

Chloromethylation and Quaternization of Poly(aryl ether ketone sulfone)s with Clustered Electron-rich Phenyl Groups for Anion Exchange Membranes

Lei Xiong^a, Yuan-Fang Hu^a, Zi-Gui Zheng^a, Zai-Lai Xie^{b*}, and Dong-Yang Chen^{a*}

^a College of Materials Science and Engineering, Fuzhou University, Fuzhou 350116, China

^b College of Chemistry, Fuzhou University, Fuzhou 350116, China

Abstract Ion segregation is critically important for achieving high ion conductivity for anion exchange membranes (AEMs). Herein, a new bisphenol monomer bearing ten electron-rich phenyl groups was designed and polymerized with various amounts of electron-deficient 4,4'-dihydroxydiphenylsulfone and 4,4'-difluorobenzophenone to yield dense and selective reaction sites for chloromethylation and quaternization. As the most challenging step, chloromethylation was optimized by tuning the reaction temperature, reaction time, and reactant ratios. Ion exchange capacity, water uptake, anion conductivity, mechanical stability, and alkaline stability of the resulting AEMs were characterized in detail. It is found that chloromethylation reaction needed to be carried out at low equivalent of chloromethylation agents to avoid undesirable crosslinking. The QA-PAEKS-20 sample with an IEC of 1.19 mmol·g⁻¹ exhibited a Cl⁻ conductivity of 11.2 mS·cm⁻¹ and a water uptake of 30.2% at 80 °C, which are promising for AEM applications.

Keywords Anion exchange membrane; Chloromethylation; Poly(aryl ether); Ion-segregation; Anion conductivity

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INTRODUCTION

Polymer electrolyte membrane fuel cells have attracted widespread attention as clean power sources for transportations in recent years.^[1–3] Two major types among them, namely proton exchange membrane fuel cells (PEMFCs) and anion exchange membrane fuel cells (AEMFCs), are extensively investigated. As a key component of the fuel cells, the membrane, either proton exchange membrane (PEM) or anion exchange membrane (AEM), separates the positive and negative electrodes from direct contact while allowing the transport of specific ions (H⁺ for PEM and OH⁻ for AEM) across it to complete the circuit during cell operation. The most well-known PEM is Nafion®, which exhibits excellent chemical stability, moderate mechanical strength, and outstanding proton conductivity.^[4,5] However, it has a high cost itself and requires the use of noble metal as catalyst, which restricts its commercial application in electric vehicles. Therefore, many works have been devoted to the development of alternative PEMs and lately AEMs to lower the capital cost and improve the cell performance.^[6–8]

The adoption of AEMs in fuel cells not only enables the use of non-noble catalyst but also improves the kinetic of oxygen

reduction.^[9–14] By means of rational molecular design, high anion conductivity and good mechanical integrity can be achieved. The polymeric backbone structure and the cationic group species are the two main aspects for molecular design. To date, a variety of polymer backbones, such as poly(phenylene oxide)s,^[15,16] poly(phenylene)s,^[17] polyimides,^[18] polystyrenes,^[19] poly(aryl ether)s,^[20,21] and poly(olefin)s,^[22] and a variety of cationic groups, such as quaternary ammonium,^[23,24] imidazolium,^[25,26] pyrrolidinium,^[27] guanidinium,^[28] and phosphonium^[29,30] groups, have been reported. The different combinations of the polymer backbone and cationic group have given rise to a broad range of different properties of the resultant AEMs.

Generally, ion conductivity can be increased by increasing ion exchange capacity (IEC) of ionomers. A membrane that has no distinct hydrophilic-hydrophobic phase separation requires a high value of IEC to obtain considerable ion conductivity. However, large water uptake and severe swelling are also encountered at high IECs. To balance the ion conductivity and dimensional stability, many strategies focusing on the development of ion-segregated structures have been reported. For example, Chen *et al.*^[31] prepared a series of poly(aryl ether)s with clustered quaternary ammonium groups. A superior Br⁻ conductivity of 5.2 mS·cm⁻¹ was achieved at an IEC of 2.23 mmol·g⁻¹ at 25 °C. Zhang *et al.*^[32] prepared poly(arylene ether sulfone)s with hydrophilic-hydrophobic multi-

* Corresponding authors, E-mail: zlxie@fzu.edu.cn (Z.L.X.)

E-mail: dongyang.chen@fzu.edu.cn (D.Y.C.)

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block structures. A high OH^- conductivity of $29 \text{ mS}\cdot\text{cm}^{-1}$ was achieved at an IEC of $1.62 \text{ mmol}\cdot\text{g}^{-1}$ at room temperature. Shen *et al.*^[33] prepared a series of comb-shape poly(arylene ether ketone)s with hyperquaternized pendant chains. A good Cl^- conductivity of $13 \text{ mS}\cdot\text{cm}^{-1}$ was achieved at an IEC of $1.58 \text{ mmol}\cdot\text{g}^{-1}$ at 20°C .

Poly(aryl ether)s have been widely studied as the backbones of AEMs for their low production cost plus good thermal and chemical stabilities.^[34,35] In addition, poly(aryl ether)s can be easily functionalized with benzyl quaternary ammonium groups by chloromethylation and quaternization in tandem.^[24,36,37] To enhance ion segregation for high anion conductive AEMs, herein, a new bisphenol monomer bearing ten electro-rich phenyl groups was designed and polymerized with electron-deficient monomers to yield an unique poly(aryl ether) backbone, namely poly(aryl ether ketone sulfone). Due to different electron densities, the subsequent chloromethylation/quaternization can be selectively directed to the new monomer segments, leading to the formation of highly clustered cationic groups. The reaction conditions and properties of the resulting AEMs have been studied in detail.

