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SULFONATED POLY(ETHER-KETONE)S CONTAINING HEXAFLUOROISOPROPYLIDENE GROUPS

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ABSTRACT

An aromatic poly(ether-ketone) derived from 4,4'-(hexafluoroisopropylidene)-diphenol and 4,4'-difluorobenzophenone has been sulfonated by using chlorosulfonic acid in 1,2-dichloroethane, in the presence of trimethylchlorosilane. The resulting modified polymers had different degrees of sulfonation depending on the reaction conditions. The sulfonation reaction with chlorosulfonic acid did not cause much degradation of the initial polymer. The sulfonated polymers are soluble in various polar solvents such as N,N-dimethylacetamide, N,N-dimethylformamide, pyridine, some in methanol, and could be cast into flexible tough films. The polymers were characterized by elemental analyses, infrared and ^{1}H NMR spectroscopy, gel permeation chromatography, and thermogravimetric analyses. The degree of sulfonation was determined by ^{1}H NMR spectroscopy. Some correlations between the conditions of sulfonation and the properties of resulting polymers have been made.

Key Words: Poly(ether-ketone); Hexafluoroisopropylidene group; Sulfonation reaction.

INTRODUCTION

Aromatic poly(ether-ketone)s are considered as high performance engineering thermoplastics which are characterized by high thermo-oxidative stability, tough mechanical properties and good solvent resistance [1]. Despite these attri-

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butes, poly(ether-ketone)s have relatively low glass transition temperature (T_g). In order to increase the T_g of these polymers, different rigid groups have been introduced into the macromolecular chains such as naphthalene [2] or biphenyl units [3] or different heterocyclic rings such as imide [4, 5], 1,3,4-oxadiazole, 1,2,4-triazole [6] or phenylquinoxaline [7] rings. Another way to improve the characteristics of poly(ether-ketone)s is the introduction of hexafluoroisopropylidene (6F) units [8, 9]. Frequently, the incorporation of 6F units increased solubility, flame resistance, thermal stability, and T_g, while decreasing color, crystallinity, dielectric constant, and moisture absorption. Many polymers with 6F units have been studied for application as films or coatings in microelectronics, optoelectronics, or in the manufacture of gas separation membranes [10]. Another way to obtain better and more useful properties is through chemical modification of poly(ether-ketone)s [11]. Sulfonation is a route to polymer modifications, particularly suitable for aromatic polymers. Sulfonation of poly(ether-ketone)s is expected to provide materials that show good permeability to water due to their more open structure and hydrophilicity and thus providing good membrane materials. Several sulfonating reagents have been described including concentrated sulfuric acid [12, 13], chlorosulfonic acid [14, 15], pure or complex sulfur trioxide [15, 16, and acetylsulfate [17]. Electron donating substituents will favor the reaction of sulfonation, whereas electron-withdrawing groups will not. In the case of poly(ether-ketone)s, phenylene rings between two ether links can be sulfonated under relatively mild conditions [18]. Another method is to sulfonate the polymers in sulfuric acid as already cast films [19]. Also, polymers with natrium sulfonate groups can be obtained by polymerization of carbonyl-5,5’-bis(2-fluorobenzensulfonate) with 2,2-bis-(hydroxyphenyl)-propan [20].

In the present paper, we have investigated the sulfonation of a poly(ether-ketone) containing hexafluoroisopropylidene groups which was obtained by the reaction of 4,4'-(hexafluoroisopropylidene)-diphenol with 4,4'-difluorobenzofenone, under relatively mild conditions, by using chlorosulfonic acid and trimethylchlorosilane [21].

EXPERIMENTAL

Starting Materials

4,4'-(hexafluoroisopropylidene)-diphenol, 4,4'-difluorobenzofenone, chlorosulfonic acid and trimethylchlorosilane were provided by different commercial sources and used as received.

Synthesis of Poly(ether-ketone) A

8.40 g (0.025 mol) of 4,4'-(hexafluoroisopropylidene)-diphenol, 5.45 g (0.025 mol) of 4,4'-difluorobenzofenone, 6.9 g potassium carbonate, 75 ml N,N-dimethylacetamide (DMAc), and 45 ml toluene were introduced in a three necked-flask equipped with a Dean Stark trap, magnetic stirrer, and heating bath. The reaction mixture was heated for 4 hours, under inert atmosphere at 150-160°C, while water was removed by azeotropic distillation. Toluene was then removed from the reaction flask by distillation and the reaction mixture was further heated at 170-180°C for approximately 6 hours. After cooling to room temperature, the viscous polymerization mixture was diluted with DMAc, and it was added dropwise into water. The precipitated polymer was isolated, washed with water and methanol, filtered, and vacuum dried. Yield: 95%.

