

Ester–Amide Exchange in Blends of Liquid-Crystalline Copolyester and Polyamide 6

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ABSTRACT: The kinetics of the ester–amide exchange in solution blends of the random liquid-crystalline polyester copoly(oxybenzoate-terephthalate) (P64) and polyamide 6 (PA6) were studied with carbon nuclear magnetic resonance. With second-order reversible reactions assumed, the activation energy of the ester–amide interchange in 30/70, 50/50, and 70/30 P64/PA6 blends were all about 24.0 kcal/mol. The pre-exponential factors for the ester–amide exchange in 30/70, 50/50, and 70/30 P64/PA6 blends were 2.01×10^{11} , 2.59×10^{10} , and $2.74 \times 10^{12} \text{ min}^{-1}$, respectively. © 2000 John Wiley & Sons, Inc. *J Polym Sci B: Polym Phys* 38: 2124–2135, 2000

Keywords: copolyester; polyamide 6; exchange; activation energy; kinetics

INTRODUCTION

Thermotropic liquid-crystalline polymers (TLCPs) usually exhibit low melt viscosity and high modulus in the oriented direction in the solid form. Blending TLCPs with engineering plastics can lower the melt viscosity of the blend and form organic polymer composites *in situ*.^{1–4} However, the enthalpy of mixing TLCPs with a flexible-coil polymer is mostly positive. The entropy is usually small in the mixing of these two polymers. Therefore, the free energy of mixing is mostly positive. In other words, most TLCPs blends are immiscible or become phase-separated systems. However, it is well known that high molecular weight polyesters can have midchain ester–ester exchange with themselves or other polymers at high temperatures. Several studies report that the miscibility of polyester blends increases with the extent of interchange reactions.^{5,6} In particular, the midchain ester–ester interchange^{7–9} in blends of thermotropic copoly(oxybenzoate-ethylene tere-

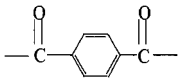
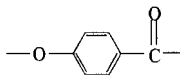
phthalate) (POB–PET) and polycarbonate has resulted in a partially miscible system, as evidenced from a single glass-transition temperature in differential scanning calorimetry measurement.¹⁰

At high temperatures, amide–amide and ester–amide interchanges also have occurred in polyamide/polyamide blends^{11–15} and polyester/polyamide blends, respectively.^{16,17} The physical properties of these blends were greatly affected by the interchange reactions. However, very little has been reported on the kinetics of the ester–amide interchange reactions in polyester/polyamide blends, which often take place in industrial processes.^{16,17} We are, therefore, motivated to study the kinetics of the ester–amide interchange reactions in POB–PET/polyamide 6 (PA6). The kinetics of the interchange reaction in four-component copolycondensates^{18–21} and in five-component copolycondensates^{9,10} have been investigated with high-resolution nuclear magnetic resonance (NMR). In this work, the kinetics of the ester–amide interchange reaction in blends of POB–PET and PA6 were determined from two-dimensional (2D) NMR heteronuclear multiple-bond correlation (HMBC) spectra and quantitative ¹³C NMR analyses.

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Table I. The Codes Used in the Dyads of the P64/PA6 Blend

| | | | |
|---------|---|---|---|
| POB-PET | $\text{—OCH}_2\text{CH}_2\text{O—}$ |  |  |
| | A ₁ | B ₁ | (AB) ₁ |
| PA6 | $\begin{array}{c} \text{H} \\ \\ \text{— N —} \\ \\ \text{—CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{—} \end{array} \begin{array}{c} \text{O} \\ \\ \text{C —} \end{array}$ | | |
| | (AB) ₂ | | |

EXPERIMENTAL

Liquid-crystalline POB-PET at a molar ratio of 60/40 was obtained from Unitika Ltd., Japan, and was termed P64. PA6 (Zytel) was purchased from DuPont. The intrinsic viscosity value of PA6 was 1.33 dL/g at 25 °C, obtained from a dilute solution of PA6 (0.5 dL/g) in *m*-cresol.²² This indicated that the concentration of the terminal groups for PA6 was about 0.6%. The solution blending of P64 and PA6 was carried out by both polymers being dissolved in 100 mL of a mixed solvent of phenol and tetrachloroethane (50/50 by weight). The concentration of the solution containing P64 and PA6 was 2% by weight. The weight ratios of P64 to PA6 in the solution were 30/70, 50/50, and 70/30. The solution was stirred and maintained at 60 °C. After the polymers were dissolved and became a one-phase solution for 60 min, the solutions were precipitated in a 10-fold excess volume of methanol. The precipitated blends were washed five times, each time with 500 mL of methanol. The blends were then dried in a vacuum oven at 100 °C for 5 days. The thermal gravimetric analysis of the dried blends showed no appreciable weight loss up to 350 °C, indicating a complete removal of the solvent. The blends were annealed at 260, 270, and 280 °C in a high-temperature oven for different times under a purge of nitrogen at 100 cm³/min.

A model compound study performed by the reaction of 20/80 terephthalate acid (TPA)/6-aminocaproic acid (ACA) at 270 °C and 80/20 4-acetoxybenzoic acid (ABA)/ACA at 250 °C for 2 h was carried out. The products from the reacted TPA/ACA and ABA/ACA were then dissolved in a mixed solvent of phenol and deuterated chloroform (80/20 by volume). 2D ¹H-¹³C HMBC NMR analyses were carried out with a Bruker DMX-600 spectrometer. Both the freshly prepared and

annealed blends of P64/PA6 (50/50) were partially dissolved in deuterated trifluoroacetic acid. A mixed solvent of phenol and deuterated chloroform (80/20 by volume) and tetramethylsilane as the standard were used in quantitative ¹³C NMR analyses. The concentration of the blend in the mixed solvent was about 5%. The intrinsic viscosity of the blends in a mixed solvent of phenol and tetrachloroethane, 50/50 by weight, was measured with an Ubbelohde viscometer at 30 °C.

