



# Synthesis of multi-block poly(arylene ether sulfone) copolymer membrane with pendant quaternary ammonium groups for alkaline fuel cell

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## ABSTRACT

A series of multi-block poly(arylene ether sulfone)s are synthesized via the copolymerization of bis(4-hydroxyphenol) sulfone, 3,3', 5,5'-tetramethylbiphenol and 4,4'-difluorodiphenyl sulfone. The resulting multi-block copolymers are brominated by using N-bromosuccinimide (NBS) as bromination reagent. The bromomethylated copolymer is solution cast to form clear, creasable films, and subsequent soaking of these films in aqueous trimethylamine to give benzyltrimethylammonium groups. The anion exchange membranes obtained by the solution hydroxide exchange with aqueous sodium hydroxide show varying degrees of ionic conductivity depending on their ion exchange capacity. The highest hydroxide conductivity  $0.029 \text{ S cm}^{-1}$  is achieved with the QBPEs-40 membrane having IEC value of  $1.62 \text{ mequiv g}^{-1}$  at room temperature and 100% RH. The obtained anion exchange membranes also have good mechanical properties and dimensional stability, which greatly facilitates the preparation of a MEA and the cell operation.

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## 1. Introduction

Anion exchange membrane fuel cells (AEMFCs) have been attracting extensive attention, for it can combine the advantage of proton exchange membrane fuel cells and traditional alkaline fuel cells [1]. They have the potential to solve the problems of catalyst cost and stability while obtaining high power and energy density by changing acidic medium into a basic one [2]. In basic condition, the cathode oxygen reduction over-potential will reduce substantially, resulting in high fuel cell efficiency. Non-noble metal catalysts can be used in AEMFCs because of the facile cathode kinetics, thus the cost of the fuel cell can be reduced significantly [3–6]. The polymer electrolyte membrane is an important part of fuel cells. It serves as the partition that separates the fuel from the oxidant and the support of the catalyst. However, there are no commercially available anion exchange membranes (AEMs) as Nafion does in the field of proton exchange membranes. For AEMFCs applications, AEMs need necessary conductivity, mechanical strength and chemical stability. At present, most commercial AEMs are based on cross-linked polystyrene, and they often blend with some other inert polymer or fabric supports to enhance mechanical properties. The cross-linked polystyrene is not very stable in basic environment and the inert

polymer or fabric supports cannot contribute to the conductivities, these drawbacks limit their further application in AEMFCs [7].

Many efforts have been direct to develop new AEMs materials. Partially or completely fluorinated polymers such as poly(ethylene-co-tetrafluoroethylene) (ETFE), poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), poly(vinylidene fluoride) (PVDF) [8–10], poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) [11–14], poly(phenylene) [15] poly(vinyl alcohol) [16,17], and poly(arylene ether sulfone) [18–21] have been investigated as candidates for AEM materials. Among these materials, poly(arylene ether sulfone) was considered as a promising material for AEMFCs application for their excellent mechanical, thermal and chemical stability [22,23]. The traditional synthetic route of poly(arylene ether sulfone) based AEMs typically included a chloromethylation reaction and quaternization step [18]. But the chloromethylation reaction needs toxic chloromethylation reagent, and gelation often occurs during the reaction. Hickner et al synthesized poly(arylene ether sulfone) with bromomethyl function group via bromination route, and prepared AEMs based on brominated poly(ether sulfone) [24]. This route avoided using toxic reagent, and got improved conductivities.

The conductivity is a key factor of AEMs. In the research of proton exchange membranes, it had been found that ionomers with ordered microphase structure could form better ionic transport tunnels and have higher conductivities [25]. There are two main methods to obtain proton exchange membranes with ordered microphase structure. First, synthesizing block copolymer membrane materials [26–30]. Second, making the ionic groups distribute densely on the polymer backbone [31–34]. Most of the

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previous research of AEMs dealt with random copolymers, and there have no report on block copolymers. In this article, we prepared AEMs based on multi-block poly(arylene ether sulfone). To investigate the effect of copolymers structure on conductivity, AEMs based random copolymers and sequence copolymers with similar ionic exchange capacity were prepared, and we found that AEMs based on block copolymer show the highest conductivity among the three kind AEMs.

## 2. Materials and methods

### 2.1. Materials

Bis(4-hydroxyphenyl) sulfone (BPS), 3,3',5,5'-tetramethyl-4,4'-biphenol (TMBP) and 4,4'-difluorodiphenyl sulfone were purchased from Aldrich. N-Bromosuccinimide (NBS) and azodiisobutyronitrile (AIBN) were purchased from Institute of Chemical Engineering of Beijing (China). N-Methyl-2-pyrrolidinone (NMP) was stirred over CaH<sub>2</sub> for 24 h, then distilled under reduced pressure, and stored over 4 Å molecular sieves. All other reagents were obtained from commercial sources and used as received.

