

Synthesis, Characterization and Biological Activity of Saturated and Unsaturated Copolyesters Based on Bisphenol-A

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SATURATED copolyesters were prepared by copolyesterification of bisphenol-A (BPA) and phthalic anhydride or tetrabromophthalic anhydride with ethylene glycol, diethylene glycol, 1,3-propane diol, 1,5-pentane diol, 1,6-hexane diol and cis-2-butene-1,4-diol. Also, unsaturated copolyesters were prepared by copolyesterification of bisphenol-A and maleic anhydride with the same glycols. All the copolyester resins obtained have been characterized; unsaturated copolyesters were found to cure with styrene. The properties of the copolyester in the form of films were determined. Also, the fire retardancy of polyesters was evaluated as varnish films on plywood strips. IR and ¹HNMR spectroscopy were used for characterization of the copolyester resins. The antimicrobial activity of the copolyesters obtained was examined against gram-positive and gram-negative bacteria.

Keywords: Copolyesters, Tetrabromophthalic anhydride glycols, Bisphenol-A and Antimicrobial activity.

Bisphenol-A (BPA) is a high-volume production chemical used to make epoxy resins and polycarbonate plastic products, including some kinds of water bottles, baby bottles, and food storage and heating containers⁽¹⁾. It is also used in the lining of metal food cans and in dental sealants, and is an additive to certain plastics used in children's toys. The chemical was first developed as a synthetic estrogen and was later polymerized to produce polycarbonate. Bisphenol-A mimics estrogen activity and is known as an "endocrine disruptor," a chemical that interferes with the hormonal system in animals and humans and contributes to adverse health effects. Bisphenol-A also causes a variety of impacts through mechanisms of action that are probably unrelated to estrogenic properties⁽²⁻⁵⁾. It is also a precursor to the flame retardant polymers⁽⁶⁻⁸⁾.

Saturated and unsaturated polyesters are conveniently prepared by melt copolyesterification at elevated temperature above the melting point of the reactant^(9,10). Curing of the unsaturated polyesters with styrene to form solid thermoset materials may have markedly improved properties^(9,11). It was stated previously^(12,13) that, some polyesters were prepared by the reaction of bis-

(dicarboxymethoxy)benzene phthalic anhydride and maleic anhydride with some glycols. In the present work, the synthesis of polyesters based on the condensation of bisphenol-A with phthalic anhydride, tetrabromophthalic anhydride and maleic anhydride with some glycols are described and their biological activity screened. Further, the aim was to investigate the factors affecting reactions between the unsaturated copolyesters and styrene.

Experimental

Materials

Maleic anhydride, phthalic anhydride, tetrabromophthalic anhydride and phenol benzoyl peroxide, styrene monomer, glycols (ethylene glycol, diethylene glycol, 1,3-propane diol, 1,5-pentane diol, 1,6-hexane diol and cis-2-butene-1,4-diol), dimethyl formamide (DMF), chloroform and dioxane were obtained from Aldrich, BDH, Merck and were employed as received.

Preparation of bisphenol-A

Bisphenol-A was prepared by the condensation of acetone with two equivalents of phenol in the presence of sulphuric acid⁽¹⁴⁾.

Methods

Polyesterification reactions

Bulk polyesterification reactions were carried out by the reaction of Bisphenol-A with acid anhydride and diols. Thus, the copolyesters were prepared by the reaction of bisphenol-A and acid anhydride [phthalic anhydride, tetrabromophthalic anhydride or maleic anhydride] with glycol in the molar ratio 1: 2: 1, respectively. The reactions were carried out by heating the mixture in the presence of oxygen-free nitrogen. The time-temperature program for each copolyester is illustrated in Tables 1 & 2. The copolyesters prepared were purified twice from chloroform solution by precipitation with light petroleum and then dried under reduced pressure.

Curing of polyester resins

The unsaturated polyester prepared in each case was cured⁽¹⁵⁾ with styrene, in the weight ratio of 70:30, using benzoyl peroxide as a free radical initiator (1%) weight ratio and dioxane as solvent. The cured copolyesters were casted as films on glass and tin plates. The plates were subjected to aging at 70°C for 24 hr, at 100°C for 24 hr, at 130°C for 6 hr, and finally, at 150°C for 6 hr. The films were tested for their resistance to acid and alkali solutions⁽¹⁶⁾ and to cold and hot water⁽¹⁷⁾.

