Kinetic Evaluation of an Oligomeric Amidation Reaction

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ABSTRACT: Homopoly(amides) similar to those of liquid crystalline poly(oxybenzoate) were prepared by acidolysis of the monomer *p*-acetamidobenzoic acid. The kinetics of catalyzed and uncatalyzed acidolysis of the 4-acetamidobenzoic acid were investigated at 265, 275, and 285°C. A second-order rate model, which can analyze kinetic parameters of two different kinetic regimes, was used to interpret the experimental data for 18 different experimental sets. It is observed that the correlation coefficient between observed and calculated values range between 0.98 and 0.99, confirming the validity of the stated model. The nature of the kinetic behavior in the two regimes was found to be independent of both catalyst type and concentration. In effect second-order rate law adequately describes the entire kinetic behavior of this system. The Arrhenius constants and activation energy parameters for this system have been reported. Differential scanning calorimetry (DSC) results of the oligomers indicate that the homopoly-(amides) melt around 360°C with degradation. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2534–2543, 2001

Key words: kinetics; liquid crystal; melt polymerization; acidolysis; polyamidation

INTRODUCTION

Xydar and Vectra, commercial acidolysis-type thermotropic liquid crystal polyesters, are synthesized by transesterification between aromatic diacids and diacetates. Wholly aromatic polyesters based on 1,4-disubstituted benzenes melt at too high temperatures to be melt processed.[1,2] Melt-processable thermotropic rigid rod polyesters can be obtained by copolyesterification through partial replacement with different monomers that have substituents, provide kinks, or change the directional effect of the ester[3] groups to suppress the crystal–mesophase transition temperature.

Direct polyesterifications between diacids and diols at high temperatures do not generate high molecular weight polyesters.[4–6] At least one reactive monomer such as acid chloride, diacetate, or diphenate is essential to get high molecular weight polyester.[7–10]
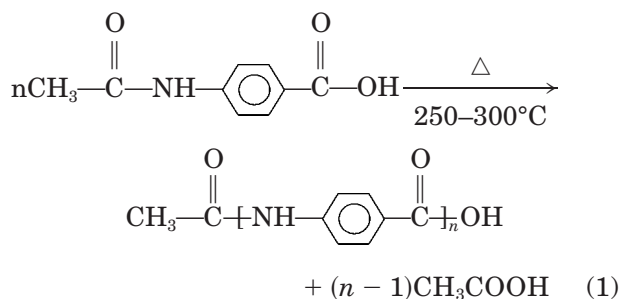
Kinetics of polyesterification reactions were previously investigated by Flory,[11,12] Carothers and Natta,[13] Rolfe and Hinshelwood,[14] Davis,[15] Korshak and Vinogradova,[16] Korshak et al.,[17] and Davis and Hill.[18] Variable orders, observed by these researchers were shown to be the result of differing polarities of the medium.[19–21] Kinetic investigations of melt acidolysis have been rather few. Vulic and Schulpen[22] studied 4-ethoxy benzoic acid, biphenol diacetate, and terephthalic acid systems with and without catalyst. Mathew et al.[23] investigated melt acidolysis of 4-acetoxy benzoic acid. Amir et al.[24] investigated the homopolymerization of 4-propionoxybenzoic acid via melt polymerization. Appicella et al.[25] examined in some detail the kinetics and catalytic aspects of

poly(ethylene terephthalate) (PET) using model molecules. This scant literature is surprising, given that acidolysis has been known since 1958 and the synthesis of many thermotropic polyesters was investigated by Jin et al.[26] There are uncertainties about kinetic order, activation energy, and the like of the reaction in the melt. This scarcity in the literature can be attributed to the intrinsic complexity of the polymerization reaction. The other possible causes of kinetic uncertainty could be the result of side reactions, insolubility of the diacids, stoichiometric imbalance, or diffusion constraints.

$$nCH_3-\overset{O}{\overset{\|}{C}}-NH-\langle\bigcirc\rangle-\overset{O}{\overset{\|}{C}}-OH \xrightarrow[250-300°C]{\triangle}$$

$$CH_3-\overset{O}{\overset{\|}{C}}\!\!\left[\!NH-\langle\bigcirc\rangle-\overset{O}{\overset{\|}{C}}\!\right]_n\!\!OH$$

$$+ (n-1)CH_3COOH \quad (1)$$

In the present work the development of the homopoly(amides) with specific properties of interest by a reaction scheme as indicated in eq. (1) was accomplished. It is thus important that the kinetics of homopolymerization be examined first and later check whether the structural randomization is attainable on incorporation of PET or PBT through melt copolyester amidation.

