Poly(aryl ether ketone)s with Bromomethyl Groups: Synthesis and Quaternary Amination

Wenjia Ma, Chengji Zhao, Haidan Lin, Gang Zhang, Hui Na

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

ABSTRACT: A series of bromomethylated poly(arylene ether ketone)s (PAEKs) with different contents of bromine tethered to the benzyl groups were successfully synthesized and characterized in this work. For this purpose, poly(arylene ether ketone) with 3,3′,5,5′-tetramethyl-4,4′-dihydroxybipheny moiety (PAEK-TM) was prepared by the aromatic nucleophilic polycondensation, and then the PAEK-TM has benzylic methyl groups that were converted to bromomethyl groups by a radical reaction using *N*-bromosuccinimide. Then, the bromomethylbenzyl groups in the membrane was converted to quaternary ammonium moieties in TMPAEK-NOH. ^{1}H-NMR measurements were used to characterize and confirm the structures of the resulting PAEK-*x*-BrTM and TMPAEK-NBr derivatives (*x* refers to the molar percentage of bromine introduced per repeating units). TGA analysis showed that PAEK-*x*-BrTM exhibited a very low-decomposition temperature at about 200°C corresponding to the C—Br bond cleavage. The hydroxide conductivity of TMPAEK-NOH membrane was 8 mS cm^{-1} at room temperature, while the water uptake of TMPAEK-NOH membrane was 22.3% at 20°C and 32.6% at 60°C. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3477–3483, 2011

Key words: poly(ether ketones); functionalization of polymers; membranes; ion exchangers; swelling

INTRODUCTION

Poly(arylene ether ketone)s (PAEKs), as a class of high-performance engineering thermoplastic materials, are widely used in the fields of traffics, aeronautics, astronautics, medicines, etc., due to high-glass transition temperature, high-thermal stability, advanced mechanical properties, and excellent resistance to hydrolysis and oxidation.[1–3] For example, the glass-transition temperature (T_g), the melting point temperature (T_m), and the thermal decomposition temperature of PAEK are 143, 334, and 530°C, respectively.[4] However, the solvent resistance and high-melting temperature make PAEKs difficult to process and fabricate. Therefore, chemical modifications are frequently required to obtain some specific physical–chemical properties for special applications. Several approaches have been proposed to functionalize the aromatic rings of the PAEKs structure, because the aromatic rings are extremely lively to electrophilic substitution reactions. Functionalized PAEKs, such as sulfonated PAEKs, brominated PAEKs, and carboxylated PAEKs, can be applied to a variety of biomaterials,[5,6] coatings,[7,8] electrodialysis devices, and electrolyte membranes for fuel cells.[9–11] For example, Lin et al.[12,13] have synthesized several series of sulfonated PAEK by postsulfonation on the activated pendants of corresponding parent polymers or by aromatic nucleophilic polycondensation of sulfonated monomers for applications in proton-exchange membrane fuel cells. Moreover, the benzylic methyl groups are also versatile reactive handle for selective modifications of PAEKs. The methyl-substituted PAEKs can be chemical modified and introduced some functional groups. Wang et al.[14] synthesized carboxylic acid functionalized PAEKs by chemical modification of methyl-substituted polymer. Furthermore, Miyatake et al.[15] gave the quaternized poly(phenylene sulfide) (PPS) through the reaction of bromomethylated PPS with tertiary amines.

The synthesis of bromomethylated polyaromatic ether classes and bromomethylated poly(phenylene) had received much attention in the recent years, because the bromomethylated polymer had been used as precursors for the synthesis of cationic polymer for direct methanol fuel cells (DMFCs).[16–20] Xu and Hibbs had recently reported the bromination of benzylic methyl groups in poly(2,6-dimethyl-1,4-phenylene oxide) and poly(phenylene), respectively. The study of modified high-performance polymers with functional groups for various applications and different purposes, such as membrane materials, was carried out by many groups. Roovers et al.[21]

have reported a series of functionalization reactions starting from the bromomethyl group. PAEK with 3,3′,5,5′-tetramethyl-4,4′-dihydroxybipheny moiety (PAEK-TM), with four active benzylic methyl groups in a repeating unit, is an ideal polymer for preparing of bromomethylated PAEKs. In this work, we describe the successful synthesis of PAEK with bromomethyl groups. ^{1}H-NMR measurement was used to prove the bromination process. Furthermore, the quaternary amination of bromomethylated PAEK with trimethylamine (TMA) in tetrahydrofuran (THF) solution was also described in the present article. The hydroxide conductivity, methanol crossover, water uptake, and the selectivity of the resulted anion exchange membranes were then investigated elementarily.