The cured copolyesters were subjected to alkaline hydrolysis according to the method reported earlier⁽¹⁸⁾. The product in each case was characterized by studying its IR and ¹HNMR spectra.

TABLE 1. Time-temperature programs for saturated copolyesters (I-XII) .

Temp °C	Time (min)					
	Saturated copolyesters					
	I	II	III	IV	V	VI
70	-	30	30	30	30	30
80	60	30	30	30	30	30
90	-	30	30	30	30	30
100	60	30	30	30	30	30
110	-	30	30	30	30	30
120	60	30	30	30	30	30
130	-	30	30	30	30	30
140	60	30	30	30	30	30
150	-	30	30	30	30	30
160	60	30	30	30	30	30
170	-	30	30	30	30	30
180	60	30	30	30	30	30
190	-	30	-	-	30	30
200	60	-	-	-	-	30
210	-	-	-	-	-	-
220	60	-	-	-	-	-
230	-	-	-	-	-	-
240	60	-	-	-	-	-
250	-	-	-	-	-	-
260	60	-	-	-	-	-

TABLE 1. Cont.

Temp. °C	Time (min)					
	Saturated copolyesters					
	VII	VIII	IX	X	XI	X II
70	30	-	-	-	-	-
80	30	60	-	-	-	-
90	30	-	-	30	-	30
100	30	60	30	30	30	30
110	30	-	30	30	30	30
120	30	60	30	30	30	30
130	30	-	30	30	30	30
140	30	60	30	30	30	30
150	30	-	30	30	30	30
160	30	60	30	30	30	30
170	30	-	30	30	-	30
180	30	60	-	-	30	-
190	30	-	-	-	-	-
200	-	60	-	-	-	-
210	-	-	-	-	-	-
220	-	60	-	-	-	-

TABLE 2. Physical properties of saturated copolyester resins (I-XII).

Polyester	Nature of polyester	Med. Wt	Acid value	n	$\eta_{int.}$
I	Viscous material	4007	25.1	7	0.0671
II	Viscous material	1336	84.1	2.18	0.0231
III	Viscous material	2671	42	4.5	0.0524
IV	Low melting solid	1002	112.2	1.6	0.0354
V	Viscous material	4007	28	6.5	0.084
VI	Viscous material	2004	56.11	3.2	0.0233
VII	Viscous material	8014	14	6.8	0.0981
VIII	Viscous material	8014	14	6.5	0.0415
IX	Viscous material	4007	28	3.36	0.0561
X	Viscous material	2003	56.11	1.66	0.0854
XI	Viscous material	8014	14	6.57	0.0724
XII	Viscous material	4007	28	3.2	0.0651

Characterization of polyesters

Viscosity measurements were carried out by an Ostwald viscometer using a 1% by weight solution in dioxane at 30°C. The average molecular weight of the prepared copolyesters were determined by the end-group analysis for carboxylic groups using KOH⁽¹⁹⁾. IR spectra were recorded (KBr pellet) on a Pye-Unicam Sp-883 Perkin Elmer spectrophotometer. ¹H NMR spectra were recorded on a Varian Gemini 200 spectrometer, operating at 200 MHz for proton; Cairo University.

Preparation of varnish films

Polywood of dimensions 5 x 0.5 x 0.05 cm were varnished by dipping in solution of polyester in DMFR. The weight of the dried varnish film is equal to the difference between the weight of polywood strip before and after dipping. The strips are prepared for flammability test.

