

# Structure and Properties of *o*-Carboxymaleanilic Polyester Resins

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## Synopsis

Polyester resins were prepared by the reaction of *o*-carboxymaleanilic acid with ethylene, trimethylene, propylene, hexamethylene, diethylene, or 1,4-butenediol. All the polyester resins obtained have been characterized and were found to cure with styrene, except the polyester from diethylene glycol. The properties of the cured products in the form of films were determined. Infrared, UV, and NMR spectroscopy were used for both qualitative and quantitative analyses of the polyester resins and their hydrolyzate products, after curing with styrene.

## INTRODUCTION

A large number of linear polyesters have been prepared since the pioneering work of Carothers and co-workers,<sup>1</sup> and the preparation of linear unsaturated polyesters in which the unsaturated carbon is adjacent to a carbonyl group is complicated by the side reactions leading to crosslinking. Polyesters from *o*-carboxymaleanilic acid 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 unsaturated polyesters based on the condensation of *o*-carboxymaleanilic acid with glycols. In the present investigation, IR, UV, and 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

### Materials and Methods

*o*-Carboxymaleanilic acid was prepared by the method of King et al.<sup>2</sup> by treating anthranilic acid with maleic anhydride in methanol. The product was recrystallized twice from methanol, mp 193°C. All chemicals and solvents used were of A.R. or equivalent grade. The polycondensation reactions were carried out by heating a mixture of the acid and glycol (1:1.05 moles) in the presence of oxygen-free nitrogen. The polyesters were purified twice by dissolving in chloroform and precipitating with light petroleum, then dried under reduced pressure.

Viscosity measurements were carried out in an Ostwald viscometer at 30°C using dioxane as solvent. The molecular weights of the prepared polyesters were determined at 37°C using an instrument made by Knauer, Berlin, which is based on lowering the solution vapor pressure using benzene as solvent. The infrared spectra were run on a Carl Zeiss 1200 spectrophotometer. Electronic spectra

were measured with a Carl Zeiss spectrophotometer type PAQ 11. NMR spectra (in  $\text{CDCl}_3$ ) were run by a Varian 60 A instrument.

### Preparation of Polyester Resins

**Poly-*o*-carboxymaleanilate of Ethylene Glycol (I).** A mixture of the acid and ethylene glycol was heated for 2 hr at 180°C under nitrogen at atmospheric pressure. The temperature was increased to 200°C and the reaction mixture was allowed to stand at this temperature for a further 2 hr. The temperature was gradually increased at the rate of 20°C/hr until it reached 240°C; then the mixture was heated at this temperature for 1 hr. The unreacted monomers and the other by-products were removed from the reaction mixture by evacuation for 1/2 hr at 240°C. The polyester after purification and drying was obtained as brown powder.

**Poly-*o*-carboxymaleanilate of Trimethylene Glycol (II).** A mixture of *o*-carboxymaleanilic acid and trimethylene glycol was heated for 2 hr at 180, 200, and 220°C, respectively. The temperature was raised to 240°C for 1/2 hr and then vacuum was applied for a further 1/2 hr. After purification the product was obtained as a viscous pale-brown resin.

**Poly-*o*-carboxymaleanilate of Propylene Glycol (III).** A mixture of the acid and glycol was heated at 160°C for 1 hr. The reaction mixture was further heated at 180°C for 2 hr, at 200°C for 2 hr, at 220°C for 1 hr, and then at 240°C for 1/2 hr. Vacuum was applied for a further 1/2 hr at 240°C. The product after purification was a brown, soluble resin.

**Poly-*o*-carboxymaleanilate of Hexamethylene Glycol (IV).** A mixture of the acid and glycol was heated at 160°C for 1 hr, at 180°C for 2 hr, and at 200°C for a further 2 hr. The resin was an amber-yellow, viscous soluble material after purification and drying.

