

# Crosslinked Sulfonated Poly(arylene ether ketone) with Pendant Carboxylic Acid Group via Poly(ethylene glycol) for Proton Exchange Membrane

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Received 11 October 2009; accepted 4 February 2010

DOI 10.1002/app.32439

Published online 14 July 2010 in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Novel proton exchange membranes are solvent-cast from *N,N*-dimethylacetamide (DMAc) solutions of the crosslinked poly(arylene ether ketone) copolymer with pendant carboxylic acid group (C-SPAEEK) via poly(ethylene glycol) (PEG) with different amounts. These membranes are formed as a result of physical and chemical crosslinking. In this study, <sup>1</sup>H-NMR and FTIR have been used to confirm the chemical structures of the copolymers. Mechanical and thermal properties, swelling and proton conductivity are affected by the crosslinker (PEG) content in the copolymers. Compared to the noncrosslinked C-SPAEEK membrane, the

crosslinked membranes become more flexible and greatly reduced water uptake and swelling ratio with only slight sacrifice in proton conductivities. And the crosslinked membranes keep higher proton conductivities without a sharply decrease at higher temperature. These results show that the crosslinked membranes have potential applications as proton exchange membranes for fuel cell. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 3318–3323, 2010

**Key words:** sulfonated; crosslinked; proton exchange membrane

## INTRODUCTION

Recently, the proton exchange membrane fuel cells (PEMFCs) have attracted increasing interests because they are considerably much cleaner and more efficient than traditional energy converters, particularly for automotive vehicles or stationary power applications.<sup>1–3</sup> A key component of a PEMFC is proton exchange membrane (PEM), which serves as a separator of fuels between anode and cathode and also provides channels for protons to pass through. Therefore, their properties such as proton conductivities and water maintenance are crucial. Traditional PEMs are perfluorinated ionomers (PFI) containing hydrolytically and thermally stable backbones, such as Nafion produced by Du Pont or Nafion-like polymers supplied by Dow, Ballard, and other companies.<sup>4</sup> Despite of many advantages of perfluorinated polymers, such as good electrochemical performance and long-

term stability due to the hydrophobicity of the fluorinated polymer backbone and the hydrophilicity of the sulfonic acid side chain groups, there are still many disadvantages. For example, the conductivity will decrease dramatically with the increase of the temperature above 80°C due to the dehydration of the membrane. Moreover, the high price also limits the large scale commercialization of PEMFC.<sup>5</sup>

These shortcomings of PFI membranes stimulated many efforts to design and synthesize PEM based on fluorine free hydrocarbon ionomer membranes as alternatives to PFI membranes, such as polysulfones,<sup>6,7</sup> polyimides,<sup>8,9</sup> polybenzimidazoles,<sup>10</sup> and so on. Among all such polymers, poly(aryl ether ketone) possesses excellent mechanical properties, high thermal stability, chemical resistance,<sup>11</sup> and some certain conductivity when sulfonated, thus becomes a promising candidate for PEMFC.<sup>12–14</sup>

Recently, Kim et al.<sup>15</sup> has reported the preparation of sulfonated poly(arylene ether sulfone) copolymers containing rigid carboxylic acid groups on rigid backbone. They observed that the carboxylic acid groups did not influence the proton conductivity of the membranes because of the space resistance. To overcome this drawback, Zhang et al.<sup>16</sup> has synthesized SPAEK copolymers with carboxylic acid groups tethered to the flexible aliphatic chains. They observed that the proton conductivity was influenced obviously by the existence of the carboxylic acid groups on flexible aliphatic side chains,

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Contract grant sponsor: National 863 Project; contract grant number: 2007AA03Z324.

Contract grant sponsor: National 973 Project; contract grant number: 2007CD936203.

