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Pendant Functional Group Copolyether Sulfones. I. Synthesis and Characterization of New Copolyether Sulfones with Pendant Aldehyde Groups Modified Into Phenolic Azomethine Groups

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PENDANT FUNCTIONAL GROUP COPOLYETHER SULFONES. I. SYNTHESIS AND CHARACTERIZATION OF NEW COPOLYETHER SULFONES WITH PENDANT ALDEHYDE GROUPS MODIFIED INTO PHENOLIC AZOMETHINE GROUPS

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ABSTRACT

New functional copolyether sulfones with pendant aldehyde groups were synthesized by the classical polycondensation reaction between 4,4'-dichlorodiphenyl sulfone (**I**) and various bisphenols such as 5,5'-methylene bis-salicylaldehyde (**II-2**), 2,2-bis(4-hydroxyphenyl)propane (**III**), and 2,6-bis(4-hydroxybenzylidene)cyclohexanone (**IV**). Condensation reaction with 4-aminophenol led to pendant phenolic azomethine groups containing copolyether sulfones. The structures of the resulting

polymers were confirmed by IR, $^1\text{H-NMR}$ spectra, and elemental analyses. The polymers were characterized by reduced viscosity, solubility, thermal stability, DSC, and x-ray diffraction measurements.

INTRODUCTION

Functional aromatic polyether sulfones containing pendant groups have received much attention in recent years [1–6].

Chemical modification of polysulfones by sulfonation [7–10], chloromethylation [11–13], lithiation [14, 15] and bromination-methylation [16–18] allowed preparation of reactive polysulfone intermediates, which by further conversion led to functional polymers.

For example, polysulfone with pendant aldehyde groups has been obtained by direct oxidation with DMSO or tetrabutyl ammonium dichromate of the halomethylated polysulfone benzyl halide groups [19].

All these transformations are classical reactions in organic synthesis, yet, in the case of sensitive polymers as modified functional polysulfones, the exact conditions for clean and complete transformations require considerable empirical probing, and further work is needed to provide modified polysulfone.

Functional polymers are suitable for the formation of membranes, coatings, ion-exchange resins, ion-exchange fibers, selectively permeable barrier films, etc.

Carboxaldehyde polysulfone may be useful in biotechnological applications such as membrane affinity chromatography [20, 21].

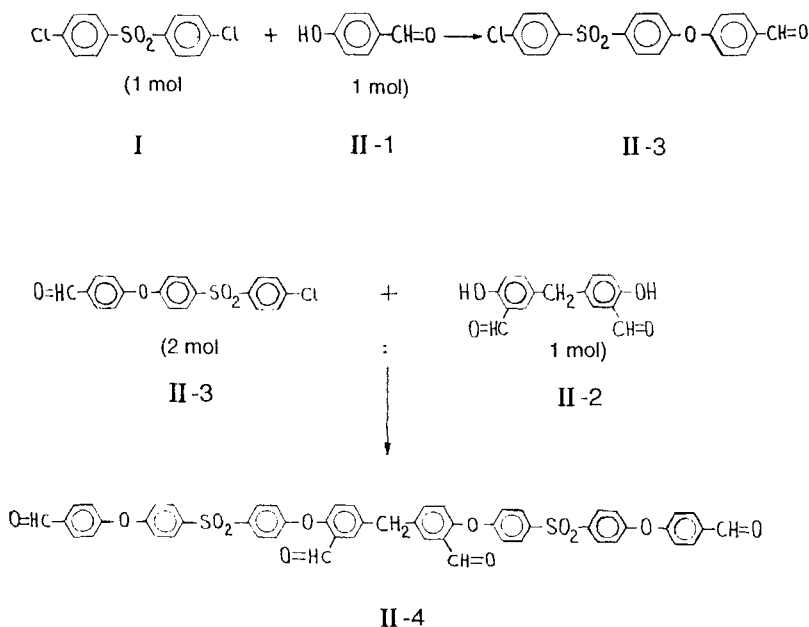
The main objective of this study was to synthesize functional polymers of sufficient quality to serve for the aforementioned applications. Our work on this subject deals with the synthesis and characterization of new functional copolyether sulfones carrying pendant aldehyde groups which were then modified via condensation reaction with 4-aminophenol into pendant azomethine phenolic group copolyether sulfones.

TABLE I. The Properties of Polymers VI–XI

Polymer	Yield, %	Softening range, °C	Reduced viscosity, ^a dL/g
VI	53	215–235	0.16
VII	82	> 310	0.36 ^b
VIII	87	> 310	0.39 ^b
IX	80	240–> 310	0.29
X	89	> 310	0.47 ^b
XI	95	> 310	0.13

^aMeasured in NMP at a concentration of 0.2 g/dL at 25°C.

^bPartially soluble in NMP.



SCHEME 1.

