

Plasticizing Polyesters of Dimer Acid and Butane Diol

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SYNOPSIS

The polyesterification reaction between dimer acid and 1,4-Butane diol under different experimental conditions has been studied to obtain the optimum conditions for synthesizing poly(1,4-butanediol)dimerate plasticizers. The effect of varying molar ratio and catalyst concentration on acid number, intrinsic viscosity, and molecular weight have been investigated. It has been found that *p*-toluene sulfonic acid is an effective catalyst for the polyesterification reaction. © 1992 John Wiley & Sons, Inc.

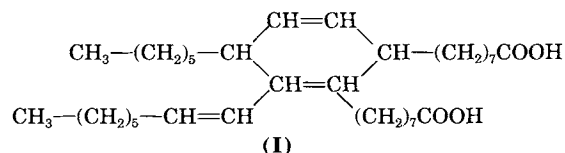
INTRODUCTION

Polyesterification reactions are very common in the polymer field and a large number of polyesters are commercially available. Cyclic dimer acids have rarely been studied for the polyesterification reactions.¹⁻³ Polyesters have found extensive applications as fibers, in surface coating, and as adhesives, polyurethanes, plasticizers, etc. Polyester plasticizers are employed mainly in poly(vinyl chloride) compositions for use in applications where minimal plasticizer loss is required. The polymeric plasticizers are less volatile and are more resistant to solvent extraction than are conventional monomeric plasticizers.

Bifunctional esterification necessarily leads to low molecular weight (< 10,000), linear, saturated polyesters that are used as plasticizers. Polyester plasticizers are usually prepared by diol-dicarboxylic acid condensation. Many workers have reported the preparation of polyesters with glycols and unsaturated dibasic acids.¹⁻³ We have undertaken the study of the synthesis of polyesters using dimer acid and diols, which may find applications as plasticizers.

Dimer acid (DA)⁴ (I), a cyclic dicarboxylic acid, is a light yellow-colored viscous and sticky liquid.

These polybasic acids are actually mixtures 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:



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

EXPERIMENTAL

Reagents

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 was a dimer of ricinoleic acid. 1,4-Butane diol (Ferek, Berlin, Germany) was used as such. Alcoholic KOH (0.1N) was standardized by titrating against 0.1N oxalic acid.

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Technique

The apparatus, technique, and formula for calculating the acid number and molecular weight were identical to those by Bajpai et al.⁵ A reaction mixture containing the calculated amount of DA, BD, and *p*-toluene sulfonic acid as catalyst (when used) was kept at $160 \pm 0.1^\circ\text{C}$, under an oxygen-free nitrogen atmosphere. After fixed intervals of time, aliquots (≈ 0.2 g each) of hot resin were withdrawn for acid group determination. This reaction was continued for 5 h. The polyester obtained was a viscous liquid of dark brown color.

The increase in molecular weight during the course of polyesterification reaction has been studied by end-group analysis.⁶ The molecular weight of the polymer is calculated by multiplying the molecular weight of the monomer by the degree of polymerization D_p . The degree of polymerization of the product for polyesterification may be represented by eq. (1)^{7,8}:

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

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 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 carboxylic group initially present (acid number) and N is 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 by noting the efflux time of the pure solvent (benzene) and of the polymer solution through a capillary tube viscometer at 28°C . The specific viscosity at zero polyester concentration was calculated by extrapolating the curve plotted between n_{sp} vs. concentration and this was considered as the intrinsic viscosity.⁹

RESULTS AND DISCUSSION

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

The effect of molar ratio (DA : BD) on the polymerization reaction in absence of the catalyst was studied by estimating the acid number at various time intervals, keeping other parameters constant. Different molar ratios, viz., 1 : 1, 1 : 1.1, 1 : 1.2, 1 : 1.3, 1 : 1.4, and 1 : 1.5 (DA : BD), were taken. It was observed that acid number decreases in a regular manner as the reaction proceeds and becomes constant when the reaction reaches toward completion. Results are given in Table I.

