

# Copolyesters of Poly(Butylene Terephthalate), 1,4-Naphthalene Dicarboxylic Acid, and Hydroquinone Diacetate: A Simple Rate Model

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Received 18 April 2003; accepted 5 June 2003

**ABSTRACT:** The kinetics of novel liquid crystalline copolyesters between poly(butylene terephthalate) (PBT), 1,4-naphthalene dicarboxylic acid (1,4 NDCA), and hydroquinone diacetate (HQDA) are examined by using the melt polymerization route. Three different copolyester compositions (i.e., PBT 70 mol % + 1,4 NDCA 15 mol % + HQDA 15 mol %, PBT 50 mol % + 1,4 NDCA 25 mol % + HQDA 25 mol %, and PBT 30 mol % + 1,4 NDCA 35 mol % + HQDA 35 mol %) were synthesized via the melt polymerization route. Sodium acetate and zinc acetate, 1.0 mol %, concentrations were tried as the polymerization catalysts. The reaction temperatures were 260, 270, and 280°C for PBT 70 and PBT 50 mol % compositions. PBT 30 mol % compositions were synthesized at 245, 255, and 265°C by using the above catalysts. Lower temperatures were employed for PBT 30 mol % reactions to avoid degradation reactions. The kinetics of complex systems are analyzed by methods analogous to solution kinetics. Few assumptions are proposed and tried

to simplify the kinetics of this complex system and to make the kinetic analysis tractable. Two different models containing different rate constants,  $k_1$  and  $k_2$ , are considered in this work. A key postulation is that the reaction originates between 1, 4 NDCA and HQDA to form a dimer. This dimer copolymerizes with the PBT chain with evolution of acetic acid (model 1) or without (model 2). The subsequent coupling of PBT segments reforms the PBT chain in the case of model 1 with random incorporation of 1, 4 NDCA–HQDA units; whereas blocks of PBT units and 1, 4 NDCA + HQDA units are formed in the case of model 2. The kinetic analysis reveals the implicit simplicity of complex systems. The number of moles of acetic acid, generated in both homopolyesterification and copolyesterification channels, is monitored to follow the rate of the reaction and evaluate the individual rate constants. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 92: 2817–2832, 2004

## INTRODUCTION

Polyesterification is an important polycondensation reaction from both the scientific and the technological point of view. Many investigations into polyesterification reactions have been carried out and a variety of conclusions have been reached regarding the kinetic order and, hence, the mechanism of the reaction.<sup>1–7</sup>

The structural organizations in the thermotropic liquid crystalline aromatic copolyesters are well documented.<sup>8–13</sup> These are specifically synthesized via melt copolyesterification route to tailor-made structures that depict desired properties. These structures help in imparting definite physiochemical properties to the system that are attributable to the major component. The major component principally consists of benzene rings fastened exclusively at *para* positions by ester groups. A recourse to polyesterification is sought to incorporate flexible moieties and rigid kinks in the product, which are important for inducing a change in

the transition temperature without compromising the mechanical properties.

Transesterification reaction between hydroquinone diacetate (HQDA) and 1,4-naphthalene dicarboxylic acid (1,4 NDCA) generates a system that differs from polyethylene terephthalate–oxybenzoate only in the direction of the ester bridging group in the mesogenic core.

Practical synthesis of high molecular weight polymers requires a knowledge of the kinetics of the polymerization reaction. Step polymerization proceeds in a stepwise manner with the molecular weight increasing with reaction time. At any time, only two molecules (whether they are dimer–dimer or dimer–trimer or dimer–monomer pairs) take part in the reaction. The monomer normally decreases in the early stages of the reaction. The rate of step polymerization is thus the sum of the rates of reaction between molecules of various sizes. The kinetics of such a situation are normally difficult to analyze. Three assumptions are made to simplify the kinetics. One, the observed reactivity of a functional group is dependent on the collision frequency of the group and not on the diffusion rate of the whole molecule. Two, the terminal functional group of a monomer or a growing chain has a greater mobility than could be expected for a polymer molecules as a whole. Three, at low diffusion

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Contract grant sponsor: Research Administration of Kuwait University.

rates two functional groups undergo more collisions before diffusing apart.

Polyesterification reactions are normally carried out by melt polymerization techniques, which allow the application of temperatures in the range of 150–400°. The temperatures employed are normally selected so that there is no thermal degradation of the monomers or polymers. To reduce the effect of thermal oxidation, polycondensation is normally conducted under an inert gas flow, which, in addition, promotes the removal of low molecular weight products from the reaction media.

Literature survey gives no evidence of kinetic explorations of the melt transesterifications of the ternary poly(butylene terephthalate) (PBT)–HQDA–1,4 NDCA system. Here, we explore the kinetics of a three-component system by using two different reaction models.

The investigations were conducted with the following objectives: (1) to identify plausible routes to simplify the kinetics of a three-component system involving PBT, HQDA, and 1,4 NDCA; (2) to develop a mathematical model capable of analyzing the system that involves two competitive parallel reactions generating a common by-product (acetic acid); and (3) to predict the rate of acetic acid production by assuming that the acetic acid is only produced by 1,4 NDCA and HQDA reacting with itself or its oligomers and not with PBT.

The two following different mathematical models capable of analyzing the systems are considered: (1) two competitive reactions occur, giving a common product (acetic acid); and (2) only the dimer formation giving acetic acid. The kinetic parameters are determined at various temperatures for both catalyzed and uncatalyzed runs to see whether kinetic order changes with catalyst type. The kinetic parameters are determined for three different compositions at three different temperatures by using two different catalyst types. A simple second-order reaction sequence is developed to analyze the experimental work.

Last, physicochemical characterization of PBT–1,4 NDCA–HQDA copolyesters is carried out by using differential scanning calorimetry.

## EXPERIMENTAL

### Materials

PBT (1600  $\mu\text{m}$ ), of intrinsic viscosity 0.56 (M/S Century Enka Private Ltd., Pune, India), was used as received. HQDA and 1,4 NDCA were purchased from a local chemical company in U.K. Infrared analysis was used to check the purity of the monomers. The melting temperature of 1,4 NDCA was greater than 300°C and that of HQDA was between 121 and 123°C, respectively.

### Melt polymerization

A 250-mL hastalloy-based and electrically heated reactor, as indicated in Figure 1, was used for the melt transesterification kinetics.

### Preparation of polymers

The transesterifications were conducted with the objective of analyzing the kinetics in the initial stage of the reaction, wherein the distillation of the side product (acetic acid) was complete under atmospheric pressure. Reactions were conducted to generate a series of copolyesters of varying compositions. Copolyesterification kinetics were investigated for three compositions, as follows: PBT 70 mol %/(1,4 NDCA + HQDA) 30, PBT 50 mol %/(1,4 NDCA + HQDA) 50, and PBT 30 mol %/(1,4 NDCA + HQDA) 70. PBT melted around 230°C and degraded around 300°C when maintained isothermally for 15 min at atmospheric pressure. The melting temperature of both PBT and 1,4 NDCA has limited the temperature range for kinetic experimental investigations. The isothermal temperatures chosen for the kinetic estimations were determined after many trial experiments. Dry nitrogen blanket was maintained throughout the experiments to prevent oxidative degradations. The rate of evolution of side product, acetic acid, was monitored volumetrically to estimate the kinetic parameters. Minor quantities of HQDA were found to sublime during the course of the reaction. They were collected, dissolved in acetone, and quantified, using a gas chromatograph. The loss was found to be less than 0.00515 mol. The purity of acetic acid formed was estimated at different isothermal kinetic temperatures. This was found to be around 95% at lower temperatures and 93% at higher temperatures, respectively. Maximum conversion noted, based on moles of acetic acid, was 75%. The light tan and opaque copolyesters were powdered and acetone was extracted to remove unreacted initial reactants, if any, prior to the characterization. It is observed that as the percentage of PBT decreases, the reaction has to be carried out at low temperatures to avoid degradation reactions.

### Measurements

Thermal transitions were obtained with a Mettler DSC 30 apparatus interfaced with a thermal analysis data station under nitrogen atmosphere using a sample size of 10–15 mg. A heating rate of 10°C/min was employed in all the cases. Indium was used to calibrate the enthalpy values. A three-metal alloy (In–Pb–Zn) was used to calibrate the temperature scale. Samples were heated in the temperature range of 40 to 300°C in both heating and cooling cycles.

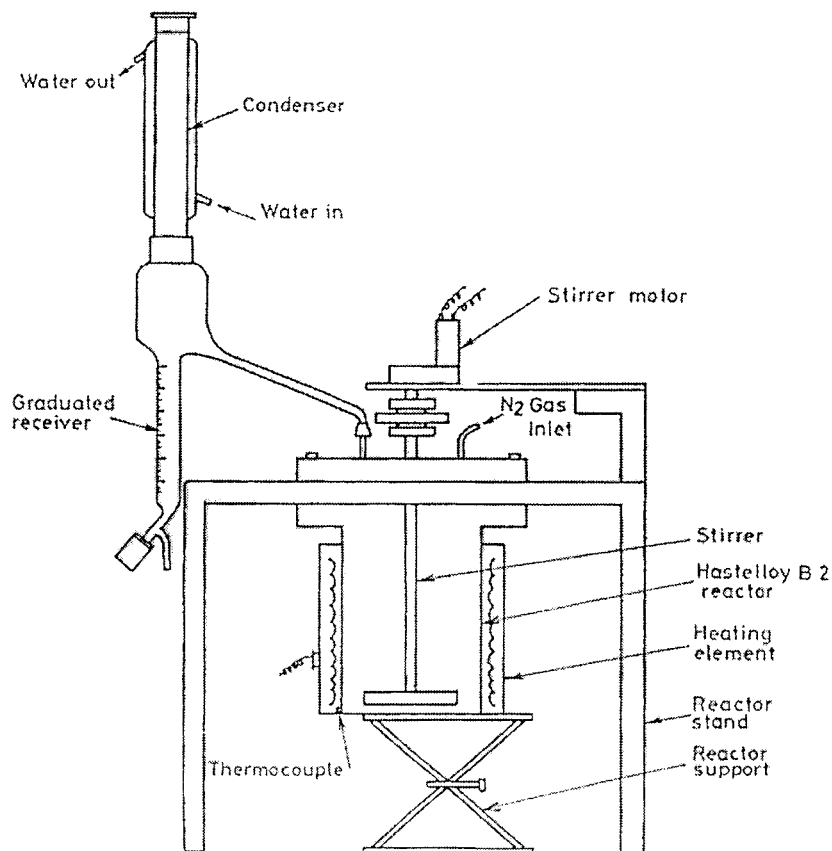


Figure 1 Polymerization reactor.

