

# Preparation of a New Type of Ion-Exchange Membrane Based on Sulfonated Poly(ether ether ketone)s

Xianfeng Li, Chengji Zhao, Hui Lu, Zhe Wang, Wei Jiang, Hui Na

Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, 130012, People's Republic of China

Received 24 August 2003; accepted 4 March 2005

DOI 10.1002/app.22456

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Novel sulfonated poly(ether ether ketone)s were prepared directly by nucleophilic polycondensation. They showed excellent thermal stability and good solubility and could be easily cast into tough membranes. The sulfonated membranes showed swelling of 16.08–26.71% and an ion-exchange capacity of 1.01–1.57. The transport

properties of different cations ( $H^+$ ,  $Na^+$ , and  $K^+$ ) of membranes based on these polymers were evaluated. The potential for ion-exchange membranes looks good. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2481–2486, 2005

**Key words:** membranes; copolymerization; swelling

## INTRODUCTION

Ion-exchange membranes are now widely used in electrodialysis for the desalination of brackish water, the recovery of acids or alkalis from waste acids or alkalis, the production of table salts, and many other purposes.<sup>1,2</sup>

For the purpose of applying electrodialysis under severe conditions such as high temperatures and strongly oxidizing conditions, a more stable ion-exchange membrane should be developed. Perfluorocarbon ion-exchange membranes have been developed and successfully applied under those conditions, but only a few industrial applications have been found, other than those in the chloralkali industry, primarily because of the high cost. New types of ion-exchange membranes that are cheap but have good electrochemical properties and excellent resistance to degradation should be developed.

Poly(arylene ether ketone)s (PAEKs) are one kind of high-performance engineering thermoplastic. They have good mechanical properties and high thermooxidative stability. Thus, sulfonated PAEKs are of interest as ion-exchange membranes. Sulfonated PAEKs were earlier prepared via the modification of the polymer; sulfonated groups were achieved on the polymer chain by a sulfonating agent such as concentrated sulfuric acid, complex sulfuric trioxide, chlorosulfuric acid, or methanesulfuric acid.<sup>3–6</sup> An attractive alternative approach is the direct copolymerization of sulfo-

nated monomers.<sup>7,8</sup> The latter way is preferable to polymer modification. We can control the degree of sulfonation (Ds) by changing the ratio of the sulfonated monomers and can avoid the side reactions associated with sulfonation. Poly(ether ether ketone)s (PEEKs), members of the PAEK family, also have excellent properties, including especially good thermal stability and good mechanical properties, in comparison with poly(ether ketone)s. In this study, novel sulfonated poly(ether ether ketone)s (SPEEKs) derived from copolymerization were prepared and characterized. The transport properties of membranes based on these polymers were evaluated.

## EXPERIMENTAL

### Materials and measurement

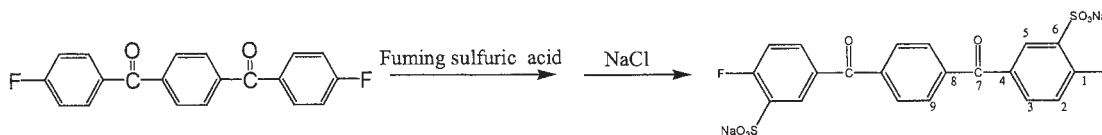
1,4-Bi(4-fluorobenzoyl)benzene was purchased from Longjing Chemical Plant (China). 3,3',5,5'-Tetramethyl diphenyl-4,4'-diol was made in our laboratory and recrystallized with ethanol. 1,4-Bi(3-sodium sulfonate-4-fluorobenzoyl)benzene was obtained through the sulfonation of 1,4-bi(4-fluorobenzoyl)benzene. Potassium carbonate was dried at 180°C for 10 h before use. Other reagents and solvents were obtained commercially and used without further purification.

### Synthesis of the sulfonated monomer

The synthesis of the sulfonated monomer [1,4-bi(3-sodium sulfonate-4-fluorobenzoyl)benzene] was performed according to a procedure described in our previous work.<sup>9,10</sup> As shown in Scheme 1, 1,4-bi(4-fluorobenzoyl)benzene was first sulfonated with fuming sulfuric acid, and this was followed by neutraliza-

Correspondence to: H. Na (huina@jlu.edu.cn).

