Unsaturated Polyesters from PET Waste: Kinetics of Polycondensation*

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Synopsis

PET waste was glycolyzed by propylene glycol at different weight ratios. The glycolyzed products were analyzed for hydroxyl value, number average molecular weight, and the amount of free glycol. The glycolyzed products were reacted with maleic anhydride at a hydroxyl to carboxyl ratio of 1.1. The control resin was a general purpose unsaturated polyester prepared by reacting phthalic anhydride, maleic anhydride, and propylene glycol. The heating schedule of the polyesterification was comparable to that normally employed in the industrial process, with two isothermal plateau of 3–4 h at 180 and 200°C. The rate of reactions and rate constants were determined separately at 180 and 200°C. The kinetics of the PET-based unsaturated polyesters was compared with that of the general purpose resin. It was found that the PET waste could be depolymerized by propylene glycol to a molecular weight range of 276–480. The polyesterification reactions followed a third-order kinetics. The rates of polyesterification of PET based systems were higher than that of the general purpose resin. PET-based systems took about 10 h to reach an acid value of 32 mg KOH/g whereas the general purpose resin took about 25 h to reach the same acid value.

INTRODUCTION

The unsaturated polyester (UP) resins are used extensively as a matrix for fiber-reinforced composites, which are replacing conventional structural materials like steel and wood in a variety of engineering applications. The fiber-reinforced plastics, termed FRP, offer excellent chemical resistance, weatherability, high strength to weight ratio, versatility of product design, and ease of fabrication. The widespread use of UP resins in the FRP industry is due to their low cost and the wide variety of grades available to meet specific property requirements.

The mechanical performance and chemical resistance characteristics of UP resins are generally modified by appropriate choice of the diols and diacids used as the building blocks of the polymer. The most commonly used diacids are orthophthalic anhydride, isophthalic acid and maleic anhydride, whereas the diols include ethylene glycol (EG), propylene glycol (PG), and neopentyl glycol (NPG).[1] It has been demonstrated[2-5] that glycolyzed poly(ethylene terephthalate) (PET) waste can be effectively used to produce UP resins with performance characteristics comparable to the conventional grades. This enables one to synthesize UP resins based on terephthalic acid (TPA) without

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much processing difficulties. This process is commercially important since it converts a waste material into a useful value-added product.

In spite of the commercial importance of unsaturated polyesters, little published data are available on the kinetics of polycondensation under industrial reaction conditions. Generally the kinetic investigations are carried out under isothermal conditions. However, in a commercial process, the initial reaction temperatures are kept low in order to avoid the loss of glycol. The temperature is raised to a higher value in the final stages of the reaction to accelerate the rate. It is, therefore, important to conduct the kinetic experiments with heating cycles comparable to those employed in industrial reactions.

In the present investigation, the PET was glycolyzed with propylene glycol. The kinetics of the polycondensation of maleic anhydride with glycolyzed PET waste was studied. The rate data are compared with the kinetics of the synthesis of conventional general purpose UP resin. In the heating cycle employed in the investigation, two distinct isothermal reaction regimes were investigated at 180 and 200°C.

EXPERIMENTAL

Materials. Fiber grade poly(ethylene terephthalate) with a number average molecular weight ($\bar{M}_n$) ranging between 18,000 and 20,000 was obtained from M/s Century Enka, Pune, India. Propylene glycol (LR) was supplied by M/s IDPL, Hyderabad, India. Zinc acetate (LR) and maleic anhydride (LR) were obtained from M/s High Purity Chemicals Pvt. Ltd., Delhi. Phthalic anhydride and hydroquinone were obtained from M/s Loba Chemie, Bombay, India.

Glycolysis of PET Waste. The PET waste was depolymerized at different weight ratios of PET to PG using 0.5% w/w zinc acetate, based on weight of PET, as catalyst. The reaction was carried out at about 200°C under reflux for 8 h in nitrogen atmosphere. The reactor used was a four-necked round bottom flask of 2-L capacity having a reflux condenser, gas bubbler, thermowell, and stirrer assembly.

Thus three oligomeric diols, coded GPET-1, GPET-2, and GPET-3, were prepared by glycolyzing PET with 37.5, 50, and 62.5% w/w PG, respectively. The total charge was about 1200 g for all the batches.