RESULTS AND DISCUSSION

The chemical structures of P64 and PA6 were divided into four components. The notations A₁, A₂, and (AB)₁ represent the ethylene dioxide, terephthalate, and oxybenzoate in the monomeric unit in P64, respectively, and (AB)₂ represents the amide in the monomeric unit of PA6, as given in Table I. From the model compound study, the carbonyl regions of the ¹³C NMR spectra of ACA, ABA, and 20/80 TPA/ACA reacted at 270 °C and 80/20 ABA/ACA reacted at 250 °C are displayed in Figure 1. In Figure 1(a), the C_α peak at 177.9 ppm in the ¹³C NMR spectra of ACA represented the carbonyl group in ACA. The C_β peak at 171.5 ppm and the C_χ peak at 169.6 ppm resulted from the carbonyl group and acetoxy group in ABA, respectively, as shown in Figure 1(b). The new peaks C_{η*} at 168.8 ppm and C_δ at 175.7 ppm were caused by the dyad terephthalate-amide [B₁(AB)₂] and by the dyad amide-amide [(AB)₂(AB)₂], respectively, as indicated in Figure 1(c). In Figure 1(d), the new peak C_{η**}, caused by the dyad oxybenzoate-amide [(AB)₁(AB)₂] also appeared at 168.8 ppm, whereas the new peak C_ε, caused by the dyad [(AB)₁(AB)₁], was located at 165.2 ppm.

The chemical structure changes that resulted from the ester-amide exchange in the P64/PA6

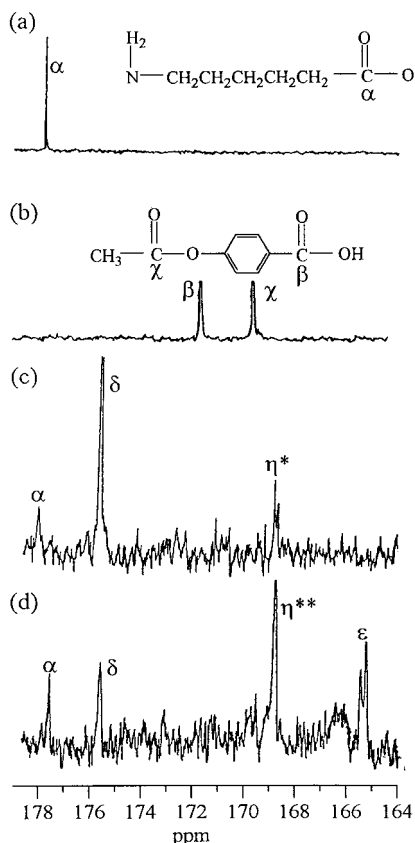


Figure 1. Carbonyl region of the ^{13}C NMR spectra of (a) ACA, (b) ABA, (c) 20/80 TPA/ACA reacted at 270 °C, and (d) 80/20 ABA/ACA reacted at 250 °C (for the model compound study).

blends could not be identified because the C_{η^*} and the $\text{C}_{\eta^{**}}$ peaks appeared at the same location, 168.8 ppm, in the one-dimensional (1D) NMR spectrum. Therefore, 2D ^1H - ^{13}C NMR analyses of the P64/PA6 blends were required. The 2D ^1H - ^{13}C NMR spectra of the freshly prepared 50/50 P64/PA6 blend are presented in Figure 2(a). Two new crosspeaks appear at 7.5–168.8 ppm (crosspeak I) and 3.3–168.8 ppm (crosspeak II) in the ^1H - ^{13}C HMBC NMR spectra of the 50/50 blend after the blend annealed at 270 °C for 60 min, as shown in Figure 2(b). In Figure 2(b), the new proton peak H_k , caused by the dyads $[\text{B}_1(\text{AB})_2]$ and $[(\text{AB})_1(\text{AB})_2]$, was overlapped at 7.5 ppm. Additionally, C_{η} was attached to H_k of the oxybenzoate or the terephthalate at crosspeak I, and C_{η} was also attached to the aromatic H_b of PA6 at crosspeak II, indicating C_{η} belonged to the carbonyl carbon of the amide group. By comparing the results of the 1D ^{13}C NMR analysis to those of the 2D ^1H - ^{13}C HMBC NMR analysis of the an-

nealed P64/PA6 blend, we concluded that the new peak C_{η} was actually caused by a superposition of the peaks from the dyads terephthalate–amide and oxybenzoate–amide. The assignments of the partial carbon peaks for the original and new dyads in the P64/PA6 blend were, therefore, determined and are given in Table II.

The partial ^{13}C NMR spectra of the 50/50 P64/PA6 blends annealed at 270 °C are displayed in Figure 3. In Figure 3, the intensity of the new peak C_{η} , representing the carbonyl group in the ^{13}C NMR spectra, increases with annealing time. Through the integration of the area under these ^{13}C peaks, the transient dyad molar fractions in the 30/70, 50/50, and 70/30 P64/PA6 blends annealed at 260, 270, and 280 °C are given in Table III. Before the exchange starts, we have B_1A_1 , $(\text{AB})_1\text{A}_1$, $\text{B}_1(\text{AB})_1$, $(\text{AB})_1(\text{AB})_1$, and $(\text{AB})_2(\text{AB})_2$. The initial dyad molar fractions of B_1A_1 , $(\text{AB})_1\text{A}_1$, $\text{B}_1(\text{AB})_1$, $(\text{AB})_1(\text{AB})_1$, and $(\text{AB})_2(\text{AB})_2$ are $F_{\text{B}_1\text{A}_1,0}$, $F_{(\text{AB})_1\text{A}_1,0}$, $F_{\text{B}_1(\text{AB})_1,0}$, $F_{(\text{AB})_1(\text{AB})_1,0}$, and $F_{(\text{AB})_2(\text{AB})_2,0}$, respectively, and they can be calculated from the initial molar fractions of P64 and PA6. In Table III(a–c), $F_{\text{B}_1\text{A}_1}$, $F_{(\text{AB})_1\text{A}_1}$, and $F_{(\text{AB})_1(\text{AB})_1}$ decrease with both increasing annealing time and temperature in different blends. Because the new peak C_{η} was due to an overlap of the peaks, $F_{\text{B}_1(\text{AB})_2}$ and $F_{(\text{AB})_1(\text{AB})_2}$ cannot be decoupled directly from their ^{13}C NMR spectra. We first obtained the integral under the new peak C_{η} . Then, $F_{\text{B}_1(\text{AB})_2}$ and $F_{(\text{AB})_1(\text{AB})_2}$ could be determined by the following formula:

$$F_{\text{B}_1(\text{AB})_2} = (F_{\text{B}_1(\text{AB})_2} + F_{(\text{AB})_1(\text{AB})_2}) \times \text{mole fraction of PET in P64}$$

$$F_{(\text{AB})_1(\text{AB})_2} = (F_{\text{B}_1(\text{AB})_2} + F_{(\text{AB})_1(\text{AB})_2}) \times \text{mole fraction of POB in P64}$$

The calculated values of $F_{\text{B}_1(\text{AB})_2}$ and $F_{(\text{AB})_1(\text{AB})_2}$ are given in Table III(a–c). In Table III, $F_{\text{B}_1(\text{AB})_2}$ and $F_{(\text{AB})_1(\text{AB})_2}$ in the 30/70, 50/50, and 70/30 P64/PA6 blends increase with annealing time and temperature. For the 50/50 P64/PA6 blend, the molar fractions of $F_{\text{B}_1(\text{AB})_2}$ become 0.022 after 30 min of annealing and 0.038 after 60 min of annealing at 270 °C. Furthermore, $F_{\text{B}_1(\text{AB})_2}$ in the 50/50 P64/PA6 blend is 0.024 after 30 min of annealing at 280 °C.