IR (film, cm^{-1}): 1665 (C=O stretching), 1250 (C-O-C), 1210 and 1180 (6F). ^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 7.82$ (dd, 4H), $\delta = 7.42$ (dd, 4H), $\delta = 7.10$ (m, 8H). Elem. Anal. Calcd.: $C_{28}H_{16}O_3F_6$: C, 65.38%; H, 3.11%. Found C, 64.96%; H, 3.25%.

Sulfonation of Poly(Ether-Ketone) A

Polymer **A** was dissolved in 1,2-dichloroethane under inert atmosphere, then trimethylchlorosilane was added. A mixture of chlorosulfonic acid in 1,2-dichloroethane was then added during 1 hour. The reaction was continued for several hours under stirring at a fixed temperature. After that, the reaction mixture was cooled to 0°C by using an ice-water bath and methanol was added during 1 hour. The precipitated polymer was filtered and washed several times with methanol and water. For the polymers which were soluble in methanol, the solvent was removed by vacuum distillation and the polymer was precipitated into water. Table 1 presents additional conditions for the preparation of sulfonated fluorinated poly(ether-ketone)s **AS1-AS9**.

IR (film, cm^{-1}): 1665 (C=O stretching), 1250 (C-O-C), 1210 and 1180 (6F), 3450-3400 (OH), 1490 and 1470 (aromatic di- and tri-substituted), 1080 (symmetric vibrations O=S=O).

^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 8.02$ (s, H *orto* position to sulfonic acid groups), $\delta = 7.90$ (m, 4H), $\delta = 7.51$ (dd, H *orto*,), to 6F groups), $\delta = 7.15\text{-}7.30$ (m, H *orto* to ether linkages).

Chlorosulfonation of Poly(Ether-Ketone) A

1.5 g of polymer **A** were dissolved in 30 ml of chlorosulfonic acid and the solution was stirred at 80°C for 2 hours. Then, the solution was cooled to room temperature and poured slowly over a quantity of crushed ice. The white precipitated polymer **AS10** was washed several times with water and dried at room temperature under reduced pressure.

IR (film, cm^{-1}): 1665 (C=O stretching), 1250 (C-O-C), 1210, and 1180 (6F), 3450-3400 (OH), 1490 and 1470 (aromatic di- and tri-substituted), 1080 (symmetric vibrations O=S=O).

Table 1. Preparation of Sulfonated Fluorinated Poly(Ether-Ketone)s [In all the Experiments the Amount of Initial Poly(Ether-Ketone) Was 1.5 g and the Volume of 1,2-Dichloroethane was 30 ml]

Sulfonated polymer	Trimethyl-chlorosilane (ml)	Chlorosulfonic acid (ml)	T_s[a] (°C)	t_r[b] (h)	X[c]
AS1	0.5	0.5	50	3	0.008
AS2	1.0	1.0	50	3	0.0120
AS3	2.0	2.0	50	3	0.250
AS4	4.0	4.0	50	3	0.450
AS5	6.0	6.0	50	3	0.570
AS6	2.0	2.0	20	3	0.011
AS7	2.0	2.0	50	9	0.660
AS8	2.0	2.0	85	3	0.900
AS9	4.0	4.0	65	6	1.100
AS10	—	30	80	2	2.000

[a] Temperature of the sulfonation process.
[b] Duration of the sulfonation process at T_s.
[c] Degree of sulfonation.

^{1}H NMR ($CDCl_3$, 250 MHz): $\delta = 7.97$ (s, H *orto* to sulfonic acid groups), $\delta = 7.79$ (m, 4H), $\delta = 7.32$ (dd, H *orto* to 6F groups), $\delta = 7.15$-7.20 (m, H *orto* to ether linkages).

Film Casting

Polymers Soluble in Chloroform

A dried polymer sample (0.2 g) was dissolved in 4 ml of chloroform to give 5% (w/v) solution which was filtered onto a glass plate and carefully spread to the edges. The films were allowed to dry slowly under a petri dish for 24 hours, and then dried for 2 hours under reduced pressure. The polymer films were released from the glass plates by placing them in water. The resulting films were dried once again in vacuum at 50°C.

Polymers Soluble Only in Dimethylformamide (DMF)

A dried polymer sample was dissolved in DMF to obtain a 10-15% solution (w/v) which was cast onto a glass plate and after evaporating the solvent at a temperature up to 150°C, a flexible film was obtained which was stripped of the plate by immersion in water. The film was dried under vacuum at 50°C.

Measurements

Infrared spectra were recorded on a Specord M-80 Spectrophotometer using KBr pellets or polymer films with a thickness of 2-5 µm.

^{1}H NMR spectra were recorded using a Bruker AC 300 instruments.