Contract grant sponsor: NSFC; contract grant numbers: 20674027, 50873045.

however, the water uptake is still much higher. It is well known that the water uptake is a key consideration for proton exchange membranes. Too low water uptake induces the reduction of the proton conductivity due to the less water absorption, while extreme water uptake will cause the loss of the dimensional stability and mechanical strength.<sup>17,18</sup> Crosslinking is an efficient means to overfull water uptake, also enhance stabilities and mechanical properties of the membranes.<sup>19–21</sup> Therefore, in this article, we prepared the SPAEK copolymer with carboxylic acid groups tethered to the flexible aliphatic chains. We proposed that the carboxylic group in the SPAEK copolymer side chain is an active pendant group, which could react with a crosslinking agent containing a hydroxyl group to form a cross-linked membrane material. And we prepared cross-linked SPAEK/poly(ethylene glycol) (PEG) membrane, in which PEG was used as crosslinker. Herein, we prepared a series of SPAEK/PEG membranes with different PEG content and discuss several important properties including mechanical and thermal properties, swelling behavior, and proton conductivity.

## EXPERIMENT

### Materials

4,4'-Difluorobenzophenone was purchased from Longjing Chemical plant, China, 4,4'-Bis(4-hydroxyphenyl)valeric acid (DPA) was purchased from Shanghai Chemical plant, China. Sodium 5,5'-Carbonyl-bis(2-fluorobenzenesulfonate) was synthesized by sulfonation of 4,4'-Difluorobenzophenone according to the procedure described by Wang et al.<sup>22</sup> Potassium carbonate was dried at 120°C for 12 h before use. PEG with molecular weight of 1500 was purchased from Shanghai Chemical works, China. Other solvents and reagents were obtained from Beijing chemical company and used without further purified.

### Synthesis of sulfonated poly(arylene ether ketone) copolymer with pendant carboxylic acid groups (C-SPAEK)

C-SPAEK copolymer, which has 50 mol % sulfonated polymer unit incorporated in the C-SPAEK copolymer composition. A typical synthetic procedure to prepare C-SPAEK ( $D_s = 1.0$ ) was as follows: A 250 mL, three-neck, round-bottomed flask equipped with a magnetic stirring bar, a  $N_2$  inlet, and a Dean-Stark trap with a condenser was charged with 4,4'-Difluorobenzophenone (0.02 mol), 4,4'-Bis(4-hydroxyphenyl)valeric acid (DPA) (0.04 mol), 5,5'-Carbonyl-bis(2-fluorobenzenesulfonate) (0.02 mol), and anhy-

drous  $K_2CO_3$  (0.065 mol). Then 50 mL DMSO and 15 mL toluene were added into the reaction flask. The mixture was heated to 140°C for 3 h. And then heated to 180°C, the temperature was maintained for 6 h. The viscous solution was cooled to 100°C and poured into 500 mL HCl (0.02M) solution. The obtained polymer was smashed to powder and washed with deionized water several times and dried at 100°C for 18 h. Intrinsic viscosity of SPAEK was measured in a concentration of 5.00 gL<sup>-1</sup> DMF solution at 25°C using an Ubbelohde viscometer. The resulting polymer had higher viscosity of 0.67 g dL<sup>-1</sup>

### Preparation of noncrosslinked and crosslinked C-SPAEK membranes

The noncrosslinked C-SPAEK membrane was prepared by pouring the solution of 10 wt % C-SPAEK in *N,N*-dimethylformamide (DMF) into a clean glass plate and dried at 80°C for 10 h and then at 100°C for 48 h in vacuum oven until most of the solvent was removed. To obtain the membrane in acid form, the membrane was immersed in 2M HCl solution for 24 h, rinsed with deionized water to remove any excess acid, and then dried at 100°C under vacuum.

The crosslinked C-SPAEK membranes were formed according to the following procedure: the solution of 10 wt % C-SPAEK (in acidic form) in DMF was prepared and then the different amounts of PEG (C-SPAEK-10 is 10 wt %, C-SPAEK-20 is 20 wt % and C-SPAEK-30 is 30 wt %) and *N,N*-dimethylacetamide (DMAc) (as the catalyst for the crosslinking reaction) were added to the above solution. And the solution was intensively agitated at 80°C for the formation of a homogeneous viscose solution. This was then cast onto petri dishes and held at a constant temperature of 80°C for 48 h to complete the crosslinking reaction. The thickness of the membranes was in the range 60–80  $\mu\text{m}$ .