With these dyad concentrations available from the ^{13}C NMR spectra, we needed to build reaction

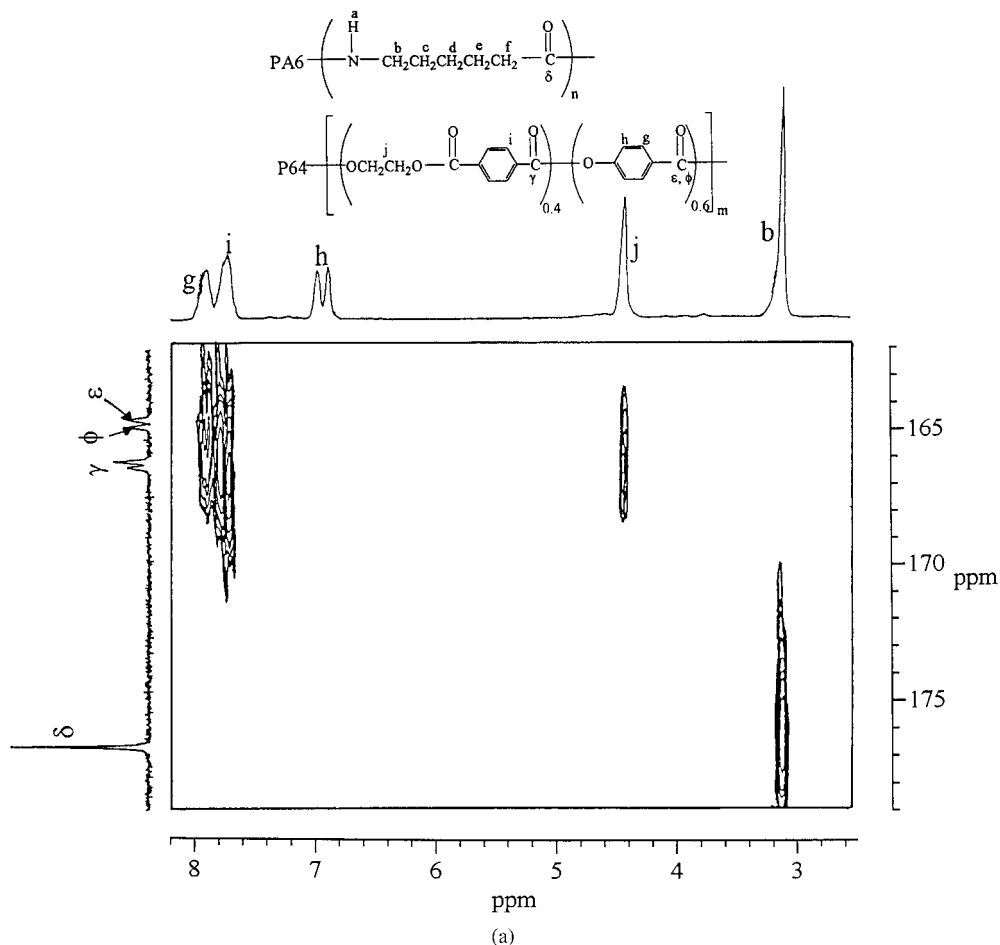
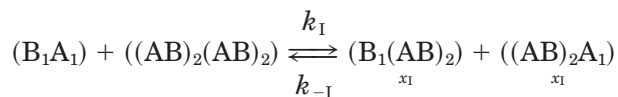


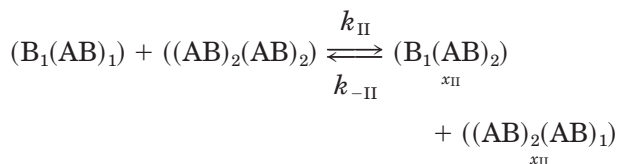
Figure 2. 2D ^1H - ^{13}C NMR spectra of (a) the freshly prepared 50/50 P64/PA6 blend and (b) the 50/50 P64/PA6 blend annealed at 270 °C for 60 min.

equations for obtaining the kinetics parameters. The possible ways for the ester-amide interchange in terms of dyads in P64/PA6 are given in the following reactions:

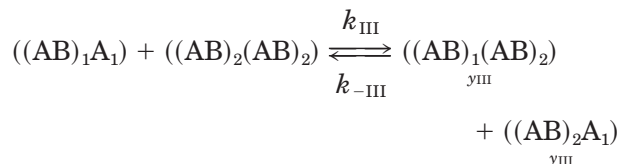
Reaction I



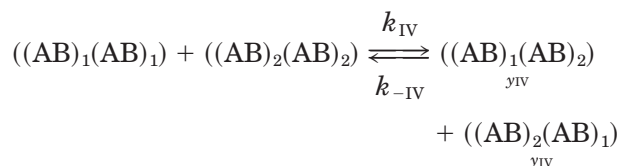
Reaction II



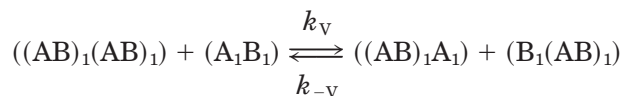
Reaction III



Reaction IV



Reaction V



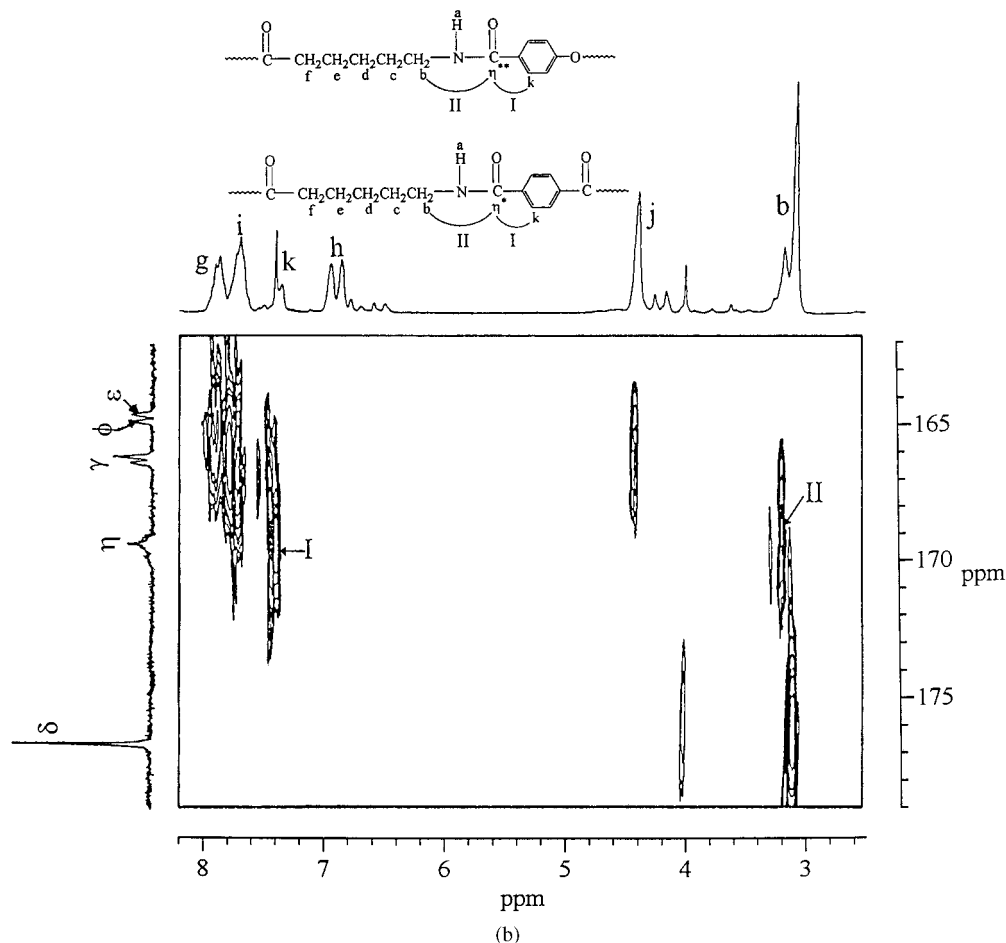


Figure 2. (Continued from the previous page)

where k_i and k_{-i} ($i = \text{I, II, III, IV, and V}$) stand for the forward and reverse reaction rate constants for each reaction, respectively. The concentrations of these new dyads are defined on the basis of their individual reactions in the following:

$$x_{\text{I}} = (F_{\text{B}_1(\text{AB})_2})_{\text{I}} = (F_{(\text{AB})_2\text{A}_1})_{\text{I}},$$

$$x_{\text{II}} = (F_{\text{B}_1(\text{AB})_2})_{\text{II}} = (F_{(\text{AB})_2(\text{AB})_1})_{\text{II}}$$

$$y_{\text{III}} = (F_{(\text{AB})_1(\text{AB})_2})_{\text{III}} = (F_{(\text{AB})_2\text{A}_1})_{\text{III}},$$

$$y_{\text{IV}} = (F_{(\text{AB})_1(\text{AB})_2})_{\text{IV}} = (F_{(\text{AB})_2(\text{AB})_1})_{\text{IV}}$$

$$x = F_{\text{B}_1(\text{AB})_2} = x_{\text{I}} + x_{\text{II}}$$

$$y = F_{(\text{AB})_1(\text{AB})_2} = y_{\text{III}} + y_{\text{IV}}$$

where the subscripts I, II, III, and IV indicate the resulting reaction. P64 is a random co-

polyester identified from its ^{13}C NMR and ^1H NMR spectra in previous studies.²³⁻²⁵ Reaction V is in equilibrium during the synthesis of random P64. Hence, reaction V is not considered here.

Second-order reversible reactions were assumed for all cases in this study.²⁶ The dyad terephthalate-amide $[\text{B}_1(\text{AB})_2]$ is produced in reactions I and II. We assumed that x and y are decoupled during the reactions. Then, we obtained eqs 1 and 2 from reactions I and II in the following forms, respectively:

Reaction I

$$\frac{dx_{\text{I}}}{dt} = k_{\text{I}}(F_{(\text{AB})_2(\text{AB})_2,0} - (x + y))(F_{\text{B}_1\text{A}_1,0} - x_{\text{I}}) - k_{-\text{I}}(x_{\text{I}} + x_{\text{II}})(x_{\text{I}} + y_{\text{III}}) \quad (1)$$

Table II. Assignment of the Partial Carbon Peaks in the P64/PA6 Blend

| Peak | Dyad | Structure | Chemical Shift |
|---------------|----------------|-----------|----------------|
| δ | $(AB)_2(AB)_2$ | | 175.8 ppm |
| ε | $(AB)_1(AB)_1$ | | 164.9 ppm |
| ϕ | $(AB)_1A_1$ | | 165.1 ppm |
| | B_1A_1 | | |
| γ | $B_1(AB)_1$ | | 166.8 ppm |
| | $B_1(AB)_2$ | | |
| η | $(AB)_1(AB)_2$ | | 168.8 ppm |

Reaction II

$$\frac{dx_{II}}{dt} = k_{II}(F_{(AB)2(AB)2,0} - (x + y))(F_{(AB)1B1,0} - x_{II}) - k_{-II}(x_I + x_{II})(x_{II} + y_{IV}) \quad (2)$$

By adding eq 1 to eq 2, we obtained eq 3:

$$\begin{aligned} \frac{dx}{dt} &= \frac{dx_I}{dt} + \frac{dx_{II}}{dt} \\ &= k_I(F_{(AB)2(AB)2,0} - (x + y))(F_{B1A1,0} - x_I) \\ &\quad - k_{-I}(x_I + x_{II})(x_I + y_{III}) + k_{II}(F_{(AB)2(AB)2,0} \\ &\quad - (x + y))(F_{(AB)1B1,0} - x_{II}) \\ &\quad - k_{-II}(x_I + x_{II})(x_{II} + y_{IV}) \quad (3) \end{aligned}$$

The dyad oxybenzoate-amide $[(AB)_1(AB)_2]$ is produced in reactions III and IV:

Reaction III

$$\frac{dy_{III}}{dt} = k_{III}(F_{(AB)2(AB)2,0} - (x + y))(F_{A1(AB)1,0} - y_{III}) - k_{-III}(y_{III} + y_{IV})(y_{III} + x_I) \quad (4)$$

Reaction IV

$$\frac{dy_{IV}}{dt} = k_{IV}(F_{(AB)2(AB)2,0} - (x + y))(F_{(AB)1(AB)1,0} - y_{IV}) - k_{-IV}(y_{IV} + y_{III})(y_{IV} + x_{II}) \quad (5)$$

By adding eq 4 to eq 5, we obtained eq 6.

$$\begin{aligned} \frac{dy}{dt} &= \frac{dy_{III}}{dt} + \frac{dy_{IV}}{dt} \\ &= k_{III}(F_{(AB)2(AB)2,0} - (x + y))(F_{A1(AB)1,0} - y_{III}) \\ &\quad - k_{-III}(y_{III} + y_{IV})(y_{III} + x_I) \\ &\quad + k_{IV}(F_{(AB)2(AB)2,0} - (x + y))(F_{(AB)1(AB)1,0} \\ &\quad - y_{IV}) - k_{-IV}(y_{IV} + y_{III})(y_{IV} + x_{II}) \quad (6) \end{aligned}$$

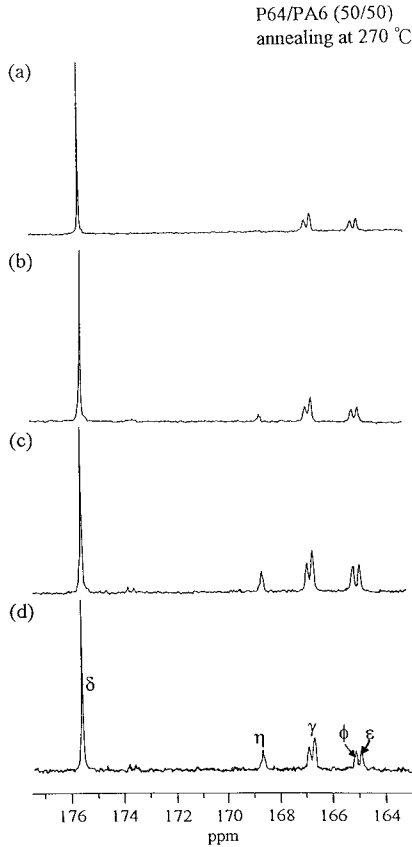


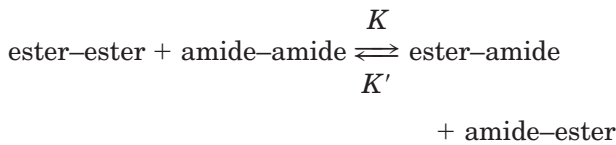
Figure 3. Partial ^{13}C NMR spectra of the 50/50 P64/PA6 blends annealed at 270 °C for (a) 0 min, (b) 15 min, (c) 30 min, and (d) 60 min.

$F_{\text{B1(AB)2}}$ and $F_{\text{(AB)1(AB)2}}$ increase with annealing temperature and annealing time at about the same rate given in Table III. If the rate constants k_i and k_{-i} ($i = \text{I, II, III, IV, and V}$) have the same order of magnitude,

$$k_{\text{I}} \cong k_{\text{II}} \cong k_{\text{III}} \cong k_{\text{IV}} \cong K$$

$$\text{and } k_{-\text{I}} \cong k_{-\text{II}} \cong k_{-\text{III}} \cong k_{-\text{IV}} \cong K' \quad (7)$$

Therefore, the ester–amide exchange of P64 (ester group) and PA6 (amide group) was lump-summed in the following:



Z is defined as

$$Z = x + y = x_{\text{I}} + x_{\text{II}} + y_{\text{III}} + y_{\text{IV}} = F_{\text{B1(AB)2}} + F_{\text{(AB)1(AB)2}} \quad (8)$$

By combining eqs 3 and 6, we obtained eq 9 in the following form:

$$\frac{dZ}{dt} = \frac{d(x + y)}{dt}$$

$$= k_{\text{I}}(F_{\text{(AB)2(AB)2,0}} - (x + y))(F_{\text{B1A1,0}} - x_{\text{I}}) - k_{-\text{I}}(x_{\text{I}} + x_{\text{II}})(x_{\text{I}} + y_{\text{III}}) + k_{\text{II}}(F_{\text{(AB)2(AB)2,0}} - (x + y))(F_{\text{(AB)1B1,0}} - x_{\text{II}}) - k_{-\text{II}}(x_{\text{I}} + x_{\text{II}}) \times (x_{\text{II}} + y_{\text{VI}}) + k_{\text{III}}(F_{\text{(AB)2(AB)2,0}} - (x + y)) \times (F_{\text{A1(AB)1,0}} - y_{\text{III}}) - k_{-\text{III}}(y_{\text{III}} + y_{\text{IV}})(y_{\text{III}} + x_{\text{I}}) + k_{\text{IV}}(F_{\text{(AB)2(AB)2,0}} - (x + y))(F_{\text{(AB)1(AB)1,0}} - y_{\text{IV}}) - k_{-\text{IV}}(y_{\text{IV}} + y_{\text{III}})(y_{\text{IV}} + x_{\text{II}})$$

$$= (F_{\text{(AB)2(AB)2,0}} - (x + y)) \times \left(k_{\text{I}}(F_{\text{B1A1,0}} - x_{\text{I}}) + k_{\text{II}}(F_{\text{(AB)1B1,0}} - x_{\text{II}}) + k_{\text{III}}(F_{\text{A1(AB)1,0}} - y_{\text{III}}) + k_{\text{IV}}(F_{\text{(AB)1(AB)1,0}} - y_{\text{IV}}) \right) - \left(k_{-\text{I}}(x_{\text{I}} + x_{\text{II}})(x_{\text{I}} + y_{\text{III}}) + k_{-\text{II}}(x_{\text{I}} + x_{\text{II}})(x_{\text{II}} + y_{\text{IV}}) + k_{-\text{III}}(y_{\text{III}} + y_{\text{IV}})(y_{\text{III}} + x_{\text{I}}) + k_{-\text{IV}}(y_{\text{IV}} + y_{\text{III}})(y_{\text{IV}} + x_{\text{II}}) \right)$$

