A Kinetic Study of the Hydrolytic Degradation of Polyethylene Terephthalate at High Temperatures

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SYNOPSIS

The hydrolytic depolymerization of molten PET in excess water was studied using a 2 L stirred pressure reactor at temperatures of 250, 265, and 280°C. Rate constants for hydrolysis are calculated from the initial rate data. At initial water : PET charge ratios (w/w) exceeding 5.1, essentially complete depolymerization to monomer is possible at 265°C. At lower water: PET initial charges, an equilibrium is established. The equilibrium constants are calculated for 2 g water/g PET at three temperatures. A kinetic model is proposed to describe the hydrolysis reaction. The model is shown to fit experimental data and to yield good predictions for the equilibrium concentration of carboxyl groups. Carboxyl-group concentrations are measured using an end-group analysis technique. Potentiometric titrations are carried out in one of two solvent systems, dimethylphenol:chloroform or dimethylsulfoxide, depending on the extent of hydrolysis. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

The chemical recycling of waste polymers has been gaining greater attention in recent years as a means of obtaining valuable products from waste plastics.[1] In chemical recycling, plastic waste is treated chemically to recover low-molecular-weight fractions of monomers or other useful oligomers. Because of the wide variety of polymers commercially available, several different types of chemical treatment are necessary.

Condensation polymers, such as polyesters and polyamides, can be treated by hydrolysis, alcoholysis, and transesterification. For polyethylene terephthalate (PET) alcoholysis,[2,3] glycolysis[4-7] and hydrolysis[8-10] have all been proposed as chemical recovery techniques. Most of the hydrolytic techniques found in the literature rely on strongly acidic or basic conditions and temperatures below 200°C. One process has recently been outlined that uses high-temperature hydrolysis of molten PET in water.[8] The kinetics of PET hydrolysis in water have been studied at temperatures below the melting range.[11-14] Thermal and hydrolytic degradation in

PET melts has also been recently examined.[15] However, little effort has been made to investigate the kinetics of the high temperature, hydrolytic depolymerization of PET. In this study, the kinetics of PET hydrolysis are studied using a high temperature, high pressure batch reactor.
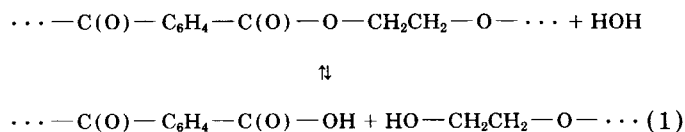
ANALYTICAL TECHNIQUES

The major difficulty to be overcome in studying the hydrolytic depolymerization of PET is a method for quantifying the hydrolysis extent as a function of reaction time. Methods outlined in the literature that have been used to measure the extent of hydrolysis include intrinsic viscosity, infrared spectroscopy, end group analysis, and gel permeation chromatography. These methods have been shown to be satisfactory for quantifying hydrolytic reactions in PET films below the melting range.[11-14] In the case of complete hydrolytic depolymerization, however, a method is required that would be capable of determining depolymerization extent for samples ranging from unreacted polymer to the final monomers. Infrared spectroscopy was found to be inadequate over this broad range of molecular weights. It is difficult, for example, to measure changes of

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carbonyl to carboxyl groups from the infrared spectra alone. The other known techniques all require suitable solvents. Unfortunately, solvent systems that solubilize the polymer are predominantly nonpolar organic ones.[16-22] These solvents do not solubilize the polar monomer, terephthalic acid, nor other small oligomers. Therefore none of the sol-

vents commonly used for PET analysis are satisfactory over the entire range of interest. Multiple solvent systems were thus examined.

End-group analysis was chosen to follow the hydrolysis reaction because it yields results that can be directly related to reaction kinetics. The hydrolysis of PET involves the chemical scission of an ester linkage by a water molecule as shown below:

$$\cdots\mathrm{-C(O)-C_6H_4-C(O)-O-CH_2CH_2-O-}\cdots\mathrm{+HOH}$$

$$\updownarrow$$

$$\cdots\mathrm{-C(O)-C_6H_4-C(O)-OH+HO-CH_2CH_2-O-}\cdots(1)$$

Each chain scission uses up one water molecule and creates one carboxyl end group. Hence, the extent of reaction can be followed by measuring the number of carboxyl ends present after various reaction times. The number of free carboxyl ends was determined by titrating solutions of hydrolysed sample with ethanolic KOH in appropriate solvent systems. It was found that two solvent systems were required because of the differences in the solubilities of the macromolecule, oligomers, and monomers of PET outlined above. The first solvent system used was a mixture of dimethylphenol : chloroform, as outlined by Garmon.[16] This system forms a metastable solution capable of solubilizing the polymer as well as degraded samples containing up to 0.8 meq carboxyl groups/g polymer. The second solvent used was dimethylsulfoxide (DMSO). This solvent was found to dissolve oligomers as well as pure terephthalic acid.