Contract grant sponsor: National Nature Science Foundation of China; contract grant number: 20320120169.



Scheme 1 Preparation of the sulfonated monomer.

tion with NaOH and precipitation with NaCl. The crude product was recrystallized with a mixture of methanol and water. The yield of this monomer was 81%. The chemical structure was confirmed by Fourier transform infrared (FTIR) and H-NMR.

IR (KBr,  $\text{cm}^{-1}$ ): 1656 (C=O), 1211, 1093, 621 (Ar—SO<sub>3</sub>Na). <sup>1</sup>H-NMR [500 MHz, dimethyl sulfoxide (DMSO), ppm]: 8.12–8.15 (dd, 2.3 Hz, 4.5 Hz, H<sub>5</sub>), 7.87 (s, H<sub>9</sub>), 7.81–7.84 (m, 2.5 Hz, 2.0 Hz, 5.3 Hz, H<sub>3</sub>), 7.34–7.38 (dd, 5.3 Hz, 5.3 Hz, H<sub>2</sub>). <sup>13</sup>C-NMR (500 Hz, DMSO, ppm): 194.74 (C<sup>7</sup>), 163.34 (C<sup>1</sup>), 161.29 (C<sup>1</sup>), 141.01 (C<sup>8</sup>), 133.98 (C<sup>4</sup>), 133.91 (C<sup>3</sup>), 132.81 (C<sup>6</sup>), 131.66 (C<sup>9</sup>), 130.29 (C<sup>5</sup>), 117.53 (C<sup>2</sup>).

### Polymer synthesis

To a 250-mL, three-necked, round flask equipped with a Dean–Stark trap, a reflux condenser, a nitrogen inlet, and a thermometer, 1,4-bis(4-fluorobenzoyl)benzene (kmol), 1,4-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene (mmol), 3,3',5,5'-tetramethyl diphenyl-4,4'-diol, dihydrous potassium carbonate, and DMSO were added. Toluene was used to take off the water that was produced in the reaction. The mixture was stirred at 140°C for 4 h and then raised to 170°C for 6 h. The reaction mixture was cooled to room temperature and poured into acetone. The inorganic salts were removed by washing with boiling water. Then, the pure samples of the polymer were obtained by drying. For SPEKK-2, the IR (KBr,  $\text{cm}^{-1}$ ) data were as follows: 1247, 1082, 690 (Ar—SO<sub>3</sub>Na), 1154 (—O—), 1654 (C=O), and 2969 (—CH<sub>3</sub>). For SPEKK-4, the <sup>1</sup>H-NMR (500 MHz, DMSO, ppm) data were as follows: 8.30 (H<sub>1</sub>), 7.86 (H<sub>2</sub>), 7.75–7.77 (H<sub>3</sub>), 7.51 (H<sub>4</sub>), and 6.49–6.51 (H<sub>5</sub>).

### Preparation of the membranes

The sulfonated polymers were first dissolved in dimethylformamide (DMF) to form a 5–10% solution, and the resulting mixture was cast onto a glass plate. The membranes (50–100 μm) of the sulfonated polymers were prepared and dried at 85°C for 10 h and then dried in a vacuum oven at 100°C for 48 h.

FTIR was carried out on a Nicolet Impact 410 FTIR spectrometer (Waltham, MA), and a Bruker Avance 500 (Germany) was used to determine <sup>1</sup>H-NMR with DMSO as a solvent and tetramethylsilane as an internal standard. Thermogravimetric analysis (TGA) mea-

surements were performed on a Netzsch STA449C (Germany) in air at the heating rate of 10°C/min. The specific viscosity was measured with an Ubbelohde viscometer.

Ds was obtained from the number of sodium sulfonate groups per repeating unit, as described in our previous report.<sup>8,9,11</sup> Ds was determined by titration with NaOH. Before titration, the polymers were acidified by an excess HCl solution to make the sodium sulfonate groups (—SO<sub>3</sub>Na) into sulfonate acid groups (—SO<sub>3</sub>H).

