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Mohamed A. Abd-alla[a]; Kamal I. Aly[a]
[a] Polymer Lab. 507 Department of Chemistry Faculty of Science, Assiut University, Assiut, Egypt

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ARYLIDENE POLYMERS. IX. SYNTHESIS, CHARACTERIZATION, AND MORPHOLOGY OF NEW POLYESTERS OF DIARYLIDENECYCLOALKANONES CONTAINING THIANTHRENE UNITS

MOHAMED A. ABD-ALLA* and KAMAL I. ALY

Polymer Lab. 507
Department of Chemistry
Faculty of Science
Assiut University
Assiut, Egypt 71516

ABSTRACT

New polyesters containing thianthrene tetraoxide were synthesized by the interaction of 2,7-dichloroformylthianthrene-5,5′,10,10′-tetraoxide with 2,5-bis(*p*-hydroxybenzylidene)cyclopentanone, 2,5-divanillylidenecyclopentanone, 2,6-bis(*p*-hydroxybenzylidene)-cyclohexanone, 2,6-divanillylidenecyclohexanone, and 2,7-bis(*p*-hydroxybenzylidene)cycloheptanone by using the interfacial polycondensation technique. The resulting polyesters were characterized by elemental and spectral analyses. All the synthesized polymers readily dissolved at room temperature in dimethylsulfoxide. The thermal properties of the polymers were evaluated and correlated to their structural units by TGA and DSC measurements. X-ray analysis of polymers showed that all the polyesters are amorphous. Moreover, the morphology of a new high performance polyester, poly[oxycarbonyl-2,7-thianthrene-5,5′,10,10′-tetraoxidecarbonzeoxyl(2-methoxy-*p*-phenylene)methylidyne(2-oxo-1,3-cyclohexanediylidenemethylidyne)methylidene(3-methoxy-*p*-phenylene)], has been investigated by scanning electron microscopy.

INTRODUCTION

This article reports on the continuation of our scientific program on the synthesis and characterization of new polymers containing diarylidenecycloalkanone moieties [1-8] which possess interesting semiconducting and good mechanical properties, attractive morphology, and LC behavior. The preparation and properties of new polyesters including thianthrene tetraoxide units are reported.

High performance, thermally stable thermoplastic polymers are currently receiving considerable attention for their potential use as structural resins or resin/fiber composites in commercial aircraft, aerospace vehicles, and engineering materials [9, 10]. High temperature polymers (H-T) are known that have tricyclic aromatic and/or heterocyclic fused rings such as phenoxathine, dibenzo-*p*-dioxine, thianthrene, phenoxaphosphine, and phenazasiline moieties in their main chain [11-15]. The literature reveals that many polyamides and polyimides containing different heterocyclic moieties have been prepared and studied [16-21]. Recently Prema and Srinivasan reported the preparation and properties of polyamides containing thianthrene units [22]. Up to this date, no report has appeared on the synthesis of linear unsaturated polyesters with thianthrene units in the polymer backbone.

The work presented here outlines the synthesis and characterization of new polyesters of diarylidenecycloalkanones that include thianthrene moieties. A major target for this work was to study the effect of cycloalkanone ring size on the thermal stability properties of the polyesters. The crystallinity, solubility, and morphologic properties of this new class of polyesters are also examined.

EXPERIMENTAL

Measurements

The elemental analyses were done on a Perkin-Elmer 240C instrument. The IR spectra were recorded on a Pye Unicam SP3 100 spectrophotometer by using the KBr pellet technique. ^{1}H-NMR spectra were run on a Varian EM-390 90 MHz NMR spectrometer at room temperature in $CDCl_3$ or in DMSO using TMS as the internal reference. The reduced viscosities of polymer solution (0.5% w/v) in DMSO were determined at 30°C by using an Ubbelohde suspended level viscometer.

The solubilities of the polymers were examined by using 0.02 g polymer in 3-5 mL solvent at room temperature. X-ray diffractographs were obtained with a Philips X-ray PW 1710 diffractometer, using Ni-filtered CuK_α radiation. The TGA and DSC thermograms were recorded in air with Du Pont Models 951 and 910, and with Du Pont 1090 thermal analyzers, respectively, at a heating rate of 10°C/min. Pellets for electrical conductivity measurements were pressed at a constant pressure of 1000 psi with an IR die. Silver paste was used to make the contacts, and the pellets were sandwiched between two graphite electrodes. The conductivities were measured at room temperature under air by using a 610°C Keithley electrometer. The morphology of the polymers was examined by a SEM Model Jeol, JSM T 200.

Monomer Synthesis

Thianthrene

Thianthrene was prepared as described in the literature [23].