Before analysis of carboxyl groups could begin, it was necessary to relate the equivalence points encountered in each system. Stearic acid was found to be soluble in both solvent systems. Hence potentiometric titrations of stearic acid were carried out in both systems (Fig. 1). The equivalence points in each system were determined from Figure 1. These results were used to correct all titrations in dimethylphenol:chloroform to their DMSO equivalents. It was also necessary to determine whether hydrolysis of the sample would continue during the actual titrations. Titrations performed after hydrolysed samples had been in solution for 30 min showed no measurable increases in carboxyl group content in either system. A typical titration was performed in 20 min.

The data obtained from titrations in the described method cannot be used for kinetic analysis without first choosing a standard-weight basis. Initially, virgin PET contains 2 mol of ester linkages per mol of repeat unit (whose molar mass is 192 g/mol), or

0.0104 mol/g PET. Terephthalic acid monomer contains 2 mol of carboxyl groups per mole of acid (molar mass is 166 g/mol), or 0.01205 mol/g acid. The difference in these numbers is due to the ethylene glycol component that is originally present in the polymer. When ethylene glycol monomer is formed in the hydrolysis reaction, it is drawn into the aqueous phase. Hence, as the depolymerization proceeds, the fraction of glycol-based units will become lower in the solid phase. As described in the next section, it is only necessary to titrate the solid phase. Therefore, the weight basis of titration changes with reaction time. It is thus necessary to account for the ethylene glycol present in the aqueous phase, in order to express the equivalence point as moles of carboxyl groups per gram of PET.
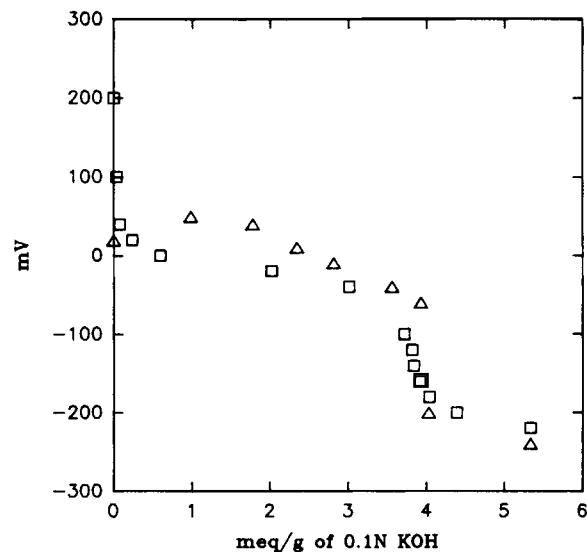

Figure 1   The titration of stearic acid in two different solvent systems. (□) dimethylphenol/chloroform; (△) DMSO.

Ethylene glycol concentration was therefore obtained as a function of reaction time for an initial charge of 2 g water/g PET at 265°C. It will be shown in the Results and Discussion section that large quantities of ethylene glycol are formed only late in the reaction. This information can be used to correct all titrations performed on hydrolysed samples for the ethylene glycol present in the aqueous phase at that reaction time. In this way, all final values obtained from the titrations denote carboxyl group concentration based on weight of original polymer, and are expressed in units of mol COOH/g PET.

EXPERIMENTAL

The PET used in all experiments was blow-moulding grade Eastman Kodak 9921 natural resin (IV = 0.80 as measured in 60% phenol/40% tetrachloroethane). The water used was high purity HPLC grade. Before being fed to the reactor, the PET pellets were pressed into 0.010" sheet on a Carver laboratory press at 250°C. The sheet was then cut into 0.5" × 0.5" flakes in order to create maximum surface area for heat and mass transfer in the reactor.

A 2-L capacity Parr pressure reactor was used for all hydrolysis experiments. The reactor was equipped with rotors to ensure proper mixing. It was also equipped with high-power heaters in order to reach the reaction temperature as quickly as possible. To further minimize the polymer–water heat-up time, the reactor vessel and water were preheated to between 80 and 85°C prior to the addition of the PET flakes. The vessel was then heated to a predetermined reaction temperature. All reaction temperatures investigated were above the melting range of the virgin PET. The melting range of the resin was determined to be from 230–245°C by differential scanning calorimetry. The time required for the polymer to melt completely in the reaction vessel depends on the initial water : PET charge ratio, and varies between 25 and 35 min as shown in Figure 2. 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 a minute of quenching. The vessel was subsequently opened, and the product removed.