$$= (F_{\text{(AB)2(AB)2,0}} - Z) \times \left(K(F_{\text{B1A1,0}} + F_{\text{(AB)1B1,0}} + F_{\text{A1(AB)1,0}} + F_{\text{(AB)1(AB)1,0}}) - K(x_{\text{I}} + x_{\text{II}} + y_{\text{III}} + y_{\text{IV}}) \right) - K'(x(x + y) + y(x + y))$$

$$= K(F_{\text{P64,0}} - Z)(F_{\text{PA6,0}} - Z) - K'Z^2 \quad (9)$$

where $F_{\text{P64,0}}$ and $F_{\text{PA6,0}}$ are the initial molar fraction of P64 and PA6, respectively, and they are given in terms of the dyads molar fractions:

$$F_{\text{P64,0}} = F_{\text{B1A1,0}} + F_{\text{(AB)1B1,0}} + F_{\text{A1(AB)1,0}} + F_{\text{(AB)1(AB)1,0}}$$

$$F_{\text{PA6,0}} = F_{\text{(AB)2(AB)2,0}}$$

Table III. The Transient Dyad Mol for Fractions of Various Dyads Obtained from Quantitative ^{13}C NMR Analyses

| Annealing Temperature | Annealing Time | $F_{(\text{AB})2(\text{AB})2}$ | $F_{\text{B1}(\text{AB})2}$ | $F_{(\text{AB})1(\text{AB})2}$ | F_{B1A1} | $F_{(\text{AB})1\text{A1}}$ | $F_{(\text{AB})1(\text{AB})1}$ |
|---|----------------|--------------------------------|-----------------------------|--------------------------------|-------------------|-----------------------------|--------------------------------|
| (a) 30/70 P64/PA 6 Blends Annealing at 260, 270, and 280 °C | | | | | | | |
| ^a 260 °C | 0 min | 0.754 | 0 | 0 | 0.022 | 0.076 | 0.072 |
| | 150 min | 0.744 | 0.004 | 0.006 | 0.021 | 0.073 | 0.069 |
| | 30 min | 0.732 | 0.009 | 0.013 | 0.020 | 0.069 | 0.065 |
| 270 °C | 60 min | 0.704 | 0.020 | 0.030 | 0.019 | 0.060 | 0.057 |
| | 15 min | 0.733 | 0.008 | 0.013 | 0.021 | 0.069 | 0.066 |
| | 30 min | 0.703 | 0.020 | 0.031 | 0.018 | 0.060 | 0.057 |
| 280 °C ^a | 60 min | 0.673 | 0.032 | 0.049 | 0.015 | 0.051 | 0.048 |
| | 10 min | 0.724 | 0.012 | 0.018 | 0.019 | 0.067 | 0.063 |
| | 20 min | 0.699 | 0.022 | 0.033 | 0.017 | 0.059 | 0.056 |
| 30 min | 0.675 | 0.032 | 0.047 | 0.014 | 0.052 | 0.049 | |
| Annealing Temperature | Annealing Time | $F_{(\text{AB})2(\text{AB})2}$ | $F_{\text{B1}(\text{AB})2}$ | $F_{(\text{AB})1(\text{AB})2}$ | F_{B1A1} | $F_{(\text{AB})1\text{A1}}$ | $F_{(\text{AB})1(\text{AB})1}$ |
| (b) 50/50 P64/PA6 Blends Annealing at 260, 270, and 280 °C | | | | | | | |
| ^a 260 °C | 0 min | 0.558 | 0 | 0 | 0.039 | 0.137 | 0.129 |
| | 15 min | 0.544 | 0.010 | 0.014 | 0.037 | 0.126 | 0.119 |
| | 30 min | 0.524 | 0.018 | 0.026 | 0.035 | 0.120 | 0.113 |
| 270 °C | 60 min | 0.495 | 0.029 | 0.044 | 0.032 | 0.111 | 0.105 |
| | 15 min | 0.537 | 0.012 | 0.019 | 0.036 | 0.124 | 0.117 |
| | 30 min | 0.512 | 0.022 | 0.034 | 0.034 | 0.116 | 0.110 |
| 280 °C ^a | 60 min | 0.472 | 0.038 | 0.058 | 0.030 | 0.104 | 0.098 |
| | 10 min | 0.528 | 0.016 | 0.024 | 0.035 | 0.118 | 0.011 |
| | 20 min | 0.508 | 0.024 | 0.036 | 0.034 | 0.115 | 0.108 |
| 30 min | 0.485 | 0.033 | 0.050 | 0.031 | 0.108 | 0.102 | |
| Annealing Temperature | Annealing Time | $F_{(\text{AB})2(\text{AB})2}$ | $F_{\text{B1}(\text{AB})2}$ | $F_{(\text{AB})1(\text{AB})2}$ | F_{B1A1} | $F_{(\text{AB})1\text{A1}}$ | $F_{(\text{AB})1(\text{AB})1}$ |
| (c) 70/30 P64/PA6 Blends Annealing at 260, 270, and 280 °C | | | | | | | |
| ^a 260 °C | 0 min | 0.361 | 0 | 0 | 0.057 | 0.198 | 0.186 |
| | 15 min | 0.331 | 0.012 | 0.018 | 0.055 | 0.188 | 0.178 |
| | 30 min | 0.311 | 0.020 | 0.030 | 0.053 | 0.182 | 0.172 |
| 270 °C | 60 min | 0.271 | 0.036 | 0.054 | 0.051 | 0.169 | 0.160 |
| | 15 min | 0.314 | 0.019 | 0.028 | 0.053 | 0.183 | 0.173 |
| | 30 min | 0.276 | 0.034 | 0.051 | 0.050 | 0.171 | 0.162 |
| 280 °C ^a | 60 min | 0.225 | 0.054 | 0.082 | 0.046 | 0.155 | 0.147 |
| | 10 min | 0.030 | 0.024 | 0.037 | 0.053 | 0.178 | 0.169 |
| | 20 min | 0.262 | 0.039 | 0.060 | 0.049 | 0.167 | 0.157 |
| 30 min | 0.231 | 0.052 | 0.078 | 0.047 | 0.157 | 0.148 | |

^a Because of high-temperature, long-time degradation, the experiment was performed up to only 30 min.

