Homopolymerization of 4-Propionoxybenzoic Acid: A Kinetic Study

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ABSTRACT: A kinetic study of the synthesis of poly(4-oxybenzoate) by melt-step growth polymerization using *para*-propionoxybenzoic acid is reported. The polycondensations obey second-order kinetics, irrespective of whether the reaction was catalyzed or uncatalyzed. Breaks are observed in the kinetic plots, suggesting the presence of different kinetic regimes during the course of the reaction. An elaborate kinetic model that presupposes precipitation of oligomers predicts two-stage kinetics as well as breaks in the rate plots and fits experimental data well throughout the course of the reaction and the performance of two transesterification catalysts are estimated. No isokinetic temperature is displayed for the transesterification reaction. Activation energy values for catalyzed reactions are found to be higher than the uncatalyzed reaction, indicating that entropy factors drive the reaction to completion. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 467–476, 1999

Key words: homopolymerization; 4-propionoxybenzoic acid

INTRODUCTION

The synthesis and properties of poly(4-oxybenzoate) have been the object of numerous investigations¹⁻¹⁰ and patent claims.¹¹⁻¹⁴

As early as 1882, Schieff and Kepl attempted the thermal condensation of free 4-hydroxy benzoic acid; but these efforts failed due to decarboxylation and etherification of the hydroxy groups. During the last 4 decades several research groups have reported the synthesis of poly(4-oxybenzoate) from 4-hydroxybenzoic acid. These condensations were conducted at temperatures less than 120°C in solution using dehydrating agents such as trifluoroacetic anhydride, thionyl chloride, and phosphorous derivatives; however, only oligomers were obtained.

Information on molecular weight and other properties of poly(4-hydroxybenzoate) are lacking because oligomers of 4-hydroxybenzoic acid with DPs ≥ 6 are insoluble in all common solvents and not meltable. It is likely that condensations in solution at low temperatures yield high molecular weight poly(4-oxybenzoate), regardless of the condensing reagent used.

Because poly(4-oxybenzoate) is not meltable and insoluble in all common solvents, it is difficult to process it, and its properties depend on both the nature of the monomer and the reaction conditions used in the synthesis work.

Most samples of poly(4-oxybenzoate) described in the literature were prepared by thermal condensation of 4-acetoxy benzoic acid (4-ABA) in an inert reaction medium like Therminol or Marlotherm- S^{15-19} [eq. (1)].

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$$n CH_{3} CO - O \longrightarrow CO_{2} H \xrightarrow{(\geq 300^{\circ}C)}_{-CH_{3} COOH} + O \longrightarrow CO \xrightarrow{1}_{n} (1)$$

Such polycondensations are usually conducted in concentrated monomer solutions (5-10 wt %) with stirring at $300-350^{\circ}$ C.

Though synthesis of poly(4-oxybenzoate) by melt polymerization was known since the 1950s,⁸ the kinetic study of this process was not reported. Mathew et al.²⁰ reported the melt polymerization kinetics of poly(4-oxybenzoate) by melt stepgrowth polymerization using 4-acetoxybenzoic acid. The performance of three transesterification catalysts were also investigated. The polycondensations were found to obey a second-order kinetics, irrespective of whether the reactions were catalyzed or uncatalyzed. Breaks were observed in the kinetic plots, suggesting the presence of different kinetic regimes during the course of the reaction.

The major aim of the present work is to study the reactivity of 4-propionoxybenzoic acid in the synthesis of poly(4-oxybenzoate) and the underlying unique features in such reactions.

The work was carried out with the following objectives: (1) develop a novel catalytic synthesis route for poly(4-oxybenzoate) through melt polymerization using 4-propionoxy benzoic acid as the monomer; (2) optimization of catalyst performance; (3) a detailed kinetic analysis; and (4) characterization of the polymer.