### 2.2. Synthesis of multi-block poly(arylene ether sulfone)s containing tetramethyl groups (BPES-y)

The block copolymers were synthesized via a typical procedure. Firstly, the F-terminated oligomers and the phenol-terminated oligomers were synthesized independently. Then the oligomers were mixed and block copolymer was prepared via nucleophilic substitution reaction. Taking the synthesis procedure of BPES-40, where 40 refers to the feed percent of TMBP, as an example: to a 100 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a Dean-Stark trap with a condenser were added TMBP (0.9692 g, 4 mmol), 4,4'-difluorodiphenyl sulfone (0.9153 g, 3.6 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (1.3821 g, 10 mmol), NMP 10 mL, and toluene 15 mL. The mixture was kept at room temperature with stirring to make the monomers dissolve in NMP adequately. After that the mixture was allowed to reflux for 4 h, and then the toluene was removed. The reaction mixture was heated to 170 °C for 16 h. To another 100 mL three-necked flask with same equipment, were added BPS (1.5016 g, 6 mmol), 4,4'-difluorodiphenyl sulfone (1.6272 g, 6.4 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (1.3821 g, 10 mmol), NMP 10 mL, and toluene 15 mL. The procedure was the same as previous. Then the two kind oligomers were mixed after cooled to room temperature. The polymerization was carried out at 180 °C for 16 h. After cooling to room temperature, the mixture was diluted with 15 mL NMP and filtered to remove the salt byproduct. The copolymer was isolated by precipitation in deionized water and washed with hot water three times. The fiber-like copolymer was dried under vacuum before used. Yield: 98%.

### 2.3. Synthesis of sequence poly(arylene ether sulfone)s containing tetramethyl groups (SPES-y)

The sequence copolymers were synthesized as follows: firstly, the TMBP unit oligomers were prepared. After that, BPS and 4,4'-difluorodiphenyl sulfone were added to the reaction mixture, and sequence copolymers were prepared. Taking the synthesis procedure of SPES-40 as an example: to a 100 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a Dean-Stark trap with a condenser were added TMBP (0.9692 g, 4 mmol), 4,4'-difluorodiphenyl sulfone (0.9153 g, 3.6 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (1.3821 g, 10 mmol), NMP 20 mL, and toluene 15 mL. The mixture was heated to reflux for 4 h, and then toluene was removed. The mixture was heated to 180 °C for 16 h. After that, the mixture was cooled to room temperature, and BPS (1.5016 g,

6 mmol), 4,4'-difluorodiphenyl sulfone (1.6272 g, 6.4 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (1.3821 g, 10 mmol), NMP 10 mL were added into it. The following step was similar as the foregoing. The sequence copolymer was isolated by precipitated in deionic water. The copolymer was washed with hot water several times and dried under vacuum before used.

### 2.4. Synthesis of random poly(arylene ether sulfone)s containing tetramethyl groups (RPES-y)

The random copolymers with different molar ratio of TMBP to BPS were synthesized via nucleophilic substitution reaction. Taking the synthesis procedure of RPES-40 as an example: To a 100 mL three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a Dean-Stark trap with a condenser were added TMBP (0.9372 g, 4 mmol), BPS (1.5016 g, 6 mmol), 4,4'-difluorodiphenyl sulfone (2.5425 g, 10 mmol), anhydrous K<sub>2</sub>CO<sub>3</sub> (2.7642 g, 20 mmol), NMP 10 mL, and toluene 15 mL. The mixture was kept at room temperature with stirring to make the monomers dissolve in NMP adequately. After that the mixture was allowed to reflux for 4 h, and then the toluene was removed. The reaction mixture was heated to 170 °C for 8 h. After cooling to room temperature, the mixture was diluted with 15 mL NMP and filtered to remove the salt byproduct. The copolymer was isolated by precipitation in deionized water and washed with hot water three times and dried under vacuum before used.

