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# Preparation of anion exchange membranes by an efficient chloromethylation method and homogeneous quaternization/crosslinking strategy

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ABSTRACT

A novel chloromethylation method and homogeneous quaternization/crosslinking strategy for a series of polymers are demonstrated in this paper. The chloromethylation is accomplished by using 1, 4-bis (chloromethoxy) butane (BCMB) as the chloromethylating reagent and concentrated sulfuric acid as the solvent and catalyst. BCMB is a kind of high-efficient, non-carcinogenic and inexpensive chloromethylating reagent, and concentrated sulfuric acid replaces toxic halogenated hydrocarbon. Study results indicated that BCMB had higher reactivity than chloromethyl octyl ether under similar reaction conditions. The chloromethylated poly (phthalazinon ether sulfone ketone) (PPESK) was then crosslinked and quarternized by using N, N, N′, N′-tetramethyl-1, 6-hexanediamine (TMHDA) as the homogeneous quaternizing and crosslinking agent during the solvent evaporation. The ion exchange capacity (IEC) of the crosslinked membranes (C-QAPPESK/OH) was very close to the theoretical value, higher than that of the membranes quaternized by trimethylamine (TMA) aqueous solutions (QAPPESK/OH). In addition to higher IEC, C-QAPPESK/OH membranes possessed greater hydroxide conductivity and chemical stability than that of QAPPESK/OH membranes. The results suggest that this efficient chloromethylation together with the homogeneous quaternizing and crosslinking method is a time-saving strategy with potential application in the preparation of anion exchange membranes.



## 1. Introduction

Recently, considerable attention has been paid to anion exchange membrane fuel cells (AEMFCs) because of their numerous advantages in comparison with polymer electrolyte membrane fuel cells (PEMFCs), such as faster electrode kinetics, desirable applicability of non-precious metals as catalyst and milder corrosion environment [1]. Therein, the anion exchange membrane (AEM) plays an inherently significant role in improving fuel cell performance, thus it is attracted special research interests [2]. AEMs are usually composed of polymer matrix and cationic charged groups. Up to now, chloromethylation followed by quaternization and alkalization is one of the most frequently used methods to fabricate AEMs [2]. Among them, chloromethylation and quaternization are the most important steps.

Chloromethylation introduces chloromethyl groups onto the phenyl ring via electrophilic substitution reaction between chloromethylation reagents and polymers [2,3]. Chloromethyl methyl ether (CMME), paraformaldehyde/HCl and trimethylchlorosilane are the commonly used chloromethylation reagents. Nevertheless, the activity of paraformaldehyde/HCl and trimethylchlorosilane is low, thus prolonged reaction time is required [2]. Despite the high activity, chloromethyl methyl ether is a well known toxic and carcinogenic compound. As a consequence, long acyclic chloromethyl octyl ether (CMOE) with low toxicity and volatility was used to conduct chloromethylation [3–8]. Unfortunately, the activity of CMOE is lower than that of CMME, because the molecule size of CMOE is larger than that of CMME, leading to the difficulty for CMOE to attack polymers caused by steric blocking effects. Additionally, the chloromethylation reaction reported in literature was usually carried out in halogenated hydrocarbon (e.g., chloroform) with Lewis acid (e.g., $SnCl_4$) as the catalyst [2,8,9]. Generally, the halogenated hydrocarbon should be dried before use and the Lewis acid is humidity sensitive, so air and water free conditions are required, resulting in the complication of facilities and production process. Furthermore, the halogenated hydrocarbon solvent is prone to volatilize and the vapor is harmful to environment and human health. Therefore, a "green" chloromethylation method needs to be developed in urgency.

Followed by chloromethylation, quaternary ammonium (QA) groups are introduced to the polymer by quaternization process. This is usually accomplished by treating the pre-formed chloromethylated polymer membranes in trimethylamine (TMA) aqueous solutions [3,4,6–11]. This is a heterogeneous quaternization method which proceeds in solid membranes and takes prolonged time. Meanwhile, TMA is highly volatilizable and carcinogenic, which makes the membrane fabrication process not environmental friendly. Consequently, the homogeneous quaternization

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method, i.e., the transformation of chloromethyl groups to QA was accomplished before or during the membrane formation, is desirable [12–15]. N, N, N′, N′-tetramethyl-1, 6-hexanediamine (TMHDA) can be used to quaternize chloromethyl groups [13,15,16] and it is less volatilizable, thus TMHDA can be utilized as a safer and homogeneous quaternization reagent. More importantly, the crosslinking of membranes will be realized simultaneously if diamines are used. Crosslinking has been proved to be a simple and effective method to improve the mechanical and chemical stability of QA-based AEMs [13,14,17–19], which is required for the fuel cell applications.

Herein, we demonstrated a new chloromethylation and crosslinking method to prepare anion exchange membranes. The chloromethylation was accomplished by using concentrated sulfuric acid and 1, 4-bis (chloromethoxy) butane (BCMB) as the solvent and chloromethylating reagent, respectively. In addition to the nonvolatile nature, concentrated sulfuric acid has good solubility for many polymers and it can be also used as catalyst in the chloromethylation reaction [6,8]. BCMB is a non-carcinogenic and inexpensive chloromethylating reagent [20,21]. Then we adopted N, N, N′, N′-tetramethyl-1, 6-hexanediamine (TMHDA) to quaternize and crosslink chloromethylated polymers during the solvent evaporation in the membrane formation. The crosslinked quaternized membranes have higher IEC and hydroxide conductivity than that of the membranes quaternized by TMA in the conventional method. In addition, the chemical stability of crosslinked quaternized membranes is significantly enhanced simultaneously.

## 2. Experimental

### 2.1. Chloromethylation

In this paper we utilized three commercially available polymers, i.e., poly (ether ether ketone) (PEEK, Victrex, medium melt viscosity grade 450PF), poly (ether sulfone) (PES, reduced viscosity = 0.36 dL $g^{-1}$ in N, N-Dimethylformamide (DMF) at 25 °C, Changchun Jilin University Special Plastic Engineering Research) and poly (phthalazinone ether sulfone ketone) (PPESK, molar ratio of sulfone/ketone = 1:1, Dalian Polymer New Material Company, its reduced viscosity in Dimethylacetamide (DMAc) at 25 °C is measured to be 0.42 dL $g^{-1}$ in our laboratory), to demonstrate the new chloromethylation method.

Typically, 1 g polymer was dissolved into 30 mL (for PES and PPESK) or 60 mL (for PEEK) ice-cold 98% concentrated $H_2SO_4$ followed by addition of a given volume of 1, 4-bis (chloromethoxy) butane (BCMB) (≥95%, Xi'an Langene Bioscience Co. Ltd, China). Subsequently, the reaction was kept in the ice-water bath (for PES and PPESK) or ice-salt bath (for PEEK) for some time and the product was separated by precipitation the mixture in ice water, followed by thorough washing with de-ionized water, and then drying at 50 °C in air. Then the chloromethylated polymers (CMPES, CMPPESK and CMPEEK) were obtained.

### 2.2. Membrane preparation

For preparing the crosslinked membranes, 0.4 g CMPPESK was dissolved in 1-methyl-2-pyrrolidone (NMP) to make a 3 wt.% solution, followed by addition of a given volume of N, N, N′, N′-tetramethyl-1,6-hexanediamine (TMHDA) (99%, Xi Ya Reagents, China). The mixture was stirred for 60–90 s and then poured onto a glass plate to cast the membrane and dried in oven at 70 °C for 24 h. This quaternization method is called homogeneous quaternization method (Scheme 1). The membranes obtained were denoted as C-QAPPESK/Cl-n, where *n* was the ratio of the actual added amount of TMHDA to the theoretical amount. Subsequently, the C-QAPPESK/Cl membranes were immersed in a 1 M KOH solution for 24 h, converting the membranes from the $Cl^-$ form into the $OH^-$ form (C-QAPPESK/OH), followed by washing with de-ionized water several times and storing in de-ionized water for another 48 h to completely remove the residual KOH prior to further experiments.

