Catalytic Synthesis of Poly(4-oxybenzoate) by Melt Polymerization: A Detailed Kinetic Study[†]

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ABSTRACT: Kinetic study of the synthesis of poly(4-oxybenzoate) by melt step growth polymerization is reported. The performances of three transesterifiation catalysts are estimated. 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. A detailed kinetic analysis reveals that acid catalysis by product cannot explain the breaks. An elaborate kinetic model which presupposes precipitation of oligomers with degree of polymerization $n \geq n_c$, predicts two-stage kinetics as well as breaks in the rate plots and fits experimental data particularly well in the later stages of the reaction. A model based on interfacial polymerization of monomers (on the precipitated oligomers) also explains second-order kinetics and rate enhancement toward the later stages. A novel feature stemming from the kinetic studies is that even though activation energies of catalyzed reactions are larger in comparison to the uncatalyzed route, entropy factors drive the reaction, suggesting the interplay of some kind of compensation effect.

Introduction

Poly(4-oxybenzoate) is a novel thermally stable polymer with proven manifold applications.[1] The first attempts at the synthesis by thermal condensation of 4-hydroxybenzoic acid (unsuccessful due to decarboxylation and etherification) dates back to the end of the 18th century.[2,3] Polymerization attempts in the last 3 decades at temperatures below 120 °C by incorporating dehydrating reagents (trifluoroacetic anhydride[4] and thionyl chloride[5,6]) resulted in oligomers. Solution polycondensations of monomers like *p*-tolyl 4-hydroxybenzoate, 4-(pivaloyloxy)benzoic acid, and 4-(trimethylsiloxy)benzoyl chloride have been successful.[7] The molecular weight of polymer by bulk polycondensation is less than 10 000 while that by solution polycondensations are in the range 20 000–50 000. Regardless of the monomer, condensation first yields a precipitation of oligomer crystals with $\overline{\mathrm{DP}}$ in the range 6–8. Intra- and intercrystalline transesterifications cause chain growth even in the absence of monomer or solvent. The thermal stability of the polymers depends on both the degree of polymerization and crystal modification.[7] Though synthesis of poly(oxybenzoate) by melt polymerization has been known since the 1950s,[8] a kinetic study of this process has not been reported, excepting that in an inert solvent.[9] The major aim of the present work is to demonstrate the efficacy of catalysts 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) a novel catalytic synthesis of poly(4-oxybenzoate) through melt polymerization; (2) a detailed optimization of catalyst performance; (3) a kinetic analysis which also accounts for the added complexity of oligomer precipitation; (4) characterization of the polymer. The work is presented as follows: A number of catalysts are employed to identify the optimal catalyst and the 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 second-order kinetics and rate acceleration is then postulated. Lastly, characterization of a typical oligomer using infrared spectroscopy, optical microscopy, and differential scanning calorimetry is illustrated.

Experimental Section

Materials. 4-Acetoxybenzoic acid was prepared by sodium hydroxide catalyzed reaction of 4-hydroxybenzoic acid with acetic anhydride and was recrystallized with methanol. The product yield was 85% and had a melting point of 186 °C.

Reactor Fabrication. An 80-mL glass-lined electrically heated reactor depicted in Figure 1 was used for polymer synthesis. The reactor had two ports for charging/stirring the reactants and for nitrogen purging. 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 0.05 mol (9.008 g) of 4-acetoxybenzoic acid. A dry nitrogen purge was used throughout the reaction to prevent oxidation and degradation. The temperatures chosen for catalyzed as well as uncatalyzed reactions were 250, 275, 300, 325, and 350 °C. It is of some technological interest to estimate catalyst effects in the melt polymerization of 4-acetoxybenzoic acid. Three catalysts (i) sodium acetate, (ii) zinc acetate, and (iii) dibutyltin oxide were studied to evaluate the acidolysis type transesterification. These catalysts have hitherto not been employed for the synthesis of poly(4-oxybenzoate). Concentrations (0.1, 0.5, and 1.0 mol %) of catalysts were varied to optimize their performance. All experiments were conducted at atmospheric pressure. The amount of 4-acetoxybenzoic acid lost by sublimation at 325 and 350 °C accounted for a maximum of 0.5% of the monomer charged.

The progress of the reaction was monitored by measuring the rate of formation of side product acetic acid as a function of time. The purity of acetic acid was checked by gas chromatography. At 250 °C the purity of acetic acid was almost 99% whereas at 275, 300, 325, and 350 °C it decreased to about 94%. The average degree of polymerization ($\bar{X}_n$) was computed on the basis of the moles of acetic acid produced.

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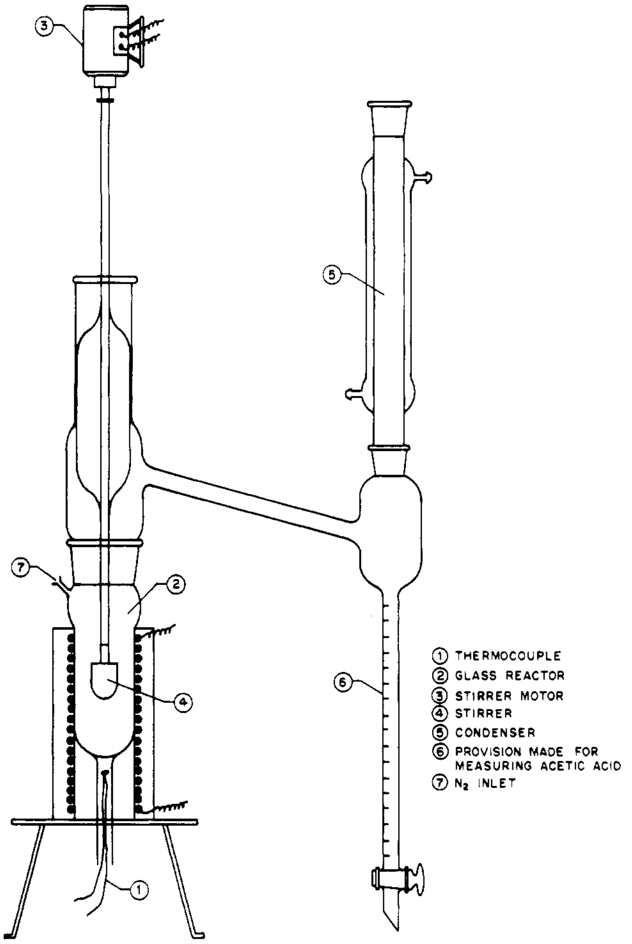

Figure 1. Laboratory scale reaction setup for the synthesis of poly(4-oxybenzoate).

