

NOTE

*Polyester Polyols from Glycolized PET Waste: Effect of Glycol Type on Kinetics of Polyesterification**

INTRODUCTION

Polyurethanes (PU) are prepared by the reaction of polyhydroxy compounds (polyols) with isocyanates. The use of different types of polyols and isocyanates in the synthesis of polyurethanes is discussed by many authors.^{1,2} Polyester polyols represent a versatile class of PU building blocks. The structure of the polyol can be changed to get a broad spectrum of properties, by proper selection of monomers.

Poly(ethylene terephthalate), commonly known as PET, is extensively used for making synthetic fibers, films, injection-molded articles, and blow-molded containers. The PET waste can be depolymerized by glycolysis to obtain oligomeric diols. These oligomers can be further reacted with aliphatic diacids to form polyester polyols.³⁻⁶ The advantages of this route include the utilization of PET waste to generate value-added products and synthesis of polyester polyols having linear terephthalic acid moieties in the polymer backbone, which is otherwise difficult.

The effect of the amount of ethylene glycol on the extent of depolymerization and subsequent polyesterification is already reported by the authors in an earlier publication.⁶ The kinetics of the polyesterification of the glycolized PET with adipic acid at a different hydroxyl to carboxyl ratio is reported.⁶

The present article describes a comparative study on the glycolysis of PET waste using three types of glycol and the subsequent polyesterification of the glycolized waste with adipic acid. The PET waste was glycolized with ethylene glycol, propylene glycol, and diethylene glycol at a fixed weight ratio of PET to glycol. The oligomeric diols were then reacted with adipic acid at a fixed hydroxyl to carboxyl ratio, to obtain the polyester polyols. The kinetics of polyesterification of the three glycolized PET products with adipic acid under conditions comparable to commercial scale processing is reported. Conventionally the kinetic investigations are carried out under isothermal reaction conditions. However, in a commercial process, the reactants are generally heated gradually from room temperature to a cook temperature lower than the boiling point of the glycol. Then, at this temperature, the reaction is carried out to hook the glycol moieties for minimizing glycol loss. The temperature is subsequently raised to a higher value to accelerate the rate of the reaction. A similar heating cycle was employed in the present work and the kinetics was studied for the two isothermal plateaus in the heating cycle.

EXPERIMENTAL

Materials. Fiber grade PET waste, with number average molecular weight ranging between 18,000 and 20,000, was obtained from M/s Century Enka, Pune (India). Ethylene glycol (LR) was obtained from M/s SD Fine Chem. Pvt. Ltd., Boisar (India). Propylene glycol (LR) was supplied by M/s IDPL, Hyderabad (India). Diethylene glycol (LR) was obtained from M/s Sarabhai Chemicals, Bombay (India). Adipic acid (LR) was procured from M/s High Purity Chemicals, Delhi (India). Zinc acetate (LR) was procured from M/s Glaxo, Bombay (India). *Para*-toluene-sulfonic acid was supplied by M/s Sisco Laboratories, Bombay (India).

Glycolysis of PET Waste. The PET waste was depolymerized to get low molecular weight diols by refluxing it with 62.5% w/w, ethylene glycol (EG), propylene glycol (PG), and diethylene glycol (DEG). The depolymerization reaction was carried out in the presence of 0.5% w/w zinc acetate, based on the weight of PET, at the reflux temperature of the glycol for 8 h. Thus three oligomeric diols coded GPET-6, GPET-3, and GPET-9 were prepared by depolymerizing PET waste with ethylene glycol, propylene glycol, and diethylene glycol, respectively. The glycolized

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products were analyzed for the amount of free glycol, by the water extraction method⁷ and for the hydroxyl value by the acetylation method.⁸ The glycolized 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 solvent system.

Synthesis of Polyester Polyols. Polyester polyols were prepared by reacting the glycolized PET oligomers with adipic acid at a fixed hydroxyl to carboxyl ratio of 1.5. Thus, three polyester polyols coded UVAW-69, -81, and -82 were prepared by reacting 78.7 g of GPET-6 with 73 g of adipic acid, 90 g of GPET-3 with 73 g of adipic acid and 129 g of GPET-9 with 73 g of adipic acid. *p*-Toluene sulfonic acid, 0.1 mol%, based on the moles of the diacid, was used as catalyst.

The polyesterification reaction was carried out in a 500-mL round-bottom glass reactor having a stirring assembly, a thermowell, a gas bubbler, and a distillation condenser. The reactants were gradually heated from room temperature to 110°C in about 0.5 h and then from 110 to 170°C in 1 h. The reaction mixture was held at 170°C for 3 h, and subsequently heated to 200°C in about 0.5 h. The reaction was carried out at 200°C until the required acid value was attained. The water of reaction was removed continuously. The acid value was measured, every 0.5 h, throughout the course of the reaction. The acid value was determined by titrating solution of the sample in acetone, with standard alcoholic KOH. The acid value is defined as the mg KOH required to neutralize 1 g polymer sample.

