

Transesterifications of Poly(bisphenol A carbonate) with Aromatic and Aliphatic Segments in Ethylene Terephthalate–Caprolactone Copolyester

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ABSTRACT: In this article, transesterification of poly(bisphenol A carbonate) (PC) with an ethylene terephthalate–caprolactone copolyester at a weight ratio 50/50 (TCL50) was investigated by infrared spectroscopy (IR), proton nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$), and a model compound. The IR and $^1\text{H-NMR}$ results showed that transesterification occurred between PC and ethylene terephthalate (ET) segments in TCL50 and resulted in the formation of bisphenol A–terephthalate ester units as in the annealed blend of PC with the PET homopolyester. By comparison with a model compound, the new signal at 2.55 ppm in the $^1\text{H-NMR}$ spectrum confirmed the appearance of bisphenol A–caprolactone ester units resulting from the exchange reaction of PC with caprolactone (CL) segments. The $^1\text{H-NMR}$ analysis of the transesterification rates revealed that the reactions of PC with aromatic and aliphatic segments in TCL50 proceeded in a random or free manner. In addition, we separately examined the interchange reaction between a PC and poly(ϵ -caprolactone) (PCL) homopolyester in an annealed blend. It was found that in the presence of a Ti compound catalyst the predominant reaction was a transesterification rather than a thermooxidative branching reaction. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 1558–1565, 2001

Key words: transesterification; poly(bisphenol A carbonate); ethylene terephthalate–caprolactone copolyester; poly(ϵ -caprolactone)

INTRODUCTION

Recently, polyester blends have attracted a great deal of attention. The focus of the interest is invariably directed to their ester-exchange reactions occurring between functional groups. For both academic purposes and industrial applica-

tion, considerable research efforts have been made on the subject.^{1–14}

Extensive investigations relating to transesterification were performed mainly in the homopolyester blends, including aromatic and aliphatic polyester. Different conclusions were made. In the poly(bisphenol A carbonate)/poly(ethylene terephthalate) (PC/PET) blend, transesterification can take place between carbonate and terephthalate groups and result in the formation of four-component copolycondensates.^{4,12} It has been shown that the reaction can be accelerated by a residual PET polymerization catalyst^{8–11}; in fact, no transesterification was observed in a

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PC/purified PET blend.^{8,9} For the blend of PC with aliphatic polyester such as poly(ϵ -caprolactone) (PCL),⁶ the interchange reaction can also take place between the components during the melt processing, but a gelled product, which could only be swollen in methylene chloride (CH_2Cl_2), was obtained. The solvent extraction, FTIR, and NMR results demonstrated that transesterification did not predominate and thermooxidative branching mainly occurred and caused the gelation between the components.

So far, transesterifications related to a copolyester have seldom been reported.⁵ However, in some cases, a copolyester can be used as a compatibilizer in polyester blends to improve the miscibility.¹² The copolyester as a third component has an unavoidable exchange reaction with blending polymers in the melt processing. Thus, in this study, special interest was given to the characterization of interchange reactions between a polyester and a copolyester.

Ethylene terephthalate–caprolactone (TCL) is a random copolyester synthesized from monomers in our laboratory.^{15–17} Since aromatic and aliphatic ester groups exist in the ethylene terephthalate (ET) and caprolactone (CL) segments, respectively, it provides a possibility that the transesterifications of the carbonate group in PC with two different kinds of ester groups can be studied in a single reaction simultaneously. Especially, we wonder if transesterification takes place randomly or in a preferential manner. In the present article, transesterifications of PC with ET and CL segments in TCL were studied in detail. At the same time, transesterification between PC and the corresponding PCL homopolyester was also a topic of this study.

EXPERIMENTAL

Materials

A random copolyester of TCL at a weight ratio 50/50 was synthesized from monomers following the method reported by Luo et al.^{15–17} and was termed TCL50 in this study. The intrinsic viscosity is 0.70 dL/g in tetrachloroethane at 30°C. Poly(bisphenol A carbonate) (PC) was kindly supplied by the Changzhou Organic Chemical Factory (China), with $M_n = 38,000$. PCL was purchased from Scientific Polymer Products (New York), with $M_n = 43,000$.

