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### Arylidene Copolyether Sulfones. II. Synthesis and Characterization of Some New Copolyether Sulfones Containing Dibenzylidene Cyclohexanone Moieties

E. Butuc<sup>a</sup>; V. Cozan<sup>a</sup>; A. Stoleriu<sup>a</sup>; M. Rusu<sup>b</sup>; Yushan Ni<sup>c</sup>; Mengxian Ding<sup>c</sup>

<sup>a</sup> "Petru Poni" Institute of Macromolecular Chemistry Romanian Academy, Jassy, Romania <sup>b</sup> Faculty of Chemical Technology, Technical University, Jassy, Romania <sup>c</sup> Changchun Institute of Applied Chemistry Chinese Academy of Sciences, Changchun, People's Republic of China

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## ARYLIDENE COPOLYETHER SULFONES. II. SYNTHESIS AND CHARACTERIZATION OF SOME NEW COPOLYETHER SULFONES CONTAINING DIBENZYLIDENE CYCLOHEXANONE MOIETIES

E. BUTUC, V. COZAN, and A. STOLERIU

“Petru Poni” Institute of Macromolecular Chemistry  
Romanian Academy  
Aleea Grigore Ghica Voda, No. 41 A, RO 6600 Jassy, Romania

M. RUSU

Faculty of Chemical Technology  
Technical University  
RO 6600 Jassy, Romania

YUSHAN NI and MENGXIAN DING

Changchun Institute of Applied Chemistry  
Chinese Academy of Sciences  
Changchun 130022, People's Republic of China

### ABSTRACT

New copolyether sulfones containing 2,6-bis(*p*-oxo-benzylidene)-cyclohexanone and 2,6-bis(*o,p*-dioxo-benzylidene)cyclohexanone moieties were prepared in the conventional literature manner by condensing the dipotassium salts of 2,6-bis(*p*-hydroxybenzylidene)cyclohexanone (III), 2,6-bis(*o,p*-dihydroxybenzylidene)-cyclohexanone (V), and 2,2-bis(*p*-hydroxyphenyl)propane (Bisphenol A, VII) with 4,4'-dichlorodiphenyl sulfone (VI), or by condensing the dipotassium salts of III and VII with a new benzylidene cyclohexanone sulfone macromer (X). Fi-

nally, the polycondensation reaction of sulfonyl bis(*p*-benzaldehyde-oxo-*p*-phenylene) (IX) with cyclohexanone leads to an unsaturated copolymer (XVI). The resulting copolyether sulfones were confirmed by IR, <sup>1</sup>H-NMR, viscometry, elemental analysis, thermo-optical (TOA), x-ray, and thermogravimetric (TGA) measurements.

## INTRODUCTION

Aromatic polysulfones are known to be thermally quite stable. They have suitable properties for use as high temperature thermoplastic composite materials.

There are few literatures available concerning unsaturated aromatic copolyether sulfones.

In our previous work [1] we reported the synthesis and some properties for copolyether sulfones containing dibenzylidene cyclopentanone moieties on the backbone.

In this paper we focus on continuing this series with copolyether sulfones containing dibenzylidene cyclohexanone moieties on the backbone.

## EXPERIMENTAL

### Measurements

The IR spectra were recorded on a Specord M90 Carl Zeiss Jena spectrophotometer by using the KBr pellet technique. <sup>1</sup>H-NMR spectra were run on a Jeol 60 MHz NMR spectrometer at 60°C in DMSO-*d*<sub>6</sub> using TMS as the internal reference. The reduced viscosities of copolymer solutions (0.2% w/v) in NMP were determined at 25 ± 0.1°C by using an Ubbelohde suspended level viscometer. Melting and softening points were determined with a Gallenkamp hot-block melting point apparatus. TGA was carried out in air with an F. Paulik Derivatograph at a heating rate of 12°C/min. X-ray measurements were made with a Rigaku IIB x-ray diffractometer. TOA was carried out as described in the literature [2].

### Reagents and Materials

4,4'-Dichlorodiphenyl sulfone (Aldrich) was recrystallized from toluene (mp 146–149°C). Bisphenol A (Fluka) and 4-hydroxybenzaldehyde (Aldrich) were used as received. 2,4-Dihydroxybenzaldehyde was synthesized according to the literature cited procedure, mp 135–137°C (literature: 135°C) [3]. NMP was vacuum distilled over P<sub>2</sub>O<sub>5</sub>. Chlorobenzene (Aldrich) and 1,4-dioxane (Merck) were used as received. Anhydrous potassium carbonate was dried at 120°C in a vacuum oven before use.