The principal aim of the present work was to investigate the kinetics of the acidolysis reaction of 4-acetamidobenzoic acid, a lyotropic liquid crystalline polyamide.

The present work was carried out with the following objectives: (1) to carry out kinetic analysis of catalyzed and uncatalyzed homopoly-(amides); (2) to compare the kinetic behavior between catalyzed and uncatalyzed reactions; (3) to ascertain whether simple kinetic laws are valid in melt/slurry as in solution polymerization; and (4) to test a simple second-order kinetic model for the homopolymerization reaction.

EXPERIMENTAL

Materials

4-Aminobenzoic acid of 99% purity was purchased from M/s. Aldrich Chemical Company (Gillingham, Dorset, UK). 4-Acetamidobenzoic acid was prepared by conventional acetylation of 4-amino-

benzoic acid with acetic anhydride (sulfuric acid catalyst). The product yield was 60% and had a melting point of 250°C.

Reactor Details

A 300-mL Hastelloy-B2–based reactor (shown in Fig. 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. It 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 0.28 mol of the monomer 4-acetamidobenzoic acid. Dry nitrogen (15 mL/min) was used throughout the reaction to prevent oxidation and degradation reactions. The temperatures chosen for the catalyzed and uncatalyzed reactions were 265, 275, and 285°C. The melting point of homopolyamides was expected to be very high (>400°C). It is of some technological interest to study the effects of three different polycondensation catalysts (sodium acetate, zinc acetate, and antimony trioxide) employed for the synthesis of p-acetamidobenzoic acid homopolymers. Concentrations (0.25, 0.5, and 1.0 mol %) of catalysts were varied to select and optimize their performance. The amounts of p-acetamidobenzoic acid lost as a result of 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 chromatograph. At 265°C the purity was 98%, whereas at 275 and 285°C the purity was 96%. The average degree of polymerization ($\bar{x}_n$) was found based on the moles of acetic acid produced. (The maximum degree of chain length attained was 5.) The solid-state polymerization reaction of the pure oligomer was not appreciable and was of no kinetic significance with respect to acetic acid extraction. 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 using a sample size of 10–15 mg. A heating rate of 20°C/min was employed in all
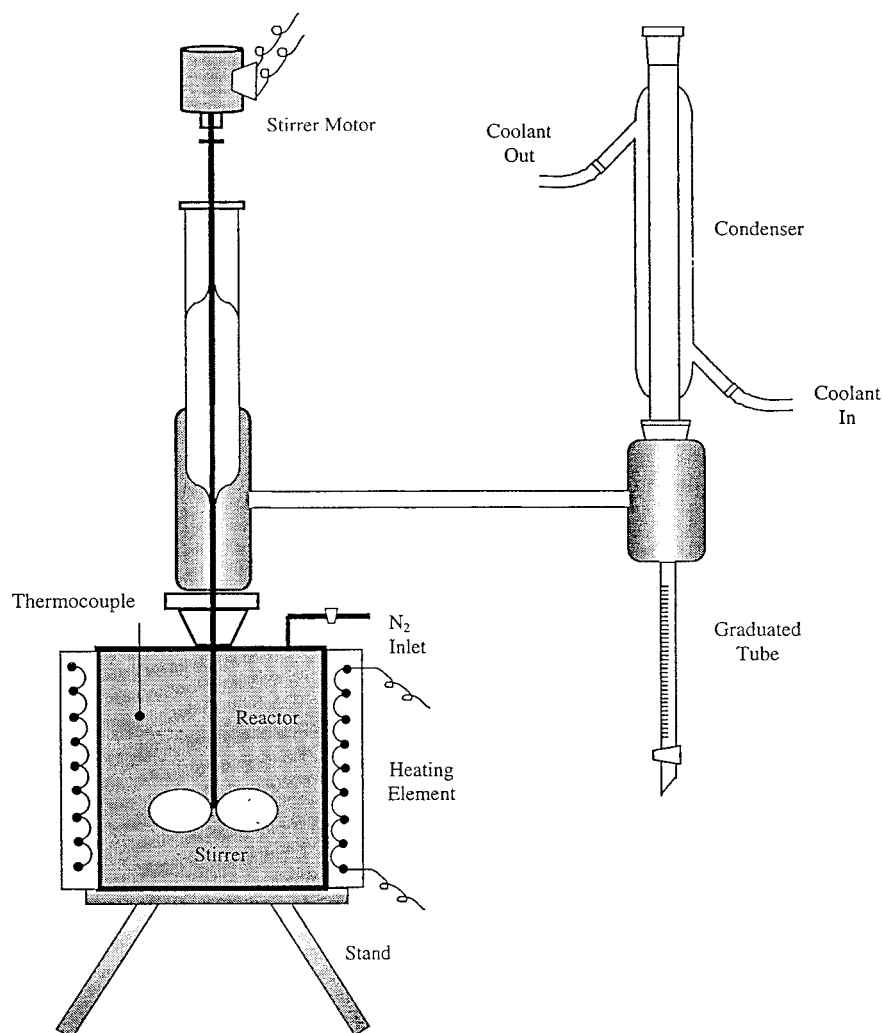
Figure 1   Experimental apparatus.

