

Miscibility and Transesterification in Bisphenol-A Polycarbonate/Ethylene Terephthalate–Caprolactone Copolyester Blends

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SYNOPSIS

The miscibility and microstructure of blends of bisphenol-A polycarbonate (PC) with ethylene terephthalate (ET)–caprolactone (CL) copolyesters (TCL) were studied by differential scanning calorimetry (DSC), infrared spectroscopy (IR) and phase contrast microscopy (PCM). The DSC results showed that PC were immiscible or partially miscible with the copolyesters having ethylene terephthalate contents higher than 60 (wt %), and miscible with the copolyesters having ET contents lower than 60 (wt %). After annealing at elevated temperature, homogenization will take place in the immiscible or partially miscible blends of PC with higher ET-content copolyesters. The IR and PCM results revealed that the homogenization of the blend are caused by the transesterification between the PC and copolyesters. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

It is well known that interchange reactions take place in polymer blends between the different functional groups involved in mixtures of some polycondensation polymers, such as polyesters and polyamides.^{1,2} This type of interaction may greatly affect the miscibility between different components in the blends.^{2–4} It opens a new route to improve the miscibility of the immiscible polymer blend pairs and prepare the novel copolymers with various degrees of randomness and composition. For reasons of both industrial application and academic interest, some research efforts have been made in this subject.^{2–6}

The blends of the poly(bisphenol-A carbonate) (PC) with aromatic and aliphatic polyesters have been extensively studied. The divergent conclusions on the miscibility behavior of the mixtures, especially of the PC with aromatic polyesters such as PC/poly(ethylene terephthalate) (PET), have been obtained. In the PET/PC blends, different miscibility behavior has been reported from completely

miscible for all compositions,⁷ partially miscible,^{8,9} to completely immiscible for all compositions.^{4,10–12}

These different conclusions about the miscibility of this system are probably attributed to the transesterification between two components which may affect by residual polymerization catalysts, other impurities, and blending conditions.^{3,4,12} For PC with aliphatic polyesters such as polycaprolactone, the interchange reaction also takes place at elevated temperature and a small amount of insoluble gel that could only be swollen in methylene chloride CH_2Cl_2 was obtained. As characterized by Fourier transform infrared spectroscopy (FTIR), ^1H and ^{13}C -NMR, it was found that transesterification did not predominate and thermo-oxidative branching reactions caused the gelation of the two components.¹³

Recently, a series of poly(ethylene terephthalate-co-caprolactone) (TCL) with different compositions has been synthesized in our laboratory^{14,15} and its miscibility with other polymers has been studied. In the present paper, we report the miscibility of the blends of the PC with synthesized copolyesters. The variation of the miscibility in these blends with the changes of ET content in the TCL and the thermal history of the blend samples was examined by differential scanning calorimetry (DSC), phase-con-

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trast microscopy (PCM) and FTIR, and the results are discussed based on the transreaction between two components.

EXPERIMENTAL

A list of the polymers used in the present work with their ET contents, intrinsic viscosity (η), and glass transition temperature (T_g) are given in Table I. The copolyesters were synthesized in our laboratory^{14,15} and purified by precipitation in large amounts of methanol from a 5% (w/v) chloroform solution. The ET content was determined by nuclear magnetic resonance spectroscopy as described previously.¹⁶ Bisphenol-A polycarbonate was provided by Idemitsu Petrochemical Co. (Idemitsu polycarbonate N2200, $M_n = 14,400$, $M_w = 29,000$).

Blend films were prepared by casting from chloroform solution at room temperature. The blend samples were further dried in a vacuum oven at a temperature of 50°C until they reached constant weight.

