

Application of Different Kinetic Models to Analyze the Reaction Rates of Liquid Crystalline Homopolyesters

H. Al-Adwani, A. E. Bishara, Y. Al-Roomi, J. Mathew, H. I. Shaban

Chemical Engineering Department, Kuwait University, P.O. Box 5969, 13060 Safat, Kuwait

Received 2 December 2003; accepted 25 February 2004

DOI 10.1002/app.20570

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Kinetics of homopolyesterification between methyl hydroquinone diacetate (MHQDA) and 1,4-naphthalene dicarboxylic acid (1,4-NDCA) in the melt were analyzed using three different rate models. The three different techniques used to evaluate the kinetic parameters for the homopolymerization reaction were as follows: simple second-order textbook equation, a simple second-order kinetic model, and Mathew's model. A simple second-order reaction mechanism previously reported by Mathew et al. is found to summarize the catalyzed and uncatalyzed reactions between MHQDA and 1,4-NDCA. Close comparison was obtained between the experimental and theoretical data

by using the Mathew's model. Mathew's model was found to perfectly fit the experimental data. The kinetic analysis of the studied system reveals the implicit simplicity of complex systems. The percentage error for the fit was found to be <5% for the Mathew's model. These novel homopolymers were analyzed for their thermal properties by using a differential scanning calorimeter. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 1118–1128, 2004

Key words: homopolymers; kinetics; liquid crystalline polymers

INTRODUCTION

The structural organization in thermotropic liquid crystalline aromatic polyesters principally consists of benzene rings fastened exclusively at *para* positions by ester groups and may be present as a sequence of 4-oxybenzoate, or 1,4-oxyphenylene oxy and 1,4-carboxyphenylene groups. The parent polyesters of the major components have such a high melting point (>650°C) that degradation precedes melting. Recourse is sought in the polyesterification, by the incorporation of a monomer which acts similar to a rigid kink to reduce the transition temperature without adversely affecting the mechanical properties.

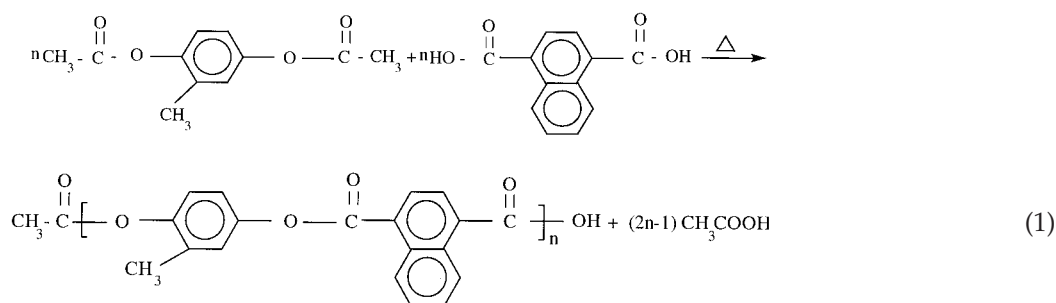
The kinetics of polyesterification reactions have been previously investigated.^{1–6} Variable orders, observed by these researchers, have been shown to be due to differing polarities of the medium.^{7,8} Kinetic investigations of melt acidolysis have been rather few. Fradet and Marechal⁹ studied 4-acetoxy benzoic acid, biphenol diacetate, and terephthalic acid system with and without catalyst. Mathew et al.¹⁰ investigated melt acidolysis of 4-acetoxy benzoic acid. Amir et al.¹¹ investigated the homopolymerization of 4-propionoxybenzoic acid via melt polymerization. Applicella et al.¹² examined in some detail the kinetics. Hans¹³ synthesized poly(ethylene terephthalate) (PET), poly(pro-

pylene terephthalate) (PPT), and PET–PPT copolyesters. He also calculated the monomer reactivity ratios of bis(2-hydroxy ethyl) terephthalate (BHET) and bis(2-hydroxy-*n*-propyl) terephthalate (BHPT) in his polymerization work by applying the copolymerization kinetic equation by using a gas chromatograph to obtain the rate constants and catalytic aspects of PET by using model molecules. Dotson et al.¹⁴ reported on the kinetics of copolycondensation of bis(4-hydroxy butyl) terephthalate and bis(2-hydroxy ethyl) terephthalate by the ester interchange reaction. This scant literature is surprising because acidolysis has been known since 1930 and the synthesis of many thermotropic polyesters have been investigated by Won et al.¹⁵

Amir et al.¹⁶ studied the kinetics of development of copolyesters of poly(butylene terephthalate) (PBT), hydroquinone diacetate (HQDA), and terephthalic acid (TA). They determined the kinetic order with respect to the homopolymers of HQDA and TA as well as the copolymers of PBT, HQDA, and TA. This complex system was modeled by using second-order kinetics; the rate constants and activation energy for this system were reported. There are uncertainties about the kinetic order, activation energy, etc. of the reaction in the melt. This dearth of open literature can be attributed to the intrinsic complexity of the polymerization reaction. Other possible causes of kinetic uncertainties could be due to side reactions, insolubility of the diacids, stoichiometric imbalance, or diffusion constraints.

In the present work, the development of homopolyesters with specific properties of interest was studied by a reaction scheme as indicated below:

Correspondence to: H. I. Shaban (mj_maths@hotmail.com).



It is important that the kinetics of homopolymerization be examined first. Later, we checked whether the structural randomization on incorporation of PET or PBT through melt transesterification reactions is attainable.

The present work focuses on the kinetics of step homopolymerization for a system containing a kink monomer. The work was carried out with the following objectives: (1) to conduct kinetic analysis of catalyzed and uncatalyzed homopolyesters; (2) to compare kinetic behavior between catalyzed and uncatalyzed reactions; (3) to investigate whether simple kinetic laws are valid in melt/slurry as in solution polymerization; and (4) to test three second-order kinetic models for the present homopolymerization reaction, to decide the best model for the present system.

EXPERIMENTAL

Materials

1,4-Naphthalene dicarboxylic acid (1,4-NDCA) and methyl hydroquinone diacetate (MHQDA) of 99% purity were purchased from Aldrich Chemie GmbH, Deisenhofer, Germany. 1,4-NDCA has a melting point $> 300^\circ\text{C}$, whereas MHQDA melts around 50°C .

Reactor details

A 300-mL Hastelloy-B2 based reactor shown in Figure 1 was used for the polymer synthesis. The reactor had four ports for charging/stirring the reactants, nitrogen gas inlet, side product collection, and vacuum measurement. The reactor could be maintained isothermally at any temperature between ambient and 400°C . A provision for measuring the side product was made, as shown in Figure 1.

Preparation of polymers

All melt polymerization studies were conducted with equal moles of the two monomers. Dry nitrogen 15 mL/min was used throughout the reaction to prevent oxidation and degradation reactions. The tempera-

tures employed for the catalyzed and uncatalyzed reactions were 235, 240, 245, and 250°C . The melting point of homopolyesters was expected to be high ($>400^\circ\text{C}$).