**Poly-*o*-carboxymaleanilate of Diethylene Glycol (V).** The acid and glycol mixture was heated at 160°C for 2 hr, at 200°C for 2 hr, at 220°C for 1 hr, and at 240°C for 1/2 hr; then vacuum was applied for 1/2 hr at 240°C. The product obtained after purification was a brown, viscous soluble material.

**Poly-*o*-carboxymaleanilate of 1,4-Butenediol (VI).** The reaction mixture was heated at 160°C for 1 hr, at 180°C for 2 hr, at 200°C for 2 hr, and at 210°C for 2 hr; then vacuum was applied for a further 1/2 hr at 210°C. The product was an amber-yellow, viscous material.

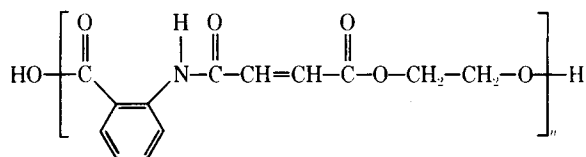
**Copolyester of *o*-carboxymaleanilic Acid, Phthalic Anhydride, and Ethylene Glycol (VII).** A mixture of *o*-carboxymaleanilic acid, phthalic anhydride, and ethylene glycol (1:1:2 moles), was heated at 160°C for 2 hr, at 180°C for 2 hr, and at 200°C for a further 3 1/2 hr. The product was purified and was obtained as pale-brown, viscous material.

**Curing of the Polyester Resins with Styrene.** A mixture of the polyester resin and styrene (70:30 w/w) was copolymerized, using benzoyl peroxide as catalyst (1.5%).<sup>3</sup> The cured polyesters in the form of films were tested for hardness,<sup>4</sup> and resistance to hot and cold water<sup>5</sup> and to acids and alkalis.<sup>6</sup>

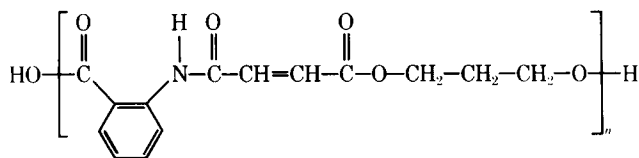
**Degradation of the Cured Polyesters.** The cured polyesters were subjected to alkaline hydrolysis,<sup>3</sup> and the soluble product was purified and characterized by studying its IR, UV, and NMR spectra.

**RESULTS AND DISCUSSION**

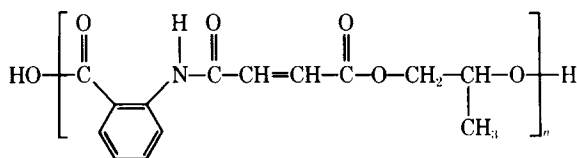
In the present study, unsaturated polyester resins (I–VI) were prepared from *o*-carboxymaleanilic acid with the following diols: ethylene glycol, trimethylene glycol, propylene glycol, hexamethylene glycol, diethylene glycol, and 1,4-butanediol. Also, a copolyester (VII) was prepared from the reaction of *o*-carboxymaleanilic acid, phthalic anhydride, and ethylene glycol:



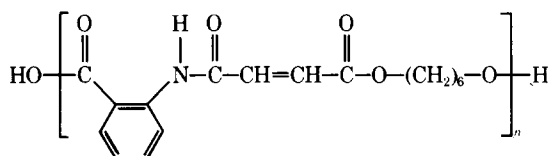
I



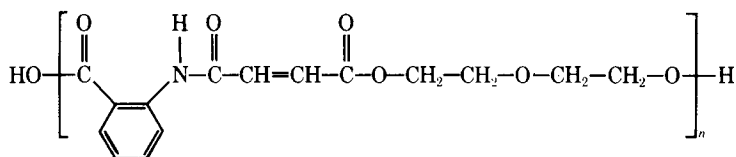
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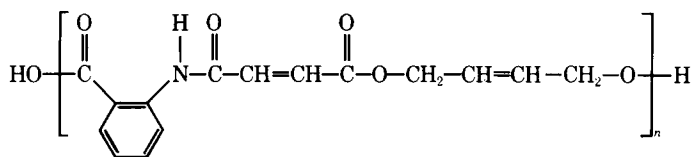
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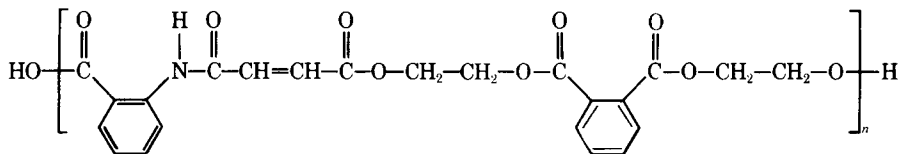
IV



V



VI



VII

The prepared polyesters (I–VII) were brown or amber-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 these polyesters are presented in Table I. Trials to prepare polyesters with higher molecular weights by increasing the reaction temperature or the condensation time failed because of the formation of an insoluble gel during the synthesis due to the maleate double bonds. This behavior was clear in the case of polyester VI, which contains a butene and a maleate double bond.

The structures of *o*-carboxymaleanilic acid as well as the prepared polyester resins (I–VII) were established by studying their IR, UV, and NMR spectra. Table II shows the important bands in their IR and electronic spectra which provide confirmation for the assigned structures. Baddar et al.<sup>7</sup> reported that trials to calculate the value of *n* (number of repeating units) by electronic spectroscopy gave low values, and this may be attributed to the complex nature of the polyesters. This finding is in agreement with our present work.

The NMR spectrum of *o*-carboxymaleanilic acid (Fig. 1) shows a broad signal centered at  $\delta$  5.8 which is probably due to the two OH protons of the carboxylic groups, the NH proton, and also two protons from the water of crystallization.

TABLE I  
Characteristics of Prepared Polyester Resins

Polyester	Acid value	Mole wt.	<i>n</i>	Viscosity	
				$\eta_{rel}$	$[\eta]$
I	4.6	1575	6	1.060	0.037
II	9.0	687	2.5	1.069	0.038
III	4.4	720	2.6	1.034	0.028
IV	37.4	1198	3.8	1.079	0.065
V	11.6	867	2.8	1.040	0.025
VI	55.7	332	1.1	1.050	0.034
VII	16.6	545	1.2	1.074	0.063

TABLE II  
IR and UV Spectral Data of *o*-Carboxymaleanilic Acid and Prepared Polyester Resins

Component	IR, $\text{cm}^{-1}$		UV	
	C=O	—NH and —OH	$\lambda_{max}$ , nm	$\epsilon_{max}$
Acid	1700	3250–3500	230	19816
Polyester				
I	1700	3250–3400	230	29332
II	1750	3200–3450	230	27310
III	1750	3300–3500	230	28260
IV	1750	3250–3450	230	34440
V	1780	3200–3500	230	28177
VI	1740	3100–3350	230	17637
VII	1700	3100–3400	235	35340