### Monomer Synthesis

4-(*p*-Chlorophenylene-sulfonyl-*p*-phenoxy)benzaldehyde (VIII) and Sulfonyl Bis(*p*-benzaldehyde-oxo-*p*-phenylene) (IX)

The monomers were synthesized from 4-hydroxybenzaldehyde (II) and 4,4'-dichlorodiphenyl sulfone (VI) according to their corresponding molar ratios.

TABLE I. The Properties of Monomers of III, V, and VIII-X

Monomer	Yield, %	mp, °C	Elemental analysis							
			C, %		H, %		S, %		Cl, %	
			Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
III	89	284-285 <sup>a</sup>	78.41	78.24	5.92	5.98	—	—	—	—
V	88	222-228	70.99	70.95	5.36	6.03	—	—	—	—
VIII	75	50-60 <sup>b</sup>	61.21	59.94	3.51	3.91	8.60	10.86	9.51	8.91
IX	70	90-115 <sup>b</sup>	68.11	66.34	3.96	4.40	6.99	9.86	0	1.90 <sup>c</sup>
X	97	130-140 <sup>b</sup>	65.42	64.71	3.99	4.16	7.94	7.48	8.78	8.64

<sup>a</sup>Literature: 282-288 [6].<sup>b</sup>Softening range.<sup>c</sup>Comments in text.

TABLE 2. Properties of Copolyether Sulfones XI-XVI

Copolymer	Yield, %	Color	Softening point, °C	$\eta_{red}$ , dL/g <sup>a</sup>	$R^b$
XI	70	Brown	> 360	0.99	—
XII	84	Brown-black	> 300	<sup>c</sup>	—
XIIIA	35	Orange	> 300	0.21	1.23
XIIIB		Orange	180–190	0.04	0.48
XIV	83	Orange	> 300	0.42	—
XV	45	Brown	> 300	0.13	0.79
XVI	87	Red	> 300	<sup>c</sup>	—

<sup>a</sup>Measured at a concentration of 0.2 g/dL in NMP at 25 + 0.1°C.

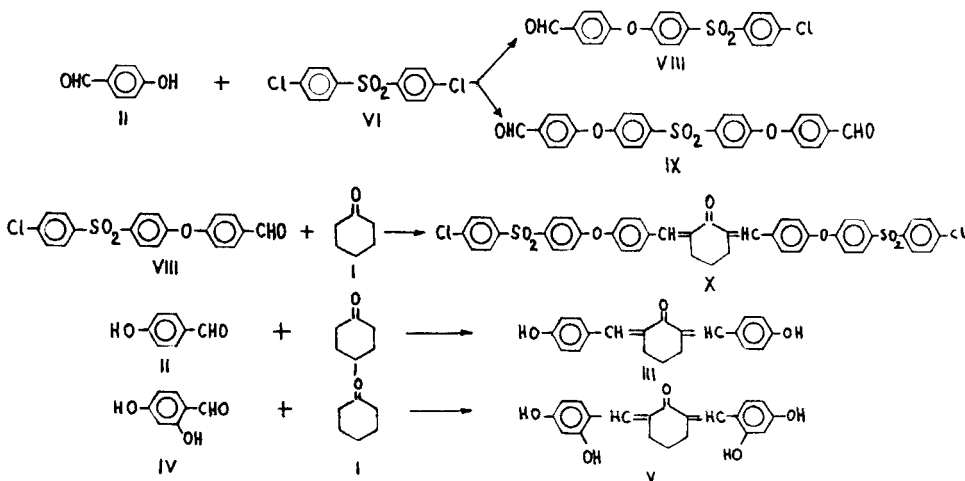
<sup>b</sup>Calculated from <sup>1</sup>H-NMR ( $R = D4CH$  units/BisA units).

<sup>c</sup>Insoluble.

