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Transesterification in poly(ethylene terephthalate) and poly(ethylene naphthalate 2,6-dicarboxylate) blends: model compounds study

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Abstract

Kinetics of transesterification reaction in poly(ethylene terephthalate)–poly(ethylene naphthalate 2,6-dicarboxylate), PET–PEN, blends resulting from melt processing was simulated using model compounds of ethylene dibenzoate (BEB) and ethylene dinaphthoate (NEN). The exchange reaction between BEB and NEN was followed by ^{1}H NMR spectroscopy using signals from the aliphatic protons of ethylene glycol moieties at 4.66 and 4.78 ppm, respectively. The first-order kinetics was established under pseudo-first-order conditions for both reactants. Thus, the overall transesterification reaction was second order reversible. The reversibility was confirmed experimentally by heating a mixed sequence of 1-benzoate 2-naphthoate ethylene (BEN) under similar conditions. Both forward reaction of the equimolar amounts of the reagents and reverse reaction came to equilibrium at the same molar ratio of the reactants and reaction products of roughly 0.25:0.50:0.25 for BEB, BEN, and NEN, respectively. The rate equation for the transesterification reaction in the model system was modified using half-concentration of BEN, which is the only effective in the intermolecular exchange. Direct ester–ester exchange was deduced as a prevailing mechanism for the transesterification reaction under the conditions studied, and the values of equilibrium and rate constants, as well as other basic thermodynamic and kinetic parameters were determined. The use of $Zn(OAc)_2$ as a catalyst resulted in a significant decrease in the activation enthalpy of transesterification, which might be due to the partial switch of the reaction mechanism from primarily pseudo-homolytic to more heterolytic where Zn^{II} acts as a Lewis base which binds to the ester carbonyl oxygen. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ethylene terephthalate)/poly(ethylene naphthalate 2,6-dicarboxylate); Transesterification; Blending

1. Introduction

Transesterification reactions in the condensation polymers have been extensively studied due to their strong effect on the miscibility and physical properties of polyester/polyester blends [1,2]. It was shown that miscibility of these polymers could be improved via formation of copolymers resulting from intermolecular exchange reactions. Such a compatibilization is of particular importance in the melt blending of the industrial polyesters like poly(ethylene terephthalate), PET, and poly(ethylene naphthalate 2,6-dicarboxylate), PEN, to produce a variety of blends combining economic advantage of PET with higher heat resistance and better barrier properties of PEN [3–5].

Early works revealed that immiscibility of these polymers could be overcome only when the intermolecular exchange reaction leading to the formation of mixed terephthalate–ethylene glycol–naphthalate (TEN) sequences reaches certain conversion [5–8]. The resulting copolymer initially has a block structure but deeper transesterification leads to its randomization [9]. Molar fraction and randomness of this newly formed species (i.e. transesterification degree) was found to control phase behavior, optic clarity, and physical properties of PET/PEN blends, including their ability for crystallization, solubility, transition temperatures, etc. [1–13].

The basic approach to kinetics and mechanism of the intermolecular transesterification reaction was developed in the early works by Devaux et al. [14–16] on the blends of poly(butyleneterephthalate)/polycarbonate (PBT/PC) and PET/PC. Data obtained led to the conclusion that

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transesterification in polyester/PC systems occurs primarily as a 'direct ester–ester exchange' and can be described as a second-order reversible reaction. However, further extension of this approach toward PET/PEN blends generated controversies and resulted in a long-going discussion over kinetics and mechanism of transesterification reaction in this particular system.

Using Devaux's method, Stewart et al. [6] concluded that transesterification between PET and PEN may be modeled as a first-order reaction, although the method is only applicable to a second-order reaction. This was noted by Kenwright et al. [11], who in their turn suggested alcoholysis mechanism for the trans-exchange between PET and PEN by the reaction of hydroxyl end groups. Strong contribution of both intermolecular alcoholysis and acidolysis reactions was also stressed by Collins et al. [17] in a recent study using small-angle neutron scattering. In addition, no final agreement has been reached in the literature over the role of factors such as blend composition, possible presence of residual catalysts, inhibitors, or technological additives, etc. Their straightforward comparison is complicated due to the distinct origin of the industrial polyesters and unequal processing techniques, and conditions used by different research groups.