When the degree of polymerization is around 6–8, the resulting oligomers are not meltable even at the highest temperature (350 °C) used in our experiments. However, the solid-state reaction of the pure oligomer product charged was not appreciable and was of no kinetic consequence so far as the production of acetic acid was concerned. Most of the experimental runs were completed in a span of 20–40 min. On the other hand the acetic acid produced by pure solid-state reaction over a period of 1.5 h was only 1–2% of the overall rate of acetic acid generation.

Measurements. Infrared spectra of all the samples were recorded on a Shimadzu IR 470 spectrophotometer using KBr disks. The polymers were examined under a polarizing microscope equipped with a Koffler hot stage. A small amount of polymer was mounted between a glass slide and a cover slip and was then heated on the stage at a constant rate. The polymers were observed under crossed polarizers. Thermal transitions were obtained with a Mettler DSC 30 apparatus interfaced with a thermal analysis data station under nitrogen atmosphere using a sample size of 10–15 mg. A heating rate of 10 K/min was employed in all cases. Indium was used to the calibrate the enthalpy values. A three-metal (In–Pb–Zn) standard was used to calibrate the temperature scale. Samples were analyzed in the temperature range 40–385 °C in both heating and cooling cycles.

Results and Discussion

Simplified Second-Order Kinetics. Formation of poly(4-oxybenzoate) proceeds by a bimolecular reaction through the mechanism[10] outlined below.

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

$$\mathrm{HA} \overset{k_i}{\rightleftharpoons} \mathrm{H}^+ + \mathrm{A}^- \tag{1}$$

$$\mathrm{HA} + \mathrm{H}^+ \overset{k_p}{\rightleftharpoons} \mathrm{H_2A}^+ \tag{2}$$

$$\mathrm{H_2A}^+ + \mathrm{A}^- \xrightarrow{k_r} \mathrm{P} + \mathrm{A_cH} \tag{3}$$

$$\mathrm{A_cH} \overset{kA_c}{\rightleftharpoons} \mathrm{A_c}^- + \mathrm{H}^+ \tag{4}$$

where A^-, H_2A^+, P, and A_cH denote the 4-acetoxybenzoate anion, protonated monomer, growing chain (dimer, trimer, etc.), and acetic acid, respectively. k_i, k_p, k_r, and kA_c denote the ionization constant, protonation constant, rate constant, and ionization constant of acetic acid in that order.

Within the purview of the above mechanism, if x denotes the number of moles of acetic acid (product) formed, then

$$dx/dt = k_r[\mathrm{H_2A}^+][\mathrm{A}^-] \tag{5}$$

$$k_i = [\mathrm{H}^+][\mathrm{A}^-]/[\mathrm{HA}] \tag{6}$$

$$k_p = [\mathrm{H_2A}^+]/[\mathrm{HA}][\mathrm{H}^+] \tag{7}$$

Combining eqs 5–7, we get

$$dx/dt = k_r k_p k_i [\mathrm{HA}]^2 \tag{8a}$$

$$dx/dt = k_r k_p k_i (c_0 - x)^2 \tag{8b}$$

$$dp/dt = k_r k_p k_i c_0 (1 - p)^2 \tag{8c}$$

where c_0 is the initial concentration of monomer and p is the fractional conversion.

The concentration cannot be expressed in absolute units since the molar volume of the melt is not precisely known. For the pure melt the assumed initial concentration $c_0 = 1$. A second-order initial rate will be given on this basis by numerical value of the rate constant itself but will have units moles per second.

It is obvious therefore that the reaction follows second-order kinetics since it is essentially bimolecular. Figure 2 depicts a second-order plot which is indeed followed quite generally. Figure 3 indicates that the reaction rate is adequately modeled by second-order kinetics even for catalyzed reactions. As an illustration we have used dibutyltin oxide at 1 mol % concentration. It is easily noticed that the differences between the catalyzed and uncatalyzed rate plots are mainly quantitative and not qualitative. Thus breaks in the second-order kinetics plot and an induction period are present for both these rate plots. However, the breaks in $1/(1 - p)$ occur for lower values in the case of uncatalyzed reactions. Also if we attribute physical meaning to $1/(1 - p)$ as the number average mean degree of polymerization, it is obvious that for the catalyzed reaction this quantity is larger on the average. A physical interpretation and a qualitative explanation of these breaks in $1/(1 - p)$ is deferred to a later section.

The natures of the plots are not altered by increasing the dibutyltin oxide concentration from 0.5 to 1.0 mol % (Figure 3), but the rates are slightly enhanced. This in turn means that the turnover number (number of reaction events in (mol/s/site) decreases with an increase in concentration of the catalyst molecules, suggesting that

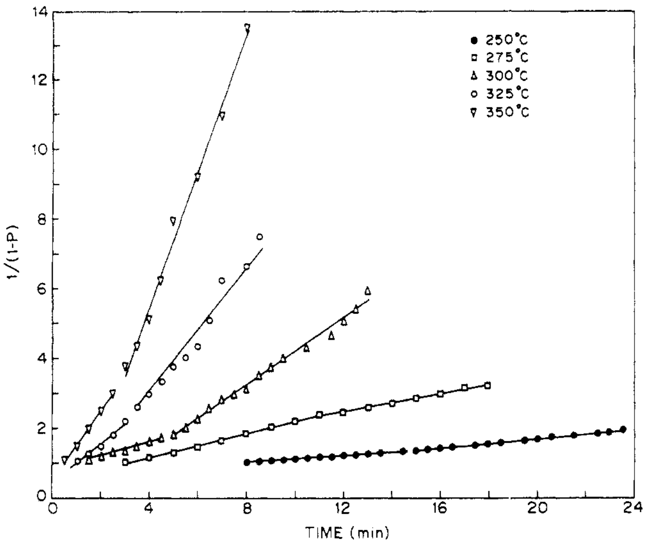

Figure 2. Second-order plot illustrating the effect of temperature for uncatalyzed reactions.

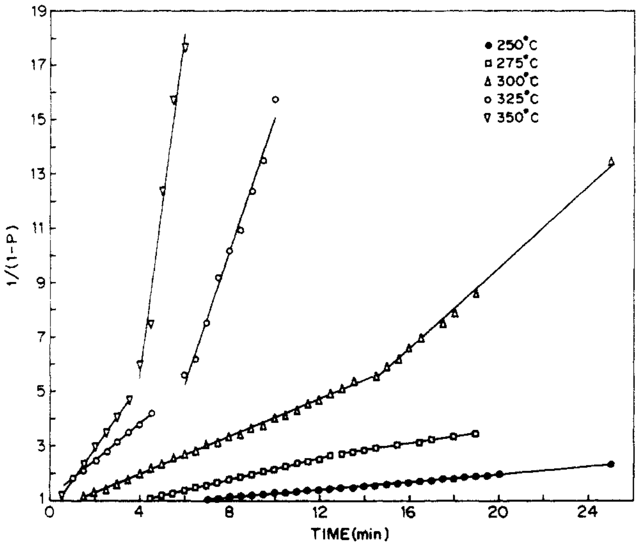

Figure 3. Second-order plot illustrating the effect of temperature for dibutyltin oxide catalyzed reactions (1 mol % concentration).