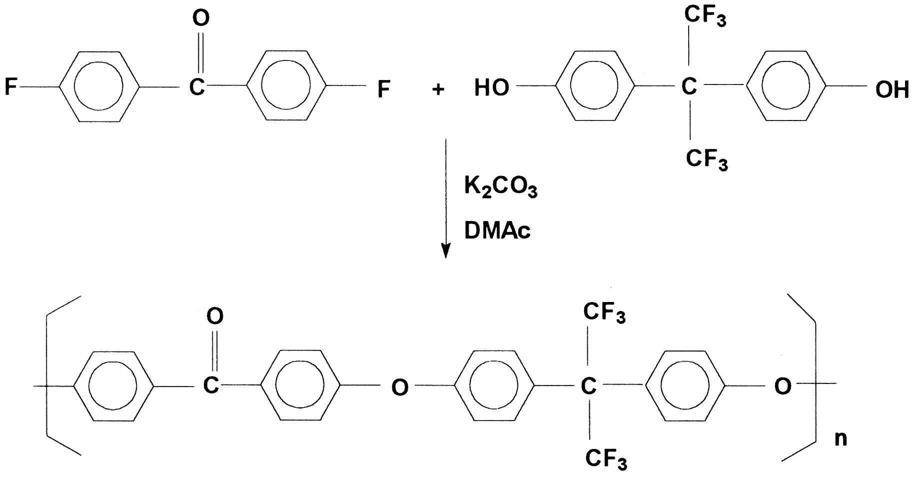
GPC analyses were run with a Waters Chromatography System with a Permagel 10^3-10^6 Å column. Polystyrene was used as a standard and tetrahydrofurane or DMF as eluent.

Thermogravimetric analyses were performed on a Mettler TC 10A at a heating rate of 10°C/min under a nitrogen atmosphere.

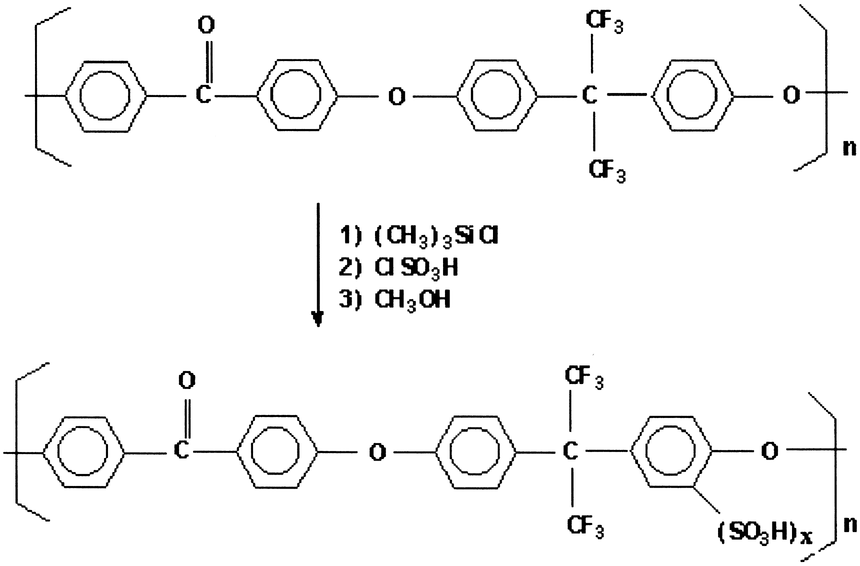
RESULTS AND DISCUSSION

The fluorinated poly(ether-ketone) **A** was obtained by the reaction of 4,4'-fluorobenzophenone with 4,4'-(hexafluoroisopropylidene)-diphenol, as shown in Scheme 1. The polymerization was carried out by heating an equimolar mixture of monomers and potassium carbonate in DMAc as solvent, under inert atmosphere, using toluene to remove the water formed during reaction. The mixture was first stirred at 150-160°C for 4 hours and, finally heated at 180°C. After a visible increase of viscosity, the reaction was stopped and the polymer was precipitated with methanol, filtered, and dried.

