

Structure and Properties of *p*-Carboxysuccinanic Polyester Resins

MICHAEL H. NOSSEIR, NINETTE L. DOSS, and SOHAIR Y. TAUFIK, *Polymer and Pigment Lab., National Research Centre, Cairo, Egypt*

Synopsis

Polyester resins were prepared by the reaction of *p*-carboxysuccinanic acid ethyl ester with ethylene glycol and 1,4-butanediol. Also, unsaturated polyester resins were prepared by the copolymerization of *p*-carboxysuccinanic acid ethyl ester and maleic anhydride with ethylene glycol, 1,6-hexanediol, 1,4-butanediol, and 2-butyne-1,4-diol. All the polyester resins and the copolyesters have been characterized and were found to cure with styrene, except those prepared in the absence of maleic anhydride. The properties of the cured products in the form of films were determined. Infrared and nuclear magnetic resonance (NMR) spectroscopy were used for both qualitative and quantitative analyses of the polyester resins and their hydrolyzate products after curing with styrene.

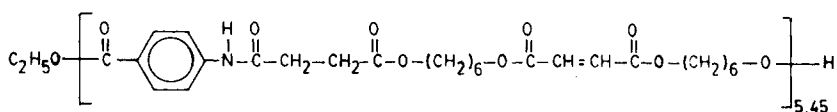
INTRODUCTION

In previous publications,^{1,2} the optimal general conditions for the synthesis of *p*- and *o*-carboxymaleinanilic polyester resins were reported. Polyesters from *p*-carboxysuccinanic 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 copolymerization of *p*-carboxysuccinanic acid ethyl ester and maleic anhydride with glycols. In the present investigation infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy are used to elucidate the structure of the prepared polyesters. Also, the reactivity of these unsaturated polyesters toward styrene have been studied.

MATERIALS AND METHODS

p-Carboxysuccinanic acid ethyl ester was prepared according to the method of Doss et al.² by treating benzocaine with succinic anhydride in acetone. The product was recrystallized twice from ethanol, m.p. 164°C. All chemicals and solvents used were A.R. or equivalent grade. The polycondensation reactions were carried out by heating a mixture of the half ester, maleic anhydride, and glycol (1 : 1 : 2 mol) in the presence of *p*-toluenesulfonic acid (1% of the total weight) in oxygen-free nitrogen. The copolymers were purified twice by dissolving in chloroform and precipitation with light petroleum, then dried under reduced pressure.

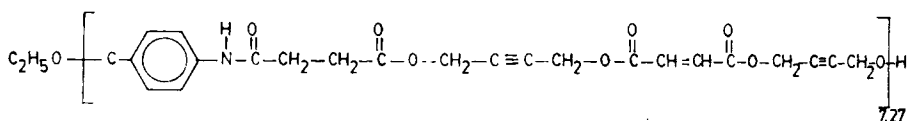
Viscosity measurements were carried out in an Ostwald viscometer at 25°C using dioxan as a solvent. The molecular weights of the prepared polyesters and copolyesters were determined at 37°C using an instrument made by



IV

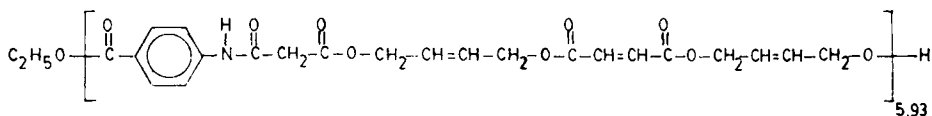
160°C for 2 h, 180°C for 2 h, 195°C for 2 h, and then at 200°C for 1/2 h under vacuum. The product was purified and was obtained as brown viscous material.

Copolyester of *p*-carboxysuccinanilic acid ethyl ester, maleic anhydride, and 2-butyne-1,4-diol (V). A mixture of *p*-carboxysuccinanilic acid ethyl ester, maleic anhydride, and 2-butyne-1,4-diol (1 : 1 : 2 mol) was heated at 150°C for 2 h, at 170°C for 4 h, at 190°C for 2 h, then vacuum was applied for a further 1 h at 190°C. The product was purified and was obtained as dark brown resin.