In comparison, the CMPPESK was quaternized by the conventional method using trimethylamine (TMA). Briefly, 0.4 g CMPPESK was dissolved in 1-methyl-2-pyrrolidone (NMP) to make a 3 wt.% solution, followed by pouring the solution onto a glass plate to cast the membrane and drying in oven at 70 °C for 24 h. Then the CMPPESK membrane was soaked into 125 mL 33 wt.% trimethylamine aqueous solution at 50 °C for 12 h to prepare the quaternized PPESK membranes (QAPPESK/Cl). This quaternization method is called conventional quaternization method (Scheme 2). Subsequently, the QAPPESK/Cl membranes were immersed in a 1 M KOH solution for 24 h, converting the membranes from the $Cl^-$ form into the $OH^-$ form (QAPPESK/OH), followed by washing with de-ionized water several times and storing in de-ionized water for another 48 h to completely remove the residual KOH prior to further experiments.

### 2.3. Characterization

The degree of chloromethylation (DCM) for the chloromethylated polymer was determined by $^1H$ NMR spectroscopy on a Bruker Avance II 400 NMR spectrometer at a resonance frequency of 400.13 MHz, using tetramethylsilane (TMS) as an internal standard. The Fourier transform infrared (FT-IR) absorption spectra of membranes after drying at 60 °C under vacuum overnight were recorded by using a Bruker Tensor 27 spectrophotometer.

For the measurements of ion exchange capacity (IEC), water uptake (WU) and swelling ratio (SR) of membranes, the $OH^-$ form membranes were dried at 60 °C under vacuum overnight.

The IEC of membranes was determined by the back titration method. Briefly, the dried $OH^-$ form membranes were immersed in 30 mL 0.01 M HCl aqueous solutions for 24 h, followed by back titration of 0.01 M NaOH solution with phenolphthalein as the indicator. The 30 mL 0.01 M HCl solution was used as the blank sample for the control experiment. The measured IEC (mmol $g^{-1}$) of the membrane was calculated as follows:

$$IEC = \frac{(V_b - V_a)c_{HCl}}{m_{dry}} \quad (1)$$

where $V_b$ and $V_a$ were the consumed volumes (mL) of the NaOH solution for the blank sample and the membrane sample, respectively, $c_{HCl}$ was the concentration of HCl solutions (mol $L^{-1}$), $m_{dry}$ was the mass of dry membrane.

The water uptake of the $OH^-$ form membranes were measured by the following equation:

$$WU = \frac{m_{wet} - m_{dry}}{m_{dry}} \quad (2)$$

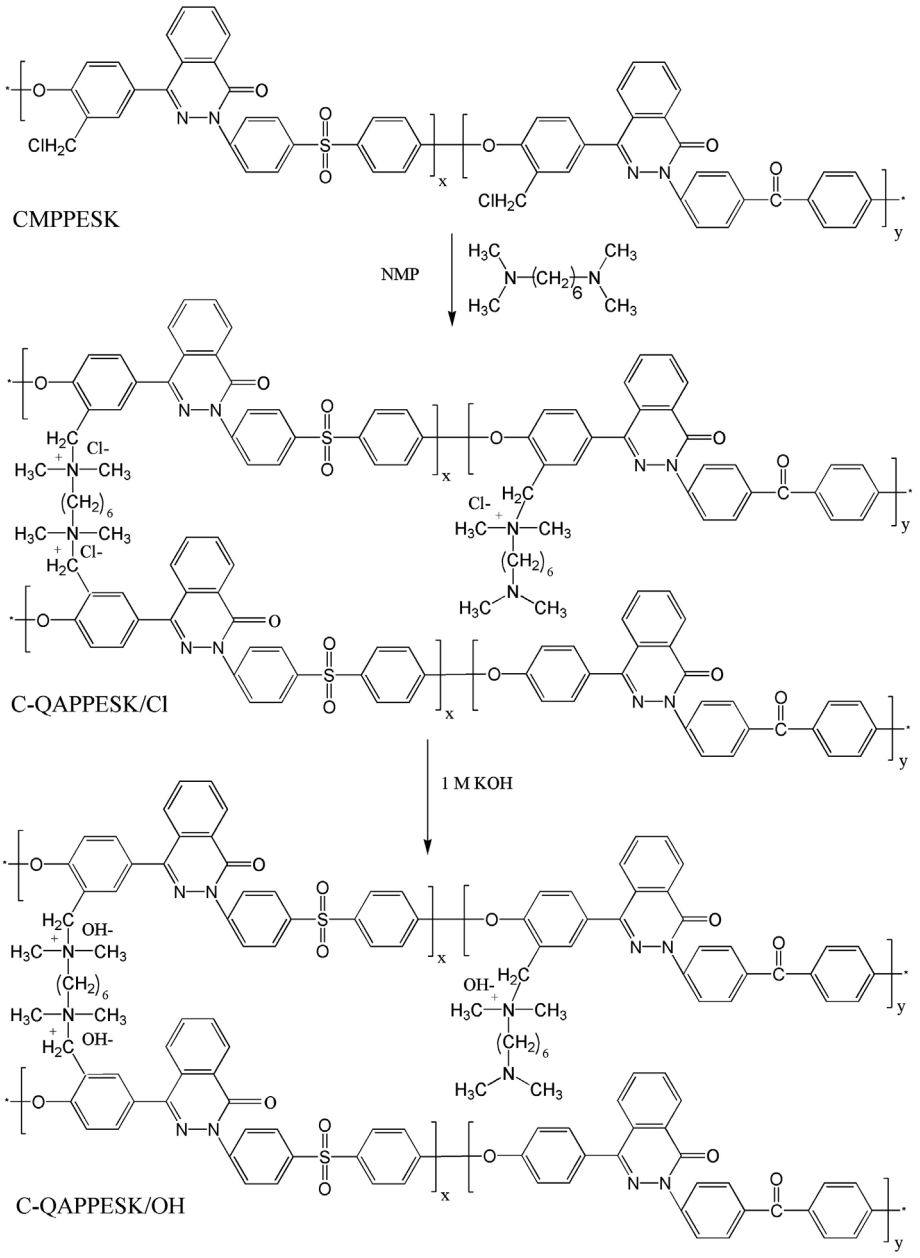
where $m_{wet}$ and $m_{dry}$ were the mass of wet and dry membranes, respectively.

The swelling ratio of the $OH^-$ form membranes in plane ($SR_p$) and in thickness ($SR_t$) direction were measured by the following equations:

$$SR_p = \frac{l_{wet} - l_{dry}}{l_{dry}} \quad (3)$$

$$SR_t = \frac{t_{wet} - t_{dry}}{t_{dry}} \quad (4)$$

where $l_{wet}$ and $l_{dry}$ were the average length [$l_{wet} = (a_{wet} \cdot b_{wet})^{1/2}$, $l_{dry} = (a_{dry} \cdot b_{dry})^{1/2}$] of wet and dry membrane samples, respectively, in which, $a_{wet}$, $b_{wet}$ and $a_{dry}$, $b_{dry}$ were the lengths and widths of wet and dry membrane samples, respectively. $t_{wet}$ and $t_{dry}$ were the thickness of wet and dry membranes, respectively.




