

TRANSESTERIFICATION OF POLY(ETHYLENE TEREPHTHALATE) WITH POLY(ϵ -CAPROLACTONE)*

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Abstract Transesterification of poly(ethylene terephthalate) (PET) with poly(ϵ -caprolactone) (PCL) was investigated by means of NMR spectroscopy, extraction experiments, differential scanning calorimetry (DSC) and phase contrast microscopy (PCM). The ^1H -NMR results show that transesterification takes place in the melt blends and leads to the formation of the PET-PCL copolyester with a chemical structure similar to ethylene terephthalate- ϵ -caprolactone copolyester (TCL) synthesized directly from monomers. However, even in the blend that has been transesterified for 8 h, the random PET-PCL copolyester, PET-PCL copolyester with long PET or long PCL segments and the unreacted PET and PCL homopolymers may coexist. Due to the low mobility of PET and PCL chains and the high viscosity of the two macromolecules, the transesterification proceeds with difficulty. Furthermore, PET is incompatible with PCL, the transesterification can only occur at the interface or in the interfacial region between two phases, and finally the reaction can only reach a local equilibrium. These results indicate that in fact the transesterification in the melt blend between two incompatible homopolymers could not lead to the formation of completely random or typical block copolyesters.

Keywords Transesterification, Poly(ethylene terephthalate), Poly(ϵ -caprolactone), Crystallization, Phase structure

INTRODUCTION

In recent years, considerable efforts have been invested in the investigation of polyester blends. Attention is invariably directed toward their ester exchange reaction ability to form homogeneous mixtures with themselves^[1-14]. This reaction has been studied for both academic interest and with a view industrial applications.

The transesterification of poly(bisphenol-A carbonate) (PC) with aromatic and aliphatic polyesters has been extensively studied and different conclusions drawn. For the PC/PET blends, transesterification can occur in the melt blends and give rise to the four-component copolycondensates^[4]. The exchange reaction may take place between PC and PET according to the three types of reaction mechanisms proposed by Kotliar^[2], i.e. alcoholysis, acidolysis and ester-ester exchange. Godard *et al.*^[4] remarked that as in their PC/PBT study^[3], an ester exchange between carbonate and terephthalate groups was the first reaction. On the other hand, it is easy to imagine that by varying the transesterification extent the compatibility between the two components in the blend will be changed too^[9-14]. For the blend of PC with aliphatic polyester such as poly(ϵ -caprolactone) (PCL), the chemical reaction could also take place between the components during the melt processing. Porter^[7] found that a gel-like product which could only be swollen in methylene chloride was obtained. In his work, the results obtained from solvent extraction, FTIR and NMR analysis demonstrated that the transesterification was not the dominant reaction, but the thermal-oxidative branching reaction mainly occurred and caused the gelation between components.

Up till now, no study on the exchange reaction of the PET/PCL blend has been reported only their immiscibility was shown by Ma *et al.*^[15]. In our laboratory, ethylene terephthalate- ϵ -caprolactone copolyesters

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(TCL) have been synthesized from the monomers^[16–18]. Due to the unavoidable transesterification between ET and CL segments, TCL copolyesters are segmented copolyesters with certain random copolymerization characteristics^[18]. For TCL copolyesters with high (> 70%) or low (< 30%) hard segment content, the hard ET or soft CL segments can crystallize, exhibiting the property of single-segmented copolymers; in other cases, TCL copolyesters exhibit certain properties^[19] of random copolymers. However, it is interesting that in any TCL copolyester, the CL and ET segments cannot crystallize simultaneously. This property can be used to distinguish TCL copolyesters from other typical segmented copolymers^[19].

In the present paper, it will be shown that transesterification can occur in the melt PET/PCL blend. The chemical structure and composition of the product were elucidated by NMR, DSC and extraction experiments. The changes of the phase structures with the transesterification extent were observed using the phase contrast microscope. The characteristics of the transesterification reaction for the PET/PCL blends were also discussed.

EXPERIMENTAL

Poly(ethylene terephthalate) (PET) having a molecular weight $M_w = 58,000$ was available from Aldrich Chemical Co. poly(ϵ -caprolactone) (PCL) with $M_w = 40,000$ was supplied by Scientific Polymer Products Inc.

The blending of PET/PCL was carried out by dissolving both PET and PCL in a mixed solvent composed of phenol and tetrachloroethane (50/50, *W/W*) at room temperature. The polymers in the solution were precipitated by adding a 10-fold volume of methanol. The precipitation blends were carefully washed with methanol, and then dried to constant weight in a vacuum oven at 50°C for one week. The dried blend was placed in a nitrogen-purged glass tube and heated in a salt bath at 270°C. Under the protection of nitrogen flow, the transesterification proceeded for different periods of time. An ethylene terephthalate- ϵ -caprolactone copolyester (TCL48, 48 represents the ET hard segment content) was synthesized directly from the monomers by a method similar to that reported by Luo *et al.*^[16, 17].