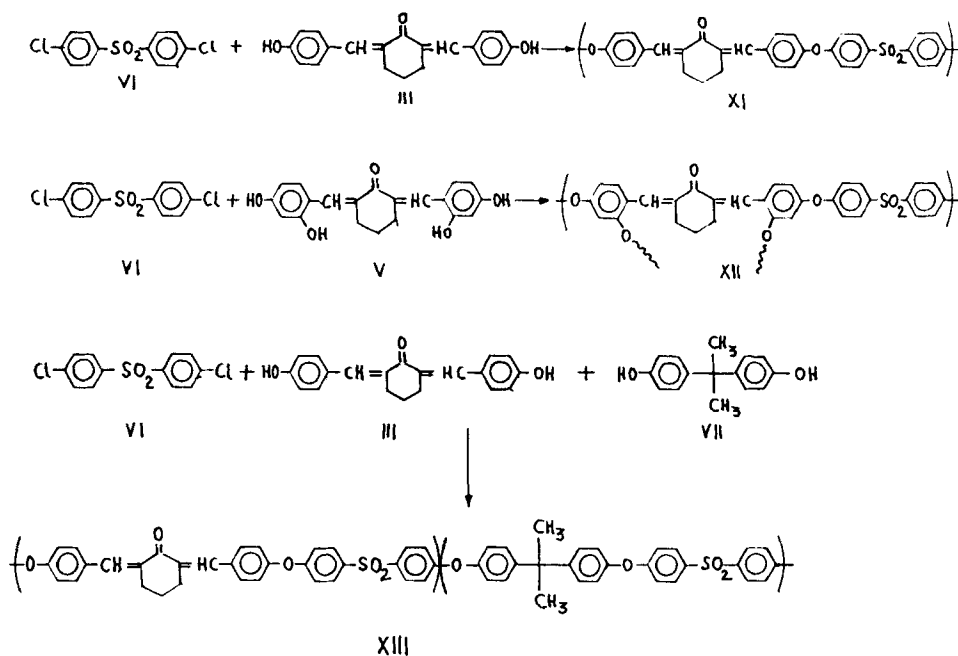
### Monomer VIII

To a solution of 4-hydroxybenzaldehyde (II) (3.70 g, 0.0303 mol) in dimethylsulfoxide (DMSO) (15 mL) was added 4,4'-dichlorodiphenyl sulfone (VI) (8.70 g, 0.0303 mol) and anhydrous potassium carbonate (5.0 g, 0.03618 mol). The solution was mechanically stirred at 140–150°C under nitrogen for 7 hours. The brown mixture was cooled to room temperature and poured into 1 L water. The brown solid was filtered, washed with several portions of water, and stirred in methanol for 16 hours. The product was filtered and dried at 35°C in vacuum for 16 hours. The properties of Monomer VIII are listed in Table 1.

**Spectral Data.** IR (cm<sup>-1</sup>): 1705 (—CH=O), 1325 (—SO<sub>2</sub>— asymmetrical vibrations), 1250 (C—O—C aromatic ether), 1160 (—SO<sub>2</sub>— symmetrical vibra-



SCHEME 1.



SCHEME 2.

tions), 1015, 840 (aromatic ring).  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , TMS):  $\delta = 6.94\text{--}7.12$  (m, 4H, ortho to  $-\text{O}-$ ),  $7.30\text{--}7.44$  (m, 2H, ortho to  $-\text{Cl}$ ),  $7.74\text{--}7.93$  (m, 4H, ortho to  $-\text{SO}_2-$ , 2H ortho to  $-\text{CH}=\text{O}$ ),  $10.12$  (s, 1H,  $-\text{CH}=\text{O}$ ).

