

Catalyzed Hydrolysis of Polyethylene Terephthalate Melts

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SYNOPSIS

The effect of zinc catalysts on the hydrolytic depolymerization of polyethylene terephthalate (PET) melts in excess water was studied using a 2-L stirred pressure reactor at temperatures of 250, 265, and 280°C. The main products of the reaction were found to be terephthalic acid, ethylene glycol, and diethylene glycol. Rate constants were calculated from initial rate data at each temperature and found to be about 20% greater than the corresponding rate constants for uncatalyzed hydrolysis. The catalytic effect of zinc, as well as sodium, salts is attributed to the electrolytic destabilization of the polymer-water interface during hydrolysis. The depolymerization rate data at 265°C were found to fit a kinetic model proposed earlier for the uncatalyzed hydrolysis of PET. The effect of zinc and sodium salts on the activation energy of hydrolysis, or on the formation of ethylene glycol monomer is unclear. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The depolymerization of polyethylene terephthalate (PET) for the recovery of monomers has been studied extensively in recent years.¹⁻³ The hydrolytic depolymerization of PET in a high pressure autoclave with excess water is known to yield high purity terephthalic acid and ethylene glycol.⁴ The rates of PET hydrolysis have been measured at temperatures between 250 and 280°C, and for initial reactor loadings of 2–10 g water/g PET.⁵ The last study suggested that essentially complete depolymerization could be obtained within 2 h at 265°C for an initial reactor loading of 5.1 g water/g PET. It would be desirable to reduce the reaction time, for example through the use of appropriate catalysts, in order to facilitate the development of an economic continuous depolymerization process.

The catalysis of PET melt hydrolysis in excess water has not been investigated in detail. However, the hydrolysis of some simple esters in aqueous solutions is known to be catalyzed by metal salts.⁶ Studies done on the polymerization of polyesters indicate that divalent metals such as titanium, zinc, lead, manganese, and cadmium are effective trans-

esterification catalysts.^{7,8} For PET, zinc acetate has been found to be a particularly effective catalyst for thermal and glycolytic degradation.^{9,10} Therefore, the catalysis of PET hydrolysis in excess water was investigated using zinc salts.

EXPERIMENTAL

Eastman 9921 virgin PET resin was used in combination with technical grades of zinc acetate dihydrate (Anachemia) and zinc stearate (Aldrich) as catalysts. High performance liquid chromatography (HPLC) grade water supplied by Fisher Scientific was used as the hydrolysis reagent.

The hydrolysis experiments were carried out in a 2-L capacity Parr pressure reactor. The procedure used in these experiments has been described in detail elsewhere.⁵ In all cases, the catalyst was added to the water in the pressure vessel and preheated to between 80 and 85°C prior to the addition of the PET resin. The vessel and contents were then heated to a reaction temperature between 250 and 280°C. The reactor vessel was quenched in an ice bath after a specified time interval. Solid and aqueous phases were separated using a sintered glass filter.

The reaction extent was determined by analyzing the solid phase for carboxyl group content. The ti-

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tration procedure, using one of two solvent systems, depending on the extent of hydrolysis, has also been described elsewhere.⁵ It was found, however, that samples containing zinc catalysts caused the formation of a precipitate in the 2,6-dimethylphenol:chloroform solvent system. This difficulty was overcome by repeating the solids grinding and washing procedure prior to dissolving the sample. The presence of zinc catalysts had no noticeable effect on the solubility of hydrolyzed samples in the other solvent used, dimethyl sulfoxide (DMSO).

Gas chromatography (GC) of the aqueous phase was used to determine ethylene glycol concentrations. HPLC was used to analyze the solid phase for terephthalic acid content.

RESULTS

The product mixture in the reactor vessel consisted of a solid phase and an aqueous phase for all reaction times studied. Upon quenching the vessel, the solid phase was normally frozen onto the sides and bottom of the vessel for reaction times less than 15 min at 265°C for an initial reactor loading of 2 g water/g PET. For longer reaction times, the solids formed a suspension in the water phase upon cooling. Similar behavior was noted after characteristic reaction times for higher initial reactor loadings and at all temperatures studied.

