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Synthesis and characterization of poly(ether sulfone ether ketone ketone) grafted poly(sulfopropyl methacrylate) for proton exchange membranes via atom transfer radical polymerization

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Abstract A series of copolymers of poly(ether sulfone ether ketone ketone) grafted poly(sulfopropyl methacrylate) (PESEKK-*g*-PSPMA) were successfully synthesized by atom transfer radical polymerization (ATRP) of sulfopropyl methacrylate (SPMA) after chloromethylation of poly(ether sulfone ether ketone ketone) (PESEKK) backbone. The structure of the chloromethyl PESEKK and the copolymers were carefully investigated. Variation of the polymerization time leads to the formation of copolymers with different degree of sulfonation (DS). The properties of the proton exchange membranes such as water uptake, ion exchange capacity, proton conductivity, and methanol permeability are studied with compared to those of Nafion 117 membranes and could be modulated simply by control of the ATRP time. The copolymers exhibited much lower methanol permeability and higher proton conductivity as compared with Nafion 117.

Introduction

As a primary component of polymer electrolyte membrane fuel cells (PEMFCs), the polymer electrolyte membrane (PEM) is required to perform a number of functions that include gas separation, acting as an electrical insulator and providing an ionic path for proton transport from anode to cathode [1–3]. Nafion membranes have achieved the greatest success, providing the most attractive, commercially available combination of performance, durability, and reliability. However, the high cost, low stability at high temperatures due to low glass transition temperature, and high methanol crossover of Nafion limit the extent of its further application and commercialization [4–6]. Thus, many efforts have been spent to develop alternative PEM materials [7–27].

Alternatively, sulfonated aromatic polymers, including sulfonated poly(aryl ether ketone)s (SPAEKs), among others, have low inherent costs, high proton conductivity, and high thermo-oxidative properties as well as good chemical and mechanical stability [20–23]. In order to obtain and maximize their conductive properties, these polymers must be introduced to sulfonic acid groups, which can be accomplished by either post-sulfonation of the polymers or directly polymerizing sulfonated monomers [28]. In general, sulfonated polymers with sulfonic acid groups on pendant phenyl rings are more stable to hydrolysis than those with sulfonic acid groups attached directly to the polymer backbone, as sulfonic acid groups can accelerate the hydrolysis of ether [29, 30]. Furthermore, the use of polymers makes it possible to improve the microphase separation of hydrophilic and hydrophobic domains that contribute to a broader ionic channel. The use of self-organized, nanophase-separated structures can allow better control of both the sulfonation degree and the distribution of sulfonic acid groups [31, 32].

As reported [33], the comb-shaped copolymer based on a highly fluorinated and rigid polyaromatic backbone containing mododisperse α-methylpoly(styrenesulfonic acid) side chains was successfully synthesized, and it was found that the copolymer PEMs exhibited very low hydration-

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based dimensional changes at elevated operating temperatures with similar proton conductivity and water uptake values when compared to Nafion. The well-defined polymer brushes can be introduced onto the backbone of the aromatic rings via the use of atom transfer radical polymerization (ATRP) process. As the initiators of ATRP, reactive alkyl halide groups in the polymer main chains are necessary. The chloromethyl groups are generally introduced into the main chain of the aromatic polymer chains via the chloromethylation by the electrophilic Friedel–Crafts substitution of the aromatic rings [34–36].

Designing new PEMs to enhance their proton conductivity, chemical/thermal stability, and mechanical property and to reduce the swelling is an ongoing effort. In our earlier study, a series of sulfonated poly(ether sulfone ether ketone ketone) (SPESEKK) with different degree of sulfonation were prepared by the post-sulfonation of PESEKK using chlorosulfonic acid as sulfonating agent and concentrated sulfuric acid as solvent. Since sulfonation is an aromatic electrophilic substitution reaction, electron-withdrawing sulfone groups deactivate the reaction. The more powerful sulfonic reagent of chlorosulfonic acid was employed, which could lead to the breakdown of the polymer main chain. In this study, to improve the stability of the resulting polymers and introduce the microphase separation structure, the copolymers of poly(ether sulfone ether ketone ketone) grafted poly(sulfopropyl methacrylate) (PESEKK-*g*-PSPMA) containing hydrophobic and hydrophilic segments were synthesized by the ATRP initiated from the chloromethyl groups of the backbone. The structure, as well as the properties of membranes including water uptake, proton conductivity, and methanol permeability, was investigated.