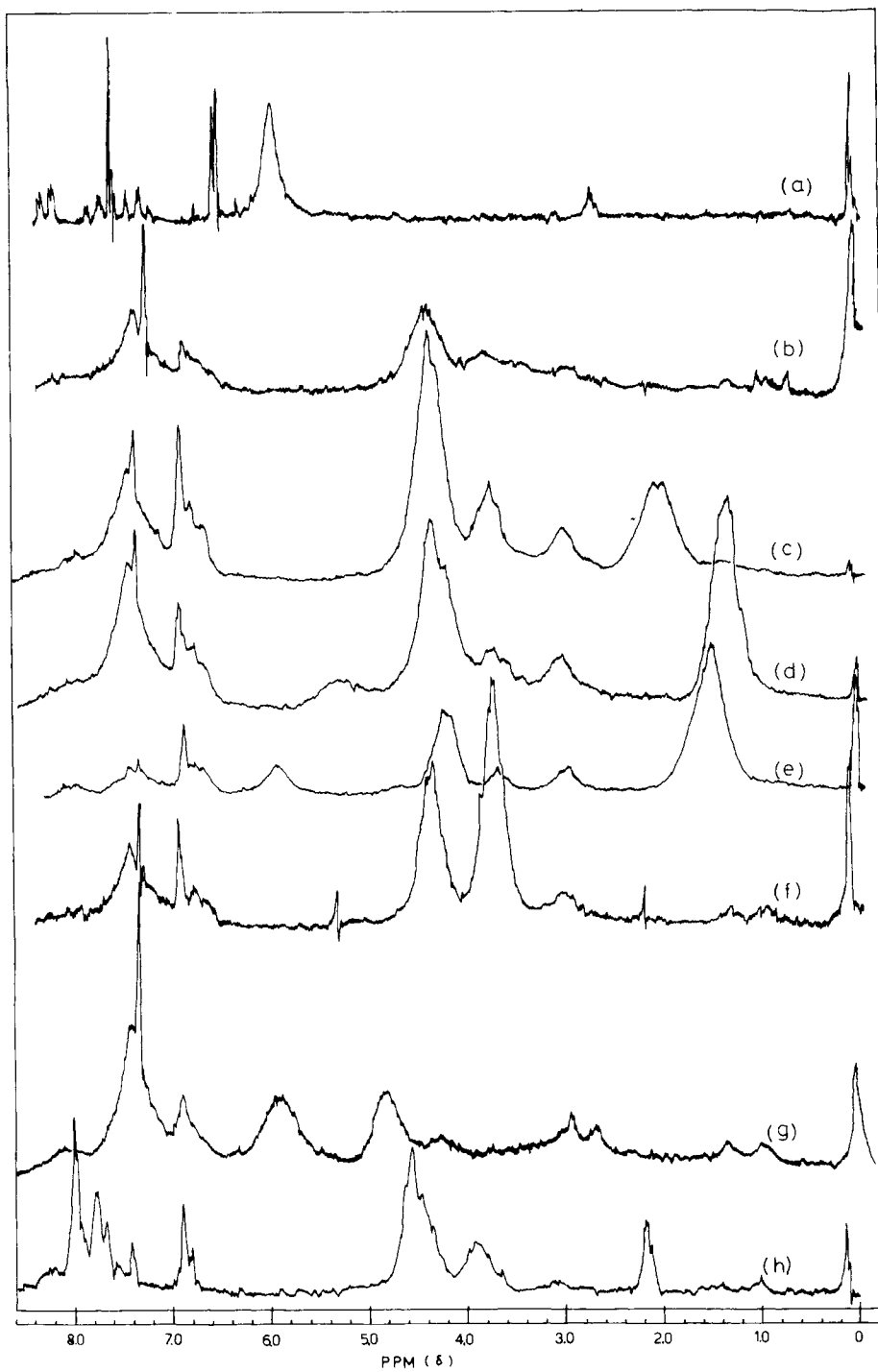


Fig. 1. NMR spectra of (a) *o*-carboxymaleanilic acid; (b)–(h) polyesters I–VII, respectively.