### Swelling of the membranes

The swelling was determined from the difference in the weights between the drying and swollen membranes. The weight of the drying membrane ( $W_{\text{drying}}$ ) was determined, and then the membrane was soaked in water until the weight remained constant. It was then taken out and wiped with blotting paper, and the weight of the membrane ( $W_{\text{wet}}$ ) was determined again. The swelling percentage ( $S_w$ ) was calculated with eq. (1):

$$S_w = (W_{\text{wet}} - W_{\text{drying}}) / W_{\text{drying}} \times 100\% \quad (1)$$

### Ion-exchange capacity (IEC)

IEC was determined through titration. The membranes in the H<sup>+</sup> form were immersed in a 1M NaCl solution for 24 h to liberate the H<sup>+</sup> ions (the H<sup>+</sup> ions in the membrane were replaced by Na<sup>+</sup> ions). The H<sup>+</sup> ions in solution were then titrated with 0.01M NaOH.

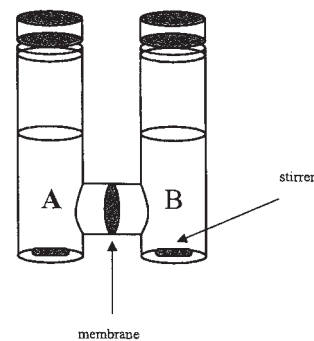
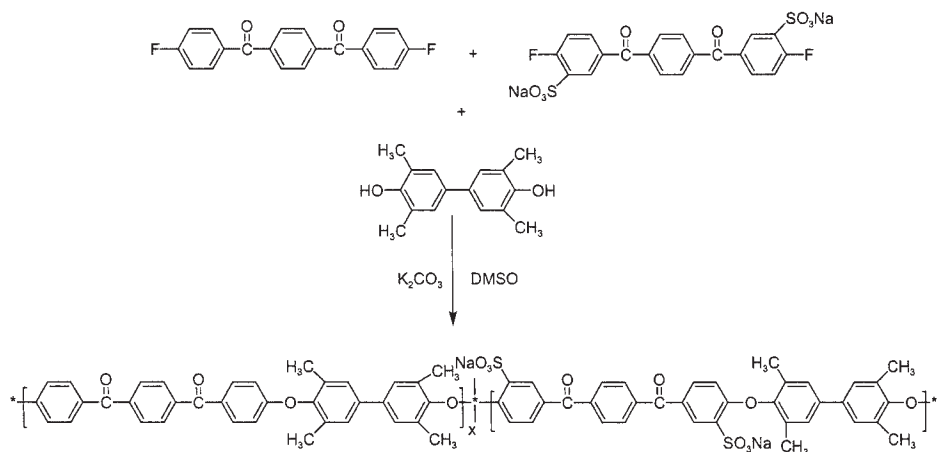


Figure 1 Diffusion cell.



Scheme 2 Synthesis of the sulfonated polymers.

The fixed ion concentration ( $A_f$ ) was calculated as follows:

$$A_f = \text{IEC} / S_w \quad (2)$$

The calculated IEC value from  $D_s$  was obtained from eq. (3):

$$\text{IEC} = \frac{D_s \times 684}{D_s \times 684 + (1 - D_s) \times 522} \quad (3)$$

The ion diffusion coefficient ( $D^+$ ) was determined with the cell in Figure 1. HCl, NaCl, and KCl were placed on one side of the cell, and water was placed on the other side of the diffusion cell. DDS-11C (Shanghai Leichi, China) was used to record the conductivity changes versus the time in solution B.  $D^+$  of the membranes was obtained from the slope of the conductivity versus the time.<sup>11–13</sup>

## RESULTS AND DISCUSSION

### Preparation and characterization of the polymers

A series of samples were prepared through the aromatic nucleophilic substitution polycondensation of 3,3',5,5'-tetramethyl diphenyl-4,4'-diol with different

ratios of 1,4-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene to 1,4-bis(4-fluorobenzoyl)benzene (Scheme 2) in a DMSO/toluene solvent system; the temperature of round flask was maintained at 140°C for 3 h to remove all the water azeotropically with toluene from the reaction mixture. The polymerization results and analytical data are displayed in Table I. When we changed the ratio of 1,4-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene to 1,4-bis(4-fluorobenzoyl)benzene, samples with different  $D_s$  values were obtained. The specific viscosities of all the polymers indicated that the polymers had high molecular weights, so we could obtain the polymer samples by polycondensation. The compositions and structures of the polymers were confirmed with FTIR (Fig. 2) and <sup>1</sup>H-NMR (Fig. 3). Figure 1 shows the IR spectrum of SPEEKK-2. The absorption bands at 1247, 1082, and 1027  $\text{cm}^{-1}$  can be assigned to asymmetric and symmetric O=S=O stretching vibrations of sodium sulfonate groups. The absorption band at 690  $\text{cm}^{-1}$  can be assigned to the S—O stretching of sodium sulfonate groups. As shown for non-sulfonated PEEKK, there is no related stretching for —SO<sub>3</sub>Na. That no peaks are attributed to the aromatic sulfone group in the range of 1140–1110  $\text{cm}^{-1}$  indicates that no crosslinking occurred during copolymerization.