EXPERIMENTAL

Measurements

The IR spectra were recorded on a Specord M 80 Carl Zeiss, Jena Spectrophotometer using the KBr pellet technique. Proton NMR spectra were run on a Jeol 60 MHz NMR spectrometer at 60°C in DMSO-*d*₆ using TMS as the internal reference. The reduced viscosities of polymer solutions (0.2% w/v) in NMP were determined at 25°C by using an Ubbelohde Suspended Level Viscometer. The solubilities of polymers were examined using 0.1 g polymer in 1–2 mL solvent at room temperature. The melting and softening points were measured using a Gallenkamp hot-block melting-point apparatus. Thermogravimetric curves were obtained in air with an F. Paulik Derivatograph at a heating rate of 12°C/min. DSC measurements were made in air using a Mettler TA instrument DSC 12 E at a heating rate of 10°C/min. X-ray measurements were made with a Rigaku IIB x-ray diffractometer.

Reagents and Materials

4,4'-Dichlorodiphenyl sulfone (Aldrich) was recrystallized from toluene (mp 146–149°C). Bisphenol A (Fluka) was used as received. 5,5'-Methylene bis-salicylaldehyde was synthesized as described in the literature [22] (mp 142–146°C; Ref. 22, 141–142°C). 2,6-Bis(4-hydroxybenzylidene)cyclohexanone was synthesized according to the literature [23] (mp 284–285°C; Ref. 24, 282–288°C). 4-Aminophenol and 4-hydroxybenzaldehyde (Aldrich) were used as received. Chloro-

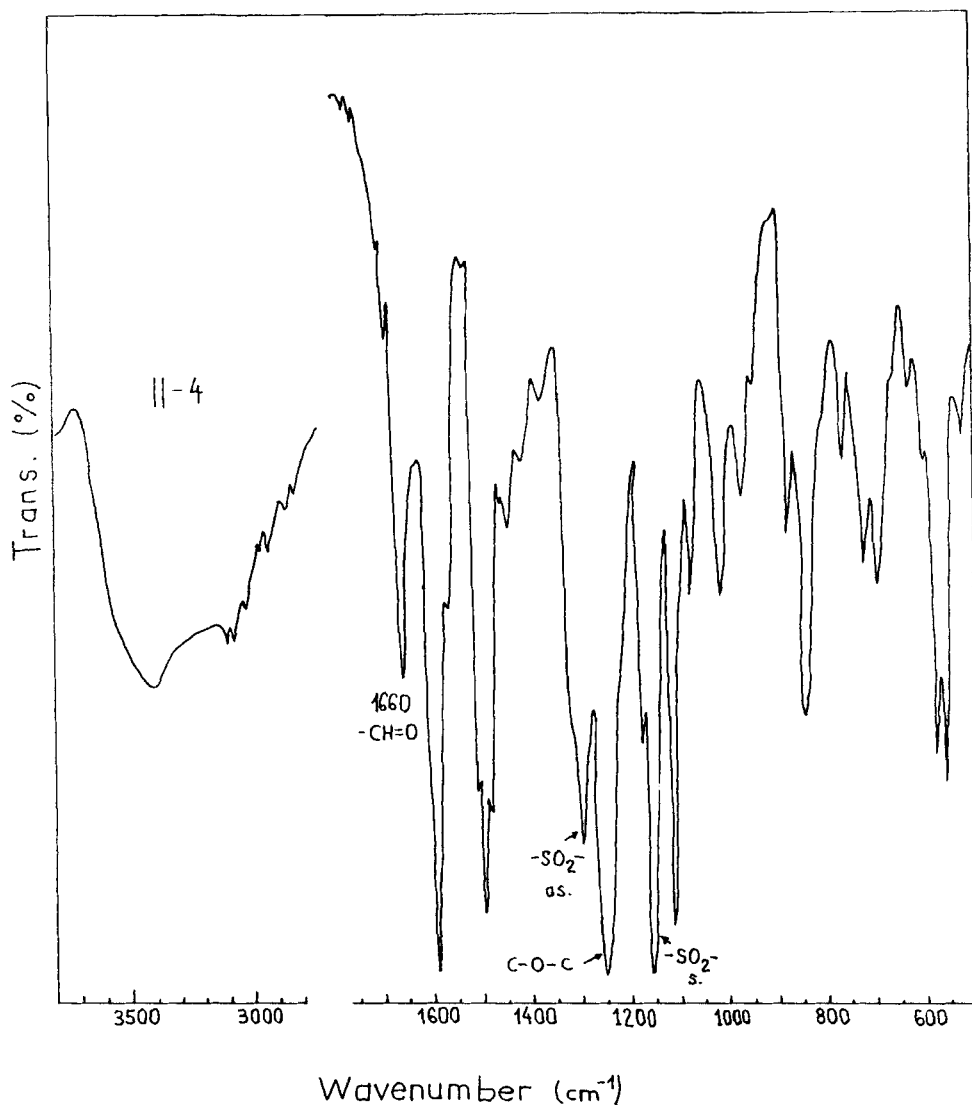
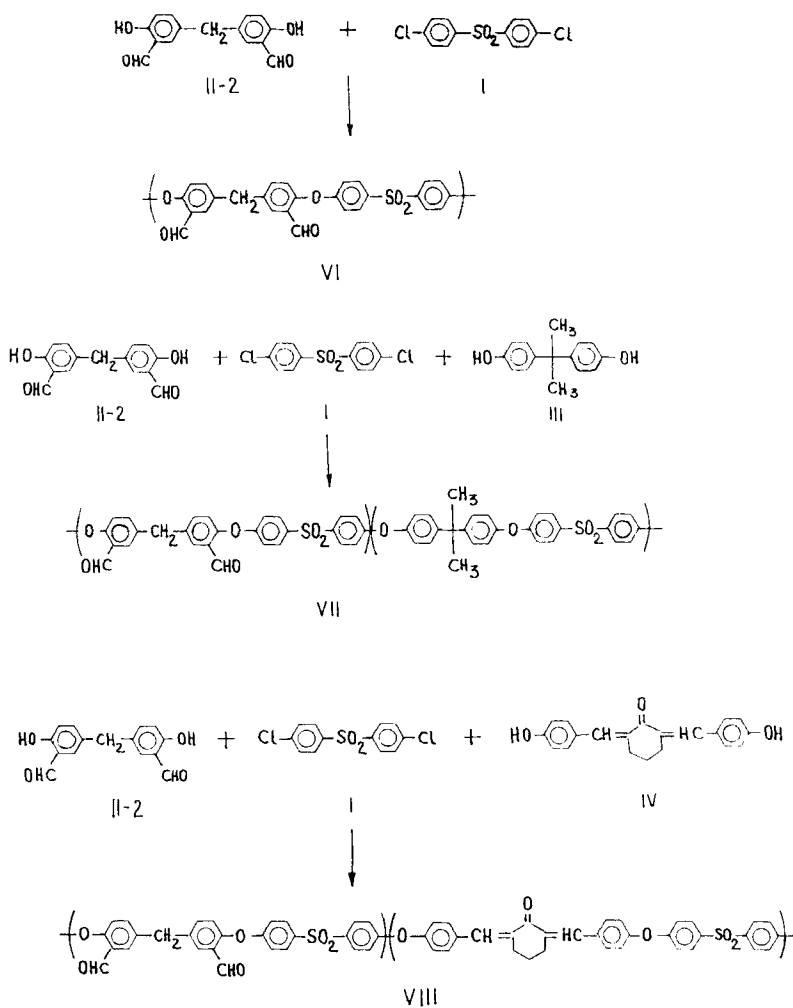