V

Copolyester of *p*-carboxysuccinanilic acid ethyl ester, maleic anhydride, and 1,4-butenediol (VI). A mixture of the half ester, maleic anhydride, and 1,4-butenediol (1 : 1 : 2 mol) was heated at 160°C for 2 h, at 180°C for 2 h, at 195°C for 1 h, then vacuum was applied for 1 h at 200°C. The product was purified and was obtained as a brown resin.



VI

Curing of the polyester resins with styrene. A mixture of the copolyester resin and styrene (70 : 30 w/w) was copolymerized using benzoyl peroxide as a catalyst (1%).³ The cured polyesters in the form of films were tested for hardness⁴ resistance to hot and cold water⁵ and to acid and alkalis.⁶

Degradation of the cured polyesters. The cured polyesters were subjected to alkaline hydrolysis,³ and the soluble product was purified and characterized by studying its IR and NMR spectra.

RESULTS AND DISCUSSION

In the present study, unsaturated polyester resins (III–VI) were prepared from *p*-carboxysuccinanilic acid ethyl ester and maleic anhydride with the following diols: ethylene glycol, hexamethylene glycol, 1,4-butenediol, and 2-butyne-1,4-diol. Also, polyester resins (I and II) were prepared from *p*-carboxysuccinanilic acid ethyl ester with ethylene glycol and 1,4-butenediol. The prepared polyesters (I–VI) were brown viscous materials, soluble in

TABLE I
 Characteristics of Prepared Polyester Resins

Polyester	Acid value	Mol. wt.	n	Viscosity [η]
I	2.2	2607	9.9	0.0180
II	3.9	4325	14.5	0.0400
III	zero	3057	7.6	0.0290
IV	1.3	2820	5.5	0.0195
V	2.1	3295	7.3	0.0320
VI	3.0	2708	5.9	0.0170

 TABLE II
 IR Spectral Data of *p*-carboxysuccinilic ethyl ester and
 Prepared Polyester Resins

Component	IR, cm^{-1}	—NH and —OH	
	C=O		
Acid	1700–1750	3300	3420
I	1740	3300–3500	
II	1700–1740	3360	3480
III	1700–1740	3380	3500
IV	1720–1740		3400
V	1720–1760	3380–3550	
VI	1700–1750	3380	3500

various organic solvents except *n*-hexane, petroleum ether, and methanol. 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 polyesters (II–VI) which contain a butene and a maleate double bond.

The structure of *p*-carboxysuccinilic ethyl ester as well as the prepared polyester resins (I–VI) were established by studying their IR and NMR spectra. Table II shows the important bands in their IR which provide conformation for the assigned structure. Baddar et al.⁷ 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.

The NMR spectrum (τ) of *p*-carboxysuccinilic ethyl ester (Fig. 1) shows a quartet centered at 5.5 which is probably due to the OH proton of the carboxylic group and methylene protons. The broad signal centered at 6.8 indicates an —NH proton. This was based on the assumption that this band disappeared completely when the spectrum was run in D_2O . The band at 8.6 is due to the methyl proton of the carboethoxy group, whereas the bands between 1.8 and 2.6 are due to the four aromatic protons. The NMR spectra of the prepared resins (I–VI) are shown in Figure 1. The method of Baddar