Experimental

Materials

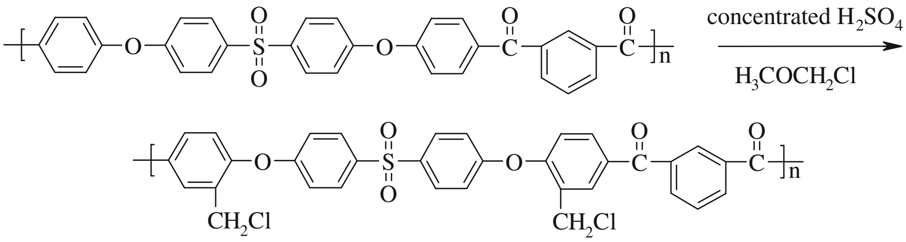
Isophthaloyl chloride (IPC) was purchased from Shuanglin Chemical Co. of China and purified by distillation under vacuum to give m.p. 43–44 °C. Ethylene dichloride was purified by distillation and dried over 0.5-nm molecular sieve. *N*-Methylpyrrolidone (NMP) of C.P. was purified by distillation and dried over a 0.5-nm molecular sieve. Concentrated sulfuric acid (98%) (H_2SO_4) was used as received. Anhydrous aluminum chloride ($AlCl_3$) was used as received without further purification. 4,4′-Bis(phenoxy)diphenyl sulfone (DPODPS) was prepared according to the literature [37]. Chloromethyl methyl ether (CME) was purchased from Shanghai Haiqu company, and 1,1,4,7,10,10-hexamethyl triethylene tetramine (HMTETA) was purchased from Aldrich. 3-sulfopropylmethacrylate (SPMA) was purchased from Tokyo Kasei Kogyo Co., Ltd. They are all used as received without further purification. Copper(I) bromide (CuBr) was purchased from Sinopharm Chemical Reagent Co. Ltd. and was purified according to procedures described in the literature [35]. The other solvents and chemicals were used as received without further purification.

Synthesis of PESEKK

The poly(ether sulfone ether ketone ketone) was synthesized as following procedures. The anhydrous aluminum chloride (18 g) was stirred in ethylene dichloride (60 mL) with the addition of the mixtures of NMP (6 mL) and ethylene dichloride (60 mL) at 0 °C. Then, the DPODPS (8.04 g) and IPC (4.06 g) were added at −15 °C and the reaction mixture was stirred at normal temperature for 8 h, followed by the addition of several drops of diphenyl ether. Finally, the methanol (100 mL) was added dropwise into the reaction mixture after 2 h to terminate the reaction. The received polymer was dried at 100 °C in vacuum overnight before sulfonation.

Chloromethylation of PESEKK

The synthesis procedure of chloromethyl poly(ether sulfone ether ketone ketone) (CMPESEKK) was illustrated in Scheme 1. The PESEKK (1.07 g) was dissolved in a three-neck flask containing 30 mL of concentrated H_2SO_4 under nitrogen and vigorous stirring for 1 h at room temperature. The flask was cooled to 5 °C in the ice bath, followed by the addition of CME in dropwise under vigorous stirring. After reaction for 2.5 h, the mixture was precipitated into a large excess of ice-cold deionized water. The polymer precipitate was filtered and washed with distilled water



Scheme 1 Synthetic procedure of CMPESEKK

until the filtration was neutral. The received polymer was then dried at 80 °C under vacuum for 24 h.