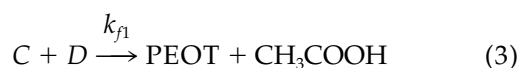
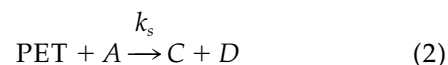
## RESULTS AND DISCUSSION

Reactions between PBT, NDCA, and HQDA were carried out by using the melt polymerization route. The maximum temperatures were chosen to obtain high enough rates, while avoiding the loss of the components by volatilization. This was 280°C in the case of PBT 70 mol % (1,4 NDCA + HQDA) 30, PBT 50 mol % (1,4 NDCA + HQDA) 50, and 265°C in the case of PBT 30 mol % (1,4 NDCA + HQDA) 70. The catalysts selected for the study were already known to be effective for aromatic polycondensation, namely, metal acetates.

Catalysts loadings up to 1 mol % of the highest concentration of monomer were employed, to the expectation that satisfactory polycondensation rates would then be obtained at much higher temperatures. In this open system, the maximum theoretical yield of acetic acid obtained was 75% for PBT 30 mol %, 72% for PBT 50 mol %, and 68% for PBT 70 mol %.

Mathew et al.<sup>14</sup> studied the copolymerization kinetics of PET and 4-acetoxybenzoic acid. Their objectives were to develop a mathematical model capable of analyzing the system which involves two parallel reactions generating a common byproduct acetic acid.

The major reactions they considered were



where  $A$  and  $(A)_2$  are acetoxy benzoic acids and dimers,  $k_h$ ,  $k_s$ , and  $k_{f1}$ , are rate constants of homopolymerization, PET chain scission, and chain re-formation with insertion of an oxybenzoate unit, respectively. Species  $C$  and  $D$  are intermediate in nature. They are generated in reaction (2) and consumed in reaction (3). The concentration of these species could not be monitored directly for kinetic evaluation. On adding reaction schemes 2 and 3, they obtained



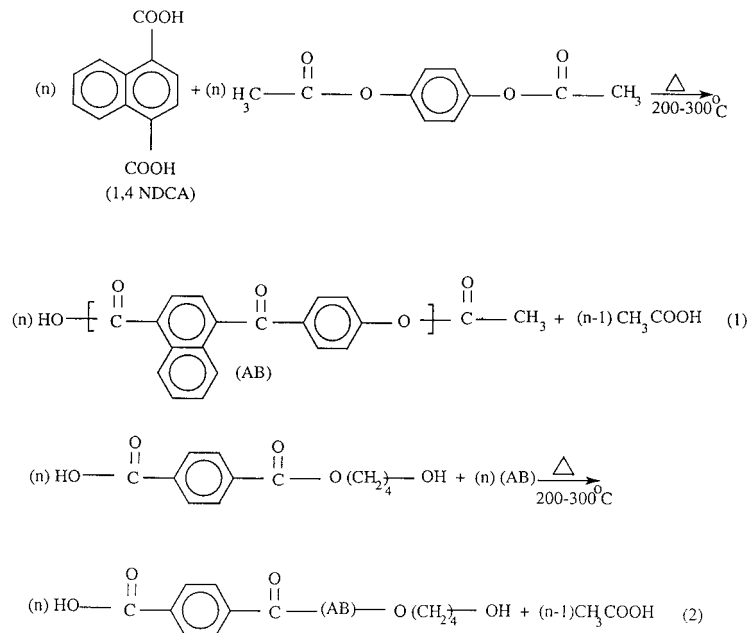


Figure 2 Reaction scheme for model number 1.

where PEOT is the random copolymer and  $k_c$  is the net result of rate constants  $k_s$  and  $k_f$ . The rate constant for the decrease in the concentration of ABA, which is also equal to the rate of formation of acetic acid as given by Mathew et al.,<sup>14</sup> is

$$\frac{-d[A]}{dt} = k_d[A]^2 + k_c[A][\text{PET}] \quad (5)$$

whereas for PET, the equation obtained was

$$\frac{-d[\text{PET}]}{dt} = k_c[A]_2[\text{PET}] \quad (6)$$

### Kinetics and mechanism

In the present work, the melt transesterification of ternary PBT-1,4 NDCA-HQDA system is analyzed.

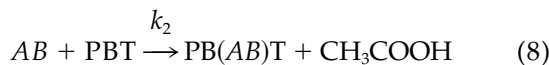
The reactions that occur when PBT, 1,4 NDCA, and HQDA are heated together or maintained isothermally at temperatures in excess of the isotropization temperature of crystalline PBT may be visualized as depicted in Figures 2 and 3.

The entire gamut of reactions, in a step polymerization reaction if accounted for, will result in very complex and unwieldy rate expressions, which will have very little practical utility. Hence, in the following section, we consider simple reaction models.

Two different kinetic models are developed by considering the following two major competing reactions: (1) dimerization of 1,4 NDCA + HQDA and (2) insertion of oligomer of the later reaction into the PBT chain, with or without the elimination of acetic acid. In

all the reactions, it is noted that the maximum degree of polymerization attained is five.

A simple reaction sequence to account for the major steps involved in the first approach (henceforth considered as model 1) in this work is outlined as



where  $A$ ,  $B$ ,  $AB$ ,  $\text{PB(AB)T}$  represent HQDA, 1,4 NDCA, dimer of HQDA and 1,4 NDCA, and copolymer of PBT, while  $k_1$  and  $k_2$  are assumed as the homo- and copolymerization rate constants.

If  $P_1$  represents concentration of  $A$  and  $B$  and  $P_2$ ,  $P_3$ , and  $P_4$  represent that of dimer of homopolymer ( $AB$ ), PBT, and homopolymer inserted into PBT, then the rate equations can be written as:

$$\frac{d(P_1)}{dt} = -k_1(P_1)(P_1) \quad (9)$$

$$\frac{d(P_2)}{dt} = k_1(P_1)(P_1) - k_2(P_2)(P_3) \quad (10)$$

$$\frac{d(P_3)}{dt} = k_2(P_2)(P_3) \quad (11)$$

and

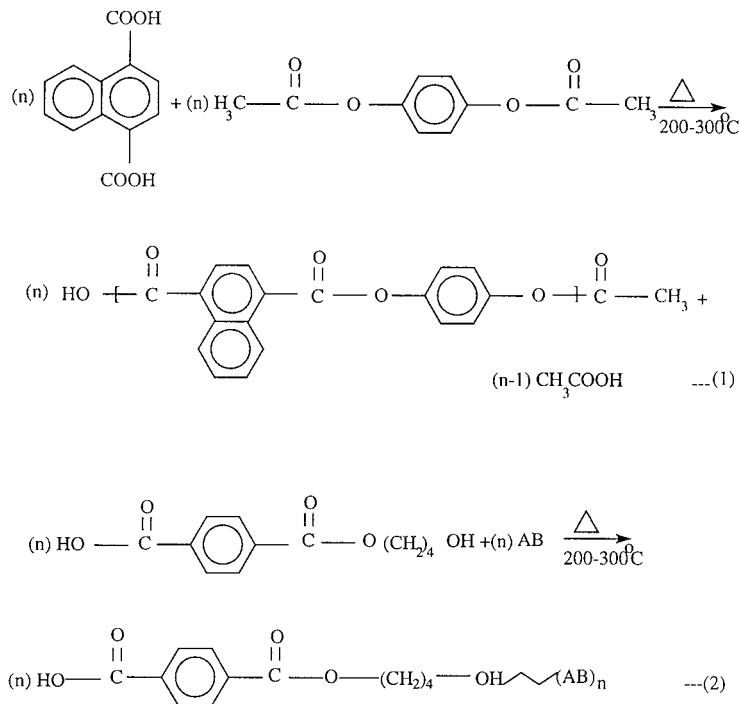


Figure 3 Reaction scheme for model number 2.

$$\frac{d(P_4)}{dt} = k_2(P_2)(P_3) \quad (12)$$

These differential equations have been solved numerically by using MATLAB with initial conditions:  $P_1 = [\text{HQDA}]_0 = [1,4 \text{ NDCA}]_0$ ,  $P_2 = 0$ ,  $P_3 = [\text{PBT}]_0$ , and  $P_4 = 0$ .

The total amount of acetic acid generated ( $T_1$ ) is calculated as

$$T_1 = P_2 + 2P_4 \quad (13)$$

The computed values of acetic acid are compared with the experimentally collected amount and the two rate constants are optimized by using a differential algebraic optimization technique.<sup>15</sup>

For the second model, the following assumptions are considered



where  $A$ ,  $B$ ,  $AB$ , and  $\text{PBT}(AB)$  represent HQDA, 1,4 NDCA, dimer of HQDA and 1,4 NDCA, and block copolymer of PBT. Two different rate constants,  $k_1$  and  $k_2$ , are assigned for this reaction network.

If  $P_1$  represents the concentration of  $A$  and  $B$  and  $P_2$ ,  $P_3$ , and  $P_4$  represent that of dimer of homopolymer ( $AB$ ), PBT, and block copolymer of PBT, then the rate equations are given as:

$$\frac{d(P_1)}{dt} = -k_1[P_1][P_1] \quad (16)$$

$$\frac{d(P_2)}{dt} = k_1[P_1][P_1] - k_2(P_2)(P_3) \quad (17)$$

$$\frac{d(P_3)}{dt} = -k_2[P_2][P_3] \quad (18)$$

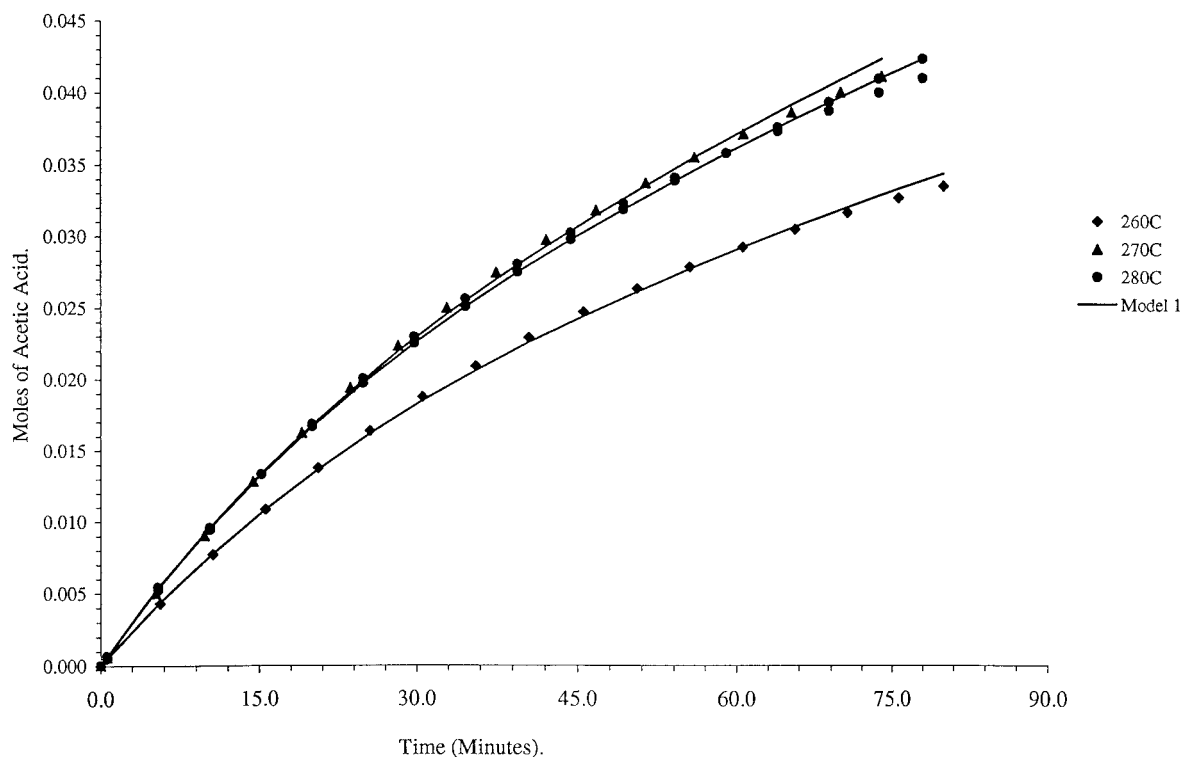
and

$$\frac{d(P_4)}{dt} = k_2[P_2][P_3] \quad (19)$$

The above differential equations were also solved by using MATLAB with initial conditions,  $P_1 = [\text{HQDA}]_0 = [1,4 \text{ NDCA}]_0$ ,  $P_2 = [\text{PBT}]_0$ ,  $P_3 = 0$ , and  $P_4 = 0$ . The total amount of acetic acid generated ( $T_2$ ) is calculated as:

$$T_2 = P_2 \quad (20)$$

The computed values of acetic acid were compared with the experimentally collected amount and the two

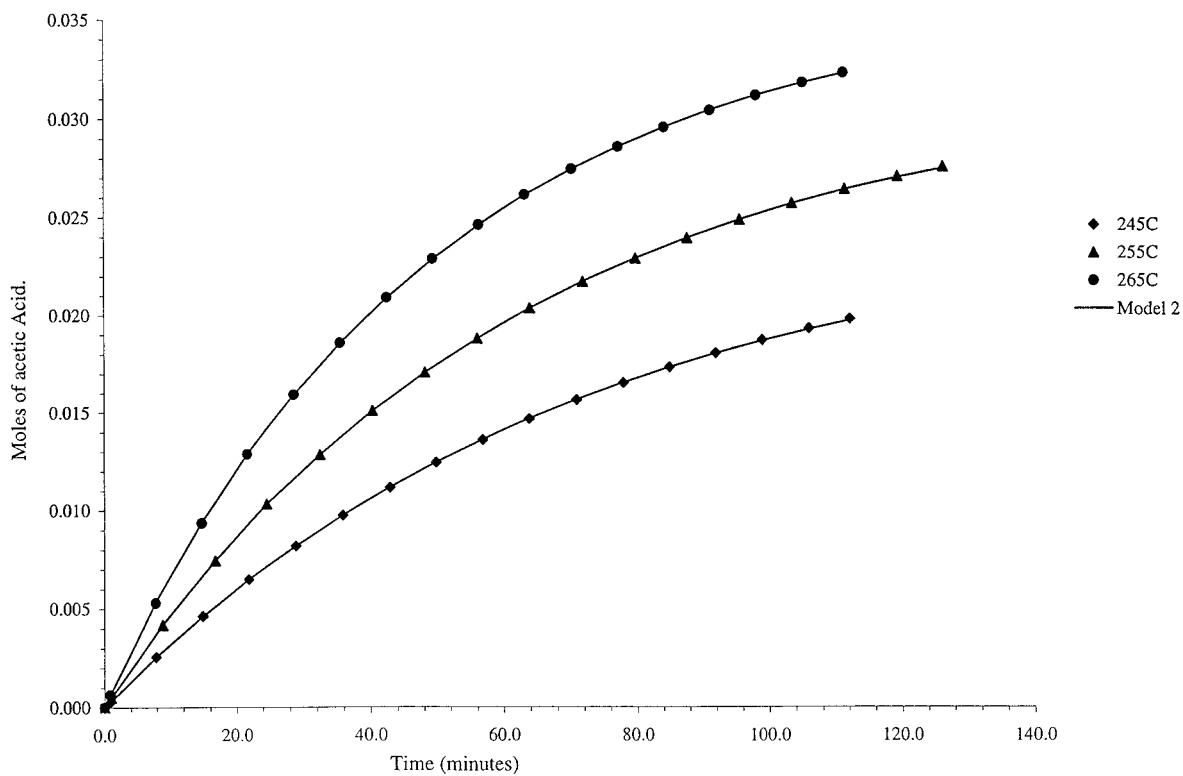


**Figure 4** Second-order plot for uncatalyzed PBT 50 mol %/(1,4 NDCA + HQDA) 50 reactions.

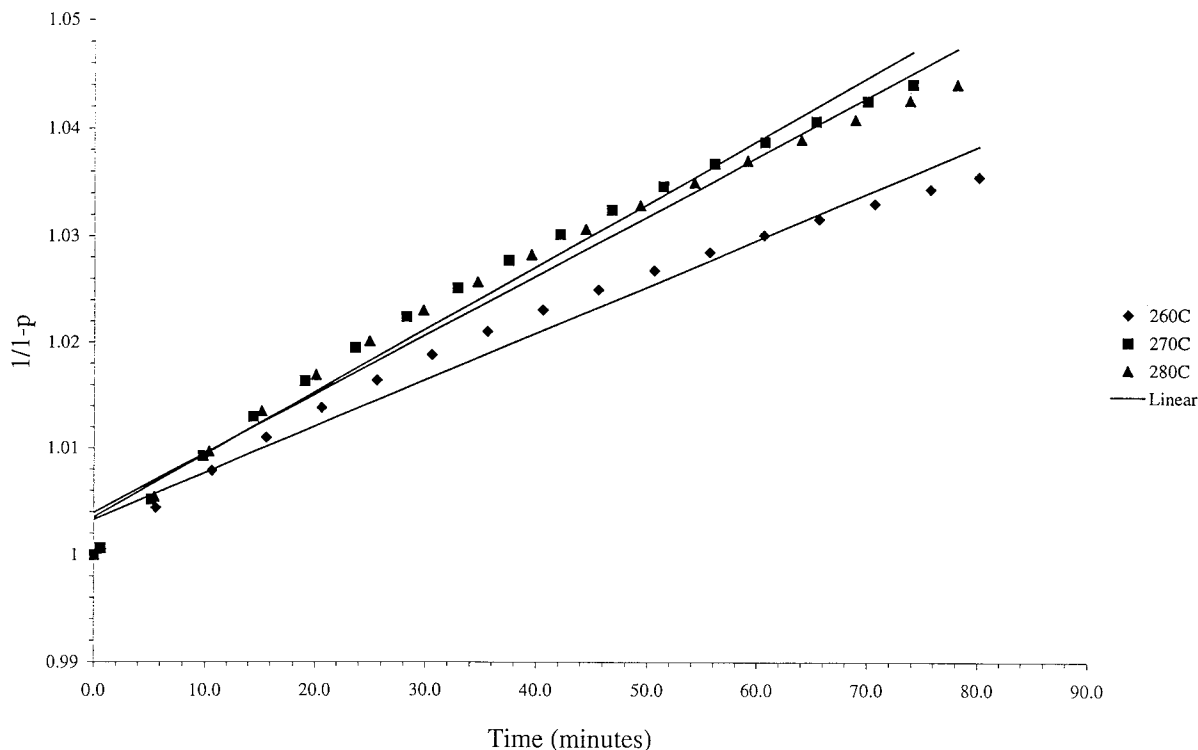
rate constants were optimized by using a similar procedure as indicated for model 1.

Two typical figures (Figs. 4 and 5) illustrate the

comparison of theoretical acetic acid production with that of experimental measurements (for uncatalyzed reactions at different PBT concentrations) for the two



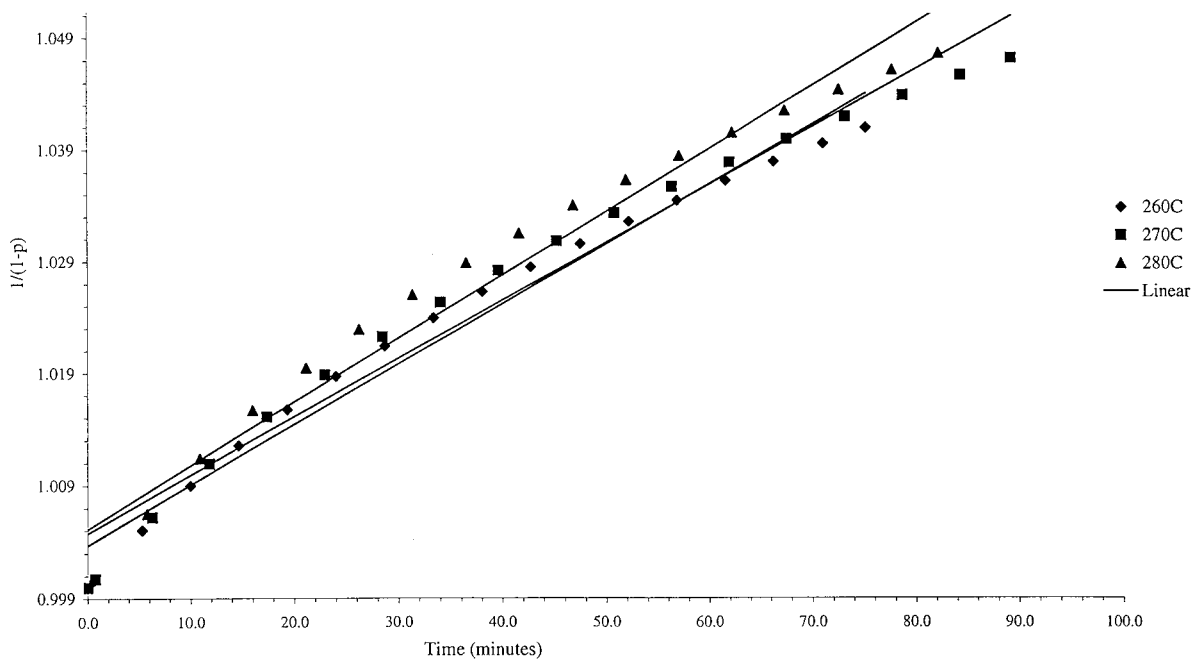
**Figure 5** Second-order plot for uncatalyzed PBT 30 mol %/(1,4 NDCA + HQDA) 70 reactions.