EXPERIMENTAL

Materials

N,N-dimethylformamide (DMF), *N,N*-dimethylacetamide (DMAc), 1,3-dimethyl-2-imidazolidinone (DMI), 4-phenoxyphenol, boron tribromide, dimethoxymethane (DMM), thionyl chloride, tin(IV) chloride ($1.0 \text{ mol}\cdot\text{L}^{-1}$ in methylene chloride), 1,1,2,2-tetrachloroethane, 1,2-dichloroethane, dichloromethane, chloroform, calcium hydride, potassium carbonate, trimethylamine aqueous solution (30 wt%), ethyl acetate, cyclohexane, ethanol, toluene, methanol, 4,4'-difluorobenzophenone, and 4,4'-dihydroxydiphenylsulfone were obtained from commercial sources and used as received. 4,4'-((Perfluoro-1,4-phenylene)bis(oxy))bis(methoxybenzene) (compound **a**) was synthesized according to our previous report.^[38]

Monomer Synthesis

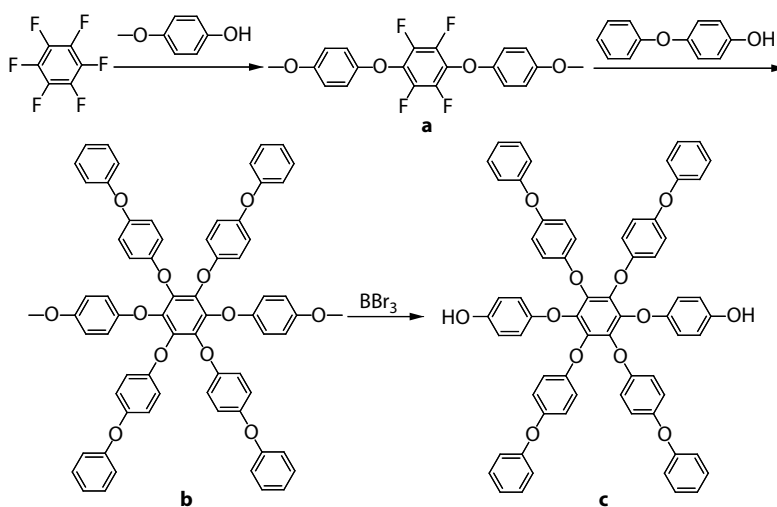
The synthesis of new bisphenol monomer bearing ten electron-rich phenyl groups is depicted in Scheme 1. To a 25 mL three-

necked round-bottom flask equipped with a magnetic stirrer, a condenser and a Dean-Stark trap, compound **a** (2.37 g, 6 mmol), 4-phenoxyphenol (6.70 g, 36 mmol), potassium carbonate (4.97 g, 36 mmol), DMI (24 mL), and toluene (15 mL) were charged. The mixture was stirred at $145\text{--}150^\circ\text{C}$ for 2 h to remove the produced water. Then, the reaction mixture was heated at $160\text{--}165^\circ\text{C}$ for 24 h and 220°C for another 24 h. Finally, the reaction mixture was poured slowly into $1 \text{ mol}\cdot\text{L}^{-1}$ NaOH aqueous solution to precipitate the crude product of compound **b**, which was filtrated and purified by column chromatography on silica gel (dichloromethane:hexane = 1:2, V:V). Yield: 59%.

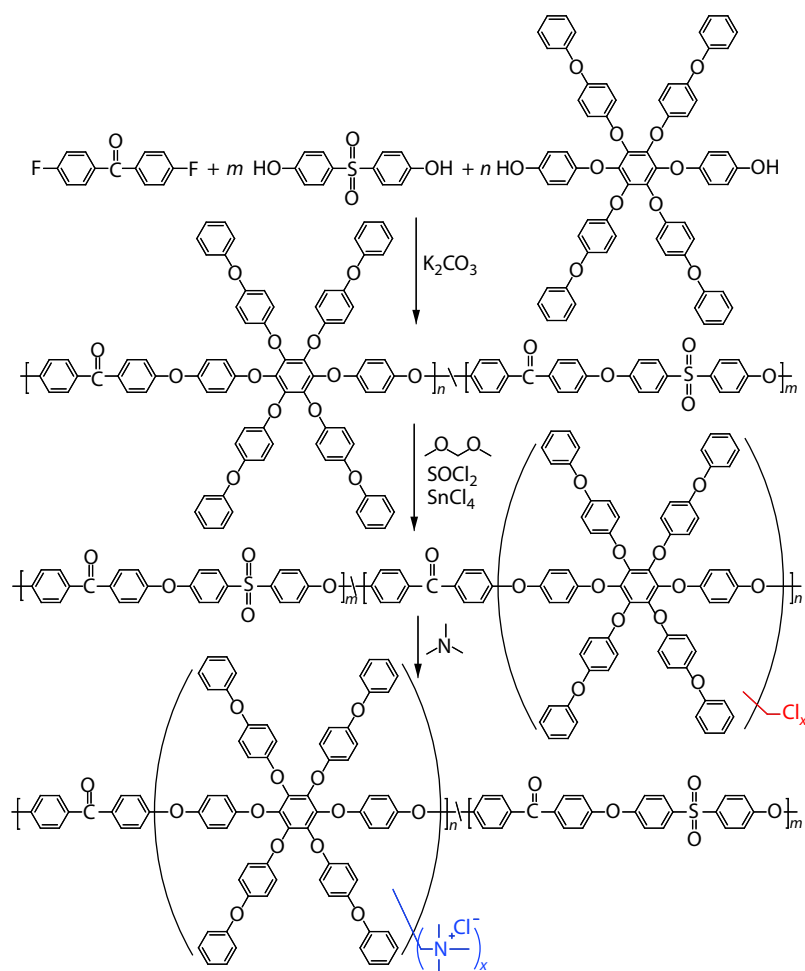
To a 50 mL three-necked round-bottom flask, compound **b** (1.06 g, 1 mmol) and 20 mL of dry dichloromethane were charged. The solution was cooled to about -78°C and 2.4 mL of BBr_3 (2.4 mmol) was added dropwise. The reaction was maintained at -78°C for 1 h and at room temperature for another 12 h. Then, the reaction mixture was diluted with CH_2Cl_2 , extracted with water, and concentrated under vacuum. The obtained solid was purified by column chromatography on silica gel (ethyl acetate:hexane = 1:5, V:V). 0.95 g of the bisphenol monomer bearing ten electron-rich phenyl groups (compound **c**) was then obtained with a yield of 92%.