The product was separated into solid and aqueous phases using a sintered glass filter. The solid phase was further washed with cold water to remove any residual water-soluble components, such as ethylene glycol monomer. The solids were then dried at 40–
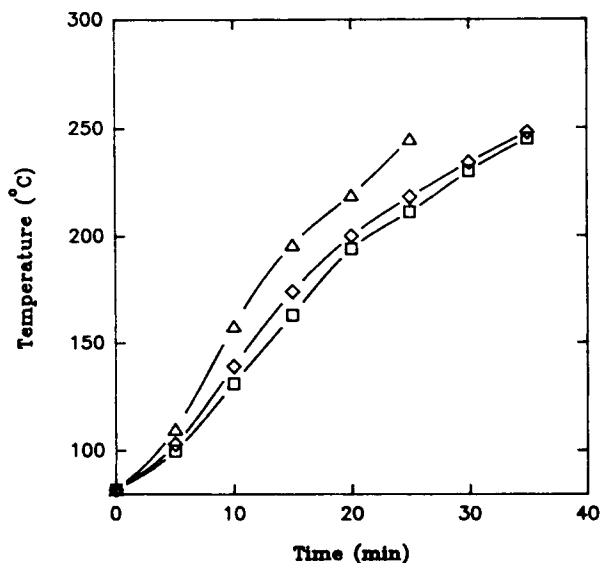

Figure 2 The temperature profile in the Parr pressure reactor for various charge ratios. (△) 2 g water/g PET; (◇) 5.1 g water/g PET; (□) 10 g water/g PET.

50°C under vacuum to constant weight. After drying, the solids were ground up into a fine powder using a mortar and pestle. Representative samples of this powder were used for analysis. The aqueous phase from the reactor was retained for testing in a Varian ultraviolet spectrophotometer.

The titration procedure was as follows. A carefully measured amount of dry powder (1–2 g in dimethylphenol : chloroform, 0.1–0.2 g in DMSO) was added to 25 mL of solvent in a stirred beaker. The KOH solution (0.1N standardized against potassium hydrogen phthalate) was then added with a buret after the powder had dissolved completely. The end point was determined potentiometrically with a pH/mV meter. In the case of monomer and some highly hydrolysed oligomers, precipitates were evident in the beaker at the end of the titration. However, this did not seem to affect the excellent reproducibility of the results, nor did it affect the analysis of carboxyl groups. Figure 3 shows typical titration curves of hydrolysed samples. In all cases, the equivalence points are characterized by dramatic potential breaks. The largest standard deviation encountered in the end points obtained by titration was 2.7%.

The titrations described were carried out solely on the solid phase recovered from the reactor. Some small oligomers and terephthalic acid monomer were found to be present in the aqueous phase. Their concentrations were quantified by determining the UV absorbance at 240 nm. It was found that the phthalate groups were only sparingly soluble in the
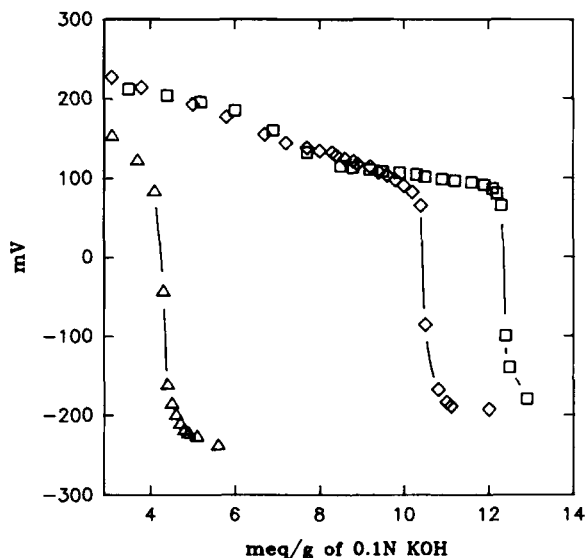
Figure 3 The titration in DMSO of PET samples hydrolysed at 265°C, at an initial charge ratio of 2 g water/g PET. (△) sample A, hydrolysed for 15 min; (◇) sample B, hydrolysed for 65 min, (□) sample C, terephthalic acid.

water phase, and did not need to be accounted for in subsequent titrations.

RESULTS AND DISCUSSION

Hydrolysis Rate Data

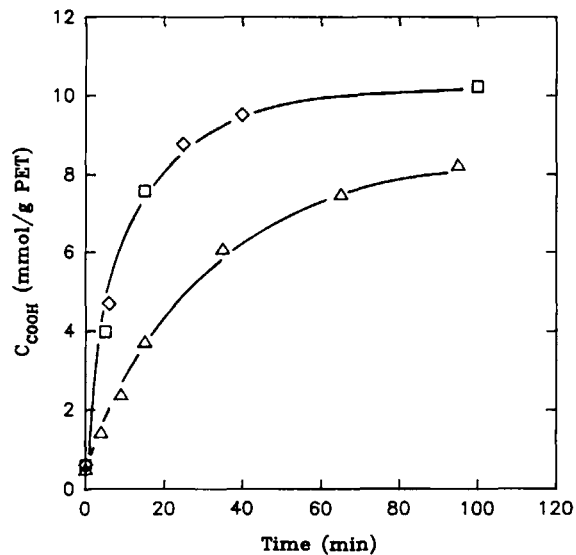Figure 4 presents the data for carboxyl group concentration as a function of reaction time at 265°C.