The study of the effects of two different polycondensation catalysts, sodium acetate and zinc acetate, for the synthesis of the MHQDA and 1,4-NDCA homopolymers holds some technological interest. Concentrations (1.0 mol %) of catalyst were used to select and optimize their performance. The amounts of MHQDA lost due to sublimation accounted for a maximum of 0.1% of the monomer charged. The progress of the reaction was measured by monitoring the rate of acetic acid formed as a function of time. The purity of acetic acid was checked by gas chromatography. At 240°C , the purity was 98%, whereas at 245 and 250°C the purity was 96%. The average degree of polymerization (\bar{x}_n) was measured on the basis of the moles of acetic acid produced. The maximum degree of chain length attained was five. The solid-state polymerization reaction of the pure oligomer was not appreciable and was of no kinetic significance as far as the extraction of acetic acid was concerned. Most of the experimental runs were completed in a span of 2.5 h.

Measurements

Thermal transitions of the oligomers were obtained with a Mettler DSC apparatus, interfaced with a thermal analysis data station under nitrogen atmosphere by using a sample size of 10–15 mg. A heating rate of $20^\circ\text{C}/\text{min}$ was employed in all cases. Indium was used to calibrate the enthalpy values. A three-metal (In–Pb–Zn) standard was used to calibrate the temperature scale.

RESULTS AND DISCUSSION

The goal of chemical kinetic measurements for well-stirred mixtures is to validate a particular functional form of the rate law and determine numerical values for one or more rate constants that appear in the rate law.

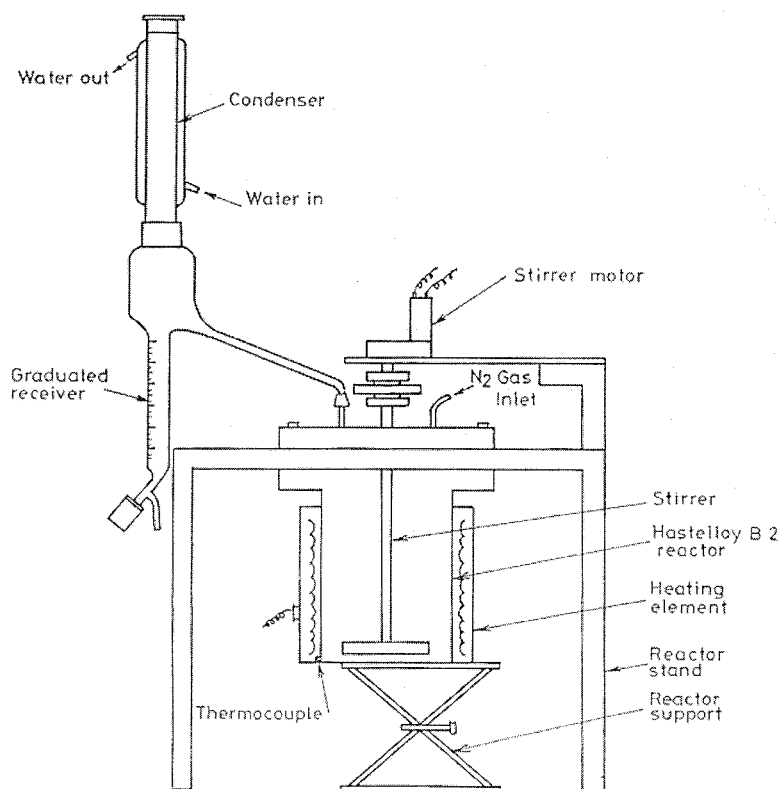


Figure 1 Polymerization reactor.

Employing the concept that the functional group reactivity is independent of molecular weight, the study of the kinetics of stepwise polymerization is significantly simplified.

If only bifunctional reactants are present and no side reactions occur, the number of unreacted carboxyl groups equals the total number of molecules (N) in the system. If acid or hydroxyl groups separate and (not in pairs) are defined as structural units, the initial

number of carboxyl moieties present is equal to the total initial number of structural units present (N_0). The number-average degree of polymerization (\bar{x}_n) is defined as

$$\bar{x}_n = \frac{N_0}{N} = \frac{c_0}{c} = \frac{1}{1-p} \quad (2)$$

where c_0 is the initial concentration; c is the final concentration; and $p = c_0 - c/c_0 =$ fractional conversion.

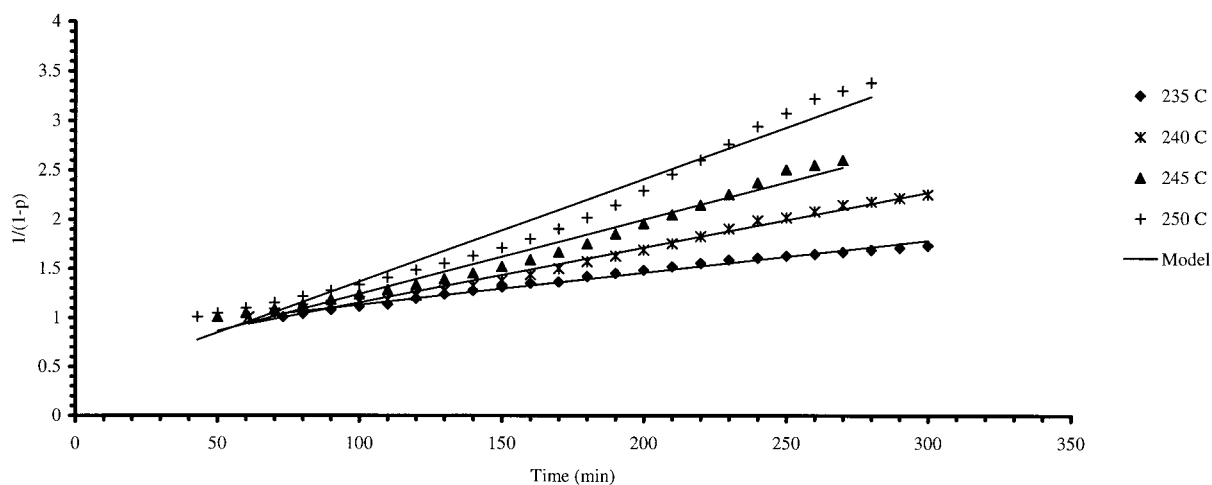


Figure 2 Second-order plot of $1/(1-p)$ versus time for uncatalyzed reaction of MHQDA and 1,4-NDCA.