EXPERIMENTAL

Materials

3,3′,5,5′-Tetramethyl-4,4′-biphenol (TMBP) and N-bromosuccinimide (NBS) were obtained from Shanghai Jiachen Chemical Company. 4,4′-Difluorobenzophenone (DFBP) was obtained from Yanbian Longjing Chemical Company, and benzoyl peroxide (BPO) used as initiator was provided from Lanzhou Aokai Chemical Company and used without any further purification. TMA was obtained from Sinopharm Chemical Reagent Co. All other solvents were obtained from Tianjin Tiantai Chemical Company and treated by a standard method before use.

Synthesis of PAEKs based on TMBP

PAEK-TM was synthesized by the aromatic nucleophilic polycondensation of 3,3′,5,5′-Tetramethyl-4,4′-biphenol (TMBP) and DFBP according to a procedure reported by our previous work,[22] and the reaction process was showed in Scheme 1. The bulk polymer was characterized by ^{1}H-NMR, shown in Figure 1. A typical procedure was described as follows: a 500-mL three-necked flask was equipped with a mechanical stirrer, a Dean–Stark trap with a reflux condenser, and purged with pure nitrogen. Then (50 mmol, 10.9 g) of DFBP, (50 mmol, 12.1 g) of TMBP, (55 mmol, 7.59 g) of anhydrous potassium carbonate, 51 mL of sulfolane, and 30 mL of toluene were added to the flask to form a solvent system of a solid concentration of 25 wt %. The reaction mixture was heated and stirred slowly until the toluene beginning to reflux at about 140°C. After keeping this temperature for 3 h, the temperature was raised to 210°C to remove most of water and toluene, with the mixture getting more viscously. After about 6 h, the viscous mixture was poured into water and strip

shaped precipitation was obtained. The precipitated copolymer was broken into pieces with muller, then washed for several times with deionized water, and dried in a vacuum oven for 24 h. Yield: 97.4%.
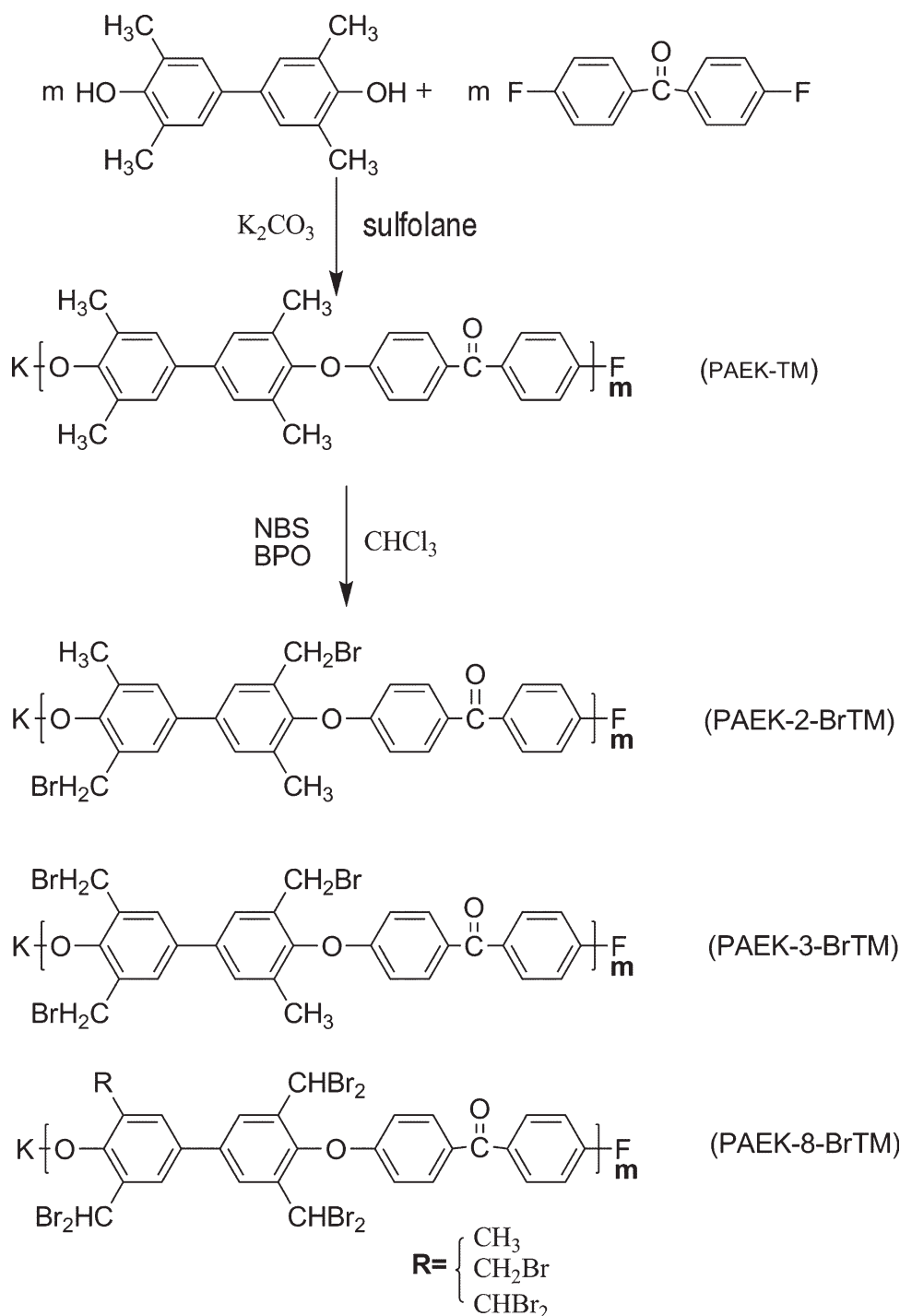
Synthesis of bromomethylated PAEKs

