

TRANSESTERIFICATION OF POLY(BISPHENOL A CARBONATE) WITH AROMATIC AND ALIPHATIC SEGMENTS IN BUTYLENE TEREPHTHALATE-CAPROLACTONE COPOLYESTER

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Abstract In this article, the transesterification of poly(bisphenol A carbonate) (PC) with butylene terephthalate-caprolactone copolyester at a weight ratio 50/50 (BCL(21)) was thoroughly investigated by proton nuclear magnetic resonance spectroscopy ($^1\text{H-NMR}$), in conjunction with a model compound. The $^1\text{H-NMR}$ results of the annealed blend PC/BCL(21) show that the formation of bisphenol A-terephthalate ester units is the same as in the annealed blend of PC with PBT, and the transesterification actually occurs between PC and butylene terephthalate (BT) segments in BCL(21). By comparison with the model compound bisphenol A dibutyrate, the new signal appearing at $\delta = 2.56$ in the $^1\text{H-NMR}$ spectrum confirms the existence of bisphenol A caprolactone ester units resulting from the exchange reaction of PC with caprolactone (CL) segments. $^1\text{H-NMR}$ analysis of the transesterification rates reveals that the reaction of PC with aromatic and aliphatic segments in BCL(21) proceeds in a random manner. The miscibility of the blend PC/BCL(21) copolyester is favorable for the transesterification of PC with BT segments and CL segments.

Keywords Transesterification, Poly(bisphenol A carbonate), Butylene terephthalate-caprolactone copolyester, $^1\text{H-NMR}$

INTRODUCTION

Investigations of polyester blends possess both academic and practical interest. For polyester blends, transesterification is the most important problem. Transesterification can influence the miscibility, phase behavior and phase structure, crystallization and crystalline morphology of the blends, and even their consequent properties.

The blend of polycarbonate (PC) with polyethylene terephthalate (PET) has been proved to be immiscible, but transesterification can change it from a heterogeneous system to a homogeneous one and make it miscible^[1–5]. Blends of polycarbonate and polybutylene terephthalate (PBT) have been studied extensively, but different conclusions were drawn regarding their states of miscibility, due to the complex melting behavior of PC/PBT blends. During the melting process, transesterification reactions between the homopolymers, liquid-liquid phase separation and crystallization of PBT may occur simultaneously. However, a recent time-resolved light scattering study^[6] unequivocally showed that a 50/50 PC/PBT blend exhibits a lower critical solution temperature (LCST) type phase behavior with a spinodal temperature (T_s).

Paul and his coworkers^[7–9] have indicated that poly(ϵ -caprolactone) (PCL) is miscible with polycarbonate of bisphenol A in the amorphous state. This blend exhibits a LCST behavior of phase separation. Coleman *et al.*^[10] have proved the presence of specific chemical interaction between PCL and PC in the amorphous state, which infers that they are miscible. However, Jonza and Porter^[11] have convincingly shown that a single glass transition was found across the compositional diagram of PCL/PC blends of either PC or PCL. Therefore, the Flory interaction parameter (χ) must be zero or slightly positive for those blends. In PC/PCL blends the interchange

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reaction can also take place between the components during melt processing, but a gelled product, which could only be swollen in methylene chloride, was obtained. Solvent extraction, FT-IR, and NMR experimental results demonstrated that transesterification did not predominate and that thermooxidative branching occurred and caused the gelation among the components.

