

# Miscibility in Blends of Liquid Crystalline Poly(*p*-oxybenzoate-*co*-*p*-phenyleneisophthalate) and Polyarylate

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**ABSTRACT:** The miscibility of liquid crystalline poly(*p*-oxybenzoate-*co*-*p*-phenyleneisophthalate) (HIQ35) and polyarylate (PAr) coprecipitated from a mixed solvent of phenol/tetrachloroethane was investigated with differential scanning calorimetry. It was found that the amorphous phase of HIQ35 and PAr formed a partially miscible blend at low concentration of HIQ35. No measurable interaction between HIQ35 and PAr occurred when the weight fraction of HIQ35 was close to or less than that of polyarylate, as evidenced by wide-angle X-ray diffraction results. Upon annealing at 315°C for several minutes, the apparent miscibility of HIQ35 with polyarylate appeared as a result of an initial reaction between the polymers. For longer annealing time, the thermal degradation of HIQ35 joined in the reaction. This reaction or degradation in the blend was confirmed by nuclear magnetic resonance analysis and the intrinsic viscosity measurement of the blend. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 68: 1581–1589, 1998

**Key words:** miscibility; liquid crystalline poly(*p*-oxybenzoate-*co*-*p*-phenyleneisophthalate); differential scanning calorimetry

## INTRODUCTION

Thermotropic liquid crystalline polymer (TLCP) blends have been studied extensively in recent years. Mostly, the purpose was to use the high modulus of liquid crystalline polymers in its oriented direction to reinforce flexible-coil polymers in forming *in situ* composites.<sup>1–5</sup> Additionally, liquid crystalline polymers can reduce the overall viscosity of the blend, and they are a good processing aid.<sup>6,7</sup> Blending TLCP with flexible-coil polymers can provide the above two advantages without incurring the high cost of the TLCP. On

the other hand, liquid crystalline polymer chains are very stiff and of a rigid-rod nature. The enthalpy of mixing a rigid-rod polymer with a flexible-coil polymer was mostly positive. The small increase in entropy due to the mixing of these two polymers was not able to compensate for the enthalpy effect. Therefore, phase separation of the TLCP blends occurred with relative ease.<sup>8</sup>

To be of use in industrial applications where high stress and temperature exist in processing, at least partial miscibility in TLCP blends is needed. The miscibility of liquid crystalline polymer and flexible polymer becomes a major obstacle in the application of TLCP blends. A few research groups have been working on the miscibility of TLCP blends. Studies of poly(*p*-oxybenzoate-*co*-ethylene terephthalate) (POB-PET) with poly(butylene terephthalate) (PBT),<sup>9</sup> polycarbonate (PC),<sup>10,11</sup> poly(hexamethylene terephthal-

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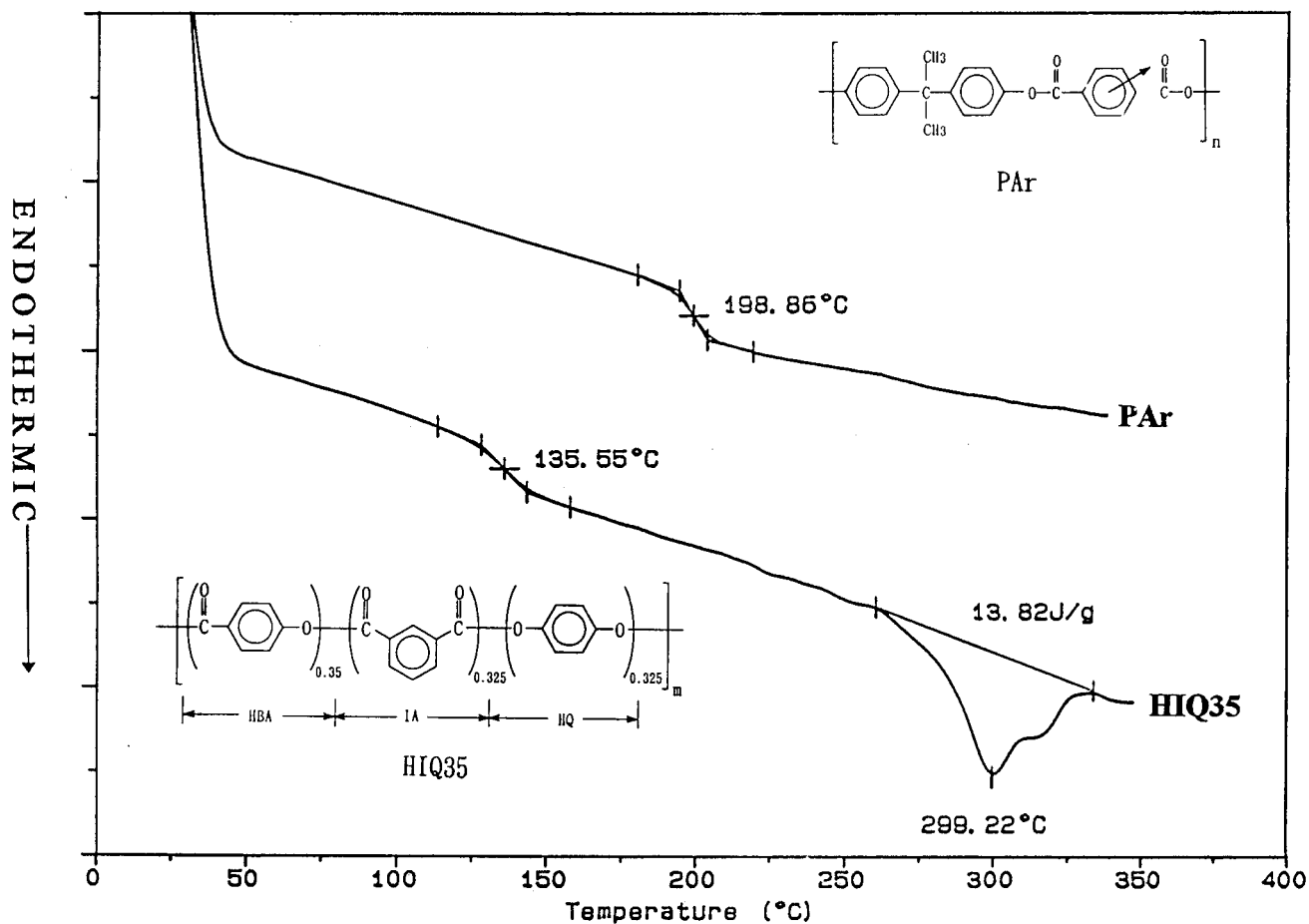