The glycolyzed products were then analyzed for hydroxyl value and the amount of free glycols as follows:

a. Determination of hydroxyl value: The hydroxyl values were determined by the conventional acetic anhydride/pyridine method.[6]

b. Determination of free glycol: A weighed quantity of the glycolyzed product was extracted with water and filtered. The filtrate containing water, free glycol, and some soluble oligomers was concentrated by evaporation of water and then chilled in order to precipitate out the water-soluble oligomers. This was filtered again. The second filtrate thus obtained contained water and free glycol. The residues remaining after the first and second filtrations were dried and weighed together. The difference between the original and the final weight represents the amount of free glycol removed by water extraction.

The glycolyzed products were also analyzed by thin layer chromatography (TLC) using chloroform/ethanol solvent system as the mobile phase and silica gel as stationary phase.

In order to check the extent of depolymerization, the glycolyzed products were analyzed after the removal of free glycol, for hydroxyl value and the number average molecular weight ($\overline{M}_n$). The hydroxyl value was determined as per procedure described earlier. The $\overline{M}_n$ was determined by vapor pressure osmometry (VPO) using a Knaur vapor pressure Osmometer. Ethyl acetate was used as solvent and benzil as the standard. The temperature of the solvent chamber was 50°C.

Preparation of Unsaturated Polyesters. The UP resins were prepared by reacting the glycolyzed products with maleic anhydride at a fixed value of the hydroxyl to carboxyl ratio of 1.1. The hydroxyl number of the glycolyzed product without separation of free glycol was used to determine the amount of maleic anhydride.

Thus three UP resins coded UVMW-57, -58, and -59 were prepared by reacting 449.6 g GPET-1 with 184.2 g maleic anhydride, 409.6 g GPET-2 with 223.2 g maleic anhydride, and 373.1 g GPET-3 with 277.0 g maleic anhydride, respectively.

A conventional general purpose (GP) resin was prepared by reacting 198.1 g maleic anhydride, 296.2 g phthalic anhydride with 334.8 g propylene glycol, keeping the hydroxyl to carboxyl ratio constant at 1.1.

The polyesterification reaction was carried out in a 2-L round-bottom flask having a distillation condenser, a gas bubbler, a thermowell, and a stirring assembly. The reactants were heated from the room temperature to 180°C in about 1–1.5 h. The temperature was then held at 180°C for about 3 h and finally raised to 200°C and maintained till the acid value reached 32 mg KOH/g. The same heating schedule was employed for all the batches. The water of reaction was removed and periodically measured throughout the course of the reaction. The acid value was monitored during the reaction. The acid value was determined by titrating the solution of the weighed quantity of resin in acetone, with about $0.2N$ standard alcoholic KOH solution using phenolphthalein indicator.

The UP resins were analyzed for hydroxyl value and number average molecular weight as described earlier.

RESULTS AND DISCUSSION

The PET waste could be depolymerized by glycolyzing it with PG, as evident from the data given in Table I. The extent of depolymerization increased with increasing amount of PG. The number average molecular weight of the glycolyzed PET, after removal of free glycol, varied between 480 and 276. These values are comparable to the molecular weight of bis(hydroxyethyl) terephthalate and bis(hydroxypropyl) terephthalate. This suggests that the extent of depolymerization is significant.

TLC of the glycolyzed products showed five to six spots with considerable tailing, indicating the presence of a number of oligomers. Thus the molecular weight distribution (MWD) of the glycolyzed products was quite broad. The

TABLE I
Characterization of Glycolyzed PET Waste

Sample no.	Glycolyzed product	PET/PG weight ratio for glycolysis	Analysis of glycolyzed product			
			Before free glycol removal		After free glycol removal	
			Free glycol (% w/w)	Hydroxyl value (mg KOH/g)	M_n (VPO)	Hydroxyl value (mg/KOH/g)
1	GPET-1	62.5/37.5	35	516	480	240
2	GPET-2	50/50	47	717	399	295
3	GPET-3	37.5/62.5	60	933	276	326

major fractions of the glycolyzed products could be represented by the following species: PG–TPA–PG, PG–TPA–EG,EG–TPA–EG, PG, and EG (slight quantity). The moieties shown above are linked through ester linkages. These glycolyzed products when polyesterified with maleic anhydride gave unsaturated polyesters which were compatible to styrene and could be cured with the conventional initiator/accelerator systems.[7,8]

It is a general practice to carry out a reaction at constant temperature for investigating kinetics. However, as stated earlier, in the commercial process, a gradual heating cycle with isothermal plateau is normally used to control the reaction rate and to minimize the loss of the diol.

