Polyester Polyols for Polyurethanes from PET Waste: Kinetics of Polycondensation*

U. R. VAIDYA and V. M. NADKARNI,[†] *Polymer Science and Engineering Group, Chemical Engineering Division, National Chemical Laboratory, Pune, 411 008, India*

Synopsis

The kinetics of polyesterification of the glycolyzed PET waste with adipic acid is reported. Glycolysis of PET waste was carried out with ethylene glycol at three different ratios of PET waste to glycol. The glycolyzed products could be readily polyesterified by reacting with adipic acid, to give polyester polyols with low acid number. Kinetics of polyesterification of the glycolyzed product made from 62.5% ethylene glycol (EG) and 37.5% waste were investigated further at different hydroxyl to carboxyl ratios. Reaction conditions were nonisothermal, comparable to the industrial process scheme consisting of two isothermal regions at 170° and 200°C. The kinetic results of the polyesterification of glycolyzed PET waste are compared to the polyesterification of pure diols, namely ethylene glycol and *bis*(hydroxyethyl) terephthalate (BHET) with adipic acid. The reactions follow second-order kinetics at 170°C and the rate of polyesterification of the mixed diol system from PET waste lies intermediate between those of the pure diols, namely, EG and BHET. Ethylene glycol exhibited the highest reactivity. At 200°C the kinetic plots of the mixed diols from PET waste were nonlinear, and thus the reaction may not follow second-order kinetics. The nonlinearity is explained in terms of the different reactivities of the different diol species in the reaction mixture. The polyester polyols, when cured with polymeric 4,4' diphenyl methane diisocyanates, gave polyurethane rigid foams and elastomers.

INTRODUCTION

Polyurethanes (PU) represent a versatile class of polymers used in a variety of applications as adhesives, coatings, rigid foams, flexible foams, and cast elastomers. Polyurethanes are prepared by reacting polyols with diisocyanates. The most commonly used polyols include polyester polyols and polyether polyols. Polyester polyols are used mainly for elastomers, rigid foams, adhesives, and sealants, whereas polyether polyols are largely used in flexible and semirigid foams, microcellular elastomers, and coatings. Polyethers are preferred over polyesters for their better hydrolytic resistance. However, polyesters are equally important, since they can be tailor made through proper selection of monomers. One can vary the molecular weight, level of branching, and the relative amounts of the rigid and flexible segments in the chain to generate a broad spectrum of properties.

Polyester polyols are prepared by the reaction of diacids with diols. The most commonly used diacids include adipic acid, succinic acid, sebacic acid, and phthalic anhydride. The aliphatic acids impart flexibility, whereas the

---

aromatic moieties improve rigidity. The commonly used glycols include ethylene glycol (EG), propylene glycol (PG), diethylene glycol (DEG), and 1,4-butanediol (BD). Usually small amounts of polyfunctional alcohols, having a functionality more than two, are added to obtain branching in the polyol structure for eventual network formation through crosslinking. These include glycerol, trimethylol propane, pentaerythritol, etc. Molecular weight can be controlled by varying the molar ratio of the alcohol to acid monomers. An excess of alcohol is always required to obtain hydroxyl termination. A controlled level of carboxyl end groups may be maintained for eventual foaming through carbon dioxide generation. The polyesterification reactions can be catalyzed by acid catalysts like p-toluene sulfonic acid, phosphoric acid, and so on.

Poly(ethylene terephthalate) [PET] is a thermoplastic used extensively in fibers, extruded films, blow-molded bottles, and injection-molded components. The various possibilities for utilization of PET waste include glycolysis by glycols such as EG, PG, and DEG.[1]

The glycolyzed products may be used in the synthesis of polyester polyols. The process is commercially important first because it converts a waste material into a value-added product, and second, it enables one to synthesize polyester polyols based on terephthalic acid (TPA) moiety with *para-para* linkages, circumventing the sublimation problems associated with the direct use of pure terephthalic acid in polyol synthesis.

As described in our earlier publication,[2] it is more relevant to carry out the kinetic investigations under nonisothermal conditions, encompassing two or three isothermal regions, normally employed on industrial-scale production.

