Solubility and Esterification Kinetics of Terephthalic Acid in Ethylene Glycol III. The Effects of Functional Groups

K. S. YANG,[1,*] K. H. AN,[1] C. N. CHOI,[1] S. R. JIN,[1] and C. Y. KIM[2]

[1]Department of Textile Engineering, Chonnam National University, Yongbong-Dong 300, Puk-Ku, Kwangju 500-757, Korea; [2]Korea Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul, Korea

SYNOPSIS

Clear time (t_{cl}), the time required for the turbid mixture of terephthalic acid (TPA) and ethylene glycol (EG) to be clear, was measured to examine the effect of poly(ethylene terephthalate) (PET) prepolymer (DP of 1–5) on the kinetics of dissolution and/or esterification of TPA with EG. The t_{cl} of the mixture of TPA/EG (1 : 1.5 in molar ratio) was reduced to 1 : 2.2 or 1 : 3.5 by addition of 30 wt % of PET prepolymer or bis-(2-hydroxyl ethyl) terephthalate (BHET), respectively. Diethyl terephthalate (DET) as an additive was used as a model compound to examine the effects of the — OH group on the esterification reaction of TPA/EG. The t_{cl} value increased with addition of DET. The effect of the carbonyl group was also examined by determining esterification rates of benzoic acid (BA) with either ethylene glycol monobezoate (EGMB) as a compound with carbonyl group, or 2-penoxyethanol (2-PhE) as a compound without the carbonyl group. The reaction rate of BA with EGMB was much higher than that of BA with 2-PhE, which indicates that the carbonyl group gave an increasing effect of the esterification rate. Fourier transform infrared spectra showed that the — OH group in both BHET and EGMB formed intramolecular hydrogen bonding with the ester carbonyl group. On the basis of these observations, we concluded that the electron density of oxygen in the hydroxyl group increased through the formation of the intramolecular hydrogen bond. The increased electron density gave the — OH group easier access to the carbonyl carbon in BA, leading to an increase in the esterification rate. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a very important polymer, considering its global production of about 9 million tons in the year 1994. The end uses of the PET are on expansion, i.e., fiber, film, and bottle, etc. In consideration of the production size, an enhancement of productivity has been recognized as a primary goal in order to conserve costs.

PET has been synthesized from esterification of terephthalic acid (TPA) with ethylene glycol (EG) or from transesterification of dimethyl terephthalate with EG. The former process is more popular recently.

The synthesizing process of PET consists of esterification and polycondensation steps. PET prepolymer (DP of 1–5) is obtained from the esterification step and the prepolymer is processed for polycondensation at more severe conditions to obtain higher molecular weight, such as low pressure in the presence of a catalyst.

TPA is crystalline and sublimed at 300°C, showing low solubility in EG or bis-(2-hydroxy ethyl) terephthalate (BHET).[1] It has been recognized that the TPA in EG is consumed mainly by esterification reaction and minorly by dissolution. In the commercialized process, TPA/EG slurry is supplied into the reactor containing PET prepolymer synthesized from the previous cycle. It normally takes 5–6 h for the esterification and 2 h for the polycondensation. Without the PET prepolymer, it was found that the t_{cl} (clear time, the time required for the turbid TPA/EG mixture to clarify) for the turbid mixture of 50

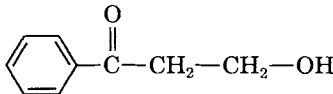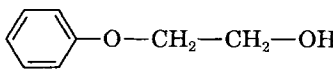mole % TPA/EG was 25 h at 230°C (near boiling point).[2]

It is well known that the rate-determining step in the esterification reaction is the accessibility of hydroxyl oxygen to the carbonyl carbon of the carboxylic acid. In attempting to shorten the long esterification time of the TPA/EG system, this work is focused on illuminating the factors that affect the rate-determining step by examining the role of the PET prepolymer in the esterification reaction. BHET was used as a model compound of the PET prepolymer and was compared with other compounds with different functional groups: diethyl terephthalate (DET), ethylene glycol monobenzoate (EGMB), and 2-penoxyethanol(2-PhE).