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

Thermodynamic Treatment of Rate Constants

Simple Second-Order Kinetic Treatment

The rate expression for polymerization of this process can be represented by second-order kinetics.[28]

$$A + B \underset{k_f}{\overset{k_r}{\Leftrightarrow}} C + D \qquad (2)$$
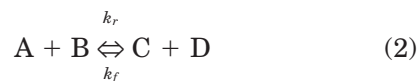
The concentration[29] distribution for the second-order reversible reaction for $[A_0] = [B_0]$ and $[C_0] = [D_0] = 0$ at $t = 0$ is

$$\frac{X_{Ae} - 2(X_{Ae} - 1)X_A}{X_{Ae} - X_A} = \exp\left[2k_f\left(\frac{1}{X_{Ae}} - 1\right)[A_0]t\right]$$

$$(3)$$

where

$$K = \frac{k_f}{k_r}, \quad X_A = \frac{[A]}{[A_0]} \quad \text{and} \quad X_{Ae} = \frac{[A_e]}{[A_0]} = \frac{\sqrt{K}}{1 + \sqrt{K}}$$

$$(4)$$

In the initial stages of polymerization, the reverse reaction is negligibly slow, and changes in
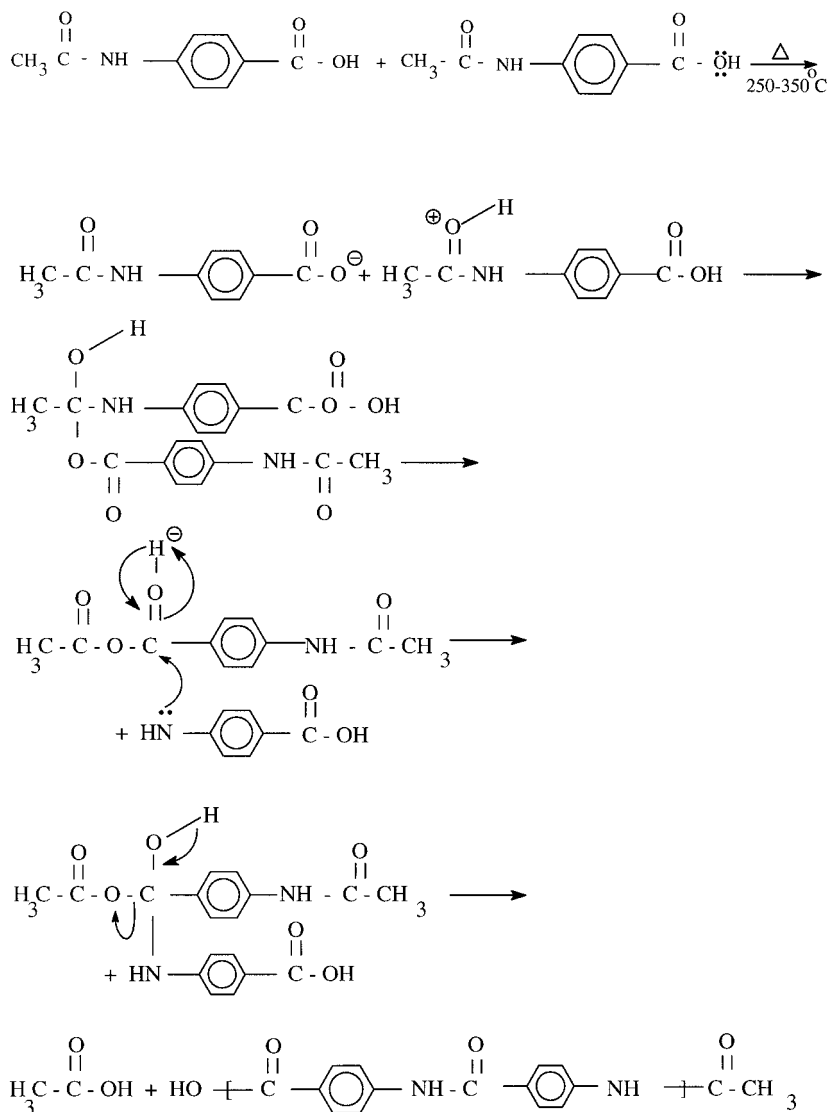
Figure 2 Reaction mechanism for the formation of poly(amide).