In the present investigation, the PET waste was glycolyzed with EG at different weight ratios. The polyester polyols were prepared by reacting the oligomeric products of PET glycolysis with adipic acid at different ratios of hydroxyl to carboxyl groups. The kinetics of those reactions is compared with the kinetics of polyesterification of adipic acid with the pure monomers, namely, EG and *bis*(hydroxyethyl) terephthalate (BHET). The kinetic data were evaluated over two isothermal reaction regions at 170 and 200°C.

EXPERIMENTAL

Materials

Fiber-grade PET with a number-average molecular weight (M_n) range of 18,000–20,000 was obtained from M/s Century Enka, Pune, India, ethylene glycol (LR) was obtained from M/s S. D. Fine Chem. Pvt. Ltd. Boisar, India. Zinc acetate (LR) was obtained from M/s Glaxo, Bombay, India. Adipic acid (LR) was supplied by M/s High Purity Chemicals, Delhi, India, and p-toluene sulfonic acid was obtained from M/s Sisco Laboratories, Bombay, India.

Bis(hydroxy ethyl) terephthalate was isolated from the glycolyzed PET by hot water extraction followed by recrystallization. It was in the form of white crystalline solid (MP, 109°C) with 99% purity.

Glycolysis of PET Waste

The PET waste was depolymerized at different weight ratios of PET to EG, using 0.5% w/w zinc acetate, based on weight of PET, as catalyst. The details

of the glycolysis reaction procedure are described in earlier publications by the authors.[1,2] Thus, three oligomeric diols, coded GPET-4, -5, and -6, were prepared by glycolyzing PET waste with 37.5%, 50%, and 62.5% w/w of EG, respectively. The glycolyzed products were analyzed for hydroxyl value[3] and free glycol.[1] The glycolysed products were also analyzed by thin layer chromatography (TLC) using chloroform/ethanol solvent system as the mobile phase and silica gel as the stationary phase. Sample solutions were prepared in phenol/tetrachloroethane.[4,5]

Synthesis of Polyester Polyols

Since polyester polyols based on GPET-4 and -5 were in the form of a nonflowing paste at room temperature, only GPET-6 was used for preparation of polyols by reacting with adipic acid. Polyester polyols based on GPET-6 were free-flowing liquids at room temperature. The polyesterification reactions were carried out at three different ratios (r) of hydroxyl to carboxyl group concentrations.

Thus, three polyester polyols, UVAW-68, UVAW-69, and UVAW-71 were synthesized by reacting 68.2 g GPET-6 with 73 g adipic acid ($r = 1.3$), 78.7 g GPET-6 with 73 g adipic acid ($r = 1.5$), and 94.5 g GPET-6 with 73 g adipic acid ($r = 1.8$), respectively. Catalyst was 0.1 mol% of p-toluene sulfonic acid, based on the amount of diacid.

Polyesterification was carried out in a 500 mL round-bottom flask having a distillation condenser, a gas bubbler, a thermowell, and stirring assembly. The reactants were heated from room temperature to 100°C in about half an hour and then from 110°C to 170°C in one hour. The temperature was held at 170°C for 3 hours. It was then raised to 200°C in half an hour and held at 200°C till the end of the reaction. The water of reaction was removed continuously. The acid value was determined by titrating the solution of the sample in acetone, with standard alcoholic KOH.

The 'control' samples of polyester polyols were prepared by using pure monomeric diols, namely EG and BHET, at a hydroxyl to carboxyl group ratio equal to 1.5. Thus UVAB-74 and UVAE-77 were prepared by reacting 108.8 g of BHET with 41.7 g adipic acid and 58.2 g EG with 91.4 g adipic acid, respectively.
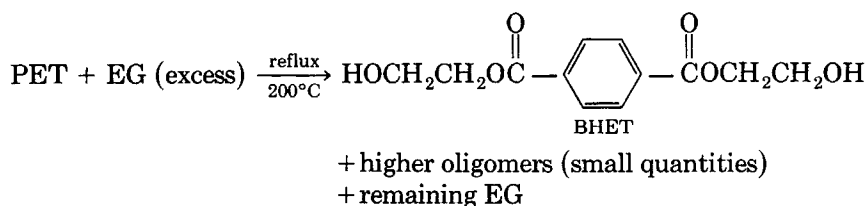
RESULTS AND DISCUSSION