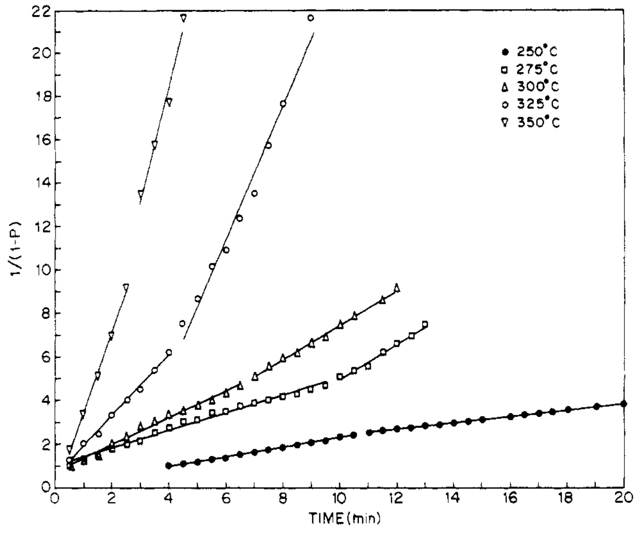

Figure 4. Second-order plot illustrating the effect of temperature for sodium acetate catalyzed reactions (1 mol % concentration).

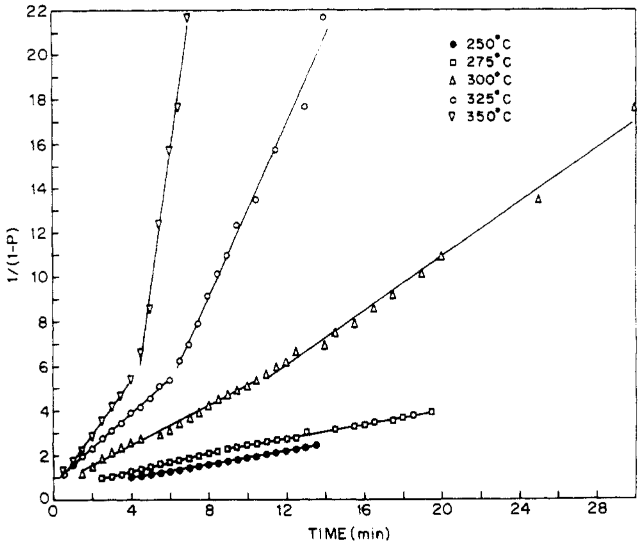

Figure 5. Second-order plot illustrating the effect of temperature for zinc acetate catalyzed reactions (1 mol % concentration).

all the catalyst sites are not uniformly accessible for the second-order reaction.

A wide range of temperatures (from 250 to 350 °C) has been employed and this range is covered in five equal intervals. As anticipated, the higher temperature runs show sharp breaks for both the catalyzed and uncatalyzed reactions. These are not prominent in the low temperature runs.

Figures 4 and 5 denote the corresponding rate behavior for sodium acetate and zinc acetate at 1 mol % concentrations and five different temperatures. From Figures 3–5 we note that the time at which the break occurs varies with temperature. The breaks decrease from 16 to 2 min as the temperature is increased from 250 to 350 °C (for both catalyzed and uncatalyzed experiments). Similar observations have been recorded in the step growth synthesis of poly(phenylene sulfide).[11,12]

The most common trait of all these plots from Figures 3–5 is that for high-temperature runs the breaks in $1/(1-p)$ occur at $\overline{DP} = 5$. There have been reports of oligomer precipitation with $\overline{DP} \geqslant 5$ in the polymerization of acetoxybenzoic acid,[7] and the breaks may have a physical explanation in terms of this mechanism. This possibility has already been spelled out earlier in the Experimental Section. A quantitative development of this idea is given in the next section. The other plausible explanations for these breaks are (i) activity level of the catalyst can change with time for the catalyzed reaction, (ii) reactivity of the end carboxylic acid group may depend on the degree of polymerization, and (iii) heterogeneous (lamellar) chain growth of the oligomer may occur on the surface of the precipitate by stepwise addition of the monomer. The other common sense explanation of a change in effective reaction order with time could not explain the breaks.

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 $k_2 > k_1$. The highest values of k_2/k_1 are displayed by the dibutyltin oxide (which is $\cong 25$) in our studies. However, the differences in the ratios of k_2/k_1 are marginal for the three catalyst systems.

It is instructive to study the influence of concentration of the catalyst on the rate constant. The highest temperature employed in our rate measurements is 350 °C. Some monomer decomposition may intrude and add complexity, as reported previously.[13] It is thus desirable to restict the temperature to 325 °C for comparison of different catalyst activity. The essential idea is to check whether the turnover number (number of molecules

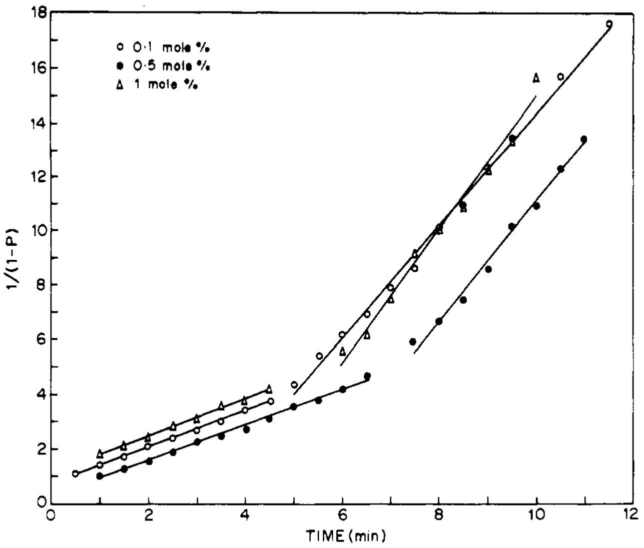

Figure 6. Effect of concentration for dibutyltin oxide catalyzed reactions at 325 °C.

