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V. Cozan[a]; A. Butuc[a]; A. Stoleru[a]; M. Rusu[b]; Yushan Ni[c]; Mengxian Ding[c]
[a] "Petru Poni" Institute of Macromolecular Chemistry Romanian Academy Aleea Grigore Ghica Voda, Jassy, Romania [b] Faculty of Chemical Technology, Polytechnic Institute, Jassy, Romania [c] Changchun Institute of Applied Chemistry Chinese Academy of Sciences, Changchun, People's Republic of China

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ARYLIDENE COPOLYETHER SULFONES. I. SYNTHESIS AND CHARACTERIZATION OF SOME NEW COPOLYETHER SULFONES CONTAINING DIBENZYLIDENE CYCLOPENTANONE MOIETIES

V. COZAN,* E. BUTUC, and A. STOLERU

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

M. RUSU

Faculty of Chemical Technology
Polytechnic Institute
Jassy 6600, 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 2,5-bis(4-oxo-benzylidene)-cyclopentanone moieties were prepared in the conventional literature manner by condensing the dipotassium salts of 2,5-bis(4-hydroxybenzylidene)cyclopentanone (I) and 2,2-bis(4-hydroxyphenyl)propane (Bisphenol A, III) with 4,4′-dichlorodiphenyl sulfone (II), or by condensing the dipotassium salts of I with chlorine-terminated Bisphenol A-4,4′-dichlorodiphenylsulfone copolymers (V). The resulting copolyether sul-

fones were confirmed by IR, viscometry, DSC measurements, thermooptical analysis (TOA), and thermogravimetric analysis (TGA).

INTRODUCTION

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

The curing process of such polymers can be complicated by liberated side products that form voids in the material and cause a reduction in the structural strength.

Polymers that contain substituted acetylene, butadiene, or both types of units in the polymer chain backbone can be cured without giving off volatiles [1].

New processable polyaromatic ether-keto-sulfones with acetylene and 1,3-butadiene units were prepared from aromatic acid chlorides and 4,4′-diphenoxydiphenyl sulfone by a Friedel–Crafts-type of polymerization [2, 3]. These polymers have good solubility before curing and improved thermal and chemical resistance after curing.

High-molecular-weight polysulfones that contain 1,3-enyne linkages in the polymer backbone were prepared by the polycondensation reaction of potassium disalts of (E)-1,3-bis(3-hydroxyphenyl)-1-butene-3-yne with 4,4′-dihalodiphenyl sulfones in dimethylsulfoxide–sulfolane solvent mixtures [4].

The goal of this paper is to present the synthesis and characterization of some new unsaturated copolyether sulfones containing 2,5-bis(4-oxo-benzylidene) cyclopentanone moieties in the backbone. In future work we intend to study the behavior of these unsaturated copolyether sulfones during thermal curing.

EXPERIMENTAL

Measurements

The IR spectra were recorded on a Specord M80 Carl Zeiss Jena spectrophotometer by using the KBr pellet technique. The reduced viscosities of polymer 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. Thermogravimetric analysis (TGA) was carried out in air with an F. Paulik Derivatograph at a heating rate of 12°C/min. Differential scanning calorimetry (DSC) measurements were made using a Perkin-Elmer 7 Series Thermal Analysis System, with a heating rate of 20°C/min, in air. Thermooptical analysis (TOA) was carried out as described in the literature [7].

Reagents and Materials

4,4′-Dichlorodiphenyl sulfone (Aldrich) was recrystallized from toluene (mp 146–149°C). Bisphenol A (Fluka) was used as received. NMP was vacuum distilled over P_2O_5. Chlorobenzene (Aldrich) was used as received. Anhydrous potassium carbonate was dried at 120°C in a vacuum oven before use.

Monomer Synthesis

2,5-Bis(4-hydroxybenzylidene)cyclopentanone (I) was synthesized and purified according to the literature [5].

Chlorine-Terminated PSF Oligomers (V) Synthesis

Various chlorine-terminated PSF oligomers were synthesized and purified by a classical procedure [6]. Their characteristics are listed in Table 2.

