

# Kinetics of Diethylene Glycol Formation from Bishydroxyethyl Terephthalate with Proton Catalyst in the Preparation of Poly(ethylene terephthalate)

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**ABSTRACT:** This research focused on the kinetics of diethylene glycol (DEG) formation from the bishydroxyethyl terephthalate (BHET) monomer with a proton catalyst. In this study, the effect of proton concentration and of reaction temperature on DEG formation are discussed. Also, the rate equation of DEG formation from the BHET monomer with a proton catalyst is described. It was found that, as far as kinetics is concerned, the reactivity of the hydroxyl end groups of BHET with protons is greater than that of ethylene glycol (EG) with protons in DEG formation. In addition, the activation energy of BHET with protons is much lower than that of BHET with itself, that is, as protons emerge during the process of PET synthesis from BHET, they catalyze DEG formation. This study provides additional kinetics data to that described in our studies previously published (*J Polym Sci Polym Chem Ed* 1998, 36,3073; 1998, 36, 3081). © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 75: 1221–1228, 2000

**Key words:** BHET; PET; DEG; protons; kinetics

## INTRODUCTION

The formation of diethylene glycol (DEG) is an important side reaction in the preparation of poly(ethylene terephthalate) (PET). The amount of DEG in PET molecules influences many important properties of the polymer; for instance, temperature, light stability, and melting point, which decreases by about 5°C for each percent increase in DEG concentration.<sup>1</sup>

The major raw materials for the production of PET are dimethyl terephthalate (DMT), terephthalic acid (TPA), and ethylene glycol (EG). During the early stages of PET manufacturing, most polyester manufacturers used DMT exclusively as the starting raw material, due to the difficulty in obtaining TPA at a high level of purity. However, the availability of higher-purity TPA and improvements in the reaction process

have made direct esterification using TPA the preferred process because of its higher reaction rate, reduced catalyst requirements, and the elimination of methanol as a by-product.

PET made by the direct esterification of TPA generally contains more DEG than does PET made by the transesterification of DMT.<sup>2</sup> In particular, the esterification stage is the period most critical to DEG formation during PET synthesis through direct esterification.<sup>3</sup> The more TPA added at the initial feed, the more DEG formed during the PET synthesis.<sup>4</sup> It is reasonable to suppose that this is because TPA releases protons, which catalyze the direct dehydration of two hydroxyl end groups to form DEG.<sup>5</sup> Therefore, it is critical to research DEG formation from the hydroxyl end groups of BHET with protons and EG with protons.

In a previous study, the authors considered the kinetics of EG with protons in the etherification reaction. It was found that the rate constant of EG with protons was significantly greater than that of pure EG with itself in the etherification

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reaction. Above all, the activation energy of EG with protons was found to be much lower than that of EG with itself.<sup>4</sup> Information concerning the kinetics of the BHET monomer with protons as model molecules in the etherification reaction, however, is scarce.

This work was based on studies used to compare the reactivity of BHET–OH functional groups and EG–OH functional groups with the proton catalyst in the DEG-formation reaction and the interpretation of experimental data to establish the rate expression of DEG formation with protons.

## EXPERIMENTAL

### Materials

Phenol and 1,1,2,2-tetrachloroethane were reagent grade and used for measurement of the viscosity; benzyl alcohol (internal standard), 1-propanol, DEG, and potassium hydroxide were reagent grade and used for the measurement of DEG. All these chemicals were used without further purification. *p*-Toluenesulfonic acid was reagent grade and used as a proton catalyst. The BHET oligomer with a number-average molecular weight ( $\bar{M}_n$ ) range of 1750–1800 (measured by GPC) was obtained from the Industrial Technology Research Institute, Hsinchu, Taiwan.

### Purification of BHET Monomer

Fixed amounts of the BHET oligomer, EG, and the zinc acetate catalyst were charged to a four-necked flask, which was fitted with a stirrer, reflux condenser, nitrogen inlet, and thermometer. The reactor was heated in an oil bath. The glycolysis reaction was allowed to proceed for 8 h at a temperature of 190°C. This process was reported by Baliga and Wong.<sup>6</sup> The product of the BHET oligomer glycolysis was vigorously agitated with water to dissolve unreacted EG and the catalyst, while most of the glycolyzed products were precipitated out. After filtration, distilled water was added and brought to the boiling point. The boiling solution was quickly filtered to separate the BHET oligomer ( $n > 1$ ) from the monomer. The mother liquid was cooled to 5°C and crystals of the BHET monomer were recovered by filtration. The monomer crystals were then vacuum-dried in an oven at 70°C for 24 h. The monomer obtained was melted at a temperature range of 109–110°C.