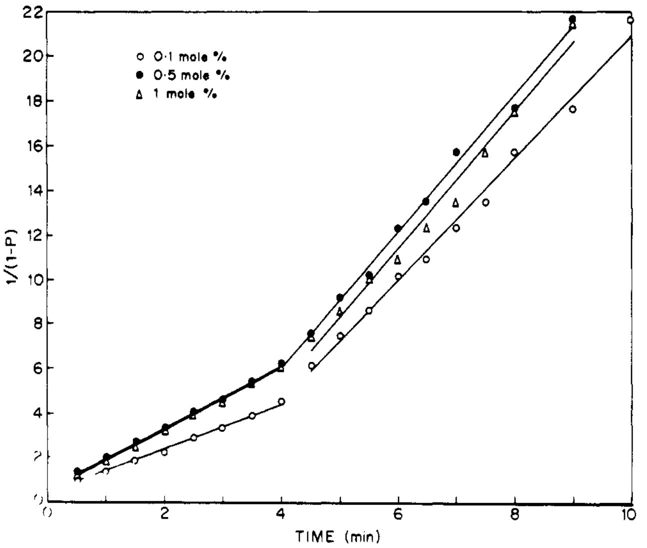

Figure 7. Effect of concentration for sodium acetate catalyzed reactions at 325 °C.

converted per site per second) 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 6–8 for dibutyltin oxide, sodium acetate, and zinc acetate, respectively. While the plots for sodium acetate and dibutyltin oxide are close together at two concentrations, at least for zinc acetate they are wide apart. It appears out that the turnover numbers uniformly decrease with increasing catalyst concentration. This suggests that at higher concentration all the catalytic sites are not uniformly accessible for the reaction. Alternatively, if the lamellar step addition mechanism[14] is operative, then at the interface of the precipitated oligomer, the extent of dispersion of the catalyst is important in deciding the rates. At best this explanation is speculative, but nevertheless cannot be ruled out in our studies. The rates insensitivity to further increase in catalyst concentration suggests this route. However, for at least one catalyst system a slight temperature rise can make a totally different picture, as shown in Figure 9 for dibutyltin oxide. There is appreciable influence of temperature as compared to Figure 6.

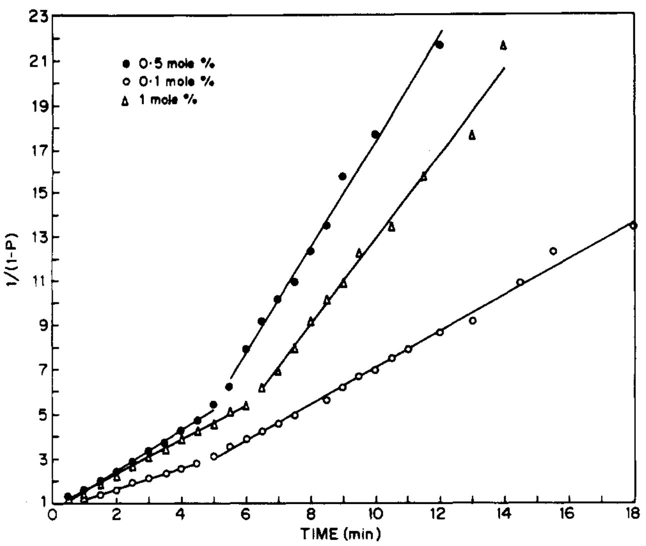

Figure 8. Effect of concentration for zinc acetate catalyzed reactions at 325 °C.

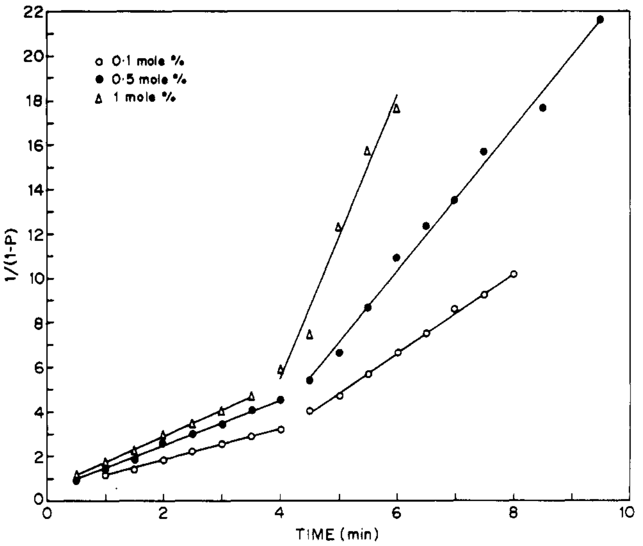

Figure 9. Effect of concentration for dibutyltin oxide catalyzed reactions at 350 °C.

The breaks in all the second-order plots are clearly indicative of two rate constants. It is necessary to determine Arrhenius parameters for each of these regions separately. In Figure 10, three catalysts are analyzed for a typical catalyst concentration of 0.5 mol %. The parallel straight lines evident from these plots imply almost identical activation energies. The activation energies are presented in Table I. In conclusion there is no distinguishing feature of the catalyst present in the first part of the reaction (k_1).

It is also borne out from Table I that the rate constant k_2 are larger than k_1 even though the activation energies of the second stage are larger than the first stage. This points to a higher free energy of activation for the first stage. This means that the entropy of activation becomes more positive and drives the reaction. A detailed thermodynamic analysis will be presented in a subsequent section.

Complex Kinetics with Step Growth Addition and Oligomer Precipitation. In this section we explore the quantitative development of the idea that oligomer precipitation is important and decidedly affects the kinetics of the overall process. As a prelude to this, we envisage the following step growth addition polymerization mechanism (see Appendix):

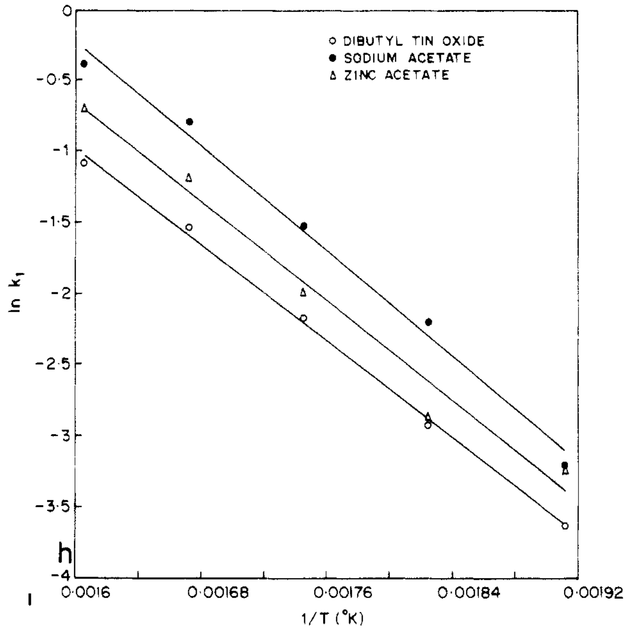

Figure 10. Arrhenius plots for dibutyltin oxide, sodium acetate, and zinc acetate catalyzed reactions (0.5 mol % concentration).

$$P_1 + P_1 \xrightarrow{k_1} P_2$$

$$P_2 + P_1 \xrightarrow{k_1} P_3$$

$$P_3 + P_1 \xrightarrow{k_1} P_4$$

$$- - - - - - - - - - - -$$

$$P_{n-2} + P_1 \xrightarrow{k_1} P_{n-1}$$

$$P_{n-1} + P_1 \xrightarrow{k_{n-1}} P_n \ldots \downarrow$$

If we assume that oligomers with $\overline{\mathrm{DP}} \geq n = n_c$ precipitate out of system (as indicated by inverted arrow), then further growth of the polymer chain has to be an interfacial reaction between the adsorbed monomer and the oligomeric lamella.[7] This in turn is supposed to take place at a much lesser rate than the reactions between monomers and the oligomeric ($\overline{\mathrm{DP}} \leq n - 1$) species.