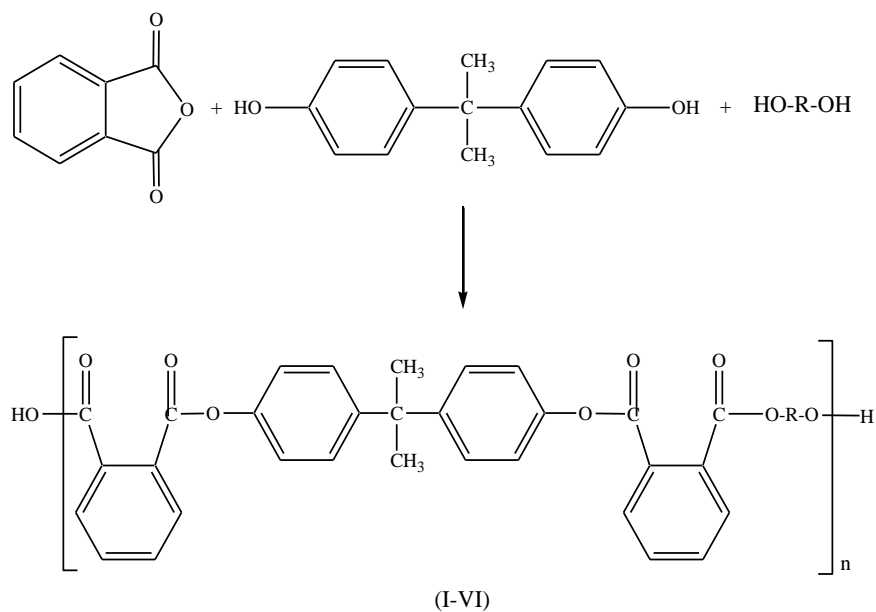
Results and Discussion

Synthesis and structure of saturated copolyester resins

In the present study, saturated copolyesters (I-VI) were synthesized by the reaction of bisphenol-A and phthalic anhydride with ethylene glycol, diethylene glycol, 1,3-propane diol, cis-2-butene-1,4-diol, 1,5-pentanediol and 1,6-hexane thylene diol.

SYNTHESIS, CHARACTERIZATION AND BIOLOGICAL ACTIVITY ...

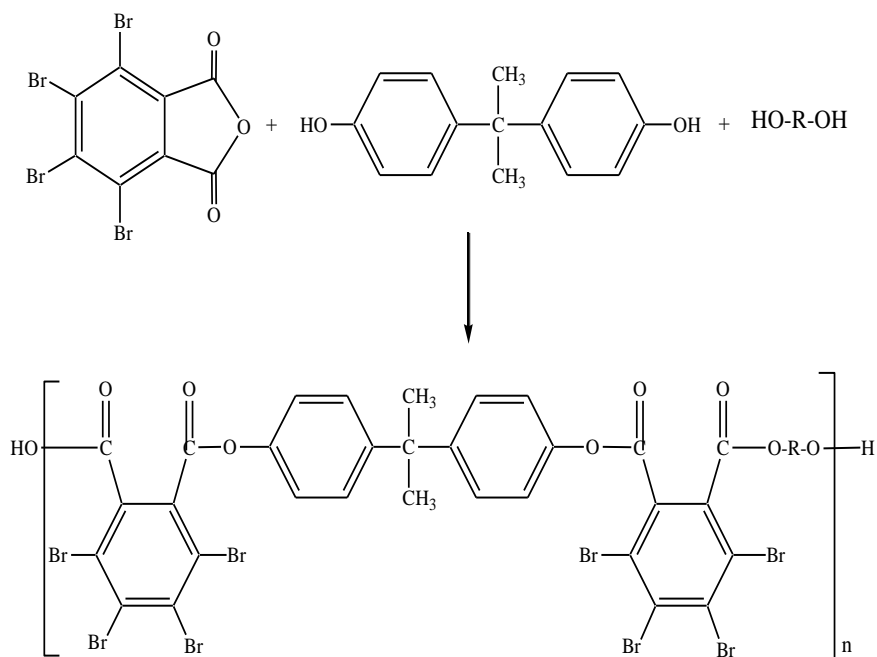
The structure of the prepared copolyesters (I-VI) can be illustrated as follows:

**Where:**

- R = I, -CH₂-CH₂-
 II, -CH₂CH₂OCH₂CH₂-
 III, -CH₂CH₂CH₂-
 IV, -CH₂-CH=CH-CH₂-
 V, -CH₂CH₂CH₂CH₂CH₂-
 VI, -CH₂CH₂CH₂CH₂CH₂CH₂-

Also, saturated copolyesters containing bromine (VII, XII) were prepared similarly by the reaction of bisphenol-A and tetrabromophthalic anhydride with the same glycols.

The structure of the prepared copolyesters (VII, XII) can be illustrated as follows:



Where

- R = VII, -CH₂-CH₂-
 VIII, -CH₂CH₂OCH₂CH₂-
 IX, -CH₂CH₂CH₂-
 X, -CH₂-CH=CH-CH₂-
 XI, -CH₂CH₂CH₂CH₂CH₂-
 XII, -CH₂CH₂CH₂CH₂CH₂CH₂-

The time-temperature program for each copolyester is illustrated in Table 1.

Fig. 1&2 shows the acid number versus time of unsaturated copolyester resins (I-XII).

