# Miscibility and Transesterification in Blends of Liquid Crystalline Copolyesters and Polyarylate

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**ABSTRACT:** Blends of poly(oxybenzoate-*p*-ethylene terephthalate) (POB-PET) and polyarylate were confirmed to be a partially miscible system by differential scanning calorimetry. When 60/40 POB-PET/PAr blend was annealed at high temperature (above 270°C) for several minutes, the ester−ester interchange (transesterification) in the blend took place immediately, as evidenced by Fourier Transformed infrared analyses. The analysis of the blend annealed at 290°C by [1]H-^{13}C nuclear magnetic resonance disclosed that there were four new diads appearing in 15 min and an additional one produced in 60 min during the heat treatment. The miscibility between POB-PET and polyarylate increased with the mol concentration of these new diads judging from differential scanning calorimetry. The evolution of the concentration of the diad ethylene glycol-isophthalate during the annealing can be described by a second-order reaction. The activation energy of forming the diad ethylene glycol-isophthalate was 26.5 kcal/mol, and the preexponential factor for the transesterification reaction is $3.7 \times 10^8$ min$^{-1}$. © 1998 John Wiley & Sons, Inc. J Polym Sci B: Polym Phys 36: 1959−1969, 1998
**Keywords:** miscibility; transesterification; kinetics; polyarylate; liquid crystalline copolyesters

## INTRODUCTION

Thermotropic liquid crystalline polymers (TLCP) have drawn much research attention since their arrival. TLCP contained rigid-rod-type chemical structures, and therefore had high mechanical and thermal properties. Due its high raw material cost, TLCP were frequently melt blended with engineering plastics to form fibril structure to reinforce the engineering plastics *in situ*.[1−4] In this respect, TLCP blends can form organic/organic composites. The compatibility between the TLCP and the matrix polymer seemed the most critical one in deciding the mechanical properties of these composites because most failures appeared at the interfaces. However, due to its stiff structure, TLCP were usually immiscible with flexible-coil amorphous polymers.[5,6] Phase separation occurred when the TLCP blends were subject to high stress and high temperature.[7]

For a reduction in phase separation and better interfacial adhesion in TLCP composites, partial miscibility is needed. In our laboratory, we have studied the miscibility in blends of liquid crystalline poly(oxybenzoate-*p*-ethylene terephthalate)(POB-PET) and polycarbonate (PC)[8,9] and found that they are miscible due to intensive ester−ester interchange (transesterification). In another case, we found partial miscibility existing in blends of POB-PET/polyetherimide (PEI).[10] In adding POB-PET to the originally immiscible TLCP and amorphous PC or PEI has been found to enhance the interfacial adhesion between the TLCP and PC or PEI.[10,11] The mechanical properties of ternary blends of poly(oxybenzoate-*p*-naphthalate)(Vectra), POB-PET, and PC[11] or PEI[10] were always higher than that of their corresponding binary blends of Vectra/PC and Vectra/PEI.

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For polyarylate (PAr), it is an amorphous polymer, and has a high glass transition temperature of 199°C. We are interested in the miscibility in blends of POB-PET and polyarylate for its application to *in situ* composites. Previously, Porter's group[12] reported the miscibility of blends of POB-PET and PAr, and found that POB-PET and PAr were partially miscible by differential scanning calorimetry and polarizing optical microscopy. They concluded that there was transesterification between POB-PET and PAr, but gave no detailed mechanism on transesterification. Transesterification between copolyesters has been well analyzed in blends of polyethylene terephthalate and polyethylenesebacate[13] and in blends of bisphenol A polycarbonate and polybutylene terephthalate[14] with nuclear magnetic resonance.

In this article, we will attempt to analyze the chemical structure change in both polymers during transesterification with Nuclear Magnetic Resonance spectroscopy. Additionally, the kinetics of the transesterification in the blend will be discussed. This result will bring us a quantitative understanding on the relationship between miscibility and transesterification.

## EXPERIMENTAL

Poly(oxybenzoate-*p*-ethylene terephthalate) at a molar ratio of 60/40 (POB-PET) was provided by Unitika Corp., Japan. Polyarylate (PAr) with a 1 : 1 isophthalate/terephthalate ratio (trade name U-100) was also supplied by Unitika. The intrinsic viscosities of POB-PET and PAr are 0.466 dL/g and 0.652 dL/g, respectively. The solution blend of POB-PET/PAr was prepared by dissolving 2 g of the polymers at the proper weight ratio in a 100 cm$^3$ mixed solvent of 50/50 phenol/tetrachloroethane by weight. The temperature of the solvent was maintained at 55°C. The solution was precipitated in a 10-fold volume of methanol after the solution became one phase for 1 h. The precipitated polymers were washed four times in hot methanol. The blend was dried in a vacuum oven at 100°C for 4 days before thermal analysis. The thermal gravimetric analysis of the dried blends showed no appreciable weight loss up to 300°C, indicating a complete removal of the solvent.

The thermal analysis of the blend at different temperature for different annealing time was carried out with a Dupont 2910 differential scanning calorimetry (DSC). For DSC analysis, the samples were heated up from 30 to 290°C, at a heating rate of 20°C per min. At 290°C, the samples were annealed for 30 s. Subsequently, the samples were quenched down to 25°C. The samples were heated again from 25 to 300°C at the same heating rate.