### 2.5. Synthesis of bromomethylated poly(arylene ether sulfone)s

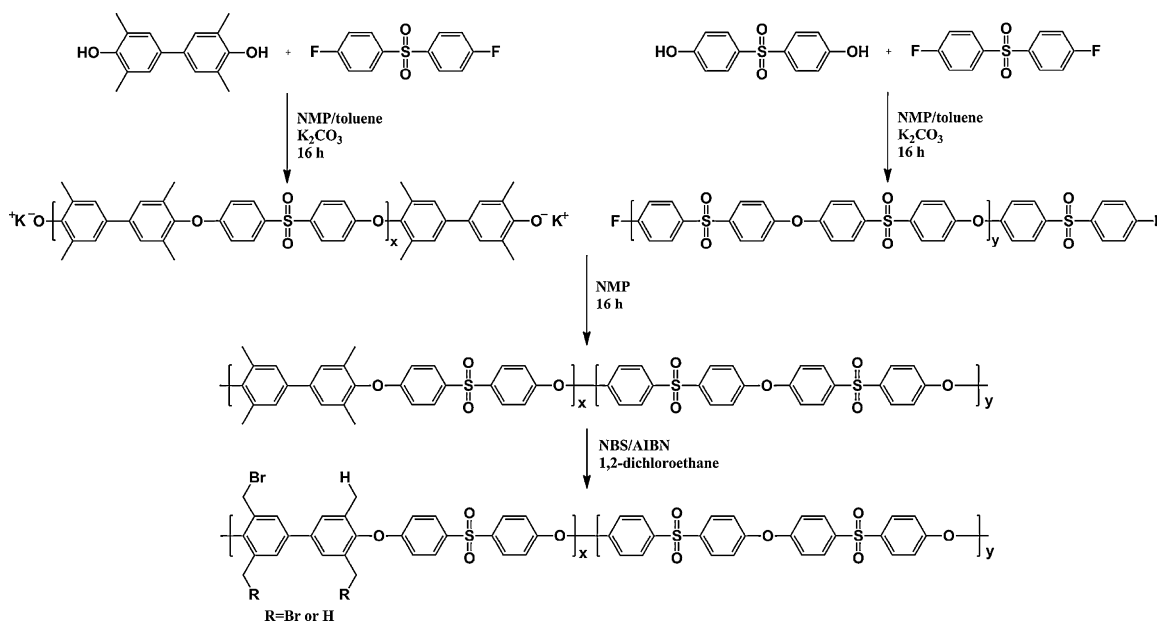
A typical procedure for preparing random bromomethylated copolymer RPES-40 (RPESBr-40) was as follows. To a three-necked flask equipped with mechanical stirrer, nitrogen inlet and condenser were added RPES-40 (2.0 g) and 40 mL 1,2-dichloroethane. The mixture was stirred adequately to form homogeneous solution. Then NBS (1.66 g, 9 mmol) and AIBN (0.1 g) were added to the solution. The solution was heated to 80 °C for 8 h, after the NBS and AIBN dissolved. The mixture was cooled to room temperature and coagulated in ethanol with vigorous stirring. The resulting polymer was washed with ethanol several times and dried under vacuum for 24 h at 40 °C. The sequence and block bromomethylated copolymers were prepared in the same procedure.

### 2.6. Preparation of the anion exchange membranes

The bromomethylated copolymer (0.6 g) was dissolved in 10 mL N,N-dimethylacetamide (DMAc). The solution was filtrated and cast onto a flat glass plate. The membrane was dried at 80 °C for 12 h, and at 100 °C under vacuum for 24 h to remove the casting solvent. Then it was peeled off and immersed in 33% trimethylamine aqueous solution for 48 h at 30 °C to make the membrane quaternary-aminated. After that the membrane was kept in 1 mol L<sup>-1</sup> NaOH aqueous solution for 48 h to obtain OH<sup>-1</sup> form membrane. Finally, the membrane was wash thoroughly and immersed in deionized water for 48 h to remove residual NaOH. The quaternary-aminated membrane was kept in deionized water before used.

### 2.7. Measurement

<sup>1</sup>H NMR spectra were measured at 300 MHz on an AV300 spectrometer. The reduced viscosities were determined with an Ubbelohde capillary viscometer at 30 ± 0.1 °C on 0.5 g dL<sup>-1</sup> concentrations of polymer in NMP. Thermogravimetric analysis (TGA) was performed in nitrogen or air atmosphere with a Perkin-Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C min<sup>-1</sup>. Molecular weights of brominated poly(arylene ether sulfone)s



Scheme 1. The synthetic route of BPESBr-*y* copolymers.

were also determined by gel permeation chromatography (GPC) using a Waters 515 HPLC pump, coupled with a Waters 410 differential refractometer detector and a Waters 996 photodiode array detector operating at a wavelength of 260 nm.  $\text{CHCl}_3$  was used as eluent. Tensile measurements were carried out with an Instron-1211 mechanical testing instrument at a speed of  $10 \text{ mm min}^{-1}$ .