Glass transition temperature (T_g) of the copolyesters and their blends were measured using a Perkin-Elmer DSC-2C. The temperature at the half height of the corresponding heat capacity jump was defined as the T_g . The temperature was calibrated with ultra-pure indium and all measurement was carried out under nitrogen atmosphere. In order to

obtain a temperature as low as 200K, the Intra-cooling II was used. In the DSC apparatus, the samples were first heated at a rate of 20K/min to 530K, maintained at that temperature for 1 min, and quenched to 200K. They were then heated from 200 K, at a rate of 20K/min to 530K to measure the glass transition temperature of the first run. After that process, the sample was annealed at 530K for a different time and then quenched to 200K to determine the effect of the thermal history on the miscibility. The T_g s of the samples with different annealing times were measured by heating at 20K/min from 200K to 500K. A sample is considered miscible if it gives at each composition a single T_g intermediate between those of the individual components. Thus, a sample exhibiting two T_g s at a given composition is considered immiscible or partially miscible.

FTIR measurements were conducted with a Nicolet 170SX FTIR spectrometer. Thin films were cast onto a NaCl window from 1% (w/v) chloroform solutions. Spectra were obtained at room temperature from the samples with and without thermal treatment. The thermally treated samples were obtained from this process: the original casting films covered with another NaCl crystal were first heated to 530K on a hot stage and kept at that temperature for different times, and then quenched to room temperature. All spectra were recorded with a resolution of 2 cm⁻¹.

Phase contrast microscopy (Olympus IMT-2) observation at a series of annealing temperatures was also carried out for the blends to determine the phase behavior. Before observation under the phase contrast microscope, samples sandwiched between two cover glasses were annealed at a temperature for different times on a hot stage equipped with a temperature controller, and then quenched to room temperature.

A solubility experiment examined the ester interchange which may occur at elevated temperatures. The samples, after annealing at different temperatures, were put into chloroform to find signs of insoluble materials or gelation. The intrinsic viscosity of the blend samples with and without thermal treatment was measured in *m*-cresol at 30°C.

Table I Description of the Polymers Used in This Study

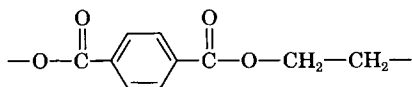
TCL Copolyesters	ET Content ^a (wt %)	$[\eta]^b$ (100 ml/g)	T_g^c (K)
TCL82	82	0.837	306
TCL72	72	0.955	291
TCL62	62	0.994	270
TCL58	58	0.851	262
TCL48	48	0.866	246

^a Determined by NMR spectroscopy.

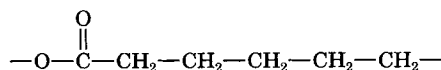
^b Measured in *m*-cresol at 30°C.

^c Determined by DSC for the TCL quenched from 510 K.

ET:



CL:



RESULTS AND DISCUSSION

The Miscibility of PC with TCL Copolyesters

Thermal analysis is a common method of detecting the miscibility behavior of polymer blends. Figures 1 and 2 give two typical DSC thermograms of mis-

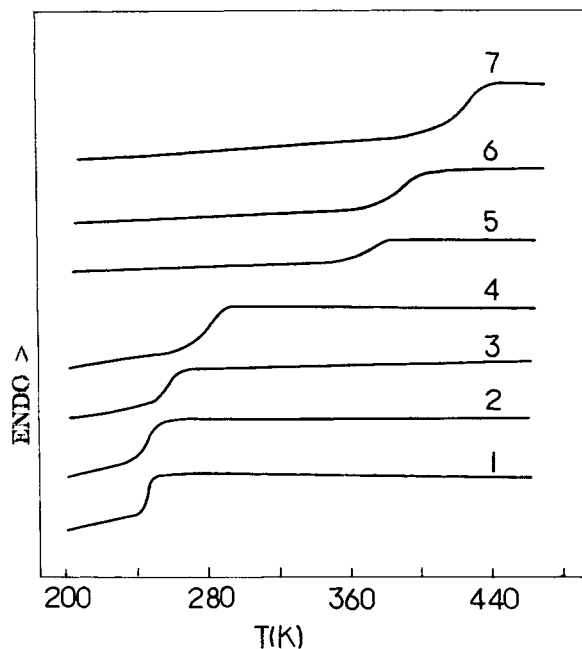


Figure 1 DSC thermograms of PC/TCL48 blends having different composition quenched from 530K to 200K. (1) TCL48; (2) TCL48/PC (9 : 1); (3) TCL48/PC (8 : 2); (4) TCL48/PC (5 : 5); (5) TCL48/PC (2 : 8); (6) TCL48/PC (1 : 9); (7) PC.