Ma et al.^[12, 13] have proved that blends of PCL and PET are immiscible, and their DSC curves for each composition show two evident T_g 's which approach those of the homopolymers. Blending of butylene terephthalate- ϵ -caprolactone (BCL) copolyester with poly(ϵ -caprolactone) has demonstrated that they are immiscible when the hard segment content in the copolyester is higher than 60%. Therefore it can be concluded that PBT is certainly immiscible with PCL. However, in the melt mixture of PET (or PBT) and PCL, the occurrence of transesterification between them is inevitable. For this reason, the normal segmented copolyester cannot be obtained from dimethyl terephthalate, ethylene glycol (or 1,4 butanediol) and ϵ -caprolactone. In our laboratory, two series of random copolyesters [ethylene terephthalate- ϵ -caprolactone copolyester (TCL) and BCL] were synthesized and characterized^[14–18]. When the hard segment content in the copolyester was lower than 60%, TCL copolyester was miscible with PC^[19, 20]. The miscibility of BCL copolyester with PC behaved similarly to that of TCL copolyester with PC, but the miscibility window is wider^[21].

It has been found that the transesterification product between PET and PC is a random copolyester that can exert great influence on the miscibility of PC/PET blend as a compatibilizer^[22]. The TCL copolyester can also play a role as a compatibilizer for PC/PET blend^[23]. For a better understanding of the compatibilizing effect of TCL copolyester, the transesterification of PC with aromatic and aliphatic segments in TCL copolyester has been investigated^[24]. Naturally, the transesterification of PC with aromatic and aliphatic segments in BCL copolyester is also of interest. In this article, the transesterification has been studied more thoroughly by $^1\text{H-NMR}$.

EXPERIMENT

Materials

Poly(bisphenol A carbonate) (PC) with $M_n = 38,000$, was kindly supplied by the Changzhou Organic Chemical Plant (China).

ϵ -Caprolactone (CL) monomer (from Fluka Chemica, Switzerland) was vacuum distilled.

1,4-Butanediol (BD) was first purified with molecular sieves for a week and then distilled under a reduced pressure. Dimethyl terephthalate (DMT) was an analytically pure product.

Analytically pure zinc acetate $\text{Zn}(\text{OAc})_2$ and antimony acetate $\text{Sb}(\text{OAc})_3$ were used as catalysts without further purification.

Butylene Terephthalate-Caprolactone Copolyester (BCL) Synthesis

The whole synthesis was divided into two steps: In the first step, DMT, BD, and $\text{Zn}(\text{OAc})_2$ were added into a nitrogen-purged reaction vessel and then heated to 170–220°C to start esterification and condensation. In the second step, CL monomer and $\text{Sb}(\text{OAc})_3$ were added to start ring-opening polymerization (about 2 h at 170–180°C in N_2 atmosphere) and then to proceed to polycondensation in a high vacuum (< 14 Pa) at 240–250°C to ensure complete conversion of monomer materials. The polymer products were obtained under the protection of N_2 .

During the synthesis, all the monomer materials (DMT, CL, and BD) were added to the autoclave in proportion and the amount of catalysts used was one-thousandth of the total amount of DMT and CL. By changing the reactant mixture ratio, we can synthesize a series of BCL copolyesters with different hard-segment contents.

Synthesis of Model Compound Bisphenol A Dibutyrate

The model compound bisphenol A dibutyrate was synthesized through two steps: Firstly, butanoic acid (12 g) and an excess of thionyl chloride (SOCl_2) were placed in a 250 mL flask; refluxing was continued until HCl vapor was no longer released. The unreacted thionyl chloride was removed under reduced pressure and butanoyl chloride was obtained. In the second step, bisphenol A (4 g) was dissolved in 80 mL mixed solvent of benzene

and pyridine (50/50, *V/V*). Under stirring, an excess amount of butanoyl chloride was carefully added dropwise to the solution cooled with iced water. The reaction mixture was stirred for 24 h at room temperature and then poured into 250 mL iced water and neutralized by HCl. The oil layer was separated and washed with 5% aqueous NaHCO₃ (3 × 50 mL) and distilled water (3 × 50 mL). After being dried with Na₂SO₄ for 24 h, the crude product was vacuum distilled and the yellow residue was re-crystallized from chloroform. Bisphenol A dibutylate was obtained.