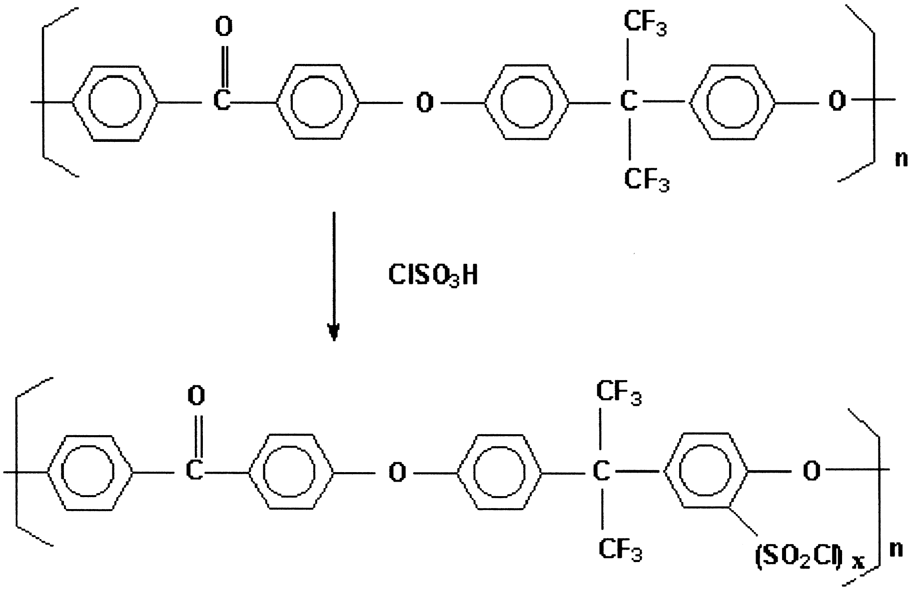
The sulfonation reaction is presented in Scheme 2. The reaction was carried out in 1,2-dichloroethane by using chlorosulfonic acid and trimethylchlorosilane. In order to correlate the degree of sulfonation of the resulted polymers with the reaction conditions, the process of sulfonation was carried out by varying in some limits different parameters such as the quantity of chlorosulfonic acid, tempera-



Scheme 1. Preparation of fluorinated poly(ether-ketone) **A**.



Scheme 2. Preparation of sulfonated fluorinated poly(ether-ketone) **AS1-AS9**.



Scheme 3. Preparation of chlorosulfonated poly(ether-ketone) **AS10**.

ture, and time of reaction. The conditions of sulfonation of reaction and the degree of sulfonation, as determined by ^{1}H NMR specroscopy, are presented in Table 1. A chlorosulfonated polymer was obtained by the reaction of fluorinated poly(ether-ketone) **A** with pure chlorosulfonic acid, for 2 hours at 80°C, as shown in Scheme 3.

From Table 1, it can be seen that the degree of sulfonation depends on the quantity of chlorosulfonic acid, temperature, and duration of the reaction. By increasing the quantity of chlorosulfonic acid for the same quantity of initial polymer **A**, a higher degree of sulfonation was obtained. Thus, polymers **AS4** and **AS5,** which were obtained by using a higher quantity of chlorosulfonic acid had a higher degree of sulfonation (0.45 and 0.57, respectively) when compared with polymer **AS2,** which was obtained by using a smaller quantity of chlorosulfonic acid and had a degree of sulfonation of 0.25. Also, it was evidenced that by increasing the reaction temperature, a higher degree of sulfonation resulted. Thus, the polymer **AS6,** which was synthesized at room temperature, had very low degree of sulfonation (0.011). The polymer **AS3**, which was obtained at 50°C, had a higher degree of sulfonation (0.25). By increasing the temperature to 85°C for 3 hours, in the case of polymer **AS8,** the degree of sulfonation became even higher (0.96). Also, by increasing the duration of sulfonation process, the degree of sulfonation was also increased. Thus, polymer **AS7,** which was prepared by running the reaction at 50°C for 9 hours had a degree of sulfonation of 0.66 when compared with the polymer **AS2,** whose reaction time was only 3 hours and therefore, had a lower degree of sulfonation (0.25). When the sulfonation reaction was performed with pure chlorosulfonic acid for 2 hours, a very high degree of chlorosulfonation (2.0) resulted. In order to obtain polymers with a high degree of sulfonation, it is possible to increase in some limits these three parameters. Thus, in the case of polymers **AS9**, the sulfonation process was carried out with a relatively higher quantity of chlorosulfonic acid at high temperature (65°C), and during a longer time, which led to a degree of sulfonation of 1.1.

The solubility of the initial poly(ether-ketone) A and the sulfonated poly(ether-ketone) AS1-AS10 is presented in Table 2. The solubility of sulfonated

Table 2. The Solubility of the Poly(Ether-Ketone) **A** and of the Sulfonated Poly(Ether-Ketone)s **AS1-AS10**

	Solvent						
Polymer	DMSO	DMF	Pyridine	THF	Chloroform	Benzene	Methanol
A	−	+	+	+	+	+	−
AS1	−	+	+	+	+	+	−
AS2	−	+	+	+	+	+	−
AS3	+	+	+	sw	sw	sw	−
AS4	+	+	+	sw	sw	−	−
AS5	+	+	+	sw	sw	−	−
AS6	sw	+	+	+	+	−	−
AS7	+	+	+	−	−	−	+
AS8	+	+	+	−	−	−	+
AS9	+	+	+	−	−	−	+
AS10	+	+	sw	sw	−	−	−

+; soluble; −, insoluble; sw, swell.