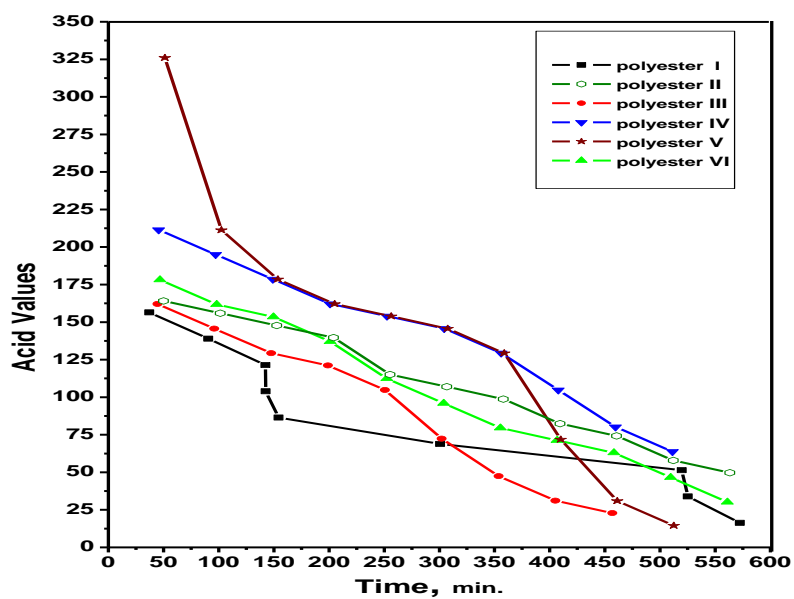


Fig. 1. The acid number versus time for saturated copolyesters resin .

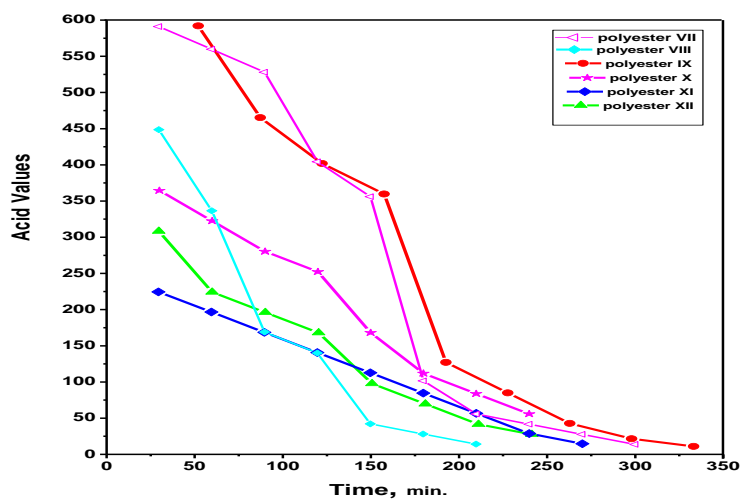


Fig. 2. The acid number versus time for saturated copolyesters resin.(VII-XII).

The structure of the prepared copolyesters was established by studying their IR and ^1H NMR spectra. The IR spectra of the prepared copolyesters showed absorption bands at $3485\text{-}3417\text{cm}^{-1}$ of μ_{OH} , $2950\text{-}2920\text{cm}^{-1}$ μ_{CH_2} (aliphatic) and $1735\text{-}1720\text{cm}^{-1}$ $\mu_{\text{C=O}}$ (ester).

The ^1H NMR spectra of copolyester (V) showed signals at $\delta 6.5\text{-}8.2$ (m, 16H) due to aromatic protons, at $\delta 4.2$ due to aliphatic protons ($-\text{CH}_2\text{OCO}$) group, at $\delta 0.7\text{-}1.7$ due to two methyl groups of bisphenol-A and $-\text{CH}_2$ group as shown in Fig. 3.

