Synthesis of Plasticizing Polyesters of Dimer Acid and Propane–Diol

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SYNOPSIS

The polyesterification of dimer acid with propane–diol under different experimental conditions has been studied to obtain the optimum conditions for synthesizing the poly(propane–diol)dimerate plasticizers. The effect of varying molar ratio, temperature, and catalyst concentration on the course of the reaction, acid number, intrinsic viscosity, and molecular weight of the resultant polyester has been investigated. p-Toluene sulfonic acid (PTSA) was found to be an effective catalyst for the polyesterification reaction. The kinetics of polyesterification in the presence and absence of a catalyst has been found to follow the second-order rate equation in equimolar concentrations of the reactants. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Polyesters have found extensive applications as plasticizers in industrial applications. The polymeric plasticizers are less volatile and more resistant to solvent extraction than are the conventional monomeric plasticizers.

Bifunctional esterification necessarily leads to low molecular weight ($< 10,000$), linear, saturated polyesters, which are useful as plasticizers. Polyester plasticizers are normally prepared by a diol–dicarboxylic acid condensation. Many workers have reported the preparation of polyesters with glycols and aliphatic diacids.[1-3] The kinetics of polyesterification of dibasic acids and glycols have been reported by various authors.[4-6]

Cyclic dimer acids have rarely been studied for polyesterification reactions.[7] We have recently studied the polyesterification between dimer acid and various diols.[8,9] Dimer acid (DA),[7] a cyclic dicarboxylic acid, is a light yellow-colored viscous and sticky liquid. It is actually a mixture of dibasic acids with 18 C atoms in length per carboxylic group and other mono- and polybasic fractions. DA may be represented as HOOC———D———COOH:

$$CH_3(CH_2)_5CH \underset{CH-CH}{\overset{CH=CH}{<>}} CH-(CH_2)_7-COOH$$
$$CH_3(CH_2)_5-HC=HC \qquad (CH_2)_7COOH$$

Dimer Acid

where D is a C-34 divalent hydrocarbon radical. It does not crystallize and contributes to the flexibility in polymers derived from it. In the present article, we report the synthesis of polyesters of DA and propane–diol (PD). The effect of varying molar ratio, catalyst, and temperature on acid number, intrinsic viscosity, and molecular weight of the resulting polyesters and the kinetics of polyesterification have been studied.

EXPERIMENTAL

Reagents

All chemicals used were of AnalaR grade. The dimer acid 1010, a gift from Vikram Sarabhai Space Centre, Trivandrum, India, was used without further purification. It had the following composition: 98% DA + 2% trimer acid, and it was a dimer of ricinoleic acid. 1,3-Propane–diol (E. Merck) was of A.R. grade. Methanolic NaOH ($0.1N$) was standardized by titrating against $0.1N$ oxalic acid.

TECHNIQUE

The apparatus, technique, and formula for calculating the acid number and molecular weight were identical to those by Bajpai et al.[8]

The polyesterification was carried out by taking the calculated amount of DA, PD, and catalyst (when used) at 160 ± 0.1°C under an oxygen-free N_2 atmosphere. The reaction was followed by estimating the unreacted carboxyl end groups left in aliquots of hot resin ($\simeq$ 0.2 g) withdrawn at fixed time intervals. The increase in molecular weight during the course of the polyesterification reaction was studied by end-group analysis.[10] The molecular weight of the polyester is calculated by multiplying the molecular weight of the monomer by the degree of polymerization (D_p). The D_p of the product may be represented by eq. (1) (Refs. 11 and 12):

$$D_p = (1 + r)/[2r(1 - p) + (1 - r)] \quad (1)$$

If this polymer, in general, is represented as an A-A-B-B type, then r is the ratio of A-A to B-B molecules and p is the extent of the reaction or the fraction of end groups that has already reacted at that particular time, i.e.:

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

where N_0 is the amount of the carboxylic group initially present (acid number), and N, the quantity left after a given interval of time. For complete conversion of reactive groups (i.e., when $p = 1$), eq. (1) reduces to $D_p = (1 + r)/(1 - r)$. Thus, an excess

of either glycol or dicarboxylic acid regulates the molecular weight of the resulting polymer and the nature of the end groups. 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[13]

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

$[\eta]$ is the intrinsic viscosity and η_r, the specific viscosity at C, which is the concentration of the polymer solution.