Table I indicates that the acid number decreases as the concentration of BD increases over DA. The molecular weight was found to increase gradually with time. The reactants with molar ratios up to 1 : 1.2 (DA : BD) give polyesters having molecular

Table I Variation of Acid No., Molecular Weight (Given in Parentheses), and Intrinsic Viscosity with Time at Different Molar Ratios of DA and BD; Temp. $160 \pm 0.1^\circ\text{C}$

Sample No.	Molar Ratio DA : BD	Time (in h)						[η]
		0	1	2	3	4	5	
1	1 : 1	155.37	92.40	64.97	48.15	35.81	30.63	—
		(850)	(1400)	(2000)	(2600)	(3500)	(4100)	
2	1 : 1.1	149.22	62.24	57.12	43.63	33.85	27.18	0.046
		(850)	(1800)	(2000)	(2500)	(3100)	(3600)	
3	1 : 1.2	147.70	75.49	48.85	34.71	30.85	25.41	0.044
		(850)	(1500)	(2100)	(2700)	(2900)	(3200)	
4	1 : 1.3	138.68	73.86	44.07	32.18	29.38	21.03	0.024
		(900)	(1500)	(2000)	(2400)	(2600)	(3000)	
5	1 : 1.4	122.65	55.49	38.98	28.28	19.83	16.84	—
		(980)	(1700)	(2000)	(2400)	(2700)	(2900)	
6	1 : 1.5	105.03	65.50	36.46	26.44	18.73	15.45	0.013
		(1100)	(1500)	(2000)	(2200)	(2500)	(2600)	

Table II Variation of Acid No. and Molecular Weight with Time at Different Concentrations of *p*-Toluene Sulfonic Acid (Catalyst), Keeping Molar Ratio DA : BD Constant at 1 : 1.3

Sample No.	Catalyst Concentration (g %)	Time (in min)					
		0	30	60	90	120	150
1	0.006	130.60 (950)	99.11 (1200)	69.10 (1500)	61.78 (1600)	38.14 (2200)	28.93 (2600)
2	0.025	84.15 (1300)	46.79 (2000)	27.56 (2600)	15.26 (3300)	9.61 (3900)	6.30 (4200)
3	0.05	129.17 (950)	45.95 (2000)	22.44 (2900)	14.85 (3400)	7.88 (4000)	4.20 (4500)
4	0.10	150.00 (800)	66.35 (1600)	33.12 (2400)	14.09 (3500)	11.9 (3700)	6.36 (4200)

weight in the range 1000–4000. At molar ratio 1 : 1.3, the molecular weight of the resulting polyester was almost the same as found in the 1 : 1.2 molar ratio. On further increasing of the concentration of BD over DA, the molecular weight of the polyester was lowered.

In the reactions of dicarboxylic acids with glycols, the latter are relatively volatile and some portion of the initial charge may be lost by the distillation of the glycol with liberated steam with the consequent limitation of molecular weight of the resulting polyester. Therefore, a slight excess of BD over DA favors the polyesterification. The excess of BD over DA in the system restricts the formation of a homogeneous mixture and, thus, inhibits the normal process of polyesterification, and this may be the reason for low molecular weights at higher concentration of BD.

Effect of Catalyst

The direct polyesterification is self-catalyzed by carboxylic groups of the acid components, but because of the reduction in the concentration of these groups with the increasing conversion, other catalysts are often employed to maintain the rate of the reaction. The rate of polycondensation reaction between DA and BD was found to be influenced by the type of the catalyst and its concentration.

The effect of various catalysts that are commonly used for the polyesterification reaction such as antimony trioxide, calcium acetate, and sulfonic acids was studied on the polycondensation reaction between DA and BD. We found that antimony trioxide as well as calcium acetate do not effect the rate at all in our studies and only *p*-toluene sulfonic acid has been found to be an effective catalyst. The effect

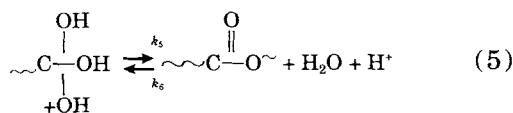
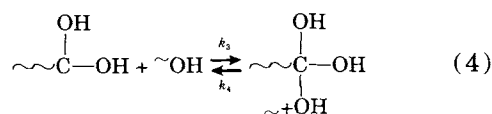
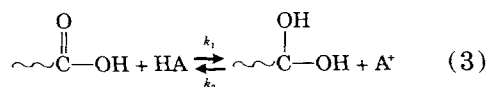
Table III Variation of Acid No. and Molecular Weights with Time at Different Molar Ratios of DA and BD at Fixed Concentration of *p*-Toluene Sulfonic Acid (0.05 g %) Catalyst

