

Synthesis and Kinetic Analysis of 1,4-Naphthalene-di(carboxylic acid) and Hydroquinone Diacetate Based Homopolyesters

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ABSTRACT: A variety of high temperature liquid crystalline polymers can be developed using the homopolyester of 1,4-naphthalene di(carboxylic acid) (1,4-NDCA) and hydroquinone diacetate (HQDA) as a spacer. In such cases the monomer 1,4 NDCA acts as a kink. Kinetic studies of the synthesis of homopolyesters by melt polymerization using 1,4-NDCA and hydroquinone diacetate (HQDA) are reported. The performance of two transesterification catalysts are estimated for this system. In this study, initial stage polymerization kinetics of the homopolyesters were examined. The side product, acetic acid, evolved in the homopolymerization of 1,4-NDCA and HQDA, was used to estimate the progress of the reaction. The polycondensations were found to obey second order kinetics, regardless of whether the reaction was catalyzed or uncatalyzed.

A set of twelve differential equations containing four different rate constants, k_1 , k_2 , k_3 and k_4 has been developed and computed, to study the initial stage kinetics. The computed values of acetic acid are compared with the experimentally collected amounts, and the four rate constants are optimized using a differential algebraic optimization technique. The present model represents the data with an acceptable accuracy and with an average percentage error of less than 5% for the entire experimental range. The correlation coefficient values range from 0.95 to 0.99 for all experimental data. The kinetic constants and activation energy values are reported.

Differential scanning calorimetric (DSC) analysis of the homopolyesters indicate that 1,4 NDCA-HQDA had the highest melting temperature, around 350°C. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 1808–1817, 2003

INTRODUCTION

Discovery of wholly aromatic main chain lyotropic liquid crystalline polymers in the research laboratories of DuPont¹ triggered intensified research directed toward the evolution of main chain thermotropic systems. Here, a number of strategies have been employed to lower aspect ratios in wholly aromatic systems so as to lower the liquid crystalline transition temperatures to such a level that organized phases are displayed prior to degradation.² Another, perhaps only marginally less significant, approach has been to increase the aspect ratio in the thermoplastic systems through the incorporation of rigid and collinear structural moieties.³ The commercialized systems in the former category are copolyesters from (i) 4-hydroxy(benzoic acid); 4,4'-dihydroxybiphenyl, and terephthalic acid and (ii) 4-hydroxy(benzoic acid) and 6-hydroxy-2-(naphthoic acid). The most prominent system related to the latter group is the copolyester of poly(ethylene terephthalate) and 4-acetoxy(benzoic acid) (PET-

oxybenzoate). These systems have predominantly random structures. The academic research in this field has overwhelmingly stressed the synthesis of novel mesogens, with aspect ratios ranging between 3 and 6.4, which are coupled through aliphatic spacers to form ordered rigid rod-flexible spacer type polymer systems. The most significant of these have been the substantial contributions by Lenz's group relating to the synthesis of a sweeping variety of thermotropic structures and establishing thermal property correlations.^{4–15}

The copolyester PET-oxybenzoate was synthesized by Jackson et al.³ through high temperature melt transesterification. However, intricate details pertaining to the polyesterification kinetics have remained unexamined. In this system, insertion of 4-oxybenzoate moieties, with stiff rodlike conformations, into flexible PET chains fosters the development of thermotropic character within a definitive range of copolyester composition. Structural elucidations have generated conflicting data for the latter system.

1,4-NDCA used as a monomer in the present system has a bulky phenyl substituent that can act as a kink and disrupt crystallinity in rigid rod systems. 1,4-NDCA and HQDA monomers also react to form polymers with high melting temperatures.

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The foregoing discussion clearly shows that while there is considerable information available on the structural and chemical properties of polymer systems, there is a total lack of kinetic information in the area of melt polymerization kinetics. There is a need to understand homopolyesterification kinetics, since precise control of the polymer properties and of the process productivity is one of the key issues in designing or optimizing the melt transesterification process.¹⁶

This work is an attempt to formulate a plausible kinetic model for the 1,4-NDCA-HQDA melt homopolyesterification reaction.

The work was carried with the following objectives: (i) to develop a mathematical model capable of analyzing the system which involves competitive parallel reactions generating a common byproduct (acetic acid); (ii) to determine the kinetic order with respect to the concentrations of both 1,4-NDCA and HQDA segments; (iii) to predict the rate of acetic acid production by assuming a definite sequence distribution for the homopolyester; (iv) to determine whether a procedure analogous to those involved in modeling solution kinetics can adequately describe melt polyesterification kinetics from a phenomenological point of view. To achieve the last objective, an elaborate rate model has been proposed.

The work is presented as follows. First a mathematical model capable of analyzing systems in which many competitive reactions occur is considered. The kinetic order is determined at various temperatures for both catalyzed and uncatalyzed runs to determine whether kinetic order changes with catalyst. A realistic reaction model accounting for all of the possible reaction sequences leading to a maximum average degree of polymerization of four will be shown to result in kinetic expressions which lead to a realistic kinetic model. Lastly, physico-chemical characterization of 1,4-NDCA-HQDA homopolyesters using differential scanning calorimetry is considered.

EXPERIMENTAL

Materials

HQDA and 1,4-NDCA were purchased from MDA Chemicals, Lancaster, UK. Differential scanning calorimeter was used to determine the melting temperature 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.

Melt polymerization

A 250 ml Hastelloy-B2-based, electrically heated reactor was used for the melt transesterification kinetics, as indicated in Figure 1.