In the present study, the kinetics of transesterification reaction between PET and PEN was studied using a model reaction of ethylene dibenzoate (BEB) and ethylene dinaphthoate (NEN). The reaction was carried out under precisely controlled conditions, which can hardly be attained using a polymer system.

2. Experimental

2.1. Materials

Benzoyl chloride (99%), 2-naphthoyl chloride (98%), and zinc(II) acetate (99.99%) were supplied by Aldrich Chemical, Co. Ethylene glycol (99.9%) was obtained from J.T. Baker Inc. The reagents were used as received without further purification.

2.2. Synthesis of model compounds

BEB and NEN were obtained by esterification of ethylene glycol with benzoyl or naphthoyl chloride, respectively. The reagents in the molar ratio 2:1 (acid chloride/ethylene glycol) were stirred at 110 °C for 4 h under nitrogen. The reaction product was cooled to room temperature, washed with 0.1 M NaOH and thereafter with water. The resulting solids (yield above 90%) were repeatedly precipitated from ethanol and dried to constant weight under vacuum. The obtained compounds (BEB) and (NEN) were purified by sublimation under reduced pressure of 10^{-2} Torr at 65 and 100 °C, respectively.

Synthesis of 1-benzoate 2-naphthoate ethylene (BEN) was performed via esterification of equimolar amounts of 2-hydroxyethylbenzoate with 1-naphthoyl chloride at 110 °C for 4 h under nitrogen flow. The 2-hydroxyethylbenzoate was prepared by reaction of excess of ethylene glycol with benzoyl chloride at 110 °C for 4 h under nitrogen. Neutralization of the resulting mixture with 0.1 M NaOH led to phase separation. The denser phase constituted by the solution of 2-hydroxyethylbenzoate in ethylene glycol was separated using a separating funnel and repeatedly washed with water. Fractional vacuum distillation of the obtained liquid gave 2-hydroxyethylbenzoate (yield 83%, mp 34 °C, lit.: 35 °C [18]). All the model compounds were characterized by mass spectroscopy and analytical ^{1}H, and ^{13}C NMR spectral data. BEB: white crystals, mp 76 °C (lit. 75 °C [16]); ^{13}C NMR (δ, $CDCl_3$): 166.38 (C=O), 62.73 (CH_2), 130.16 (1′C), 128.41 (3′,5′C), 129.71 (2′,6′C), 133.16 (4′C). EI-MS *m/z* (rel. int. %): 227 (17, [M^+], $C_{10}H_{14}O_4$), 105 (100, [M^+] − 165, C_7H_5O), 77 (33, [M^+] − 193, C_6H_5). Found: C 70.85, H 5.15%; calculated for $C_{16}H_{14}O_4$: C 71.10, H 5.22%. NEN: white crystals, mp 96 °C; ^{13}C NMR ($CDCl_3$): 166.5 (C=O), 62.89 (aliphatic carbon), 135.60, 132.45, 128.35 (quaternary carbons of the naphthyl ring), 131.32, 129.39, 126.67, 127.04, 127.75, 128.23, 125.21 (tertiary carbons of the naphthyl ring). EI-MS *m/z* (rel. int. %): 370 (87.5, [M^+], $C_{24}H_{18}O_4$), 199 (53, [M^+] − 171, $C_{13}H_{11}O_2$), 127 (62, [M^+] − 243, $C_{10}H_7$), 155 (100, [M^+] − 215, $C_{11}H_7O$), 185 (9, [M^+] − 185, $C_{12}H_9O_2$). Found: C 77.79%, H 4.87%; calculated for $C_{24}H_{18}O_4$: C 77.82%, H 4.89%. BEN: white crystals, mp 68 °C; ^{13}C NMR ($CDCl_3$):166.36 (C=O benzoyl), 166.51 (C=O naphthoyl), 62.75 (aliphatic carbon next to benzoyl), 62.84 (aliphatic carbon next to naphthoyl), 130.16 (substituted carbon of the phenyl ring), 133.16 (*p*-carbon of the phenyl ring), 129.71 (*o*-carbon of the phenyl ring), 128.41 (*m*-carbon of the phenyl ring), 132.45, 135.60, 128.35 (quaternary carbons of naphthyl ring), 131.32, 129.39, 126.67, 127.04, 127.75, 128.23, 125.21 (tertiary carbons of naphthyl ring). EI-MS *m/z* (rel. int. %): 320 (89, [M^+], $C_{20}H_{16}O_4$), 155 (100, [M^+] − 165, $C_{11}H_7O$), 105 (47, [M^+] − 215, C_7H_5O), 149 (61, [M^+] − 171, $C_9H_9O_2$), 127 (64, [M^+] − 193, $C_{10}H_7$), 77 (25, [M^+] − 243, C_6H_5), 171 (15, [M^+] − 149, $C_{11}H_7O_2$). Found: C 74.76%, H 4.96%; calculated for $C_{20}H_{16}O_4$: C 74.99%, H 5.03%.

