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Miscibility in blends of liquid crystalline poly(*p*-oxybenzoate-co-*p*-phenyleneisophthalate) and polycarbonate

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The miscibility of liquid crystalline poly(*p*-oxybenzoate-co-*p*-phenyleneisophthalate) (HIQ) and polycarbonate (PC) was investigated with differential scanning calorimetry (d.s.c.). It was found that blends of liquid crystalline HIQ and PC showed a single glass transition temperature across the whole composition range. Annealing these blends at temperatures slightly above the melting point of HIQ, ester exchange occurred as confirmed both by i.r. and n.m.r. spectroscopy. The apparent miscibility of HIQ and PC was caused by this reaction. The blends retained liquid crystalline characteristics in the first few reaction minutes. As the transesterification continued, the bisphenol-A segment in PC reacted with both isophthalate and oxybenzoate segments in HIQ. This resulted in amorphous polymers. These amorphous polymers exhibited a single glass transition temperature higher than that for both pure polymers. © 1997 Elsevier Science Ltd.

(Keywords: miscibility; transesterification; liquid crystalline polymer blends)

INTRODUCTION

Liquid crystalline polymer (LCP) blends have been studied extensively in recent years[1–3]. The motivation was first to use the high tensile modulus of the liquid crystalline polymers in solid state to reinforce engineering polymers. Second, the low viscosity of the liquid crystalline polymers can reduce the overall viscosity of the blend, and is a good processing aid[4]. Blending LCP with engineering polymer can give the above two advantages without incurring the high cost of the LCP.

The miscibility of liquid crystalline polymer and engineering polymer is a major obstacle in the application of LCP blends. The homogeneity of polymer blends depends on the compatibility or the interaction between polymers. The degree of interaction between two polymers is best described by the free energy of mixing, ΔG, which contains enthalpic (ΔH) and entropic (ΔS) contributions. For a blend to be a single phase, the necessary condition is $\Delta G < 0$. The entropy terms are usually small, and the enthalpy terms dominate the free energy of mixing in polymer blends. The favourable (exothermic) heat of mixing resulted from interaction between the two polymers. The introduction of interacting groups by chemical modification of a polymer or by copolymerization can result in a negative contribution to the enthalpy of mixing. Liquid crystalline polymer chains are very stiff and of rigid-rod nature. Consequently, the enthalpy of mixing rigid-rod polymer with a flexible-coil polymer was mostly positive. Phase separation of the LCP blend occurred during processing, where high stress and high temperature existed[5]. Introducing some kind of interaction between these two dissimilar polymers is necessary to improve the miscibility of the two polymers. The previous work by our group was concerned with the miscibility of polycarbonate (PC) and liquid crystalline poly (oxybenzoate-co-ethylene terephthalate) (POB-PET)[6]. The main result was that the miscibility between the two polymers increased with ester exchange mostly between the PET segment and PC. In general, as transesterification continues, the blends convert first to block copolymers and, finally, to random copolymers[7]. Even some attempts to inhibit the ester exchange between POB-PET and PC was not very successful[8]. When the blends are in the form of random copolymers, the benefits of adding LCP to the matrix polymer will be lost. In this study, the miscibility of a wholly aromatic liquid crystalline polyester with polycarbonate was investigated.

EXPERIMENTAL

The liquid crystalline polymer used in this study is poly(*p*-oxybenzoate-co-*p*-phenyleneisophthalate) (HIQ). HIQ is a copolyester of *para*-hydroxybenzoic acid (HBA), isophthalic acid (IA) and hydroquinone (HQ). The chemical structure of HIQ and polycarbonate are shown in *Figure 1*. The 4-oxybenzoate segments impart nematic phase. The IA and HQ are known to form a crystalline structure. Consequently, HIQ exhibits biphasic morphology[9–11]. The composition of interest is HBA/IA/HQ (35/32.5/32.5) or HIQ35. In this study we used HIQ standing for HIQ35. The intrinsic viscosity of the HIQ used was 1.02 dl g^{-1}. The HIQ polymer was provided by Hoechst Celanese Co. PC was purchased from General Electric. The trade name of the PC is Lexan 121, and its molecular weight is $M_w = 158\,900$.

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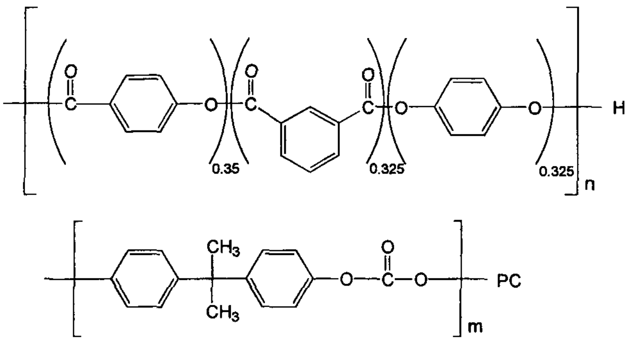

Figure 1 The chemical structures of poly(*p*-oxybenzoate-co-*p*-phenyleneisophthalate) (HIQ) and polycarbonate (PC)

The solution blending of PC and HIQ was carried out by dissolving both polymers in a mixed solvent of phenol and tetrachloroethane (50/50 by volume). The concentration of the solution containing PC and HIQ is 2% by weight. Different weight ratios of PC to HIQ in the solution were made which were 30/70, 40/60, 50/50, 60/40 and 70/30. The solution was stirred and heated up to 70°C. After the polymers were completely dissolved and became one-phase solution for $\frac{1}{2}$h, the blends were precipitated in a large volume of methanol. The blends were then washed five times, each time with 200 cm^3 methanol. The blends were then dried in a vacuum oven at 100°C for four days. The t.g.a. of the dried blends showed no appreciable weight loss up to 350°C, indicating a complete removal of the solvent. The melt blending involved drying HIQ and PC powders at 100°C under vacuum for 8 h, and then putting them, at a proper weight ratio, into a Brabender mixer. The speed of the roller blade in the mixer was 50 rpm. The blending temperature was set at 310°C. The polymers were purged with nitrogen gas during melt-blending to prevent them from degrading. Thermal transitions of blends were measured with a Du Pont 2910 d.s.c. The solution-mixed blends were heated up from 25°C to 315°C at a heating rate of 20°C min^{-1}, and were annealed at these two temperatures for different times. The samples were then quenched to room temperature with liquid nitrogen. The d.s.c. curves of the samples were taken during the second time the samples were heated up at the heating rate of 20°C min^{-1}. The melt-blended samples were measured without experiencing the annealing step. The birefringence of the melt blends was obtained with a Carl Zeiss Axiophot polarized microscope.

The chemical structure change resulting from transesterification was identified qualitatively by *FT*i.r. and n.m.r. spectroscopy. PC and its derivatives can be dissolved in chloroform but not HIQ. The ester exchange between HIQ and PC can therefore be confirmed by examining the chemical structure change of PC in the blends. HIQ/PC blends were extracted with chloroform, and the soluble portion was used for *FT*i.r. analysis. A Bomen MB100 *FT*i.r. was used for this measurement. For n.m.r. analysis, freshly prepared and annealed blends of HIQ/PC were completely dissolved in a mixed solvent of deuterated trifluoroacetic acid and deuterated dichloromethane at a weight ratio of 15/85. Two-dimensional ^1H–^1H correlation spectroscopy (COSY) analysis was conducted to identify the additional resonance peaks resulting from the reaction. In order to pinpoint the chemical structure change of the annealed blend, a model compound study was carried out by melt blending of PC/hydroxybenzoic acid (HBA) and PC/isophthalic acid (IA) at a weight ratio of 80/20, respectively. The PC/HBA and PC/IA blends were melt-blended at 220°C and 300°C, respectively, for 30 min, and were then dissolved in the same mixed solvent.

Tetramethylsilane was added to the solution as an internal reference standard. One dimensional proton analysis on these model compound solutions was performed. The resonance peaks resulting from reaction between PC/HBA and PC/IA were assigned. A Bruker DMX-600 NMR (600 MHz) was used for this study.