Characterization

High-resolution ¹H-NMR spectra were recorded with a Bruker AVANCE AE400 NMR spectrometer at 300 K; the number of scans was 8, and the sweep width was 6000 Hz. All the samples were examined as 8%–10% (g/mL) solutions in deuterated chloroform. Curves were resolved into their components with a computer program that approximates each peak to a Lorentzian shape.

DSC measurements were carried out on a Perkin-Elmer DSC-2C apparatus equipped with a TADS microcomputer and an Intracooler-II. The calorimeter was calibrated with ultra-pure indium. The samples were heated at a rate of 40 K/min to 525 K, maintained for 2 min to erase the thermal history and then quenched to 200 K. The quenched samples were then reheated at a rate of 20 K/min to 525 K for curve recording. The temperature at half height of the corresponding heat capacity jump was defined as *T_g*, while *T_m* was the peak temperature of the melting endotherm and *T_{cc}* was the peak temperature of the crystallization exotherm in heating thermograms.

The intrinsic viscosity [*η*] of BCL copolyesters was measured in 1,1,2,2-tetrachloroethane with an Ubbelohde viscometer at 30°C. The characterization data of BCL are shown in Table 1.

Table 1. Characterization data of BCL copolyester

Sample	Hard segment content (wt%)	[<i>η</i>] (dL/g)	<i>T_g</i> (K)	<i>T_{cc}</i> (K)	<i>T_m</i> (K)	Solubility in CHCl ₃
BCL	21	0.836	222	266	292	S

Blending and Annealing

The two polymers were dissolved in chloroform, yielding a 5% solution. The blend was subsequently recovered from the solution by precipitation with methanol. The blend samples were further dried in a vacuum oven at 50°C until they reach constant weights.

The newly prepared blend was placed in a nitrogen-purged glass tube and heated in a 270°C salt bath (KNO₃/NaNO₃, 48.7/51.3, wt%). Under the protection of a nitrogen flow, the blend was annealed for various lengths of time.

Measurements

All ¹H-NMR spectra were obtained on a Bruker AVANCE AV400 NMR spectrometer at 300 K; the number of scans was 64, and the sweep width was 8000 Hz, using CDCl₃ as a solvent and TMS as an internal standard. About 10% solution was prepared for this measurement.

RESULTS AND DISCUSSIONS

Transesterification of PC with BT Segments

Figure 1 displays the ¹H-NMR spectra of PC and BCL.

According to the literature^[25, 26], the peaks at $\delta = 7.22$ – 7.29 (a) are due to aromatic protons, and the peak at $\delta = 1.72$ (b) is due to methyl protons of PC. In the ¹H-NMR spectrum of BCL (21) copolyester, the peak at $\delta = 8.06$ (c) could be assigned to the protons attached to benzene nucleus, the peaks appearing at $\delta = 4.03$ (e), $\delta = 2.28$ (f), $\delta = 1.62$ (g) and $\delta = 1.36$ (h) are due to the methylene protons of $-\text{CH}_2-\text{OCO}-$, $-\text{OC}-\text{CH}_2-$ and $-(\text{CH}_2)_3-$ in CL segment respectively. The peak at $\delta = 4.32$ (d) could be assigned to the methylene protons of $-\text{OCH}_2(\text{CH}_2)_2\text{CH}_2\text{O}-$ in butanediol unit next to a terephthaloyl group.

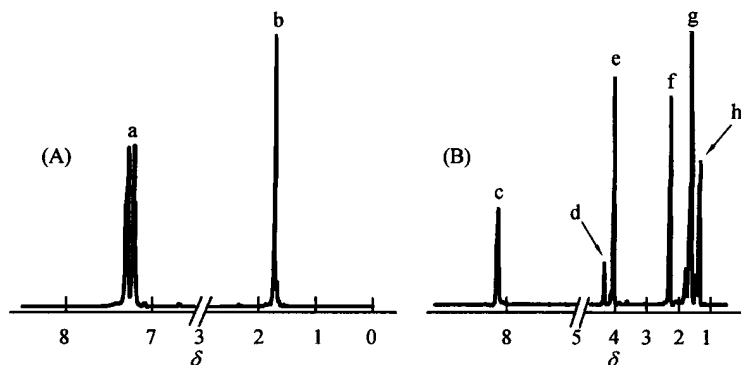


Fig. 1 ^1H -NMR spectra of PC (A) and BCL(21) (B)