2.3. Kinetic measurements

Kinetic measurements were performed during isothermal heating of an equimolar mixture of BEB and NEN at 170–210 °C with 2 mol% of zinc(II) acetate as a catalyst [18], and at 220–250 °C without use of a catalyst. The reaction order with respect to each reactant was determined using a ten-fold excess of either BEB or NEN at 250 °C. The kinetics of the reverse reaction (transesterification of BEN) was studied at 200 °C in the presence of 2 mol% of $Zn(OAc)_2$ and at 240 °C without use of a catalyst.

Reactants were carefully milled and mixed in an agate mortar. The mixtures were placed in glass ampoules (0.2 g each) and sealed under reduced pressure of 10^{-2} Torr. A set of 10 samples was immersed into a thermostated silicone bath. The ampoules were withdrawn after certain time intervals and cooled by water to room temperature. The solids obtained were dissolved in $CDCl_3$ and analyzed by ^1H NMR as described elsewhere [1,19,20].

2.4. Instrumentation

The NMR spectra (^1H: 300 MHz and ^{13}C: 75 MHz) were recorded using a VARIAN UNITY 300 spectrometer. Mass spectra (EI-MS) were obtained on a JEOL JMS-SX 102 mass spectrometer using 70 eV electron impact ion source.

3. Results and discussion

Kinetics of transesterification reaction was extensively studied by Devaux et al. [14–16] using PBT/PC and PET/PC systems. The kinetics of the equilibrated transcondensation was modeled using overall reaction mechanism:

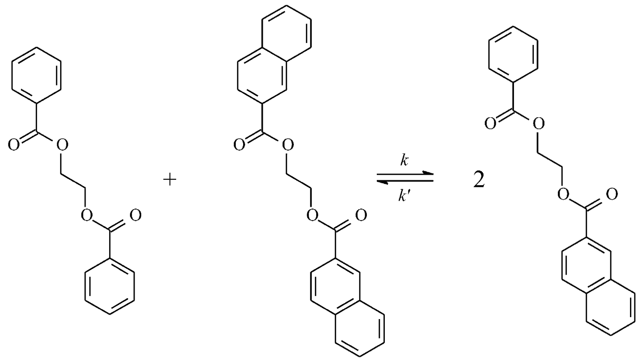
$$\underset{\text{PBT or PET}}{\sim A_1{-}B_1\sim} + \underset{\text{PC}}{\sim A_2{-}B_2\sim} \underset{k'}{\overset{k}{\rightleftharpoons}} \underset{\text{copolyesters}}{\sim A_1{-}B_2\sim + \sim A_2{-}B_1—} \quad (1)$$

The basic assumption of this approach is an equality of the rates of the forward and reverse reactions, i.e.

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

This is very logical, taking into account that the bonding energies of the broken and re-formed chemical bonds are almost the same on the right and left sides of the equation and that ester–ester interchain reaction in polyesters or polyester/PC systems is entropy driven process [1,9]. The claimed equality of k and k' presumes that the reaction of the equimolar amounts of the reactants would lead to the equal concentrations or molar fractions of all four species of Eq. (1) when transesterification reaction reaches its equilibrium.

Transesterification reaction in PET/PEN system can be presented as it is shown in Scheme 1 for the compounds of BEB and NEN modeling terephthalate–ethylene glycol–terephthalate (TET) and naphthalate–ethylene glycol–naphthalate (NEN) sequences of PET and PEN, respectively.



BEB **NEN** **BEN**

Scheme 1. Transesterification reaction between model compounds of PET and PEN.