The work is presented as follows: two different catalysts were employed to identify the most optimal catalyst and its concentration. A conventional second-order kinetic analysis is then attempted. The intrusion of oligomer precipitation and how it adds to the complexity of the kinetics (i.e., breaks in the kinetic plots) is then analyzed. The role of interfacial reaction leading to secondorder kinetics is then postulated. Lastly, characterization of a typical oligomer using hot-stage polarizing microscopy and differential scanning calorimetry is illustrated.

EXPERIMENTAL

Materials

4-Propionoxybenzoic acid was prepared by sodium hydroxide catalyzed reaction of 4-hydroxybenzoic acid with propionic anhydride and was



Figure 1 Experimental apparatus.

recrystallized with methanol. The product yield was 70%, and it had a melting point of 180°C.

Reactor Details

A 300-mL HASTELLOY- B_2 -based reactor depicted in Figure 1 was used for polymer synthesis. The reactor had four ports for charging/stirring the reactants, nitrogen gas inlet, N_2 gas/vapor outlet, 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 0.25 mol of 4-propionoxy benzoic acid. Dry nitrogen (20 mL/min) was used throughout the reaction to prevent oxidation and degradation reactions. The temperatures chosen for the catalyzed and uncatalyzed reactions were 230, 245, and 260°C. It is of some technological interest to check the effects of two different transesterification catalysts, zinc acetate, and antimony trioxide employed for the synthesis of poly(4-oxybenzoate). Concentrations (0.25, 0.5, and 1.0 mol %) of catalysts were varied to optimize their performance. The amounts of parapropionoxybenzoic acid lost by sublimation accounted to a maximum of 0.1% of the monomer charged.

The progress of the reaction was measured by monitoring the rate of side product propionic acid, formed as a function of time. The purity of propionic acid was checked by gas chromatograph. At 230°C the purity was 99%, whereas at 245 and 260°C the purity was 97%. The average degree of polymerization $(\overline{X_n})$ was found based on the mol of propionic acid produced. (The maximum degree of polymerization attained was six.)

The solid-state reaction of the pure oligomer was not appreciable, and was of no kinetic significance as far as extraction of propionic acid was concerned. Most of the experimental runs were completed in a span of 2 h.

Measurements

Thermal transitions of the polymers were obtained with a Mettler DSC 30 apparatus interfaced with a thermal analysis data station under nitrogen atmosphere using a sample size of 10-15mg. A heating rate of 10° C/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.

The polymers were examined under a Reitzner hot stage polarizing microscope. A small amount of sample was mounted between the polymer glass slide and cover slip, and was then heated at a constant rate. The polymers were observed under crossed polarizers.

RESULTS AND DISCUSSION

Kinetic Model Development

In the analysis of the kinetics of poly(4-oxybenzoate), it was first assumed that the formation of poly(4-oxybenzoate) proceeds by a bimolecular mechanism outlined below:

$$\mathrm{HA} \Leftrightarrow^{k_i} \mathrm{H}^+ + \mathrm{A}^- \tag{2}$$

$$\mathrm{HA} + \mathrm{H}^{+} \Leftrightarrow \mathrm{H}_{2}\mathrm{A}^{+} \tag{3}$$

$$\mathrm{H}_{2}\mathrm{A}^{+} + \mathrm{A}^{-} \xrightarrow{k_{r}} \mathrm{P} + \mathrm{A}_{\mathrm{c}}\mathrm{H} \tag{4}$$

$$A_{c}H \Leftrightarrow A_{c}^{-} + H^{+}$$
(5)

where A⁻, H₂A⁻, P, and A_C H denote the 4-propionoxy benzoate anion, protonated monomer, growing chain (dimer, trimer, etc.) and propionic acid respectively. k_i , k_p , k_r , and k_{AC} denote the ionization constant, protonation constant, rate constant, and ionization constant of propionic acid, in that order.