Glycolysis

PET waste could be depolymerized by glycolyzing it with EG. The data on the hydroxyl values of the glycolyzed PET are summarized in Table I. The results indicate that the hydroxyl values of the oligomeric diols, after removal of free glycol, increases with the amount of EG taken for glycolysis. This means that the extent of depolymerization increases with the amount of glycol. It is consistent with the authors' earlier reported observations.[1] The hydroxyl values are comparable to that of bis(hydroxyethyl) terephthalate implying that the extent of depolymerization is quite significant. The TLC analysis showed one prominent spot and a couple of very faint spots. The prominent spot could be assigned to BHET which constitutes the major portion of the glycolyzed product. The other spots were probably due to

TABLE I
Characterization of Glycolyzed PET Waste

Sr. no.	Glycolyzed PET code	Ratio of PET to EG (w/w)	Analysis of glycolyzed PET		
			Amount of free glycol wt. %	Hydroxyl value before removal of free glycol mg KOH/g	Hydroxyl value after removal of free glycol mg KOH/g
1	GPET-4	62.5 : 37.5	32	610	374
2	GPET-5	50 : 50	45	870	402
3	GPET-6	37.5 : 62.5	58	1070	440

traces of higher oligomers as illustrated below

$$\text{PET + EG (excess)} \xrightarrow[200°C]{\text{reflux}} \text{HOCH}_2\text{CH}_2\text{O}\overset{\overset{\text{O}}{\|}}{\text{C}} - \langle\!\langle\bigcirc\rangle\!\rangle - \overset{\overset{\text{O}}{\|}}{\text{C}}\text{OCH}_2\text{CH}_2\text{OH}$$

BHET

+ higher oligomers (small quantities)
+ remaining EG

Polyesterification

The glycolyzed PET products could be polymerized with adipic acid to get polyester polyols over a broad range of viscosity varying from 2400 cps to nonflowing paste at room temperature. The polyols were found to be cured when reacted with polymeric 4,4′ diphenyl methane diisocyanate (PMDI). In the preliminary experiments it was observed that the polyesters made from GPET-4 and -5 were in the form of nonflowing pastes at room temperature which would make their subsequent processing difficult in terms of blending them with isocyanate and subsequent casting. Therefore, only GPET-6 which gave polyols with relatively low viscosities ranging between 2400 and 24,000 cps at 25°C, was used for the investigations.

As reported earlier[2] it is essential to keep the initial temperature below the boiling point of the glycol. Therefore, the temperature was initially kept at 170°C for 3 h and then raised to 200°C.

Polyesterification is a reversible reaction

$$\text{diacid + diol} \rightleftharpoons \text{polyester + water}$$
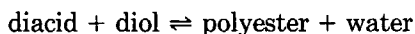
The water of condensation should be removed continuously in order to shift the equilibrium to the right-hand side of the equation. The rate of polyesterification may be defined as the rate at which the carboxyl concentration diminishes.

$$R = -\frac{d[\text{COOH}]}{dt}.$$

The polyesterification reactions are catalyzed by acids. In the absence of any external catalyst, the diacid itself acts as a catalyst and the rate equation may

be represented as

$$-\frac{d[\text{COOH}]}{dt} = k[\text{COOH}]^2[\text{OH}] \tag{1}$$

For stoichiometric proportions of the monomers, Eq. (1) becomes

$$-\frac{d[\text{COOH}]}{dt} = k\text{C}^3 \tag{2}$$

In terms of the extent of reaction p, Eq. (2) may be written as

$$\frac{1}{(1-p)^2} = 2\,\text{C}_o^2 kt + \text{constant} \tag{3}$$

where C_o is initial concentration of carboxyl groups and p is the fraction of carboxyl groups initially present, that have undergone the reaction, i.e.