This can be rewritten as:

$$\mathrm{BEB} + \mathrm{NEN} \underset{k'}{\overset{k}{\rightleftharpoons}} 2\mathrm{BEN} \quad (3)$$

In the present work, this reaction was carried out under precise time/temperature conditions in the glass ampoules sealed under reduced pressure using equimolar amounts of the reactants. The kinetics was followed by measuring integral intensities of the proton signals from ethylene glycol moieties at 4.66, 4.72, and 4.78 ppm for BEB, BEN, and NEN, respectively.

No other spectral changes were observed within the sensitivity of the method when the blends were heated at 190–240 °C for 4 h. This observation was confirmed by heating pure reactants BEB or NEN under the same conditions with or without use of $Zn(OAc)_2$ as a catalyst. Neither ^1H nor ^{13}C NMR spectroscopy detected the formation of hydroxyl, carboxyl, or any other functional groups that might result from the decomposition of the reactants. Thus, it was assured that transesterification was the only reaction under conditions chosen. Reversibility of the reaction (Eq. (3)) was confirmed experimentally by heating BEN, in the same range of temperature. It is worth noting that using model compounds may be the only way to study the reverse reaction.

Fig. 1(a) and (b) show ^1H NMR patterns of the signals from the aliphatic protons at the different stages of transesterification for the forward and reverse reactions, and the corresponding kinetics curves are presented in Fig. 2(a) and (b), respectively. It can be seen that heating BEN at 210 °C in the presence of 2 mol% of $Zn(OAc)_2$ resulted in the formation of homo compounds BEB and NEN. Both forward and reverse reactions under conditions mentioned approximated to its equilibrium after 220–250 min of heating and reached almost equal ratio between reactants and reaction products of roughly 0.25:50:0.25 for BEB, BEN, and NEN, respectively.

The equilibrium constant, K, for the reaction (Eq. (3)) can be written as

$$K = \frac{k}{k'} = \frac{[\mathrm{BEN_e}]^2}{[\mathrm{BEB_e}][\mathrm{NEN_e}]} \quad (4)$$

where $[\mathrm{BEN_e}]$, $[\mathrm{BEB_e}]$, and $[\mathrm{NEN_e}]$ are concentrations or molar fractions of the reactants and reaction product at equilibrium. It can be seen that use of the experimental values of these fractions gives $K \approx 4$ that means:

$$k \approx 4k' \quad (5)$$

Accurate equilibrium constants calculated from the concentrations equilibrated at different temperatures are summarized in Table 1. The values of K ranged from 3.68 to

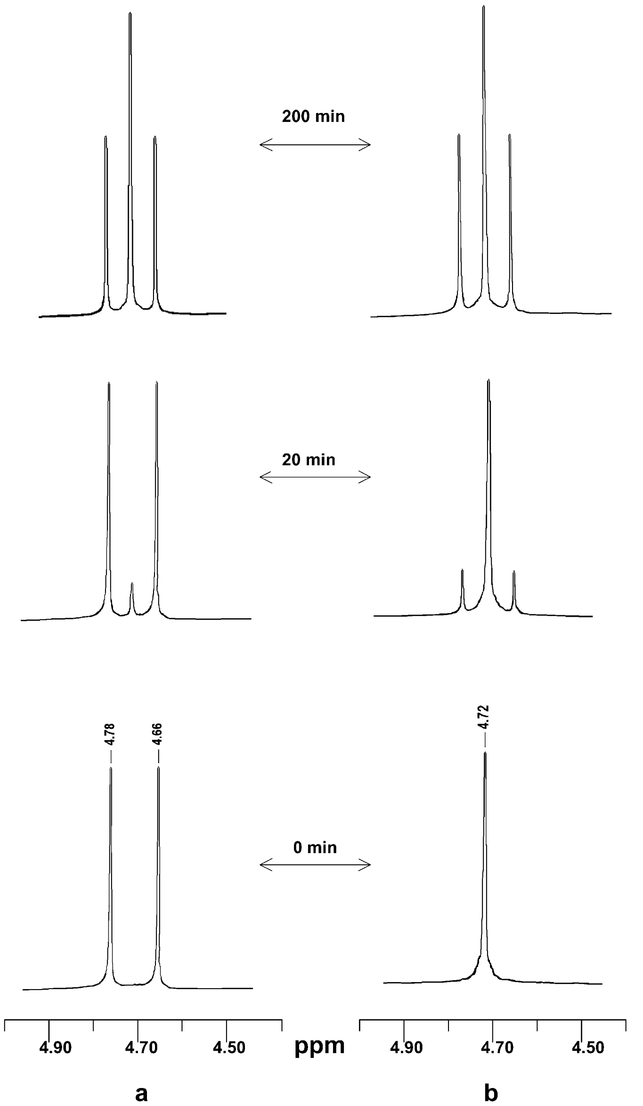


Fig. 1. Proton NMR spectra of the blend of BEB and NEN (a) and the mixed compound BEN (b) at different stages of transesterification reaction in the presence of $Zn(OAc)_2$ at 210°C.