Blending and Annealing

The two polymers were dissolved in chloroform (CHCl_3), yielding a 5% solution. The blends were subsequently recovered from the solution by precipitating them in methanol. The blend samples were further dried in a vacuum oven at 50°C until they reached a constant weight.

The freshly prepared blend was placed into a nitrogen-purged glass tube and heated in a 260°C salt bath ($\text{KNO}_3/\text{NaNO}_3$, 50/50, wt %). Under the protection of a nitrogen flow, the blend was annealed for various lengths of time.

Synthesis of Model Compound Bisphenol A Dibutyrate

The model compound bisphenol A dibutyrate was synthesized by two steps of a reaction as reported below. Butanic acid (12 g) and an excess of thionyl chloride (SOCl_2) were placed into a 250-mL flask; the refluxing was carried out until HCl vapor was no longer released. The unreacted thionyl chloride was removed under reduced pressure and butanoyl chloride was obtained. Bisphenol A (4 g) was dissolved in an 80-mL mixture solvent of benzene and pyridine (50/50, v/v). Under stirring, an excess of butanoyl chloride was carefully dropped into the solution cooled with iced water. The reactant mixture was stirred for 24 h at room temperature and then poured into 250 mL iced water and neutralized using HCl. The oil layer was separated and washed with 5% aqueous NaHCO_3 (3×50 mL) and distilled water (3×50 mL). After being dried with Na_2SO_4 for 24 h, the crude product was vacuum-distilled and the yellow residue was recrystallized in chloroform. Bisphenol A dibutyrate was obtained. Its structure and $^1\text{H-NMR}$ spectrum are presented in Figure 5. All peaks are assigned as follows: δ 6.96–7.24 (dd, 8H, aromatic **H**), 2.52 (t, 4H, $-\text{OCCH}_2\text{CH}_2\text{CH}_3$), 1.75 (m, 4H, $-\text{OCCH}_2\text{CH}_2\text{CH}_3$), 1.65 (s, 6H, $-\text{CH}_3$ in bisphenol A unit), 1.02 (t, 6H, $-\text{OCCH}_2\text{CH}_2\text{CH}_3$).

Measurements

All infrared spectra were recorded using a Nicolet 170SX FTIR spectrometer. The blends with different annealing times were dissolved in chloroform, and the solution was cast onto a NaCl pellet. After evaporating the solvent, the cast blend film was used to obtain the spectra of the blends. $^1\text{H-NMR}$ spectra were obtained on a Bruker

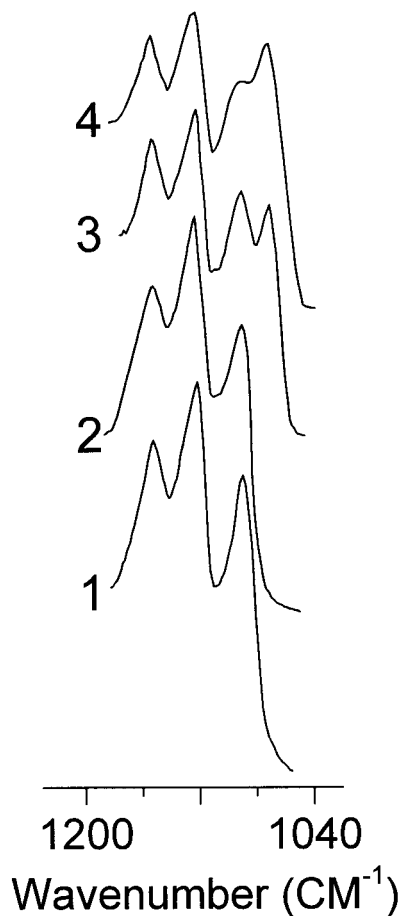


Figure 1 FTIR spectra of PC/TCL50 (50/50) blend with different annealing times at 260°C (1040–1200 cm^{-1}): (1) 0 min; (2) 30 min; (3) 60 min; (4) 90 min.