RESULTS AND DISCUSSION

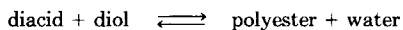
Glycolysis of PET Waste. PET waste could be glycolized by refluxing it with glycols like ethylene glycol (EG), propylene glycol (PG), and diethylene glycol (DEG). The characterization data on the glycolized products are reported in Table I. It is seen from the table that the amounts of free glycol in the three glycolized products are comparable (weight basis). However, there is a marked difference in the hydroxyl values. The hydroxyl value of GPET-6 is the highest and that of GPET-9 is the lowest. Table II gives the physical property data of the diesters of terephthalic acid with EG, PG, and DEG, namely bis(2-hydroxy ethyl)terephthalate, bis(hydroxypropyl)terephthalate and bis[2(2-hydroxyethoxy) ethyl]terephthalate. It is seen from Tables I and II that the hydroxyl value of GPET-6, after removal of the free glycol corresponds to that of bis(2-hydroxy ethyl)terephthalate (BHET). However, the hydroxyl values of GPET-3 and -9, after removal of the free glycol, are lower than those of the corresponding diesters. This shows that the extent of depolymerization is lower in GPET-3 and -9.

In the present work, the three glycols were used at the same weight percentage, based on the weight of PET waste. Thus the moles of the glycol per unit weight of PET differed in the glycolysis reaction. In our earlier investigation,⁶ it was shown that the extent of depolymerization is influenced by the moles of glycol taken for depolymerization (Table III). Therefore, the lower molar amounts of PG and DEG in the glycolysis reaction, relative to EG, may have decreased the extent of depolymerization in GPET-3 and -9.

As a result, the PET oligomers obtained by glycolysis with PG and DEG would exhibit higher molecular weight and a broader molecular weight distribution, when compared to the EG-glycolized product. The TLC analysis, shown in Figure 1, confirms this conclusion. The TLC of GPET-6 (EG-based product) shows only one prominent spot with a couple of very faint spots. The dark spot could be assigned to bis(2-hydroxy ethyl)terephthalate, whereas, in the case of GPET-3 and -9 more than three spots with considerable tailings were observed, indicating a broad molecular weight distribution.

Polyesterification. Polyesterification is a step growth reaction. The molecular weight of the polymer increases at a relatively slow rate. The reaction mixture, at any instance, consists of various sized diols, diacids, and hydroxy acid molecules. Any hydroxyl group can react with any carboxyl group. The kinetic study of such a system is greatly simplified if one assumes that the reactivity of the functional group of a bifunctional molecule remains the same, irrespective of the molecular size and whether or not the functional group at the other end has reacted. This assumption has theoretical and experimental justification.⁹

Polyesterification is a reversible reaction



In order to shift the equilibrium of the reaction towards the product side, water should be

TABLE I
Characterization Data on Glycolyzed PET

| Sample no. | Glycolyzed PET code | Glycol type | PET/Glycol (w/w) | (g mol glycol/100 g PET) | Analysis of glycolyzed products | | | Appearance after removal of free glycol |
|------------|---------------------|-------------|------------------|--------------------------|---------------------------------|---|--|---|
| | | | | | Free glycol (wt %) (approx.) | Hydroxyl value before removal of free glycol (mg KOH/g) | Hydroxyl value after removal of free glycol (mg KOH/g) | |
| 1 | GPET-6 | EG | 37.5/62.5 | 2.69 | 58 | 1070 | 440 | Crystalline |
| 2 | GPET-3 | PG | 37.5/62.5 | 2.16 | 60 | 933 | 326 | Semisolid |
| 3 | GPET-9 | DEG | 37.5/62.5 | 1.57 | 56 | 650 | 215 | Pasty |

NOTE

TABLE II
Physical Data of Diesters of Terephthalic Acid

| Diester type | Melting point (°C) | Hydroxyl value (mg KOH/g) | Molecular weight |
|---|--------------------|---------------------------|------------------|
| 1. Bis(2-hydroxy ethyl)terephthalate $\text{HO}-\text{H}_2\text{C}\cdot\text{H}_2\text{C}-\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{CH}_2\cdot\text{CH}_2-\text{OH}$ | 109 | 442 | 254 |
| 2. Bis(2-hydroxy propyl)terephthalate $\text{HO}-\underset{\text{CH}_3}{\text{HC}}\cdot\text{H}_2\text{C}-\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}-\text{CH}_2\cdot\underset{\text{CH}_3}{\text{CH}}-\text{OH}$ | 131 | 398 | 282 |
| 3. Bis(2(2-hydroxy ethoxy)ethyl)terephthalate $\text{HO}-\text{H}_2\text{C}\cdot\text{H}_2\text{C}\cdot\text{O}\cdot\text{H}_2\text{C}\cdot\text{H}_2\text{C}\cdot\text{O}-\text{C}(=\text{O})-\text{C}_6\text{H}_4-\text{C}(=\text{O})-\text{O}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{O}\cdot\text{CH}_2\cdot\text{CH}_2-\text{OH}$ | 35 | 313 | 358 |

