

Kinetics of Glycolysis of Poly(Ethylene Terephthalate) Melts

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SYNOPSIS

The reaction of poly(ethylene terephthalate) (PET) melts with ethylene glycol was examined in a pressure reactor at temperatures above 245°C. The reaction rate was found to depend on temperature and on the concentrations of liquid ethylene glycol and of ethylene diester groups in the polymer. A kinetic model proposed for the initial period of the reaction was found to be consistent with experimental data. It was found that internal catalysis by ethylene glycol does not play an important role in the glycolytic depolymerization of PET. The rate constants for glycolysis were calculated for three different temperatures, yielding an activation energy of 92 kJ/mol. Zinc salts, which have a catalytic effect on glycolysis of PET below 245°C, do not appear to influence glycolysis rates above that temperature. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The reaction of poly(ethylene terephthalate), or PET, with ethylene glycol is of great importance in the commercial polymerization of high-molecular-weight PET resins. The yield and quality of the product are strongly influenced by the kinetics and equilibria of this reaction. For this reason, early studies focused on the kinetics of the overall polymerization reaction and on the determination of equilibrium constants. Challa¹⁻³ found that the reverse, or glycolysis, rate is important in determining the maximum extent of polymerization. He determined that the glycolysis rate is first order with respect to ethylene glycol (EG) concentration. In recent years, glycolysis has been studied as a means of obtaining polyols from waste PET to be used in the production of unsaturated polyesters and polyurethanes.⁴⁻⁷ The current interest in the depolymerization of PET by glycolysis to recover bis-2-hydroxyethyl terephthalate (BHET) monomer has led to studies of glycolysis catalysts and of the composition of the products from the depolymerization of PET soda bottles.⁸

Chen et al.⁹ have recently studied the kinetics of the glycolytic depolymerization of PET in a pres-

surized reactor at temperatures between 190 and 240°C. These authors concluded that the glycolysis rate is second order with respect to EG concentration, and that EG thus acts as both reactant and catalyst in the glycolysis reaction. These conclusions contradict the earlier findings of Challa. Baliga and Wong⁸ found that zinc compounds have a catalytic effect on glycolysis below 240°C. In the present study, the glycolysis of PET melts is examined at temperatures exceeding 240°C in a pressure reactor. A kinetic model is developed to determine if EG has a discernible catalytic effect on the glycolytic depolymerization of PET. Also, the effect of zinc compounds on glycolysis is evaluated at 265°C.

EXPERIMENTAL

The PET used in this research work was blow-molding grade natural resin supplied by Eastman (IV = 0.80 in 60% phenol/40% tetrachloroethane). A reagent grade of ethylene glycol was obtained from Fisher Scientific. The PET pellets were pressed into 0.010-in. sheets in a Carver laboratory press at 250°C prior to use. The sheet was then cut into 0.5 × 0.5-in. flakes in order to maximize the surface area available for heat and mass transfer in the reactor.

A 2-L capacity Parr pressure reactor was used for all glycolysis experiments. The reactor was equipped

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with rotors to ensure proper mixing. The reaction vessel and EG reactant were preheated to between 80 and 85°C prior to the addition of the PET flakes in order to minimize the time required to reach the reaction temperature. The ratio of EG : PET used in the experiments was 2 : 1 (w/w). After a specified time interval at the reaction temperature, the reactor vessel was removed from the heating collar and quenched quickly in an ice bath. The temperature of the product mixture dropped to under 100°C within 2 min of quenching. The vessel was subsequently opened, and the product removed. The product was stored under nitrogen in a sealed jar at 5°C.

The extent of reaction was studied by determining the amount of EG remaining in the product mixture after quenching the reactor vessel. Unreacted EG was removed from the product mixture by careful drying, as follows. Samples of the product mixture, in quantities exceeding 5 g, were first dried in a vacuum oven at 90°C for 12 h. In general, 95% of the weight loss occurred during this vacuum drying step. The samples were weighed and then dried in a circulating air oven at 110°C for a further 48 h. This time was sufficient for the sample weight to reach a steady value. The dried samples were cooled to room temperature in a dessicator and weighed on an analytical balance to the nearest tenth of a milligram.

RESULTS

The heating profile of the pressure reactor charged with 300 g of EG and PET is shown in Figure 1 for set points of 255, 265, and 275°C. Within 25 min, the temperature of the reaction mixture reached 245°C. This temperature was determined to be the upper limit of the melting range of the PET resin by differential scanning calorimetry (DSC). Product mixtures quenched prior to 25 min were two-phase systems with flakes still clearly visible. Product mixtures quenched after 25 min were white, homogeneous gels.