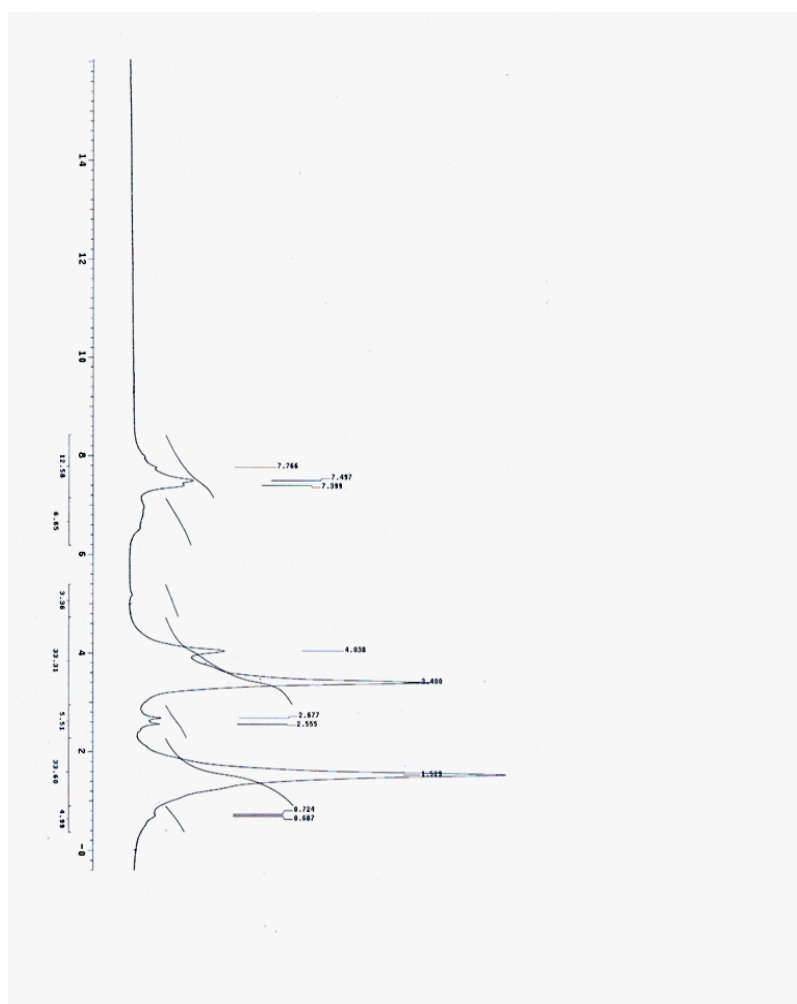


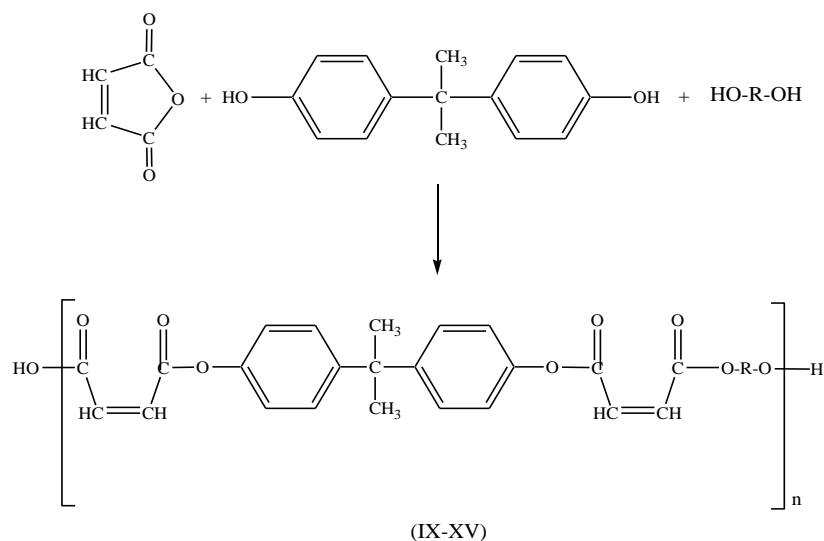
Fig. 3. ^1H NMR spectrum of copolyester (V).

Physical properties of saturated copolyester resins:

The prepared copolyesters (I-XII) were yellowish to dark brown viscous materials, soluble in various organic solvents except ethanol, n-hexane and light petroleum ether. These linear copolyesters showed great resistance to gelation after long storage periods. Some of the physical properties (acid value, molecular weight, number of repeating units and viscosity measurements) of the prepared copolyesters are illustrated in Table 2. From Table 2 it is clear that the molecular weight of the prepared copolyester resins ranged from 1002 to 8014.