DMX-500 NMR spectrometer using CDCl_3 as a solvent and TMS as an internal standard. About a 10% solution was prepared for this measurement.

A solubility experiment was carried out to examine the interchange reaction occurring during the annealing process. The samples, after annealing for different times, were put into chloroform to find signs of insoluble materials or gelation.

RESULTS AND DISCUSSION

Transesterification of PC with ET Segments

Figure 1 displays the evolution of FTIR spectra (1040–1200 cm^{-1}) of the PC/TCL50 blend (50 represents the ET segment content in TCL) with the annealing time at 260°C. At an annealing time greater than 30 min, a new absorbance peak ap-

peared at 1070 cm^{-1} and became stronger with increasing annealing time. The characteristic peak was observed in the transesterified product of the PC/PET blend.^{3,4} It should be attributed to a complex vibration of the bisphenol A-terephthalate unit. At the range of 1620–1860 cm^{-1} , the FTIR spectrum shows two carboxyl group absorbance peaks, as presented in Figure 2. As the annealing time was prolonged, the C=O stretching absorbance band of the carbonate group (1780 cm^{-1}) progressively decreased; the C=O stretching absorbance band of the aliphatic and aromatic ester groups in TCL50 (center at about 1730 cm^{-1}) gradually widened. During the transesterification process, aromatic carbonate was transferred into aliphatic carbonate. Since ethylene carbonates are unstable and ultimately disappear, the 1780 cm^{-1} band of PC was reduced with the annealing time. Furthermore, the C=O

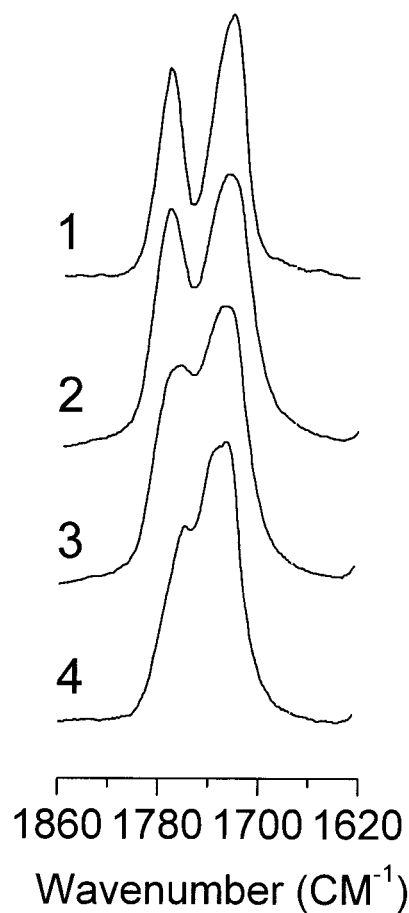


Figure 2 FTIR spectra of PC/TCL50 (50/50) blend with different annealing times at 260°C (1620–1860 cm^{-1}): (1) 0 min; (2) 30 min; (3) 60 min; (4) 90 min.

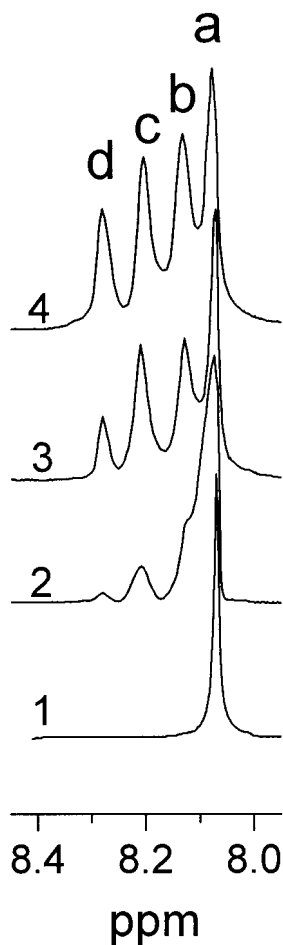


Figure 3 $^1\text{H-NMR}$ spectra (500 MHz) of PC/TCL50 (50/50) blend with different annealing times at 260°C (8.0–8.4 ppm): (1) 0 min; (2) 30 min; (3) 60 min; (4) 90 min.

stretching band of the new resultant bisphenol A-terephthalate unit is at 1740 cm^{-1} ; its overlapping with the 1730 cm^{-1} band leads to a wider peak in Figure 2.