Figure 2 shows the thermogravimetric analysis (TGA) thermogram of a glycolysate sample after drying in the manner described previously. No weight loss is noted in the sample at temperatures of 100 and 197°C, indicating the absence of water and of EG. The weight loss above 400°C is likely due to the volatilization of BHET, which is expected to be the most volatile component remaining in the reaction mixture after the removal of EG.

Figure 3 shows the thermogram of a product gel sample removed from the reaction vessel immediately after quenching and tested by TGA. A constant temperature of 197°C was maintained in the furnace, and the weight loss was recorded as a function of time. The sample weight levels off at 37.5% of the

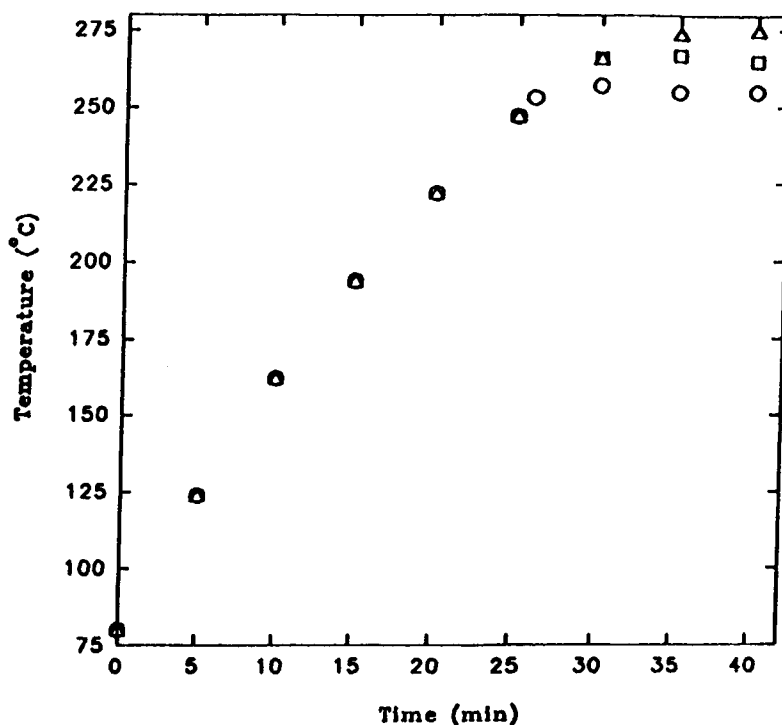


Figure 1 Reactor heating profile for three set points: (○) 255°C, (□) 265°C, (△) 275°C.

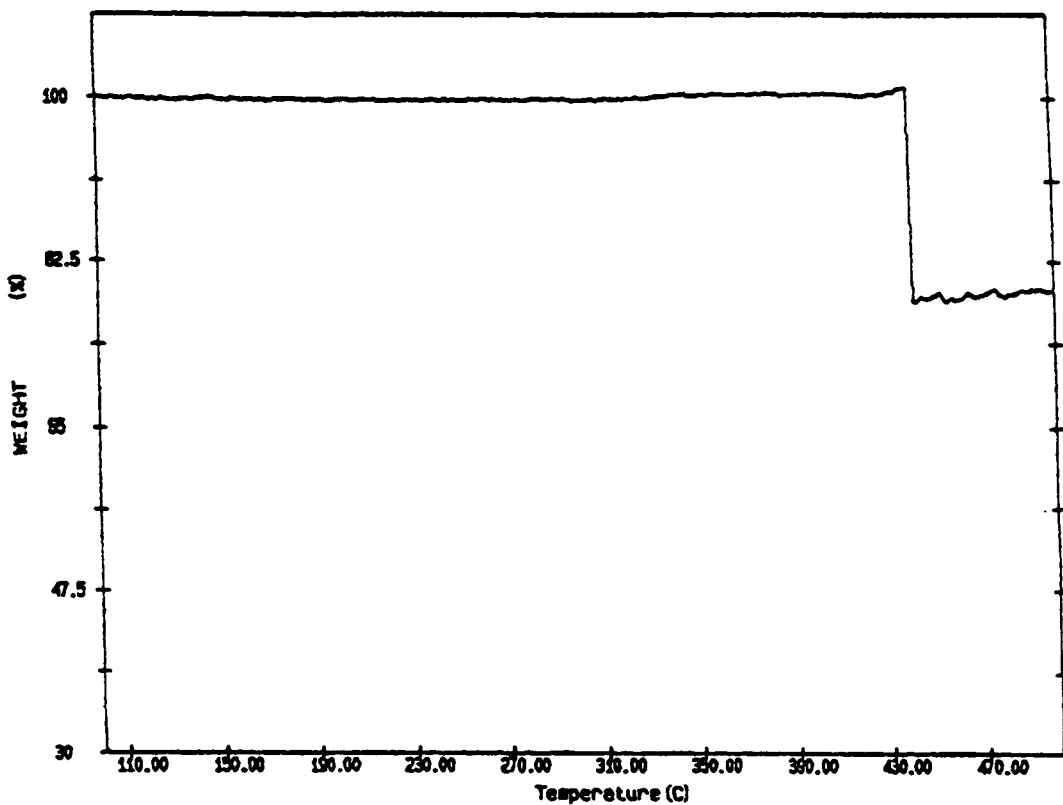


Figure 2 TGA thermogram for a dried glycolysate sample heated at 5°C/min.

