

Synthesis, Crosslinking and Degradation of Some Unsaturated Polyester Resins

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Synopsis

Some unsaturated polyester resins were prepared by the ester interchange between *p*-carbethoxymaleananilic acid and *p*-carbethoxysuccinanilic acid with saturated and unsaturated diols. Moreover, copolymers were also synthesized by the polyesterification of the aforementioned acids and maleic anhydride with the above-mentioned glycols. The structure of both the unsaturated polyester resins and copolymer resins was established by IR, UV, and NMR spectroscopy. Also, viscosity measurements and molecular weight determinations were further tools for their structural elucidation. All the products were attempted to cure with styrene in the presence of benzoyl peroxide as initiator, and the produced network structures, in the form of films, were tested as surface coating materials for glass and metals. The structure of the cured products was established after their degradation, by physical and spectroscopical means.

INTRODUCTION

In previous publications^{1,2} we have studied the polyesterification of either *p*-carbethoxymaleananilic acid (I) or *p*-carbethoxysuccinanilic acid (II), either alone or in the presence of maleic anhydride, with different glycols.

It was the aim of the present investigation to study the effect of a mixture of both the two half esters (I) and (II) in molar ratio 1 : 1 on both the physical and chemical properties of the formed polyester resins or copolymer resins in order to obtain improved film properties after curing with styrene to be used as surface coating materials.

EXPERIMENTAL

Materials and Methods

p-Carbethoxymaleananilic acid¹ and *p*-carbethoxysuccinanilic acid² were prepared and recrystallised twice from the appropriate solvents before being used. All chemicals and solvents used were A.R. or equivalent grade. The polyesterification reactions were carried out by heating a mixture of both half esters and glycols (1 : 1 : 2 mol) or a mixture of both half esters, maleic anhydride, and glycols (0.5 : 0.5 : 1 : 1.05 mol) in the presence of *p*-toluene-sulphonic acid (1% of the total weight) in oxygen-free nitrogen. The polyester resins or copolymer resins were purified three times by dissolving in chloroform and precipitating with light petroleum, and then dried under reduced pressure at 60°C.

Viscosity measurements were carried out in an Ostwald viscometer at 25°C using dioxane as a solvent. The molecular weights of the resins were determined at 37°C, using an instrument made by Knauer, Berlin, which is based on lowering the solution vapor pressure using benzene as a solvent. The IR spectra were run on a Carl Zeiss 1200 spectrophotometer. NMR spectra (in CDCl_3) were run on a Varian 60 A instrument.

Preparation of the Polyester Resins

General Procedure. A mixture of *p*-carbethoxymaleanilic acid (I) (0.5 mol) and *p*-carbethoxysuccinilic acid (II) (0.5 mol) were thoroughly powdered, mixed and added to the glycols, namely, ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,6-hexanediol, and 2-butene-1,4-diol (1.05 mol) in a two necked round-bottomed flask, provided with a magnetic stirrer and a condenser, in a stream of oxygen-free nitrogen, in presence of *p*-toluenesulphonic acid (1% of total weight). The mixture was heated for 2 h at 160°C. The temperature was raised 20°C each 2 h till it reached 220°C; then the mixture was evacuated for 0.5 h at 160°C to remove the unreacted monomers and the other byproducts. The remaining resin was purified and dried in an oven at 60°C.

Preparation of Copolymer Resins

General Procedure. A mixture of the half ester I (1/3 mol), half ester II (1/3 mol), maleic anhydride (1/3 mol) and the glycol (1.05 mol) was heated at 160°C, in the presence of *p*-toluenesulphonic acid (1% of total weight). The same procedure described above was followed in each case. The resin was then purified as usual and dried.