**Scheme 1.** Homogeneous quaternization method.

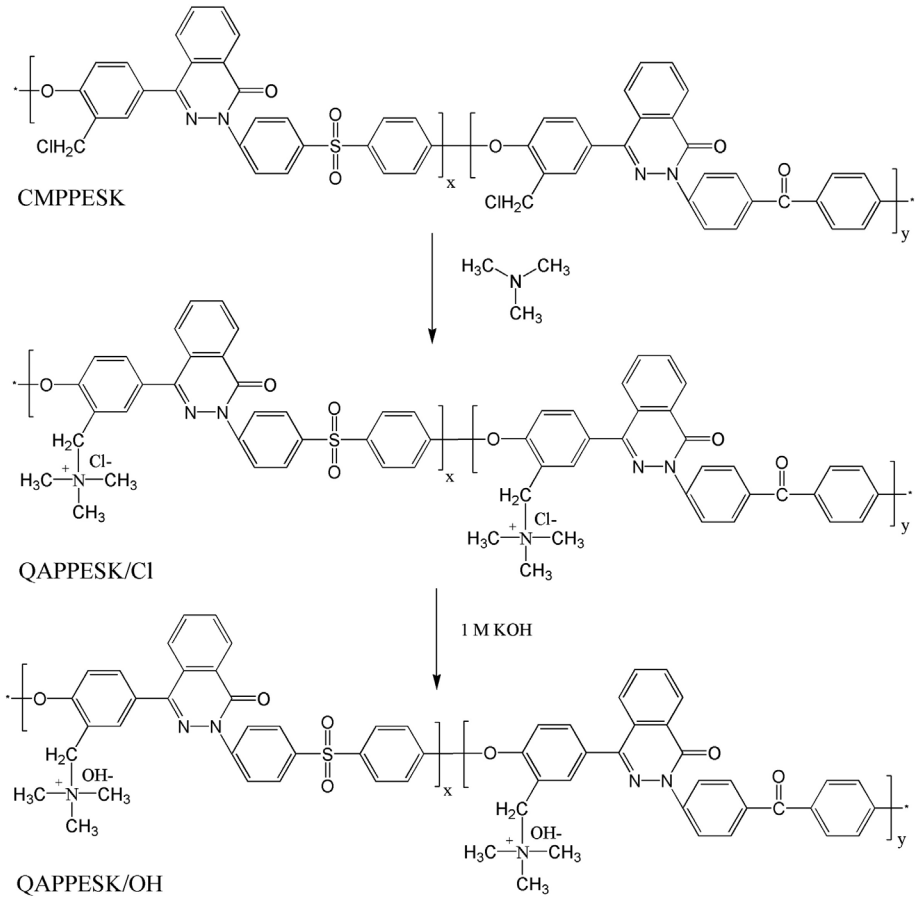
The ionic conductivity of AEMs was measured by a two-probe AC impedance spectroscopy with a Solartron 1260 frequency response analyzer (Solartron Analytical, UK) interfaced with a 1287 potentiostat/galvanostat. The AEMs were immersed in the freshly made ultrapure water after alkalization, and the container was sealed to minimize its exposure to ambient $CO_2$. At measurement, the membrane was taken out from the ultrapure water as quickly as possible, and then sealed between two plates with electrodes of testing fixture, which was placed in freshly made ultrapure water to keep a relative humidity of 100%. Moreover, water was refreshed before every measurement at different temperature. The measurement was conducted in the potentiostatic mode over frequencies ranging from 10 MHz to 10 Hz with a potentiostatically controlled AC potential of 20 mV. Ionic conductivity, $\sigma$ (mS cm$^{-1}$), was calculated according to the following equation:

$$\sigma = \frac{l}{wdR} \tag{5}$$

where $l$ was the length of the membrane (cm) between two electrode, $w$ and $d$ was the membrane width and thickness, respectively, $R$ was the measured membrane resistance (mΩ).

For the scanning electron microscope (SEM) and composition measurement, the $OH^-$ form membranes were first ion-exchanged to $Br^-$ form by immersing the membrane in 0.01 M HBr solutions for 24 h, then the $Br^-$ form membranes were stored in deionized water for another 24 h and finally dried at 60 °C overnight under vacuum. The morphology and elemental distribution of the cross-sectional $Br^-$ form membranes were detected by JEOL JSM-6360LV SEM equipped with an Oxford Inca EDX detector.

The thermal properties of the membranes were tested by using a TGA analyzer (Mettler Toledo TGA/SDTA851). Before test, the membrane samples were vacuum-dried at 60 °C for 24 h. Then samples were heated from 100 to 800 °C at a heating rate of 10 °C min$^{-1}$ under air flow (80 mL min$^{-1}$). Derivative thermogravimetry (DTG) curves were obtained by making the first order differential of TGA curve on temperature.




**Scheme 2.** Conventional quaternization method.

The mechanical properties of water-saturated $OH^-$ form membranes were measured on a WDW Electromechanical Universal Testing Machine (Changchun KeXin Corporation, China) at room temperature. The membrane was cut into specimens with 10 mm in width and kept in de-ionized water before test. The stretching test was carried out using a programmed elongation rate of 0.5 mm $min^{-1}$.

The chemical stability of the quaternized membranes was evaluated by monitoring the variation of IEC in de-ionized water or 1 M KOH at a

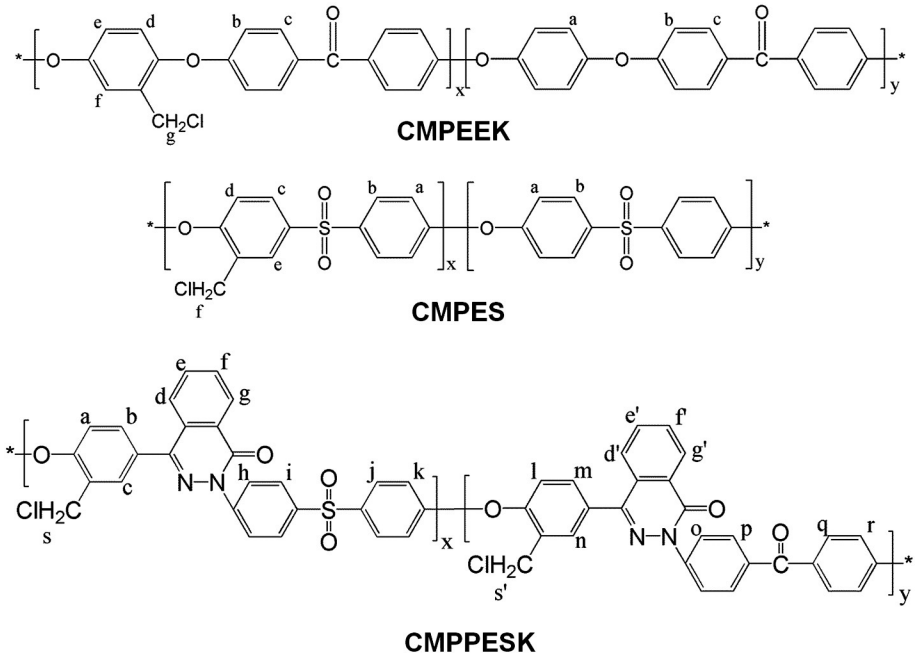



**Fig. 1.** The chemical structures of CMPEEK, CMPES and CMPPESK.

given temperature. After a given time, a piece of membrane was put out and the IEC was measured by the method mentioned above.

## 3. Results and discussion

### 3.1. Chloromethylation of polymers

The chemical structures and the corresponding $^1$H NMR spectra of CMPPESK, CMPEEK and CMPES are shown in Figs. 1 and 2, respectively. The hydrogen atoms for the three chloromethylated polymers are denoted as $H_x$, where x represents the position marked in Fig. 1. The peaks in the range between 4.5 and 5.0 ppm are attributed to the hydrogen atoms in chloromethyl groups ($-CH_2Cl$) [5,6,8], confirming the chloromethylated polymer has been successfully synthesized. As an electrophilic substitution, the reaction of polymers would preferentially take place in the benzene rings next to the ether bond due to the highest electron-density [8]. For CMPPESK, the protons on chloromethyl groups (s and s′) show double peaks on $^1$H NMR spectra, which can be can be ascribed to the different chemical environment of s and s′ protons, because s and s′ protons on $-CH_2Cl$ groups are close to the sulfone and ketone groups, respectively [22]. In addition, owing to the low reaction temperature and short reaction time, the sulfonation of polymers was avoided [8]. The DCM of CMPEEK, CMPES and CMPPESK was calculated as follows: $DCM_{PEEK} = 2\ A(H_g)/A(H_c)$, $DCM_{PES} = 2\ A(H_f)/[A(H_b) + A(H_c) + A(H_e)]$, $DCM_{PPESK} = [A(H_s) + A(H_{s'})]/[A(H_g) + A(H_{g'})]$, where $A(H_x)$ represents the area of the peaks corresponding to $H_x$ in the $^1$H NMR spectra. The concentration of chloromethyl groups (mmol $g^{-1}$) can be evaluated by Eq. (6):

$$c_{CM} = \frac{1000 \cdot DCM}{M_{\mathbf{Polymer}} - 1 \cdot DCM + M_{CM} \cdot DCM} \tag{6}$$

where $M_{Polymer}$ was the molecular weight of the repeat unit of PEEK, PES or PPESK; $M_{CM}$ was the molecular weight of chloromethyl group.

For comparison, the DCM of the three chloromethylated polymers reported in literature and the corresponding used amount of chloromethyl octyl ether (CMOE) are displayed in Table 1. Although the reaction time was shorter and amount of chloromethylation reagent was smaller, higher DCM can be obtained when BCMB was utilized, illustrating the superior activity of BCMB than CMOE. The higher activity of BCMB may probably result from two reasons. The first is that there are two chloromethyl groups in a single BCMB molecule. And the smaller molecule size may be another reason, which is beneficial for BCMB to attacking the polymer. Thus, it can be deduced from the results above that the combination of sulfuric acid and BCMB is highly active for preparation of chloromethylated polymers with high DCM even when the reaction is carried out at a very low temperature and so small amount of BCMB is used.