removed continuously. The rate of polyesterification may be defined as the rate at which the reactant concentration diminishes¹⁰:

$$R = \frac{-d[\text{COOH}]}{dt} \quad (1)$$

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

$$-\frac{d[\text{COOH}]}{dt} = k[\text{COOH}]^2[\text{OH}] \quad (2)$$

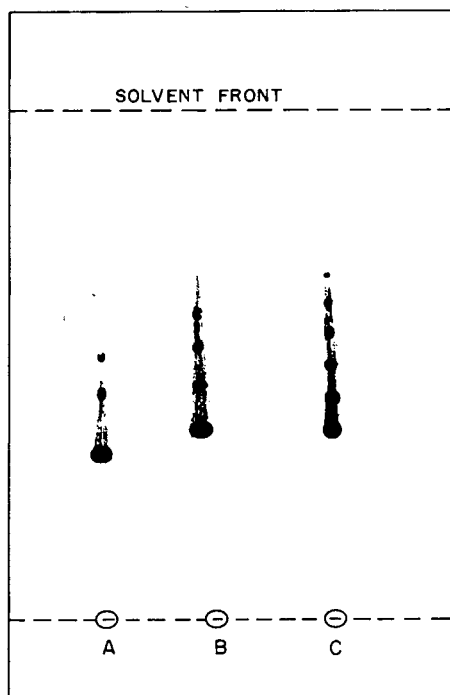
For stoichiometric proportion of monomers, eq. (2) becomes

$$-\frac{d[\text{COOH}]}{dt} = kC_0^3 \quad (3)$$

TABLE III
Effect of the Amount of Glycol on Extent of Depolymerization⁶

| Glycolyzed PET code | Weight ratio EG/PET | (g mol EG/100 g PET) | Extent of depolymerization ^a |
|---------------------|---------------------|----------------------|---|
| GPET-4 | 37.5/62.5 | 0.97 | 0.8461 |
| GPET-5 | 50/50 | 1.61 | 0.9095 |
| GPET-6 | 62.5/37.5 | 2.69 | 0.9955 |

$$^a \text{Extent of depolymerization} = \frac{\text{hydroxyl value of GPET after removal of free glycol}}{\text{hydroxyl value of BHET}}$$



A = GPET-6, B = GPET-3, C = GPET-9

Fig. 1. TLC analysis of glycolyzed PET waste.

In terms of the extent of reaction, p , eq. (3) may be written as

$$\frac{1}{(1-p)^2} = 2C_0^2 kt + \text{const} \quad (4)$$

where

$$p = \frac{C_0 - C}{C_0} \quad (5)$$

and C_0 represents initial concentration. Similarly for acid-catalyzed reaction the rate equation can be written as

$$\frac{1}{1-p} = C_0 kt + \text{const} \quad (6)$$

For catalyzed reactions with nonstoichiometric amounts of monomers, the equation needs to be modified¹¹ as follows:

$$\ln \frac{[B]}{[A]} = \ln r + [A]_0(r-1)kt \quad (7)$$

where r is the ratio of concentrations of functional groups and is never less than one. Thus $[B]$ represents the concentration of the reactant which is in excess. In the present work, the hydroxyl

groups are in excess; therefore,

$$\ln \frac{[\text{OH}]}{[\text{COOH}]} = \ln \frac{[\text{OH}]_0}{[\text{COOH}]_0} + [\text{COOH}]_0 \{ ([\text{OH}]_0 / [\text{COOH}]_0) - 1 \} kt \quad (8)$$

where $[\text{OH}]_0$ and $[\text{COOH}]_0$ represent initial concentrations of the hydroxyl and the carboxyl groups. Thus for the reaction to be of second order, the plot of $\ln[\text{CH}]/[\text{COOH}]$ vs. time should be linear.

Though the assumption of constant reactivity of functional groups is widely accepted, a large change in the reactivity of the reaction system with time has been noted. In several systems a difference in the reactivity of the monomer compared to its oligomeric species has also been