RESULTS AND DISCUSSION

The d.s.c. curves of HIQ and PC are shown in *Figure 2*. The glass transition temperature (T_g) of HIQ is 134°C, indicating the presence of an amorphous phase. Three small endothermic peaks appearing for HIQ are located at 300.52, 312.23 and 334.74°C. As the heating rate increased from 60°C min^{-1} to 100°C min^{-1}, these three peaks converged to a broad endothermic peak shown in *Figure 3*. This phenomenon is similar to the recrystallization behaviour after melting exhibited by Nylon 6[12]. The appearance of triple endothermic peaks was possibly caused by the double recrystallization temperatures at 302°C and 317°C. To confirm this, HIQ films were prepared by completely dissolving HIQ pellets in a mixed solvent of 50/50 phenol/tetrachloroethane and then casting the solution onto glass slides. The HIQ films were washed four times in hot methanol before they were put in a vacuum oven at 100°C for four days to eradicate residual solvent. The melt-crystallized HIQ films were prepared by annealing HIQ films at 302°C and 312°C, respectively, for 3 min in a vacuum tube, and were then quenched in liquid nitrogen. The X-ray diffraction patterns of these HIQ films, powder (precipitated from methanol) and as-received pellets are shown in *Figure 4*. *Figure 4* shows a diffraction peak at $2\theta = 30°$ for the as-cast HIQ film. For the HIQ film annealed at 302°C, additional diffraction peaks appeared at $2\theta = 28°$ and 22°. After annealing at 312°C, there were four major diffraction peaks appearing at $2\theta = 30°$, 28°, 26.5° and 22°. This clearly manifested that the multiple peaks in the d.s.c. curves of HIQ pellets resulted from recrystallization after melting. The corresponding d.s.c. curves for these HIQ films were shown in *Figure 5*, which further supported the recrystallization argument. For a solution blend of 40/60 HIQ/PC, there was only one T_g appearing, as shown in *Figure 6*. This might be caused by two facts. First, the T_g of HIQ is quite broad, and the two T_g of HIQ and PC are close to each other. The onset of the T_g of PC is overlapped with the endpoint of the T_g of HIQ. Second, HIQ and PC are miscible. The T_g of the 40/60 HIQ/PC blends annealed at 315°C for 3 min was 144°C, as shown in *Figure 6*. In *Figure 6*, when annealing time increased to 9 and 12 min, the T_g of the 40% HIQ blend increased to around 150°C and 155°C, respectively. There was only one small melting peak at 308°C for the 40/60 HIQ/PC blend after annealing for 1 min. For higher HIQ concentration, there was still only one T_g appearing, and these T_gs increased with annealing time once the melting peak disappeared. As shown in *Figure 7*, the T_g was 147.39°C after annealing for 6 min, and became 155.84°C after annealing for 12 min at