The IECs of the copolymer membranes in  $\text{OH}^{-1}$  form were measured by titration. The  $\text{OH}^{-1}$  form membranes were immersed in 100 mL HCl (0.02 M) standard for 48 h. Then the HCl solution was titrated with a standardized NaOH solution using phenolphthalein as an indicator.

The water uptake and swelling ratio of the copolymer membranes were measured as follows: The membranes were dried under vacuum at  $100^\circ\text{C}$  until their weight did not change any more to obtain dry materials. They were immersed in deionized water for 4 h at a given temperature. Then the membranes were wiped with tissue paper, and measured their weight quickly. The water uptake (WU) of QXPES-*y* membranes were calculated according to:

$$\text{WU (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100 \quad (1)$$

where  $W_{\text{dry}}$  and  $W_{\text{wet}}$  are the weight of the dry and the corresponding water-swollen membranes, respectively.

The dry membranes were chopped into circular samples, and measured their diameter. Then the samples were immersed in deionized water for 4 h at given temperature. They were taken out and measured their diameter and thickness. The swelling ratio (SR) of the membranes was calculated from:

$$\text{SR (\%)} = \frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} \times 100 \quad (2)$$

Here,  $l_{\text{dry}}$  and  $l_{\text{wet}}$  are the lengths of the dry and wet samples, respectively.

The hydroxide conductivities ( $\sigma$ ,  $\text{Scm}^{-1}$ ) of the copolymer membranes (size:  $1 \text{ cm} \times 4 \text{ cm}$ ) were obtained using  $\sigma = d/L_s W_s R$  ( $d$ : distance between reference electrodes, and  $L_s$  and  $W_s$  are the thickness and width of the membrane respectively). Here, ohmic resistance ( $R$ ) was measured by four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (Solatron 1260) and an electrochemical interface (Solatron 1287, Farnborough

Hampshire, ONR, UK). The membranes were sandwiched between two pairs of gold-plate electrodes. 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 thermo-controlled chamber in liquid water for measurement. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in liquid water. All samples were equilibrated in water for at least 24 h prior to measurement. At a given temperature, the samples were equilibrated for at least 30 min before any measurements. Repeated measurements were then taken at that given temperature with 10-min interval until no more change in conductivity was observed.

### 3. Results and discussion

#### 3.1. Synthesis and characterization of the copolymers

The synthetic route of bromomethylated multi-block poly(arylene ether sulfone)s is shown in Scheme 1. The TMBP and BPS unit oligomers were synthesized independently, and then the oligomers were mixed. The polymerization was carried out for 16 h at  $180^\circ\text{C}$ . For the preparation of sequence copolymers, the TMBP unit oligomers were synthesized firstly, after that BPS and 4,4'-difluorodiphenyl sulfone were added to the reaction mixture, then the sequence copolymers were obtained via nucleophilic substitution polycondensation. For all the TMBP unit oligomers, the length was controlled in 10 repeat units. For the BPS unit oligomers, the length was controlled in 15 (BPES-40) and 20 (BPES-20). The random copolymers were prepared by polycondensation of 4,4'-dichlorodiphenyl sulfone, BPS and TMBP. The  $^1\text{H}$  NMR spectra of the TMBP unit oligomer and BPS unit oligomer in  $\text{CDCl}_3$  are shown in Fig. 1. For the TMBP unit, the peaks at  $\delta$  2.1 could be assigned to the protons on methyl. The peaks at  $\delta$  6.8, 7.7 and 7.3 were attributed to the chemical shifts of Ar-H which attached to sulfone groups and Ar-H at ortho position of methyl, respectively. For the BPS unit, the peaks at  $\delta$  7.1 and 8.0 were assigned to the protons of meta position and ortho position Ar-H of sulfone group. The  $^1\text{H}$  NMR spectra of sequence (SPES-40) and block (BPES-40) copolymers are shown in Fig. 2. The chemical shifts of both TMBP and BPS repeat unit can be found in the spectrum. The bromomethylated poly(arylene ether sulfone)s

