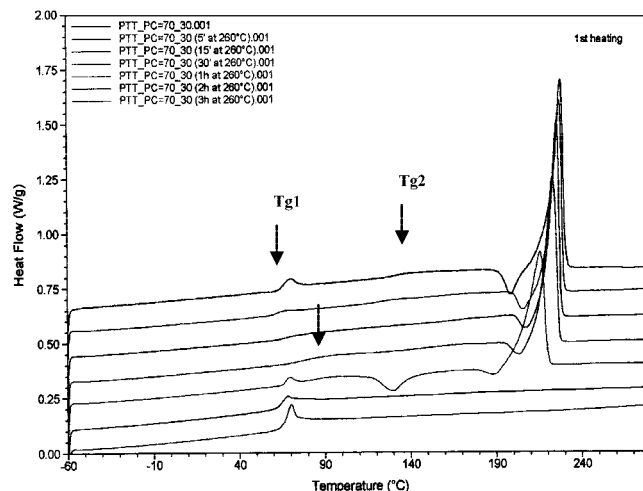


Figure 11. DSC thermograms of the PTT/PC 70/30 blend annealed at 260 °C (0–180 min).

annealing time, which gives the *apparent* transesterification constant k_2 as slope.^{15d} Again, an induction period appears for both blends followed by the expected linear dependence which gives a higher k_2 value for the PTT/PC 70/30 blend. Because k_2 depends on the concentration of catalysts used in the polyester synthesis,^{15d} it can be assumed that the higher PTT content also causes the higher transesterification rate for the 70/30 blend.

3.3. Wide-Angle X-ray Scattering. The WAXS patterns for the blends PTT/PC 70/30 and 50/50 annealed at 260 °C for different times (0–180 min) are shown in Figures 9 and 10, respectively. Both systems showed the semicrystalline behavior corresponding to three subphases—crystalline PTT, amorphous PTT, and amorphous PC—due to the immiscibility of the blend partner. In the case of unannealed 70/30 blends, the intensity of crystalline diffraction peaks is nearly the same as that of the neat PTT. As the annealing time increased in steps from 5 to 180 min, the peak intensity decreases gradually, indicating reduction in crystallinity of the PTT to different degrees. The PTT/PC 70/30 blend annealed for 1 h shows the minimum PTT crystallinity and when it was annealed for 2 and 3 h gives only an amorphous halo, indicating the complete absence of crystallinity. Thus, WAXS data showed reduced peak intensities upon annealing at 260 °C from 5 to 180 min. The amorphous halo of PTT was found out for crystallinity calculation. The background was adapted considering the air scattering in the scattering region around $\sim 8^\circ$ in 2θ . Therefore, the relative ordering parameter α_X (“crystallinity”) calculated using the equation $\alpha_X = I_{cr}/(I_{cr} + I_a)$ based on peak-area method (ratio of relevant crystalline scattering to total scattering, integral method in the range $2\theta = 5^\circ$ – 36°) with applying an amorphous scattering curve. The results obtained here are the overall crystallinities assuming $I_{cr} = I_{cr(PTT)}$ and $I_a = I_{a(PTT)} + I_{a(PC)}$. The calculated crystallinity data for 70/30 and 50/50 blends are shown in Table 3. As expected, at the beginning of the annealing procedure, i.e. at 5 min, a small, but non-negligible, improvement of the crystalline structure and/or increasing of the crystallinity α_X was found, caused by healing effects of the ordered phase.

