Saturated and Unsaturated Polyesters Based on 1,3-(Dicarboxymethoxy)benzene

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Synopsis

Saturated polyesters were prepared by the reaction of 1,3-(dicarboxymethoxy)benzene with ethylene, diethylene, tetramethylene, and hexamethylene glycols. Also, unsaturated polyesters were prepared by the reaction of 1,3-(dicarboxymethoxy)benzene and maleic anhydride with the same glycols. All the polyester resins obtained have been characterized, and the unsaturated polyesters were found to cure with styrene. The properties of the cured polyesters in the form of films were determined. IR and ^{1}H-NMR spectroscopy were used for both qualitative and quantitative analyses of the polyesters as well as their hydrolyzate products, after curing with styrene.

INTRODUCTION

Polyesters form a class of industrially useful materials. By varying the type and amount of glycols and dicarboxylic acids, polyesters with a wide range of physical and mechanical properties[1,2] can be obtained. Polyesters from 1,3-(dicarboxymethoxy)benzene have not yet been reported. The aim of the present work is to find the optimal general conditions for the preparation of a number of saturated and unsaturated polyesters based on 1,3-(dicarboxymethoxy)benzene. In the present investigation, IR and ^{1}H-NMR spectroscopy are used to elucidate the structure of the prepared polyesters. Also, the reactivity of these unsaturated polyesters towards styrene has been studied.

EXPERIMENTAL

1,3-(Dicarboxymethoxy)benzene[3] was prepared through the reaction of resorcinol with chloroacetic acid and the product was recrystallized twice from methanol, mp 195°C. All chemicals and solvents used were of A.R. or equivalent grade.

Polyesterification Reactions. The polyesterification reactions were carried out by heating equimolar amounts of the acid and glycol in presence of oxygen-free nitrogen. The time–temperature program for each polyester is illustrated in Table I. The polyesters were purified twice by dissolving in chloroform and precipitating with light petroleum, and then dried under reduced pressure. Unsaturated polyesters were prepared and purified in the same manner by the reaction of 1,3-(dicarboxymethoxy)benzene, maleic

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TABLE I
Time-Temperature Programs for the Preparation of Saturated-
(I–IV) and Unsaturated- (V–VIII) Polyesters

Temp (°C)	Time (h)							
	I	II	III	IV	V	VI	VII	VIII
140	—	—	—	—	$1/2$	1	—	1
150	—	1	1	1	1	1	$1/2$	$1/2$
160	1	1	1	1	1	1	1	1
170	1	1	1	1	1	1	$2/3$	1
180	1	1	$3/4$	1	1	1	—	$1/2$
190	1	1	$1/2$	—	1	$1/3$	—	—
200	1	1	$1/2$	—	$1/2$	—	—	—
210	—	1	—	—	—	—	—	—

anhydride, and glycol in the molar ratio 1:1:2, respectively. Table I also shows the time–temperature programs for the preparation of unsaturated polyesters (V–VIII).

Curing of the Polyester Resins with Styrene. Each of the prepared unsaturated polyesters was copolymerized[4] with styrene, in the molar ratio of 70:30, using benzoyl peroxide as initiator (1%) and dioxane as solvent. The cured polyesters were casted as films on glass and tin plates. The films were tested for resistance to hot and cold water[5] and to acids and alkalies.[6]

Degradation of the Cured Polyesters. The cured polyesters were subjected to alkaline hydrolysis,[4] and the soluble product in each case, was purified and characterized by studying its IR and ^{1}H-NMR spectra.

Viscosity measurements were carried out by an Ostwald viscometer using a 1% solution in dioxane at 30°C The molecular weight of the prepared polyesters were determined by the end group analysis for —COOH using KOH.[7] The infrared spectra were recorded by a Beckman 4220 Infrared Spectrophotometer in the range 4000–600 cm^{-1}. The proton magnetic resonance spectra (in CDCl$_3$ as a solvent and using TMS as a zero reference) were obtained at room temperature with a Varian EM-390 Spectrometer operating at 90 MHz.

TABLE II
Physical Characteristics of the Polyester Resins

| Polyester	Nature of polyester	Acid value	Mol wt	n	$[\eta]_{int}$
I	Low melting solid	37.2	3029	12.0	0.048
II	Viscous material	53.2	2108	7.1	0.028
III	Viscous material	32.3	3267	11.7	0.035
IV	Viscous material	13.8	8159	26.5	0.050
V	Viscous material	9.9	10018	25.4	0.048
VI	Low melting solid	11.6	9642	20.0	0.046
VII	Viscous material	15.6	7217	16.0	0.036
VIII	Viscous material	24.9	4776	9.4	0.042

