The Glycolysis of Poly(ethylene terephthalate)

JONG-WU CHEN, LEO-WANG CHEN

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan, Republic of China

ABSTRACT: The experiments were carried out in excess ethylene glycol (EG) and poly(ethylene terephthalate) (PET) oligomer in the presence of zinc acetate as catalyst at 190°C. It was found that during the glycolysis reaction, the monomer and dimer were contained in the liquid phase. After 2 h of the glycolysis reaction, an equilibrium state between the monomer and dimer was seen to approach. The equilibrium value of 0.51 between the monomer and dimer obtained at 190°C was in good agreement with previously published values. It was found that the catalyst concentration facilitated equilibrium and increased the glycolysis rate. A reduced amount of EG in the initial feed resulted in a decrease in the glycolysis rate. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 35–40, 1999

Key words: ethylene glycol; poly(ethylene terephthalate); zinc acetate; glycolysis rate

INTRODUCTION

Poly(ethylene terephthalate), PET, is a thermoplastic polyester widely used in the manufacture of high-strength fibers, photographic films, and soft-drink bottles. In 1987, the volume of PET consumed in the beverage industry alone was more than 700 million pounds, corresponding to more than three billion bottles.[1]

To ease the burden of waste disposal, it is critical that PET polymer be recycled. One method of recycling PET has been the depolymerization of the polymer into the monomer and higher oligomers. This can be accomplished by glycolysis with excess amounts of glycols such as ethylene glycol (EG), propylene glycol, and diethylene glycol. The resulting oligomer diols can be used in polyurethane formations or reacted further to make unsaturated polyester resins.[2–9]

PET is commonly synthesized either by reacting terephthalic acid (TPA) and EG, or dimethyl terephthalate (DMT) and EG. Both polymerization schemes first form the monomer, bis(hydroxyethyl)terephthalate (BHET). After adding stabilizer and additives, the prepolymer is polymerized through polycondensation by releasing EG:

$$n \text{ BHET} \leftrightarrow \text{PET}_n + (n-1)\text{EG}$$

Vaidya and Nadkarni reported the preparation of unsaturated polymer through the glycolysis of the products of PET waste by propylene glycol in the presence of zinc acetate as a catalyst.[2,3] They showed that the glycolyzed products consisted mostly of a hydroxyl-terminated monomer, dimer, and trimer. Later on, they repeated the glycolysis study using EG,[4] their results showed that in excess EG, the glycolyzed products contained mostly monomer.

S. Baliga et al.[1] reported that PET recycled from soft-drink bottles was depolymerized by glycolysis in excess EG at 190°C in the presence of metal acetate catalysts. The glycolyzed products consisted mostly of a monomer and dimer. No other higher PET oligomers were detected, and an

equilibrium was established between monomers and dimers, with an equilibrium constant lying between 1.13 and 1.53 at 190°C.

In the present work, the experiments were carried out in excess EG with PET oligomer in the presence of zinc acetate as a catalyst at 190°C under a pressure of 1 atmosphere. To study the glycolysis reaction in more detail, samples were taken at the beginning of and during the two-phase stage (liquid and solid). The glycolysis rate of samples was examined by analyzing the hydroxyl number of samples. The effect of catalyst and EG amount in the initial feed on glycolysis rate was studied. Moreover, the equilibrium constant between the monomer and dimer and EG molecules was discussed.

EXPERIMENTAL

PET oligomers, with a number-average molecular weight ($\overline{M_n}$) range of 1750–1800 (measured by Gel Permeation Chromatography), were obtained from the Industrial Technology Research Institute, Taiwan.

In all the experiments, 50 g of PET oligomer flakes were added to 65 g of EG, such that the molar ratio of PET oligomer to EG was 1 : 4. The mixture, together with 0.25 g of zinc acetate catalyst (0.5% by weight of PET oligomer), was charged to a four-necked flask, which was fitted with stirrer, reflux condenser, nitrogen inlet, and thermometer. The reactor was heated in an oil bath and the temperature was brought up to 190°C in 40 min. The glycolysis reaction was allowed to proceed up to 10 h with small samples removed periodically.