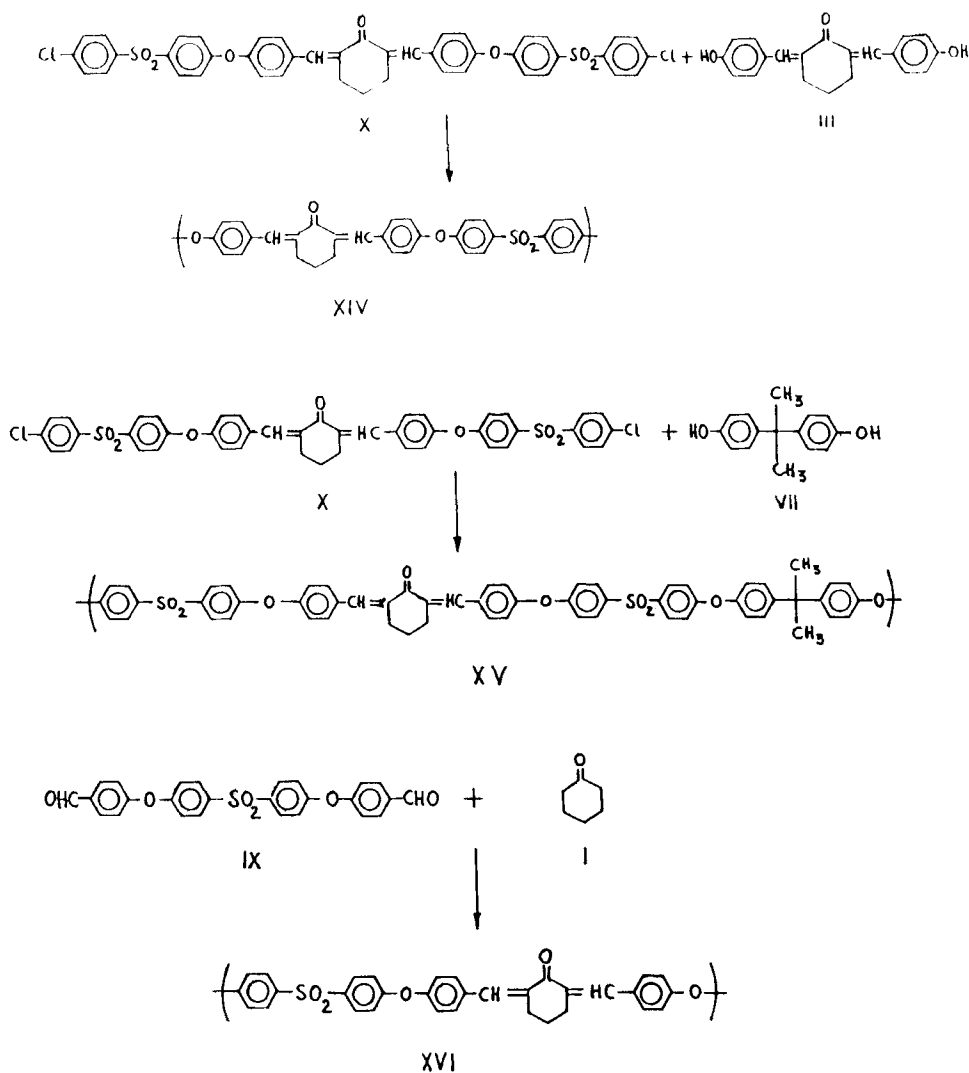
### Monomer IX

To a solution of II (5.20 g, 0.04258 mol) in DMSO (15 mL) was added VI (5.80 g, 0.02019 mol) and anhydrous potassium carbonate (7.0 g, 0.05065 mol). The solution was mechanically stirred at  $150\text{--}155^\circ\text{C}$  under nitrogen for 10 hours. The brown mixture was cooled to room temperature and poured into 1 L water. The purification procedure is identical with that for monomer VIII. The product was dried at  $50^\circ\text{C}$  in vacuum for 18 hours. The properties of monomer IX are listed in Table 1.

**Spectral Data.** IR ( $\text{cm}^{-1}$ ): 1700 ( $-\text{CH}=\text{O}$ ), 1330 ( $-\text{SO}_2-$  asymmetrical vibrations), 1250 ( $\text{C}-\text{O}-\text{C}$  aromatic ether), 1165 ( $-\text{SO}_2-$  symmetrical vibrations), 1025, 840 (aromatic ring).  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ , TMS):  $\delta = 6.87\text{--}7.31$  (m, 8H, ortho to  $-\text{O}-$ ),  $7.62\text{--}7.73$  (m, 2H, ortho to  $-\text{Cl}$ , monomer VIII traces),  $7.88\text{--}8.05$  (m, 4H, ortho to  $-\text{SO}_2-$ , 4H ortho to  $-\text{CH}=\text{O}$ ),  $10.17$  (s, 2H,  $-\text{CH}=\text{O}$ ).

### 2,6-Bis(*p*-chlorophenylene-sulfonyl-*p*-phenoxy-benzylidene)cyclohexanone (X)

To a solution of VIII (6.20 g, 16.63 mmol) in 1,4-dioxane (30 mL) was added cyclohexanone (I) (0.81 g, 8.25 mmol). The solution was magnetical stirred at  $50\text{--}$



SCHEME 3.

60°C while dry hydrogen chloride gas was introduced as a catalyst. After 4 hours of stirring, a red solid product separated out. The solid material was filtered off, washed with a great amount of water until HCl traces were completely removed. The product was heated in methanol under reflux for 6 hours. After filtration the product was dried at 50°C in vacuum for 20 hours. The properties of macromer X are listed in Table 1.

*Spectral Data.* IR ( $\text{cm}^{-1}$ ): 2940, 2880 ( $-\text{CH}_2-$ ), 1665 ( $\text{C}=\text{O}$ ), 1325 ( $-\text{SO}_2-$  asymmetrical vibrations), 1245 ( $\text{C}-\text{O}-\text{O}$  aromatic ether), 1155 ( $-\text{SO}_2-$  symmetrical vibrations), 1015, 835 (aromatic ring).  $^1\text{H-NMR}$  ( $\text{DMSO}-d_6$ ,