The X-ray diffraction analysis of the solution blend of 60/40 POB-PET/PAr annealed at 290°C for different time was carried out in a D5000 diffraction meter (Siemens Corp., Germany) operated at 40 KV and 30 mA. CuK$\alpha$ radiation was used. The chemical structure change resulting from transesterification was identified by Fourier Transformed infrared (FTIR) and Nuclear Magnetic Resonance (NMR) spectroscopy. POB-PET does not dissolve in chloroform. Only PAr and its derivatives can be dissolved in chloroform. The ester exchange between POB-PET and PAr can, therefore, be confirmed by examining the chemical structure change of PAr in the blends. POB-PET/PAr blends were extracted with chloroform first, and then the solution containing microparticles was filtered with a syringe containing a 0.5-micron pore-size filter. The soluble portion was used for FTIR analysis. A Bomem MB100 FTIR was used for this measurement. For NMR analysis, freshly prepared and annealed blends of POB-PET/PAr were completely dissolved in a mixed solvent of deuterated chloroform and deuterated trifluoacetic acid at volume ratio of 60/40. Two-dimensional $^1$H-$^{13}$C Heteronuclear Multiple Bond Correlation (HMBC) analysis on these blends was conducted on a Bruker DMX-600 spectrometer to identify the new resonance peaks resulted from the new structures evolved during transesterification.

## RESULTS AND DISCUSSION

The DSC curves and the chemical structures of POB-PET and PAr are shown in Figure 1. The glass transition temperatures ($T_g$) of POB-PET and PAr are located at 62.2 and 198.7°C, respectively. The miscibility in solution blends of POB-PET and PAr was studied through the difference in their glass transition temperature ($T_g$) in the blends. The $T_g$s of solution blends of POB-PET/ PAr at different compositions are displayed in Figure 2. In Figure 2, the low $T_{g1}$ was exhibited by POB-PET, and the high $T_{g2}$ stood for PAr. There were two distinctive $T_g$s when the weight fraction of PAr is less than or equal to 0.6 in the blend. The $T_{g1}$ was almost independent of the concentration of PAr in these compositions, and the $T_{g2}$ increased with the concentration of PAr in
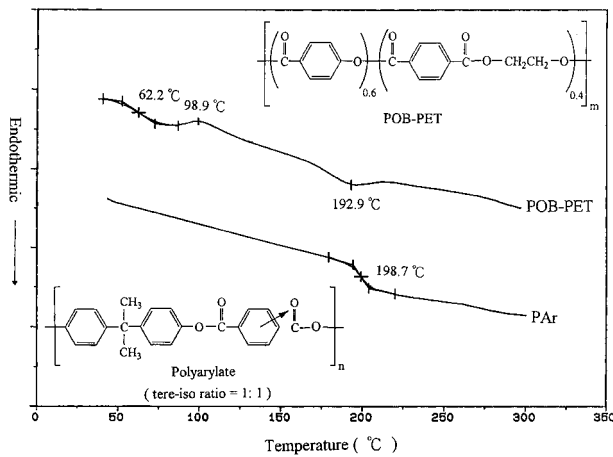
**Figure 1.** The chemical structures and the DSC curves of poly(oxybenzoate-p-ethylene terephthalate) and polyarylate.

these blends. A totally immiscible binary polymer blend prepared by the solution method will become completely phase separated when the blend is heated up to the melt state. The amorphous phases of the completely phase-separated blend will display two glass transition temperatures contributed from each component, and the two $T_g$s are independent of the relative weight fraction of each polymer. If there is a slight miscibility in the binary blends, the $T_g$ of each component will be affected by the existence of the partially miscible region. As the partially miscible region increases,
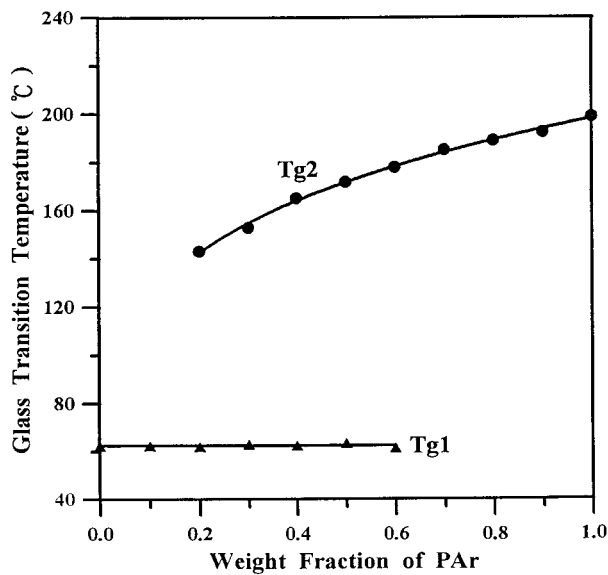


**Figure 2.** The glass transition temperature of blends of POB-PET and PAr at different compositions.
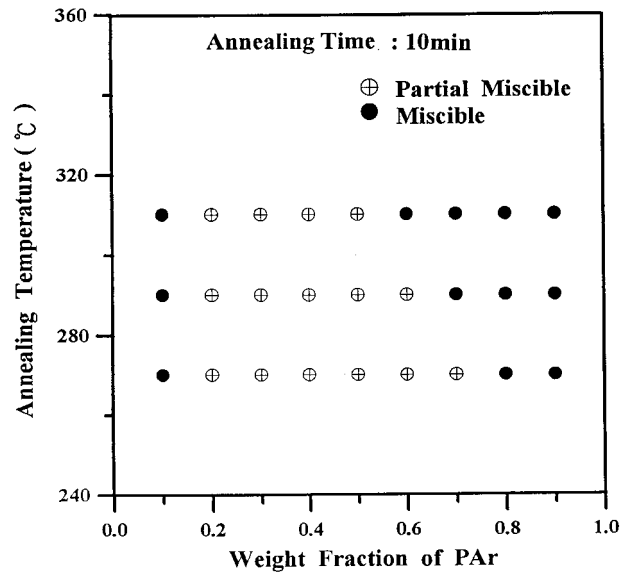


