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## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### **Arylidene Polymers. XVI. Synthesis, Characterization, and Morphology of New Polyesters of Diarylidene-cycloheptanone Containing Azo and Azomethine Groups in the Main Chain**

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**To cite this Article** Abd-alla, Mohamed A. , Aly, Kamal I. and Geies, Ahmed A.(1991) 'Arylidene Polymers. XVI. Synthesis, Characterization, and Morphology of New Polyesters of Diarylidene-cycloheptanone Containing Azo and Azomethine Groups in the Main Chain', *Journal of Macromolecular Science, Part A*, 28: 3, 269 – 282

**To link to this Article:** DOI: 10.1080/00222339108052142

**URL:** <http://dx.doi.org/10.1080/00222339108052142>

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## ARYLIDENE POLYMERS. XVI. SYNTHESIS, CHARACTERIZATION, AND MORPHOLOGY OF NEW POLYESTERS OF DIARYLIDENECYCLOHEPTANONE CONTAINING AZO AND AZOMETHINE GROUPS IN THE MAIN CHAIN

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### ABSTRACT

A new class of linear unsaturated polyesters of diarylidene-cycloheptanone containing azo or azomethine groups in the polymer main chain has been synthesized by interfacial polycondensation of 4,4'-azodibenzoyl chloride, 3,3'-azodibenzoyl chloride, and 4,4'[1,4-phenylene bis(methylidenenitrilo)]dibenzoyl chloride with 2,7 bis(*p*-hydroxybenzylidene)cycloheptanone at ambient temperature. The resulting polyesters were characterized by elemental analyses, IR spectroscopy, solubility, and viscometry measurements. The thermal properties of the polymers were evaluated by TGA and DTA measurements. The crystallinity of the polymers was examined by x-ray analysis. The morphology of a high performance polyester, namely poly[oxycarbonyl-3,3'-azobenzene-carbonyloxy-*p*-phenylene-methylidyne (2-oxo-1,3-cycloheptanediylidene) methylidyne-*p*-phenylene], has been investigated by scanning electron microscopy. The UV-visible spectra of polymers V and VI were

measured in *m*-cresol solution and showed characteristic absorption bands at 468 and 490 nm due to  $n-\pi^*$  transition. In addition, the electrical properties of the polymers were measured.

## INTRODUCTION

In recent years, polymers containing certain chromophoric groups in the main chain have received the attention of synthetic polymer chemists [1, 2]. The aromatic azo group is of special interest due to the existence of *cis-trans* isomerism and its effect on the photochromic properties of the polymers [3, 4]. Some aromatic polyamides containing azo groups exhibiting liquid crystalline behavior have been spun into high strength high modulus fibers [5]. Therefore, polymers that contain the azo group have potential use in a variety of applications [6-9], especially polyazoarylenes, which have been reported to be highly conducting materials upon doping [10]. In addition, the azomethine linkage ( $-\text{CH}=\text{N}-$ ) has special interest due to its *syn-anti* isomerism and its effect on the thermal and photochromic properties [11].

In recent work we reported the synthesis and characterization of new linear unsaturated polyesters of diarylidencycloalkanones (five- or six-membered ring) containing azo or azomethine linkage with interesting chromophoric and electrical properties [12, 13].

The work reported in this article outlines the synthesis, characterization, and morphology of new polyesters of diarylidencycloheptanone based upon aromatic azo or azomethine moiety.

A major target of this work has been a study of the effects of the inclusion of a seven-membered ring in the polymer backbone on polymer properties. The crystallinity, morphology, photochromic, and electrical properties of the synthesized polymers were also investigated.

## EXPERIMENTAL

### Measurements

The elemental analyses were done on a Perkin-Elmer 240 C instrument. The IR spectra were recorded on a Pye Unicam SP 3 1000 spectrophotometer by using the KBr pellet technique.  $^1\text{H-NMR}$  spectra were run on a Varian EM-390 90 MHz NMR spectrometer at room temperature in

DMSO, using TMS as the internal reference. The inherent viscosity of a polymer solution (0.5% w/v) in *m*-cresol was determined at 30°C by using an Ubbelohde suspended level viscometer.