Preparation of polymers

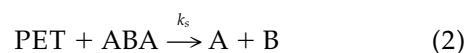
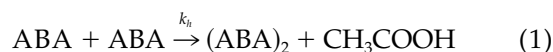
The transesterifications were conducted with the objective of analyzing the kinetics in the initial stage of the reaction, wherein the distillation of the side product, acetic acid, was complete under atmospheric pressure. Reactions were conducted to study the kinetics at different temperatures. Homopolyesterification kinetics were investigated at equal mole ratios of the reactants (HQDA : 1,4-NDCA). The melting temperature of HQDA and 1,4-NDCA has limited the temperature range for kinetic experimental investigations. The isothermal temperatures (240, 250 and 260°C) chosen for the kinetic estimations were determined after many trial experiments. A dry nitrogen blanket was maintained throughout the experiments to prevent oxidative degradations. The rate of evolution of the side product, acetic acid, was monitored volumetrically to estimate the kinetic parameters. HQDA lost due to sublimation was monitored and was found to be less than 0.075 mol % of the initial reactant charged. Therefore, no correction was made for loss in the overall mass balance. The purity of the acetic acid formed was estimated at different isothermal kinetic temperatures. It was found to be around 95% at lower temperatures and 93% at higher temperatures. The maximum conversion noted, based on moles of acetic acid, was 75%. The light tan and opaque homopolyesters were powdered and acetone extracted to remove unreacted initial reactants, if present, prior to the characterization.

Measurements

Thermal transitions were obtained with a Mettler DSC 30 apparatus interfaced with a thermal analysis data station under a nitrogen atmosphere using a sample size of 10–15 mg. A heating rate of 20°C/min was employed in all cases. Indium was used to calibrate the enthalpy values. A reference sampling containing (In-Pb-Zn) was used to calibrate the temperature scale. Samples were analyzed in the temperature range of 40 to 400°C in the heating cycle and cooling cycles.

Kinetic model

Mathew et al.¹⁷ have proposed a simple, second order kinetic model for the transesterification of 4-acetoxybenzoic acid (ABA) and poly(ethylene terephthalate) (PET). The consumption of ABA was found to be mainly due to homo and copolymerization reactions:



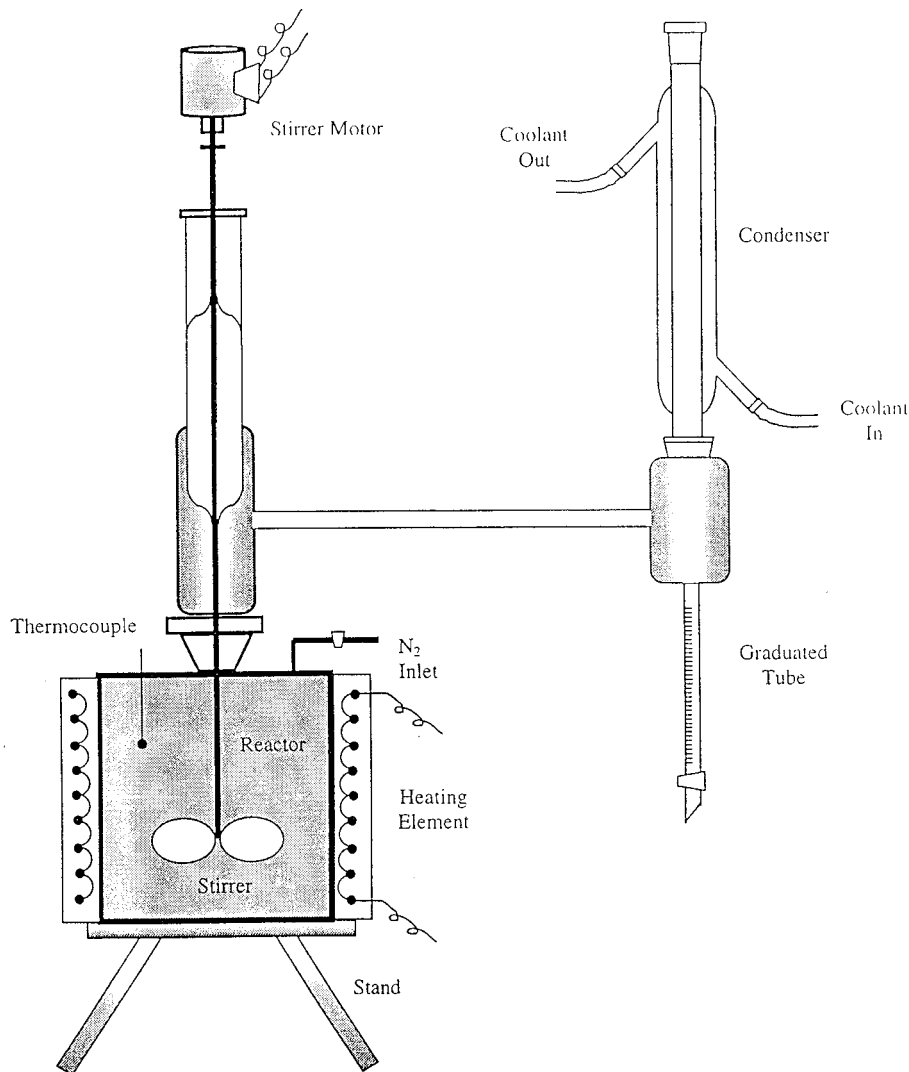
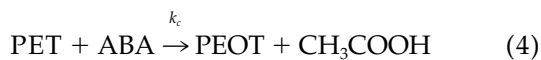


Figure 1 : Experimental setup.



Here, k_h , k_s and k_{fi} are the rate constants for homopolymerization, PET chain scission, and chain re-formation with the insertion of an oxybenzoate unit, respectively. Species A and B are intermediate in nature. These are generated as shown in reaction (2) and consumed as shown in reaction (3).