Because the reaction is equilibrium, Z_e is at its optimal value, which equals $F_{\text{P64},0}F_{\text{PA6},0}$. $Z_e = F_{\text{P64},0}F_{\text{PA6},0}$ and $F_{\text{P64},0}F_{\text{PA6}} + F_{\text{PA6},0} = 1$ were put into eq 9, and the following equation was obtained:

$$\frac{dZ_e}{dt} = K(F_{\text{P64},0} - Z_e)(F_{\text{PA6},0} - Z_e) - K'Z_e^2 = 0$$

$$K(F_{\text{P64},0}F_{\text{PA6},0} - Z_e(F_{\text{P64},0} + F_{\text{PA6},0}) + Z_e^2) = K'Z_e^2$$

$$K(Z_e - Z_e + Z_e^2) = K'Z_e^2$$

$$K = K' \quad (10)$$

By putting eq 10 into eq 9, we obtained eq 11:

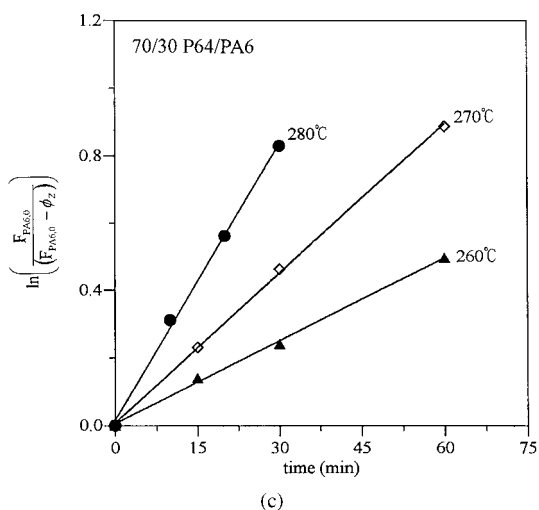
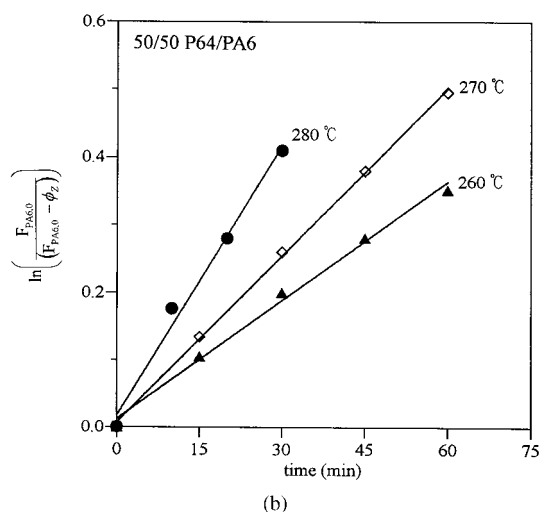
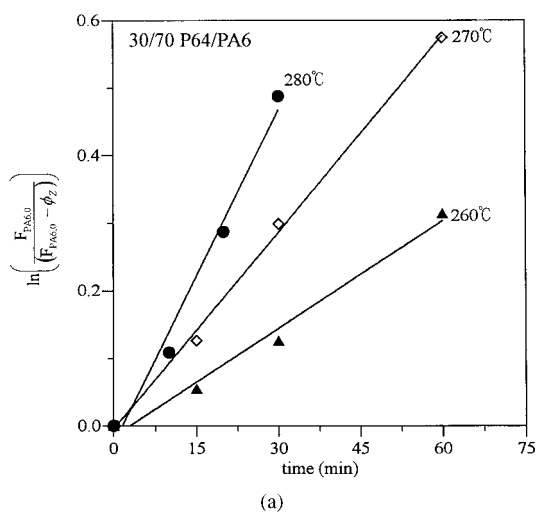


Figure 4. Plots of the kinetics expression of the ester–amide exchange in different weight ratios of P64 to PA6: (a) 30/70, (b) 50/50, and (c) 70/30.

Table IV. Rate Constants of Ester–Amide Exchange in P64/PA6 Blends Annealed at Different Temperatures

| P64/PA6 | Annealing Temperature (°C) | $K \times 10^3$ (min ⁻¹) |
|---------|----------------------------|--------------------------------------|
| 30/70 | 260 | 5.30 |
| | 270 | 9.66 |
| | 280 | 16.41 |
| 50/50 | 260 | 4.80 |
| | 270 | 8.23 |
| | 280 | 13.84 |
| 70/30 | 260 | 8.15 |
| | 270 | 14.70 |
| | 280 | 27.32 |

$$\frac{dZ}{dt} = K(F_{P64,0}F_{PA6,0} - Z) \quad (11)$$

By integrating eq 11 and using the amide–ester exchange reaction ratio, $\phi_z = Z/F_{P64,0}$, for these reactions, we can obtain a simple kinetics expression:

$$\ln\left(\frac{F_{PA6,0}}{F_{PA6,0} - \phi_z}\right) = Kt \quad (12)$$

By plotting $\ln[F_{PA6,0}/(F_{PA6,0} - \phi_z)]$ against time, we can obtain the rate constant K from the slopes of these lines, as shown in Figure 4. The rate constant K for the ester–amide exchange in P64/PA6 blends at different temperatures and different compositions is given in Table IV. We can fit the rate constants into the Arrhenius expression:

$$\ln K = \ln A - \frac{E_a}{RT} \quad (13)$$

where A is the pre-exponential factor, E_a is the activation energy, R is the gas constant [$R = 1.987$ cal/(mol K)], and T is the absolute temperature. In Figure 5, the slopes of these lines were $-E_a/R$, and the activation energy obtained was about 24.0 kcal/mol for P64/PA6 blends of different compositions. This activation energy for the ester–amide exchange reaction in P64/PA6 is smaller than that for the ester–ester exchange in the formation of the dyad bisphenol A–oxybenzoate (94.6 kcal/mol) and the dyad bisphenol A–terephthalate (41.8 kcal/mol).¹⁰ The pre-exponential factors in the ester–amide exchange in

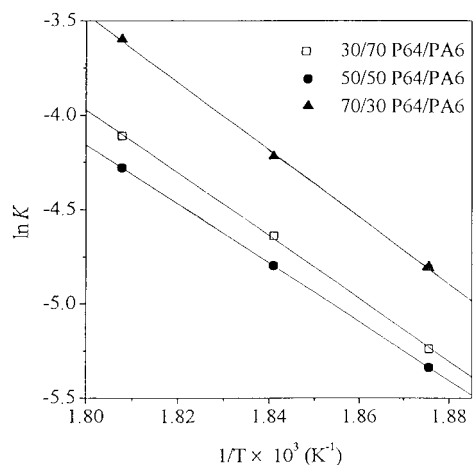


Figure 5. Rate constants of the ester–amide exchange in 30/70, 50/50, and 70/30 P64/PA6 blends at different temperatures.