RESULTS AND DISCUSSION

In the present study, saturated polyester resins (I–IV) were prepared from the reaction of 1,3-(dicarboxymethoxy) benzene with ethylene, diethylene, tetramethylene, and hexamethylene glycols, respectively. Unsaturated polyesters (V–VIII) were prepared by reaction of 1,3-(dicarboxy-methoxy)benzene and maleic anhydride with ethylene, diethylene, tetramethylene and hexamethylene glycols, respectively.
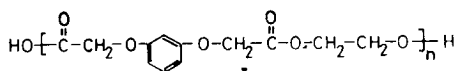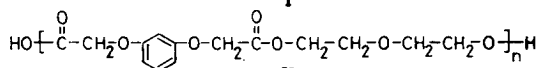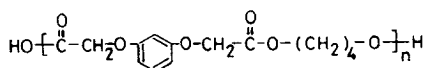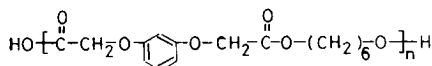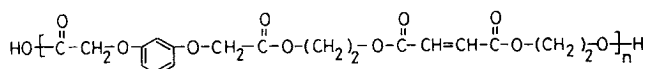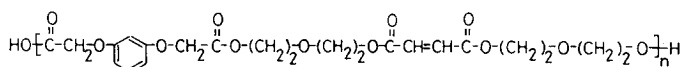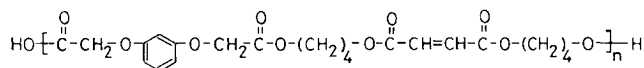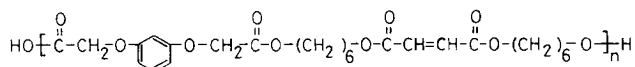

The prepared polyesters (I–VIII) were transparent pale yellow, viscous materials, soluble in various organic solvents except alcohol, n-hexane, and light petroleum. These linear polyesters showed greater resistance to homopolymerization and remained soluble after long storage periods. Some of the physical properties of the prepared saturated and unsaturated polyesters are presented in Table II.

The structure of 1,3-(dicarboxymethoxy)-benzene as well as the prepared polyesters (I–VIII) were established by studying their IR and ^{1}H-NMR spectra. The infrared spectra of the eight prepared saturated and unsaturated polyesters show bands at 3480–3500, 2850–2950, 1730–1760, and 770–780 cm^{-1}, characteristic for ν_{OH}, ν_{CH_2}, $\nu_{C=O}$, and δ_{CH} of aromatic (three adjacent),

TABLE III
^{1}H-NMR Spectral Data of Polyesters (I–VIII)

Polyester	Component	Chemical shift (ppm)	Assignment	Peak areas (integration)	Relative mol amount	Mol %
I	Glycol	4.4	$-O-CH_2-CH_2-O-$	40.5	10.13	50
	Acid	4.6 and 6.35–7.35	$2(-O-CH_2-\overset{O}{\underset{\|\|}{C}})$ and 4Ar	81.0	10.13	50
II	Glycol	3.6 and 4.3	CH_2-O-CH_2 and $2(CH_2O-\overset{O}{\underset{\|\|}{C}})$	34.0	4.25	50
	Acid	4.6 and 6.55–7.40	$2(OCH_2-\overset{O}{\underset{\|\|}{C}})$ and 4Ar	34.0	4.25	50
III	Glycol	1.6 and 4.2	CH_2-CH_2- and $2(CH_2O-\overset{O}{\underset{\|\|}{C}})$	90.0	11.25	50
	Acid	4.6 and 6.55–7.40	$2(OCH_2-\overset{O}{\underset{\|\|}{C}})$ and 4Ar	90.0	11.25	50
IV	Glycol	1.10–1.80 and 4.25	$(CH_2)_4$ and $2(CH_2O-\overset{O}{\underset{\|\|}{C}})$	75	6.25	50
	Acid	4.55 and 6.50–7.35	$2(OCH_2-\overset{O}{\underset{\|\|}{C}})$ and 4Ar	50	6.25	50