The bromination of the benzylmethyl-bearing poly (aryl ether ketone)s was carried out in chloform, using NBS as the bromination agent and BPO to initiate the radial reaction. A typical procedure was as follows: PAEK-TM (10 mmol, 2.42 g), NBS power(90 mmol, 16.0 g), BPO (0.05 g), and chloroform (50 mL) were added into a 250-mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, and a condenser. When the mixture was heated to 84°C, tetrachloromethane began to reflux, and the mixture turned to blood red. After 2 h, the mixture was poured into 50 wt % ethanol and water mixture. A yellow precipitate termed PAEK-2-BrTM was obtained under vigorous stir. The precipitate was washed with ethanol for several times and dried in a vacuum oven for 24 h. The other two bromomethylated PAEKs were prepared through a period of 4 and 12 h under the same reaction procedure.

Quaternary amination of bromomethylated PAEKs

A typical synthesis procedure of TMPAEK-NOH was as follows, a 100-mL three-necked round-bottomed flask equipped with a nitrogen inlet, and a dropping funnel was charged with PAEK-2-Br (3.17 g, 50 mmol) and THF (50 mL). TMA (1.16 mL, 50 mmol) was dripped into the reactions from the dropping funnel drop by drop. The mixture was kept at 40°C for 4 h, then a homogeneous solution was received, then the resulting solution was cast directly onto clean glass plate. After carefully dried at room temperature for 3 h and vacuum-dried at 120°C for 24 h, tough and flexible membrane of TMPAEK-x-NBr was obtained. The membrane was transformed to the alkaline form (TMPAEK-NOH) by hydroxyl ions exchange in 1M NaOH for 24 h at room temperature. Then, the membrane was soaked and washed thoroughly with deionized water.

Measurement

^{1}H-NMR spectra were recorded on a Bruker 400 MHz spectrometer using deuterochloroform (CDCl$_3$) as solutions for PAEK-TM and PAEK-x-BrTM series and dimethyl sulfoxide-d_6 for PAEK-NOH. The bromine content per repeat unit of the PAEK-BrTM was evaluated by integration and comparison of the ^{1}H-NMR signals arising from the methyl protons and from the brominated methyl protons. The degree of

Scheme 1 Synthetic route of bromomethylated poly(arylene ether ketones).

bromine groups (DBr) was calculated by the following eq. (1):

$$D_{Br} = 12A_{Hd}/(3A_{Hd} + 2A_{He}) \qquad (1)$$

where A_{Hd} is the peak area of brominated methyl protons, and A_{He} corresponds to the peak area of methyl protons.