It is evident that the data for initial reactor charges of 5.1 and 10 g water/g PET fall on the same rate curve at 265°C. There would therefore appear to exist a water concentration, C_{WATERc}, above which the extent of depolymerization remains effectively constant. Experiments were carried out at 265°C to show that C_{WATERc} corresponds to an initial reactor loading of 0.283 mol water/g PET, or 5.1 g water/g PET, as summarized in Figure 5. This initial loading gives a carboxyl group concentration that falls within the 95% confidence limit of 10.4 mmol COOH/g PET, yielding essentially complete depolymerization.

At an initial charge of 2 g water/g PET, an equilibrium state is reached when C_{COOH} = 0.00868 mol/g PET, and complete depolymerization is not possible. This equilibrium value was verified by approaching it from an initial monomer state as well. Water, terephthalic acid, and ethylene glycol were loaded into the reactor vessel in the right proportions, taking into account the water present in the acid and diol, to give the same initial charge of 2 g water/g PET. The reactor was then run at 265°C for 5 h. The product was removed and filtered to separate the solids. The solids were washed, dried, and titrated as described previously. The carboxyl group content was again found to be 0.00868 mol/g PET. Since the equilibrium value can be approached from both polymer and monomer starting points, it can be concluded that any impurities present in the commercial resin, such as residual poly-
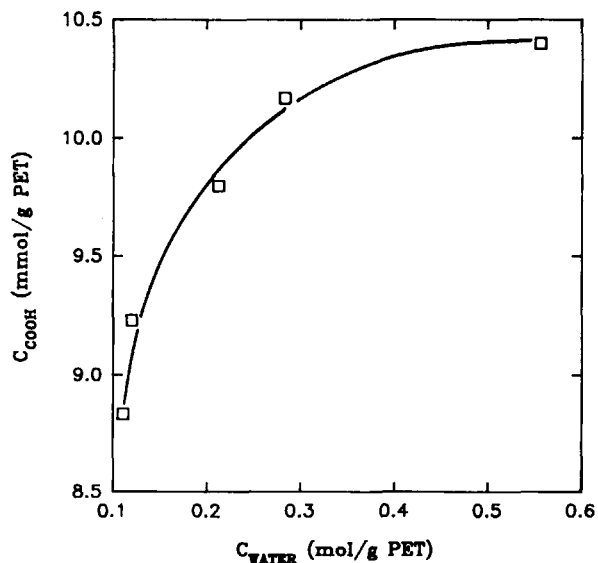

Figure 4 Increase in carboxyl group concentration with time at 265°C, for three initial charge ratios. (△) 2 g water/g PET; (◇) 5.1 g water/g PET; (□) 10 g water/g PET.

Figure 5 Equilibrium values of carboxyl group concentration as a function of initial water concentration at 265°C.

condensation catalyst, do not have a measurable effect on the equilibrium point.

In order to determine the nature of the hydrolysis mechanism, the concentration of ethylene glycol in the aqueous phase was monitored using gas chromatography for an initial charge ratio of 2 g water/g PET. The results are summarized in Figure 6. The bulk of the ethylene glycol monomer is seen to appear relatively late in the reaction, after 35 min. This time corresponds to a carboxyl-group concentration of 0.00610 mol/g PET. Lower reaction times show very little glycol present. The smooth increase noted in Figure 4 for C_{COOH} is not evident. The data in Figure 6 are therefore consistent with a random chain scission mechanism.

Determination of Rate and Equilibrium Constants

Equation (1) shows the chemical reaction for the hydrolysis of PET. The rate of appearance of carboxyl groups can be expressed as follows:

$$dC_{COOH}/dt = kC_{EL}C_{WATER} - k'C_{COOH}C_{OH} \quad (2)$$

where C_{EL} represents the concentration of ester linkages at any reaction time, and k and k' refer to the reaction-rate constants for the hydrolysis and condensation reactions, respectively.

For small reaction times, $C_{COOH}C_{OH} \ll C_{EL}C_{WATER}$. Therefore, the second term in eq. (2) can be ne-

glected. In all experiments performed $C_{WATER} \gg C_{EL}$ by at least an order of magnitude for small reaction times. C_{WATER} can thus be considered constant. It must be noted that C_{WATER} refers specifically to the concentration of liquid water in the reactor at a specified temperature. Liquid-water concentrations were calculated by assuming that the only contributions to pressure in the reactor vessel were due to saturated water vapour and to air. For small t, eq. (2) becomes:

$$dC_{COOH}/dt = (kC_{WATER})C_{EL}. \quad (3)$$

Since one carboxyl group breaks one ester linkage, C_{EL} can be expressed as follows:

$$C_{EL} = C_{ELp} - C_{COOH} \quad (4)$$

where C_{ELp} is the initial concentration of ester linkages in the polymer.

Substituting for C_{EL} in eq. (3) and integrating from time 0 to t, and from carboxyl group content C_{COOHo} to C_{COOH}, gives:

$$\ln[(C_{ELp} - C_{COOHo})/(C_{ELp} - C_{COOH})]$$
$$= (kC_{WATER})t. \quad (5)$$

In all kinetic studies, reaction time zero is taken to be the time at which the reactor vessel temperature is 245°C, that is, when all the PET is molten.