Synthesis of PESEKK-*g*-PSPMA copolymer

The synthesis procedure of PESEKK-*g*-PSPMA copolymers was illustrated in Scheme 2. The CMPESEKK (0.628 g) and sulfopropyl methacrylate (SPMA) (2.51 g) were dissolved in 25 mL of dimethyl sulfone (DMSO) under vigorous stirring at room temperature. After the formation of homogeneous solution, CuBr (0.014 g) and HMTETA (0.03 mL) were added under nitrogen and stirred for 0.5 h. The flask was then sealed and placed in the 120 °C oil bath for the predetermined time of 3, 7, and 12 h, respectively. The mixture was precipitated into a large excess of methanol, and the collected polymer was washed by the mixture of ethanol and water (1:1 in volume) for several times. The received polymer was then dried at 80 °C under vacuum for 24 h.

Membrane preparation

Membranes were prepared from casting solution containing PESEKK-*g*-PSPMA in DMSO at 5 wt%. The solution was cast onto a glass sheet and dried in an oven at 100 °C for 24 h. Consequently, the transparent membranes with the thickness of 40–60 μm were obtained.

Water uptake

Water uptake was determined by weighing vacuum dried membrane and fully equilibrated membrane with water. The surface of the membrane sample was quickly wiped with an absorbent tissue to remove the excess of water and the sample was then weighed. The water uptake of the membrane was determined from:

$$\text{Water uptake } (\%) = (W_s - W_d)/W_d \times 100\% \qquad (1)$$

where W_d and W_s are the weights of dried and wet membranes, respectively.

Ion exchange capacity (IEC)

Ion exchange capacity of the membranes was measured by the classical titration method. The PESEKK-*g*-PSPMA membranes were soaked in 1.5 M NaCl solution for at least 72 h before measuring IEC. The protons released due to the exchange reaction with Na ions were titrated with 0.005 M standardized NaOH solution, using phenolphthalein as an indicator. The IEC of the PESEKK-*g*-PSPMA membranes was calculated from the following equation:

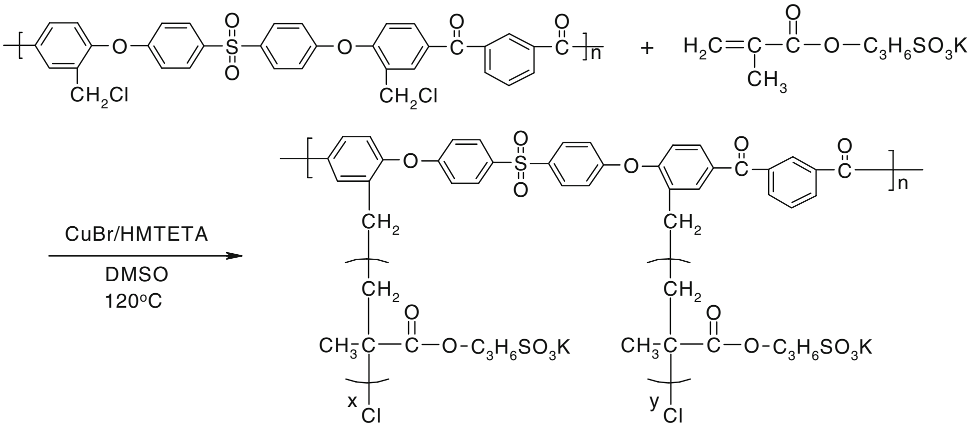
$$\text{IEC} = \frac{V(\text{NaOH}) \times C(\text{NaOH})}{M(\text{membrane})} \qquad (2)$$

where V(NaOH) is the volume (mL) of NaOH solution consumed, C(NaOH) is the normality of NaOH solution, and M(membrane) is the weight of the PESEKK-*g*-PSPMA membranes.