The PAEK-TM and PAEK-BrTM series were cast onto glass plates from their NMP solutions (10 wt %) and then placed in a vacuum oven at 80°C for 12 h and at 120°C for another 12 h to remove the residual solvent completely. The glass plates were subsequently immersed in water solutions until the membranes were peeled off the glass plates. The mechanical properties of PAEK-TM and PAEK-BrTM membranes were investigated using a SHIMADZU AG-I 1KN instrument. Before tensile test, these membranes were dried in vacuum oven. Then, the test was carried out at room temperature at a constant crosshead speed of 2 mm min⁻¹. The
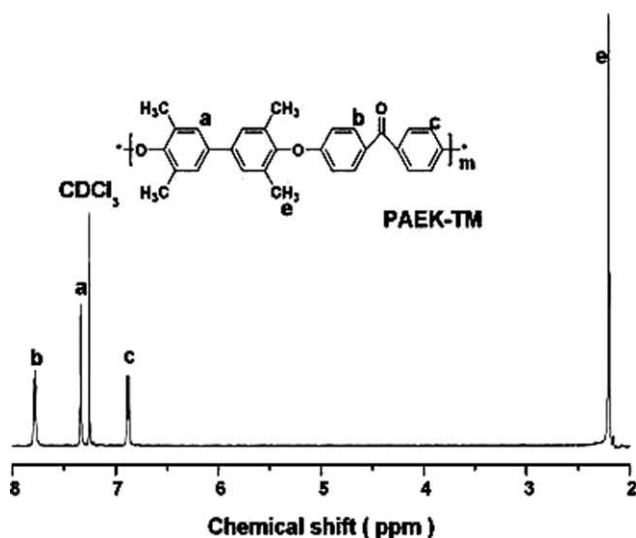
Figure 1 ^{1}H-NMR spectra of PAE-TM in CDCl$_3$.

Figure 3 ^{1}H-NMR spectra of PAEK-3-BrTM in CDCl$_3$.

uniaxial tensile measurements were conducted on membrane samples of 4 mm width and 15 mm length.

Thermogravimetric analysis was conducted using a Perkin–Elmer TGA-7. The samples were heated at a rate of 10°C min^{-1} under N$_2$ atmosphere. Before testing, all the membranes were preheated to 120°C and kept at this temperature for 20 min to remove any residual moisture and solvent. Differential scanning calorimetry (DSC) measurements were carried on a Mettler Toledo DSC 821^e instrument at a heating rate of 20°C min^{-1} under nitrogen protection.

Gel permeation chromatograms (GPCs) using polystyrene as a standard were obtained on a Waters 410 instrument using dichloromethane (CH$_2$Cl$_2$) as an eluent at a flow rate of 1 mL min^{-1}.

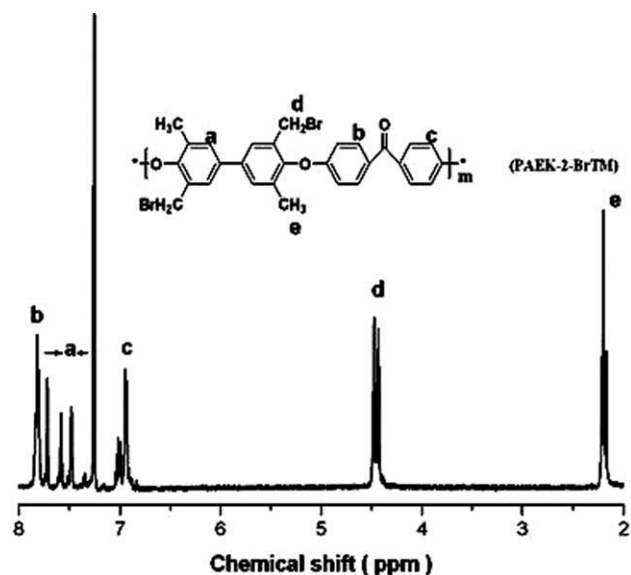The hydroxide conductivities parallel to the surface (in-plane) of the TMPAEK-x-NOH membranes were determined by alternating-current impedance spectroscopy using a modified four-probe AC impedance method from 0.1 Hz to 100 kHz, 10 mV AC perturbation, and 0.0 V DC rest voltage using a Princeton Applied Research Model 2273 potentiostat/galvanostat/FRA. The membranes and the electrodes were set in a Teflon cell, and the distance between the reference electrodes was 1 cm. The cell was placed in a thermocontrolled chamber in liquid water for measurement. The impedance measurements were performed from 20 to 70°C under 100% relative humidity (RH). The hydroxide conductivities (σ, S cm^{-1}) of the copolymer membranes were obtained using $\sigma = d/L_s \times W_s \times R$ (d is the distance

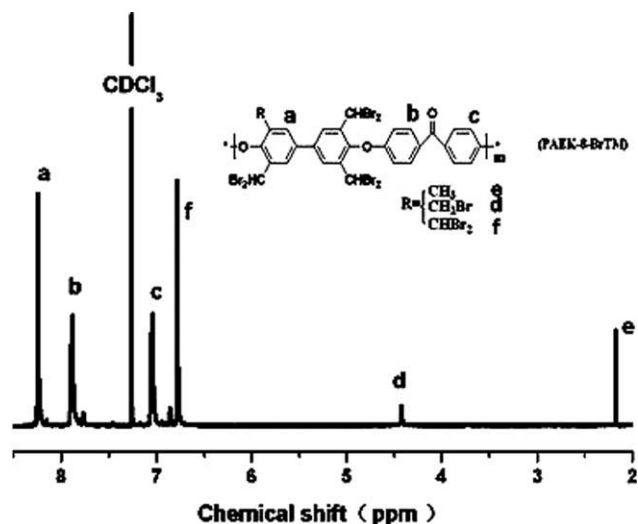**Figure 2** ^{1}H-NMR spectra of PAEK-2-BrTM in CDCl$_3$.

