

# Sulfonation of Poly(Ether Ether Ketone)(PEEK): Kinetic Study and Characterization

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Received 19 July 2001; accepted 24 January 2001

**ABSTRACT:** Hydrophobic poly(ether ether ketone) (PEEK) were modified by sulfonation at different temperatures (22, 36, 45, and 55°C) and varying period of time with concentrated sulfuric acid used as solvent. A kinetic study was carried out based on the assumption that sulfonation reaction is a second-order reaction, which takes place preferentially in the aromatic ring between the two ether (—O—) links (the first type substitution), and there is only one substituent attached to each repeat unit of the PEEK before the complete substitution of this preferred aromatic ring. More than 100% substitution was observed in experiment. All the data with substitution degree less than 95% agree fairly well with the kinetic behavior of the second-order reaction. The reaction rate coefficient and activation energy for first type substitution were obtained. The sulfonated PEEK samples were characterized in terms of ion-exchange capacity (IEC), <sup>1</sup>H-NMR, contact angle, and solubility. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 82: 2651–2660, 2001

**Key words:** poly(ether ether ketone) (PEEK); ion-exchange capacity (IEC); contact angle; sulfonation; kinetics; characterization

## INTRODUCTION

Membranes are one of the important applications of polymers. Many engineering plastics (e.g., polystyrene, polysulfone, polyethersulfone, and polyphenyl oxide) have found broad uses in membrane manufacturing. It is generally accepted that one single material does not possess all the excellent properties required for membranes. Therefore, for a specific application, polymer materials may need some modification to improve their performances.

Sulfonation is a frequently used means for polymer modification. Many polymers<sup>1–6</sup> have

been sulfonated to improve their expected properties in terms of better wettability, higher water flux, higher antifouling capacity, better permselectivity, and increased solubility in solvents for processing.

The earlier sulfonation treatments were mainly focused on improving the hydrophilicity of membranes, since the hydrophilic membranes can offer and retain a relatively higher water flux because of the enhanced antifouling capacity and favorable hydrodynamic environment of the membranes. Recently, sulfonation has been directed to the performance enhancement of pervaporation and gas separation membranes.<sup>7,8</sup> It is well known that the solution–diffusion theory is the basis for the mass transport through homogeneous membranes; sulfonation modification can increase the affinity interaction between the membrane material and one of the components to be separated; therefore, the preferential permeation of this species can be expected.

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Contract grant sponsor: Natural Sciences and Engineering Research Council of Canada (NSERC).

*Journal of Applied Polymer Science*, Vol. 82, 2651–2660 (2001)  
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In the case of the polyelectrolyte membranes for dehydration of solvents by pervaporation, some researchers<sup>9</sup> have proposed a novel transport mechanism (the so-called “fixed carrier” theory), which holds that there are separate channels in the membrane for the transport of water and alcohol molecules, and the water molecules transport exclusively through the fixed carrier sites. Based on this theory, it can be concluded that the sulfonation of membrane material is favorable to the preferential permeation of water. This effect is particularly prominent for the less hydrophilic membrane materials.

Poly(ether ether ketone) (PEEK) is a new generation of polymers with high thermal and mechanical stabilities, both of which are the properties required for the polymeric membranes in practical applications, especially for pervaporation separation processes, where a stronger interaction and phase change are involved. There have been some reports of the applications of sulfonated PEEK in ultrafiltration. In this work, an attempt is made to sulfonate the PEEK for pervaporation application, where the sulfonation degree of the polymer is important to the separation performance, as a hydrophilicity–hydrophobicity balance should be manipulated to achieve the preferential permeation toward one of the components of the mixture and simultaneously suppress the excessive swelling of membranes.

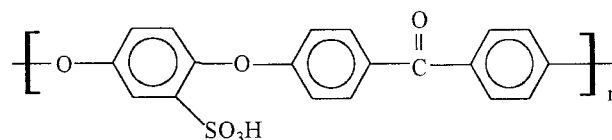
Concentrated sulfuric acid and the chlorosulfuric acid are usually employed as sulfonating solvents.<sup>10</sup> It is well known that chlorosulfuric acid is a much stronger solvent than concentrated sulfuric acid because of the weak Cl–S bond. This often makes the sulfonation reaction less controllable, and more importantly, the sulfonation is generally accompanied with side reactions.<sup>11–13</sup> Concentrated sulfuric acid was used as the solvent for sulfonation of PEEK in this study.

In this work, the mechanism of the sulfonation of PEEK was analyzed and the sulfonation kinetics was investigated. Sulfonated PEEK samples were characterized in terms of ion-exchange capacity (IEC), sulfonation degree, <sup>1</sup>H-NMR, contact angle and solubility in some common solvents.