TABLE I  
Data of the Sulfonated Polymers

Polymer	$m$ (mmol)	$k$ (mmol)	$m/k^a$	Yield (%)	$\eta_{sp}/c^b$	$D_s$	$T_{10\%loss}$ (°C) <sup>c</sup>
SPEEKK-1	16	24	4:6	93	0.89	0.78	434
SPEEKK-2	20	20	5:5	90	1.10	0.97	423
SPEEKK-3	24	16	6:4	93	1.41	1.23	399
SPEEKK-4	40	0	10:0	90	1.36	1.86	394

<sup>a</sup> Ratio of 1,4-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene to 1,4-bis(4-fluorobenzoyl)benzene.

<sup>b</sup> Viscosity at a concentration of 5.00 g/L in DMF at 25 ± 0.1°C.

<sup>c</sup> Temperature at 10% weight loss.

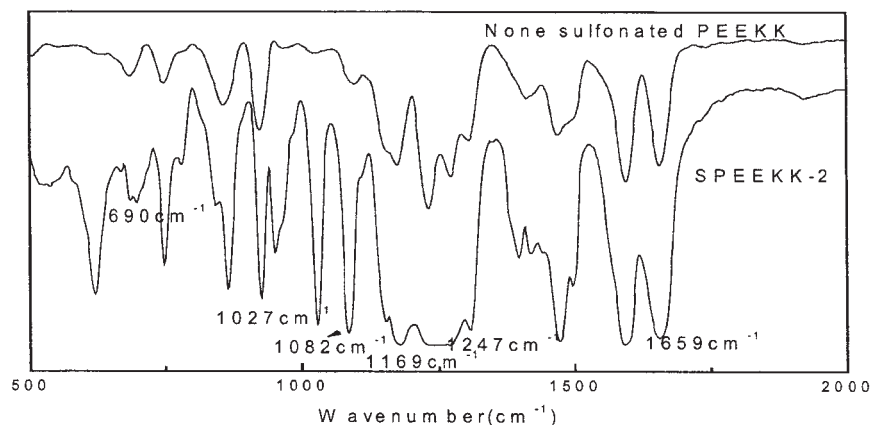


Figure 2 FTIR spectra of SPEKK-2 and non-sulfonated PEEKK.

The absorption at 1659 (C=O) and 1169 (—O—) was also found in FTIR.  $^1\text{H-NMR}$  spectroscopy was used for the structure confirmation of SPEKK-4.  $^1\text{H-NMR}$  spectra (Fig. 3), along with the peak assignments, indicated the structure of SPEKK-4.

#### Thermal properties of the polymers

The thermal properties of the polymers were examined with TGA and differential thermal analysis (DTA) under an air atmosphere at heating rate of  $10^\circ\text{C}/\text{min}$ . No glass-transition temperatures were observed in SPEKKs in a temperature range of  $100\text{--}400^\circ\text{C}$  from DTA. This may be explained by the strong intermolecular interaction due to the introduction of  $-\text{SO}_3\text{Na}$ . No crystalline peaks were found in SPEKKs. They showed the amorphous structures of

the polymers. From the TGA curve, we found that the polymers all had excellent thermal stability; the 10% weight loss temperatures are shown in Table I. The sulfonated polymers were stable at about  $400^\circ\text{C}$ . The 10% weight loss temperatures of the polymers decreased as the content of sodium sulfonate groups increased. Two weight-loss steps can be observed in Figure 4. The first weight-loss step at  $350\text{--}400^\circ\text{C}$  is attributed to the splitting-off of sulfonic acid groups of SPEKK. The second weight-loss step at about  $450^\circ\text{C}$  corresponds to the main polymer chain decomposition.