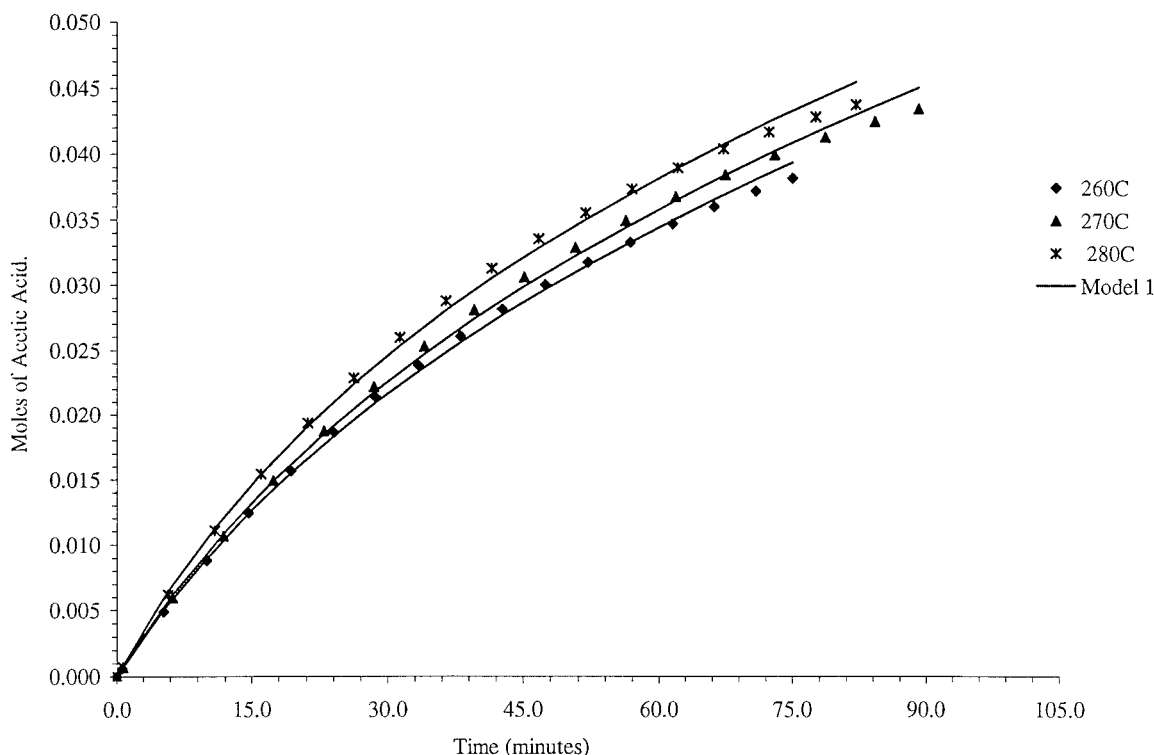
**Figure 6** Second-order plot of  $1/1 - p$  as a function of time for uncatalyzed PBT 50 mol %/(1,4 NDCA + HQDA) 50 reactions.

models. Figures 4 and 5 show that second-order kinetics using both models can be adopted to study the copolymerization of (1,4 NDCA + HQDA) and PBT. The figures also indicate that both models fit the experimental data well.

In the study of Mathew et al.<sup>14</sup> on the melt polymerization kinetics of poly(4-oxybenzoate) with poly(ethylene terephthalate), the authors observed breaks in the kinetic plots of  $1/(1 - p)$  versus time. Because there are two competing reactions, a second-order plot



**Figure 7** Second-order plot of  $1/1 - P$  as a function of time for catalyzed PBT 50 mol %/(1,4 NDCA + HQDA) 50 reactions.



**Figure 8** Second-order plot for PBT 50 mol %/(1,4 NDCA + HQDA) 50, sodium acetate (1 mol %) catalyzed reactions.

of  $1/(1 - p)$  versus time (Figs. 6 and 7) did not yield straight lines and, hence, were not used for the determination of the kinetic parameters. However, if there is a significant oligomer (homopolymer of 1,4 NDCA + HQDA) precipitation, then an *a priori* one would expect two kinetic stages and consequently breaks in the rate (slope) of acetic acid production curves. Because breaks are not observed in the kinetic analysis, it can be concluded that in all probability, oligomer precipitation (arising out of homopolymerization of 1,4 NDCA + HQDA) does not occur to a significant degree.

Figures 8 and 9 indicate the adherence of both models to catalyzed data for different temperatures. A perfect match is found to exist between the experimental data points and the model.

The data can be classified into three different types, as follows: (1) those emanating from variance in temperature for different polymer compositions, as presented in Figures 4–9; (2) that obtained at constant temperature as the catalyst type is varied (Figs. 10–12); and (3) that obtained at constant temperature while varying compositions of reaction mixture (Figs. 13–15).

A common feature in all these plots is the general adherence to second-order kinetics, which is fairly obeyed, thus warranting that the suggested models adequately fit the experimental runs.

The kinetic constants  $k_1$  and  $k_2$  (Tables I and II) obtained in this study are within 5–7% error limits relative to the theoretical prediction. It is found that

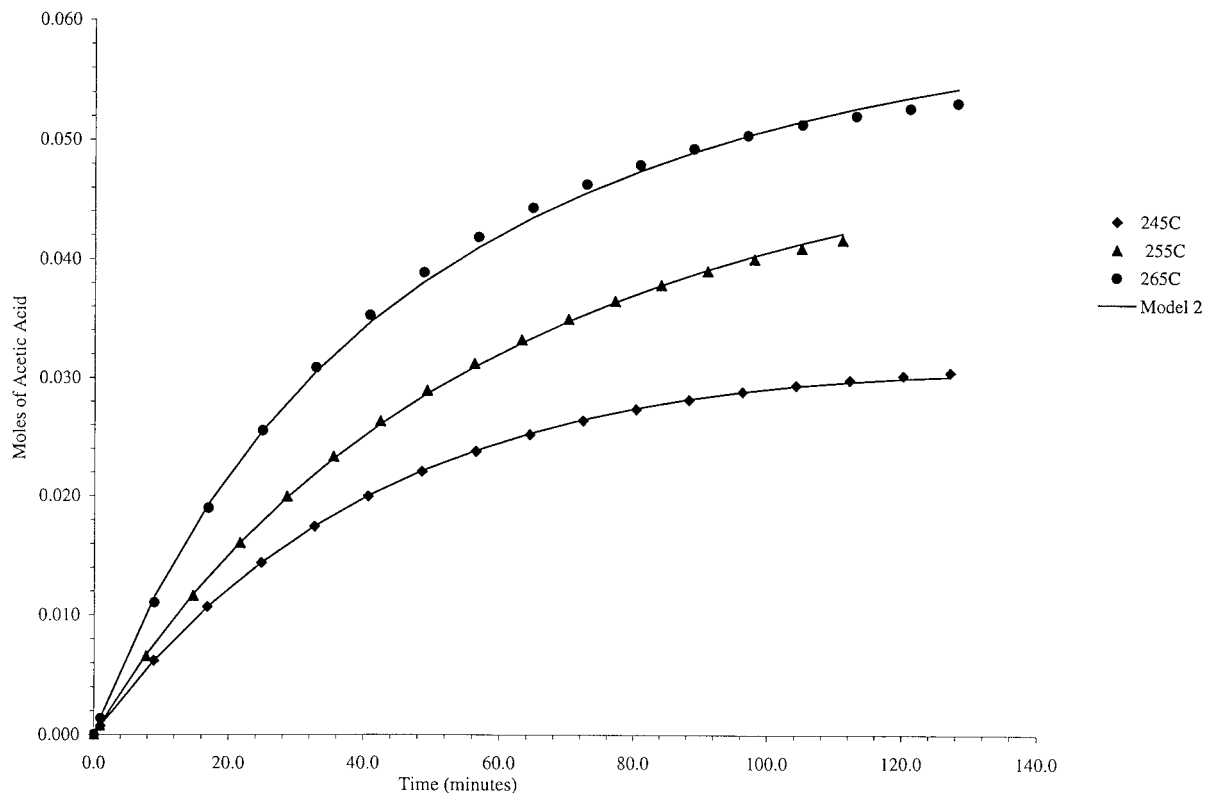
both models give equal values for the first kinetic constant ( $k_1$ ).

As seen from Table I, model 1 can be used to determine the random copolymerization rate constants  $k_1$  and  $k_2$  for the compositions of PBT 50 mol %/(1,4 NDCA + HQDA) 50 and PBT 70 mol %/(1,4 NDCA + HQDA) 30, while model 2 (Table II) can be used to determine the copolyesterification kinetics of a block copolymer composition consisting of PBT 30 mol %/(1,4 NDCA + HQDA) 70 system. Both tables clearly indicate that the homopolymerization step occurs at a faster rate compared to copolymerization step. The rate constant,  $k_2$ , for copolymerization reaction indicates that the incorporation of the monomer into PBT with the evolution of acetic acid (model 1) or without (model 2). The low values of  $k_2$  might be qualitatively attributed to the high melt viscosity of PBT.

A comparison of the uncatalyzed and catalyzed plots indicates that the difference between the two plots is mainly quantitative. No breaks are found in these plots. The uncatalyzed reactions exhibit no appreciable improvement in the average degree of polymerization.