## KINETIC CONSIDERATIONS

### Substitution Sites

Sulfonation is an electrophilic substitution reaction, and the active site for substitution is deter-



**Figure 1** Repeat unit of sulfonated poly(ether ether ketone).

mined mainly by the electron density of the site. It can be judged that the substitution will preferentially take place in one of the four positions of the aromatic ring as specified in Figure 1, which shows the repeat unit of the polymer. Since the electron density of the other two aromatic rings in the repeat unit is relatively low due to the electron-attracting nature of the neighboring carboxyl group, under ordinary sulfonation conditions, for example, at room temperature and with the concentrated sulfuric acid used as solvent, there is only one —SO<sub>3</sub>H group (first type substitution) attached to each of the repeating units. However, at higher temperatures and/or long period of reaction time, the substitution in the other two aromatic rings (the second type substitution) is also possible. The first type substitution is preferred because of the lower energy barrier of this type of reaction. Based on this consideration, the following assumptions can be made:

1. Substitution first takes place only in one of the four sites specified in Figure 1 (the first type substitution).
2. Four sites have equal chance for the substitution.
3. The first-type substitution is a second-order reaction.
4. After the first type substitution is complete, further substitution (the second-type substitution) can happen in the other two identical aromatic rings.
5. The reverse reaction is neglected for the high acid concentration.
6. Volume change during reaction is ignored.

Actually, there can not be a clear-cut boundary between the first type and second type substitution. At a high degree of sulfonation, the second type substitution may be initiated. These two types of substitutions definitely display different kinetic behavior.

According to our experimental observations, when the sulfonation degree is approaching 100%, the sulfonated PEEK becomes water solu-

**Table I Polymer/Acid Concentration Ratio (a/b) Employed in Sulfonation Experiments**

PEEK/H <sub>2</sub> SO <sub>4</sub>	PEEK Conc. (a)	H <sub>2</sub> SO <sub>4</sub> Conc. (b)	(a/b)
5/95 (w/v)	0.176 mol/L	17.7 mol/L	0.01
10/90 (w/v)	0.356 mol/L	17.0 mol/L	0.02

Density of PEEK: 1.32 g/cm<sup>3</sup>, H<sub>2</sub>SO<sub>4</sub> concentration: 18.4 mol/L.

ble, it is impossible to recover all the SPEEK used in the titration experiment, as a result, the sulfonation degree determined by titration method is somewhat questionable. Therefore, the kinetic study is confined to the first type substitution in this work.

### Sulfonation Kinetics

The sulfonation reaction can be described as follows:

PEEK + HOSO <sub>3</sub> H = PEEK - SO <sub>3</sub> H + H <sub>2</sub> O				
Initial conc.	<i>a</i>	<i>b</i>	0	0
At time <i>t</i>	<i>a - c</i>	<i>b - c</i>	<i>c</i>	<i>c</i>

Based on the previous assumption, the reaction rate can be written as

$$\frac{dc}{dt} = k(a - c)(b - c) \quad (1)$$

where *k* is the reaction rate coefficient, *a* and *b* are the initial concentrations of PEEK repeat unit and concentrated sulfuric acid, respectively, and *c* is the concentration of the sulfonated PEEK repeat unit. Usually a large concentration ratio of acid/polymer is maintained (Table I), so that an effective sulfonation will be achieved:

$$b \gg a > c$$

$$(b - c) \approx b$$

Therefore, equation (1) is reduced to

$$\frac{dc}{dt} = kb(a - c) \quad (2)$$

$$\ln \frac{a - c}{a} = -kbt \quad (3)$$

$$\ln \left( \frac{1}{1 - SD} \right) = kbt \quad (4)$$

where SD = *c/a* is the ratio of the concentration of sulfonated PEEK repeat unit to that of the total initial repeat unit of PEEK, can be regarded as the sulfonation degree (SD). The reaction rate coefficient can be expressed as

$$k = k_0 e^{-E_a/RT}$$

$$\ln k = \ln k_0 - \frac{E_a}{RT} \quad (5)$$

The sulfonation degree (SD) can be determined experimentally using titration method, and therefore the rate coefficients can be obtained using equation (4), the activation energy of the sulfonation reaction can thus be evaluated using equation (5).

## EXPERIMENTAL

### Materials

Concentrated sulfuric acid was provided by Fisher Scientific, with a specified concentration of 95–97 wt %. The PEEK was obtained from the Victrex US Inc. in powder form (<80 μm), with a molecular weight *M<sub>w</sub>* 39,200, and density 1.26–1.32 g/cm<sup>3</sup>. dimethyl-formamide (DMF), dimethyl-acetamide (DMAC) and acetone are provided by Aldrich Chemical Co. Inc.

### Sulfonation Reaction

The initial concentration ratio of PEEK/sulfuric acid was maintained at 5/95 (w/v) in all the experiments. PEEK is dissolved in concentrated sulfuric acid at room temperature to suppress the heterogeneous sulfonation. After complete dissolution of PEEK (~1 h), the polymer solution was brought to the normal reaction temperature. After different length of reaction times (varying from 1 to 24 h), the sulfonated PEEK solution was then quenched in deionized water under mechanical agitation to recover the modified polymer, which is then immersed in deionized water to

remove the residual sulfuric acid until the pH value of the washing water is  $>5$ .