P64/PA6 blends were determined from the intercepts. In Table V, the pre-exponential factors were 2.01×10^{11} , 2.59×10^{10} , and 2.74×10^{12} min^{-1} for the 30/70, 50/50, and 70/30 P64/PA6 blends, respectively. From the hard-sphere collision theory,²⁷ the pre-exponential factor, A , can be written as the following:

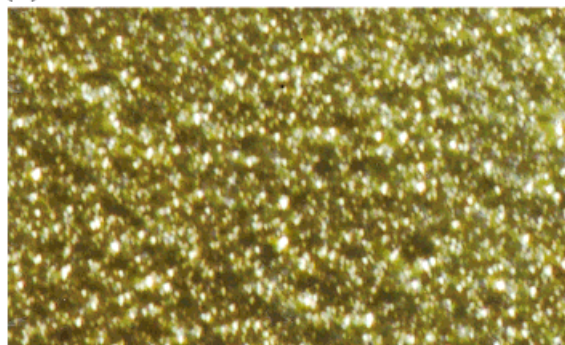
$$A = \frac{B_{\text{P64PA6}}}{N_{\text{A}}[\text{P64}][\text{PA6}]} e^{1/2} \quad (14)$$

where [P64] and [PA6] indicate the concentrations of P64 and PA6, respectively. $B_{\text{P64 PA6}}$ is the total number of P64/PA6 collisions per unit time per unit volume. N_{A} is Avogadro's number. From eq 14, the pre-exponential factor A is proportional to $B_{\text{P64 PA6}}$. The ester–amide exchange takes place in the interfaces between P64 and PA6 domains. As binary blends become more miscible, the domain size in the blends is decreasing, and the total surface area of all domains on a per weight basis will be increasing. In other words, the number of exchange collisions is increasing in

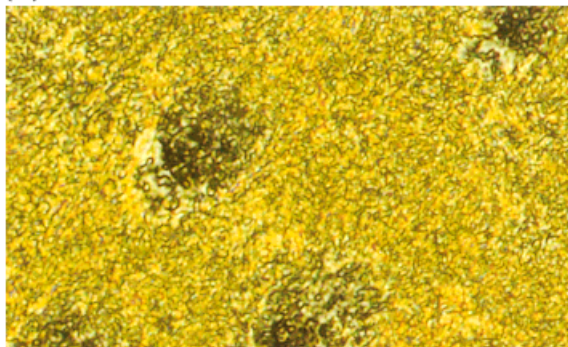
Table V. The Pre-Exponential Factor of the P64/PA6 Blends

| P64/PA6 | Pre-Exponential Factor (A) (min^{-1}) |
|---------|---|
| 30/70 | 2.01×10^{11} |
| 50/50 | 2.59×10^{10} |
| 70/30 | 2.74×10^{12} |

25 μm
(a) 30/70 P64/PA6



(b) 50/50 P64/PA6



(c) 70/30 P64/PA6



Figure 6. Polarized micrographs of (a) 30/70, (b) 50/50, and (c) 70/30 P64/PA6 blends annealed at 270 °C for 5 min.

more miscible blends. Hence, the pre-exponential factor for the ester–amide exchange in P64/PA6 blends can be explained by the miscibility of the

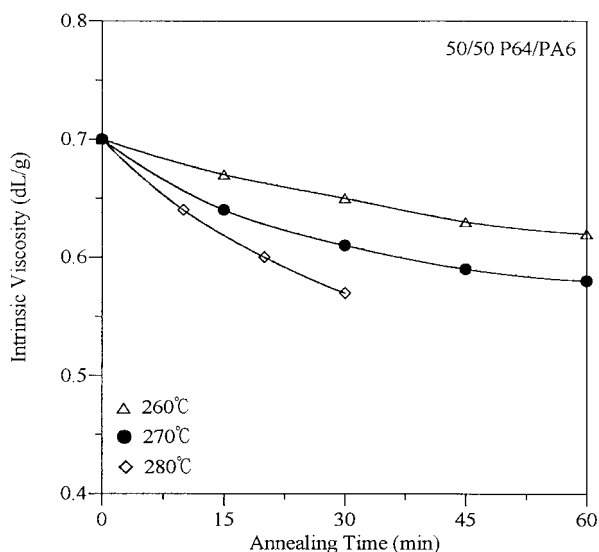


Figure 7. Intrinsic viscosity of the 50/50 P64/PA6 blend annealed at different times and different temperatures.

blend in the melt state. A simple observation on the morphologies of P64/PA6 blends in the melt state can be obtained from polarized micrographs of P64/PA6 blends annealed at 270 °C for 5 min, as shown in Figure 6. For the 30/70 P64/PA6 blend, the amorphous phase of PA6 and the small liquid-crystalline domains of P64 coexisted, as shown in Figure 6(a). For the 50/50 P64/PA6 blend, a partial phase separation was observed, as shown in Figure 6(b). As the amount of P64 increased to 70%, a more homogeneous phases appeared, indicating miscibility in blends of P64 and PA6. Therefore, the 50/50 P64/PA6 blend has the lowest pre-exponential factor.

The effect of the ester–amide exchange on the molecular weights of P64 and PA6 can be determined from their intrinsic viscosity. The intrinsic viscosity of the 50/50 P64/PA6 blend decreased with annealing time and temperature, as presented in Figure 7. The reduction of the intrinsic viscosity of the annealed blend was caused by both the ester–amide exchange and chain degradation. The ester–amide exchange caused P64 to lose its rigid-rod nature and, therefore, reduced its intrinsic viscosity. Additionally, acidolysis, aminolysis, and amidolysis in PA6 and partial hydrolysis of P64 led to chain degradation.

CONCLUSION

The kinetics of the ester–amide exchange in the solution blends of random liquid-crystalline polyester P64 and PA6 were studied with ^{13}C NMR. With second-order reversible reactions assumed, the activation energies of the ester–amide interchanges in the 30/70, 50/50, and 70/30 P64/PA6 blends were all about 24.0 kcal/mol. The pre-exponential factors for the ester–amide exchange in the 30/70, 50/50, and 70/30 P64/PA6 blends were 2.01×10^{11} , 2.59×10^{10} , and $2.74 \times 10^{12} \text{ min}^{-1}$, respectively. The lowest pre-exponential factor appearing in the ester–amide exchange in the 50/50 P64/PA6 blend possibly may have been caused by its partial phase-separated system.

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