However, in principle one would argue that the formation of an oligomer ($\overline{\mathrm{DP}} = n$) can occur due to $(n-1)/2$ reaction pathways for an odd oligomer (n = odd) and $n/2$ pathways for an even oligomer (n = even). For low degrees of conversion (and hence degrees of polymerization) the sequences outlined are of chief importance. Even if other reactions occur, their rate expression will be formally identical to the one given here (see Appendix). The net rate of acetic acid production is given by

$$\text{rate} = \sum_{i=2}^{n} \frac{\mathrm{d}P_i}{\mathrm{d}t} \tag{9}$$

which results in an expression of the form

$$\mathrm{d}(\mathrm{CH_3COOH})/\mathrm{d}t = k_1 P_1^2 + k_{n-1} P_1 P_{n-1} \tag{10}$$

Here the P_n denotes the concentration of the nth oligomer.

Some qualitative statements are in order, as to why we choose k_1 and k_{n-1} differently. Analysis of our data seems to necessitate this; not only that, but k_{n-1} has to be chosen higher than k_1, to obtain the rate enhancement in the second stage.

The standard procedure involved in the derivation of the Flory–Schulz distribution assumes $k_1 = k_i$ at all stages of the reaction. However, when oligomer precipitation occurs, this assumption seems to break down, especially if rate acceleration is observed following the precipitation. Now if we assume Flory–Schulz distribution (see Appendix) up to the $(n-1)$th oligomer stage, we have

$$\mathrm{d}p/\mathrm{d}t = k_1(1-p)^2 + k_{n-1}(1-p)p^{n-2}(1-p) \tag{11a}$$

$$\mathrm{d}p/\mathrm{d}t = k_1(1-p)^2[1 + (k_{n-1}/k_1)p^{n-2}] \tag{11b}$$

where p is the degree of conversion of 4-acetoxybenzoic acid at any given instant.

A glance at Figures 11 and 12 predict that agreement with the new model is especially good toward the later stages of the reaction. In the initial stages, however, the predictions of the model are systematically larger in comparison to the experimental values. *Another interesting point to note is that the k_2 and k_1 values are almost close in numerical agreement to earlier values which are determined by assuming the usual second-order kinetics for both these stages.* It is observed that the cutoff value $n = n_c$ for the degree of polymerization increases monotonically with temperature and has to be determined experimentally as the best fit parameter. To site an example, the value of $n_c = 6$ is the best least squares estimate observed for the dibutyltin oxide catalyzed reaction at 350 °C. The value of n_c is also in agreement with the value reported earlier.[7]

Thus we conclude that a more sophisticated kinetic model which takes into account precipitation does not really add much to the understanding of the overall kinetics. Besides for the low degree of polymerization, the fit is much worse.

Role of Interfacial Catalysis. Lastly, a qualitative mechanism which explains the second-order kinetics and rate enhancement can be sought as follows. It is assumed that the catalyst is better dispersed on the precipitated oligomer. Then the following steps presumably occur:

$$\text{catalyst} + \text{oligomer(solid)} \rightarrow \text{catalyst(supported)}$$

$$\text{HA} + \text{catalyst(supported)} \rightarrow \text{HA(ads)}$$

$$\text{HA(ads)} + \text{HA(ads)} \rightarrow \text{dimer} + \mathrm{A_cH}$$

$$\text{HA(ads)} + \text{oligomer}(n-1) \rightarrow \text{oligomer}(n)\downarrow + \mathrm{A_cH}$$

where HA denotes 4-acetoxybenzoic acid, $\mathrm{A_cH}$ is the acetic acid, and the nth oligomer is a solid.

For steric reasons the reaction of HA(ads) with an $n-1$ oligomer will be slow. Also it will generate a fresh catalyst surface and acetic acid and *kinetically display first-order dependence on HA. Since this is not observed experimentally in the later stages of the reaction, we effectively rule out this mechanism.* The other chief contributing reaction (dimerization of HA) then will be kinetically second order, provided we invoke the reasonable assumption that the surface concentration of adsorbed monomers HA will be in direct proportion to the concentration in the bulk (which will be very low in any case, at a high degree of conversion).

The rate enhancement is thus due to the catalytic reaction processes at the interface, which improves the overall efficacy of the catalyst. This involves a further assumption that the dimer is desorbed fast and replenishes

Table I
Activation Energy for Second-Order Plots (Catalyzed and Uncatalyzed Reactions)

catalyst type	catalyst concn	ln A_1	activation energy, E_1 (kcal/mol)	ln A_2	activation energy, E_2 (kcal/mol)	ln (A_2/A_1)
uncatalyzed		13.95 ± 0.27	18.63 ± 2.20	22.16 ± 0.05	26.60 ± 0.41	8.21
sodium acetate	0.1	14.20 ± 0.17	18.15 ± 1.37	29.02 ± 0.32	32.98 ± 2.62	14.82
	0.5	14.55 ± 0.13	18.30 ± 1.03	28.32 ± 0.35	32.00 ± 2.90	13.77
	1.0	14.61 ± 0.27	17.56 ± 2.17	26.62 ± 0.53	29.44 ± 4.35	12.01
zinc acetate	0.1	14.00 ± 0.18	13.71 ± 1.50	23.37 ± 0.27	27.52 ± 4.35	9.37
	0.5	13.95 ± 0.18	17.32 ± 1.50	28.47 ± 0.73	32.77 ± 2.21	14.52
	1.0	14.55 ± 0.09	15.36 ± 0.76	30.36 ± 0.47	31.60 ± 5.94	15.81
dibutyltin oxide	0.1	13.08 ± 0.29	16.82 ± 2.40	29.40 ± 0.87	34.91 ± 7.15	16.32
	0.5	14.65 ± 0.05	16.97 ± 0.46	32.60 ± 0.61	37.65 ± 5.00	17.95
	1.0	14.98 ± 0.12	17.96 ± 0.99	33.13 ± 0.44	37.85 ± 3.58	18.15