## MEASUREMENTS

### Characterization

<sup>1</sup>H-NMR experiments were carried out on a Bruker 510 spectrometer by using DMSO-*d*<sub>6</sub> as solvent. FTIR spectra were measured on a Nicolet Impact 410 Fourier-transform infrared spectrometer. Differential scanning calorimeter (DSC) measurements were performed on a Mettler Toledo DSC821<sup>e</sup> instrument at a heating rate of 20°C min<sup>-1</sup> from 50 to 300°C under nitrogen. Thermogravimetric analysis (TGA) on a PerkinElmer Pyris-1 thermal analyzer system was employed to assess thermal stability of the membranes. Before testing, the membranes were dried and kept in the TGA furnace at 150°C under

an air atmosphere for 15 min to remove water. The samples were evaluated in the range of 80–700°C at a heating rate of 10°C min<sup>-1</sup> under nitrogen atmosphere.

### Water uptake measurements

The membranes were immersed into deionized water at 20°C for 2 days to make the membranes fully hydrated. The weight of the membranes was measured after blotting by filter paper. Then the membranes were dried at 80°C in vacuum for 24 h and measured again. All the experimental results were based on three measurement of each testing and averages were given. The weight gained from water was calculated with reference to the weight of the dry specimen using the following equation:

$$\text{Water uptake (WU)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%$$

where  $W_{\text{dry}}$  and  $W_{\text{wet}}$  stand for the masses of the dried and wet samples, respectively.

$$\text{Swelling ratio (\%)} = [(L_{\text{wet}} - L_{\text{dry}})/L_{\text{dry}}] \times 100\%$$

where  $L_{\text{wet}}$  and  $L_{\text{dry}}$  are the lengths of the wet and dry membranes, respectively.

### Ion exchange capacity of membrane

Ion exchange capacity (IEC) indicates the ion exchangeable groups of a polymer and reflects the proton transport action capacity of PEM from another point of view. Membrane samples were immersed in 1M NaCl solution for at least 48 h to liberate the hydrogen ion (the H<sup>+</sup> ions in the membrane were replaced by Na<sup>+</sup> ions). Then the H<sup>+</sup> ions were titrated by back titration with 0.01M NaOH using phenolphthalein as an indicator. All the experimental results were based on three measurement of each testing and averages were given.

### Proton conductivities

The proton conductivities of the membranes were measured by a four-electrode AC impedance spectroscopy technique over a frequency range of 0.1–10<sup>5</sup> Hz, 10 mV ac perturbation and 0.0 V dc rest voltage using a Princeton Applied Research Model 273A Potentiostat (Model 5210 frequency response detector, EG&G PARC, Princeton, NJ). The samples were all immersed in deionized water for at least 24 h to completely hydrated before testing and then sandwiched between two stainless steel blocking electrodes of an open cell in 100% relative humidity. The

testing temperature range of the impedance measurements was varied from 20°C to 80 °C.

The conductivity  $\delta$  of the samples was calculated using the following equation:

$$\sigma = L/RA$$

where  $L$  and  $A$  stand for the thickness and face area of the sample, and  $R$  is derived from the low intersect of the high frequency semicircle on a complex impedance plane with the Re ( $Z$ ) axis. The impedance data were corrected for the contribution from empty and short circuited cell.

### Mechanical properties

Mechanical properties of the membranes were evaluated at room temperature on Shimadzu AG-I 1KN at a strain rate of 2 mm min<sup>-1</sup>, and a 500 N load cell was used. The samples were prepared by being cut into a 15 × 4 mm dumbbell shape. At least three measurements for each membrane were taken and average value was calculated.