$$p = \frac{\text{C}_o - \text{C}}{\text{C}_o} \tag{4}$$

Similarly for acid-catalyzed reactions, the equation can be written as

$$\frac{1}{1-p} = \text{C}_o\,kt + \text{constant} \tag{5}$$

For catalyzed reactions wherein the monomers are present in nonstoichiometric amounts, Eq. (5) does not hold good and is to be modified[6] as follows

$$\text{Ln}\frac{[B]}{[A]} = \text{Ln}\,r + [A]_o(r-1)kt \tag{6}$$

where r is the ratio of reactants and is always greater than one; thus $[B]$ is the concentration of the group which is in excess. In the present case, the diol was used in excess of the stoichiometric amount. Therefore,

$$\text{Ln}\frac{[\text{OH}]}{[\text{COOH}]} = \text{Ln}\frac{[\text{OH}]_o}{[\text{COOH}]_o} + [\text{COOH}]_o\left(\left(\frac{[\text{OH}]_o}{[\text{COOH}]_o}\right) - 1\right)kt \tag{7}$$

Thus for the reaction to be second order, the plot of

$$\text{Ln}\frac{[\text{OH}]}{[\text{COOH}]} \text{ versus time should be linear.}$$

Figure 1 shows the variation of the extent of reaction, p, with time. The extent of reaction is calculated using Eq. (4). The rate of reaction of PET-based
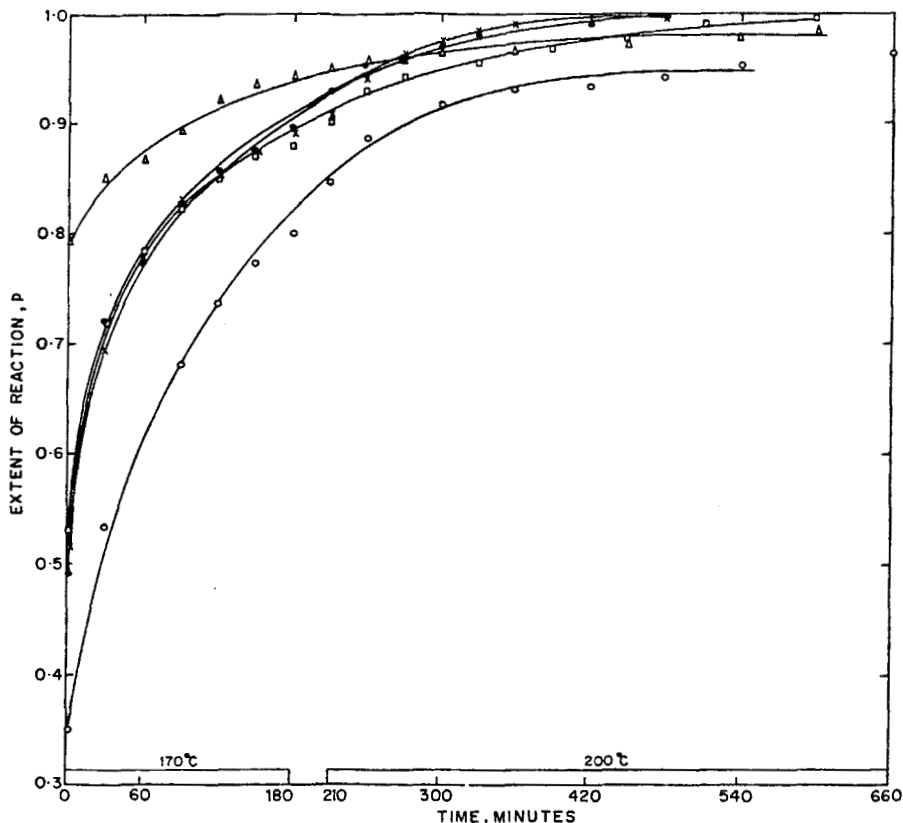
Fig. 1. Change in the extent of reaction with time. (□) UVAW-68; (×) UVAW-69; (●) UVAW-71; (△) UVAE-77; (○) UVAB-74.

systems are comparable. The reactivity of EG-based systems is the highest in the initial stages but drops down significantly in the later stages at 200°C. BHET-based systems exhibit the lowest reactivity throughout the course of reaction.

The kinetic data of polyesterification of UVAW-68, -69, and -71 were analyzed based on Eq. (7). The data are reported in Figure 2 in the form of plots of $Ln \dfrac{[OH]}{[COOH]}$ versus time. The plots are fairly linear at 170°C for all the three polyols, but at 200°C considerable deviations from linearity are observed. This could be attributed to the presence of a number of diol structures in the reaction system, with different reactivities towards adipic acid.