Fig. 3 shows the dependence of DCM of CMPPESK on the used volume of BCMB ($V_{BCMB}$) per gram of PPESK. The reaction time was limited to 4 h. The DCM of CMPPESK increases rapidly with $V_{BCMB}$ in the low concentration level. When $V_{BCMB}$ exceeds ca. 2.5 mL, the DCM reaches a flat level (around 1.60). The reason may result from the space block and electronic effect, because chloromethylation is an electrophilic substitution, while chloromethyl groups are electron-withdrawing groups which will decrease the electron density on benzene rings and hence reduce the reaction ability.

In the following preparation of AEMs, PPESK was selected as the polymer matrix to be studied in detail due to the high glass-transition temperatures (263–305 °C), superior mechanical strengths, good solubility, and good chemical resistances of PPESK [6]. It is necessary to be pointed out that the homogeneous quaternization/crosslinking strategy

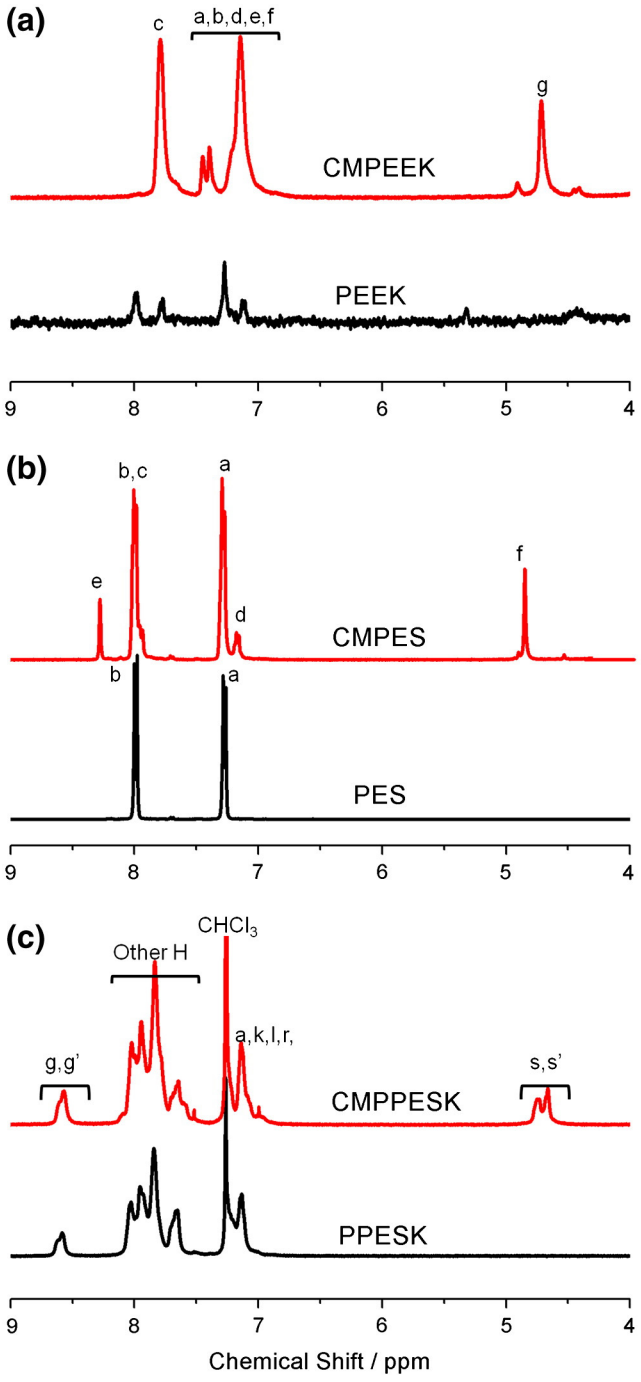



**Fig. 2.** $^1$H NMR spectra of CMPEEK, CMPES and CMPPESK. The solvent for CMPEEK and CMPES is DMSO-$d_6$, and for CMPPESK is $CDCl_3$.

**Table 1**
Comparison of DCM and the chloromethylation conditions for different polymers in this work and literature. Both solvent and catalysts used are concentrated sulfuric acid.

| Polymer | CR[a] | $V^b$ (mL) | $T^c$ | $T^d$ (h) | $c_{CM}{}^e$ mmol $g^{-1}$ | Reference |
|---|---|---|---|---|---|---|
| PEEK | BCMB | 4.62 | Ice-salt bath | 0.5 | 3.16[f] | This work |
| | CMOE | 20 | Ice-salt bath | 1.67 | 2.91[f] | [8] |
| PPESK | BCMB | 2.8 | Ice-water bath | 4 | 1.83[f] | This work |
| | CMOE | 5 | 0 °C | 9 | ~1.65 | [6] |
| PES | BCMB | 2.5 | Ice-water bath | 7 | 2.68[f] | This work |
| | CMOE | 5 | Ice-water bath | n.a. | 1.32 | [7] |

[a] Chloromethylating reagent.
[b] Volume of chloromethylating reagent for 1 g polymer.
[c] Reaction temperature.
[d] Reaction time.
[e] Concentration of chloromethyl groups for the obtained chloromethylated polymers.
[f] Data evaluated by Eq. (6).

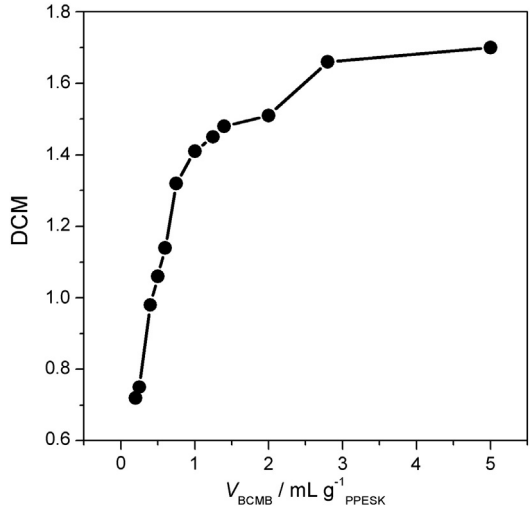



**Fig. 3.** Dependence of DCM of CMPPESK on the used volume of BCMB. The reaction was carried out in the ice-water bath for 4 h.

can be also applied to PEEK and PES, but these results are not given in the manuscript owing to the limitation of the length of one article.

### 3.2. Quaternization and crosslinking of CMPPESK with TMHDA

The quaternized and crosslinked CMPPESK was prepared by adding TMHDA to the casting solution containing CMPPESK (DCM = 1.47) followed by evaporation the solvent at 70 °C. During the formation of membrane, the amine groups of TMHDA will interact with chloromethyl groups ($-CH_2Cl$) to give QA groups and the polymer lines are crosslinked at the same time. After alkalization, the membranes were converted from the $Cl^-$ form to the $OH^-$ form (C-QAPPESK/OH). The effect of the used amount of TMHDA on the resulting IEC of C-QAPPESK/OH was studied. The theoretical amount of TMHDA needed ($V_t$) was calculated by Eq. (7), assuming one molecule of TMHDA interacts with two chloromethyl groups.

$$V_t = \frac{mc_{CM}M_{TMHDA}}{2\rho_{TMHDA}} \tag{7}$$

where $m$ was the mass of CMPPESK; $M_{TMHDA}$ and $\rho_{TMHDA}$ was the molecular weight and density of TMHDA, respectively.