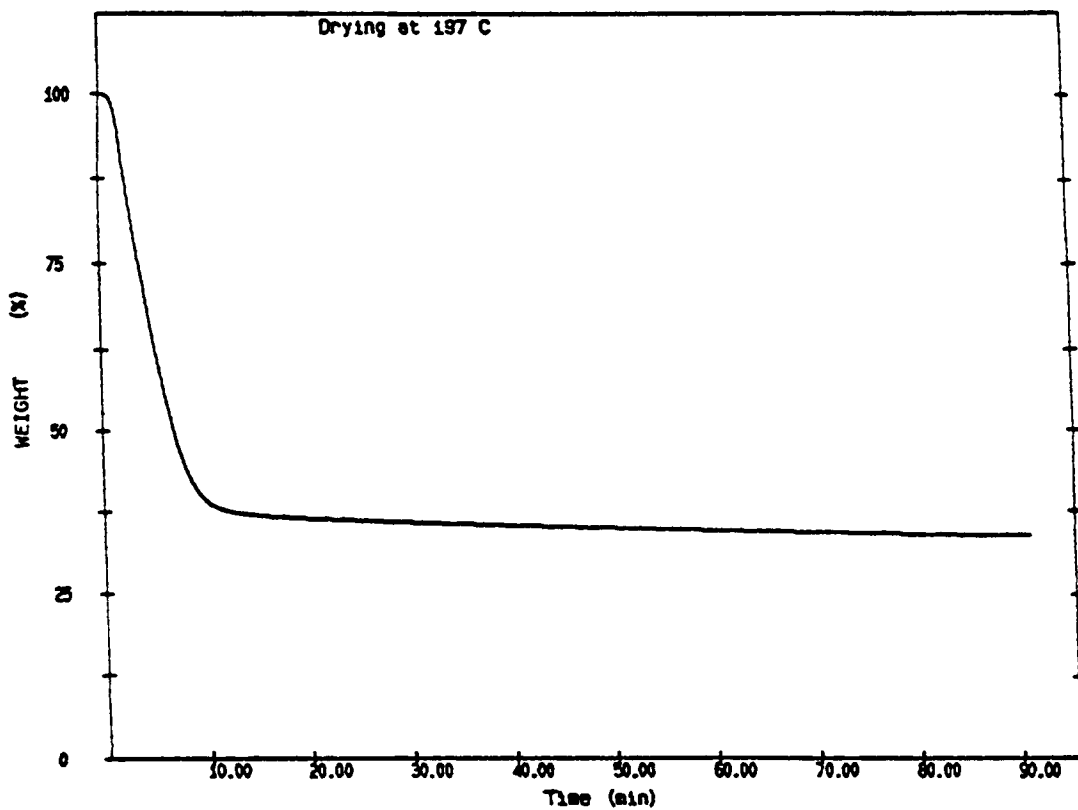


Figure 3 TGA thermogram for a glycolysate sample held at 197°C for 90 min.

Table I Gravimetric Analysis of Control Samples

Sample	Doped With	Initial Sample Weight (wt %)	Final Sample Weight (wt %)	Comments
Ethylene glycol	—	100	0	No sample was left
PET	Ethylene glycol	50.284	50.198	% Change ≤ 1.0
Dried glycolysate	Ethylene glycol	10.643	10.461	% Change -1.7
BHET	Ethylene glycol	10.863	10.746	% Change -1.1

initial value after about 15 min. The residue weight for a sample from the same experiment was found to be 37.876% when dried according to the procedure described previously. Hence, the agreement between the methods is excellent.

In order to verify that only EG is removed during drying, a series of control experiments were run. Samples that had been doped with known quantities of EG were subjected to the drying procedure, and initial and final weights were recorded. The results are shown in Table I. Pure EG evaporates completely upon drying, as expected. Ethylene glycol and PET are also separated with great accuracy. The glycolysate sample in Table I had been previously dried prior to the addition of a measured amount of EG. Both it and the BHET sample exhibit a weight loss greater than the added amount of EG. However, this additional loss results in an error of only 1.7%, at most. The maximum standard deviation in constant

weight value for any set of glycolysate samples was determined to be 0.89%.