polymers is a clear indication that these polymers differ from the initial one. The solubility of the polymers seems to be connected very closely with the degree of sulfonation. Thus, the fluorinated poly(ether-ketone) A was soluble in solvents such as DMF, Pyridine (Py), tetrahydrofurane (THF), chloroform, and benzene. The polymers, having a low degree of sulfonation AS1, AS2, and AS6 had similar solubility with the initial polymer A. The polymers with a higher degree of sulfonation, AS3, AS4, and AS5, were partially soluble in solvents like chloroform or tetrahydrofurane and were soluble in polar solvents like dimethylsulfoxide (DMSO), DMF, Py. Polymers with the highest degree of sulfonation (AS7, AS8) from this series were soluble only in polar solvents. They were also soluble in methanol. Polymer AS9 was soluble in methanol and boiling water. By cooling the water solution, the polymer was still soluble. The polymer containing chlorosulfonic groups AS10 was soluble in DMF, swell in Py and THF, and was insoluble in chloroform, benzene, or methanol. The change in solubility when compared with the initial polymer could be explained by the presence of the polar sulfonic groups along the macromolecular chains. The good solubility of these polymers in different organic solvents indicates that the crosslinking reactions were limited in the conditions of the experiment.

The infrared spectra of fluorinated poly(ether-ketone) **A** and of the sulfonate derivative **AS4** are shown in Figure 1. All the polymers showed a characteristic absorption band at 1665 cm^{-1} due to C=O stretching of ketone groups, at 1250 cm^{-1} due to C-O-C stretching of aryl ether groups and at 1210 cm^{-1} and 1180 cm^{-1} due to 6F groups.

Few modifications can be observed for the polymers having a low degree of sulfonation and the intensities of the bands which characterize the sulfonic groups increased with increasing the level of sulfonation relative to the intensities of bands associated with the initial polymer. In the IR spectra of the polymers having a higher degree of sulfonation, the broad band appearing at 3450-3450 cm^{-1} was assigned to O-H vibration from sulfonic acid groups. The aromatic C-C band at 1490 cm^{-1} was observed to split upon sulfonation. A new absorption band at 1470 cm^{-1} appeared. Thus, the splitting of skeletal vibration is indicative of trisubstitution [12]. The absorption band at 1080 cm^{-1} was assigned to sulfur-oxygen symmetric vibrations O=S=O.

For the initial poly(ether-ketone) and sulfonated polymers the ^1H NMR was recorded. Figure 2 presents the ^1H NMR of the poly(ether-ketone) **A**. The protons which are in *orto* position to carbonyl groups (*Ha*), appeared as a doublet at δ = 7.82, and the protons which are in *orto* position to 6F groups (*Hd*) appeared as a doublet at δ = 7.42. The protons being in *orto* position to ether linkages (*Hb* and *Hc*) appeared as a triplet at δ = 7.10. Figure 3 presents the ^1H NMR of the sulfonated poly(ether-ketone) **AS8.** In this case the protons in *orto* position to carbonyl groups (*Ha*) appeared at δ = 7.90 as a doublet, the protons in *orto* position to 6F groups (*Hd*) appeared as a doublet at δ = 7.51, and the protons in *orto* position to ether linkages (*Hb* and *Hc*) appeared at δ = 7.14 as a multiplet. The protons which are in *orto* position to sulfone groups (*He*) appeared at δ = 8.05 as a singlet.