Within the preview of the above mechanism if *x* denotes the number of moles of propionic acid (product) formed then,

$$\frac{dx}{dt} = k_r [\mathrm{H}_2 \mathrm{A}^+] [\mathrm{A}^-]$$
(6)

$$k_i = \frac{[\rm{H}^+][\rm{A}^-]}{[\rm{HA}]}$$
(7)

$$k_{p} = \frac{[\mathrm{H}_{2}\mathrm{A}^{+}]}{[\mathrm{H}\mathrm{A}][\mathrm{H}^{+}]}$$
(8)

combining eqs: (6), (7), and (8) we get,

$$\frac{dx}{dt} = k_r k_p k_i \,[\text{HA}]^2 \tag{9}$$

where c_0 is the initial concentration of monomer.

The concentration cannot be expressed in absolute units because molar volume of the melt is not known. For the pure melt the assumed initial concentration $c_0 = 1$.

Let $k = k_r$, k_p , k_i , and let P denote the factional conversion (i.e., $P = x/c_0$), then eq. (9) can be transformed to:

$$\frac{dx}{dt} = kc_o^2 (1-P)^2$$
 (10)

or

$$\frac{dP}{dt} = kc_o(1-p)^2 \tag{11}$$

Separating variables and integration gives:

$$\frac{1}{(1-P)} = kc_o t + 1 \tag{12}$$

The above equation indicates that a plot of 1/(1 - P) vs. time should give a straight line. This was not the case for the experimental runs that were undertaken (see, for instance, Fig. 2). This leads us to the conclusion that a simple biomolecular reaction mechanism is not enough to describe the kinetics of poly(4-oxybenzoate). The reason is probably due to precipitation of an



Figure 2 Second-order plots for uncatalyzed reaction at various temperatures.

oligomer that affects the kinetics of the overall process. To quantitatively prove that oligomer precipitation is important and affects the kinetics of the process we give the following mechanism for a step-growth polymerization reaction. The main consequences of oligomer precipitation with $\overline{DP} \gg n_c$, where n_c is the precipitated oligomers is considered below.

Chain growth occurs by step additions where at a given time only two molecules react;

$$P_{1} + P_{1} \xrightarrow{k_{1}} P_{2}$$

$$P_{1} + P_{2} \xrightarrow{k_{1}} P_{3}$$

$$P_{3} + P_{1} \xrightarrow{k_{1}} P_{4}$$

$$\dots$$

$$P_{n-2} + P_{1} \xrightarrow{k_{1}} P_{n-1}$$

$$P_{n-1} + P_{1} \xrightarrow{k_{n-1}} P_{n} \downarrow$$

As per the assumptions involved in the Flory-Schulz distribution, the end group reactivity remains the same irrespective of the degree of polymerization. This assumption is valid till the (n - 1)th oligomer stage.

If we assume further that oligomers with $\overline{DP} \ge n = n_c$ precipitate out of system (as indicated by the inverted arrow), then further growth of the

polymer chains has to be an interfacial reaction between the absorbed monomer and oligomeric lamella.²¹ This, in turn, is supposed to take place at a much lesser rate than the reactions between monomers and the oligomeric ($\overline{DP} \leq n - 1$) species. However, in principle, one would argue that the formation of an oligomer ($\overline{DP} = n$) can occur due to (n - 1)/2 reaction pathways for odd oligomer and n/2 pathways for even oligomer. For low degrees of conversion, the sequences outlined are important. The net rate of propionic acid production is given by

$$\text{Rate} = \sum_{i=2}^{n} \frac{dP_i}{dt}$$
(13)

which results in an expression of the form

$$\frac{d(\text{CH}_{3}\text{CH}_{2}\text{COOH})}{dt} = k_{1}P_{1}^{2} + k_{2}P_{1}P_{n-1} \quad (14)$$

here, P_n denotes concentration of *n*th oligomer. If we assume Flory-Schulz distribution up to the (n - 1)th oligomer stage, we have

$$\frac{dP}{dt} = k_1 (1-P)^2 \left[1 + \frac{k_2}{k_1} P^{n-2} \right]$$
(15)

where P is degree of conversion of 4-propionoxybenzoic acid at any instant.