For NMR measurements, about 10% solutions were prepared by dissolving the blends in a 20:1 (*V/V*) mixture of deuterated chloroform and trifluoroacetic acid. The ¹H-NMR spectra were obtained with a Bruker DMX-500 spectrometer. Extraction experiments were employed to separate the ingredients in the melt-processed blends. The samples were first extracted with CCl₄ (a solvent for PCL, a nonsolvent for PET) in a Soxhlet extractor. The undissolved fraction was dried and then extracted with CHCl₃ (a solvent for copolyesters, a nonsolvent for PET and TCL copolyester with high ET content $\geq 80\%$). The differences in the solubility of transesterified samples in CCl₄ and CHCl₃ at different transesterification times were analyzed, respectively. DSC measurements were carried out with a Perkin-Elmer DSC-2 calorimeter. Both cooling and heating curves were recorded at a scanning rate of 20 K/min. The temperature was calibrated with ultrapure indium. The change of phase structures with transesterification time was observed by a phase contrast microscope (Olympus IMT-2). Before observation, the sample sandwiched between two cover glasses was molten on a hot stage equipped with a temperature controller for 1 min, and then quenched in liquid nitrogen.

RESULTS

NMR Analysis of the Transesterification

Figure 1 shows the ¹H-NMR spectrum of the freshly prepared PET/PCL (50/50, wt%) blend. The peaks centered at $\delta = 8.06$ (a) and $\delta = 4.68$ (b) should be attributed to the protons of the benzene ring and the ethylene dioxy group of PET; the peaks at $\delta = 4.04$ (c), $\delta = 2.35$ (d) and $\delta = 1.0\text{--}2.0$ (e) to methylene protons of $-\text{CH}_2-\text{OCO}-$, $-\text{OCCCH}_2-$ and $-(\text{CH}_2)_3-$ in PCL, respectively. Obviously, this spectrum is a simple additive spectrum of PET and PCL homopolymers. Thus, the original blend is a mechanical mixture of the two homopolymers. After the blend was annealed at 270°C for a sufficiently long time, four new peaks (f, i, j, k) appeared in the range of $\delta = 4.0\text{--}5.0$ between peak b and c, and became stronger with increasing annealing time, as shown in Fig. 2. It is notable that the chemical shifts of these four peaks coincide with those of the four characteristic peaks of ethylene terephthalate- ϵ -caprolactone copolyester (TCL48) synthesized from the

monomers, as shown in Fig. 3. Through a model compound study, Luo *et al.*^[16–18] attributed these peaks to the protons in the different linkage patterns between terephthalate and caprolactone units, resulting from an unavoidable exchange reaction between ET and CL segments. Their spectral assignments are summarized in Table 1.

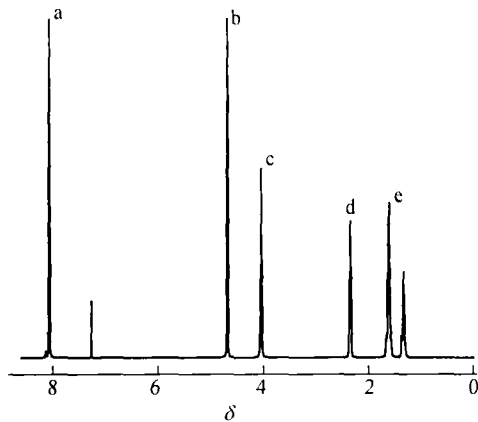


Fig. 1 500MHz ¹H-NMR spectrum of PET/PCL blend (50/50)