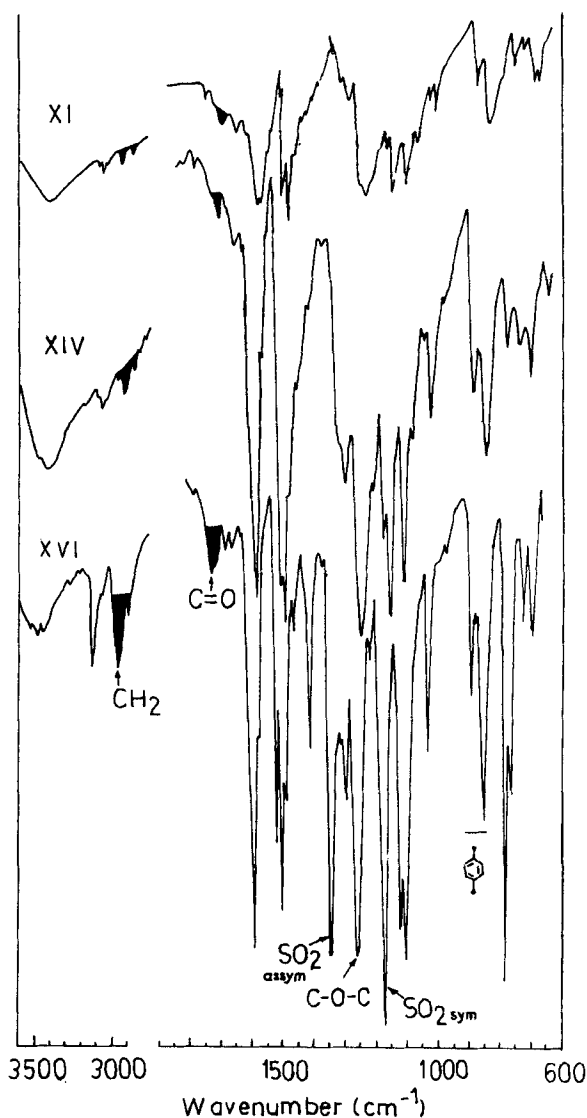


FIG. 1. The IR spectra of unsaturated copolyether sulfones (XI, XIV, XVI).

TMS):  $\delta = 1.85$  (m broad, 2H,  $\gamma$ -cyclohexanone ring), 2.95 (m broad, 4H,  $\beta, \beta'$ -cyclohexanone ring), 7.04–7.27 (m, 8H, ortho to  $-\text{O}-$ , 2H,  $-\text{CH}=\text{}$ ), 7.47–7.65 (m, 4H, ortho to  $-\text{Cl}$ , 4H, ortho to  $-\text{CH}=\text{}$ ), 7.82–7.97 (d, 8H, ortho to  $-\text{SO}_2-$ ).

2,6-Bis(*p*-hydroxybenzylidene)cyclohexanone (III),  
2,6-Bis(*o,p*-dihydroxybenzylidene)cyclohexanone (V)

The monomers were obtained by using the corresponding hydroxyaldehydes (II, IV) and cyclohexanone (I) as described in the literature [5].



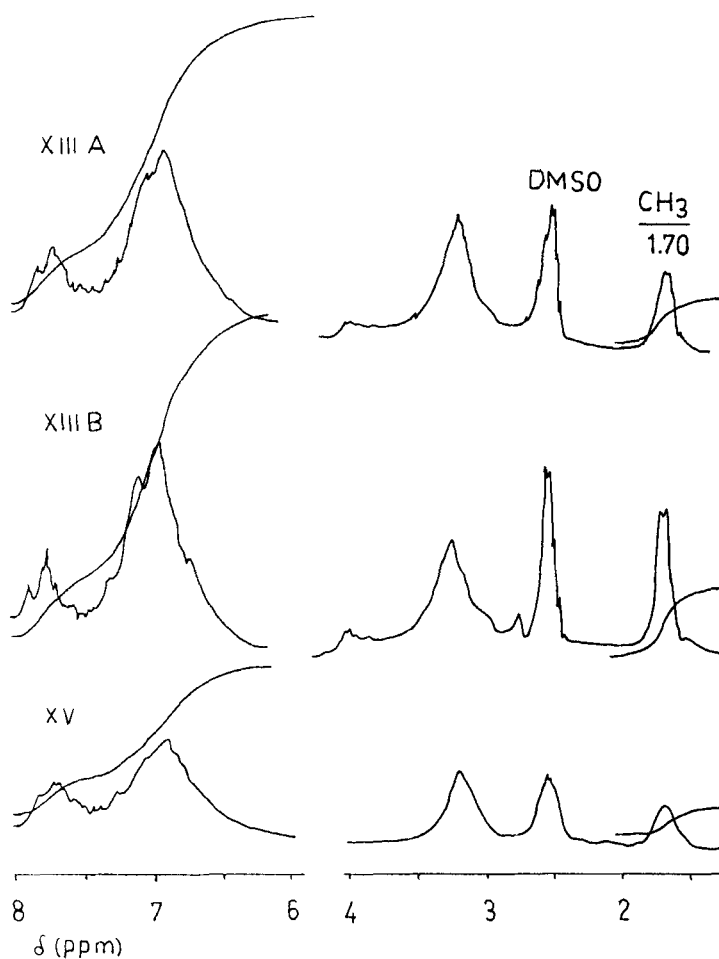


FIG. 2. The  $^1\text{H-NMR}$  spectra of unsaturated copolyether sulfones (XIII A, XIII B, XV).

