

SULFONATION OF A NEW POLYETHER-ETHERKETONE PREPARED FROM PHENOLPHTHALEIN

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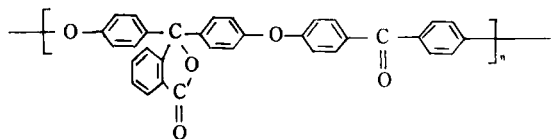
ABSTRACT

A novel polyetheretherketone (PEK-C) prepared from phenolphthalein has been synthesized. In order to improve some of its properties for application in high performance membrane, the PEK-C has been sulfonated with concentrated sulfuric acid. Degree of sulfonation can be regulated by controlling the temperature and time of sulfonation. The characterization of the sulfonated PEK-C in sodium salt form has been made by IR, ^1H NMR and ^{13}C NMR etc. It is shown that the sulfonation appears to take place exclusively in the ortho position to phenolic ether of phenolphthalein unit. The result is in agreement with theoretical deduction. Some properties of the sulfonated PEK-C, such as solubility, transition temperature, thermal degradation and hydrophilicity have also been discussed.

INTRODUCTION

Polyaryl ether ketones are characterized by their toughness, thermal and oxidative stability and good resistance against hydrolysis. Unlike polyarylsulfones, most of PEEK compounds exhibit partial crystallinity which makes them impossible to proceed solution processes. Chemical modifications of these polymers are of interest. Sulfonation is a powerful and versatile method of polymer modification. Marvel^[1] reported the sulfonation of a polyaryletherketone synthesized from iso- or terephthaloyl chloride and diphenyl ether by using chlorosulfonic acid as the sulfonating agent in 1984. Jin^[2] and Norman^[3] described the sulfonation of PEEK in 1984 and 1985 respectively aiming at enhancing the solubility of PEEK.

In our laboratory a polyetheretherketone (PEK-C) of the structure:



has been synthesized^[4]. It is an amorphous polymer with high glass transition temperature (T_g , 228 °C) and similar to PEEK in mechanical properties. PEK-C is soluble in a few aprotic polar solvents such as DMF, NMP and chlorohydrocarbons and thus can be solution-casted to asymmetric membrane. A recent report^[5] has described the preparation and properties of PEK-C UF membranes.

In this paper a controlled sulfonation of PEK-C with concentrated sulfuric acid, the characterization of PEK-C and the effect of the degree of sulfonation on its properties are described. It is expected to provide a good membrane material.

EXPERIMENTAL

1. Materials

PEK-C samples ($\eta_{sp}/C = 0.47$, $\overline{M}_w = 20,000$, T_g , 228 °C) were synthesized in our laboratory; H_2SO_4 (95—98%).

2. Sulfonation

The following is a typical sulfonation procedure for preparing a 0.8 $SO_3H/PEK-C$ composition. Other degrees of sulfonation can be achieved by varying the condition of reaction.

PEK-C in powder form was dissolved in H_2SO_4 to form a 10% w/v solution and stirred at 70 °C for 8 hrs. The resulting sulfonated polymer was precipitated by dropping it in ice-water at 0 °C under stirring. After removing the excess acid by washing, the polymer was cut up and shredded in a blender, washed thoroughly free from acid, then filtered and dried under vacuum at 60 °C. A yellow-brown product was obtained. Polymers with higher degree of sulfonation were difficult to wash due to their swelling in H_2O .

3. Neutralization

The $SO_3H/PEK-C$ samples were neutralized with enough 25% CH_3ONa solution in methanol or $NaOH$ aqueous solution. The neutralized polymers were filtered, washed several times with methanol and water, then dried under vacuum to give $SO_3Na/PEK-C$ polymers.

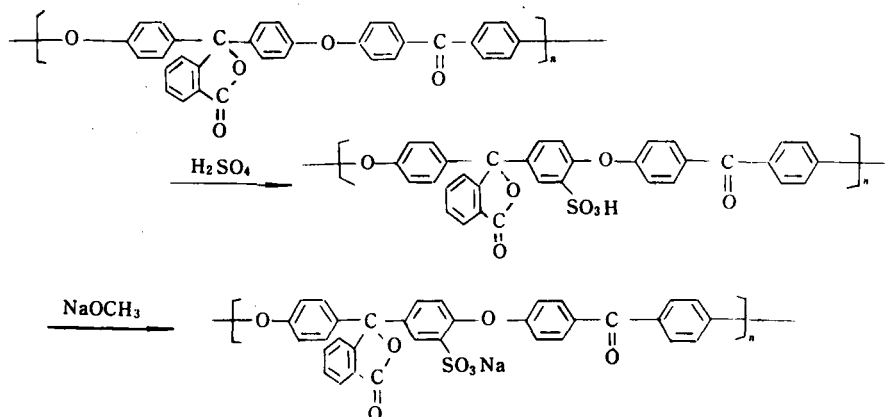
4. Determination of degree of sulfonation

Average degrees of sulfonation (X_s) per repeating unit (containing four phenyl rings) were calculated from ion exchange capacity (IEC) determined by titration as described in reference^[6].