The method for purification of the BHET monomer was described in the literature.<sup>7</sup>

### Etherification of BHET with Proton Catalyst

#### *Apparatus for the Study of the Kinetics of BHET with Proton Catalyst in the Etherification Reaction*

A fixed amount of the BHET monomer and *p*-toluenesulfonic acid were charged to a four-necked flask, which was fitted with a reflux condenser and heated in an oil bath. Oxygen entry was prevented under nitrogen.

#### *Process*

The reaction was run at four different temperatures (120, 130, 140, and 150°C). A sample was removed at fixed intervals.

### Quantitative Analysis

#### *Determination of the Number-average Molecular Weight of BHET*

The number-average molecular weight of samples taken was not great. Furthermore, the samples could be dissolved in an acetylating solution; therefore, the number-average molecular weight of the samples was obtained by appropriate titration to analyze unreacted hydroxyl end groups. This method is briefly described as follows: A 0.5-g sample was weighed accurately and added to 10 mL of the acetylating solution, which contained 88:12 (v/v) pyridine and acetic anhydride, in a round-bottomed flask.

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

#### *Determination of DEG Content*

PET was depolymerized by saponification with potassium hydroxide in 1-propanol under reflux, following neutralization with hydrochloric acid in 1-propanol and removal of the precipitate. The liberated DEG was measured by gas chromatography (GC-FID). The method was referred to in the literature.<sup>8,9</sup> Benzyl alcohol was used as the internal standard. The GC column used was a Stabiwax-DA capillary column and analysis was

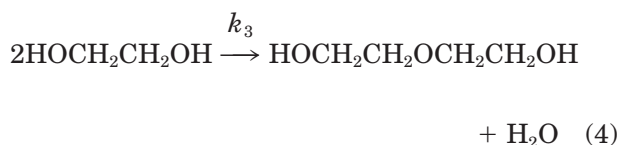
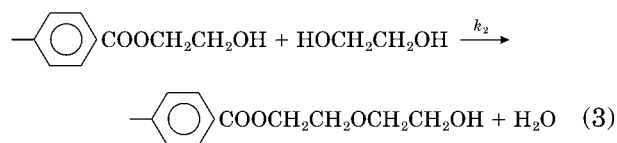
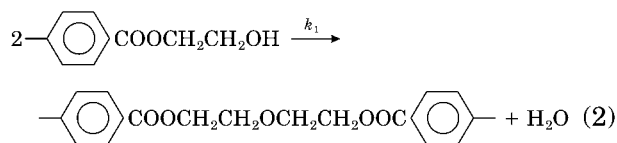
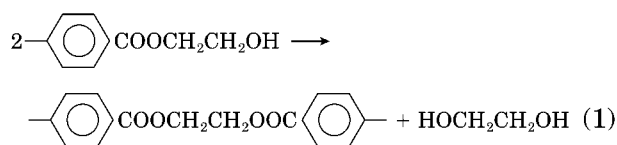
made at 140–200°C with 20 cc/min of nitrogen as the carrier gas.

### Determination of EG Content

EG was removed from the sample by vigorously stirring with water for 24 h. The method of removing EG was described by Baliga and Wong.<sup>6</sup> The time of 24 h was found to be appropriate. The water in which the EG was dissolved was removed to be analyzed by GC.

## RESULTS AND DISCUSSION

### Kinetics of Etherification of BHET Monomer with Proton Catalyst



The BHET monomer was charged to the reactor. Owing to the polymerization reaction, EG was produced, as shown in eq. (1). In eq. (2),  $k_1$  is the reaction rate constant of DEG formation from BHET on its own with protons. In eq. (3),  $k_2$  is the reaction rate constant of DEG formation from BHET with EG with protons. In eq. (4),  $k_3$  is the reaction rate constant of DEG formation from EG on its own with protons.

A small amount of water is produced during the etherification reaction. This was purged out immediately using nitrogen gas. However, it was

observed that only a minute amount of water was produced during the etherification reaction. This indicates that the concentration of water was negligible; therefore, the reverse reaction in eqs. (2)–(4) was also reasonably assumed to be negligible.