Polymerization

Poly(aryl ether ketone sulfone)s (PAEKSs) were synthesized through polycondensation of compound **c** with 4,4'-dihydroxydiphenylsulfone and 4,4'-difluorobenzophenone, as depicted in Scheme 2. Typically, to a 25 mL three-necked round-bottom flask equipped with a Dean-Stark trap, condenser, magnetic stirrer, and gas inlet and outlet were charged 4,4'-difluorobenzophenone (1.3092 g, 6 mmol), 4,4'-dihydroxydiphenylsulfone (1.2014 g, 4.8 mmol), compound **c** (1.2373 g, 1.2 mmol), potassium carbonate (1.2447 g, 9 mmol), 16 mL of solvent DMAc, and toluene (6 mL). The reaction mixture was heated at $145\text{--}150^\circ\text{C}$ for 2 h to remove the produced water and 170°C for 16 h to polymerize. Finally, the reaction mixture was cooled and poured into deionized water (500 mL) to precipitate the product PAEKS-20. Changing the above loading amounts of 4,4'-dihydroxydiphenylsulfone and compound **c** to 5.4 and 0.6 mmol yielded PAEKS-10 (10 mol% of compound **c** in bisphenol monomers).



Scheme 1 Synthetic route to the bisphenol monomer bearing ten electron-rich phenyl groups.



Scheme 2 Synthetic routes to PAEKs, CM-PAEKs, and QA-PAEKs.

Chloromethylation of PAEKs

The PAEKs were chloromethylated by dimethoxymethane (DMM), SOCl_2 , and SnCl_4 . A typical procedure of chloromethylation reaction is as follows. PAEKs-20 (1.0 g) and 1,1,2,2-tetrachloroethane (20 mL) were charged into a 50 mL three-necked round bottom flask equipped with gas inlet and outlet. After the copolymer dissolved completely, 3 mL of DMM was added slowly under vigorous magnetic stirring. Then, 2.4 mL of SOCl_2 and 0.2 mL of SnCl_4 were added dropwise to the mixture. The reaction was carried out at room temperature for 48 h to obtain light red mixture. The reaction mixture was poured into 500 mL of methanol to precipitate a fibrous product. After being dried at 60 °C under vacuum for 24 h, the chloromethylated copolymer CM-PAEKs-20 was obtained.

Membrane Preparation and Quaternization

CM-PAEKs (1.0 g) was dissolved in 25 mL of 1,2-dichloroethane, filtered and then cast onto a leveled glass plate. Drying at 60 °C under ambient pressure for 8 h and vacuum for another 8 h yielded thick, transparent, and tough membranes. The membranes were peeled off and immersed in 15% trimethylamine aqueous solution at room temperature for 1 week. Quaternized copolymer QA-PAEKs were obtained, which were washed with deionized water for several times and stored in deionized water prior to use.

Characterizations

High-resolution mass spectra (HRMS) were measured on the Thermo Scientific Executive plus Mass spectrometer equipped with electrospray ionization (ESI) source. ^1H nuclear magnetic resonance (^1H -NMR) spectra were measured on a Bruker Avance III 400 spectrometer. Fourier transform infrared (FTIR) spectra were measured on a Thermo Nicolet 5700 FTIR spectrometer. Gel permeation chromatography (GPC) was performed on a Waters Breeze system equipped with a Waters Styragel column, Waters 515 HPLC pump, and Waters 2414 refractive index detector. Thermogravimetric analysis (TGA) was conducted on SDT-Q600 under nitrogen atmosphere with a heating rate of 10 °C·min⁻¹. The tensile properties of membranes were measured on a Suns universal testing instrument UTM 6502X. Small-angle X-ray scattering (SAXS) patterns were measured on an Anton Paar SAXSess mc² instrument.

Ion exchange capacity (IEC) was determined by titration. 0.2 g of membrane in Cl^- form was immersed in 50 mL of 0.2 mol·L⁻¹ NaNO_3 solution for 24 h. The released Cl^- was titrated by 0.1 mol·L⁻¹ AgNO_3 using K_2CrO_4 as the colorimetric indicator. IEC was calculated by the following equation:

$$\text{IEC} = \frac{\Delta V_{\text{AgNO}_3} c_{\text{AgNO}_3}}{m_d} \quad (1)$$

where m_d is the mass of the dry membrane, ΔV_{AgNO_3} is the volume of added AgNO_3 solution, and c_{AgNO_3} is the concen-

tration of AgNO_3 solution ($0.1 \text{ mol}\cdot\text{L}^{-1}$).

Water uptake (WU) was calculated from the following equation:

$$\text{Water uptake} = \frac{W_1 - W_0}{W_0} \times 100\% \quad (2)$$

where W_1 and W_0 refer to the weights of the wet and dry membranes, respectively.

Swelling ratio was calculated from the following equation:

$$\text{Swelling ratio} = \frac{l_1 - l_0}{l_0} \times 100\% \quad (3)$$

where l_0 and l_1 refer to the lengths of the wet and dry membranes, respectively.