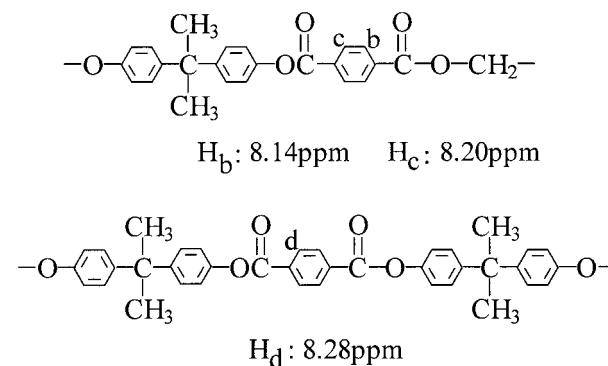
Further information about structural changes can be obtained by nuclear magnetic resonance measurement. Figure 3 shows the $^1\text{H-NMR}$ spectra of the blend before and after annealing at 260°C . In Figure 3, the original blend exhibited a peak (a) at 8.10 ppm which belonged to aromatic protons in the ET segments. However, three new peaks (b: 8.14 ppm, c: 8.20 ppm, d: 8.28 ppm) appeared in the resonance region of the aromatic proton after the blend was annealed at 260°C . The peak at 8.28 ppm should be assigned to the aromatic protons of terephthalate substituted symmetrically by bisphenol A, and the peaks at

8.20 and 8.14 ppm, to the aromatic protons of terephthalate substituted by bisphenol A and aliphatic groups.^{3,4} Their structures are depicted in Scheme 1.

Therefore, the IR and $^1\text{H-NMR}$ results demonstrate that during the annealing process transesterification can take place between PC and ET segments in TCL50 and result in the formation of new copolycondensates as in the exchange reaction of PC with the PET homopolymer.⁴

Transesterification of PC with CL Segments

Figure 4 shows another change of the $^1\text{H-NMR}$ spectrum with the annealing time. The resonance peak (e) at 2.35 ppm is due to the methylene protons neighboring carboxyl group ($-\text{CH}_2\text{COOCH}_2-$) in CL segments of TCL50. However, it is interesting that an additional new peak (f) appeared at 2.55 ppm in the $^1\text{H-NMR}$ spectrum when the blend PC/TCL50 (50/50) was annealed at 260°C for 30 min. With increasing annealing time, the new peak gradually increased. But it was not observed in the $^1\text{H-NMR}$ spectrum of the annealed PC/PET blend,⁴ that is, the peak is not related to the transesterification of PC with the ET segments. From the chemical shift, the new peak may result from methylene protons next to the carboxyl group in new resultant bisphenol A-CL unit (see Scheme 2). Because the benzene ring of bisphenol A has stronger electronegativity than that of the aliphatic chain, the linkage pattern probably causes a downfield shift of about 0.2 ppm of the corresponding resonance peak (e: 2.35 ppm) in the original caprolactone segments. The assumption can be confirmed by comparison with the $^1\text{H-NMR}$ spectrum of a model compound bisphenol A dibutyrate.



Scheme 1

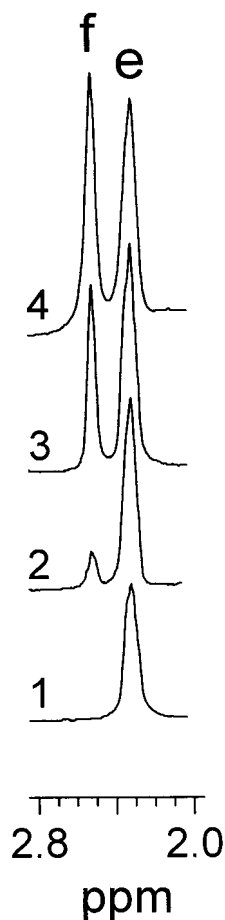
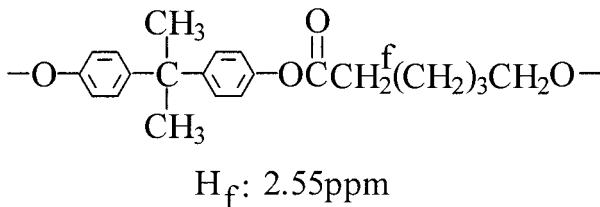


