

# Synthesis and Characterization of Saturated and Unsaturated Copolyesters Based on Bis-1,4-(dicarboxymethoxy) Benzene

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## SYNOPSIS

Saturated copolyester were prepared by copolyesterification of bis-1,4-(dicarboxymethoxy) benzene and phthalic anhydride with diethylene glycol, triethylene glycol, tetraethylene glycol 1,4-butane diol, 1,2-propane diol, and 1,6-hexamethylene glycol. Also, unsaturated copolyesters were prepared by copolyesterification of bis-1,4-(dicarboxymethoxy) benzene and maleic anhydride with the same glycols. All the copolyester resins obtained have been characterized and unsaturated copolyesters in the form of films were determined. IR and <sup>1</sup>H-NMR spectroscopy were used for both qualitative and quantitative analysis of the copolyesters resins and their hydrolyzate products, after curing with styrene. © 1992 John Wiley & Sons, Inc.

## 1. INTRODUCTION

Saturated and unsaturated polyesters<sup>1,2</sup> are conveniently prepared by melt copolyesterification at elevated temperatures above the melting point of the resulting polyesters. Curing of the unsaturated polyesters with styrene to form solid thermoset materials may have markedly improved properties.<sup>1,3</sup> It was stated previously<sup>4,5</sup> that some polyesters were prepared based on bis-1,3-(dicarboxymethoxy) benzene. The work is now extended to find the optimal general conditions for the preparation of a number of copolyesters based on the condensation of bis-1,4-(dicarboxymethoxy) benzene, phthalic anhydride, and maleic anhydride with some glycols. Further, the aim was to investigate the reactions between the unsaturated copolyesters and styrene.

## 2. EXPERIMENTAL

### 2.1. Materials

Maleic anhydride, phthalic anhydride, hydroquinone, monochloroacetic acid, sodium hydroxide, and

sodium carbonate were pure-grade products of Merck Co. (Germany) and were used directly. Glycols (diethylene, triethylene, tetraethylene, 1,4-butane, 1,2-propylene, and 1,6-hexamethylene) were products of E. Merck, Darmstadt. All solvents used were of A.R. or equivalent grade.

### 2.2. Preparation of Bis-1,4-(dicarboxymethoxy) Benzene

Bis-1,4-(dicarboxymethoxy) benzene<sup>6</sup> was prepared by the reaction of hydroquinone with chloroacetic acid and the product was recrystallized twice from water; mp was 250–252°C.

### 2.3. Polyesterification Reactions

Copolyesterification of bis-1,4-(dicarboxymethoxy) benzene (0.2 mol), phthalic anhydride (0.2 mol), and glycol (0.4 mol) were carried out by heating the reaction mixture in the presence of oxygen-free nitrogen. Unsaturated copolyesters of bis-1,4-(dicarboxymethoxy) benzene, maleic anhydride, and glycol were prepared and purified in the same manner. The time–temperature program for each copolyester is illustrated in Table I. The copolyesters prepared were purified twice from chloroform solution by precipitating with light petroleum and then dried under reduced pressure.

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**Table I** Time-Temperature Programs for the Copolyesters (I-XII)

Temp	Time (h)											
	Saturated Copolyesters						Unsaturated Copolyesters					
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII
90	1	1	—	1	—	1	—	—	—	—	—	—
110	1	1	1	1	1	1	1	1	—	—	—	—
120	1	1	—	—	1	1	1	1	—	1	—	—
130	—	1	1	1	—	—	1	1	—	1	—	—
140	1	—	—	—	1	1	1	1	—	1	1	—
150	1	1	1	1	—	1	1	1	—	1	1	—
160	1	1	1	—	1	—	1	1	1	1	1	—
170	1	—	—	1	—	1	1	1	1	1	1	1
180	1	1	1	1	1	1	1	1	1	1	1	1
190	1	1	1	1	1	1.5	1	1	1	1	1	1
200	1.5	1.5	1	1	1	—	1	1	1	1	1	1
210	—	—	1	—	1	—	—	1	1	—	—	1
220	—	—	—	—	—	—	—	1	—	—	—	—

#### 2.4. Curing of Unsaturated Copolyester Resins with Styrene

The unsaturated polyester prepared in each case was copolymerized<sup>7</sup> with styrene, in the molar ratio of 70 : 30, using benzoyl peroxide as a free radical initiator (1%) and dioxane as solvent. The cured copolyesters were cast as films on glass and tin plates. The plates were stored at 70°C for 24 h, at 100°C for 24 h, at 120°C for 5 h, and, finally, at 150°C for 5 h. The films were tested for resistance to acid and alkali solutions<sup>8</sup> and to cold and hot water.<sup>9</sup>

The cured copolyesters were subjected to alkaline hydrolysis according to the method reported earlier.<sup>7</sup> The product in each case was characterized by studying its IR and <sup>1</sup>H-NMR spectra.