The properties of the obtained monomers are listed in Table 1.

#### Synthesis of Copolymers XI–XV

This series of unsaturated copolyether sulfones was synthesized in the same manner as described previously [1] (Schemes 2 and 3). The copolymers were refluxed in boiling methanol, then filtered and dried under vacuum at  $80^\circ\text{C}$  overnight. Their properties are listed in Table 2.

#### Synthesis of Copolymer XVI

Monomers IX and I were reacted in the same conditions as described for the synthesis of macromer X (Scheme 3). The purification procedure was similar with the one described above. The properties of copolymer XVI are listed in Table 2.

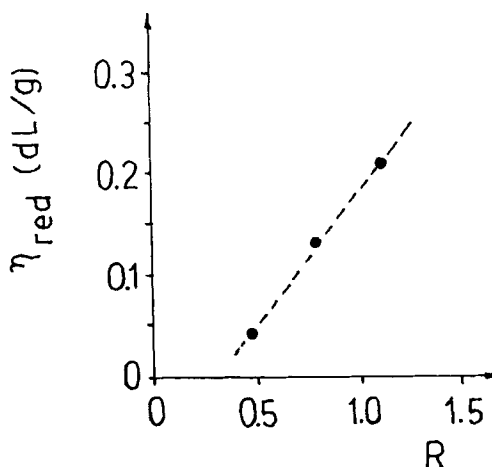


FIG. 3. The dependence of  $\eta_{red}$  of copolymers XIII A, XIII B, and XV on  $R$  values.

## RESULTS AND DISCUSSION

The first step in obtaining the desired copolymers was the preparation of five types of monomers with different structures in order to have a large range of properties in the resulting copolymers (Scheme 1).

Therefore, mono- and dialdehyde sulfone monomers (VIII, IX) were obtained by reaction between hydroxyl and chlorine functional groups of the corresponding compounds (II, VI).

Elemental analysis data of monomer IX showed the presence of chlorine. This unexpected phenomenon was confirmed by the  $^1\text{H-NMR}$  spectra of this monomer where the peaks at  $\delta = 7.62\text{--}7.73$  ppm clearly showed the presence of protons ortho to chlorine, as cited in the literature [4]. This fact is due to an incomplete reaction of the monoaldehyde (VIII) formed in the first step with 4-hydroxybenzaldehyde (II). So the obtained dialdehyde (IX) contains a small amount of monoaldehyde (VIII). Further separation into pure monomers is very difficult and not yet perfected.

By reacting the monoaldehyde prepared (VIII) with cyclohexanone (I), the unsaturated sulfone macromer (X) was obtained.

The same procedure mentioned above was used to react the hydroxyaldehydes (II, IV) with I to obtain the unsaturated monomers (III, V).

Two procedures were used to obtain the unsaturated copolymers. The first one was the classical polycondensation reaction between VI and various bisphenols such as III, V, and VII, resulting in the corresponding copolymers (XI, XII, XIII) (Scheme 2). The second procedure consisted of the polycondensation reaction of the unsaturated sulfone macromer (X) with III or VII bisphenols to obtain the corresponding copolymers (XIV, XV), or the polycondensation reaction of IX with I to obtain the copolymer (XVI) (Scheme 3).

The resulting copolyether sulfones were characterized by IR and  $^1\text{H-NMR}$  spectral, elemental analysis, reduced viscosity, TOA, x-ray, and TGA measurements.