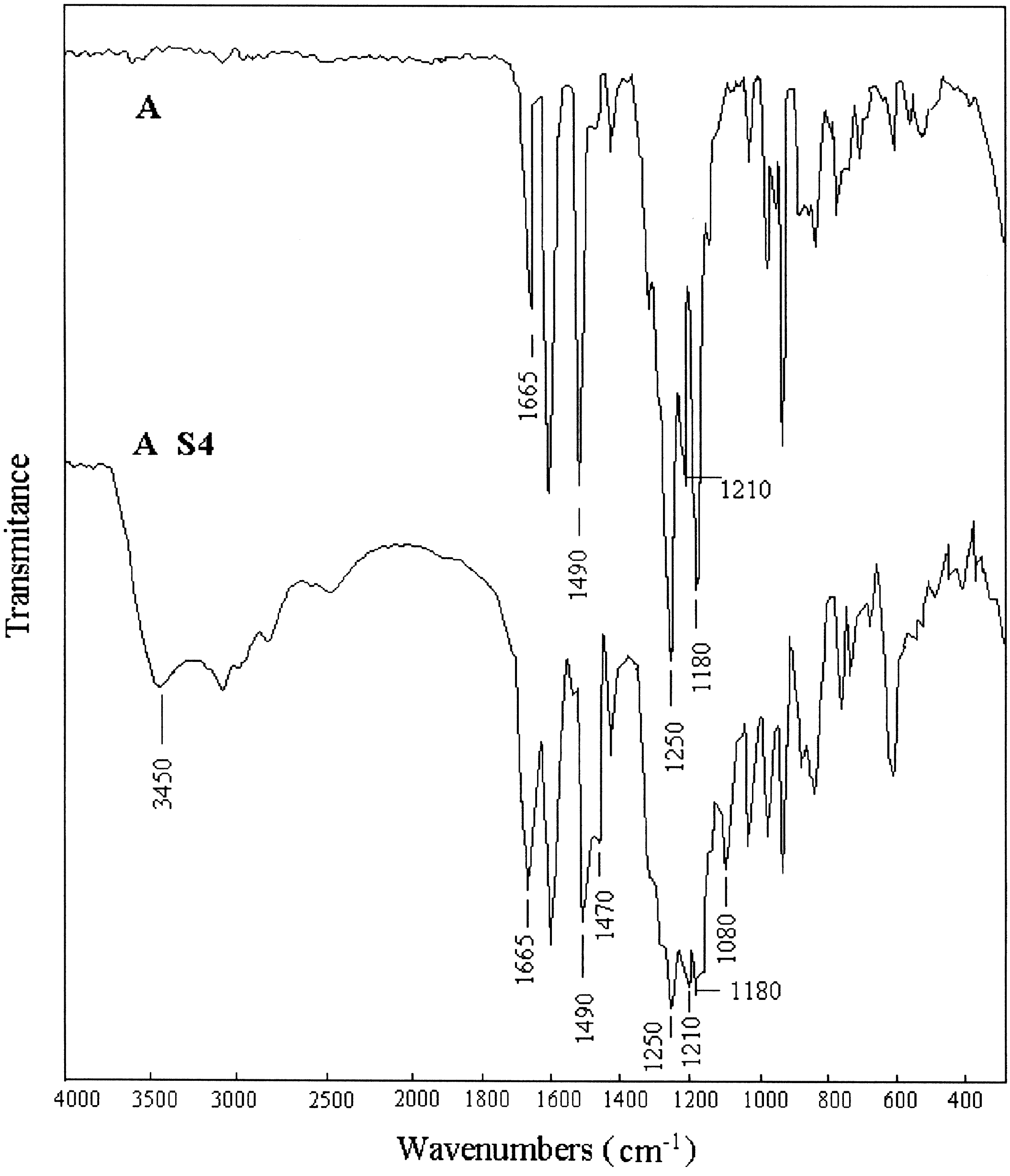


Figure 1. Infrared spectra of poly(ether-ketone) **A** and of sulfonated poly(ether-ketone) **AS4.**

It is possible to compare the integrals corresponding to the *He* protons with the integral corresponding to *Ha* protons and to determine the degree of sulfonation. Thus, in Table 1 the degree of sulfonation determined from ^{1}H NMR spectra is presented.