EXPERIMENTAL

Materials

TPA (Samsung Petroleum Chemical Co., Yochon, Korea; average size of 165 μm) and EG (Honam Ethylene Co., Yochon, Korea) used were fiber-forming grade. Moisture was removed from EG by boiling and condensing it at 110°C. Prior to use, the TPA was dried at 60°C under vacuum overnight. PET prepolymer (S. Co., Korea) synthesized from TPA and EG was ground to powder and a given amount was added to the reactor at the beginning of the reaction. The saponification value and the number average molecular weight of the PET prepolymer were received as 10.8 and 1,074, respectively. BHET (Nisso Co., Japan) was used without further purification. For the model reactions, DET and EGMB[3] were synthesized in the laboratory and 2-PhE (first grade, Aldrich Chemical Co., St. Louis, MO.) was used as received. The characteristics of EGMB and 2-PhE appear in Table I.

Table I Characteristics of EGMB and 2-PhE

Chemical Structure	Molecular Weight	Boiling Point (°C)
O‖ ⟨benzene⟩—C—CH$_2$—CH$_2$—OH EGMB	116	150
⟨benzene⟩—O—CH$_2$—CH$_2$—OH 2-PhE	138	245
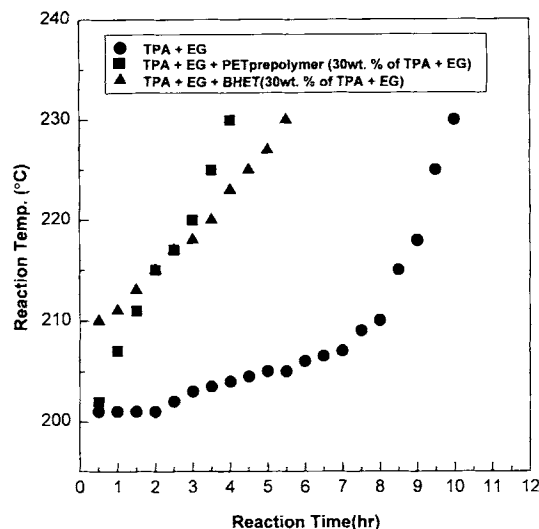
Figure 1 Temperature profile of the system with time of TPA/EG (1 : 1.5 in molar ratio) at 230°C.

Esterification

Esterification reaction between TPA and EG was performed in a four-necked round flask installed in a silicon oil bath with a temperature controller. The water formed from the reaction was removed by condensing the EG at 110°C. After preparing a slurry with a given molar ratio of TPA/EG in a reactor, DET or BHET was added; an isothermal reaction was then performed by stirring at 100 rpm and at the temperature set previously.

Esterification % (EV) was calculated from the acid value (AV) and saponification value (SV) using eq. (1).

$$EV\ (\%) = \frac{SV - AV}{SV} \times 100 \qquad (1)$$

The AV was determined by acid–base titration of the dissolved portion in the reaction mixture. The soluble portion was powdered and dissolved in dimethyl sulfoxide to be titillated with 1 : 10N NaOH methanol solution by using a pH meter (Fisher Accumet pH Meter, Model 805 MP, USA). The AV was calculated on the basis of eq. (2).

$$AV(\text{meq/g}) = \frac{f \times t}{10 \times w} \qquad (2)$$

where w is the weight of the sample in grams, t is mL of 0.1N NaOH used for titration, and f is the factor of 0.1N NaOH.