WAXS analysis of PTT/PC 50/50 blends also showed the same behavior. PTT diffraction peaks are clearly seen in the WAXS pattern of unannealed blends. For annealed blends, as the annealing time increased in steps from 5 to 180 min, the PTT crystallinity is decreased to different degrees. The PTT/PC 50/50 blend annealed for 1 h shows the minimum PTT crystallinity and when it is annealed for 2 and 3 h gives only

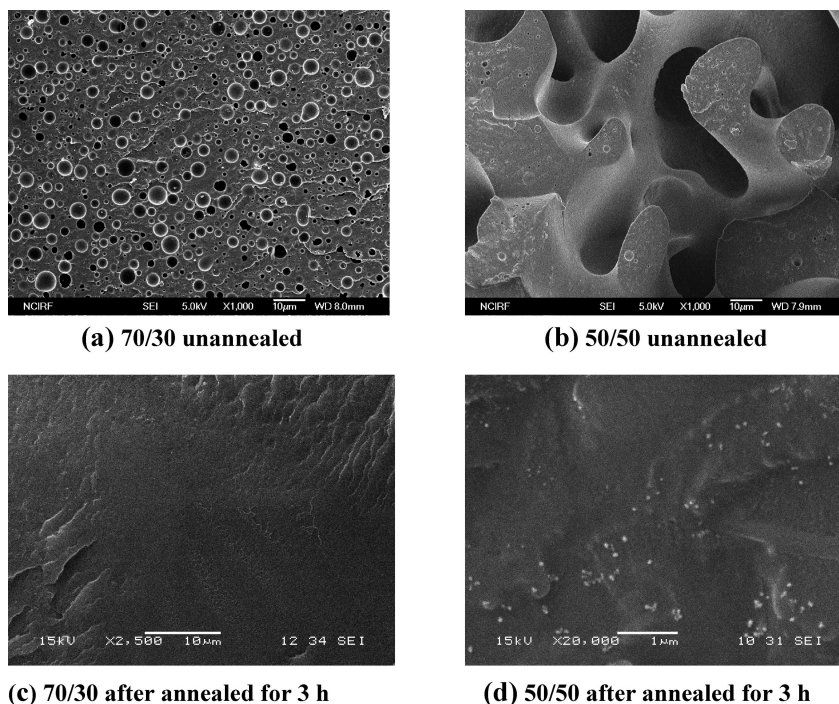


Figure 12. SEM pictures of annealed and unannealed blends of PTT/PC 70/30 and 50/50: (a) 70/30 unannealed, (b) 50/50 unannealed, (c) 70/30 annealed for 3 h, and (d) 50/50 annealed for 3 h.

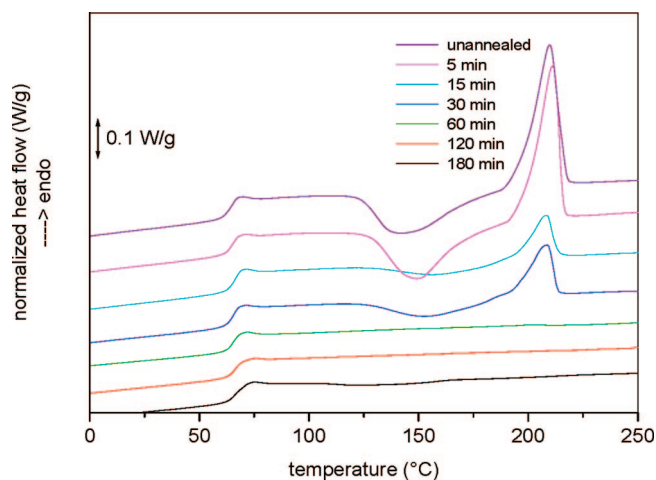


Figure 13. Second heating scans of the PTT/PC 70/30 blends after first heat treatment.

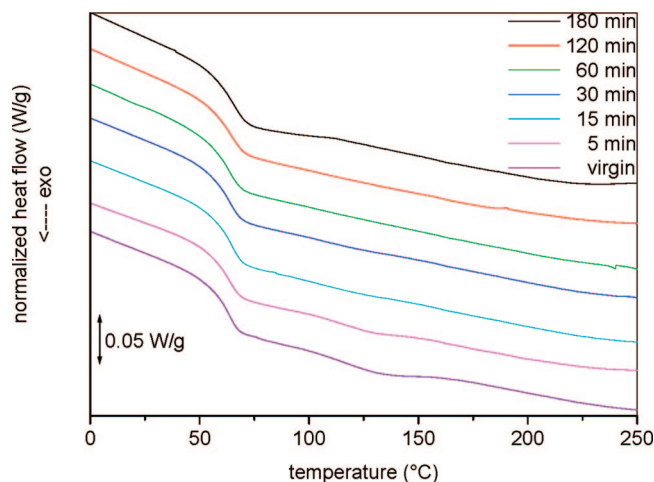


Figure 14. DSC cooling scans of the 70/30 blend.

amorphous halo, which indicates the complete disappearance of crystallinity.

