Preparation and Characterization of Some New Unsaturated Polyesters based on 3,6-Bis(methoxymethyl)durene

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ABSTRACT: A series of unsaturated polyester resins based on 3,6-bis(methoxymethyl)-durene with different diacids or anhydrides, namely, phthalic anhydride, maleic anhydride, and succinic acid, and different glycols, namely, 1,2-propylene glycol, triethylene glycol, 1,4-cyclohexane diol, and 3,6-bis(benzyloxymethyl)durene, were prepared. Infrared and nuclear magnetic resonance spectra were used to characterize the unsaturated polyester resins obtained qualitatively and quantitatively. The average-number molecular weight (M_n) was determined by end-group analysis. These polyesters were found to cure with styrene at room temperature. The thermal behavior of the styrenated polyesters was studied via thermogravimetrical analysis and differential scanning calorimetry (TGA and DSC). © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 3388–3398, 2001

Key words: 3,6 bis(methoxymethyl)durene; curing; unsaturated polyesters; thermal behavior

INTRODUCTION

Durene is an essentially aromatic hydrocarbon produced from various petroleum fractions that can be converted into a valuable chemical reagent, for example, bis-halomethylated aromatic hydrocarbons. It was discovered by many workers[1–3] that linear polymeric resinous polyesters can be made from the reaction of 3,6-bis(chloromethyl)durene, mp 192–195°C, and 3,6-bis(hydroxymethyl)durene, mp 245 ± 1°C, with different monomers. Aromatic and heterocyclic rings are widely used in thermally stable polymers. This is because the primary bond strength is the single most important factor contributing to heat resistance. The bond dissociation energy of a carbon–carbon single bond is 83.6 kcal/mol, and that of a carbon–carbon double bond, 145.8 kcal/mol. In aromatic systems, the double-bond dissociation energy is much higher by a value ranging from 39.2 to 68.6 kcal/mol due to resonance stabilization.[4]

The aim of the present work was to make use of 3,6–bis(chloromethyl)durene by reacting it with methyl alcohol and benzyl alcohol in the presence of a sodium hydroxide solution in order to prepare monomers with melting points lower than the corresponding 3,6-bis(hydroxymethyl)durene. Also, we plan to convert these monomers into polyesters having a symmetrical, compact, and fully substituted aromatic ring with relatively high thermal stability as compared with the aliphatic ones.

EXPERIMENTAL

Materials

1-3,6-Bis(chloromethyl)durene was supplied by the Aldrich Co. Poly(hydric alcohol) (1,2-propylene glycol, 1,4-cyclohexane diol, triethylene glycol), phthalic anhydride, succinic acid, maleic anhydride, and styrene were reagent grade and used without further purification, supplied by E. Merck. Methyl ethyl ketone peroxide (MEKP) as

Table I   Temperature Programming of Polyester Resins (III–VII)