SV was determined by back titration of the excess KOH with HCl after saponification reaction of the

Table II   Clear Time Dependence of TPA/EG on Molar Ratio of TPA : EG, Additive, or Reaction Temperature

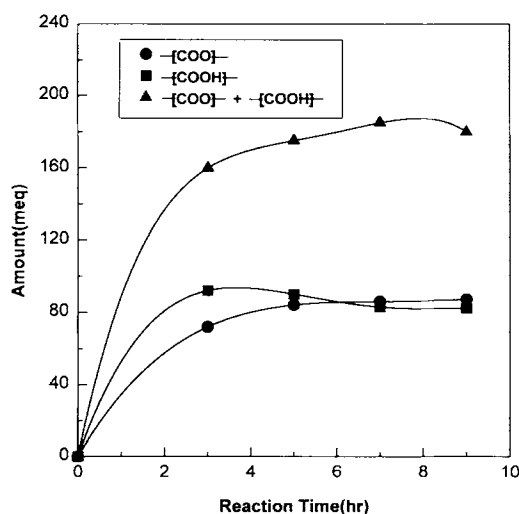| TPA : EG Molar Ratio	Reaction Temp. (°C)	Additive	Clearing Time (min)
1 : 3	210	None	610
		DET	675
		PET prepolymer	590
		BHET	495
1 : 1.5	230	None	1,500
		PET prepolymer	680
		BHET	430

esterified products. The titration was performed by saponifying the product in 0.5N KOH ethanol solution by boiling; adding distilled water; refluxing the mixture for 1 h; and back-titillating the remaining KOH by 0.5N HCl at room temperature. The SV was calculated by using eq. (3).

$$SV(\text{meq/g}) = \frac{f(B - t)}{2w} \qquad (3)$$

where f is the factor of 0.5N HCl, B is mL of 0.5N HCl consumed for blank test, t is mL of 0.5N HCl used in back titration, and w is the weight of the sample in grams.

Model Reaction

The model compounds for the esterification reactions used were EGMB or 2-PhE as an alcohol and benzoic acid (BA) as an acid. The model reactions were performed to estimate the reactivities of BA in an excess of EGMB or 2-PhE, stirring at 100 rpm. No phase separations were observed between BA and alcohols. The molar ratios of BA to EGMB or to 2-PhE were 1 : 13.5 or 1 : 27.0 for each compound, and temperatures chosen were 180, 190, 200, and 210°C. The conversion of BA was determined by back titration of the remaining BA with 1 : 20N KOH solution in tetrahydrofuran solvent at room temperature.

Measurement

The t_{cl} was determined by the observation of the time required for TPA particles to be consumed clearly at a given temperature.
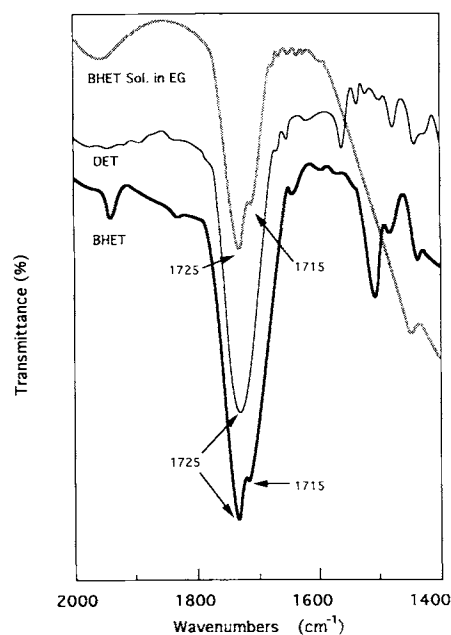

Figure 2   Dependence of contents of carboxylic acid and ester in soluble portion of the reaction mixture on reaction time; 182°C, TPA/EG = 1 : 10 in molar ratio.

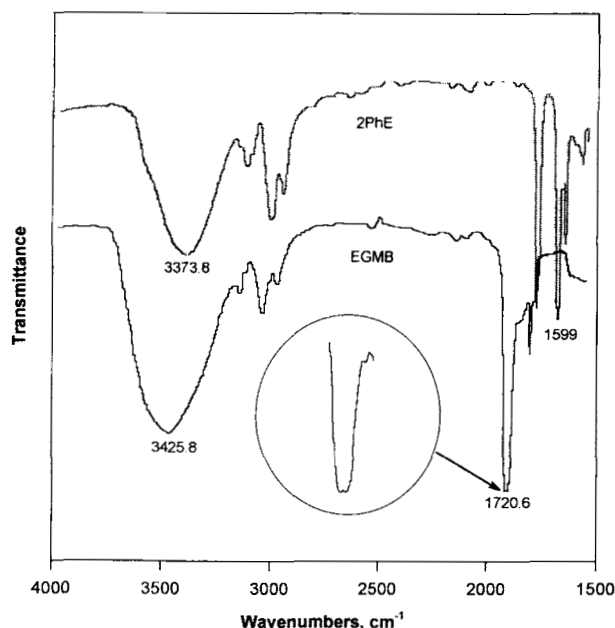**Figure 3**   FTIR spectra of DET, BHET, and 25 wt % BHET solution in EG.