In order to confirm this hypothesis polyester polyols were prepared by reacting pure monomers, namely EG and BHET, with adipic acid at r equal to 1.5. For both the systems, coded UVAE-77 and UVAB-74, the plot of $Ln \dfrac{[OH]}{[COOH]}$ versus time was linear (Fig. 3) over both the isothermal regions. The reactivity of EG-based system was observed to be much more than the BHET-based systems. The difference in the reactivities of EG- and BHET-
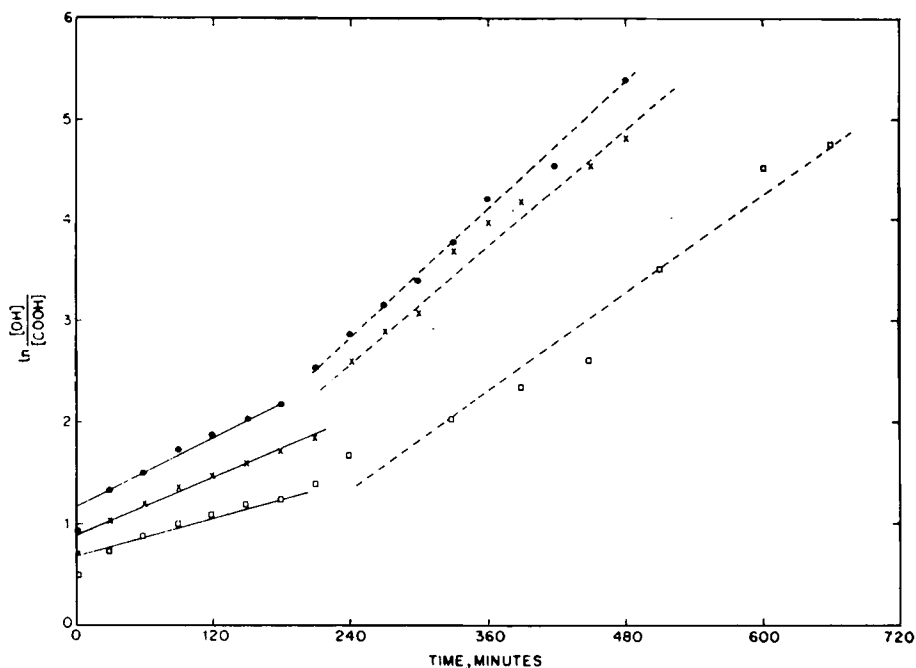
Fig. 2. Plot of Ln $\dfrac{[OH]}{[COOH]}$ versus time, for systems based on PET waste. Continuous and dotted lines represent data at 170°C and 200°C, respectively. (□) UVAW-68; (×) UVAW-69; (●) UVAW-71.
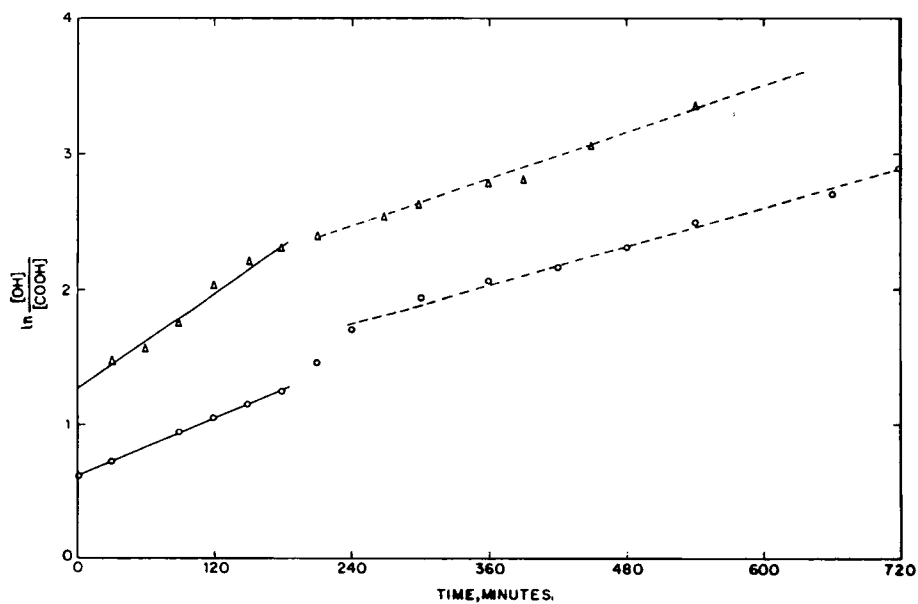