FIG. 1. The IR spectra of model compound II-4.

benzene and DMSO (Aldrich) were used as received. Anhydrous potassium carbonate was dried at 120°C in vacuum before use.

Model Compound (II-4) Synthesis

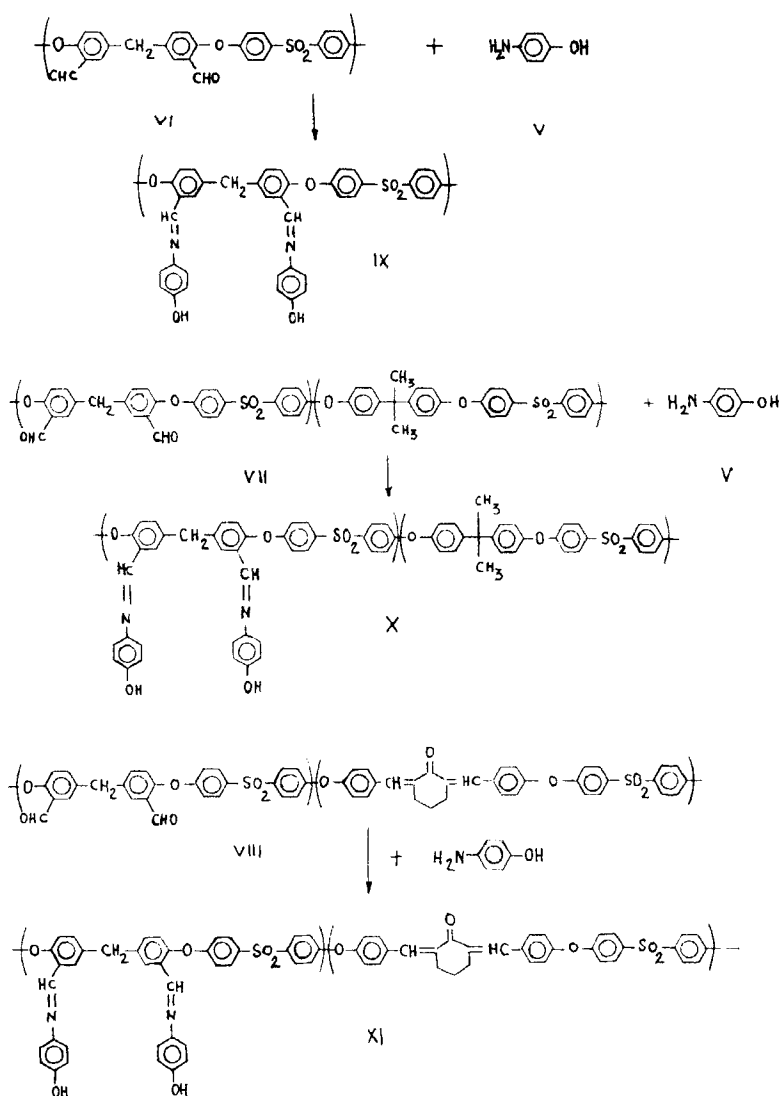
The synthesis and purification of the model compound (II-3) were described elsewhere [25]. The same synthesis system was charged with 2.7 g (7.242×10^{-3} mol) II-3, 0.9 g (3.512×10^{-3} mol) II-2, 30 mL DMSO, and 30 mL chlorobenzene. The system was heated 1 hour at about 80–90°C under a continuous flow of dry



