Polyesterification of Dimer Acid and Diethylene Glycol

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ABSTRACT

The polyesterification of dimer acid with diethylene glycol under different experimental conditions has been studied to obtain the optimum conditions for synthesizing poly(diethylene glycol) dimerate plasticizers. The effects of varying molar ratio, temperature, and catalyst concentration on the course of polyesterification, acid numbers, intrinsic viscosities, and molecular weights of the resultant polyesters have been observed. Uncatalyzed and catalyzed polyesterification have been found to follow the second- and third-order rate equations, respectively, in equimolar concentrations of the reactants.

INTRODUCTION

Polyesters have found extensive applications as fibers, film-forming materials, surface coatings, adhesives, plasticizers, precursors of polyurethanes, etc. Low molecular weight ($< 10,000$) aliphatic polyesters have found application as polymeric plasticizers or prepolymeric oligomers. Polymeric plasticizers are more processable, less volatile, and more resistant toward extraction of solvents than are conventional monomeric plasticizers. Recently, the dimer-acid-based polymers have drawn the attention of researchers due to their resistance toward heat, moisture, and chemicals. The polyesterification of cyclic dimer acid has rarely been studied [1–4].

The dimer acid (DA, I) [5], a cyclic dicarboxylic acid, is a light yellow colored viscous and sticky liquid. These polybasic acids are mixtures of dibasic acids of 18 carbon atoms in length per carboxylic group and other mono- and polybasic fractions. DA may be represented as HOOC—D—COOH:

$$CH_3(CH_2)_5—HC \overset{\displaystyle CH=CH}{\underset{\displaystyle CH-CH}{}} CH(CH_2)_7COOH$$

$$CH_3—(CH_2)_5—CH=CH \qquad (CH_2)_7COOH$$

(I)
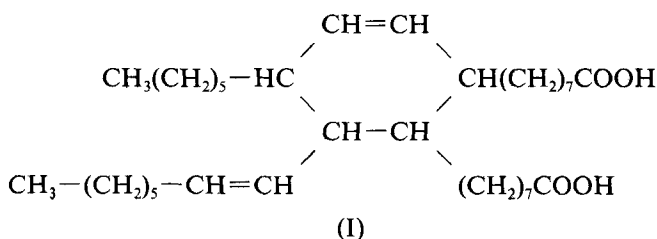
where D is a C-34 divalent hydrocarbon radical. It does not crystallize, and it contributes to the flexibility of polymers derived from it. We have undertaken the study of polyesterification reactions of dimer acid with various glycols [6-8]. The present communication reports the synthesis of polyesters of dimer acid with diethylene glycol (DEG) and its kinetic studies. The effect of the molar ratio of DA to DEG, catalyst concentration, and temperature on the course of reaction were studied.

EXPERIMENTAL

Materials

All the chemicals used were of AR grade. Dimer acid 1010, a gift from Vikram Sarabhai Space Centre, Trivandrum, India, was used without further purification. It had the composition of 98% DA and 2% trimer acid, and it was the dimer of ricinoleic acid. Diethylene glycol (E. Merck, India) was used as such. Methanolic NaOH (0.1 N) was standardized by titrating against 0.1 N oxalic acid.

Technique

The polyesterification was accomplished by direct condensation of DA and DEG. A reaction mixture containing the calculated amount of DA, DEG, and a catalyst, p-toluene sulfonic acid (pTSA) (when used), were condensed at 160 ± 1°C in a three-necked flask equipped with thermometer, N_2 gas inlet, and condenser. The reaction was followed by estimation of the unreacted carboxyl end-groups in aliquots of hot resin (~0.2 g) withdrawn at fixed time intervals. The reaction was carried out for 5 hours.