### Neutralization of the Sulfonated Poly(Ether Ether Ketone) (SPEEK-H)

The wet SPEEK-H was immersed in a 50/50 (v/v) aqueous acetone solution 5 min and then in pure acetone 10 min to remove water from the SPEEK-H. Finally, the acetone-wet SPEEK-H was air dried. A sample of about 0.5 g was then neutralized in 200 mL of 0.01 M sodium hydroxide aqueous solution for 3 days, so that the SPEEK-H was fully converted into its sodium salt form SPEEK-Na.

### Backtitration of NaOH Solution

Dilute sulfuric acid (0.003M) is employed to back titrate the NaOH aqueous solution, which has been partially neutralized by the SPEEK-H. Universal indicator is adopted to predict the neutral point. By measuring the amount of the sulfuric acid consumed in the titration, the molar quantity of the  $-\text{SO}_3\text{H}$  contained in the sample of the SPEEK-H can be determined using equation (6):

$$N_{\text{SPEEK-H}} = (MV)_{\text{NaOH}} - 2(MV)_{\text{sulfuric acid}} \quad (6)$$

where  $M$ ,  $V$  are the molar concentration and volume of the standard solutions, respectively. The ion-exchange capacity (IEC) can thus be determined by

$$\text{IEC} = (N_{\text{SPEEK-H}}/W_{\text{sample}}) \cdot 1000 \text{ (meq/g)} \quad (7)$$

where  $W_{\text{sample}}$  is the weight of the SPEEK-Na sample.

It is known that SPEEK-Na is a copolymer that consists of a PEEK- $\text{SO}_3\text{Na}$  unit and a PEEK unit; the sulfonation degree can thus be defined as

SD

$$= \frac{\text{molar number of the PEEK} - \text{SO}_3\text{Na unit}}{(\text{molar number of the PEEK} - \text{SO}_3\text{Na unit} + \text{molar number of the PEEK unit})} \quad (8)$$

The molar number ( $N_1$ ) of the PEEK- $\text{SO}_3\text{Na}$  unit in 1 g sulfonated PEEK copolymer is

$$N_1 = 0.001 \cdot \text{IEC} \quad (9)$$

The molar number ( $N_2$ ) of the PEEK unit in 1 g sulfonated PEEK copolymer is

$$N_2 = \frac{(1 - 0.001 \cdot \text{IEC} \cdot M_1)}{M_2} \quad (10)$$

where  $M_1$ ,  $M_2$  are the molecular weights of the SPEEK- $\text{SO}_3\text{Na}$  unit, and the PEEK unit, respectively:

$$M_1 = 390 \text{ (dalton)}$$

$$M_2 = 288 \text{ (dalton)}$$

With these and inserting equations (9) and (10) into equation (8) gives

$$\text{SD} = \frac{288 \cdot \text{IEC}}{(1000 - 102 \cdot \text{IEC})} \quad (11)$$

When  $\text{SD} = 100\%$ , we can get the limit IEC of the sulfonated PEEK (100% first type substitution of the aromatic ring)

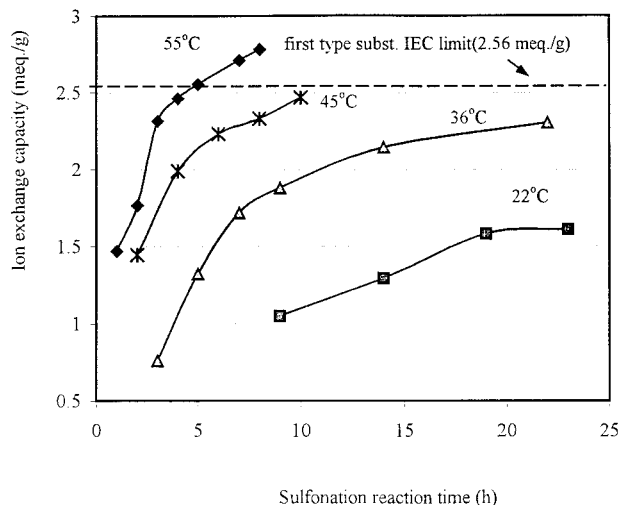
$$(\text{IEC})_{\text{max}} \approx 2.56 \text{ (meq/g)}$$

### $^1\text{H-NMR}$

The sulfonated PEEK samples of different sulfonation degrees were dissolved in DMSO- $d_6$  solvent to obtain 3 wt % polymer solutions for NMR analysis using an Avance 500 (Bruker Instrument). The  $^1\text{H-NMR}$  spectra were recorded at a resonance frequency of 500.13 MHz at a temperature of 298 K.

### Contact Angle Characterization

A dry SPEEK-Na sample was dissolved in DMF solvent to form a 5 w/w % polymer solution, which was filtered and debubbled 2 days before the membrane casting on a glass plate with a knife gap of 250  $\mu\text{m}$ . The cast polymer solution film was transferred to an oven to evaporate the solvent at 70°C for 2 days. The resulting membrane is transparent with a thickness of 15  $\mu\text{m}$  (measured with a MITUTOYO micrometer). The membranes are further cleaned with deionized water, dried in a vacuum descissor 1 day before being cut into a square form of 2  $\times$  3 cm for contact angle characterization, using the facility of Axisymmetric Shape Image Profile Analysis (ASIPA).