A single run was also performed without a catalyst. It was found that even after 10 h, a considerable amount of PET oligomer flakes remained in the reactor and the system was still two-phase. By comparison, with the catalyst, the PET oligomer flakes disappeared after 2 h. This implies that the presence of zinc acetate as a catalyst is critical to facilitate the glycolysis of PET oligomers. This result is the same as the PET polymer depolymerization experiments in excess EG in the presence of zinc acetate as a catalyst, as described by S. Baliga.[1]

The sample was allowed to cool to room temperature under a nitrogen atmosphere. Water was used to dissolve any unreacted EG and catalyst. About 1 L of deionized water was added, and the solution was agitated vigorously, while most of the glycolyzed products precipitated out. After filtration, a small amount of dissolved PET oligomers was recovered.

Analysis

The hydroxyl values of reaction samples and the extracted glycolyzed products were analyzed. This method is briefly described as follows: 0.5 g of the sample was accurately weighed and added to 10 mL of acetylating solution, containing 88 : 12 (v/v) pyridine and acetic anhydride, in a round-bottomed flask.

The flask was fitted with a vertical reflux condenser and heated with stirring in a boiling water bath for about 2 h. The mixture was then cooled to room temperature and hydrolyzed by 100 mL of chilled water. Under vigorous stirring, 20 mL of benzene was added. The resulting solution was titrated against 0.1 N KOH standard using phenolphthalein as indicator.

RESULTS AND DISCUSSION

This research used PET oligomer, of a polymerization degree of between 9 to 10, to replace the PET polymer used by Baliga et al. The authors chose to conduct the experiment using PET oligomer derived from direct esterification without catalyst, so that variables like the presence of impurities, including the catalyst, could be minimized. In all the experiments, PET oligomer was glycolyzed in excess EG. The PET oligomer was cut into grains to maximize the surface area available for heat and mass transfer in the reactor.

Glycolysis Reaction

The system was two phases (solid and liquid) during the first 2 h of the glycolysis reaction. One sample was taken from the liquid phase at base time (the time at which the temperature of 190°C was reached). Further samples were taken from the liquid phase during the two-phase stage at 30, 60, and 90 min after base time. After 2 h, the reaction entered the homogenous (liquid) phase. During this stage, samples were removed every 2 h, that is, at 2, 4, 6, and 8 h after base time. A final sample was removed at 10 h, when the reaction was terminated. The samples removed were solid at room temperature. After removing EG from the samples with deionized water, the

Table I   The Hydroxyl Number (mq KOH/g) of Sample Obtained from the Liquid Phase

Reaction Time (min)	EG/PET Oligomer = 3	EG/PET Oligomer = 4
base	300	315
30	310	320
60	325	327
90	330	335

samples were titrated to analyze the hydroxyl values. Table I shows that the hydroxyl number of the samples increased with reaction time. Even at the base time of the reaction, the hydroxyl number of the sample obtained from the liquid phase was high and fell between that of the monomer and dimer. The hydroxyl number of the monomer and dimer is 441.5 and 251.3 mq KOH/g, respectively. It was confirmed using DSC and thin liquid chromatography (TLC) that no other PET oligomer higher than the dimer existed in the liquid phase.

Figure 1 displays the DSC scans of the samples after EG had been removed. The samples were taken from the liquid phase at base time and the first 90 min of the glycolysis reaction. The DSC scans of both samples consists of two endothermic peaks: the first peak is centered around 108°C, and can be reasonably associated with the melting point of the monomer (109–110°C). The second peak, centered at around 149°C, is quite

Figure 1   DSC scans of the sample removed from the liquid phase: (a) at the base time, and (b) at the first 90 min of the glycolysis reaction.

broad and, hence, not readily identifiable with the melting point of the dimer (170–174°C). However, the presence of only two peaks suggests that the liquid phase consists predominantly of the monomer and dimer. The fact that the peaks do not exactly correspond with the melting points of the momomer and dimer is explained by S. Baliga et al.[1] Baliga reports that the monomer and dimer may interact at elevated temperatures causing a shift forward in the second peak.