Synthesis and structure of unsaturated copolyester resins

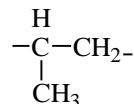
Also, in the present work, unsaturated copolyesters containing maleate unsaturation (XIII- XVIII) were prepared by the reaction of bisphenol-A and maleic anhydride with the following glycols: ethylene glycol, diethylene glycol, 1, 2- propane diol, cis-2- butene-1,4-diol, 1,5-pentane diol, and 1,6-hexane diol as follows:

**Where**

R = XIII, $-\text{CH}_2 - \text{CH}_2-$

XIV, $-\text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2-$

XV,



XVI, $-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2$

XVII, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$

XVIII, $-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2-$

The time-temperature program for each copolyester is illustrated in Table 3. Fig. 4 shows the acid number versus time (XIII-XVIII).

TABLE 3. Time-temperature programs for unsaturated copolyesters (XIII - XVIII).

Temp. °C	Time (min)					
	Unsaturated copolyesters					
	XIII	XIV	XV	XVI	XVII	XVIII
70	30	30	60	30	30	30
80	30	30	-	30	30	30
90	30	30	60	30	30	30
100	30	30	-	30	30	30
110	30	30	60	30	30	30
120	30	30	-	30	30	30
130	30	30	60	30	30	30
140	30	30	-	30	30	30
150	30	30	60	30	30	30
160	30	30	-	-	30	30
170	30	30	60	-	30	30
180	30	30	30	-	30	30
190	30	30	30	-	30	-
200	-	-	30	-	30	-
210	-	-	30	-	30	-

The structure of the prepared copolyesters was established by studying their IR and ¹HNMR spectra. The IR spectra of some prepared copolyesters showed bands at 3450-3400 cm⁻¹ (ν_{OH}), 2920-2900 cm⁻¹ ν_{CH₂} (aliphatic) and 1720-1700 cm⁻¹ ν_{C=O} (ester).

The ¹HNMR spectra of copolyester showed signals at δ6.2-8.0 (m, 12H) due to aromatic protons and -CH=CH- (olefinic protons), at δ4.2 due to aliphatic protons (-CH₂OCO) group, at δ1.7 due to two methyl groups of bisphenol-A, and at δ1.2 due to protons of -CH₂ group.