Figure 1 Chemical structures and DSC curves of PAR and HIQ35.

ate) (PHMT),<sup>12</sup> poly(ethylene terephthalate) (PET),<sup>13,14</sup> and polyarylate (PAR)<sup>15</sup> have been reported. The apparent miscibility in blends of POB-PET/PC, POB-PET/PBT, and POB-PET/PAR was found to result from ester interchange at high temperatures. The apparent miscibility in the blend of POB-PET/PHMT is caused by a reaction in the

Table I Transition Temperatures of HIQ35 Under Different Heating Rates

Heating Rate (°C/min)	$T_g$ (°C)	$T_c$ (°C)	$T_m$ (°C)
5	132.0	309.8	300.3
20	135.6	322.3	299.2
60	142.9	a	302.5
80	146.7	a	304.6
100	150.6	a	309.1

$T_c$ , crystallization temperature.

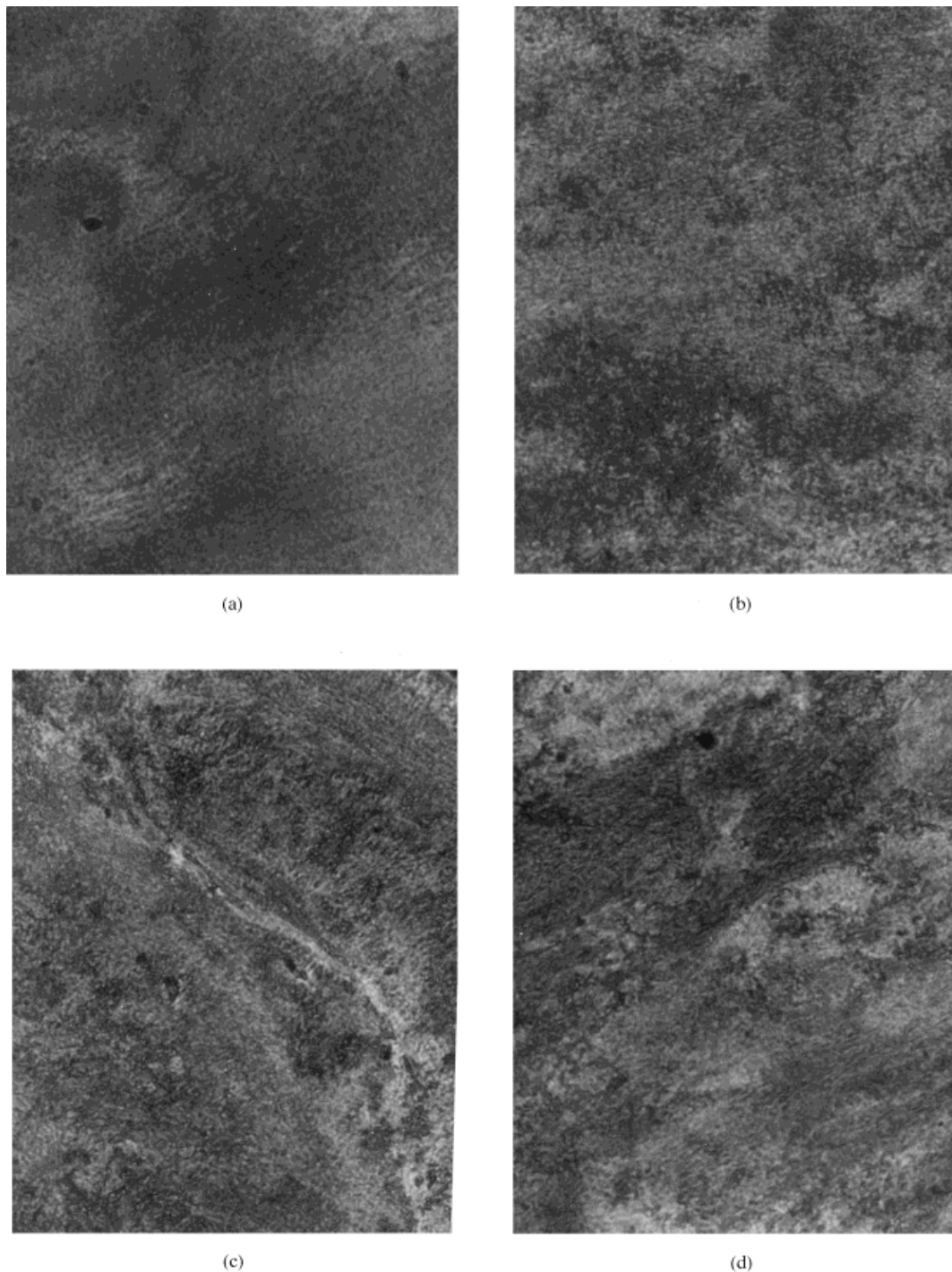
<sup>a</sup> Not existing.