In the present investigation, the reaction temperature was maintained at 180°C for the initial 3–4 h. It was then raised to 200°C. The polycondensation of glycolyzed PET waste with maleic anhydride was completed in about 9 h, whereas the phthalic-anhydride-based GP resin batch took about 26 h to reach comparable conversion.

Figure 1 shows the decrease in the acid value with reaction time. The acid value decreased more rapidly in the PET-based reactions relative to the GP resin batch.

The kinetics of the reaction was followed by monitoring the acid group concentration. The extent of the reaction and the degree of polymerization were then determined from the acid number with reference to the theoretical considerations in the kinetics of polyesterification described below.

Polyesterification is a reversible reaction and can be represented as

$$\text{diacid + diol} \rightleftharpoons \text{polyester + water}$$

Flory[9] therefore suggested that the rate of disappearance of the reactants can be interpreted as the overall rate of the reaction. Generally, the rate of polyesterification is monitored by measuring the rate of depletion of the carboxyl groups of the acid or anhydride. It is known that polyesterification reactions are catalyzed by acids, and, in the absence of any added catalyst, the diacid itself acts as a catalyst. Therefore, in the absence of an external catalyst, the rate of polyesterification could be represented as

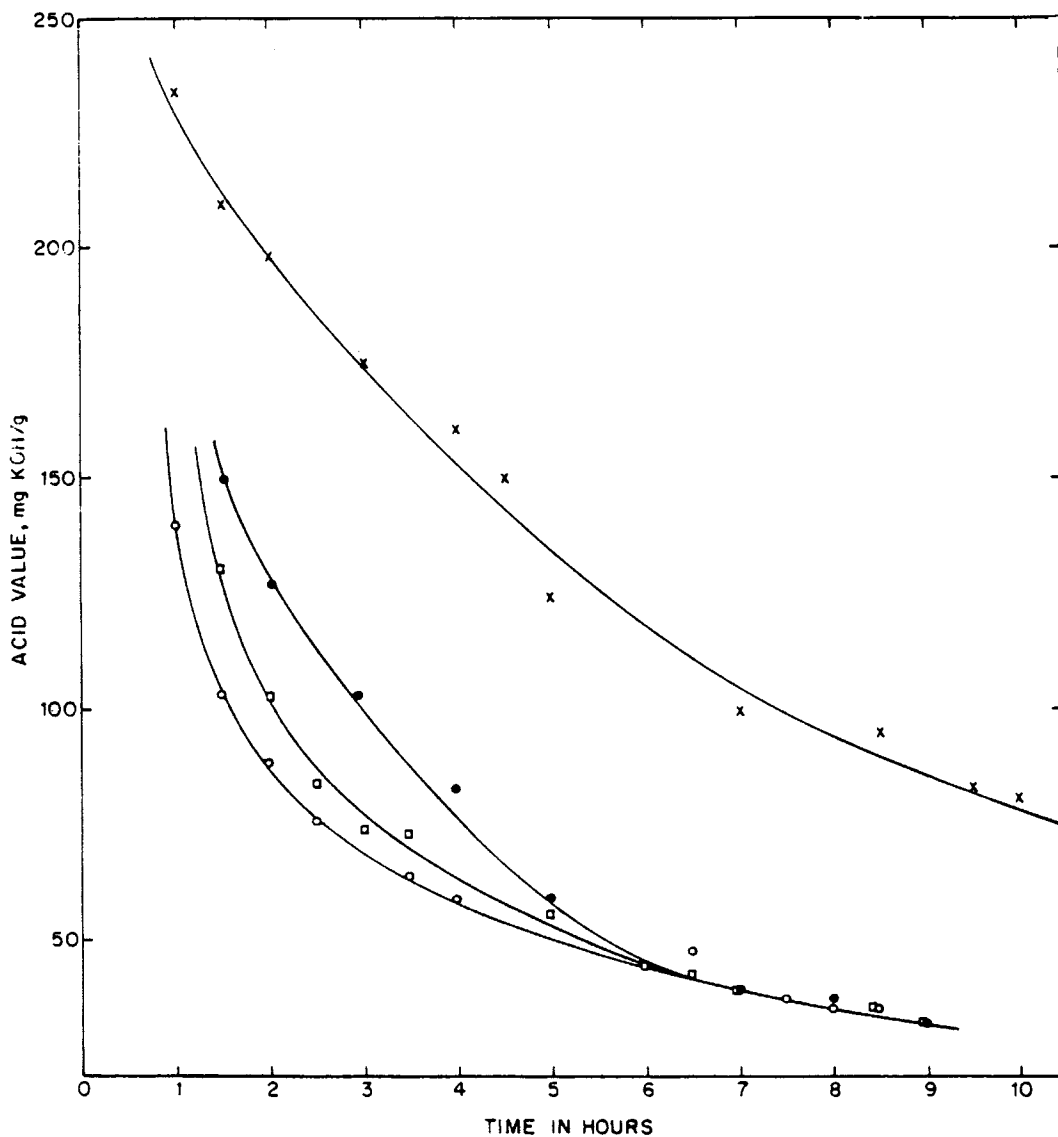$$R = \frac{-d[\text{COOH}]}{dt} = k[\text{COOH}]^2[\text{OH}] \tag{1}$$