**Figure 2** Time dependence of ion-exchange capacity (IEC) of sulfonated poly(ether ether ketone).

## RESULTS AND DISCUSSION

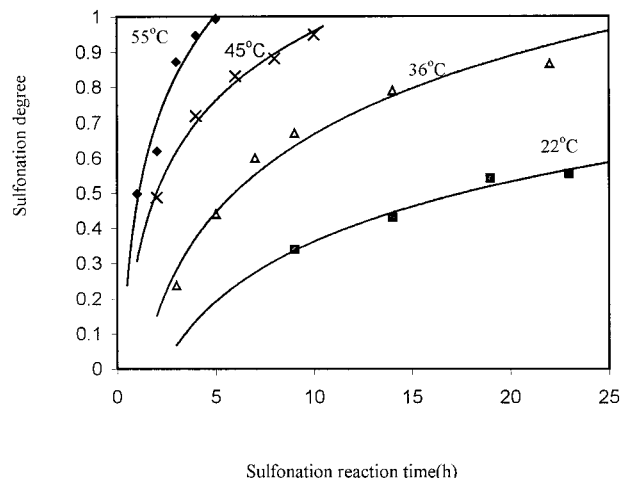
### Sulfonation Kinetics

Figure 2 presents the time and temperature dependence of the ion exchange capacity of the sulfonated PEEK. At room temperature (22°C), the IEC increases slowly with sulfonation time and almost reaches a plateau at about 1.7 (mEq/g), suggesting that it is impossible to obtain a higher degree of sulfonation within a short time. In contrast, at higher temperature (e.g., 55°C), the IEC increases sharply, the first-type substitution nearly comes to an end in about 5 h. Therefore temperature plays an important role in the sulfonation of PEEK.

Figure 2 shows that IEC data of some samples surpass the limit value (2.56 mEq/g), which corresponds to 100% substitution based on first type reaction. Implying that the second type substitution has been initiated at higher temperature (55°C), more than one sulfonic group has been attached to one repeating unit of PEEK.

Figure 3 presents the kinetic behavior of the sulfonation reaction at 22, 36, 45, and 55°C. The data with more than the maximal IEC are not included in this Figure. It can be seen that the sulfonation degree increases with reaction time in an exponential manner.

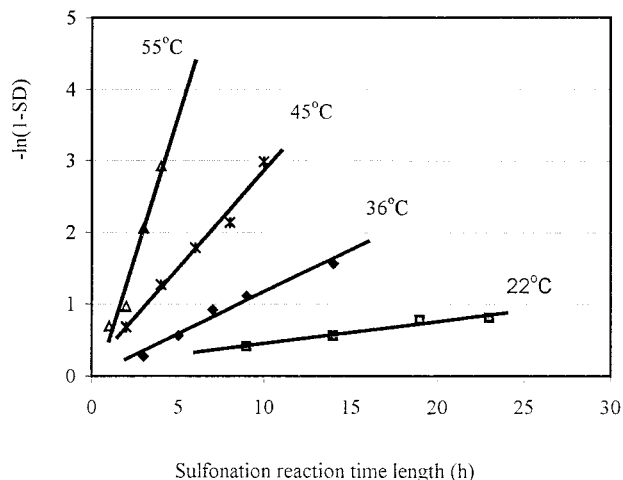
As mentioned previously, at a certain high degree of sulfonation, the second type substitution can be initiated, therefore only the lower IEC data can be employed to determine the reaction rate coefficients for the first type substitution. It



**Figure 3** Dependence of sulfonation degree on reaction time.

was found that data of samples with IEC lower than 95% of the limiting value are adequate.

Figure 4 plots  $-\ln(1-SD)$  versus reaction time at different temperatures of 22, 36, 45, and 55°C, respectively. Based on our previous analysis, there should be a linear relation between  $-\ln(1-SD)$  and the reaction time with a slope of  $bk$  and zero intercept. It can be found that the intercepts of the four lines are very close to zero. The deviation from zero may be attributed to the experimental errors as well as the heterogeneous sulfonation reaction occurring in the PEEK dissolution phase, since the first 1 h for dissolution of PEEK in concentrated sulfuric acid at room temperature (22°C) is not included in the reaction



**Figure 4** Plot of  $-\ln(1-SD)$  against reaction time at 22, 36, 45, and 55°C.

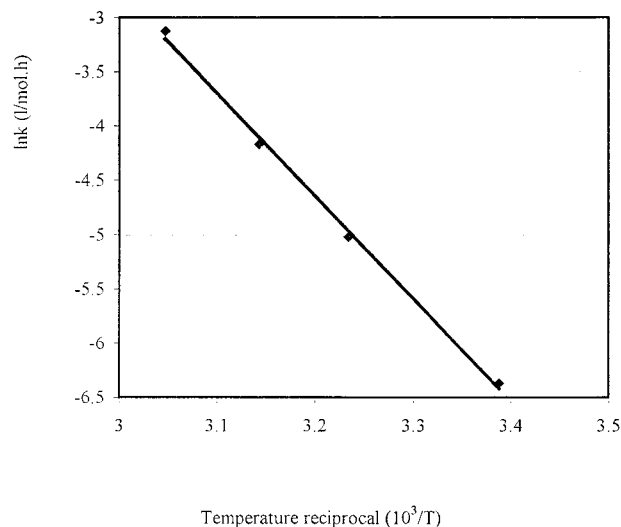
**Table II** Parameters of  $bk$  and  $k$  at Different Temperatures