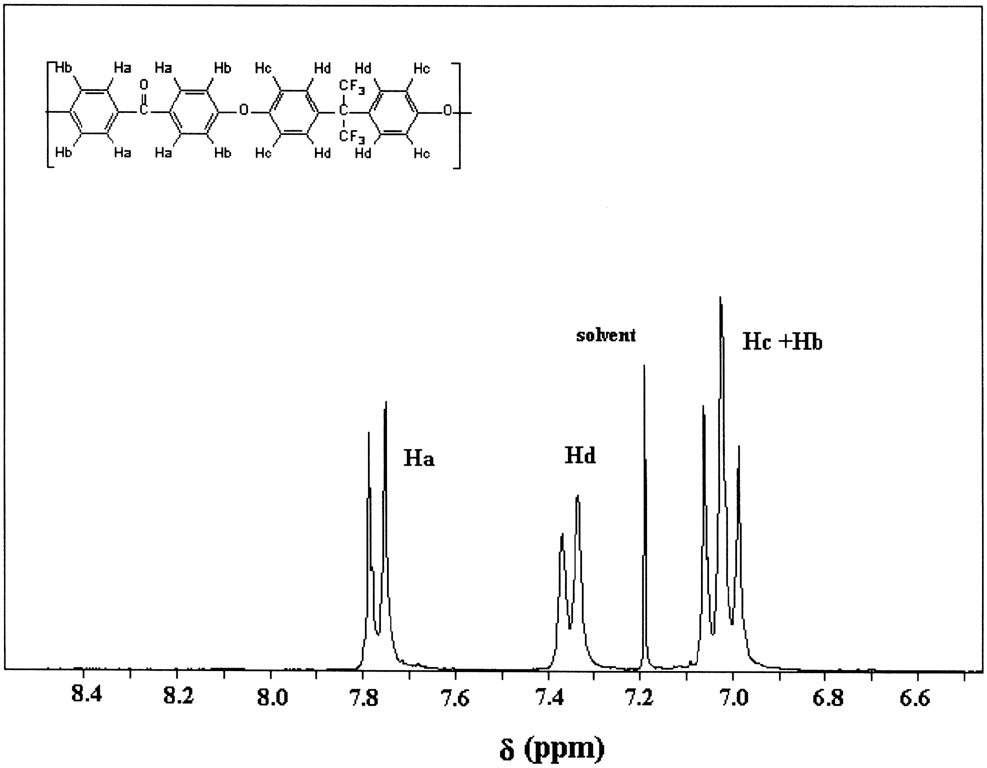


Figure 2. ^{1}H NMR of poly(ether-ketone) **A.**

GPC analyses were used to determine the molecular weight of the initial poly(ether-ketone) **A** and of sulfonated poly(ether-ketone) **AS1 – AS10**. Polymer **A** has $M_n = 9.98 \times 10^4$ g mol^{-1} and $M_w = 1.28 \times 10^5$ g mol^{-1}. The polymers which were sulfonated by using a lower quantity of chlorosulfonic acid and lower temperature, **AS1**, **AS2,** and **AS6,** had unimodal molecular weight distributions with no evidence of degradation compounds. In the case of polymers, which were sulfonated in stronger conditions **AS3**, **AS4**, **AS5**, **AS7,** and **AS8,** the molecular weight distributions were still unimodal, but an increase of M_n and M_w probably appeared due to some crosslinking. The overall aspect of GPC curves being unimodal, even when the polymers were sulfonated under strong conditions, shows that the present fluorinated poly(ether-ketone)s are more chemically stable than their non-fluorinated counter parts [22]. In the case of polymer **AS10,** which was obtained in pure chlorosulfonic acid at high temperature, the presence of a small quantity of products whith lower molecular weight was observed.

The films of the sulfonated poly(ether-ketone)s cast from chloroform or DMF were tough and flexible. The quantity of absorbed water of the films depends on the degree of sulfonation. For example, the polymers **AS1** and **AS2** absorbed a very small quantity of water, while polymers **AS3**, **AS4,** and **AS5**

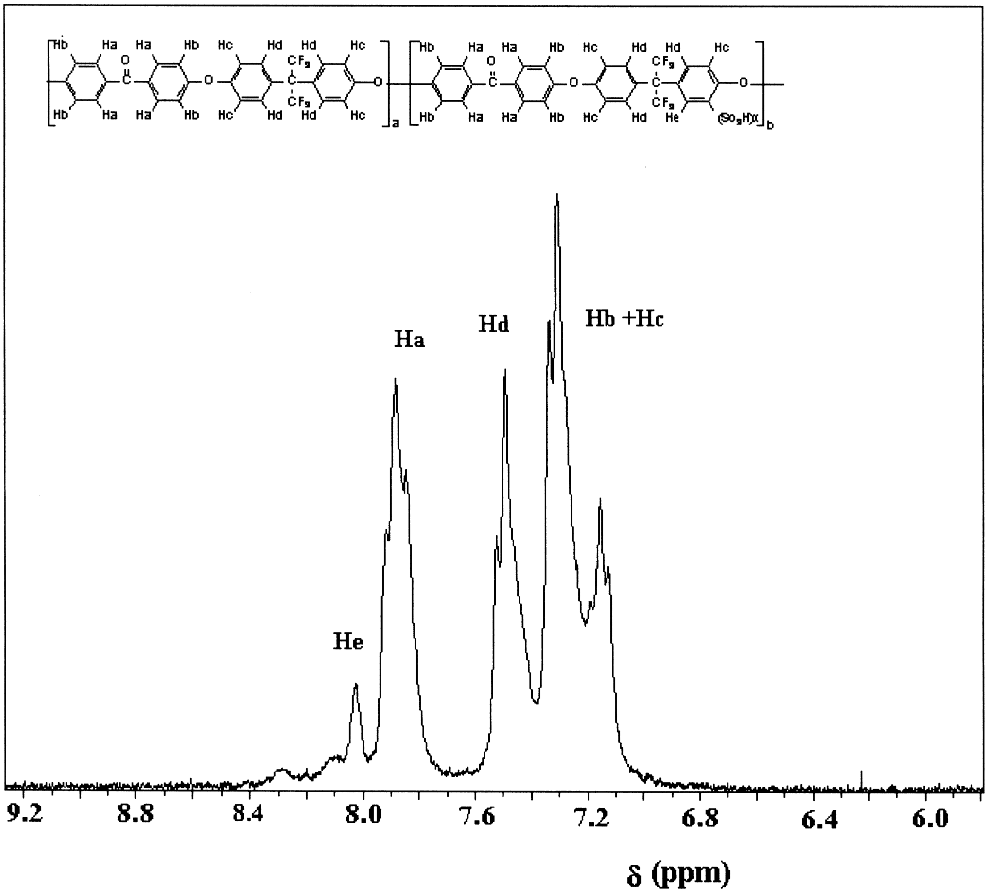


Figure 3. ^{1}H NMR spectrum of sulfonated poly(ether-ketone) AS8.

absorbed a higher quantity of water. The films with higher degree of sulfonation **AS7**, **AS8,** and **AS9** absorbed water significantly and they swelled to double or triple the original size.