Fig. 1. Change in acid value with time: (○) UVMW-57; (□) UVMW-58; (●) UVMW-59; (×) GP resin.

If the concentrations of carboxyl and hydroxyl groups are equal, then eq. (1) becomes

$$\frac{-d[\text{COOH}]}{dt} = kC^3 \qquad (2)$$

where C is the concentration of the carboxyl or hydroxyl groups, or

$$2kt = 1/C^2 = \text{const} \qquad (3)$$

The extent of the reaction, p, is defined as the fraction of the functional

groups (carboxyl) initially present that have undergone reaction in a given time t, that is,

$$p = \frac{C_0 - C}{C_0} \qquad (4)$$

where C_0 is the initial concentration of carboxyl groups.
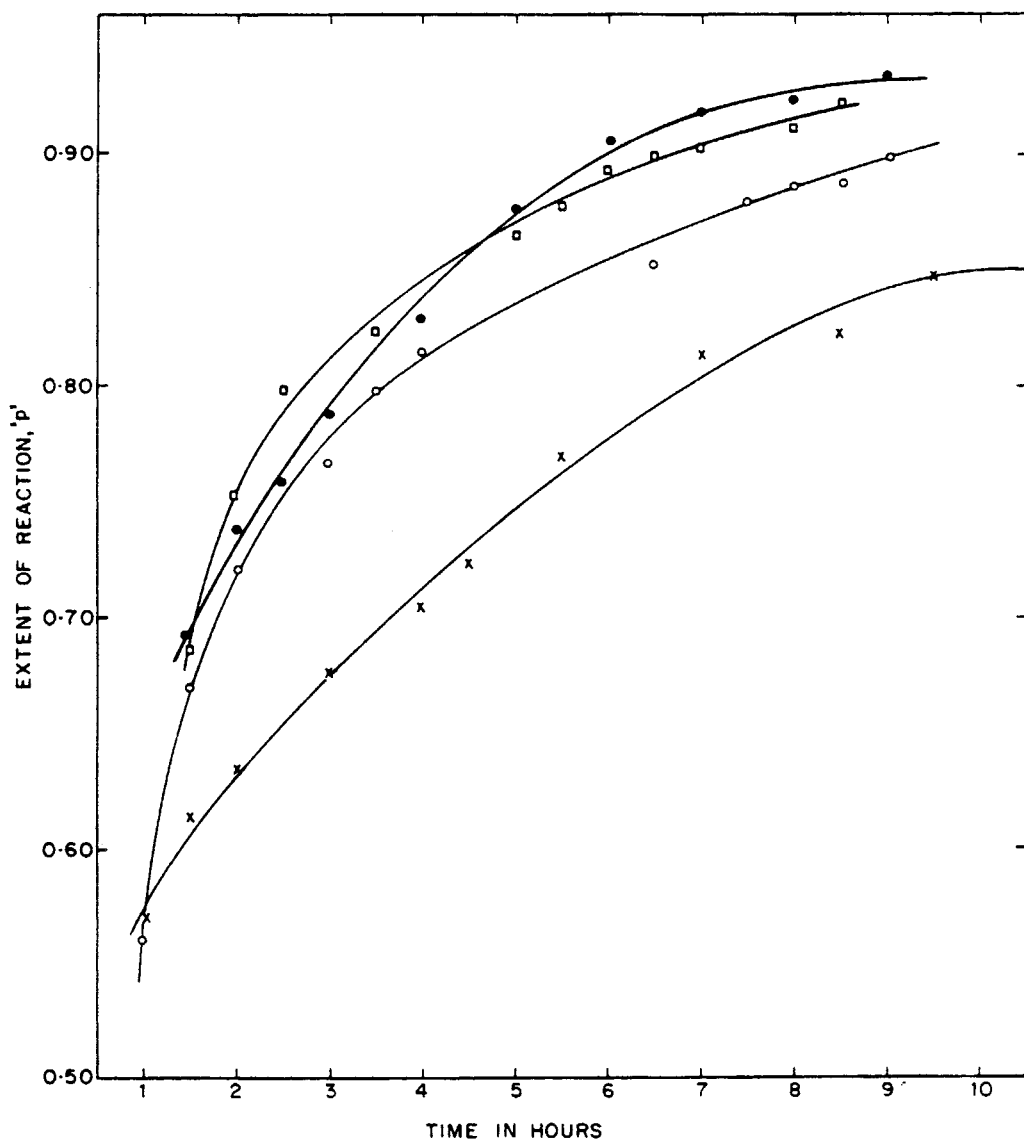
$$\therefore C = C_0(1 - p) \qquad (5)$$