2,7-Diacetylthianthrene (I)

A solution of thianthrene (8.89 g, 0.04 mol) in 50 mL of dry CS_2 was added dropwise to a stirred mixture of acetyl chloride (25.76 g, 0.326 mol) and anhydrous $AlCl_3$ (22.4 g, 0.364 mol) in 150 mL CS_2. During the addition, the temperature of the reaction was kept at 10°C. After the end of the addition, the reaction mixture was stirred at ambient temperature for 20 h and then poured onto crushed ice/HCl. The solid product formed was filtered off, washed with water, dried, and recrystallized from an ethanol-benzene mixture (4:1) as pale yellow needles, Yield 70%, mp 175°C, literature [12] 175°C. IR (KBr) 1695 cm^{-1} (C=O); ^1H NMR ($\delta/CDCl_3$) showed at 7.35-8.15 (m, 6H of Ar—H) and at 2.65 (s, 6H of $2COCH_3$) ppm.

Preparation of 2,7-Thianthrenedicarboxylic Acid-5,5′,10,10′-tetraoxide (II)

Compound II was prepared in 89% yield by oxidation of I by using a procedure similar to that given in Ref. 22; mp > 300, IR (KBr) 1715 cm^{-1} (C=O), 3350-3100 cm^{-1} (—OH) 1310, 1165, 1130 cm^{-1} ($>SO_2$), ^1H NMR (δ/DMSO): 7.5-8.45 (m, 6H of Ar—H), 5.8 (s, 2H of —COOH) ppm.

Analysis, Calculated for $C_{14}H_8O_8S_2$: C, 45.69; H, 2.77; S, 17.56. Found: C, 45.53; H, 2.09; S, 17.59.

Preparation of 2,7-Dichloroformylthianthrene-5,5′, 10,10′-tetraoxide (III)

A mixture of diacid II (7.2 g, 0.02 mol) was boiled in 50 mL thionyl chloride in the presence of few drops of pyridene as catalyst. The excess of thionyl was distilled off and the residual matter was recrystallized from benzene-petroleum ether, bp 60–80 (1:1), yield 85%, mp 180°C (contrary to the report by Prema and Srinivasan [22]). IR (KBr) 1765 cm^{-1} (C=O) and at 1320, 1180, 1120 cm^{-1} ($>SO_2$ group).

Analysis. Calculated for $C_{14}H_{16}O_6S_2Cl_2$: C, 41.58; H, 1.48; S, 15.84; Cl, 17.32. Found: C, 41.50; H, 1.50; S, 15.70; Cl, 17.21.

Synthesis of Bis(*p*-Hydroxybenzylidene)cycloalkanone Derivatives

2,5-Bis(*p*-hydroxybenzylidene)cyclopentanone (IV), 2,5-divanillylidenecyclopentanone (V), 2,6-bis(*p*-hydroxybenzylidene)cyclohexanone (VI), 2,6-divanillylidenecyclohexanone (VII), and 2,7-bis(*p*-hydroxybenzylidene)cycloheptanone (VIII) were synthesized as reported in our previous papers [2, 3] and recrystallized twice before use.

Polymer Synthesis

In a three-necked flask equipped with a mechanical stirrer (2000 rpm/min), dry nitrogen inlet and outlet, and dropper, a mixture of 0.01 mol diarylidenecycloalkanones (IV–VIII), 25 mL methylene chloride, and sodium hydroxide solution (0.02 mol) was introduced. After mixing, 0.01 mol of III, dissolved in 25 mL methylene chloride, was added over a period of 2 min at 25°C and vigorously stirred. After complete addition of acid chloride, the stirring was continued for 2 h, and a solid polymer separated out. The solid polymer was filtered off, washed with water, hot alcohol, and hot acetone, and dried under reduced pressure (1 mmHg) at 100°C for 2 days. Table 1 summarizes the polyester yield, elemental analysis, color, and reduced viscosity.

Bis-phenol C was prepared according to the literature [24] and recrystallized twice from benzene before use.

TABLE 1. Elementary Analyses, Yield, Color, and Reduced Viscosity of Polyesters IX_{a-e}

Polymer	Analysis						Yield, %	Color	η_{red}, dL/g[a]
	C, %		H, %		S, %				
	Calcd	Found	Calcd	Found	Calcd	Found			
IX_a	64.49	63.87	3.25	3.27	10.42	11.13	89	Yellow	0.80
IX_b	61.40	60.98	3.50	3.38	9.35	9.03	91	Yellow	0.87
IX_c	63.94	63.28	3.44	3.41	10.03	9.83	87	Pale yellow	0.75
IX_d	66.06	65.83	3.98	3.91	9.79	9.64	83	Pale yellow	0.78
IX_e	64.42	64.13	3.68	3.53	9.82	9.79	85	Yellowish	0.91

[a] Reduced viscosity measured in DMSO at 30°C.