Parameter Estimation

The parameters to be evaluated in the kinetic model described earlier are the rate constants k_1 and k_2 , and the degree of polymerization of precipitated oligomer (n). A total of 21 experiments were carried out to evaluate these parameters. As indicated in the experimental section, different sets of conditions (temperatures and initial concentrations), were used for the catalyzed and uncatalyzed reactions. Furthermore, the concentration of catalyst used was also varied. The parameters in the model were estimated using a differential algebraic optimization technique due to Cuthrell and Biegler.²² This technique is a nonlinear programming method based on sequential quadratic programming (Reklaitis),²³ whereby the differential equations modeling the kinetics of the system are converted to a set of approximating algebraic equations by using orthogonal collocation. First, the degree of conversion P is parameterized as a piece-wise polynomial written in Langangian form:

$$P_{k+1}(t) = \sum_{i=0}^{k} P_i \phi_i(t)$$
 (16)

where

$$\phi_{i}(t) = \prod_{k \neq i}^{k} \frac{(t - t_{k})}{(t_{i} - t_{k})}$$
(17)

 $P_{k+1}(t)$ s in eq. (16) denote (k + 1)th order polynomials. The notation $k \neq i$ indicates that $k = 0, \ldots, i - 1, i + 1, \ldots, k$. Equation (16) substituted into eq. (15), gives the residual equation:

$$\sum_{i=0}^{k} (P_i \phi_i(t)) = k_i (1 - P_{k+1}(t))^2 \times \left[1 + \frac{k_2}{k_1} P_{k+1}^{n-2}(t) \right]$$
(18)

Discretization of the above residual yields the following set of algebraic equations:

$$R(t_i) = \sum_{i=0}^{k} \left(P_i \dot{\phi}_i(t) \right) - k_1 (1 - P_i^2) \left[1 + \frac{k_2}{k_1} P_i^{n-2} \right]$$
(19)

$$i=1,\ldots,k.$$

The objective of the optimization model is to minimize the sum of square residuals (SSE) between the calculated values of the fractional conversion and the experimental values; i.e.,

Minimize
$$\sum_{d=1}^{N_d} \{ [P]_d^{\exp} - [P]_d^{\operatorname{cal}} \}^2$$
(20)

where N_d is the number of experimental points.

The optimization problem to estimate the kinetic parameters can now be summarized as follows:

Find k_i , k_{n-1} , and n so as to:

Minimize
$$\sum_{d=1}^{N_d} \{ [P]_d^{\exp} - [P]_d^{\operatorname{cal}} \}^2$$
(20)

Subject to:

$$R(t_i) = \sum_{i=0}^{k} P_i \dot{\phi}_i(t) - k_1 (1 - P_i^2) \left[1 + \frac{k_2}{k_1} P_i^{n-2} \right]$$
(19)

 $P_0 = [P]_0$, initial fractional conversion

$$i = 1, ..., k$$

In the above model, the degree of oligomer precipitation is an integer number. Thus, the above model (p) is actually a mixed nonlinear integer program. However, if we enumerate over *n*, model (p) can still be solved via a sequential quadratic programming technique. It has been shown²⁰ that *n* varies from 1 to 6. This is not a wide range that will pose difficulties in an enumeration procedure. It is appropriate, therefore, to fix n in the model to a certain integer number and solve the resulting NLP problem to calculate the SSE and the parameters k_i and k_{n-1} . A given degree of oligomer precipitation n is first assumed, and the model is solved for the minimum SSE. The degree of precipitation n is then increased by 1, and a new SSE is recorded. The n leading to the best SSE is retained as the degree of oligomer precipitation that best describes the kinetic system. The corresponding kinetic parameters are taken as the best parameter estimates. The results of the optimization process for the various experiments are shown in Table II.