RESULTS AND DISCUSSION

Effect of Varying Molar Ratio (DA : PD) on Acid Number and Molecular Weight

The effect of the molar ratio (DA : PD) in the absence of the catalyst on the polyesterification reaction was studied at different molar ratios, viz., 1 : 1, 1 : 1.1, 1 : 1.2, 1 : 1.3, 1 : 1.4, and 1 : 1.5 (DA : PD), keeping the other parameters constant. It was observed that acid number decreases in a regular manner as the reaction proceeds and becomes constant when the reaction proceeds toward completion (Table I).

Table I shows that the acid number decreases as the concentration of PD increases over DA. The molecular weight was found to increase gradually with time.

Table I   Variation of Acid Number, Molecular Weight (in Parentheses), and Intrinsic Viscosity [η] with Time at Different Molar Ratios of DA and PD at Temp 160 ± 0.1°C

Sample No.	Molar Ratio DA : PD	Time (in h)						[η]
		0	1	2	3	4	5	
1	1 : 1	121	115	100	95	84	82	0.057
		(736)	(774)	(890)	(937)	(1060)	(1100)	
2	1 : 1.1	97	87	82	75	—	65	0.041
		(910)	(1000)	(1061)	(1154)		(1300)	
3	1 : 1.2	124	101	89	85	79	73	0.061
		(727)	(872)	(974)	(1000)	(1100)	(1153)	
4	1 : 1.3	135	115	108	91	64	—	0.081
		(683)	(780)	(822)	(947)	(1250)		
5	1 : 1.4	118	116	91	88	82	78	0.060
		(767)	(780)	(950)	(965)	(1000)	(1056)	
6	1 : 1.5	120	108	93	74	66	61	0.061
		(760)	(830)	(922)	(1100)	(1169)	(1230)	
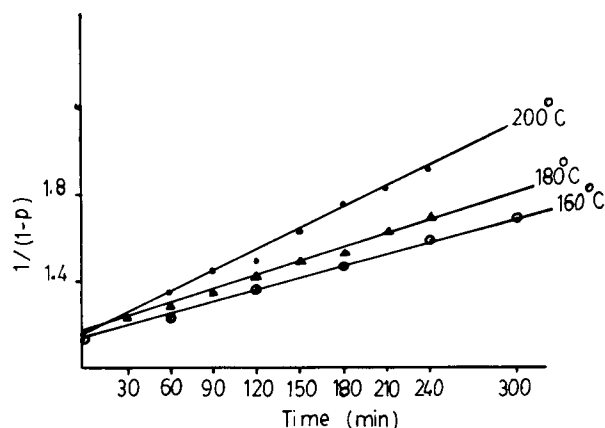
Figure 1 Plots representing $1/(1 - p)$ vs. time of uncatalyzed polyesterification of DA and PD.

Effect of Catalyst

The degree of polyesterification ($D_p = 1/1 - p$) vs. time shows that uncatalyzed polyesterification requires quite a long time to reach a high degree of polymerization (Fig. 1). Greater success is achieved by adding to the system a small amount of catalyst, whose concentration was constant throughout the reaction. The rate of polyesterification of DA with PD was found to be influenced highly by the catalyst type and concentration.

p-Toluene sulfonic acid has been found to be an effective catalyst and its effect on the polyesterification reaction was studied using 0.025, 0.05, 0.075, 0.10, and 0.25 g % of the catalyst and a molar ratio of 1 : 1.3 (DA : PD) and a temperature of 160 ± 0.1°C. Reaction time was found to decrease remarkably in the presence of the catalyst (Table II).