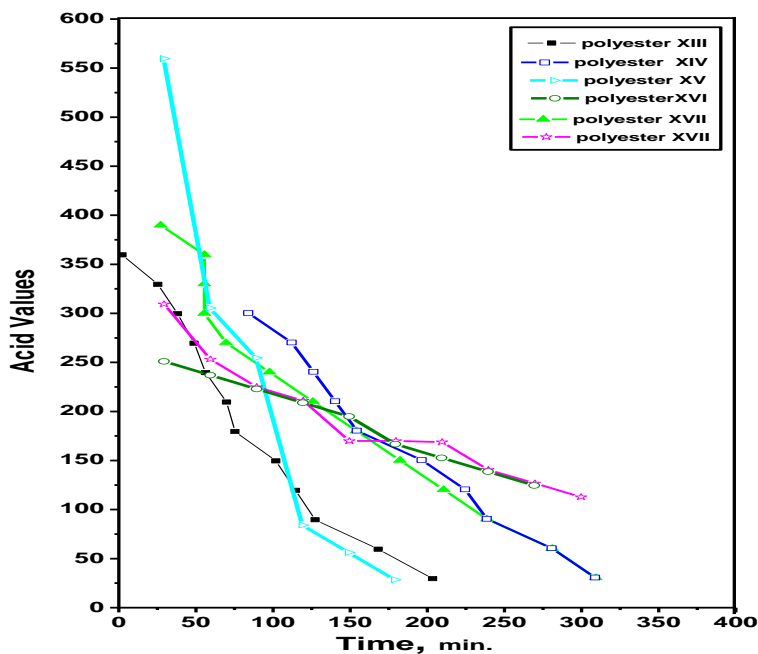


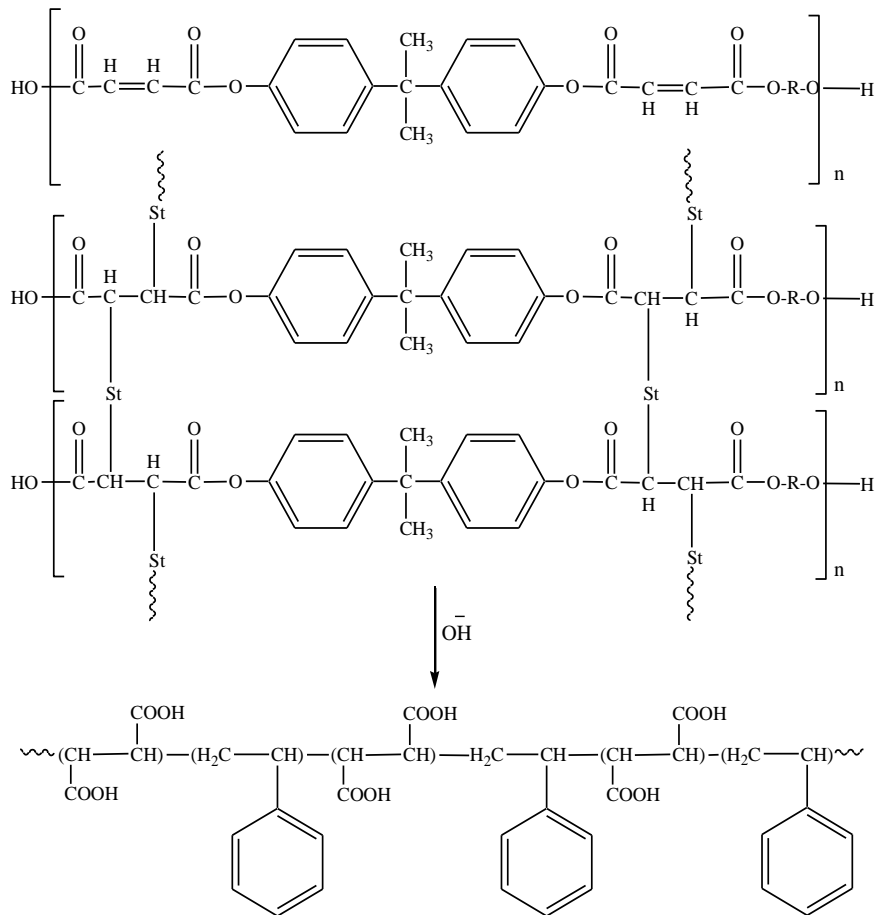
Fig. 4. The acid number versus time for unsaturated copolyesters resin (XIII-XVIII).

Physical properties of unsaturated copolyester resins

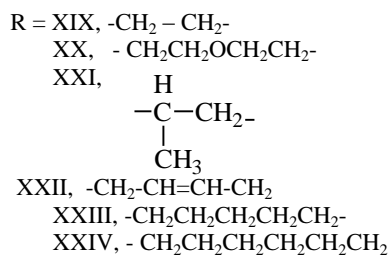
The prepared copolyesters (XIII-XVIII) were yellowish to dark brown viscous materials, soluble in various organic solvents except alcohol, n-hexane and light petroleum. The copolyesters prepared show great resistance to gelation after long storage periods. Some of the physical properties of the prepared copolyesters are illustrated in Table 4. From Table 4 it is clear that molecular weight of the prepared copolyesters resins ranged from 890 to 4007.

TABLE 4. Physical properties of unsaturated polyester resins (XIII-XVIII).

Polyester	Nature of polyester	Mol. wt	Acid value	n	η_{int}
XIII	Viscous material	4007	2.26	85.6	0.0245
XIV	Low melting solid	1002	112.22	1.9	0.0445
XV	Viscous material	4007	28.05	8.3	0.0381
XVI	Low melting solid	890	126.1	1.8	0.011
XVII	Viscous material	4007	28	7.8	0.0682
XVIII	Low melting solid	1336	84.1	2.5	0.0745



Where



Curing of unsaturated copolyester resins with styrene

The prepared unsaturated copolyesters (XIII-XVIII) were found to cure with styrene (St) to form insoluble crosslinked polymers (XIX-XXIV). The properties of these cured polyesters in the form of films showed that they have a considerable good film properties on glass and metal plates as shown in Table 5.

The cured polyesters were subjected to hydrolysis, and the hydrolyzate products (styrene-fumaric acid copolyesters) were characterized by IR and ¹HNMR spectra. Thus, their IR spectra showed bands at 3500 cm⁻¹ of ν_{OH}, at 3020 cm⁻¹ of ν_{CH} aromatic, at 1720 cm⁻¹ of ν_{C=O} and 750 & 700cm⁻¹ of aromatic five adjacent protons respectively. Also, their ¹HNMR spectra showed signals at δ6.5 to δ7.2(m,8H) due to phenyl protons of styrene units and at s1 to 2.5 (broad) due to the aliphatic protons in fumaric and styrene units.