Figure 4 FTIR spectra of EGMB and 2-PhE.

Synthesis of DET

Terephthaloil chloride and excess ethanol (1 : 5 in molar ratio) were reacted for 5 h at room temperature. The product was precipitated in distilled water and dried. The unreacted terephthaloil chloride and TPA in DET were removed by recrystallizing in acetone, and the acetone remaining in the DET was washed with distilled water 5–6 times, repeatedly. The DET produced was identified with characteristic infrared (IR) bands.

Analysis

Fourier transform infrared (FTIR) spectroscopies were obtained from liquid samples in a liquid cell or from the solid samples in a KBr pellet by using a Jasco A-202 IR spectrometer at room temperature.

RESULTS AND DISCUSSION

Effects of PET Prepolymer and BHET

The boiling-point variations with time could be traced with the temperature profile of the system, as in Figure 1. The temperature range was from 198°C (the boiling point of EG) to set temperature 230°C. The increasing rate of the temperature was in the order of TPA/EG with PET prepolymer, that with BHET and that without any additive. For the system without additive, it took 10 h to reach 230°C.
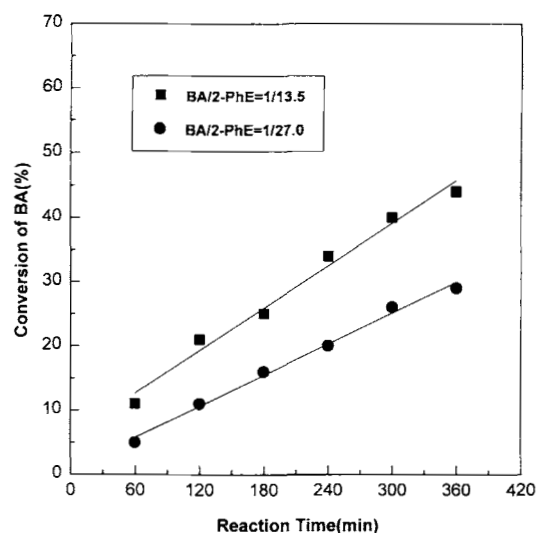

Figure 5 Conversion of BA in 2-PhE at 200°C.

At the lowest rate of the TPA/EG system, it is recognized that the boiling point of the system increased at a low rate due to a slow increase in molecular weight. The boiling point of the system with an additive increased rapidly due to the rapid increase in molecular weight. The increasing rate of temperature of the TPA/EG/PET prepolymer system is higher than that of the TPA/EG/BHET system. In consideration of the higher molecular weight as well as the higher dissolution temperature of PET prepolymer than BHET, the dissolution of the PET prepolymer itself contributed higher rate of temperature increase.
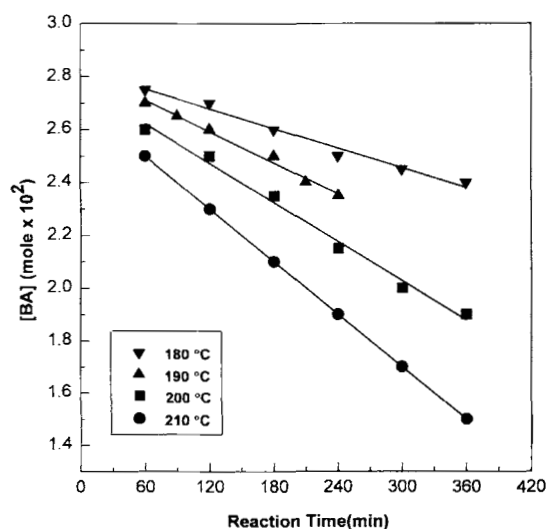

Figure 6 [BA] versus reaction time in 2-PhE (1 : 27 in molar ratio).