SCHEME 2.

nitrogen. Then 2.4 g anhydrous potassium carbonate was added and the temperature was increased slowly to 130–134°C and maintained there for 6 hours until the water–chlorobenzene azeotrope was completely eliminated. The temperature was increased slowly to 150°C and maintained for 10 hours at 150–155°C. The mixture was allowed to cool to room temperature, then filtered to remove the inorganic salts, and poured into a large amount of water:methanol (3:1 v/v). After 6 hours of vigorous stirring the brown product was filtered, washed three times with water, and then with methanol. The product was finally dried under vacuum at 50°C for 18 hours. The brown powder (2 g, 61%), mp 146–150°C, was characterized by elemental analysis and IR spectroscopy.

Analysis. Calculated for $\text{C}_{53}\text{H}_{36}\text{S}_2\text{O}_{12}$: C, 68.52; H, 3.91; S, 6.90; Cl, 0.0%. Found: C, 64.95; H, 4.14; S, 10.98; Cl, 0.51%. IR (KBr, cm^{-1}): 1700, 1660



SCHEME 3.

(CH=O); 1585, 1500 (aromatic); 1300 (—SO₂— as); 1250 (C—O—C); 1160 (—SO₂— s); 1115, 1025, 880, 850 (aromatic).

Polymers Containing Aldehyde Pendant Group (VI–VIII) Synthesis

A typical synthesis procedure for polymers with aldehyde pendant groups (VI–VIII) is as follows. A 500-mL four-necked flask, equipped with a mechanical stirrer, thermometer, dry nitrogen inlet, a Dean-Stark trap with condenser, and a Claisen adaptor, was charged with a mixture of 0.03005 mol (7.70 g) bisphenol-dialdehyde (II-2), 0.03002 mol (8.62 g) 4,4'-dichlorodiphenyl sulfone (I), 0.07235