## RESULTS AND DISCUSSION

### Polymer synthesis and characterization

The chemical structures of the sulfonated copolymers were confirmed by <sup>1</sup>H-NMR spectra and the results are listed in Figure 1. The peaks at 2.36, 2.04, and 1.59 ppm were assigned to the aliphatic side chain. The low-field signals (6.5–8.5 ppm) were characteristic resonances of the aromatic hydrogen atoms. The introduction of the sulfonic acid group results in H<sub>5</sub> signal shift downfield. The signal at 8.18 ppm was assigned to the H<sub>5</sub> at the ortho position to the electron-withdrawing sulfonic acid groups. The calculated Ds of 0.89 was also measured by the NMR technique.<sup>23–25</sup>

The chemical structures of the polymers and cross-linked polymers were also confirmed by FTIR spectroscopy. The spectra of C-SPAEEK and C-SPAEEK-X are listed in Figure 2. The crosslinking by esterification between –OH in PEG and –COOH in C-SPAEEK, the strong intra- and intermolecular hydrogen bonds between proton-donor (–SO<sub>3</sub>H or –COOH) and proton-acceptor (–O– ether) groups in the C-SPAEEK/PEG membrane system were confirmed by FTIR. Figure 2 shows the FTIR spectra of the C-SPAEEK/PEG membranes crosslinked PEG and noncrosslinked C-SPAEEK system. The comparative analysis of C-SPAEEK with different amount of PEG membrane spectra shows significant changes in the spectra for the polymer after partial crosslinking by the PEG macromolecules. An the increase in intensity of –CH<sub>2</sub>– bands (between 2850 cm<sup>-1</sup> and 2930 cm<sup>-1</sup>) with the increase of PEG can be observed. It was reported that the

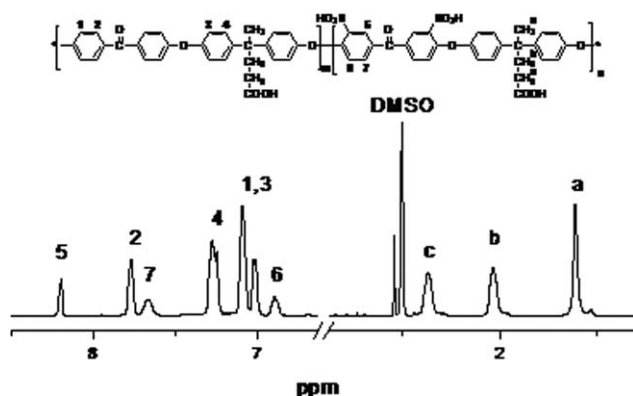


Figure 1  $^1\text{H-NMR}$  spectra of sulfonated polymer (C-SPAEEK).

absorption band of ester ( $-\text{COO}-$ ) appeared at  $1730\text{--}1735\text{ cm}^{-1}$ .<sup>26</sup> The absorption band at  $1733\text{ cm}^{-1}$  can be observed [Fig. 3(b,c)], but the absorption band of carboxylic group ( $-\text{COO}-$  in  $-\text{COOH}$  groups) appeared at  $1707\text{ cm}^{-1}$  in pure C-SPAEEK membrane [Fig. 2(a)]. And the intensity of the ester bond increased with the amount of the PEG [Fig. 2(b,c)]. Deformation bands ( $1351\text{ cm}^{-1}$ ) of  $\text{CH}_2\text{-O}$  groups of PEG crosslinked linkages can be also observed. All these results proved the formation monoester linkage as a result of partial monoesterification-crosslinking reaction of C-SPAEEK with PEG.

### Mechanical property

Besides the excellent thermal stability, the membranes applied in fuel cell should also possess good mechanical property. The mechanical properties of the C-SPAEEK/PEG membranes as functions of PEG content have been investigated. The results obtained are shown in Figure 3 and Table I where the effects of PEG content on tensile strength and flexibility are summarized. As

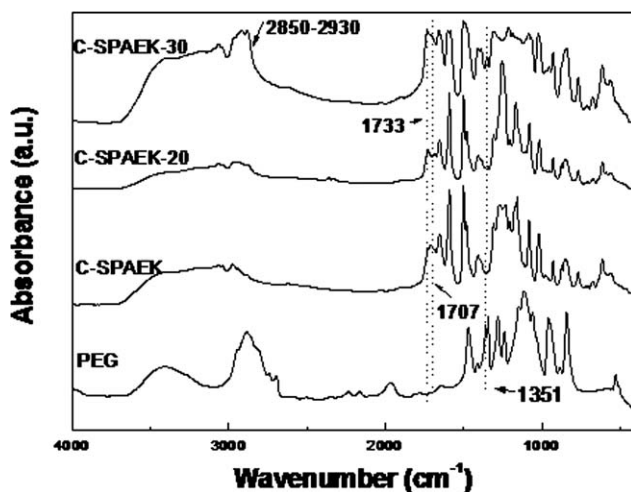


Figure 2 Comparative FTIR spectra of C-SPAEEK and crosslinked C-SPAEEK-x.