Polyester Resin	Temperature Programming (°C)	Total Reaction Time (h)	Acid Value After Purification (mg KOH g^{-1})	Number-Average Molecular Weight ($\overline{M}_n$)	Curing Time (At Room Temperature 28 ± 2°C) (h)
III	140–200 every hour, 2 h at 210	8	43.9	1278.13	1.5
IV	160–210 every hour	5	39	1438.72	3
V	130–190 every 1 h, 2 h at 200	8	42	1335.95	2
VI	140–190 every hour, 2 h at 200	7	54	1039.07	3.5
VII	140–200 every hour, 2 h at 210	8	48	1168.96	1
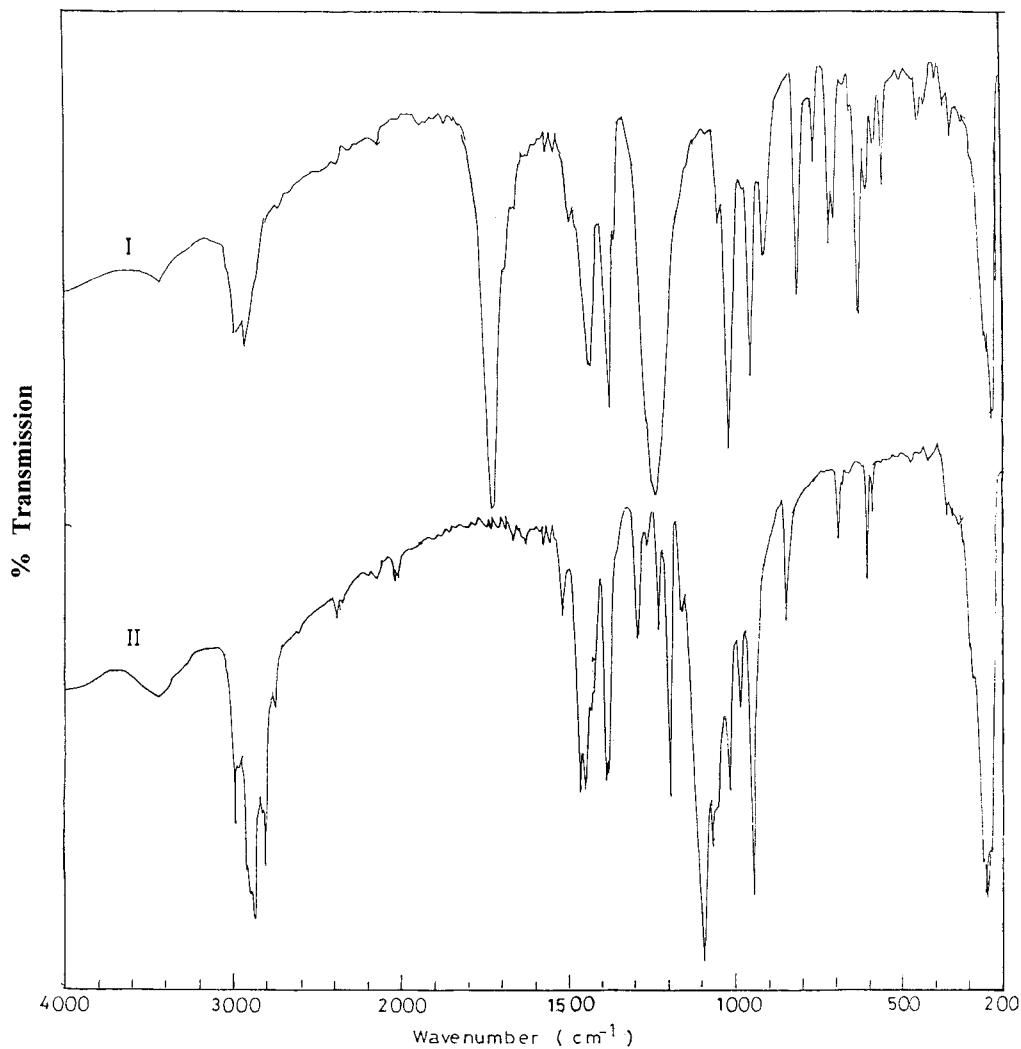
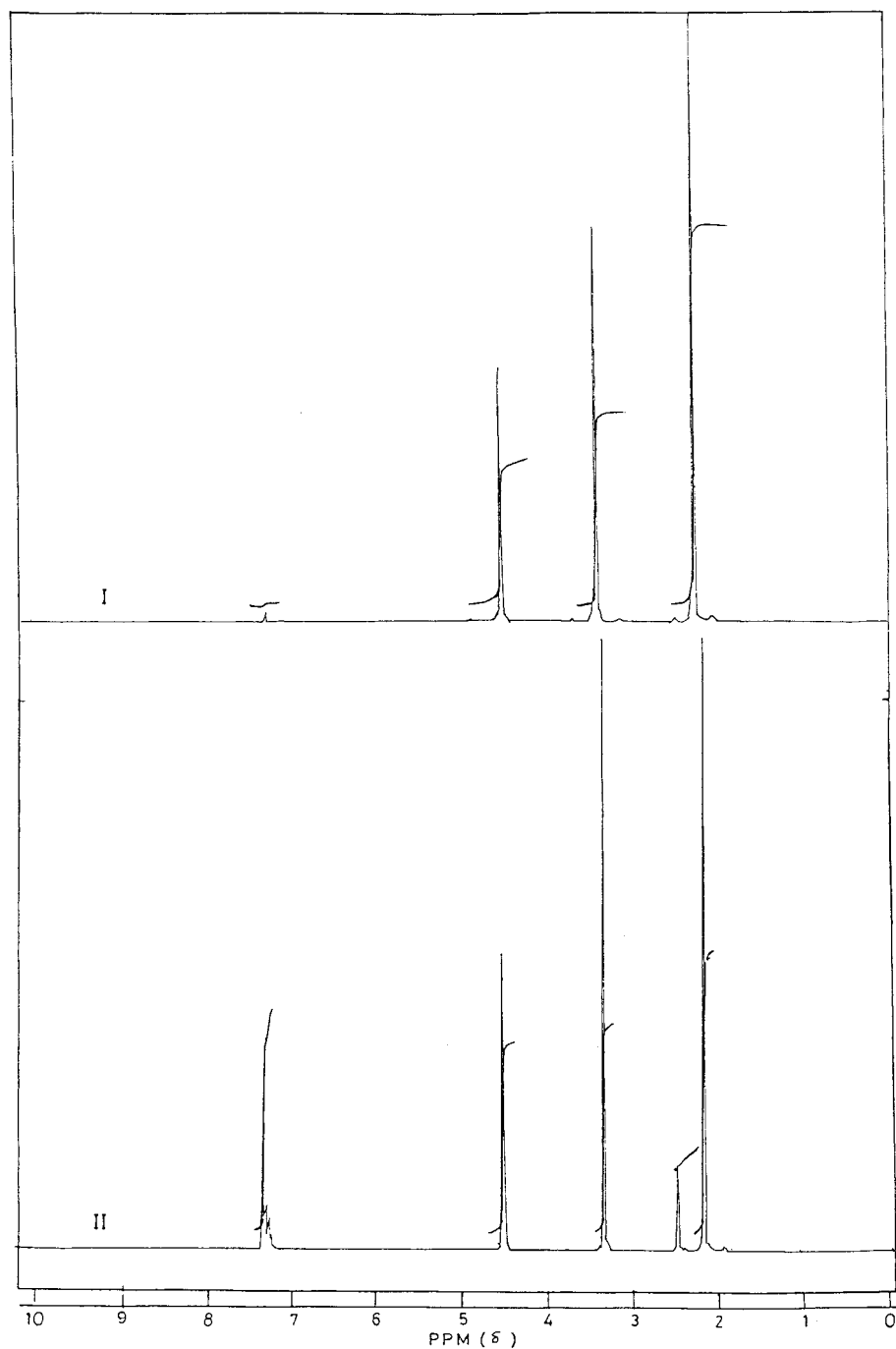**Figure 1**   IR spectra of monomers **I** and **II**.