Figure 4 ^{1}H-NMR spectra of PAEK-8-BrTM in CDCl$_3$.

TABLE I
^{1}H-NMR Data for PAEK-TM and PAEK-x-BrTM Membranes

^{1}H	—CH$_3$	—C$_6$H$_{2a}$—	—C$_6$H$_{4b}$—	—C$_6$H$_4$c—	—CH$_2$Br	—CHBr$_2$
PEEK-TM	2.20	7.34	6.89	7.79	–	–[a]
PEEK-2-BrTM	2.20	7.36–7.71	6.94	7.82	4.48	–
PEEK-3-BrTM	2.19	7.49–7.73	7.02	7.82	4.43	–
PEEK-8-BrTM	2.17	8.24	7.05	7.87	4.41	6.79

[a] No peak was observed in ^{1}H-NMR spectrum.

between reference electrodes, and L_s and W_s are the thickness and width of the membrane, respectively).

The water uptake, membrane swelling, and ionic exchange capability of PAEKs anion exchange membrane derivative were measured by a traditional method, which was described previously in our literature.[23]

RESULTS AND DISCUSSION

Synthesis of bromomethylated poly(ether ether ketone)s

The structure of PAEK-TM is shown in Scheme 1. Figure 1 shows the ^{1}H-NMR spectra of PAEK-TM copolymer. The peaks around 2.18 ppm correspond to the methyl protons, and the peaks above 6 ppm are assigned to the hydrogen atoms of deactivated aromatics. The number–average molecular weight is 27700 g mmol^{-1}, indicating that PAEK with high-molecular weight was obtained.

The synthesis of PAEK-BrTM is also shown in Scheme 1. Their structures were confirmed by their ^{1}H-NMR spectrums. The ^{1}H-NMR of PAEK-2-BrTM corresponding to the bromomethylated poly(aylene ether ketone)s with two bromine per repeating unit was shown in Figure 2. The typical peak of brominated benzyl groups was observed at δ = 4.43 ppm

(—CH$_2$—). The typical peaks of benzyl groups were observed at about δ = 2.18 ppm (—CH$_3$). The integration ratio of the H_d to H_e was assigned for the composition of quaternary bromine. As for PAEK-2-BrTM, the integration ratio of the H_d to H_e is 0.704 and the D_{Br} is 2.05, which successfully proved the PAEK-2-BrTM. And the number–average molecular weight of PAEK-2-BrTM is 24 171 g mmol^{-1}. For PAEK-3-BrTM, the integration ratio of the H_d to H_e was 2.04, and the D_{Br} = 3.02, and the ^{1}H-NMR spectra of PAEK-3-BrTM were shown in Figure 3. The typical peaks of benzylmethyl group with two bromine atoms were observed at about δ = 6.78 ppm (—CHBr$_2$) as shown in Figure 4. The proton a signals of 3,3′,5,5′-tetramethyl-4,4′-dihydroxybipheny were shifted to higher frequencies at δ = 8.24 ppm due to deshielding from the bromine atoms of benzyl. From the integration ratio of H_d to H_f, we find that most of the benzyl are brominated by two bromine atoms because of steric hindrance effect. More details of ^{1}H-NMR data for PAEK-TM and PAEK-x-BrTM copolymers are shown in Table I. PAEK-TM was smoothly brominated by treatment with NBS in chloform. Mild reaction conditions and simple preparation provide a practical and commercially available route for the synthesis of bromomethylated polymers in high yields.

