

Crystallization-induced Sequential Reordering in Poly(trimethylene terephthalate)/Polycarbonate Blends

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Abstract: Transesterification between poly(trimethylene terephthalate) (PTT) and bisphenol-A-polycarbonate (PC) is studied by differential scanning calorimetry (DSC) and nuclear magnetic resonance (NMR) spectroscopy. When the blend of PTT/PC is annealed at higher temperatures, the samples do not show any melting peak at an initial stage, indicating the samples completely lose their crystallinity due to the formation of random copolymers. However, when the random copolymer is annealed at temperatures lower than the melting temperature of PTT, a melting peak is observed, indicating that the random copolymers are sequentially reordered. The melting point and the heat of fusion of crystals formed from the crystallization-induced sequential reordering depend upon the annealing temperature and time. The average sequence length determined from NMR is increased as the blocks are regenerated.

Keywords: poly(trimethylene terephthalate), polycarbonate, crystallization-induced sequential reordering.

Introduction

Interchange reactions between two polycondensates may offer an attractive alternative for producing new copolymers. It is well known that transreactions such as alcoholysis, acidolysis, and transesterification commonly occur at the melt state in polyester blends. It has also been found by many investigators¹⁻⁶ that transreactions between component polyesters in immiscible polyester blends can play an important role in their miscibility. It is generally accepted that transreactions between two homopolymers produce first block copolymers and then the block copolymers are transformed into random copolymers due to a large entropy increase. However, it was observed that random copolyesters prepared from immiscible or miscible polyester blends, in which either of component polyesters is crystalline, were sequentially reordered when they are annealed below their melting temperatures. This process has been termed crystallization-induced sequential reordering (CISR) and its driving force is believed to be the lower enthalpy state of crystallites. Lenz *et al.*⁷ observed first the CISR when the blend of poly(4-oxybenzoate-co-ethylene terephthalate) and poly(3-

chloro-4-oxybenzoate-co-ethylene terephthalate) was heated below their melting temperatures. Recently, Fakirov *et al.*⁸ also observed the CISR in the blend of poly(ethylene terephthalate) (PET) and polycarbonate (PC), but they did not show clear evidence of CISR in a quantitative sense. In this study, we examine the CISR in the blend of poly(trimethylene terephthalate) (PTT) and PC more quantitatively by measuring precisely the sequence length of each block.

PTT is an aromatic polyester synthesized by the polycondensation of 1,3-propane diol with either terephthalic acid or dimethyl terephthalate. Since it is reported that PTT has better elastic recovery and resilience than both PET and poly(butylene terephthalate) (PBT),⁹ PTT and its blends with other engineering plastics may have strong potential to be used as an engineering plastic. In this regard, it is significant to elucidate the mechanism of ester interchange reactions between PTT and PC in designing the blend system.

Experimental

Materials. PTT was supplied by Shell Chemical Co., and PC was supplied by Cheil Ind.. Chemical structures of two polymers are shown in Figure 1. All the samples were vacuum-dried at 80°C for 24 h, prior to blending. PTT/PC blends with various weight ratios (20/80, 50/50 and 80/20)

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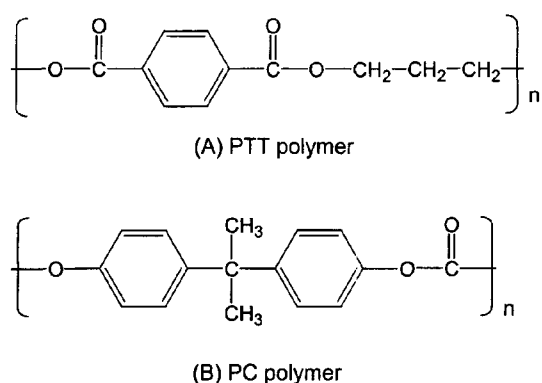


Figure 1. Chemical structures of PTT and PC polymers.

with 2 wt% stabilizer (Irganox1010) were prepared by using a Mini-Max molder at 270 °C for 5 min. It was assumed that transreaction did not occur significantly during the mixing, since the NMR analysis showed that the degree of randomness and the average sequence length of the mixture were 0.2 and 50, respectively. Therefore, the blends are regarded as a mechanical mixture. The samples were ground into fine powder and vacuum-dried at 80 °C for 24 h prior to further treatment. This powder is used as an initial sample for CISR.