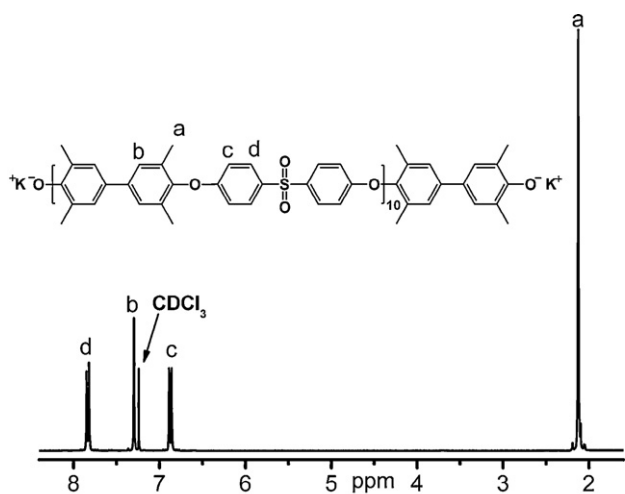


Fig. 1. The  $^1\text{H}$  NMR spectra of TMBP unit and BPS unit oligomer in  $\text{CDCl}_3$ .

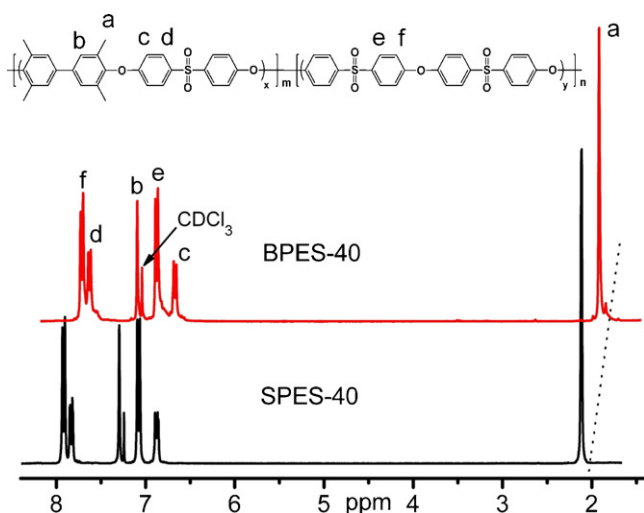


Fig. 2. The  $^1\text{H}$  NMR spectra of BPES-40 and SPES-40 in  $\text{CDCl}_3$ .

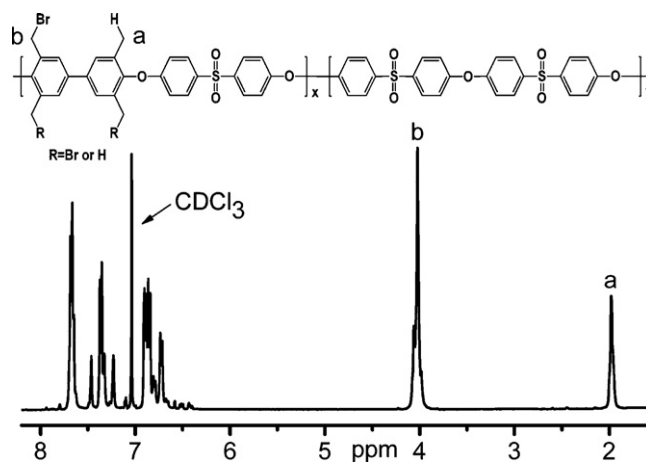


Fig. 3. The  $^1\text{H}$  NMR spectra of RPESBr-40 in  $\text{CDCl}_3$ .

were prepared using NBS as the bromination reagent and AIBN as the initiator. The reaction temperature was  $80^\circ\text{C}$ , the reaction time was 8 h, and 1.0 equiv of NBS to  $\text{Ar}-\text{CH}_3$  was used. Fig. 3 shows the  $^1\text{H}$  NMR spectrum of BPESBr-40. The peaks at about  $\delta$  2.0 are the chemical shift of the methyl groups. The peaks at about  $\delta$  4.5 are the chemical shift of protons on the bromomethyl. The degree of functionalization (DF) is calculated from the ratio of the signal intensity of  $-\text{CH}_2\text{Br}$  to the sum of  $-\text{CH}_3$  and  $-\text{CH}_2\text{Br}$ . Other bromomethylated copolymers' DF was calculated in the same way. Table 1 summarizes the DF, inherent viscosity and GPC data of the bromomethylated copolymers. The DF value of the copolymers was in range of 70–79%. As shown by inherent viscosity and GPC, all the copolymers have high molecular weight. The random copolymers' typical number average molecular weight ranged from 87,000 to 90,000, and for the sequence and block copolymers, it ranged from 55,000 to 74,000.