The ^1H -NMR spectrum of PC and BCL blend is a simple superposition of their respective spectra. But it would change greatly after the blend is annealed, and the spectrum changes could give further information about structural changes. Figure 2 shows the changes of ^1H -NMR spectrum of the blend annealed at 270°C for different lengths of time.

The bands indicated by arrows show great changes and several new peaks appear. These changes resulted from the transesterification in annealing.

The bands between $\delta = 8.5\text{--}8.0$ in Fig. 3 are related to the changes of chain structure in the neighborhood of terephthalate group.

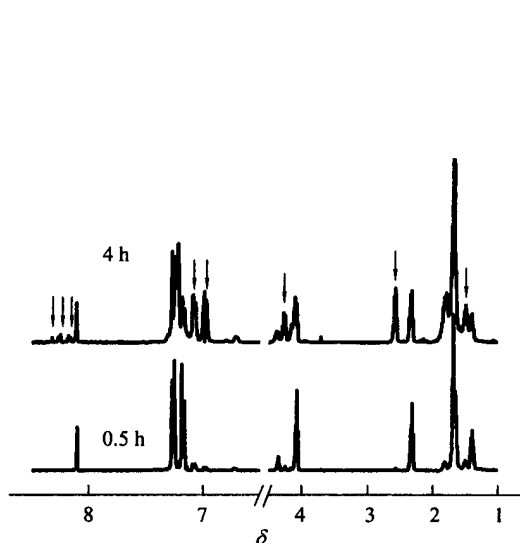


Fig. 2 ^1H -NMR spectra of PC/BCL50 (21) blend after different annealing times at 270°C

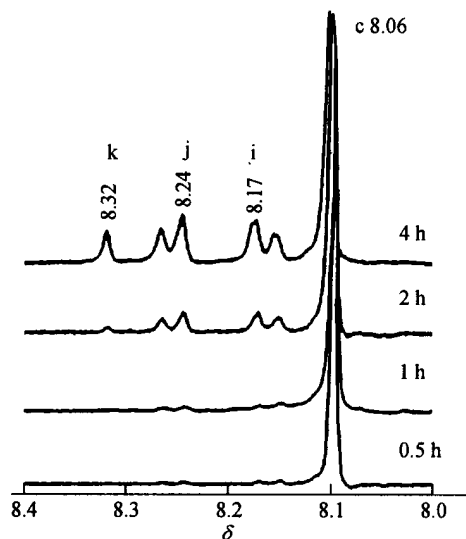


Fig. 3 The ^1H -NMR spectra of PC/BCL(21) blend in $\delta = 8.5\text{--}8.0$ after annealing for different periods of time.

Devaux and his coworker^[27] have synthesized a model compound, bisphenol-A terephthalate and its ^1H -NMR spectrum exhibits one strong peak at $\delta = 8.3$ that belongs to the protons of terephthalate. Therefore the peak at $\delta = 8.32$ could be assigned to the aromatic protons of terephthalate substituted symmetrically by bisphenol A. And the peaks at $\delta = 8.24$ and $\delta = 8.17$ are ascribed to the aromatic protons of terephthalate substituted by bisphenol A and aliphatic groups. Their structures are depicted in Scheme 1.

The new peaks of ^1H -NMR spectrum shown in Fig. 4 in the region of $\delta = 6.5$ and $\delta = 7.5$ reflect the changes of groups bonded to bisphenol A carbonate.