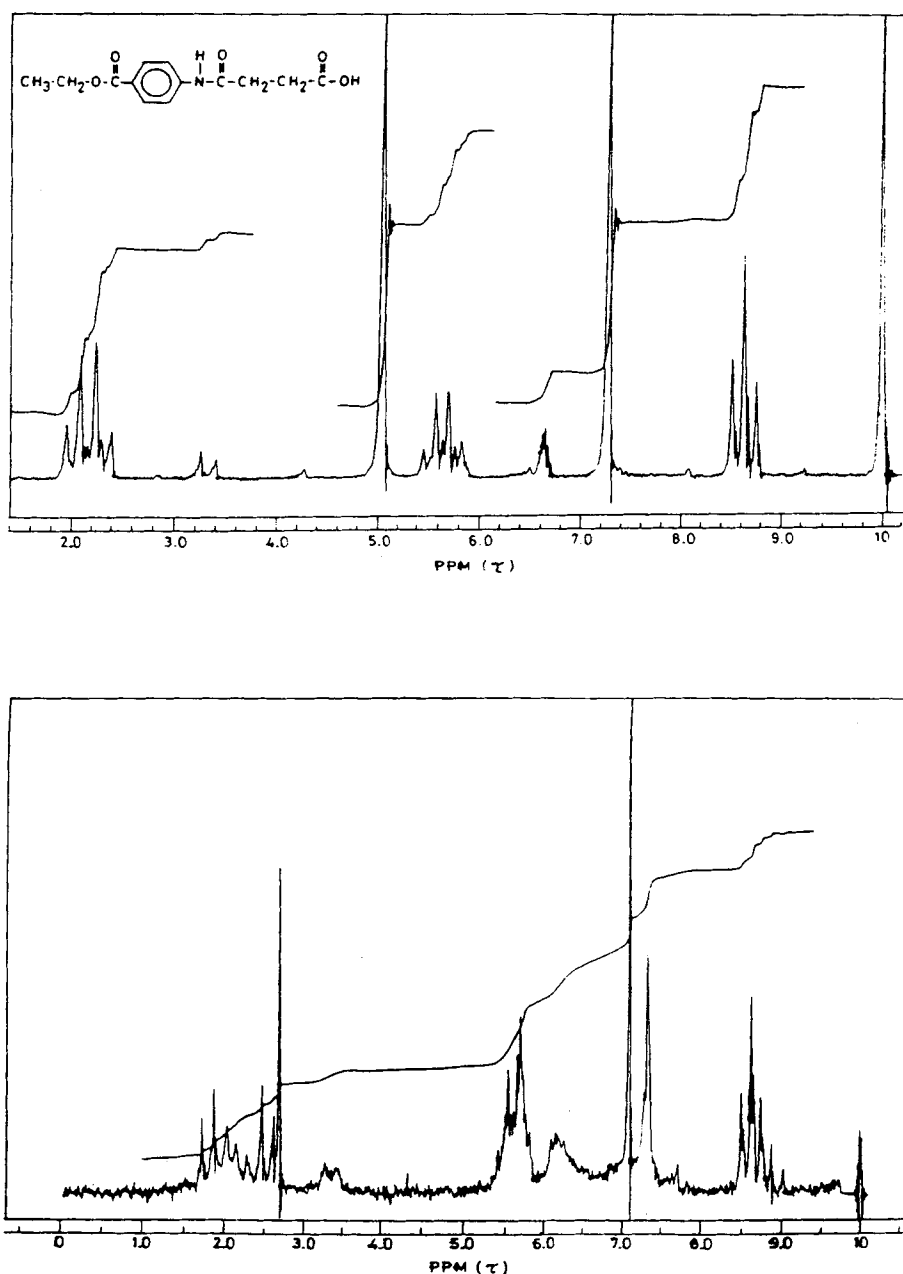


Fig. 1. NMR spectra of (a) *p*-carboxysuccinanic acid (b)–(g) polyesters I–VI, respectively.

et al. was used in our present work for the quantitative and qualitative analyses of the polyester resins as shown in Table III. From Table III it is clear that the mol% ratios of the glycol to the acid, calculated for polyesters (I–VI) are 50 : 50.

The prepared polyesters were found to cure with styrene to form insoluble crosslinked polymers, except polyesters I and II, which did not contain maleic