Figure 4 $^1\text{H-NMR}$ spectra (500 MHz) of PC/TCL50 (50/50) blend with different annealing times at 260°C (2.0–3.0 ppm): (1) 0 min; (2) 30 min; (3) 60 min; (4) 90 min.

Figure 5 presents the $^1\text{H-NMR}$ spectrum of the model compound. The detailed chemical shifts in the $^1\text{H-NMR}$ spectrum are given in the Experimental section. The methylene protons next to the carboxyl group show a resonance peak at 2.52 ppm, which is nearly identical with the chemical shift of the new peak in the annealed blend of PC/TCL50. The results indicate that the new



Scheme 2

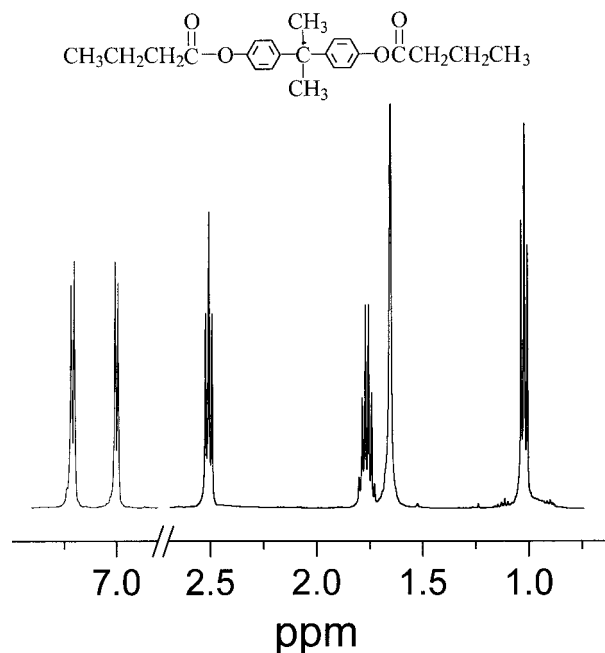


Figure 5 $^1\text{H-NMR}$ spectrum (500 MHz) of a model compound bisphenol A dibutyrate.

peak at 2.55 ppm represents the resultant bisphenol A-caprolactone unit as depicted in Scheme 2. So, we can conclude that the transesterification between PC and the CL segment occurred and gave rise to a new linkage pattern. The transesterified product could be dissolved in chloroform (CHCl_3); no insoluble material or gelation was detected in the solubility experiment, meaning that the thermooxidative branching reaction is negligible here.

From the experimental facts above, we naturally assume that transesterification can also occur between PC and the PCL homopolymer. Figure 6 shows the $^1\text{H-NMR}$ spectrum of the PC/PCL blend before and after annealing at 260°C for 60 min. However, as reported in the literature,⁶ the spectrum of the annealed blend is the same as that of the original blend, therefore excluding the occurrence of transesterification. Unexpectedly, adding a 2% (wt) $\text{Ti}(\text{O}i\text{Bu})_4$ catalyst to the annealed blend also caused a new resonance peak (m) at 2.55 ppm, as shown in Figure 7. Its relative intensity increased with the annealing time. This resonance signal is coincident with the characteristic peak stemming from the transesterification of PC with CL segments in TCL50, which indicates the formation of the bisphenol A-caprolactone unit in the annealed PC/PCL blend. In addi-

tion, neither gel was detected for the annealed samples in the solubility experiment. These results revealed that in the presence of a catalyst transesterification obviously took place between PC and the PCL homopolymers and the thermooxidative branching reaction, which caused the gelation of the two components, was also negligible. On the other hand, it further confirms the above interpretation of the signal at 2.55 ppm for the annealed PC/TCL50 blend.