Table III   Comparisons of Kinetic Data of Esterification of BA in 2-PhE or in EGMB (1 : 27 in Molar Ratio)

		BA/2-PeE	BA/EGMB
Rate Const.	180°C	1.30×10^{-5} (M/L min)	3.44×10^{-2} (L/M min)
	190°C	1.83×10^{-5}	7.28×10^{-2}
	200°C	2.53×10^{-5}	14.69×10^{-2}
	210°C	3.23×10^{-5}	31.40×10^{-2}
Ea (kcal/M)		13.46	28.57
Reaction Order		0	2

The t_{cl} value as a measure of TPA consumption rate is tabulated in Table II. Regardless of reaction conditions, the t_{cl} was reduced by addition of PET prepolymer or BHET. The slurry TPA/EG (1 : 1.5 molar ratio) in the absence of an additive became clear in 1,500 min at 230°C. On the contrary, with 30 wt % of PET prepolymer or BHET, t_{cl} reduced to 1 : 2.2 and to 1 : 3.5 with respect to the control, respectively. These phenomena indicate that both the PET prepolymer and the BHET contributed to consumption of TPA in EG and BHET more predominantly.

The kinetics of esterification are shown in Figure 2. The [—COOH] concentration determined by acid value increases sharply and then decreases with reaction. The concentration of ester increases continuously, exceeding the acid concentration, eventually to flatten out. This behavior shows that some TPA was dissolved first and then esterified later. Otton and Ratton[4] reported that the solubilities of TPA in EG or in BHET are 1.338(—COOH) eq/kg and

0.386(—COOH) eq/kg at 230°C, respectively; the solubilities are trivial considering the total consumption of the TPA in the system. Thus the TPA consumption seems to be certainly accelerated by the esterification reaction in the following steps: TPA dissolution in EG in the early stage of the reaction, resulting in rapid AV increase; formation of PET prepolymer through esterification reaction; and further esterification reaction of TPA, mainly with the PET prepolymer and trivially with EG. This will be discussed further.

Effects of Functional Groups

The effects of the addition of PET prepolymer or BHET on t_{cl} are shown in Table II. The t_{cl} decreased with addition of BHET, but on the other hand, the t_{cl} increased with addition of DET. These results imply that the DET itself neither participated in nor contributed to TPA consumption.