In this study, the reaction temperature was below 270°C; thus, DEG formation due to the degradation reaction was not considered and the contribution of the degradation reaction to the formation of ether links is less important.<sup>9</sup>

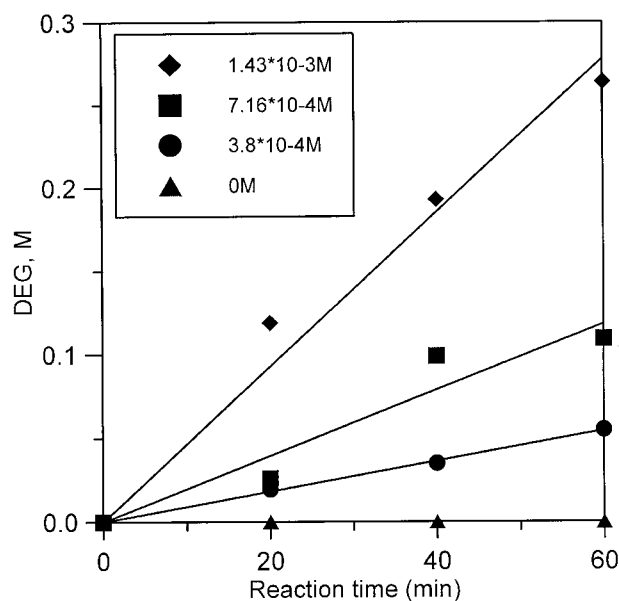
Therefore, the reaction rate equation is expressed as the following:

$$\frac{d[\text{DEG}]}{dt} = k_1[\text{BHET}]^2 + k_2[\text{BHET}][\text{EG}] + k_3[\text{EG}]^2 \quad (5)$$

where [EG] and [BHET] are the concentrations of EG and BHET ( $\text{---} \text{C}_6\text{H}_4 \text{---} \text{COOCH}_2\text{CH}_2\text{OH}$ ) respectively. They can be expressed as the following equations:

$$[\text{EG}] = \left( \frac{\text{EG wt \%}/M_{\text{EG}}}{100} \right) \times \rho \times 1000 \quad (6)$$

$$[\text{BHET}] = \left( \frac{\rho}{M_{\text{BHET}}} \right) \times 1000 \quad (7)$$



**Figure 1** Relationship between [DEG] and reaction time ( $t$ ) for various proton concentrations at the same temperature (150°C).

**Table I** Comparison of  $k_3[EG]_{\max}^2$  and  $(d[DEG])/dt$  for Various Proton Concentrations

$[H^+]$ in mol/L	$k_3^a$	$[EG]_{\max}$	$k_3[EG]_{\max}^2$	$\frac{d[DEG]}{dt}$
$1.43 \times 10^{-3}$	$1.63 \times 10^{-5}$	0.619	$6.3 \times 10^{-6}$	$4.60 \times 10^{-3}$
$7.16 \times 10^{-4}$	$8.17 \times 10^{-6}$	0.467	$1.8 \times 10^{-6}$	$1.97 \times 10^{-3}$
$3.80 \times 10^{-4}$	$4.33 \times 10^{-6}$	0.367	$5.8 \times 10^{-7}$	$9.10 \times 10^{-4}$

<sup>a</sup> [4].

The rate constant of  $k_3$  is expressed in the following equations:

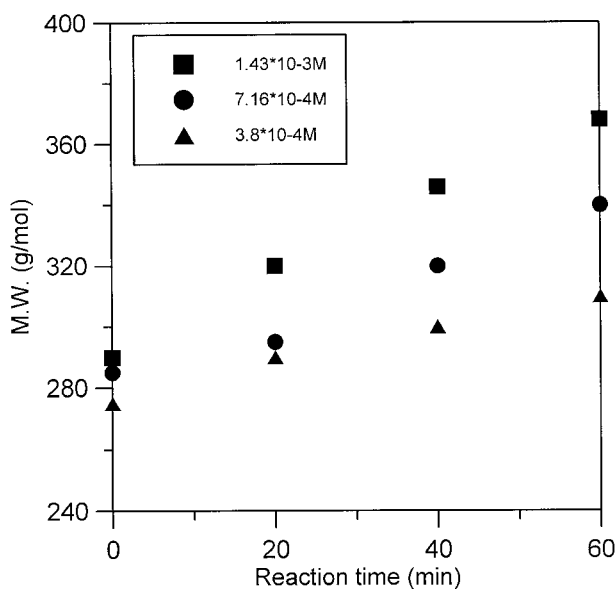
$$k_3' = 3.59 \times 10^{13} \times e^{(-125500/RT)} \quad (8)$$