The results above suggest that the Ti compound catalyst induces very rapid transesterification in the melt blend. Hence, it is understandable that owing to lack of a catalyst the occurrence of transesterification was not observed in the literature.⁶ A similar behavior was reported on the interchange reaction of PC with the PET homopolymer.^{8,9} It is necessary to note that the Ti compound catalyst was also used in the synthesis of the TCL50 copolyester. Residue of the catalyst was confirmed by X-ray fluoroscopy. From the transesterification behaviors of PC with PCL and PET, it can be imagined that both transesterifications of PC with ET and CL segments were certainly accelerated by the residue of the polymerization catalyst.

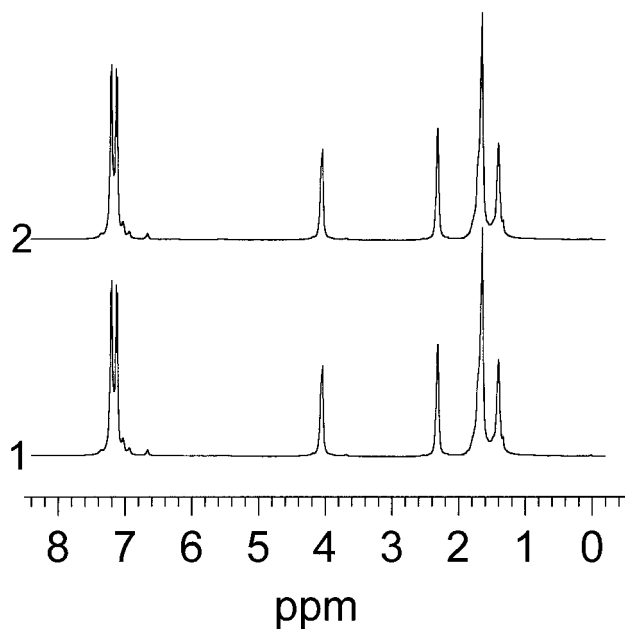


Figure 6 $^1\text{H-NMR}$ spectrum (500 MHz) of PC/PCL (50/50) blend: (1) original blend; (2) after annealed for 60 min at 260°C.

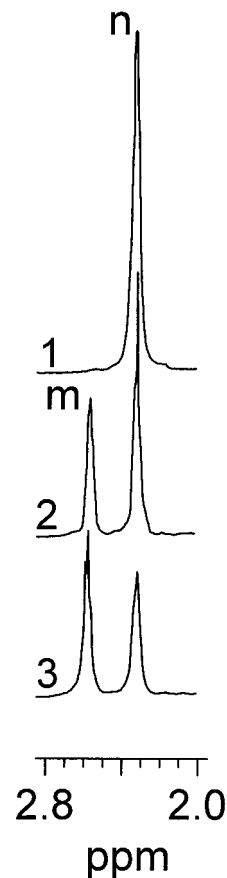


Figure 7 $^1\text{H-NMR}$ spectra (500 MHz) of PC/PCL (50/50) blend [adding 2% $\text{Ti}(\text{OBu})_4$] with different annealing times at 260°C (2.1–2.8 ppm): (1) 0 min; (2) 60 min; (3) 90 min.

Transesterification Rates of PC with ET and CL Segments

In our previous work,¹⁴ it was shown that homogenization of the PC/TCL blend can be caused by transesterification of PC with the TCL copolyester during the annealing process. By the present further study, we can determine that in addition to ET segments CL segments simultaneously take part in the reaction with PC.