5. Structure characterization

IR spectra were obtained on a Perkin-Elmer 599B spectrometer, samples were prepared from solution cast film on NaCl plates. ^1H and ^{13}C NMR spectra were measured on a JNM-100 spectrometer ^{13}C irradiation frequency of 25 MHz at 34 °C in $DMSO-d_6$ (for sulfonated samples) and in $CDCl_3$ (for unsulfonated sample using tetramethylsilane as an internal standard).

RESULTS AND DISCUSSION



Synthesis

As described in the experimental section, the sulfonation reaction of PEK-C is as follows:

PEK-C was sulfonated to different degrees as shown in Table 1 and Fig. 1.

Table 1 Sulfonation reaction of PEK-C

Sample	Condition of sulfonation reaction				X_s^*
	Conc. of H_2SO_4 (%)	Polymer / H_2SO_4 (g / ml)	Temp. ($^{\circ}C$)	Time (h)	
PEK-C	95-98	8-10%	25	24	0.3
	95-98	8-10%	60	3	0.3
	95-98	8-10%	60	12	0.7
	95-98	8-10%	60	36	1.0
PEEK**	95.5	1-4%	25	4.5	0.3
	97.4	1-4%	25	24.5	0.7
	97.4	1-4%	25	792	1.0

*: X_s , number of SO_3H per repeating unit

**: Data from reference [2].

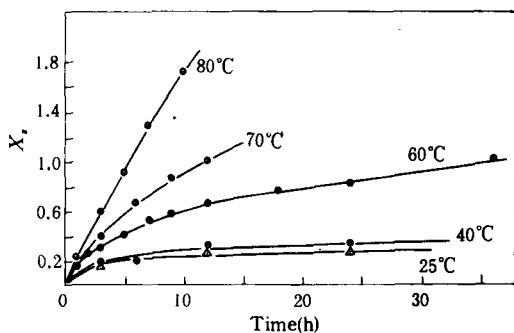


Fig.1 The sulfonation reaction of PEK-C at different temperatures and times

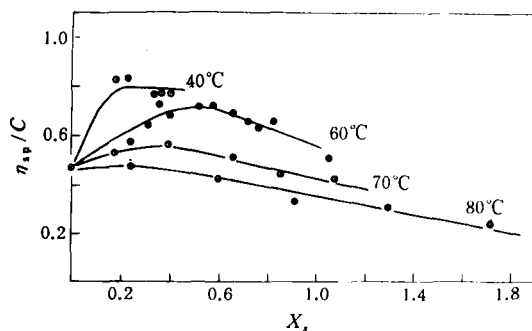


Fig.2 The relationship between X_s and η_{sp}/C for sulfonated PEK-C

In the case of sulfonated PEK-C this degradation is not serious. The sulfonated PEK-C sample ($X_s=1.0$) with good mechanical strength can be made at $80^{\circ}C$. However, serious degradation was occurred when polyether-sulfone (PES-C) was sulfonated at $80^{\circ}C$ [7] so that the mechanical strength of its film was lost. In comparison with PES-C, PEK-C is much more stable in H_2SO_4 . It can be concluded that H_2SO_4 is very suitable for the sulfonation of PEK-C and the appropriate reaction temperature of sulfonation is from $40^{\circ}C$ to $60^{\circ}C$.

Characterization

The solubility characteristics of sulfonated PEK-C in the free acid and sodium salt form with different degrees of sulfonation are shown in Table 2. The high X_s sulfonated PEK-C is soluble only in strong polar aprotic solvents such as DMF, DMAc, DMSO and NMP. The solubility of the neutralized sample is

similar to that of the free acid form. PEK-C is a typical amorphous polymer. It is soluble in some chlorohydrocarbons such as chloroform, 1, 2-dichloroethane. The sulfonated PEK-C is no more soluble in all of chlorohydrocarbons.