Figure 3 depicts a second-order plot that takes precipitation into consideration. The plot indicates that the reaction rate is adequately modeled by second-order kinetics for uncatalyzed reactions. Figure 4 indicates that a similar trend is followed for catalyzed reactions. As an illustration, we have used antimony trioxide (1 mol % concentration). It is easily noticed that the differences between uncatalyzed and catalyzed rate plots are quantitative and not qualitative. Thus, breaks in the kinetics plot and an induction period are present for both the plots. The point at which the break occurs as a function of temperature for a few typical runs are indicated in Table I. As seen in the table, the value for breaks increases with temperature. The breaks occur at a higher value for catalyzed reaction relative to uncatalyzed reactions. A physical interpretation and a qualitative explanation of these breaks is deferred later. The nature of the plots are not al-

No.	Reaction	Temperature	S.S.E k_1/k_2	$\ln A_1$	Activation Energy E_1 (Kcal/mol)	$\ln A_2$	Activation Energy E_2 (Kcal/mol)
1	Uncatalyzed	230°C	+0.01 0 102/15 67	41 65	44 7	29.8	27 18
1	e neutury zeu	245°C	+0.01 0.033/21.76	11.00	11.1	20.0	21.10
		260°C	+0.39 0.322/73.11				
2	Zinc Acetate	230°C	$+0.018\ 0.03/3.54$	68.05	71.96	50.6	49.30
	(0.25 mol %)	245°C	$+0.003 \ 0.062/18.77$	00.00	11.00	00.0	10.00
	(0.20 1101 /0)	260°C	± 0.08 1.762/57.08				
	Zinc Acetate	230°C	$\pm 0.003 \ 0.015/13.48$	80.4	84.04	35.5	28.32
	(0.5 mol %)	$245^{\circ}\mathrm{C}$	$\pm 0.008 \ 0.986/69.12$				
		260°C	$\pm 0.012 \ 1.565/81.85$				
	Zinc Acetate	230°C	$\pm 0.006 \ 0.024/22.30$	66.8	70.1	31.6	28.32
	(1.0 mol %)	$245^{\circ}\mathrm{C}$	$\pm 0.009 \ 0.77/76.45$				
		260°C	$\pm 0.007 \ 1.227/109.5$				
3	Antimony trioxide	230°C	$\pm 0.005 \ 0.053/13.6$	60.29	62.9	34.5	31.45
	(0.25 mol %)	$245^{\circ}\mathrm{C}$	$\pm 0.005 \ 0.884/49.6$				
		260°C	$\pm 0.005 \ 1.811/81.03$				
	Antimony trioxide	230°C	$\pm 0.004 \ 0.012/10.17$	61	64.7	36.5	34
	(0.5 mol %)	$245^{\circ}\mathrm{C}$	$\pm 0.011 \ 0.54/55.36$				
	· · · · ·	$260^{\circ}\mathrm{C}$	$\pm 0.010 0.45/68.13$				
	Antimony trioxide	$230^{\circ}\mathrm{C}$	$\pm 0.017 \ 0.004/10.03$	99	104.05	37.8	35.4
	(1.0 mol %)	$245^{\circ}\mathrm{C}$	$\pm 0.019 \ 0.434/37.80$				
		260°C	$\pm 0.010 \ 1.381/73.38$				

Table II Rate Constants and Activation Energies for Catalyzed and Uncatalyzed Reactions

tered by increasing the antimony trioxide concentration from 0.5 to 1.0 mol %, but the rates are slightly enhanced. This, in turn, means that the turnover number (number of reaction events) decreases with an increase in concentration of the catalyst molecules, suggesting that all the catalyst sites are not uniformly accessible for the second-order reaction.