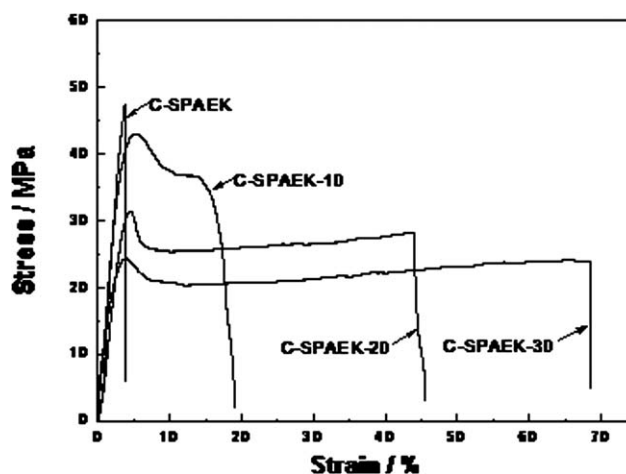


Figure 3 Stress-strain of C-SPAEEK-x membranes.

seen in Figure 3, the tensile strength of the membranes decreased significantly with increasing PEG content, while they became much more flexible (much higher elongation at break values). This may be attributed to the crosslinking by esterification and the formation of strong intermolecular H-bonding linkages between  $-\text{COOH}$  or  $-\text{SO}_3\text{H}$  and  $-\text{OH}$  in the film-forming process. It was noted that with increasing the content of PEG, the elongation at break was also elevated. From Table I, the samples in the dry state had tensile strength of  $25.32\text{--}47.27\text{ MPa}$ , and Young's moduli of  $0.81\text{--}1.65\text{ GPa}$ . The increase of the flexible aliphatic chains (from PEG) in C-SPAEEK/PEG structures resulted in the decrease in the tensile strength and Young's moduli. But both of them were obviously higher than Nafion 117 of  $22.7\text{ MPa}$  and  $0.046\text{ GPa}$  at the same testing condition in our lab. The mechanical properties suggested these crosslinked membranes were flexible and strong enough for usage in fuel cells.

### Thermal stability

The thermal stabilities of the copolymers were investigated by TGA measurement (Fig. 4). The C-SPAEEK had three weight loss steps. The first weight loss was observed around  $100^\circ\text{C}$ , which was attributed to the loss of the absorbed moisture by the hygroscopic sulfonic acid and carboxylic acid groups. The second weight loss was attributed to the splitting-off of sulfonic acid groups. All the other crosslinked C-SPAEEK-X in acid form also exhibited three step degradation patterns. The first stage at around  $190^\circ\text{C}$  is related to the dehydration of the hygroscopic sulfonic acid and carboxylic acid groups in the membranes. The second stage at around  $270^\circ\text{C}$  is associated with decarboxylation, degradation of PEG linkages and the splitting-off of sulfonic acid groups. The last degradation step of all the membranes at around  $430^\circ\text{C}$  corresponded to the main chain decomposition.<sup>27</sup>

TABLE I  
Mechanical Properties of Membranes

Polymer	Tensile modulus (MPa)	Tensile strength (MPa)	Elongation (%)	Solubility in DMAc
C-SPAEEK	1648.49	47.27	3.78	Yes
C-SPAEEK-10	1305.70	42.20	18.95	Swollen
C-SPAEEK-20	1063.25	31.34	45.57	Swollen
C-SPAEEK-30	810.78	25.32	68.55	Swollen