cible and immiscible PC/TCL blends, and Table II summarizes the thermal analysis results of blends of PC with copolyesters having different ET contents. According to the single T_g criterion, blends of PC/TCL48 are miscible in entire composition. Blends of PC with TCL having ET content higher than 60 (wt %) give two T_g s, which indicates that these blends are immiscible or partially miscible. These thermal analysis results show that a miscibility limit specified by ET content in TCL copolyester exists in PC/TCL blends and its value is about 60% (wt). The ϕ_{COO} (volume fraction of ester group, given by group contribution of molar volume¹⁷) in the TCL with 60 wt % ET content is 0.249; this value is close to the ϕ_{COO} of PBT, 0.266.

For the mixtures of PC with aliphatic polyesters, Cruz et al¹⁸ found that PC is miscible with aliphatic polyesters having CH_2/COO ratios in their repeat units between 2 (ϕ_{COO} is 0.373) and 5 (ϕ_{COO} is 0.192), partially miscible for ratios up to 7, and immiscible for ratios greater than 7. This miscibility window gives the upper miscibility limit of ϕ_{COO} to be 0.373; this upper limit of the PC/aliphatic polyester blends is evidently greater than that of PC with the TCL copolyesters. From the works of Suzuki et al. and others,^{4,10-12} the conclusion has been made that the blends of PC/PET are immiscible in all composition

and the blends of PC/PBT are partially miscible without transesterification between two components.¹⁹⁻²³ From the miscibility behavior and upper miscibility limits of ϕ_{COO} in blends of PC with aromatic polyesters, aliphatic polyesters, and copolyesters, we found that the miscibility behavior of PC with synthesized TCL copolyesters is similar to that of the blends of PC with aromatic polyesters. That means the presence of the benzene ring in the repeat units of polyester makes the upper miscibility limit of ϕ_{COO} shift to the smaller fraction. The results show that the miscibility behavior of PC with polyesters is very sensitive to both ester moiety concentration and steric restriction in the molecular chain of the polyesters. There is an optimum ϕ_{COO} range in polyesters concerning the miscibility of these mixtures, and the benzene ring in polyesters affects the miscibility limits because of the steric effect of this big and stiff group.

For the blends of PC with TCL having relatively higher ET content, such as PC/TCL82, two distinct T_g s for all compositions were obtained before the thermal treatment of the samples (Fig. 3), which suggested the formation of two phase in these mixtures. However, comparison of the T_g of the blends with the T_g s of the corresponding pure components showed that the higher T_g related to the PC de-