The solubility of the polymers was determined by using 0.02 g polymer in 3–5 mL solvent at room temperature. X-ray diffractograms were obtained by using a Philips X-ray PW 1710 diffractometer with Ni-filtered  $\text{CuK}_\alpha$  radiation. The TGA and DTA thermograms were carried out in air by using DuPont Model 951, 910, and DuPont 1090 thermal analyzers at a heating rate of 10°C/min. The morphology of the polymers was examined by a SEM Model Jeol, JSM T 200. Pellets for electrical conductivity measurements were prepared by pressing at constant pressure (1000 psi) with an IR die. Silver paste was used to make the contacts, and the samples were sandwiched between two graphite electrodes. Conductivity was determined at ambient temperature in air by using a 610 C Keithley Electrometer.

### Synthesis of the Acid Chlorides

4,4'-Azodibenzoyl chloride (I) and 3,3'-azodibenzoyl chloride (II) were prepared according to the method reported by Tomlinson [14]. 4,4'-[1,4-Phenylene bis(methylidenenitrilo)]dibenzoyl chloride (III) was prepared by the Subramanian method [15].

### Synthesis of 2,7-Bis(*p*-hydroxybenzylidene)cycloheptanone (IV)

This monomeric compound was synthesized as described in our previous papers [16, 17].

### Polymerization

A mixture of 0.01 mol 2,7-bis(*p*-hydroxybenzylidene)cycloheptanone (IV), 25 mL dry methylene chloride, and a suitable quantity of sodium hydroxide (3 mmol, soluble in 30 mL water) was introduced into a three-necked flask (500 cm<sup>3</sup> volume) equipped with a mechanical stirrer (2000 rpm/min), dry nitrogen inlet and outlet, and dropper. After mixing, 0.01 mol acid chloride (I–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 a further 3 h, at which time a highly orange solid separated out. The solid polymer was filtered off, washed with excess water, ethanol, and hot

acetone, and finally dried under reduced pressure (1 mmHg) at 70°C for 2 days. All the polyesters produced, their yield, and some physical properties are listed in Table 1. For the identification of each polymer, refer to Scheme 1.

## RESULTS AND DISCUSSION

The preparation of this new class of unsaturated polyesters was based on 2,7-bis(*p*-hydroxybenzylidene)cycloheptanone (IV). This monomer was synthesized in good yield by condensation of 2 mol *p*-hydroxybenzaldehyde with 1 mol cycloheptanone under the same conditions as reported in our previous work [16, 17].

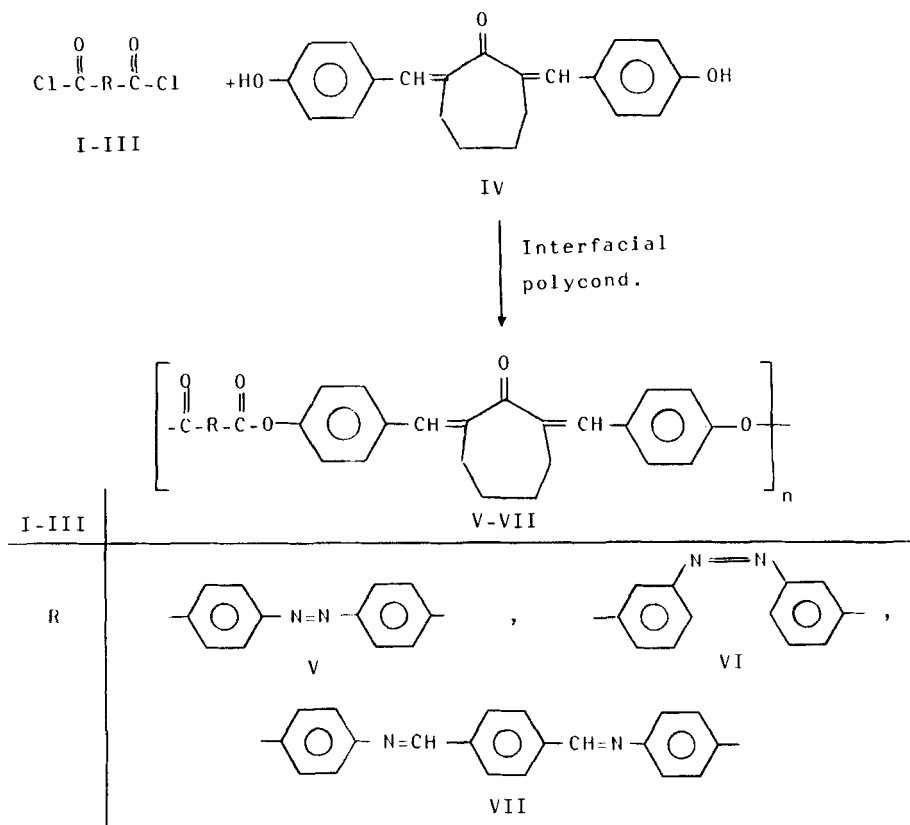
The new polyesters of diarylidencycloheptanone containing azo and azomethine groups in the polymer backbone were synthesized by the interaction of equimolar quantities of 4,4'-azodibenzoyl chloride (I), 3,3'-azodibenzoyl chloride (II), or 4,4'-[1,4-phenylene bis(methylidene)nitrite]dibenzoyl chloride (III) with 2,7-bis(*p*-hydroxybenzylidene)cycloheptanone (IV) by using an interfacial polycondensation technique in the presence of benzyltriethylammonium chloride as a phase-transfer catalyst at ambient temperature. The synthesis of these polyesters is represented in Scheme 1.