The result is given by the overall reaction:



where k_c is the net result of rate constants k_s and k_{fi} and PEOT is the homopolymer formed. The net result is given by the overall reactions:

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

and $[\text{PET}]$ is

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

Dividing equation (5) by equation (6) results in the following form:

$$\frac{d[\text{ABA}]}{d[\text{PET}]} = \frac{k_h}{k_c} \frac{[\text{ABA}]}{[\text{PET}]} + 1 \quad (7)$$

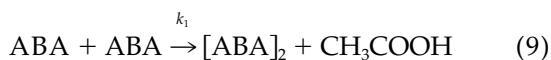
This equation is analytically solved with the initial conditions: $[\text{PET}] = [\text{PET}]_0$ and $[\text{ABA}] = [\text{ABA}]_0$

$$\text{Let } \frac{k_h}{k_c} = k_r$$

$$[\text{ABA}] = [\text{ABA}]_0 \left(\frac{[\text{PET}]}{[\text{PET}]_0} \right)^{k_h/k_c} + \frac{[\text{PET}]}{1 - k_h/k_c} \left(1 - \left[\frac{[\text{PET}]}{[\text{PET}]_0} \right] \right) \left(\frac{k_h}{k_c} \right)^{-1} \quad (8)$$

The concentration of ABA, designated [ABA], as function of [PET] can be substituted into equation (2) and solved numerically to yield [PET] at any time.¹⁸ The concentration of ABA can be back calculated from equation (8) to provide the extent of the reaction. The values of rate constants had to be optimized using a constrained non-linear optimization technique proposed by Rosenbrock¹⁹ to match the acetic acid yield, which was determined experimentally. This model fits well for short reaction times but failed to provide a comprehensive fit for the entire experimental time.

Another approach was suggested by Shaban and Mathew²⁰ for the copolyesterification of PET, hydroquinone diacetate, and terephthalic acid, treated as ABA. This analysis is based on two differential equations given as



Assuming conversion x in first reaction and y in the second,

$$\frac{dx}{dt} = k_1([\text{ABA}]_0 - x)^2 \quad (11)$$

$$\frac{dy}{dt} = k_2(x/2 - y)([\text{PET}]_0 - y) \quad (12)$$

where x and y are the converted concentrations of ABA and PET. These equations were numerically solved using the fourth order Runge Kutta Method reported by Chapra and Canale.¹⁸ The values of rate constants were evaluated using the constrained non-linear optimization technique¹⁹ by minimizing the objective function

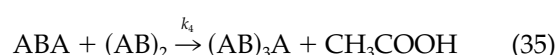
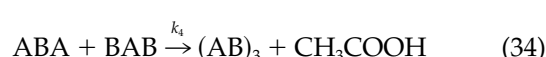
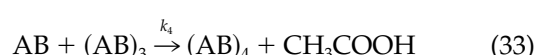
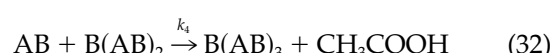
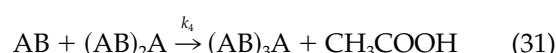
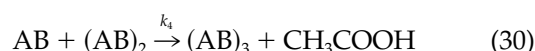
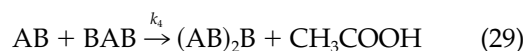
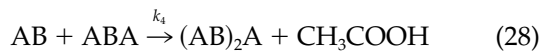
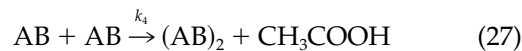
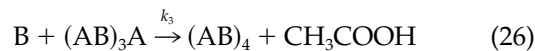
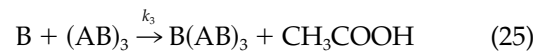
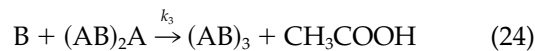
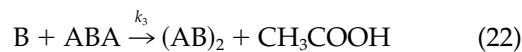
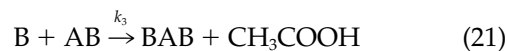
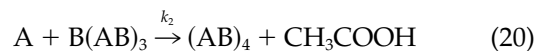
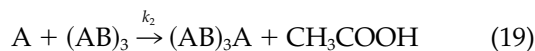
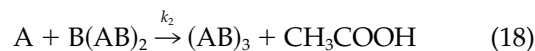
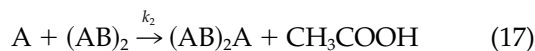
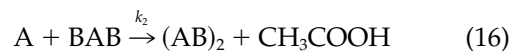
$$\sum_{i=1}^{N(\text{obs})} [\text{AC}_i - (x_i/2 + y_i)]^2 \quad (13)$$

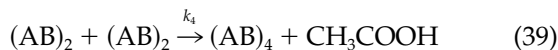
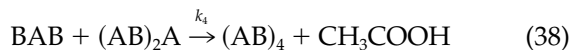
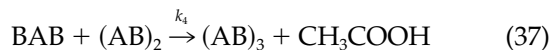
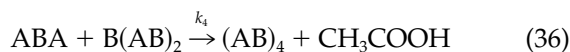
where AC_i is the experimentally collected amount of acetic acid at any time t .

In another kinetic work, Santacesaria et al.²¹ proposed 58 reactions and six rate expressions for melt

transesterification of dimethyl terephthalate with ethylene glycol.