Figure 2 NMR spectra of monomers **I** and **II**.

an initiator and cobalt naphthenate (8% cobalt) as a promoter were obtained from the Aldrich Co.

Methods

Methods of Preparation

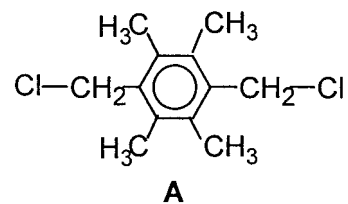*Preparation of Monomers.* Two monomers were prepared[5] from 3,6-bis(chloromethyl)durene (**A**):

A

Table II Main Absorption Bands from IR Spectra of Polyesters Resins (III–VII)

Absorption (cm^{-1})	Assignment
3550	Stretching —OH terminal carboxyl
2800–2980	Stretching frequency of CH_2, CH_3, aromatic and olefinic
1700–1740	Carbonyl group C=O stretching
1580	Stretching aromatic and olefinic —C=C—
1150–1380	Stretching —C—O—C ester
670, 750, 880	*cis*-Olefinic and aromatic residues

- 3,6-Bis(methoxymethyl)durene (**I**) was obtained by reacting **A** (1 mol) with a sodium hydroxide solution (2.3 mol) and methanol (20 mol). The reaction was performed under reflux for 2 h with continuous stirring. Colorless shiny crystals were obtained (mp 114°C; yield 91.7%).
- 3,6-Bis(benzyloxymethyl)durene (**II**), on the other hand, was prepared by refluxing a mixture of **A** (1 mol) with a sodium hydroxide solution (4 mol) and benzyl alcohol (23 mol) for 20 h with continuous stirring. Two layers were obtained, and the organic layer was extracted with ether and evaporated. Shiny colorless crystals were obtained and recrystallized from ethanol (mp 110°C; yield 60%).

Preparation of Polyesters **III–VII**. The polycondensation reaction of poly(hydric alcohol) and the dibasic acids and anhydrides was carried out by heating the mixtures at temperatures high enough to melt the solid reagents. Heating was continued in a nitrogen atmosphere until the reaction progressed to the desired extent. After completion of the reaction, the polyesters were purified by dissolving them in chloroform and precipitating with petroleum ether 40°–60° (twice). They were dried under a vacuum at 40°C. Polyester **III**, based on 3,6-bis(methoxymethyl)durene (**I**), 1,2-propylene glycol, phthalic anhydride, and maleic anhydride, was prepared by mixing 11.65 g (0.525 mol) of monomer **I**, 7.4 g of phthalic anhydride (0.5 mol), 4.9 g (0.5 mol) of maleic anhydride, and 3.99 g (0.525 mol) of propylene glycol. The mixture was heated in an oil bath for 1 h at 140°C; then, the temperature was increased gradually every 1 h until it reached 200°C and then was heated for 2 h at 210°C. The unreacted monomers and the other by-products were removed from the reaction mixture by vacuum-distillation for 30 min at 200°C. The total reaction period was 8 h. The polyester obtained was a viscous light brown resin. The other unsaturated polyester resins, based on 3,6-bis(methoxymethyl)-durene with 1,4-cyclohexane diol, succinic acid, maleic anhydride (polyester **IV**), triethylene glycol, phthalic anhydride, maleic anhydride (polyester **V**), triethylene glycol, succinic acid, maleic anhydride (polyester **VI**), 3,6-bis(benzyloxymethyl)durene (monomer **II**), phthalic anhydride, and maleic anhydride (polyester **VII**), were prepared following the previous procedure with polyester **III**. The products obtained were either light or dark brown resins, except polyester **VII**, which was a solid, and were purified as usual. The temperature programming of these polyesters are listed in Table I.

Methods of Analysis

Thermogravimetric Analysis (TGA). A Shimadzu-TGA-50H analyzer was used for the TG analysis. Platinum pan samples of 4–5 mg were heated from 25 to 800°C. The rate of heating was 10°C/min.

Differential Scanning Calorimety (DSC). DSC measurements were made on a Shimadzu DSC-D20. Samples weighing about 5 mg were placed in a platinum cell. The samples were heated at a rate of 10°C/min to 600°C

Infrared (IR) and Nuclear Magnetic Resonance Spectra (NMR). The IR spectra were performed using a JASCOO FTIR 300 E Fourier transform infrared spectrometer, while the NMR spectra were performed at 260 MCP using a JEOL-Ex-270 NMR spectrometer.