Comparison of Tables I and II indicates that  $k_1$  is higher than  $k_2$  for the uncatalyzed and catalyzed PBT 30 mol % and PBT 50 mol % reactions. For PBT 70 mol %, the magnitude of the rate constant  $k_2$  is more than twice than that of  $k_1$ . This could possibly be due to faster incorporation of dimer segments into a large

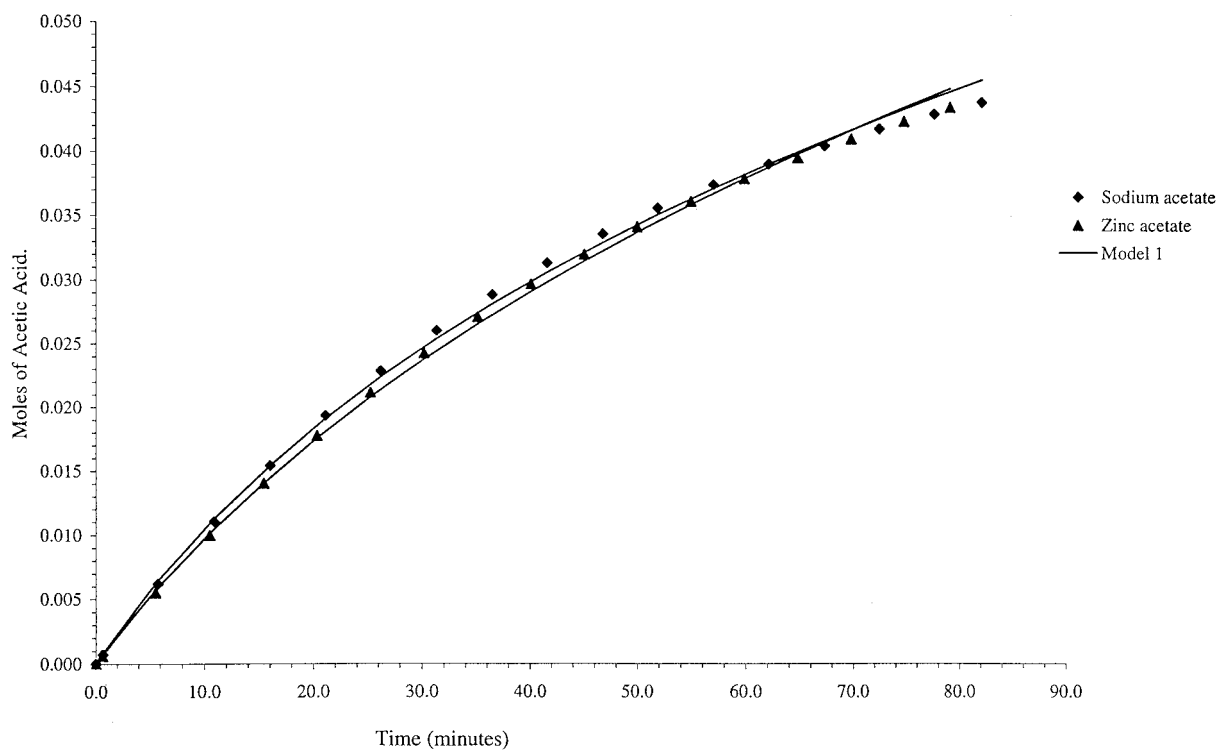




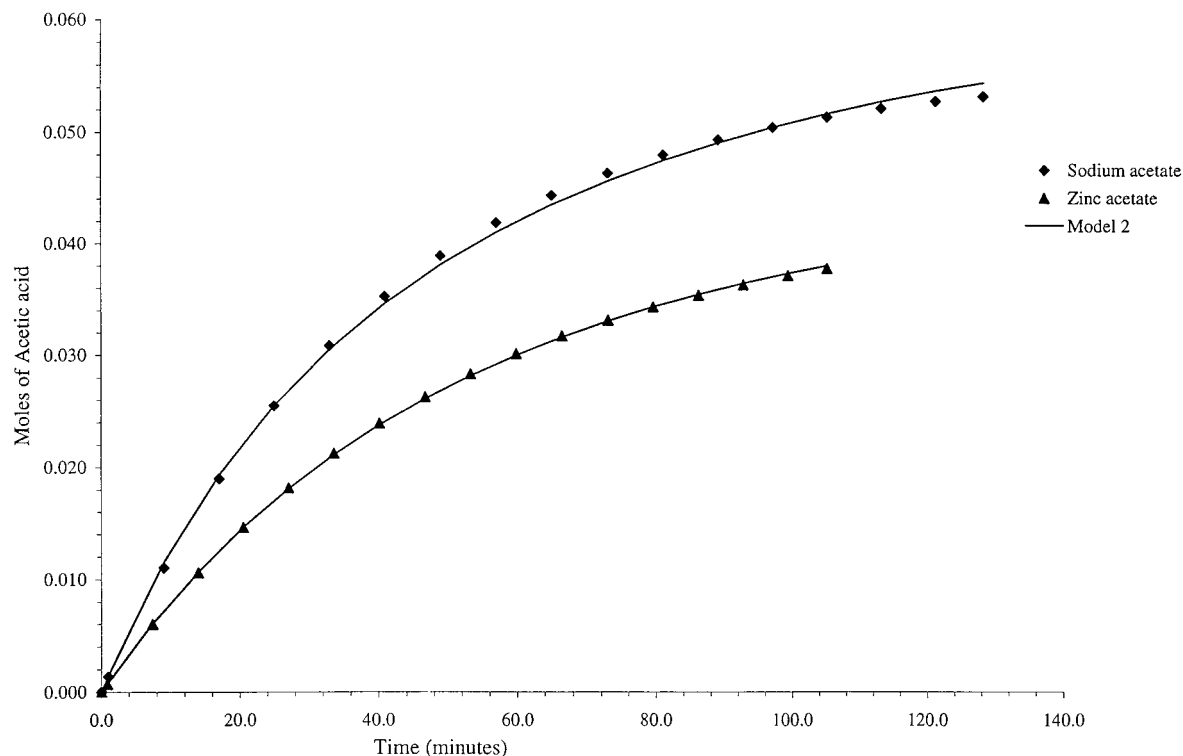
**Figure 9** Second-order plot for sodium acetate (1 mol %) catalyzed PBT 30 mol % / (1,4 NDCA + HQDA) 70 reactions.

quantity of PBT. Both models indicate the highest  $k_1$  value is for zinc acetate catalyzed PBT 70 mol % reactions.

The rate constants  $k_1$  and  $k_2$ , representing the homo- and copolymerization reactions, are indicated in Tables I and II. Comparison of the rate constant values of



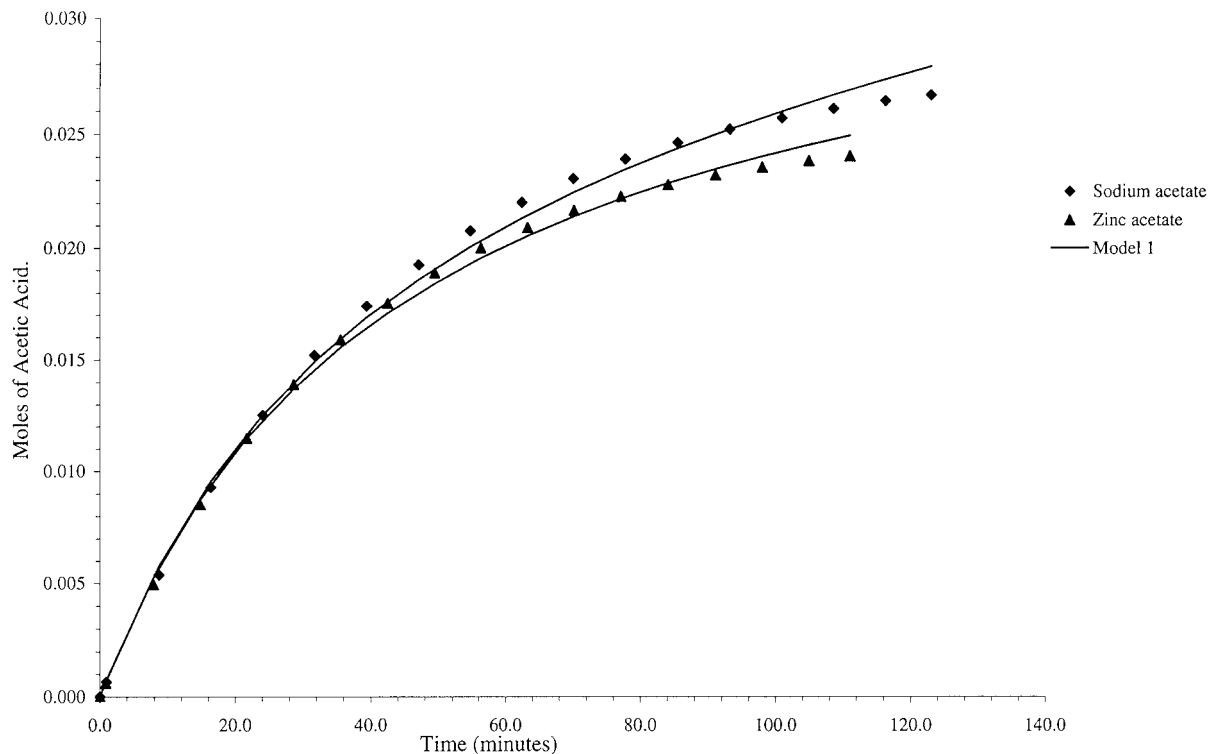
**Figure 10** Second-order plot for different catalysts (1 mol % concentration) variation for PBT 50 mol % / (1,4 NDCA + HQDA) 50 reactions at 280°C.



**Figure 11** Second-order plot for different catalysts variations (1 mol % concentration) for PBT 30 mol %/(1,4 NDCA + HQDA) 70 reactions at 265°C.

the uncatalyzed and catalyzed PBT 30 mol % indicates that the values are low for uncatalyzed reactions. The  $k_2$  values are found to be zero. The reason for this could not be explained.