The thermal stability of the polymers was studied by thermogravimetric analysis. The polymers with a low degree of sulfonation **AS1**, **AS2,** and **AS6** exhibit similar decomposition temperature when compared with the initial polymer **A.** The polymers with a higher degree of sulfonation exhibited two steps of weight loss: the first step of weight loss is at about 325°C and corresponds to the degradation of sulfonic acid groups. The second step of weight loss appeared at a temperature above 520°C, and it was attributed to polymer degradation (Figure 4). Comparison with related aromatic poly(ether-ketone)s and sulfonated poly(ether-ketone)s which do not contain hexafluoroisopropylidene groups and whose decomposition temperature are of about 285°C and 490°C, respectively, shows that the present fluorinated poly(ether-ketone)s and sulfonated fluorinated

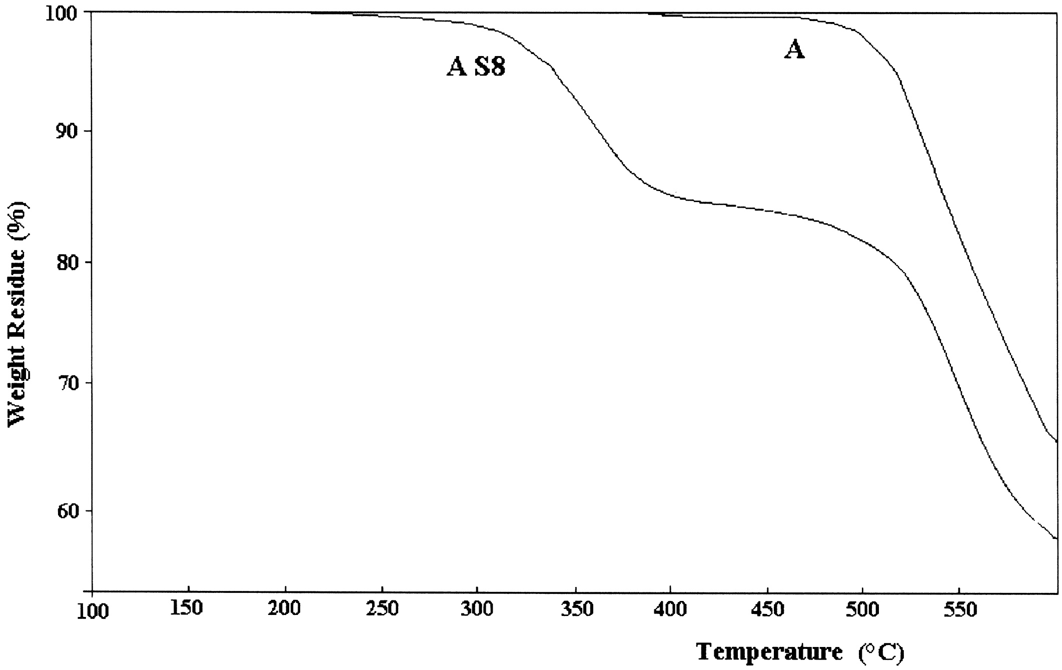


Figure 4. TGA curves of poly(ether-ketone) **A** and of sulfonated poly(ether-ketone) **AS8**.

poly(ether-ketone)s have a higher decomposition temperature, being more thermostable [22].

CONCLUSION

Sulfonated poly(ether-ketone)s containing hexafluoroisopropylidene groups were prepared by the reaction of the corresponding poly(ether-ketone)s with chlorosulfonic acid in 1,2-dichlorethane, in the presence of trimethylchlorosilane, at relatively low temperature. The conditions of the reaction did not produce strong degradation of the initial polymer. The degree of sulfonation was determined by ^{1}H NMR spectroscopy and it was increasing with increasing the quantity of chlorosulfonic acid, temperature, and duration of sulfonation process. Sulfonated poly(ether-ketone)s having a degree of sulfonation up to 1.1 per unit structure were obtained. The solubility of the sulfonated polymers depends on the degree of sulfonation: polymers with a high degree of sulfonation, above 0.6, were soluble even in methanol and swelled in water. These polymers can be cast in flexible tough films. They were stable up to 325°C and after this temperature appeared the thermal degradation of sulfonic acid groups. The presence of hexafluoroisopropylidene groups determined a higher decomposition temperature of the present polymers when compared with related sulfonated poly(ether-ketone)s without such groups.

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