Three different temperatures 230, 245, and 260°C were employed for the reaction. As anticipated, the higher temperature shows sharp breaks for both catalyzed and uncatalyzed runs. These are not prominent in the low-temperature runs. Figure 5 denotes the corresponding rate



Figure 3 Second-order plot indicating the effect of temperature for uncatalyzed reactions.



Figure 4 Second-order plot illustrating the effect of temperature for antimony trioxide-catalyzed reactions (1 mol %).

Figure No.	Catalyst	$\left(rac{1}{1-P} ight)$ at 230°C	Time (min)	$\left(rac{1}{1-P} ight)$ at 245°C	Time (min)	$\left(rac{1}{1-P} ight)$ at 260°C	Time (min)
2 3 4	Uncatalysed Antimony Trioxide (1 mol %) Zinc Acetate (1 mol %)	$1.33 \\ 2.1 \\ 1.77$	$\begin{array}{c} 122\\ 88\\ 32 \end{array}$	$1.7 \\ 3.56 \\ 2.52$	30 57 28	$2.98 \\ 3.15 \\ 3.15$	22 23 18

Table I Breaks Noted for Typical Uncatalyzed and Catalyzed Polymerization Reactions

behavior for zinc acetate-catalyzed reactions at 1 mol % concentration at three different temperatures. From Figures 3–5 we note that the time at which the break occurs varies with temperature. The breaks decrease from 122 to 22 min as the temperature is increased from 230 to 260°C, while for catalyzed reactions, the decrease in time varies from 90 to 10 min. The most common trial of all these plots is that for the high temperature runs the break occurs at $\overline{DP} \ge 3.15$. There have been reports of oligomer precipitation with \overline{DP} ≥ 5 in the polymerization of acetoxybenzoic acid,²¹ and the breaks may have a physical explanation in terms of mechanism. This possibility is already spelled out in the experimental section. A quantitative development of this idea is deferred below. The other explanations for the breaks are (a) activity level of the catalyst can change with time for catalyzed reaction; and (b) reactivity of the end carboxylic acid group may depend on the \overline{DP} .



Figure 5 Second-order plot illustrating the effect of temperature for zinc acetate-catalyzed reactions (1 mol %).

Influence of Catalyst Concentration on Rate Constant in the Two Stages

From Figures 3–5 it is obvious that two kinetic constants are displayed for both stages of the reaction with $k_2 > k_1$ (Table II).

It is instructive to study the influence of concentration of the catalyst on the rate constant. The highest temperature employed in our studies is 260°C, because monomer decomposition may intrude and add complexity. It is, thus, desired to check the effects at 245°C (Fig. 6), for comparison of different catalyst activity. The essential idea is to check whether the turnover number is independent of catalyst concentration. If the turnover number is independent of catalyst concentration, then one can state that all catalyst sites are equally accessible. To test this, the degree of polymerization is plotted as a function of time in Figures 6 and 7 for antimony trioxide and zinc acetate at 245°C. Although the plots for antimony trioxide are apart at three concentrations, at one concentration they are close together for zinc acetate. It appears that the turnover number de-



Figure 6 Plot illustrating the effect of concentration for antimony trioxide-catalyzed reactions at 245°C.



Figure 7 Plot indicating the effect of concentration for zinc acetate-catalyzed reactions at 245°C.

creases with increasing catalyst concentration. This suggests that at higher concentration all the catalytic sites are not uniformly accessible for the reaction. The rates, further insensitive to rise with catalyst concentration, suggest this route. However, for at least one catalyst system a slight temperature rise can make a totally different picture, as shown in Figure 8 for antimony trioxidecatalyzed reaction. There is appreciable influence of temperature compared to Figure 6. The breaks in all the plots are indicative of two rate constants. The Arrhenius parameters for each of these regions are shown separately in Table II. In Figure 9, two catalysts are analyzed for a typical concentration of 1 mol %. The lines differ from each other, indicating different activation ener-



Figure 8 Effect of concentration for antimony trioxide-catalyzed reactions at 260°C.