It has been known that the band at $\delta = 7.22$ belongs to aromatic protons of bisphenol A carbonate. In the

transesterification of butylene terephthalate units with bisphenol A carbonate units, bisphenol A also can be substituted by terephthalate group symmetrically or unsymmetrically (as shown in Scheme 2). Such substitutions will certainly influence the bands of aromatic protons in the bisphenol A group. In fact, the intensity of the band at $\delta = 7.22$ changes with annealing time, on the left side of this band the intensities of other bands are intensified while those on the right side are reduced. The cause of this change is quite complicated and needs further investigation.

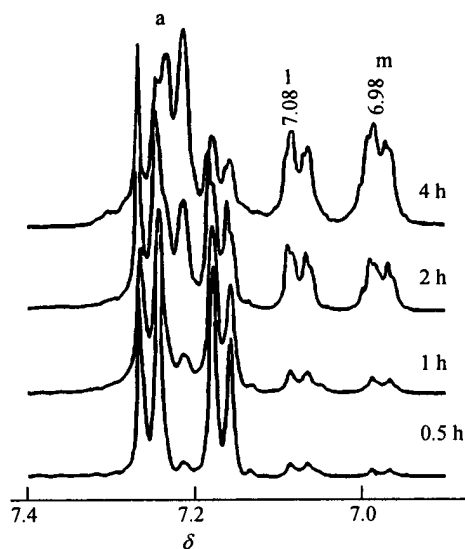
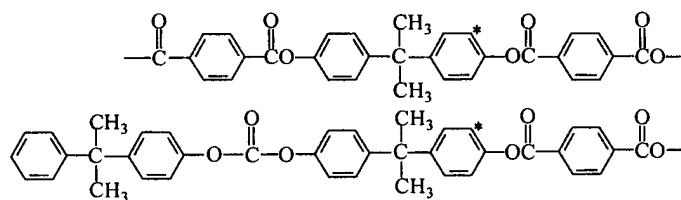
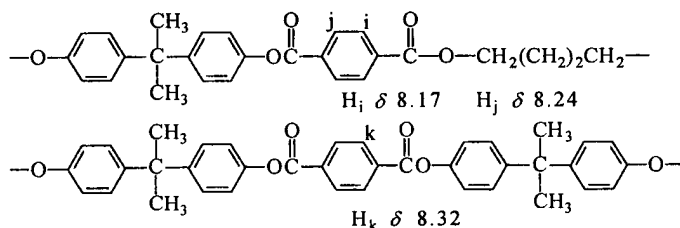
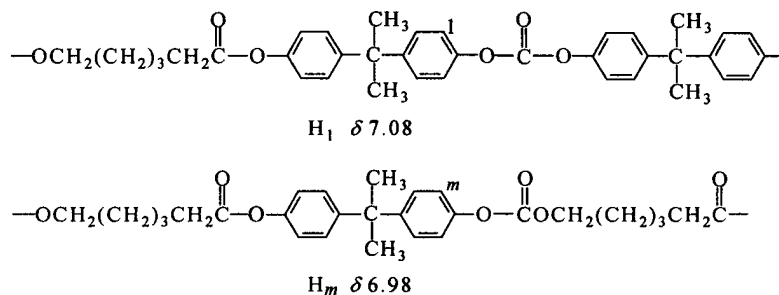


Fig. 4 The ^1H -NMR spectra of PC/BCL(21) blend in $\delta = 6.5\text{--}7.5$ after annealing for different periods of time

The changes of the proton bands above $\delta = 8.0$ and around $\delta = 7.22$ have proved that the transesterification reaction between butylene terephthalate units and bisphenol A carbonate units actually occurs.