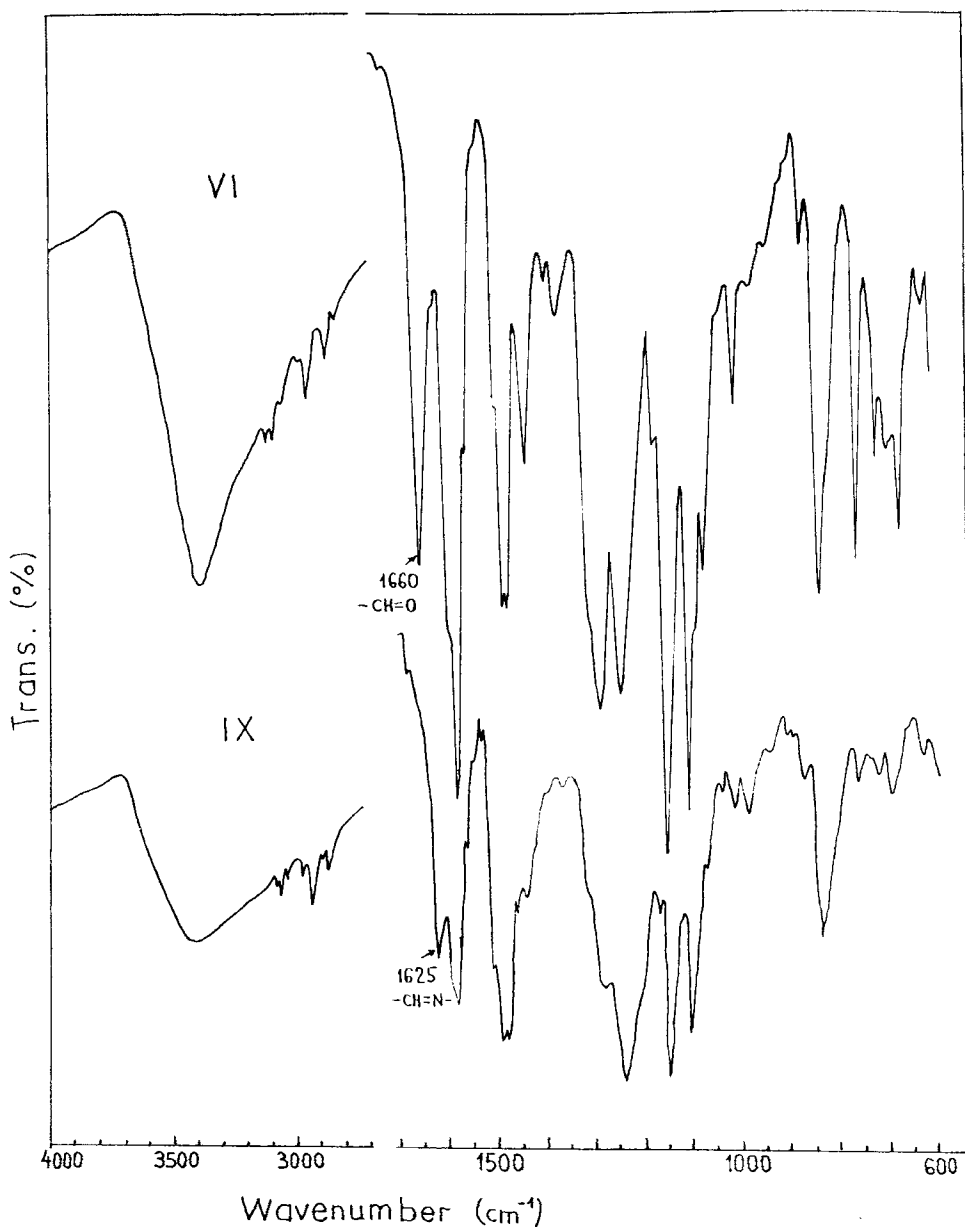


FIG. 2. The IR spectra of polymers VI and IX.

mol (10.0 g) potassium carbonate anhydrous, 40 mL dimethylsulfoxide (DMSO), and 50 mL chlorobenzene (PhCl). The mixture was heated under stirring at 134°C for about 1 hour to remove the PhCl-water azeotrope. The temperature was increased to 160–165°C and the stirring maintained for 6 hours. The mixture was allowed to cool and then filtered to remove inorganic salts. The polymer was coagulated into a large amount of water, filtered, washed with water, and then dispersed

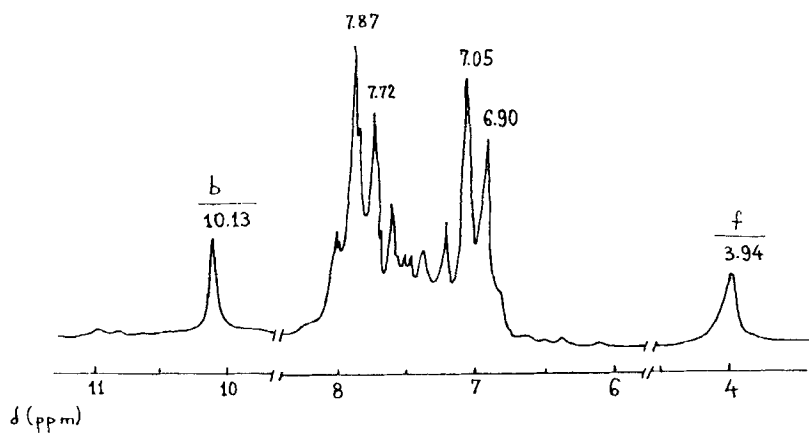
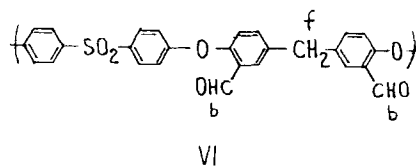
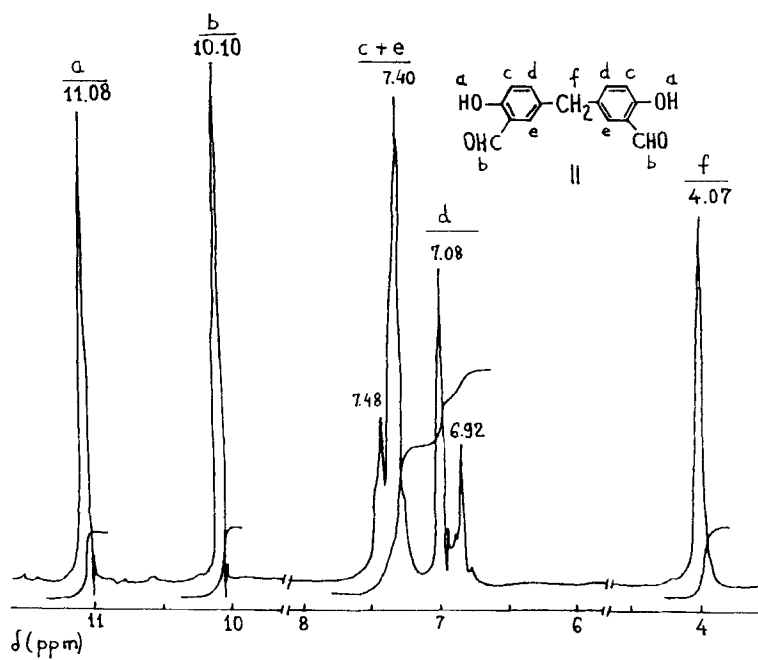


FIG. 3. The ¹H-NMR spectra of monomer II-2 and polymer VI.