Flamability test

Flamability test was used to evaluate the fire retardancy of polyesters (I-XII) as varnish films. Table 6 illustrates the time of burning of coated plywood strips. From Table 6 it is clear that the time of burning of coated plywood strips is greater than that of uncoated plywood strips. It is attributed to the presence of the aromatic moiety and the halogen atoms in the polyester backbone which increase the resistance to flammability.⁽¹⁸⁾

TABLE 6. Time of burning of polyesters (I-XII) as varnish films.

Polyester	Time (min.)
I	1.9
II	2.7
III	3.07
IV	2.9
V	2.5
VII	3.07
VIII	4.9
IX	5
X	5.03
XII	5.01
Uncoated strip	1.05

Antimicrobial activity

The antimicrobial activity of the synthesized compounds was determined in vitro using the hole plate and filter paper method⁽²⁰⁾ against a gram +ve and gram -ve bacteria. The tested compounds were dissolved in DMSO, different concentration have been chosen (150, 200 and 250 µg/ml). The inhibition zones of microbial growth produced by different compounds were measured in millimeters at the end of an incubation period of 48hr at 28°C. DMSO alone showed no inhibition zone. The gram -ve bacteria were Escherichia coli, Strepto bacillus and the gram +ve bacteria were Staphylococcus aureus, Bacillus subtilis. The results are illustrated in Table 7. The investigation of antibacterial screening data revealed that all tested compounds showed moderate to good activity compared to the broad spectrum antibacterial drugs used. It has been observed that most of the synthesized compounds have remarkable antimicrobial activity towards the selected bacteria

TABLE 7. Biological activity of some polyesters.

Compound No	Gram (-ve) bacteria				Gram (+ve) bacteria			
	Escherchia coli		Streptobacillus		Staphylococcus aureus		Bacillus subtilis	
	MIC	A	MIC	A	MIC	A	MIC	A
I	250	+	200	+	150	+	150	+
III	250	++	150	+	150	++	150	+++
IV	150	+	200	+	200	+	250	++
VII	150	++	150	++	250	+	250	+
IX	150	++ +	150	++	200	++	200	++
XII	150	++	200	+	150	+	150	+
XIII	150	++	150	++	200	+	150	++
XV	200	++	200	+	150	++	200	+
XVI	150	++ +	150	+++	200	++	150	++

A = antimicrobial activity of tested compounds

(+, ++ and +++) represent the extent of the zone diameter (mm) inhibition of either fungal growth or bacterial cell.

(-) no inhibition was observed.

(+) 75mm, slightly active.

(++) 77mm, modelatly active.

(+++) 79mm highly active

MIC = minimum inhibitory concentration.

Nutrient agar medium have been utilized for growing test organisms.

(DMF) was used as control for each comparison.

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تخليق وتوصيف البولي استرات المشبعة والغير مشبعة المحتوية على بس فينول- A ودراسة تأثيرها البيولوجي

أحمد عبد السلام خليل ، أمال أحمد محمود و ليلي محمد رضا
قسم الكيمياء - كلية العلوم - جامعة بنها - بنها - مصر .

في هذا البحث تم تحضير البولي استرات المشبعة من تفاعل بس فينول-A مع انهيديد حمض الفيتاليك أو رباعي بروموانهيديد حمض الفيتاليك مع الإيثيلين جليكول، ثنائي إيثيلين جليكول، أو ٣-بروبان دايلول، ٥-و١-بنتان دايلول، ١ و٦-هكسان دايلول و سيس-٢-بيوتين-١ و٤-دايلول. وأيضا تم تحضير بعض البولي استرات الغير مشبعة من تفاعل بس فينول-A وحمض المالبك اللامائي مع نفس الجليكولات السابقة. وقد تم دراسة بعض الخواص الفيزيائية للبولي استرات المحضرة، كما تم تحضير بعض البولي استرات ذات التركيبات الشبكية بتفاعلها مع المونومرات الفينيلية مثل الاستيرين لاستخدامها كأفلام على السطوح الزجاجية والمعدنية وكذلك دراسة مقاومتها للأوساط المختلفة. أيضا تم دراسة معدل الإحتراق والنشاط البيولوجي للبولي استرات المحضرة. وكذلك تم إثبات تركيب هذه البولي استرات بواسطة الأشعة تحت الحمراء والرنين النووي المغناطيسي.