### 3.2. Thermal stability of the copolymer containing quaternary ammonium groups

Films of the bromomethylated copolymers were prepared by casting dimethylacetamide (DMAc) solution under vacuum at  $80^\circ\text{C}$  for 12 h, and  $100^\circ\text{C}$  for 24 h. These films were then immersed in an aqueous solution of trimethylamine to form the quaternary ammonium functional groups by substitution of the bromine atoms in the bromomethyl groups. The copolymer membranes (in the hydroxide form) were obtained by treating quaternary ammonium membranes in an excess of 1 M NaOH (aq) at  $30^\circ\text{C}$  for two days. The thermal stability of all the AEMs was determined by TGA technique in nitrogen atmosphere. The TGA curves of the AEMs are shown in Fig. 4. Because the membrane became hydrophilic after quaternary-

**Table 1**  
Inherent viscosity, molecular weight and DF of the bromomethylated copolymers.

Sample <sup>a</sup>	$\eta_{\text{inh}}$ ( $\text{dL g}^{-1}$ ) <sup>b</sup>	$M_n \times 10^4$ $\text{g mol}^{-1}$	$M_w \times 10^4$ $\text{g mol}^{-1}$	PD <sup>c</sup>	DF (%) <sup>d</sup>
RPES-20	0.55	9.1	14.9	1.63	70.2
RPES-40	0.60	10.4	17.0	1.64	72.3
SPES-20	0.49	9.0	16.3	1.61	79.3
SPES-40	0.45	8.7	14.3	1.64	77.5
BPES-20	0.42	7.4	13.5	1.65	76.5
BPES-40	0.40	5.5	10.6	1.68	74.6

<sup>a</sup> RPES, SPES, and BPES represent random, sequence and block copolymer, respectively. The number (20 or 40) is the molar percentage of TMBP in the feed.

<sup>b</sup> Inherent viscosity measured at a concentration of  $0.5 \text{ g dL}^{-1}$  in NMP at  $30^\circ\text{C}$ .

<sup>c</sup> Polydispersity.

<sup>d</sup> Degree of functionalization calculated from  $^1\text{H}$  NMR spectra.

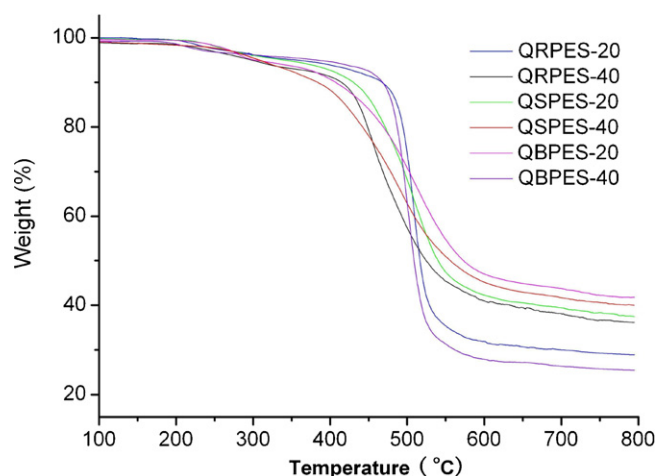


Fig. 4. The TGA curves of XPES-y membranes in N<sub>2</sub>.

aminated and absorbed water from the atmosphere, slight weight loss between 50 and 120 °C, which corresponded to the evaporation of absorbed water, was observed. The similar behavior has been also found in other polymeric ion exchange membranes. As shown in Fig. 4, all the AEMs have two thermal degradation steps except for the loss of absorbed water. The first weight loss starting from 200 °C is related to the degradation of quaternary ammonium groups, and the second weight loss starting from 300 °C is related to the degradation of the polymer backbone. The thermal stability of the AEMs is lower than poly(arylene ether sulfone)s without quaternary ammonium groups. This behavior is similar to the previous report [35].

### 3.3. IEC, water uptake and dimension stability of the AEMs

The IEC value, water uptake and swelling ratio of the AEMs are listed in Table 2. The theoretical value of IEC was calculated according to DF assuming that all the benzyl bromide groups are converted to benzyltrimethylammonium groups and all the bromide ions are exchanged for hydroxide ions. The experimental value was obtained by titration method. The theoretical IEC value is controlled at about 1.35 and 2.10 mequiv g<sup>-1</sup>, and the experimental IEC value is at about 1.00 and 1.50 mequiv g<sup>-1</sup>. It can be concluded by comparing the theoretical IEC values to the experimental IEC values of the membranes that 70–75% benzyl bromide can be converted to benzyltrimethylammonium groups in hydroxide form. The similar result was reported previously in the quaternization process of chloromethylated polysulfone under the similar conditions [21]. This is because the quaternization process was carried out in solid membranes rather than in solutions, the benzyl bromide groups cannot contact with trimethylamine adequately,