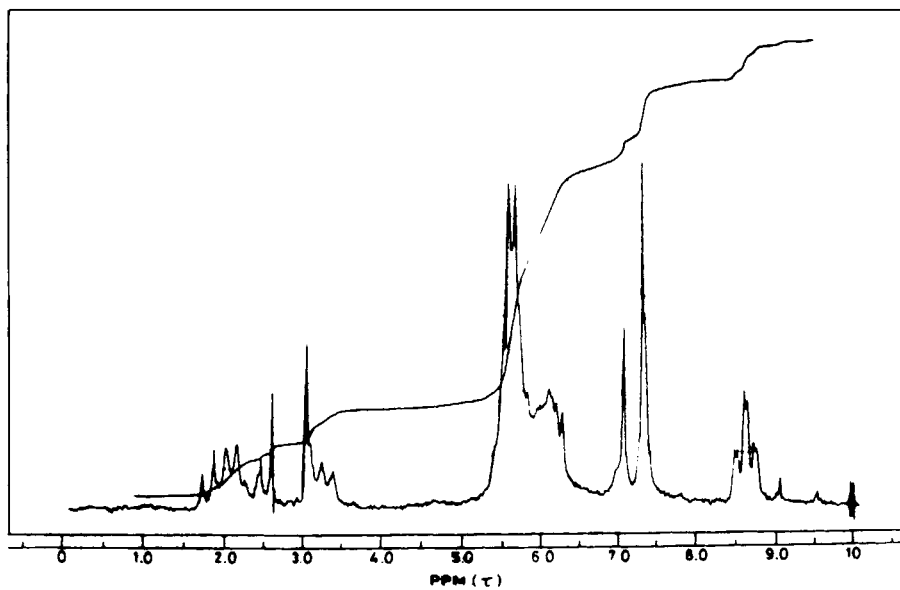
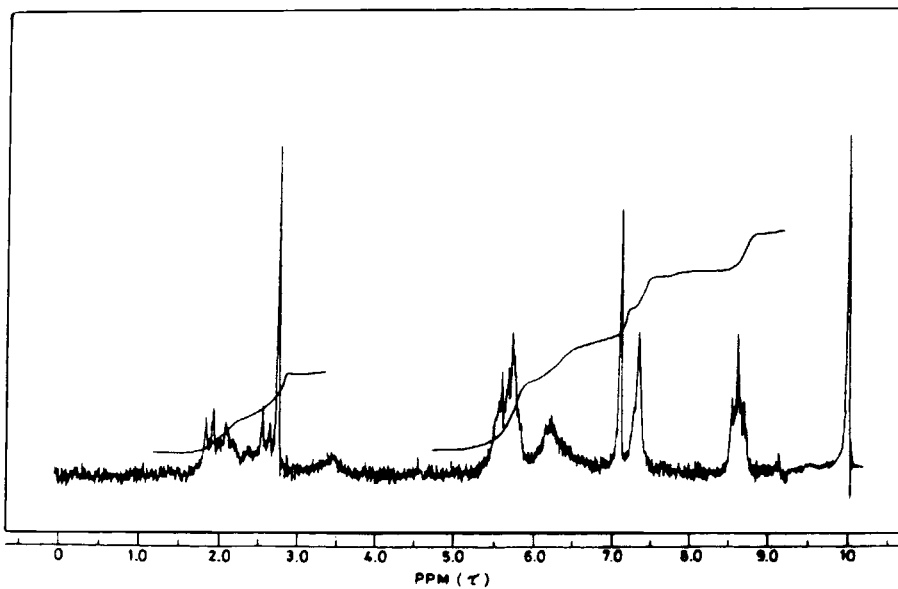


Fig. 1. (Continued from the previous page.)