The resulting polymers were characterized by elemental analysis, IR spectra, solubility, viscometry, thermogravimetric analysis (TGA), differential thermal analysis (DTA), ultraviolet spectra, x-ray analysis, and morphology. The elemental analysis of all the polymers coincided with the characteristic repeating units of each polymer, and revealed the introduction of new two nitrogen atoms in the repeating unit. These data are included in Table 1. The IR spectra of the polymers showed the appearance of new absorption bands at 1730–1735  $\text{cm}^{-1}$ , characteristic of the carbonyl groups of esters, and at 1665  $\text{cm}^{-1}$  (C=O of cycloheptanone). It should be pointed out that the  $\text{—N=N—}$  absorption band of the aromatic azo compound in polymers V and VI is difficult to identify in the IR spectra because of the interference of the C=C ring stretching vibration [18, 19], while an absorption band at 1610  $\text{cm}^{-1}$ , characteristic of C=N—, appears in polymer VII. The absorption bands at 825 and 750  $\text{cm}^{-1}$  belong to the out-of-the-plane vibration of hydrogen in the aromatic ring. In addition, other characteristic absorption bands, due to specific groups present in the rest of macromolecule, are also evident in the IR spectra.

TABLE 1. Results of Elementary Analyses, and Some Physical Properties of Polymers V-VII

Polymer	Analysis						Yield, %	Color of the polymer	$\eta_{inh}$ , dL/g <sup>a</sup>
	C, %		H, %		N, %				
	Calcd	Found	Calcd	Found	Calcd	Found			
V	75.81	75.52	4.69	4.57	5.05	4.92	92	Orange	0.73
VI	75.81	75.38	4.69	4.43	5.05	4.91	89	Pale orange	0.83
VII	76.03	75.79	5.48	5.23	4.79	4.63	83	Yellowish	0.65

<sup>a</sup>Inherent viscosity measured in *m*-cresol.



SCHEME 1.

The inherent viscosity of a polymer solution (0.5%, w/v) in *m*-cresol was determined at 30°C by using a Ubbelohde suspended level viscometer (see Table 1).

The solubility characteristics of polymers V-VII were tested in various solvents including NMP, DMA, DMF, DMSO, CH<sub>2</sub>Cl<sub>2</sub>, *m*-cresol tetrachloroethylene, a CHCl<sub>3</sub>-acetone mixture, concentrated H<sub>2</sub>SO<sub>4</sub>, and methanesulfonic acid (MSA). A 10% (w/v) solution was taken as a criterion for solubility. It was found that all the polymers dissolved readily in concentrated H<sub>2</sub>SO<sub>4</sub> or methanesulfonic acid to give a violet solution. Polymer VII, which contains the azomethine linkage, is more soluble in tetrachloroethylene than polymers V and VI, which possess