The molecular weight of the resulting polyester was found to increase with increase in catalyst concentration.

The effect of the catalyst was also studied by keeping its concentration and other parameters constant, i.e., using 0.075 g % and varying the molar ratios of DA : PD in the range of 1 : 1, 1 : 1.1, 1 : 1.2, 1 : 1.3, 1 : 1.4, 1 : 1.5, etc. The acid number was found to decrease with time in all runs. The molecular weight of the resulting polyesters was found to increase with time (Table III). It has been found that the catalyst addition almost doubles the reaction rate as well as the molecular weight of resulting polyester.

Effect of Temperature

We studied the polycondensation reaction between DA and PD at various temperatures, viz., 140, 160, 180, and 200°C. The rate of reaction of both catalyzed and uncatalyzed reactions were found to increase with increase in temperature, as is apparent from the k values in Table IV. At 140°C, the reaction in the absence of the catalyst is extremely slow in obtaining the oligoesters of the desired molecular weight, as is evidenced by the negligible decrease in carboxyl groups even after 4 h. On the other hand, in presence of catalyst at 140°C, the reaction is not as slow as that of the uncatalyzed one and it is also not of the same order as that of reactions at other temperatures. On plotting log k vs. $1/T$, the value of log k at 140°C does not lie on the straight line (Fig. 2).

At other temperatures, viz., 160, 180, and 200°C, the reaction is relatively fast. In the presence of 0.05

Table II Variation of Acid Number and Molecular Weight (in Parentheses) with Time at Different Concentrations of p-toluene Sulfonic Acid, Keeping the Molar Ratio DP : PD Constant at 1 : 1.3

Sample No.	Catalyst Concentration	Time (in h)					
		0	1	2	3	4	5
1	0.025	114	98	78	53	38	32
		(800)	(930)	(1100)	(1450)	(1800)	(2000)
2	0.050	118	82	78	52	40	32
		(763)	(1030)	(1070)	(1450)	(1740)	(2000)
3	0.075	118	59	45	—	30	25
		(763)	(1330)	(1600)		(2100)	(2300)
4	0.100	120	61	39	27	—	26
		(750)	(1300)	(1800)	(2200)		(2260)
5	0.250	117	51	33	31	30	—
		(800)	(1500)	(2000)	(2042)	(2100)	

Table III   Variation of Acid Number, Molecular Weight (in Parentheses), and Intrinsic Viscosity with Time at Different Molar Ratios of DA and PD at a Fixed Catalyst Concentration (0.075 g%) at Temp 160 ± 0.1°C

Sample No.	Molar Ratio DA : PD	Time (in h)						$[\eta]$
		0	1	2	3	4	5	
1	1 : 1	124	98	79	75	68	59	0.090
		(720)	(908)	(1127)	(1190)	(1310)	(1530)	
2	1 : 1.1	119	106	87	72	63	59	0.08
		(750)	(840)	(1030)	(1197)	(1352)	(1440)	
3	1 : 1.2	127	78	52	41	38	36	0.10
		(716)	(1100)	(1500)	(1830)	(1930)	(2000)	
4	1 : 1.3	118	58	45	—	30	25	0.13
		(763)	(1330)	(1600)		(2100)	(2300)	
5	1 : 1.4	129	78	—	51	35	28	0.11
		(700)	(1060)		(1400)	(1800)	(2000)	
6	1 : 1.5	123	88	50	47	38	35	
		(760)	(1000)	(1400)	(1440)	(1600)	(1700)	

g % of p-toluene sulfonic acid and at 200°C, a very viscous polyester is obtained that is not completely soluble in acetone, the solvent we used for determining acid number. Therefore, we found 160°C to be a suitable temperature for the study of various effects on polyesterification of DA and diols.