$$k_3 = [H^+]k_3' \quad (9)$$

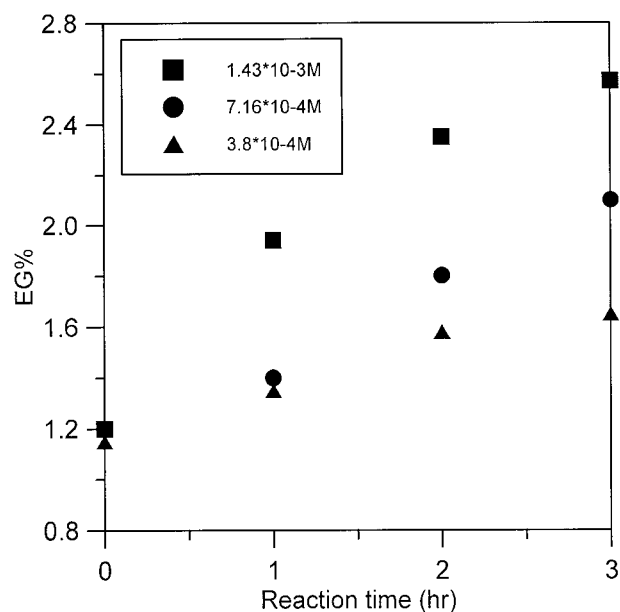
where  $[H^+]$  is the concentration of the protons. The process to derive the value of  $k_3$  was previously reported by Chen and Chen,<sup>4</sup> where EG wt % is defined as the weight percentage of EG contained in the sample;  $M_{EG}$ , as the molecular weight of EG;  $M_{BHET}$ , as the number-average molecular weight of BHET; and  $\rho$ , as the density of the sample. The volume of EG in the sample was assumed to be negligible because the EG content in the sample was small.

The term diethylene glycol (DEG) is generally applied to the dimer of glycol molecules. The ether bond structure ( $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$ ) also appears in the main chain of PET. This structure is also usually referred to as DEG. It is assumed that the reactivity of functional groups does not depend on the polymer chain length. DEG content in the final product is obtained through depolymerization of the sample. Hornof found that DEG is not likely to be removed immediately from the reaction time by distillation because of its rather high boiling point ( $245^\circ\text{C}$ ).<sup>10</sup> The volume of DEG in the sample was assumed to be negligible because the DEG content in the sample was small. The concentration of DEG is expressed as the following equation:

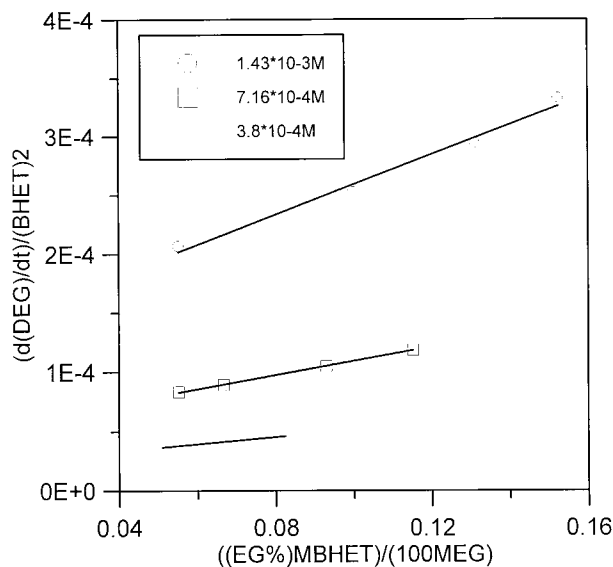
$$[\text{DEG}] = \frac{(\text{DEG wt \%})M_{\text{DEG}}}{100} \times \rho \times 1000 \quad (10)$$



**Figure 2** Relationship between number-average molecular weight of BHET and reaction time ( $t$ ) for various proton concentrations at the same temperature ( $150^\circ\text{C}$ ).



**Figure 3** Relationship between  $[\text{EG}]$  and reaction time ( $t$ ) for various proton concentrations at the same temperature ( $150^\circ\text{C}$ ).



**Figure 4** Plot according to eq. (12) for various proton concentrations with BHET at the same temperature (150°C). The slope gives  $k_2$  and the intercept gives  $k_1$ .