TABLE 2. Elemental Analysis of Polymers VI-XI

Polymer	C, %		H, %		S, %		Cl, %	N, %	
	Calcd.	Found	Calcd.	Found	Calcd.	Found	Found	Calcd.	Found
VI	64.54	65.96	3.61	3.24	7.83	8.05	0.41		
VII	66.05	67.26	4.03	3.54	8.01	8.24	2.74		
VIII	66.71	67.89	3.94	3.71	7.52	7.41	1.62		
IX	65.47	66.00	3.86	4.19	6.82	6.11	1.68	2.98	2.89
X	67.77	68.64	4.23	3.87	6.96	6.27	2.24	2.03	2.00
XI	70.23	69.34	4.29	5.12	6.09	6.68	1.85	2.13	3.03

well into methanol. After filtration, the polymer was heated in methanol for 4 hours under reflux, filtered, and finally dried in vacuum at 50°C for 20 hours. The properties of the polymers are listed in Table 1.

Chemical Modification into Azomethine Phenolic Groups (IX-XI)

Functional copolyether sulfones with pendant aldehyde groups (VI-VIII) were modified by continuous azeotropic solution condensation with 4-aminophenol into pendant azomethine phenolic group copolyether sulfones [26]. A typical procedure is as follows. The same synthesis system presented above was charged with 4 g

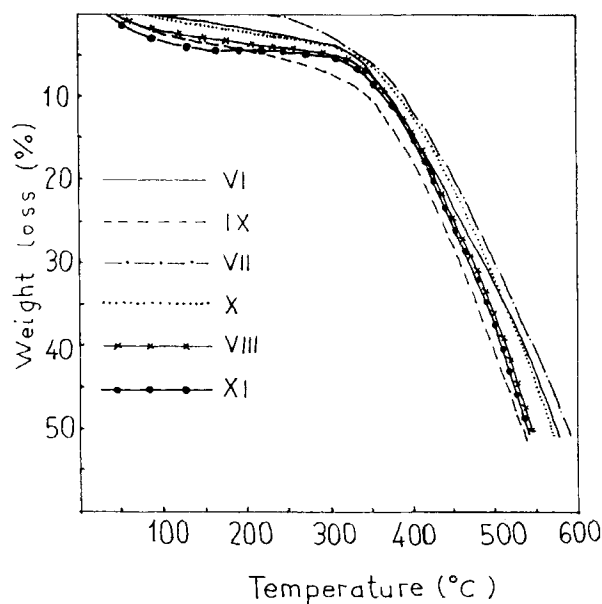


FIG. 4. The TGA curves of polymers VI-XI.

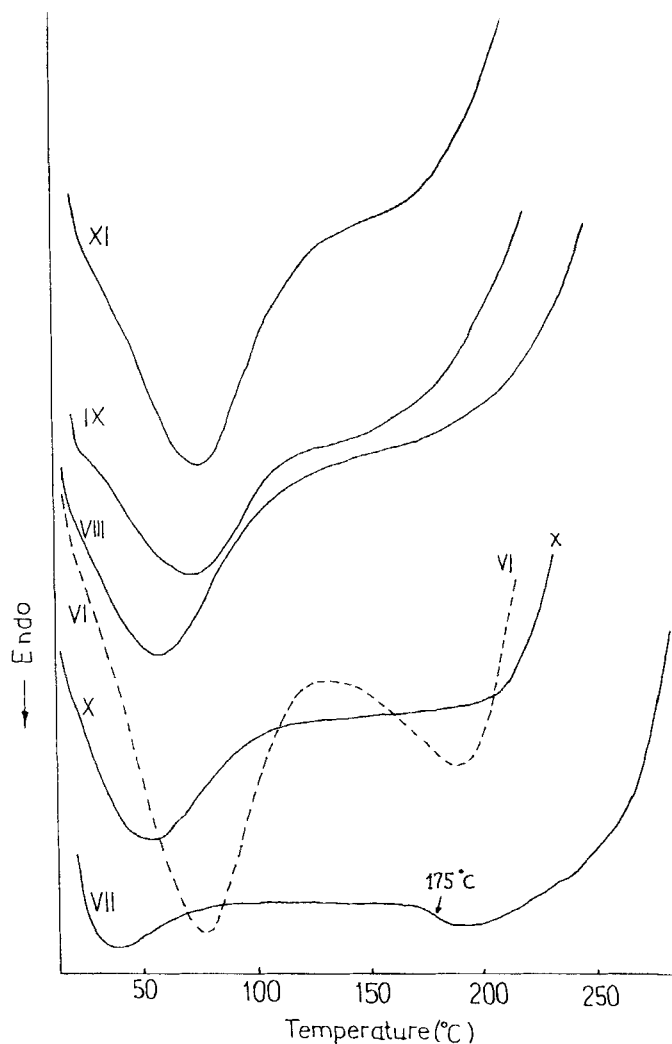


FIG. 5. The DSC curves of polymers **VI-XI**.

polymer (**VI**), 0.02291 mol (2.50 g) 4-aminophenol (**V**), 20 mL DMSO, and 25 mL PhCl. The mixture was heated at 134°C for about 1.5 hours until all water was removed as the PhCl-water azeotrope. The temperature was increased to 160°C and the stirring maintained for 8 hours. The solution was allowed to cool. The polymer was coagulated into a large excess of water, washed with water and methanol, and the polymer was heated in methanol 4 hours under reflux, filtered, and finally dried in vacuum at 60°C for 20 hours.