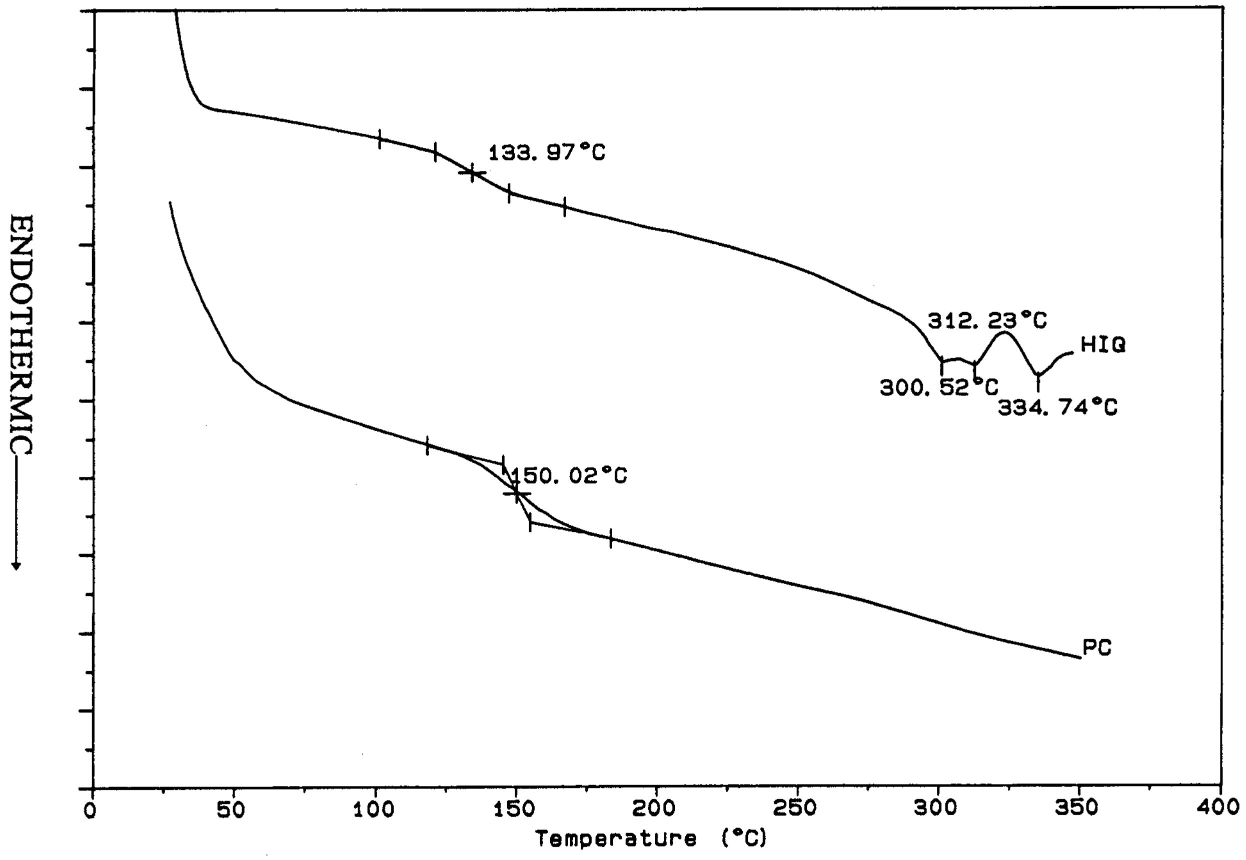

Figure 2 The d.s.c. curves of HIQ and PC at a heating rate of 20°C min^{-1}

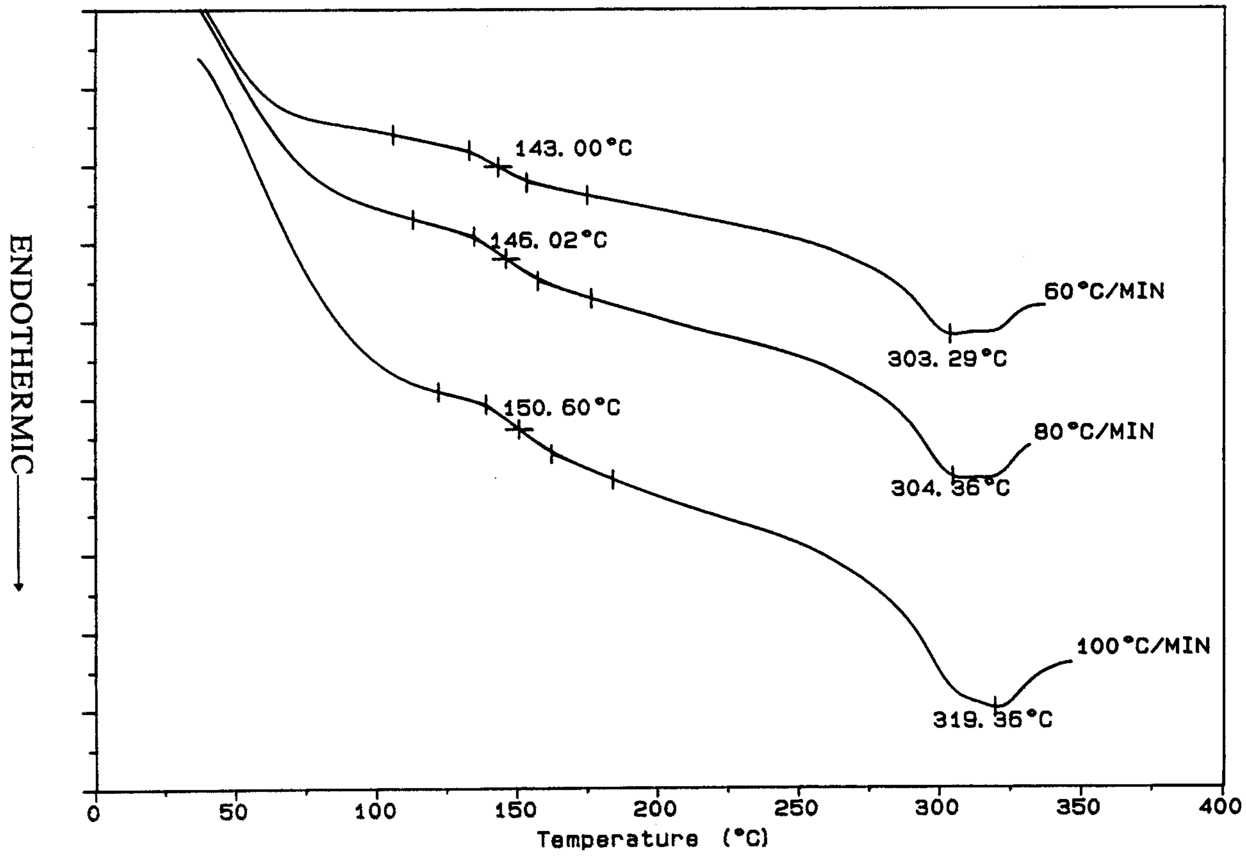

Figure 3 The d.s.c. curves of HIQ at different heating rates

315°C for the 50/50 HIQ/PC blend. Similar behaviour was observed for the 60% HIQ blend annealed at 315°C. The more dramatic change in T_g of the HIQ blend took place at a higher annealing temperature. The T_g of the 40% HIQ blend increased to 156.06°C after annealing for 6 min and to 158.84°C after annealing for 12 min at 325°C, as shown in *Figure 7*. Noticeably, after annealing for more than 6 min, the d.s.c. curves of these blends

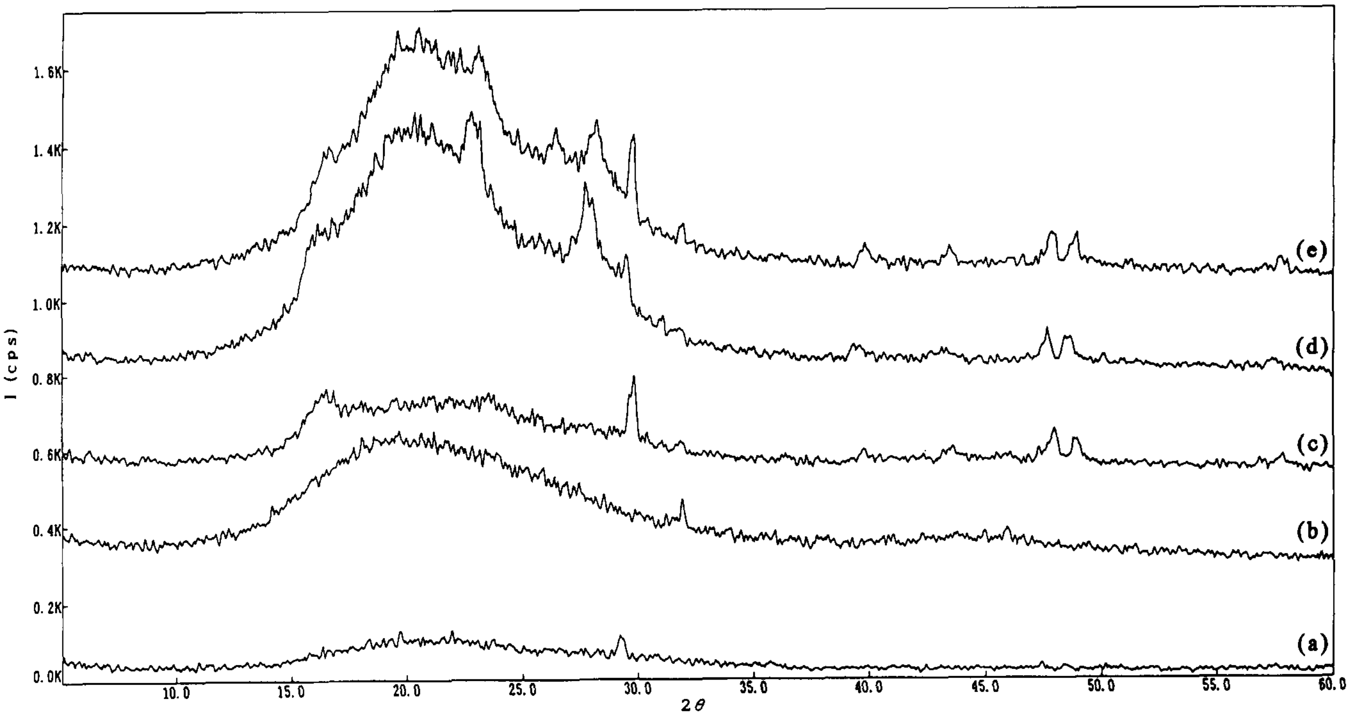

Figure 4 X-ray diffraction peaks of: (a) HIQ pellets; (b) HIQ powders; (c) HIQ film as cast; (d) HIQ film annealed at 302°C; and (e) HIQ film annealed at 312°C