Thermal Analysis and Crystallization-induced Sequence Reordering (CISR) Process. Transreactions of PTT/PC blends were carried out in a sample pan using Perkin-Elmer DSC-7 under nitrogen atmosphere. Each initial sample as a mechanical mixture was heated up to 270 °C and kept at this temperature for a given period of time to induce transreaction in the blends. This annealing was followed by rapid cooling to room temperature, and then the sample was again heated up to 270 °C to observe its melting behaviors. The melting endotherm becomes smaller and finally vanishes as the annealing time is increased. The blends without melting endotherms were cooled to 140 °C, corresponding to the maximum crystallization temperature of pure PTT (T_c), and annealed at this temperature for 120 min. This annealing was followed by rapid cooling to room temperature, and then heated up to 270 °C to observe its crystallization behavior. In order to induce CISR, the blends were again annealed for a given period of time at temperatures below T_m of PTT. Three different temperatures (140, 185 and 195 °C) were selected in this work to investigate the effect of annealing temperature. After rapid cooling to room temperature, the samples were then heated up to 270 °C in order to observe its restoration of melting endotherms. The whole cycle of thermal analysis is schematically represented in Figure 2.

^1H NMR Analysis. ^1H NMR spectra were obtained using a 300 MHz Bruker spectrometer. Samples were dissolved in a mixed solvent of trifluoroacetic acid (TFAA)/deuterated chloroform (CDCl_3) (5/5, v/v). Tetramethylsilane (TMS) was used as an internal reference.

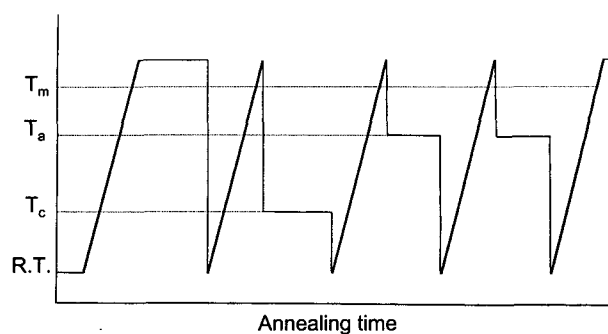


Figure 2. Schematic heating-annealing-cooling cycles in DSC, where T_m , T_a , and T_c are melting temperature, annealing temperature and crystallization temperature, respectively. The heating rate is 20 °C/min.

Results and Discussion

The DSC heating curves for a PTT/PC (50/50, w/w) blend, annealed for different periods of time at 270 °C, 140 °C, 185 °C are shown in Figure 3. As can be seen in Figure 3, after annealing for 120 min at 270 °C, the samples did not show any melting peak, indicating that the sample completely loses its crystallinity. When this amorphous sample was then heated for 120 min at 140 °C, corresponding to the maximum crystallization temperature of pure PTT (T_c), any significant melting peak was not observed on DSC thermogram, indicating that the annealing at T_c for 120 min did not produce enough amounts of blocks to crystallize under this condition. However, when the amorphous sample was annealed for 180 min at 185 °C, a small melting peak is observed at about 200 °C, as shown in Figure 3. This indicates that the block sequence restored from random copolymers is long enough to crystallize. When the annealing temperature was increased to 195 °C, larger melting peak is observed at 201 °C as compared with the case of 185 °C annealing, as

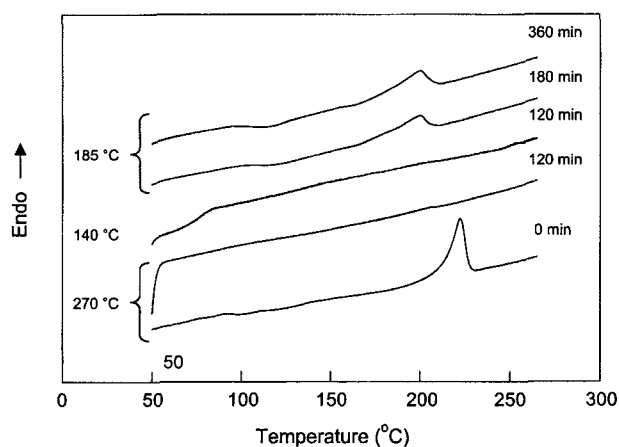


Figure 3. DSC thermograms of PTT/PC blends (50/50), after the amorphous sample is annealed at 185 °C.