Polymerization of Bis-phenol C and 2,7-Dichloroformylthianthrene-5,5′,10,10′-tetraoxide

The polymerization method described here for the preparation of polymers $IX_{a\text{-}e}$ was applied, and the resulting polymer was purified and dried under vacuum at 1 mmHg. IR (KBr): 1745 cm^{-1} ($>$C=O of ester group), 1315, 1160, 1125 cm^{-1} ($>$SO$_2$).

Analysis. Calculated for $C_{32}H_{24}O_8S_2$: C, 64.00; H, 4.00; S, 10.67. Found: C, 63.81; H, 3.92; S, 10.37.

RESULTS AND DISCUSSION

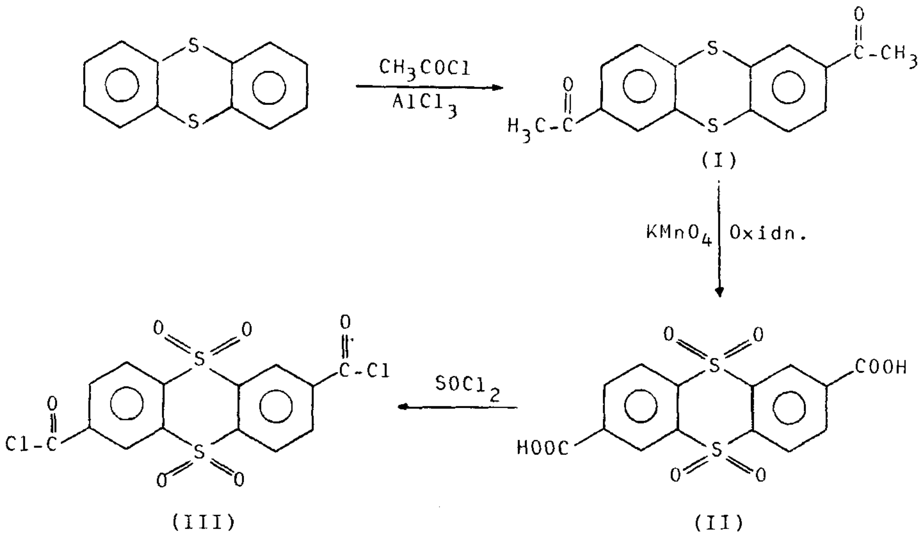
The preparation of these polyesters was based on the interaction of 2,7-dichloroformylthianthrene-5,5′,10,10′-tetraoxide (III) with various bis(*p*-hydroxybenzylidene)cycloalkanone derivatives (IV–VIII) at low temperature by using the interfacial polycondensation method. A typical synthesis and elucidation of the structure of III was performed by the following route. A thianthrene precursor was prepared as described in the literature [23] by reaction of sulfur and benzene with $AlCl_3$ in the presence of carbon disulfide as a reaction medium to afford thianthrene in good yield. Acetylation of thianthrene with acetyl chloride by a Friedel-Crafts reaction catalyst was used to obtain I. By oxidation of I with $KMnO_4$ in weak basic medium at pH 8.5, II was established in good yield, mp > 300°C. The corresponding acid chloride, III, was acquired in 87% yield by the interaction of the diacid II with excess thionyl chloride and a few drops of pyridene as catalyst. All steps followed for the preparation of III are depicted in Scheme 1.

All the structures shown in Scheme 1 are consistent with those reported in the literature [12, 22, 23], and they were confirmed by microanalysis and spectral data.

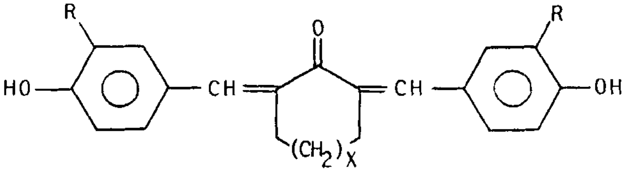
It should be noted that the melting point of the acid chloride III reported here is lower than that mentioned in the reported work by Prema and Srinivasan [22]. This may be attributed to a typing error by the authors.

The various bis(*p*-hydroxybenzylidene)cycloalkanone derivatives IV–VIII were prepared as reported in our previous papers, and their structures are represented as shown in Scheme 2.