Before considering the temperature variation of the rate constants, it is important to check whether diffusion will mask the true activation energies. In these reactions, the melt-phase viscosities are fairly high



**Figure 12** Second-order plot for different catalyzed PBT 70 mol %/(1,4 NDCA + HQDA) 30 reactions at 280°C.

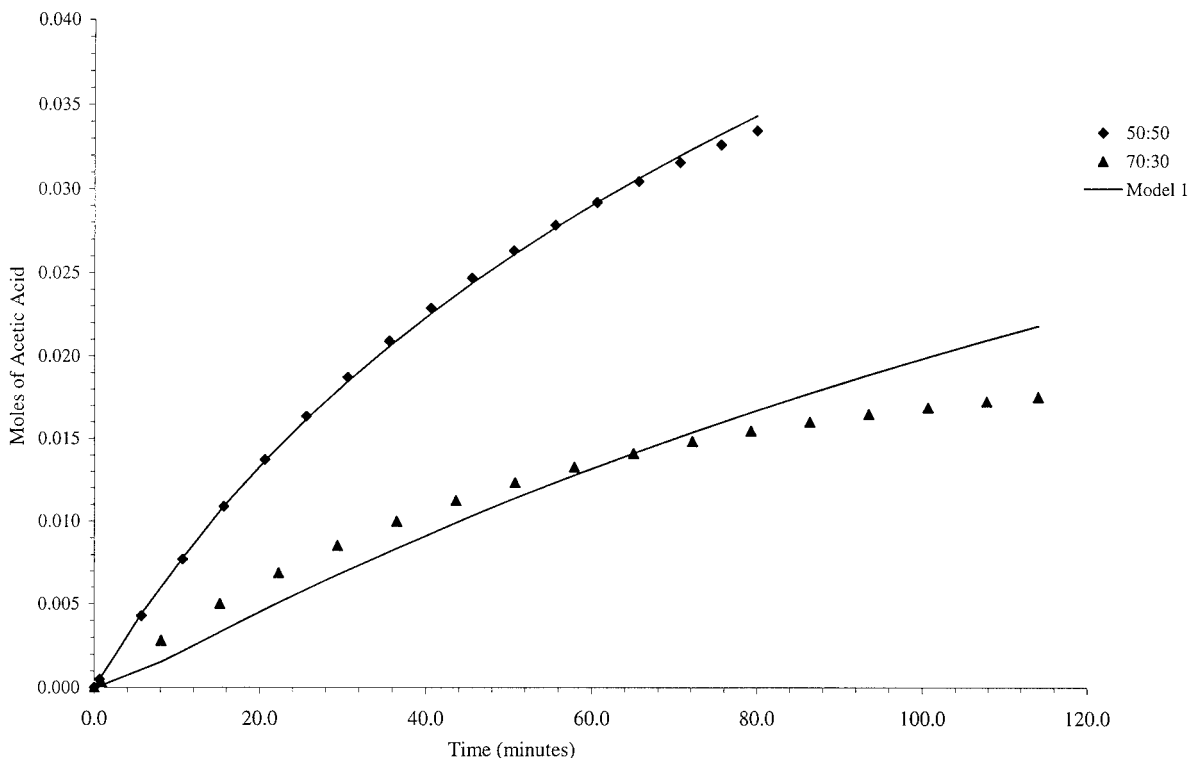


Figure 13 Second-order plot for uncatalyzed composition variation at 260°C.

and in such cases the diffusivities are inversely proportional to the viscosity. If the melt reaction is a diffusion-controlled process, then it can be expected

that there will be a lowering of activation energy (slope) signaling the transition to a diffusion-controlled regime. There is no observance of such behav-

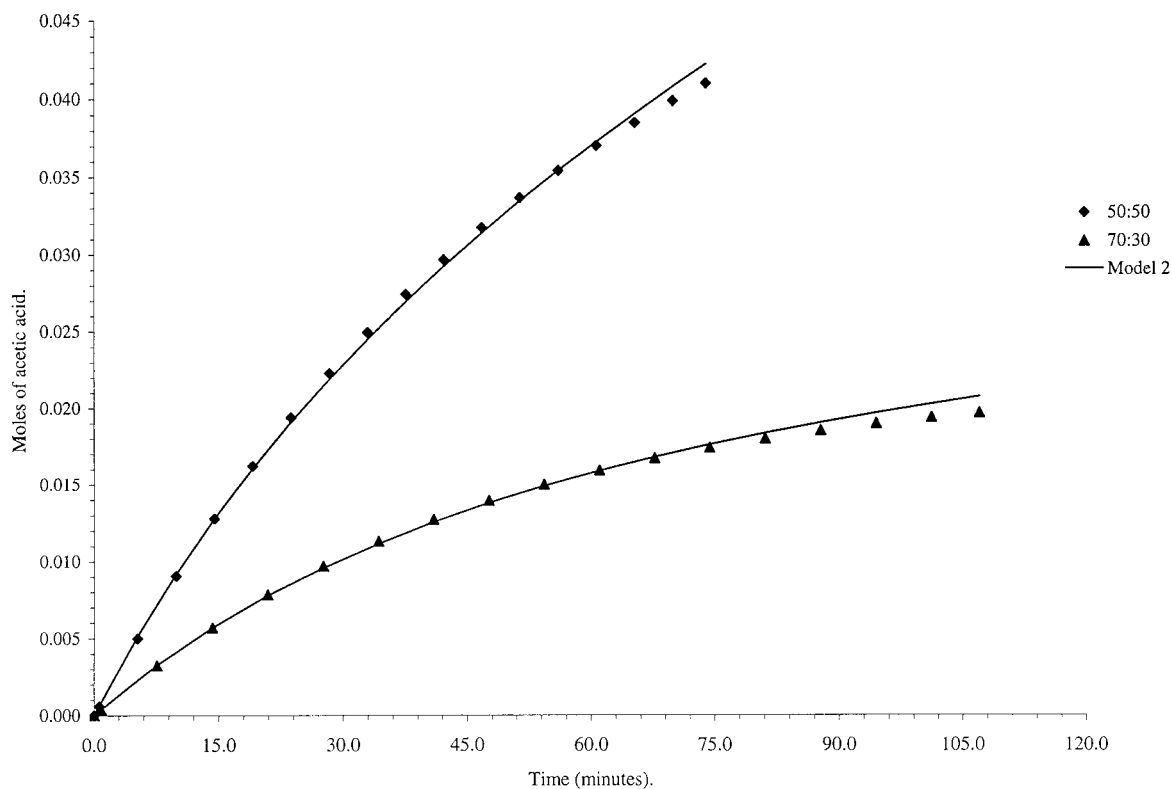
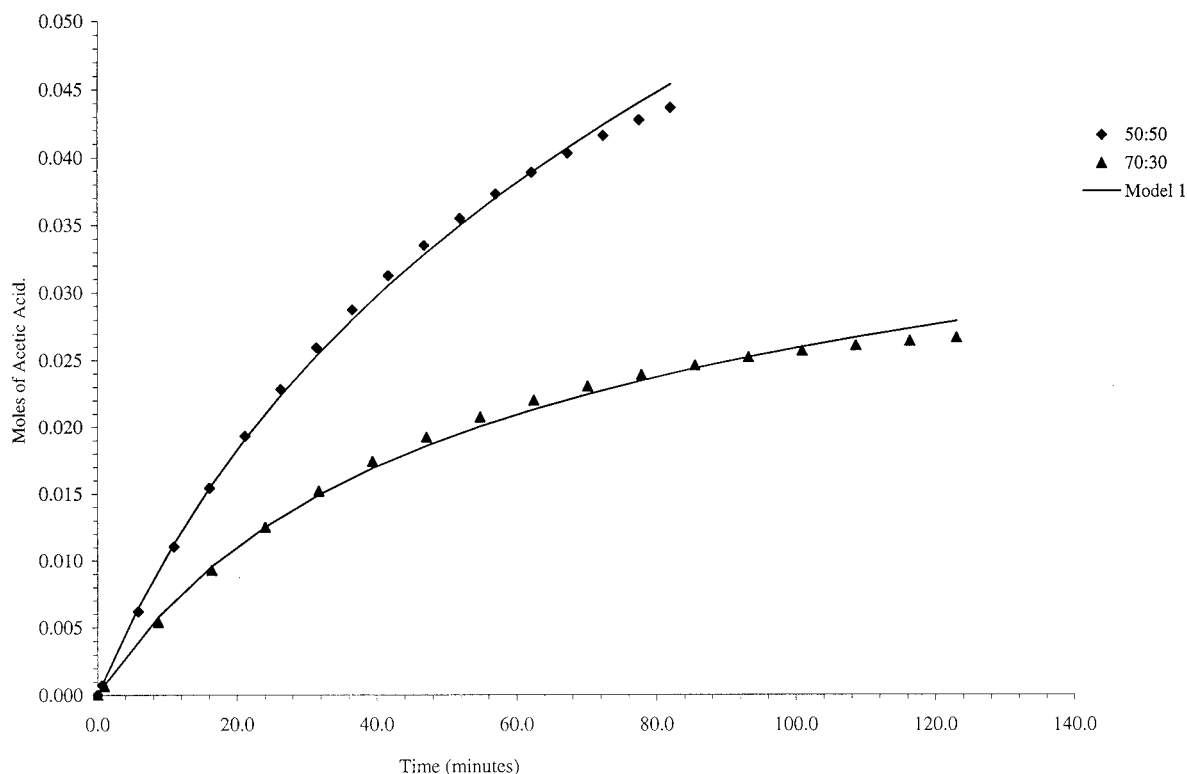


Figure 14 Second-order plot illustrating uncatalyzed compositions variations at 270°C.



**Figure 15** Second-order plot illustrating composition variations at 260°C for 1 mol % sodium acetate catalyzed reactions.

ior in the Arrhenius plots (Figs. 16-18), indicating that the reaction rate is not influenced by diffusion. This assumption will be confirmed in further experimentation by the authors.

Values of the correlation coefficient ( $R^2$ ) for all the Arrhenius plots are greater than 0.93. Only three temperatures are available for experimentation. The copolyesterification reaction between PBT 50 mol %/(1,

**TABLE I**  
Values of Kinetic Parameters Obtained Using Model Number 1

Composition (mol %)	Temperature (°C)	Catalyst type	$k_1$ (L/mol S)	$k_2$ (L/mol S)	$E_1$ (kJ/mol)	$R^2$
30 PBT	245	—	0.041	0		
30 PBT	255	—	0.0602	0	Uncat 92	0.99
30 PBT	265	—	0.0914	0		
30 PBT	245	NaC	0.0802	0		
30 PBT	255	NaC	0.1297	0	Cat 108	0.98
30 PBT	265	NaC	0.2038	0		
30 PBT	265	ZnC	0.1176	0		
50 PBT	260	—	0.2419	0.0175		
50 PBT	270	—	0.3072	0.0569	Uncat 30	0.93
50 PBT	280	—	0.309	0.0459		
50 PBT	260	NaC	0.2972	0.0363		
50 PBT	270	NaC	0.3132	0.0407	Cat 23	0.95
50 PBT	280	NaC	0.3576	0.0411		
50 PBT	280	ZnC	0.3237	0.0552		
70 PBT	260	—	0.1181	1		
70 PBT	270	—	0.1478	1	Uncat 50	0.98
70 PBT	280	—	0.1779	1		
70 PBT	260	NaC	0.3355	0.0083		
70 PBT	270	NaC	0.1534	1	Cat 81	0.99
70 PBT	280	NaC	0.2251	1		
70 PBT	280	ZnC	0.6519	0		

—, uncatalyzed reaction; NaC, sodium acetate; ZnC, zinc acetate.