The carboxyl group concentration, C_{COOH} , was determined for hydrolysate samples that were reacted for 9 min at 265°C, for an initial reactor loading of 2 g water/g PET. The effect of zinc salts and other compounds on C_{COOH} was investigated. The results are summarized in Table I.

Control experiments to determine whether the components of the additives had any effect on the titration itself (but not on the hydrolysis) are also summarized in Table I. The control sample was hydrolyzed without any additive. Subsequent to the hydrolysis, 0.1% w/w PET of zinc stearate (1.58×10^{-3} mmol Zn^{+2} /g PET) was added to the solid phase. The presence of the salt had a negligible effect on C_{COOH} , which was determined to be 2.40 mmol/g PET in DMSO, the same value obtained for the control sample. Stearic and acetic acids, which are the anionic components in the salts tested, were added to the reaction mixture prior to hydrolysis. Again, no perceptible increase in C_{COOH} was noted after 9 min at 265°C. Any residual acid present in the solid phase after filtration may have been removed by the washing procedure. It can thus be concluded that the presence of the catalysts them-

Table I Effect of Various Additives on C_{COOH} after 9 min at 265°C

Additive	Concentration		C_{COOH} mmol/g PET
	wt %	mmol/g PET	
Control	—	—	2.40
Stearic acid	1.0	3.52×10^{-2}	2.40
Acetic acid	1.0	1.67×10^{-1}	2.40
Zinc stearate	0.01	1.58×10^{-4}	2.41
	0.05	7.91×10^{-4}	2.70
	0.1	1.58×10^{-3}	2.76
	1.0	1.58×10^{-2}	2.77
Zinc acetate	0.1	4.56×10^{-3}	2.76
Sodium acetate	0.026	3.17×10^{-3}	2.83
	1.0	1.22×10^{-1}	2.85

Initial reactor loading of 2 g water/g PET.

selves does not interfere with the titration of hydrolyzed samples.

The effect of salt concentration on the hydrolysis reaction was examined using zinc stearate. Four different concentrations were used as summarized in Table I. It can be seen that 1.58×10^{-4} mmol Zn^{+2} /g PET has a negligible effect on C_{COOH} . A concentration of 7.91×10^{-4} mmol Zn^{+2} /g PET leads to a 12% increase in the value of C_{COOH} . The increase in the value of C_{COOH} levels off at just over 15% (i.e., 2.76 mmol/g PET) for concentrations of 1.58×10^{-3} and 1.58×10^{-2} mmol Zn^{+2} /g PET. Thus, a molar concentration of zinc of 1.58×10^{-3} mmol/g PET is sufficient to give maximum increase in C_{COOH} after a 9-min reaction time at 265°C. Increasing the amount of zinc beyond that value does not cause a further increase in the carboxyl group content.

The effect of zinc on the rate of hydrolysis was studied using both zinc stearate and zinc acetate at concentrations equal to or exceeding 1.58×10^{-3} mmol Zn^{+2} /g PET. Zinc acetate is readily water soluble; zinc stearate is quite hydrophobic. The zinc catalysts were added to 5.1 g water/g PET and reacted at 265°C for various times. The increase in C_{COOH} with time is shown in Figure 1. The points from the two zinc salts tested, zinc stearate and zinc acetate, are seen to lie on the same curve.

The effect of temperature on carboxyl group formation was studied for an initial reactor loading of 5.1 g water/g PET with zinc acetate at an ionic concentration of 4.56×10^{-3} mmol Zn^{+2} /g PET. The results in Figure 2 show an increase in the initial rate with reaction temperature.