Interaction of equimolar quantities of III with different bis(*p*-hydroxybenzylidene)cycloalkanones (IV–VIII), and the application of



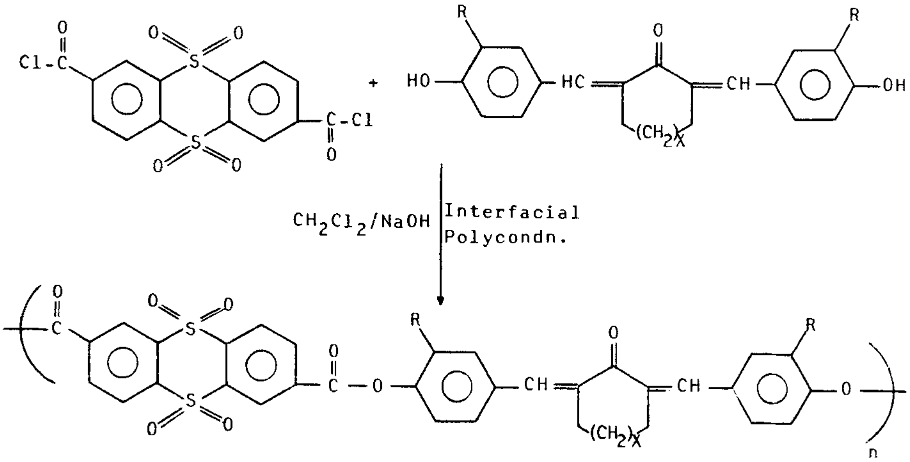
SCHEME 1.



(IV-VIII)

IV R=H, X=0 ; V R=OCH_3, X=0;
VI R=H, X=1 ; VII R=OCH_3, X=1;
VIII R=H, X=2

SCHEME 2.



IX$_a$ (R=H, X=0) ; IX$_b$ (R=OCH$_3$, X=0)
IX$_c$ (R=H, X=1) ; IX$_d$ (R=OCH$_3$, X=1)
IX$_d$ (R=H, X=2)

SCHEME 3.

low temperature interfacial polycondensation with NaOH/CH_2Cl_2, afforded new polyesters IX$_{a\text{-}e}$, shown in Scheme 3.

The resulting polymers were characterized by elemental analysis, IR spectra, solubility, viscometry, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and x-ray analysis. The elemental analysis of all the polymers coincided with the characteristic repeating units of each polymer, which revealed the introduction of new two sulfur atoms in the repeating unit. The data are included in Table 1.

The IR spectra of all polymers showed the appearance of absorption bands at 1740 ± 10 cm^{-1} (characteristic of the carbonyl groups of esters), at 1675 ± 10 cm^{-1} (C=O of cycloalkanone moieties), and at 1315, 1180, and 1125 cm^{-1} (characteristic of SO_2 stretching). Different ring stretching vibrations at 1515 cm^{-1} were shown by all the polymers with varying intensity. Besides, other characteristics absorption bands due to specific groups present in the various polymers were also shown, see Fig. 1.

The solubilities of the polyesters were tested in various solvents including a DMF-DMA mixture, NMP, DMSO, *m*-cresol, a $CHCl_3$-acetone mixture (1:1 ratio), trifloroacetic acid, concentrated H_2SO_4, and

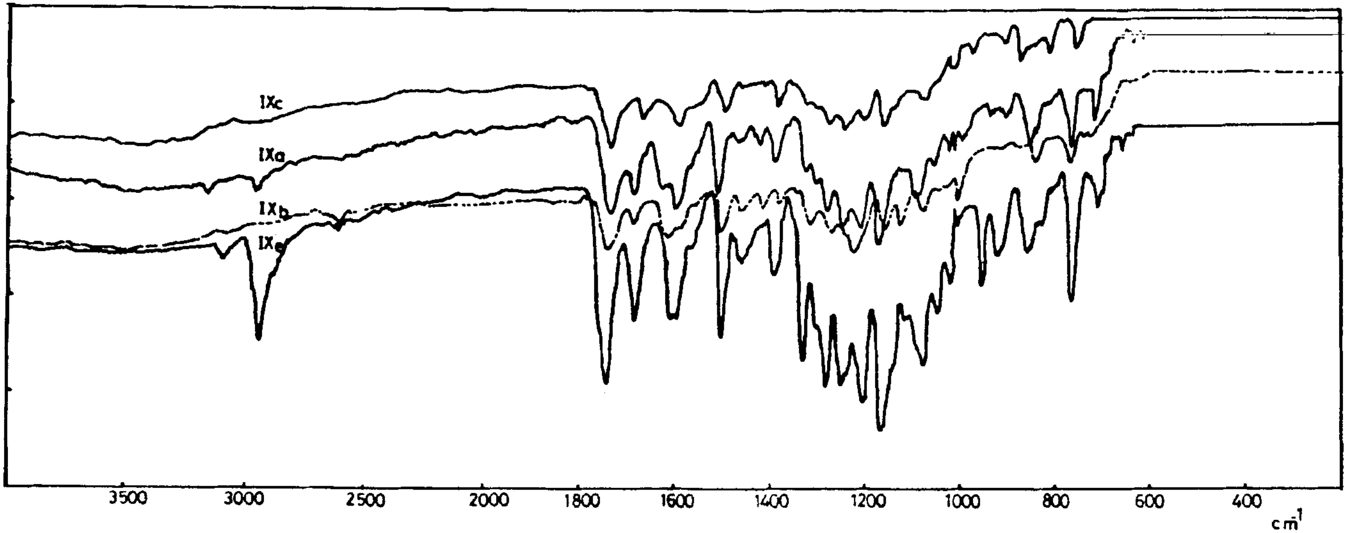


FIG. 1. The IR spectra of polymers IX_a, IX_b, IX_c, and IX_e.