#### Effect of Proton Concentration

*p*-Toluenesulfonic acid is a strong acid and is used as a proton donor in the etherification reaction.<sup>11</sup>  $H^+$  ions are easily released by *p*-toluenesulfonic acid under the condition that a solution exists even with a minutely small amount of water and at a high temperature. Therefore, it can be assumed that protons were perfectly released from *p*-toluenesulfonic acid in this study.

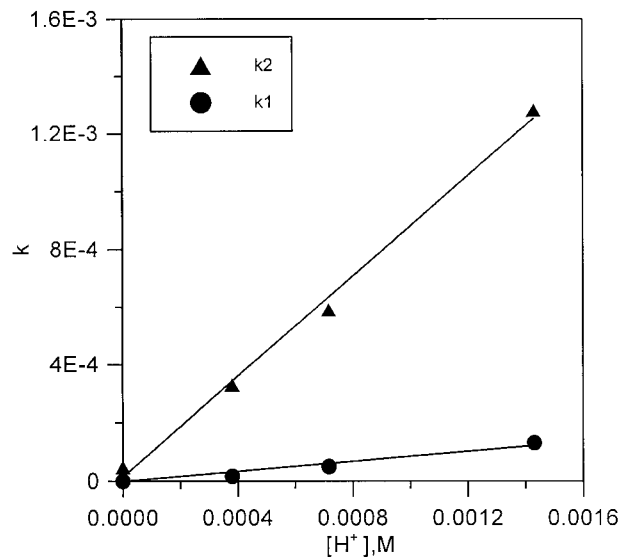
The kinetics of the BHET monomer with various concentrations of proton in the etherification reaction were considered at the same temperature (150°C). The relationship between the concentration of DEG with the reaction time ( $t$ ) is shown in Figure 1. The values of [DEG] shown in Figure 1 represent the incremental amount of [DEG], that is, the total amount of [DEG] at a certain time minus the amount of [DEG] at the

**Table II** Effect of Proton Concentrations on the Reaction Rate Constants

$[H^+]$ in mol/L	$k_1$	$k_2$
$1.43 \times 10^{-3}$	$1.31 \times 10^{-4}$	$1.28 \times 10^{-3}$
$7.16 \times 10^{-4}$	$5.02 \times 10^{-5}$	$5.90 \times 10^{-4}$
$3.80 \times 10^{-4}$	$1.70 \times 10^{-5}$	$3.30 \times 10^{-4}$
0	$9.28 \times 10^{-7}$ <sup>a</sup>	$4.76 \times 10^{-5}$ <sup>b</sup>

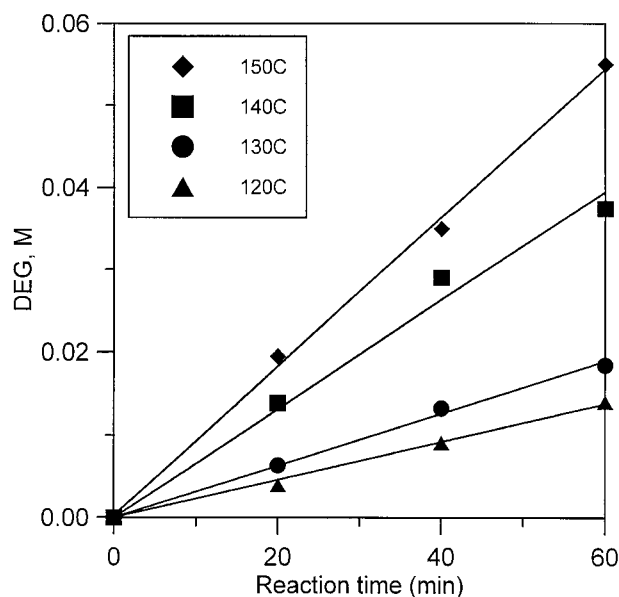
<sup>a</sup> [3].

<sup>b</sup> [2].



**Figure 5** Relationship between the reaction rate constants  $k_1$  and  $k_2$  and proton concentrations.

base time. In this study, during comparison of  $k_3[EG]^2$  with  $d[DEG]/dt$ , the value of  $k_3[EG]^2$  was considered negligible in eq. (5), as shown in Table I. The values of [EG] listed in Table I represent the amount of EG present in the reaction medium at the end of the reaction, that is, the maximum amount of EG in the reaction. Therefore, eq. (5) can be divided by  $[BHET]^2$  to derive eq. (11), which is expressed in the following equation:



**Figure 6** Relationship between [DEG] and reaction time ( $t$ ) for four different temperatures at the same proton concentration ( $3.8 \times 10^{-4}$  M).