Gas chromatograms of the aqueous phase showed the presence of two products. These products were

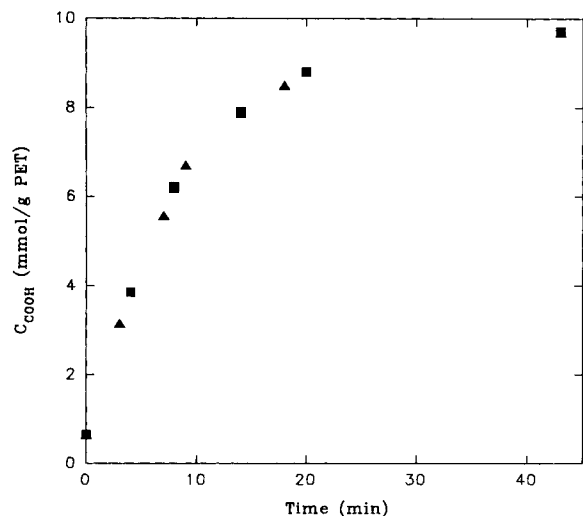


Figure 1 Increase in carboxyl groups during hydrolysis at 265°C for 5.1 g water/g PET: (■) zinc acetate (4.56×10^{-3} mmol Zn^{+2} /g PET), (▲) zinc stearate (1.58×10^{-3} mmol Zn^{+2} /g PET).

identified to be ethylene glycol and diethylene glycol. The formation of diethylene glycol from ethylene glycol in a dimerization side reaction is to be expected at high temperatures.¹⁰ Figures 3 and 4 summarize the GC data for ethylene glycol and diethylene glycol, respectively.

Hydrolysis experiments at an initial reactor loading of 5.1 g water/g PET at 265°C for 2 h were used to obtain solid phase samples for terephthalic acid analysis. The control experiment contained no

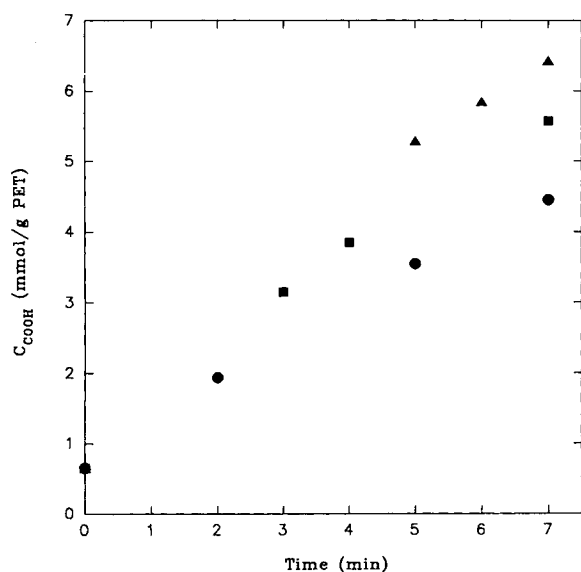


Figure 2 Carboxyl group concentrations for short reaction times during hydrolysis with zinc acetate (4.56×10^{-3} mmol Zn^{+2} /g PET): (●) 250°C, (■) 265°C, (▲) 280°C.

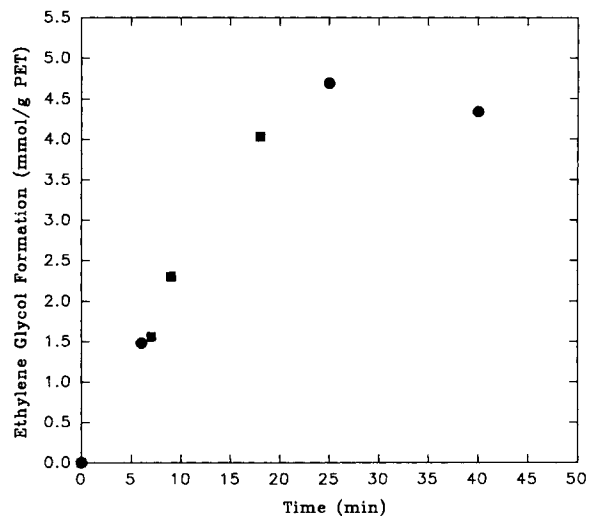


Figure 3 Ethylene glycol formation at 265°C: (●) 5.1 g water/g PET, (■) 5.1 g water/g PET with zinc acetate (4.56×10^{-3} mmol Zn^{+2} /g PET).

additives; zinc stearate (1.58×10^{-3} mmol Zn^{+2} /g PET) was used in the other experiment. In both cases, the terephthalic acid content of solid phase samples was determined by HPLC relative to a terephthalic acid standard. Both samples were found to have terephthalic acid contents of $96.0 \pm 0.5\%$.