In-plane anion conductivity (σ) was measured on a Solartron 1260A frequency response analyzer using a previously reported setup.^[39] The samples were submerged in ultrapure water at different temperatures during the measurement. σ was calculated from the following equation:

$$\sigma = \frac{L}{RA} \quad (4)$$

where L is the distance between the two electrodes, A is the cross-sectional area of the membrane sample, and R is the resistance derived from the diameter of the semicircle in the electrochemical impedance spectrum.

The alkaline stability was evaluated by immersing the membranes in $1 \text{ mol}\cdot\text{L}^{-1}$ NaOH solution at 60°C for 120 h and recording the change in both IEC and Cl^- conductivity.

RESULTS AND DISCUSSION

Monomer Synthesis

The new bisphenol monomer bearing ten electron-rich phenyl

groups (compound **c**) was synthesized by a three-step process. The electron-rich phenyl groups were designed as reaction sites for dense chloromethylation, which can be converted to clustered quaternary ammonium groups quantitatively in the final products. The chemical structures of compounds **b** and **c** were confirmed by ^1H -NMR spectra, as shown in Fig. 1(a). For compounds **b**, the singlet at 3.76 ppm is attributed to the methoxyl protons, and the resonance signals between 6.73 and 7.34 ppm are attributed to the phenyl protons. The precise assignment is confirmed by the 2D ^1H - ^1H COSY NMR spectrum, as shown in Fig. 1(b). For compound **c** (bottom of Fig. 1a), the signal attributed to the methoxyl protons totally disappears and a new signal at 4.70 ppm is observed, which can be assigned to the phenol protons. The mass of c-H^+ is measured to be 1029.2914 (Fig. 1c), matching well with the theoretical value of 1029.2911. All these data suggests the successful synthesis of the compounds **b** and **c**.

Polymerization and Chloromethylation

Polycondensations of compound **c** with 4,4'-difluorobenzophenone and 4,4'-dihydroxydiphenylsulfone were carried out by a conventional K_2CO_3 -activated protocol.^[23] The polymer structure is confirmed by ^1H -NMR, as shown in Fig. 2(a). The number-average molecular weights of PAEKS-10 and PAEKS-20 characterized by GPC are 4.32×10^4 and 3.98×10^4 , respectively, and the polydispersity indices of PAEKS-10 and PAEKS-20 are 1.9 and 2.1, respectively. Regarding the chloromethylation, to avoid the handling of the highly toxic chloromethylation reagent chloromethyl methyl ether (CMME), *in situ* generation of CMME using dimethoxymethane and thionyl chloride was employed.^[40,41] Since the desired chloromethyl group can fur-

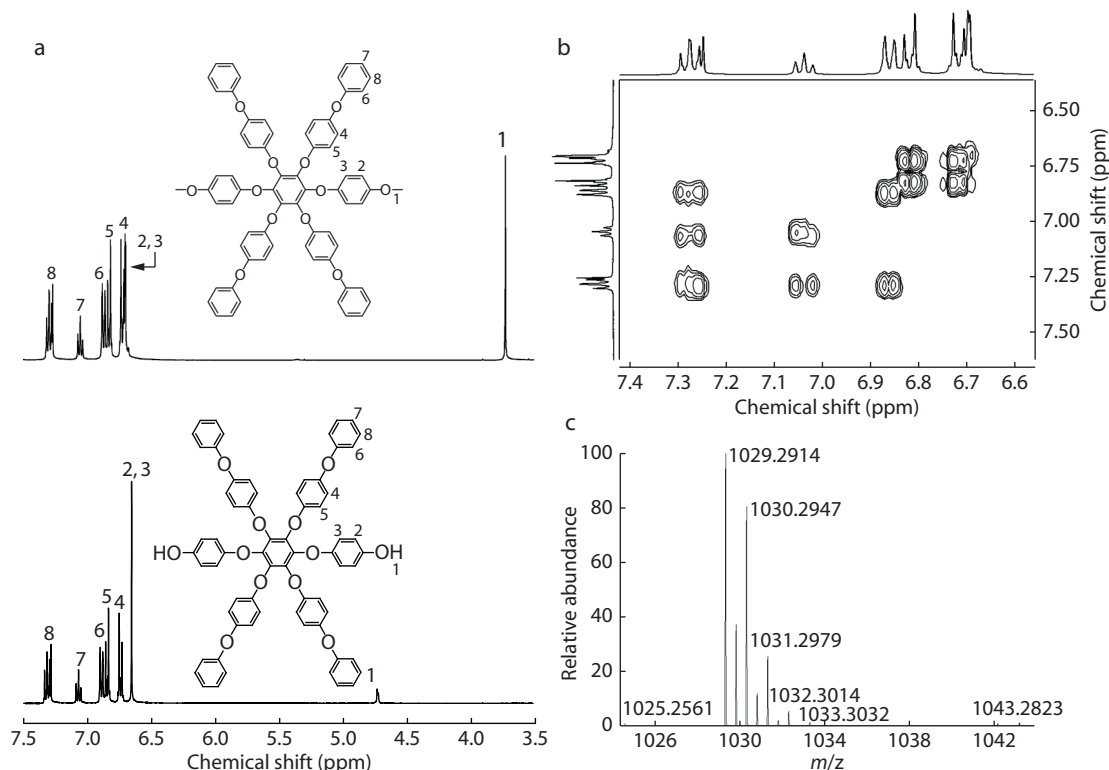


Fig. 1 (a) ^1H -NMR spectra of compounds **b** (above) and **c** (bottom) in CDCl_3 , (b) 2D ^1H - ^1H COSY NMR spectrum of compound **b** in CDCl_3 , and (c) high resolution ESI mass spectrum of compound **c**.