the concentration of reactant can be considered to result from the forward reaction alone. As the reaction proceeds, one product (acetic acid) is continuously recovered, rendering the possibility of reverse reaction to the minimum. The following equation represents the rate of the forward reaction:

$$-\frac{dx}{dt} = k[\text{COOH}][\text{OAC}] \qquad (5)$$

where OAC is the concentration of the acetyl functional group. Given that the functionalities remain equal in the charges fed to the reactor, eq. (5) changes to

$$-\frac{dc}{dt} = k[c]^2 \qquad (6)$$

where c is the concentration of unreacted functional groups. If c_0 is the initial concentration and p is the fractional conversion, then

$$c = c_0(1 - p) \quad \text{and} \quad \frac{dc}{dt} = -c_0 dp/dt \qquad (7)$$

and so

$$c_0 kt = \frac{1}{1 - p} + \text{constant} \qquad (8)$$

The concentration cannot be expressed in absolute units because the molar volume in the melt is not precisely known. A second-order initial rate will be given on this basis, by numerical value of the rate constant itself, but will have units of moles per minute. The rate law plots show that the kinetics is adequately represented by simple second-order behavior. The explanation to this behavior was previously discussed by Mathew et al.[23] They developed a reaction model based on the precipitation of oligomers that affects the kinetics of the overall process. They suggested a step-growth mechanism using the Flory–Schulz distribution, stating that the end-group reactivity is not influenced by the degree of polymerization until one step before the last. The net rate of polymerization or the production of an acetic acid is given by

$$\text{Rate} = \sum_{i=2}^{n} \frac{dp_i}{dt} \quad (9)$$

which results in an expression of the form

$$\frac{d(\text{CH}_3\text{COOH})}{dt} = k_1 p_1^2 + k_{n-1} p_1 p_{n-1} \quad (10)$$

where p_{n-1} and k_{n-1} represent the concentration of the $(n - 1)$th oligomer and the corresponding rate constant.

Using Flory–Schulz distribution up to $(n - 1)$th oligomer stages, the rate expression is given as

$$\frac{dp}{dt} = k_1 (1 - p)^2 \left[1 + \frac{k_2}{k_1} p^{n-2} \right] \quad (11)$$

The experimental data, that is, the amount of acetic acid collected as a function of time for each set, were analyzed for the estimation of k_1, k_2, and n. Equation (11) was solved by numerical integration using the Romberg algorithm.[30] A nonlinear optimization technique[31] was also used to estimate the parameters by minimizing the sum of squares of errors between measured and calculated values.

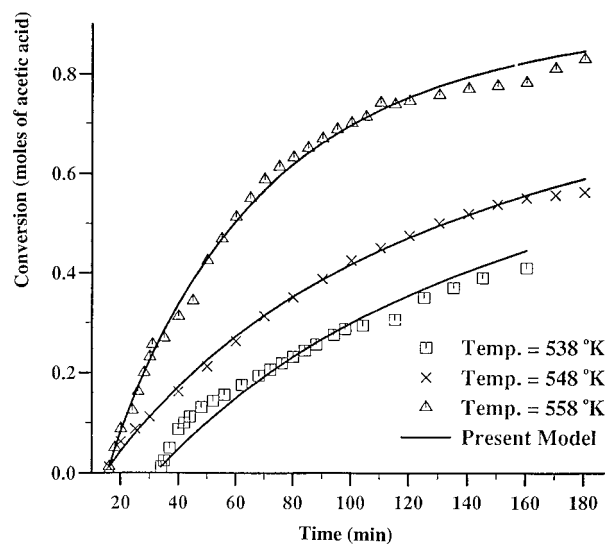$$\text{Minimize} \sum_{j=1}^{N} ([p]_j^{\text{exp}} - [p]_j^{\text{cal}})^2 \quad (12)$$

Figure 3 Second-order plot illustrating effect of temperature for homopolymerization of 4-acetamidobenzoic acid (uncatalyzed reactions).

where N is the number of observations. The calculated values fitted with experimental data for the entire range, with the exception of near the start of the reaction. To overcome this problem the objective function was redefined as a sum of squares of percentage errors, to eliminate the influence of magnitude of p, and provide equal weightage to all the points uniformly.

$$\text{Minimize} \sum_{j=1}^{N} \left[\frac{[p]_j^{\text{exp}} - [p]_j^{\text{cal}}}{[p]_j^{\text{exp}}} \times 100 \right]^2 \quad (13)$$

To improve the solution of the differential equation, a modified form of the fourth-order Range–Kutta equation was used to obtain accurate solution. The choice of the step size was made to reduce the unnecessary computation without affecting the accuracy of the results. A search subroutine was also added to match the corresponding experimental value to the calculated one for each time step, to obtain the value of the objective function to be minimized for the selected variables using nonlinear optimization with specified constraints. The values of rate constants are positive ($k_1 > 0$; $k_2 > 0$) and the degree of polymerization n is an integer; therefore, three constraints were implemented: $k_1 > 0$ and n is an integer in the optimization program.