Figure 4 summarizes the initial reaction rate data obtained from the drying of glycolysate samples at three different temperatures. The decrease in EG concentration, in mol/L, is shown as a function of residence time in the reactor vessel.

DISCUSSION

Glycolysis Rate Data

The glycolysis of PET is an equilibrium reaction, the reverse reaction being the well-known polycondensation:

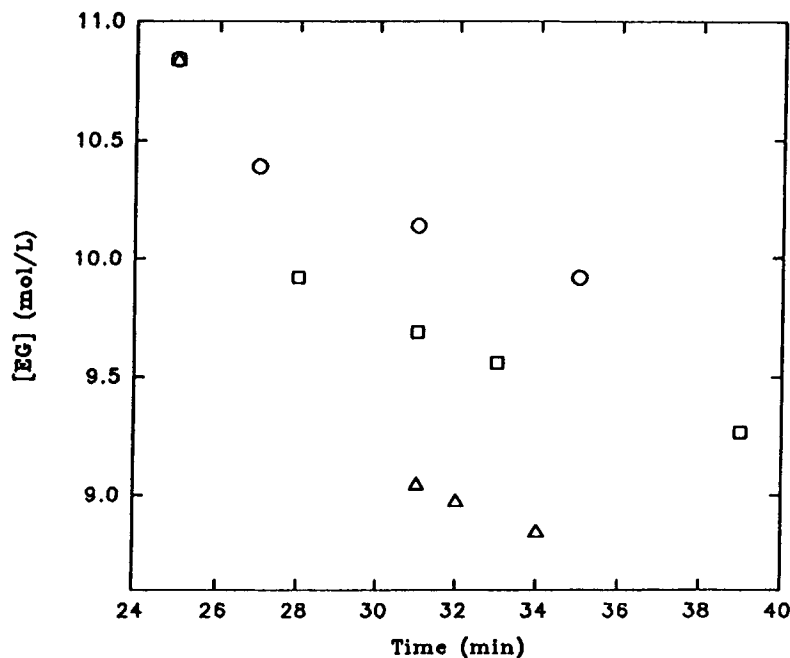
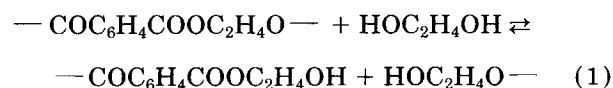


Figure 4 Decrease in [EG] as a function of residence time in the reactor vessel for three temperatures: (○) 255°C, (□) 265°C, (△) 275°C.

In the initial stages of PET glycolysis, the polycondensation reaction is not important and can be ignored. The rate of glycolysis can thus be expressed as follows:

$$-\frac{d[\text{EG}]}{dt} = -\frac{d[\text{EDE}]}{dt} = k_G[\text{EG}]^a[\text{EDE}] \quad (2)$$

where $[\text{EG}]$ is the concentration of liquid ethylene glycol at reaction temperature, $[\text{EDE}]$ is the concentration of ethylene diester groups, and k_G is the rate constant for glycolysis. The constant a can have a value of 1 or 2, depending on whether the reaction is internally catalyzed by EG. All concentrations are in units of mol/L.

Equation (2), with $a = 1$, is in agreement with the model first proposed by Challa.¹ However, results reported recently by Chen et al.⁹ for the glycolytic depolymerization of PET suggest that the initial rate of PET glycolysis is proportional to $[\text{EG}]^2$. In the very early stages of the reaction, $[\text{EG}]$ and $[\text{EDE}]$ in Eq. (2) can be approximated by their initial values, $[\text{EG}]_i$ and $[\text{EDE}]_i$, respectively. Equation (2) can be rewritten to give an expression for the initial depolymerization rate:

$$\text{Rate} = k_G[\text{EG}]_i^2[\text{EDE}]_i \quad (3)$$

Chen et al.⁹ used a special form of Eq. (3), where $[\text{EDE}]_i$ may be considered constant. Therefore, they lumped the concentration $[\text{EDE}]_i$ with the reaction rate constant k_G to obtain a new rate constant k_i :

$$\begin{aligned} \text{Rate} &= k_i[\text{EG}]_i^2 \\ k_i &= k_G[\text{EDE}]_i \end{aligned} \quad (4)$$

Figure 5 plots the initial depolymerization rates obtained by Chen et al. as functions of both $[\text{EG}]_i$ and $[\text{EG}]_i^2$. In this case only, the EG concentration is in mol/mol PET repeat unit. It is seen that the better agreement is obtained with $a = 1$ in Eq. (4). The conclusion of Chen et al. that EG catalyses the glycolysis reaction cannot thus be justified based solely on the data from Figure 5. In subsequent discussion, Eq. (2) will be used to analyze the data obtained in the present work without the assumption of pseudo-first-order kinetics implied in Eq. (4).