3.84 that are fairly close to 4. It is important to note that K was independent of temperature or use of the catalyst. This confirms that there is no gain of enthalpy in the transesterification reaction (Eq. (3)), i.e. $\Delta H^0 \approx 0\ \mathrm{kcal\ mol^{-1}}$. The reaction appears to be driven by the slight release of entropy: $\Delta S^0 = 2.6\ \mathrm{cal\ mol^{-1}\ K^{-1}}$, due to the formation of the final composition of products enriched with more 'disordered' mixed sequences of BEN.

Studies of equimolar blends of PET and PEN by different research groups also indicated exceeding concentration of mixed sequences terephthalate–ethylene glycol–naphthalate, TEN, when the reaction approached to equilibrium [11–13,21]. The ^{1}H NMR patterns and the final ratio of approximately 0.25:0.50:0.25 for TET, TEN and NEN, respectively, reported in the papers mentioned looked very similar to the results obtained in the present work on the model compounds. However, no equilibrium data have been yet reported for the polymer systems.

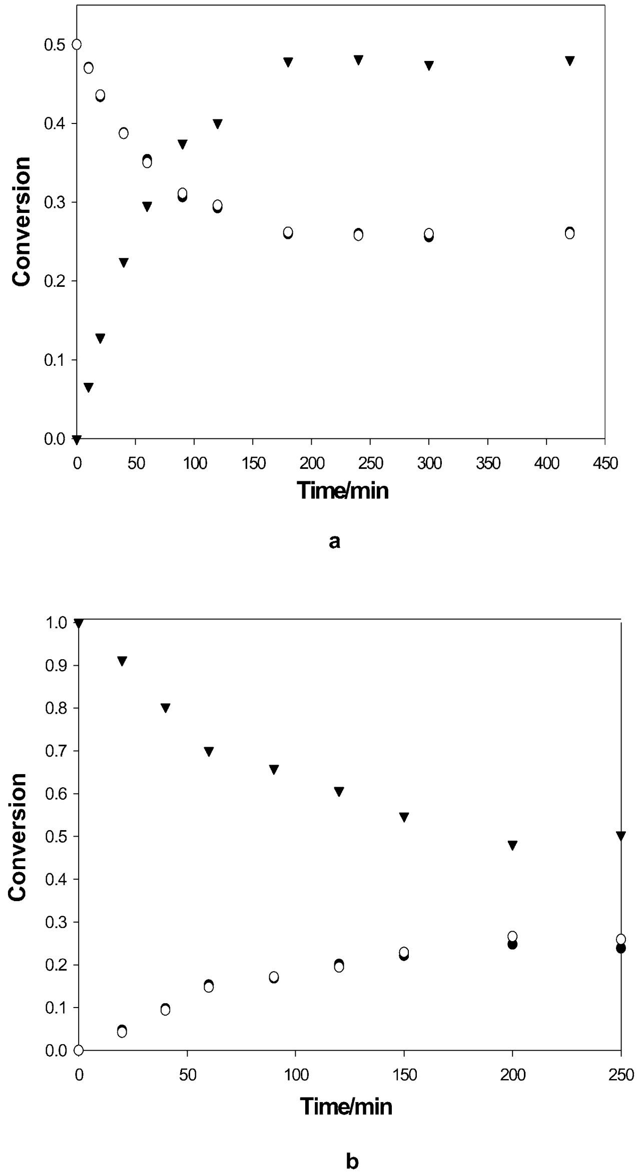


Fig. 2. Kinetics of consumption of the reagents (BEB and NEN for the forward (a) and BEN for the reverse (b) reactions) and formation of the products (BEN for the forward (a) and BEB and NEN for the reverse (b)) in the presence of $Zn(OAc)_2$ at 210 °C.