Synthesis of Unsaturated Copolyether Sulfones (IV)

A 500-mL three-necked flask, equipped with a mechanical stirrer, dry nitrogen inlet, a Dean-Stark trap with condenser, and a Claisen adaptor, was charged with a mixture of 0.05 mol (14.61 g) 2,5-bis(4-hydroxybenzylidene)cyclopentanone (I), 0.05 mol (11.41 g) Bisphenol A (III), 0.10 mol (28.72 g) 4,4'-dichlorodiphenyl sulfone (II), 0.20 + 0.03 mol% (31.79 g) anhydrous K_2CO_3, 100 mL NMP, and 100 mL chlorobenzene. The entire system was purged with N_2 for 10 minutes. The mixture was heated at 155°C for 8 hours. During this time the PhCl-H_2O azeotrope was collected in the Dean-Stark trap. Then the temperature was raised to 180°C. After 5 hours, the PhCl was completely distilled and the temperature was increased to 187°C for 2 hours. The mixture was allowed to cool and then filtered to remove inorganic salts. The polymer was coagulated into a large excess of MeOH, filtered, washed with water and MeOH, and finally dried in vacuum at 80°C for 12 hours.

The properties of the polymers are listed in Table 1.

Synthesis of Unsaturated Copolyether Sulfones (VI)

The same synthesis system presented above was charged with 0.00342 mol (1.0 g) I, 100 mL NMP, and 50 mL PhCl. The system was continuously purged with dry N_2, slowly heated to 130-140°C to remove the moisture, and then cooled to about 100°C. Then 0.01447 mol (2 g) anhydrous K_2CO_3 was added, and the system was reheated at 140°C for 2 hours, after which 50 g chlorine-terminated PSF oligomer (V), dissolved in 100 mL PhCl, was added as fast as possible. The temperature was maintained at 140°C for 2 hours, at 150-155°C for 3 hours, and finally at 180°C for 4 hours while PhCl was removed from the trap. The mixture was allowed to

TABLE 1. The Properties of Unsaturated Copolyether Sulfones (IV-1-3)

Polymer number	Polymer composition, mol%			Cl, %	η_{red},[a] dL/g	Softening point, °C
	I	II	III			
IV-1	100	100	0	0.82	0.28	330
IV-2	50	100	50	0.78	0.42	250-335
IV-3	25	100	75	0.59	0.34	180-335

[a] Measured at a concentration of 0.2 g/dL in NMP at 25°C.

TABLE 2. The Properties of the Chlorine-Terminated PSF Oligomers (V) and of the Corresponding Unsaturated Copolyether Sulfones (VI)

Oligomer number	$\overline{M}_n$[a]	Softening point, °C	Cl, %	η_{red},[b] dL/g	Polymer number	Softening point, °C	η_{red},[b] dL/g
V-1	38,000	246-248	0.20	0.50	VI-1	330	0.61
V-2	38,000	246-248	0.20	0.50	VI-2	230-300	0.51
V-3	15,960	199-210	0.51	0.24	VI-3	258-260	0.30
V-4	4,600	160-190	1.65	0.015	VI-4	145-200	0.07
V-5	31,400	–	1.36	0.36	VI-5	330	0.31

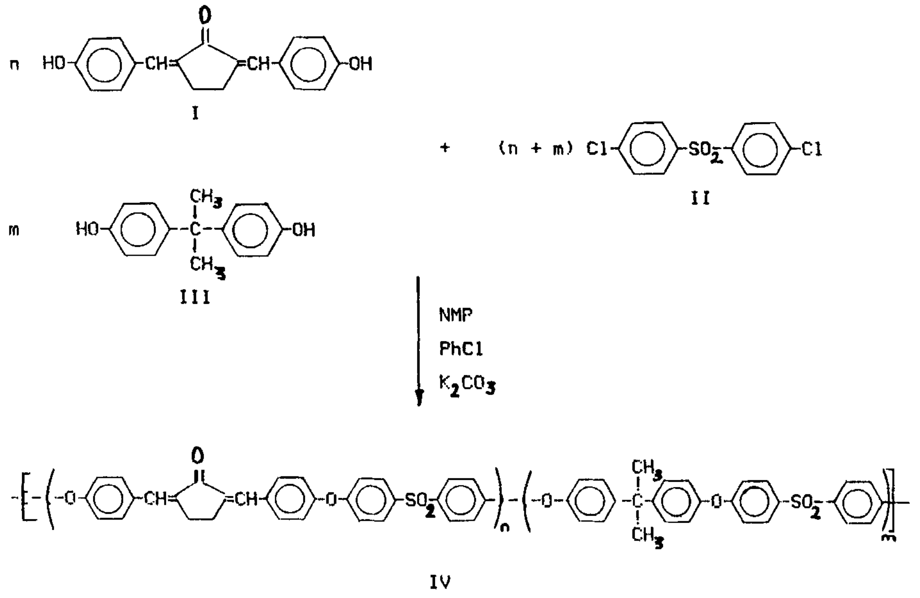
[a] Calculated from osmometric and viscometric measurements.
[b] Determined as in Table 1.