Fig. 3. Plot of Ln $\dfrac{[OH]}{[COOH]}$ versus time, for systems based on *bis*(hydroxy ethyl) terephthalate, and ethylene glycol. Continuous and dotted lines represent data at 170°C and 200°C, respectively. (▲) UVAE-77; (○) UVAB-74.

TABLE II
Determination of Rate Constants at 170°C and 200°C

Sr. no.	Polyester code	170°C			200°C		
		Extent of reaction p^a	[COOH] (eg/kg)	Rate constant, k (kg/eq min^{-1})	Extent of reaction p^b	[COOH] (eq/kg)	Rate constant, k (kg/eq min^{-1})
1	UVAW-68	0.5314	3.317	3.2×10^{-3}	0.9025	0.690	36.8×10^{-3}
2	UVAW-69	0.5182	3.174	2.9×10^{-3}	0.9058	0.620	34.8×10^{-3}
3	UVAW-71	0.4897	3.046	2.2×10^{-3}	0.9313	0.410	30.8×10^{-3}
4	UVAB-74	0.3833	2.340	3.0×10^{-3}	0.8464	0.583	8.0×10^{-3}
5	UVAE-77	0.7928	0.786	32.3×10^{-3}	0.9506	0.187	14.8×10^{-3}

[a] Extent of reaction when temperature reached 170°C.
[b] Extent of reaction when temperature reached 200°C.

based systems may explain the nonlinear kinetic behavior of the mixed systems based on PET waste at 200°C.

The plots of Ln $\dfrac{[OH]}{[COOH]}$ versus time at 170°C are fairly linear (Figs. 2 and 3) for the PET waste-based systems and also the polyols from EG and BHET. Therefore, the rate constants could be calculated from the slopes of the graphs. Table II presents the rate constants at 170°C. The initial concentrations of the reactants were calculated from the acid value of the reaction mixture when the temperature reached 170°C. Thus the starting point ($t = 0$) for kinetic analysis was assumed to be the time when the reaction mixture reached 170°C. Since each system had undergone different extents of reaction during the initial heating period up to 170°C (Fig. 1 and Table II), it is more logical to compare the rates of the reaction at equivalent extent of the reaction than to compare the rate constants. Referring to Figure 4 which depicts the variation of the rate of polymerization with the extent of reaction at 170°C for the five systems, it is apparent that the reactivity of the EG-based system is the highest and that of the BHET-based system is the lowest. The three PET waste-based systems have comparable reactivity and these exhibit kinetic behavior intermediate to the EG- and BHET-based systems. The difference in the reactivity of EG and BHET can be seen from the fact that the EG-based system had already undergone about 80% conversion whereas BHET-based system had undergone only 38% reaction, when the reaction mixture reached 170°C (Table II).