The properties of the polymers are listed in Table 1.

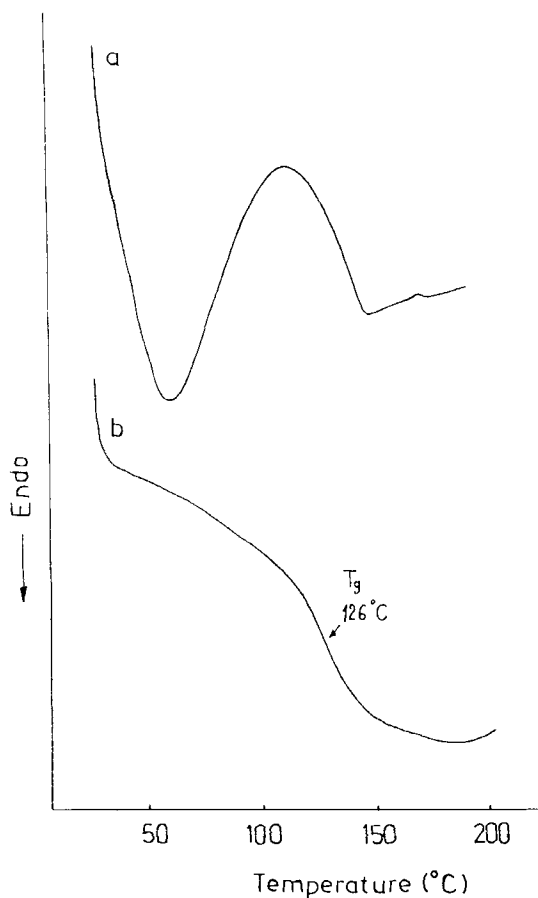


FIG. 6. The DSC curves of model compound **II-4**: (a) first heating, (b) second heating.

RESULTS AND DISCUSSION

A model compound (**II-4**), which describes well the chemical structure of the polymers, was synthesized (Scheme 1). As can be seen, the elemental analysis data are acceptable. We note that a higher purification of this product is very difficult due to its great solubility, as we observed previously for such kinds of products [25]. However, the IR spectra (Fig. 1) showed the presence of such characteristic absorption bands as $1700, 1660\text{ cm}^{-1}$ ($\text{CH}=\text{O}$), $1300, 1160\text{ cm}^{-1}$ ($-\text{SO}_2-$), 1250 cm^{-1} ($\text{C}-\text{O}-\text{C}$), $880, 850\text{ cm}^{-1}$ (aromatic).

The preparation of the copolyether sulfones with aldehyde pendant groups (**VI-VIII**) was based on the polycondensation reaction of 4,4'-dichlorodiphenyl sulfone (**I**) and various bisphenols such as 5,5'-methylene bis-salicylaldehyde (**II-2**), 2,2-bis(4-hydroxyphenyl)propane (Bisphenol A, **III**), and 2,6-bis(4-hydroxy-

SAMPLE NAME: VI-XI DATE: 93.09.21
 TARGET/FILTER(MONOCHR): Cu
 VOLTAGE/CURRENT: 40kV 20mA
 SLITS: DS 1 RS .15 SS 1
 SCAN SPEED: 2 DEG/MIN.
 STEP/SAMPLING: 02 DEG
 PRESET TIME: 0 SEC
 SMOOTHING: 0

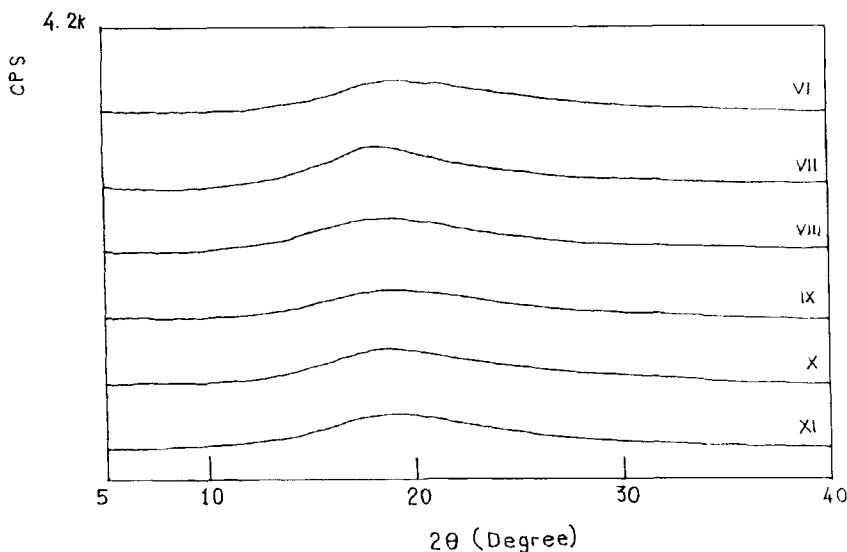


FIG. 7. The x-ray diffraction curves of polymers **VI-XI**.

benzylidene)cyclohexanone (**IV**) in the presence of DMSO, PhCl, and anhydrous potassium carbonate (Scheme 2).

