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### Aspects of the Chemistry of Poly (Ethylene Terephthalate). IV. Hydrolysis of Poly(Ethylene Terephthalate) in the Melt Phase

T. H. Shah<sup>a</sup>; G. A. Gamlen<sup>a</sup>; D. Dollimore<sup>b</sup>; J. I. Bhatt<sup>c</sup>

<sup>a</sup> Department of Chemistry and Applied Chemistry, University of Salford, Salford, England <sup>b</sup>

Department of Chemistry, University of Toledo, Toledo, Ohio <sup>c</sup> Mineral Resources Research Center, University of Minnesota, Minneapolis, Minnesota

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## Aspects of the Chemistry of Poly(Ethylene Terephthalate). IV. Hydrolysis of Poly(Ethylene Terephthalate) in the Melt Phase

T. H. SHAH and G. A. GAMLEN

Department of Chemistry and Applied Chemistry  
University of Salford  
Salford M5 4WT, England

D. DOLLIMORE

Department of Chemistry  
University of Toledo  
Toledo, Ohio 43606

J. I. BHATTY

Mineral Resources Research Center  
University of Minnesota  
Minneapolis, Minnesota 55440

### ABSTRACT

The effect of water vapor pressure on the molecular weight of molten poly(ethylene terephthalate) has been followed by measurement of the changes which occur in the intrinsic viscosity and the end-group concentrations upon hydrolysis. It was found that phosphoric acid is highly effective as a stabilizer; the hydrolysis rate constant ( $K_h$ ) decreasing from  $7.6 \times 10^{-7} \text{ mol}^{-1} \text{ s}^{-1}$  for nonstabilized to  $2.5 \times 10^{-7} \text{ mol}^{-1} \text{ s}^{-1}$  for the stabilized polyester at  $290^\circ\text{C}$  and water vapor pressure of 20 mmHg.

## INTRODUCTION

It is well known that when poly(ethylene terephthalate) (PET) is spun in the melt phase, a certain amount of hydrolytic degradation of the polyester can take place if the material is not well dried prior to melt spinning.

In spite of high industrial production of PET fiber and film, there is very little published information about the hydrolysis of the polymer, especially the melt phase.

## EXPERIMENTAL

All the chemicals used in this study were supplied by the Imperial Chemical Industries, Fibres Division, Harrogate, United Kingdom. No further purification of these chemicals was performed. The monomer bis(hydroxyethyl) terephthalate was of commercial grade.

Polycondensation of the monomer to PET and the subsequent hydrolysis of the formed polymer were carried out on a 1.5-kg scale in the melt phase, using a vacuum autoclave, as schematically shown in Fig. 1.

The monomer was polymerized at 290°C to an intrinsic viscosity value of about 0.67, using antimony trioxide (500 ppm) catalyst and

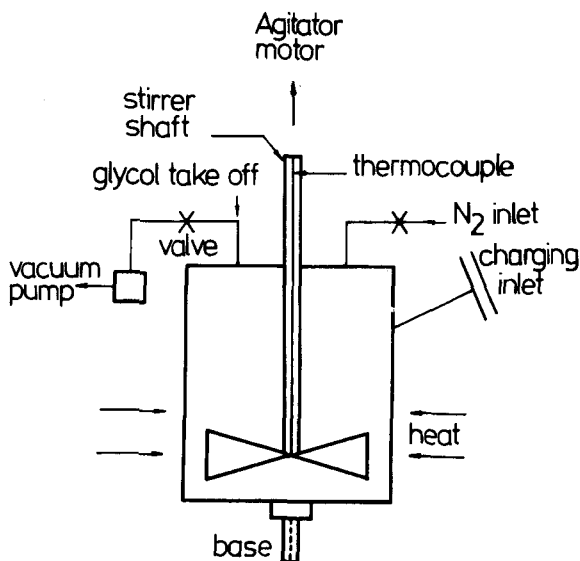


FIG. 1. Schematic diagram of polycondensation autoclave.