Thermal stability

The thermal properties of the PAEK and PAEK-x-BrTM series are investigated by TGA under N$_2$ atmosphere at a heat rate of 10°C min^{-1}. As shown in Figure 5, PAEK-TM copolymers exhibited a typical degradation at about 491°C. It is believed to be
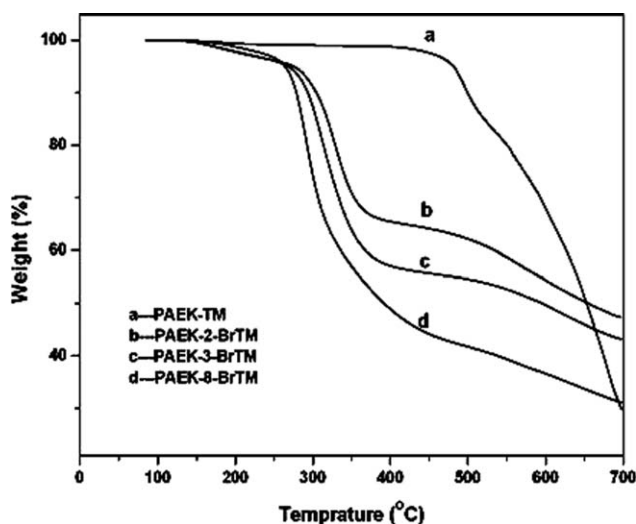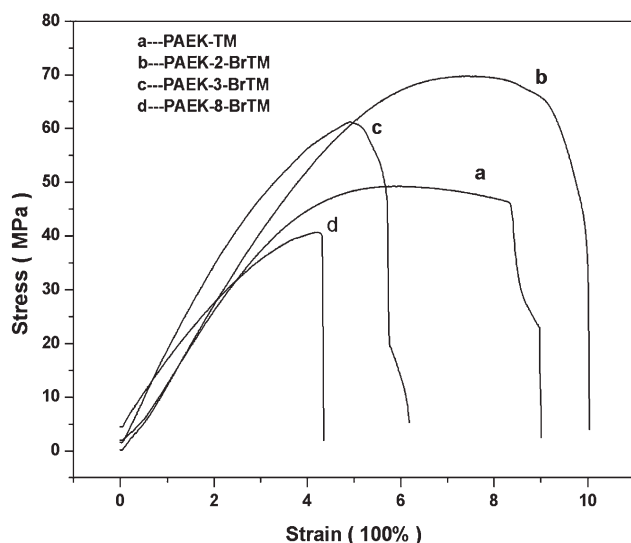

Figure 5 TGA curves of PAEK-TM and PAEK-x-BrTM membranes.

TABLE II
The Thermal Properties of PAEK-TM and PAEK-x-BrTM Membranes

Polymer	T_g (°C)	T onset (°C)	T_d (°C) (5%)[a]	(10%)[b]
PAEK-TM	253.27	491.14	481.94	499.75
PAEK-2-BrTM	158.17	148.17	275.74	304.59
PAEK-3-BrTM	163.67	165.20	268.88	293.49
PAEK-8-BrTM	165.98	180.64	264.40	278.84

[a] The temperature of 5% weight loss.
[b] The temperature of 10% weight loss.

Figure 6 Stress–strain of PAEK-TM and PAEK-x-BrTM membranes.

associated with the decomposition of polymer main chain. Meanwhile, the PAEK-BrTMs exhibit a two-step degradation. The first decomposition temperature corresponding to the C—Br bond cleavage is at about 200°C, while the second decomposition temperature above 500°C was associated with the main-chain degradation. Despite the lower decomposition temperature of bromine groups, the PAEK-x-BrTM series exhibited a much slower degradation rate than PAEK-TM, which proved that higher thermal stability was obtained due to the crosslinking structure forming in the PAEK-BrTM series due to the crosslinking structure forming between the bromines at the pendant during temperature-programmed heating.[24]

T_gs of copolymers are investigated by DSC analysis, which is listed in Table II. The results show that the thermal behavior of both PAEK and PAEK-x-BrTM series exhibit a high-flowing temperature. It was expected that PAEK-x-BrTM has a higher T_g than PAEK due to the effect of steric hindrance. However, the observed T_gs of PAEK-x-BrTM are

lower. It is assumed that a partial degradation of the backbone occurs during the bromination reaction.

Mechanical properties

The PAEK-x-BrTM membranes exhibit excellent mechanical properties with tensile stress at maximum load of 54.0–72.8 MPa, and elongations at break of 5.0–15.2% while the PAEK-TM has an elongation at break of 12.9% and a tensile stress at maximum load of 54.3 MPa. The stress–strain data are shown in Figure 6. Compared to PAEK-TM, the tensile stress of PAEK-x-BrTM membranes is enhanced. However, PAEK-x-BrTM membranes get brittler when more bromine atoms were introduced. The bromine atoms increase the special hindrance effect, making the molecule chains hard to move, which decrease the flexibility. The PAEK-2-BrTM membrane exhibits the most outstanding tensile impact resistance and toughness.