TABLE 2. Solubility Characteristics of Polyesters ($IX_{a\text{-}e}$)[a]

Polymer	DMF DMA	NMP	DMSO	*m*-Cresol	$CHCl_3$ acetone	MSA	TFA	Conc H_2SO_4
IX_a	−	−	+	−	−	+	±	+
IX_b	−	−	+	−	−	+	±	+
IX_c	−	−	+	−	−	+	±	+
IX_d	−	−	+	−	+	+	±	+
IX_e	±	±	+	±	+	+	+	+

[a](+) Soluble at RT; (±) partially soluble at RT; (−) insoluble.

methanesulfonic acid. It was found that polymers $IX_{a\text{-}d}$ are insoluble in a DMF-DMA mixture, NMP, *m*-cresol, and an acetone-$CHCl_3$ mixture, while polymer IX_e is slightly insoluble in those solvents. All the polymers are completely soluble in DMSO. In strong protic solvent such as concentrated H_2SO_4 and methanesulfonic acid, all the polymers were readily soluble, giving a violet color. The greater solubility of polymer XI_e may be attributed to the greater flexibility of the cycloheptyl ring in the polymer main chain [25]; see Table 2.

The x-ray diffractographs of polymers $IX_{a\text{-}e}$ in Fig. 2 indicate an overall amorphous pattern in the $2\theta = 5\text{-}35°$ region. Attempts to crystallize any of the five prepared polymers from DMSO failed to produce a crystalline polymer. The inability to crystallize can be attributed to the unsymmetrical orientation of the polymer chains caused by the presence of the thianthrene tetraoxide moiety [26, 27].

The thermal behavior of polymers $IX_{a\text{-}e}$ was evaluated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in air at a heating rate of 10°C/min. The TG curves of these polymers are given in Fig. 3, and Table 3 gives the temperatures for various percentage weight losses. All the polymers showed similar decomposition patterns. The temperature for a 10% weight loss is considered to be the polymer decomposition point, and it ranged between 450 and 525°C. The effect of ring size on the thermal stability of polyesters can be seen from Table 3; polymers $IX_{a,\ b}$, which contain the cyclopentanone ring, are more thermally stable than other polymers. Introduction of the cyclohexanone ring in a polymer decreases stability: polymer IX_c loses 10% at 475°C and polymer IX_d loses 10% at 460°C. This decrease of stability may be attributed to the flexibility of the cyclohexyl ring. The introduction of

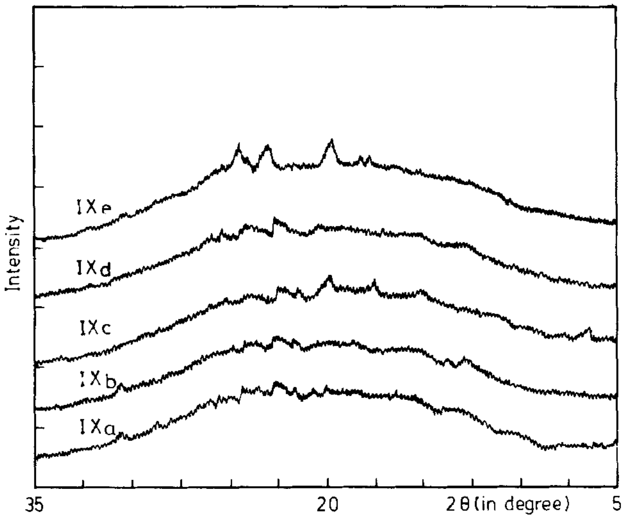


FIG. 2. X-ray diffraction patterns of polyesters IX_{a-e}.

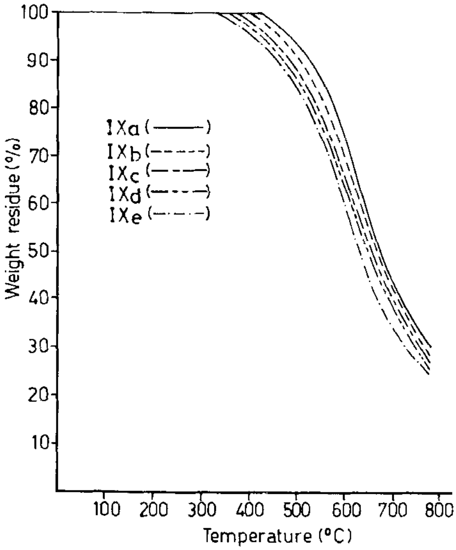
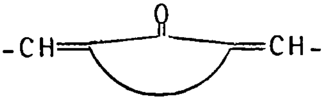


FIG. 3. Thermogravimetric curves of polyesters IX_{a-e}.