Using the preceding approach the experimental data points were analyzed to obtain the rate constants for the two kinetic regimes. From the
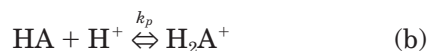
Table I   Rate Constants and Thermodynamic Parameters for Second-Order Plots for Homopolymerization of *p*-Acetamidobenzoic Acid

| System | Induction Time (min) | Temperature (°C) | Rate Constant (s^{-1}) | | EOA[a] | | | | | | | |
			k_1	k_2	EA$_1$	EA$_2$	ln A_1[b]	ln A_2[b]	ΔH_1[c]	ΔH_2[c]	ΔS_1[c]	ΔS_2[c]
Uncatalyzed	34	265	.00525	0.008	155.75	640.60	29.50	—	147	631	−18.7	879
	16	275	.00156	0.027								
	16	285	.0255	0.0161								
Zn(OAC)$_2$ (1 mol %)	32	265	.00708	.0097	181.10	199.84	35.5	40.43	172	191	42	74
	21	275	.0245	.1194								
	19	285	.0262	.0410								
Sb$_2$O$_3$ (1 mol %)	43	265	.00525	.008	219.10	96.90	42.83	17.17	210	88	114	−110
	26	275	.00156	.027								
	21	285	.0255	.016								
NaOAC (1 mol %)	50	265	.00611	.001	259.0	532.9	52.82	—	250	524	189	696
	22	275	.0374	.0061								
	19	285	.0396	.0468								
NaOAC (0.5 mol %)	38	265	.0064	—	208	—	41.22	—	−199	—	93	—
	27	275	.0130	—								
	20	285	.0287	0.1645								
NaOAC (0.25 mol %)	37	265	0.0106	—					43.6	103	−210	−85
	26	275	0.0172	0.001	52.6	112.40	7.26	—				
	19	285	0.0155	0.0015								

[a] EOA = energy of activation (kJ/mol).
[b] ln A = frequency factor.
[c] ΔH = enthalpy of activation (kJ/mol) and ΔS = entropy of activation (J mol); 1 and 2 represent corresponding values for two kinetic regimes.

plots it can be generalized that the reactions (both uncatalyzed and catalyzed) follow a second-order pathway. A possible mechanism for the formation of homopolyamides is indicated in Figure 2.

If HA denotes an un-ionized molecule of 4-acetamidobenzoic acid, the following steps can be presumed in the polymerization reaction:

$$\text{HA} \overset{k_i}{\Leftrightarrow} \text{H}^+ + \text{A}^- \qquad \text{(a)}$$

$$\text{HA} + \text{H}^+ \overset{k_p}{\Leftrightarrow} \text{H}_2\text{A}^+ \qquad \text{(b)}$$

$$\text{H}_2\text{A}^+ + \text{A}^- \overset{k_r}{\rightarrow} \text{P} + \text{A}_c\text{H} \qquad \text{(c)}$$

$$\text{A}_c\text{H} \overset{k_{AC}}{\Leftrightarrow} \text{A}_c^- + \text{H}^+ \qquad \text{(d)}$$

where A$^-$, H$_2$A$^+$, P, and A$_c$H denote the 4-acetamido benzoic anion, protonated monomer, growing chain (dimer, trimer, etc.), and acetic acid, respectively; k_i, k_p, k_r, and k_{AC} denote the ionization constant, protonation constant, rate constant, and ionization constant of the acetic acid, in that order.

All the reactions are characterized by two kinetic regimes in the second-order plots, which is indicative of different kinetic behavior in the two regimes. This change in kinetic behavior in both catalyzed and uncatalyzed reactions became more apparent at higher temperatures. The reported conversion values of the reaction lie in the range of 80% conversion. Although Flory[12] reported that kinetic data above $\overline{DP} > 5$ should be considered for studying the mechanism of a reaction, many authors[32–34] have reported the kinetics for the early stages of step-growth polymerization, where

changes in the polarity of the medium occur when conversion increases. Based on similar approaches efforts, were taken to analyze the reaction kinetics of the para acetamido–benzoic acid homopolymer system.

The treatment of the kinetic data was carried out on the assumption that the reaction medium existed in a molten state. Although the slight possibility of the existence of molten versus solid phase could exist in the reaction medium, the actual phase of each could not be determined because of experimental constraints.