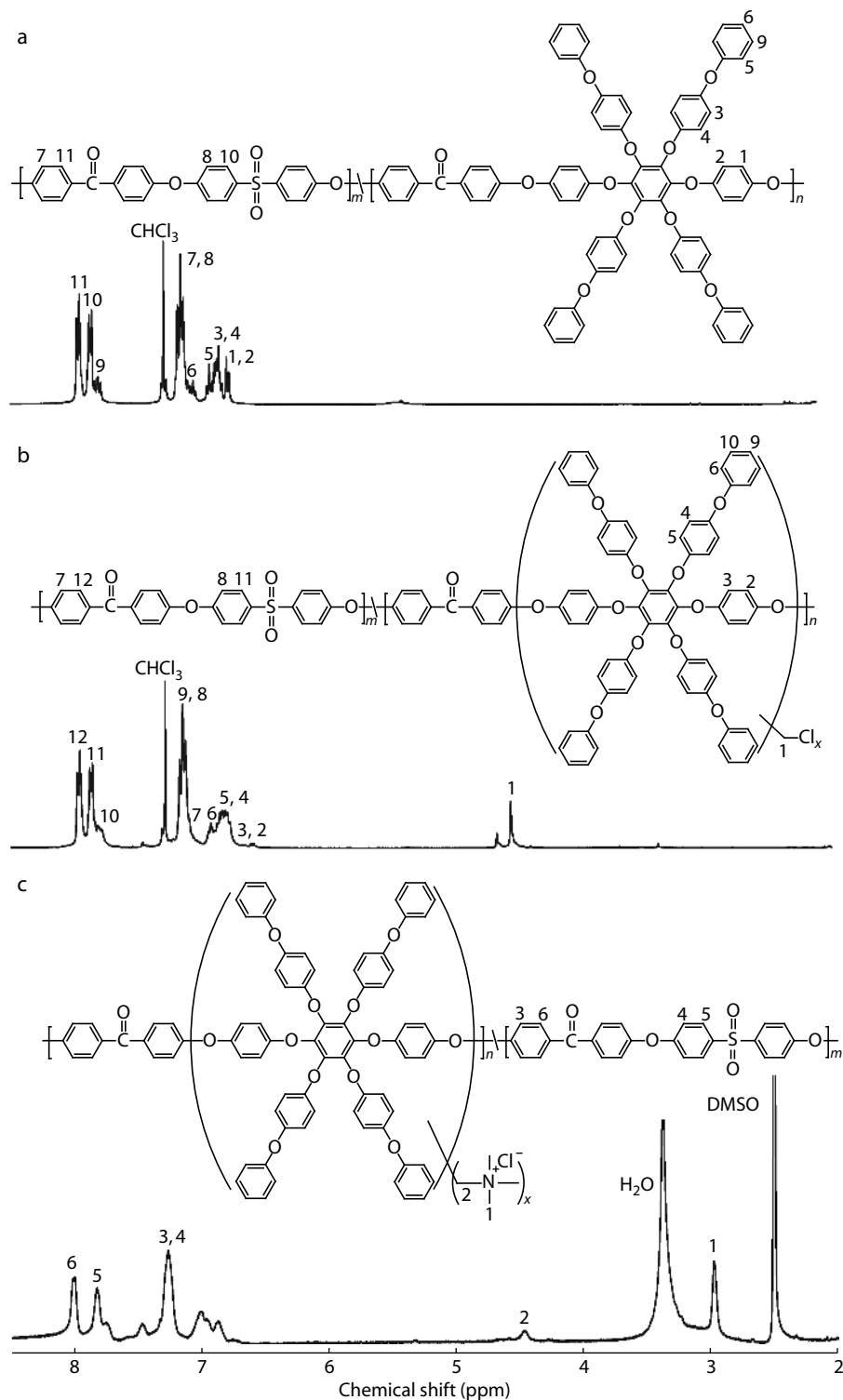


Fig. 2 ^1H -NMR spectra of PAEKs-20, CM-PAEKs-20 in CDCl_3 , and QA-PAEKs-20 in $\text{DMSO}-d_6$.

ther react with the remaining electron-rich phenyl groups to cause crosslinking, the effects of reaction temperature, reactant ratio, and reaction time on chloromethylation of CM-PAEES-20 were examined and are summarized in [Table 1](#). It can be seen that crosslinking easily occurs at 60 °C when the equivalent of SnCl_4 is higher than 0.125. Lowering the reaction temperature

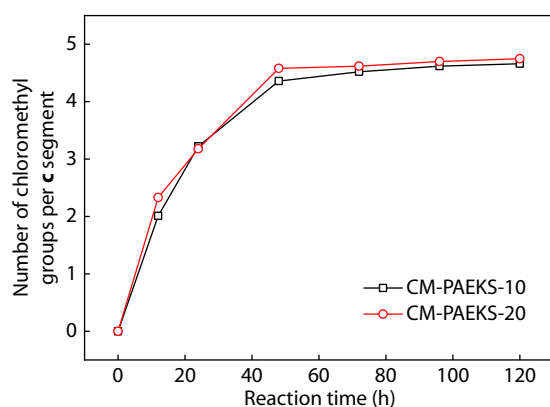
avoids crosslinking, but the degree of chloromethylation (number of reacted phenyl groups per **c** segment, which was calculated from the integral ratio of the methylene protons at 4.56–4.67 ppm (signal 1 in Fig. 2b) to the phenyl protons at 7.96–7.98 ppm (signal 12 in Fig. 2b) in ^1H -NMR spectra) decreases. At room temperature, the degree of chloromethylation

Table 1 Reaction conditions and results of chloromethylation (CM-PAEKs-20).