Equation (2) can be solved by writing a component balance for liquid EG:

$$[\text{EG}] = [\text{EG}]_i - [\text{EG}]_{\text{Reacted}} \quad (5)$$

According to Eq. (1), the amount of EG that has reacted at any time is related by stoichiometry to

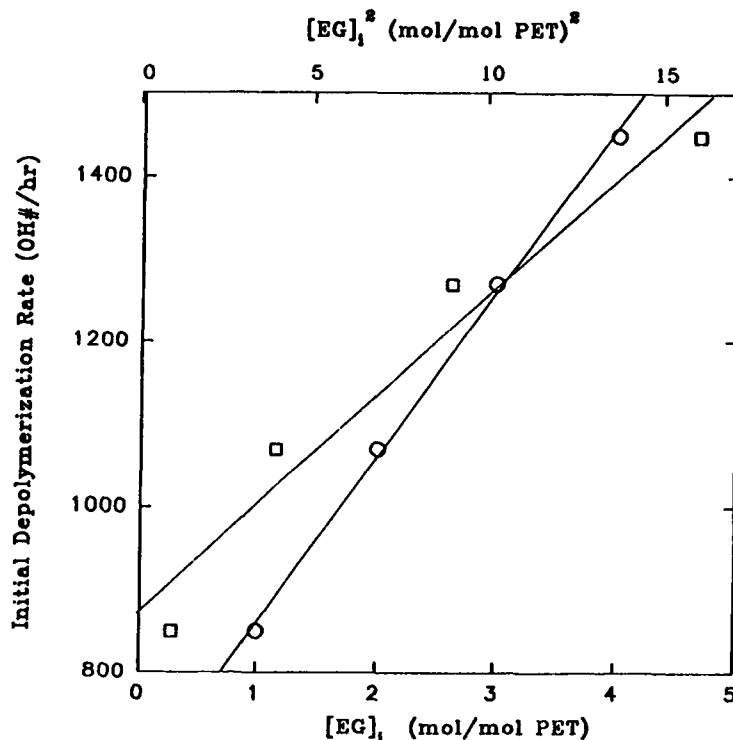


Figure 5 Initial depolymerization rates from Ref. 9 as functions of (○) $[\text{EG}]_i$ and (□) $[\text{EG}]_i^2$.

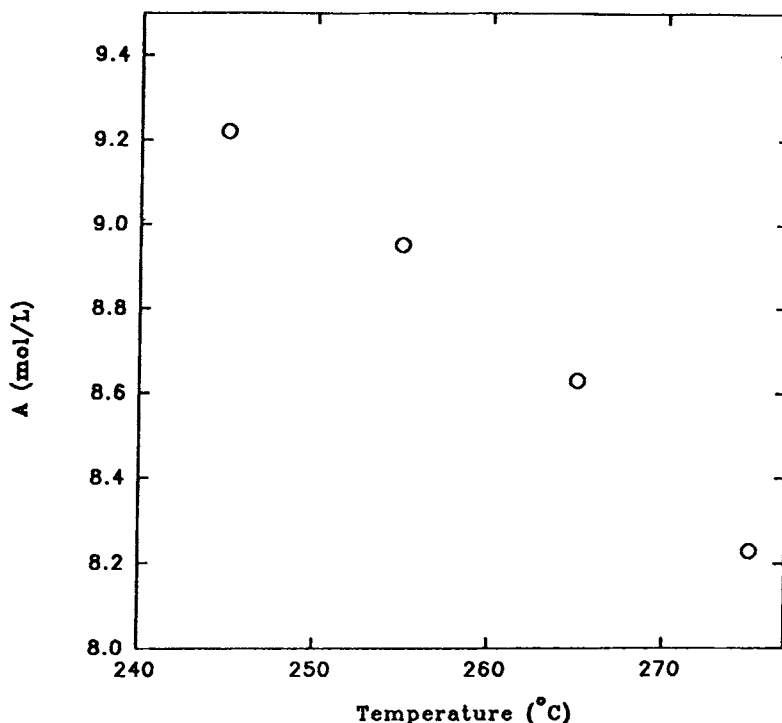


Figure 6 Variation of parameter A with reaction temperature.

the amount of EDE groups remaining in the PET as follows:

$$[\text{EG}]_{\text{Reacted}} = [\text{EDE}]_i - [\text{EDE}] \quad (6)$$

where $[\text{EDE}]_i$ is the concentration of EDE groups initially present in the polymer.