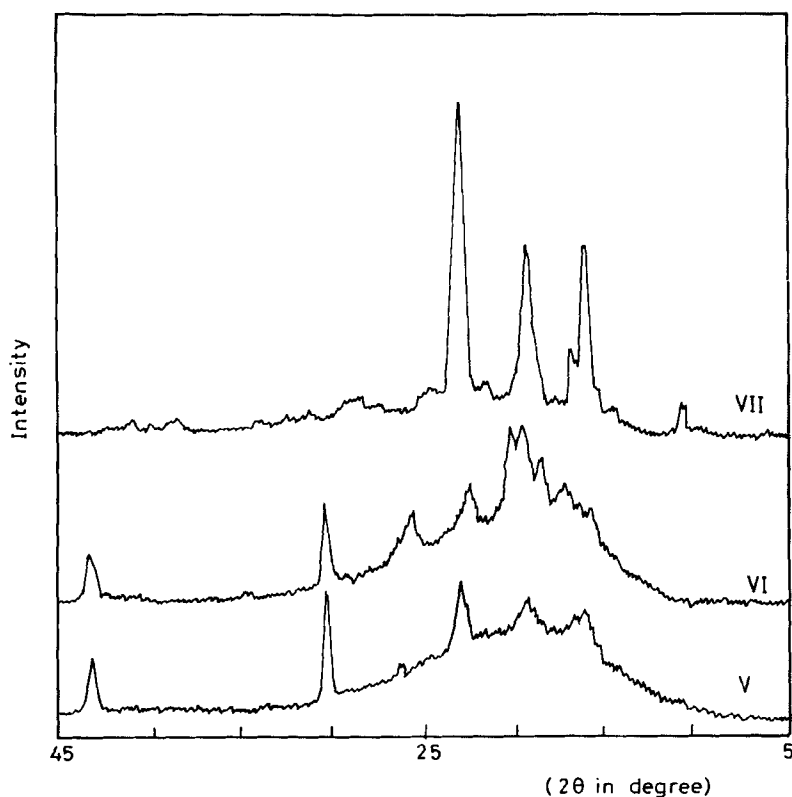


FIG. 1. X-ray diffraction patterns of polymers V-VII.

the azo group. Moreover, a polyester that contains a 3,3'-azo linkage is more soluble than polymer VII which is connected through the 4,4'-position. This may be attributed to the close packing of the polymer chain in the latter polymer [20, 21]. In addition, the increase in the solubility of these polymers which contain a cycloheptanone moiety may be attributed to the flexibility of the cycloheptanone ring which possesses two types of conformation (boat and chair), causes unsymmetrical orientation in the polymer macrochain, prevents close packing of polymer molecules, and thereby makes solvation easier [22].

X-ray diffractographs of polymers V-VII in Fig. 1 show a few reflections of sharpness peaks intermediate between crystalline and amorphous interferences in the  $2\theta = 5-45^\circ$  region. The presence of



—N=N— or —CH=N— as polar groups, in addition to the high level of —C=C— bonds, induces some degree of crystallinity [12, 23]. X-ray diffractograms in Fig. 1 also show that a polymer based on azomethine linkage VII has a high degree of crystallinity in comparison to those based on a para-azo linkage or a meta-azo linkage (V, VI).

The thermal behavior of polymers V–VII were evaluated by thermogravimetric analysis (TGA) and differential thermal analysis (DTA) in air at a heating rate of 10°C/min. TG curves of the polymers are shown in Fig. 2, and Table 2 gives the temperatures for various percentage weight losses. All the polymers showed similar patterns of decomposition. The first step in the thermal decomposition of polymers V and VI, which contain an azo linkage, is the elimination of the azo group as molecular nitrogen. This observation is in agreement with that of Bach and Black [1]. The temperature at which 10% weight loss occurs is considered to be the polymer decomposition temperature, and it ranges between 255 and 295°C. Polymer VII, which contains an azomethine linkage, is less thermally stable than those containing an azo linkage. More particularly, polymer VI, which is based on the meta-azo linkage, is less thermally stable than polymer V, which is based on the para-azo linkage, and this may be attributed to differences in stereoregularity. The 4,4'-structure leads to more compact packing of the polymer chain [20].

The ultraviolet and visible spectra of polymers V and VI were measured in a *m*-cresol solution  $1 \times 10^{-3}$  (w/v). The UV spectra of the polymers showed a broad absorption band at  $\lambda_{\max}$  468 nm for polymer VI, and at  $\lambda_{\max}$  490 nm for polymer V. The appearance of a broad absorption band in the UV spectra is attributed to the  $n-\pi^*$  transition of the —N=N— group present in the polymer main chain (see Fig. 3).