Concerning the discussion of the induction period of the transesterification, the randomization became more significant after annealing times in the range above 30 min. In the same range a perceptible decrease of the crystallinity in both blend systems is found. On the other hand, this decrease of crystallinity corresponds very well with the shortening of the **PT** sequences connected each other in a segment, which is notable to crystallize if the length fall below a certain length.

3.4. Thermal and Morphological Analysis. Figure 11 shows the DSC thermograms of the Sorona/PC 70/30 blend annealed at 260 °C for increasingly longer times from 0 to 180 min. Two well-defined glass transition temperatures (T_g s) can be seen in the DSC curves of the unannealed blends and indicate that the system is immiscible. Upon annealing, the glass transition temperatures of the amorphous PTT- and PC-rich phases shift to higher and lower temperatures, respectively. After annealing

at 260 °C for more than 30 min, the original two T_g s merged in the blends to a single and sharp T_g . In addition, the melting temperature (T_m) decreases with increase of the annealing time imposed on the blends. Eventually, at extended annealing times (e.g., 120 min or longer), T_m of the blends disappear which indicates the transition from semicrystalline to an amorphous state. Furthermore, the annealed blends seemed to reach a final state where one glass transition was observed. This behavior is due to the compatibilizing effect of the copolyester formed as a result of transesterification. Similar homogenization of the blend upon annealing at high temperatures was reported elsewhere.^{28,30} With the increase in annealing time the heat of fusion and the peak temperature decreased.³¹ The T_m s of the blends eventually disappeared, and the T_g stayed constant for the samples annealed at 260 °C for 120 min or longer.

Figure 12 shows the SEM pictures of annealed and unannealed blends of PTT/PC 70/30 and 50/50. These pictures show that the melt compounded PTT/PC 70/30 blend exhibits phase separated domains, while the same blend that had been heated

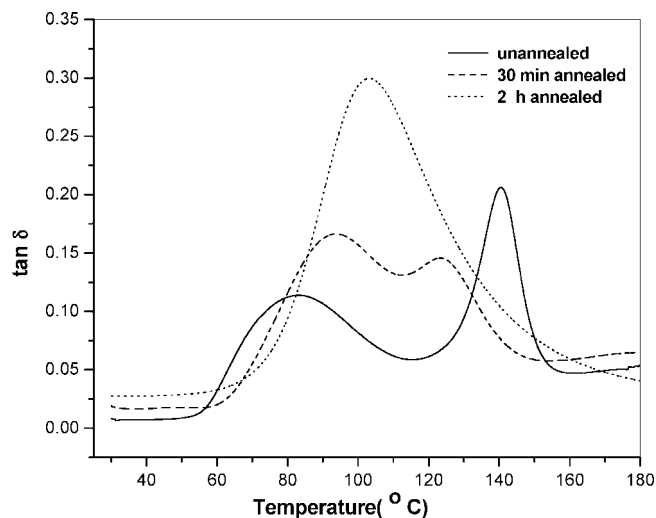


Figure 15. DMA spectra showing the $\tan \delta$ of PTT/PC 70/30 blends annealed at 260 °C from 0 to 120 min.