Table II  $T_g$ ,  $T_m$ , and  $\Delta H_m$  of HIQ35/PAR Blends at Different Weight Ratios

HIQ35/PAR	$T_{g1}$ (°C)	$T_{g2}$ (°C)	$T_m$ (°C)	$\Delta H_m$ (J/g) (normalized against HIQ35)
0/100		198.9	a	a
10/90	a	193.3	a	a
20/80	a	191.5	a	a
30/70	a	188.1	310.0	5.3
40/60	139.2	183.0	308.5	8.8
50/50	138.5	184.2	306.5	9.3
60/40	137.7	183.2	305.2	11.5
70/30	137.6	179.4	304.1	11.6
80/20	136.4	172.8	305.9	11.8
90/10	136.3	a	302.8	12.0
100/0	135.6	a	299.2	13.8

$T_{g1}$ , low-temperature  $T_g$ ;  $T_{g2}$ , high-temperature  $T_g$ ;  $\Delta H_m$ , enthalpy of fusion.

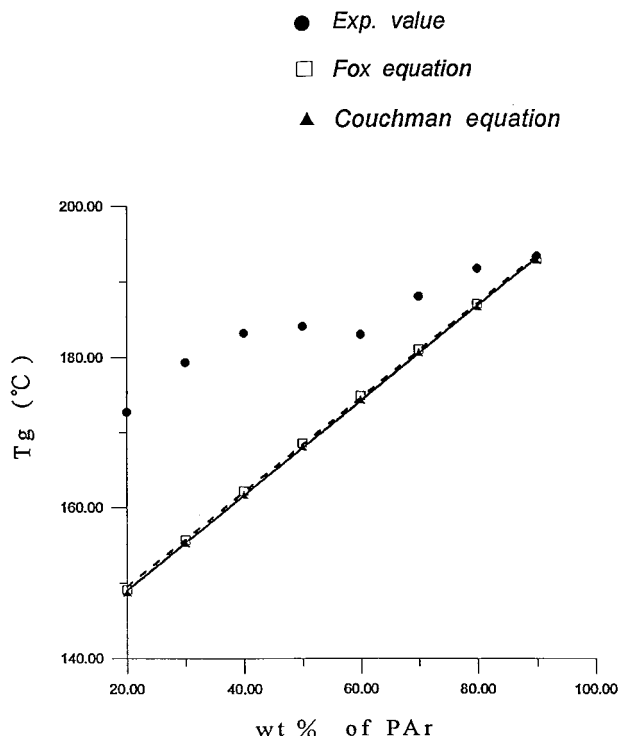
<sup>a</sup> Not existing.



**Figure 2** Room-temperature birefringence pictures of blends of HIQ35/PAr at weight ratios: (a) 30/70; (b) 50/50; (c) 70/30; (d) 80/20.

melt. Poly(*p*-oxybenzoate-*co-p*-phenyleneisophthalamate) is a copolyester of *para*-hydroxybenzoic acid (HBA), isophthalic acid (IA), and hydroquinone (HQ), and is termed HIQ. The 4-oxybenzoate segments impart nematic phase. The IA and HQ are

known to form a crystalline structure. Consequently, HIQ exhibits biphasic morphology.<sup>16,17,18</sup> Blends of liquid crystalline HIQ and PC exhibit complete miscibility due to strong transesterification, as concluded from our previous study.<sup>19</sup>



**Figure 3** Comparison between measured  $T_g$ s and values predicted by Fox and Couchman equations in blends of HIQ35/PAR.

Although transesterification enhances the miscibility in liquid crystalline polyester blends, it has two serious effects. First, it results in lower molecular weights of the polymers. Second, the transesterification also causes a loss of liquid crystalline character in the TLCP blends.<sup>20</sup> In this study, we chose a blend of polyarylate and liquid crystalline HIQ. Polyarylate is more stable at high temperature than PC, and therefore is less susceptible to ester exchange reaction. Additionally, both HIQ and PAR contain isophthalate units in their structures. We would like to know if they can form a miscible system because of similar chemical structures in part of the polymer chains.