TABLE 3. Thermal Properties of Polyesters (IX_{a-e}) and Polyester Reference X

	Temperature (°C) for various percentage decompositions				
Polymer	10	20	30	40	50
IX_a	525	575	615	640	675
IX_b	505	545	580	620	655
IX_c	475	530	560	605	635
IX_d	460	520	550	585	630
IX_e	450	515	545	580	615
X	275	300	315	350	375

the cycloheptyl ring in a polymer chain also decreases thermal stability (10% weight loss for polymer IX_e at 450°C). Comparison of the thermal stability of our polyesters with another polyester (X) derived from bisphenol C and III under the same conditions reported here showed that the thermal stability of the latter (10%, 275°C; 20%, 300°C; 30%, 315°C; 40%, 350°C; 50%, 375°C) is much more lower than the former polymers, so the thermal stability of the polyesters of diarylidenecycloalkanones may be attributed to the compactness of conjugated system  in the polymer main chain. Figure 4 shows typical TGA traces of poly[oxycarbonyl-2,7-thianthrene-5,-5′,10,10′-tetroxidecarbonyloxy-*p*-phenylene(*p*-phenyl-1″,1″-cyclohexane)].

A typical DSC trace of polymer IX_a, as a selected example in Fig. 5, shows a broad exotherm which appears above 300°C. This is attributed to a curing reaction involving olefinic bonds [28]. Furthermore, the DSC thermogram shows a weak glass transition temperature at 225°C.

The prepared polymer IX_b was cast into a self-supporting film from a dichloromethane solution (5% w/v). The cast film was compact and transparent, with a faint yellow color.

The morphology of the synthesized polyester IX_d was examined by scanning electron microscopy. The SEM sample was prepared by evaporating a dilute solution of polymer IX_d on a smooth surface of aluminum foil and subsequently examined in a scanning electron microscope, Jeol,

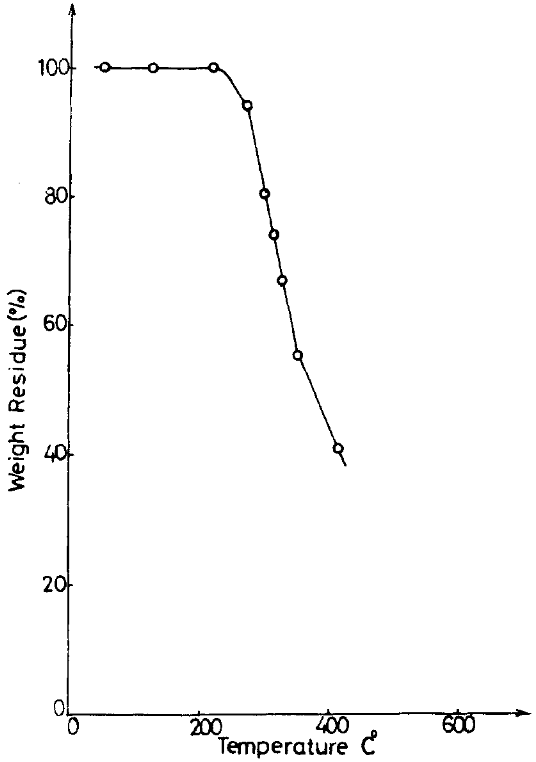


FIG. 4. Thermogravimetric curve of polymer X.

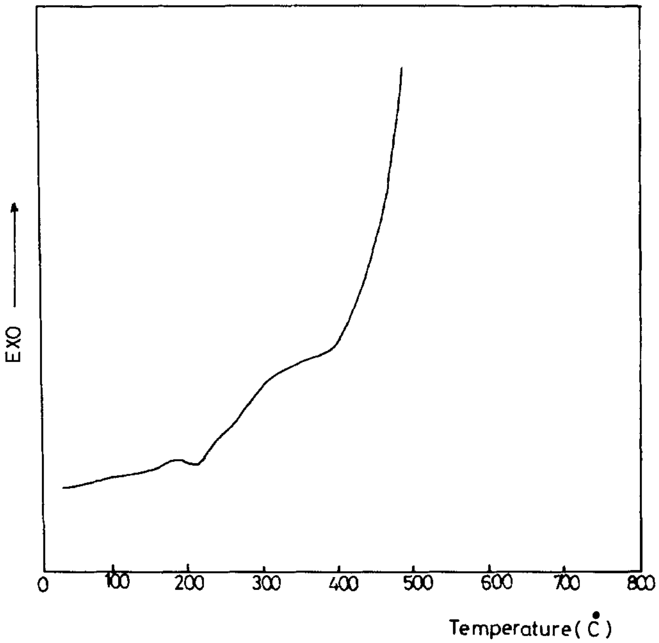


FIG. 5. DSC thermogram of polymer IX_a.