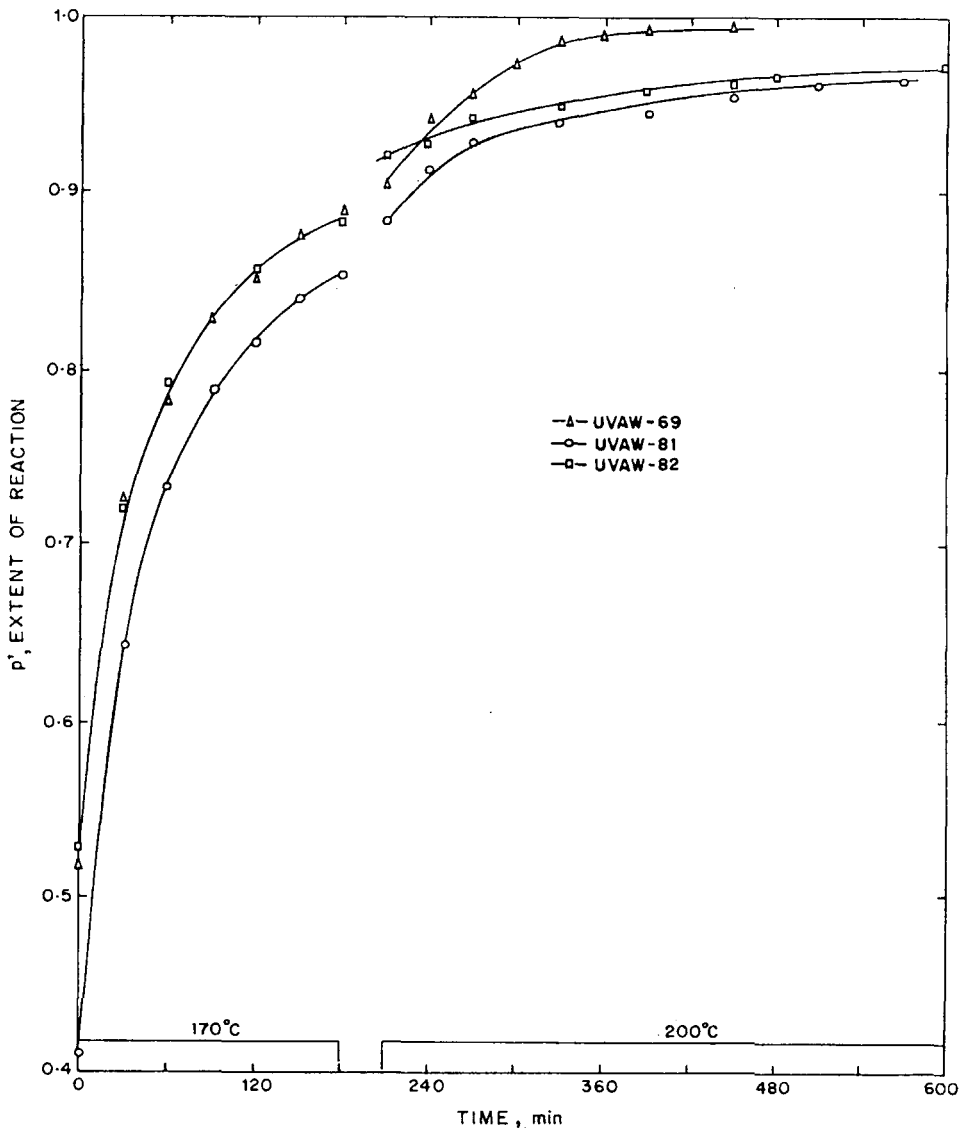


Fig. 2. Change in the extent of reaction with time: (Δ) UVAW-69; (\circ) UVAW-81; (\square) UVAW-82.

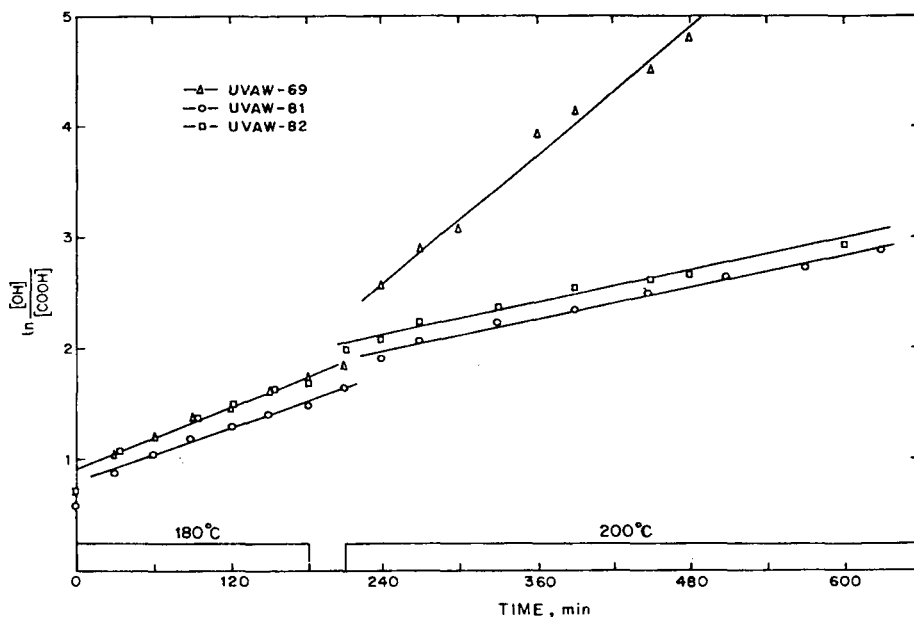


Fig. 3. Plot of $\ln [\text{OH}]/[\text{COOH}]$ vs. time: (Δ) UVAW-69; (\circ) UVAW-81; (\square) UVAW-82.

observed.^{12,13} This behavior usually occurs with monomers having two functional groups in close proximity, and the polymerization brings about considerable changes in the electron donating or withdrawing ability of the functional group. The other reason for the decrease in the reactivity with increasing molecular weight is the large changes in the polarity of the reaction medium.