Substituting Eqs. (5) and (6) into Eq. (2) gives

$$-\frac{d[\text{EDE}]}{dt} = k_G[\text{EDE}]([\text{EDE}] + A) \quad (7)$$

where the constant A is defined as:

$$A = [\text{EG}]_i - [\text{EDE}]_i \quad (8)$$

Since the volatility of ethylene glycol changes with temperature, the value of A is dependent on the reaction temperature, and on the reactor vessel volume that is unoccupied by the liquid reactants. Measurements of temperature and pressure in the reactor suggest that a vapor-liquid equilibrium exists in the closed vessel at each temperature. Therefore, the value of $[\text{EG}]_i$ can be readily calculated at each reaction temperature using thermodynamic data for ethylene glycol¹⁰ to determine the quantity of EG present as vapor in the 2-L reactor. Figure 6 summarizes the dependency of A on reaction tempera-

tures between 245 and 275°C. The variation in A over this range is about 10%.

Equation (7) can be rearranged to separate the variables and integrated between the limits of time 0 and t , and the corresponding ethylene diester concentrations $[\text{EDE}]_0$ and $[\text{EDE}]$, respectively, to give

$$\frac{1}{A} \ln\left(\frac{1}{1-x}\right) = k_G t \quad (9)$$

$$x = \frac{A([\text{EDE}]_0 - [\text{EDE}])}{[\text{EDE}]_0([\text{EDE}] + A)} \quad (10)$$

The variable x represents a degree of conversion or reaction, with a value of 0 when $[\text{EDE}] = [\text{EDE}]_0$ at reaction time 0, and with a value of 1 when $[\text{EDE}] = 0$. For convenience, reaction time 0 is considered to be the time when the reaction temperature is first attained in the reactor vessel. Figure 7 shows a plot of x versus reaction time. The values of $[\text{EDE}]$ were calculated from the data in Figure 3 using Eqs. (5) and (6). The value of $[\text{EDE}]_0$ was measured for each set of reaction conditions. This value was employed in Eq. (10) to carry out the corresponding kinetic analysis.

The glycolysis rate constant can be obtained by plotting $1/A \ln(1/1-x)$ versus t , as shown in Figure 8 for three different temperatures. The initial rate

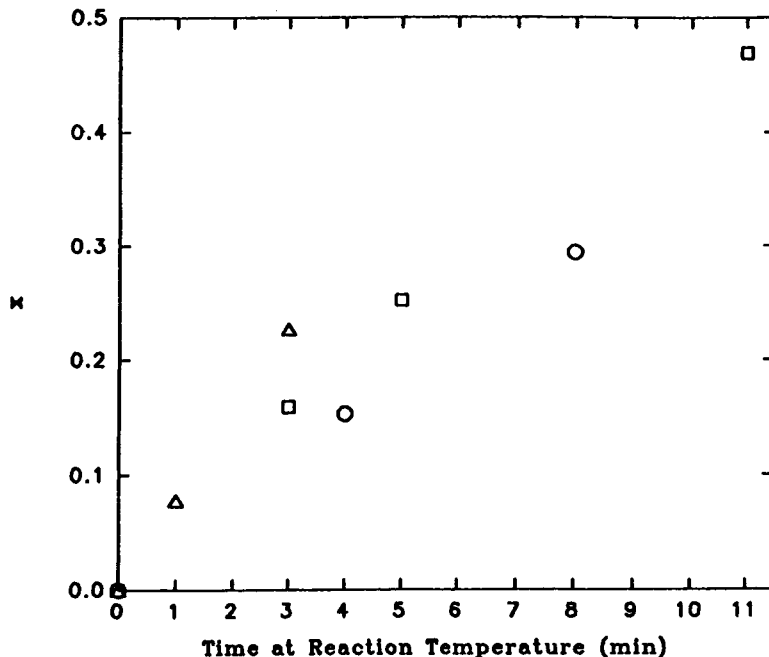


Figure 7 Reaction extent, x , as a function of reaction time for three temperatures: (○) 255°C, (□) 265°C, (△) 275°C.

model, Eq. (9), is seen to provide a good fit for the experimental data. It can thus be concluded from Figures 5 and 8 that the glycolytic depolymerization rate of PET expressed in Eq. (2) is applicable to the entire temperature range from 190 to 275°C.