In addition, there are two new resonance peaks at $\delta = 7.08$ (l) and $\delta = 6.98$ (m) occurring after annealing. The two new peaks appear upfield, and this means that the two sides of bisphenol A group may be substituted by aliphatic groups. It is reasonable to conclude that the bisphenol A groups have been substituted by caprolactone units symmetrically or unsymmetrically (as shown in Scheme 3). According to the shield theory, the peak at $\delta = 6.98$ is due to the bisphenol A aromatic protons substituted by caprolactone units symmetrically while the peak at $\delta = 7.08$ is due to the bisphenol A aromatic protons substituted unsymmetrically.

It is interesting to note that the intensity of the peak at $\delta = 7.08$ is stronger than that of the peak at $\delta = 6.98$ before it is annealed for 120 min, but after annealing for 240 min the situation is reversed. This phenomenon indicates that the bisphenol A group symmetrically substituted by the caprolactone units became predominant.



Scheme 3

After the substitution of carbonate for caprolactone, the bisphenol A carbonate units as the neighbor to the caprolactone units can also exert an influence on the proton bands of the CL units. The $\delta = 2.2$ and $\delta = 2.7$ bands in Fig. 5 exhibit the changes of chain structure of the CL segment neighborhood with annealing time. The resonance peak (f) at $\delta = 2.32$ still belongs to the methylene protons neighboring the carboxyl group ($\text{---CH}_2\text{COOCH}_2\text{---}$) of CL segments in BCL copolyester. It is more important that an additional new peak (n) appeared at $\delta = 2.56$ when the blend PC/BCL (50/50) was annealed at 270°C for 30 min. With the increase of annealing time, the new peak gradually intensifies. This peak was not observed in the $^1\text{H-NMR}$ spectrum of the annealed PC/PBT blend^[24], that means, it is not related to the transesterification of PC with the BT segments. This new peak may result from methylene protons next to the carboxyl group in the resultant bisphenol A-CL linkage (see Scheme 4) in annealing.

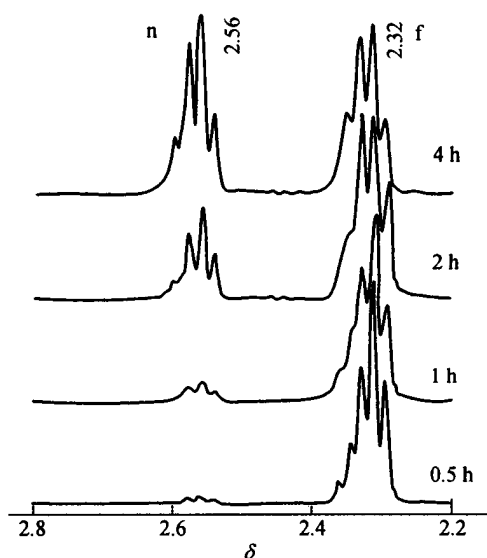
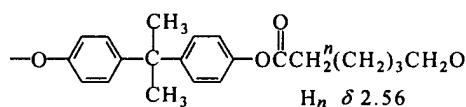
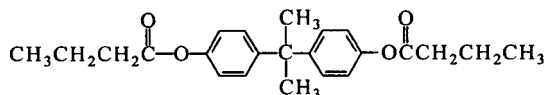


Fig. 5 The $^1\text{H-NMR}$ spectra of PC/BCL(21) blend in $\delta = 2\text{--}3$ after annealing for different periods of time

Because the benzene ring of bisphenol A has a stronger electronegativity than the aliphatic chain, the linkage pattern probably causes a downfield shift of about $\delta = 0.2$ of the corresponding resonance peak (f: $\delta = 2.32$) in the original caprolactone segments.

Such an understanding can be confirmed by the proton spectrum of a model compound, the chemical structure of which is shown in Scheme 5.



Scheme 5

The proton spectrum of the model compound is shown in Fig. 6.