In this work a new comprehensive kinetic model was tried successfully. This model hypothesizes the steps involved in the reaction mechanism of the transesterification of 1,4-NDCA and HQDA. If A and B represent HQDA and 1,4-NDCA, respectively, then the reactions sequence can be given as





The rate equations are as follows:

$$\begin{aligned} \frac{dP_1}{dt} = & -k_1(P_1)(P_2) - k_2(P_1)(P_3) - k_2(P_1)(P_5) - k_2(P_1)(P_6) \\ & - k_2(P_1)(P_8) - k_2(P_1)(P_9) - k_2(P_1)(P_{11}) \quad (40) \end{aligned}$$

$$\begin{aligned} \frac{dP_2}{dt} = & -k_1(P_1)(P_2) - k_3(P_2)(P_3) - k_3(P_2)(P_4) - k_3(P_2)(P_6) \\ & - k_3(P_2)(P_7) - k_3(P_2)(P_9) - k_3(P_2)(P_{10}) \quad (41) \end{aligned}$$

$$\begin{aligned} \frac{dP_3}{dt} = & -k_1(P_1)(P_2) - k_2(P_1)(P_3) - k_3(P_2)(P_3) - k_4(P_3)(P_3) \\ & - k_4(P_3)(P_4) - k_4(P_3)(P_5) - k_4(P_3)(P_6) - k_4(P_3)(P_7) \\ & - k_4(P_3)(P_8) - k_4(P_3)(P_9) \quad (42) \end{aligned}$$

$$\begin{aligned} \frac{dP_4}{dt} = & -k_2(P_1)(P_3) - k_3(P_2)(P_4) - k_4(P_3)(P_4) - k_4(P_4)(P_5) \\ & - k_4(P_4)(P_6) - k_4(P_4)(P_8) \quad (43) \end{aligned}$$

$$\begin{aligned} \frac{dP_5}{dt} = & -k_2(P_1)(P_5) + k_3(P_2)(P_3) - k_4(P_3)(P_5) - k_4(P_4)(P_5) \\ & - k_4(P_5)(P_6) - k_4(P_5)(P_7) \quad (44) \end{aligned}$$

$$\begin{aligned} \frac{dP_6}{dt} = & -k_2(P_1)(P_5) - k_2(P_1)(P_6) + k_3(P_2)(P_4) - k_3(P_2)(P_6) \\ & + k_4(P_3)(P_3) - k_4(P_3)(P_6) - k_4(P_6)(P_4) - k_4(P_6)(P_5) \\ & - k_4(P_6)(P_6)/2 \quad (45) \end{aligned}$$

$$\begin{aligned} \frac{dP_7}{dt} = & -k_2(P_1)(P_6) - k_3(P_2)(P_7) + k_4(P_3)(P_4) \\ & - k_4(P_3)(P_7) - k_4(P_5)(P_7) \quad (46) \end{aligned}$$

$$\begin{aligned} \frac{dP_8}{dt} = & -k_2(P_1)(P_8) + k_3(P_2)(P_6) + k_4(P_3)(P_5) \\ & - k_4(P_3)(P_8) - k_4(P_4)(P_8) \quad (47) \end{aligned}$$

$$\begin{aligned} \frac{dP_9}{dt} = & -k_2(P_1)(P_8) - k_2(P_1)(P_9) + k_3(P_2)(P_7) - k_3(P_2)(P_9) \\ & + k_4(P_3)(P_9) + k_4(P_4)(P_5) \quad (48) \end{aligned}$$

$$\begin{aligned} \frac{dP_{10}}{dt} = & -k_2(P_1)(P_9) - k_3(P_2)(P_{10}) + k_4(P_3)(P_7) + k_4(P_4)(P_6) \quad (49) \end{aligned}$$

$$\begin{aligned} \frac{dP_{11}}{dt} = & -k_2(P_1)(P_{11}) - k_3(P_2)(P_9) + k_4(P_3)(P_8) + k_4(P_5)(P_6) \quad (50) \end{aligned}$$

$$\begin{aligned} \frac{dP_{12}}{dt} = & -k_2(P_1)(P_{11}) - k_3(P_2)(P_{10}) + k_4(P_3)(P_9) + k_4(P_4)(P_8) \\ & + k_4(P_5)(P_7) + k_4(P_6)(P_6)/2 \quad (51) \end{aligned}$$

where $P_1, P_2, P_3, P_4, P_5, P_6, P_7, P_8, P_9, P_{10}, P_{11}$ and P_{12} represent the concentration of A, B, AB, ABA, . . . (AB)₄, respectively. The total amount of acetic acid generated can be calculated as follows:

$$\begin{aligned} \text{Total acetic acid} = & P_3 + 2(P_4) + 2(P_5) + 3(P_6) + 4(P_7) \\ & + 4(P_8) + 5(P_9) + 6(P_{10}) + 6(P_{11}) + 7(P_{12}) \quad (52) \end{aligned}$$

The computed amount of acetic acid was compared with experimentally collected amount and four rate constants were optimized using a differential algebraic optimization technique reported in Amir Al-Haddad, et al.²²

Figure 2 illustrates the comparison of the theoretical acetic acid production with the experimental measurements for uncatalyzed 1,4-NDCA-HQDA reactions. Figure 2 shows that second order kinetics are followed for 1,4-NDCA-HQDA uncatalyzed reactions at 240, 250 and 260°C.

Mathew et al.¹⁷ plotted $\frac{1}{1-p}$ as a function of time to study the second order kinetics of the homopolymerization of poly(oxybenzoate). In this study, plots of $\frac{1}{1-p}$ versus time (Fig. 3) were made in order to obtain the second order rate constants. A break is noted in all the plots. As seen in the plot, simple second order kinetics was not found to be valid for the homopolymerization of 1,4-NDCA-HQDA uncatalyzed reactions. Figure 4 is a typical plot indicating the adherence of second order kinetics to catalyzed reactions.

The data can be classified into two different types: (i) those emanating from variation in temperature as presented in Figures 2 and 4 and (ii) those obtained at a constant temperature (260°C) with variations in catalyst type (Fig. 5).