**Table III Comparison of  $k_3[EG]_{\max}^2$  with  $(d[DEG])/dt$  for Four Different Temperatures**

Temperature (°C)	$k_3^a$	$[EG]_{\max}$	$k_3[EG]_{\max}^2$	$\frac{d[DEG]}{dt}$
150	$4.33 \times 10^{-6}$	0.367	$5.8 \times 10^{-7}$	$9.1 \times 10^{-4}$
140	$1.83 \times 10^{-6}$	0.312	$1.8 \times 10^{-7}$	$6.6 \times 10^{-4}$
130	$7.37 \times 10^{-7}$	0.267	$5.3 \times 10^{-8}$	$3.2 \times 10^{-4}$
120	$2.84 \times 10^{-7}$	0.223	$1.4 \times 10^{-8}$	$2.3 \times 10^{-4}$

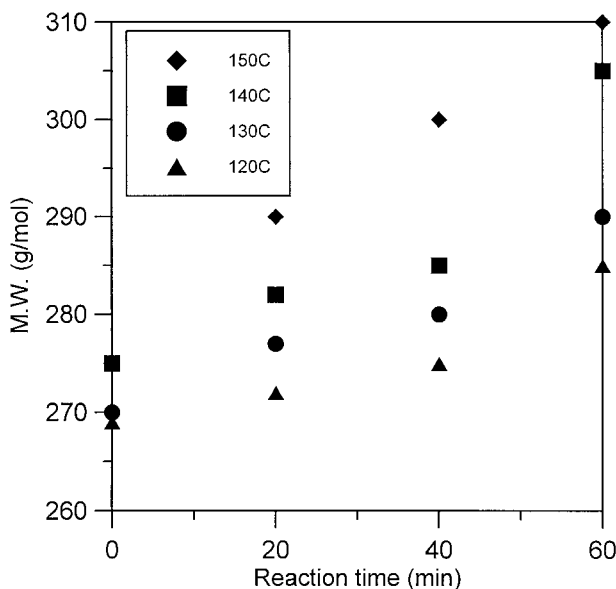
<sup>a</sup> [4].

$$\frac{\left(\frac{d[DEG]}{dt}\right)}{[BHET]^2} = k_1 + k_2 \left(\frac{[EG]}{[BHET]}\right) \quad (11)$$

By substituting eqs. (6) and (7), eq. (11) can be derived to reach eq. (12), as expressed in the following equation:

$$\frac{\left(\frac{d[DEG]}{dt}\right)}{[BHET]^2} = k_1 + k_2 \left(\frac{(\text{EG wt \%})M_{BHET}}{100M_{EG}}\right) \quad (12)$$

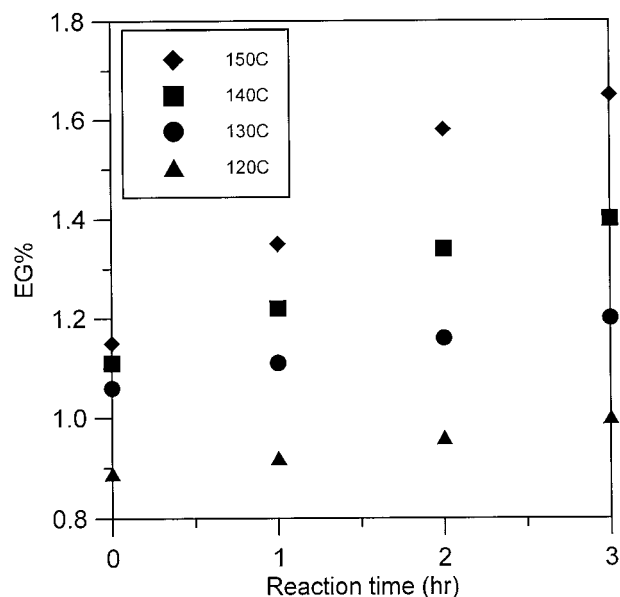
The value of  $M_{BHET}$  is derived through the measurement of hydroxyl end groups ( $-\text{OH}$ ) during sampling. Figure 2 shows the relationship between  $M_{BHET}$  and the reaction time ( $t$ ) with var-