Table 2 Solubility of PEK-C and sulfonated PEK-C at room temperature

Solvent	Sulfonated PEK - C				PEK - C
	$X_s=1.0$		$X_s=0.6$		
	Free acid	Na salt	Free acid	Na salt	
Dimethyl formamide	S	S	S	S	S
Dimethyl acetamide	S	S	S	S	S
N-Methyl pyrrolidone	S	S	S	S	S
Dimethyl sulfoxide	S	S	S	S	SW
1,1,2 - Trichloroethane	I	I	SW	SW	S
1,2 - Dichloroethane	I	I	SW	SW	S
Chloroform	I	I	I	I	S
Tetrahydrofuran	I	I	I	I	SW
1,4 - Dioxane	I	I	I	I	SW
Ethanol	I	I	I	I	I
Acetone	I	I	I	I	I
Toluene	I	I	I	I	I

S. soluble; I. insoluble; SW. swollen.

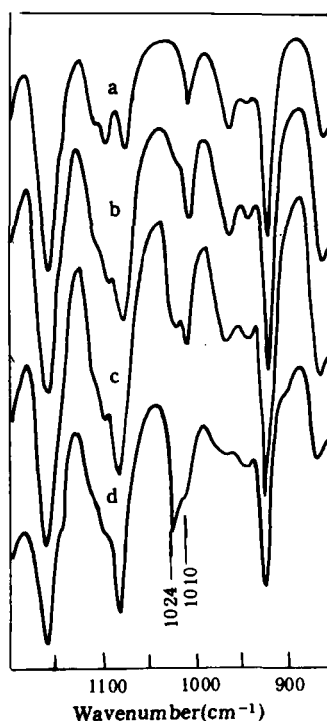


Fig.3 The IR spectra of sulfonated PEK-C
a) PEK-C; b) $X_s=0.3$;
c) $X_s=0.6$; d) $X_s=1.0$

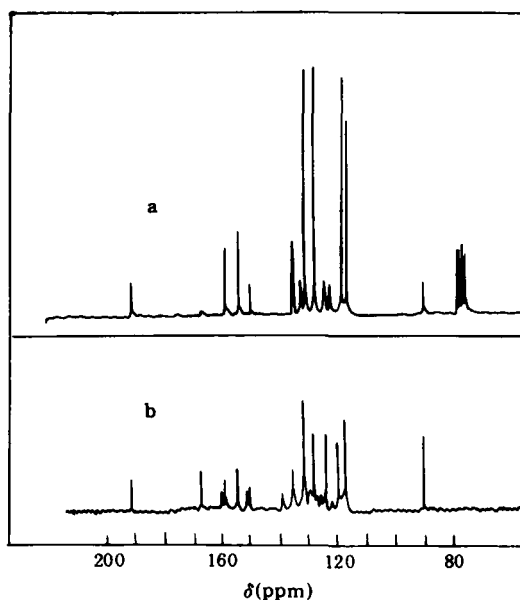


Fig.4 ^{13}C NMR spectra of PEK-C(a) and sulfonated PEK-C(b)

The infrared spectra of PEK-C and its sulfonated derivatives with different degrees of sulfonation are shown in Fig. 3. The IR spectra of sulfonated PEK-C deviate significantly from the spectrum of PEK-C. The presence of absorption at 1024 cm^{-1} (e. g. symmetric S=O stretching) is associated with sulfonic acid group. The intensity of this band increases with increasing level of sulfonation relative to intensity of the band associated with the backbone (at 1010 cm^{-1}). The change observed in the IR spectra indicates the presence of $-\text{SO}_3\text{H}$ groups.

The ^1H and ^{13}C NMR spectra for sulfonated PEK-C and PEK-C are shown in Figs. 4, 5 and Table 3. Analysis of these spectra indicates that sulfonation occurs predominantly in one position and that the position is in the ortho position to phenolic ether of phenolphthalein unit. This result agrees with theoretical deduction.

Properties

Glass transition behavior: It is of interest to compare how the degree of sulfonation influences the glass transition temperature (T_g) of sulfonated PEK-C. T_g values are determined by DSC. The introduction of $-\text{SO}_3\text{H}$ groups into PEK-C increases T_g as much as 50°C . This is probably due to increased intermolecular association through the polar ionic sites, i. e. an ionomer effect, and also due to the increased molecular bulkiness^[8]. The increase in T_g is proportional to the degree of sulfonation (see Fig. 6). In determination of T_g values we found that it is important to use well-purified and carefully dried samples for obtaining well-defined and reproducible T_g data.

Thermal stability: PEK-C is a highly heat-resistant polymer. The onset of significant weight loss for PEK-C is at about 460°C (Fig. 7)

Table 3 The ^{13}C NMR data of PEK-C and sulfonated PEK-C

PEK-C		Sulfonated PEK-C	
Carbon	(ppm)	Carbon	(ppm)
A	193.99	A	193.30
B	132.62	B	132.58
C	132.21	C	132.28
D	119.58	D	119.82
E	160.59	E	160.07
F	156.08	F	155.62
G	117.76	F'	151.41
H	128.94	G	117.89
I	136.60	H	128.95
J	90.91	H'	127.40
		I	136.61
		I'	136.43
		J	90.45
		K	139.70

As discussed briefly in another report^[9], the onset of weight loss might be the result of main chain decomposition of polymer occurring at the triaryl-substituted carbon atom in the lactone ring for PEK-C. In comparison with PEK-C, it