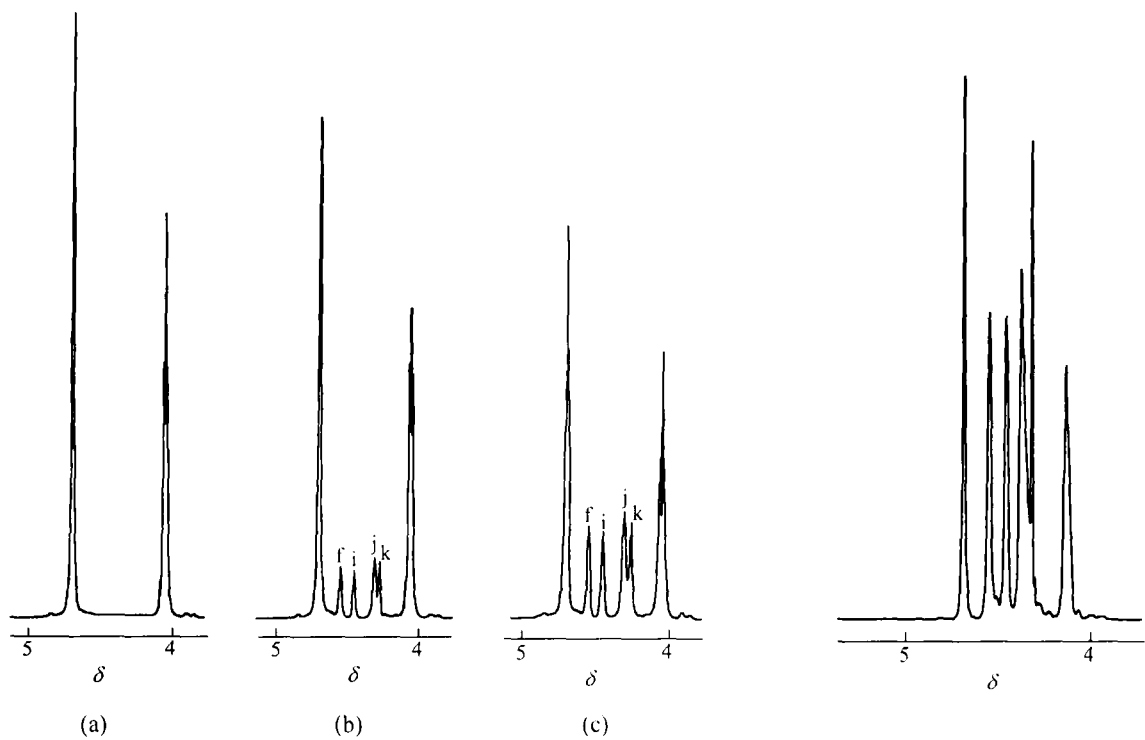


Fig. 2 500 MHz ¹H-NMR spectra of PET/PCL blend (50/50) with different annealing times at 270°C
a) Original blend; b) 4 h; c) 8 h

Fig. 3 500MHz ¹H-NMR spectrum of TCL48 copolyester

From the above assignments, we can conclude that the transesterification took place between PET and PCL homopolymers in the annealing stage, and resulted in the formation of PET-PCL copolyesters similar to TCL48 copolyester. The reaction process can be described as follows:

The part insoluble in CCl_4 was dried and then extracted with CHCl_3 . Figure 5 shows the extraction results. The amount of the fraction soluble in CHCl_3 increases with the annealing time. The ^1H -NMR spectrum of the soluble part reveals that PET-PCL copolyesters were extracted in the experiment (Fig. 6). Figure 5 also shows that part of the blend annealed for 8 h was still insoluble in CHCl_3 . In the previous study^[18], it was shown that the solubility of the TCL copolyester in CHCl_3 is related to the ET segment content, and the copolyesters with high ET content ($> 80\%$) are insoluble in this solvent. These results imply that the insoluble part may consist of both PET and the PET-PCL copolyesters with high ET segment content.

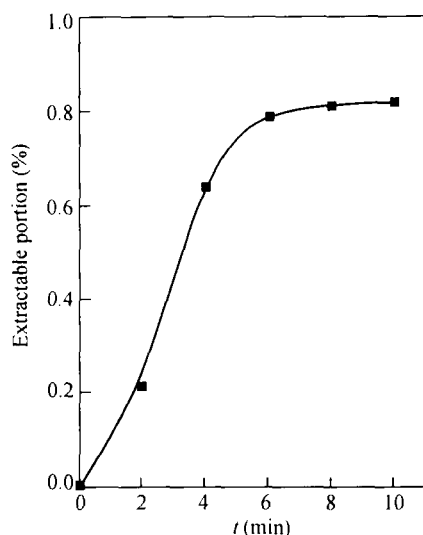


Fig. 5 Solubility of the CCl_4 unextractable fraction in CHCl_3 as a function of annealing time at 270°C

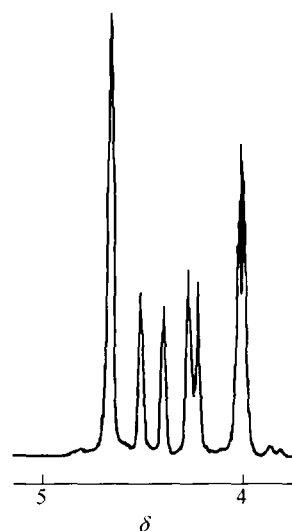


Fig. 6 500 MHz ^1H -NMR spectrum of the CHCl_3 extracted fraction of the blend annealed at 270°C for 8 h