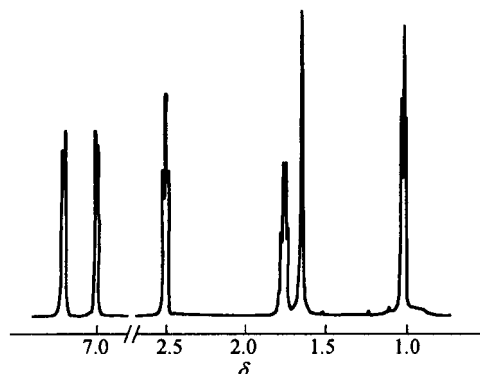


Fig. 6 ^1H -NMR spectrum of a model compound (bisphenol A dibutyrate)

The proton signals of all peaks are assigned as follows: at $\delta = 6.96\text{--}7.24$ (aromatic H), $\delta = 2.52$ ($-\text{OCCH}_2\text{CH}_2\text{CH}_3$), $\delta = 1.75$ ($-\text{OCCH}_2\text{CH}_2\text{CH}_3$), $\delta = 1.65$ ($-\text{CH}_3$ in bisphenol A unit), $\delta = 1.02$ ($-\text{OCCH}_2\text{CH}_2\text{CH}_3$). The methylene protons next to the carboxyl group show a resonance peak at $\delta = 2.52$, which is nearly identical with the chemical shift of the new peak in the annealed blend of PC/BCL21. The results indicate that the new peak at $\delta = 2.56$ represents the resultant bisphenol A-caprolactone unit as depicted in Scheme 4.

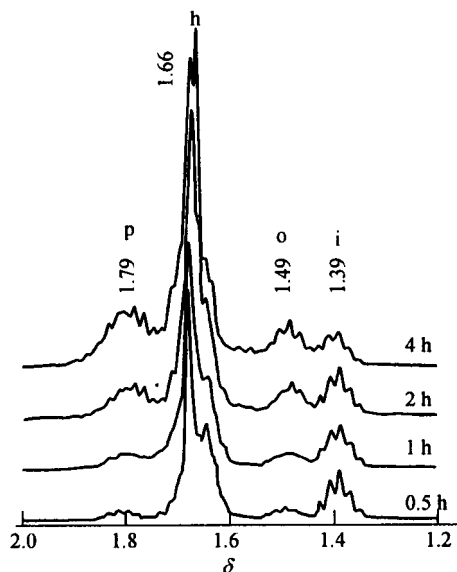


Fig. 7 The ^1H -NMR spectra of PC/BCL(21) blend in $\delta = 1\text{--}2$ after annealing for different periods of time

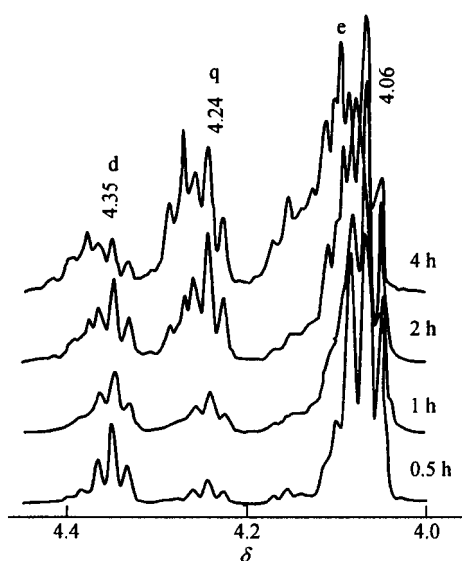


Fig. 8 The ^1H -NMR spectra of PC/BCL(21) blend in $\delta = 3.5\text{--}4.5$ after annealing for different periods of time

Figure 7 and Fig. 8 show the changes of bands at $\delta = 1-2$ and at $\delta = 4-4.5$. The CL unit has five methylenes. The protons bonded to carbonyl and to oxide are described above. The bands of three methylenes in the middle of the CL unit changed accordingly after substituted reaction. Their bands shift downfield so two new peaks appeared at $\delta = 1.49$ (o) and $\delta = 1.79$ (p). The band at $\delta = 1.79$ belongs to the side methylene protons; the band at $\delta = 1.49$ belongs to the central methylene protons of CL segment.