### Water uptake and swelling ratio

The water uptake is one of the crucial properties of proton exchange membranes, which is closely related to IEC, proton conductivity and mechanical strength. Higher proton conductivity requires higher water uptake, because the protons are in the form of hydronium ions when they pass through the hydrophilic regions of the membrane. However, excessive water uptake in a PEM leads to unacceptable dimensional change or loss of dimensional shape, which can lead to weakness or a dimensional mismatch when incorporated into a membrane electrode assembly (MEA).<sup>28</sup> The water uptakes of various membranes were shown in Figure 5 and Table II. It could be seen that the water uptake of the crosslinked membranes (C-SPAEEK-X) were lower than that of pure C-SPAEEK membrane under the same conditions. This result can be attributed to the decrease amount of carboxylic or sulfonic acid protons of the ionomers. The carboxylic or sulfonic acid groups were partially consumed by acid-base interaction between the carboxylic groups and hydroxyl groups of the PEG component. And also, the membrane after crosslinking had denser network structure than pure C-SPAEEK, leading to the reduction of space to retain water around sulfonic acid groups and eventually restricted the water uptake of the membranes.<sup>29</sup>

Dimensional stability of membranes is also important for using in PEM. Therefore, appropriate levels

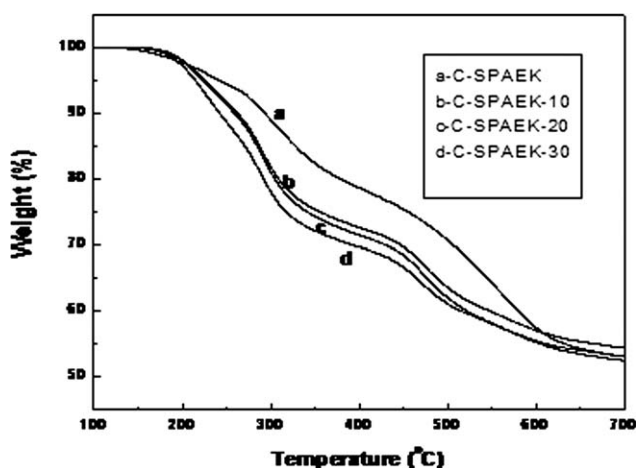


Figure 4 TGA curves of C-SPAEEK-x membranes.

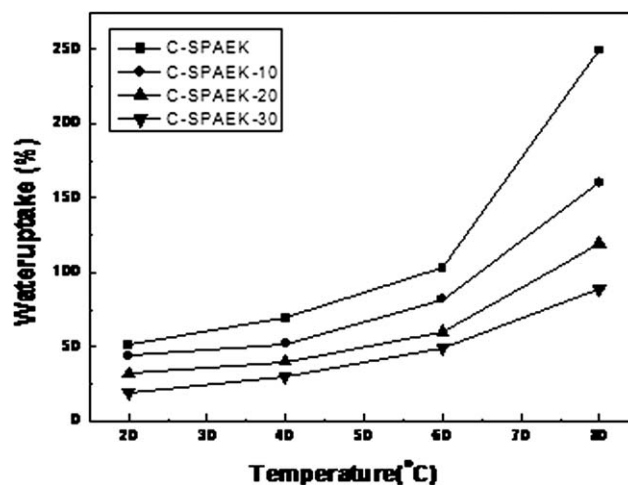


Figure 5 Water uptake of C-SPAEEK-x membranes as a function of temperature.

of water uptakes and dimensional stability of membranes are the critical demands for their application as PEMs. The swelling ratio (SR) values were also listed in Table II. As seen from these data, the SR decreases from 25.3% to 14.5% with the increasing PEG content at room temperature. And the SR values at 80°C were also listed in Table II. The lower SR was attributed to the formation of the network. It was clear that the interaction led to the membranes more compact. The result also suggested that one can control swellability of the membranes simply by changing the content of crosslinking PEG molecules. The membranes with excellent dimensional stability were remarkably promising to be used as proton exchange membranes in PEMFCs.