cool and filtered to remove the inorganic salts. The polymer was coagulated into a large excess of MeOH, filtered, washed with water and hot MeOH, and finally dried in vacuum at 80°C for 20 hours.

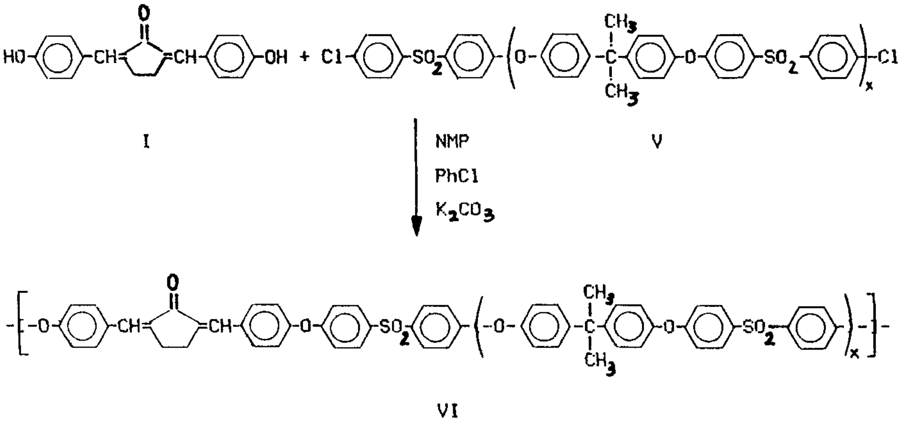
The properties of the polymers are listed in Table 2.

RESULTS AND DISCUSSION

The preparation of the unsaturated copolyether sulfones (IV) was based on the polycondensation reaction of 2,5-bis(4-hydroxybenzylidene)cyclopentanone (I) and 2,2-bis(4-hydroxyphenyl)propane (Bisphenol A, III) with 4,4′-diclorodiphenyl sulfone (II) in the presence of NMP, PhCl, and anhydrous K_2CO_3 (Scheme 1).



SCHEME 1.



SCHEME 2.

The same procedure was applied for the synthesis of the unsaturated copolyether sulfones (VI) by the polycondensation reaction of I with various chlorine-terminated polysulfone oligomers (V), as shown in Scheme 2.

The resulting copolyether sulfones were characterized by IR spectroscopy, viscometry, DSC, TOA, and TGA measurements.

The IR spectra of polymers (Fig. 1) showed the appearance of the absorption band of the C=O group of cyclopentanone at 1695 cm^{-1}, and at 1300 and 1155 cm^{-1} for the $-SO_2-$ group, assigned to the stretching asymmetrical and symmetrical vibrations, respectively. There are also other characteristic absorption bands for the rest of the structure.

As can be seen from Tables 1 and 2, the softening points of the unsaturated copolyether sulfones are in the 145 to 335°C range, generally higher than those of the oligomers (V).