Temp. (°C)	$b$ (mol/L)	$bk$ (1/h)	$k$ (L/mol · h)
22	17.7	0.0303	1.712E-3
36	17.7	0.0894	5.051E-3
45	17.7	0.2732	1.544E-2
55	17.7	0.7777	4.394E-2

time. As a matter of fact, at room temperature of 22°C, the sulfonation reaction took place very slowly, this behavior is demonstrated by a small slope of the line corresponding to 22°C in Figure 4. This is the basis that the time period for PEEK dissolution was not included as the reaction time. The slopes and their corresponding reaction rate coefficients at four temperatures are summarized in Table II.

The rate coefficient is plotted in Figure 5 as a function of temperature reciprocal. The activation energy of the first type substitution and the pre-exponential factor of the rate coefficient are determined from the slope and the intercept, and the results are shown in Table III, where the relevant data<sup>14</sup> of the sulfonation of some aromatic monomers are also included for comparison.

In general, the activation energy for sulfonation of PEEK is relatively larger than that for the sulfonation of aromatic monomers as shown in the case of monomer 4-MeC<sub>6</sub>H<sub>4</sub>NHMe and monomer C<sub>6</sub>H<sub>5</sub>NHMe. This is because after sul-

**Figure 5** Plot of  $\ln k$  against temperature reciprocal.**Table III** Sulfonation Activation Energies  $E_a$  and Pre-exponential Factors:  $k_0$  of PEEK and Some Aromatic Monomers

Material	$E_a$ (kcal/mol)	$k_0$ (L/mol · h)
PEEK	18.8	1.31E11
4-MeC <sub>6</sub> H <sub>4</sub> NHMe	13.3	2.00E07
C <sub>6</sub> H <sub>5</sub> NHMe	15.3	6.31E07
4-MeC <sub>6</sub> H <sub>4</sub> NO <sub>2</sub>	19.5	6.31E10

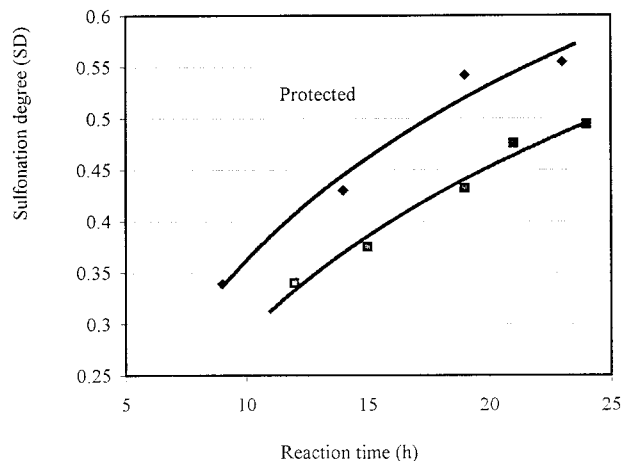
fonation the polymer chains tend to curl up due to the electrostatic interaction between the ion couples, further substitution on the curled chains will become more difficult. However, there is no such orientation barrier for sulfonation of these two monomers, sulfonation reaction is thus easier to occur.

The activation energy of monomer 4-MeC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub> is a little higher than that of PEEK. The most probable reason for this is the existence of the —O<sub>2</sub> group in the aromatic ring of the monomer, which possesses a strong electron-withdrawing property, leading to a much lower electron density in the aromatic ring of 4-MeC<sub>6</sub>H<sub>4</sub>NO<sub>2</sub>. Obviously, in this case, the electron-density difference in aromatic rings also significantly affects their reaction activity.

#### Effect of Moisture Contamination

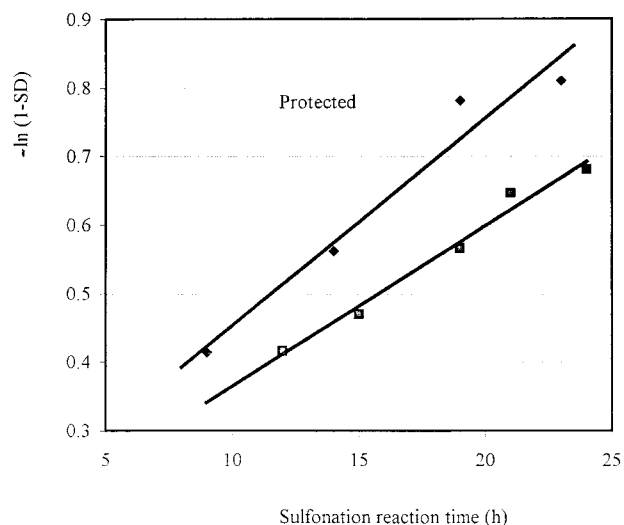
It is known that the reaction rate depends on the concentrations of the reacting species. In this work, the concentrated sulfuric acid is used as the reagent, which has a strong tendency to uptake the moisture from the air. Usually the sulfonation reaction is slow, the reaction time is quite long. If there is no protective measure to prevent the moisture uptake, the concentration of the reagents can be diluted. Figure 6 shows the effect of the moisture contamination on the sulfonation degree (SD) of the sample at room temperature. The relative humidity of the environment is 60–70%. It can be seen that SD values of the SPEEK samples without nitrogen blanketing decreased significantly.