Quaternary amination of bromomethylated PAEKs and the elementary properties as anion exchange membranes

Flexible and tough TMPAEK-NBr membrane-bearing benzyltrimethylammonium groups was achieved from quaternization of the resulting TMPAEK-2-Br copolymer and subsequent film-forming process. Finally, novel anion exchange membranes, TMPAEK-NOH, was obtained by an anion exchange of TMPAES-NBr membranes with 1M NaOH, and the reaction process was shown in Scheme 2. The ^{1}H-NMR spectrum of the ammoniated derivaty is shown in Figure 7, in which the signal of —CH$_2$—N(CH3)$_3^+$ changed from 3.21 to 3.15 ppm when R is converted from Br to quaternary amination group. The integration of these two peaks can be used to calculate the percentage conversion. Then, the IEC, hydroxide conductivity, water uptake, and water swelling ratio of TMPAEK-NOH anion exchange membrane were investigated and listed in Table III. The hydroxide conductivity of the
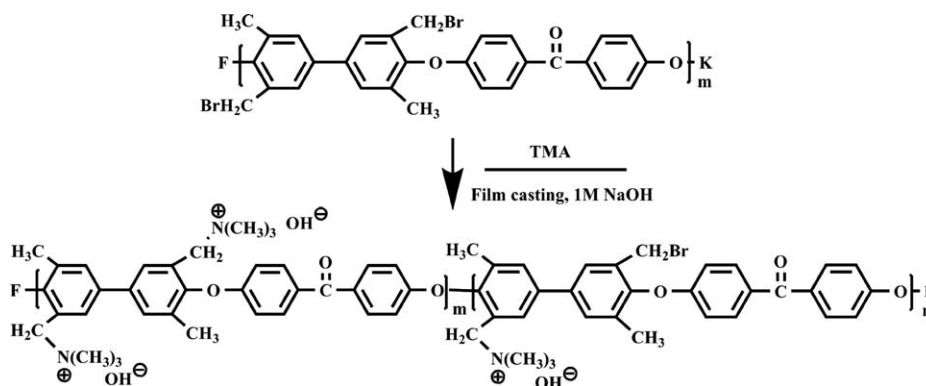
Scheme 2 Quaternary animation of bromomethylated poly(arylene ether ketones).

TABLE III
Hydroxide Conductivities, Anion Exchange Capability, Water Uptake, Methanol Permeability, and Membrane
Swelling Ratio of Anion Exchange Membrane

| | Hydroxide conductivity (mS cm^{-1}) | IEC (mmol g^{-1}) | WU[a] | | MS[b] | | DK ($\times 10^{-8}$ cm^2 s^{-1}) |
			20°C	60°C	20°C	60°C	
Sample	8	0.96	22.3	32.6	2.7	7.8	4.11

[a] The water uptake was calculated from $WU = 100(m_{wet} - m_{dry})/m_{dry}$.
[b] The membrane swelling ratio was calculated from $MS = 100(l_{wet} - l_{dry})/l_{dry}$, where l is the length of the membrane.

TMPAEK-NOH membrane was measured at 100% RH under room temperature. The anion exchange derivative exhibits a hydroxyl conductive of 8×10^{-3} S cm^{-1} at room temperature but low-water uptake and swelling ratio. The selectivity Φ (the ratio of proton conductivity to methanol permeability coefficient) of TMPAEK-NOH anion exchange membrane was 1.95×10^5 S s cm^{-3}, which was even lower than the Nafion 117 because of its lower methanol permeability coefficient. These properties enable the potential use of TMPAEK-NOH membrane as anion exchange membrane for DMFCs and sewage treatment. Further research of water and proton dynamic behaviors in anion exchange membranes is necessary.

CONCLUSIONS

A series of novel bromomethylated PAEKs were synthesized. The bromine connected to the benzyl group was very active, and it was more convenient to introduce functional group to the benzene ring. PAEK-2-BrTM membrane has more outstanding mechanical properties with an elongation at break of 15.2% and a tensile stress at maximum load of 72.8 MPa. GPC results show no significant degrada-

tion after bromomeathylation. Furthermore, the TMPAEK-NOH, obtained from quaternary amination of PAEK-2-BrTM, showed excellent hydroxide conductivity (0.008 S cm^{-1}) and low-water uptake of 22.3% at 20°C and 32.6% at 60°C. A more detailed study of replacing bromine by nucleophilic substitution to functional groups used as anion exchange membrane will be reported soon.