#### Properties of the membranes

$S_w$ , IEC, and  $A_f$

All the sulfonated polymers could be readily cast into tough membranes. All the membranes were prepared

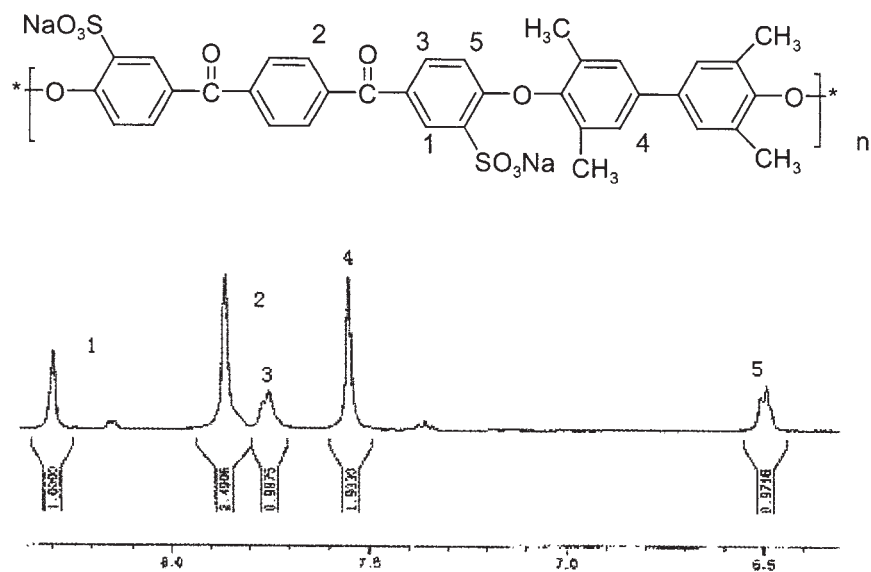


Figure 3  $^1\text{H-NMR}$  spectrum of SPEKK-4.

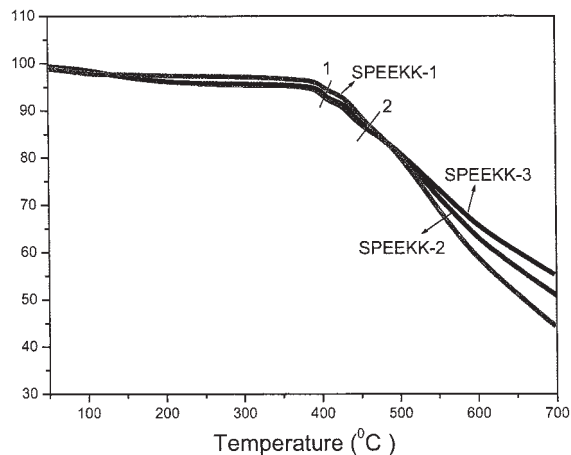


Figure 4 Thermogravimetric curves of SPEEKs.

by the redissolution of the copolymers in DMF and cast directly onto a glass substrate. The property data for the membranes are summarized in Table II.

These SPEEKK membranes showed increased IEC with increasing  $D_s$ . As shown in Table II, the SPEEKKs with  $D_s$  values of 0.8, 1.0, and 1.2 exhibited IECs of 1.01, 1.36, and 1.57. The experimental IEC values listed in Table II are in good agreement with the calculated IEC values, under the assumption that all the sulfonated

TABLE II  
Properties of the Membranes

Polymer	SPEEKK-2	SPEEKK-3	SPEEKK-4
$D_s$	0.8	1.0	1.2
$S_w$ (%)	16.08	23.95	26.71
IEC (m)	1.01	1.36	1.57
IEC (c)	1.36	1.65	1.93
$A_f$ (mequiv/g of H <sub>2</sub> O)	6.28	5.68	5.87
$D_{H^+}$ ( $\times 10^{-11}$ )	14.3	20.6	22.6
$D_{Na^+}$ ( $\times 10^{-11}$ )	3.94	8.13	19.1
$D_{K^+}$ ( $\times 10^{-11}$ )	8.54	19.1	31.4

IEC(c), IEC calculated from  $D_s$ ; IEC(m), IEC measured with titration;  $D_{H^+}$ ,  $D_{Na^+}$ , and  $D_{K^+}$ , diffusion coefficient of H<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>.