## EXPERIMENTAL

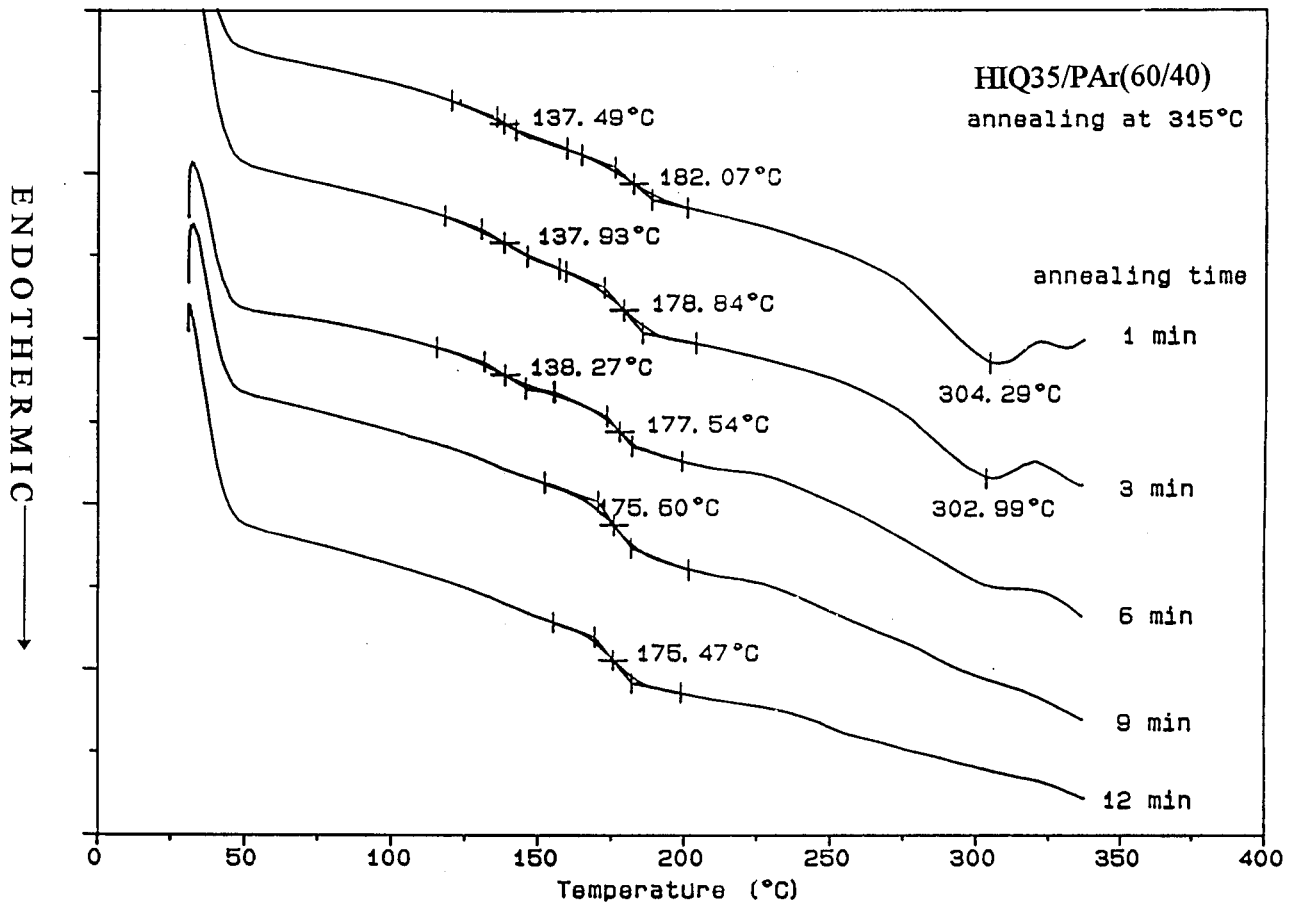
The HIQ composition of interest is HBA/IA/HQ (35/32.5/32.5), or HIQ35. The intrinsic viscosity of the HIQ35 and polyarylate were 0.785 and 0.698 dL/g, respectively. The HIQ35 polymer was provided by Hoechst Celanese Co. (Summit, NJ), PAR was obtained from Unitika Corporation (Osaka, Japan). The unit ratio of isophthalate to

terephthalate in PAR is 1 : 1; the trade name of PAR was U-100. The solution blending of PAR and HIQ35 was carried out by dissolving both polymers in a mixed solvent of phenol and tetrachloroethane (50/50 by weight). The concentration of the solution containing PAR and HIQ35 is 2% by weight. The different HIQ/PAR weight ratios used were 10/90, 20/80, 30/70, 40/60, 50/50, 60/40, 70/30, 80/20, and 90/10. The solutions were stirred and heated to 70°C. After the polymers were completely dissolved and became a one-phase solution for 30 min, the blends were precipitated in a 10-fold volume of methanol. The blends were then washed 5 times, each time with 200 cc methanol. The blends were then dried in a vacuum oven at 100°C for 4 days. The thermogravimetric analysis of the dried blends showed no appreciable weight loss up to 350°C, indicating a complete removal of the solvent. Thermal transitions of the HIQ35/PAR blends were measured with a Du Pont 2910 differential scanning calorimeter (DSC). The blends were heated from 25 to 315°C at a rate of 20°C/min, and the samples were immediately quenched to room temperature with liquid nitrogen. The DSC curves of the samples were taken the second time the samples were heated at the rate of 20°C/min.