Differential Scanning Calorimetry (DSC) Measurements

Figure 7 presents the DSC cooling curves of the PET/PCL blends (20/80, 50/50 and 80/20 by weight) after different annealing times. The 20/80 blend shows a distinct exothermic peak at low temperature, which could be attributed to the crystallization of PCL segments. As the annealing time was prolonged, the peak height gradually reduced and moved toward lower temperature. For the 80/20 blend, the crystallization peak of PET segments at high temperature exhibited the same tendency. However, the 50/50 blend shows two exothermic peaks (belonging to PCL and PET segments, respectively) in its DSC curves. After the blend was annealed for 8 h, the two weak crystallization peaks were still observable. In the heating run, the melting temperature and enthalpy of the PCL and PET segment crystals decrease simultaneously with the annealing time, as depicted in Fig 8. Such changes of the thermal behavior indicate that due to the exchange reaction between the two different ester groups, PET and PCL homopolymer chains are broken and the crystallization ability of the PET and PCL components is reduced. Similar results were observed for poly(butylene succinate)/poly(butylene terephthalate) blends^[6].

DISCUSSION

As shown above, the four new peaks in the ^1H -NMR spectra of the transesterified blends became stronger with increasing annealing time. However, after annealing for 8 h, their peak intensity was still much weaker than that of the TCL48 copolyester, that is to say, after 8 h the amount of the random copolyester structure units in the transesterified blend was considerably less than that in TCL48 copolyester synthesized from monomers. The results obtained from the extraction experiments also support such a deduction. In fact, in the transesterified

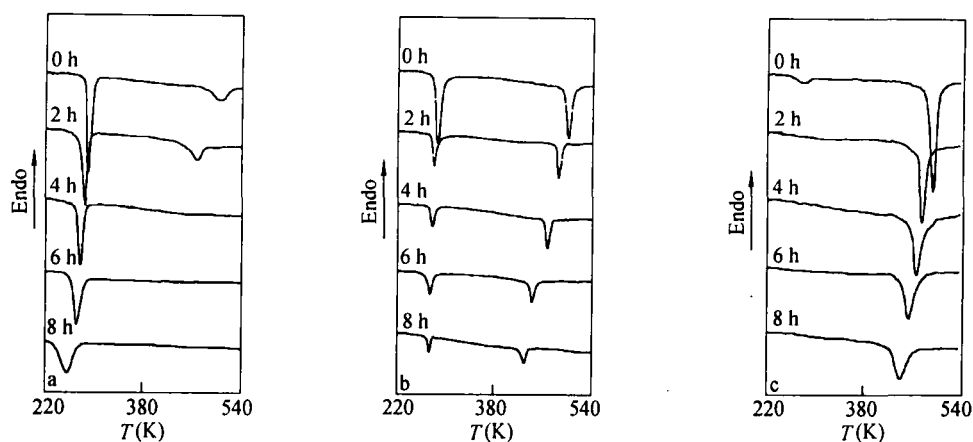


Fig. 7 DSC cooling curves of PET/PCL blends with different annealing time at 270°C
a) 20/80, b) 50/50, c) 80/20

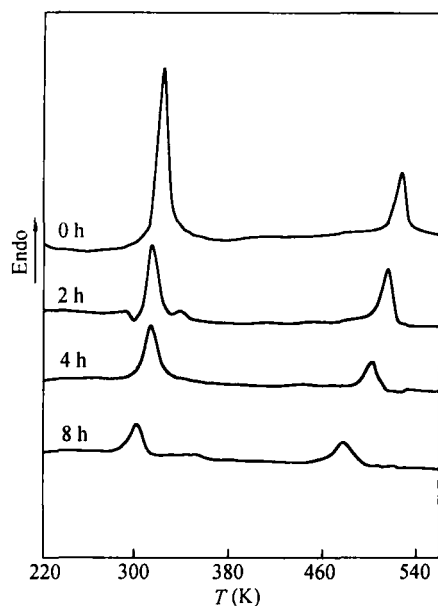


Fig. 8 DSC heating curves of PET/PCL blend (50/50) with different annealing time at 270°C

blend both PET and PCL homopolymers were still retained. This means that in such an incompatible blend, the transesterification reaction proceeds with great difficulty. On the other hand, the crystallization behavior illustrates the characteristic chain structure more clearly. It is important that even in the transesterified blend (50/50) for 8 h, both PCL and PET components still retain their crystallization ability to some extent. However, both the hard and the soft segments in TCL48 copolyester cannot crystallize^[19]. This shows that the chain structures of the transesterified blend PET/PCL (50/50) have not approached the degree of randomness as in TCL48 copolyester. Therefore, it can be concluded that in fact the transesterified PET/PCL blend (50/50) for 8 h is a mixture composed of PET-PCL copolyester with certain random degree, PET-PCL copolymers with long PET or PCL segments, PET and PCL homopolymers.