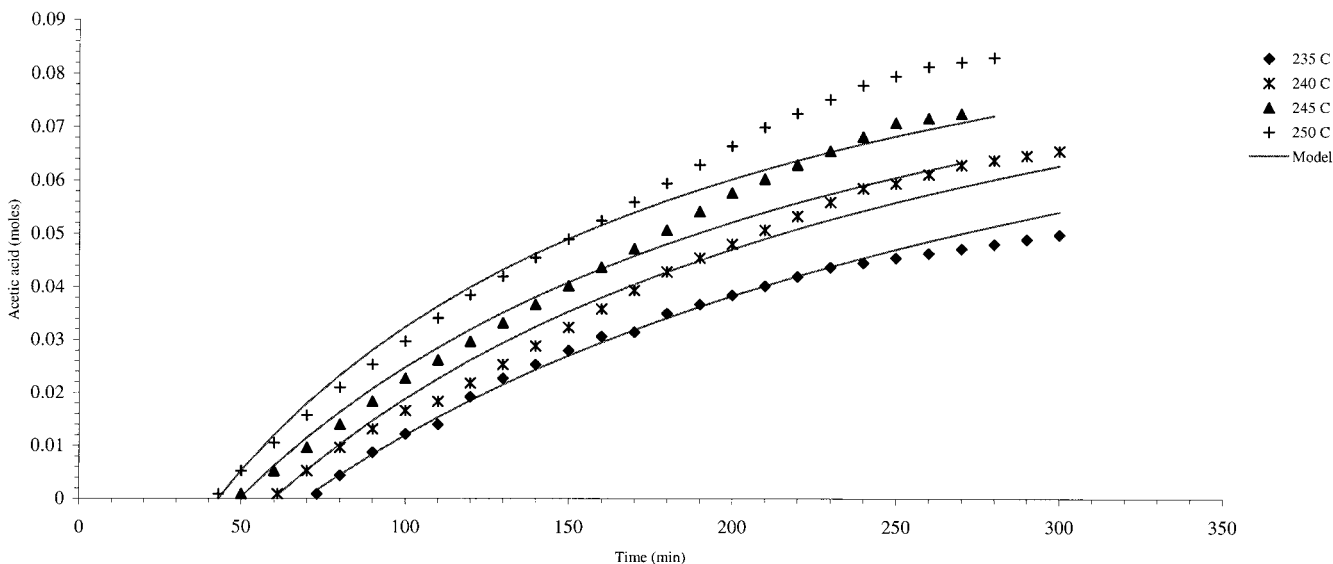


Figure 3 Simple second-order kinetic model plot for uncatalyzed reaction of MHQDA and 1,4-NDCA.

The second-order rate equation takes the form

$$-\frac{d[\text{COOH}]}{dt} = k'[\text{COOH}][\text{OH}] \quad (3)$$

or differently

$$-\frac{dc}{dt} = k'c^2 \quad (4)$$

where c is the concentration of $[\text{OH}]$ groups which are considered to be equal. Integration of (4) gives

$$c_0 k' t = \frac{1}{1-p} + \text{const.} \quad (5)$$

where c_0 is the initial concentration of $[\text{OH}]$ or $[\text{COOH}]$ groups, k' is rate constant, and t is the time of reaction.

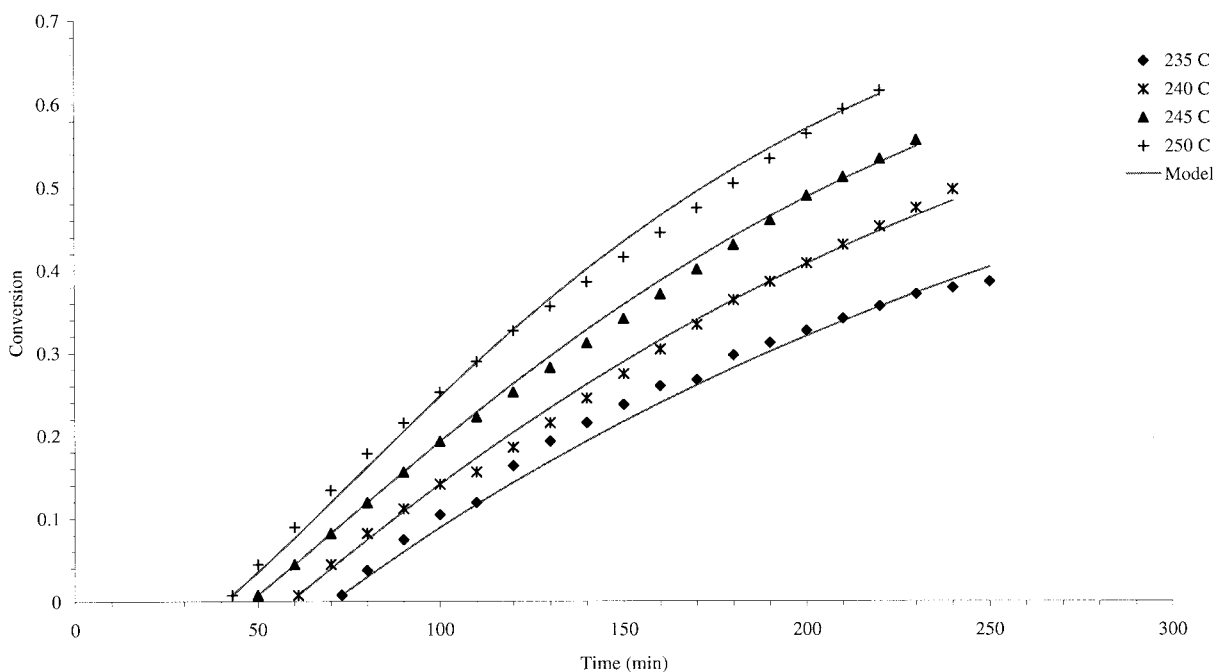


Figure 4 Second-order plot of uncatalyzed reaction of MHQDA and 1,4-NDCA (Mathew model).

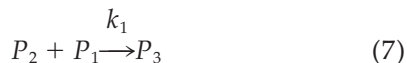
TABLE I
Kinetic Parameters Obtained by Plotting
1/(1-p) versus Time

Composition (mole) MHQDA : 1,4 NDCA	Catalyst type	Temperature (°C)	k_1 (Lit mol ⁻¹ min ⁻¹)	% Error
1 : 1	—	235	0.0033	1.58
1 : 1	—	240	0.0056	2.42
1 : 1	—	245	0.0076	4.56
1 : 1	—	250	0.0104	7.23
1 : 1	NaC	235	0.0047	1.60
1 : 1	NaC	240	0.0116	9.79
1 : 1	NaC	245	0.0165	14.86
1 : 1	NaC	250	0.0301	37.70
1 : 1	ZnC	250	0.0190	17.76

— = No catalyst; NaC = sodium acetate; ZnC = zinc acetate.

Oligomer precipitation model

Mathew et al.¹⁰ assumed that step growth homopolymerization of poly(oxybenzoate) could be described by simple second-order kinetics. They assumed that the largest oligomer contained n monomers, where n was claimed to range typically from 6 to 8. The polymerization process is described as



where $n, P_1, P_2, P_3 \dots P_{n-2}, P_{n-1}$, and P_n represent the chain length, monomer, dimer, trimer, the last $(n - 2)$, and $(n - 1)$ stage oligomer, and the precipitated oligomer.