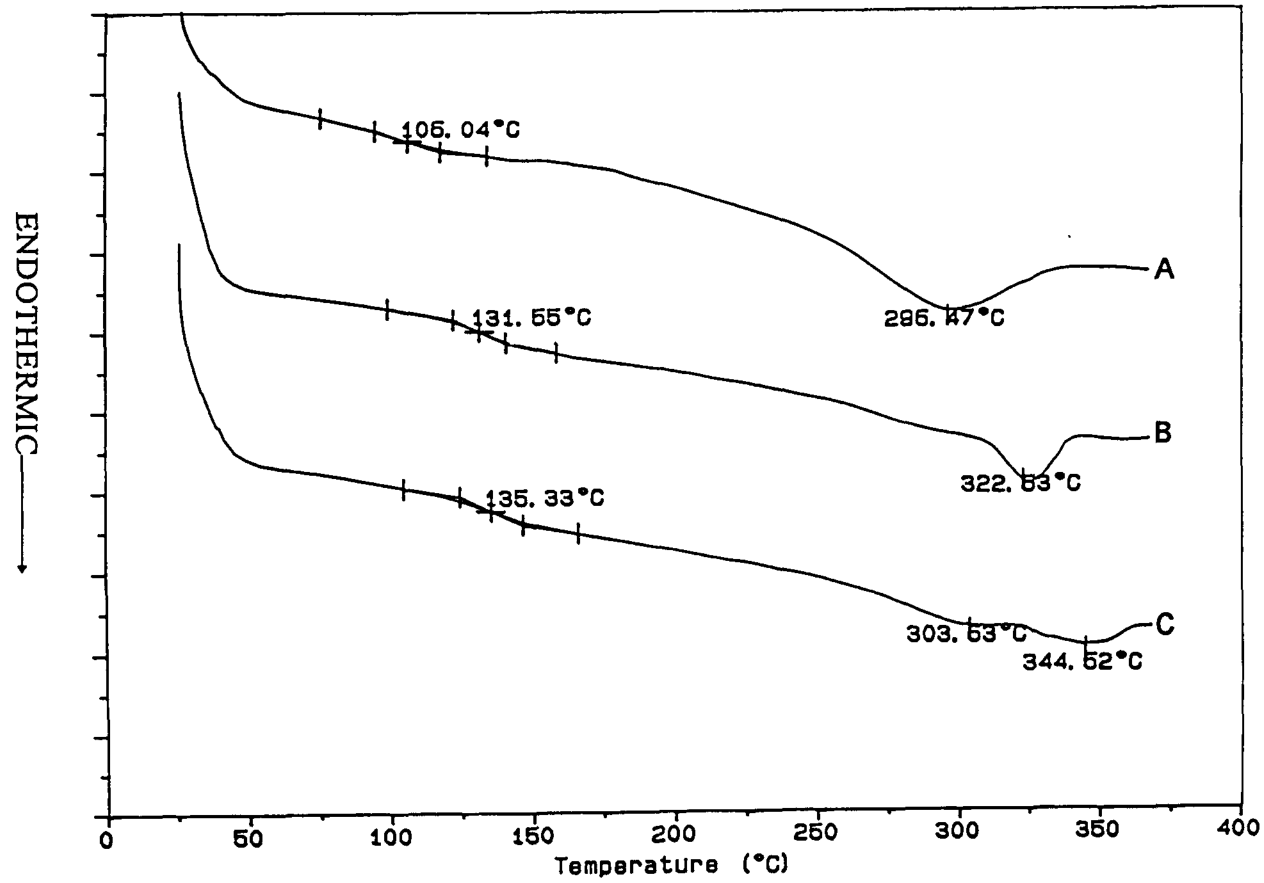

Figure 5 The d.s.c. curves of HIQ film as cast (A), HIQ film annealed at 302°C for 3 min (B) and HIQ film annealed at 312°C for 3 min (C)

behaved like that of amorphous polymers. Moreover, the colour of the blend also changed from a non-transparent milk colour to an almost transparent brown colour after annealing for 9 min. A parallel t.g.a. on these HIQ blends did not show any weight loss when they were annealed at 325°C for 20 min. This phenomenon indicated that HIQ blends were miscible, and ester exchange in the blends resulted in a homogeneous phase upon annealing. A number of equations have been proposed to describe the composition dependence

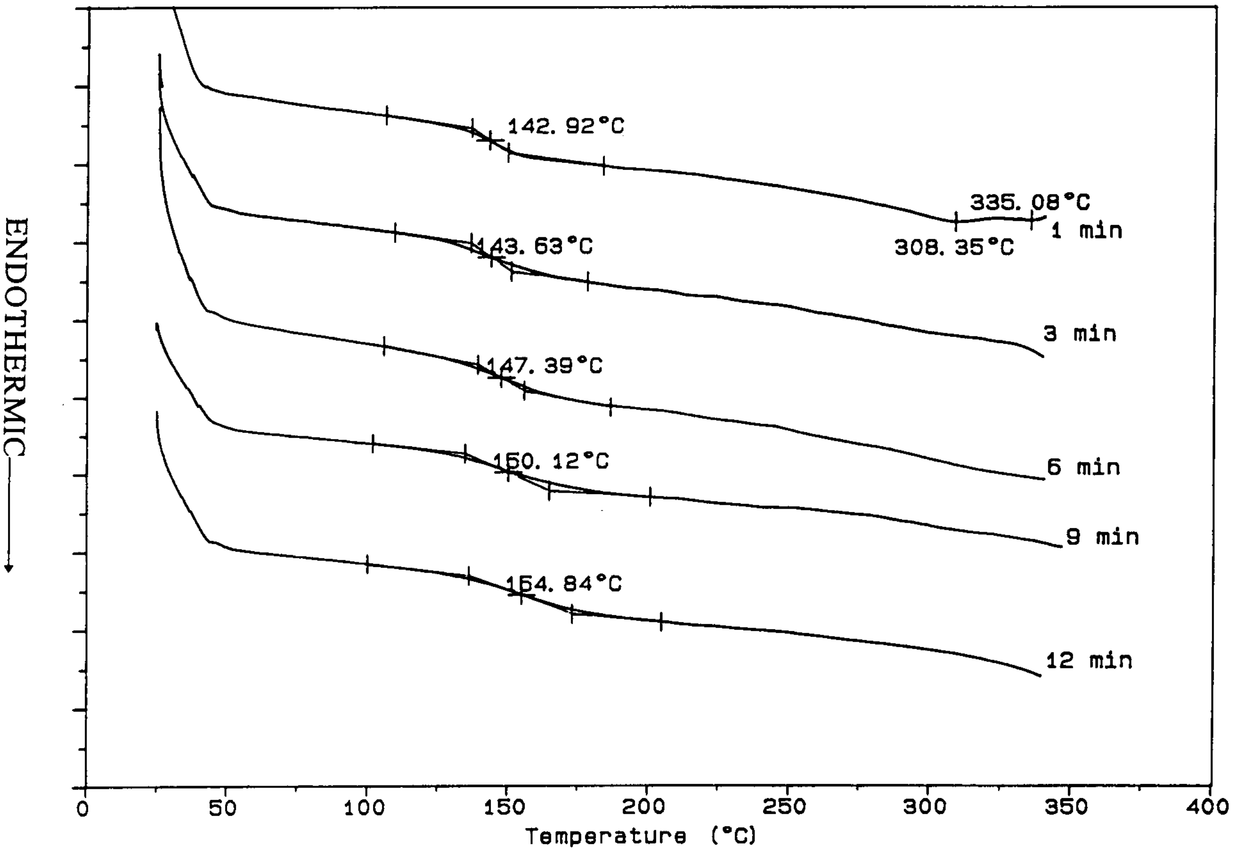

Figure 6 The d.s.c. curves of 40/60 HIQ/PC blends annealed at 315°C for different times

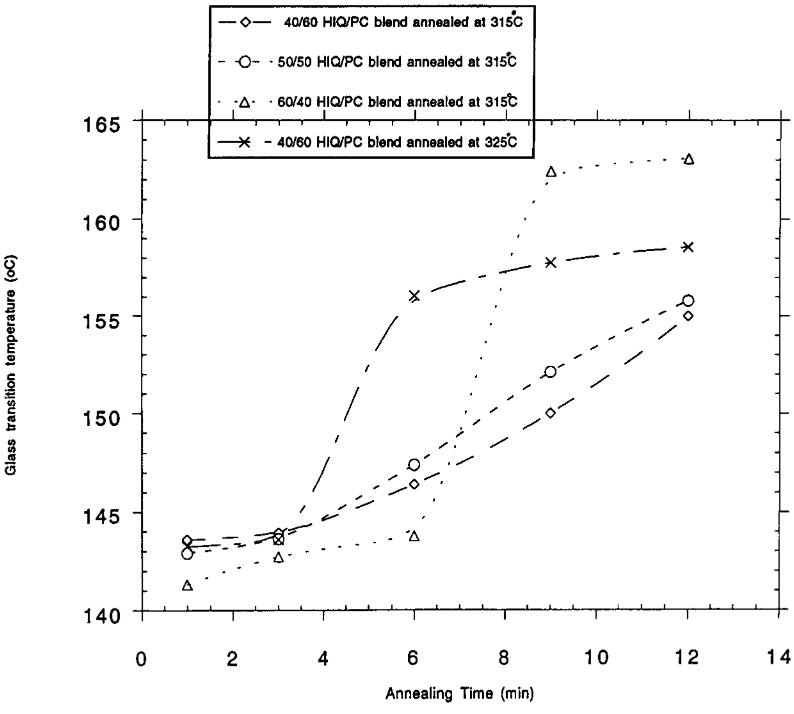

Figure 7 The glass transition temperature of HIQ/PC blends at different composition after annealing at 315°C and 325°C for different times

of T_g for polymer blends[13–15]. Two of them are as follows.

Fox:

$$1/T_g = W_1/T_{g1} + W_2/T_{g2}$$

Couchman:

$$\ln T_g = \{W_1 \ln(T_{g1}) + (\Delta C_{p2}/\Delta C_{p1}) W_2 \ln(T_{g2})\}/\{W_1 + (\Delta C_{p2}/\Delta C_{p1}) W_2\}$$

The ΔC_p values for PC and HIQ are 0.242 and 0.146 J g^{-1}°C, respectively. To reduce the complication of transesterification on T_g, the T_g of HIQ/PC blends annealed at 315°C for 1 min is used for comparison. In *Figure 8a*, the composition dependence of T_g for HIQ/PC blends is plotted. Due to the fact that the T_g for pure HIQ is quite broad, the T_g width for the blends increases with the concentration of HIQ. The measured T_g of various blends agreed well with the predicted values by the Couchman equation, but not the Fox equation, as shown in *Figure 8b*. The d.s.c. curve of the 30/70 HIQ/PC blends which were melt-mixed at 310°C is shown in *Figure 9*. The T_g of the blends followed the trend of that of the solution blends upon heating. After 9 min, there was only T_g, 159.37°C, but no melting peak. The blend behaved as an amorphous polymer. Judging from the T_g, the transesterification seemed saturated after 12 min.