DISCUSSION

Effect of Catalyst on Hydrolysis Mechanism

The rate constant for hydrolysis, k_c , can be calculated by plotting the quantity $(C_{WATER})^{-1} \ln[1/(1 - e)]$ versus reaction time for short reaction times.⁵

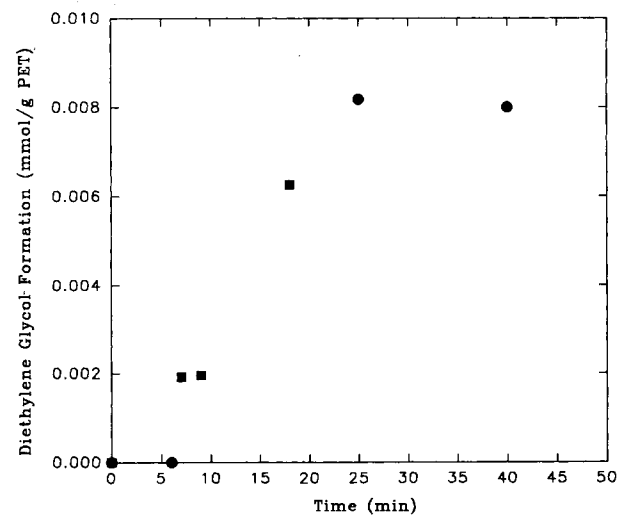


Figure 4 Diethylene glycol formation at 265°C: (●) 5.1 g water/g PET, (■) 5.1 g water/g PET with zinc acetate (4.56×10^{-3} mmol Zn^{+2} /g PET).

The parameter e is a dimensionless reaction extent defined by the following expression:

$$e = \frac{C_{\text{COOH}} - C_{\text{COOH}_0}}{C_{\text{ELP}} - C_{\text{COOH}_0}}$$

The data for an initial reactor loading of 5.1 g water/g PET, with either zinc acetate or zinc stearate, and for a reaction temperature of 265°C are shown in Figure 5. The data fall on a straight line, as expected, with a slope of 0.425. The value of k_c is therefore 0.425 g PET mol⁻¹ min⁻¹. The corresponding value of k from Campanelli et al.⁵ at 265°C is 0.360 g PET mol⁻¹ min⁻¹. The addition of the zinc salts resulted in an 18% increase in the rate of the hydrolysis reaction. It can thus be concluded from the data at 265°C that the addition of at least 1.58×10^{-3} mmol Zn⁺²/g PET leads to a modest increase in the rate of PET hydrolysis.

The mechanism of the enhancement of the reaction is not readily apparent. The results reported here suggest a behavior different from that usually observed for the catalysis of polyester polymerization reactions in that both zinc acetate and sodium acetate appear to have equivalent effects on the reaction rate (Table I). Sodium acetate is, however, known to be a very poor catalyst compared to zinc acetate for the polymerization of polyesters.⁸ In order to explain this behavior, it is proposed that both the sodium and zinc salts enhance the rate of hydrolysis by affecting the morphology of the reaction mixture as discussed below.

The hydrolysis reaction apparently occurs at the

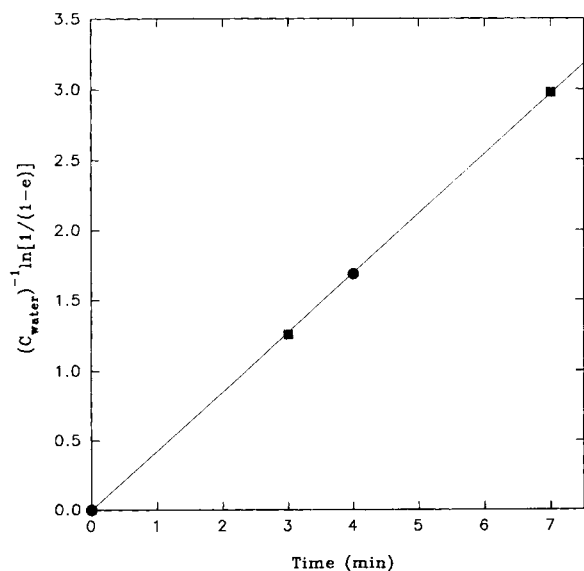


Figure 5 Initial hydrolysis rate data for 5.1 g water/g PET at 265°C: (●) zinc acetate (4.56×10^{-3} mmol Zn⁺²/g PET), (■) zinc stearate (1.58×10^{-3} mmol Zn⁺²/g PET).