### IEC and proton conductivity

Ion exchange capacity (IEC) is a method to indicate the exchangeable ions of polymer membranes. The IEC values play a definitive role in determining the proton conductivity of the membranes. The IEC of the C-SPAEEK-X membranes with different PEG content are presented in Table II. As seen from these data, the IEC values decrease from 1.69 to 1.18 mmol g<sup>-1</sup> with the increasing PEG content, which

TABLE II  
Ds, SR, Water Uptake, and IEC of the Polymers

Polymer	IEC (mmol g <sup>-1</sup> )	Swelling Ratio (%)		Water uptake (%)	
		20°C	80°C	20°C	80°C
C-SPAEEK	1.69 ± 0.1	25.3 ± 0.2	135 ± 3	51 ± 2	249 ± 4
C-SPAEEK-10	1.54 ± 0.1	17.9 ± 0.1	93 ± 2	44 ± 1	160 ± 2
C-SPAEEK-20	1.36 ± 0.2	16.3 ± 0.3	67 ± 2	32 ± 2	119 ± 1
C-SPAEEK-30	1.18 ± 0.1	14.5 ± 0.1	49 ± 2	19 ± 3	89 ± 1
Nafion117	0.91 ± 0.1	12.6 ± 0.1	23.5 ± 1	18 ± 2	30 ± 4

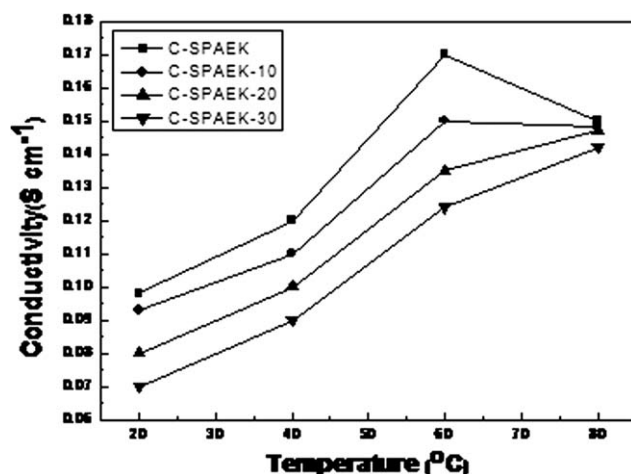


Figure 6 Proton conductivities of C-SPAEEK-x films as a function of temperature.

can be also attributed to the decrease amount of carboxylic or sulfonic acid protons of the ionomers.

Four-probe technique was used in the determination of the proton conductivity of the C-SPAEEK/PEG membranes. Proton conductivities of the membranes were measured at 100% RH in the temperature range of 25–80°C and the data are depicted in Figure 6. It was expected that proton conductivity depends significantly on water uptake and IEC. As seen from Figure 6, in all cases the conductivity decreased with increasing PEG content of the membranes. The decrease in water uptake and IEC with increasing PEG content can be the reason for the observed decrease in productivity. However, the excess water content dilutes the proton concentration at high temperature, thus resulting in a sharp decrease of the proton conductivity of pure C-SPAEEK membrane. And an important finding has been found in the proton conductivities at 80°C. With the crosslinking extent improve, the proton conductivities at 80°C become from decreasing to increasing already. This trend could be based on the fact that proton conductivity is a function of ion exchange capacity and water uptake, both of which are affected by the crosslinking extent. The crosslinking extent here was controlled by adjusting the content of PEG. The crosslinked membranes have more network than uncrosslinked one, which also resists water absorption and water percolation, and results in the good the mechanical stabilities of the crosslinked at higher temperature (80°C). As a result, the introduction of the crosslinker PEG in copolymers leads to a significant increase in proton conductivity at higher temperature.

## CONCLUSION

In this study, a series of novel C-SPAEEK/PEG membranes have been prepared and characterized. These

membranes were formed as a result of physical (via H-bonding) and chemical (via PEG) crosslinking. The C-SPAEEK/PEG membranes showed more flexible property and lower water uptake. The SR decrease from 25.3% to 14.5% with the increasing PEG content at room temperature. The result also suggested that one can control swellability of the membranes simply by changing the content of crosslinking PEG molecules. And the C-SPAEEK/PEG membranes showed higher proton conductivity at higher temperature (80°C). All the results showed that these membranes may be a potential PEM material for PEMFC applications.