The reduced viscosities of the polymer solutions (IV, VI) are in the 0.28-0.61 dL/g range (except for the 0.07 value of sample VI-4, which is the smallest molecu-

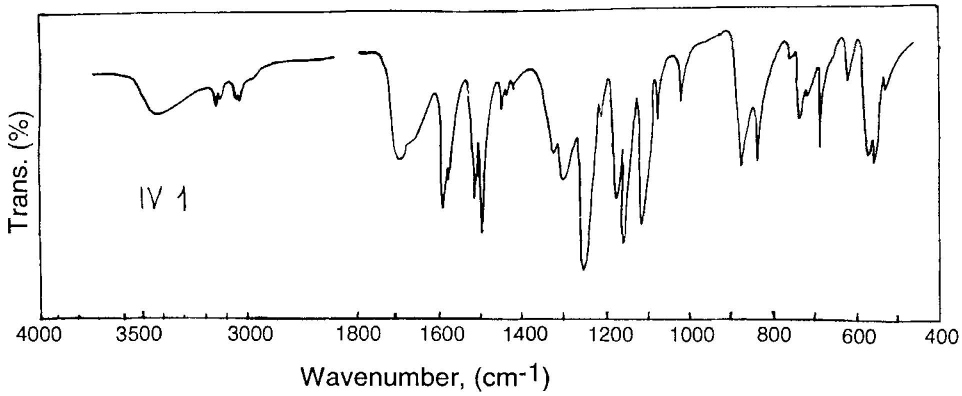


FIG. 1. Infrared spectra of unsaturated copolyether sulfone IV-1.

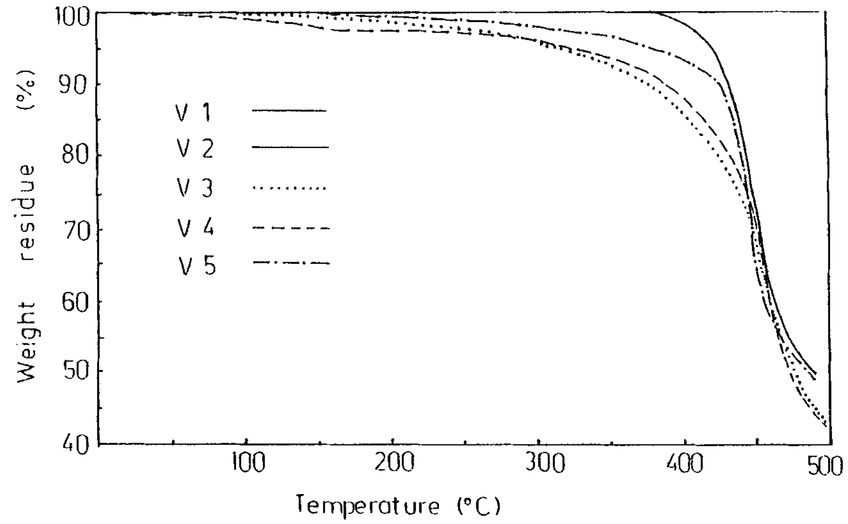


FIG. 2. Thermogravimetric curves of chlorine-terminated polysulfone oligomers (V-1-5).

lar weight product). The VI series shows an increase of reduced viscosity values versus the oligomers V, with the exception of sample VI-5, which is smaller than the V-5 sample.

The thermal stabilities of the unsaturated copolyether sulfones (IV, VI) were evaluated by thermogravimetric analysis in air at a heating rate of 12°C/min.

The TG curves of the polymers are given in Figs. 2-4. Table 3 gives the temperatures for various percentage weight losses. All the polymers showed similar

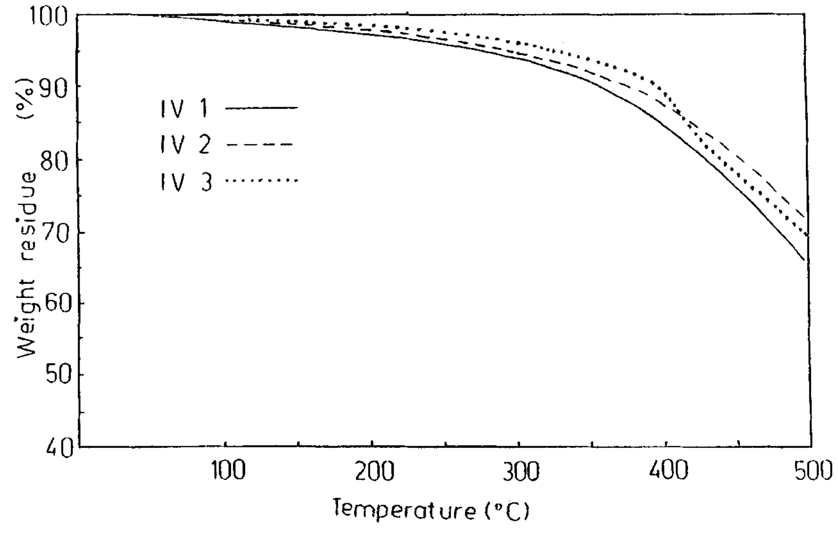


FIG. 3. Thermogravimetric curves of unsaturated copolyether sulfones (IV-1-3).