DISCUSSION

Even though both the methoxymethyl and the benzyloxymethyl derivatives of durene were prepared, our study was restricted mainly to the
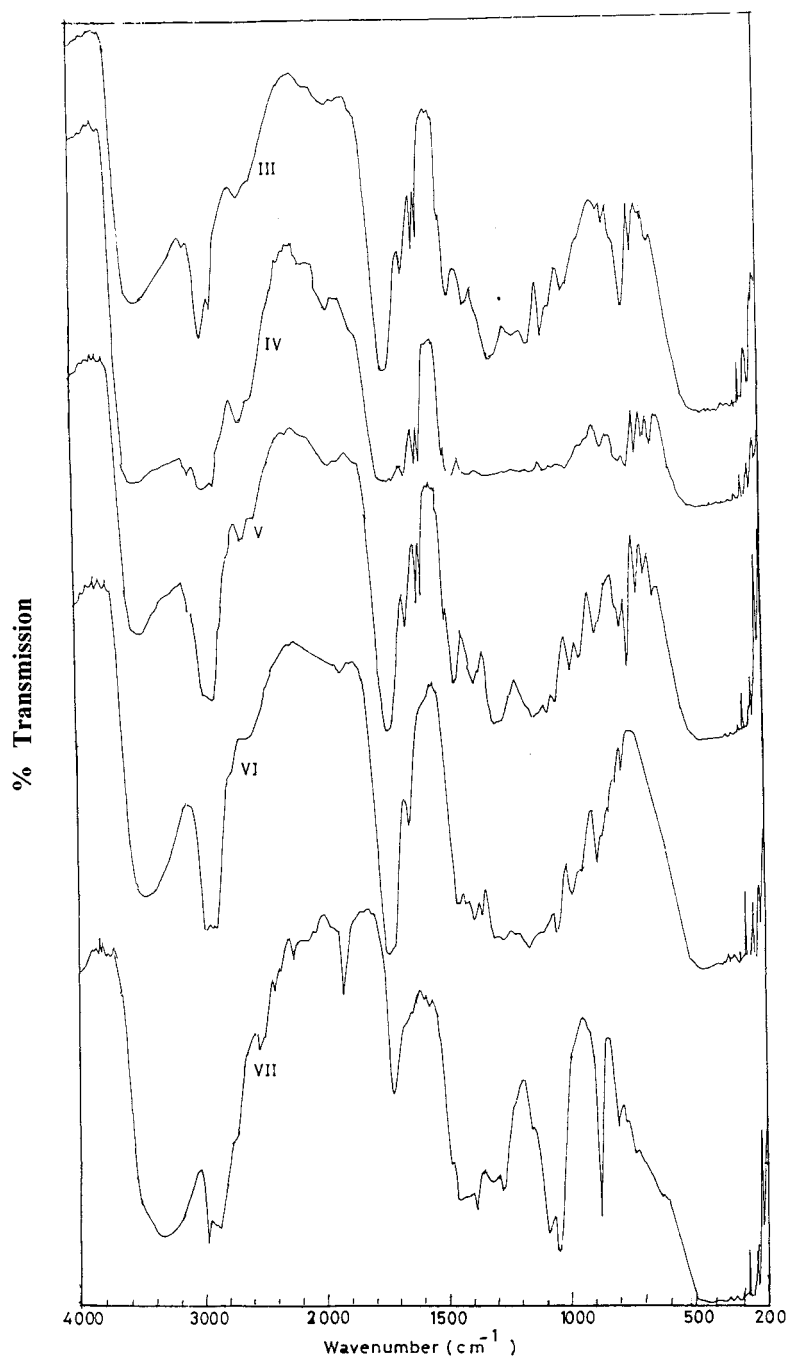
Figure 3   IR spectra of unsaturated polyester resins **III**–**VII**.

former one due to its ease of preparation and for its better yield (see Experimental section). The structure of monomers **I** and **II** was investigated by IR and NMR (Figs. 1 and 2). The NMR spectrum of monomer **I** showed a sharp signal at δ 4.5 ppm, which is most probably due to the methyl group protons (C$\underline{\text{H}}_3$—O) of the methyl alcohol residue.[6] The NMR spectrum of monomer **II** showed a signal centered at δ 7.4 ppm,

characteristic of the aromatic protons, together with a signal at δ 3.4 ppm, characteristic of the methylene protons (Ar—C$\underline{\text{H}}_2$—O—) of the benzyl alcohol residue. For both monomers **I** and **II**, the methylene protons of —C$\underline{\text{H}}_2$—O and the methyl group protons attached to the durene moieties appeared at δ 4.5 and 2.2 ppm, respectively. The IR spectrum of monomers **I** and **II** showed the appearance of a C—O—C band at