Curing the Polyester and Copolymer Resins with Styrene

It was carried out as previously reported.³ The cured polyesters or copolymers in the form of films were tested for hardness,⁴ resistance to hot and cold water,⁵ and to acid and alkalis.⁶

Degradation of the Cured Polyesters and Copolymers

The cured polyesters or copolymers were subjected to alkaline hydrolysis,³ and the soluble product was purified and identified by studying its IR and NMR spectra.

RESULTS AND DISCUSSION

In the present investigation, unsaturated polyester resins (III–VII) were prepared by the ester interchange between *p*-carbethoxymaleanilic acid (I), *p*-carbethoxysuccinilic acid (II) with ethylene glycol, diethylene glycol, 1,2-propylene glycol, 1,6-hexanediol, and 2-butene-1,4-diol. They were brown viscous resins, soluble in most organic solvents except in *n*-hexane and light petroleum but sparingly soluble in methanol and ethanol. They show greater resistance to homopolymerization and remained soluble after long storage

TABLE I
 Physical Data of the Prepared Polyester Resins

Resins	Acid value after purification	Mol wt	<i>n</i>	Viscosity [η]
III	0.0	554		0.040
IV	1.8	793	1.2	0.021
V	2.5	598	1.0	0.010
VI	4.1	1082	1.6	0.020
VII	4.3	622	1.2	0.025

periods. The physical properties of these polyester resins are included in Table I.

Also, copolymer resins (VIII–XII) were prepared in a similar way and maleic anhydride was added. These resins were brown or dark brown viscous resins, soluble in all organic solvents, except *n*-hexane or ligroin and sparingly soluble in ethanol or methanol. Table II shows the physical properties of these copolymers.

The structure of the prepared resins (III–XII) were established by studying their IR, UV, and NMR spectra. Table III shows the important bands in their IR which provide conformation for the proposed structure.

The electronic spectra of the resins (III–XII) in dioxane are quite similar to those of equimolar mixture of the two half esters (I and II) in acetonitrile and is quite an indication of the presence of both maleananilic and succinanilic acid residues in the backbone structure of these resins.

The NMR spectral data (τ) of the polyester resins and the copolymer resins (cf. Table IV) are used in this investigation for the quantitative analyses of these resins. From this table, it is clear that the mol % ratios of the two half esters to the glycol are 50 : 50.

The prepared polyester resins failed to cure with styrene which may be attributed to their low molecular weights (cf. Table I) and hence a few number of double bonds susceptible to be attached by styrene, except that prepared from *p*-carbethoxymaleananilic acid, *p*-carbethoxysuccinanilic acid, and 1,6-hexanediol, which may be attributed to the fact that the two OH groups in the diol are far apart from each other. On the other hand, the prepared copolymer resins were found to cure with styrene to form insoluble crosslinked polymers. The properties of these cured resins in the form of films (Table V) showed that they have considerable surface hardness and adhere well to glass and metal plates. The films, however, are brittle and lack

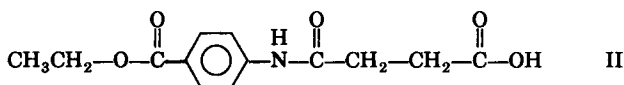
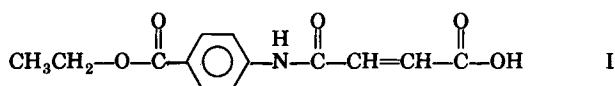
TABLE II

Copolymer resin	Acid value after purification	Mol wt	<i>n</i>	Viscosity [η]
VIII	2.8	952	1.2	0.045
IX	3.6	846	1.13	0.034
X	2.9	868	1.20	0.015
XI	1.8	3413	3.90	0.060
XII	4.5	1800	2.28	0.060

TABLE III
 IR Spectral Data of the Prepared Resins (III–XII)