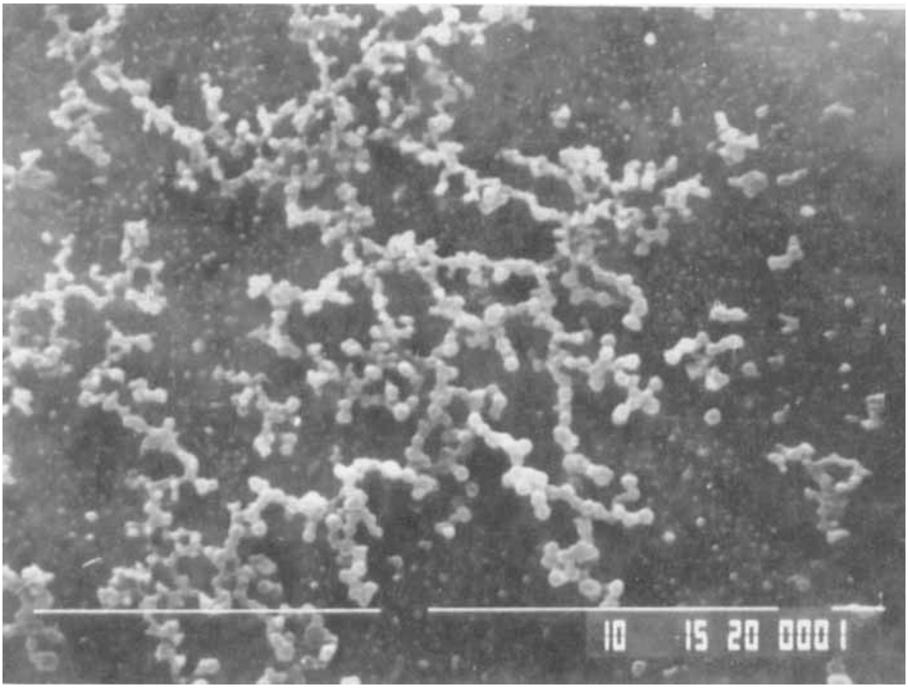


FIG. 6. SEM image of polymer IX_d.

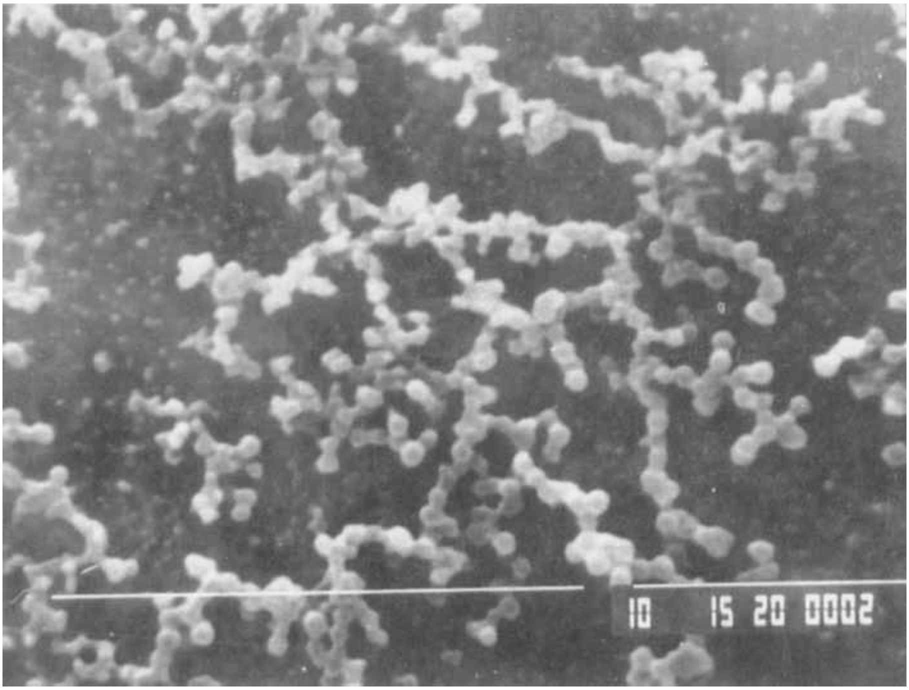


FIG. 7. SEM image of polymer IX_d.