Figure 9 Arrhenius plot for antimony trioxide and zinc acetate reactions (1 mol %).

gies. In conclusion, there is difference in the activity of the catalyst present in the two regimes k_1 and k_2 . Higher values for the activation energy are found in the initial stages of the reaction and the values decrease for the second regime.

It is also borne out from Table II that the rate constant k_2 is higher than k_1 , even though activation energies of the second stage are lower than the first stage. This points to a lower free energy of activation for the first stage. This indirectly points to a lower entropy of activation causing the reaction to slow down. Figure 10 was plotted to check the presence of an isokinetic temperature for three group of runs (three varying catalyst concentrations). The lines do not cross each other, thus overruling the existence of an isokinetic temperature for this system. It appears in Figure 11 that two rate curves belonging to two different catalysts do not cross over to give a temperature



Figure 10 Plot to check the existence of an isokinetic temperature for zinc acetate-catalyzed reaction.



Figure 11 Plot to check the existence of isokinetic temperature for antimony trioxide and zinc acetate-catalyzed reactions at 0.25 mol %.

called the isokinetic temperature. However, this behavior is evident at only $0.25 \mod \%$ concentration and is not universal.

Polymer Characterization

The DSC thermograms shown in Figures 12 and 13 exhibit endotherms (heating cycles) and exotherms (cooling cycles) depicting the liquid crystalline nature of poly(4-oxybenzoate). Table III shows the values for a typical set wherein the catalyst concentration is varied at constant time and temperature. The reversible first-order transition (Fig. 13) points to either (a) reversible change between two crystalline modifications, or (b) crystallization of oligomeric poly(4-oxybenzo-



Figure 12 DSC endotherms of the first heating cycle of uncatalyzed and catalyzed reactions at three catalyst concentrations (0.25, 0.5, and 1.0 mol %) at 260°C.



Figure 13 DSC exotherms of the first cooling cycle of uncatalyzed and catalyzed reactions at three catalyst concentrations (0.25, 0.5, and 1.0 mol %) at 260°C.

ate) during the cooling cycle. Microscopic observations were made in the temperature range over which first-order transitions were noted in DSC. This did not reveal phase change or volatilization, which would arise from postpolycondensation. In the absence of high temperature X-ray data we can only speculate regarding the nature of transition. The comparable values of enthalpy on heating (ΔH_h) and cooling (ΔH_c) discounts the occurrence of degradation reactions on heating the polymer till 350°C.

CONCLUSIONS

Two transesterification catalysts were employed in the synthesis of poly(4-oxybenzoate) by melt polymerization. Second-order kinetics was found to be valid for both catalyzed and uncatalyzed reactions. It appears that two kinetic regimes are present in the course of reaction. For both these regimes, second-order kinetics is found to be valid. A model that takes into account oligomer precipitation also displays two-stage kinetics.

Even though activation energies are larger for the catalyzed reaction (in comparison to the uncatalyzed) entropy factors could possibly be driving the reaction to completion. No isokinetic temperature is displayed for these runs.

The optimal concentrations needed for synthesis have been listed. Our data shows that zinc acetate is a more suitable catalyst. Optical microscopic analysis reveals solid to solid crystalline modification occurs at high temperature. DSC

No.	Reaction	$T_h^{\mathbf{b}}$ (°C)	$\Delta H_h{}^{\rm c}~(\rm kJ/g)$	T^b_c (°C)	$\Delta H_c^{\ \rm c} \ ({\rm kJ/g})$
1	Uncatalyzed	305.4	0.0127	256	0.0146
2	Zinc Acetate (2.5 mol %)	310.7	0.028	264	0.0095
3	Zinc Acetate (0.5 mol %)	325.5	0.0068	273.4	0.0153
4	Zinc Acetate (1.0 mol %)	309.3	0.016	258.7	0.0113

Table IIITransition Temperature and Thermodynamic Data for Catalyzedand Uncatalyzed Reactions^a

^a Reaction temperature 260°C, reaction time 2 h.