The decrease in the rate of reaction may not be due to a decrease in the reactivity of the functional groups, but to a decrease in the concentration of free functional groups with time. The other factor governing the rate of polyesterification is the removal of water of reaction. Since polyesterification is a reversible reaction, the water should be removed in order to shift the equilibrium toward the product side. With the progress of reaction, the molecular weight increases and so does the viscosity, which makes the removal of water from the reaction mixture increasingly difficult. Thus the overall reaction rate of any system would depend on a number of factors stated above.

Figure 2 shows the variation of the extent of polyesterification reaction with time for the three types of glycolized PET products. For the plot, the zero time has been taken to be the time at which the reaction mixture reached 170°C. For the initial period, the increase in the extent of reaction for the EG-glycolized product (UVAW-69) and the DEG-glycolized product (UVAW-82) is comparable. The rate of the PG-glycolized product (UVAW-81) is comparatively lower.

However, at 200°C, there is a marked increase in the rate of reaction of UVAW-69, whereas UVAW-81 and -82 proceed at relatively lower rates.

Figure 3 illustrates the plots of $\ln [\text{OH}]/[\text{COOH}]$ vs. time as per eq. (8). It is seen that, in spite of the presence of monomers and oligomers of different sizes in the reaction mixture, the plots are fairly linear at a given temperature. Thus the reactions follow second-order kinetics. The slight nonlinearity in the initial stages at 170°C may be attributed to the large changes in the concentration of the reactive groups and polarity of the reaction medium.

The rate constants of the reactions were calculated from eq. (8) separately for the two regions at 170 and 200°C. For computation of the rate constants, the initial concentration of the carboxyl groups was obtained from the acid value of the reaction mixture at the time when it reached 170 and 200°C, respectively (Table IV). At 170°C covering the extent of reaction from 0.4 to 0.9, the DEG-based polyester exhibits the highest rate constant, followed by EG-based system and then the PG-based system. This trend is consistent with the reported observations that the reactivity of DEG is higher than that of EG¹⁴ and that the presence of a secondary hydroxyl group on PG

TABLE IV
Kinetic Rate Constants of the Polyesterification Reactions

| Sample no. | Polyester code | Type of diol used for polyesterification | 170°C | | 200°C | |
|------------|----------------|--|-----------------------------|--|-----------------------------|--|
| | | | (COOH) ^a (eq/kg) | Rate constant k , (kg eq ⁻¹ min ⁻¹) | (COOH) ^b (eq/kg) | Rate constant k , (kg eq ⁻¹ min ⁻¹) |
| 1 | UVAW-69 | GPET-6 (EG-based) | 3.174 | 2.9×10^{-3} | 0.620 | 34.8×10^{-3} |
| 2 | UVAW-81 | GPET-3 (PG-based) | 3.613 | 2.4×10^{-3} | 0.724 | 10.5×10^{-3} |
| 3 | UVAW-82 | GPET-9 (DEG-based) | 2.340 | 3.7×10^{-3} | 0.388 | 10.5×10^{-3} |

(COOH)^a = concentration of carboxyl groups when reaction reached 170°C.

(COOH)^b = concentration of carboxyl groups when reaction reached 200°C.