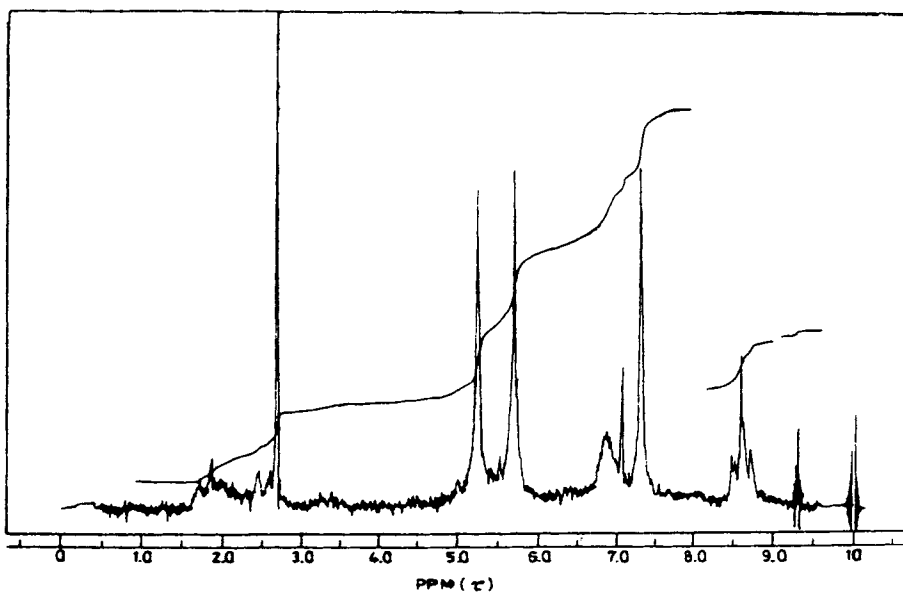
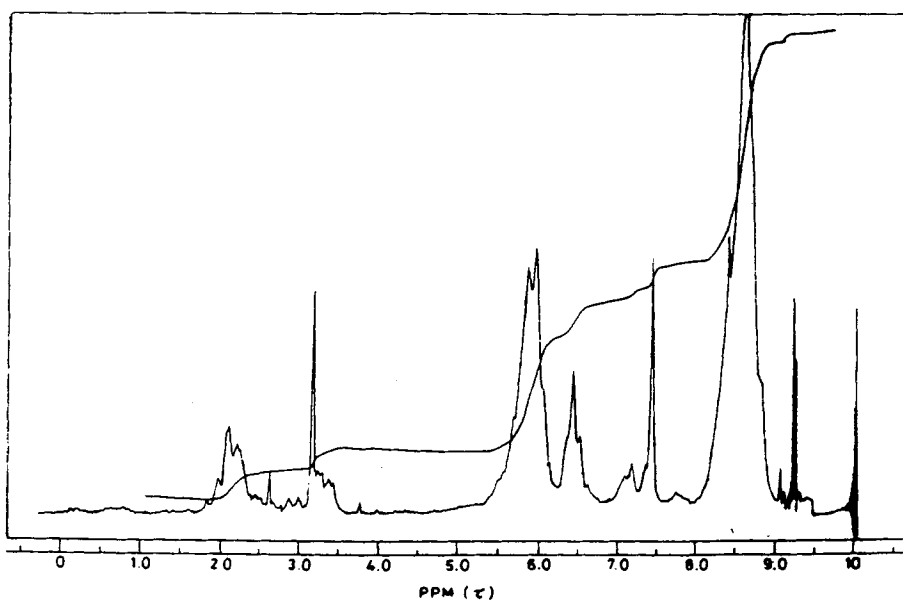


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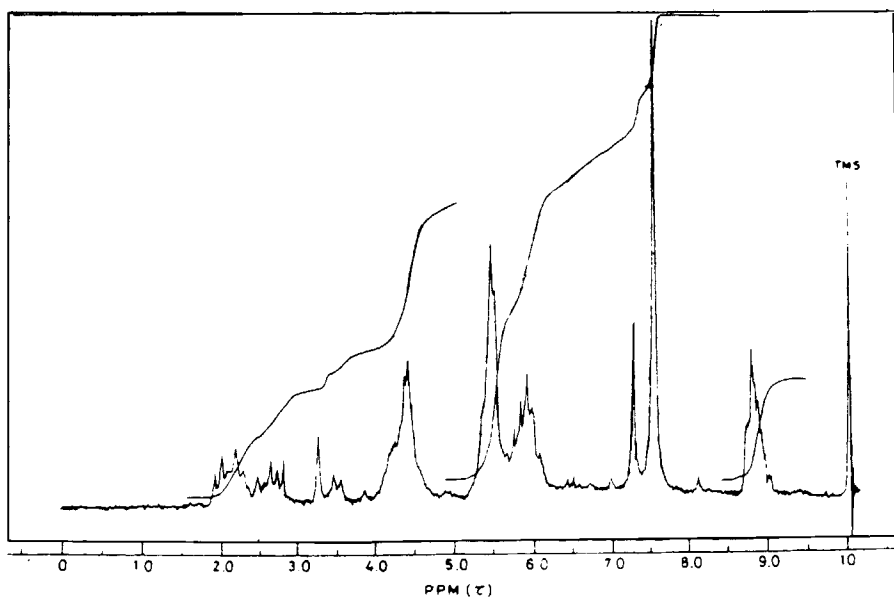


Fig. 1. (Continued from the previous page.)