Fig. 2. Increase in the extent of reaction with time: (○) UVMW-57; (□) UVMW-58; (●) UVMW-59; (×) GP resin.

TABLE II
Uncatalyzed Polyesterification of UVMW-57

Sample no.	Time (min)	Temp (°C)	Acid value (mg KOH/g)	Water evolved, (mL)	p	$1/(1-p)^2$
1	0	Room temp	317.7	—	—	—
2	30	110	—	—	—	—
3	100	180	139.9	4.0	0.5596	5.156
4	130	180	103.7	13.0	0.6735	9.381
5	160	180	89.1	16.0	0.7195	12.710
6	190	180	76.8	18.0	0.7583	17.118
7	220	180	74.6		0.7652	18.137
8	250	180	64.0	21.5	0.7985	24.629
9	280	180	58.9	24.0	0.8146	29.092
10	430	200	47.0	25.5	0.8521	45.715
11	490	200	38.0	28.0	0.8804	69.910
12	520	200	36.4		0.8854	76.143
13	540	200	35.8		0.8873	78.732
14	580	200	32.0	29.0	0.8992	98.419

Figure 2 shows the increase in the extent of reaction, p, with time. It is clear from the figure that, in PET-based systems, the extent of reaction increases much more rapidly than in the GP resin. The extent of reaction in case of UVMW-59 is less than UVMW-58 at 180°C, but it increases rapidly at 200°C. At the end of the reaction, the extent follows the order UVMW-59 > UVMW-58 > UVMW-57 > GP resin.

Combining eqs. (3) and (5), one obtains

$$\frac{1}{(1-p)^2} = 2C_0^2 kt + \text{const} \tag{6}$$

As per eq. (6) a plot of $1/(1-p)^2$ vs. time should be linear for a third-order kinetics.

The experimental data illustrated in Table II for a typical run were used to generate the plots of $1/(1-p)^2$ vs. time for the polyesterification reactions.

TABLE III
Determination of Rate Constants at 180 and 200°C

Serial no.	Polyester code	180°C			200°C		
		[COOH][a] (eq. mol/kg)	Slope	Rate constant k (kg^2 eq. mol^{-2} min^{-1})	[COOH][b] (eq. mol/kg)	Slope	Rate constant k (kg^2 eq. mol^{-2} min^{-1})
1	UVMW-57	2.49	0.1133	9.14×10^{-3}	0.98	0.3513	18.28×10^{-2}
2	UVMW-58	3.10	0.1788	9.30×10^{-3}	1.03	0.4825	22.70×10^{-2}
3	UVMW-59	3.47	0.1555	6.46×10^{-3}	1.23	0.6944	22.90×10^{-2}
4	GP resin	4.17	0.037	1.06×10^{-3}	2.67	0.0926	0.65×10^{-2}

[a] Concentration of carboxyl groups when temperature reached 180°C.
[b] Concentration of carboxyl groups when temperature reached 200°C.

Although a modification is required for cases wherein the ratio of hydroxyl to carboxyl, that is, r is much greater than unity, eq. (6) holds good at small variations from unity such as at the value of 1.1 used in the present study.