shown in Figure 4. An increase of annealing time at 195 °C results in an increase of melting temperature by 6 °C accompanying with an increase of the heat of fusion, as can be seen in Table I. This indicates that the higher annealing temperature and longer annealing time result in an increase in restored enthalpy and crystal size. Since it is generally known that with increasing annealing temperature the rate of crystallization decreases whereas the rate of ester interchange reaction increases, it is concluded that an increase in the rate of ester interchange reaction mainly contributes to an increase in restored enthalpy as the annealing temperature is increased.

In order to examine the effect of the blend ratio on the CISR of PTT/PC blends, the blends with different blend

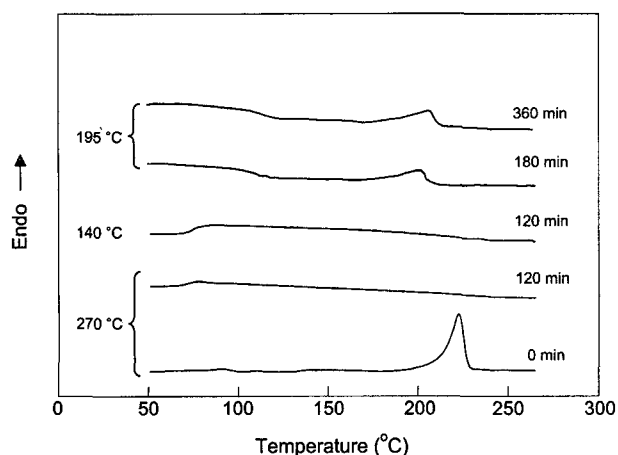


Figure 4. DSC thermograms of PTT/PC blends (50/50), after the amorphous sample is annealed at 195 °C.

Table I. The Glass Transition Temperature, Melting Temperature and the Heat of Fusion of PTT/PC (50/50) Mixture when Measured by DSC

Composition	Annealing Conditions		Transition Temperature		Heat of Fusion (J/g)
	(T/°C)	(Time/min)	(T _g /°C)	(T _m /°C)	
PTT/PC (50/50)	270	0	95, 135	222	28
	270	120	71	-	-
	140	120	-	-	-
	185	180	110	200	11
	185	360	104	200	13
	195	180	-	201	18
	195	360	-	207	24

ratios were annealed for different periods of time at 195 °C. The blend of PTT/PC (20/80) does not show CISR, as shown in Figure 5, because the amount and sequence length of PTT in the random copolymer are too small and too short, respectively, to induce crystallization. The blend with a lower PTT content (20/80) requires a shorter time (90 min) for losing the crystallinity of PTT as compared with the blends with higher PTT contents in the blends, i.e., the PTT/PC (50/50) and PTT/PC (80/20) blends require 120 min and 150 min of annealing, respectively, for complete loss of their crystallinities, as shown in Figure 3 and Figure 6. It is noteworthy that all PTT/PC random copolymers except for the PTT/PC (20/80) blend restore the ability to crystallize when the samples are annealed at temperatures (185 °C and 195 °C) below T_m of PTT, as shown in Table II.