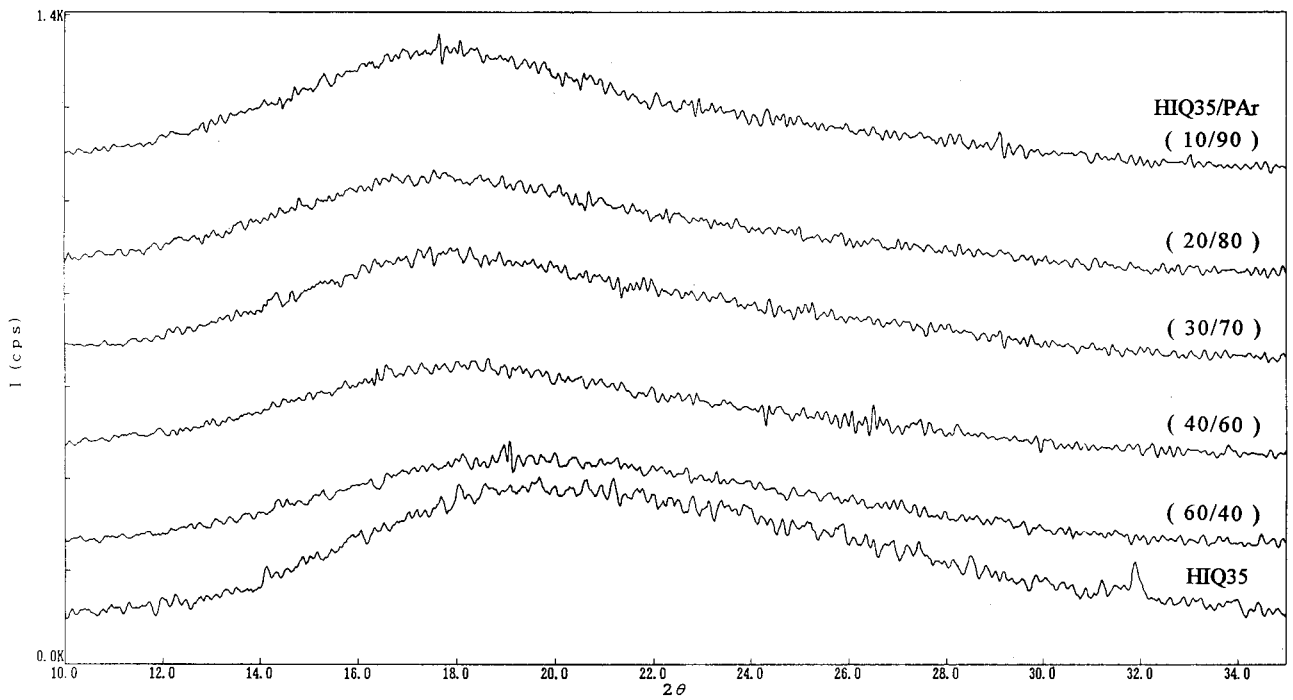
Annealing of HIQ35/PAR blends in different compositions was performed by two methods. The first was carried out in the DSC, and the second was executed in a vacuum tube for nuclear magnetic resonance (NMR) analysis. The blends in powder form were heated on a hot plate to form a melt, and then squeezed onto a glass slide to form a film for birefringence observation. The birefringence pictures of the blends were obtained with a Carl Zeiss Axiophot polarized microscope. X-ray diffraction was carried out with a diffraction meter, Model Science MXP-3, MAC Corp., Japan. For NMR analysis, 6% solutions of PAR dissolved in deuterated chloroform and HIQ35 dissolved in CD<sub>2</sub>Cl<sub>2</sub>/CF<sub>3</sub>COOD (70/30 by volume) were prepared. For the annealed 60/40 HIQ35/PAR blend, there was no proper solvent found in this study; therefore, the soluble fraction of the annealed blends in deuterated chloroform was analyzed. The NMR spectra were obtained on a Bruker DMX-600 spectrometer. The Heteronuclear Multiple Bond Correlation NMR spectrum of the soluble fraction of the annealed blend was obtained.