The linear plots of $1/(1 - p)^2$ vs. time in Figure 3 indicate that the reactions follow third-order kinetics for both the temperature regimes. It is also seen that the rate of reaction increases remarkably with the temperature,
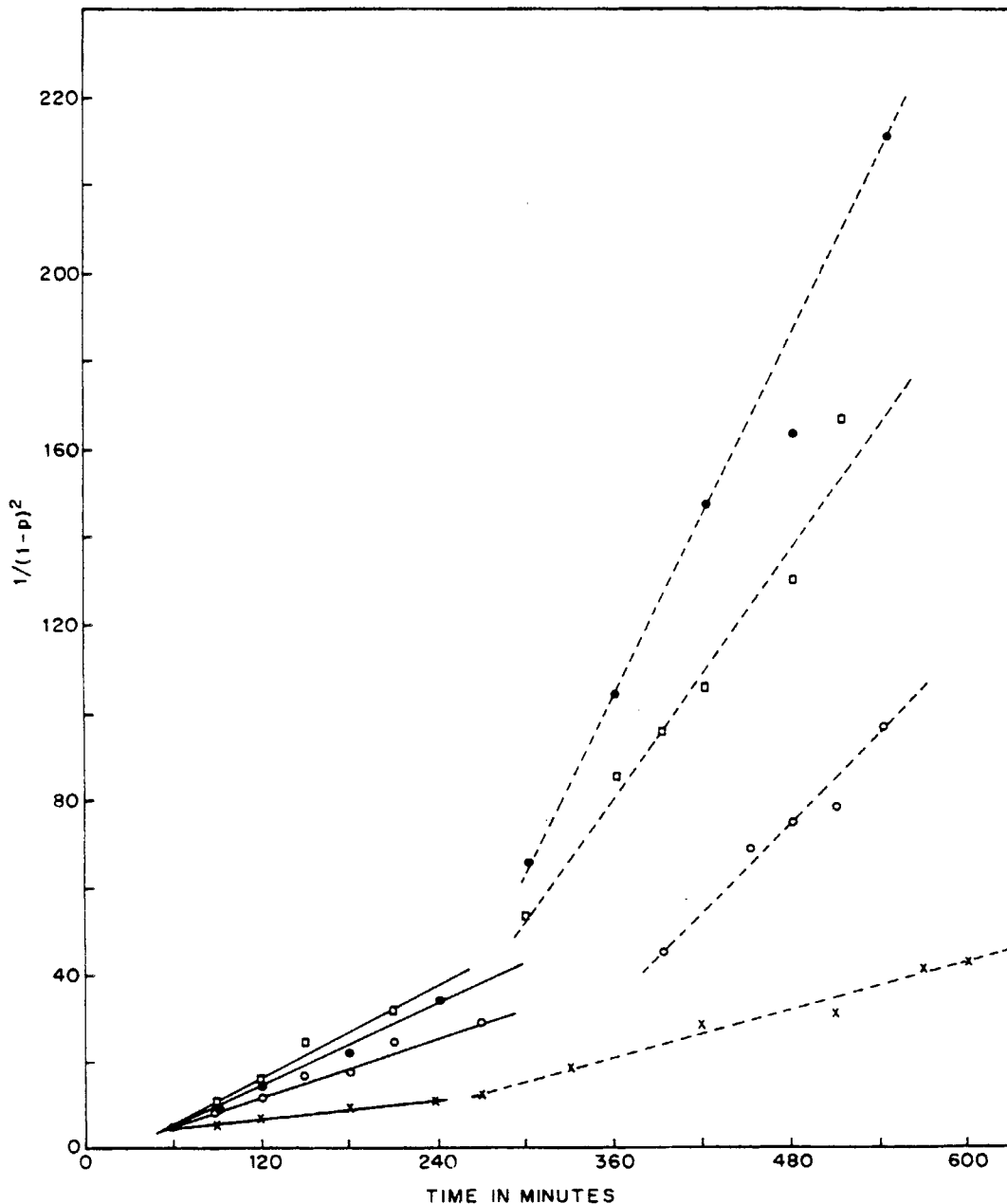