Synthesis of the copolyether sulfones with pendant azomethine phenolic groups (**IX-XI**) was realized by continuous azeotropic solution condensation of the polymers carrying aldehyde pendant groups (**VI-VIII**) with 4-aminophenol in DMSO + PhCl, as shown in Scheme 3. The structures of the resulting copolyether sulfones (**VI-XI**) were confirmed by IR and $^1\text{H-NMR}$ spectroscopy, and elemental analysis. The polymers were characterized by viscometry, solubility, thermogravimetric analysis (TGA), DSC, and x-ray measurements.

The IR spectra of polymers (Fig. 2) showed the appearance of the characteristic absorption band of the $-\text{CH}=\text{O}$ group at 1660 cm^{-1} and at 1290, 1240, and 1150 cm^{-1} for the $-\text{SO}_2-$ group (asymmetrical), $\text{C}-\text{O}-\text{C}$ (aromatic ether), and $-\text{SO}_2-$ (symmetrical) stretching vibrations, respectively. There are also other characteristic absorption bands for the rest of the structure.

The IR spectra of polymers **IX-XI** showed the complete disappearance of the $-\text{CH}=\text{O}$ absorption band at 1660 cm^{-1} , and the appearance of the characteristic absorption band of the $-\text{CH}=\text{N}-$ group at 1625 cm^{-1} . All other bands mentioned above are also present.

A typical example of the $^1\text{H-NMR}$ spectra of polymers is shown in Fig. 3, with the corresponding assignment of peaks. As can be seen, the singlet from 11.08 ppm due to hydroxylic protons (a) of bisphenol (II-2) disappeared after reaction while the singlet from 10.10 ppm due to aldehydic protons (b) remained.

The elemental analysis data of polymers (Table 2) showed good agreement between calculated and found values. The small differences in C content for samples VI–VIII could be due to an incomplete purification of these polymers.

The reduced viscosities of polymer solutions VI–XI are in the 0.13–0.47 dL/g range. The copolyether sulfones with pendant azomethine phenolic groups (IX, X) showed increased reduced viscosity values versus the starting polymers (VI, VII), while sample XI showed a decreased η_{red} value versus the starting polymer (VIII), probably due to a fractionation effect which occurs in the purification step.

The thermal stabilities of polymers VI–XI were evaluated by TGA in air at a heating rate of 12°C/min. The TGA curves of the polymers are given in Fig. 4. As can be seen, only sample VII is completely stable up to about 230°C while the other polymers are lost in the range of 3–5% below 200°C. The higher thermal stability for polymer VII could be due to the presence of the bisphenol A units in the chemical structure, as observed by us previously for similar systems [27].

The DSC curves (first heating, Fig. 5) showed an endotherm below 100°C for all polymers. To elucidate this phenomenon, we studied the thermal behavior of the model compound (II-4). As can be seen (Fig. 6), in the first heating cycle the endotherm at about 60°C is still present. It disappeared in the second heating cycle, where a distinct glass transition temperature (T_g) can be observed at 126°C. The endotherm existing below 100°C in both the model compound and the polymers could be due to the elimination of absorbed water; these products have an increased hydrophilic character due to the presence of pendant aldehyde and hydroxyl groups. A study of a possible correlation with the chemical structure will be made in future work. The thermal stability discussed above for TGA curves is reflected by the occurrence of an exothermal peak. The higher the thermal stability in the 1–5% range, the higher the temperature onset for the exothermal peak. This is the reason why a distinct T_g at 175°C could only be detected for sample VII. For the rest of the polymers, T_g seems to be greater than the decomposition temperature.

The polymers were completely or partially soluble in aprotic dipolar solvents such as DMSO and NMP, but insoluble in common solvents.

The x-ray diffraction curves of polymers VI–XI (Fig. 7) showed them all to be amorphous.

CONCLUSIONS

Functional copolyether sulfones with pendant aldehyde groups were prepared via the classical polycondensation reaction of various bisphenols with 4,4'-dichlorodiphenyl sulfone. They were then modified by condensation reactions with 4-aminophenol into the corresponding polymers carrying phenolic azomethine groups.

Their expected structures were confirmed by IR and $^1\text{H-NMR}$ spectroscopy, and their properties were determined using current analysis methods.

X-ray diffraction measurements showed that the polymers obtained are amorphous.

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