## References

- Hickner, M. A.; Ghassemi, H.; Kim, Y. S.; Einsla, B. R.; McGrath, J. E. *Chem Rev* 2004, 104, 4587.
- Gamburzev, S.; Appleby, A. J. *J Power Sources* 2002, 107, 5.
- Dimitrova, P.; Friedrich, K. A.; Vogt, B.; Stimming, U. *J Electroanal Chem* 2002, 532, 75.
- Souzy, R.; Ameduri, B. *Prog Polym Sci* 2005, 30, 644.
- Kreuer, K. D. *J Membr Sci* 2001, 185, 29.
- Genova-Dimitrova, P.; Baradie, B.; Foscallo, D.; Poinsignon, C.; Sanchez, J. Y. *J Membr Sci* 2001, 185, 59.
- Wang, F.; Hickner, M.; Kim, Y. S.; Zawodzinski, T. A.; McGrath, J. E. *J Membr Sci* 2002, 197, 231.
- Asano, N.; Aoki, M.; Suzuki, S.; Miyatake, K.; Uchida, H.; Watanabe, M. *J Am Chem Soc* 2006, 128, 1762.
- Fang, J. H.; Guo, X. X.; Harada, S.; Watari, T.; Tanaka, K.; Kita, H.; Okamoto, K. *Macromolecules* 2002, 35, 9022.
- Wainright, J. S.; Fontanella, J. J.; Wintersgill, M. C.; Savinell, R. F.; Litt, M. *Electrochim Acta* 1998, 43, 1289.
- Rikukawa, M.; Sanui, K. *Prog Polym Sci* 2000, 25, 1463.
- Li, X. F.; Liu, C. P.; Lu, H.; Zhao, C. J.; Wang, Z.; Xing, W.; Na, H. *J Membr Sci* 2005, 255, 149.
- Gil, M.; Ji, X. L.; Li, X. F.; Na, H.; Hampsey, J. E.; Lu, Y. F. *J Membr Sci* 2004, 234, 75.
- Muthu Lakshmi, R. T. S.; Choudhary, V.; Varma, I. K. *J Mater Sci* 2005, 40, 1.
- Kim, D. S.; Shin, K. H.; Park, H. B.; Chung, Y. S.; Nam, S. Y.; Lee, Y. M. *J Membr Sci* 2006, 278, 428.
- Zhang, Y.; Cui, Z. M.; Zhao, C. J.; Shao, K.; Li, H. T.; Fu, T. Z.; Na, H.; Xing, W. *J Power Sources* 2009, 191, 253.
- Decker, C. *Prog Polym Sci* 1996, 21, 593.
- Lin, C. W.; Thangamuthu, R.; Yang, C. J. *J Membr Sci* 2005, 253, 23.
- Chen, J. H.; Asano, M.; Yamaki, T.; Yoshida, M. *J Power Sources* 2006, 158, 69.
- Qiao, J. L.; Hamaya, T.; Okada, T. *Polymer* 2005, 46, 10809.
- Chen, S. L.; Benziger, J. B.; Bocarsly, A. B.; Zhang, T. *Ind Eng Chem Res* 2005, 44, 7701.
- Wang, F.; Chen, T. L.; Xu, J. P. *Macromol Chem Phys* 1998, 199, 1421.
- Li, Z. L.; Liu, X. C.; Chao, D. M.; Zhang, W. J. *J Power Sources*, to appear.
- Xing, P. X.; Robertson, G. P.; Guiver, M. D.; Mikhailenko, S. D.; Kaliaguine, S. *J Polym Sci Part A: Polym Chem* 2004, 42, 2866.
- Shi, Z. Q.; Holdcroft, S. *Macromolecules* 2005, 38, 4193.
- Rhim, J. W.; Lee, S. W.; Kim, Y. K. *J Appl Polym Sci* 2002, 85, 1867.
- Devrim, Y. G.; Rzaev, Z.; Pişkin, R. *Macromol Chem Phys* 2007, 208, 175.
- Zhao, C. J.; Li, X. F.; Wang, Z.; Dou, Z. Y.; Zhong, S. L.; Na, H. *J Membr Sci* 2006, 280, 643.
- Zhong, S. L.; Cui, X. J.; Cai, H. L.; Fu, T. Z.; Shao, K.; Na, H. *J Power Sources* 2007, 168, 154.