Fig. 3.   Plot of $1/(1 - p)^2$ vs. time: (—) data at 180°C; (- - -) data at 200°C; (○) UVMW-57; (□) UVMW-58; (●) UVMW-59; (×) GP resin.
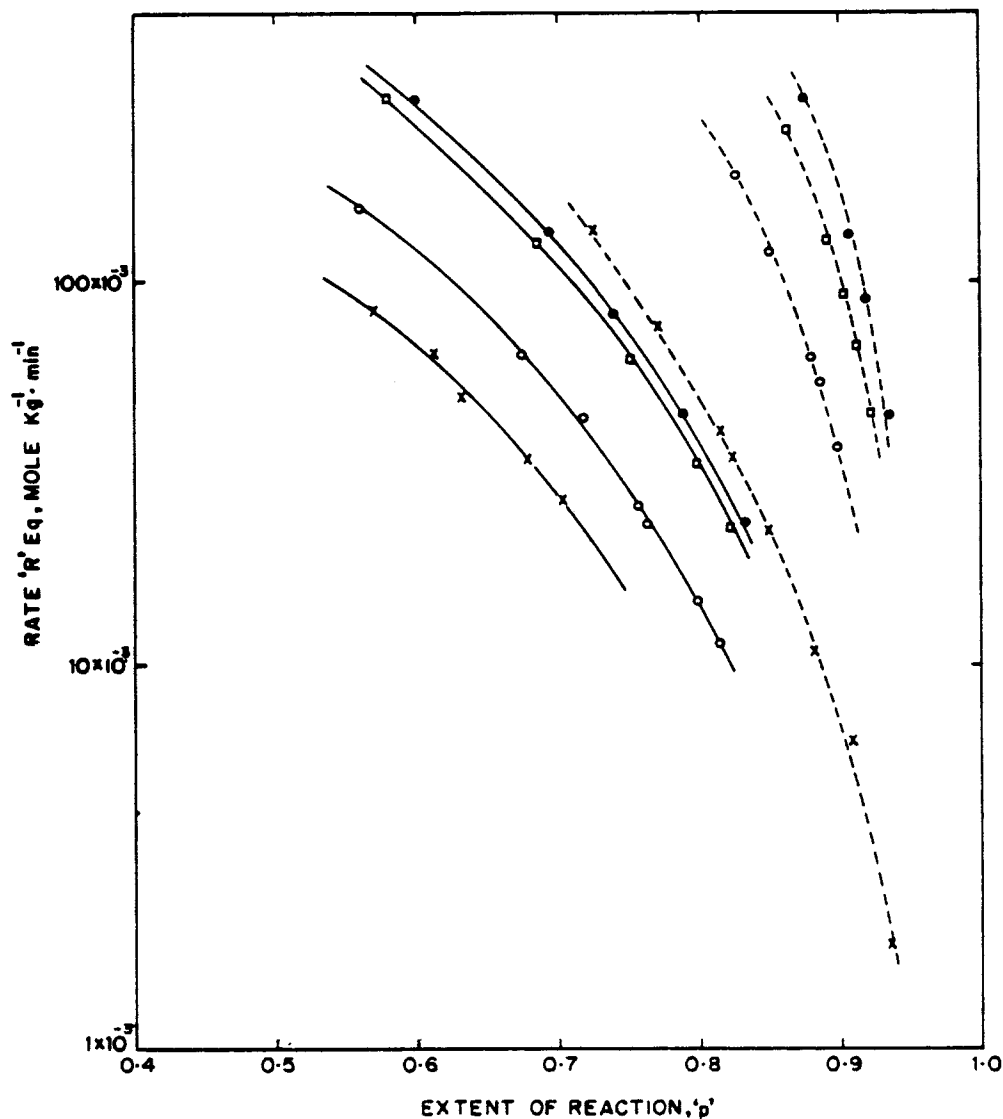
Fig. 4.   Decrease in the rate of reaction with extent of reaction: (—) data at 180°C; (- - -) data at 200°C; (○) UVMW-57; (□) UVMW-58; (●) UVMW-59; (×) GP resin.

and this increase is more prominent in the case of resins based on glycolyzed PET, compared to GP resin.

The rate constants at 180 and 200°C were calculated for all the four reactions using eq. (6). The initial concentrations at 180 and 200°C were calculated from the acid values of the reaction mixture at the time of reaching the respective temperature. The rate constants are given in Table III. The rate constants of the reactions based on glycolyzed PET are much higher than that of phthalic anhydride based GP resins.