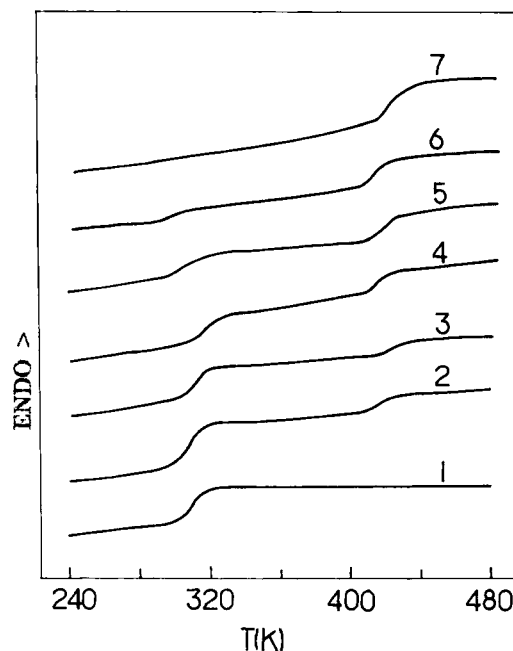
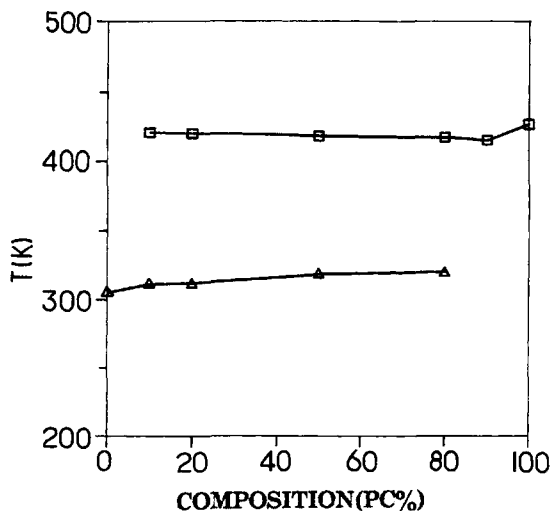
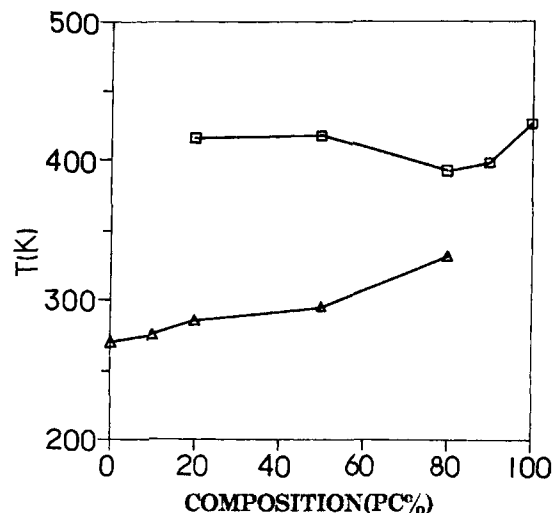


Figure 2 DSC thermograms of PC/TCL82 blends having different composition quenched from 530K to 200K. (1) TCL82; (2) TCL82/PC (9 : 1); (3) TCL82/PC (8 : 2); (4) TCL82/PC (5 : 5); (5) TCL82/PC (2 : 8); (6) TCL82/PC (1 : 9); (7) PC.

Table II Thermal Properties of TCL Copolyesters/PC Blends

Copolyesters	PC Content (wt %)	T_g (K) (First Run)	T_g (K) (Final Run)
TCL82	0	306	307
	10	312	421
	20	312	420
	50	319	415
	80	320	417
	90	320	415
	100	427	427
TCL72	0	291	
	30	294	414
	50	300	410
	70	298	406
	100	427	
TCL62	0	270	270
	10	275	275
	20	285	416
	50	295	418
	80	332	393
	90	399	399
	100	427	427
TCL58	0	262	
	30	273	
	50	293	
	70	371	
	100	427	
TCL48	0	246	
	10	249	
	20	256	
	50	284	
	80	355	
	90	397	
	100	427	

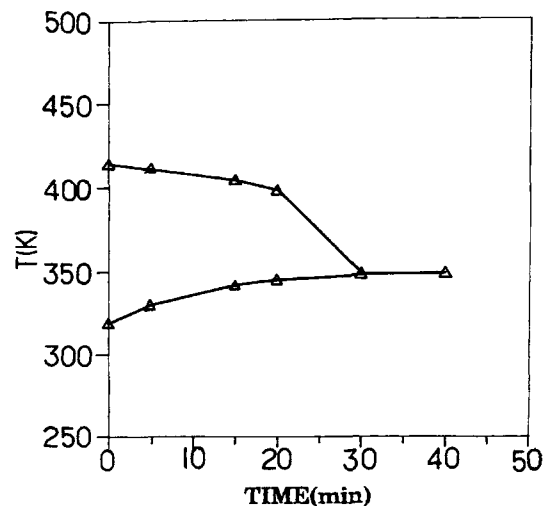
creased slightly and the lower T_g corresponding to TCL82 increased a little, which means the two polymers are partially miscible with each other. The ex-

**Figure 3** Glass transition temperature versus composition of PC/TCL82 blends.**Figure 4** Glass transition temperature versus composition of PC/TCL62 blends.

isting two phases are a PC-rich phase with a small amount TCL82, and a TCL82-rich phase with a small amount of PC. Figure 4 shows the T_g s of another PC/TCL copolyester blend system with different composition. Here, the ET content in TCL copolyester (ET 62 wt %) is lower than that in TCL82, and the shift of T_g s in these blends is more apparent than that in PC/TCL82 blends. Thus, the lower ET content in copolyester is favorable to the miscibility of these blends.