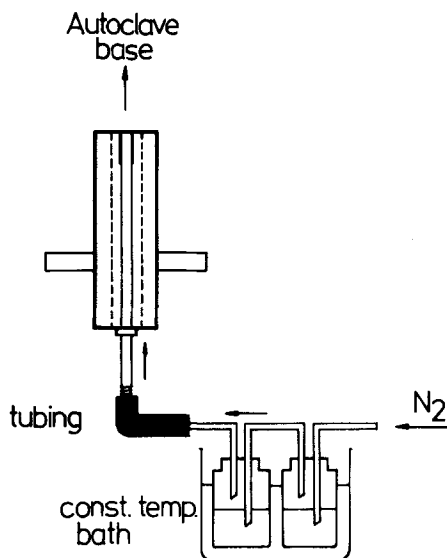


FIG. 2. Device used for introducing water vapor into the autoclave.

orthophosphoric acid (300 ppm) as stabilizer. The PET formed was then hydrolyzed in the melt phase at  $290^{\circ}\text{C}$ , using various water vapor pressures. The water vapor was introduced into the autoclave by attaching the device shown in Fig. 2 to the base of the autoclave.

Throughout this study the flow rate of nitrogen was maintained at 5 L/min. The hydrolyzed polymer was sampled at various stages of the reaction, and samples were then analyzed for intrinsic viscosity and endgroup concentration values. The intrinsic viscosity (I.V.) of the polymer was measured using a phenol/tetrachloroethane (1:1 w/w) mixture as solvent at  $20^{\circ}\text{C}$  in a capillary viscometer. The carboxyl and hydroxyl endgroup concentrations were determined using the infrared spectroscopic method reported by Alderman and Zichy [1]. A Perkin-Elmer model 521 grating infrared spectrophotometer was employed.

## RESULTS AND DISCUSSION

The rates of hydrolysis, oxidation, and thermal degradation of poly(ethylene terephthalate) in the solid phase were studied by McMahon et al. [2] as a function of temperature, relative humidity, and film thickness. They found that the rate of hydrolysis was very much faster than the rates of the other two reactions.

Poly(ethylene terephthalate) is fundamentally an ester, hence water

can react with it, hydrolyzing the ester links in the polymer chain. Various authors [3-5] have stated that this polymer is qualitatively resistant to hydrolysis in the solid phase, but no measurements of the rate of the reaction have been presented which would indicate the stability of the polyester when exposed to moisture in the melt phase. Some other workers [2, 6] have published the rate of hydrolysis of PET in the solid phase. However, no published detailed work has been traced on the hydrolysis of PET in the melt phase.

In this investigation the hydrolysis of stabilized PET in the melt at 290°C has been carried out. The hydrolytic reaction was followed by changes in the endgroup concentration and the fall in the viscosity of the polymer.

The results obtained from the experiments performed at various water vapor pressures (w.v.p.) (20, 92, 232, 468 mmHg) are presented in Figs. 3 and 4. Figure 3 represents the changes occurring in the I.V. of the polymer upon hydrolysis, and Fig. 4 illustrates how the total endgroup concentration of the hydrolyzed polymer varies with time. These figures show that the I.V. of the polyester falls upon hydrolysis and that the total endgroup concentration increases linearly with time. In general, this behavior is true for all values of w.v.p. used. However, the fall in the I.V. is very much sharper at the initial stages of hydrolysis, especially at higher w.v.p. The I.V. continues to fall until a limiting intrinsic value ( $[\eta]_1$ ) is reached.

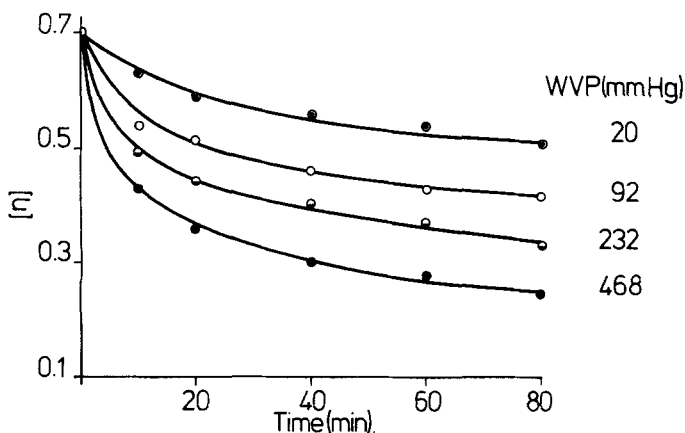


FIG. 3. Hydrolysis of PET in the melt using various water vapor pressures (w.v.p.) at 290°C.