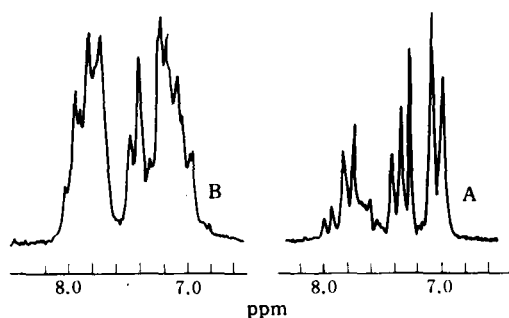
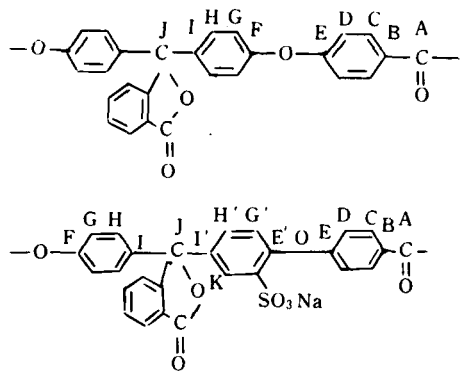


Fig.5 ^1H NMR spectra of PEK-C (A) and sulfonated PEK-C (B)

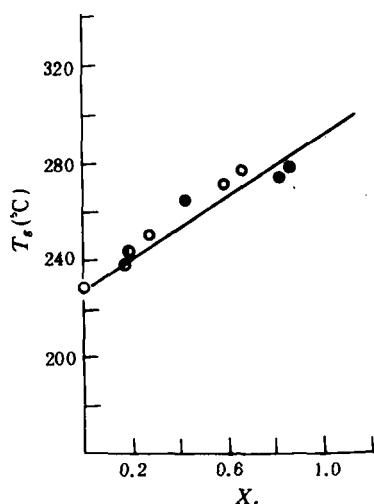


Fig.6 The effect of X_s on T_g of sulfonated PEK-C

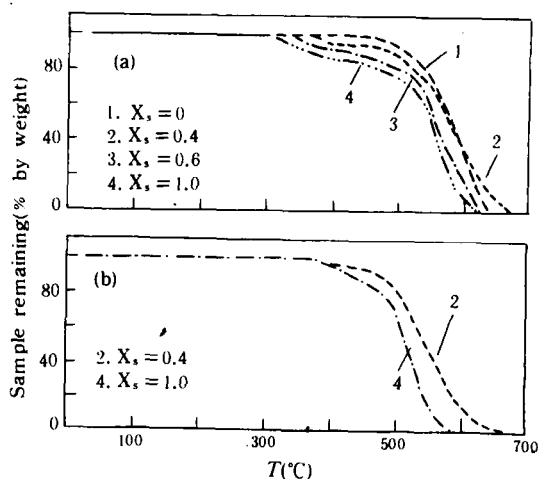


Fig.7 TGA data of sulfonated PEK-C
(a) $-\text{SO}_3\text{H}$ form; (b) $-\text{SO}_3\text{Na}$ form

was found that the initial weight loss temperature of sulfonated PEK-C decreased with increasing sulfonation levels for both free acid and salt forms. In Fig. 7(a), it is noted that there are two weight loss processes on TGA curves for samples of high and medium degrees of sulfonation in their free acid form. The first weight loss step in the temperature region of $300-400^\circ\text{C}$ is probably associated with the decomposition of sulfonic acid groups. In Fig. 7(b), the initial weight loss temperature seems to be shifted to higher temperature after neutralization. It can be concluded that the alkali metal counter-ions improve the thermal stability.

Hydrophilicity: The enhancement of hydrophilicity produced by the sulfonation of PEK-C is illustrated by the water-film contact angle data shown in Table 4. Sulfonation to the extent of 1.0 $\text{SO}_3\text{Na}/\text{PEK-C}$ reduced the contact angle of PEK-C by 13° .

The ion exchange capacities of compositions (X_s 0.6 and 1.0 $\text{SO}_3^-/\text{PEK-C}$) were found to be 1.2 and 1.84 meq/g. The effect of degree of sulfonation on hydrophilicity is illustrated by the water sorption behavior of cast film upon immersion in water at room temperature for 24 hrs., the water uptake was 7.3% and

13.2% respectively. Hydrophilicity, as determined by water sorption and contact angle measurements, can be varied over a wide range by controlling degree of sulfonation.

Table 4 Effect of sulfonation on hydrophilicity

Degree of sulfonation X_s	Ion exchange capacity, meq / g	Water sorption % weight increase	Contact angle degree °
1.0	1.84	13.2	60
0.6	1.20	7.3	66
0	0	1.6	73

Keywords :

Polyetheretherketone; Phenolphthalein; Sulfonation.

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