The change in slope noted in both catalyzed and uncatalyzed reactions decreased with higher temperatures, as indicated in Figure 3. The reactions are found to follow the same order in both the kinetic regimes as observed by the fit. The low values for the slope at higher temperatures could be the result of (1) a decrease in the reactivity of the functional groups, causing no appreciable increase in the degree of polymerization; and (2) slow chain growth (because of high temperature) occurring within the precipitated oligomer by stepwise addition of the monomer. Second-order rate constants k_1 and k_2 were evaluated from the solution of eq. (11) by numerical integration and nonlinear optimization. The values of rate constants are listed in Table I and the experimental data and model results are shown in the kinetic plots (Figs. 3–7).

An induction period is noted at all temperatures (Table I). The induction period is found to decrease with an increase in reaction temperature. The geometries of the reactor and condenser are the possible causes of the occurrence of an induction period.

Figure 3 shows a second-order plot that is indeed followed quite generally for the uncatalyzed homopolymers at three different temperatures. Figure 4 indicates that the reaction rate is adequately modeled by second-order kinetics, even for catalyzed reactions. It is seen from Figures 3 and 4 that the difference between them is mainly quantitative. Different polycondensation catalysts like zinc acetate, antimony trioxide, and sodium acetate (1 mol % concentration) were tried at the highest temperature (285°C) to determine the best catalyst. These catalysts were not found to be very promising, with the exception of sodium acetate at 0.25 mol % concentration. If we attribute a physical meaning to the term fractional conversion as the amount of monomer units converted to oligomers it is obvious from the plots that the catalysts do not play a major role in increasing the average degree of polymerization.
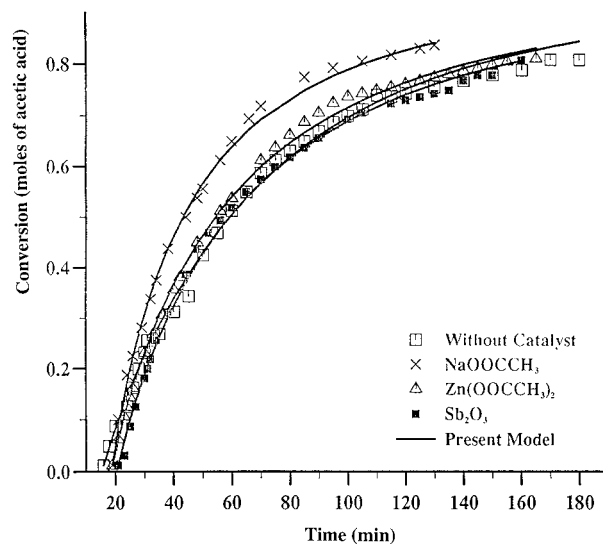

Figure 4 Second-order plot illustrating effect of nature of catalyst (1 mol % concentration) for the homopolymerization of 4-acetamidobenzoic acid at 285°C.

Experiments were conducted for each temperature. The values of energy of activation and frequency factor were evaluated by using the least-squares fit. A glance at Table I reveals that the catalyst sodium acetate (precisely 0.25 mol %) plays only a marginal role in decreasing the energy of activation. The activation energy values for the second-order rate constants k_2 are found to be more comparable to those of k_1, the rate constant obtained for the initial stages of the reaction. The rate constants indicated in Table I are found to increase only marginally as a function of temperature in an individual set. The activation energy values for catalyzed reactions are found to be high compared to those of uncatalyzed reactions. This observation is also apparent from Figures 5a and 5b. It is true that the plots are good, given that an acceptable error is noticed between the experimental points and the modeled line.

Table I depicts that the activation energies are higher in the second kinetic regime. This indirectly implies a decrease in rate of reaction in this regime at the working temperature, although this observation is not valid based on the values for k_2 noted in Table I. The expression for the rate constant is within the format of the theory of reaction rates.