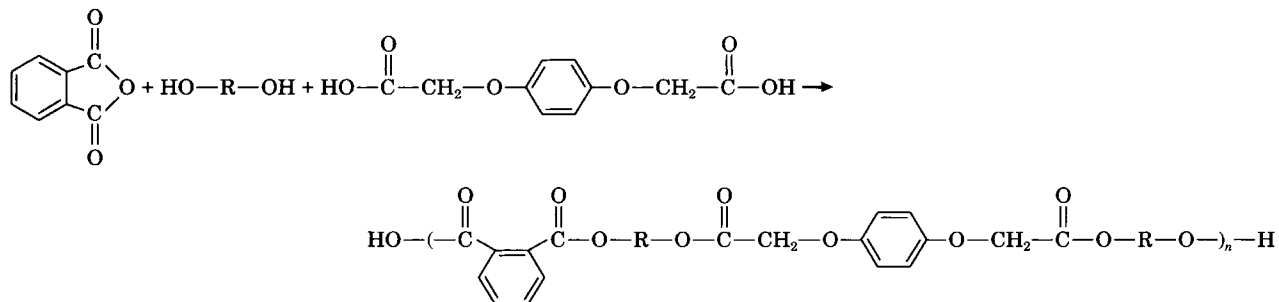
#### 2.5. Characterization of Polyesters

Viscosity measurements were carried out by an Ostwald viscometer using a 1% solution in dioxane at

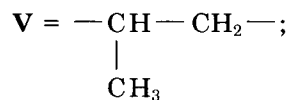
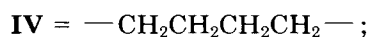
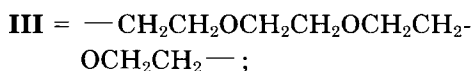
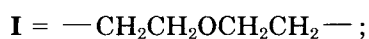
30°C. The molecular weight of the prepared copolyesters were determined by the end-group analysis for —COOH using KOH.<sup>10</sup> The infrared spectra were recorded by a Beckman 4220 infrared spectrophotometer. The proton magnetic resonance spectra (in CDCl<sub>3</sub> using TMS as reference) were measured with a Varian EM-390 spectrometer operating at 90 MHz.

### 3. RESULTS AND DISCUSSION

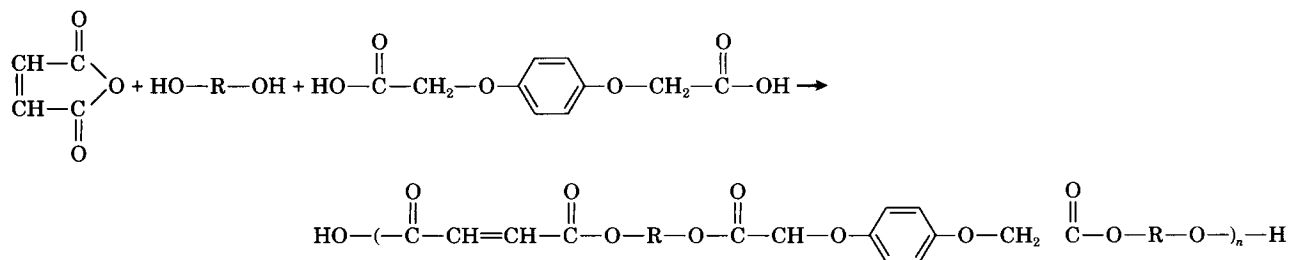
In the present work, saturated copolyesters (I-VI) were synthesized by the reaction of bis-1,4- (dicarboxymethoxy) benzene and phthalic anhydride with diethylene, triethylene, tetraethylene, 2,4-butylene, 1,2-propylene, and 1,6-hexamethylene glycols as follows:



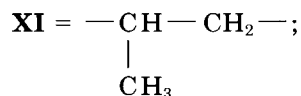
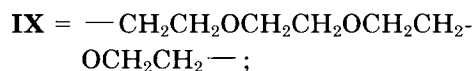
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Also, unsaturated copolyesters (VII–XII) were prepared by the reaction of bis-1,4-(dicarboxymethoxy) benzene and maleic anhydride with the same glycols, as follows:



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The prepared copolyesters (I–XII) were yellowish to dark brown viscous materials, soluble in var-

ious organic solvents except alcohol, *n*-hexane, and light petroleum. The copolyesters prepared showed greater resistance to gelation and remained soluble after long storage periods. Some of the physical properties of the prepared copolyesters are illustrated in Table II.