interface of a PET in water emulsion. This hypothesis is supported by the observation that the solid hydrolysis products form a distinct phase and not a precipitate upon cooling the reactor vessel, indicating a very low degree of miscibility between PET and water. Thus, additives that affect the emulsion properties would be expected to influence the hydrolysis reaction rate. The solubility characteristics of additives in either the disperse or continuous phases do not seem to be important because zinc acetate and zinc stearate have essentially the same effect on PET hydrolysis (Fig. 1). However, the electrolytic properties of the sodium and zinc salts tested would have a serious impact on the PET-water interface in the emulsion.

It is well known that ionic species influence the stability of emulsions by affecting the surface charge of the disperse phase droplets.¹² Below a critical concentration of electrolyte, little effect on emulsion stability is observed. Above the critical concentration, which is a characteristic of both electrolyte and other emulsion components, the overall effect is to destabilize the emulsion. Elworthy et al.¹³ studied the effect of sodium nitrate and calcium nitrate on chlorobenzene in water emulsions stabilized by a nonionic surfactant. They found rapid increases in coalescence rates after critical concentrations of 6.2×10^{-3} and 7.2×10^{-4} mol/L for the sodium and calcium salts, respectively. Becher et al.¹⁴ examined the effect of sodium chloride and calcium chloride on mineral oil in water emulsions stabilized by a nonionic surfactant. They noted a rapid decrease in the zeta potential after critical concentrations of about 10^{-5} and 10^{-7} mol/L for the sodium and calcium salts, respectively. Thus, the overall effect of electrolytes is to weaken the electrostatic repulsion between disperse phase droplets, thereby increasing the rate of coalescence.

Figure 6 shows C_{COOH} after 9 min at 265°C as a function of the logarithm of ionic strength for the PET-water system. At low salt concentrations, there is little effect on C_{COOH} . At concentrations exceeding about 10^{-4} mol/L, however, there is a marked increase in C_{COOH} . These results correspond directly to the earlier findings discussed above.^{13,14} Because the electrolytes decrease the stability of the PET-water interface, less thermal and mixing energy is required to form an interface than in the absence of electrolytes. The net effect thus appears to be an increase in interfacial area, and a subsequent increase in the rate of hydrolysis.

Effect of Catalysts on Hydrolysis Kinetics

The activation energy for catalyzed hydrolysis is readily obtained by using the data in Figure 2 to

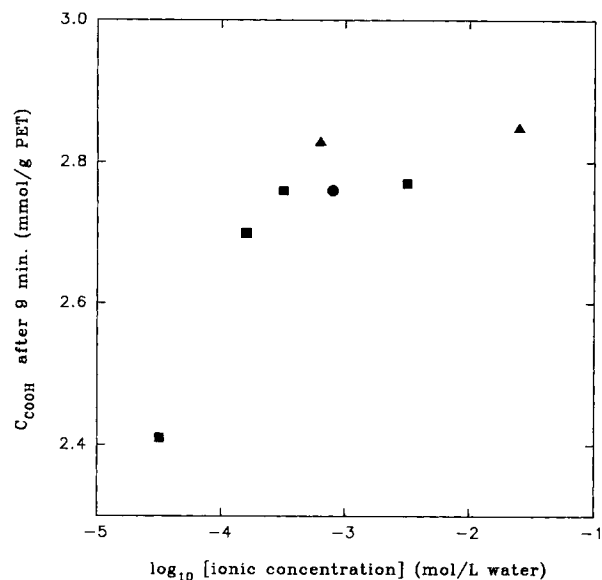


Figure 6 Effect of electrolyte concentration on C_{COOH} after 9 min at 265°C: (●) zinc acetate, (■) zinc stearate, (▲) sodium acetate.