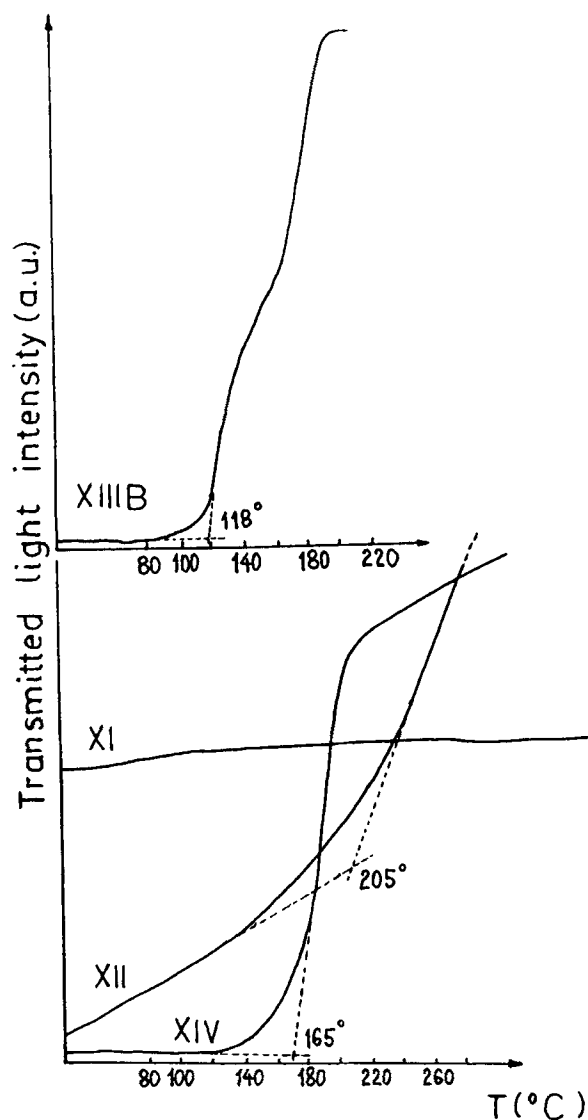


FIG. 4. TOA curves of copolymers XI, XII, XIII B, and XIV.

The terpolymer (XIII) was fractionated by refluxing in methanol and gave two fractions: XIII A ( $\eta_{\text{red}}$  0.21 dL/g) and XIII B ( $\eta_{\text{red}}$  0.04 dL/g).

The IR spectra of copolymers (Fig. 1) showed the absorption band of the C=O group of cyclohexanone at  $1700\text{ cm}^{-1}$  and the  $-\text{SO}_2-$  group at  $1320$  and  $1150\text{ cm}^{-1}$ , assigned to the stretching asymmetrical and symmetrical vibrations, respectively.

The  $^1\text{H-NMR}$  spectra of copolymers (Fig. 2) showed the characteristic peak at  $1.70\text{ ppm}$  assigned to the  $(\text{H}_3\text{C})_2\text{C}=\text{C}$  protons and aromatic peaks at about  $8.0$ – $6.7\text{ ppm}$ . The ratio of corresponding integrals of peaks for 2,6-bis(*p*-oxo-benzyl-

TABLE 3. Elemental Analysis of Copolymers XI-XVI

Copolymer	Empirical formula (formula weight)	S, %		Cl, %, Found
		Calcd	Found	
XI	$(C_{32}H_{24}SO_5)_n$ (520.58) <sub>n</sub>	6.16	6.19	1.51
XII	$(C_{32}H_{24}SO_7)_n$ (552.58) <sub>n</sub>	5.80	5.06	3.13
XIIIA	$(C_{57}H_{46}S_2O_9)_n$ (939.07) <sub>n</sub>	6.83	7.27	1.43
XIV	$(C_{32}H_{24}SO_5)_n$ (520.58) <sub>n</sub>	6.16	6.85	1.18
XV	$(C_{57}H_{46}S_2O_9)_n$ (939.07) <sub>n</sub>	6.83	7.12	3.31
XVI	$(C_{32}H_{24}SO_5)_n$ (520.58) <sub>n</sub>	6.16	7.13	3.46 <sup>a</sup>

<sup>a</sup>Comments in text.

idene)cyclohexanone (D4CH) units versus Bisphenol A (BisA) units,  $R$ , was calculated (Table 2). In Fig. 3 the dependence of  $\eta_{red}$  values is plotted versus  $R$ , and this indicates a linear dependence of  $\eta_{red}$  values on  $R$  values.

Table 3 shows good agreement between calculated and found values for %S of copolymers (XI-XVI).

The presence of the chlorine content in the copolymer (XVI) proceeded from the traces of monomer (VIII) [contained in the monomer (IX), as discussed] which terminates the chain growth.

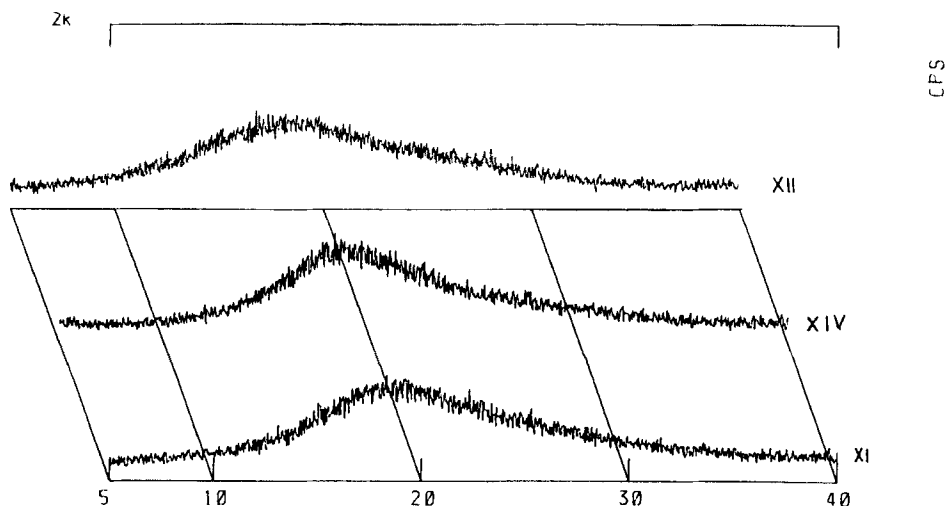


FIG. 5. X-ray diffraction curves of copolymers XI, XII, and XIV.