TABLE III  
 NMR Spectral Data of Polyesters I-VII

Poly- ester	Compo- nent	Resonance signal $\delta$	Assignment	Peak areas (integra- tion)	Relative amount	Mole %
I	Glycol	4.4	—CH <sub>2</sub> —CH <sub>2</sub> —	9	2.25	50
	Acid	6.5–8.5	4 Ar + 2 olefinic + NH	16	2.28	50
II	Glycol	2.0 and 4.3	—CH <sub>2</sub> and —CH <sub>2</sub> —O—	64	10.6	61.9
	Acid	6.4–8.3	4 Ar + 2 olefinic + NH	46	6.53	38.0
III	Glycol	1.3 and 4.3	—CH <sub>3</sub> and —CH—CH <sub>2</sub> —	96	16.0	58.0
	Acid	6.0–8.5	4 Ar + 2 olefinic	70	11.6	42.0
IV	Glycol	1.2 and 4.3	—(CH <sub>2</sub> ) <sub>4</sub> — and 2 —CH <sub>2</sub> —O—	84	7.0	50.0
	Acid	5.5–5.8	4 Ar + 2 olefinic + NH	49	7.0	50.0
V	Glycol	3.3–4.7	—(CH <sub>2</sub> —CH <sub>2</sub> )—O—	36	4.5	60.0
	Acid	6.5–8.4	4 Ar + 2 olefinic	18	3.0	40.0
VI	Glycol	4.8 and 5.9	—CH <sub>2</sub> —CH=CH—CH <sub>2</sub> —	64	10.6	49.7
	Acid	6.5–8.5	4 Ar + 2 olefinic + NH	77	11.0	50.3
VII	Glycol	4.4	—CH <sub>2</sub> —CH <sub>2</sub> —	60	7.5	50.7
	Acid	6.5–8.5	8 Ar + 2 olefinic + NH	80	7.27	49.2

This was based on the assumption that this band disappeared completely when the spectrum was run in D<sub>2</sub>O. The band, at  $\delta$  6.4 is due to the olefinic —CH=CH—, whereas the bands between  $\delta$  7.0 and 8.6 are due to the four aromatic protons. The NMR spectra of the prepared resins (I–VII) are shown in Figure 1; the method of Baddar et al.<sup>7</sup> was used in our present work for the quantitative analysis of these polyesters by 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 the mole % ratios of the glycol to the acid, calculated for polyesters I, IV, VI, and VII, are 50:50, while in the case of polyesters II, III, and V the ratios are 60:40. These results may be due to the low acid values of these polyesters accompanied by their low molecular weights (Table I).

The prepared polyesters were found to cure with styrene to form insoluble crosslinked polymers, except polyester V, which contain diethylene glycol. The properties of these cured polyesters in the form of films (Table IV) show that they have considerable surface hardness and adhere well to glass and metal plates. The films, however, are brittle and lack elasticity. The cured polyesters were subjected to hydrolysis, and the hydrolyzate products were characterized by IR, UV, and NMR spectra. Thus, their IR spectra show bands at 1725, 700–750, 2900, and 3100–3600 cm<sup>-1</sup> characteristic of the stretching frequencies of the C=O, C—H aromatic, CH<sub>2</sub>, and O—H groups, respectively. The electronic spectra of these hydrolyzate products in dioxan are identical and show a maximum at 260 nm,  $\epsilon_{\max}$  5100. Also, their NMR spectra show signals at  $\delta$  7.2 which represents the aromatic protons of polystyrene, at  $\delta$  3.6 due to the CH protons, and at  $\delta$  2.0 for the CH<sub>2</sub> protons. The ratio of styrene to maleic acid in the hydrolyzate products, calculated quantitatively from the NMR spectrum of copolyester I, for example, was found to be 3.9.

TABLE IV  
Film Properties of the Styrene-Cured Polyesters

	I	II	III	IV	VI	VII
Pendulum hardness, sec	163 at 15 $\mu$	162 at 12 $\mu$	169 at 10 $\mu$	168 at 10 $\mu$	177 at 15 $\mu$	165 at 15 $\mu$
Cold water resistance	not affected	not affected	not affected	not affected	not affected	not affected
Boiling water resistance	damaged	damaged	damaged	damaged	damaged	not affected
Alkali resistance						
5% NaOH	damaged	damaged	damaged	damaged	damaged	not affected
5% Na <sub>2</sub> CO <sub>3</sub>	damaged	not affected	damaged	not affected	damaged	not affected
Acid resistance						
5% H <sub>2</sub> SO <sub>4</sub>	damaged	not affected	damaged	not affected	damaged	not affected
% Extractable material	20	7.5	24.5	17.5	18.5	76.5

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