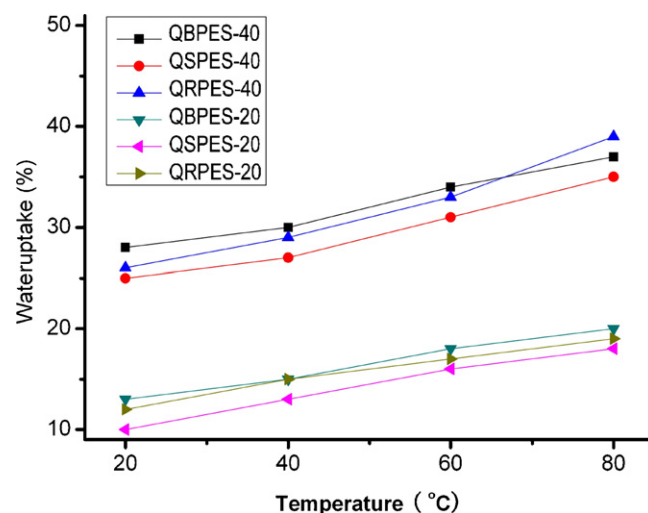


Fig. 5. Water uptake curves of XPES-y membranes at different temperature.

although the membranes became more hydrophilic and took up water in the quaternization process, some of bromomethyl groups do not come into contact with the aqueous trimethylamine reagent [15].

The water uptake values of the AEMs in hydroxide form were measured at 20 °C, 40 °C, 60 °C and 80 °C as presented in Fig. 5. The water uptake values for all the membranes are increased with the increasing of IEC, and there is no significant difference among the three series AEMs at similar IEC. It can be also found that the AEMs have higher water uptake values at higher temperature. Take QRPEs-40 membrane as an example, the water uptake value is 19% at 20 °C, 20% at 40 °C, 25% at 60 °C, and 27% at 80 °C. In general, the AEMs showed lower water uptakes than previously reported AEMs prepared from chloromethylated polysulfone. For example, with the same IEC of 1.62 mequiv g<sup>-1</sup>, QXPES-40 shows a smaller water uptake (<30%) than AEMs prepared from chloromethylated polysulfone (>40%) [21]. The lower water uptake of QXPES-y would be caused by its longer hydrophobic segments compared to chloromethylated polysulfone based AEMs.

The swelling ratio is a parameter that relate to the mechanical properties of the AEMs. The AEMs cannot be used in cell applications if it swells too much in water. The swelling ratio data in the lengthwise direction of AEMs are listed in Table 2. It can be found from these data that the AEMs have good dimension stability. For example, the swelling ratio of QBPEs-40 is 12% at 20 °C, which is much lower than that of chloromethylated polysulfone based membrane with the similar IEC [21]. All the obtained AEMs have good mechanical strength as shown in Table 3. Taking QBPEs-20 as an example, the tensile strength is 60.3 MPa, tensile modulus

Table 2

IEC, water uptake, swelling ratio and hydroxide conductivity of the QXPES-y membranes.

Sample (S cm <sup>-1</sup> ) <sup>a</sup>	IEC (mequiv g <sup>-1</sup> )		Water uptake (%)		Swelling ratio (%) <sup>d</sup>		Conductivity
	Theoretical <sup>b</sup>	Experimental <sup>c</sup>	20 °C	60 °C	20 °C	60 °C	
QRPEs-20	1.32	0.96	12	17	4	4	0.009
QRPEs-40	2.09	1.50	26	32	10	12	0.021
QSPES-20	1.35	1.04	10	15	4	5	0.019
QSPES-40	2.21	1.56	25	30	9	12	0.027
QBPEs-20	1.40	1.12	13	18	6	7	0.021
QBPEs-40	2.14	1.62	27	33	12	14	0.029

<sup>a</sup> QRPEs, QSPES and QBPEs represent the quaternary-aminated RPES, SPES, and BPES membranes respectively.

<sup>b</sup> Calculated from <sup>1</sup>H NMR spectra.

<sup>c</sup> Determined by titration.

<sup>d</sup> The swelling ratio was in the lengthwise direction.