(a)
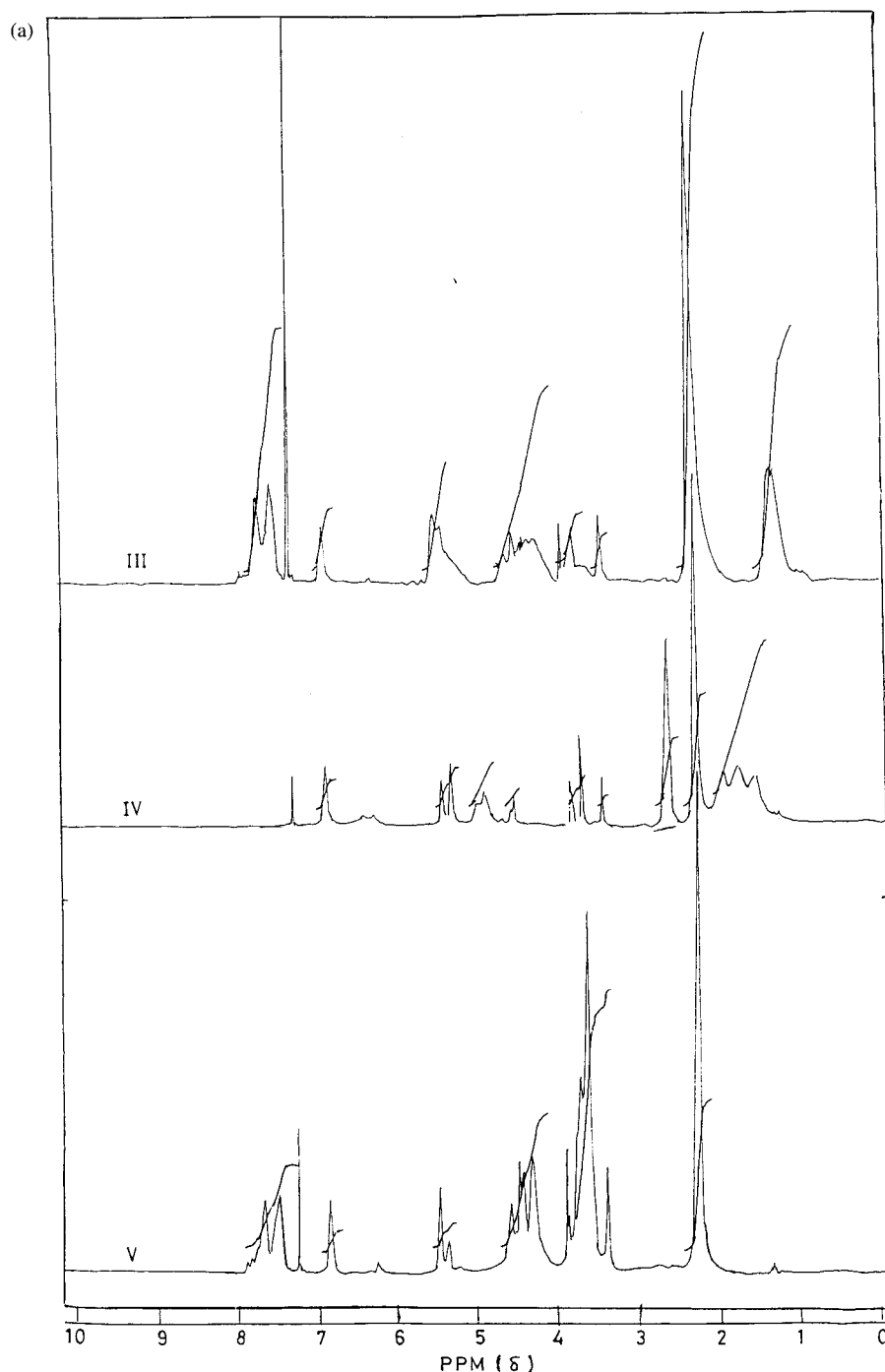
Figure 4 NMR spectra of unsaturated polyester resins: (a) **III–V**; (b) **VI** and **VII**.

1100 cm^{-1} and the absence of an —OH band at 3800–3400 cm^{-1}. The band at 2950–2980 cm^{-1} stands for the CH stretching frequency of CH$_2$, CH$_3$, and aromatic groups. The bands at 650 and 890 cm^{-1} are indicative of the presence of aromatic residues. Thus, monomers **I** and **II** can be assigned the following structures:

(b)
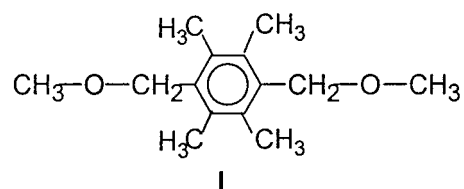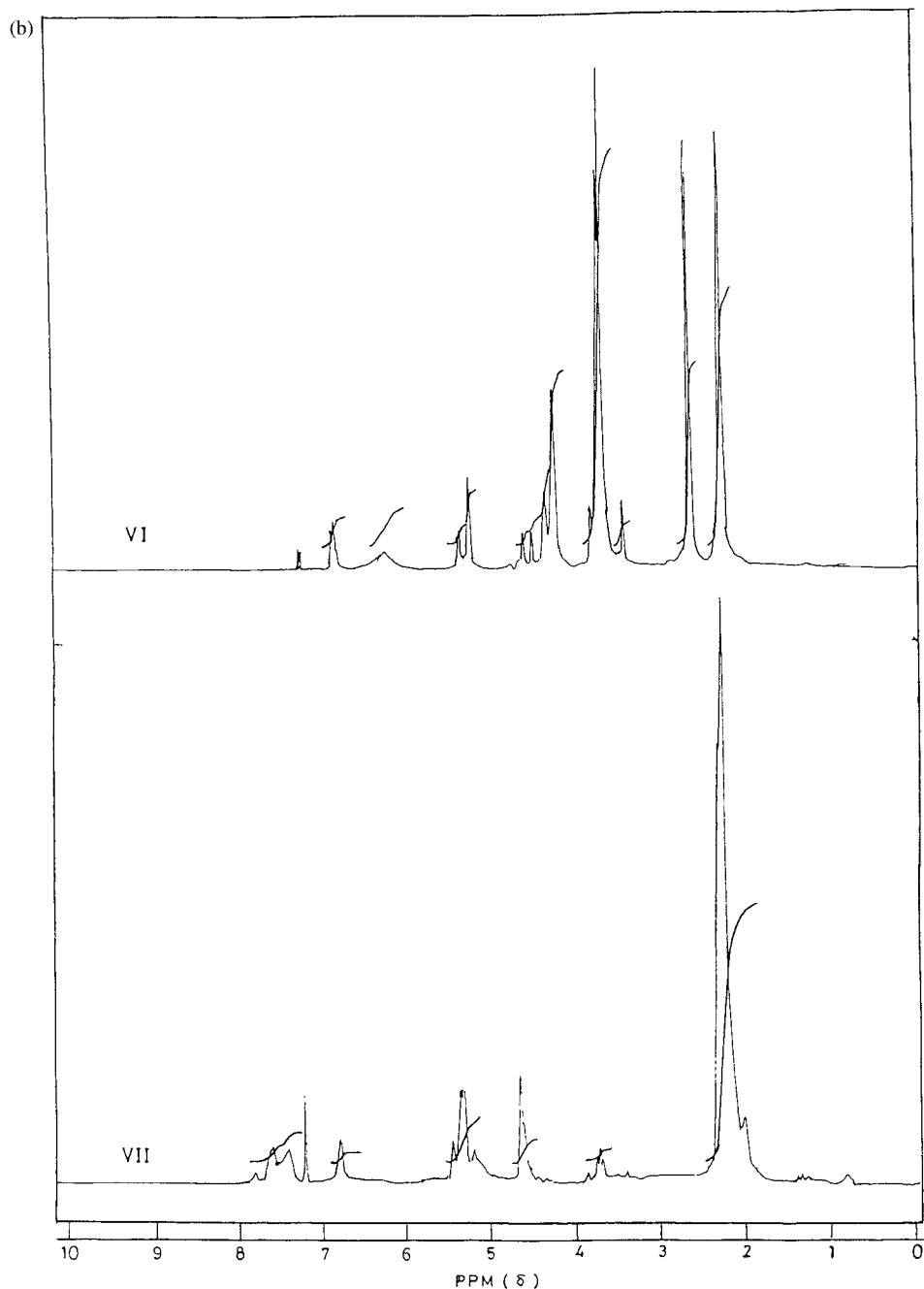
Figure 4 (*Continued from previous page*)