The increase in molecular weight during the course of polyesterification was determined by end-group analysis [9]. The molecular weight of the polyester was calculated by multiplying the molecular weight of the repeating unit by the degree of polymerization, DP. The degree of polymerization may be represented by Eq. (1) [10, 11]:

$$DP = (1 + r)/[2r(1 - p) + (1 - r)] \qquad (1)$$

where r is the ratio of dicarboxylic acid to glycol molecules and p is the extent of reaction or the fraction of end groups that has already reacted at a particular time, i.e.,

$$p = N_0 - N/N_0 \qquad\qquad (2)$$

where N_0 is the amount of carboxylic group initially present and N is the quantity left after a fixed time interval. The intrinsic viscosity of the polymer was determined viscometrically at 25 ± 0.1°C by noting the efflux time of the pure solvent (benzene) and of the polymer solution of 0.5 g/100 mL of the solvent, and calculated by using the relation [12]:

$$[\eta] = [2(\eta_{sp} - \ln \eta_r)]^{1/2} C^{-1} \qquad\qquad (3)$$

$[\eta]$ is the intrinsic viscosity, η_r is the reduced viscosity, and η_{sp} is the specific viscosity at C, the concentration of the polymer solution.

RESULTS AND DISCUSSION

Effect of Molar Ratio

The effect of the molar ratio of DA and DEG on the polymerization reaction in the presence and absence of catalyst was studied by estimating the acid number at various time intervals by keeping the other parameters constant. Different molar ratios, viz., 1:1, 1:1.3, 1:1.5, and 1:2 (DA:DEG), were taken, and the reactions were performed at 160 ± 1°C with a catalyst concentration 0.1 g% (when used). The pattern of decrease in acid numbers with increase in time in all the molar ratios was found to be similar. Figure 1 reveals that the acid number decreases as the concentration of DEG increases over DA in both the catalyzed and uncatalyzed reactions.

The molecular weight was found to increase gradually with time. The polyesters were obtained with molecular weight ranging from 1000 to 5000. Due to the volatility of glycols, some portion of the initial charge may be lost by distillation. Consequently, a limitation of the molecular weights of the products was observed. Therefore, a slight excess of glycol over DA favors polyesterification. In addition, it provides hydroxy-terminated polyesters which may find application as polyurethane precursors.

Effect of Catalyst Concentration

The direct polyesterification reactions are known to be acid-catalyzed. In the absence of catalyst, a second molecule of the acid undergoing esterification functions as a catalyst, but because of the reduction in the concentration of the acid with increasing conversion, other catalysts are often employed to maintain the rate of the reaction. p-Toluene sulfonic acid has been found to be an effective catalyst, and its effect on the polyesterification of DA and DEG (equimolar) was performed by varying its concentration, viz., 0.05, 0.075, 0.1, and 0.2 g%, at 160 ± 1°C. The reaction time was found to decrease remarkably in the presence of catalyst. Table 1 shows that catalyst addition almost doubles the rate as well as the molecular weight of the polyester. The rate of polyesterification was found to increase with an increase in catalyst concentration. The rate of polyesterification was found to be
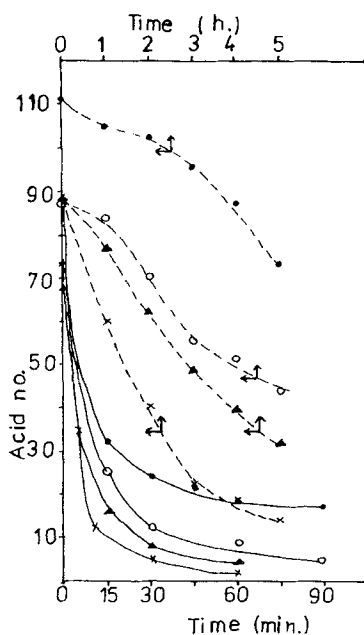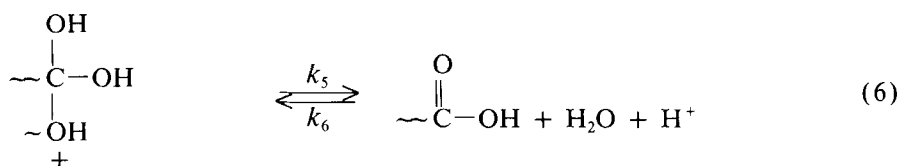
FIG. 1.   Acid number vs time for the catalyzed (——) and uncatalyzed (---) polyesteri-
fication of DA and DEG at varying molar ratios [(●) 1:1, (○) 1:1.3, (▲) 1:1.5, and (×)
1:2] at 160 ± 1°C.