**Figure 3.** The miscibility diagram of the 60/40 POB-PET/PAr blend annealed at different temperatures for 10 min.

the two $T_g$s will shift toward each other. In the case of the POB-PET/PAr blend, the $T_{g2}$ contributed by PAr followed the above argument. However, owing to the stiff segment of POB and the partial crystallinity of the PET segment in the POB-PET copolymer, the $T_{g1}$ contributed by the PET segment was not affected by the presence of the partially miscible region. From this behavior, one can infer that there is partial miscibility existed between POB-PET and PAr. This result is similar to Porter's result.[12] The miscibility diagram of POB-PET/PAr blends annealed at different temperatures for 10 min is presented in Figure 3. In Figure 3, after being annealed at 270°C, the POB-PET/PAr blend is partially miscible when the weight fraction of PAr is between 0.2 and 0.7. In the case of the weight fraction of PAr being more than 0.8 or less than 0.1, the POB-PET/PAr blends become miscible. Compared to the thermal analysis result of the freshly prepared POB-PET/PAr blend, there was a small decrease in the miscibility region that might be caused by thermodynamics-induced phase separation. However, as the annealing temperature increased to 310°C, the miscible composition in the POB-PET/PAr blend increased as shown in Figure 3. This behavior indicated that there might be some reaction involved in the annealing process. The glass transition temperatures ($T_g$s) of the annealed POB-PET/PAr blend are given in Table I.

**Table I.**  The $T_g$s of Solution Blends of POB-PET/PAr at Different Compositions Annealed at Different Temperature for 10 Min

| POB-PET/PAr | 270°C | | 290°C | | 310°C | |
|---|---|---|---|---|---|---|
| | $T_{g1}$ | $T_{g2}$ | $T_{g1}$ | $T_{g2}$ | $T_{g1}$ | $T_{g2}$ |
| (80/20) | 62.2 | 125.5 | 63.3 | 122.6 | 64.2 | 120.9 |
| (70/30) | 63.2 | 142.4 | 64.1 | 137.3 | 64.6 | 132.6 |
| (60/40) | 62.7 | 152.2 | 62.9 | 148.9 | 66.5 | 142.9 |
| (50/50) | 65.0 | 160.0 | 65.9 | 156.7 | 65.6 | 152.8 |
| (40/60) | 62.7 | 160.9 | 64.8 | 157.0 | a | 152.4 |
| (30/70) | 64.2 | 175.2 | a | 170.9 | a | 168.9 |
| (20/80) | a | 178.1 | a | 176.9 | a | 171.9 |

<sup>a</sup> Not existing.

When the 60/40 POB-PET/PAr blend was annealed at 290°C in vacuum, the $T_{g2}$ decreased with the annealing time, as shown in Figure 4. In specific, the $T_{g2}$ dropped from 165 to 153°C in 10 min, and became stabilized at 145°C after 90 min annealing. The $T_{g1}$ increased only slightly. The drop in $T_{g2}$ increased with the annealing temperature, as demonstrated in Figure 4. The fresh 60/40 POB-PET/PAr blend was prepared from a solution precipitated process, and therefore contained a small amount of inhomogenity as displayed in the polarized optical micrograph (POM) of the
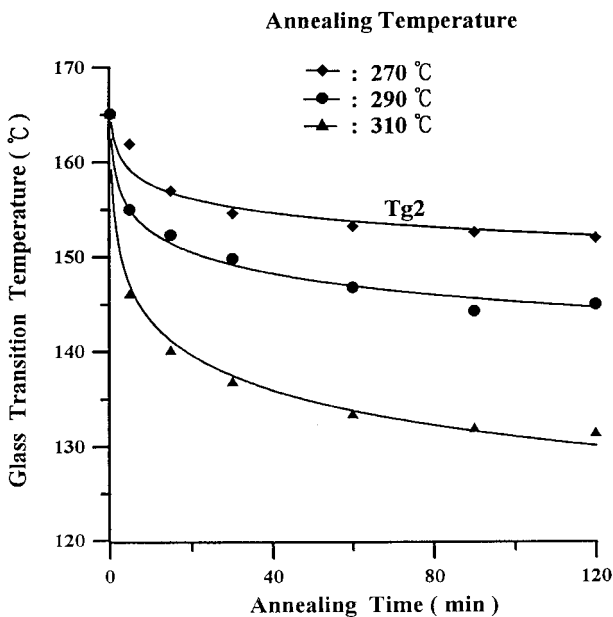


**Figure 4.**  The glass transition temperatures contributed by PAr in the blend of 60/40 POB-PET/PAr annealed at different temperature in vacuum for different time.

blend [see Fig. 5(a)]. The DSC result of this blend also indicated that it is a partial miscible blend. The morphology of the 60/40 POB-PET/PAr blend becomes more homogeneous as the annealing time increased, shown in Figure 5(b) and (c). From the DSC and the POM result of the 60/40 POB-PET/PAr blend, we concluded that the change in the domain morphology of the blend seemed dominated mostly by the reaction during annealing. The phase separation in the blend caused by thermodynamics is relatively small in this case.

The X-ray diffraction result of the annealed 60/40 POB-PET/PAr blend was displayed in Figure 6. In curve (a) of Figure 6, the wide-angle X-ray diffraction pattern of POB-PET is characterized by a sharp diffraction peak at $2\theta = 19.5°$ with a shoulder at $2\theta = 28.2°$ and one relatively weak broad peak at $2\theta = 43.3°$. The POB sequences of the POB-PET copolyesters apparently adopt the crystal structures of the parent homopolymer, poly(oxybenzoate).[15] As the blend was annealed at 290°C, the 28.2° peak disappeared after 15 min, and the 19.5° peak decreased with annealing time steeply, as shown in curves (b), (c), (d), (e), and (f) of Figure 6. This indicated that the crystal structure of POB-PET has been reduced due to the reaction with PAr.