Higher rate of the direct reaction in the model system ($k \approx 4k'$) looks like a seeming contradiction to the equality of the rates of the forward and reverse exchange reactions ($k \approx k'$) claimed by Devaux for the polyester/PC blends [1,9,14–16]. In both these systems BEB/NEN and polyester/PC, transesterification occurs without notable gain in enthalpy and the reaction is driven by entropy. Thus, the difference between the rate constants of the forward and reverse reactions in Eqs. (1) and (3) should be explained by their distinct statistics.

There are four species in the PET/PC or PBT/PC blends and each effective collision between the reaction

Table 1
Equilibrium (K), rate constants (k) and corresponding thermodynamic and activation parameters for the transesterification reaction (Eq. (3)) obtained in the absence and in the presence of the catalyst

T (°C)	K	ΔH^0 (kcal mol^{-1}) ΔS^0 (cal K^{-1} mol^{-1})	$k \times 10^2$ (min^{-1})	$\Delta H^{\neq}$ (kcal mol^{-1}) $\Delta S^{\neq}$ (cal K^{-1} mol^{-1})
Without catalyst				
220	–		0.09 ± 0.01	
230	3.74	$\Delta H^0 \approx 0$	0.34 ± 0.05	$\Delta H^{\neq} = 37.8 \pm 5.3$
240	3.82	$\Delta S^0 \approx 2.6$	0.64 ± 0.09	$\Delta S^{\neq} = 3.4 \pm 0.7$
250	3.79		1.17 ± 0.25	
In the presence of 2 mol% of Zn(OAc)$_2$				
170	–		0.28 ± 0.02	
180	3.68	$\Delta H^0 \approx 0$	0.54 ± 0.04	$\Delta H^{\neq} = 20.8 \pm 1.5$
190	3.81	$\Delta S^0 \approx 2.6$	0.92 ± 0.09	$\Delta S^{\neq} = -31.7 \pm 4.4$
200	3.84		1.53 ± 0.17	
210	3.77		2.16 ± 0.23	

products $-A_1-B_2-$ and $-A_2-B_1-$ results in the formation of two initial reactants $-A_1-B_1-$ and $-A_2-B_2-$ as it is shown in Eq. (1). In case of PET/PEN or BEB/NEN, effective collisions of the reactants lead to the formation of two mixed sequences TEN or BEN, respectively. However, the reverse reaction is only half as effective because 50% of the collisions BEN + BEN (or TEN + TEN) would result in the recombination of the parts of these molecules without formation of the initial reactants [22]. Thus, kinetics of the transesterification reaction (Eq. (3)) should be described using only half-concentration of BEN (i.e. [BEN]/2), which would be effective in the reverse reaction.

The reaction orders with respect to each of the reactants were determined to verify the overall order of transesterification reaction in the model system. The reaction was carried out at 250 °C under pseudo first-order conditions using 10-fold excess of either BEB or NEN. Kinetics was followed by the consumption of the reagent taken in deficiency as well as by the formation of the reaction product BEN. Kinetic data obtained (Fig. 3) were treated in terms of first-order kinetics: $\ln a = kt$. Linearity of the plots $\ln a$ vs. time, shown in the insert to Fig. 3, indicates that the reaction is first order with respect to each reagent. The average rate constant determined from the gradients of the lines was of $(1.50 \pm 0.12) \times 10^{-2}\ \mathrm{min}^{-1}$ giving the half-life of the reaction $t_{1/2} = (\ln 2)/k = 46.2$ min. As it can be seen from Fig. 3, the reaction follows first-order kinetics for more than six half-life periods. Thus it should be concluded that the overall order of the reaction (Eq. (3)) is second order reversible with respect to the resulting product BEN.

Using the effective half-concentration of BEN as it was justified above, the rate equation for the transesterification reaction (Eq. (3)) can be written in the following way

$$\frac{1}{2}\frac{\mathrm{d[BEN]}}{\mathrm{d}t} = [\mathrm{BEB}][\mathrm{NEN}] \tag{6}$$

or in the differential form

$$\frac{1}{2}\frac{\mathrm{d[BEN]}}{\mathrm{d}t} = k[\mathrm{BEB}][\mathrm{NEN}] - k'[\mathrm{BEN}]^2 \tag{7}$$

where [BEB], [NEN] and [BEN] are concentrations of BEB, NEN, and BEN at time t.