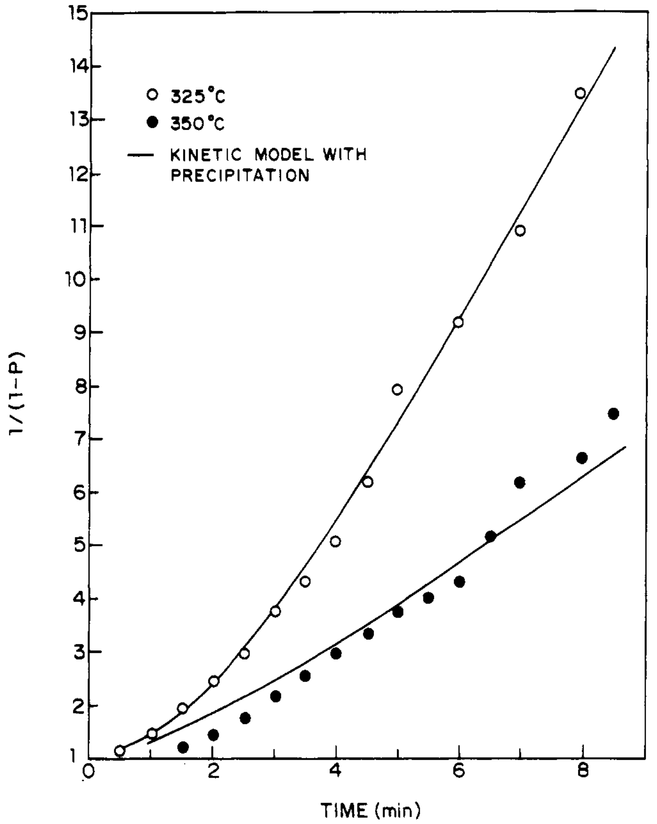

Figure 11. Second-order plot for uncatalyzed reactions compared with the precipitation model.

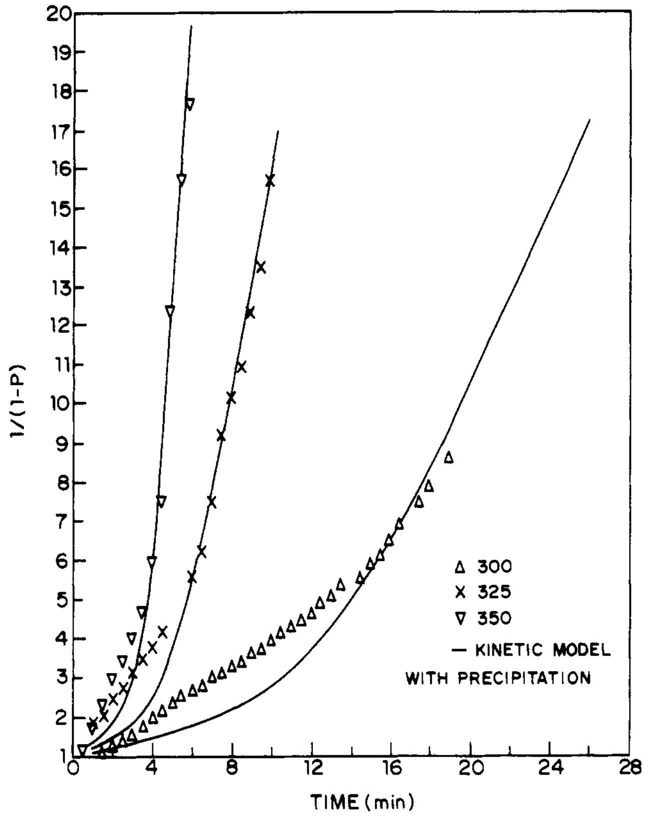

Figure 12. Second-order plot for dibutyltin oxide catalyzed reactions (1 mol % concentration) compared with the precipitation model.

the surface. The acceleration of the rate can be understood because every *n*th oligomer surface newly created is effectively participating in the interfacial catalysis.

Further direct experiments are necessary to prove this conjecture, but qualitatively it points out the correct trends.

Thermodynamic Analysis of the Rate Constants. The detailed considerations given in the previous sections show that, irrespective of the intricacies of the kinetic mechanism, in all the catalyzed reactions $k_2 > k_1$. The temperature behavior of these kinetic constants showed a few surprises however. A quick look at Table I tells us that even though the activation energies are larger, the rate constants (k_2) are numerically larger than k_1 by virtue of large preexponential factors. Thus entropy factors are important and it is best to interpret the results in terms of the theory of absolute reaction rates and a quasi thermodynamic interpretation.[15]

In general, the entropy of activation is usually negative for a second-order reaction (two monomers adding to form a dimer). The expression for the rate constant is within the format of the theory of absolute reaction rates

$$k = e^2(kT/h)e^{\Delta S^*/R}e^{-E_{\mathrm{exp}}/RT} \qquad (12)$$

$$E_{\mathrm{exp}} = \Delta H^* + 2RT \qquad (13)$$

The symbols ΔS^* and E_{exp} represent the entropy and experimental energy of activation when two monomers dimerize. From a priori theoretical considerations[15] (eq 12) ΔS^* has to be negative for a second-order reaction in the liquid state. Now, with the increase in enthalpy of activation, if entropy of activation also proportionately increases, then entropy factors can outweigh the enthalpy increase and drive the reaction in the forward direction. If the reaction rate constant is represented as

$$k = Ae^{-E/RT} \qquad (14)$$

where A is the preexponential factor and E is the energy of activation, then

$$\ln A = bE + C \qquad (15)$$

where b and C are constants. This is referred to as the compensation effect in the literature.[16] One of the consequences of the compensation effect is that a temperature called the isokinetic temperature is displayed

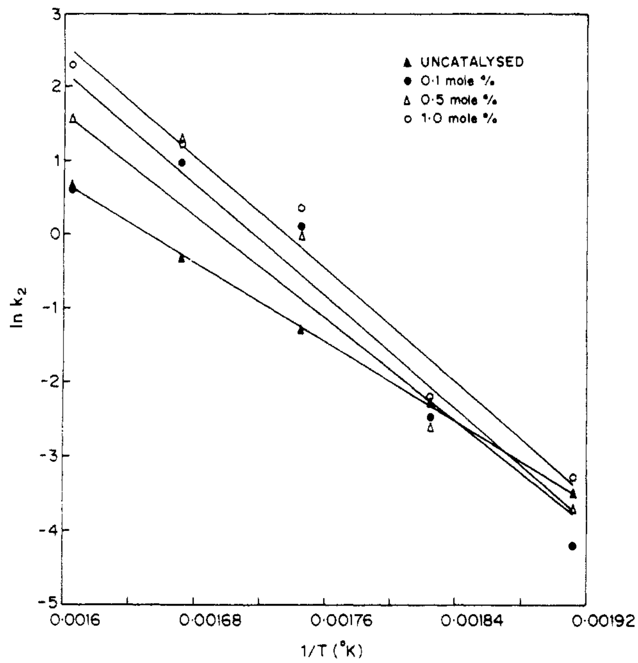

Figure 13. Plot illustrating the existence of an isokinetic temperature for dibutyltin oxide catalyzed reactions at variable catalyst concentration.