The FTIR spectra of PAr and POB-PET are displayed in Figure 7. As indicated in Figure 7, the aryl ester absorbency peaks appeared at 1739 and 1070 cm$^{-1}$ for PAr, and there was an alkyl ester absorbency peak at 1715 cm$^{-1}$ other than the two aryl peaks at 1739 and 1064 cm$^{-1}$ for POB-PET. The annealed 60/40 POB-PET/PAr blends were extracted with chloroform, and the suspensions were then filtered to obtain clear solutions. The
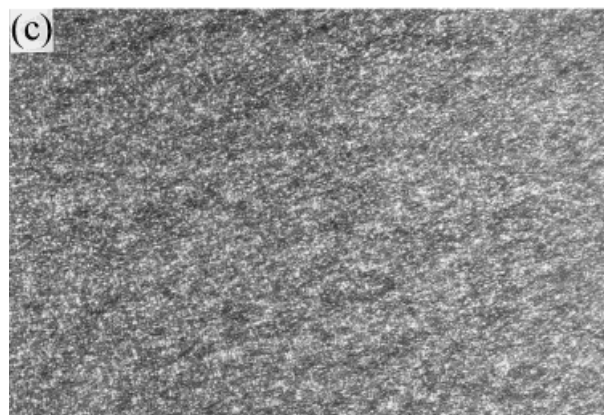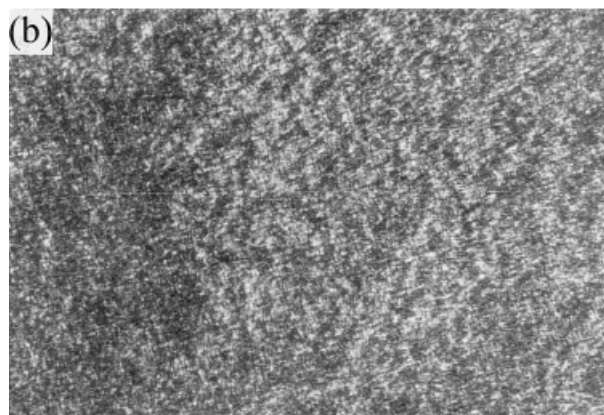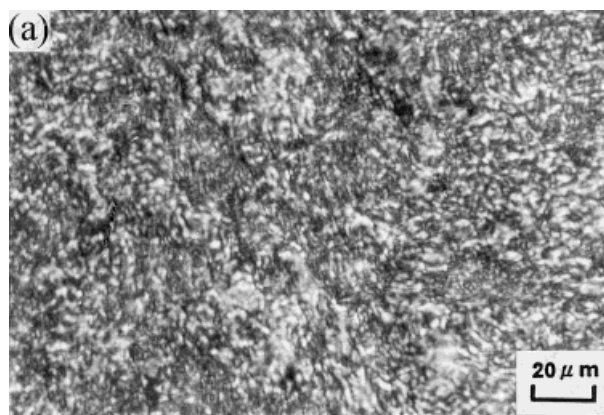
**Figure 5.** The polarized optical micrographs of the 60/40 POB-PET/PAr blend annealed at 290°C for (a) 0 min, (b) 15 min, (c) 60 min.

FTIR spectra of the resulting solutions were illustrated in Figure 8. POB-PET does not dissolve in chloroform. There was no additional peak appearing other than the main peaks of PAr for the chloroform-extracted solution out of freshly prepared 60/40 POB-PET/PAr blend, as displayed in Figure 8. The appearance of the alkyl group at
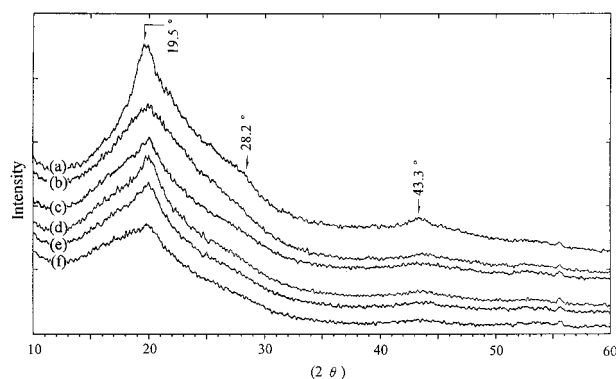


**Figure 6.** The wide-angle X-ray diffraction curves of (a) POB-PET, (b) 60/40 POB-PET/PAr blend freshly prepared, (c) annealed for 15 min, (d) annealed for 30 min, (e) annealed for 60 min, (f) annealed for 90 min at 290°C.

1716 cm$^{-1}$ in the FTIR spectra of the extracted blend after 15 min annealing indicated that the alkyl ester has been attached to the PAr molecules. This particular alkyl ester peak also grew with the annealing time. This is initial and direct evidence that transesterification indeed took place.

Further study on the change in the chemical structures of POB-PET and PAr was carried out with NMR. Because the annealing of the blend
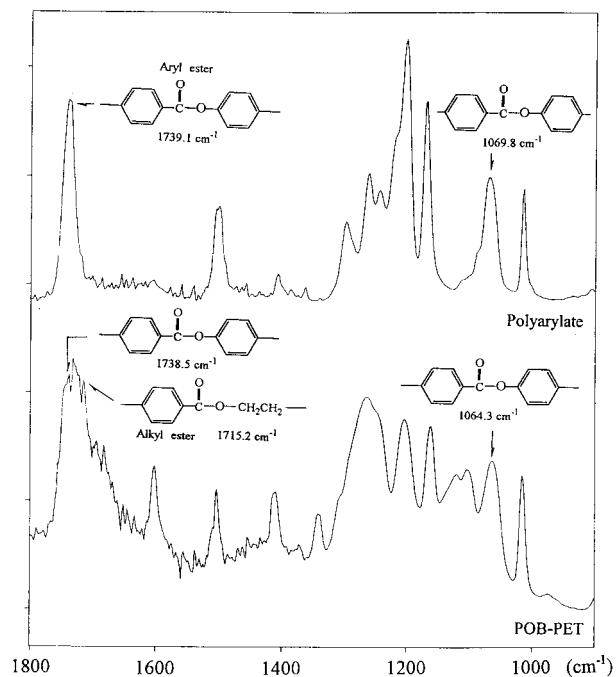