Sequence reordering is analyzed in terms of the degree of randomness and the number average sequence length. Exchange reactions in molten PC-PTT mixtures lead to the

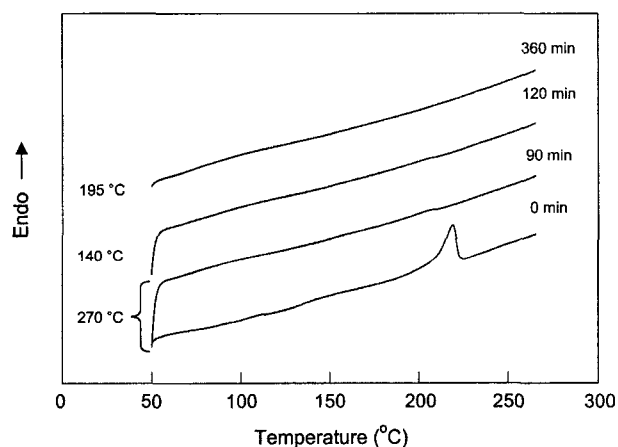


Figure 5. DSC thermograms of PTT/PC blends (20/80), after the amorphous sample is annealed at 195 °C.

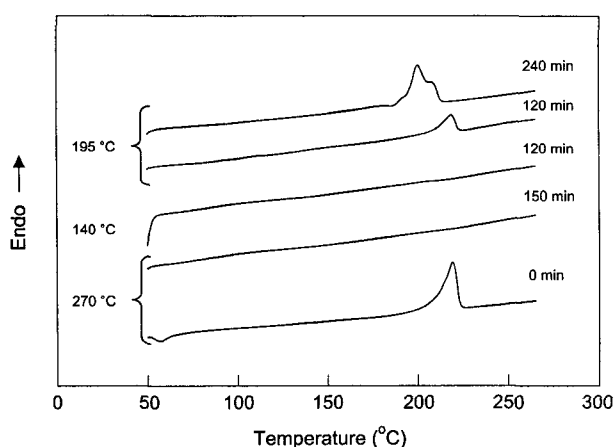


Figure 6. DSC thermograms of PTT/PC blends (80/20), after the amorphous sample is annealed at 195 °C.

Table II. The Glass Transition Temperature, Melting Temperature and the Heat of Fusion of PTT/PC (20/80) and (80/20) Blends when Determined by DSC

Composition	Annealing Conditions		Transition Temperature		Heat of Fusion (J/g)
	(T ^o C)	(Time/min)	(T _g ^o C)	(T _m ^o C)	
PTT/PC (20/80)	270	0	135	219	14
	270	90	151		
	140	120			
	195	360			
	270	0	135	219	14
PTT/PC (80/20)	270	0		219	50
	270	150			
	140	120			
	195	120	87, 136	218	14

formation of a four-component copolycondensate, which can be represented by the general formula $[(A_1B_1)_x (A_2B_2)_y]_m [(A_1B_2)_z (A_2B_1)_w]_n$, where A_1 , A_2 , B_1 , and B_2 denote trimethylene, bisphenol, terephthalate and carbonate unit, respectively. Taking into account that the fraction of triads $A_iB_jA_k$ is equal to that of triads $A_kB_jA_i$, the triad analysis gives the degree of randomness (DR)¹⁰:

$$DR = f_{A_iB_jA_k} \left(\sum_{i=1}^2 \frac{1}{F_{A_i}} \right) \quad (i \neq k) \quad (1)$$

where $f_{A_iB_jA_k}$ and F_{A_i} denote the fraction of triads $A_iB_jA_k$ and the mole fraction of A_i units, respectively. The average sequence length (N) can be computed from the fraction of either dyad or triad.¹⁰ For example, the average length of trimethylene terephthalate (A_1B_1) sequences is equal to the ratio of the average number of A_1B_1 sequences to the average number of $A_1B_1A_2$ sequences:

$$N = \frac{f_{A_1B_1A_1}}{f_{A_1B_1A_2}} + 1 \quad (2)$$

NMR analysis would provide us with a direct evidence for sequence reordering. Typical NMR spectra for mechanical mixture, random copolymer and restored copolymer prepared from PTT/PC (50/50) blends are shown in Figure 7. It is revealed that the spectrum of mechanical mixture (Figure 7A) is similar to that of the sample annealed at 195°C for 360 min (Figure 7C), indicating that the block sequence was restored when the sample was annealed at 195°C for 360 min. From analysis of the NMR signals in the range of 8.30–8.50 ppm, we can evaluate the degree of randomness and the number average sequence length. When the sample is annealed at 195°C for 360 min, the number average sequence length becomes larger as compared with the case of annealing at 270°C for 120 min, as can be seen in Table