The structure of the prepared copolyesters (I–XII) was established from IR and <sup>1</sup>H-NMR spectra. The IR spectra of the prepared copolyesters (I–XII) show bands around 3485 cm<sup>-1</sup> (νOH), 2920 cm<sup>-1</sup> (νCH<sub>2</sub>), and 1720 cm<sup>-1</sup> (νC=O). The <sup>1</sup>H-NMR spectra (Table III) of the copolyesters (I–XII) were studied, and the method of Baddar et al.<sup>11</sup> was used in our present work for the quantitative analysis of these copolyesters by <sup>1</sup>H-NMR spectroscopy. The results of both qualitative and quantitative analysis

Table II Physical Properties of Saturated and Unsaturated Copolyester Resins

Polyester	Nature of Polyester	Mol. Wt.	Acid Value	<i>n</i>	Int. η
I	Viscous material	3325.51	40.57	7.2	0.050
II	Viscous material	4533.99	39.12	8.4	0.072
III	Viscous material	4994.40	22.49	9.1	0.054
IV	Viscous material	3467.46	42.40	7.8	0.066
V	Viscous material	5928.26	51.72	13.7	0.056
VI	Viscous material	4510.07	33.11	9.5	0.066
VII	Viscous material	2926.40	24.74	7.1	0.043
VIII	Viscous material	2134.6	17.70	4.7	0.056
IX	Viscous material	4778.88	4.24	9.6	0.041
X	Viscous material	3771.28	40.86	8.3	0.058
XI	Viscous material	2134.75	62.64	5.6	0.185
XII	Viscous material	4805.33	3.62	11.3	0.057

**Table III** <sup>1</sup>H-NMR Spectral Data of Saturated and Unsaturated Copolyesters (I–XII)

Polyester	Component	Chemical Shift (ppm)	Assignment	Peak Areas (Integration)	Relative Mol Amount	Mol %
<b>I</b>	Glycol	3.6 and 4.3	2(CH <sub>2</sub> OCH <sub>2</sub> ) and 4(CH <sub>2</sub> OC)    O	76	4.75	50.91
	Acid	4.5 and 6.7–7.8	2(OCH <sub>2</sub> C) and 8 Ar    O	55	4.58	49.09
<b>II</b>	Glycol	3.6 and 4.2	4(CH <sub>2</sub> OCH <sub>2</sub> ) and 4(CH <sub>2</sub> OC)    O	105	4.38	49.32
	Acid	4.5 and 6.7–7.9	2(OCH <sub>2</sub> C) and 8 Ar    O	54	4.5	50.68
<b>III</b>	Glycol	3.6 and 4.2	6(CH <sub>2</sub> OCH <sub>2</sub> ) and 6 (CH <sub>2</sub> OC)    O	117	3.25	50.00
	Acid	4.6 and 6.8–7.8	2(OCH <sub>2</sub> C) and 8 Ar    O	39	3.25	50.00
<b>IV</b>	Glycol	1.8 and 4.2	2(CH <sub>2</sub> ) <sub>2</sub> and 4(CH <sub>2</sub> OC)    O	135	8.44	51.08
	Acid	4.6 and 6.7–7.8	2(OCH <sub>2</sub> C) and 8 Ar    O	97	8.08	48.90
<b>V</b>	Glycol	1.3, 4.1 and 5.3	2(CH <sub>3</sub> ), 2(CH <sub>2</sub> OC), and 2(CHOC)                          O                    O	116	9.67	50.89
	Acid	4.6 and 6.6–7.8	2(OCH <sub>2</sub> C) and 8 Ar    O	112	9.33	49.11
<b>VI</b>	Glycol	1.1–1.9 and 4.2	2(CH <sub>2</sub> ) <sub>4</sub> and 4(CH <sub>2</sub> OC)    O	180	7.5	50.00
	Acid	4.6 and 6.7–7.8	2(OH <sub>2</sub> CC) and 8 Ar    O	90	7.5	50.00
<b>VII</b>	Glycol	3.6 and 4.2	2(CH <sub>2</sub> OCH <sub>2</sub> ) and 4(CH <sub>2</sub> OC)    O	100	6.25	50.61
	Acid	4.5 and 6.1–6.9	2(OCH <sub>2</sub> C) and CH=CH + 4 Ar    O	61	6.10	49.39
<b>VIII</b>	Glycol	3.7 and 4.3	4(CH <sub>2</sub> OCH <sub>2</sub> ) and 4(CH <sub>2</sub> OC)    O	91	3.79	53.46
	Acid	4.6, 6.3, and 6.9	2(OCH <sub>2</sub> C), CH=CH, and 4 Ar    O	33	3.30	46.54
<b>IX</b>	Glycol	3.6 and 4.3	6(CH <sub>2</sub> OCH <sub>2</sub> ) and 4(CH <sub>2</sub> OC)    O	33	1.03	48.36
	Acid	4.6, 6.3, and 6.9	2(OCH <sub>2</sub> C), CH=CH, and 4 Ar    O	11	1.10	51.64