Further information can be extracted from Figure 7 regarding the effect of moisture contamination on the concentration of sulfuric acid. As has been discussed previously, the slope of the line of  $-\ln(1-SD)$  vs. reaction time is the product of rate coefficient ( $k$ ) and the initial concentration ( $b$ ) of the sulfonating solvent. Both experiments are

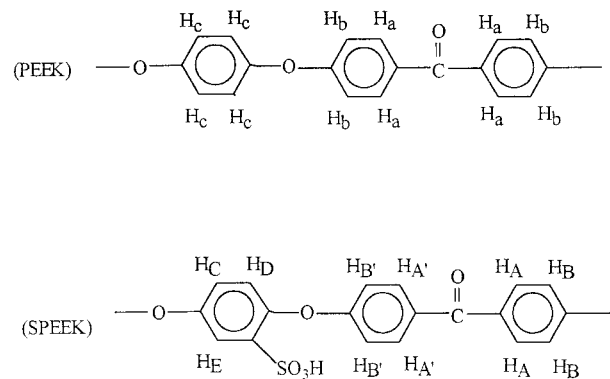


**Figure 6** Effect of moisture contamination on the sulfonation degree.

carried out at the same temperature, the variation in the slope reflects the concentration change of the reagents. In the case of the experiment with no protection of nitrogen gas, the reagent concentration varies in the entire course of the reaction for the continuous uptake of the moisture. Here, we attribute the lowered IEC of the sample only to the dilution effect of the moisture contamination and employ the concept of the “average initial concentration” of the sulfonating solvent to characterize this effect. The ratio of the two slopes in Figure 7 is 0.775. Since the reaction is second-order, both the concentrated sulfuric acid and the



**Figure 7** Influence of moisture contamination on the sulfonation degree for the estimation of the “average initial concentration” of sulfuric acid.



**Figure 8** Nomenclature of the aromatic protons for PEEK and SPEEK repeat unit.

PEEK are diluted; therefore, the concentration dilution coefficient should be equal to the square root of the ratio, which is about 0.88, implying that the concentration decreases more than 10% in nearly one day’s exposure to environment. Therefore, a proper protection against moisture contamination is necessary for the precise control of the sulfonation.