Sample No.	Molar Ratio DA : BD	Time (in h)				
		0	1	2	3	4
1	1 : 1	168.19 (750)	159.39 (900)	125.24 (1000)	73.16 (1700)	43.52 (2900)
2	1 : 1.1	162.43 (790)	151.8 (800)	111.46 (1100)	55.46 (2000)	41.78 (2600)
3	1 : 1.2	152.26 (800)	96.46 (1200)	60.10 (1800)	28.07 (3000)	16.39 (4000)
4	1 : 1.3	129.17 (900)	45.95 (2000)	27.56 (2600)	15.26 (3400)	9.61 (3900)
5	1 : 1.4	151.20 (800)	95.34 (1200)	44.61 (1900)	17.77 (2800)	15.77 (2900)
6	1 : 1.5	156.86 (800)	146.52 (850)	73.83 (1400)	63.36 (1500)	40.39 (1900)

of the *p*-toluene sulfonic acid on the polyesterification reaction was studied by using 0.006, 0.025, 0.05, and 0.1 g % at the fixed molar ratio of 1 : 1.3 (DA : BD) and temperature $160 \pm 0.1^\circ\text{C}$. Table II shows the variation of acid number with time corresponding to different catalyst concentrations. Reaction time was found to decrease remarkably in the presence of this catalyst. The molecular weight of the resulting polyester was found to increase with an increase in catalyst concentration. The polyester of desired molecular weight was obtained in the catalyst concentration of 0.025–0.05 g %.

The effect of catalyst was also studied by keeping its concentration constant and varying the molar ratio between DA and BD. The results have been shown in Table III. The molar ratios of DA : BD were varied from 1 : 1 to 1 : 1.5, keeping the catalyst concentration fixed at 0.05 g % and other parameters constant. The acid number was found to decrease with time in all the runs. The molecular weight of the resulting polyester was found to increase with time, its value being dependent on the amount of BD used. Polyester having a maximum molecular weight (around 4000) was obtained when the molar ratio of 1 : 1.3 (DA : BD) was used. On further increasing the concentration of BD over DA, the molecular weight of polyester was lowered. In presence of the catalyst, a slight excess of BD over DA also favors the polyesterification reaction, whereas excess of BD inhibits normal polyesterification.

Since the polyesterification is a well-known acid-catalyzed reaction, the polyesterification of DA and BD may also follow the same course of esterification:



In the above equations, \sim and \sim are used for all DA and BD species. The proton catalyzing eq. (3) comes from *p*-toluene sulfonic acid in the case of catalyzed polyesterification. The formation of half-ester [eq. (4)] is a rapid process and is supported by the rapid drop in acid numbers to nearly

half in the first 60 min. The polycondensation occurs by the repetition of reaction (5).

Effect of Varying Molar Ratio on the Intrinsic Viscosity

The change in intrinsic viscosity of the resulting polyesters during the course of polyesterification was studied by varying the molar ratio of DA : BD and the results are shown in Table I. The increase in intrinsic viscosity corresponds to the increase in molecular weight due to the variation in molar ratio of DA : BD, which is a normal phenomenon.

Effect of Temperature

Normally polyesterification reactions are being studied in the temperature range of $150\text{--}285^\circ\text{C}$. We studied the polycondensation reaction between DA and BD at 120, 140, 160, and 200°C to determine the optimum temperature for this reaction. At 120 and 140°C , the reaction is very very slow to get the oligoesters of the desired molecular weight. At 200°C , this reaction in the presence of catalyst is relatively very fast. In the presence of 0.05 g % of *p*-toluene sulfonic acid and at 200°C , a very viscous polyester is obtained within 1 h. This polyester is not completely soluble in acetone—the solvent that we used for determining acid number. Therefore, for our studies, we found that the temperature 160°C was quite suitable for both self-catalyzed and catalyzed reactions.

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