The electrical conductivity of the polyesters was measured by the Arrhenius method and gave values in the  $10^{-11}$  to  $10^{-12}$  ohm/cm range.

The morphology of the synthesized polyester VI was examined by scanning electron microscopy (Jeol, JSM T 200). The SEM sample was prepared by the traditional detachment thin film technique [24, 25]. SEM images were taken on Mamiya 6×7 roal film. A scanning electron photograph of polymer VI (Fig. 4) shows the surface of the polymer has the polymorph of a globular structure in continuous merging chains, whereas Fig. 5 exhibits the presence of globular, subglobular, and am-pullar structures of different sizes on the polymer surface.

Moreover, the morphological features of the longitudinal fracture surface of polyester VI were also examined by SEM at 15 kV at different

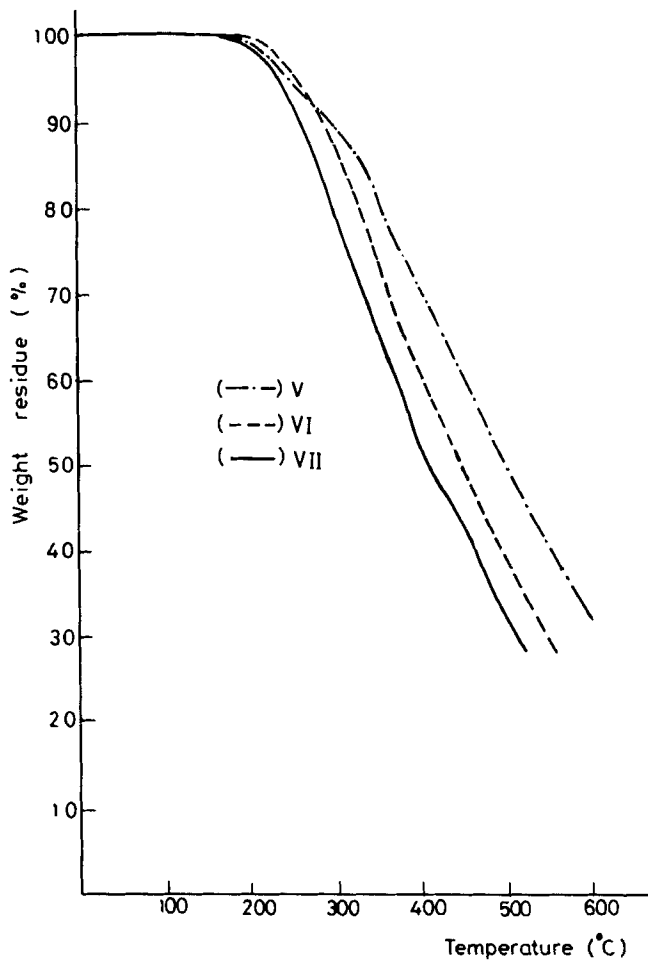


FIG. 2. Thermogravimetric curves of polymers V-VII.

TABLE 2. Thermal Properties of Polymers V-VII

Polymer	Temperature (°C) for various % decomposition				
	10	20	30	40	50
V	295	350	395	445	490
VI	280	325	360	400	450
VII	255	300	330	370	395

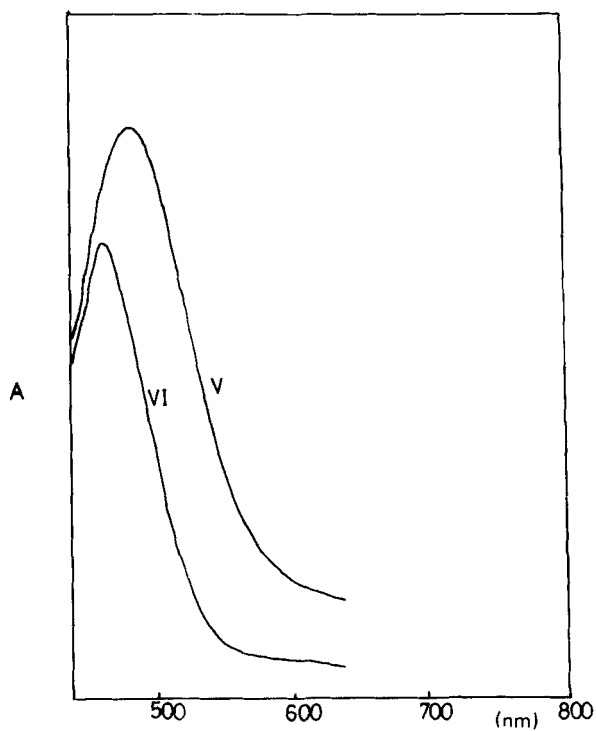


FIG. 3. The ultraviolet visible spectra of polymers V and VI.