Concentrations could be replaced with molar fractions a and b for BEB and NEN, respectively, and x for [BEN]/2 or $2x$ for [BEN]. At time $t = 0$ molar fractions of the reactants are equal ($a_0 = b_0 = 0.5$) and their current values at time t could be expressed as $a_0 - x$ or $b_0 - x$, which are equal also. Now Eq. (7) can be rewritten as following:

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a_0 - x)^2 - k'x^2 \tag{8}$$

Rearrangement of Eq. (8) taking into consideration that $k = 4k'$ and following integration give the rate equation (Eq. (9))

$$\frac{1}{2a_0}\ln\frac{a_0}{a_0 - 2x} = kt \tag{9}$$

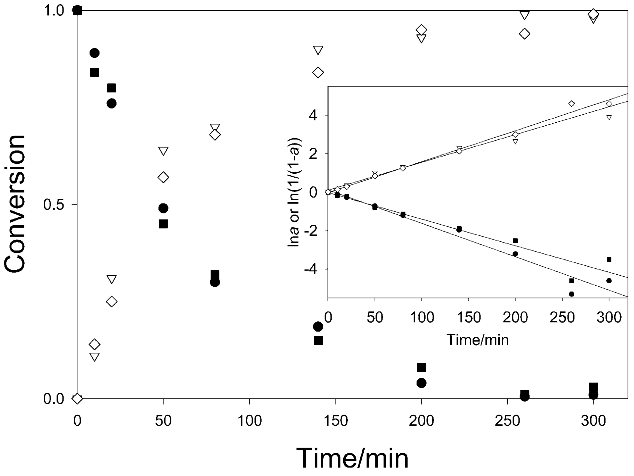


Fig. 3. Kinetics of consumption of the reagent taken in deficiency (BEB—■; NEN—●) and formation of the product (BEN—◇ and ▽ in excess of NEN and BEB, respectively) under pseudo first order conditions at 250 °C. Inset shows linearization of corresponding curves calculated by first-order.

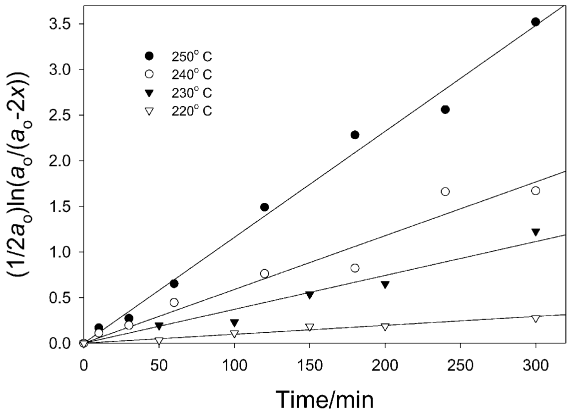


Fig. 4. Transesterification kinetics for BEB/NEN blend (50/50 by mole) without catalysts.

where a_0 is known and x can be easily determined by ^{1}H NMR as it was shown above.

The rate equation (Eq. (9)) was used to process kinetic data for transesterification reaction carried out at different temperatures with and without use of $Zn(OAc)_2$ as a catalyst. The resulting series of plots are presented in Figs. 4 and 5, respectively. Their fairly good linearity confirms that transesterification reaction in the model system BEB/NEN is second order. It should be noted that the deviation of the experimental points from the straight lines are significantly lower for the model compounds than it was previously observed for the polymers [5,6].

The rate constants calculated from the kinetic plots are given in Table 1. Their comparison with the rate constants obtained for the polymer systems could not be straightforward because transesterification reaction in polymers occurs at higher temperatures. In general, the values of k are higher by factor of 10 as compared to the rate constants for the catalyzed and uncatalyzed PBT–PC and PET–PEN exchange reactions [11,15], which might be due to the additional sterical hindrance in the polymers.

The activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) were calculated from the temperature dependence of the rate constants listed in Table 1 by plotting $\ln(k/T)$ against T^{-1} for both catalyzed and uncatalyzed reactions. The numerical values are also included in Table 1. The enthalpies of activation are very close to those obtained for the transesterification reaction in the polymer blends [11,15] and this may be considered as an additional evidence for the similarity of the reaction mechanism in the polymer and the model system studied.