|						
V	Glycol	4.4	$2(O-CH_2-CH_2-O)$	70.0	8.75	50
	Acid	4.6 and 6.35–7.35	$2(OCH_2-\overset{\overset{O}{\|\|}}{C})$ and $CH=CH + 4Ar$	87.5	8.75	50
VI	Glycol	3.70 and 4.40	$2(CH_2-O-CH_2)$ and $4(CH_2O-\overset{\overset{O}{\|\|}}{C})$	125.0	7.81	50
	Acid	4.70 and 6.40–7.40	$2(OCH_2-\overset{\overset{O}{\|\|}}{C})$ and $CH=CH + 4Ar$	78.0	7.80	50
VII	Glycol	1.70 and 4.25	$2(CH_2-CH_2)$ and $4(CH_2-O)$	68.0	4.25	48.57
	Acid	4.60 and 6.40–7.40	$2(OCH_2-\overset{\overset{O}{\|\|}}{C})$ and $CH=CH + 4Ar$	45.0	4.50	51.42
VIII	Glycol	1.20–1.90 and 4.20	$2(CH_2)_4$ and $4(CH_2-O-\overset{\overset{O}{\|\|}}{C})$	129.0	5.40	49.50
	Acid	4.70 and 6.30–7.45	$2(OCH_2-\overset{\overset{O}{\|\|}}{C})$ and $CH=CH + 4Ar$	55.0	5.50	50.50
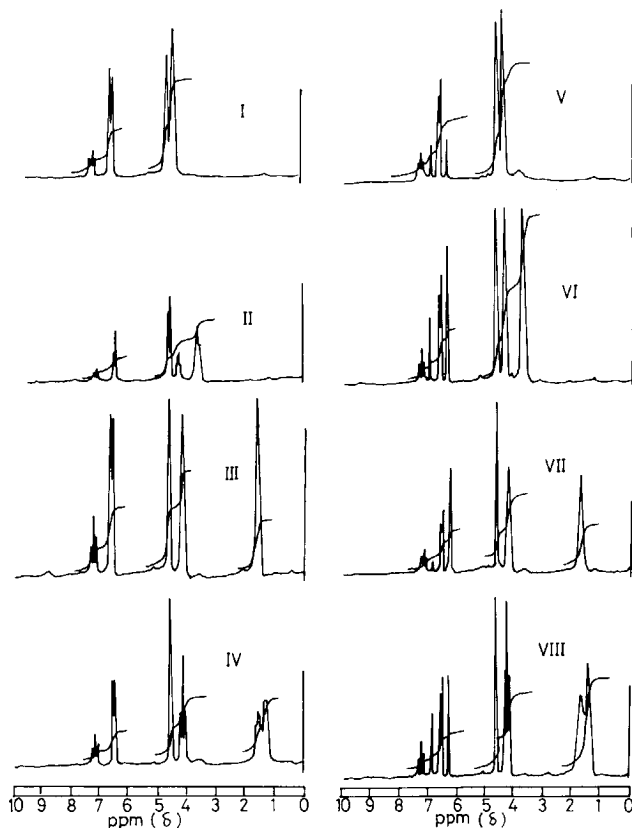
Fig. 1. ¹H-NMR spectra of polyesters (I–VIII).

respectively. The ¹H-NMR spectra (Fig. 1) of the polyester resins (I–VIII) are studied, and the method of Baddar et al.[8] was used in our present work for the quantitative analysis of these polyesters by ¹H-NMR spectroscopy. The results of both qualitative and quantitative analyses of the polyester resins are shown in Table III. From Table III, it is clear that mol % ratios of the glycol to the acid, calculated for polyesters (I–VIII) are 50:50.

The prepared polyesters were found to cure with styrene to form insoluble crosslinked polymers (IX). The properties of these cured polyesters in the form of films (Table IV) show that they have a considerable film properties on glass and metal plates. The cured polyesters were subjected to hydrolysis,

TABLE IV
Film Properties of the Styrene-Cured Polyesters

	V	VI	VII	VIII
Cold water resistance	Not affected	Not affected	Not affected	Not affected
Boiling water resistance	Not affected	Not affected	Not affected	Not affected
Alkali resistance				
10% NaOH	Damaged	Damaged	Damaged	Damaged
10% Na_2CO_3	Not affected	Damaged	Not affected	Damaged
Acid resistance				
10% H_2SO_4	Not affected	Not affected	Not affected	Not affected

TABLE V

Molar Ratio of Styrene to Fumaric Acid Residue in the Hydrolyzate Products (X) Calculated from the Oxygen Content and from ^{1}H-NMR Spectra Data

Hydrolyzate products of polyesters	Molar ratio of styrene to fumaric acid	
	Calculated from oxygen content	Calculated from ^{1}H-NMR
V	1.48	1.41
VI	1.86	1.94
VII	1.93	1.88
VIII	2.14	2.11

and the hydrolyzate products (X) were characterized by IR and ^{1}H-NMR spectra. Thus, their IR spectra show bands at 1715, 700, 750, 2900, and 3400 cm^{-1}, characteristic of $\nu_{C=O}$, δ_{CH}, of aromatic (five adjacent), ν_{CH_2}, and ν_{OH}, respectively. Also, their ^{1}H-NMR spectra show signals at $\delta_{7.3}$, which represents the aromatic protons of polystyrene, and at $\delta_{2.0}$ for the CH$_2$ protons.
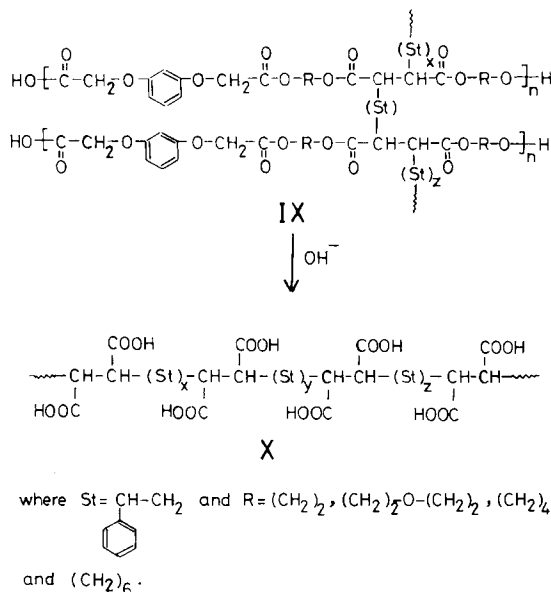
The average molar ratio of styrene (St) to fumaric acid residue in the hydrolyzate products (Table V) was deduced from the oxygen content and the ^{1}H-NMR spectral data as previously described.[9]

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