Run	Temperature (°C)	Equivalent of SnCl ₄	Equivalent of DMM	Equivalent of SOCl ₂	Reaction time (h)	Chloromethylation degree
1	60	2.000	22	20	0.5	Gelation
2	60	1.000	22	20	0.5	Gelation
3	60	0.500	22	20	0.5	Gelation
4	60	0.250	22	20	3.0	Gelation
5	60	0.125	22	20	3.0	2.02
6	40	0.125	22	20	3.0	1.89
7	35	0.125	22	20	3.0	1.12
8	25	0.125	22	20	3.0	0.08
9	0	0.125	22	20	3.0	0
10	25	0.125	22	20	24	3.18
11	25	0.125	22	20	48	4.58
12	25	0.125	22	20	96	4.70
13	25	0.250	22	20	< 48	Gelation
14	25	0.125	44	40	48	4.73
15	25	0.125	66	60	< 48	Gelation

could be increased by reaction time, but the increase of the reactant ratio of either SnCl₄ (entry 13) or DMM/SOCl₂ (entry 15) might also lead to crosslinking. The optimized reaction conditions were as follows: 25 °C, 0.125 equivalent of SnCl₄, 44 equivalent of DMM, and 40 equivalent of SOCl₂.

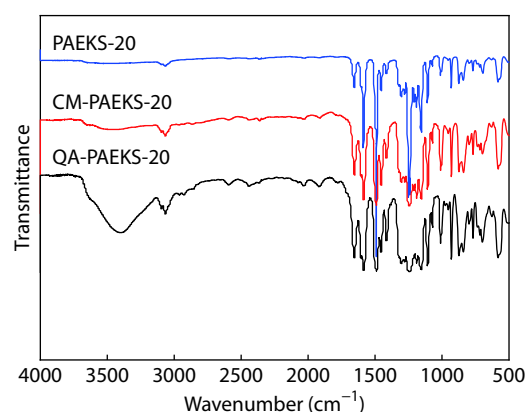
With the above optimized reaction conditions, the effects of reaction time on the degrees of chloromethylation of PAEKs-10 and PAEKs-20 were examined, as shown in Fig. 3. It can be seen that the degrees of chloromethylation increase with the increase of reaction time from 0 h to 50 h and then level off. The highest degree of chloromethylation is ~4.7 for both PAEKs-10 and PAEKs-20. This result implies that each **c** segment could be attached with ~4.7 chloromethyl groups. Since PAEKs-20 has a higher content of **c** segment than that of PAEKs-10, it has more chloromethyl groups when the degree of chloromethylation is the same.

**Fig. 3** Effect of reaction time on the degree of chloromethylation.

Membrane Formation and Conversion to QA-PAEKs

The colorless, transparent, and ductile membranes were fabricated by solution casting of PAEKs-10 and PAEKs-20. The quaternization of membranes was carried out by immersing the membranes in 15 wt% trimethylamine aqueous solution for 1 week. As shown in Fig. 2(c), the existence of signals 1 (2.99 ppm) and 2 (4.47 ppm) in the ¹H-NMR spectrum of QA-PAEKs-20 clearly demonstrates the formation of quaternary ammonium

groups. To further confirm the chemical structures of the obtained polymers, FTIR technique was employed, as shown in Fig. 4. It can be seen that all the spectra of PAEKs-20, CM-PAEKs-20, and QA-PAEKs-20 exhibit absorption bands peaked at 1586 and 1493 cm⁻¹, which can be ascribed to the stretching vibration of C=C on the benzene rings, and band at 3063 cm⁻¹, which can be ascribed to the stretching vibration of aromatic protons (Ar—H). Comparing CM-PAEKs-20 with QA-PAEKs-20, a set of bands at 2900–3000 cm⁻¹ in QA-PAEKs-20 are observed, which can be assigned to the vibration of aliphatic C—H bond on either chloromethyl groups or quaternary ammonium groups. The intensity of these bands is stronger for QA-PAEKs-20, which can be attributed to its higher content of aliphatic C—H bond. Both ¹H-NMR and FTIR results suggest the successful synthesis of QA-PAEKs.

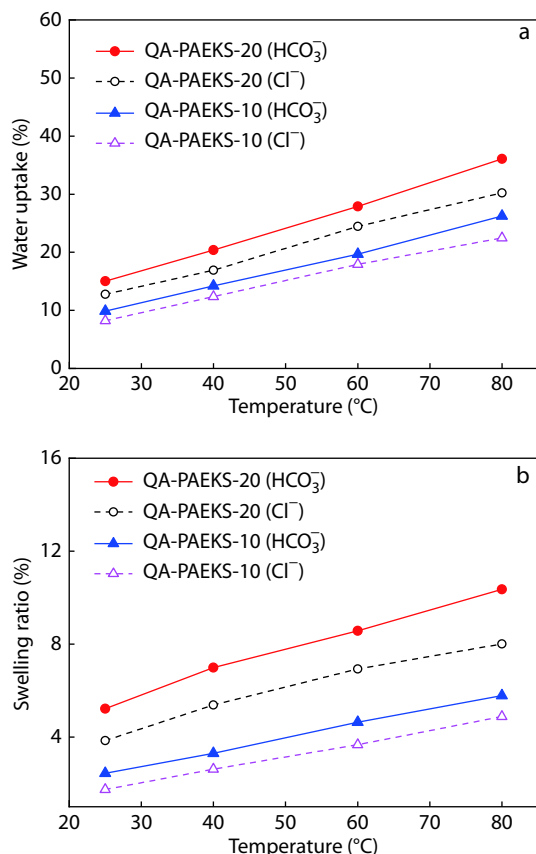
**Fig. 4** FTIR spectra of PAEKs-20, CM-PAEKs-20, and QA-PAEKs-20.

Ion Exchange Capacity (IEC), Water Affinity, and Anion Conductivity

As listed in Table 2, the titrated IECs of QA-PAEKs-10 and QA-PAEKs-20 with the counter anion of Cl⁻ are 0.76 and 1.19 mmol·g⁻¹, respectively. The water uptakes, swelling ratios, and Cl⁻ conductivities of QA-PAEKs-10 and QA-PAEKs-20 at room temperature are moderate, and increase with the increase of IEC. Besides, the water uptake and swelling ratio increase with the increasing temperatures regardless of the species of counter anions, as shown in Figs. 5(a) and 5(b). For the QA-PAEKs-10 and

Table 2 Degree of chloromethylation, IEC, water uptake, swelling ratio, Cl^- conductivity, and $T_{d-5\%}$ of QA-PAEKS-10 and QA-PAEKS-20 membranes.