Equation (5) can be simplified by introducing the reaction extent, e, as defined below:

$$e = (C_{COOH} - C_{COOHo})/(C_{ELp} - C_{COOHo}). \quad (6)$$

When $e = 0$, the carboxyl group concentration is the concentration at time $t = 0$. Similarly, when $e = 1$, the carboxyl group concentration is the concentration of all hydrolysable ester linkages. Substituting into eq. (5) gives:

$$\ln[1/(1 - e)] = (kC_{WATER})t. \quad (7)$$

The rate constant, k, can therefore be determined from a plot of $C_{WATER}^{-1} \times \ln[1/(1 - e)]$ versus t. Figure 7 shows experimental data gathered at 265°C for three water concentrations at reaction times lower than 10 min. For the case of 10 g water/g PET initial charge, C_{WATERc} is used in place of C_{WATER} in eq. (7). As predicted by eq. (7), the data fall on a straight line, giving a value of 0.360 g PET mol^{-1} min^{-1} for k.
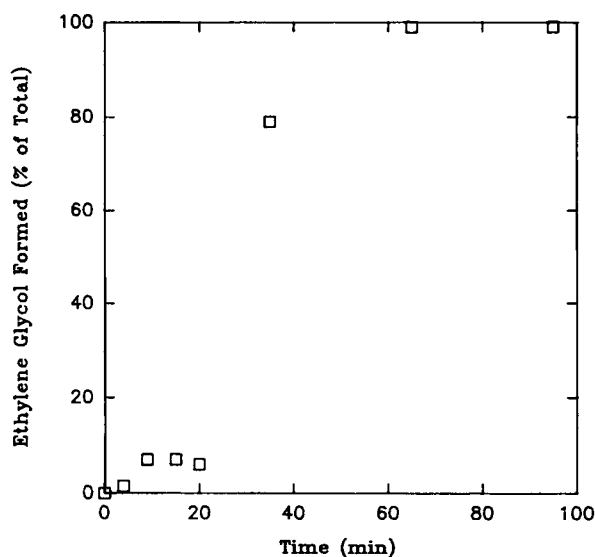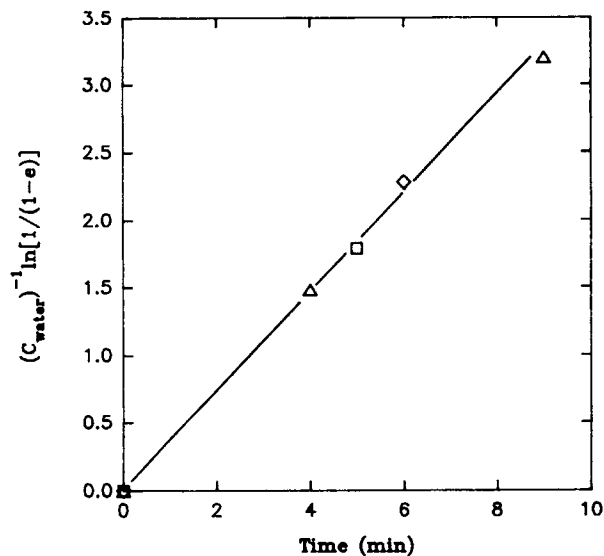

Figure 6 Increase in ethylene glycol concentration in the aqueous phase (as a percentage of the total recovery). Initial charge ratio is 2 g water/g PET, and the reaction temperature is 265°C.

Figure 7 First order model, eq. (7), fit to initial rate data at 265°C. ($\triangle$) 2 g water/g PET; ($\lozenge$) 5.1 g water/g PET; ($\square$) 10 g water/g PET.

The condensation reaction constant, k', can be calculated from the equilibrium constant, K. At equilibrium, the following equation can be written:

$$K = k/k' = (C_{COOH}C_{OH})/(C_{EL}C_{WATER}). \quad (8)$$

Since each hydrolytic chain scission forms one carboxyl and one hydroxyl group, $C_{COOH} = C_{OH}$. Equation (8) can therefore be simplified to yield:

$$K = (C_{COOH})^2/(C_{EL}C_{WATER}). \quad (9)$$

Equilibrium concentrations were obtained for the case of 2 g water/g PET initial charge at temperatures of 250, 265, and 280°C. The results are summarized in Table I. At 265°C, $K = 0.664$, and k' is therefore calculated to be 0.544 g PET mol^{-1} min^{-1}.

Equilibrium constants have been previously calculated for the polycondensation reactions of a variety of polyesters. Vancso–Szmercsanyi et al.[23] found that the equilibrium constant is independent of the acid used in the polycondensation, and only weakly dependent on temperature. Between 140 and 180°C, they found the equilibrium constant to be approximately 1.4 for ethylene glycol polyesters. This value can be inverted to 0.71 in order to give the ratio of hydrolysis rate constant to polycondensation rate constant.