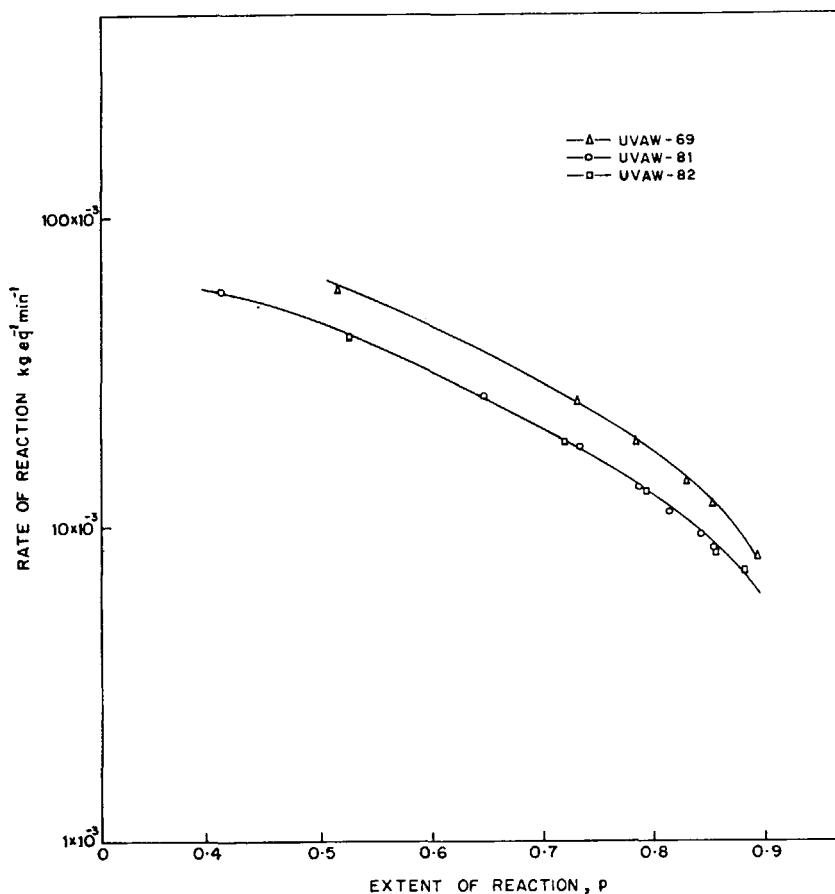


Fig. 4. Change in the rate of reaction with extent of reaction at 170°C: (Δ) UVAW-69; (\circ) UVAW-81; (\square) UVAW-82.

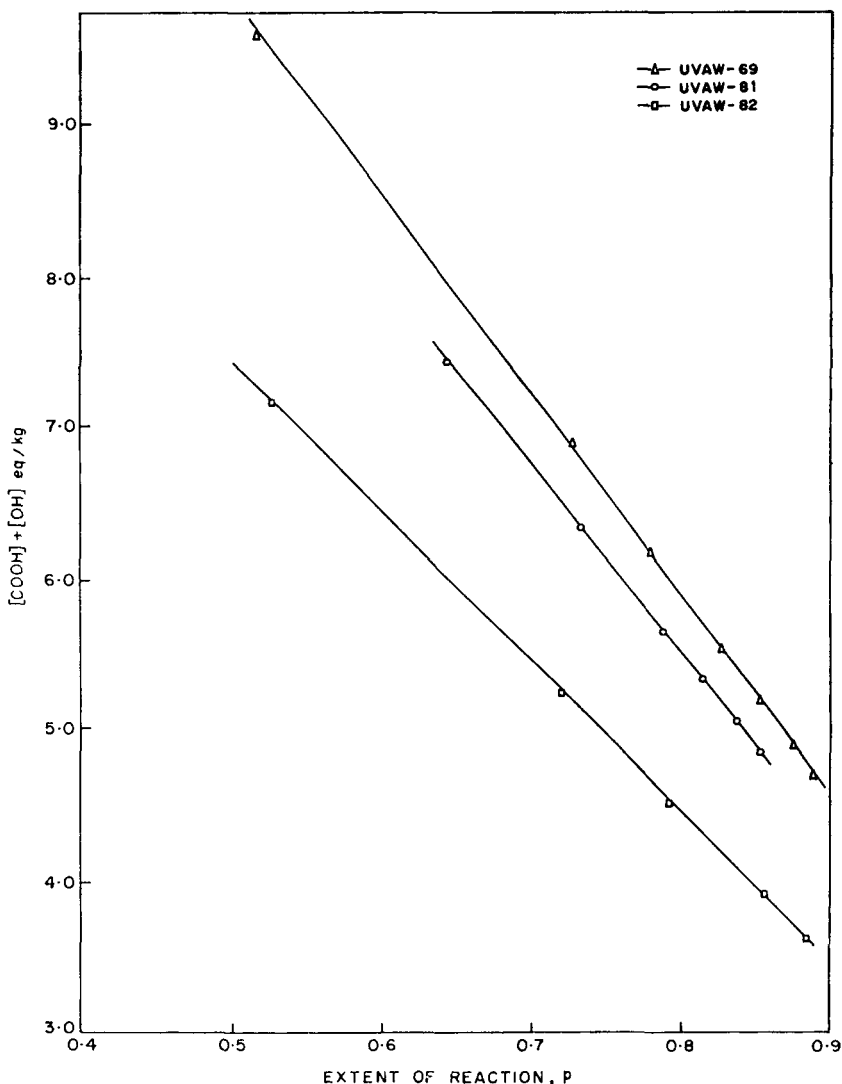


Fig. 5. Change in the total concentration of functional groups with extent of reaction at 170°C: (Δ) UVAW-69; (\circ) UVAW-81; (\square) UVAW-82.

reduces its reactivity.¹⁵ At 200°C, there is an increase in the values of the rate constant, as expected. However, the increase is the maximum for the EG-based glycolized product.