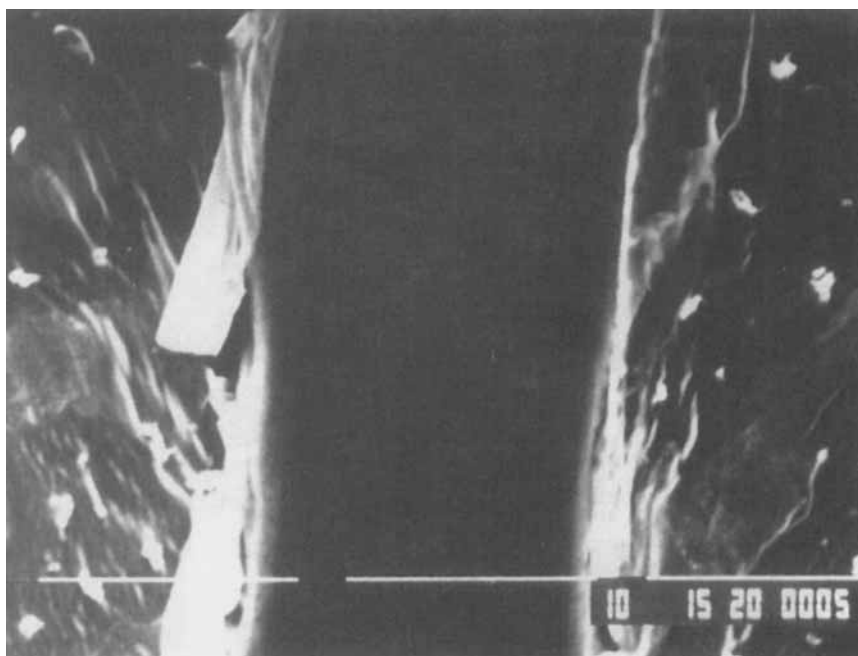


FIG. 4. SEM image of polymer surface VI.

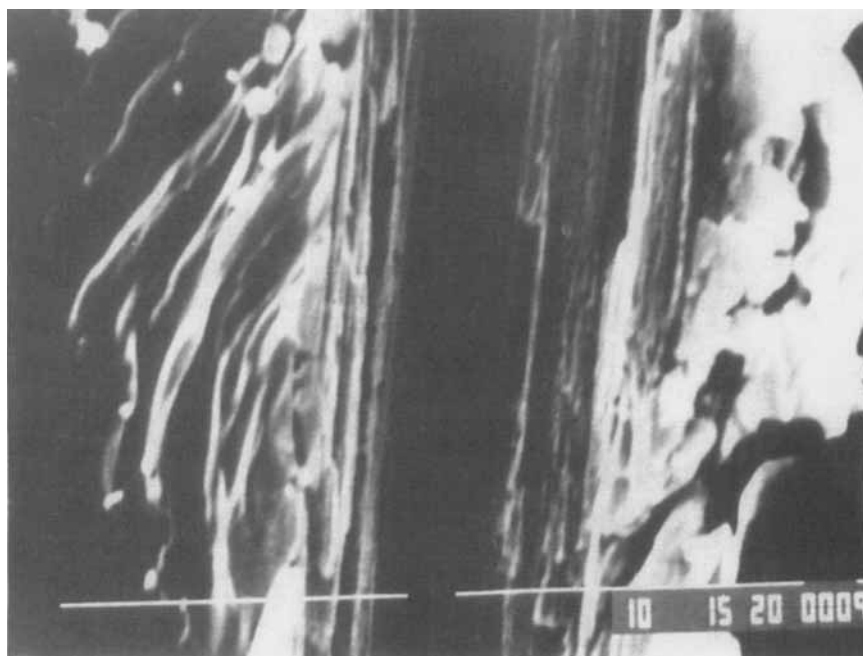


FIG. 5. SEM image of polymer surface VI.