TABLE 1.   Variation of Acid Number and Molecular Weight (in parenthesis)
with Time at Different Concentrations of p-Toluene Sulfonic Acid at
Equimolar Concentrations of DA and DEG

Catalyst concentration, g%	Time (min)						
	0	5	15	30	45	60	90
0.05	82	48	37	31	29	26	24
	(1100)	(1900)	(2460)	(2950)	(3100)	(3500)	(3780)
0.075	89	62	35	27	25	21	20
	(1000)	(1460)	(2600)	(3370)	(3600)	(4300)	(4500)
0.10	83	—	32	24	22	18	16
	(1100)		(2900)	(3800)	(4000)	(5000)	(5700)
0.20	92	55	28	24	18	12	—
	(1000)	(1650)	(3200)	(3800)	(5000)	(7500)	

maximum at a 0.2 g% concentration of p-toluene sulfonic acid. At this concentration of catalyst the molecular weight of polyester reached 7500 within an hour (Table 1). Polyesterification between DA and BD [7] has been found to be an acid-catalyzed reaction, and a plausible mechanism may be represented as

$$\underset{\overset{\|}{\underset{\text{—C—OH}}{O}}}{} + \text{HA} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{\overset{\substack{\text{OH}\\|}}{\underset{+}{\text{—C—OH}}}}{} + \text{A}^- \tag{4}$$

$$\underset{\overset{\substack{\text{OH}\\|}}{\underset{+}{\text{—C—OH}}}}{} + \sim\!\text{OH} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \underset{\underset{\underset{+}{\sim\!\text{OH}}}{\overset{\substack{\text{OH}\\|}}{\text{—C—OH}}}}{} \tag{5}$$

$$\underset{\underset{\underset{+}{\sim\!\text{OH}}}{\overset{\substack{\text{OH}\\|}}{\text{—C—OH}}}}{} \underset{k_6}{\overset{k_5}{\rightleftharpoons}} \underset{\overset{\overset{O}{\|}}{\text{—C—OH}}}{} + \text{H}_2\text{O} + \text{H}^+ \tag{6}$$
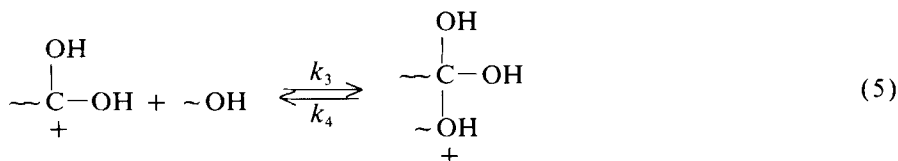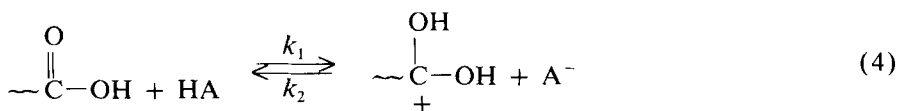
where — and ~ are used for all DA and DEG species, respectively. The proton-catalyzing Eq. (4) comes from pTSA in the case of catalyzed polyesterification. This may be the reason for the increase in reaction rate with an increase in p-toluene sulfonic acid as a catalyst.