A more logical way to compare the reactivity is to follow the variation in the rate of reaction with the extent of reaction. Figure 4 shows the change in the rate of reaction with the extent of reaction at 170°C. Figure 5 shows the change in the total concentration of functional groups with the extent of reaction at 170°C. Though the rate constant of UVAW-82 (DEG system) is higher than that of UVAW-69 (EG system), because of the higher concentration of free functional groups in UVAW-69, its rate is higher than that of UVAW-82. The rates of UVAW-81 and -82 are identical. The reactivity of diethylene glycol (monomer) is higher than that of ethylene glycol. However, the mole percent of free DEG present in GPET-9 is less than the mole percent of free EG present in GPET-6. In our earlier publication,⁶ reporting the study on kinetics of EG and BHET, it is seen that the presence of higher oligomers reduces the reaction rate. Thus the lower mole percent of free DEG and the presence of higher molecular weight oligomers in GPET-9 may

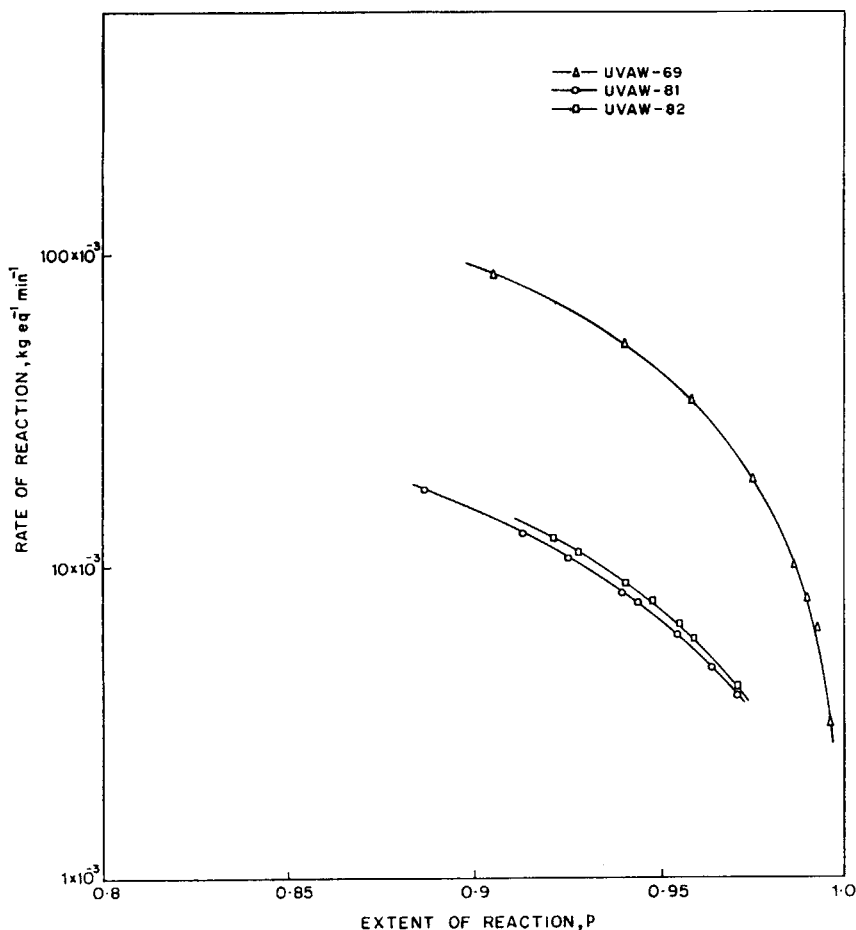


Fig. 6. Change in the rate of reaction with extent of reaction at 200°C: (Δ) UVAW-69; (\circ) UVAW-81; (\square) UVAW-82.

cause the reaction of UVAW-82 to proceed at a slower rate. Though the concentration of hydroxyl group in GPET-3 (PG-based) is higher than that of GPET-9 (DEG-based), the presence of secondary hydroxyl groups in GPET-3 reduces the overall reactivity. Therefore, the rates of UVAW-81 and UVAW-82 are almost comparable.

Figure 6 represents the change in the reaction rate with the extent of reaction at 200°C. Figure 7 shows the change in the concentration of functional groups with extent of reaction. Again the same trend is observed in the reaction rates. The rates are higher than the corresponding rates at 170°C. The lower rate of reaction of UVAW-82 (DEG-based) is observed in this region also. This may again be attributed to lower concentration of free functional groups and higher concentration of large sized oligomers.

The polyesterification reactions with the three types of glycolized PET were continued further, at higher temperature with vacuum cycle, in order to obtain an acid number below 1 mg KOH/g. The subsequent reaction conditions were not identical for the three systems. The characteristics of the polyester polyols obtained are summarized in Table V. It is seen that the hydroxyl value of UVAW-81 is less than that of UVAW-82. Since the PG-based system was the least reactive, vacuum was applied for a much longer time compared to the other two reactions, which might have resulted in the loss of glycol from UVAW-81, lowering its hydroxyl value.