calculate k_c at each temperature. The resulting values of k_c are summarized in Table II. An Arrhenius plot for these rate constants is shown in Figure 7, with the data for uncatalyzed hydrolysis included for comparison purposes. It is evident that the data for uncatalyzed hydrolysis appear to be more linear than the data for catalyzed hydrolysis. A linear regression gives an activation energy for catalyzed hydrolysis of 47.9 kJ/mol. This value is 14% lower than the activation energy of 55.7 kJ/mol obtained in uncatalyzed hydrolysis. This decrease in activation energy could, however, be an artifact due to the temperature dependence of emulsion properties on ionic strength. If, for example, only the data at 250 and 265°C are used to calculate the activation energy of catalyzed hydrolysis, a value of 55.2 kJ/mol is obtained. This value is almost identical to the activation energy calculated from the uncatalyzed data.

The kinetic model developed by Campanelli et al.⁵ for the hydrolysis of PET melts can be summarized as follows:

$$\ln \frac{B - A - C_{\text{COOH}}}{B + A + C_{\text{COOH}}} = -2B(k'_c - k_c)t + \ln \frac{B - A - C_{\text{COOH}_0}}{B + A + C_{\text{COOH}_0}} \quad (2)$$

$$A = \frac{k_c(C_{\text{ELP}} + C_{\text{WATER}_0})}{2(k'_c - k_c)} \quad (3)$$

$$B = \sqrt{A^2 + \frac{k_c C_{\text{ELP}} C_{\text{WATER}_0}}{k'_c - k_c}} \quad (4)$$

Table II Effect of Temperature on Rate Constants for Catalyzed Hydrolysis (0.1% Zinc Acetate) at 5.1 g Water/g PET

Temperature (°C)	k_c (g PET mol ⁻¹ min ⁻¹)
250	0.299
265	0.425
280	0.542

Catalyst concentration does not appear explicitly in the modelling equations. In fact, the dependency of the hydrolysis rate on the salt concentration is not a simple one. Table I shows an increase in hydrolysis rate with ionic concentration only up to a limiting value. Thus, for an ionic concentration equal to or greater than 1.58×10^{-3} mmol/g PET, the hydrolysis rate becomes independent of ionic concentration, and eqs. (2)–(4) can be used directly to model the kinetics of hydrolysis.

The values of the parameters to be used in eqs. (2)–(4) are summarized in Table III for catalyzed hydrolysis at 265°C with an initial reactor loading of 5.1 g water/g PET and an ionic concentration of at least 1.58×10^{-3} mmol/g PET. C_{ELP} is the concentration of ester linkages originally present in the PET polymer. The concentration of liquid water initially present in the reaction vessel at 265°C, C_{WATER_0} , is calculated from vapor-liquid equilibrium data. The rate constant k'_c is estimated from the equilibrium concentrations of products and reactants at 265°C for an initial reactor loading of 2 g water/g PET.

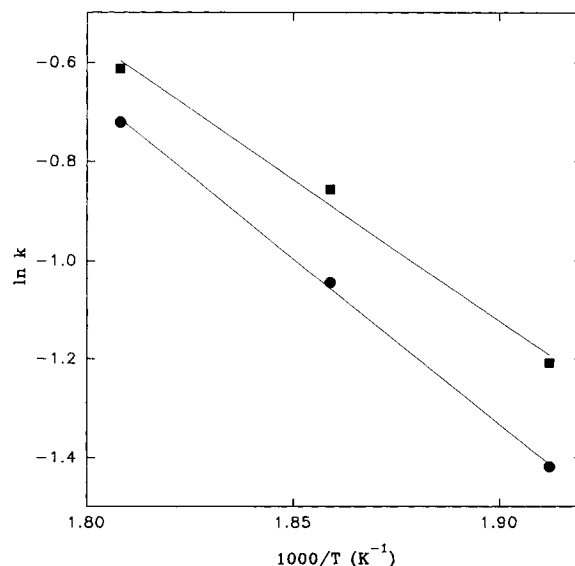


Figure 7 Arrhenius plots for hydrolysis (●) without and (■) with additives.