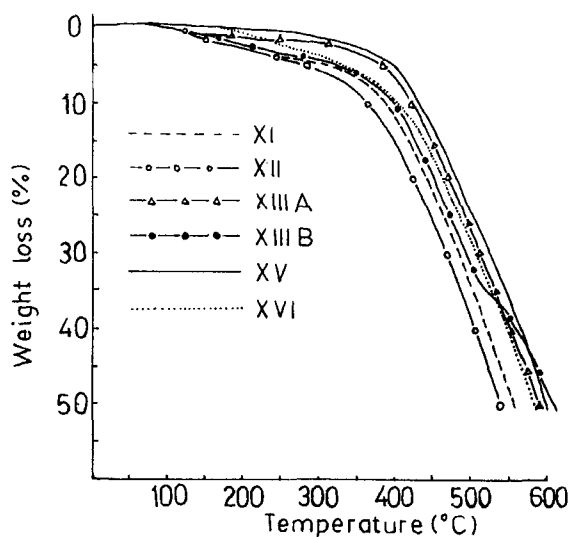


FIG. 6. TGA curves for copolymers XI, XII, XIII A, XIII B, XV, and XVI.

The glass transition temperature ( $T_g$ ) of copolymers, determined by TOA (Fig. 4) (Table 3), ranged between 118 and 212°C and seems to increase with increasing  $\eta_{red}$  values. For the copolymer (XI) with the higher  $\eta_{red}$  value (0.99 dL/g), no  $T_g$  was detected up to 350°C.

Except for sample XIII B which is an oligomer, the other copolymers possess softening points greater than 300°C and the x-ray curves in Fig. 5 show that the copolymers synthesized are amorphous.

The structure of the monomer (V) is suited for reactions in both the *p*- and *o*-positions. The copolymer (XII) is almost insoluble in aprotic dipolar solvents such as DMSO and NMP. Also, a very small peak at 3440  $\text{cm}^{-1}$ , assigned to  $-\text{OH}$

TABLE 4. The Thermal Properties of Copolymers XI-XVI

Copolymer	TGA temperatures (°C) for various % decompositions					$T_g$ , °C <sup>a</sup>
	10	20	30	40	50	
XI	390	442	483	523	558	—
XII	363	422	467	503	540	205
XIII A	425	470	510	553	590	204
XIII B	403	450	490	565	> 600	118
XIV	390	440	480	519	553	165
XV	430	480	525	565	600	212
XVI	404	463	508	550	585	155

<sup>a</sup>TOA measurements in air.

groups, led us to conclude that the structure of this copolymer is partially cross-linked.

The copolymer (XVI) is insoluble in NMP and has no softening point up to 300°C, similar to the properties of other copolymers obtained by a different synthesis route (XI, XIV).

The thermal stabilities of the copolymers were evaluated by TGA in air at a heating rate of 12°C/min.

The TG curves of copolymers are represented in Fig. 6. Table 4 gives the temperatures for various percentage weight losses. All the copolymers showed similar decomposition patterns. The temperature for a 10% weight loss ( $T_{10}$ ) is considered to be the copolymer decomposition temperature, and it is used in comparing the thermal stabilities of different copolymers.

$T_{10}$  values of copolymers range between 363 and 430°C. As can be seen, copolymers with Bisphenol A units (XIII, XV) have higher  $T_{10}$  values than others and are arranged in the following order: XV > XIII A > XIII B. The alternate copolymer (XV) possesses higher thermal stability (Table 4, Fig. 6) than the others, as expected.

Moreover, the  $T_{10}$  values at 390°C for copolymers (XIV, XI) demonstrated the common structure obtained and the good thermal stability character for these copolymers.

## CONCLUSIONS

Arylidene copolyether sulfones containing dibenzylidenecyclohexanone units were prepared by various procedures with the aim of obtaining common chemical structures.

For this purpose we used reactions between both monomers with hydroxyl and chlorine functional groups and monomers with aldehyde and active =CH<sub>2</sub> groups.

Their expected structures were confirmed by IR and <sup>1</sup>H-NMR spectra, and their properties were determined using current analysis methods.

X-ray curves proved that the copolymers are amorphous.

The  $T_{10}$  and  $T_g$  values for both the XI, XIV, XVI series and the XIII, XV series of copolymers were closely ranged in distinct domains corresponding to their common chemical structures.

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