**Figure 7.** The FTIR spectra of polyarylate and POB-PET.
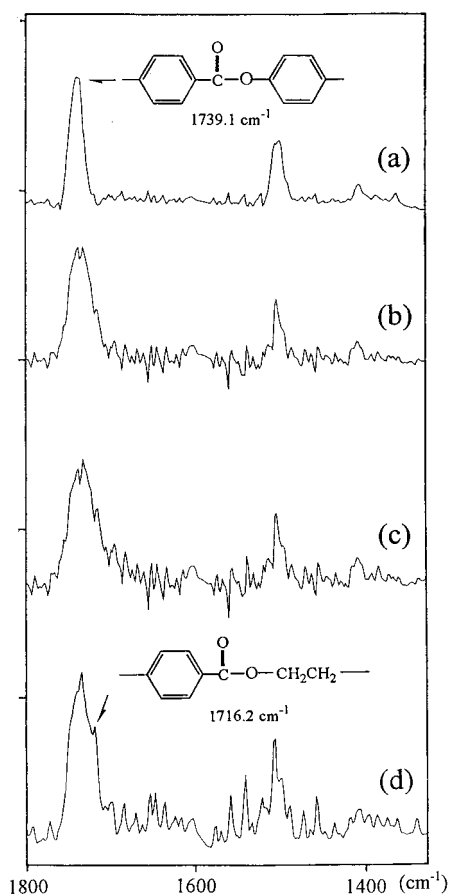
**Figure 8.** The FTIR spectra of chloroform-soluble portions of 60/40 POB-PET/PAr (a) freshly prepared, (b) annealed for 15 min, (c) annealed for 30 min, (d) annealed for 90 min at 290°C.

was carried out in vacuum, the hydrolysis of the copolyesters was reduced to a minimum. Moreover, the degree of polymerization is high enough to neglect chain end reactions. Therefore, we concentrate on ester–ester interchange. The diad codes used in analyzing ester–ester interchange and the protons and $^{13}$C in the chemical structures of POB-PET and PAr were assigned in Figure 9 for NMR identification. The $^{1}$H-$^{13}$C HMBC NMR spectra of two aromatic portions of the completely dissolved fresh and the 60/40 POB-PET/PAr blend annealed at 290°C were chosen for comparison. The first aromatic region is in between 7.1 and 7.9 ppm of $^{1}$H and in between 118 and 134 ppm of $^{13}$C-NMR spectra. The second aromatic region is in between 8.3 and 8.7 ppm of $^{1}$H and in between 130 and 140 ppm of $^{13}$C-NMR spectra.

The first aromatic regions of the $^{1}$H-$^{13}$C-NMR spectra of the 60/40 POB-PET/PAr blend are shown in Figure 10. In Figure 10(a), the reso-

nance peaks of the freshly prepared 60/40 POB-PET/PAr blend indicated that the blend is a mechanical mixing of two polymers. Upon annealing the 60/40 POB-PET/PAr blend at 290°C for 15 min, a small new crosspeak appeared at 7.17–121.9 ppm (5* peak) and the other new crosspeak showed up at 7.73–130.6 ppm (13** peak) in the $^{1}$H-$^{13}$C spectra of the blend simultaneously, as indicated in Figure 10(b). Then, the first and the second new crosspeaks grew substantially and the second new crosspeak became independent from its neighboring peaks after 60 min annealing, as shown in Figure 10(c). The first new crosspeak is near the aromatic $H_5$. From reading the relative position of $^{1}$H to $^{13}$C and from a previous model compound study,[16] we knew the first new peak was the bisphenol-A segment attached to the POB segment, and the second new peak was the ethylene glycol segment attached to the isophthalate segment. Hence, we deduced that the 5* and the