**TABLE II**  
Values of Kinetic Parameters Obtained Using Model Number 2

Composition (mol %)	Temperature (°C)	Catalyst type	$k_1$ (L/mol S)	$k_2$ (L/mol S)	$E_1$ (kJ/mol)	$R^2$
30 PBT	245	—	0.049	0.0697		
30 PBT	255	—	0.0729	0.578	Uncat 90	0.96
30 PBT	265	—	0.1065	0.0574		
30 PBT	245	NaC	0.1105	0.0842		
30 PBT	255	NaC	0.1342	0.0195	Cat 76	0.98
30 PBT	265	NaC	0.2139	0.0111		
30 PBT	265	ZnC	0.1281	0.0346		
50 PBT	260	—	0.2593	0		
50 PBT	270	—	0.3525	0	Uncat 50	0.97
50 PBT	280	—	0.3506	0		
50 PBT	260	NaC	0.3278	0		
50 PBT	270	NaC	0.3604	0	Cat 37	0.98
50 PBT	280	NaC	0.4106	0		
50 PBT	280	ZnC	0.3768	0		
70 PBT	260	—	0.326	0.009		
70 PBT	270	—	0.4032	0.0034	Uncat 72	0.98
70 PBT	280	—	0.5879	0.0045		
70 PBT	260	NaC	0.3598	0		
70 PBT	270	NaC	0.3646	0	Cat 50	0.94
70 PBT	280	NaC	0.7016	0		
70 PBT	280	ZnC	0.6527	0.0004		

—, uncatalyzed reaction; NaC, sodium acetate; ZnC, zinc acetate.

4 NDCA + HQDA) 50 and PBT 70 mol %/(1, 4 NDCA + HQDA) 30 was carried out at 260, 270, and 280°C and for PBT 30 mol %/(1,4 NDCA + HQDA)70 the temperature was 245, 255, and 265°C. The choice of these temperatures was of necessity to prevent degradation reactions occurring in the different compositions.

The  $R^2$  values, corresponding to the correlation coefficients for the determination of the activation energy values, are reported in Tables I, II, and III. These values ranged between 0.93 and 0.98, indicating a significant fit of the data.  $r$  is the correlation coefficient which is equal to  $\sqrt{r^2}$  and  $r = r^2 = 1$ , signifying that the line explains 100% of the variability of the data. It is to be recalled that a value of 1.0 for  $R^2$  signals a perfect fit.

The catalyzed and uncatalyzed Arrhenius plots for model 1 and 2 are shown in Figures 16 and 17. The

minor change in the slope in each of these two plots suggests that the catalyst plays a marginal role in enhancing the reaction rate.

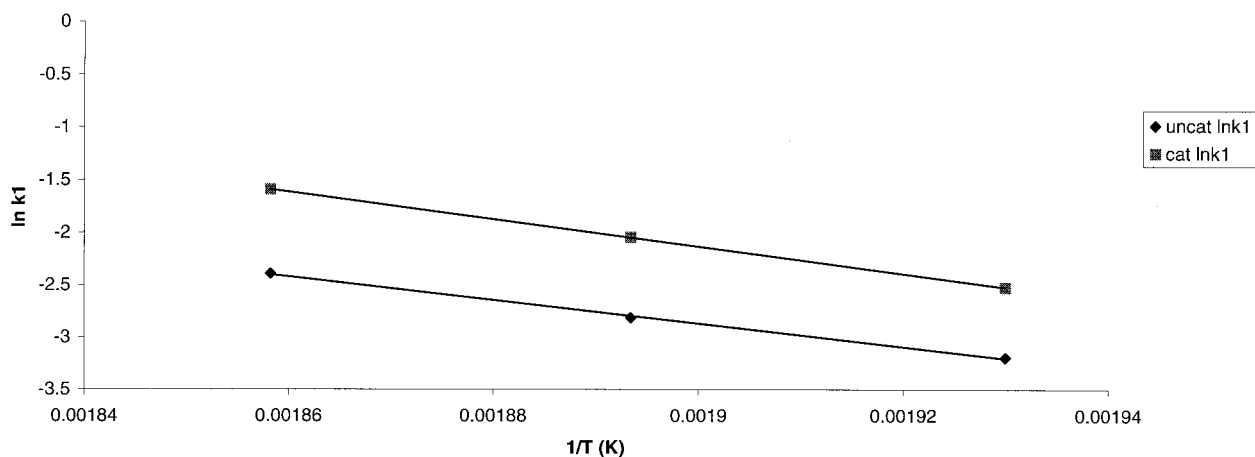
Figure 18 is a typical Arrhenius plot for PBT50 mol %/(1,4 NDCA + HQDA) 50 using model number 1. A glance at Tables I and II indicates that the activation energy values for a few catalyzed runs are actually larger than the uncatalyzed reactions, while the rate constants are found to be numerically similar. The selected catalysts thus do not play a major role in enhancing the rate of reaction.

We observe some abnormalities in the activation energies in model number 1 where the activation energy ( $E_1$ ) is larger in the case of catalyzed reactions than uncatalyzed reactions in two cases (30 PBT and 70 PBT). In light of the narrow range of temperatures

**TABLE III**  
Values of Kinetic Parameters of Homopolymer

Composition (mol %)	Temperature (°C)	Catalyst type	$k_1$	$k_2$	$k_3$	$k_4$	$E_1$ (kJ/mol)	$R^2$	$E_2$ (kJ/mol)	$R^2$
hq 1, 4	240	—	0.0435	0.0264	0	0				
hq 1, 4	250	—	0.0505	0.0428	0.0647	0				
hq 1, 4	260	—	0.0556	0.0542	0	0.0017				
hq 1, 4	240	NaC	0.0558	0.0171	0	0	Uncat 28	0.95	Uncat 82	0.97
hq 1, 4	250	NaC	0.0484	0.0532	0	0	Cat 12	0.96	Cat 73	0.06
hq 1, 4	260	NaC	0.0619	0.0326	0	0.0061				
hq 1, 4	260	ZnAc	0.0515	0.0536	0	0.0138				

—, uncatalyzed reaction; NaC, sodium acetate; ZnC, zinc acetate.

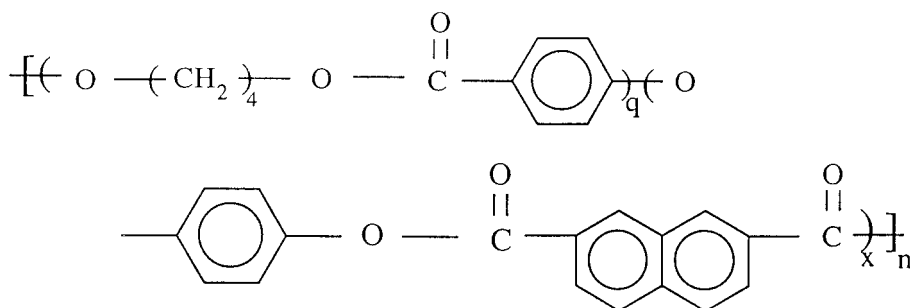


**Figure 16** Arrhenius plot for sodium acetate catalyzed and uncatalyzed rate constant ( $k_1$ ) using model 1 for PBT 30 mol %/(1,4 NDCA + HQDA) 70 compositions.

available for the reaction (245–280°C), further investigation could now be undertaken to investigate this phenomena. Future work is planned to investigate this abnormality.

### Characterization

The entities present in the copolyester can be depicted by the following global structure:



Here  $q$  and  $x$  represent the mole percents of PBT and HQDA + 1,4 NDCA units along the chain. For the composition of PBT 50 mol % (1,4 NDCA + HQDA) 50, the structures would resemble a rigid-rod flexible spacer-type thermotropic system constituting a triad mesogen with carboxylic groups coupled to 1,4 butane diol. At lower (<50) mole percentages of HQDA + 1,4 NDCA, the mesogen is diluted at the cost of PBT moieties.

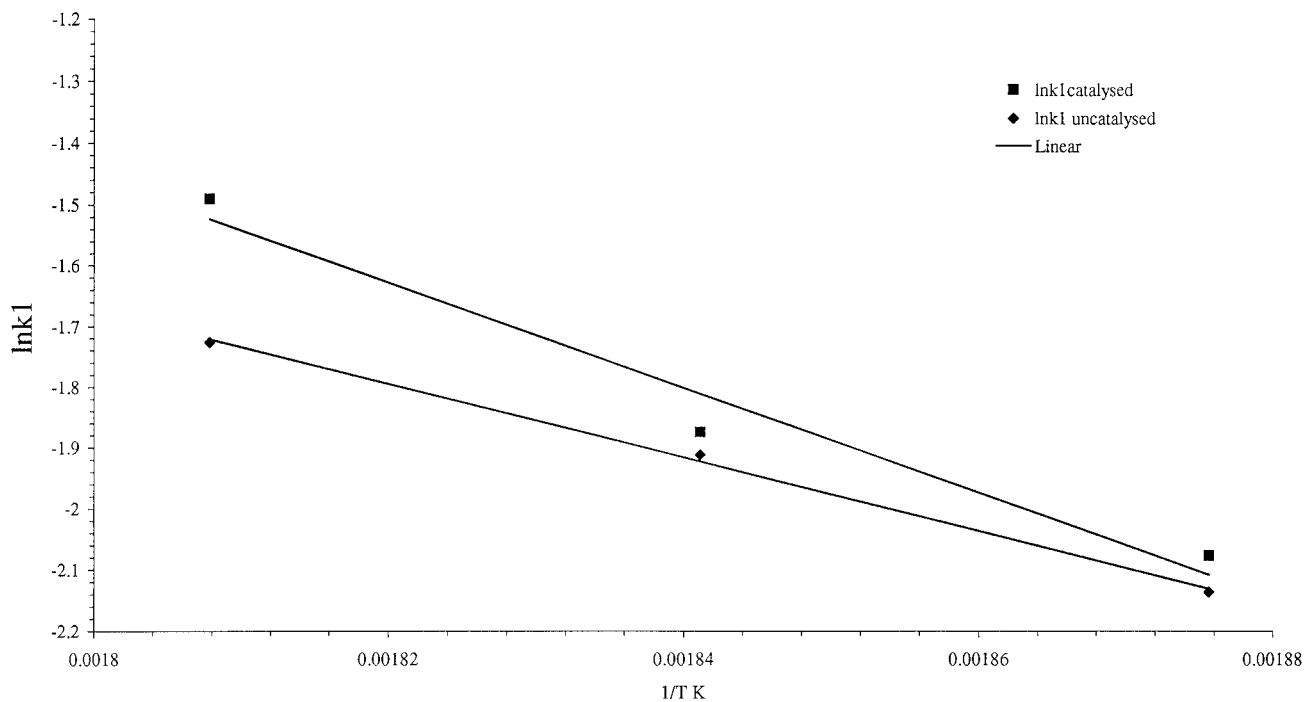
Above 50 mol % of HQDA + 1,4 NDCA in the copolyester, the averaged mesogen length increases and consists of less dibutylene units of 1,2 butane diol. At sufficiently high (>60) mole percentages of HQDA + 1,4 NDCA, the averaged mesogen formed is non-melting and the thermotropic character would disappear.