The rate of reaction follows the second-order kinetics in both the reactions, i.e., uncatalyzed and catalyzed polyesterification (Fig. 1). The energies of activation ΔE_a of the uncatalyzed and catalyzed reactions were found to be 9.8 and 10.4 kcal/mol, respectively, as calculated from the Arrhenius eq. (5). On comparing the rate of the uncatalyzed reaction with that of catalyzed one, it was found that the reaction rate in the former case is much slower than that in the latter case, even though the activation energy is almost the same. The results clearly indicate that the frequency factor in the Arrhenius equation is much greater for the reaction involving a charged catalyst and is quite apparent from the plots drawn between log k and $1/T$ (Fig. 3).

Table IV   Velocity Constants and Energies of Activation for Uncatalyzed and Catalyzed Polyesterification of DA and PD

	$k_2 \times 10^8$ mol dm³ s⁻¹			
	160°C	180°C	200°C	E* kcal mol⁻¹
Uncatalyzed	3.66	5.29	9.12	9.8
Catalyzed	10.66	17.45	31.13	10.4

Change in Intrinsic Viscosity during the Course of the Polyesterification Reaction

The intrinsic viscosity of the resulting polyesters using different molar ratios of DA : PD in the absence and presence of catalyst was calculated and is shown, respectively, in Tables I and III. The increase in intrinsic viscosity corresponds to an increase in molecular weight due to the variation in the molar ratio of DA : PD, which is a normal phenomenon.
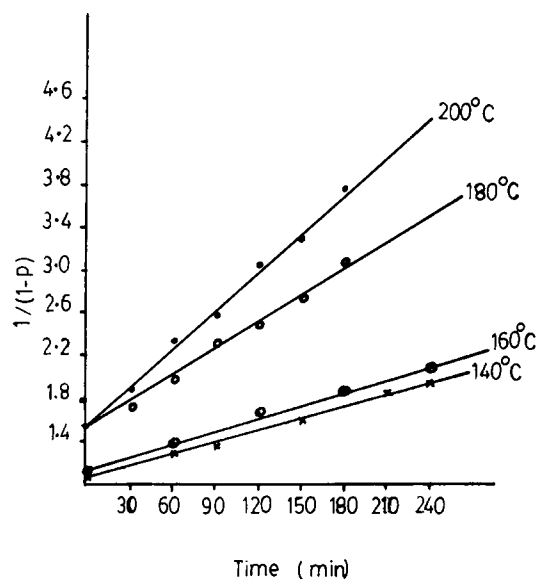
Figure 2   Plots representing $1/(1 - p)$ vs. time of catalyzed polyesterification of DA and PD.
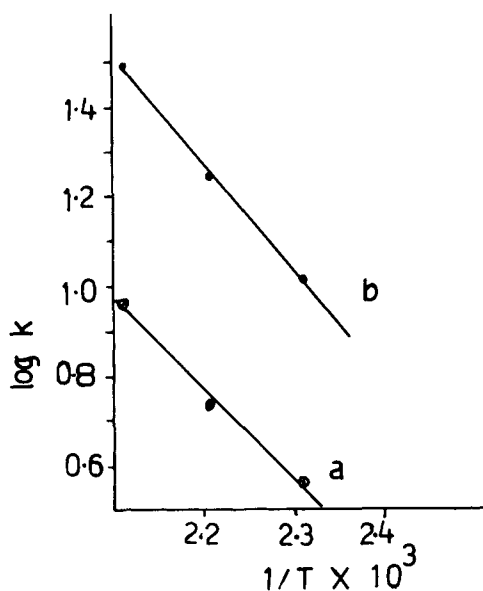
Figure 3 Plots representing $1/T$ vs. log k: (a) uncatalyzed polyesterification; (b) catalyzed polyesterification.

CONCLUSION

Thus, the desired molecular weight plasticizing polyesters may be synthesized using the proper concentration of dimer acid, propane–diol, and p-toluene sulfonic acid, which may find applications in surface coating, flexible foam formulations, etc.

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