The arrangements of functional groups in BHET in the reaction system could be enlightened
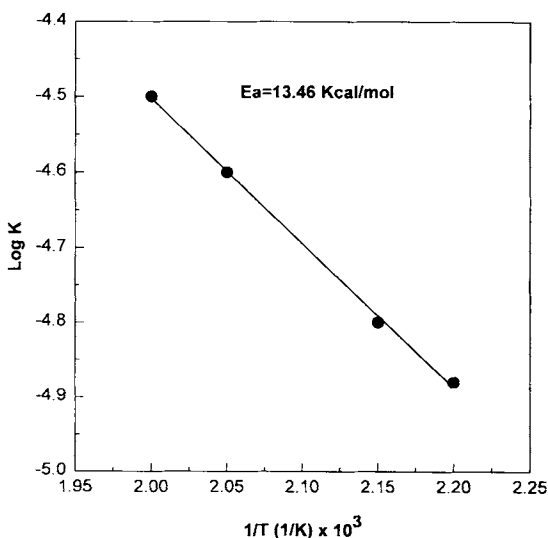
Figure 7   Arrhenius plot of the esterification of BA with 2-PhE (1 : 27 in molar ratio).
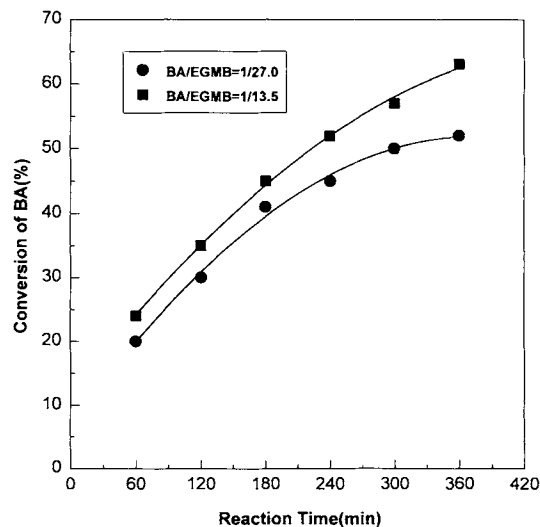
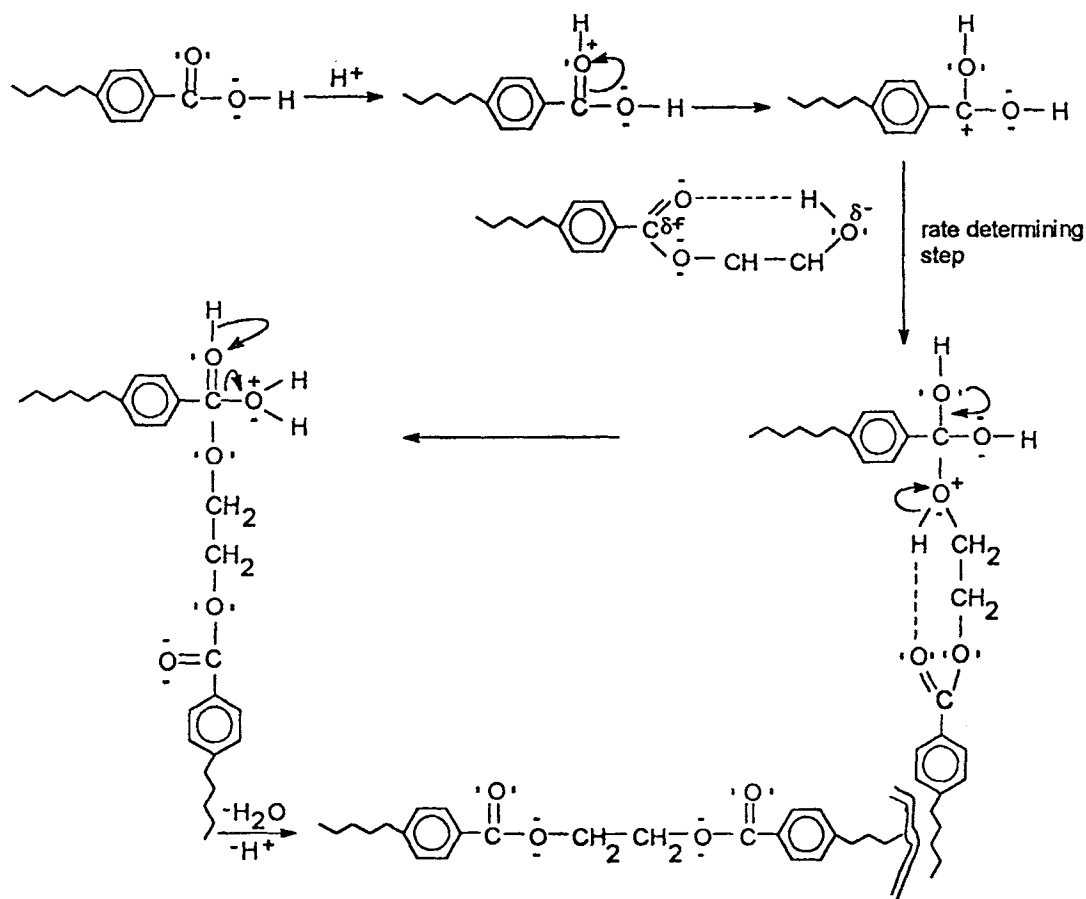**Figure 8**   Conversion of BA in EGMB at 200°C.