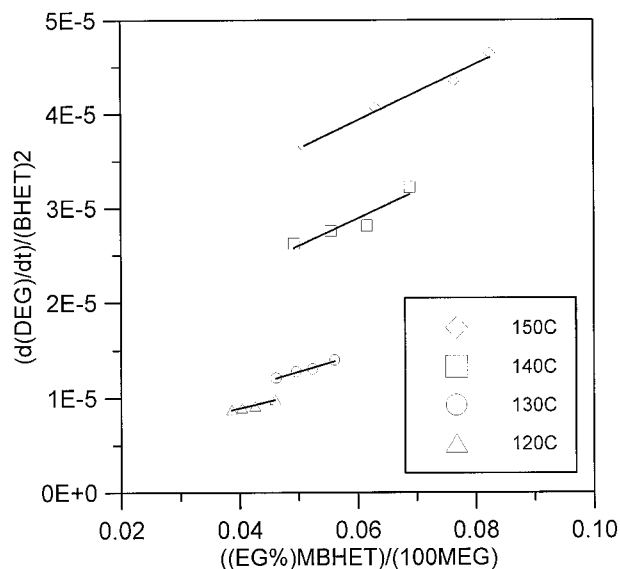
**Figure 7** Relationship between number-average molecular weight of BHET and reaction time ( $t$ ) for four different temperatures at the same proton concentration ( $3.8 \times 10^{-4} M$ ).

ious proton concentrations. The value of  $t$  at each interval was obtained using eq. (7). The relationship between the weight percentage of EG in the sample and  $t$  with various proton concentrations is shown in Figure 3. The plot indicated by eq. (12) is presented in Figure 4. The slope given in the diagram is  $k_2$  and the intercept given is  $k_1$ . Therefore, the reaction rate constants  $k_1$  and  $k_2$  could be obtained using eq. (12), as shown in Figure 4.

The relationship between proton concentrations and the values of  $k_2$  and  $k_1$  are listed in Table II and shown in Figure 5. It was found that the reaction rate constants increase linearly with the proton concentration, and both lines in the diagram are close to the original point. Therefore, the relationship between the reaction rate constant and the concentration of protons can be expressed as the following equations:



**Figure 8** Relationship between  $[EG]$  and reaction time ( $t$ ) for four different temperatures at the same proton concentration ( $3.8 \times 10^{-4} M$ ).



**Figure 9** Plot according to eq. (12) for four different temperatures at the same proton concentration ( $3.8 \times 10^{-4} M$ ). The slope gives  $k_2$  and the intercept gives  $k_1$ .

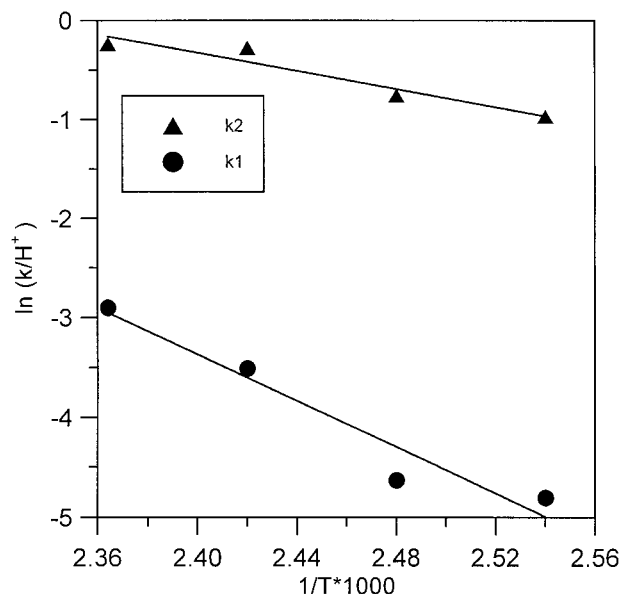
$$k_1 = [H^+]k'_1 \quad (13)$$

$$k_2 = [H^+]k'_2 \quad (14)$$

The concentration of protons is not included in the rate constants  $k'_1$  and  $k'_2$ .