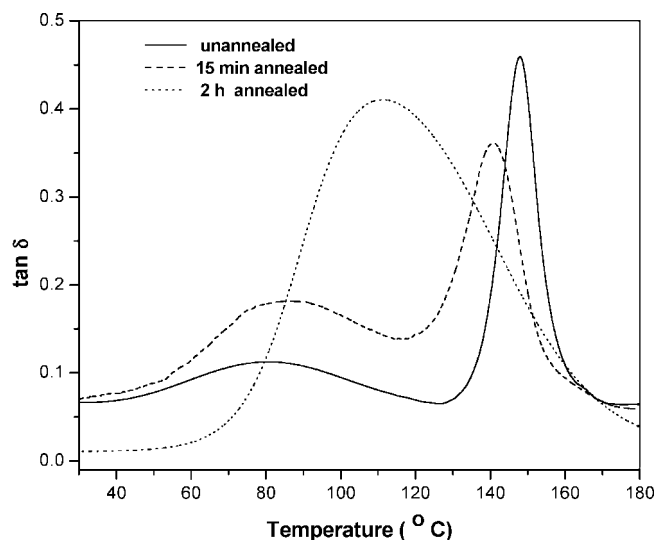


Figure 16. DMA spectra showing the $\tan \delta$ of PTT/PC 50/50 blends annealed at 260 °C from 0 to 120 min.

for 120 and 180 min is apparently free from such phase separated domains, which further indicates that the annealed blends readily underwent a homogenization process. The 50/50 blend initially having co-continuous phase morphology was also transformed to a homogeneous one after extended annealing. Therefore, it can be concluded that on progressively longer annealing, the original phase-separated morphology eventually disappear, and the morphology of the annealed PTT/PC blends turned homogeneous. It is well-known that a physical state is readily reversible, but a chemically changed state is irreversible. Figure 13 shows the second heating scans of the PTT/PC 70/30 blends after first heat treatment. The SEM and DSC results (Figures 12 and 13) show that the morphology of the annealed Sorona/PC blends was homogeneous and is different from the original phase-separated morphology of the as prepared blends and a single glass transition is apparent. In other words, the changes upon annealing of the blends were irreversible (Figure 13).

The 70/30 blend exhibited significant decrease in the endothermic (crystalline melting, T_m) peak temperatures and the degree of crystallinity (as indicated by the peak areas) upon annealing at 260 °C. This behavior is attributed to an increase in the degree of transesterification between PTT and PC, which

TABLE 2: Time Dependence Randomization of 70/30 and 50/50 Blends

annealing time (min)	PTT/PC 70/30		PTT/PC 50/50	
	B	$\ln[F(B)/(F(B) - f(BT))]$	B	$\ln[F(B)/(F(B) - f(BT))]$
5	0.00	0.00	0.00	0.00
15	0.02	0.02	0.01	0.01
30	0.04	0.04	0.02	0.02
60	0.17	0.19	0.04	0.05
120	0.70	1.20	0.33	0.41
180	0.89	2.22	0.51	0.72
(random)	1.00		1.00	

TABLE 3: Variation of Crystallinity with Annealing Time of PTT/PC 70/30 and 50/50 Blends^a

		annealing time (min)						
		0	5	15	30	60	120	180
PTT/PC 70/30	crystallinity (α_x)	0.272	0.300	0.274	0.267	0.15	0.0	0.0
PTT/PC 50/50	crystallinity (α_x)	0.188	0.192	0.180	0.144	0.05	0.0	0.0

^a $\Delta\alpha_x \geq \pm 0.015$.

produces significant quantities of statistical and short random-block copolymers, which inhibit crystallization. Figure 14 shows the DSC cooling scans of the 70/30 blend.

3.5. Dynamic Mechanical Analysis. It is well-known that miscible binary polymer blends exhibit a single T_g registered between the T_g s of the neat components. If the polymers are immiscible, the two T_g s (or the corresponding α -relaxation processes) appear well separated.⁶ Therefore, spectroscopic techniques sensitive to glass transition relaxations may provide useful information concerning local concentration fluctuations and miscibility in polymer blends.³² Sorona/PC blends (70/30 and 50/50) were annealed at 260 °C for different times. Figure 15 shows the DMA spectra of PTT/PC 70/30 blends annealed at 260 °C from 0 to 120 min. It is evident that there is a substantial difference in the $\tan \delta$ maximum with annealing time. After annealing at 260 °C for more than 15 min, the two distinct $\tan \delta$ peaks present in the unannealed blends (two T_g s) move closer to each other, and when the annealing time exceeds 60 min, the two peaks are merged to a single $\tan \delta$ peak (T_g). The single $\tan \delta$ peak at extended annealing times, e.g. 120 min or longer, indicates that the system is homogeneous. It is proved that upon progressively longer annealing the original phase-separated domains eventually disappear, and the morphology in the annealed PTT/PC 70/30 blends turns homogeneous.