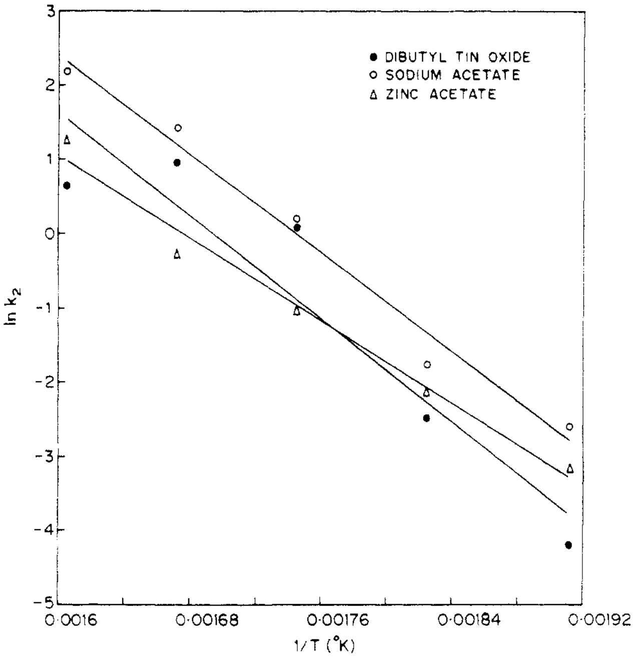

Figure 14. Plot illustrating the existence of an isokinetic temperature for dibutyltin oxide, sodium acetate, and zinc acetate catalyzed reactions at 0.1 mol % catalyst concentration.

for a group of catalysts. Irrespective of the enthalpy and entropy factors, their activities are the same at the isokinetic temperature. In other words all the Arrhenius plots cross at the isokinetic temperature. In the dibutyltin oxide catalyzed system, presented in Figure 13 as ln k_2 versus $1/T$ for four groups of runs (three varying catalyst concentrations and one without catalyst), it is probable that something resembling an isokinetic temperature can exist wherein all the rate curves cross (within the narrow limits). However, it is an open question whether different catalysts at the same concentration can display an isokinetic temperature.

It appears (Figure 14) at least two rate curves belonging to two different catalysts crossover to give a temperature which may be called an isokinetic temperature. However, this behavior is evident at only 0.1 mol % concentration and is not universal (that is, being unmanifested at all concentrations).

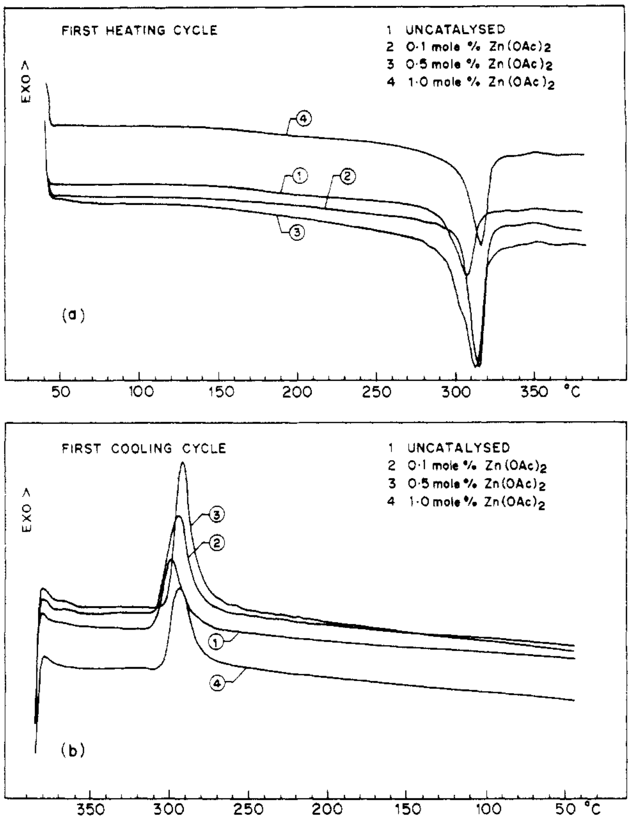

Figure 15. DSC endotherms (a) and exotherms (b) of the first heating and cooling cycle of uncatalyzed and catalyzed reactions at three different catalyst concentrations (0.1, 0.5, and 1.0 mol %) at 325 °C.

An interesting trait shown by many catalyzed runs, irrespective of whether an isokinetic temperature exists or not, is that the entropy factors have to be large and proportionately increase with an increase in enthalpy of activation so as to compensate and drive the reaction. In this sense, some sort of compensation effect is invariably present (see earlier discussion).

Polymer Characterization. The infrared spectra of 4-acetoxybenzoic acid showed a band at 1756 cm^{-1} due to C=O stretching. In poly(4-oxybenzoate) this band was shifted to 1741 cm^{-1}. The intensity of the band at 1677 cm^{-1} in 4-acetoxybenzoic acid is reduced to a great extent in poly(4-oxybenzoate). This is indicative of elimination of an acetyl C=O group as acetic acid during polymerization. The weak intensity of the band in the polymer may be due to acetyl end groups. The band at 1370 cm^{-1} due to CH_3 bending has also been reduced to a great extent in poly(4-oxybenzoate). Its position is also shifted to 1363 cm^{-1} in the polymer. This also supports the elimination of an acetyl group of 4-acetoxybenzoic acid during polymerization.