### Effect of Temperature

The kinetics of the BHET monomer at four different temperatures (120, 130, 140, and 150°C) with the same proton concentration ( $3.8 \times 10^{-4} M$ ) in the etherification reaction were considered. The relationship between the concentration of DEG and the reaction time ( $t$ ) is shown in Figure 6. The values of [DEG] shown in Figure 6 represent the incremental amount of [DEG], that is, the total amount of [DEG] at a certain time minus the amount of [DEG] at the base time. During comparison of  $k_3[EG]^2$  with  $d[DEG]/dt$ , the value of  $k_3$



**Figure 10** Apparent activation energy of the reaction rate constant  $k'$  in the etherification reaction.

was considered negligible in eq. (5), as shown in Table III. Figure 7 shows the relationship between  $M_{\text{BHET}}$  and  $t$ . The relationship between the weight percentage of EG in the sample and  $t$  at four different temperatures is shown in Figure 8. Figure 9 shows the reaction rate constants  $k_1$  and  $k_2$ , which were obtained using eq. (12) at different temperatures and are listed in Table IV. According to the Arrhenius equation, the reaction rate constants could be used to derive the activation energy and preexponential factor:

$$\ln k' = \ln A - E/RT \quad (15)$$

$\ln k'$  is plotted against  $1/T$  (see Fig. 10). The slope evaluated from the diagram gives the activation energy of ether bond formation; therefore, the rate constants  $k'_1$  and  $k'_2$  are expressed as the following equations:

$$k'_1 = 4.4 \times 10^{10} \times e^{(-96,550/RT)} \quad (16)$$

**Table IV** Effect of Temperature on Reaction Rate Constants

Temperature (°C)	$k_1$	$k'_1$	$k_2$	$k'_2$
150	$2.10 \times 10^{-5}$	$5.5 \times 10^{-2}$	$3.00 \times 10^{-4}$	$7.9 \times 10^{-1}$
140	$1.14 \times 10^{-5}$	$3.0 \times 10^{-2}$	$2.90 \times 10^{-4}$	$7.6 \times 10^{-1}$
130	$3.73 \times 10^{-6}$	$9.8 \times 10^{-3}$	$1.80 \times 10^{-4}$	$4.7 \times 10^{-1}$
120	$3.13 \times 10^{-6}$	$8.2 \times 10^{-3}$	$1.45 \times 10^{-4}$	$3.8 \times 10^{-1}$

**Table V Comparison of the Reactivity of BHET-OH and EG-OH with the Addition of Proton Catalyst**

Temperatures (°C)	$k'_3$	$k'_1$	$k'_3/k'_1$
120	$6.5 \times 10^{-3}$	$7.6 \times 10^{-4}$	9
140	$2.7 \times 10^{-2}$	$4.8 \times 10^{-3}$	6
160	$9.9 \times 10^{-2}$	$2.6 \times 10^{-2}$	4
180	$3.2 \times 10^{-1}$	$1.2 \times 10^{-1}$	3
200	$9.6 \times 10^{-1}$	$4.8 \times 10^{-1}$	2

$$k'_2 = 4.2 \times 10^4 \times e^{(-38,000/RT)} \quad (17)$$

where  $R$  is the gas constant,  $8.314 \text{ Jmol}^{-1} \text{ K}^{-1}$ .

#### Comparison of the Reactivity of BHET-OH and EG-OH with Protons in DEG Formation

According to Table V, a comparison of the reactivity of BHET-OH with protons and EG-OH with protons reveals that the value of  $k'_1$  is greater than the value of  $k'_3$ , that is, the reactivity of BHET-OH with protons is greater than that of EG-OH with protons in DEG formation.

#### Comparison of the Activation Energy of BHET with Itself and that of BHET with Protons in DEG Formation

The rate constant of DEG formation from BHET with itself is expressed as the following equation:

$$k_{10} = 8.0 \times 10^{10} \times e^{(-137,140/RT)} \quad (18)$$

The process to derive the value of  $k_{10}$  was previously reported by Chen and Chen.<sup>3</sup>

A comparison of eq. (16) with eq. (18) reveals that the activation energy of BHET with protons is much lower than that of BHET with itself, that is, as protons emerge during the process of PET synthesis from BHET, they catalyze DEG formation.

## CONCLUSIONS

The kinetics of BHET with protons was considered. Therefore, the rate equation of DEG formation from BHET with protons was described in this study. The rate constant of DEG formation from BHET on its own with protons is

$$k_1 = 4.4 \times 10^{10} \times e^{(-96,550/RT)} \times [H^+]$$

The rate constant of DEG formation from BHET and EG with protons is

$$k_2 = 4.2 \times 10^4 \times e^{(-38,000/RT)} \times [H^+]$$

It was found that, in DEG formation, the reactivity of the hydroxyl end groups of BHET with protons is greater than that of EG with protons. In addition, the activation energy of BHET with protons is much lower than that of BHET with itself, that is, as protons emerge during the process of PET synthesis from BHET, the protons catalyze DEG formation.

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