II
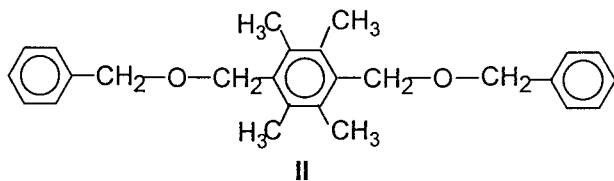
Characterization of the Unsaturated Polyester Resins

The prepared polyester resins **III–VII** based on 3,6-bis(methoxymethyl)durene were brown vis-cous resins soluble in most of the organic solvents and insoluble in *n*-hexane, petroleum ether, and methanol. The polycondensation reaction was followed by the continuous determination of the acid number (every 1 h). This was performed by titrating the resin in chloroform, with a 0.2*N* standard alcoholic potassium hydroxide solution using phenolphthalein as an indicator. These linear polyesters showed great resistance to homopolymerization and remained soluble after long storage pe-

riods. Trials to prepare polyesters with higher molecular weights by increasing the reaction temperature or the condensation time failed. This is due to the presence of sufficient alkyl substituents on the benzene ring of the bis(methoxymethyl)durene monomer which prevent the formation of a higher molecular weight polymer by steric hindrance.[7]

The linear structure of these polyester resins **III–VII** was established by studying their IR and NMR spectra.[6] Table II and Figure 3 show the important bands in their IR spectra.

The NMR spectra[6] of the prepared resins **III–VII** are shown in Figure 4. The four aromatic protons appeared between δ 7.2 and 7.6 ppm for polyesters **III**, **V**, and **VII**, while the olefinic protons for all the polyesters appeared at δ 6.4–6.8 ppm. The methyl-group protons of the durene moiety for polyesters **III–VII** are found as a signal at δ 2.5 ppm. The methylene protons are present between δ 3.5 and 5.5 ppm. The methyl group of the propylene glycol moiety in the polyester **III** backbone and the two C$\underline{H}$ protons of the cyclohexane diol residue in the polyester **IV** backbone are found at δ 1.5 ppm. Quantitative and qualitative analyses of the polyester resins by NMR spectroscopy were studied in the present work[8] (see Table III). It is evident from this table that the relative molar ratios (mol %) of the glycol to t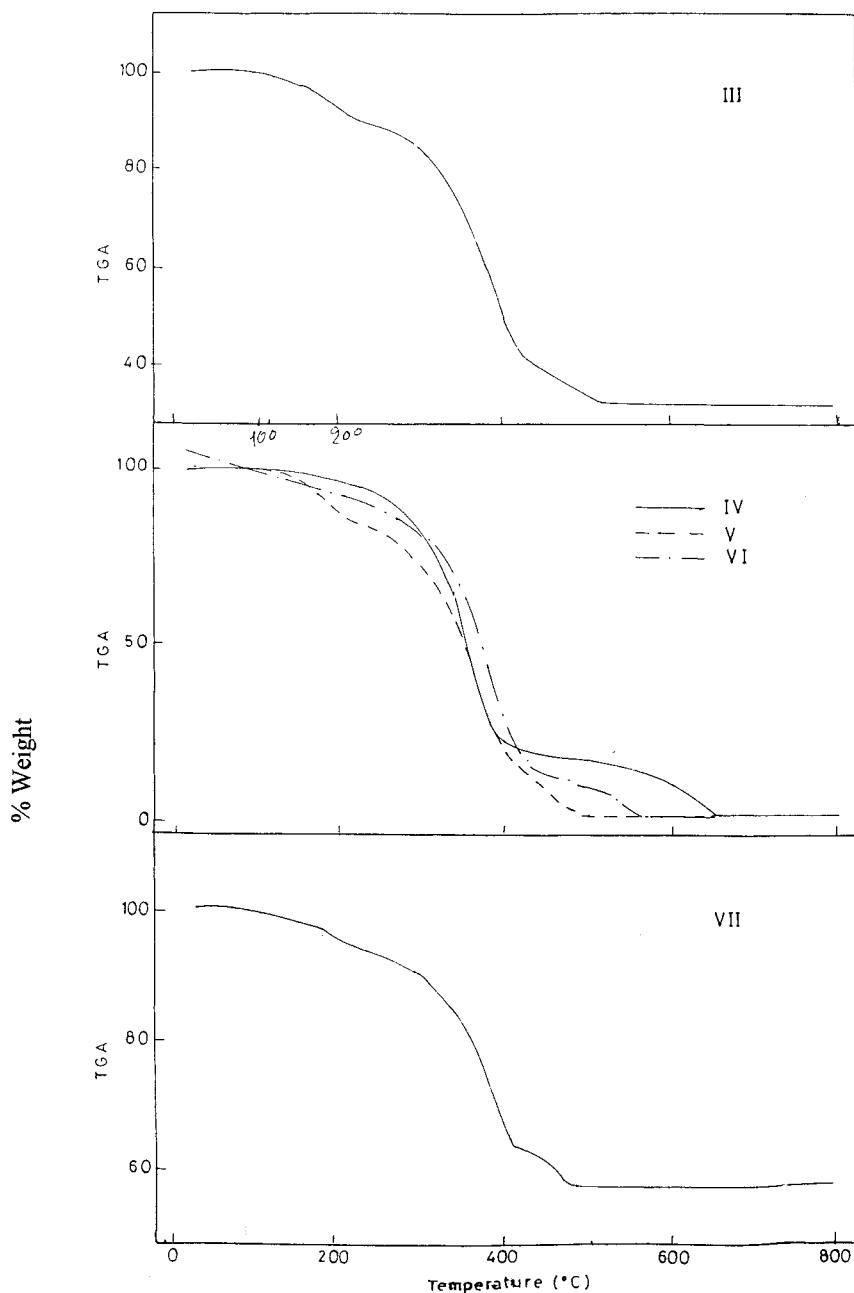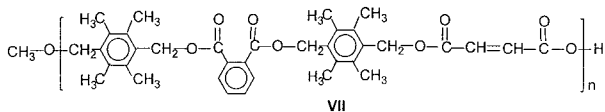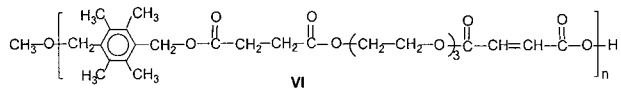he acid calculated for polyester resins **III–VII** are nearly 50:50 percent. Figures 3 and 4 illustrate the assigned structure for the polyesters **III–VII**. The prepared unsaturated polyesters were found to cure with styrene at room temperature in the ratio of 70:30 polyester/styrene wt/wt in the presence of 2% MEKP and 0.5% co-naphthenate of the total weight to form insoluble crosslinked polymers:

III

IV

V

Table III NMR Spectral Data for the Prepared Polyesters (III-VII)

Polyester	Component	Resonance Signal (δ) ppm	Assignment	Peak Area Integration	Relation Amount	Mol %
III	Acids	7.6; 6.8	4 Ar; 2 olefinic	15.10	2.52	51.45
	Glycols	3.5–5.5; 2.3; 1.5	[C$\underline{H}_3$—O, C$\underline{H}_2$—O—CO, 2(C$\underline{H}_2$—O)]; 4 (C$\underline{H}_3$ group); C$\underline{H}_3$ group of the propylene glycol	57	2.38	48.55
IV	Acids	2.5–3; 6.9	OC—(C$\underline{H}_2$—C$\underline{H}_2$)—CO; 2 olefinic	8.64	1.44	51.98
	Glycols	1.5–2; 2.1–2.5; 3.5–5	2(C$\underline{H}$—O) of cyclohexane; four [C$\underline{H}_3$ group], 4 [C$\underline{H}_2$—ocyclohexane 2[Ar—C$\underline{H}_2$—O], C$\underline{H}_3$—O	38.79	1.33	48.02
V	Acids	7.2–7.9; 6.9	4 Ar; 2 olefinic	34	5.6	44.44
	Glycols	3.5–5.5; 2.2–2.5	3[O—C$\underline{H}_2$—C$\underline{H}_2$—O—], 2[Ar—C$\underline{H}_2$—O], CH3—O four [C$\underline{H}_3$— group]	217	7	55.55
VI	Acids	6.9; 2.5–3	2 olefinic; OC— (C$\underline{H}_2$—C$\underline{H}_2$)—CO	11.14	1.85	57.64
	Glycols	3.5–5.5; 2.2–2.5	3[O—C$\underline{H}_2$—C$\underline{H}_2$—O—], 2[Ar—C$\underline{H}_2$—O], C$\underline{H}_3$O; four [C$\underline{H}_3$ group]	42.26	1.36	42.36
VII	Acids	7.5–8; 6.9	4 Ar; 2 olefinic	17	2.83	49.56
	Glycols	3.5–5.5; 1.9–2.5	[4 (Ar—C$\underline{H}_2$—O), C$\underline{H}_3$—O]; 8 [C$\underline{H}_3$— group]	101	2.88	50.43

Figure 5 TG thermograms of styrenated polyester resins **III–VII**.