The DSC thermograms shown in Figure 15 exhibit sharp endotherms (heating cycle) and exotherms (cooling cycle), depicting the highly crystalline nature of poly(4-oxybenzoate). Table II shows the values for a typical set wherein the catalyst concentration is varied at constant time and temperature. The reversible first-order transition (Figure 15) points to either (i) reversible change between two crystalline modifications or (ii) crystallization of oligomeric poly(4-oxybenzoate) during the cooling cycle. Microscopic observations were made in the temperature range over which first-order transitions were noted in DSC. This did

Table II
Transition Temperatures and Thermodynamic Data for Catalyzed and Uncatalyzed Reactions[a]

no.	reacn	T_1^b (°C)	$\Delta H_{h_1}^c$ (kJ/mol)	$\Delta H_{c_1}^d$ (kJ/mol)	T_2^b (°C)	$\Delta H_{h_2}^e$ (kJ/mol)	$\Delta H_{c_2}^d$ (kJ/mol)
1	uncatalyzed	306.5	3.365	3.603	332.0	3.771	4.083
2	zinc acetate 0.1 mol %	312.6	4.480	5.068	324.1	4.972	5.116
3	zinc acetate 0.5 mol %	312.1	3.975	4.431	327.0	4.443	4.480
4	zinc acetate 1.0 mol %	315.3	3.266	3.603	327.3	3.363	3.675

[a] Reaction temperature, 325 °C; reaction time, 2.0 h. [b] T_1 and T_2 represent the transition temperature for first and second heating cycle. [c] ΔH_{h_1} and ΔH_{h_2} represent enthalpy values on heating the polymer in the first and second heating cycle. [d] ΔH_{c_1} and ΔH_{c_2} represent enthalpy values on cooling the polymer in the first and second cooling cycle.

not reveal either 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 the transition. The values of T_2 are higher than T_1 indicating (i) alterations in the crystal size due to thermal treatments and (ii) variations in the amount of crystallites and crystal perfection. The comparable values of ΔH_{h_1} and ΔH_{c_1}, ΔH_{h_2} and ΔH_{c_2} discounts the occurrence of degradation reactions on heating the polymer to 385 °C.

Conclusions. Three transesterification catalysts were employed in the synthesis of poly(4-oxybenzoate) by melt polymerization. Second-order kinetics is shown to be valid for both catalyzed and uncatalyzed reactions. A detailed kinetic analysis shows that acetic acid (product) liberated has no influence on the rate of reaction. Nevertheless, it appears that two kinetic regimes are present in the course of reaction. For both these regimes second-order kinetics is valid. A model which also takes into account the added complexity of oligomer precipitation also displays two-stage kinetics. The agreement with experiment, though poor in the initial stages (as intuitively obvious) progressively becomes better toward the later stages, indicating that precipitation is important. An interfacial mechanism operating at this stage can make the catalyst more efficient, and rate acceleration is shown to ensue. Besides, second-order kinetics is once again followed.

Even though the activation energies are larger for the catalyzed reaction (in comparison to the uncatalyzed) the entropy factors drive the reaction by lowering the free energy of activation. It appears that some kind of a compensation effect is present. Also, a few runs show the presence of an isokinetic temperature, as one would expect a priori when the compensation effect is prevalent.

The optimal concentrations needed for synthesis also have been listed. Our data show that dibutyltin oxide is the most suitable catalyst. Optical microscopic analysis shows that solid to solid crystalline modification occurs at high temperature. DSC analyses of uncatalyzed and catalyzed samples were carried out to evaluate parameters like ΔH_h and ΔH_c. This also suggests plausible crystal–crystal modification at elevated temperatures.

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Appendix

The main consequences of oligomer precipitation with $\overline{\mathrm{DP}} \gg n_c$, where n_c is fixed, are analyzed in this section. As already mentioned in the text, the chain growth occurs by step additions where at a given time two molecules only react:

$$\mathrm{P}_1 + \mathrm{P}_1 \xrightarrow{k_1} \mathrm{P}_2$$

$$\mathrm{P}_1 + \mathrm{P}_2 \xrightarrow{k_1} \mathrm{P}_3$$

$$\mathrm{P}_3 + \mathrm{P}_1 \xrightarrow{k_1} \mathrm{P}_4$$

- - - - - - - - - - -

$$\mathrm{P}_{n-2} + \mathrm{P}_1 \xrightarrow{k_1} P_{n-1}$$

$$\mathrm{P}_{n-1} + \mathrm{P}_1 \xrightarrow{k_{n-1}} \mathrm{P}_n\downarrow$$

As per the assumptions involved in the derivation of the Flory–Schulz[17] distribution, the end group reactivity remains the same irrespective of the degree of polymerization. This assumption is maintained till the $(n - 1)$th oligomer stage. However, at the stage at which precipitation sets in, there is reason to believe that reactivity of the end group is enhanced, i.e. $k_{n-1} \gg k_1$.

We can think of other pathways in which a given oligomer can be formed. For $\overline{\mathrm{DP}} = 6$ the following pathways are possible: (1,5), (2,4), (3,3). Here the numbers in parentheses denote the degrees of the polymerization of the reactant pair. For $\overline{\mathrm{DP}} = 7$ we have (1,6), (2,5), (3,4). In general for an oligomer of even $\overline{\mathrm{DP}} = n$ there are $n/2$ ways of generation. In contrast for an odd oligomer there are $(n - 1)/2$ routes to production. Now, if we follow the Flory–Schulz distribution for f_n for each of the oligomers with $\overline{\mathrm{DP}} = n$

$$f_n = (1 - p)p^{n-1} \tag{A1}$$

where f_n is the mole fraction of the nth oligomer, p is the degree of conversion of the monomer at a given stage, which is equal to the rate at which the product (acetic acid in our example) is formed.

It can be readily seen that for the rate expression for the production of a given oligomer (e.g. for $\overline{\mathrm{DP}} = 6$), though the (1,5), (2,4), (3,3) pairs are identical formally, we use eq A1. So they can all be summed up. Thus

$$\frac{\mathrm{d}p_n}{\mathrm{d}t} = k_1\left(\frac{n}{2}\right)(1 - p)^2 p^{n-2} \qquad \mathrm{DP} = \text{even} \tag{A2}$$

$$\frac{\mathrm{d}p_n}{\mathrm{d}t} = k_1\left(\frac{n-1}{2}\right)(1 - p)^2 p^{n-2} \qquad \mathrm{DP} = \text{odd} \tag{A3}$$

The net rate of production of acetic acid is equal to the net rate of production of oligomers with $n \geq 2$ and can be obtained by summing all the even and odd oligomer production rates of the type given by eqs A2 and A3 till the nth oligomer, which precipitates.

The main consequence of the oligomer precipitation will be that the Flory–Schulz distribution will be sharply truncated at $\overline{\mathrm{DP}} = n_c$, which of course modifies the rate expression slightly, otherwise it just introduces a new normalization factor $(1 - p^{n_c})^{-1}$ as multiplicative factor in each of the terms f_n in eq A1.

For our own analysis the best agreement with experiment is obtained by a rather restrictive model in which we do not use eqs A1 and A2 and all the pathways for oligomer production but instead use the step growth mechanism in which the n*th oligomer is formed by addition of a monomer to the* $(n-1)$*th oligomer,* $n-1$ *by addition of a monomer to the* $(n-2)$*th oligomer, etc., i.e. eq 11b.*

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Registry No. 4-Acetoxybenzoic acid, 2345-34-8; 4-acetoxybenzoic acid (homopolymer), 144634-70-8; 4-acetoxybenzoic acid (SRU), 28728-97-4; sodium acetate, 127-09-3; zinc acetate, 557-34-6; dibutyltin oxide, 818-08-6.