**Figure 9.** The diad and the proton and the $^{13}$C codes assigned in POB-PET and PAr structures.

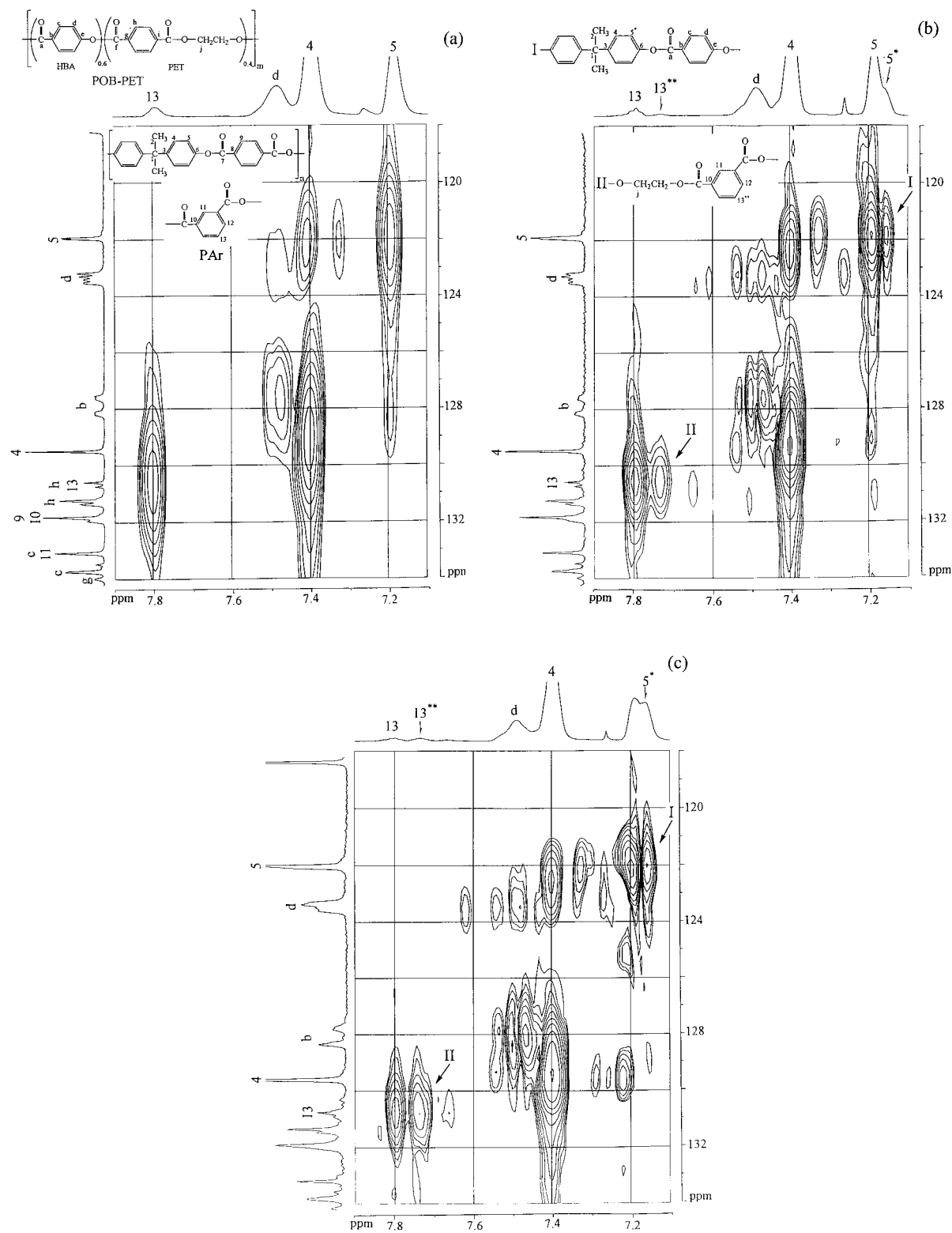**Figure 10.** The 600 MHz $^1$H-$^{13}$C NMR spectra of the first aromatic region of 60/40 POB-PET/PAr (a) freshly prepared, (b) annealed for 15 min, (c) annealed for 60 min at 290°C, new crosspeaks marked by I and II.

13** new peaks in the first region were caused by the hybrid structures (new diads) bisphenol A oxybenzoate and ethylene glycol-isophthalate, respectively.

By the same method, we can examine the second region. The second region of the freshly prepared blend is shown in Figure 11(a). We identified the third and the fourth new crosspeaks at 8.37–131.8 ppm (9** peaks) and at 8.46–131.8 ppm (9* peak), as shown in Figure 11(b) after 15 min annealing. These two new peaks were caused by the diad ethylene glycol–terephthalate and oxybenzoate–terephthalate, respectively. When the annealing time increased to 60 min, other than the growing third and fourth peak, an additional new peak appeared at 8.61–137.1 ppm (12* peak), as indicated in Figure 11(c). The fifth new peak is caused by diad oxybenzoate–isophthalate. In summary, there were four new structures appearing as a result of ester–ester interchange in heating the POB-PET/PAr blend at 290°C for 15 min in vacuum. The fifth new structure showed up in the blend when the heating time was increased to 60 min.

The quantitative analysis on the concentration of the above five new structures resulted from the 60/40 POB-PET/PAr cannot be carried out except diad ethylene glycol–isophthalate (13** peak), as shown in Figure 12. This is because only the 13** peak can be separated independently from the surrounding peaks in the proton NMR spectra. The concentration of the diad ethylene glycol–isophthalate can be calculated by the initial POB-PET and PAr concentration and the diad probability following the method as described in the previous article.[7] In Figure 13, the new diad ethylene glycol–isophthalate increased sharply with annealing time in the first 15 min, and then increased moderately near 60 min annealing time. This behavior is in synchronization to that of the glass transition temperatures ($T_{g2}$) in the 60/40 POB-PET/PAr blend, as shown in Figure 4. Therefore, it indicated that upon heating the miscibility enhancement between POB-PET and polyarylate was probably due to the ester–ester interchange. In specific, the presence of small mol fraction (about 1%) of new diad can enhance the miscibility in POB-PET/PAr blend greatly by lowering the glass transition temperature of PAr by about 10°C.

The ester–ester interchange mechanism of producing diad ethylene glycol–isophthalate can be expressed in the following.

$$-(A_2 - A_3)- + -(B_1 - B_{22})- \underset{k'}{\overset{k}{\rightleftharpoons}}$$
$$a - x \qquad\qquad b - x$$
$$-(A_2 - B_1)- + -(A_3 - B_{22})-$$
$$\text{x} \qquad\qquad \text{x}$$

where $a$ and $b$ are the initial mol fraction of PET segment in POB-PET and the initial mol fraction of the portion of bisphenol A isophthalate in polyarylate, respectively. The mol fraction of $A_2B_1$ and $A_3B_{22}$ is $x$. The codes used in the above mechanism are given in Figure 9.