The equilibrium constants presented in Table I are seen to be of the same magnitude as the polycondensation equilibrium constant. However, the K values in Table I are quite sensitive to temperature, which is not the case in polycondensation reactions. This would indicate that the polycondensation equilibrium state is different from the equilibrium encountered for hydrolysis. In fact, the rate constants upon which the polycondensation equilibrium is based are valid for high conversions of monomer to polymer. The rate constants upon which the hydrolysis equilibrium is based, on the other hand, are valid for low conversions, when only monomers, dimers, and short-chain oligomers are present. It is therefore not surprising that the equilibrium constants for polycondensation do not correspond with those for hydrolytic depolymerization.

Temperature effects on the hydrolysis rate constant, k, were also investigated. The k values were calculated from initial rate data using eq. (7) at three different temperatures. An initial charge ratio of 10 g water/g PET was used in all cases to make sure that C_{WATER} remained greater than C_{WATERc}. In this way, C_{WATERc} could be used in eq. (7) for all three temperatures. The results are listed in Table II.

The data in Table II are fitted to the Arrhenius equation in Figure 8. An activation energy for hydrolysis of 55.7 kJ/mol is obtained. Researchers working below the melting range of PET have previously studied the hydrolysis of PET films in water.

Table I Equilibrium Concentrations of Products and Reactants for an Initial Reactor Charge Ratio of 2 g Water/g PET

| Temperature (°C) | Concentrations (mmol/g PET) | | | K |
	C_{COOH}	C_{EL}	C_{WATER}	
250	9.54	0.86	73.9	1.43
265	8.68	1.72	66.0	0.664
280	7.58	2.82	53.0	0.384

Table II Hydrolysis Rate Constants From Initial Rate Data for a Reactor Charge Ratio of 10 g Water/g PET

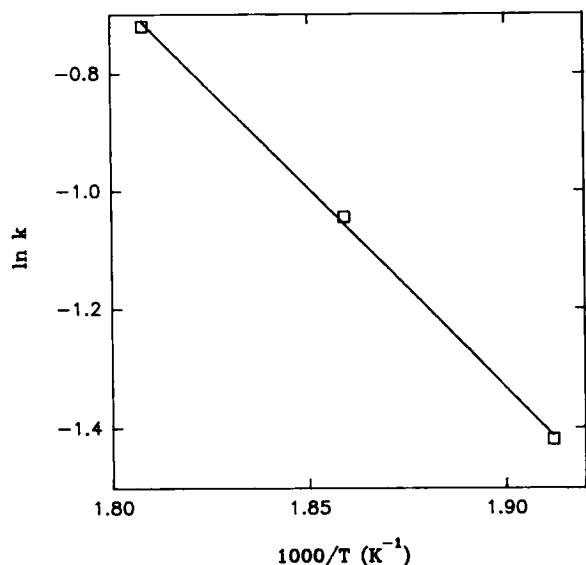| Temperature (°C)	Liquid Water Concentration (mol/g PET)	k (g PET mol^{-1} min^{-1})
250	0.524	0.242
265	0.515	0.352
280	0.505	0.487

Figure 8 Arrhenius plot for an initial charge ratio of 10 g water/g PET.

At 100°C, Zimmerman and Kim[12] found that a first-order model approximated the hydrolysis in the initial period, yielding a rate constant of 3.0×10^{-7} min^{-1} for a PET sample containing initially 0.021 meq COOH/g polymer. For further comparison, a first-order model was found to fit the data of Ravens and Ward[13] in the initial period of hydrolysis at 186°C. This model yields an initial rate constant of 2.0×10^{-4} min^{-1}. Since PET hydrolysis below the melting range is limited by physical factors such as diffusion and crystallinity, these rate constants are much lower than the values reported here for melt hydrolysis with excess water. It is possible to obtain a rough estimate about the influence of physical factors on the hydrolysis reaction at 100 and 186°C by using the Arrhenius equation to extrapolate the rate constants calculated here. At 186°C, the quantity kC_{WATERc} can be extrapolated to give a first order initial rate of 9.4×10^{-3} min^{-1}; while at 100°C, the extrapolated value of kC_{WATERc} is 3.3×10^{-4} min^{-1}. These extrapolated values are orders of magnitude greater than the experimental values given. Hence, it is clear that physical considerations easily dominate kinetic ones in solid PET hydrolysis. Hydrolysis above the melting range renders physical factors much less important, and is therefore a more effective means of hydrolysing PET.

A Kinetic Model for Melt Hydrolysis

In seeking a model for the complete hydrolysis reaction, it is necessary to retain the second term in

eq. (2), since the reverse reaction will ultimately determine the equilibrium. A simplification of this term can be made, however. As the reaction proceeds, $C_{\text{COOH}} = C_{\text{OH}}$. Equation (2) therefore becomes:

$$dC_{\text{COOH}}/dt = kC_{\text{EL}}C_{\text{WATER}} - k'(C_{\text{COOH}})^2. \quad (10)$$

By stoichiometry, it is possible to express both water and ester linkage concentrations in terms of C_{COOH}:

$$dC_{\text{COOH}}/dt = k(C_{\text{ELp}} - C_{\text{COOH}})(C_{\text{WATERo}} - C_{\text{COOH}})$$
$$- k'(C_{\text{COOH}})^2 \quad (11)$$

where C_{ELp} is the initial concentration of ester linkages; and C_{WATERo} is the liquid water concentration at reaction time zero. If C_{WATERo} is greater than C_{WATERc}, then C_{WATERc} is used in eq. (11).