Transesterification in the PC/TCL Blends

When samples were annealed at elevated temperature, the T_g s of the partially miscible blends changed with the annealing temperature and annealing time.

**Figure 5** Temporal changes of T_g s at 530K of PC/TCL82 (5 : 5).

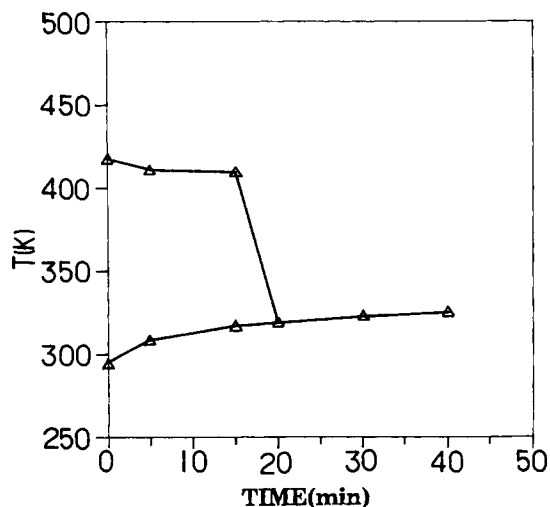


Figure 6 Temporal changes of T_g s at 530K of PC/TCL62 (5 : 5).

That may be the consequence of the interaction between the two constituents in the blends. The variations in the T_g s at a certain annealing temperature for different times are given in Figures 5 and 6. From the temporal change experiment, we found that the interval between two transition temperatures decreased and finally joined in one T_g . The annealing time which showed one T_g was related to the initial T_g s of the studied blends. The smaller the interval of the initial T_g s, comparing the interval of the original T_g s of the two pure components, the shorter the annealing time to present one T_g . This suggests that homogenization is greatly affected by the initial miscibility of the blends. The higher the degree of miscibility between two components in the blends,

the easier it is for the intermolecular interchange reaction to take place in the mixtures.

Phase structures of blend samples with different thermal treatment were investigated by phase contrast microscopy (PCM). The phase behavior change with the thermal history can be detected clearly by PCM, as shown in Figure 7. From the observation under the PCM, we found that homogenization occurred in PC/TCL62 blend more easily than that in PC/TCL82 blend. This observation result is similar to the DSC results, confirming the effect of the initial miscibility on the homogenization process in the mixtures.

These thermal analysis and PCM observation results show that the miscibility behavior of the synthesized copolyester with PC changed with the thermal treatment, perhaps because of the interaction occurring between two components in the blend. In order to confirm this conclusion, FTIR measurements were performed to investigate the temporal change in chemical structure of the constituents in the blend at elevated temperature. From the IR spectra, we can analyze the change in chemical structure of the molecular chain and detect the new components produced from the interaction. Kotliar has determined that the interchange reactions involved in the condensation polymers, such as polyesters and polyamides, are mainly three types¹: intermolecular alcoholysis, acidolysis, and transesterification. In the polyester blends, the transesterification was considered to be a general interaction occurring at an elevated temperature. Figure 8 shows the FTIR spectra of the TCL82/PC (5 : 5) annealed at 530K for different times. The absorbance peak of aromatic carbonate triads in the