In Fig. 8, a new peak appearing at $\delta = 4.24$ (q) rose with the prolongation of annealing time. According to the assignment above, the neighboring peak at $\delta = 4.06$ (e) could be assigned to the methylene protons of $-\text{O}-\text{CH}_2-$ in the CL unit next to a carbonate unit or bisphenol A group. Between the peak "d" and peak "e", the different sequence structures of butylene terephthalate and caprolactone should have the corresponding proton bands as shown in our previous work^[16]. However, the proton spectrum of BCL(21) copolyester (Fig. 1) did not exhibit any band in this region, because the butylene terephthalate content in BCL(21) was too low. In the blend of PC/BCL(21), sequence structure of butylene terephthalate and caprolactone should not exhibit any band in this region.

TRANSESTERIFICATION RATES OF PC WITH BT AND CL SEGMENTS

In the present study, it is necessary to determine the reaction rates, because both BT segments and CL segments are simultaneously involved in the transesterification reaction with PC.

In the reaction process, terephthalate and CL units in BCL are respectively transferred into bisphenol A-terephthalate and bisphenol A-CL units. Because their relative amounts are proportional to the integral intensity area under the resonance peaks, their transferring ratios X_{AB} and X_{AC} in the reaction can be calculated via the following formula:

$$X_{AB} = \frac{\frac{1}{4}I_k + \frac{1}{4}(I_i + I_j)}{\frac{1}{4}I_c + \frac{1}{4}I_k + \frac{1}{4}(I_i + I_j)} = \frac{I_k + I_i + I_j}{I_c + I_k + I_i + I_j}$$

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

A denotes bisphenol A; B denotes terephthalate; and C denotes CL.

The changes of the rates X_{AB} and X_{AC} with the annealing time are illustrated in Fig. 9.

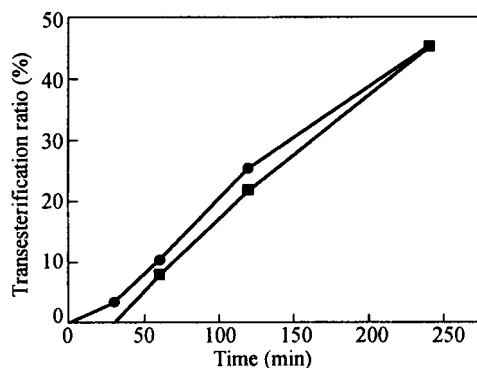


Fig. 9 Transferring mol ratios of terephthalate and CL units in BCL versus annealing time at 270°C (■) Bisphenol A-terephthalate; (●) Bisphenol A-CL

The rates X_{AB} and X_{AC} increase markedly with the progress of reaction. The rate of X_{AC} is a little faster than X_{AB} before 240 min; and the rate difference is small. Such a difference is largely related to the content of the caprolactone unit in BCL(21) copolyester. Because the BCL(21) copolyester is miscible with PC, the

transesterification rate difference between butylene terephthalate units, caprolactone units and bisphenol A carbonate units should not be large.

CONCLUSIONS

The changes in the proton spectrum of the blend PC/BCL(21) copolyester with annealing time have sufficiently proved that the transesterification reaction has happened between PC and BCL(21), moreover, butylene terephthalate units and caprolactone units exchanged with polycarbonate simultaneously.

The transesterification rate of the CL segment with PC is a little quicker than that of the BT segment with PC. The difference of their transesterification rates is small. Such experimental results are related to the miscibility between components in the blend of PC with BCL(21) copolyester.

Naturally, the transesterification between PC and BCL copolyesters with different butylene terephthalate contents will be very interesting, especially the transesterification reaction between PC and BCL copolyester with a high BT content will be different from that of the blend PC/BCL(21) copolyester. The dependence of the transesterification rate on temperature for these blends is also important.

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