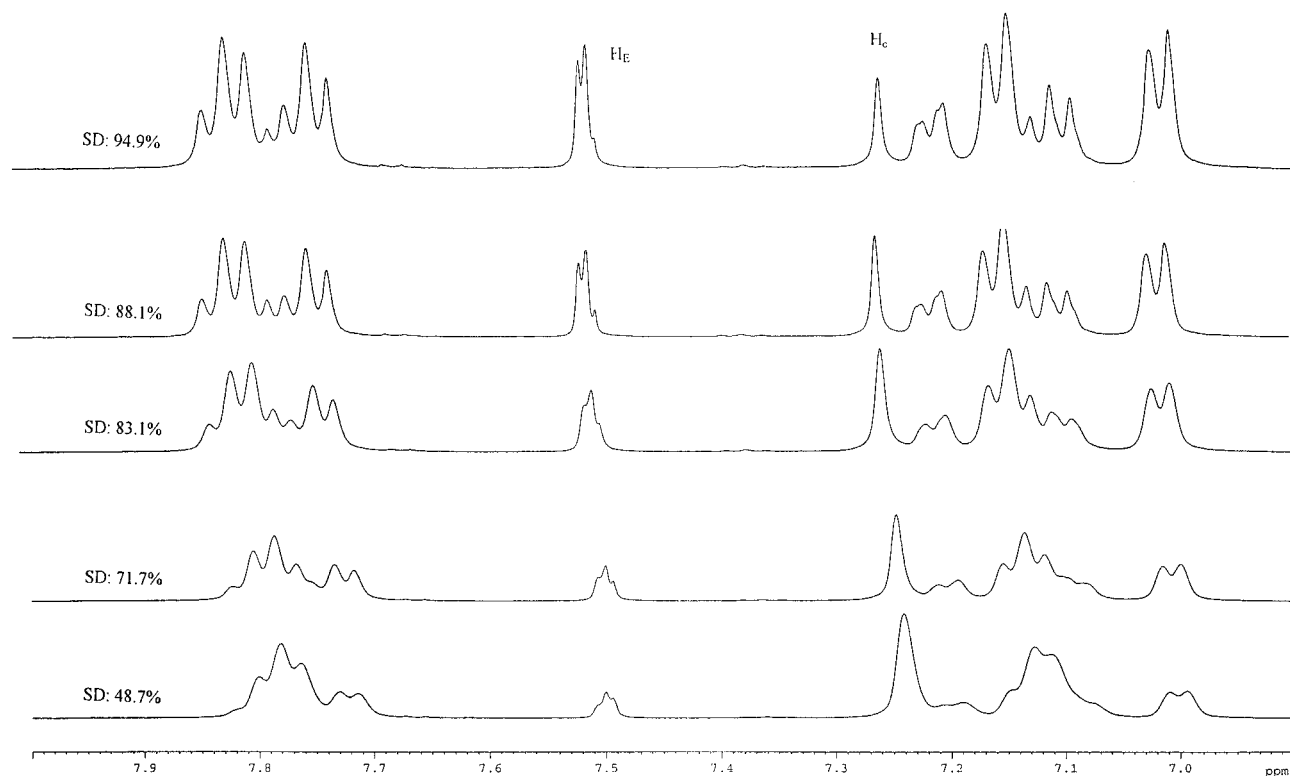
## Characterizations

### <sup>1</sup>NMR Analysis

Figure 8 presents the nomenclature of the characteristic protons in the aromatic ring in the sulfonated PEEK repeat unit. The <sup>1</sup>NMR spectra of SPEEK samples of different known sulfonation degrees are illustrated in Figure 9. The peaks at 7.25 ppm in each spectrum stand for the H<sub>c</sub> protons in PEEK repeat unit as shown in Figure 8. When the sulfonic group is attached to the aromatic ring, this type of protons is differentiated into three categories: H<sub>C</sub>, H<sub>D</sub> (the doublets at ~7.2 ppm), and H<sub>E</sub> (at 7.5 ppm as shown in Fig. 9). When more sulfonic groups are attached to the aromatic ring in the PEEK repeat unit, the intensity of these signals enhances expectedly as depicted in Figure 9. Actually, the sulfonation degree (SD) of the SPEEK samples can also be quantitatively determined by evaluating the intensity or peak area represented by all these protons as indicated in Figure 8 based on the following formula<sup>17</sup>

$$\frac{n}{12 - 2n} = \frac{A_{HE}}{\sum A_{H_{AA'BB'CDE}}} \quad (0 \leq n \leq 1)$$

$$SD = n \times 100\%$$



**Figure 9**  $^1\text{H-NMR}$  spectra of the SPEEK samples of different sulfonation degrees.

where  $A_{\text{H}_E}$  represents the area of the signal, and the integrated peak area of the signals corresponding to all the other aromatic protons.

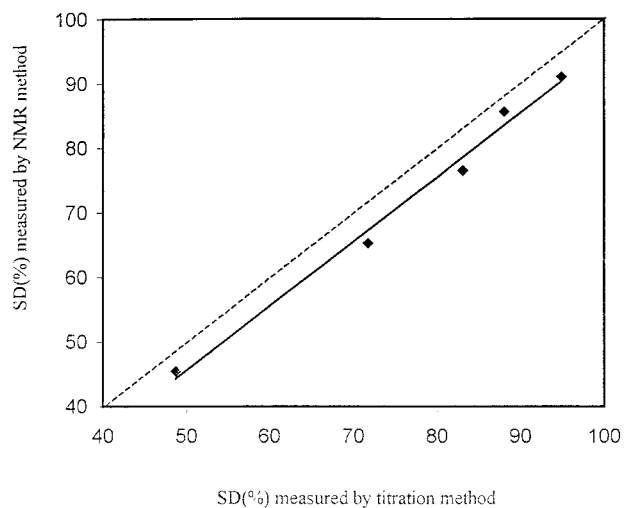
The comparison of sulfonation degree based on titration method and NMR is presented in Figure 10. It seems that there is a constant difference

between these data. This deviation can be reasonably excluded because the data were estimated from two totally different methods. If this deviation is ignored, a good agreement can be expected.

### Contact Angle

Contact angle is the measure of surface properties of materials, change in contact angle of polymer materials means change in their surface chemistry. PEEK is intrinsically hydrophobic, contact angle of parent PEEK is  $88^\circ$ .<sup>15</sup> After sulfonation of this material, there is a remarkable change (Table IV) in contact angle, which decreases with the increase of sulfonation degree of membrane materials. This also suggests that polar sulfonic group has been introduced into the polymer chains.