In order to quaternize the chloromethyl groups adequately, excessive amount of TMHDA was added to the casting polymer solution, because not all amine groups can be reacted (Scheme 1). The membrane IEC was determined by the ratio of actual added amount of TMHDA ($V_a$) to $V_t$ (denoted as $n$). The properties of C-QAPPESK/OH membranes obtained with different $n$ are presented in Table 2. The IEC of C-QAPPESK/OH membranes increased with $n$, reaching to 1.44 mmol $g^{-1}$ at $n = 5$, which was very close to the theoretical IEC (1.47 mmol $g^{-1}$) of the C-QAPPESK/OH membranes evaluated by Eq. (8):

$$IEC_{t-TMHDA} = \frac{1000 \cdot DCM}{M_{PPESK} - 1 \cdot DCM + M_{QA-TMHDA} \cdot DCM/2} \tag{8}$$

where $M_{PPESK}$ was the molecular weight of the repeat unit of PPESK; $M_{QA\text{-}TMHDA}$ was the molecular weight of the QA groups produced by chloromethyl groups with TMHDA. In sharp contrast, the IEC of QAPPESK/OH made by the conventional quaternization method, was only 1.05 mmol $g^{-1}$, while the theoretical IEC for QAPPESK/OH was 1.53 mmol $g^{-1}$ obtained by Eq. (9):

$$IEC_{t-TMA} = \frac{1000 \cdot DCM}{M_{PPESK} - 1 \cdot DCM + M_{QA-TMA} \cdot DCM} \tag{9}$$

where $M_{QA\text{-}TMA}$ was the molecular weight of the QA groups produced by chloromethyl groups with TMA. As shown in Table 2, the IEC of QAPPESK/OH was far from the theoretical value even when the TMA used in the quaternization was nearly 1000 times that of the theoretical amount. Similar phenomenon was reported previously by other researchers [8].

The degree of quaternization can be further determined by the Br:S molar ratio of the $Br^-$ form membranes. Since the Br and S elements are the characteristic elements of QA groups and backbone matrix, respectively, the Br:S molar ratio can be used as an indicator of the quaternization degree. As shown in Table 2, the Br:S molar ratio increases with $n$, reaching 61:39 at $n = 5$, which is very close to the theoretical value of the C-QAPPESK/OH membranes. In contrast, the Br:S molar ratio of the QAPPESK/OH membrane is only 45:55, far from the theoretical value (60:40). The reason for the lower IEC of QAPPESK/OH than that of C-QAPPESK/OH may be related to the fact that the quaternization reaction in solid membranes is often inadequate due to the space blocking effect and limited contact of reactants. As for the homogeneous quaternization method carried out in solution, it can overcome the disadvantages faced by the conventional quaternization method. The results above definitely indicate the higher efficiency of the homogeneous quaternization method.

### 3.3. Physical characterization of C-QAPPESK/OH

The structure of CMPPESK, C-QAPPESK/OH-5 and QAPPESK/OH membranes were characterized by FT-IR, and the absorption spectra are shown in Fig. 4. The peak at 3068 $cm^{-1}$ on the spectra is due to the stretching of C–H bond of aromatic hydrocarbon. In comparison with CMPPESK, the wide band at around 3440 $cm^{-1}$ in the FT-IR absorption spectra of QAPPESK/OH and C-QAPPESK/OH-5 is attributed to the stretching vibration of O–H bond, indicating the successful quaternization and alkalization of CMPPESK. In addition, the peaks

**Table 2**
Properties of C-QAPPESK/OH and QAPPESK/OH.

| Samples | $n$ | Br:S molar ratio[c] | IEC mmol $g^{-1}$ | WU[d] wt.% | $SR_p$[d]% | $SR_t$[d]% | $\sigma$ mS $cm^{-1}$[d] | $u$ $cm^2$ $s^{-1}$ $V^{-1}$[d] | Tensile strength[e] MPa | Elongation at break[e]% |
|---|---|---|---|---|---|---|---|---|---|---|
| C-QAPPESK/OH-2 | 2 | 52:48 | 1.09 ± 0.08 | 37.3 ± 0.9 | 17.5 ± 0.5 | 13.5 ± 1.1 | 5.4 ± 0.6 | $1.9 \times 10^{-5}$ | 10.51 | 1.2 |
| C-QAPPESK/OH-4 | 4 | 58:42 | 1.26 ± 0.01 | 36.0 ± 3.5 | 16.9 ± 0.3 | 13.4 ± 0.9 | 7.6 ± 1.4 | $2.3 \times 10^{-5}$ | 10.32 | 1.8 |
| C-QAPPESK/OH-5 | 5 | 61:39 | 1.43 ± 0.01 | 36.4 ± 2.4 | 15.9 ± 0.6 | 13.8 ± 0.4 | 10.4 ± 0.7 | $2.7 \times 10^{-5}$ | 10.21 | 1.9 |
| C-QAPPESK/OH-T[a] | 1 | 60:40 | 1.47 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| QAPPESK/OH | ~1000[f] | 45:55 | 1.04 ± 0.02 | 28.2 ± 2.8 | 13.5 ± 0.7 | 10.9 ± 1.0 | 3.4 ± 0.2 | $1.1 \times 10^{-5}$ | 13.14 | 1.2 |
| QAPPESK/OH-T[b] | 1 | 60:40 | 1.53 | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |

[a] C-QAPPESK/OH membrane with theoretical parameters.
[b] QAPPESK/OH membrane with theoretical parameters.
[c] Data measured by EDX analysis of $Br^-$ form membranes.
[d] At 25 °C.
[e] Water-saturated membranes.
[f] The molar ratio of the TMA utilized to the theoretical amount.

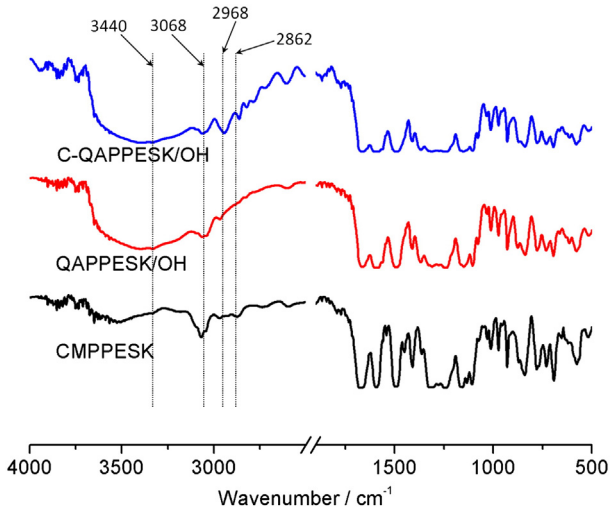



**Fig. 4.** FT-IR spectra of CMPPESK, QAPPESK/OH and C-QAPPESK/OH-5.

at 2862–2968 $cm^{-1}$ are the characteristics of $CH_2$ and $CH_3$ groups and the strength of these peaks is enhanced on C-QAPPESK/OH-5 than that of CMPPESK and QAPPESK/OH, which can be attributed to the $CH_2$ groups in TMHDA.

The SEM images and $Br^-$ elemental distribution of the C-QAPPESK/OH-5 and QAPPESK/OH membranes are presented in Fig. 5. Both of the cross-section of the two membranes are smooth and compact with thickness of ~50 μm (Fig. 5a and c). The light spots in Fig. 5b and d represent the $Br^-$ elements of membranes. As illustrated, the $Br^-$ elements can be observed throughout the cross-section and the distribution is uniform. The density of light spots for C-QAPPESK/OH-5 is larger than that of QAPPESK/OH under the same signal collecting time (4 min), indicating that the C-QAPPESK/OH-5 has larger ionic capacity than that of QAPPESK/OH.

The TG and DTG curves for C-QAPPESK/OH-5 and QAPPESK/OH membranes are shown in Fig. 6. The quaternized membranes exhibited two weight loss steps. The first step that occurred from 200 °C is mainly attributed to the elimination of decomposed products of QA groups. The second weight loss step starting at around 400 °C is ascribed to the decomposition of the polymer main chain. As shown in Fig. 6(b), the onset decomposition temperature and the fastest decomposition temperature of the first weight loss step for the two membranes are approximately the same, suggesting the similar thermal stability of C-QAPPESK/OH-5 and QAPPESK/OH. To be emphasized is that IEC of C-QAPPESK/OH-5 was higher than that of QAPPESK/OH. Therefore, it is not surprising C-QAPPESK/OH-5 would present more weight loss than QAPPESK/OH at the same temperature (Fig. 6(a)).

The mechanical properties of water-saturated AEMs were measured at room temperature and the results are listed in Table 1. It can be found that all AEMs presented a tensile strength larger than 10 MPa, and the elongation at break for all AEMs is small due to the rigid properties of backbone (PPESK). Thanks to the introduction of TMHDA containing $–CH_2–$ groups, the tensile strength of C-QAPPESK/OH was slightly decreased, but the elongation at break was increased, indicating that the ductility of C-QAPPESK/OH was improved in comparison with QAPPESK/OH, which is beneficial for the application of C-QAPPESK/OH in fuel cells.