Mathew et al. assumed that the rate constant for the termination step, denoted as k_2 , was different from that of the first $n - 1$ reactions. They justified this assumption on the basis that the reaction sequence is terminated by the formation of precipitated polymer (n -mer), which plays no further role in the polymerization process.

The rate of polymerization was related to the overall monomer conversion x as

$$\frac{dx}{dt} = k_1(1 - x)^2 + k_2(1 - x)^2x^{n-2} \tag{11}$$

where, x, t, k_1, k_2 , and n represent the monomer conversion, time in minutes, rate constant for the initial stage, rate constant for final stage, and order of the reaction, respectively.

In the analysis of their experimental data, Mathew et al. employed eq. (11) to evaluate k_1 and k_2 .

Simple second-order kinetic model

The rate constant (k) is evaluated by comparing the measured moles of side product (e.g., acetic acid) evolved as a function of time (M_{ie}) with the value of the number of M_{ic} calculated by using the present model. It may be shown that the moles of side product

TABLE II
Kinetic Parameters Obtained by Applying the New Simple Second-Order Model

Composition (mole) MHQDA : 1,4 NDCA	Catalyst type	Temperature (°C)	t_0 (min)	k_1 (Lit mol ⁻¹ min ⁻¹)	% Error
1 : 1	—	235	70.98	0.0035	4.32
1 : 1	—	240	59.34	0.0043	3.39
1 : 1	—	245	48.43	0.045	1.90
1 : 1	—	250	41.78	0.0058	4.01
1 : 1	NaC	235	55.20	0.0039	6.93
1 : 1	NaC	240	44.90	0.0059	12.14
1 : 1	NaC	245	38.90	0.0069	12.58
1 : 1	NaC	250	34.13	0.0077	14.44
1 : 1	ZnC	250	38.10	0.0074	12.17

t_0 = induction time; — = no catalyst; NaC = sodium acetate; ZnC = zinc acetate.

TABLE III
Kinetic Parameters Obtained by Applying Mathew's Model

Composition (mol) MHQDA : 1,4 NDCA	Catalyst type	Temperature (°C)	k_1 (Lit mol ⁻¹ min ⁻¹)	k_2 (Lit mol ⁻¹ min ⁻¹)	% Error	E_1 (kJ/mol)	E_2 (kJ/mol)
1 : 1	—	235	0.0032	0.0025	4.32		
1 : 1	—	240	0.0035	0.0058	3.39	23.2800	257.2767
1 : 1	—	245	0.0036	0.0100	1.90		
1 : 1	—	250	0.0038	0.0145	4.01		
1 : 1	NaC	235	0.0032	0.0052	2.85		
1 : 1	NaC	240	0.0036	0.0146	4.87	54.3644	175.0180
1 : 1	NaC	245	0.0042	0.0156	3.65		
1 : 1	NaC	250	0.0046	0.0189	4.39		
1 : 1	ZnC	250	0.0048	0.0158	3.85		

— = no catalyst; NaC = sodium acetate; ZnC = zinc acetate; E_1 and E_2 = activation energy for rate constants k_1 and k_2 .

generated is equal to the moles of monomer that have reacted to yield oligomers. Thus,

$$\sum \vartheta = \frac{\vartheta_0}{1 + k\vartheta_0 t} \quad (12)$$

$$M_{ic} = \vartheta_0 - \sum \vartheta \quad (13)$$

Substituting for $\sum \vartheta$ from eq. (12) yields

$$M_{ic} = \frac{k\vartheta_0^2 t}{1 + \vartheta_0 k t} \quad (14)$$

where ϑ_0 is the initial number of moles of monomer and ϑ is the number of moles of monomer at reaction time (t).

Eq. (14) is a linear equation with a single fitting parameter k . In practice, in polymerization reactions,

there is a delay (dead time) at the start of the experiment before a noticeable amount of side product is collected. This is due to the capacity of the condenser and the graduated tube. This dead time (t_0) is also a function of initial reaction rate, catalyst activity, and the reaction temperature. To take this factor into account, eq. (14) was modified to yield

$$M_{ic} = \frac{\vartheta_0^2 k (t - t_0)}{1 + \vartheta_0 k (t - t_0)} \quad (15)$$

In this analysis, Solver, which is a built-in function in Microsoft Excel 97, was used to calculate the best values of k and t_0 from the experimental data. The following default values dead time (2 min), number of iterations (100), and precision limit (10^{-5}) were employed in the calculations.

Equation (15) was also tried for the same experimental data and Solver was again used to calculate the

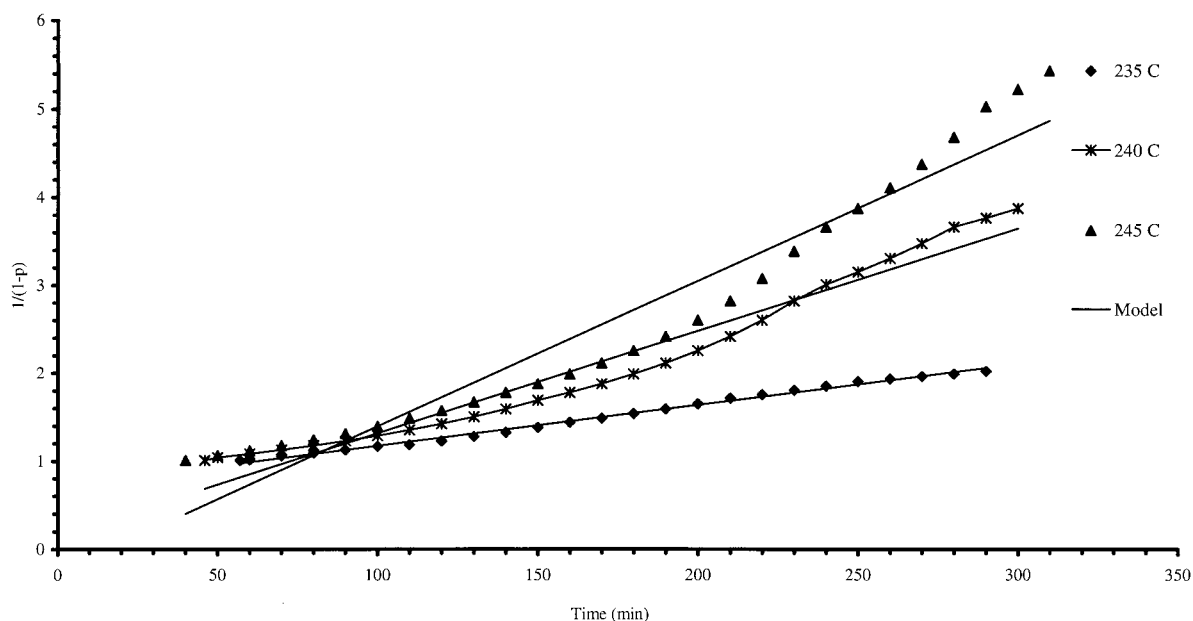


Figure 5 Second-order plot of $1/(1 - p)$ versus time for mol % sodium acetate catalyzed reaction of MHQDA and 1,4-NDCA.