Equation (11) can be solved analytically for C_{COOH}:

$$\ln \frac{|C_{\text{COOH}} + A - B|}{|C_{\text{COOH}} + A + B|}$$
$$= -2B(k' - k)t + \ln \frac{|C_{\text{COOHo}} + A - B|}{|C_{\text{COOHo}} + A + B|} \quad (12)$$

where

$$A = k(C_{\text{ELp}} + C_{\text{WATERo}})/2(k' - k) \quad (13)$$

$$B = \left(\frac{k^2(C_{\text{ELp}} + C_{\text{WATERo}})^2}{4(k' - k)^2} + \frac{kC_{\text{ELp}}C_{\text{WATERo}}}{k' - k}\right)^{1/2}. \quad (14)$$
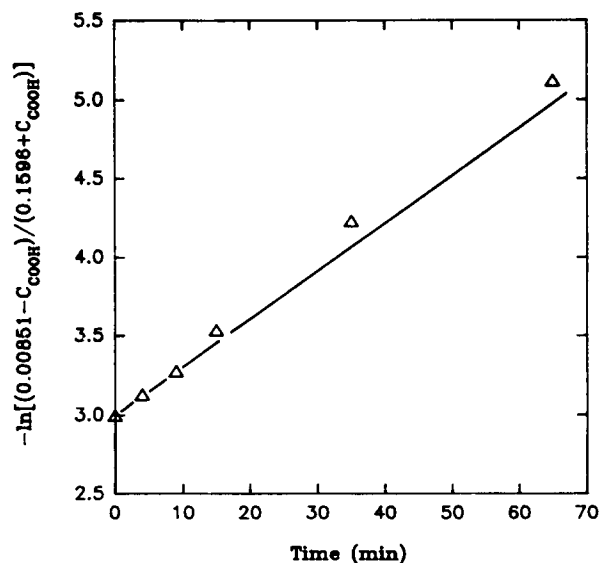

Figure 9 Proposed kinetic model, eq. (12), compared to the rate data obtained for an initial charge ratio of 2 g water/g PET at 265°C.

The data in Figure 4 are compared to eq. (12) in Figure 9, for an initial charge ratio of 2 g water/g PET, with $C_{ELp} = 0.0104$, $C_{WATERo} = 0.066$, $k = 0.360$, and $k' = 0.542$. In this case, eq. (12) becomes:

$$-\ln[(0.00851 - C_{COOH})/(0.1596 + C_{COOH})]$$
$$= 0.0306t + 3.00. \quad (15)$$

According to eq. (15), C_{COOH} cannot exceed 0.00851 mol/g PET. This value differs from the experimentally determined equilibrium concentration of 0.00868 mol/g PET by 2%.

In Figure 10, the data for initial reactor charges of 5.1 and 10 g water/g PET are compared to eq. (12) using $C_{WATERo} = C_{WATERc}$ to give:

$$-\ln[(0.00977 - C_{COOH})/(0.4972 + C_{COOH})]$$
$$= 0.0923t + 4.00. \quad (16)$$

In this case, the equilibrium concentration of carboxyl groups is predicted to be 0.00977 mol/g PET, which is 6% lower than the value for initial concentration of ester linkages, suggesting effectively complete hydrolysis.

Hence the proposed model is seen to provide good agreement with experimental results. The model also gives a satisfactory estimate of the equilibrium carboxyl-group concentration. The only parameters whose values are required a priori are the forward and reverse rate constants, the initial concentration
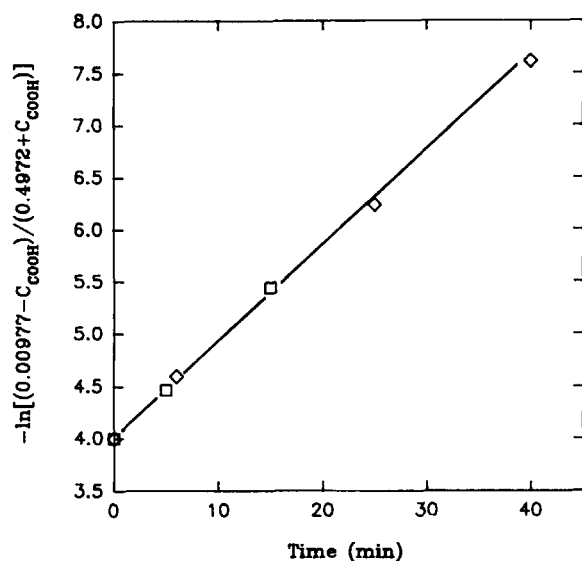
of ester linkages in the polymer, and the liquid water concentration at the reaction temperature.