### *3.4. Water uptake, swelling ratio and hydroxide conductivity of C-QAPPESK/OH*

The WU, $SR_p$ and $SR_t$ of these membranes at room temperature were listed in Table 2. As illustrated, C-QAPPESK/OH membranes have larger WU and SR than that of QAPPESK/OH, even at similar IEC. This can be explained in the sight of the structure of C-QAPPESK/OH. Since

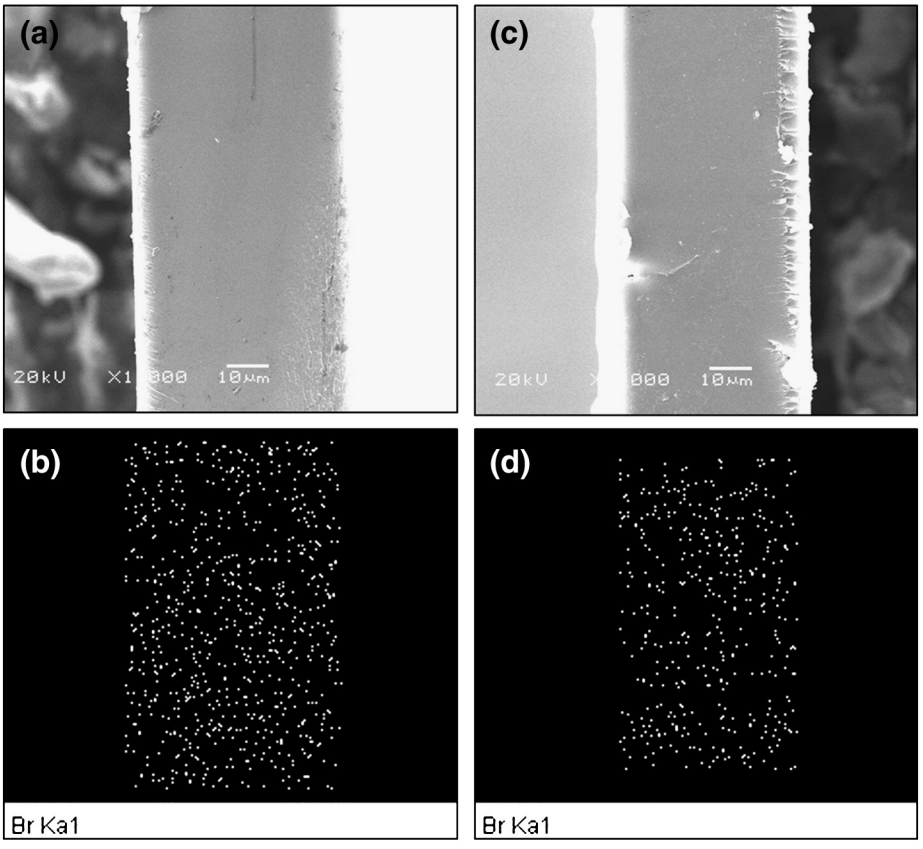



**Fig. 5.** SEM images of (a) C-QAPPESK/OH-5 and (c) QAPPESK/OH. The corresponding $Br^-$ distribution of (b) C-QAPPESK/Br-5 and (d) QAPPESK/Br.

TMHDA has six -$CH_2$, it will increase the space and reduce the interaction between adjacent polymer lines of C-QAPPESK/OH, making it easier for water molecules to enter into the membrane, resulting in the higher WU and SR of C-QAPPESK/OH than that of QAPPESK/OH. Moreover, it was found that the variation of WU and SR for C-QAPPESK/OH with the increase of $n$ was not remarkable, if any, a slight declining trend was presented. That may be explained as follows: the crosslinking network has already formed at $n = 2$, and further increasing $n$ only improved the crosslinking degree and QA group density, but it was difficult for additional water molecules to enter into the membrane owing to the tight network and enhanced interaction between adjacent polymer lines at higher crosslinking degree [23], resulting in the minor change of WU and SR with the increase of IEC. Furthermore, the WU, $SR_p$ and $SR_t$ of AEMs under different temperatures are measured (Fig. 7). It is found in Fig. 7 that, the crosslinked membrane possessed stable dimensional stability in water under elevated temperature, whereas the temperature induced swelling for the uncrosslinked membrane (QAPPESK/OH) was more significant. The high dimensional stability of C-QAPPESK/OH offers the advantage for the application in fuel cells especially under elevated temperatures.

For C-QAPPESK/OH membranes, the hydroxide conductivity increased with IEC, reaching 10.4 ± 0.7 mS $cm^{-1}$ at $n = 5$, which is much higher than that of QAPPESK/OH (3.8 ± 0.6 mS $cm^{-1}$) at 25 °C (Table 2). In order to check the effect of $CO_2$ to the results, the conductivity of $HCO_3^-$ of the membrane was measured by converting the $OH^-$ form AEMs to the $HCO_3^-$ form according to the literature [24]. We found that the calculated $OH^-$ conductivity, which was obtained from the $HCO_3^-$ conductivity using a 3.8× multiplication factor [24], was close to the measured $OH^-$ conductivity (not below), indicating the negligible effect of $CO_2$ on AEMs in our experiments. Moreover, the hydroxide