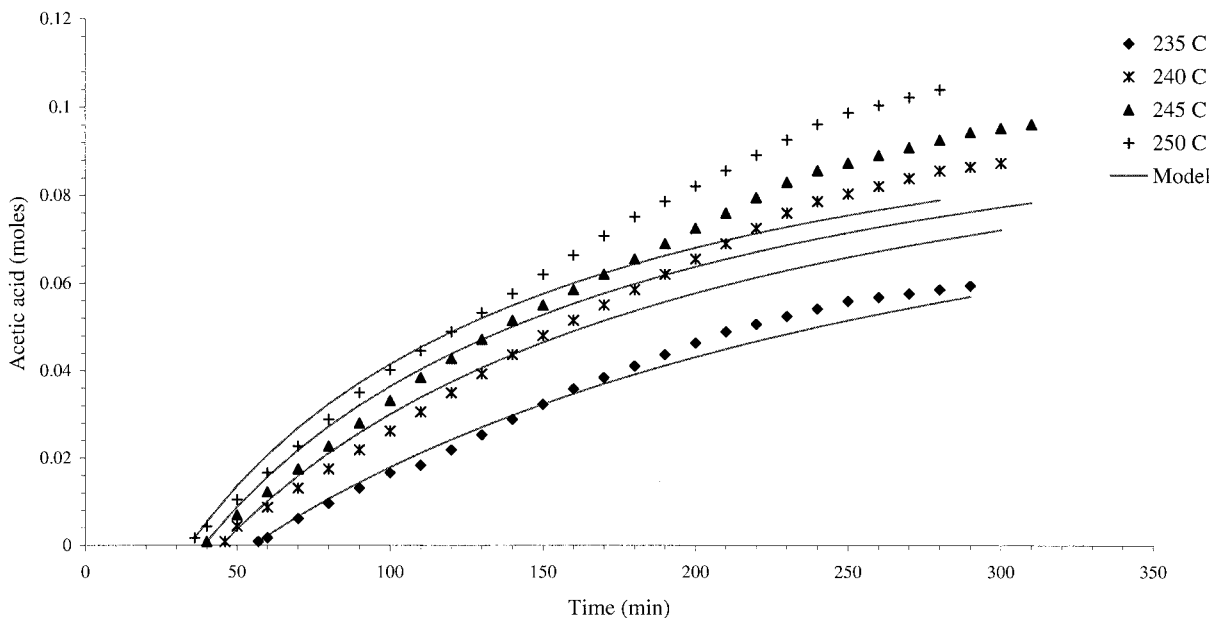


Figure 6 Simple second-order kinetic plot for 1.0 mol % sodium acetate catalyzed reaction of MHQDA and 1,4-NDCA.

best values of k from the experimental data. The objective function was defined as the sum of the percentage of absolute deviations between experimentally measured moles of acetic acid (M_{ie}), as a function of time, and the corresponding computed values (M_{ic})

$$F = \sum_{i=1}^m \frac{100 |M_{ie} - M_{ic}|}{M_{ic}} \quad (16)$$

Here m is the total number of data points. Equation (16) gives an equal weight to all experimental points from the start to the completion of the reaction, thereby facilitating the best fit and correctly assessing the optimal values of k .

The initial estimate of k was provided to Solver, which then performed a fixed number of trials (100 per variable) in which the values of the constant were

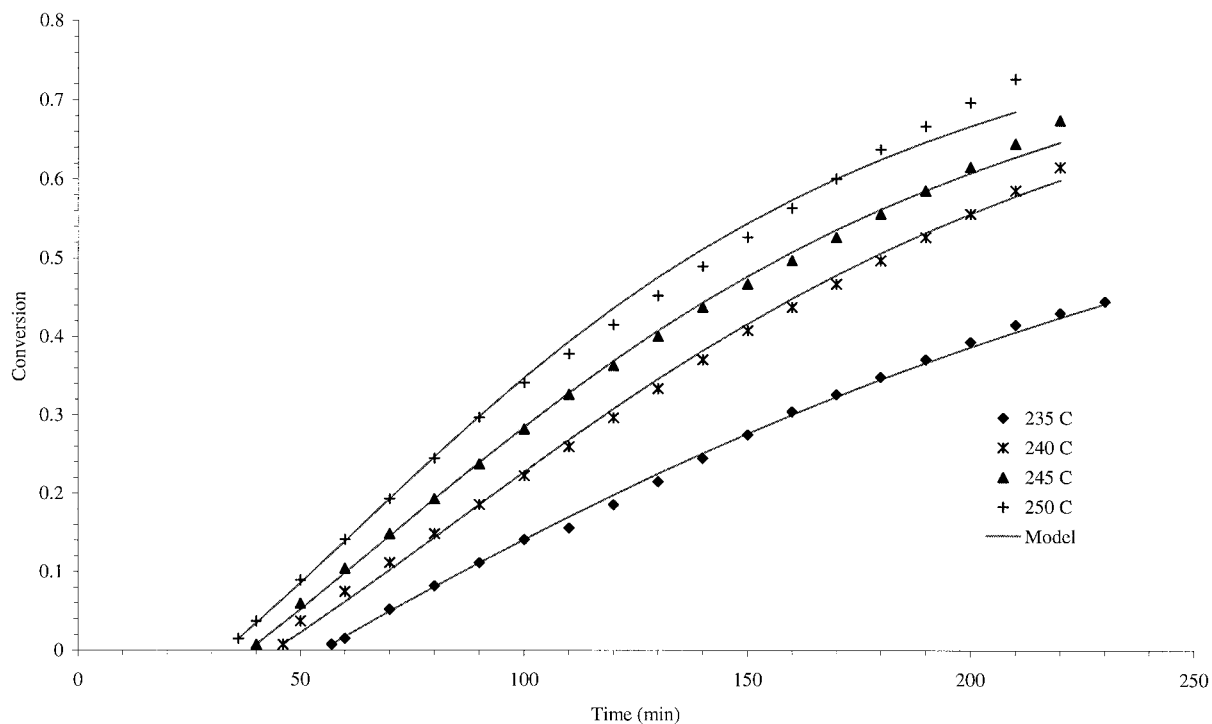


Figure 7 Second-order plot for 1.0 mol % sodium acetate catalyzed reaction of MHQDA and 1,4-NDCA (Mathew model).