## RESULTS AND DISCUSSION

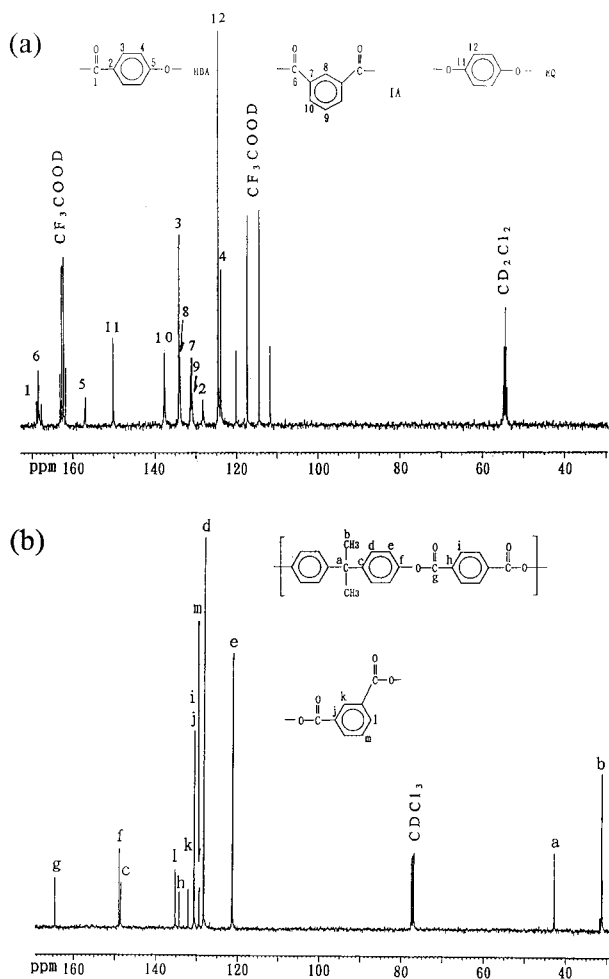
The chemical structures and DSC curves of HIQ35 and PAR are shown in Figure 1. The glass



**Figure 4** DSC curves of HIQ35/PAr (60/40) annealed at 315°C for different times.



**Figure 5** X-ray diffraction patterns of blends of HIQ35/PAr at different weight ratios.



**Figure 6** The  $^{13}\text{C}$ -NMR spectra of (a) HIQ35 dissolved in  $\text{CF}_3\text{COOD}/\text{CD}_2\text{Cl}_2$  (30/70); (b) PAR dissolved in  $\text{CDCl}_3$ .

transition temperatures ( $T_g$ s) of PAR and HIQ35 are 198.9 and 135.6°C, respectively. Two endothermic peaks were observed for HIQ35, at 299.2 and 316.3°C. As the heating rate was increased from 5°C/min to 20°C/min, these two peaks converged to a broad endothermic peak. The transition temperatures of HIQ35 under different heating rates are listed in Table I. Both the  $T_g$  and the melting temperature ( $T_m$ ) increased with the heating rate. The appearance of two endothermic peaks was caused by the double recrystallization temperatures at 309.8 and 322.3°C. This has been proven in a previous study.<sup>19</sup> The thermal properties of solution-coprecipitated blends of HIQ35/PAR at different weight ratios are listed in Table II, where the low-temperature  $T_g$  ( $T_{g1}$ ) and the high-temperature  $T_g$  ( $T_{g2}$ ) stand for the contribution by HIQ35 and PAR, respectively. Most of

these blends displayed two  $T_g$ s along with a melting endotherm. There is only one  $T_g$  for HIQ35/PAR blends at compositions of 30/70, 20/80, and 10/90. Additionally, the normalized heat of fusion ( $\Delta H_m$ ) (against the actual HIQ35 weight in blends) of these blends was either non-existent or much less than that of the pure HIQ35 (Table II). These two facts imply that the crystallization of HIQ35 was reduced due to the presence of partial miscibility between the polymers at these compositions. Another piece of data also supports this explanation. The birefringence pattern of HIQ35/PAR at composition 30/70 was more homogeneous than those of HIQ35/PAR at 50/50, 70/30, and 80/20, as shown in Figure 2.

For a miscible random polymer blend, a number of equations have been proposed to describe the composition dependence of  $T_g$  of the blend.<sup>21-23</sup> Two of them are as follows:

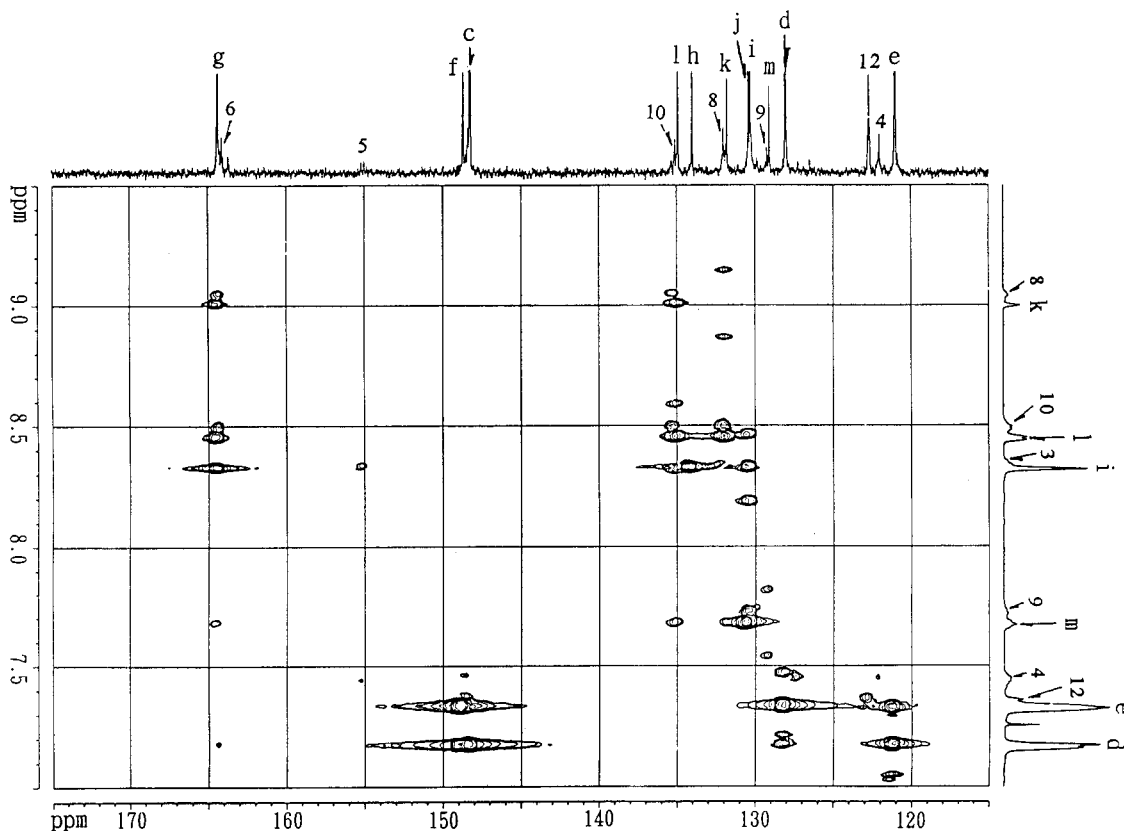
$$\text{Fox: } 1/T_g = W_1/T_{g1} + W_2/T_{g2}$$

$$\text{Couchman: } \ln T_g = \{W_1 \ln(T_{g1}) + (\Delta C_{p2}/\Delta C_{p1})$$

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

The  $\Delta C_p$  (heat capacity at constant pressure) values for PAR and HIQ35 are, respectively, 0.280 and 0.335  $\text{J g}^{-1} \text{°C}^{-1}$ . To reduce the complication of possible transesterification on  $T_g$ , the HIQ35/PAR blends were heated to 340°C and were immediately quenched in liquid nitrogen before the second DSC scan. Figure 3 shows the composition dependence of  $T_g$  of HIQ35/PAR blends. In the case of the blends exhibiting two  $T_g$ s, the higher  $T_g$  was chosen for the comparison. The single  $T_g$  exhibited by the HIQ35/PAR blends at high PAR compositions agreed reasonably well with the values predicted by the Couchman and Fox equations, indicating that the blends were partially miscible. Upon annealing at 315°C, the  $T_g$  of each component in the blend of 60/40 HIQ35/PAR shifted toward each other, as indicated in Figure 4. The difference between the two  $T_g$ s of the blends reduced with the annealing time. After 12 min annealing, there was only one  $T_g$  existing along with the disappearance of the melting peak for the 60/40 HIQ35/PAR blend. This suggests that either the blend became a miscible system or some reaction took place between HIQ35 and PAR under the thermal treatment.

For the crystalline phase in these blends, X-ray diffraction measurements were carried out. The wide angle X-ray diffraction (WAXD) pat-



**Figure 7** The 600 MHz  $^1\text{H}$ - $^{13}\text{C}$ -NMR spectrum of chloroform-extracted HIQ35/PAR (60/40) after annealing at 315°C for 12 min.

terns over the Bragg angles from 10 to 35 degrees of the 10/90, 20/80, 30/70, 40/60, and 60/40 HIQ35/PAR blends, coprecipitated from methanol and not heated, are shown in Figure 5. The diffraction patterns of these blends exhibited the general features of the HIQ35 component except at  $2\theta = 31.9$  degrees. The lack of significant variation in the  $2\theta$  positions of the HIQ35 reflection lead to the conclusion that the presence of PAR did not inhibit the crystallization of HIQ35. There is a subtle difference between the samples in WAXD and DSC. In DSC measurement, the blends were heated to 340°C and then quenched. The melt stage gave the samples a chance to reach thermal equilibrium, and the quenching step suppressed the crystallization of HIQ35 in the blends. Hence, the DSC results confirmed that partial miscibility existed in the amorphous phase of HIQ35 and PAR.