The slopes of the lines in Figure 8 give the values of the rate constants summarized in Table II. The corresponding activation energy can be calculated from the Arrhenius plot in Figure 9 to be 92 kJ/mol. This value is in good agreement with previously

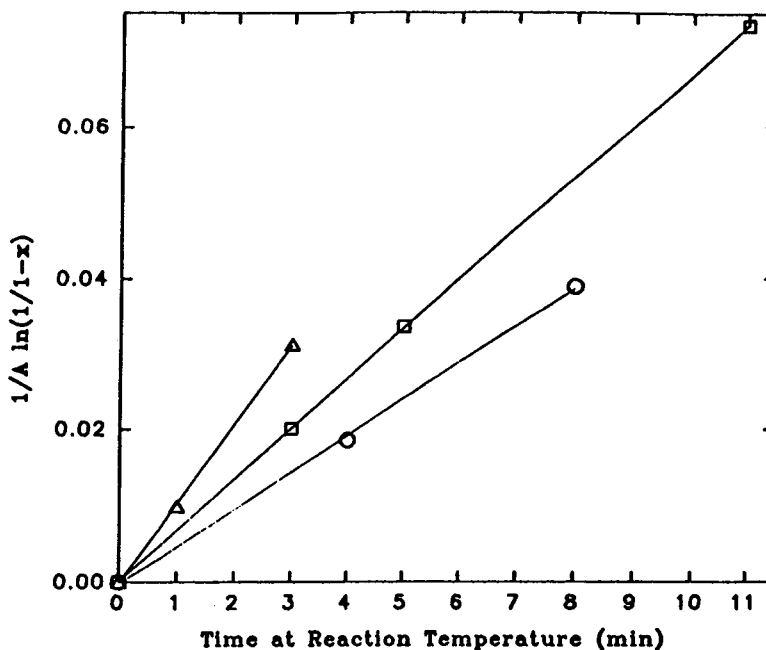


Figure 8 Initial rate data plotted according to Eq. (9) for three temperatures: (○) 255°C, (□) 265°C, (△) 275°C.

Table II Glycolysis Rate Constants

Temperature (°C)	$k_G \times 10^3$ (L mol ⁻¹ min ⁻¹)
255	4.87
265	6.67
275	10.44

published activation energies for the glycolysis of PET.^{2,3,7}

Glycolysis with External Catalysts

In earlier work, zinc compounds were found to catalyze the hydrolytic depolymerization of PET melts.¹¹ This catalytic activity was attributed to an electrolytic destabilization of the water-PET interface. Since EG is known to be a better solvent for PET oligomers¹² than water, the influence of the zinc compounds on the melt glycolysis of PET is examined in this work.

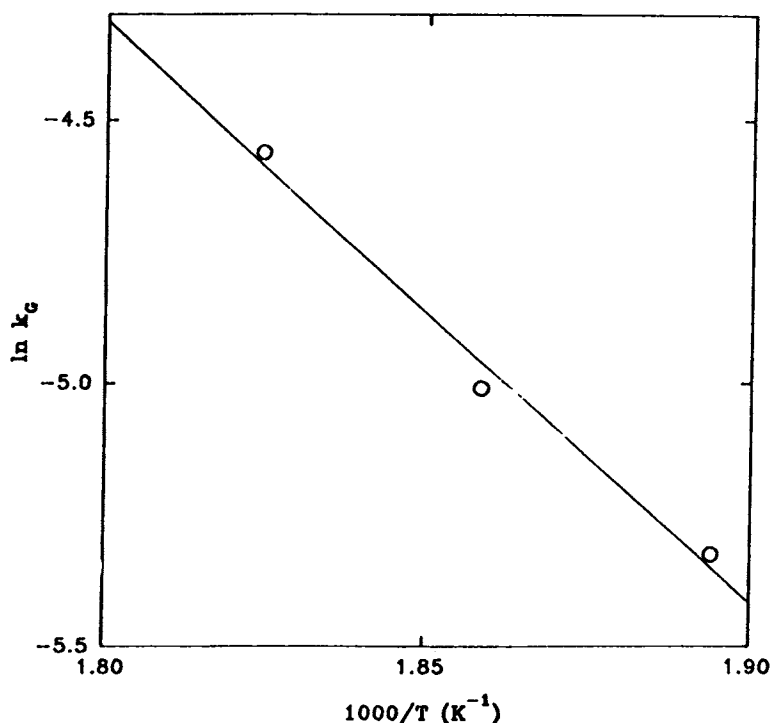
Zinc salts are known to catalyze the glycolysis of PET below its melting range.⁸ The data in Table III show the effect of zinc salts on [EG] when a temperature of 245°C is first obtained in the reactor

Table III Effect of Zinc Catalysts on [EG] at 245°C

Additive	[EG] (mol/L)	% Difference
None	10.84	—
0.1% zinc stearate	10.36	-4.5
0.1% zinc acetate	10.36	-4.5
1.0% zinc acetate	10.43	-3.8

vessel and the PET has just melted. The zinc salts do in fact lower [EG] compared to the case when they are not present, indicating a catalytic effect. The results for 0.1% zinc acetate and 0.1% zinc stearate are the same within experimental error. Increasing the concentration to 1.0% zinc acetate does not give an added benefit over 0.1%.