monomers were incorporated into the copolymer. This also indicates that sulfonated groups could be introduced into the polymer via the sulfonated monomer without any side reactions, which are often observed in the postsulfonation method. With increasing  $D_s$ , the SPEEKs showed increasing water content, from 16.08 to 26.71%. Nevertheless,  $A_f$ , expressed as the ratio of IEC to the water content, did not follow the order. This may be explained as follows: when the water content in the membrane increased, it provided more channels for co-ionic transport and led to the loosening of the membrane structure.<sup>14</sup>

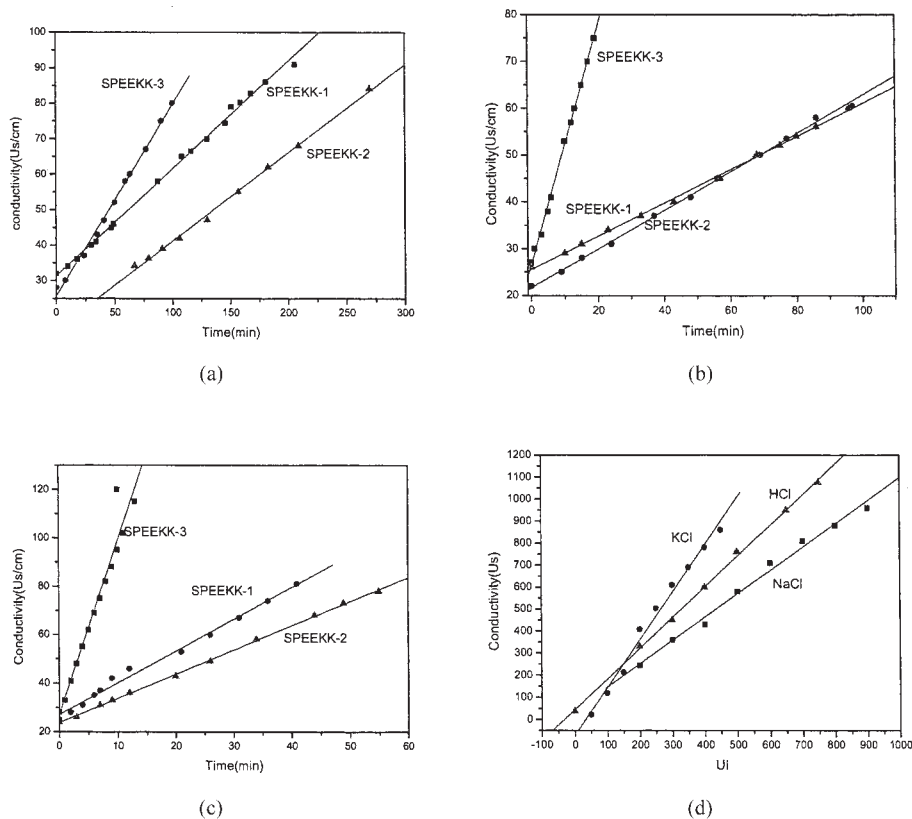
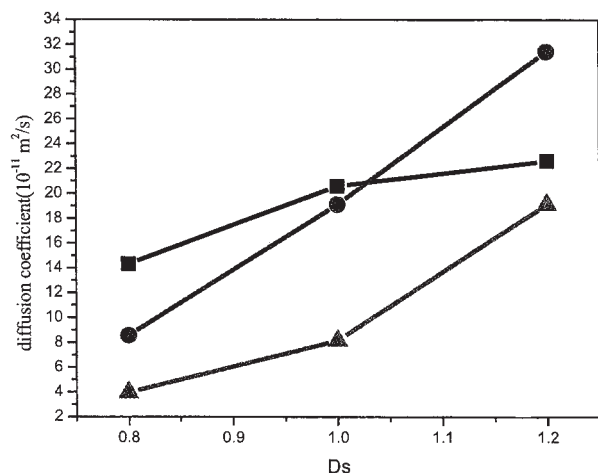


Figure 5 Conductivity–time plots of SPEEKs: (a) 0.3N HCl, (b) 1N NaCl, (c) 1N KCl, and (d) standard curves.