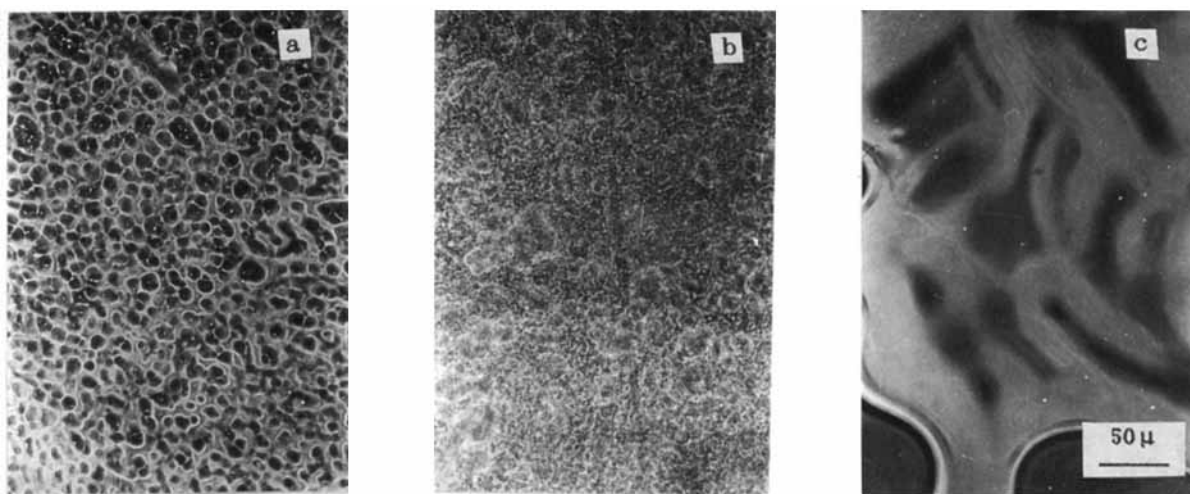


Figure 7 Phase contrast micrograph of PC/TCL82 (5 : 5) with different annealing time at 530K. (a) 1 minute; (b) 10 minutes; (c) 30 minutes.

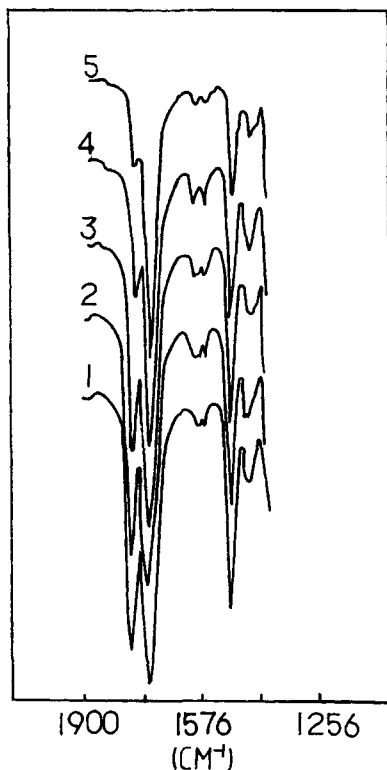


Figure 8 FTIR spectra of PC/TCL82 (5 : 5) with different annealing time at 530K. (1) Original sample; (2) 10 minutes; (3) 20 minutes; (4) 40 minutes; (5) 60 minutes.

amorphous state (1775 cm^{-1} band) decreases with increased annealing time, and carbonyl stretching of aliphatic and aromatic ester (center about 1730 cm^{-1}) increases with the annealing time. These results prove that the transesterification occurred at elevated temperature in these blends. Because of the complication of overlapped peaks, it is difficult to obtain the relative amount of the interchange reaction between the two components. Compared with the DSC results, the transesterification causing the disappearance of aromatic carbonates less than 40% is probably enough to give a homogeneous phase of the blend.

In the present study, no insoluble gel was detected for the thermal treatment samples in the solubility experiment. We also found that the intrinsic viscosity of PC/TCL82 decreased remarkably with increasing thermal treatment time (after 1 h of thermal treatment at 530K, the $[\eta]$ decreased from 0.62 to 0.47). These results mean the transesterification was predominant and the thermo-oxidative branch-

ing reactions which caused the gelation of the two components were negligible.

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