Resin	IR (cm ⁻¹)				
	$\nu_{\text{C=O}}$	$\nu_{\text{C=C}}$	$\nu_{\text{amide II}}$	ν_{OH}	ν_{NH}
III	1720	1610	1530	3490	3380
IV	1720–1740	1600–1610	1600–1610	3460	3380
V	1720	1605	1510–1530	3300–3580	3380
VI	1720	1605	1520	3430–3580	3380
VII	1720	1610	1540	3480	3380
VIII	1720	1610	1530	3500	3380
IX	1720	1610	1530	3500	3360
X	1720	1605	1510–1530	3300–3600	3300–3600
XI	1730	1600	1540	3540	3380
XII	1720		1600–1510	3200–3600	

Polyesters



Half ester of acid (I)—glycol (1)—half ester of acid (II)

III

Acid (I) = *p*-carbethoxymaleanilic acidAcid (II) = *p*-carbethoxysuccinilic acid

Glycol (1) = ethylene glycol

Half ester of acid (I)—glycol (2–5)—acid (II)—glycol (2–5)

or

Half ester of acid (II)—glycol (2–5)—acid (I)—glycol (2–5)

IV glycol 2 = diethylene glycol; V glycol 3 = propylene glycol

VI glycol 4 = 1,6-hexanediol; VII glycol 5 = 1,4-butanediol

Copolymers

Half ester of acid (I)—glycol (2–6)—acid (II)—glycol (2–6)—maleic acid—glycol (2–6)

or

Half ester of acid (II)—glycol (2–6)—acid (I)—glycol (2–6)—maleic acid—glycol (2–6)

or

Half ester of acid (II)—glycol (2–6)—maleic acid—glycol (2–6)—acid (I)—glycol (2–6)

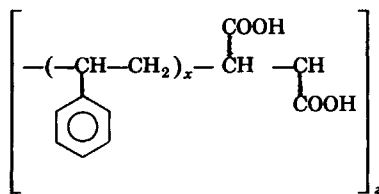
VIII, glycol 2 = ethylene glycol

IX, glycol 3 = diethylene glycol

X, glycol 4 = 2-propylene glycol

XI, glycol 5 = 1,6-hexanediol

XII, glycol 6 = 1,4-butene diol



XIII

TABLE IV
The NMR Spectral Data of Resins (IV-XII)

Polyester	Component	Resonance signal τ	Assignment	Peak area integration	Relation mol amount (%)
IV	Glycol Acids	5.2-6.8	$2-O-(CH_2-O-(CH_2) \rightarrow O-$	80	5
		1.8-3.3	8 Ar + 2 olefinic	50	
		7.1, 7.3	$(-CO-CH_2-CH_2-CO \rightarrow$ CH ₃	20	5
V	Glycol	8.6	$2 \leftarrow C \rightarrow$	27	
		4.7-5.8	$2-(CH_2-C=C \rightarrow$	30	4.7
VI	Acids	1.8-3.3	8 Ar + 20 olefinic	50	
		7.1, 7.4	$(-CO-CH_2-CH_2-CO \rightarrow$	20	5.0
	Glycol	8.5	$2 \leftarrow (CH_2)_2 - (CH_2) \rightarrow$	72	
		4.8	$2 \leftarrow O-CH_2 \cdots CH_2 \rightarrow$	37	4.5
		1.8-2.6	8 Ar + 2 olefinic	45.5	
VII	Glycol	3.3, 7.1, 7.3	$(-CO-CH_2-CH_2-CO \rightarrow$	18.8	4.6
		4.3	$2 \leftarrow C-CH=CH-C \rightarrow$	16	
	Acids	5.3-6.0	$2 \leftarrow O-CH_2 \cdots CH_2-O \rightarrow$	32	4
		1.8-2.8, 3.3		40	
		7.1, 7.3		16	4