In the reaction process, terephthalate and CL units in TCL50 are transferred into bisphenol A-terephthalate and bisphenol A-CL units, respectively. Figures 3 and 4 also show that those amounts of the two new structure units increase with the annealing time. Because the relative amounts are proportional to the integrals under the resonance peaks, their transferring ratios

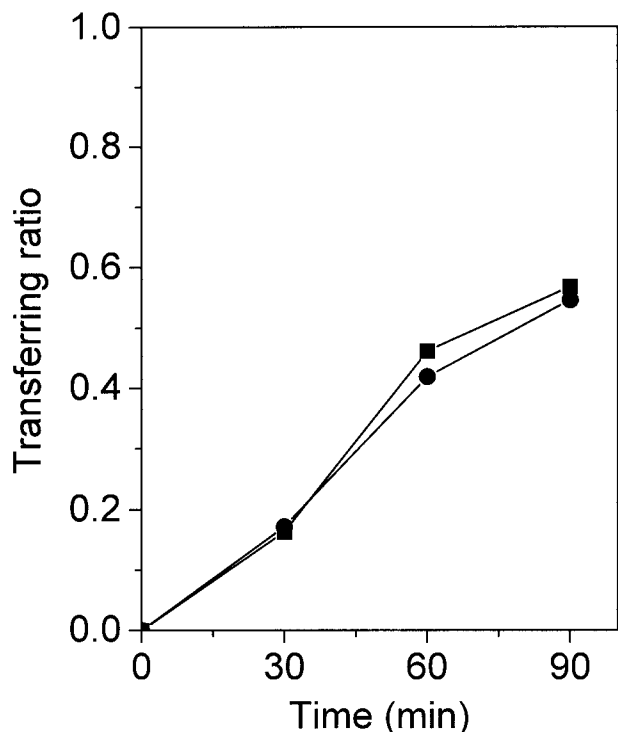


Figure 8 Transferring mol ratios of terephthalate and CL units in TCL50 versus annealing time at 260°C (obtained from $^1\text{H-NMR}$ analysis): (■) bisphenol A-terephthalate; (●) bisphenol A-CL.

X_{AB} and X_{AC} in the reaction can be calculated from

$$X_{AB} = \frac{\frac{1}{4}I_d + \frac{1}{4}(I_c + I_b)}{\frac{1}{4}I_a + \frac{1}{4}I_d + \frac{1}{4}(I_c + I_b)} = \frac{I_d + I_c + I_b}{I_a + I_d + I_c + I_b}$$

$$X_{AC} = \frac{\frac{1}{2}I_f}{\frac{1}{2}I_e + \frac{1}{2}I_f} = \frac{I_f}{I_e + I_f}$$

A is bisphenol A; B, terephthalate; and C, CL.

The changes of X_{AB} and X_{AC} with the annealing time are described in Figure 8. In Figure 8, X_{AB} and X_{AC} markedly increase as the reaction continues. When the blend PC/TCL50 was annealed for 90 min at 260°C, about 56% terephthalate and 54% CL units in TCL50 were transferred into these new linkages. However, interestingly, the increased rates of X_{AB} and X_{AC} show little

difference. Thus, we believe that the transesterifications of PC with ET segments and CL segments proceed in a random or free manner.

From theory, the reaction activities of aromatic and aliphatic ester groups differ from each other. However, the difference did not seem to cause a very preferential reaction in the blend of PC with random TCL50 copolyester. On the other hand, our previous work¹⁴ showed that PC is miscible with TCL50, suggesting that the molecular chain of PC can sufficiently contact with both ET and CL segments in the blend. Therefore, the miscibility may be beneficial to both transesterifications of PC with ET and CL segments.

CONCLUSIONS

From the results and discussion above, the conclusions are the following:

1. In the annealed blend, transesterification could occur between PC and the TCL50 copolyester. The bisphenol A unit in PC reacted simultaneously with ET and CL segments. In the reaction process, the terephthalate and CL units were progressively transferred into bisphenol A-terephthalate and bisphenol A-caprolactone units, respectively.
2. From $^1\text{H-NMR}$ analysis, the reaction rates of PC with two kinds of segments are nearly equal, that is, the transesterifications of carbonate groups with aromatic and aliphatic ester groups proceeded in a random or free manner.
3. In the presence of Ti compound catalyst, transesterification also took place between PC and PCL homopolyester and led to the formation of copolyester. However, the thermooxidative branching reaction was negligible here.

Additionally, residues of the Ti compound in TCL50 may simultaneously catalyze both transesterifications of PC with ET and CL segments, but the process needs further study in the future.

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