Crosslinking is an effective method to change the morphology and surface properties of polymer materials. We tested the effect of ionic crosslinking on the surface property by immersing the SPEEK-Na membrane (100% SD) in 0.1 M  $\text{KAl}(\text{SO}_4)_2$  aqueous solution for 20 min, expecting a change in contact angle to prove the presence of the sulfonic groups. A pronounced change in con-



**Figure 10** Comparison of sulfonation degrees (SD) measured by different methods.



**Table IV Contact Angle of SPEEK-Na With Different Sulfonation Degree**

Material	Sulfonation Degree (%)	Contact Angle <sup>a</sup>
PEEK	0	88 <sup>15</sup>
SPEEK-Na	67	58.2
SPEEK-Na	79	52.2
SPEEK-Na	87	46.7
SPEEK-Na	100	40.2
SPEEK-Al	100	58.5

<sup>a</sup> Solvent is deionized water (22°C).

tact angle is observed, which increases from 40.2° to 58.5, comparable to that of SPEEK-Na membrane of 67% SD, showing that ionic crosslinking has taken place between the sulfonic groups by this trivalent aluminum ion, and the crosslinked surface becomes less hydrophilic.

Changes in contact angle reflect alternation of the surface properties. All the membranes tested are homogeneous, there is no difference between the surface and the bulky matrix of the membranes in terms of chemical composition. Therefore, based on this change, the effectiveness of sulfonation can also be recognized.

### Solubility of SPEEK in Solvents

PEEK shows little solubility in almost all the solvents tested except some strong acids, such as concentrated sulfuric acid, CH<sub>3</sub>SO<sub>3</sub>H. The crystallinity of PEEK accounts for this solvent resistance. It is generally accepted that dissolution of PEEK in strong acids is the result of protonation of ketone groups and in some cases chemical modifications.<sup>16</sup>

Sulfonation is a feasible approach to improve the solubility of PEEK in widely used solvents. It is found that solubility of sulfonated PEEK depends on the degree of sulfonation. We tested the solubility of SPEEK-Na in solvents DMF and DMAC at room temperature, the results are summarized in Table V. Bailly et al.<sup>11</sup> studied the solubility of SPEEK-H in DMF, DMAC, and DMSO. They reported that SPEEK-H of greater than 40% SD can dissolve in these solvents at room temperature. The results obtained by our group show that SPEEK-Na samples of 55.5% SD can dissolve in DMF, DMAC; however, some fiber-like residuals can still be visually observed in the dilute polymer solution. These residuals are probably the aggregates of the network of the PEEK crystalline. Sulfonation can reduce the crystallinity of PEEK<sup>17</sup>; based on this point, the solubility of SPEEK depends on the degree of the collapse of the crystalline by sulfonation.

While sulfonation degree is high enough, it can be assumed that the crystallized population of PEEK can be broken completely, as a proof of this assumption, we find SPEEK-Na with 79% SD can dissolve perfectly in these solvents. In this case, the main interaction between the amorphous SPEEK molecular chains is the electrostatic forces between the sulfuric groups, which can be undermined by the highly polar water molecules. This is the reason the highly sulfonated PEEK can dissolve in water.

The solubility of SPEEK in water also depends on the type of counter ion as shown in Table V. SPEEK-Na (86.6% SD) is less soluble than SPEEK-H (86.6%), indicating that there is a stronger interaction between SPEEK-Na polymer chains. Based on this knowledge, it is easy to

**Table V Dependence of Solubility of SPEEK-Na on Sulfonation Degree**

Sample	Sulfonation Degree (%)	Solvent	Solubility
SPEEK-Na	33.9	DMF, DMAC	Insoluble
SPEEK-Na	43.0	DMF, DMAC	Insoluble
SPEEK-Na	54.2	DMF, DMAC	Partially soluble, solution is turbid
SPEEK-Na	55.5	DMF, DMAC	Soluble with little fiber-like residual
SPEEK-Na	67.0	DMF, DMAC	Soluble with little fiber-like residual
SPEEK-Na	79.0	DMF, DMAC	Soluble
SPEEK-Na	86.6		Soluble in 75°C water
SPEEK-H	86.6		Soluble in 60°C water
SPEEK-H	99.4		Soluble in hot water
SPEEK-H	≥100		Soluble in hot water

understand why there is a higher degree of dependence of solubility of SPEEK–Na on sulfonation degree reported by us than that of SPEEK–H reported by other researchers.<sup>11</sup>

## CONCLUSIONS

The kinetic behavior of sulfonation of PEEK can be characterized as a second-order reaction. There are two types of substitutions happening to the PEEK. The first type substitution takes place in the preferential aromatic ring between the two ether links. There is no significant degree of second type substitution happening before 95% sulfonation degree is reached. The activation energy and reaction rate coefficient of the first type substitution are obtained.

The sulfonation degree of PEEK can be well controlled by reaction time and reaction temperature. The latter is found to have a more remarkable effect on the sulfonation degree. At higher temperatures, for example 55°C, the second type substitution can be initiated; therefore, more than 100% sulfonation degree can be achieved.

The solubility of PEEK after modification is improved remarkably, which is found to be both sulfonation degree and the type of counter ion-dependent. SPEEK–Na samples of more than about 55% SD can dissolve in solvents DMF, DMAC at room temperature. SPEEK samples of high SD can dissolve in water. Sulfonated PEEK samples are characterized by IEC, <sup>1</sup>H-NMR and contact angle. All the results are consistent with each other.

The authors thank Victrex USA (Westchester, PA) for donating the PEEK samples used in this work.

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