Figure 9 Reaction mechanism suggested between BHET and TPA dissolved.

from the FTIR spectra as shown in Figure 3. The band around 1725 cm^{-1} of DET designates the ester carbonyl group free from hydrogen bonding. There are two kinds of carbonyl groups in BHET and in BHET solution in EG, i.e., one at 1725 cm^{-1} represents the carbonyl group free from hydrogen bonding, the other at 1715 cm^{-1} would be the carbonyl group involved in intramolecular hydrogen bonding between the carbonyl oxygen and 2-hydroxyl group. For BHET/EG, the relative intensity of 1715 cm^{-1} to 1725 cm^{-1} reduced from the BHET alone, implying the inhibition of the formation of intramolecular hydrogen bonding by EG. This intramolecular hydrogen bonding in BHET crystal was reported by Miyake.[5] In this work, it was found that the intramolecular hydrogen bonding is formed not only in the crystalline state but also in BHET solution in EG, which resembles the actual esterification conditions of the TPA/EG/BHET system.

The model compounds chosen were EGMB or 2-PhE as an alcohol and BA as an acid. EGMB contains a carbonyl group but 2-PhE does not. The

characteristic IR bands represent: existing —OH group (3425 cm^{-1}) and carbonyl group (involved in intramolecular hydrogen boding, double peaks around 1720 cm^{-1}) in EGMB; and —OH group (3373 cm^{-1}) in 2-PhE (Fig. 4). The wave number shift from 3425 to 3373 cm^{-1} would indicate that the hydrogen bonds in 2-PhE are stronger than those in EGMB. On the other hand, the intramolecular hydrogen bonding is more predominant in EGMB than in 2-PhE. This can be rationalized by the fact that the boiling point of EGMB is lower than that of 2-PhE by 95°C, though the molecular weight of EGMB is higher than that of 2-PhE (Table I).

The functions of the carbonyl group were investigated through the esterification rate of the model compounds. Figure 5 shows that conversion of BA in 2-PhE has a linear relationship between conversion and reaction time with the similar slopes at both molar concentrations of 1 : 13.5 and 1 : 27 (BA/2-PhE). The reaction rate may be controlled by the slow rate of proton release from BA representing the 0th order of reaction. The BA conversion in-

creases with an increase in temperature (Fig. 6). Activation energy of BA/2-PhE (1 : 27) was determined as 13.46 kcal/mole (Table III) from the Arrhenius plot of the conversion rate of BA in 2-PhE at various temperatures (Fig. 7).

In comparison, Figure 8 shows BA conversion in EGMB with reaction time. The absolute value of BA conversion % in EGMB is significantly higher than that in 2-PhE and shows a decrease in slope with reaction time. The rate coefficient of the BA/EGMB system seems to be doubled with every 10 K increase, following the rule of thumb. Otton and Ratton[4] reported that EGMB has the —OH group which is more reactive toward the carboxylic group than the first —OH group of EG. From the linear relationship between 1/(BA) and reaction time, the reaction order of BA in EGMB was determined as second. From the Arrhenius plot, the activation energy was determined as 28.57 kcal/mole (Table III), i.e., the BA in EGMB is more temperature-dependent than that in 2-PhE.

On the basis of these discussions, the esterification mechanism of EGMB is suggested in Figure 9. In comparison with 2-PhE the intramolecular hydrogen bonding in BHET increased the electrical charge on oxygen in the —OH; consequently, the increased charge density accelerated the access of alcohol to the carbonyl carbon. This implies how the esterification rate can be increased by PET prepolymer in a TPA/EG slurry.

CONCLUSIONS

The t_{cl} of TPA was shortened by the addition of PET prepolymer or BHET and more significantly by that of BHET. The results were explained on the basis of model compound reactions between BA and 2-PhE or between BA and EGMB. An enhanced accessibility of the EGMB to BA would be possible with help of the formation of intramolecular hydrogen bonding in EGMB. The shorter t_{cl} of TPA/EG with BHET, compared with that of PET prepolymer, could be rationalized by the higher equivalent concentration of the hydroxyl group forming intramolecular hydrogen bonding in BHET than in PET prepolymer.

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