TABLE III
NMR Spectral Data of Polyesters I-VI

Polyester	Component	Resonance signal τ	Assignment	Peak area integration	Relation amount	Mol %
I	Glycol	5.6	O—CH ₂ —CH ₂ —O	20	5	50
	Acid	2.5-7.3	4 Ar + C—CH ₂ —CH ₂ —CO—	40	5	50
II	Glycol	5.6, 3.3	O—CH ₂ —CH ₂ —O + CH=CH	30	5	50
	Acid	1.3-2.8, 7.3	4 Ar + CO—CH ₂ —CH ₂ —CO	40	5	50
III	Glycol	5.2-6.0	2(O—CH ₂ —CH ₂ —O)	80	10	50
	Acid	1.8-3.3	4 Ar + 6 olefine +	100	10	50
IV	Glycol	7.3-7.6	CO—CH ₂ —CH ₂ —CO—	40		
		8.6	2(—CH ₂) ₄	64	4	50
	Acid	5.3-6.3	2(O—CH ₂ —CH ₂ —O)	32		
		1.8-3.3	4 Ar + 2 olefine	24	4	50
V	Glycol	7.3	CO—CH ₂ —CH ₂ —CO—	16		
		5.6	2(O—CH ₂ —C=C—CH ₂ —O)	48	6	50
	Acid	1.8-3.3	4 Ar + 2 olefine	36	6	50
VI	Glycol	7.3	—CO—CH ₂ —CH ₂ —CO—	24		
		5.5	2(O—CH ₂ —CH ₂ —O)	41.6	5.2	52
	Acid	1.8-3.3	4 Ar + 2 olefine	28.8	4.8	48
		7.3	CO—CH ₂ —CH ₂ —CO	19.2		

residue. The properties of these 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 and NMR spectra. Thus, their IR spectra show bands at 1700-1780, 3400-3500, 2920, 3015, and 700 cm⁻¹ characteristic of the stretch-

TABLE IV
 Film Properties of the Styrene-Cured Polyesters

	III	IV	V	VI
Bendulum hardness, s	150 at 15 μ	100 at 43 μ	131 at 18 μ	95 at 30 μ
Cold water resistance	not affected	not affected	not affected	not affected
Boiling water resistance	damaged	damaged	damaged	damaged
Alkali resistance				
5% NaOH	damaged	damaged	damaged	damaged
5% Na ₂ CO ₃	not affected	not affected	not affected	not affected
Acid resistance				
5% H ₂ SO ₄	not affected	not affected	not affected	not affected
% Extractable material	15.8	20	1.4	16.7

ing frequencies of the $>C=O$, OH, aliphatic, and aromatic $-C-H$ and $-C-H$ out of plane of the ring bending,⁸ respectively. Also, their NMR spectra show signals at 8.47, 6.8, and 2.8 which represent the CH₂, CH, and aromatic protons, respectively. The ratios of styrene to maleic acid in the hydrolysate products, calculated quantitatively from the NMR spectrum of copolymer III for example was found to be 1.9.

References

1. N. N. Messiha, M. H. Nosseir, and S. H. El-Hamouly, *J. Appl. Polym. Sci.*, **25**, 51 (1980).
2. N. L. Doss, S. Y. Towfik, and M. H. Nosseir, *Ind. J. Chem.*, **18B**, 436 (1979).
3. N. A. Ghanem, M. H. Nosseir, and N. I. Hussein, *Eur. Polym. J.*, **7**, 943 (1971).
4. A. M. Erichsen, *Catalog for Paint Instruments*, A. M. Erichsen G.M.B.H. Hemer Sundwig/Westf., 1959, pp. 15, 16, 19, 26.
5. A. Gardner and G. Swad, *Physical and Chemical Examination of Paints, Varnishes, Lacquers and Colours*, Gardner Laboratory, Bethesda, Maryland, 1947, p. 514.
6. Indian Standard Specifications, Indian Standard Institution, New Delhi, IS: 1950, pp. 158, 159.
7. F. G. Baddar, M. H. Nosseir, N. N. Messiha, and N. E. Ikladious, *Eur. Polym. J.*, **12**, 361 (1976).
8. R. M. Silverstein and G. C. Bassler, *Spectrometric Identification of Organic Compounds*, John Wiley and Sons, Inc., London (1967) p. 83.

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