[EDE] values calculated from experiments with the catalysts and concentrations from Table III at 265°C are used to obtain the glycolysis extents shown in Figure 10, from Eqs. (9) and (10). From Figure 10, the data points for 0.1% zinc acetate, 0.1% zinc stearate, and 1.0% zinc acetate are seen to lie on the same line as the data for uncatalyzed glycolysis. Therefore, it appears that there is no discernible change in k_G upon addition of the zinc compounds.

**Figure 9** Arrhenius plot for glycolysis rate constants.

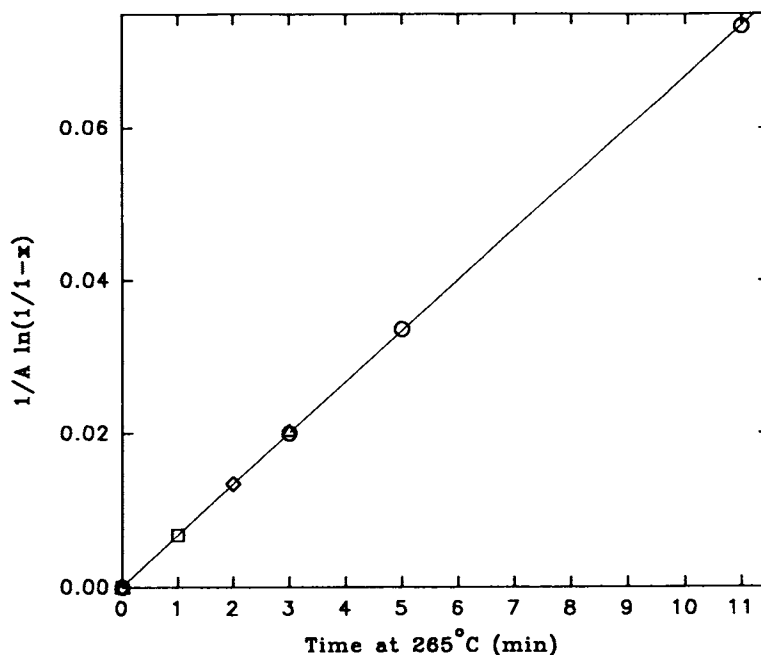


Figure 10 Glycolysis extent data at 265°C fit to Eq. (9): (○) no additives, (□) 0.1% zinc stearate, (△) 0.1% zinc acetate, (◇) 1.0% zinc acetate.

Effectiveness of Zinc Compounds for Glycolysis

The presence of zinc acetate and zinc stearate during PET glycolysis does increase the reaction extent below 245°C, although the exact mechanism is unknown.⁸ Below this temperature, the glycolysis reaction occurs between solid PET and liquid ethylene glycol. At temperatures exceeding 245°C, the glycolysis reaction occurs predominately in a single liquid phase, as evidenced by the homogeneous gel obtained upon quenching the reaction mixture. The zinc salts do not promote any further increase in the glycolysis rate at 265°C. There are two possible reasons for the apparent loss of catalytic effectiveness. First of all, the reaction rate may no longer be limited by the catalyzed step in the glycolysis mechanism. Second, the interfacial properties of the zinc salts may no longer be important in a single-phase reaction. Either or both of these explanations may be possible. However, the fact that zinc compounds have little effect on the melt glycolysis reaction strengthens the earlier conclusion that the effectiveness of zinc compounds in PET hydrolysis is due primarily to their interfacial properties.^{11,13}

CONCLUSIONS

A kinetic model for the glycolytic depolymerization of PET melts was found to be first order in both EG

and ethylene diester concentrations, for small reaction times. The proposed model appears to be consistent with data in the literature for glycolysis below 240°C as well. The results suggest that EG does not have a significant role as an internal catalyst in the glycolytic depolymerization of PET. The activation energy for glycolysis was found to be 92 kJ/mol, which is in agreement with values reported in the literature. Although zinc salts appear to have a catalytic effect on glycolysis below 245°C, they do not seem to influence rates at temperatures above 245°C. These salts did, however, catalyze melt hydrolysis in an earlier study. This difference in catalytic behavior may be due primarily to the differences in solubility of PET and its oligomers in water and in EG.

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NOTATION

- [EDE] Concentration of ethylene diester groups in the polymer, mol/L
 [EDE]₀ Concentration of ethylene diester groups initially present in the polymer, mol/L

- [EDE]₀ Concentration of ethylene diester groups in the polymer at reaction time 0, mol/L
- [EG] Concentration of liquid ethylene glycol, mol/L
- [EG]_i Initial concentration of liquid ethylene glycol at a specific reaction temperature, mol/L
- k_G Glycolysis rate constant, L mol⁻¹ min⁻¹
- k_i Pseudo-first-order rate constant

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