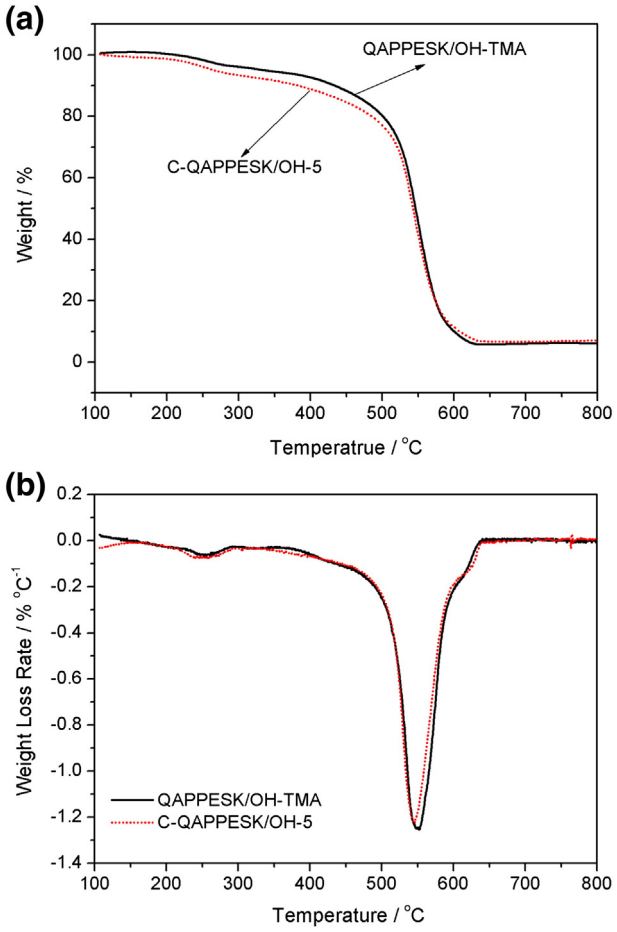



**Fig. 6.** (a) TG and (b) DTG curves of QAPPESK/OH and C-QAPPESK/OH-5.

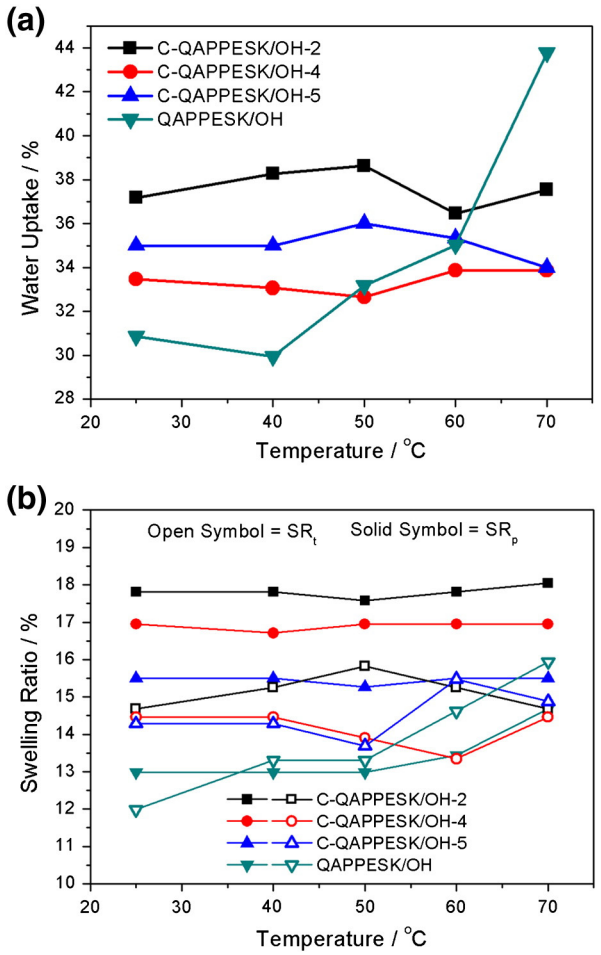



**Fig. 7.** (a) WU and (b) SR of C-QAPPESK/OH and QAPPESK/OH at different temperature.

conductivity of C-QAPPESK/OH and QAPPESK/OH membranes at different temperatures was measured. As plotted in Fig. 8, the conductivity is positively correlated to temperature, because the movement of $OH^-$ groups will speed up as long as temperature increases [8,25]. For QAPPESK/OH, the temperature-induced increase of WU (Fig. 7) might be another reason for the easier transportation of $OH^-$ in the membrane. At 70 °C, the conductivity of C-QAPPESK/OH-5 can reach as high as 17.3 mS $cm^{-1}$, which is 2.2 times that of QAPPESK/OH (~7.8 mS $cm^{-1}$).

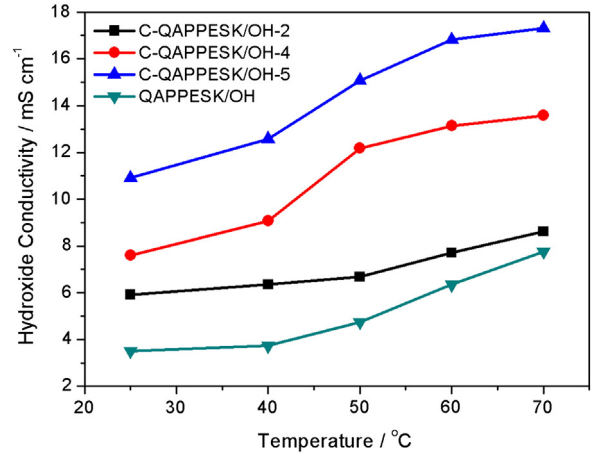



**Fig. 8.** The hydroxide conductivity of QAPPESK/OH and C-QAPPESK/OH at different temperature.

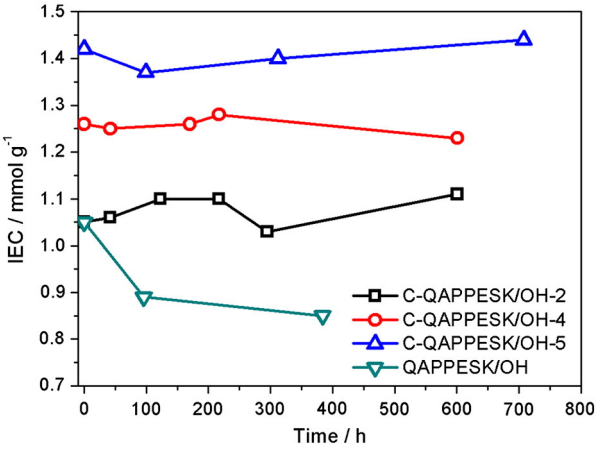



**Fig. 9.** IEC of C-QAPPESK/OH and QAPPESK/OH as a function of exposure time in deionized water at 80 °C.

For further studying the $OH^-$ conducting ability of AEMs, the mobility of $OH^-$ [$u(OH^-)$, $cm^2\ s^{-1}\ V^{-1}$] in the membranes was estimated by Nernst–Einstein Eq. (10), which is similar with the calculation of mobility of $H^+$ in proton exchange membranes [26,27]:

$$u(OH^-) = \sigma/[F \times c(OH^-)] \quad (10)$$

where $\sigma$ is the conductivity (S $cm^{-1}$), $F$ is the Faraday constant (96,485 C $mol^{-1}$), and $c(OH^-)$ is the concentration of $OH^-$ in the membrane (mol $cm^{-3}$), which can be calculated by the following equation [27]:

$$c(OH^-) = IEC \times \rho/[1000 \times WU] \quad (11)$$

where $\rho$ is the density of water (taken as 1 g $cm^{-3}$).

As shown in Table 1, the $u(OH^-)$ of C-QAPPESK/OH-2 is higher than that of QAPPESK/OH, and $u(OH^-)$ increases with the increase of IEC of C-QAPPESK/OH. For QAPPESK/OH, the low WU and IEC may inhibit the formation of ion conducting channels, resulting in the difficulty of transportation of $OH^-$ in the QAPPESK/OH. In contrast, C-QAPPESK/OH-2 has higher WU than that of QAPPESK/OH, although they have similar IEC, which is beneficial for the transport of $OH^-$. Furthermore, the ion conducting channels of C-QAPPESK/OH were further developed with the increase of IEC, and the WU did not increase simultaneously, leading to the enhancement of $u(OH^-)$ and ion conductivity.

In contrast to proton exchange membrane, high conductivity of AEMs generally requires high IEC due to the low ion mobility of $OH^-$ relative to $H^+$ [28]. Unfortunately, the WU and SR of the uncrosslinked membranes will simultaneously increase with IEC [8,28], which not only deteriorate the mechanical strength of AEMs, but also damage the interface between membrane and electrode under humidity fluctuation conditions in fuel cells. Herein, thanks to the crosslinking effect, the swelling of C-QAPPESK/OH membranes was impeded and the membrane with high conductivity together with low water uptake and good dimensional stability was obtained.

### 3.5. Chemical Stability of C-QAPPESK/OH

Besides conductivity, the chemical stability is another important index in the development of AEMs, because the stability of the cationic functional group in AEMs, typically quaternary ammonia, is usually lower than that of the sulfonic functional group in acidic polymer electrolytes such as Nafion [28]. Typically, the QA groups will be decomposed by the Hofmann elimination and nucleophilic substitution mechanisms, and the decomposition rate will be sped up at high temperature [1,29]. Herein, the chemical stability of the quaternized membranes was studied by monitoring the change of IEC with the time in water at 80 °C (Fig. 9). After 500 h or even 700 h, the IEC of C-QAPPESK/OH did not decline. In sharp contrast, the IEC of QAPPESK/OH decreased gradually and