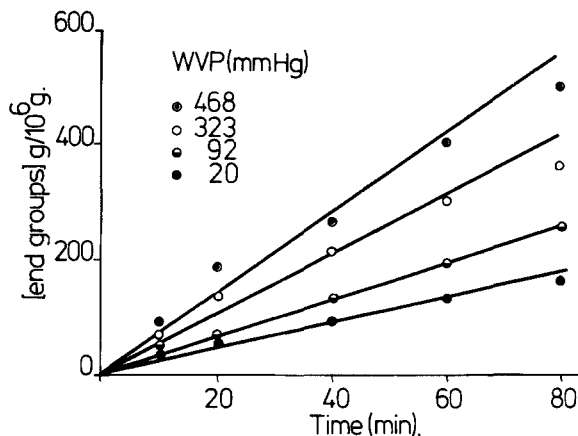


FIG. 4. Effect of water vapor pressure on the formation of end-groups during melt hydrolysis of PET at 290°C.

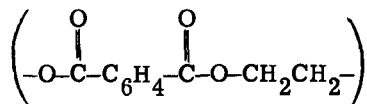
The number of unhydrolyzed ester linkages (C) were calculated from the I.V. of the polymer samples collected. The number-average molecular weights ( $\bar{M}_n$ ) were calculated from the I.V. values by using the following equation [7]:

$$[\eta] = 7.55 \times 10^{-4} \bar{M}_n^{0.685}$$

From the  $\bar{M}_n$  value of the "unhydrolyzed" polymer sample, the initial number of ester bonds (A) per mol of polymer was calculated:

$$A = (\bar{M}_n/192) - 1$$

where the molecular weight of the unit in PET



is 192.

This procedure was repeated for each sample of the hydrolyzed polymer. Assuming that the moles of ester linkages hydrolyzed per

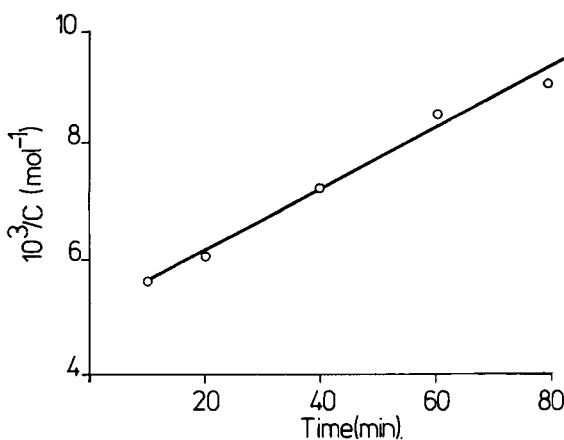


FIG. 5. Rate of hydrolysis of "nonstabilized" PET at 290°C using water vapor pressure of 20 mmHg.

mole of polymer =  $z$ , then the number of ester linkages remaining intact ( $C$ ) per mole of polymer is given by

$$C = A - z$$

Plots of  $1/C$  against time for each w.v.p. produced straight lines. A typical second-order graph at a w.v.p. of 20 mmHg is shown in Fig. 5. Similar plots at various other w.v.p. were obtained. The hydrolysis rate constant ( $K_h$ ) for each w.v.p. was determined from the slopes of these graphs.

$K_h$  increased linearly with w.v.p., as illustrated by Fig. 6. The value for  $K_h$  varies between  $2.5 \times 10^{-7}$  and  $2.9 \times 10^{-6} \text{ mol}^{-1} \text{ s}^{-1}$  for the lowest and the highest w.v.p., respectively. This magnitude of  $K_h$  is very similar to that obtained by Smith and Burn [8] who found a value of  $3.6 \times 10^{-6} \text{ mol}^{-1} \text{ s}^{-1}$  for the acid hydrolysis of aliphatic esters. Smith [9] has also reported a slightly higher values of  $K_h$  for aromatic esters. According to Chapman et al. [10], the rate coefficient for the acid hydrolysis of methyl benzoate is  $3.68 \times 10^{-6} \text{ mol}^{-1} \text{ s}^{-1}$  at 100.8°C.