Assuming a second-order reversible reaction as Murano and Yamadera[13] did, we can write

$$\frac{dx}{dt} = k(a - x)(b - x) - k'x^2 \qquad (1)$$

Because the copolyester is random at equilibrium, we have $x_e = ab$, and $a + b = 1$. Therefore, we can get

$$k = k' \qquad (2)$$

Putting eq. (2) into eq. (1), we obtained

$$\frac{dx}{dt} = k(ab - x) \qquad (3)$$

Integrating eq. (3), we can get a simple kinetic expression,

$$\frac{1}{(b - a)} \ln\left\{\frac{a(b - x)}{b(a - x)}\right\} = kt \qquad (4)$$

In Figure 14, eq. (4) was plotted, and the slopes of those lines are the rate constants at different temperatures. We can fit the reaction constants into the Arrhenius expression

$$\ln k = \ln A - E_a/RT \qquad (5)$$

where $R$ is the gas constant ($R = 1.987$ cal/(mol K)), $E_a$ is the activation energy, $A$ is the preexponential factor, and $T$ is the absolute temperature. We plotted eq. (5) in Figure 15, and obtained the activation energy of 26.5 kcal/mol. The preexponential factor for this ester–ester interchange is $3.7 \times 10^8$ min$^{-1}$.

The intrinsic viscosity of the 60/40 POB-PET/PAr blend decreased sharply with the annealing time initially, as illustrated in Figure 16. The

**Figure 11.** The 600 MHz $^1$H-$^{13}$C NMR spectra of the second aromatic region of 60/ 40 POB-PET/PAr (a) freshly prepared, (b) annealed for 15 min, (c) annealed for 60 min at 290°C, new crosspeaks marked by III, IV, and V.
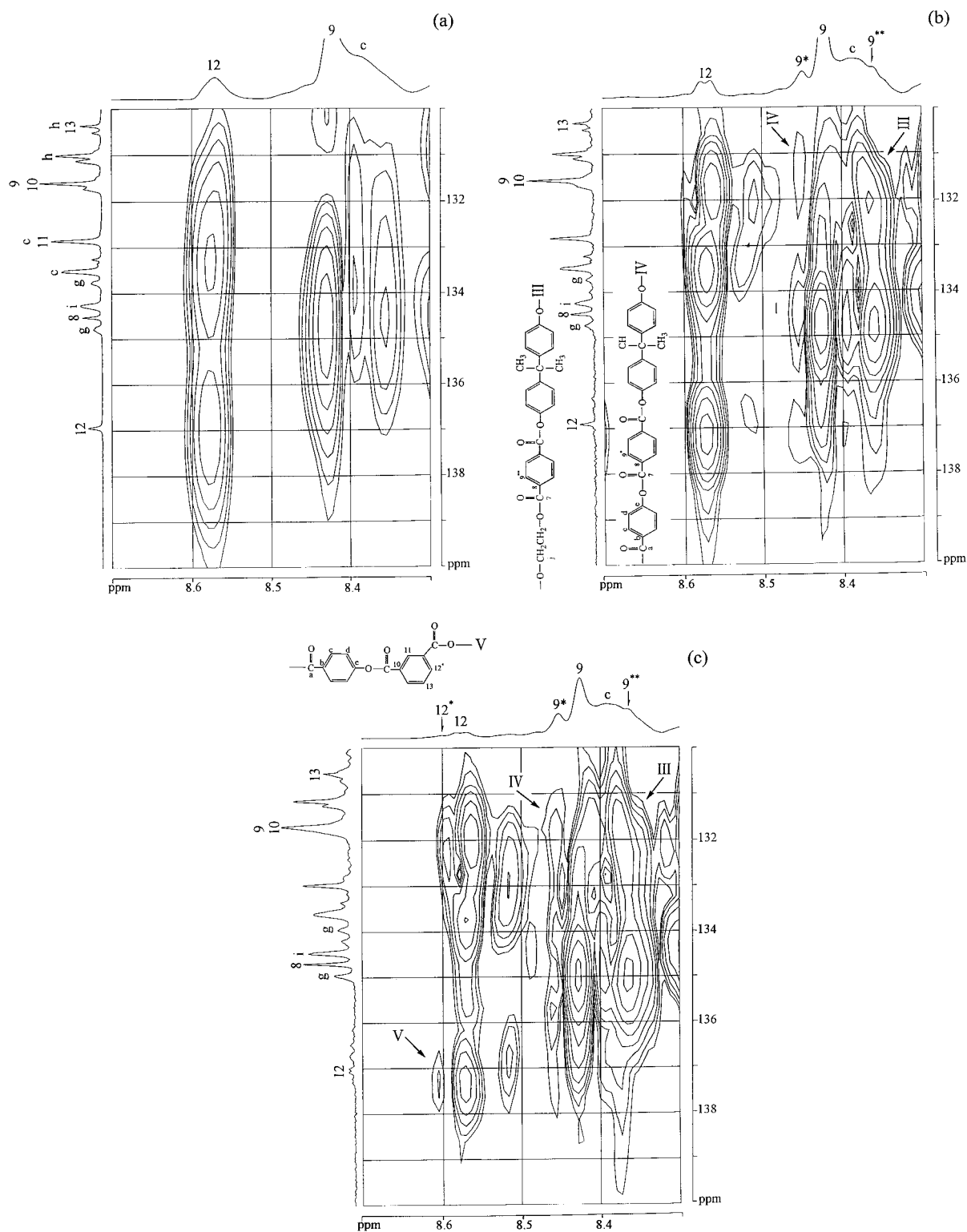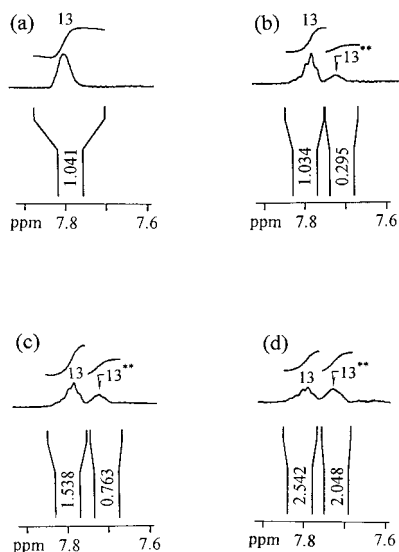
**Figure 12.** The partial proton NMR spectra of 60/40 POB-PET/PAr (a) freshly prepared, (b) annealed for 15 min, (c) annealed for 30 min, (d) annealed for 60 min at 290°C.