Sample	Degree of chloromethylation	IEC ($\text{mmol}\cdot\text{g}^{-1}$)	Water uptake ^a (%)	Swelling ratio ^a (%)	Cl^- conductivity ^a ($\text{mS}\cdot\text{cm}^{-1}$)	$T_{d-5\%}$ ($^{\circ}\text{C}$)
QA-PAEKS-10	4.72	0.76	9.9	1.7	1.4	230
QA-PAEKS-20	4.75	1.19	15.0	3.9	4.0	222

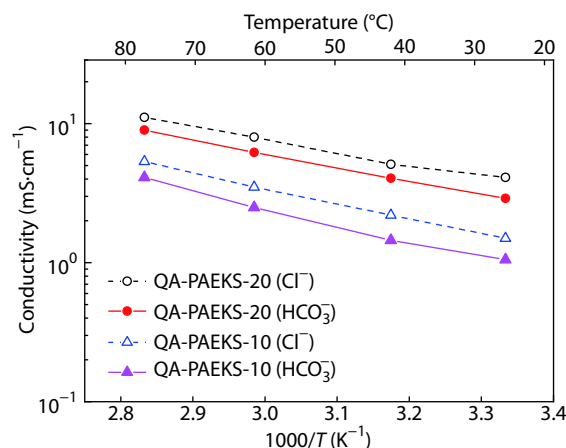
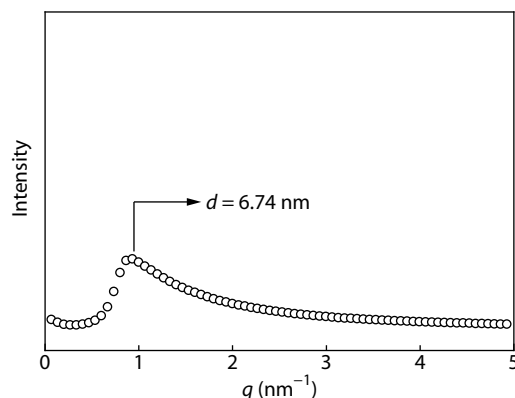
^a Measured at room temperature.**Fig. 5** (a) Water uptakes and (b) swelling ratios of QA-PAEs with Cl^- or HCO_3^- as the counter anion, plotted versus the temperature.

QA-PAEKS-20 membranes in Cl^- form, the water uptakes are 8.2% and 12.8%, and the swelling ratios are 1.7% and 3.9%, respectively. When temperature is increased to 80 $^{\circ}\text{C}$, the water uptakes of the samples increase to 22.5% and 30.2%, and the swelling ratios increase to 4.9% and 8.0%, respectively. When changing the counter anion from Cl^- to HCO_3^- , slightly higher water uptake and swelling ratio are achieved, which might be attributed to the different hydrophilicities of the corresponding anions.^[42]

The anion conductivities of QA-PAEKSs at various temperatures are shown in Fig. 6. It can be seen that for both Cl^- and HCO_3^- counter anions, the anion conductivities of QA-PAEKSs increase with the increasing temperature as expected. At the temperature of 80 $^{\circ}\text{C}$, QA-PAEKS-20 with an IEC of 1.19 $\text{mmol}\cdot\text{g}^{-1}$ shows the highest Cl^- conductivity of 11.2 $\text{mS}\cdot\text{cm}^{-1}$ and highest HCO_3^- conductivity of 9.1 $\text{mS}\cdot\text{cm}^{-1}$. At the same temperature, the membrane with Cl^- counter anion shows higher conductivities than the membrane with HCO_3^- counter anion, while the water uptake and swelling ratio are in the opposite order. Given the mobility of each ion species ($v_{\text{Cl}^-} = 7.9 \times 10^{-8}$, $v_{\text{HCO}_3^-} = 4.6 \times 10^{-8}$ in infinitely diluted aq-

ueous solution at 297 K),^[43] the higher Cl^- conductivity of QA-PAEKSs than HCO_3^- conductivity can be attributed to the greater mobility of Cl^- than HCO_3^- . In this case, water uptakes have minor influence on the anion conductivity. The anion conductivity of QA-PAEKSs exhibits an approximate Arrhenius-type dependence on temperature. Arrhenius activation energies (E_a s) for anion conduction calculated from the slopes are $\sim 20 \text{ kJ}\cdot\text{mol}^{-1}$, comparable to those of other ion-segregated AEMs.^[23,34]

The ion segregation was confirmed by small angle X-ray scattering, as shown in Fig. 7. If ion segregation exists, there would be electron density difference between ionic and non-ionic domains, yielding a scattering peak corresponding to the domain distance (d). It can be seen that a scattering peak does show up for QA-PAEKS-20 with a d value of 6.74 nm, suggesting that the design of dense quaternization for ion segregation is successful. QA-PAEKS-20 with a low IEC of 1.19 $\text{mmol}\cdot\text{g}^{-1}$ shows a high Cl^- conductivity of 4.0 $\text{mS}\cdot\text{cm}^{-1}$ at room temperature, which is comparable to the OH^- conduct-

**Fig. 6** Anion conductivities of QA-PAEKSs with Cl^- or HCO_3^- as the counter anion.**Fig. 7** Small angle X-ray scattering pattern of QA-PAEKS-20.

ivity of many advanced AEMs with similar IECs,^[44–46] despite the fact that the Cl^- mobility is less than a half of the OH^- mobility. For practical applications, an OH^- conductivity of higher than $10 \text{ mS}\cdot\text{cm}^{-1}$ may be expected. The measurement of OH^- conductivity of QA-PAEKS-20 was attempted, but inaccuracy existed because of membrane cracking during alkaline immersion prior to tests.