McMahon et al. [2] studied the effect of relative humidity on the rate of hydrolysis of PET film and yarn of varying thickness at several temperatures. The highest  $K_h$  value ( $4.5 \times 10^{-8} \text{ mol}^{-1} \text{ s}^{-1}$ ) reported by these workers is for a 0.5-mil film at 100% humidity and 130°C. This figure is very much smaller than the lowest value ( $2.5 \times 10^{-7} \text{ mol}^{-1} \text{ s}^{-1}$ ) obtained from our work on the molten polyester.

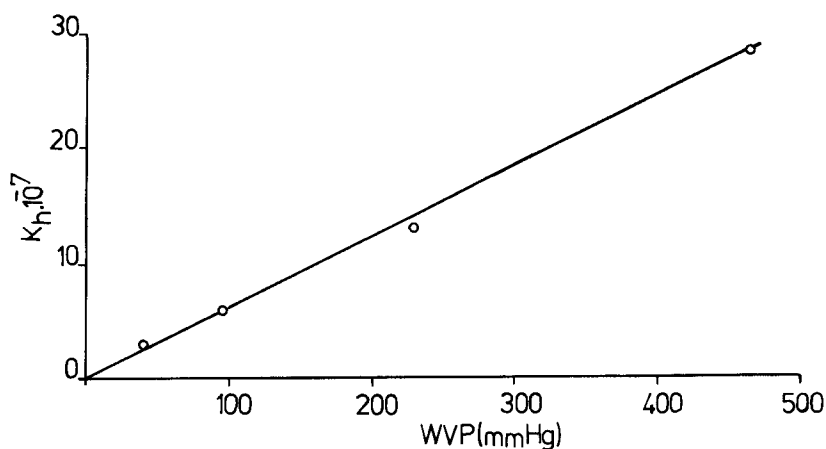


FIG. 6. Effect of water vapor pressure on the rate constant of hydrolysis of PET at 290°C.

The extent of polymer hydrolysis is related to changes in the number-average molecular weight as follows. A polymer chain  $n$  units long reacts with one molecule of water. This divides the chain into two sections with an average length of  $n/2$ . If this reacts with two molecules of water, it will divide into three chains having an average length of  $n/3$ . Thus, at the end of the hydrolysis reaction the length of the average molecular chain will be

$$\frac{n}{\text{number of water molecules reacted} + 1}$$

The molecular weight of the basic PET unit is 192. Hence the average molecular weight of the polymer before hydrolysis  $(\bar{M}_n)_0$  equals  $192n$ , and the average molecular weight after hydrolysis  $(\bar{M}_n)_t$  equals

$$\frac{192n}{\text{number of H}_2\text{O molecules reacted} + 1}$$

and

$$\frac{(\bar{M}_n)_0}{(\bar{M}_n)_t} = \frac{192n / (\text{moles H}_2\text{O} + 1)}{192n}$$



TABLE 1. Amount of Water Introduced into the PET Melt Using Various Water Vapor Pressures over a Period of 80 min (flow rate of  $N_2 = 5$  L/min)

Water vapor pressure, mmHg	Amount of $H_2O/80$ min	
	grams	moles
20	8.46	0.47
92	38.91	2.16
232	98.12	5.46
468	197.90	10.99

This means that the extent of hydrolysis is directly related to the amount of water introduced into the polymer melt.

Table 1 shows the total amount (moles) of water introduced into the polymer melt using each w.v.p. over a period of 80 min. Table 1 was drawn up using the following relationship:

$$\text{moles of } H_2 = \frac{\text{w.v.p.} \times 18 \times VN_2}{22.4 \times 760 \times 18}$$

where

$$VN_2 = \text{flow rate of nitrogen (5 L/min)}$$

The maximum amount of water (10.99 mol) introduced into the polymer melt was of a w.v.p. of 468 mmHg. The average total weight of the polymer in the autoclave was 1 500 g, and the calculated  $M_n$  value for the unhydrolyzed polymer was 21 000. From this information the initial amount of ester linkages (A) present in 0.0714 mol of PET was calculated to the 15.76 mol.

On the assumption that one molecule of water was involved for each ester linkage hydrolyzed, the complete hydrolysis of the polyester to the monomer was not possible in view of the above calculation, since only 10.99 mol of water was introduced into the autoclave containing 0.0714 moles PET (A = 15.76 mol).