At 200°C the plots of Ln $\dfrac{[OH]}{[COOH]}$ versus time are linear for the EG- and BHET-based systems (Fig. 3). Therefore, the rate constants could be calculated from the slopes. However, for PET waste-based systems, large deviations from linearity were observed (Fig. 2). Therefore, it is difficult to calculate the precise values of rate constants. Table II shows the approximate values of rate constants of PET-based systems, calculated from the mean straight line as shown in Figure 2. These values of rate constants, can give an order of magnitude indication of the differences in the rate of polyesterification be-
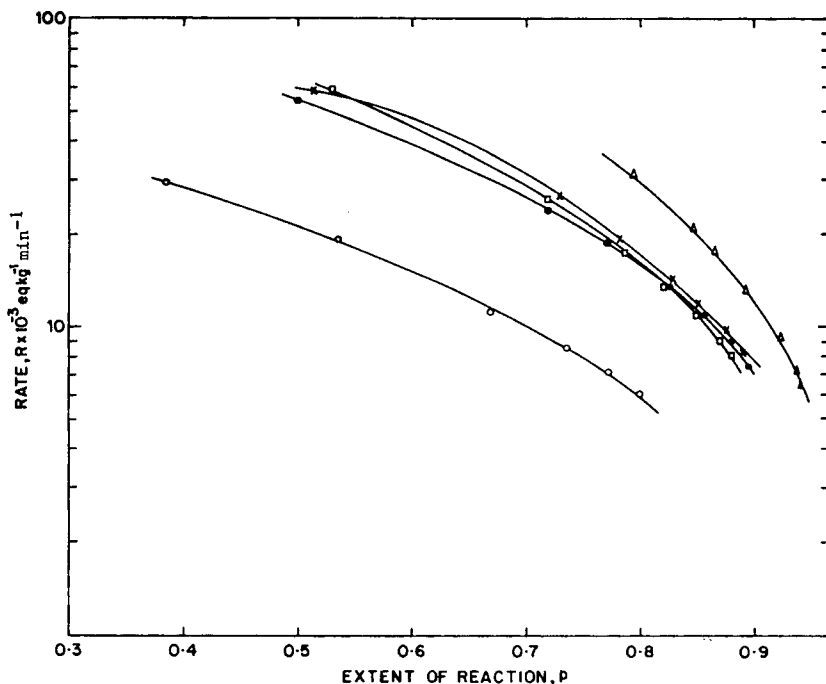
Fig. 4. Change in the rate of reaction with extent of reaction, at 170°C. (△) UVAE-77; (○) UVAB-74; (□) UVAW-68; (×) UVAW-69; (●) UVAW-71.

tween the pure diols and the mixed diol systems. The initial concentration was calculated from the acid value of reaction mixture when it reached 200°C.

It was observed that at 200°C, the PET waste-based systems are more reactive than the EG- and BHET-based systems (Fig. 5). The rates of PET-based systems are comparable.

The rates of reaction of EG- and BHET-based systems were lower at 200°C than at 170°C. This may be related to the difficulty in removal of reaction water from the reaction mixture in case of the BHET-based polyol and to the loss of EG at high temperatures in the case of the EG-based polyol. It is known that, in the later stages of the polyesterification reaction, the efficiency of removal of the reaction water and the amount of free diol influence the course of the reaction.[7] The viscosity of the pure BHET-based system was found to be very high even at the elevated reaction temperatures (Table III), which could make the removal of reaction water through the bulk of the reaction mixture very difficult. In the case of the EG-based systems, though the polyol viscosity was not as high as the BHET-based system, the unreacted glycol started distilling at 200°C. Therefore, the stirring and nitrogen flow had to be reduced which might have adversely affected the removal of water from the reaction system. The viscosities of the PET waste-based polyols were lower than the EG- and BHET-based polyols. Among the PET-based systems the rate increased with the ratio r of the diol to the diacid amounts.

The PET waste-based polyols were cured with PMDI at different isocyanate to hydroxyl ratios to obtain cast elastomers, and rigid foams with
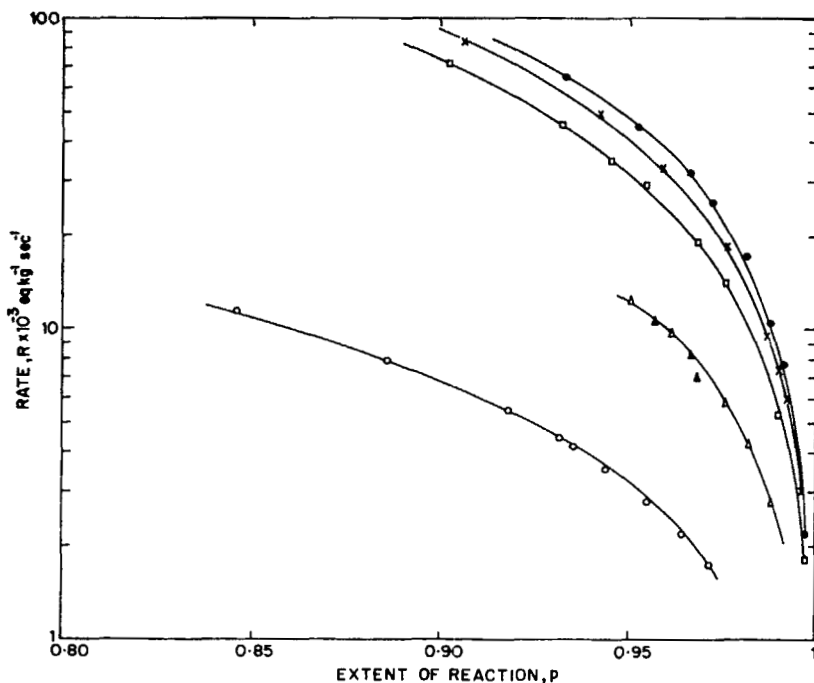
Fig. 5.   Change in the rate of reaction with extent of reaction, at 200°C. (△) UVAE-77; (○) UVAB-74; (□) UVAW-68; (×) UVAW-69; (●) UVAW-71.