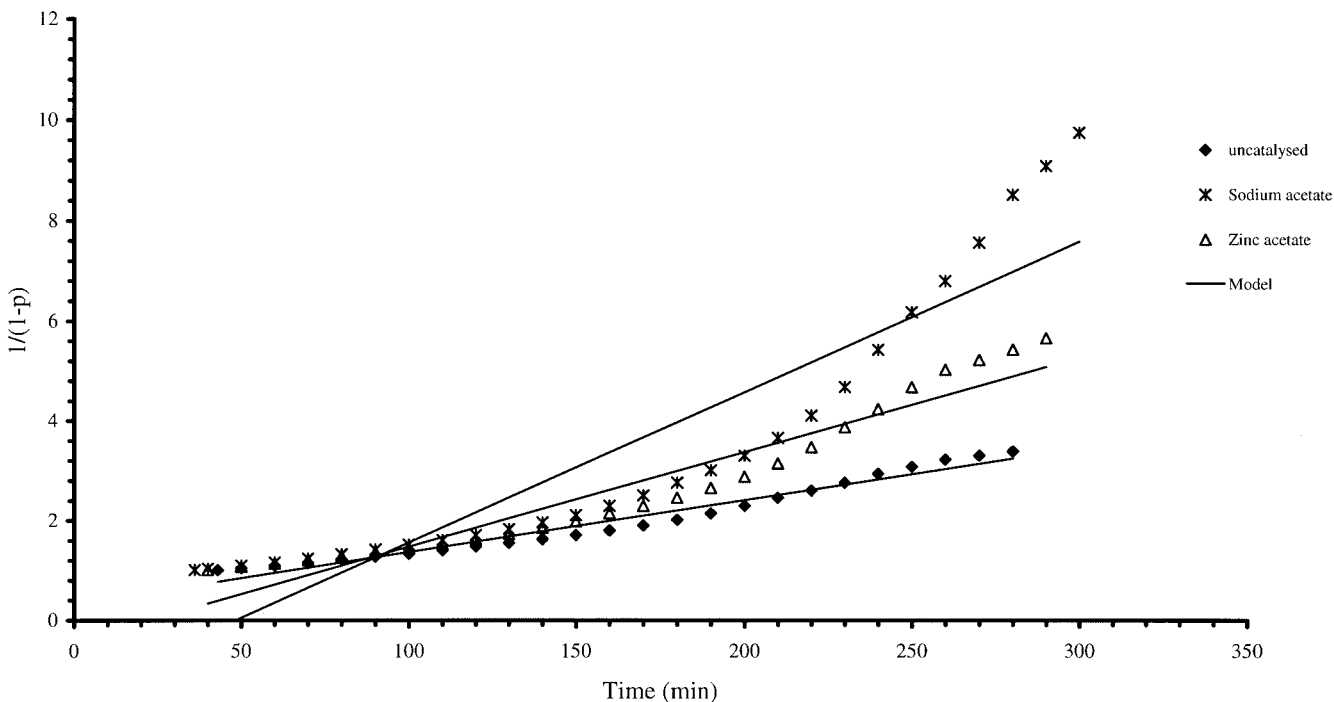


Figure 8 Second-order plot of $1/(1 - p)$ versus time for indicating the effect of catalysts (1 mol %) for reaction of MHQDA and 1,4-NDCA at 250°C.

changed until the objective function attained the least possible value.

In the Mathew et al. model, eq. (11) was solved by using a nonlinear multivariable optimization technique with the fourth-order Runge-Kutta methodology. The three parameters (k_1 , k_2 , and n) were evaluated to provide the best possible fit between the experimental and computed values of conversion (x) as

a function of time. The differential equation was solved as an initial value problem, with $t = 0, x = 0$. A step size of 0.1 min was chosen. This gave accurate results with a manageable number of computation steps.

A constraint, that the degree of polymerization (n) should be an integer value, was added. The VLook function within Excel was employed to select calcu-

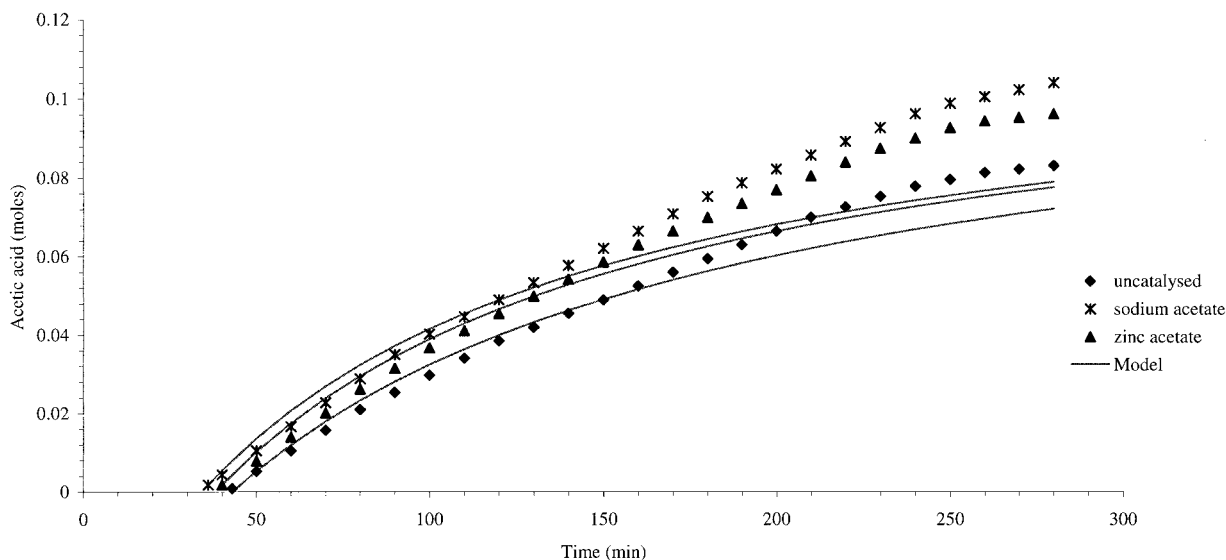


Figure 9 Simple second-order kinetic model indicating the effect of catalysts (1 mol %) for reaction of MHQDA and 1,4-NDCA at 250°C.