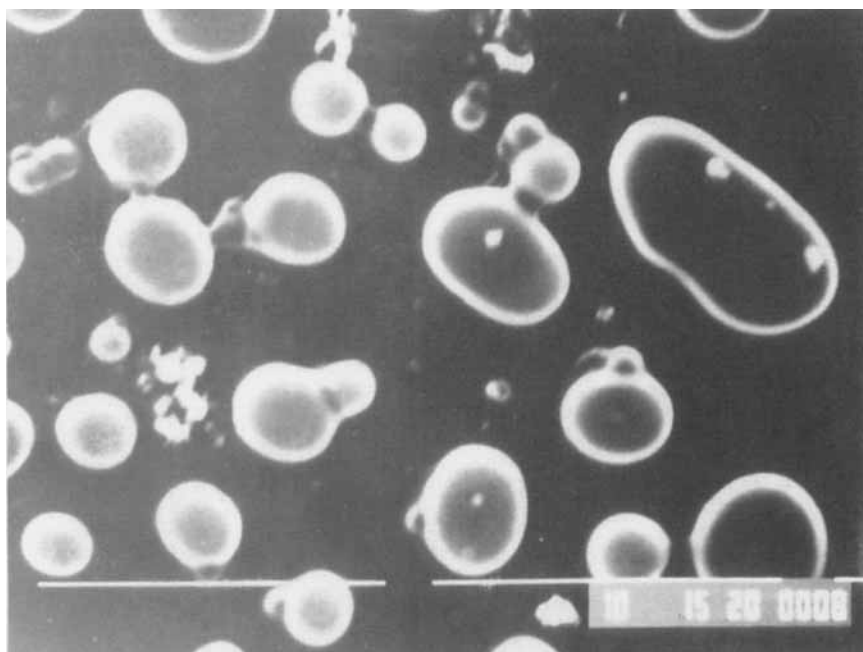


FIG. 6. SEM image of longitudinal fracture surface of polymer VI.

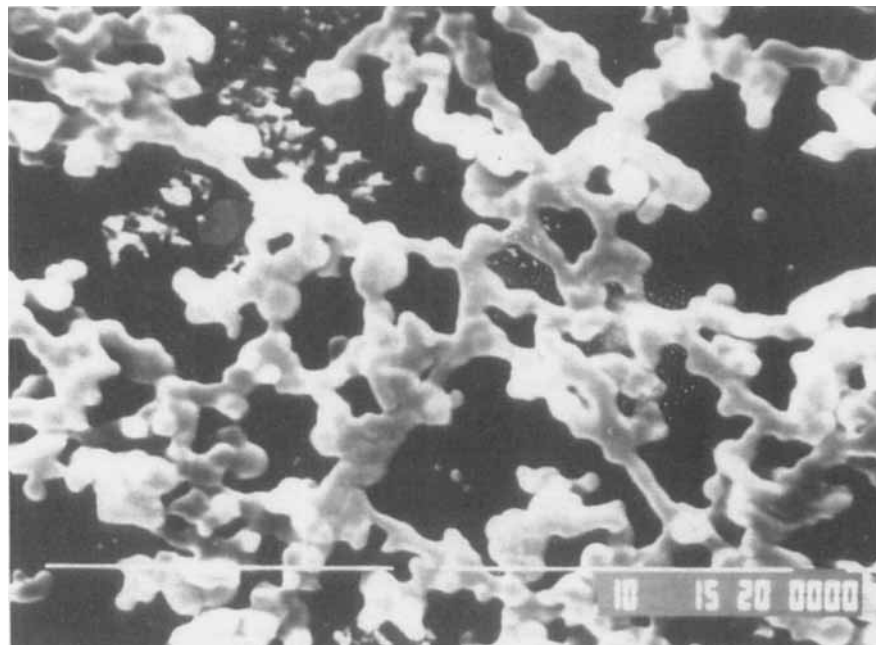


FIG. 7. SEM image of longitudinal fracture surface of polymer VI.

magnifications. The SEM image of the fracture surface of polyester VI in Figs. 6 and 7 shows that microfibril structure morphology exists.

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Received July 23, 1990

Revision received October 22, 1990