It was found that co-condensation (or transesterification) and self-condensation proceeded simultaneously during the synthesis of TCL48 copolyester^[18]. The monomers may play a role as a diluent in the synthesis. As a result, both ET hard and CL soft segments themselves grow into long segments with difficulty. So TCL

copolyester exhibited an obvious randomness. However, in the transesterification of the PET and PCL homopolymers with high molecular weight, the low mobility of polymer chains and high viscosity of the blend would reduce the reaction probability. The transesterification can only attain a certain reaction equilibrium in which the content of PET-PCL copolyester with certain random degree reaches a upper limit finally, as shown in Fig. 5. In the transesterification, it is almost impossible for the PET and PCL homopolymers to form the completely random PET-PCL copolyester like TCL copolyesters.

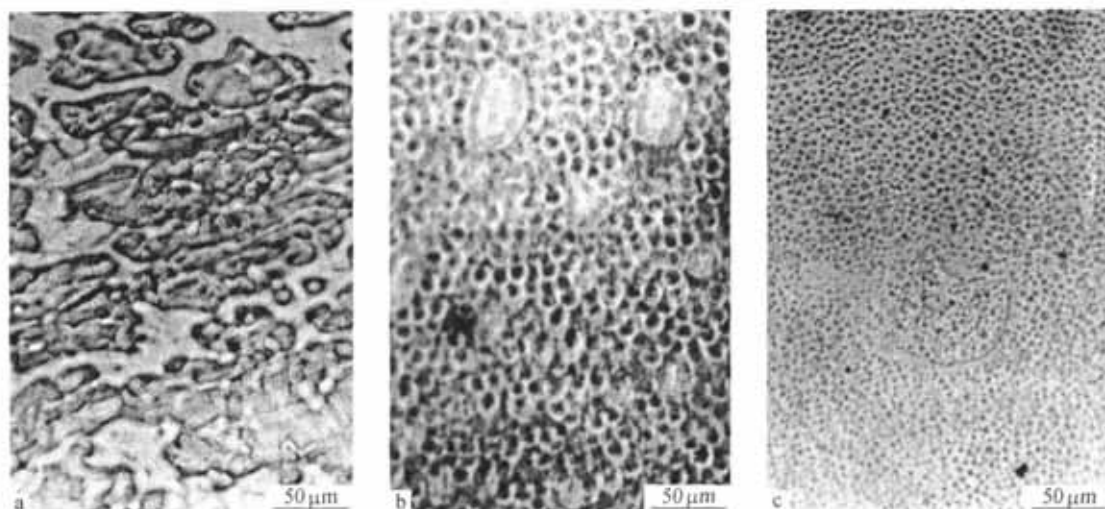


Fig. 9 Phase contrast micrographs of PET/PCL blend (50/50) with different annealing time at 270°C
a) Original blend, b) 4 h, c) 8 h

In a transesterification review^[1], Porter remarked that transesterification can occur in both compatible and incompatible blends. For the latter, the reaction presumably occurs at the interface or in the interfacial region. It has been shown that PET is incompatible with PCL, their blends with different compositions exhibit two T_g s^[15]. The phase contrast micrographs of the transesterified blend PET/PCL (50/50) are shown in Fig 9. It is evident that the PET/PCL blend exhibits a two phase structure, therefore, the transesterification in this blend should begin in interfacial regions of the two phases. It is natural that the transesterification reaction should be a progressive process and can reach only some local reaction equilibrium. At the same time, the size of the two phases in the blends became smaller and smaller, this is similar to the experimental results reported in our previous work^[20, 21]. It has been shown that poly(ethylene terephthalate) is incompatible with poly(bisphenol-A carbonate), but the transesterification product from PET and PC components, and TCL copolyester can compatibilize them. The changes of the phase structures in the transesterified PET/PCL blend also prove that the transesterification product in the PET/PCL blend can also improve the compatibility between PET and PCL components and reduce the tension between PET rich and PCL rich phase domains. It indicates that the transesterification product can act as compatibilizer in PET/PCL incompatible blends.

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