To further determine whether or not the sample removed from the liquid phase at base time and the first 90 min of the glycolysis reaction contained oligomers other than the dimer, EG was removed from the samples with deionized water, and the samples were analyzed by TLC. The sample solution was prepared by dissolving the sample in a solvent containing 4 : 1(v/v) acetone and hexane. It was found that only two points were shown on the TLC. Only one point was found when the monomer was removed from the sample. The method used to remove the monomer was reported by C. C. Lin et al.[10]

The results of DSC and TLC analysis can reasonably demonstrate that the monomer and dimer and no other higher oligomers were contained in the liquid phase. From the above, it can be supposed that during the glycolysis reaction, the PET oligomer (solid phase) was glycolyzed under the effect of zinc catalyst to produce the monomer and dimer. This monomer and dimer gradually dissolved in EG (liquid phase). The solid phase disappeared totally after 2 h, leaving only the monomer and dimer in the glycolyzed solution. Therefore, an equilibrium state between these two species was seen to approach after 2 h of the glycolysis reaction.

Equilibrium Value Between the Monomer and Dimer

The model proposed by S. Baliga et al.[1] was used to obtain the equilibrium value:

$$\text{PET} + (n_M + n_D - 1)\text{EG} \rightarrow$$
$$n_M \text{ Monomer} + n_D \text{ Dimer}   \text{(1)}$$

$$2 \text{ Monomer} \xrightarrow{K} \text{Dimer} + \text{EG}   \text{(2)}$$

where n is the number of mol, subscripts M and D stand for the monomer and dimer, respectively. From the mol balance, it can be shown that

Figure 2 The number of mol of the monomer increases with glycolysis time.

$$H_1(n_M M_M + n_D M_D) = n_M M_M H_M + n_D M_D H_D \quad (3)$$

$$m_{EG} H_{EG} + H_M M_M n_M + H_D M_D n_D = H_0 m_0 \quad (4)$$

$$\sigma = \frac{n_D}{n_M} = \frac{M_M(H_M - H_1)}{M_D(H_1 - H_D)} \quad (5)$$

$$n_M = \frac{n_{PET}}{2\sigma + 1} \quad (6)$$

$$n_D = \frac{n_{PET}\sigma}{2\sigma + 1} \quad (7)$$

$$K = \frac{n_D n_{EG}}{n_M^2} \quad (8)$$

where n_{PET} is the number of mol of PET repeating units = 0.26 mol; m_0 is the total mass of the reacting system; m_{EG} is the mass of free EG; H_0 is the hydroxyl number measured before EG removal; H_1 is the hydroxyl number measured after EG removal; and M is the molecular weight (monomer, 254; dimer, 446; EG, 62) and H_M, H_D, and H_{EG} are theoretical hydroxyl numbers of monomer (441.5), dimer (251.3), and EG (1809.7), respectively. The percentage of EG consumed is given by

$$\% \text{ EG consumed} = \left(1 - \frac{m_{EG}}{m_{EG}^0}\right) \times 100 \quad (9)$$

where $m_{EG}{}^0$ is the initial mass of EG used. The theoretically expected percentage of EG consumed is given by

Theoretical % EG consumed

$$= \left(n_M + n_D - \frac{n_{PET}}{n}\right) \frac{M_{EG}}{m_{EG}^0} \times 100 \quad (10)$$

where n is the average number of repeating units in the a PET molecule chain. In this study n = 9–10, for the PET oligomer.

The glycolysis reaction in excess EG in the presence of 0.5% zinc acetate as catalyst was studied. The relationship between the number of mol of the monomer and glycolysis time, and the relationship between the number of mol of the dimer and glycolysis time were obtained by using eqs. (5), (6), and (7), as shown in Figures 2 and 3. The number of mol of the monomer increased with glycolysis time, and the number of mol of the dimer decreased with glycolysis time. By extending the reaction time to 10 h, the authors wanted to ensure that the reaction attained a steady state, so that an equilibrium constant could be obtained. When the number of mol approached a steady value, there existed an equilibrium between the monomer and dimer. About 20.5% of the initial EG was consumed, which agrees satisfactorily with the theoretically expected value of 22.5% calculated using eqs. (9) and (10), as shown

Figure 3 The number of mol of the dimer decreases with glycolysis time.