In summary, the HIQ/PC blend showed single-phase behaviour across the whole composition range. As the strong and fast ester exchange between HIQ and PC took place, new amorphous polymer behaviour eventually

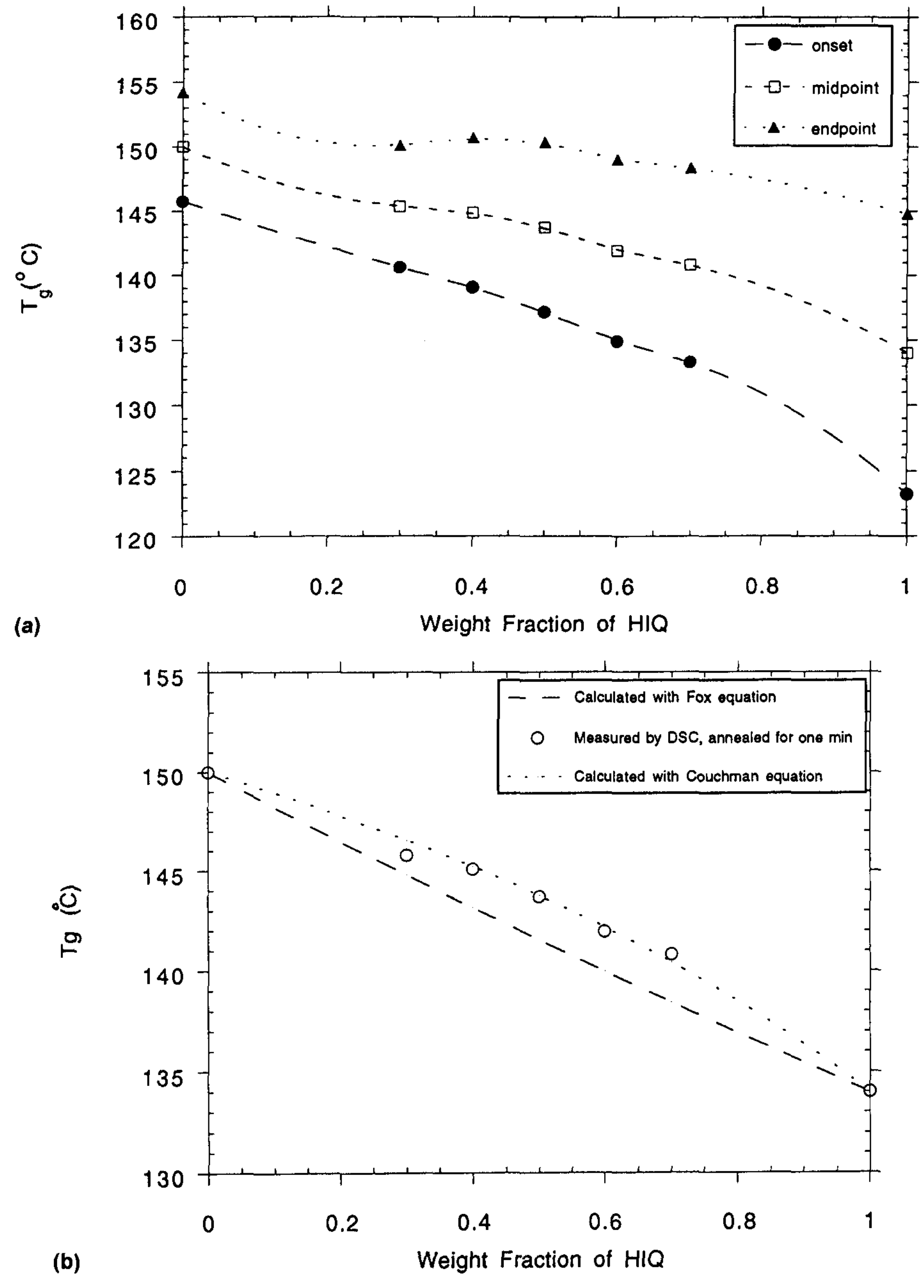

Figure 8 (a) Composition dependence of T_g for HIQ/PC blend annealed at 315°C for 1 min. (b) Comparison of measured and predicted T_g by Fox and Couchman equation

resulted, indicated by a T_g higher than T_g of both pure components.

Further evidence for the HIQ having amorphous polymer behaviour can be supported from birefringence observation. The transition of the birefringence of the 30% HIQ melt blends at different mixing times is shown in *Figure 10*. In *Figure 10a*, the birefringence pattern of the HIQ polymer cooled down from 315°C is displayed. After mixing the HIQ blend for 4 min, the HIQ was dispersed in the PC matrix as the liquid crystal phase, and PC appeared as the dark (isotropic) domains shown in *Figure 10b*. As the blending time increased to 6 min, there were large dark drops, about 0.05 mm in diameter, indicating a large isotropic phase. These are shown in the bottom right corner of *Figure 10c*. Continuing for 9 min, the birefringence or the liquid crystalline phase of the HIQ blend almost disappeared totally, as shown in *Figure 10d*. This dramatic change of the blend from the liquid crystal state to the isotropic phase detailed the forming of the amorphous polymer during the transesterification. This result corresponded very well to the d.s.c. result.

FT*i.r. and n.m.r. results*

The *FT*i.r. analysis focused on the carbonyl stretch in PC (1780 cm^{-1}), carbonyl stretch in ester (1740 cm^{-1}), and C–O bend vibration in ester (1070 cm^{-1})[16]. *Figure 11* showed the i.r. spectra of PC and HIQ, respectively. There was clearly no aryl ester peak existing in the PC spectrum. The aryl ester group (at 1740 cm^{-1} and 1070 cm^{-1}) attached to the PC molecule after blending for 4 min is shown in *Figure 12*. After 9 min, the intensity of the ester peak grew to 90% of that of the carbonate peak. This is direct evidence that the ester exchange between PC and HIQ took place. The difference between the *FT*i.r. spectra of the extracted blend at 9 min and 12 min is very small, indicating a saturation point. This result agreed with the increase in T_g of the HIQ blends with annealing time.

The analyses of reacting polyester/PC blends have been carried out on both midchain and alcoholysis with n.m.r.[17–21]. In this study, since the molecular weight of PC and HIQ is high, we only paid attention to the midchain part, which seemed the main cause of miscibility[20]. In order to pinpoint the resonance peaks caused by the chemical structure changes during transesterification, a model compound study was first carried out. Following the methods by Devaux[22] and Espinosa[23], the melt-blended PC/HBA and PC/IA both at a weight ratio of 80/20 were dissolved in the same mixed solvent as described in the previous section for n.m.r. analysis.

There was essentially no change in the methyl proton resonance peak at 1.6 ppm in the n.m.r. spectrum of PC. Therefore, only the aromatic proton n.m.r. spectra of PC, HBA, reacted PC/HBA, reacted PC/IA and HIQ are shown in *Figures 13a–e*, respectively. HBA can be dissolved in $CF_3COOD/CDHCl_2$ (15/85), while IA can not. By comparing *Figures 13a*, *b* and *c*, one can discern the additional resonance peaks A at 8.11 ppm and B at 7.34 ppm resulting from the new structure I, as indicated in *Figure 13c*.