A common feature in all of these plots is the general adherence to second order kinetics, which is fairly well obeyed.

No major differences in rate constant values are noted between the catalyzed and uncatalyzed experiments, indicating that sodium acetate is not a promising catalyst for this reaction. k_1 in the rate equation indicates depletion of the monomers, HQDA and 1,4-NDCA. k_2 indicates the depletion of HQDA after reaction with the oligomers and k_3 represents the depletion of 1,4-NDCA with the oligomers. k_4 indicates the consumption of dimers and trimers. The uncatalyzed values of k_1 are greater than those of k_2 . The highest values of k_1 and k_2 are obtained at the maximum temperature of 260°C for both the catalyzed and uncatalyzed reactions. Arrhenius plots indicating the match between the experimental data points and the

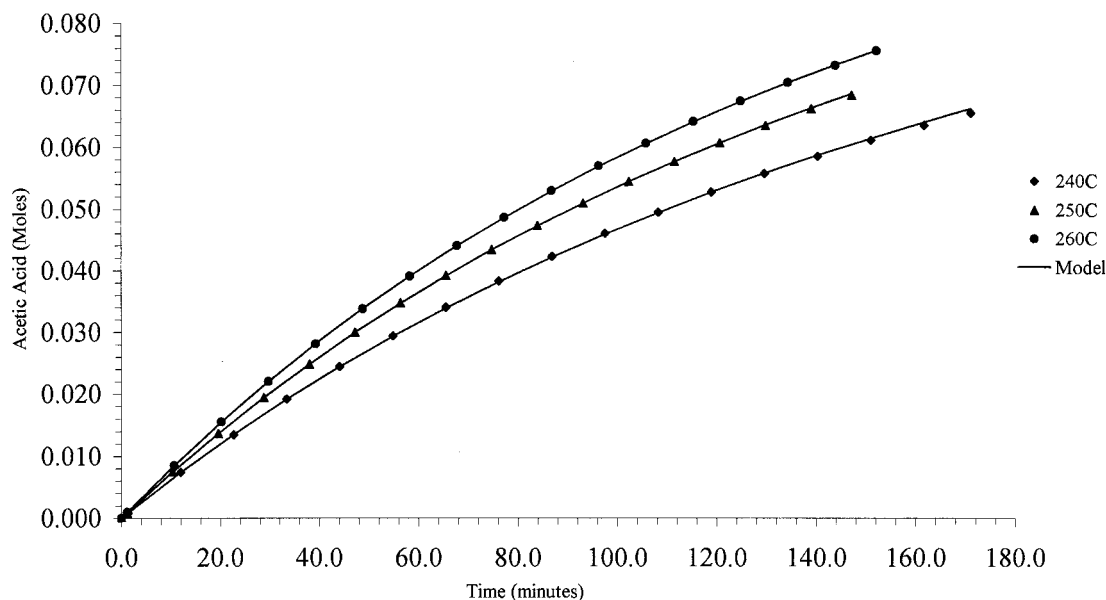


Figure 2 Second order plot for uncatalyzed 1,4-NDCA-HQDA reactions.

second order model are presented in Figures 6 and 7. The R^2 values of these plots are found to be greater than 0.95 (Table I). The energy of activation (E_1 and E_2) for the rate constants k_1 and k_2 are also listed in Table I.

The activation energy values in Table I indicate that sodium acetate is a good catalyst for this system.

Polymer characterization

The low molecular weight oligomers obtained were pale yellow in color. No sign of degradation was noted.

Differential scanning calorimeter (DSC) thermograms of the first heating cycle for 1,4-NDCA-HQDA

(50 : 50 mol % composition) is shown in Figure 8. The first heating cycle consisted of heating the sample to 400°C at a rate of 20°C/min. The thermogram consists of a melting endotherm at 294°C and another melting endotherm with a shoulder at 350°C.

The entities present in the copolyester can be given as

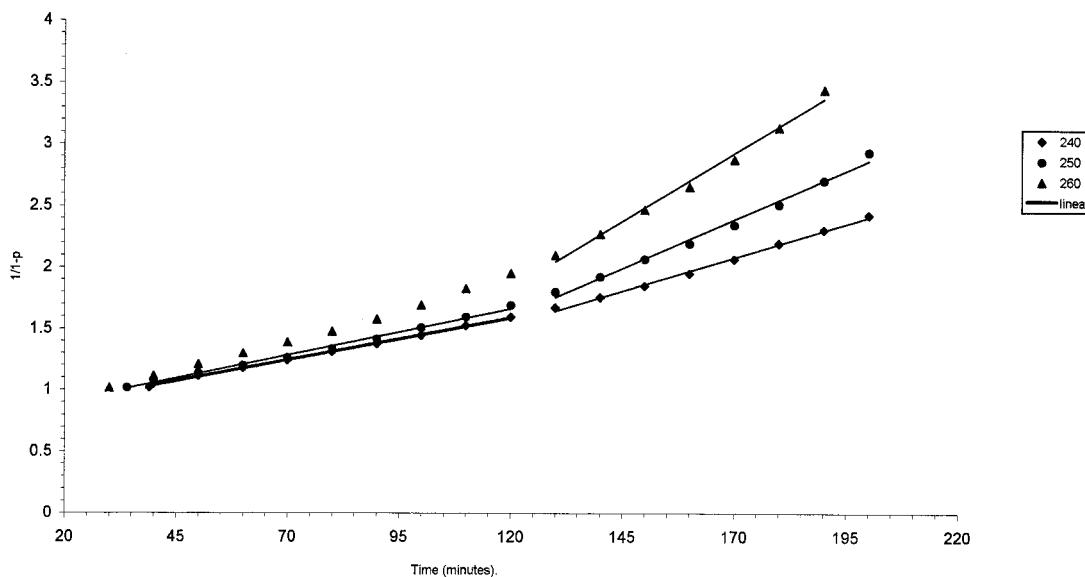
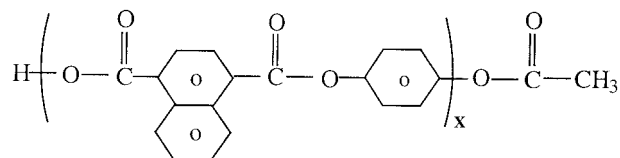


Figure 3 Plot indicating the variation of $1/(1-p)$ as a function of time.