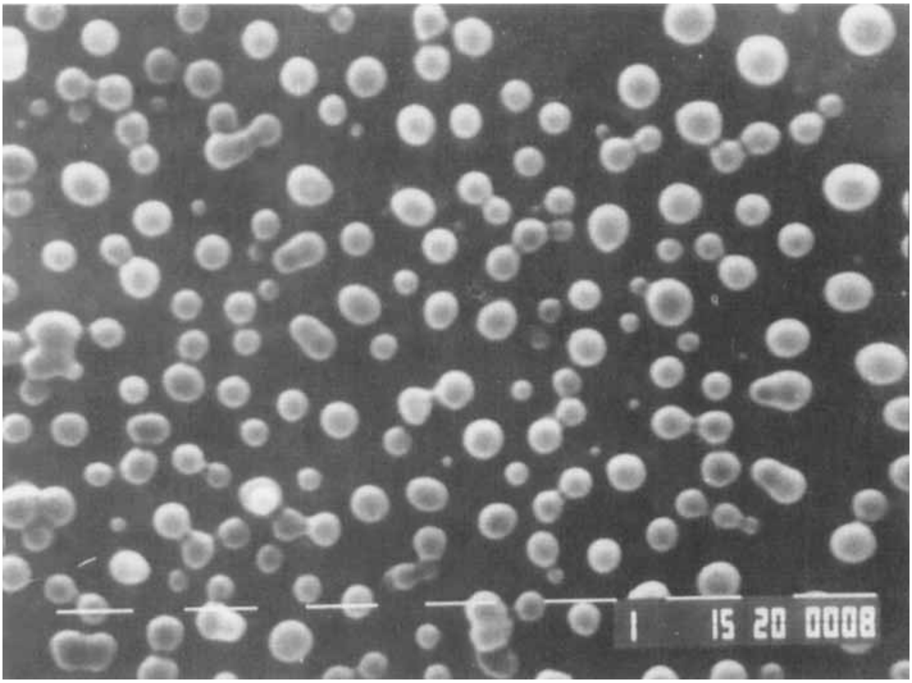


FIG. 8. SEM image of polymer IX_d.

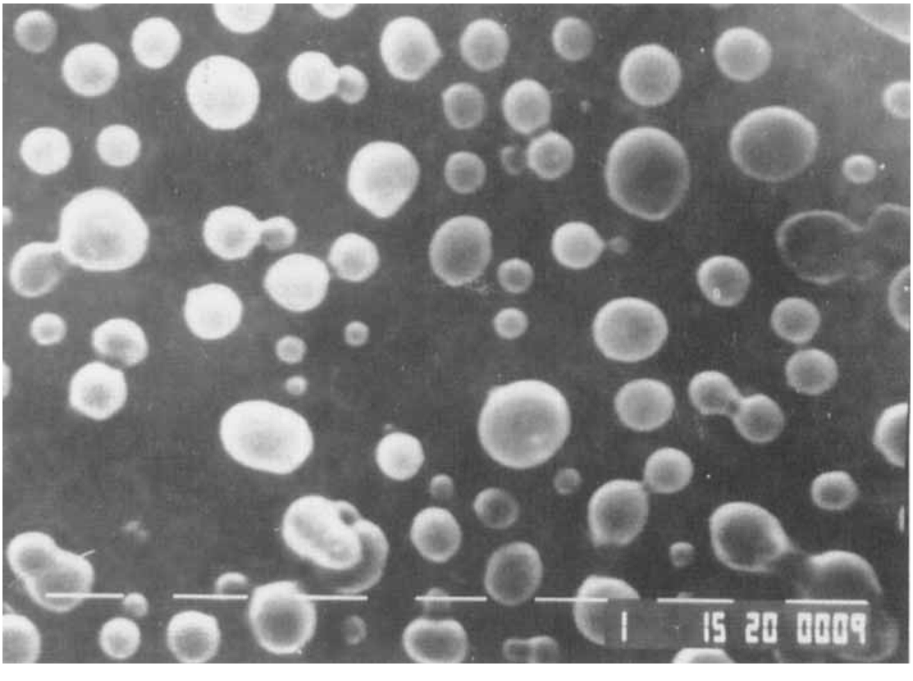


FIG. 9. SEM image of polymer IX_d.

JSM T 200, after it was coated with a gold-palladium alloy. SEM images were taken on Mamiya 6 × 7 roll film at an accelerating voltage of 10 kV by using low dose techniques. Scanning electron photographs of polymer IX_d, Figs. 6 and 7, show that the polymer surface has a polymorph globular structure in a continuous chain. Moreover, Figs. 8 and 9 exhibit globular and subglobular structures in different sizes with some coalescence.

The electrical conductivities of the prepared polyesters were tested by the Arrhenius technique. They all proved to be insulator materials (10^{-14} ohm/cm).

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