 $^{\rm b}\,T_h$ and T_c represents the transition temperature for first heating and cooling cycle.

 $^{c}\Delta H_{h}$ and ΔH_{c} represent enthalpy values on heating the polymer in first heating and cooling cycle.

analysis of uncatalyzed and catalyzed runs were carried out to evaluate enthalpy values. No degradation reactions are found to occur on heating the oligomer to 350°C during a DSC analysis.

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REFERENCES

- Braun, E. J.; Stscy, M.; Tatlow, J. C.; Tedder, J. M.; J Chem Soc 1949, 2976.
- Kametani, T.; Fukumoto, K.; Zasslic, Y. 1960, 80, 1188; Chem Abstr 1961, 55, 3589.
- Elias, H. G.; Warner, R. J. Makromol Chem 1981, 182, 681.
- Higashi, F.; Kobubo, N.; Gato, M. J Polym Sci Polym Chem Ed 1980, 18, 2879.
- Higashi, F.; Kubota, K.; Sekizuka, M.; Gato, M. J Polym Sci Polym Chem Ed 1980, 18, 2879.
- Higashi, F.; Kubota, K.; Sekizuka, M.; Gato, M. J Polym Sci Polym Lett Ed 1980, 18, 385.
- Higashi, F.; Kubota, K.; Sekizuka, M. Makromol Chem Rapid Commun 1980, 1, 457.
- Gilkey, R.; Caldwell, J. R. J Appl Polym Sci 1959, 2, 198.
- Economy, J.; Nowak, B. E.; Cottis, S. G. SAMPLE J 1970, 6, 6.

- Economy, J.; Storm, R. S.; Matkovick, M. I.; Cottis, S. G.; Novak, B. E. J Polym Sci Polym Chem Ed 1976, 14, 2207.
- Fr. 1568152, May 23, 1969, Carborundum Co., Invs: Economy, J.; Novak, B. E. Chem Abstr 1970, 72, 13412.
- Ger. Often, 2025948, Dec. 3, 1970, Carborundum Co., Invs: Economy, J.; Cottis, S. G.; Novak, B. E. Chem Abstr 1971, 74, 54559 k.
- Ger. Often 2157696, June 15, 1972; Carborundum Co., Invs.: Economy, J.; Cottis, S. G.; Novak, B. E. Chem Abstr 1972, 77, 140738 m.
- U.S. 2728 747, Dec. 27, 1955, General Mills Inc., Invs: Aelony, D.; Renfrew, M. M. Chem Abstr 1956, 50, 6098 e.
- Economy, J.; Storm, R. S.; Matkovich, M. T.; Cottis, S. G.; Nowak, B. E. J Polym Sci Polym Chem Ed 1976, 14, 2207.
- Economy, J.; Volksen, W.; Geiss, R. Mol Cryst Liq Cryst 1984, 105, 289.
- Economy, J.; Volksen, W.; Viney, C.; Geiss, R.; Siemens, R.; Karis, T. Macromolecules 1988, 21, 2777.
- Krichldorf, H. R.; Schwarz, G. Polymer 1984, 25, 520.
- Liezer, G.; Schwarz, G.; Kricheldort, H. R. J Polym Sci Polym Phys Ed 1983, 21, 1599.
- Mathew, J.; Bahulekar, R. V.; Ghadge, R. S.; Rajan, G. R.; Ponrathnam, S.; Prasad, S. D. Macromolecules 1992, 25, 7336.
- Kricheldorf, H. R.; Schwarz, G. Makromol Chem 1983, 184, 475.
- Cuthrell, J. E.; Beigler, L. T. AICHE J 1987, 33, 282.
- Reklaits, G. V. Engineering Optimization; Wiley: New York, 1983.