Equation (2) can thus be solved by substitution of all known parameters:

$$-\ln\left[\frac{0.00981 - C_{\text{COOH}}}{0.8092 + C_{\text{COOH}}}\right] = 0.1073t + 4.48. \quad (5)$$

The fit of the data in Figure 1 to the kinetic model is shown in Figure 8. A linear regression through the catalyzed hydrolysis data gives an intercept of 4.52 and a slope of 0.1059. The value of the slope is 1.3% lower than the value obtained from the model in eq. (5).

The increase in hydrolysis rate due to the use of catalyst should lead to a faster production of ethylene glycol monomer. However, the data in Figure 3 seem to show that there is little difference in the ethylene glycol production rate. The same is noted for the production of diethylene glycol in Figure 4. Figures 3 and 4 do not imply that the catalysts have no effect on the formation of ethylene glycol or its dimer. Because of the sharp increase in glycol production between 10 and 20 min, it is possible that further sampling in that region will show some differences in the rates of production of both glycols. However, because the increase in hydrolysis rate constant is only about 20% with the use of salt catalysts, their impact on monomer production may not be very great.

CONCLUSIONS

The addition of zinc and sodium salts leads to a modest increase in the reaction rate constant for PET hydrolysis. The mechanism of the catalysis is thought to involve electrolytic destabilization of the PET-water interface, resulting in a greater interfacial area exposed to the hydrolysis reaction. The kinetic model proposed by Campanelli et al.⁵ was found to fit the data for catalyzed hydrolysis of PET at 265°C. The effect of salt catalysts on the activation energy and on the formation of ethylene glycol was unclear.

Table III Kinetic Parameters for Catalyzed Hydrolysis at 265°C

Parameter	Value
C_{ELP}	0.0104 mol/g PET
$C_{\text{WATER}0}$	0.236 mol/g PET
k_c	0.425 g PET mol ⁻¹ min ⁻¹
k'_c	0.556 g PET mol ⁻¹ min ⁻¹

Initial reactor loading of 5.1 g Water/g PET.

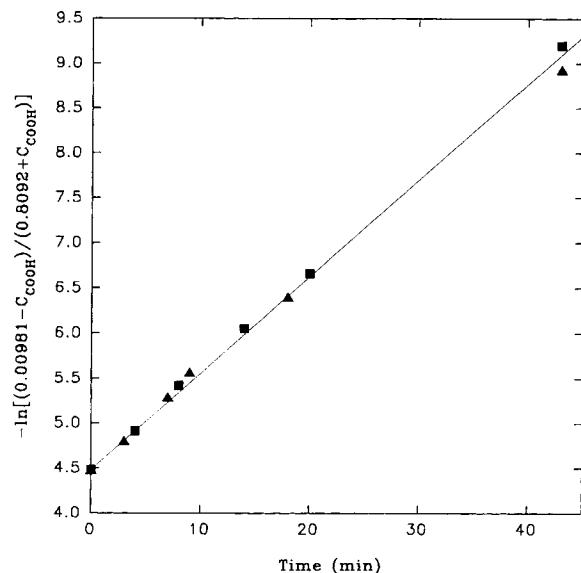


Figure 8 Fit of eq. (2) to hydrolysis data with (■) zinc acetate and (▲) zinc stearate.

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NOMENCLATURE

C_{COOH}	Carboxyl group concentration at any time, mol/g PET
$C_{\text{COOH}0}$	Carboxyl group concentration at reaction time 0, mol/g PET
C_{EL}	Concentration of ester linkages at any time, mol/g PET
C_{ELP}	Initial ester linkage concentration in the polymer, mol/g PET
C_{WATER}	Liquid water concentration at any time, mol/g PET
$C_{\text{WATER}0}$	Initial liquid water concentration at the reaction temperature, mol/g PET
e	Hydrolysis reaction extent, defined in eq. (1)
k_c	Rate constant for hydrolysis at limiting ionic concentration, g PET mol ⁻¹ min ⁻¹
k'_c	Rate constant for condensation at limiting ionic concentration, g PET mol ⁻¹ min ⁻¹

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