These polyols could be reacted with polymeric 4,4'-diphenyl methane diisocyanate (PMDI) at ambient temperature at an isocyanate index of 100 to give PU elastomers. The mechanical and

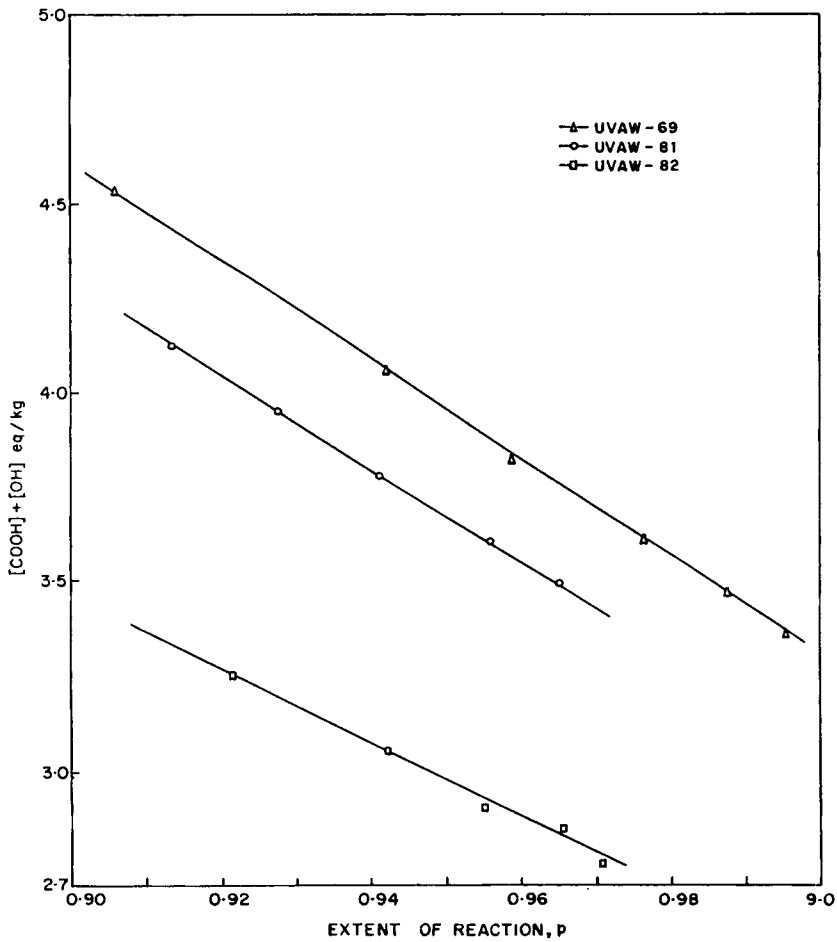


Fig. 7. Change in the total concentration of functional groups at 200°C: (Δ) UVAW-69; (\circ) UVAW-81; (\square) UVAW-82.

TABLE V
Characterization of Polyester Polyols

| Sample no. | Polyester code | Viscosity at 27°C (cP) | Hydroxyl value (mg KOH/g) |
|------------|----------------|------------------------|---------------------------|
| 1 | UVAW-69 | 4000 | 150 |
| 2 | UVAW-81 | 13000 | 110 |
| 3 | UVAW-82 | 4100 | 125 |

dynamic mechanical properties of the elastomers are being evaluated and will be reported separately.

CONCLUSIONS

PET waste can be depolymerized by glycolyzing it with glycols like EG, PG, and DEG. The extent of the glycolysis depends on the moles of the glycol present when glycolized on a weight basis, the extent of glycolysis was found to be the highest for EG, giving the diester, bis(2-hydroxy

ethyl)terephthalate. The glycolized products obtained from reaction of PET waste with PG and DEG exhibited higher number average molecular weights and broader molecular weight distributions.

The oligomeric diols thus obtained could be polyesterified with adipic acid to get polyester polyols of different molecular weights. The polyesterification reactions followed second-order kinetics for both the isothermal regions (at 170 and 200°C) employed in the reaction. At 170°C, the rate constant of DEG-based oligomers was the highest ($3.7 \times 10^{-3} \text{ kg eq}^{-1} \text{ min}^{-1}$) followed by that of the EG-based and PG-based glycolysis products, respectively (2.9×10^{-3} and $2.4 \times 10^{-3} \text{ kg eq}^{-1} \text{ min}^{-1}$). At 200°C, an increase in the value of the rate constant was observed. The increase was the maximum for the EG-glycolized product ($34.8 \times 10^{-3} \text{ kg eq}^{-1} \text{ min}^{-1}$). The rate constants of the other two polyesters made from PG- and DEG-glycolized PET were comparable ($10.5 \times 10^{-3} \text{ kg eq}^{-1} \text{ min}^{-1}$).

The rate of the reaction of the EG-based system was the highest, whereas those of the PG- and DEG-based systems were comparable for both the isothermal regions. In spite of the higher reactivity of the DEG monomer compared to that of EG monomer, the reaction of the DEG-based oligomer proceeds at a slower rate than the EG-based system. This lower rate may be attributed to the lower mole percentage of free DEG and higher concentration of higher molecular weight oligomers when compared to the EG system. The reactivity of PG-based system was lower as expected because of the presence of secondary hydroxyl groups.

These polyester polyols when reacted with polymeric 4,4'-diphenyl methane diisocyanate (PMDI) gave elastomers. The results of the characterization of the elastomers will be reported in subsequent publications.

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