Effect of Temperature

The rate of polymerization is found to be influenced remarkably by the reaction temperature. The effect of temperature on the course of polyesterification was studied at various temperatures, viz., 160, 180, 200, and 220°C, by using equimolar concentrations of DA and DEG. The rate of reaction was found to increase with an increase in temperature. At higher temperatures (220°C) the system has an extent of reaction of 0.84 and DP = 6.4 within 5 hours. For the uncatalyzed polyesterification, $1/(1 - p)$ and $1/(1 - p)^2$ have been plotted graphically against time using the least-squares method. The best linear plots were obtained by plotting $1/(1 - p)$ vs time, which indicates that the reaction satisfies second-order kinetics (Fig. 2a). pTSA-catalyzed polyesterification shows a somewhat different behavior. The reaction rate was found to be very fast compared to the uncatalyzed reaction. For the pTSA-catalyzed polyesterification, $1/(1 - p)$ and $1/(1 - p)^2$ were plotted graphically against time using the least-squares method. The best linear plots were obtained by plotting $1/(1 - p)^2$ against time, which indicates that catalyzed polyesterification follows third-order kinetics (Fig. 2b). The rate constants for both uncatalyzed and catalyzed polyesterification reactions have been calculated, and these values are presented in Table 2. The Arrhenius equation was found to be obeyed satisfactorily since good straight lines were obtained when log k were plotted vs $1/T$, as shown in Fig. 2. The energies of activation (ΔE_a) of the uncatalyzed and catalyzed reactions are found to 23.03 and 14.17 kcal·mol^{-1}, respectively. It appears that the uncatalyzed reaction is slower than the catalyzed one, in spite of the fact that ΔE_a is less in the former case. The entropy of activation (ΔS) was also
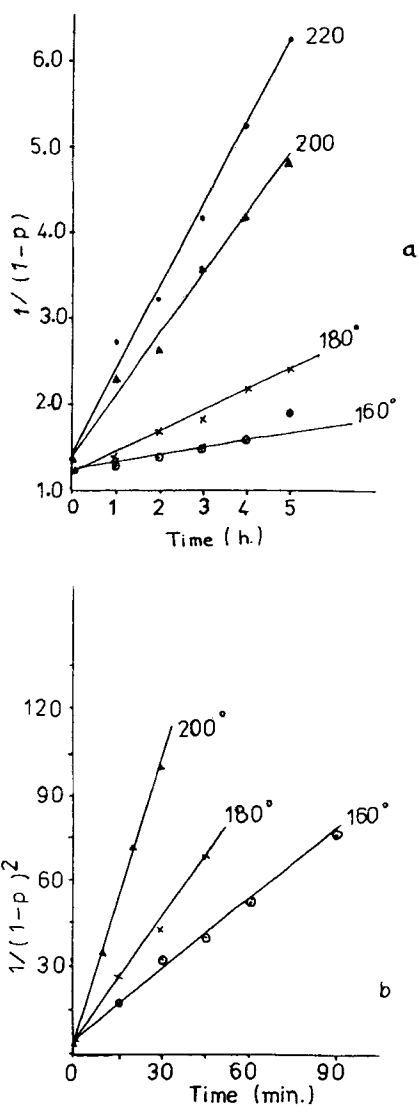
FIG. 2. (a): $1/(1 - p)$ vs time for the uncatalyzed polyesterification of DA:DEG (1:1) at different temperatures. (b): $1/(1 - p)^2$ vs time for the catalyzed polyesterification of DA:DEG (1:1) at different temperatures.

TABLE 2. Velocity Constants and Activation Parameters for Uncatalyzed and Catalyzed Polyesterification of DA and DEG (1:1)

Reaction	$k \times 10^3 \, \text{mol} \cdot \text{dm}^{-1} \cdot \text{s}^{-1}$				E_a, kcal·mol^{-1}	S, kcal·mol^{-1}
	160°C	180°C	200°C	220°C		
Uncatalyzed	0.035	0.069	0.198	0.277	14.17	−32.25
Catalyzed	5.28	22.2	52.38	—	23.03	−28.45

TABLE 3. Intrinsic Viscosities and Molecular Weights of Polyester Resin (DA:DEG = 1:1, 160 ± 1°C)

Reaction	Molecular weight	Time	$[\eta]$
Uncatalyzed	1250	5 h	0.08
Catalyzed	5700	90 min	0.144

found to increase (calculated at 180°C) for the reaction involving charged catalyst (Table 2). These results are in agreement with similar results obtained by various workers [13–15]. The low negative values of ΔS may be due to the higher viscosity of the reaction medium involving catalyst.

The intrinsic viscosity of the polyesters resulting from the equimolar reaction of DA:DEG in the absence and presence of catalyst at 160 ± 1°C was calculated (Table 3). The corresponding increase in intrinsic viscosity with an increase in molecular weight is a normal phenomenon.

The resulting polyesters are dark brown resins which are easily soluble in acetone, benzene, and chloroform, and insoluble in DMF and DMSO.

CONCLUSION

The polyesterification of DA and DEG in the presence of pTSA catalyst results in the synthesis of poly(diethylene glycol) dimerate polyester resins, which may find applications as plasticizers or polyurethane precursors.

ACKNOWLEDGMENT

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