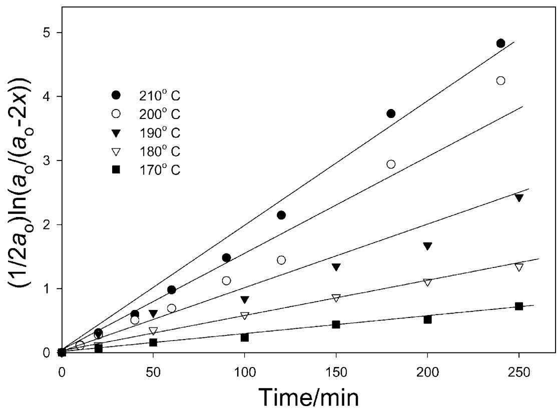
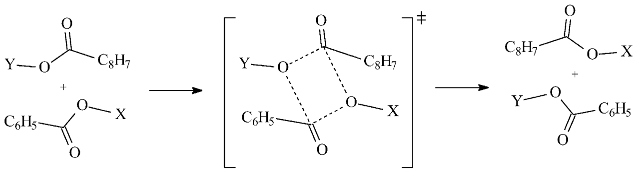


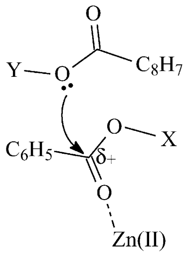
Fig. 5. Transesterification kinetics for BEB/NEN blend (50/50 by mole) in the presence of $Zn(OAc)_2$.

First order with respect to each reagent indicates unambiguously that two molecules, BEB and BEN, constitute an associative transition state. The uncatalyzed pathway is characterized by high activation enthalpy of 37.8 ± 5.3 kcal mol^{-1} suggesting the direct ester–ester exchange, in which the bond breaking plays a dominant role in the transition state. The acyl-oxygen fission mechanism [23] is very likely for the cleavage of the ester C–O bonds within the four-centered transition state.



The symmetrical transition state may not be necessarily the case and one of two C–O bonds could be elongated or cleaved to a greater extent but it is impossible to specify which of the two is most affected. The high $\Delta H^{\neq}$ is obviously the reason why the activation entropy is not very much negative as should be expected for a true second-order reaction and this might be due to the compensation effect [24]. It is also possible that there is no significant loss of entropy in the binary system free of solvent when two different molecules find each other in the transition state. It is interesting to note that the values of ΔS^0 and $\Delta S^{\neq}$ are very similar (Table 1). This similarity might reflect the fact that the uncatalyzed ester exchange is basically entropy driven process.

The effect of the catalyst on the activation parameters, and first of all on $\Delta H^{\neq}$ is very notable, and this is in good agreement with the results obtained for trans-exchange reactions in polymers [15]. The drop in $\Delta H^{\neq}$ might be due to the partial switch of the reaction mechanism from primarily pseudo-homolytic to more heterolytic where Zn^{II} acts as a Lewis base which binds to the ester carbonyl oxygen. It may be assumed that possible interaction between Zn(II) and carbonyl oxygen leads to an increase in the positive charge on the carbonyl carbon as it can be expected from the basic mechanism of Lewis acid catalysis in the reactions of carbonyl compounds [23].



As a result, the nucleophilic attack by the oxygen via the transition state becomes the dominant pathway and the activation entropy of the catalytic reaction involving extra species in the transition state decrease to significantly more negative as compared to the noncatalytic ester–ester exchange.

4. Conclusions

Transesterification reaction in PET/PEN blends was studied using model compounds of BEB, NEN and BEN, which simulate TET, NEN and TEN sequences of the polyesters. Heating of BEN above 200 °C resulted in the formation of homo sequences BEB and NEN, and this confirmed experimentally the reversibility of the trans-exchange reaction. The reaction order was determined with respect to each reagent under pseudo first-order conditions. It was found that overall transesterification reaction in the model system is second-order reversible. The rate of the forward reaction was four times higher due to the possible recombination of half of BEN molecules and kinetics of transesterification was described using the effective half-concentration of the product. Kinetic data and activation parameters indicated that direct ester–ester exchange is the primarily mechanism of transesterification in the model system. Use of $Zn(OAc)_2$ resulted in the dramatic decrease of activation enthalpy that might be due to the partial switch of the reaction mechanism from primarily pseudo-homolytic to more heterolytic where Zn^{II} acts as a Lewis base which binds to the ester carbonyl oxygen.

Acknowledgments

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