CONCLUSIONS

The hydrolytic depolymerization of PET above the melting range was studied in a batch reactor. Rate constants were calculated for the forward reaction using initial rate data. It was shown that essentially complete depolymerization could be achieved for initial water/PET (w/w) ratios of 5.1 or greater. Smaller charge ratios resulted in the establishment of an equilibrium. Equilibrium constants were calculated from equilibrium concentrations, and used to obtain rate constants for the reverse, or condensation reaction. A model was proposed for the hydrolytic depolymerization. This model was found to fit the experimental data and to provide satisfactory predictions of the equilibrium concentrations of carboxyl groups for three different initial-charge ratios. Carboxyl group concentrations were determined using end-group titration in two solvent systems.

NOTATION

C_{COOH}	carboxyl group concentration at any time, mol/g polymer
C_{COOHo}	carboxyl group concentration at reaction time zero, mol/g polymer
C_{EL}	concentration of ester linkages at any time, mol/g polymer
C_{ELp}	initial ester linkage concentration in the polymer, mol/g polymer
C_{WATER}	liquid water concentration at any time, mol/g polymer
C_{WATERc}	minimum liquid water concentration required for essentially complete depolymerization, mol/g polymer
C_{WATERo}	liquid water concentration at reaction time zero, mol/g polymer
e	hydrolysis reaction extent, defined in eq. (6)
k	hydrolysis rate constant, g PET mol^{-1} min^{-1}
k'	polycondensation rate constant, g PET mol^{-1} min^{-1}
K	equilibrium constant

Figure 10 Proposed kinetic model, eq. (12), compared to rate data obtained at 265°C. ($\Diamond$) 5.1 g water/g PET; ($\Box$) 10 g water/g PET.

REFERENCES

1. R. D. Leaversuch, *Modern Plastics,* **68,** 40–43 (1991).
2. B. Mikalajczyk, A. Lubawy, M. Djewska, P. Smo-czynski, A. Pozniak, and H. Boebel, Polish Patent PL 126,009 (1985).
3. L. A. Dupont and V. P. Gupta, ANTEC 91, Conference Proceedings, Montreal, Canada, May 5–9, 1991, 2139–2141.
4. J. Y. Chen, C. F. Ou, Y. C. Hu, and C. C. Lin, *J. Appl. Polym. Sci.,* **42,** 1501–1507 (1991).
5. U. R. Vaidya and V. M. Nadkarni, *J. Appl. Polym. Sci.,* **38,** 1179–1190 (1989).
6. S. Baliga and W. T. Wong, *J. Polym. Sci., Polym. Chem.,* **27,** 2071–2082 (1989).
7. G. A. Naik and K. A. Joshi, *J. Adhes. Sci. Technol.,* **1,** 201–207 (1987).
8. J. W. Mandoki, U.S. Patent 4,605,762 (1986).
9. S. F. Pusztaszeri, U.S. Patent 4,355,175 (1982).
10. N. D. Sharma, A. A. Vaidja, and P. Sharma, Indian Patent IN 163,385 (1988).
11. A. Ballara and J. Verdu, *Polym. Degrad. Stab.,* **26,** 361–374 (1989).
12. H. Zimmerman and N. T. Kim, *Polym. Eng. Sci.,* **20,** 680–683 (1980).
13. D. A. S. Ravens and I. M. Ward, *Trans. Farad. Soc.,* **57,** 150–159 (1961).
14. R. C. Golike and S. W. Lasoski, *J. Phys. Chem.,* **64,** 895–898 (1960).
15. K. S. Sao and J. D. Cloyd, *J. Appl. Polym. Sci.,* **42,** 845–850 (1991).
16. R. G. Garmon, *Polymer Molecular Weights, Part I,* Vol. 4, P. E. Slade, Jr., Ed., Marcel Dekker Inc., New York, 1975, pp. 54–59.
17. W. R. Sorenson and T. W. Campbell, *Preparative Methods of Polymer Chemistry,* 2nd ed., Wiley-Inter-science, New York, 1968.
18. H. Giesekus, *Polymer Fractionation,* M. J. R. Cantow, Ed., Academic Press, New York, Chap. CI, 1967.
19. H. Hendrix and W. Fester, *Shirley Inst.,* **43,** 1795 (1963).
20. M. J. Maurice and F. Huizinga, *Anal. Chim. Acta,* **22,** 363 (1960).
21. I. M. Ward, *Trans. Farad. Soc.,* **53,** 1406 (1957).
22. H. A. Pohl, *Anal. Chem.,* **26,** 1614 (1954).
23. I. Vancso–Szmercsanyi, E. Makay–Body, E. Szabo–Rethy, and P. Hirschberg, *Kinetics and Mechanism of Polyreactions,* Vol. 1, IUPAC Symposium Preprints, Budapest, 1969, pp. 103–107.