In the case of PC/IA, the additional resonance peaks C at 8.29 ppm and D at 7.56 ppm were exhibited by the structure II, as displayed in *Figure 13d*. Structure II had been identified in work of Espinosal[23]. These two model

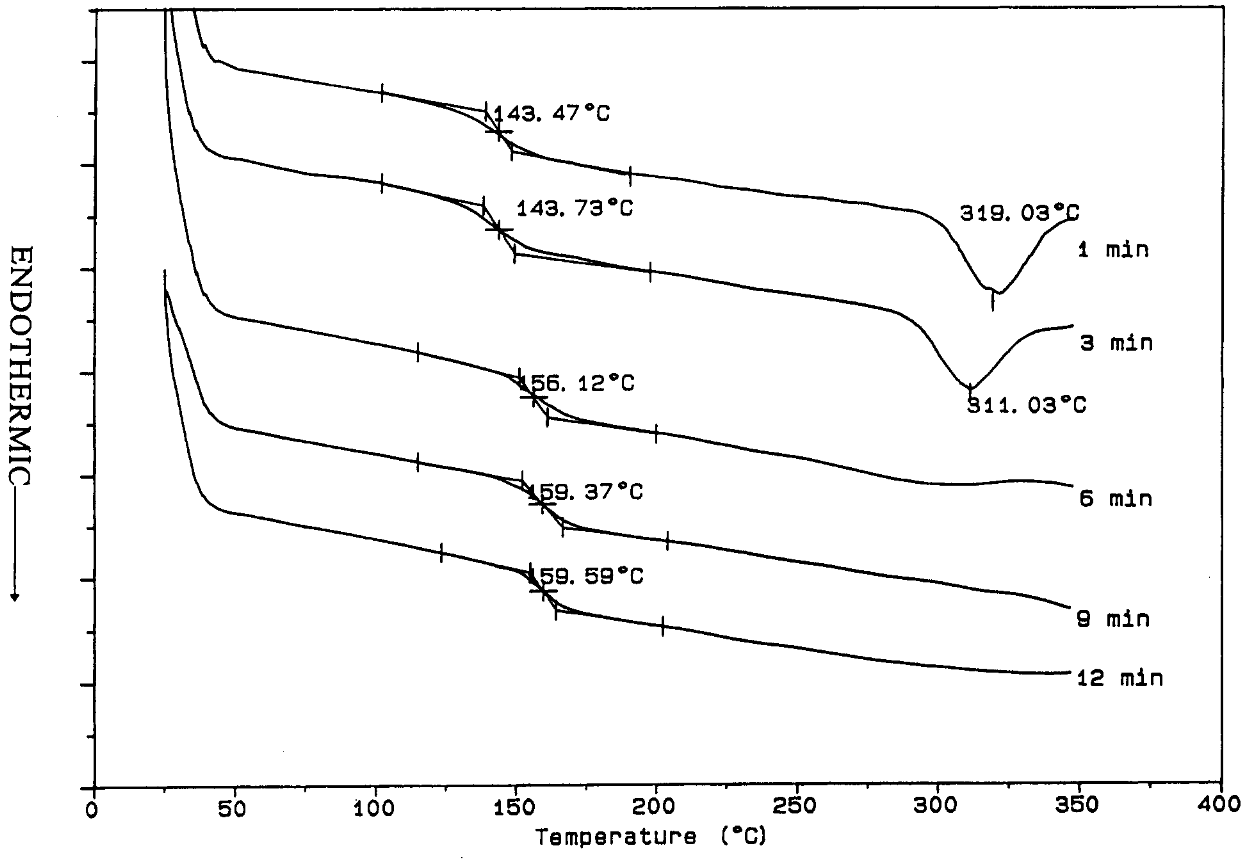

Figure 9 The d.s.c. curves of 30/70 HIQ/PC melt-mixed at 310°C for different blending times

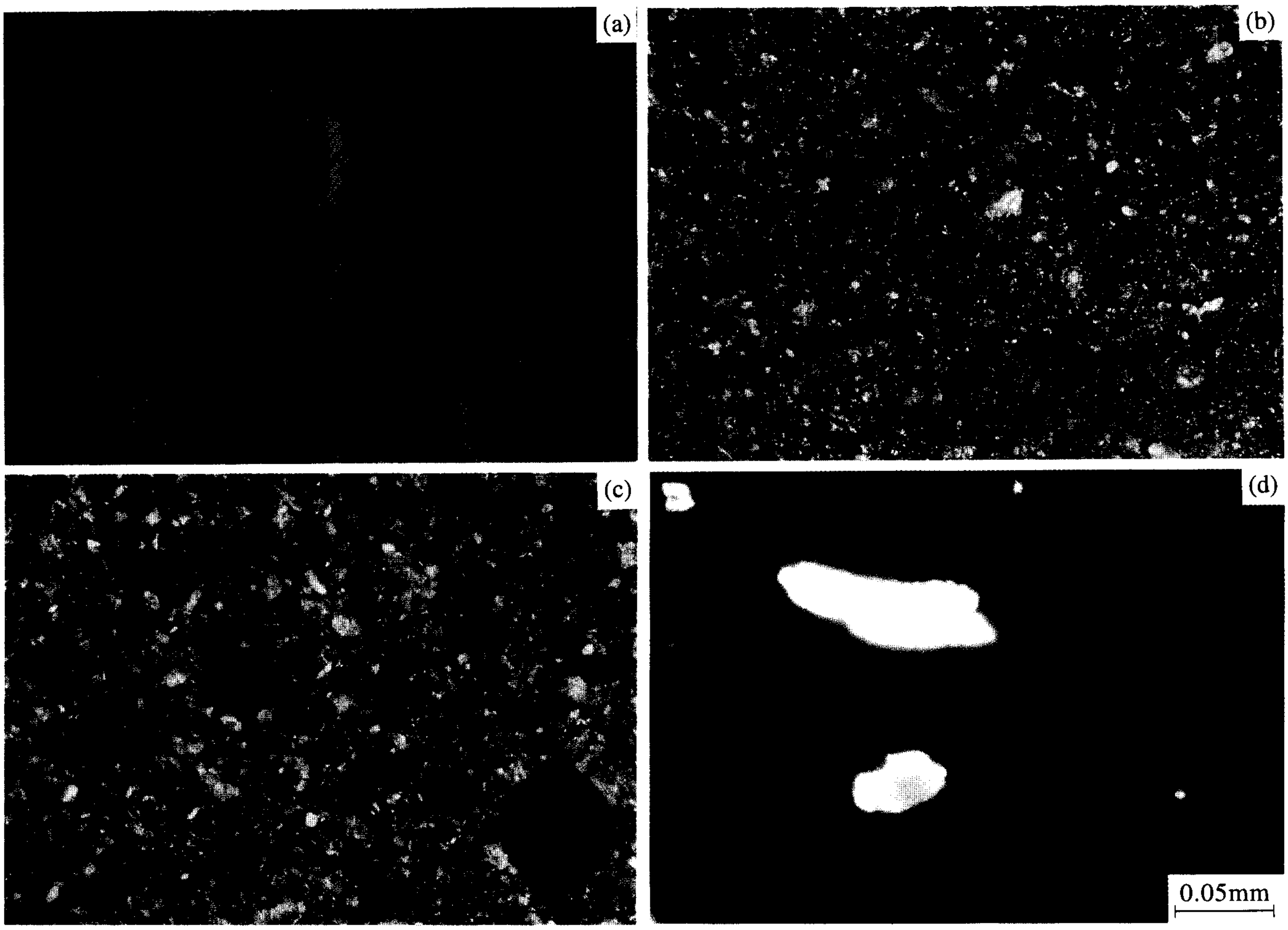

Figure 10 The birefringence pattern of (a) HIQ, (b) 30/70 HIQ/PC melt blend at blending time 4 min, (c) 6 min, (d) 9 min