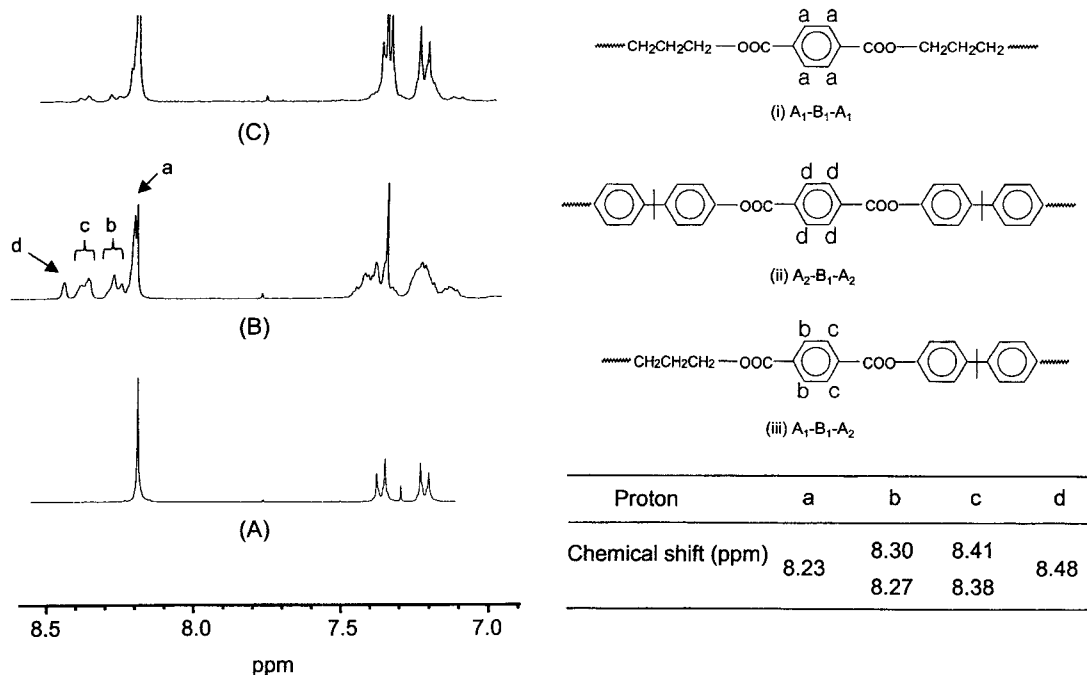


Figure 7. ¹H NMR spectrum of PTT/PC (50/50) blend (A) mechanical mixture (B) the sample annealed at 270°C for 120 min (C) the sample annealed at 195°C for 360 min.

Table III. The Degree of Randomness and the Number Average Sequence Length of Random Copolymer and Restored Block Copolymer when Determined by NMR

	Degree of Randomness (DR)	Number Average Sequence Length (N)
PTT/PC (50/50) Annealed at 270°C for 120 min	0.78	2.60
PTT/PC (50/50) Annealed at 195° for 360 min	0.25	7.84
PTT/PC (50/50) Annealed at 185° for 360 min	0.32	5.53
PTT/PC (80/20) Annealed at 195° for 240 min	0.21	11.28
PTT/PC (20/80) Annealed at 195° for 360 min	0.98	1.58

III, indicating that more blocky sequences are restored from random sequences in the mixture.

Conclusions

PTT-PC random copolymers are first prepared by heating the mixture of PTT and PC at 270°C for 120 min. Restoration of the blocky sequence is observed when the PTT-PC random copolymer is annealed at temperatures below the melting temperature of PTT. The melting temperature and the heat of fusion of crystals from the crystallization induced sequential reordering depends upon the annealing temperature and time. DSC measurements showed that higher melting temperature and longer annealing time result

in an increase in the heat of fusion and melting temperature. From analysis of the NMR spectra, the degree of randomness and the number sequence length are quantitatively determined. It is concluded that crystallization-induced sequential reordering is driven by the lower enthalpy state of crystallites.

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