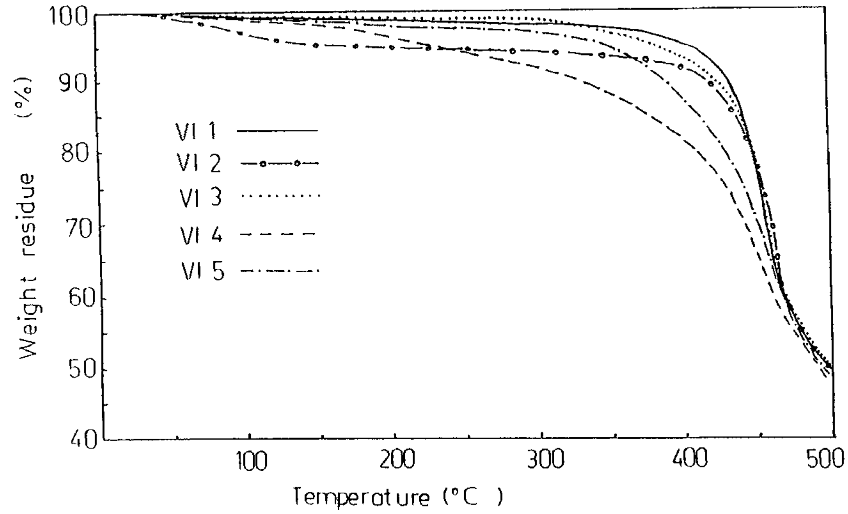


FIG. 4. Thermogravimetric curves of unsaturated copolyether sulfones (V-1-5).

decomposition patterns. The temperature for a 10% weight loss is considered to be the polymer decomposition temperature and is used in comparing the thermal stabilities of different polymers.

T_{10} values of copolyether sulfones from the IV series range between 368 and 395°C while the VI series ranges between 378 and 489°C. The T_{10} values of unsaturated copolyether sulfones can be arranged in the following order: IV series, IV-3

TABLE 3. The Thermal Properties of Polysulfones (V-5) and Copolyether Sulfones (IV-1-3, VI-1-5)

Polymer sample	TGA, temperature (°C) for various % decompositions					T_g, °C	
	10	20	30	40	50	DSC	TOA
V-1-2	492	500	510	518	550	188	
V-3	440	488	510	520	533	–	
V-4	446	493	510	520	531	–	
V-5	493	509	518	530	583	–	
IV-1	368	428	471	510	553	235	
IV-2	380	450	505	555	–	208	
IV-3	395	435	490	580	–	161	
VI-1	489	500	510	520	560	181	172
VI-2	475	502	511	522	553	188	180
VI-3	483	505	515	523	558	167	172
VI-4	378	464	495	512	568	156	146
VI-5	440	482	503	518	543	110	112

> IV-2 > IV-1; VI series, VI-1 > VI-3 > VI-2 > VI-5 > VI-4. As can be seen from a comparison of Figs. 2 and 4, the copolyether sulfones from the VI series are less thermally stable than the V series ones, with the exception of the VI-3 sample which is higher than the V-3 sample.

The glass transition temperatures (T_g) of polysulfones (V-1-2) and copolyether sulfones (IV-1-3; VI-1-5) were determined by the DSC method. For the VI-1-5 sample series we used the TOA method [7] besides DSC measurements (Table 3). As can be seen, the $T_g$values range from 110 to 235°C and the difference between the two methods does not exceed 10°C.

CONCLUSIONS

Arylidene copolyether sulfones were prepared by the classical polycondensation reaction of an unsaturated bisphenol with aromatic dihalosulfones.

Their expected structures were confirmed by IR spectroscopy, and their properties were determined using current analysis methods.

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