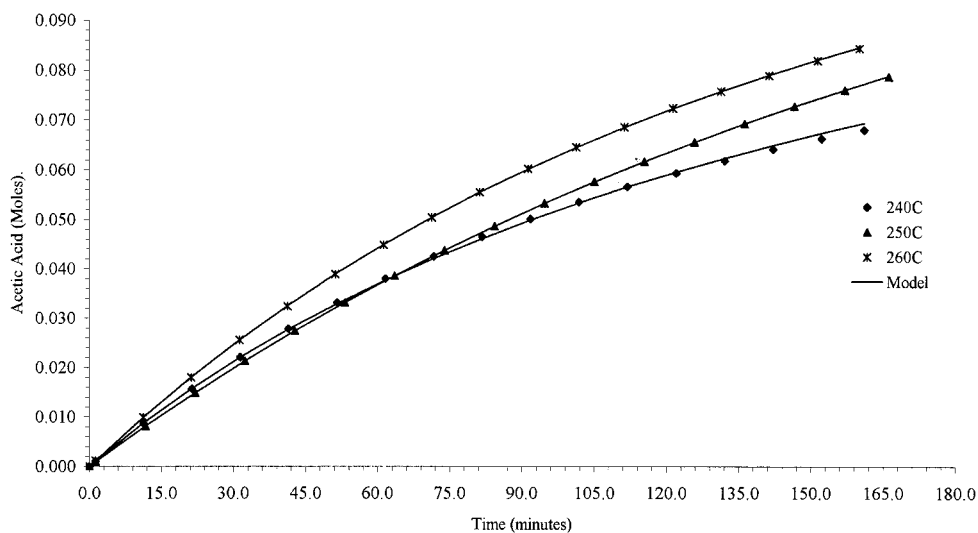


Figure 4 Second order plot for catalyzed 1,4-NDCA-HQDA reactions.

where x represents the equal mole ratio of HQDA and 1,4-NDCA units along the chain.

In a step growth polymerization, the monomer concentration progressively decreases with reaction time. Thermal analysis of a typical sample of HQDA-1,4-NDCA carried out by quench cooling the melt at 20°C/minute did not reveal a T_g value. A small exotherm, possibly of oligomeric, HQDA-1,4-NDCA was noted at 275°C (Fig. 8).

CONCLUSIONS

Two transesterification catalysts, sodium acetate and zinc acetate, were employed in the synthesis of 1,4-

NDCA-HQDA based homopolymers using melt polymerization. Acetic acid was liberated on homopolymerization of 1,4-NDCA-HQDA. An elaborate kinetic model with four different rate constants and twelve differential equations was used to analyze the homopolymerization reaction. Two different polyesterification catalysts, sodium acetate and zinc acetate, were tried. Sodium acetate was found to be a good catalyst for the homopolyesterification reactions.

Second order kinetics was found to be valid for both catalyzed and uncatalyzed reactions. Arrhenius plots reveal that the chosen catalyst has only a marginal role in the polyesterification reactions. The rate constant k_1

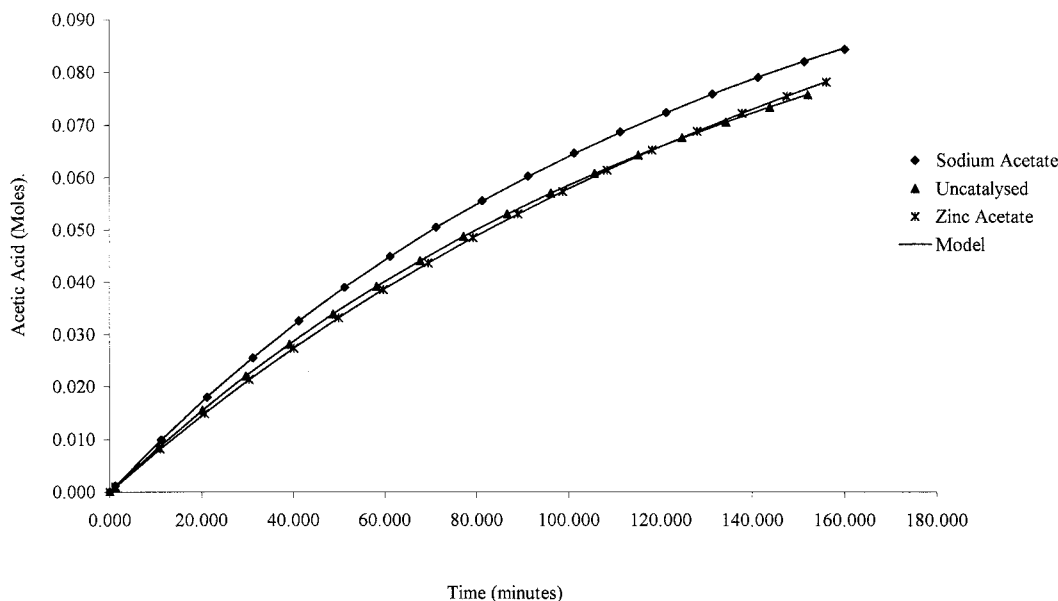


Figure 5 Second order plot indicating variation of catalyst (1 mol %) types for 1,4-NDCA-HQDA reactions.