TABLE III
Brookfield Viscosity of Polyester Polyols at 140°C

Sr. no.	Polyester code	Viscosity, cps
1	UVAW-68	73
2	UVAW-69	37
3	UVAW-71	19
4	UVAB-74	Nonflowing paste
5	UVAE-77	75

specific gravity varying between 0.25 and 0.6. The characterization and mechanical testing of these materials are in progress and will be reported in subsequent publications.

CONCLUSIONS

It is concluded that PET waste can be depolymerized by glycolysis with ethylene glycol. The extent of depolymerization increases with the amount of glycol taken for glycolysis. This observation is consistent with earlier investigations.[1,2] The oligomeric products of PET glycolysis can be readily esterified with adipic acid to get polyols with a range of molecular weight and viscosity. These polyols can be cured with polymeric 4,4'-diphenyl methane diisocyanate to give polyurethane products.

The polyesterification reactions follow second-order kinetics at 170°C as indicated by linear plots of $\text{Ln}\dfrac{[\text{OH}]}{[\text{COOH}]}$ versus time. The reactivities of the mixed diol systems based on glycolyzed PET waste lie intermediate to those exhibited in the polyesterification of pure monomers, namely, ethylene glycol and *bis*(hydroxyethyl) terephthalate. However, at 200°C, the kinetic plots of the mixed diol systems are considerably nonlinear. These deviations from linearity may be attributed to the difference in the reactivities of the different reacting diol species in the mixed systems.

The reactivities of the mixed systems were found to be higher than the systems based on pure EG and BHET at 200°C. This may be related to the difficulties in efficient removal of the water of reaction from the reaction mixture for the pure monomer-based polyesterification. The polyester polyols based on BHET exhibited very high viscosity even at high temperatures (nonflowing paste at 140°C), which would have an adverse effect on the removal of water. In the case of the EG-based polyester, at a high temperature of 200°C, the stirring and nitrogen flow had to be reduced to minimize the loss of glycol. A reduction in stirring and nitrogen flow would reduce the rate of water removal, thereby resulting in slower reaction rates.

Preliminary product development experiments have indicated that the polyols made from glycolyzed PET waste and adipic acid, when reacted with 4,4'-diphenyl methane diisocyanate, give PU elastomers and rigid PU foams. The details of product characterization will be reported in subsequent publications.

References

1. U. R. Vaidya and V. M. Nadkarni, *Ind. and Engg. Chem.-Res.*, **26**, 194–198 (1987).
2. U. R. Vaidya and V. M. Nadkarni, *J. Appl. Polym. Sci.*, **34**, 235–245 (1987).
3. J. Urbansky, W. Czerwinski, K. Janika, F. Majewska, and H. Zowall, *Handbook of Analysis of Synthetic Plastics*, Ellis Horwood Ltd., Chichester, 1977, Chap. 8.
4. S. Mori, S. Iwasaki, M. Furusawa, and T. Takeuchi, *J. Chromatogr.*, **62**, 109–113 (1971).
5. L. H. Peebles, M. W. Huffman, and C. T. Ablett, *J. Polym. Sci.*, Part A-1, **7**, 479–496 (1969).
6. G. Odian, *Principles of Polymerization*, John Wiley and Sons, New York, 1981, p. 88.
7. G. Odian, *Principles of Polymerization*, John Wiley and Sons, New York, 1981, p. 54.