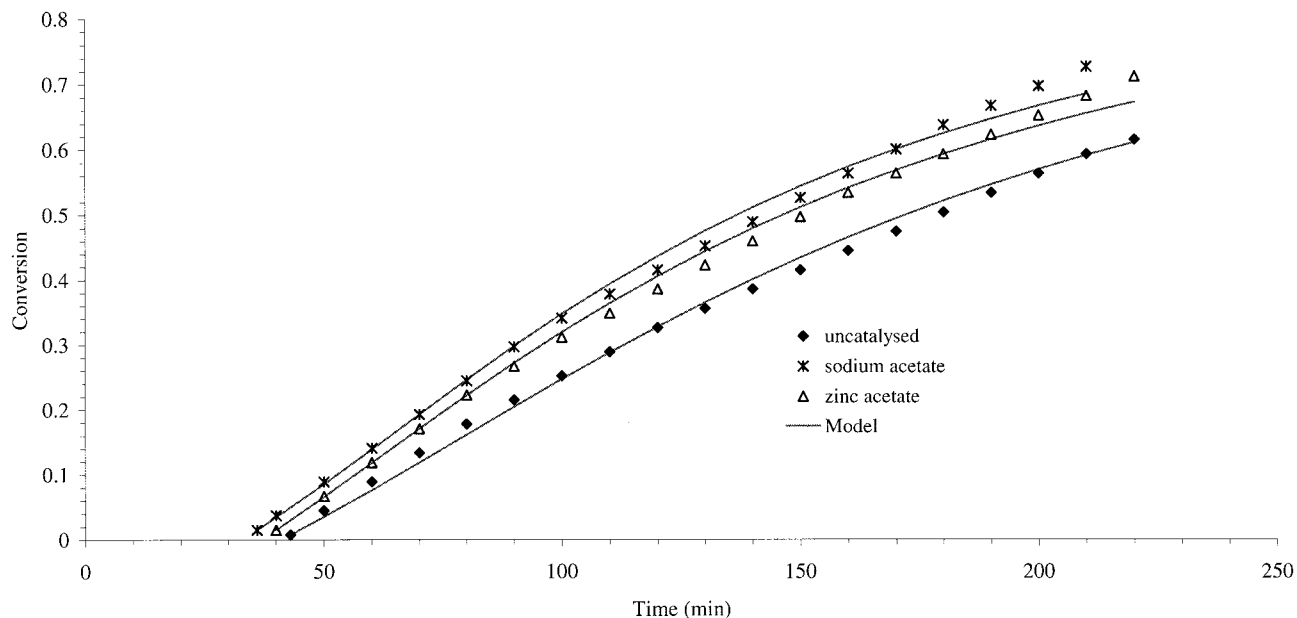


Figure 10 Second-order plot indicating the effect of catalysts (1 mol %) for reaction of MHQDA and 1,4-NDCA at 250°C (Mathew model).

lated conversions corresponding to the measured values.

The three different models, $1/(1-p)$, a simple second-order kinetic model, and Mathew's model were tested against the homopolymerization kinetic data of MHQDA and 1,4-NDCA. In evaluating the models, percentage error was used as the main factor to determine the closeness of the fit to the model. Some typical observations are presented below.

Figures 2, 3 and 4 illustrate the effect of reaction temperature for uncatalyzed reaction on the production rate of acetic acid in the homopolymerization of 1,4-NDCA and MHQDA at 235, 240, 245, and 250°C, using the three different models. In these and subsequent figures, the curves drawn through the data points depict the lines of best fit predicted by each model. As seen from the plots, Mathew's model is found to have good agreement between the measured

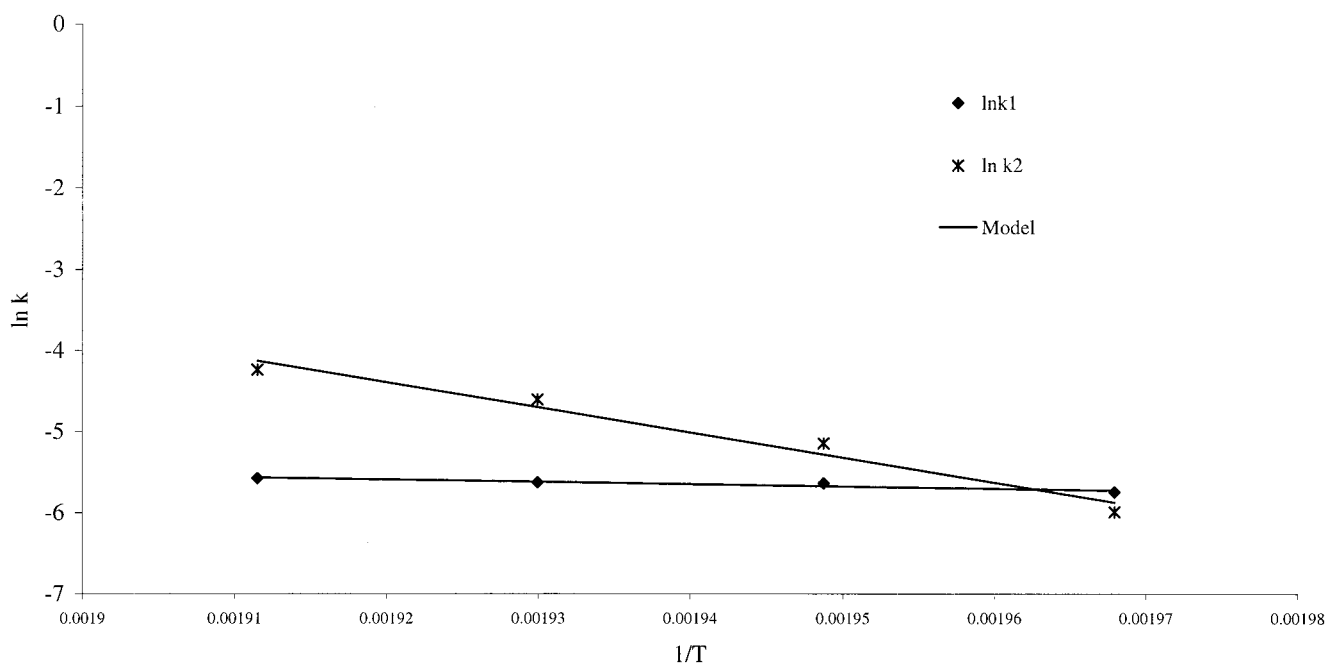


Figure 11 Arrhenius plot for uncatalyzed rate constants k_1 and k_2 (Mathew model).

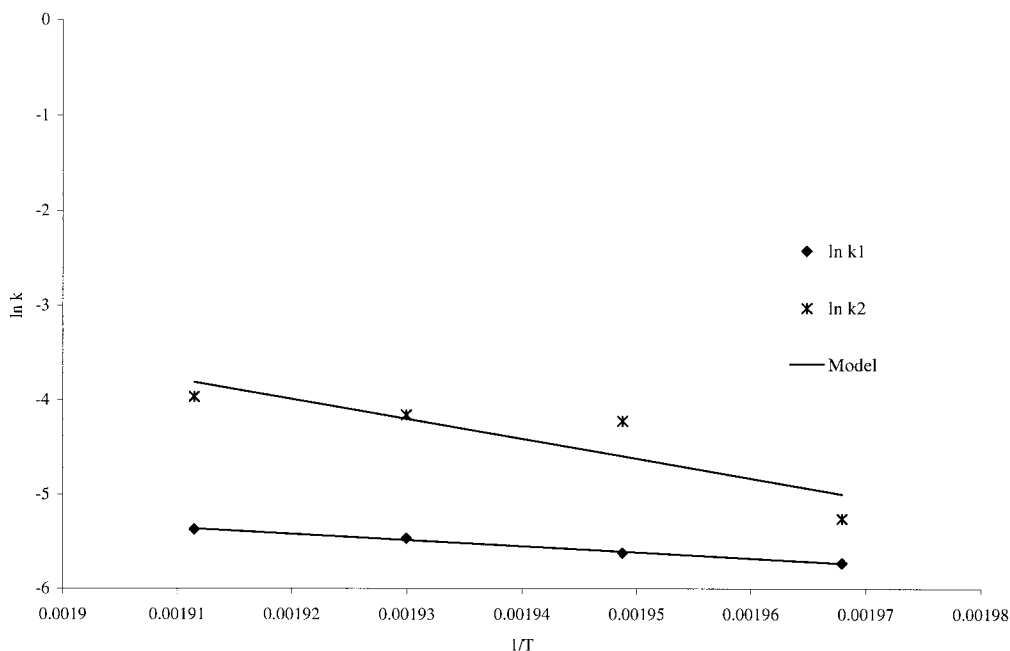


Figure 12 Arrhenius plot for 1.0 mol % sodium acetate catalyzed rate constants k_1 and k_2 (Mathew model).