Our results show (Figs. 3 and 7) that when water was introduced into the molten PET, the I.V. rapidly started to fall until it reached a limiting value. This limiting intrinsic viscosity  $([\eta])_1$  is very much dependent upon the w.v.p. used. Figure 7 shows that as the w.v.p. in

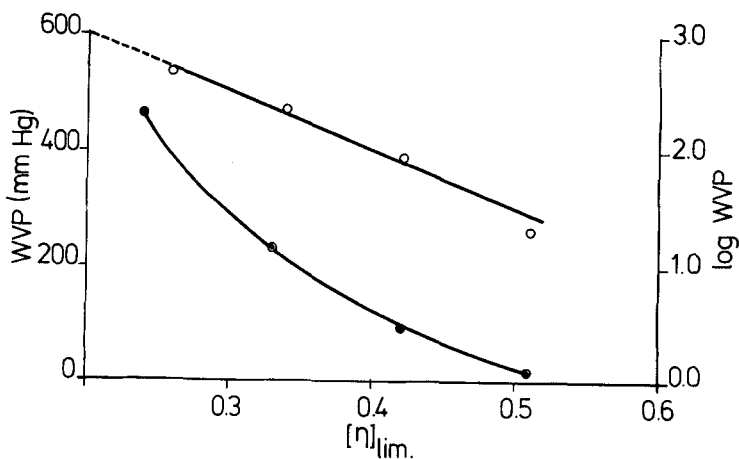


FIG. 7. Effect of water vapor pressure on limiting intrinsic viscosity of hydrolyzed PET.

the autoclave was increased, the value for  $[\eta]_1$  was lowered quite appreciably. A plot of log w.v.p. against  $[\eta]_1$  produced a straight line, as shown in Fig. 7.

#### EFFECT OF STABILIZER

The results discussed previously were for the melt hydrolysis of poly(ethylene terephthalate) which had been stabilized by the addition of 300 ppm orthophosphoric acid. In this section, hydrolysis of the polyester obtained in the absence of  $H_3PO_4$  is considered.

The polymer was hydrolyzed at  $290^\circ C$  and the water vapor introduced into the polymer melt was 20 mmHg. Figure 8 shows the effect of stabilizer addition on the extent of hydrolysis. Clearly the polymer which had been polymerized in the presence of  $H_3PO_4$  shows greater stability toward hydrolysis than the PET obtained in the absence of  $H_3PO_4$ . The fall in viscosity with time upon hydrolysis is sharper in the latter case.

The rate constant for the hydrolysis of "nonstabilized" PET, using a w.v.p. of 20 mmHg, was calculated from a plot of  $1/C$  against times. The value obtained in this case ( $7.6 \times 10^{-7} \text{ mol}^{-1} \text{ s}^{-1}$ ) was much higher than that determined for the hydrolysis of the stabilized PET ( $4.5 \times 10^{-7} \text{ mol}^{-1} \text{ s}^{-1}$ ), using the same w.v.p. (20 mmHg). It was observed that, on hydrolysis, the limiting intrinsic viscosity was

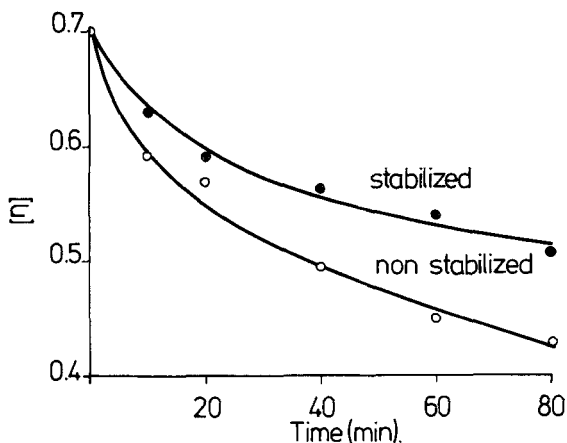


FIG. 8. Effect of stabilization on the hydrolysis of PET at 290°C and water vapor pressure of 20 mmHg.

lowered from 0.508 for the stabilized PET to 0.433 for the "nonstabilized" PET.

These results clearly show the importance of the addition of  $H_3PO_4$  during the production of commercial PET for fiber and film purposes. We have previously demonstrated [11] that  $H_3PO_4$  plays an important role in the stabilization of PET toward thermal degradation.

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