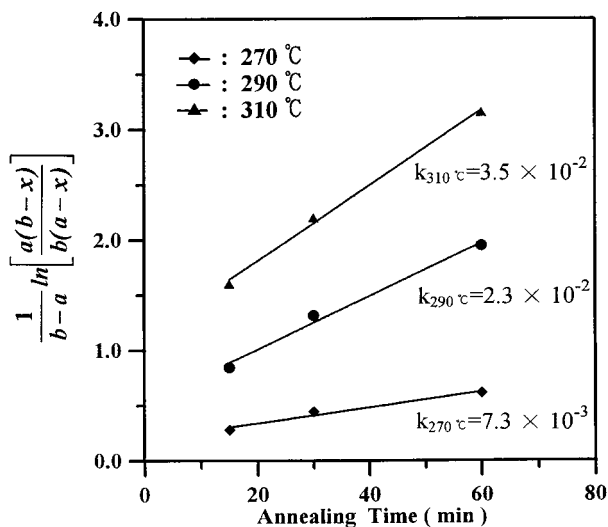**Figure 14.** The kinetics of forming diad ethylene glycol-isophthalate during transesterification in 60/40 POB-PET/PAr blend.

decrease in the intrinsic viscosity of the POB-PET/PAr blend during the annealing was caused, in fact, by simultaneous chain degradation and transesterification. The unavoidable decarboxylation of the unstable oxyethylene–carbonate diad (give off $CO_2$) must have hap-

pened. The decrease in intrinsic viscosity can also be caused by the change in the molecular weight distribution. A complete transesterification would reduce the distribution of the molecular chain length to Flory's most probable distribution ($M_w/M_n = 2$). Hence, the crucial reduction in the intrinsic viscosity of the annealed blend most likely came from decarboxylation and transesterification.
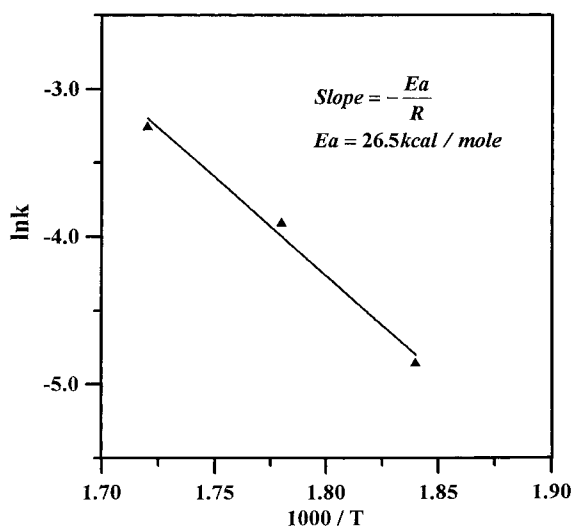
**ethylene glycol-isophthalate**



**Figure 13.** The evolution of the mol fraction of the diad ethylene glycol-isophthalate upon annealing 60/40 POB-PET/PAr blend at different temperature.



**Figure 15.** The activation energy obtained from the Arrhenius expression in forming diad ethylene glycol-isophthalate during transesterification in 60/40 POB-PET/PAr blend.
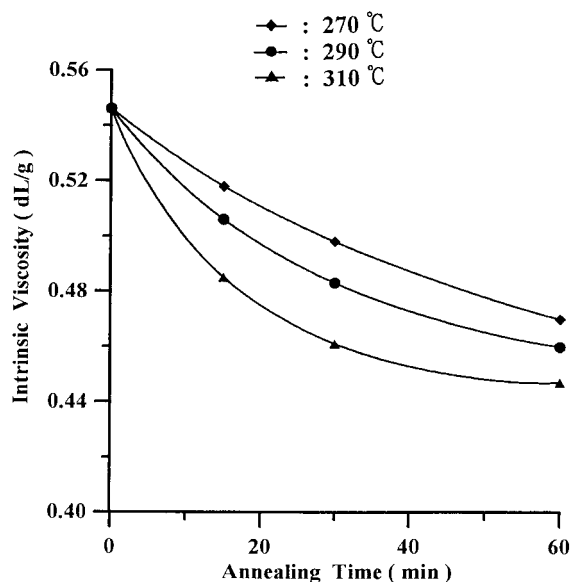
**Figure 16.** The change in the intrinsic viscosity of the 60/40 POB-PET/PAr blend with the annealing time at different temperature.

## CONCLUSIONS

The ester–ester interchange in POB-PET and polyarylate is a very fast process at high temperature even in vacuum. When the 60/40 POB-PET/polyarylate blend was annealed at 290°C for 15 min, there were four new hybrid structures (diads) produced as a result of transesterification. They are bisphenol-A–oxybenzoate, ethylene glycol–isophthalate, ethylene glycol–terephthalate and oxybenzoate–terephthalate. In an hour, an additional new diad, oxybenzoate–isophthalate, was produced.

The evolution of the concentration of the diad ethylene glycol–isophthalate during the anneal-

ing can be described by a second-order reaction. The activation energy of forming dyad ethylene glycol–isophthalate was found to be 23.4 kcal/mol, and the preexponential factor is $3.7 \times 10^{-8}$ min$^{-1}$.

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