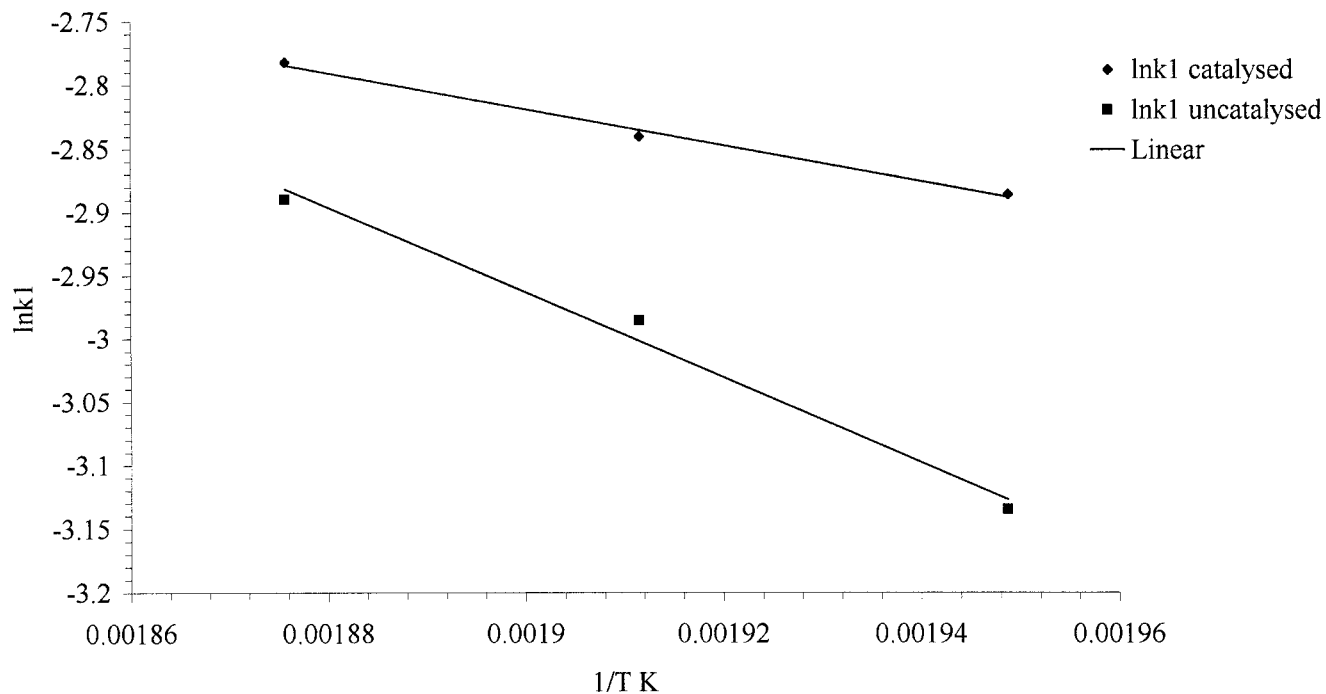


Figure 6 Arrhenius plot indicating variation of $\ln k_1$ for catalyzed and uncatalyzed reactions.

has higher value than k_2 . The value of E_2 , the energy of activation related to the rate constant k_2 , was found to be higher than E_1 . The rate constant values and activation energy values indicate that sodium acetate does not significantly enhance the reaction rate. DSC anal-

ysis of the homopolymer indicated that it melts at around 350°C.

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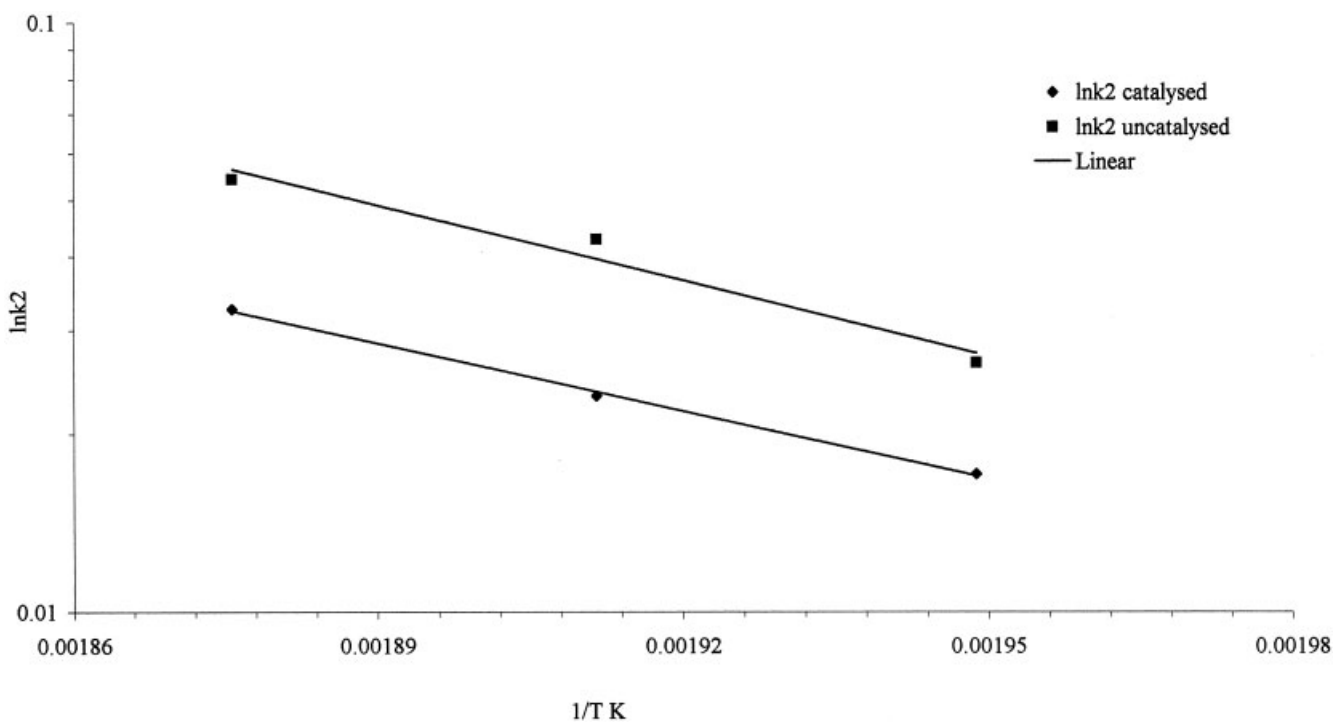