**Table 3**  
Mechanical properties of the QXPS-x membranes<sup>a</sup>.

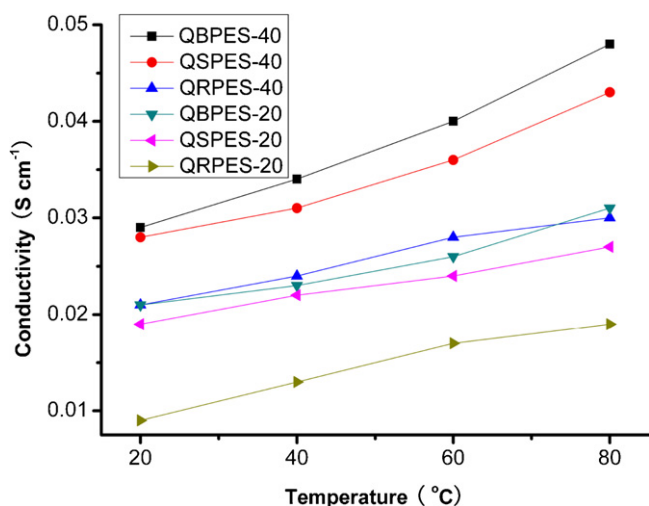
Sample	Tensile strength (MPa)	Tensile modulus (GPa)	Elongation at break (%)
QRPES-20	57.2	1.37	7.7
QRPES-40	68.2	1.43	15.3
QSPES-20	65.9	1.53	7.0
QSPES-40	67.4	1.32	13.2
QBPE-20	60.3	1.45	8.2
QBPE-40	38.8	0.86	20.2

<sup>a</sup> The samples were measured at 30 °C, 100% RH.

is 1.45 GPa and elongation at break is 8.2%. These results indicate that all the AEMs were tough and ductile enough for potential use as AEM materials.

### 3.4. Hydroxide conductivities of the AEMs

The hydroxide conductivities of the QXPES-y membranes at 100% RH as a function of temperature are displayed in Fig. 6. In general, conductivity above  $10^{-2} \text{ S cm}^{-1}$  is required for anion exchange membrane materials used in alkaline fuel cells. Almost all the obtained membranes' conductivities are above  $10^{-2} \text{ S cm}^{-1}$  at room temperature. The conductivities of the AEMs were increased with IEC and temperature, which was similar as the trend of water uptake. Not surprisingly, the conductivities of the AEMs are higher than that of AEMs prepared from chloromethylated polysulfone and random polymers with the similar IEC. For example, the conductivity of QBPE-40 membrane (experimental IEC  $1.62 \text{ mequiv g}^{-1}$ ) is  $0.029 \text{ S cm}^{-1}$ , which is almost twice of that of chloromethylated polysulfone ( $0.01 \text{ S cm}^{-1}$ , IEC =  $1.50 \text{ mequiv g}^{-1}$ ) [21] and random copolymer ( $0.015 \text{ S cm}^{-1}$ , IEC =  $1.58 \text{ mequiv g}^{-1}$ ) [35] based AEMs with the similar IEC. As we expected, the QBPE-y membranes showed the highest conductivity among the three series AEMs with the similar IEC. For example, the conductivities at room temperature of QRPE-40, QSPES-40 and QBPE-40 are  $0.021 \text{ S cm}^{-1}$ ,  $0.027 \text{ S cm}^{-1}$  and  $0.029 \text{ S cm}^{-1}$  respectively. It was proposed that the block copolymer proton exchange membranes with hydrophilic and hydrophobic segments could form continuous, ion-rich hydrophilic domains, namely, ion transport channel, and have high proton conductivity [26–30]. We speculated that the anion exchange copolymer membranes may form the ion transport channel.



**Fig. 6.** Conductivity curves of XPES-y membranes at different temperature.

## 4. Conclusions

Three series of bromomethylated poly(arylene ether sulfone)s were synthesized by the aromatic nucleophilic substitution and followed by the bromination reactions. The resulting bromomethylated poly(arylene ether sulfone)s was solution cast to form clear, creasable films, and subsequent soaking of these films in aqueous trimethylamine gave quaternary ammonium poly(arylene ether sulfone)s. The ionic conductivities of the copolymer membranes with IEC value at about  $1.50 \text{ mequiv g}^{-1}$  are over  $10^{-2} \text{ S cm}^{-1}$  at room temperature, which fulfills the basic requirement of fuel cells. By comparing the conductivities of the random, sequence and block copolymer membranes with the similar IEC value, it was found that the block copolymer membrane displayed the highest anion conductivity. The block membrane QBPE-40 displayed high room temperature conductivity of  $0.029 \text{ S cm}^{-1}$  but low swelling ratio of 12% which indicate the anion exchange membrane with high conductivity and good dimensional stability could be achieved by designing and synthesizing the block copolymer membranes.

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