$$k = \frac{kT}{h} \exp^{(\Delta S/R)} \exp^{(-\Delta H/RT)} \qquad (14)$$

$$E_{\exp} = \Delta H + 2RT \qquad (15)$$
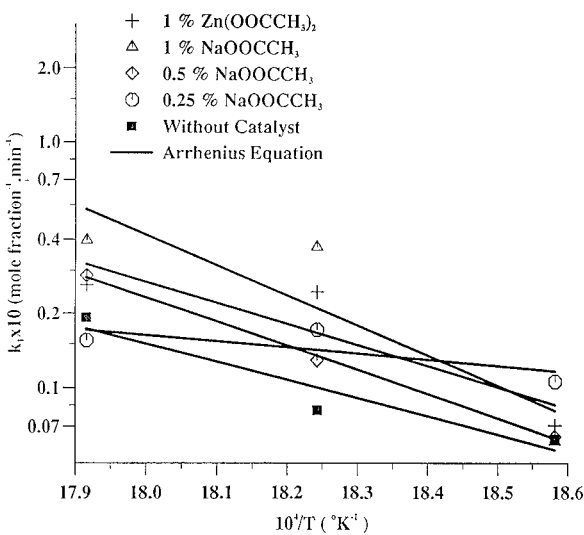
(a)
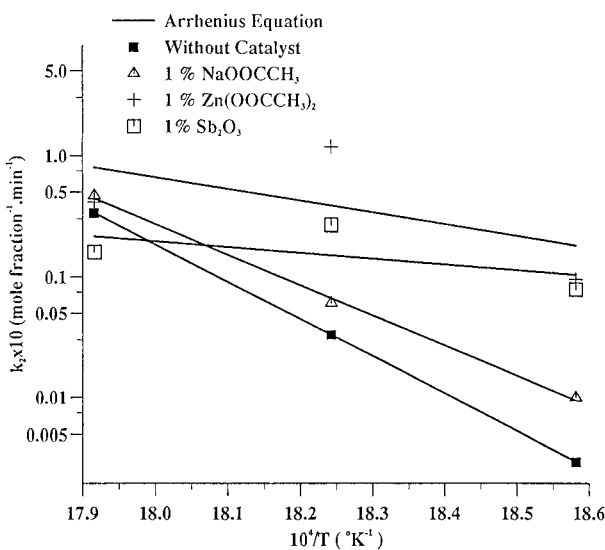
(b)

Figure 5 (a) Arrhenius plots for uncatalyzed and catalyzed homopolymerization of 4-acetamido benzoic acid for k_1. (b) Arrhenius plots for uncatalyzed and catalyzed homopolymerization of 4-acetamido benzoic acid for k_2.

where the symbols ΔS, ΔH, and $E_{\exp}$ represent, respectively, the entropy of activation, enthalpy of activation, and the experimentally determined energy of activation when two or more monomers react to form a polymer. A rise in energy of activation is also observed in the second kinetic regime. This observation is supported with the relatively high entropy values in the second regime. The overall increase in free energy of activation could thus be the probable cause for the increase in activation energy values in the second regime.
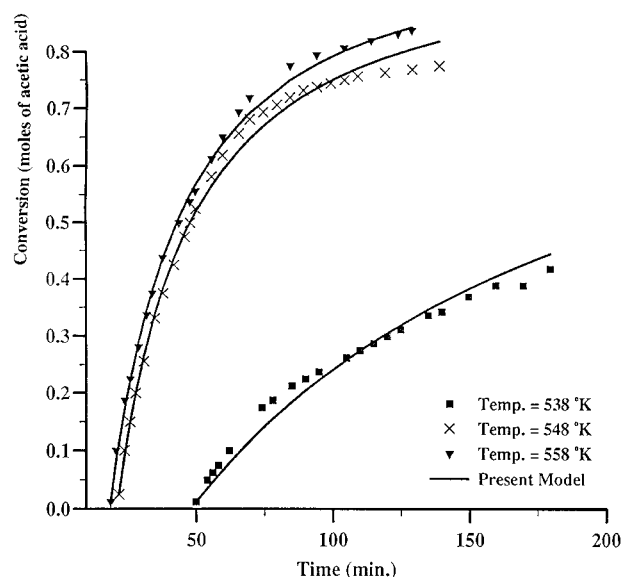

Figure 6 Second-order plot illustrating effect of temperature for 1 mol % sodium acetate catalyzed homopolymerization of 4-acetamido benzoic acid.

Figures 6 and 7 are typical plots indicating that second-order kinetics is also followed for catalyzed reactions at different temperatures and catalyst concentrations.

Characterization

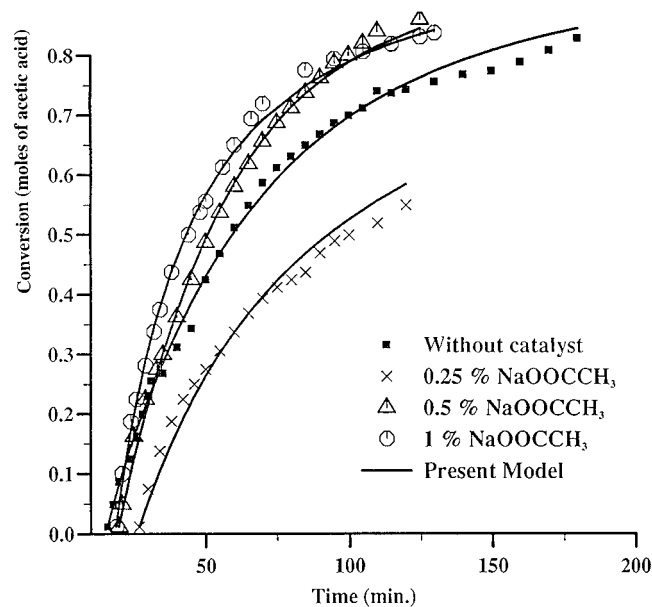Characterization of polyamides by differential scanning calorimetry (DSC) leads to a possible