References

1. Zhang, S. J.; Fu, L. X.; Yang, D. C.; Sun, H.; Wang, G. B.; Wu, Z. W. Chem J Chin Univ 2001, 22, 334.
2. Attwood, T. E.; Darrson, P. C.; Rose, J. B. Polymer 1981, 22, 1096.
3. Huang, Z. Z.; Yu, L. M.; Sheng, S. R.; Ge, W. W.; Liu, X. L.; Song, C. S. J Appl Polym Sci 2008, 108, 1049.
4. Moulinie, P.; Paroli, R. M.; Wang, Z. J. J Polym Sci Polym Chem 1995, 33, 2741.
5. Steven, M. K.; John, N. D.; Kurtz, S. M.; Devine, J. N. Biomaterials 2007, 28, 4845.
6. Schroder, K.; Meyer, A. P.; Keller, D.; Besch, W.; Babucke, G. Contrib Plasma Phys 2001, 41, 562.
7. Ilaria, C.; Nico, C.; Katja, N.; Paolo, V.; Qizhi, C.; Mary, P. R.; Aldo, R. B. Surf Coat Technol 2009, 203, 1349.
8. Koniger, T.; Munstedt, H. J Soc Inform Dis 2008, 16, 559.
9. Zaidi, S. M. J Arabian Sci Eng 2003, 28, 183.
10. Wang, J. H.; Zhao, Z.; Gong, F. X.; Li, S. H.; Zhang, S. B. Macromolecules 2009, 42, 871.
11. Shao, K.; Zhu, J.; Zhao, C. J.; Li, X. F.; Cui, Z. M.; Zhang, Y.; Na, H.; Xing, W. J Polym Sci Part A: Polym Chem 2009, 47, 5772.
12. Lin, H. D.; Zhao, C. J.; Cui, Z. M.; Ma, W. J.; Fu, T. Z.; Na, H.; Xing, W. J Power Sources 2009, 193, 507.
13. Zhang, Y.; Wan, Y.; Zhao, C. J.; Shao, K.; Zhang, G. Polymer 2009, 50, 4471.
14. Wang, F.; Roovers, J. Macromolecules 1993, 26, 5295.
15. Miyatake, K.; Zhou, H.; Watanabe, M. J Polym Sci Part A: Polym Chem 2005, 43, 1741.
16. Xu, T. J Membr Sci 2005, 263, 1.
17. Hibbs, M. R.; Fujimoto, C. H.; Cornelius, C. Macromolecules 2009, 42, 8316.
18. Yan, J. L.; Hickner, M. A. Macromolecules 2010, 43, 2349.
19. Xu, T.; Liu, Z. M.; Li, Y.; Yang, W. H. J Membr Sci 2008, 320, 232.
20. Xu, T.; Zha, F. F. J Membr Sci 1999, 203, 2002.
21. Wang, F.; Roovers, J. J Polym Sci Polym Chem 1994, 32, 2413.
22. Na, H.; Yuan, J.; Ni, Y. W.; Zhang, W. J.; Wu, Z. W.; Zhang, H. F.; Mo, Z. S. Chem Res Chin Univ 1997, 5, 23.
23. Lin, H. D.; Zhao, C. J.; Cui, Z. M.; Ma, W. J.; Li, H. T.; Na, H. J Membr Sci 2009, 345, 242.
24. Wu, D.; Fu, R. Q.; Xu, T. W.; Wu, L.W.; Yang, H. J Membr Sci 2008, 310, 522.
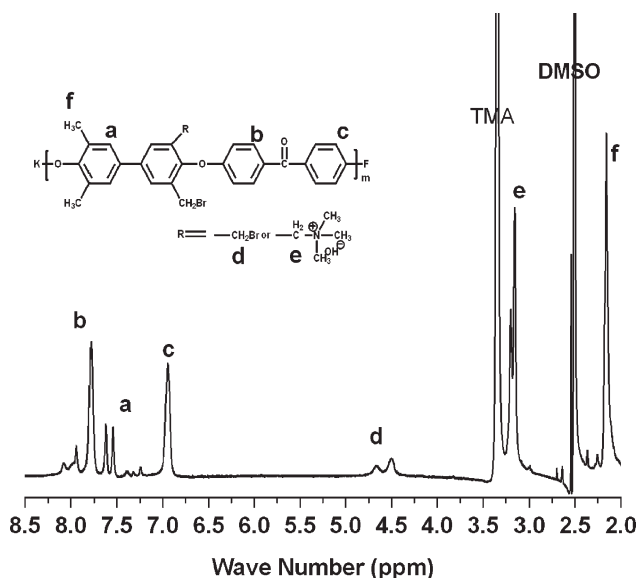
Figure 7 ^{1}H-NMR spectra of quaternary aminatied poly (arylene ether ketone)s in Dimethyl Sulfoxide-D6.