Figure 7 Arrhenius plot indicating variation of $\ln k_2$ for catalyzed and uncatalyzed reactions.

TABLE I
Table of Kinetic Parameters for the Homopolymer of 1,4-NDCA-HQDA

Composition HQDA : 1,4-NDCA (mol %)	Temperature (°C)	Catalyst type	k_1	k_2	k_3	k_4	E_1 (kJ/mole)	R^2	E_2 (kJ/mole)	R^2
0.5 : 0.5	240	*	0.0435	0.0264	0	0				
0.5 : 0.5	250	*	0.0505	0.0428	0.0647	0	Uncat. 28	0.95	Uncat. 82	0.95
0.5 : 0.5	260	*	0.0556	0.0542	0	0.0017				
0.5 : 0.5	240	NaC	0.0558	0.0171	0	0				
0.5 : 0.5	250	NaC	0.0484	0.0532	0	0	Cat. 12	0.97	Cat. 73	0.98
0.5 : 0.5	260	NaC	0.0619	0.0326	0	0.0061				
0.5 : 0.5	260	Znc	0.0515	0	0.0138					

* Uncatalyzed reaction
 NaC Sodium acetate
 ZnC Zinc acetate
 E_1 & E_2 Energy of activation for rate constant k_1 & k_2
 k_1, k_2, k_3 & k_4 Rate constants ($L \text{ mol}^{-1} \text{ sec}^{-1}$)
 Uncat Uncatalyzed reaction
 Cat Catalyzed reaction

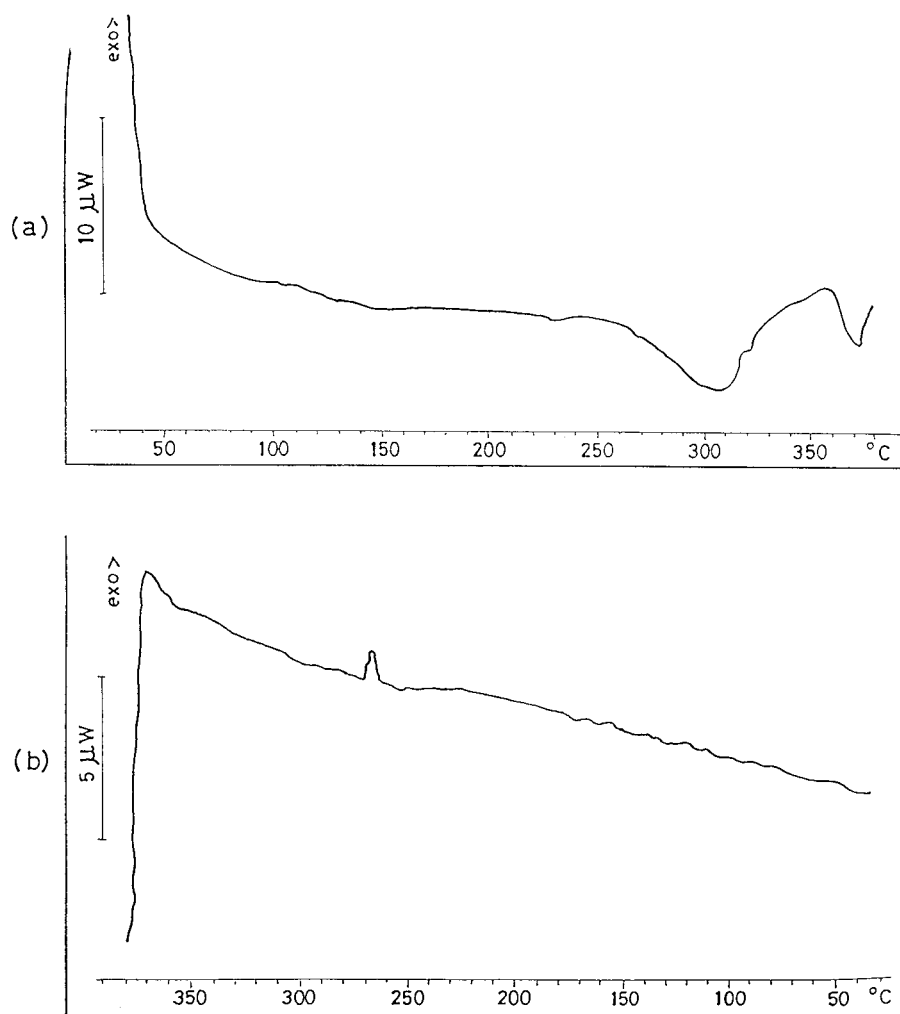


Figure 8 Thermogram indicating (a) heating and (b) cooling for the homopolymer of 1,4-NDCA-HQDA synthesized at 260°C.

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