Figure 7 Second-order plot illustrating effect of sodium acetate concentration for the homopolymerization of 4-acetamido benzoic acid at 265°C.
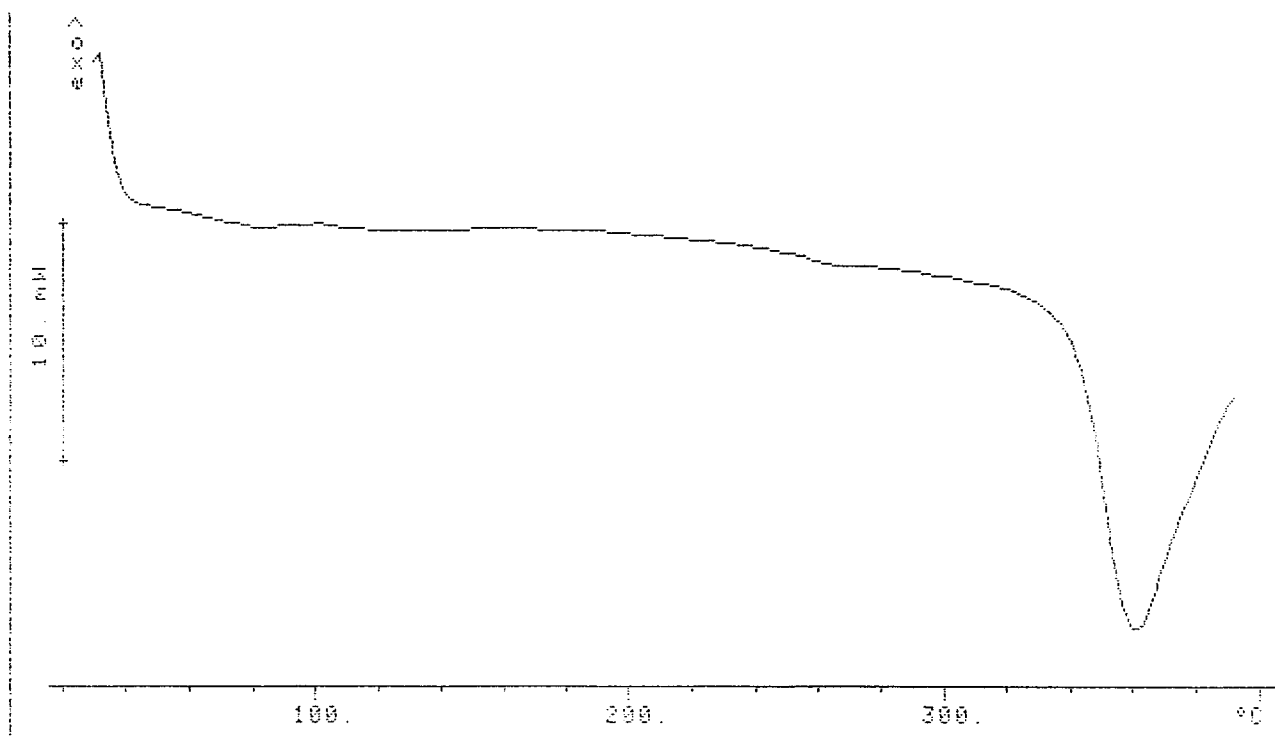
Figure 8 Thermogram indicating decomposition of the homopolyamide during the first heating cycle (20°C/min).

conclusion that the wholly aromatic polyamides formed by condensation of acetic acid degrade immediately after melting (Fig. 8).

CONCLUSIONS

High-temperature acidolysis of *p*-acetamido benzoic acid were studied at three different temperatures using three different catalysts and catalyst concentrations. All these reactions start as a slurry and progressively tend to solid-state reactions. Two different kinetic regimes were noticeable in the kinetic plots in all reactions. A simple second-order rate law is capable of analyzing the system. Reaction rates in the range of 10^{-2} to 10^{-3} conc^{-1} time^{-1} were noted for the second-order plots. Activation energies lie in the range of 53 to 640 kJ/mol for the homopolyamide system.

DSC analysis of the system indicates that the oligomers are meltable at 360°C, followed by degradation.

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