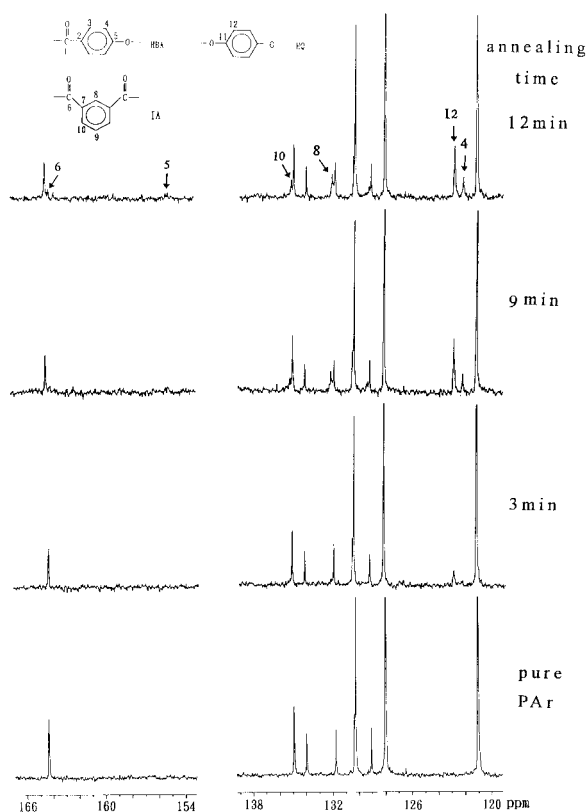
To identify the specific interaction between HIQ35 and PAR under thermal treatment,  $^{13}\text{C}$ -NMR analysis on deuterated chloroform-extracted solutions of these blends was carried out. The  $^{13}\text{C}$ -NMR spectra of HIQ35 and PAR are shown, and

various peaks are identified, in Figure 6. We could not find a proper solvent (even with various compositions of  $\text{CF}_3\text{COOD}/\text{CD}_2\text{Cl}_2$ ) to dissolve annealed blends of HIQ35/PAR completely. Hence, the extraction method was used. The  $^1\text{H}$ - $^{13}\text{C}$ -NMR spectrum of the deuterated chloroform-extracted 60/40 HIQ35/PAR blend which was annealed at 315°C for 12 min is given in Figure 7. This NMR spectrum was used to identify peaks contributed from both HIQ35 and PAR. In Figure 7, HIQ35 peaks appear in the middle of strong PAR peaks. Since HIQ35 does not dissolve in chloroform, the appearance of HIQ35 in chloroform indicates that HIQ35 either degraded thermally or reacted with PAR. Additionally, the NMR peak intensity of aromatic  $^{13}\text{C}$  in oxybenzoate and in hydroquinone of HIQ35 (peaks 3, 4, and 12) in the blends grew with the thermal treatment time, as shown in Figure 8. On the other hand, the thermogravimetric analysis of HIQ35 and 60/40 HIQ35/PAR blend showed that there was no appreciable weight loss at 315°C for 30 min. The intrinsic viscosity of 60/40 HIQ35/PAR blend increased with annealing time, reaching its maximum at 9 min, and then

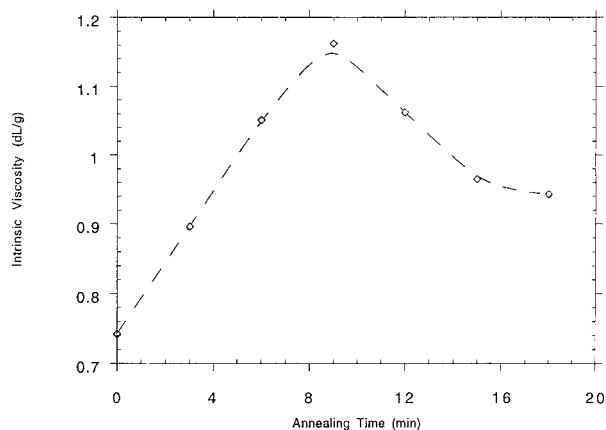
decreased slightly, as shown in Figure 9. In the annealing period of 20 min, the intrinsic viscosity of the blend was higher than that of the freshly prepared blend. This fact precluded the annealed 60/40 HIQ35/PAR blend from becoming solely thermally degraded. Rather, a molecular chain-end reaction between HIQ35 (or degraded HIQ35) and PAR must have happened initially to account for the blend's increasing molecular chain length. After a longer annealing time, the thermal degradation of HIQ35 joined the reaction in the blend, causing molecular chain length to decrease. For a more accurate analysis, we tried solid-state NMR analysis on the annealed blends, but the sensitivity and the side band problems prevented us from obtaining discernible results.

## CONCLUSIONS

The amorphous phase of HIQ35 and polyarylate formed a partially miscible system at low HIQ35 concentration, as concluded from the DSC results.



**Figure 8** The transient  $^{13}\text{C}$ -NMR spectra of deuterated chloroform-extracted 60/40 HIQ35/PAR blend after annealing at 315°C for different times.



**Figure 9** Transient intrinsic viscosity of the 60/40 HIQ35/PAR blends after annealing at 315°C for different times.

No interaction between HIQ35 and PAR occurred when the weight fraction of HIQ35 was close to or less than that of polyarylate, as evidenced by WAXD results. Upon annealing the blends at 315°C, the apparent miscibility in blends of 60/40 HIQ35/polyarylate occurred as a result of an initial reaction between HIQ35 and polyarylate. Further annealing resulted in the thermal degradation of HIQ35 joining the reaction, as confirmed by the NMR analysis and intrinsic viscosity measurement of the blend.

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