VIII	Glycol	5.5-6.3	$3(-O-CH_2-CH_2-O)-$	12	1	50
	Acids	1.8-3.3	8 Ar + 4 olefinic	12	1	50
IX		6.9, 7.2	$-CO-CH_2-CH_2-CO-$	4	3.66	50
	Glycol	5.5-6.4	$3(-O-(CH_2)_2-O-(CH_2)_2-O)-$	88		
	Acids	1.8-3.5	8 Ar + 4 olefinic	44	3.66	50
		7.1, 7.4	$-CO-CH_2-CH_2-CO-$	14		
X	Glycol	8.6	$3(-O-C-C-O-)$ CH ₃	30		
		4.7, 5.4-6.2	$3(O-C-C-H-O-)$ C	29.8	3.3	50
XI	Acids	1.8-3.4	8 Ar + 4 olefinics	38.8		
		7.1, 7.3	$-CO-CH_2-CH_2-CO-$	12	3.2	50
	Glycol	8.5	$3(\dots CH_2-CH_2-CH_2 \dots)$	96		
		5.7	$3(-O-CH_2 \dots CH_2-O)$	48	4	50
	Acids	1.8-3.3	8 Ar + 4 olefinics	48		
XII	Glycol	7.1, 7.3	$-CO-CH_2-CH_2-CO-$	16	4	50
		4.5	$3(-O-C-CH=CH-O)$	21		
		5-6	$3(-O-CH_2 \dots CH_2-O)$	63	3.5	50
	Acids	1.8-3.3	8 Ar + 4 olefinic	42		
	7.1, 7.3	$-CO-CH_2-CH_2-CO-$	16	3.6	50	

TABLE V
Film Properties of The Styrene-Cured Resins (III, VIII-XII)

Test	III	VIII	IX	X	XI	XII
Pendulum hardness (s)	100	30	152	210	94	79
Cold water resistance	Not affected	Not affected	Not affected	Not affected	Not affected	Not affected
Boiling water resistance	Not affected	Not affected	Not affected	Not affected	Not affected	Not affected
Alkali resistance						
5% NaOH	Damaged after 24 h	Damaged after 10 min	Damaged after 5 min	Damaged after 5 min	Damaged after 35 min	Damaged after 10 min
5% Na ₂ CO ₃	Not affected	Not affected	Not affected	Not affected	Not affected	Not affected
Acid resistance						
5% H ₂ SO ₄	Not affected	Not affected	Not affected	Not affected	Not affected	Not affected
% Extractable material	57.73	40.80	78.48	51.37	77.98	59.35

elasticity. They are not affected by cold water, hot water, 5% Na_2CO_3 solution, and 5% sulphuric acid solution, but they are destroyed in 5% NaOH solution at different time intervals. Comparing the film properties of these resins with those previously prepared ones,^{1,2} it was found that these cured resins (VI and VII–XII) are not affected by hot water while the previously prepared ones were damaged in hot water.

The cured resins (VI and VIII–XII) were subjected to hydrolysis and the hydrolysate products were characterized by IR, UV, and NMR spectra. Thus, their IR spectra showed bands at 1700–1720 cm^{-1} (acid >C=O)⁷ and at 3400–3600 cm^{-1} (OH).⁷ The bands at 2920 and 3015 cm^{-1} are characteristic for aliphatic CH_2 and CH stretching frequencies and aromatic C—H stretching frequency,⁸ respectively. The strong sharp bands at 700 and 770 cm^{-1} are attributed to aromatic C—H out-of-plane bending frequency.⁷

The electronic spectra of the hydrolysate products in dioxane are quite similar and showed a broad maximum at λ_{max} 275 nm ($\epsilon = 4000$) and another one at λ_{max} 280 nm ($\epsilon = 52,000$), indicating the presence of phenyl residue.

The NMR spectrum of the hydrolysate product showed signals at 2.9 (m, aromatic), 6.3 (m, CH), and 8.4 (m, CH_2). The ratio of styrene to maleic acid in the hydrolysate product, calculated quantitatively from the NMR spectrum, was found to be 1.2. The average molecular weight of the hydrolysate products (XIII) and (XIX) as examples were found to be 515 and 390, respectively.

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