Figures 19 and 20 are two first-order differential scanning transitions for PBT and a typical composition of PBT 70 mol %/(1, 4 NDCA + HQDA) 30. Figure 19 indicates that PBT melts at 230°C and on cooling the endotherm is reversed at 174°C. The

PBT-1,4 NDCA–HQDA polymers were heated at a rate of 20°C/min from room temperature to 300°C. The samples were then cooled at a rate of 20°C/min. On incorporation of the dimer into PBT, the melting transition of PBT is reduced to 210°C, thus making the PBT copolyester more amenable to processing.

### CONCLUSION

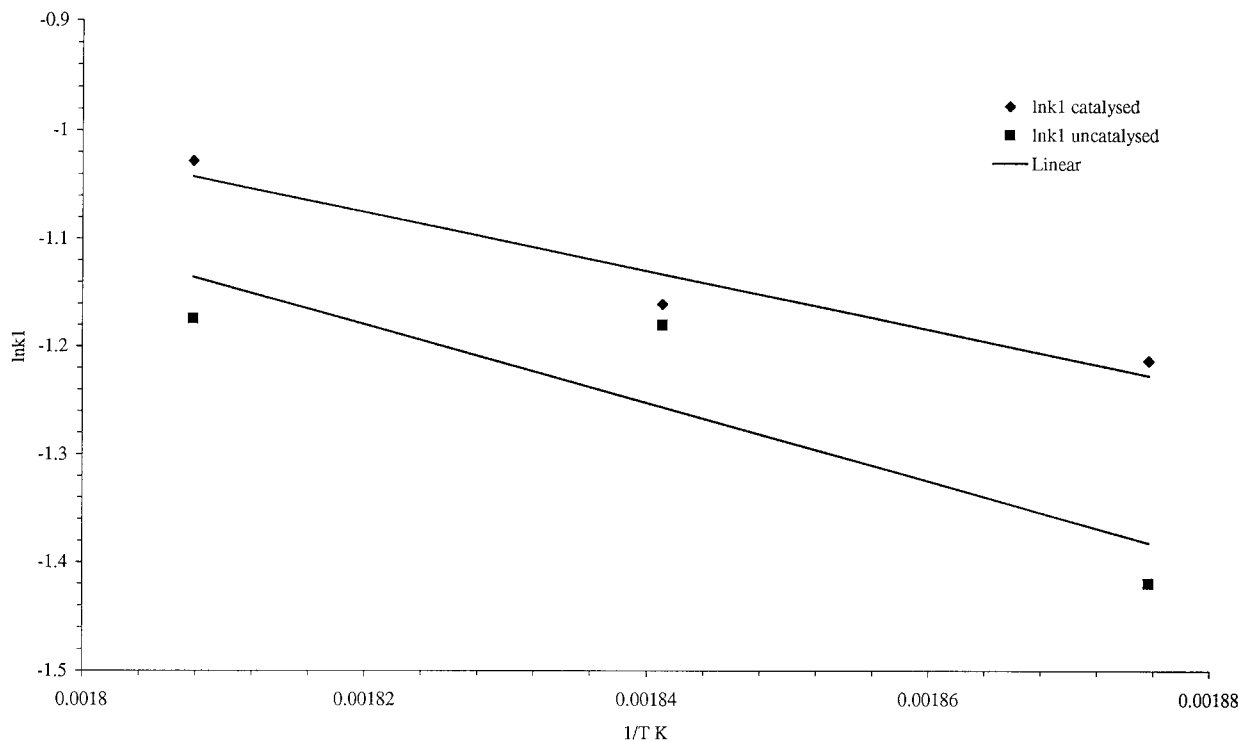
The kinetics of PBT–1, 4 NDCA–HQDA system were analyzed. The kinetic analysis was expected to be complex because of the possibility of several reactions occurring in parallel. However, to make the analysis tractable, two different models with few assumptions were made. In model number 1, it is assumed that HQDA and 1, 4 NDCA combine to form a dimer, producing acetic acid as a byproduct. This dimer then copolymerizes with the PBT chain to form random copolyesters with the liberation of acetic acid. In model number 2, it is assumed that HQDA reacts with 1, 4 NDCA with the production of acetic acid, while



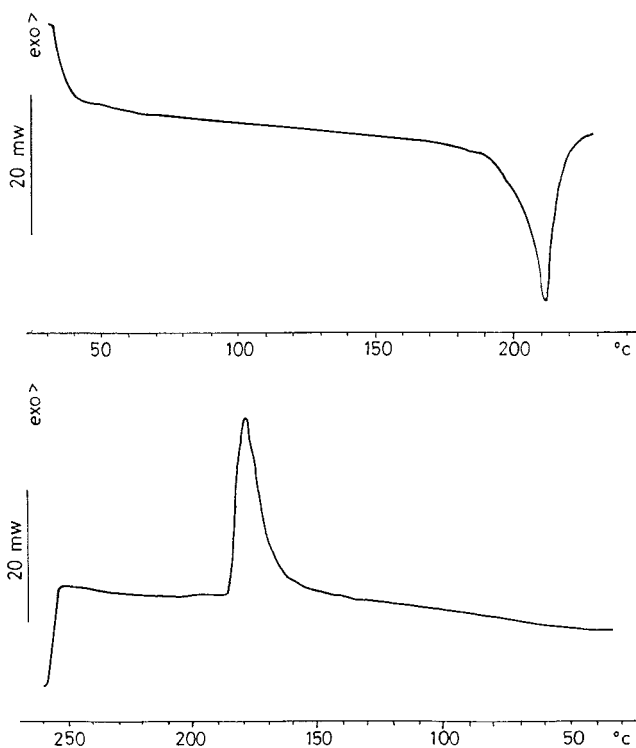
**Figure 17** Arrhenius plot for sodium acetate catalyzed and uncatalyzed rate constant ( $k_1$ ) using model 2 for PBT 70 mol %/(1,4 NDCA + HQDA) 30 compositions.

the dimer formed in the later reaction gets attached to PBT without the liberation of acetic acid. To retain the simplicity in both models, the key assumptions and

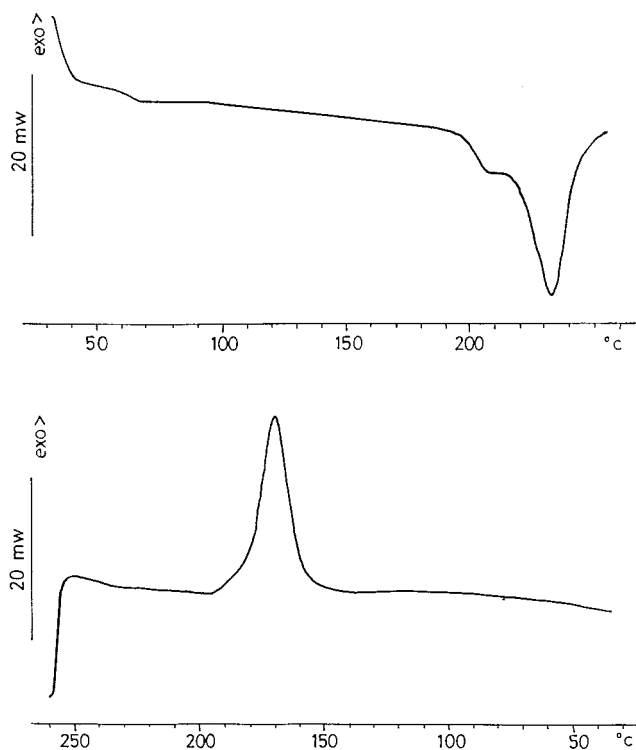
possibilities considered were (1) HQDA and 1, 4 NDCA react to form a dimer and (2) the dimer subsequently gets attached to a PBT chain.



**Figure 18** Arrhenius plot for sodium acetate catalyzed and uncatalyzed rate constant ( $k_1$ ) using model 1 for PBT 50 mol %/(1,4 NDCA + HQDA) 50 compositions.



**Figure 20** Typical DSC endotherms for uncatalyzed PBT 70 mol %/(1,4 NDCA + HQDA) 30 for the heating (top) and cooling cycle.



**Figure 19** DSC endotherms for virgin grade PBT for the heating (top) and cooling cycle.

Kinetically, both the models were assumed and shown to be of second order with respect to the reactants. In the second reaction of both models, the concentrations of PBT repeat units and dimer figure as a product. In principle, other reactions can also give rise to acetic acid in both models, such as dimer reacting with HQDA or 1, 4 NDCA. The probabilities for these processes are considered to be small in comparison to the main reaction postulated above. In short, the latter reactions are considered to be extremely slow, and hence, assumed to be of less consequence in the overall mass balance. An important finding in this work is that each model gives  $k_1$  and  $k_2$  values for a specific composition. Model number 1 is found to give  $k_1$  and  $k_2$  values for PBT 50 mol %/(1, 4 NDCA + HQDA) 50 and PBT 70 mol %/(1, 4 NDCA + HQDA) 30. The rate constant ( $k_2$ ) for PBT 50 mol % is found to be lower than  $k_1$ , while the  $k_2$  values for PBT 70 mol % is found to be more than twice the value of  $k_1$ . These  $k_2$  values possibly signify the rate of incorporation of the dimer into PBT. No  $k_2$  values are found for PBT 30 mol %, possibly indicating the formation of block copolymers. Model number 2 (Table II) shows no  $k_2$  values for PBT 50 mol % and PBT 70 mol %.

The authors thank the Research Administration of Kuwait University for the funds provided from Project EC 01/00 to carry out this research work. They are also grateful to Dr. A. R. Khan, Dr. J. Mathew, and Eng. Younis Hussain from the Chemical Engineering Department, Kuwait University for the professional help rendered in this work.

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