TG and DSC Characterization of the Styrenated Polyester Resins III–VII

The thermal behavior of the styrene-cured polyesters (styrenated polyesters **III–VII**) studied using TG and DSC thermograms are shown in Figures 5 and 6. The important data derived from these thermograms is based on the maximum weight loss from TG curves; the decomposition and combustion exotherm from the DSC curves
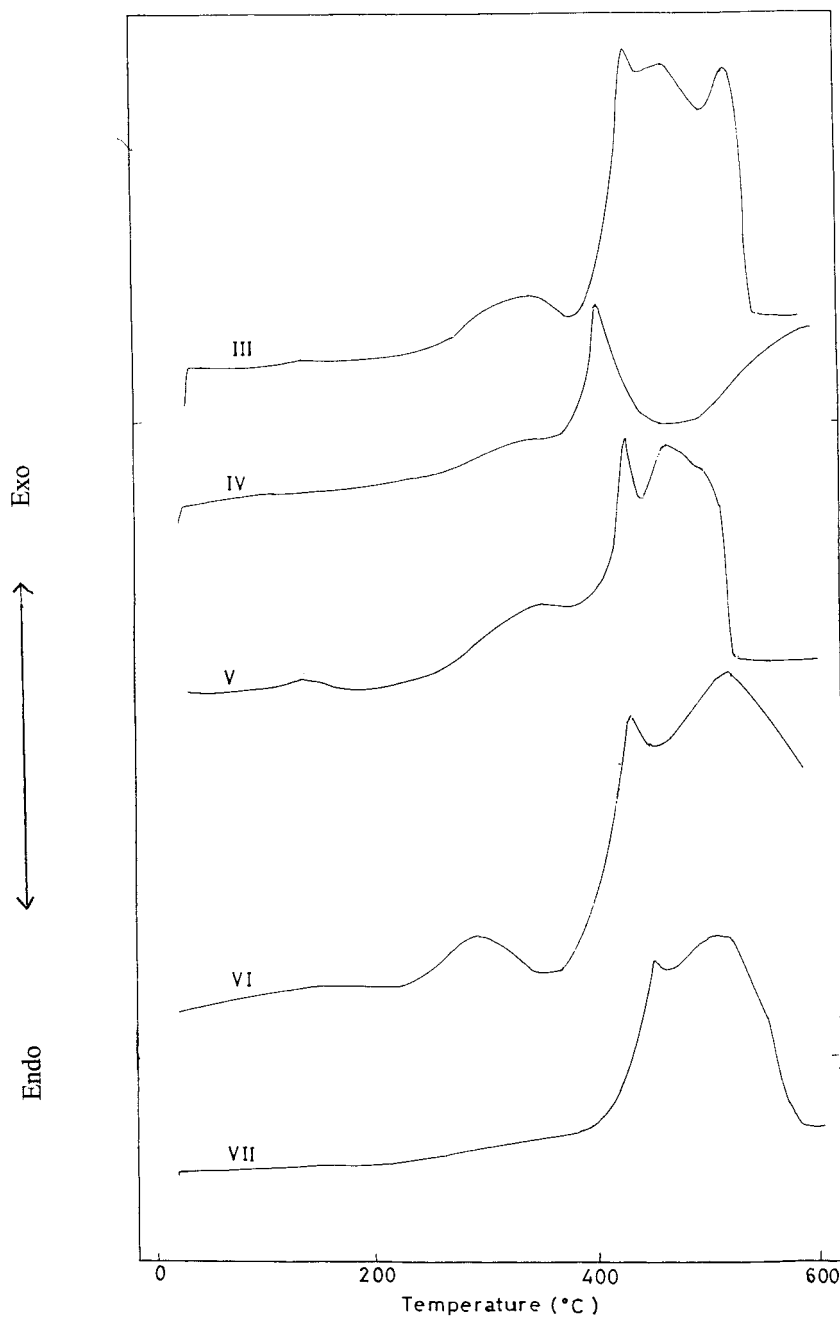
Figure 6 DSC thermograms of styrenated polyester resins **III–VII**.

are tabulated in Table IV. From the TG curves, the styrenated polyesters begin to lose negligible weight at 100–110°C and this can be attributed to the loss of water. In general, these styrenated polyesters **III–VII** begin to lose weight at an appreciable rate at about 200°C and above. Table IV shows that the maximum weight loss occurred at temperatures above 400°C. For polyester **VII**, the maximum weight loss was much lower (43.9%)

than that for polyesters **IV**, **V**, and **VI** and was relatively lower for polyester **III**, which means that polyester **VII** is relatively thermally stable. This can be attributed to its high aromaticity as compared with other investigated polyesters. On the other hand, DSC thermograms were not so illustrative for comparison as the peaks are broadened and sometimes not very distinct. The exothermic oxidative degradation started for the styrenated polyes-

Table IV   Summary of TG and DSC Data

Styrenated Polyester Resins	Maximum Weight Loss		Decomposition Exotherm		Combustion Exotherm	
	%	(Temperature °C)	Peak Temperature (°C)	ΔH (J/g)	Peak Temperature (°C)	ΔH (J/g)
III	68	(420)	428	210	518	54
IV	96.2	(460)	—	—	402	640
V	97	(440)	426	58	468	220
VI	97.5	(500)	437	100	524	72.7
VII	43.9	(450)	448	—	504	48.22

ters with the formation of low molecular weight species partially oxidized for polyester **V** at 150°C, polyester **VI** at 220°C, polyesters **III** and **IV** at 250°C, and polyester **VII** at 400°C. The decomposition and combustion exotherm of the styrenated polyesters (**III–VII**) occurred at high temperatures from 400–520°C (Table IV). At the same time, the heat of combustion recorded for the styrenated polyesters **III** and **VII** (54 and 48.27 J/g, respectively) was low. The higher temperatures at which the combustion of pyrolytic products took place, and the low heat of combustion, are indications that these polyesters can act as flame retardants. This relationship between flammability and a low heat of combustion was established by Ohe and Matsura,[9] as the lower heat of combustion means less heat being generated and radiated back to support combustion.[10,11] From the previous discussion, it may be concluded that the styrenated polyester **VII** can be considered more thermally stable, with respect to the rest of the polyesters. At the same time, polyesters **III** and **VII** may act as flame-retardants.

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