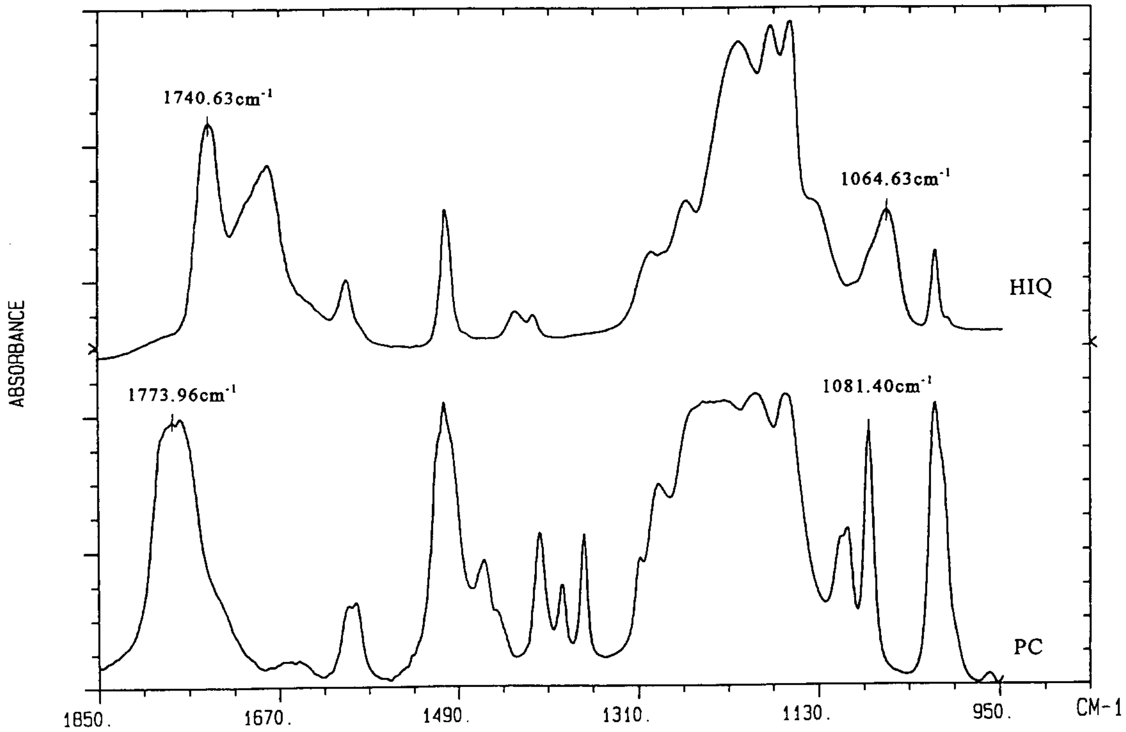

Figure 11 The *FT*i.r. spectra of HIQ in CF_3COOH and PC in chloroform

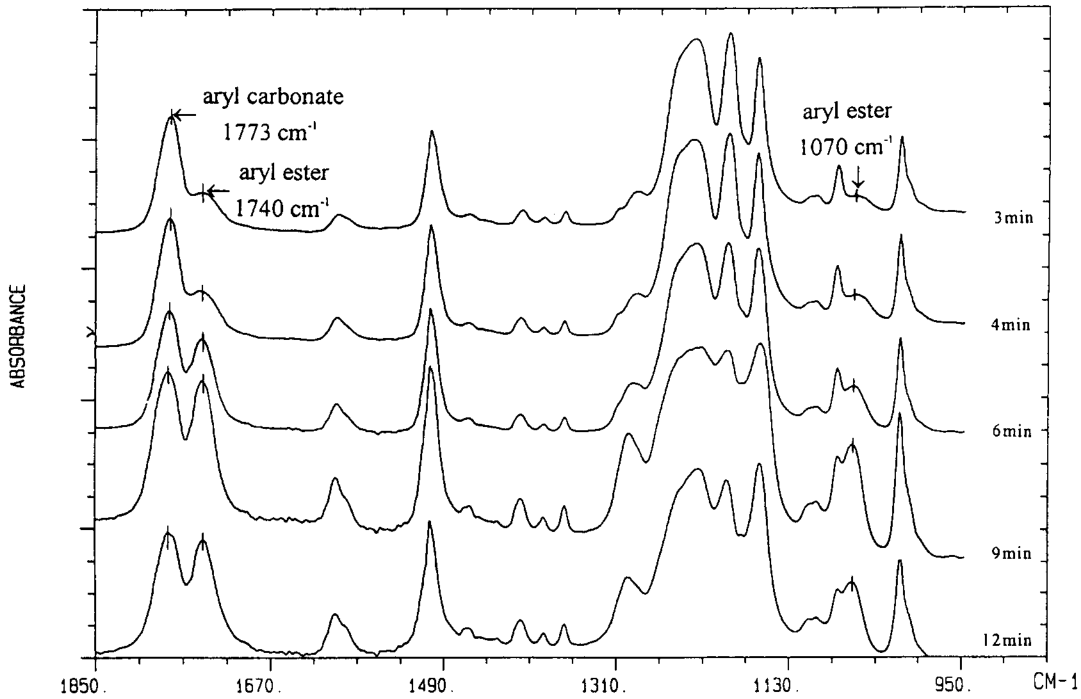

Figure 12 The transient *FT*i.r. spectra of 30/70 HIQ/PC melt blend at different blending times extracted with chloroform

compounds showed that bisphenol-A in PC can react with HBA and IA under proper conditions. Previously, new proton resonance peaks appeared in both aromatic and aliphatic regions during transesterification in PC/polyester blends[17–19]. In this case, since the reaction is between PC and the aromatic polyester, spectroscopic examination focused on the aromatic region, ignoring the methyl protons of PC. The more detailed chemical shifts for the aromatic protons for the above cases are listed in *Table 1*, which is used for studying the HIQ/PC blends. The aromatic region of the ^1H–^1H COSY spectra of freshly prepared and annealed HIQ/PC (30/70) blends, which are completely dissolved in $CF_3COOD/CHDCl_2$ (15/85), are presented in *Figures 14a* and *b*, respectively. By comparing the two COSY spectra of HIQ/PC blends, we could identify two sets of new cross peaks appearing in *Figure 14b*. The first set of new cross peaks was located at 8.07 ppm and 7.30 ppm corresponding to structure I in the model compound study. The second set of new cross peaks had coordinates of 8.25 ppm and 7.58 ppm corresponding to structure II in the model compound study. This is direct evidence that bisphenol-A in PC had reacted with isophthalate and oxybenzoate in HIQ after annealing for 12 min at 310°C. From the complex COSY spectrum of annealed HIQ/PC blend, the degradation of HIQ at high temperature may not be completely excluded in the annealing process. However, the degradation of HIQ definitely would neither cause the increase of T_g of the HIQ/PC blends with annealing time, nor produce the new cross peaks in the COSY spectrum displayed by the annealed HIQ/PC blend. Therefore, ester exchange between PC and HIQ indeed took place after annealing at high temperatures.

Table 1 Chemical shifts of aromatic protons of model compounds and polymers

Compound or polymer	Chemical shift δ (ppm)					
PC	H8 7.08	H9 7.20				
HBA	H2 6.80	H1 7.88				
PC/HBA (80/20), 220°C for 30 min	H8 7.08	H9 7.20	H2 6.78	H1 7.91	A[a] 8.11	B[a] 7.34
PC/IA (80/20), 300°C for 30 min	H8 7.08	H9 7.20	H4 8.39	H5 7.60	C[a] 8.29	D[a] 7.56
HIQ	H1 8.24	H2 7.38	H4 8.43	H5 7.67	H6 7.27	H7 7.27

[a] Additional peaks resulted from reaction

CONCLUSIONS

Blends of liquid crystalline HIQ and PC showed a single glass transition temperature across the whole composition range both because of the closeness of their individual glass transition temperature and the apparent miscibility by transesterification. When the temperature was above the melting point of HIQ, the transesterification between HIQ and PC took place immediately. In the first few minutes of the exchange reaction, the blends retained liquid crystalline characteristics. As the transesterification continued, the bisphenol-A in PC reacted with both isophthalate and oxybenzoate in HIQ. This resulted in amorphous polymers, with glass transition temperatures higher than that for both pure components.