Figure 4 shows the drop in the rate of reaction with the extent of reaction. It is seen that the drop is more steep at 200 than at 180°C. This is because of the higher extent of the polycondensation reaction at 200°C, leading to a
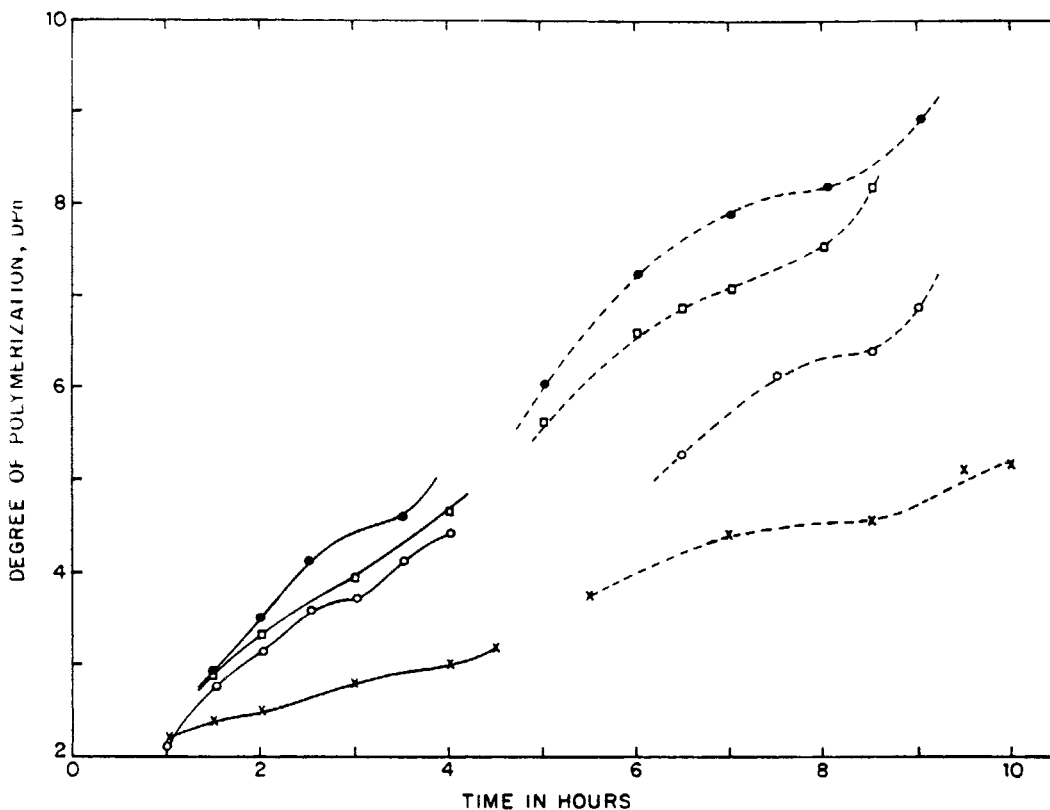
Fig. 5. Increase in degree of polymerization with time: (—) data at 180°C; (- - -) data at 200°C; (o) UVMW-57; (□) UVMW-58; (●) UVMW-59; (×) GP resin.

higher viscosity, which in turn makes the removal of water of reaction more difficult. The reaction equilibrium would thus shift to the reactant side, thereby lowering the rate. The overall rate of polycondensation increases in the order GP resin < UVMW-57 < UVMW-58 < UVMW-59.

It is known that any imbalance in the stoichiometry of the reactants, reduces the degree of polymerization (DP_n).[10] The average degree of polymerization is represented as follows:

$$DP_n = \frac{1 + r}{1 + r - 2p} \qquad (7)$$

where r is the ratio of the concentrations of two reactants and is never less than unity. Figure 5 shows the increase in DP_n with time. At any given time the average degree of polymerization is higher for PET-based systems, compared to the GP resin.

CONCLUSIONS

PET waste can be depolymerized by glycolyzing it with PG. The extent of depolymerization depends on the amount of PG used. The glycolyzed PET can be polyesterified with maleic anhydride to give unsaturated polyesters

which are miscible with styrene and can be cured by conventional curing systems.

The polycondensation reactions follow third-order kinetics. The reaction rate increases with temperature and decreases with the extent of polymerization. The systems based on glycolyzed PET (that is, terephthalic-acid-based) are more reactive than the orthophthalic-anhydride-based GP resin. Among the terephthalic-acid-based systems the reactivity increases with a decrease in the amount of terephthalic acid moiety. In other words, the rate decreases with an increase in the aromatic content.

The kinetic data generated should be useful for product development, process design, and optimization since the reaction conditions investigated are comparable to those employed on the industrial scale.

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