PTT/PC 50/50 unannealed blends also show two distinct $\tan \delta$ peaks (two T_g s) as indicated in Figure 16. Upon annealing at 260 °C for 15 min these $\tan \delta$ peaks come closer and when the annealing time is more than 120 min merged into a single peak (T_g). Hence, similarly to the PTT/PC 70/30 blend, also for the PTT/PC 50/50 blend upon progressively longer annealing the morphology turns homogeneous.

4. Conclusions

Sorona/PC melt blends were characterized by their transre-action, morphology, and thermal and crystallization behavior upon annealing using FTIR, WAXD, ¹H NMR, DSC, SEM, and DMA. These investigations showed that the unannealed blends are having heterogeneous phase morphology; i.e., Sorona and PC are inherently immiscible, and the copolyester content is exactly zero. The copolyester content increases with increase

in annealing time and the PTT content. FT-IR spectra revealed the occurrence of a transesterification reaction between PTT and PC chain segments upon annealing at 260 °C, and this exchange reaction produced the new copolymer, which acted as the compatibilizer in the PTT/PC blends in the earlier stage of the reaction. A new absorption peak present at $\sim 1070\text{ cm}^{-1}$ in the spectra of annealed blends is characteristic of the new aromatic polyester structure. ^1H NMR studies confirm the dependence of transesterification rate on the annealing time and PTT content. The sequence structures of the produced copolyesters were determined by a triad analysis, which showed that the degree of randomness increased proportionally with time of annealing. It was found that the randomness on the PTT/PC 70/30 and 50/50 blends increased with annealing time at 260 °C. Up to 180 min of reaction, the degrees of randomness B is 0.89 (for 70/30 blend) and 0.51 (for 50/50 blend), i.e., degree of randomness B approaching 1.0 upon extended annealing for the 70/30 blend, where PTT content is more compared to the 50/50 blend, indicating that fully random copolyesters (with $B \sim 1$) are finally formed after extensive reactions at 260 °C. Two well-defined glass transition temperatures present in the DSC curves of the unannealed blends are indicative of an immiscible system. After annealing at progressively longer times, the original two T_g s in the blends come closer and finally merged to a single T_g . The melting temperature (T_m) decreases with the increase in annealing time, and when it is 120 min or longer, T_m of the blends disappear, indicating transition into an amorphous state. Also, DSC measurements on the heated PTT/PC 70/30 blend showed that transesterification reaction between PTT and PC at 260 °C is irreversible. SEM analysis showed that upon annealing at 260 °C for more than 120 min the original two-phase morphology is converted into a homogeneous one. From WAXS analyses it can be seen that the Sorona/PC blends turned out to be amorphous when annealed at 260 °C for a time of 120 min or longer, hence indicating formation of random copolyesters. In DMA, the single $\tan \delta$ peak at extended annealing times indicates transition into a homogeneous system. Thus, it is clear that on extended annealing the original phase-separated domains eventually disappear, and the morphology of the annealed PTT/PC blends turned homogeneous. According to the experimental results of annealed Sorona/PC blend samples, it can be concluded that the random copolyester formed as a result of the transesterification reaction between PTT and PC is the main factor for the change in miscibility. This random copolymer formed as a result of these exchange reactions acted as a compatibilizer in the initial stages of reactions. After annealing at 260 °C for more than 1 h, this random copolymer became the main species of the product exhibiting a homogeneous phase.

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