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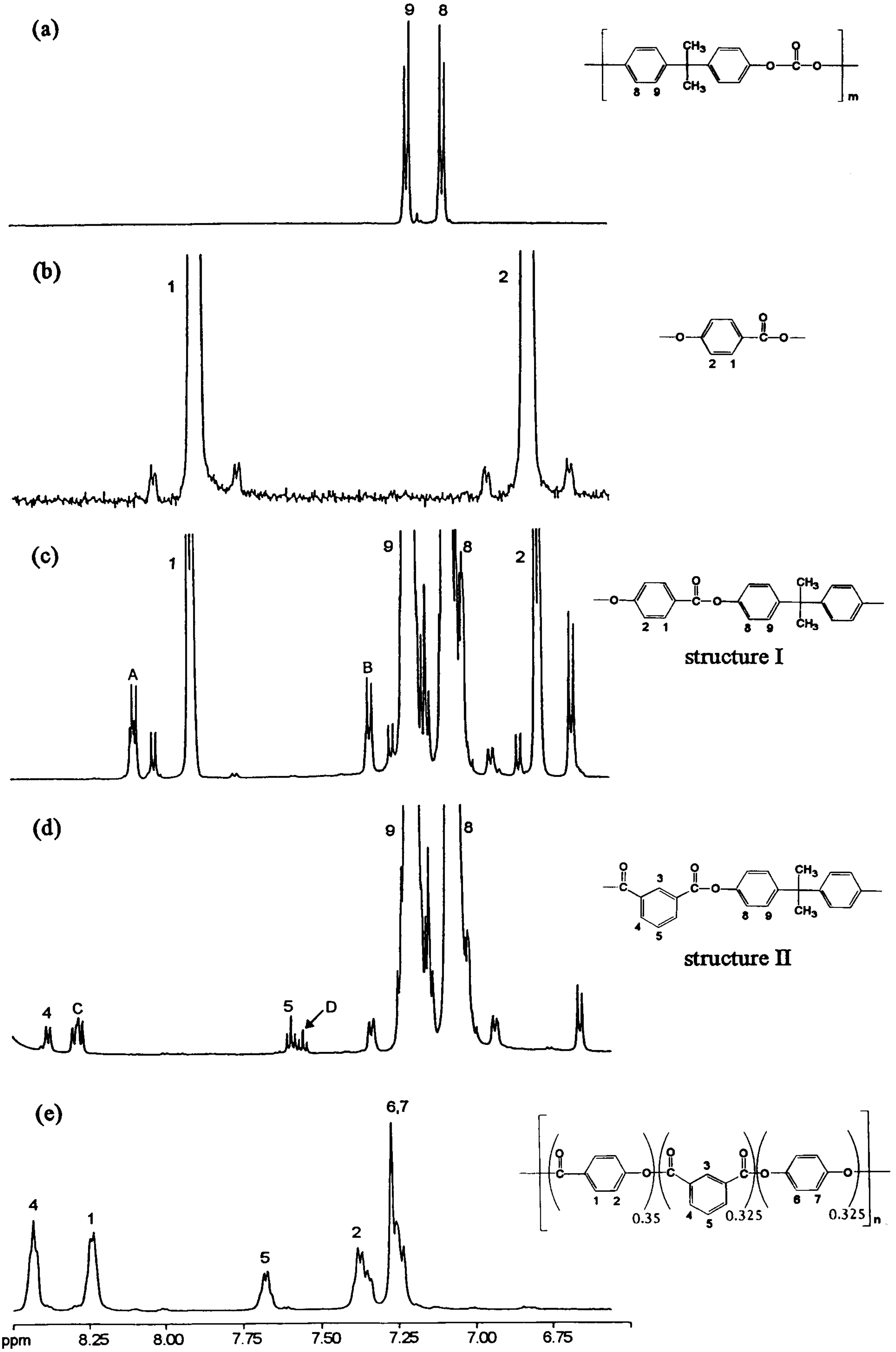

Figure 13 The aromatic proton region of 600 MHz n.m.r. spectra of: (a) PC; (b) HBA; (c)_ PC/HBA (80/20) at 220°C for 30 min; (d) PC/IA (80/20) at 300°C for 30 min; and (e) HIQ

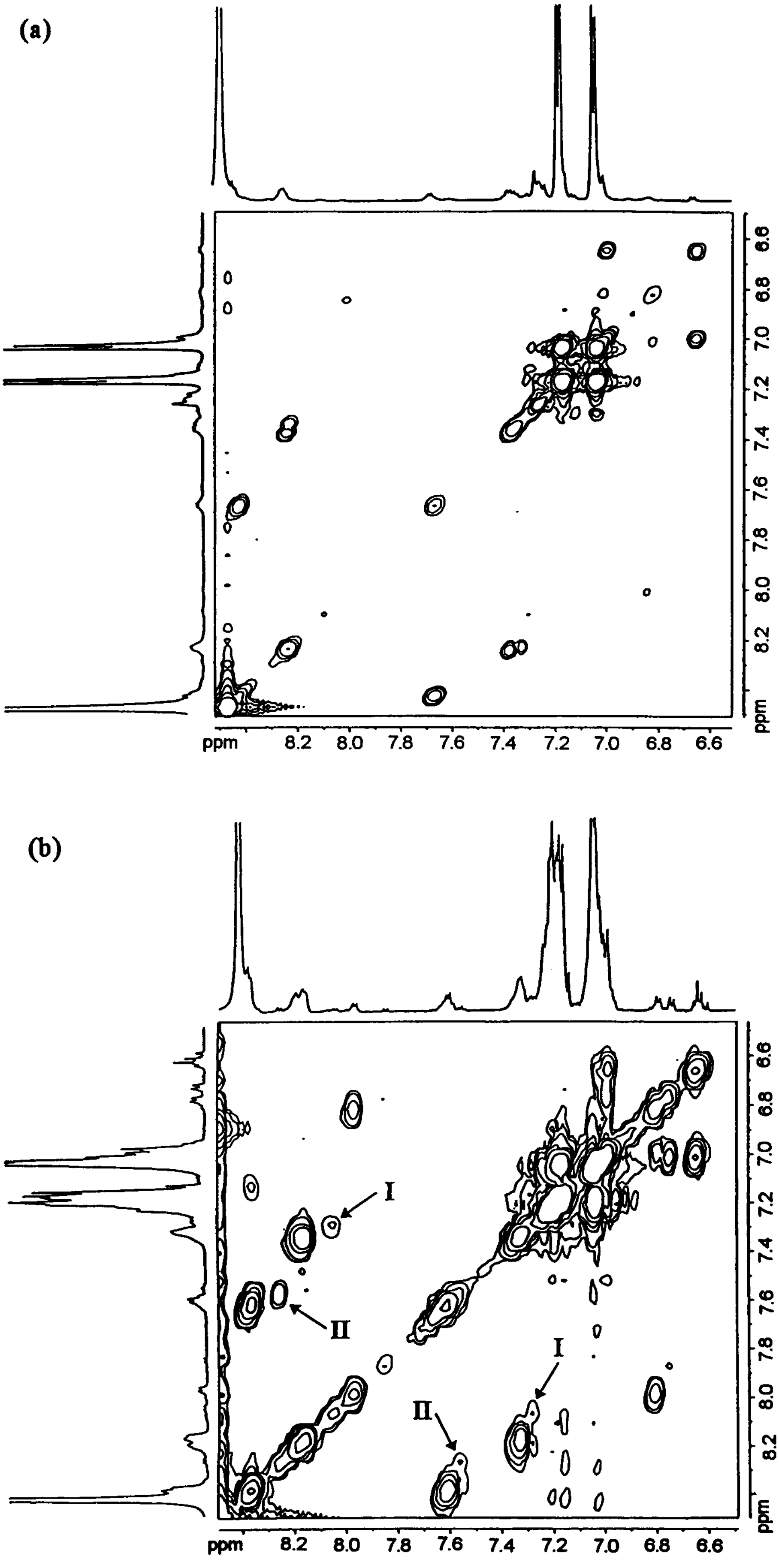

Figure 14 The aromatic region of 600 MHz $^1H-^1H$ COSY n.m.r. spectra of: (a) freshly prepared HIQ/PC (30/70) mixture; and (b) HIQ/PC (30/70) melt blend at 310°C for 12 min

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