and fitted results. The percentage error between the model values and experimental data is found to be the least for the Mathew model (<5% error). The kinetic parameters and the percentage error values for the three models are presented in Tables I-III.

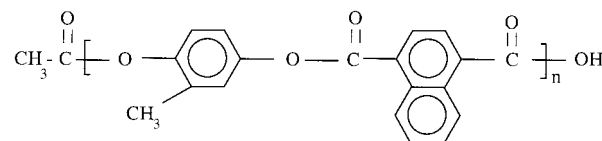
Figures 5, 6, and 7 depict similar plots by using sodium acetate (1.0 mol %) as the catalyst. An induction period is found to be present in plots 2 to 7. Figures 2-7 show that the induction time decreases with increasing temperatures. This is anticipated, as the evaporation time of the side product will be more rapid under increased temperatures. The slope of the individual curves are also found to increase with enhanced reaction rate. The values of the rate constant, obtained in each plot, are also found to increase with reaction temperature. The catalyzed homopolymerization plots also indicate a better fit with Mathew's model (Fig. 7). The percentage error values of the Mathew's model are found to be less than 5%, supporting the fact that this model can also fit catalyzed second-order homopolymerization reactions. Figures 8-10 provide typical plots in the three reaction cases at 250°C using sodium acetate catalyst, and zinc acetate catalyst, or an uncatalyzed reaction. The plots indicate larger slopes for sodium acetate catalyzed reactions. Figures 8 and 9 indicate that no match is obtained between the experimental data and the theoretically obtained values for the $1/(1-p)$ and the new second-order model. Mathew's model is again (Fig. 10) found to yield a good fit with percentage error < 5%.

Mathew's model was used to determine the activation energy for the present system. The activation energy values for the homopolymerization of MHQDA and 1,4-NDCA are indicated in Table III.

The sodium acetate catalyst gives lower activation energy values for the second rate constant k_2 . Typical Arrhenius plots are shown in Figures 11 and 12. The percentage errors of these plots are also found to be less than 5%.

Polymer characterization

In step-growth polymerization, the monomer concentration progressively decreases with reaction time. The repeat unit of a polymer of 1,4-NDCA and MHQDA can be shown as



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

Thermal analysis of a typical sample of MHQDA + 1,4-NDCA by quench cooling the melt at 20°C/min did not reveal a glass transition temperature. The heating endotherm indicates melting occurring at 310°C. A small exotherm possibly of oligomeric MHQDA + 1,4-NDCA is noted at 275°C.

CONCLUSION

Homopolymerization of MHQDA and 1,4-NDCA was carried out by using the melt polymerization route. The temperatures employed for the melt polymeriza-

tion studies were 235, 240, 245, and 250°C. Three different homopolymerization models were used to analyze the experimental data for MHQDA and 1,4-NDCA system. The models were a simple second-order textbook equation, a simple second-order kinetic model, and Mathew's model. The second-order textbook equation and the new simple second-order equation yield a single rate constant (k). Mathew's model had two rate constants (k_1 and k_2). Mathew's model was found to fit the homopolymerization data with a percentage error < 5%. An induction period is present for all the catalyzed and uncatalyzed reactions. Lower induction time was seen for higher temperatures. All the rate constants were found to increase with increasing temperature.

Activation energy values were obtained by using Mathew's model. Higher activation energy was obtained for the uncatalyzed rate constant (k_2). The lower activation energy values of uncatalyzed rate constant (k_1) could not be explained. The rate constants obtained from Mathew's model were found to be positive. An advantage of Mathew's model is the duality of the rate constants (k_1 , k_2), which signify different reaction rates for different steps involved in the step-polymerization procedure.

The authors are grateful to Dr. Abdul Rehman Khan, R. Thangakonam, and Fatma Taqui for their professional help during the course of this work.

References

1. Flory, P. J. *Principles of Polymer Chemistry*; Cornell Univ. Press: Ithaca, NY, 1953.
2. Flory, P. J. *J Am Chem Soc* 1937, 59, 466.
3. Carothers, W. H.; Natta, F. J. *J Am Chem Soc* 1930, 52, 314.
4. Rolfe, R. T.; Hinshelwood, C. N. *Trans Faraday Soc* 1934, 30, 935.
5. Davis, M. M. *Trans Faraday Soc* 1938, 34, 410.
6. Davis, M. M.; Hill, D. R. *J Trans Faraday Soc* 1953, 49, 395.
7. Vulic, I.; Schulpen, T. *J Polym Sci, Part A: Polym Chem* 1992, 30, 2725.
8. Fradet, A.; Marechal, E. *Adv Polym Sci* 1982, 43, 51.
9. Fradet, A.; Marechal, E. *J Macromol Sci Chem* 1982, A-17, 859.
10. Mathew, J.; Bahulekar, R. V.; Ghadage, R. S.; Rajan, C. R.; Ponrathnam, S. *Macromolecules* 1992, 25, 7338.
11. Amir, A. H.; Mathew, J.; Elkamel, A.; Nagdi, M. J. *Appl Polym Sci* 1999, 72, 467.
12. Applicella, B.; Serio, M. D.; Flocca, W.; Po, R.; Santacessaria, E. *J Appl Polym Sci* 1998, 69, 2423.
13. Hans, M. J. *Macromolecules* 1980, 13, 1007.
14. Dotson, N. A.; Galvan, R.; Lawrence, R. L.; Tirrell, M. *Polymerization Process Modeling*; VCH Publishers: New York, 1996.
15. Won Seok Lyoo; Joon Ho Kim; Wan Shik Ha. *J Appl Polym Sci* 1996, 62, 473–480.
16. Amir Al-Haddad; Johnson, M. *Studies in Surface Science and Catalysis*; Elsevier Science Series in Catalysis: 4th G. M. Schwab Symposium, Berlin, Germany; Froment, G. F.; Waugh, K. C., Eds.; Elsevier: Amsterdam, 2001, pp 565–574.