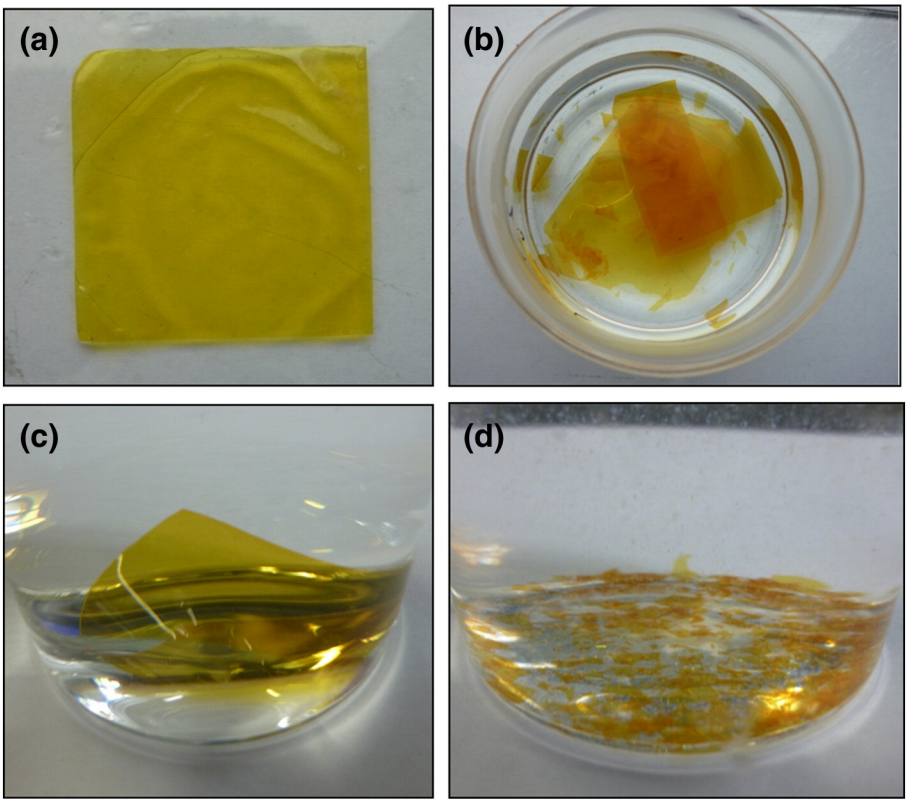



**Fig. 10.** Photo graphs of (a, c) C-QAPPESK/OH and (b, d) QAPPESK/OH (a, b) before and (c, d) after degradation test.

the loss was 20% merely after 200 h. In addition, the morphology of C-QAPPESK/OH membrane did not change after degradation testing, while the QAPPESK/OH membrane was crashed into pieces after only 96 h (Fig. 10). The Br:S molar ratio of C-QAPPESK/OH membranes after degradation testing was 53:47, 55:45 and 62:38 for C-QAPPESK/OH-2, C-QAPPESK/OH-4 and C-QAPPESK/OH-5, respectively, which was very close to the initial value. Furthermore, the microscopic morphology of C-QAPPESK/OH and the distribution of ionic clusters were not changed obviously (Fig. 11). In comparison, the ratio was decreased to 40:60 for QAPPESK/OH, i.e., an 18% loss in the Br:S molar ratio, which is consistent with the 19% IEC loss, indicating the loss of QA groups in QAPPESK/OH during the degradation testing.

To further evaluate the stability, the variation of IEC of membrane in 1 M KOH at elevated temperature was measured. Fig. 12a shows the IEC loss of C-QAPPESK/OH-5 in 1 M KOH at 50, 60, 70 and 80 °C for 48 h. It can be seen that the loss of IEC got more significant with the increase of temperature, which is consistent with the literature [30]. Furthermore, the long-term stability of C-QAPPESK/OH-5 and QAPPESK/OH was compared by monitoring the IEC loss in 1 M KOH at 60 °C for more than 300 h. As shown in Fig. 12b, the IEC of C-QAPPESK/OH-5 is decreased by 24% from 1.42 mmol $g^{-1}$ to 1.09 mmol $g^{-1}$ after 336 h, whereas a 48% loss of IEC is observed for QAPPESK/OH. The above results indicated better chemical stability of C-QAPPESK/OH membrane than QAPPESK/OH in alkaline solution under elevated temperature.

The decomposition of QA groups in QAPPESK/OH might be through the elimination of a tertiary amine to form benzyl alcohol [9]. The improved stability of TMHDA-modified membranes can be attributed to the difficulty for the β-proton abstraction of QA groups in C-QAPPESK/OH membranes, due to the increased electron density at the β-carbon shifted from γ-carbon [13]. As a result, it can be concluded that the chemical stability of quaternizing membranes can be improved by crosslinking with TMHDA, which is of great importance to the application of AEMs under the fuel cell working conditions.

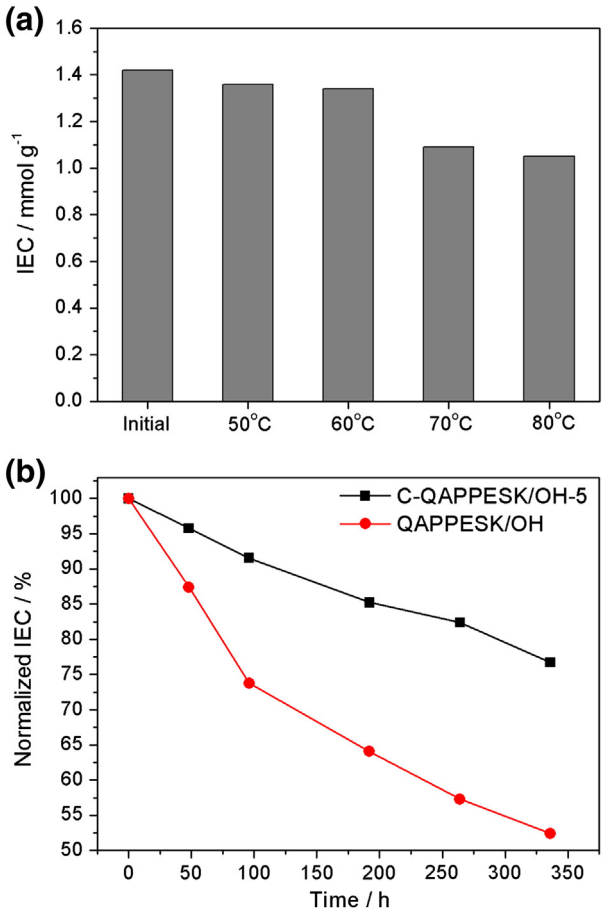



**Fig. 12.** (a) IEC of C-QAPPESK/OH-5 after immersing in 1 M KOH at 50, 60, 70 and 80 °C for 48 h, respectively. (b) IEC of C-QAPPESK/OH-5 and QAPPESK/OH as a function of exposure time in 1 M KOH at 60 °C.

## 4. Conclusions

In this work, the chloromethylation of PPESK, PEEK and PES was successfully conducted by using BCMB as the chloromethylating reagent and concentrated $H_2SO_4$ as the solvent and catalyst. As a non-carcinogenic and low-price chloromethylating reagent, BCMB has higher activity than CMOE under similar reaction conditions. Moreover, concentrated $H_2SO_4$ is selected to be the solvent and catalyst, so the use of halogenated hydrocarbon solvents and humidity-sensitive Lewis acid is avoided. Therefore, the combination of BCMB and concentrated $H_2SO_4$ is a green, highly efficient and economic chloromethylation method and it can be widely applied in the preparation of anion exchange membranes. Furthermore, quaternized and crosslinked PPESK membranes were then prepared by using TMHDA as the quaternizing and crosslinking agent. This is a simultaneous and homogeneous quaternizing and crosslinking method, that is, the crosslinking and quaternization can be accomplished at the same time during the membrane formation. The quaternization proceeds homogenously, which improves the efficiency, leading to the resulting IEC close to the theoretical value. The C-QAPPESK/OH membranes possess enhanced hydroxide conductivity and chemical stability in comparison with that of QAPPESK/OH prepared by the conventional quaternization method. This simultaneous quaternizing and crosslinking method could significantly improve the performance and chemical stability of AEMs; also it is a time-saving and efficient method, with potential use in the preparation of anion exchange membranes.

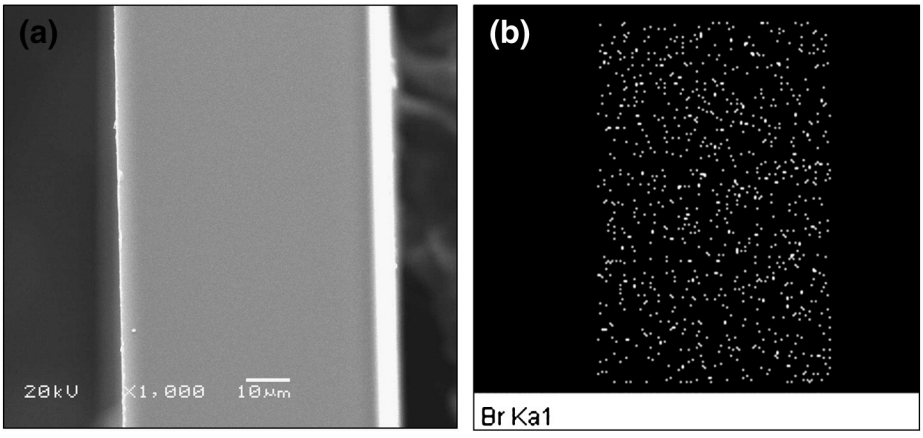



**Fig. 11.** (a) SEM image of C-QAPPESK/OH-5 and (b) $Br^-$ distribution of C-QAPPESK/Br-5 after degradation testing.

## Acknowledgements

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