Figure 4   Correlation of measured and theoretical EG consumed.

in Figure 4. Figure 5 shows that the equilibrium value was obtained using eq. (8). The equilibrium value of 0.51 at 190°C was different from the equilibrium constant of between 1.13 and 1.53 obtained by Baliga et al. The equilibrium constant of 0.51 derived by the authors was in good agreement with the result reported by Ravindranath et al.[11] and Kumar et al.[12]

Effect of Catalyst Concentration

S. Baliga et al.[1] found that, of the four metal acetate catalysts (lead, zinc, cobalt, and manga-

Figure 5   The value of $N_D N_{EG}/N_M{}^2$ decreases with reaction time and approach to the equilibrium value.

Figure 6   Effect of zinc acetate concentration on the glycolysis reaction.

nese) tested, zinc acetate was the best in the terms of the extent of depolymerization. Therefore, the effect of the concentration of zinc acetate catalyst on the glycolysis reaction was undertaken in this study. In Figure 6, the hydroxyl number increases with reaction time, and eventually approaches a steady value. The results in Figure 6 imply that the catalyst concentration facilitates the equilibrium between the monomer and dimer with EG. The catalyst concentration was also seen to increase the glycolysis rate.

Effect of EG in the Initial Feed

EG acts as both a reactant and a catalyst in the depolymerization of PET.[13] A kinetic model for the glycolytic depolymerization of PET melts was found to be first order in the EG concentration.[14] The amount of EG added in the initial feed was critical to the glycolysis reaction. The hydroxyl number of samples of EG/PET oligomer = 3 in the initial feed was smaller than that of EG/PET oligomer = 4 in the entire glycolysis reaction with the same amount of zinc acetate catalyst (0.5% by weight of PET oligomer) added. This is shown in Figure 7 and Table I. Therefore, a reduced amount of EG in the initial feed resulted in the decrease of glycolysis rate at 190°C under pressure of 1 atmosphere.

CONCLUSIONS

The experiments were carried out in excess EG with PET oligomer in the presence of zinc acetate

Figure 7 Effect of EG amount in the initial feed on the glycolysis reaction.

as the catalyst. The system was two phases during the 2 h of the glycolysis reaction at 190°C under a pressure of 1 atmosphere. It was found that during the glycolysis reaction, the monomer and dimer were contained in the liquid phase. When the solid phase disappeared, the system entered a homogeneous phase. The hydroxyl number of the sample increased with reaction time, eventually approaching a steady value. Therefore, an equilibrium state between the monomer and dimer was seen to approach after

2 h of the glycolysis reaction. The equilibrium value of 0.51 at 190°C was in good agreement with the previously published equilibrium values. A reduced amount of EG in the initial feed resulted in a decrease in the glycolysis rate. The catalyst concentration facilitated the approach of an equilibrium. The catalyst concentration was also seen to increase the glycolysis rate.

REFERENCES

1. Baliga, S.; Wong, W. T. J Polym Sci 1989, A27, 2071.
2. Vaidya, U. R.; Nadkarni, V. M. Ind Eng Chem Res 1987, 26, 194.
3. Vaidya, U. R.; Nadkarni, V. M. J Appl Polym Sci 1987, 34, 235.
4. Vaidya, U. R.; Nadkarni, V. M. J Appl Polym Sci 1988, 35, 775.
5. Vaidya, U. R.; Nadkarni, V. M. J Appl Polym Sci 1989, 38, 1179.
6. Stevenson, R. W.; Nettleton, H. R. J Appl Polym Sci A-1 1965, 6, 889.
7. Challa, G. Makromol Chem 1960, 38, 105.
8. Challa, G. Makromol Chem 1960, 38, 123.
9. Challa, G. Makromol Chem 1960, 38, 138.
10. Chen, J. Y.; Ou, C. F.; Hu, Y. C.; Lin, C. C. J Appl Polym Sci 1991, 42, 1501.
11. Ravindranath, K.; Mashelkar, R. A. J Appl Polym Sci 1981, 26, 3179.
12. Kumar, A.; Sharma, S. N.; Gupta, S. K. Polym Eng Sci 1984, 24, 1205.
13. Campanelli, J. R.; Kamal, M. R.; Cooper, D. G. J Appl Polym Sci 1994, 54, 1731.
14. Lin, C. C.; Baliga, S. J Appl Polym Sci 1986, 31, 2483.