**Figure 6** Diffusion coefficient of cations versus Ds: (●) K<sup>+</sup>, (■) H<sup>+</sup>, and (▲) Na<sup>+</sup>.

#### Diffusion coefficient of cations

Ion permeability through a membrane can be determined from salt diffusion measurements. According to Fick's first law, the salt flux through a membrane ( $N$ ) can be written as follows:

$$N = D_A \frac{C_1 - C_2}{d} \quad (4)$$

where  $D_A$  is the H<sup>+</sup> diffusion coefficient,  $C_1$  and  $C_2$  are the concentrations of ions in cells A and B, and  $d$  is the membrane thickness. According to the conservation of mass

$$V \frac{dC_1}{dt} = N = D_A \frac{C_1 - C_2}{d} \quad (5)$$

where  $V$  is the volume of solutions in each cell.

$$C_1^0 = C^0, C_2^0 = 0, C_1 + C_2 = C_1^0 \quad (6)$$

where  $C_1^0$  and  $C_2^0$  is the primary concentration of salt in cell A and B, respectively. Adapted an integral to eq. (5), we obtained the following:

$$\frac{2D_A S}{Vd} t = -\ln \frac{\Delta C}{C_1} = -\ln \frac{C_1^0 - 2C_2}{C_1^0} \quad (7)$$

where  $t$  is the time,  $\Delta C$  is the change of concentration in cell and  $S$  is the area of membranes. Because  $C_1^0 \gg C_2$ , in this experiment, eq. (7) can be expressed as follows:

$$C_2 = \frac{D_A S C_1^0}{Vd} t \quad (8)$$

In this experiment, the concentration can be expressed by the conductivity of the solutions. Equation (8) may be expressed as follows:

$$Q = \lambda C_2 = \frac{\lambda D_A S C_1^0}{Vd} t \quad (9)$$

where  $Q$  is the conductivity and  $\lambda$  is the coefficient of  $Q$  vs.  $C$  linear. From eq. (9), the diffusion coefficient of ions of the membrane could be determined from the slope of the straight line of the conductivity versus the time shown in Figure 5.<sup>12,13,15</sup> The diffusion coefficients of different ions of the membranes with different Ds values are shown in Table II. For the same cation, the diffusion coefficient showed an increasing tendency with increasing Ds (Fig. 6). This may be explained as follows: an increasing number of sulfonated groups in the membrane provided more channels for coionic transport and led to the loosening of the membrane structure, which led to the increasing diffusion of the cations.

## CONCLUSIONS

Novel SPEEKs with different Ds values were prepared and studied. Most of the polymers could easily be cast into tough membranes. The transport properties of different cations of SPEEK membranes were evaluated. The membranes showed increased ion diffusion as Ds increased. We could control the membrane properties by adjusting the Ds value of SPEEK.

## References

- Sata, T.; Nojima, S.; Matsusaki, K. *Polymer* 1999, 40, 7243.
- Gab, J.; Ohya, H. *J Membr Sci* 1998, 140, 195.
- Jia, L. D.; Xu, X. F.; Zhang, H. J.; Xu, J. P. *J Appl Polym Sci* 1996, 60, 1231.
- Daoust, D.; Devaux, J.; Godard, P. *Polym Int* 2001, 50, 917.
- Daoust, D.; Devaux, J.; Godard, P. *Polym Int* 2001, 50, 925.
- Daoust, D.; Devaux, J.; Godard, P. *Polym Int* 2001, 50, 932.
- Liu, S. Z.; Wang, F.; Chen, T. L. *Macromol Rapid Commun* 2001, 22, 579.
- Li, X. F.; Na, H.; Lu, H. *Chem J Chin Univ* 2004, 25, 1563.
- Li, X. F.; Na, H.; Lu, H. *J Appl Polym Sci* 2004, 94, 1569.
- Gab, J.; Haruhiko, O.; Toshiyuki, N. *J Membr Sci* 1999, 156, 61.
- Gil, M.; Ji, X. L.; Li, X. F.; Na, H.; Hampsey, J. E.; Lu, Y. F. *J Membr Sci* 2004, 234, 75.
- Benavente, J.; Canas, A. *J Membr Sci* 1999, 156, 241.
- Xu, T. W.; He, B. L. *Technol Water Treatment* 1996, 22, 245.
- Hu, K. Y.; Xu, T. W.; Yang, W. H.; Fu, Y. X. *J Appl Polym Sci* 2004, 91, 167.
- Daniel, M. S.; Merlin, L. B. *J Am Chem Soc* 2001, 123, 11805.