Thermal Property, Mechanical Property, and Alkaline Stability

Thermogravimetric analysis (TGA) curves of representative PAEKS-20, CM-PAEKS-20, and QA-PAEKS-20 are shown in Fig. 8. The weight loss of samples during heating is attributed to the thermal degradation. It can be seen that PAEKS-20 has no degradation until $\sim 400^\circ\text{C}$, while CM-PAEKS-20 and QA-PAEKS-20 start to degrade at $\sim 200^\circ\text{C}$. The degradation step at $\sim 200^\circ\text{C}$ for CM-PAEKS-20 and QA-PAEKS-20 could be attributed to the decomposition of the chloromethyl and quaternary ammonium groups, respectively.^[40] The 5% weight decomposition temperatures ($T_{\text{d-5\%}}$) of QA-PAEKS-10 and QA-PAEKS-20 are listed in Table 2, both higher than 220°C . This suggests the promising thermal stability of the samples for polymer electrolyte membrane fuel cells applications and all-vanadium redox flow battery application.^[47]

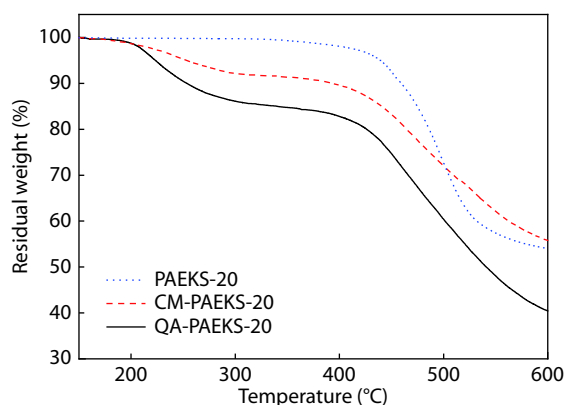


Fig. 8 TGA curves of representative PAEKS-20, CM-PAEKS-20, and QA-PAEKS-20.

The stress-strain curves of QA-PAEKS-10 and QA-PAEKS-20 are shown in Fig. 9, and the tensile strength and elongation-at-break values are listed in Table 3. It can be seen that QA-PAEKS-10 is more robust than QA-PAEKS-20, with a higher tensile strength (26.8 MPa) and a higher elongation-at-break value (9.8%). This is because QA-PAEKS-20 uptakes a larger amount of water which plasticizes the membrane. Notably, the tensile strengths of QA-PAEKSs are comparable to those of other quaternary ammonium functionalized poly(aryl ether)s with similar IECs.^[38,48]

The alkaline stability of the QA-PAEKSs was evaluated by immersing the membranes in $1 \text{ mol}\cdot\text{L}^{-1}$ NaOH solution at 60°C for 120 h. As listed in Table 3, both IEC and Cl^- conductivities decrease slightly after the immersion. The decreases are greater for QA-PAEKS-20 than for QA-PAEKS-10, which can be attributed to the larger water uptake and the more degradable sites for QA-PAEKS-20. The mechanism of the alkaline degradation of quaternary ammonium functionalized poly(aryl ether)s has been disclosed previously.^[13,49] Both the quaternary ammonium groups and the poly(aryl ether) backbones may be degraded. Therefore, the application of QA-PAEKSs in strong base at elevated temperatures is not advised; instead, the applications in acidic^[23] and neutral^[50] conditions are recommended.

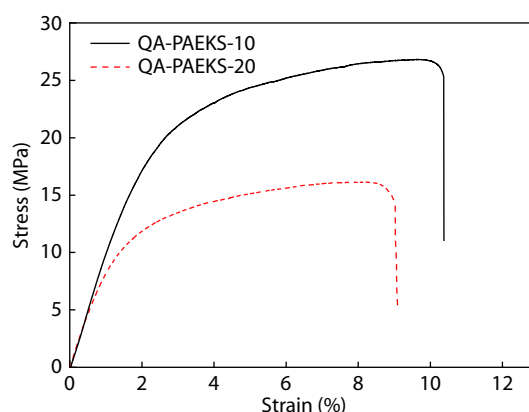


Fig. 9 Stress-strain curves of QA-PAEKSs.

Table 3 Mechanical properties and alkaline stability of QA-PAEKSs.

Membrane	Tensile strength (MPa)	Elongation at break (%)	IEC remaining (%)	Cl^- conductivity remaining (%)
QA-PAEKS-10	16.1	8.4	99.2	97.0
QA-PAEKS-20	26.8	9.8	98.9	93.7

CONCLUSIONS

A new type of bisphenol monomer bearing ten electron-rich phenyl groups was designed and polymerized successfully with electron-deficient monomers to yield poly(aryl ether ketone sulfone)s (PAEKSs) with clustered electron-rich segments. These segments were selectively chloromethylated without undesirable crosslinking by careful control of the reaction temperature, reactant ratio, and reaction time. The chloromethyl groups were converted to quaternary ammonium groups by immersion in trimethylamine solution. Quaternary ammonium functionalized poly(aryl ether ketone sulfone)s (QA-PAEKSs) were then obtained for anion exchange membrane applications. The chemical

structures were confirmed by ^1H -NMR, 2D ^1H - ^1H COSY NMR, MS, and FTIR. The membranes were prepared by solution-casting. It is found that QA-PAEKS-20 with an IEC of $1.19 \text{ mmol}\cdot\text{g}^{-1}$ features moderate water uptake and swelling ratio, high Cl^- and HCO_3^- conductivities, good mechanical strength, excellent thermal stability, and reasonable alkaline stability, which are promising metrics for AEM applications.

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