Proton conductivity

The proton conductivities (δ) of the PESEKK-*g*-PSPMA membranes at different temperatures were evaluated using three-electrode electrochemical impedance spectra. The impedance measurements were carried out on a CHI660 electrochemical workstation (CH Instruments) coupled with a computer. An organic glass diffusion cell composed of two symmetrical chambers was divided by a membrane sample. The cells were filled with the electrolyte composed of methanol (1 M) and sulfuric acid (0.5 M). The two platinum wires used as working electrode and counter electrode, as well as a calomel electrode functionalized as the reference electrode, were introduced into the electrolyte solution. The impedance spectra were recorded with the help of ZPlot/ZView software under an ac perturbation

Scheme 2 Synthetic procedure of PESEKK-*g*-PSPMA



signal of 5 mV over the frequency range of 0.1 MHz to 1 Hz. The electron resistance of the system (without membrane divided) was measured as R_1, and the electron resistance of the system (with membrane divided) was measured as R_2. Electron resistance of membrane under variable temperature (15–50 °C) at 100% humidity was obtained as the dispersion of R_2 and R_1. The proton conductivity δ of the membrane was calculated from the following equation:

$$\delta = I/(RA) \tag{3}$$

where δ, I, R, and A represent the proton conductivity, thickness of membranes, the resistance of the membrane, and the cross-sectional area of the membrane, respectively.

Methanol permeability

An organic glass diffusion cell was used to obtain the methanol permeability of the PESEKK-*g*-PSPMA membranes. The diffusion cell was composed of two chambers divided by a membrane sample. One chamber of the cell (V_1) was filled with a 5 M (C_1) methanol solution in distilled water. The other chamber (V_2) was filled with water. A sample (effective area 0.385 cm^2) was clamped between the two chambers. Methanol permeates across the membrane by the concentration difference between the two chambers. The methanol concentration in the receiving chamber as a function of time is given by:

$$C_2(t) = [ADK\,C_1(t - t_0)]/(V_2 l) \tag{4}$$

where A (cm^2) is the membrane area, l (cm) is the membrane thickness, D is the methanol diffusivity, and K is the partition coefficient between the membrane and the adjacent solution. The product DK means the membrane permeability (P).

$$P = (C_2(t)V_2\,l)/[A\,C_1(t - t_0)] \tag{5}$$

C_2 is measured several times during the permeation experiment and the methanol permeability is obtained from the slope of the straight line. The methanol concentration was measured by using a gas chromatography of Agilent GC 6820 equipped with a FID detector.

Characterization

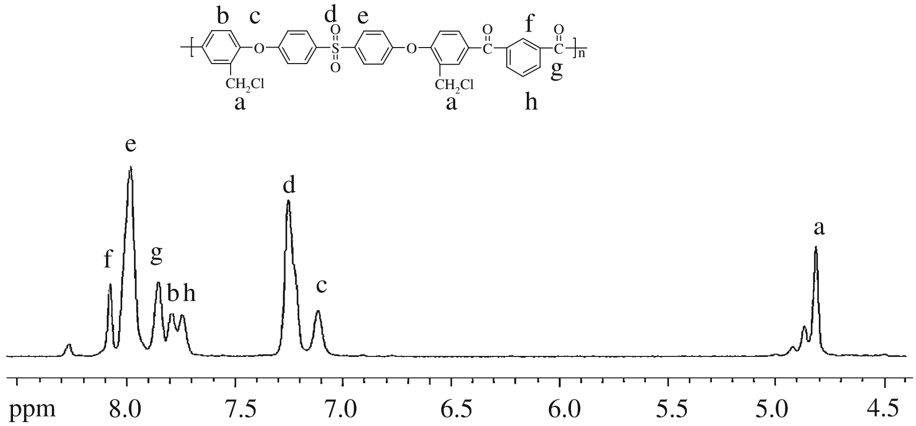
The proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Bruker ARX 400 NMR spectrometer with dimethyl sulfoxide-*d* as solvent and tetramethylsilane ($\delta = 0$) as internal reference. The thermal gravimetric analysis (TGA) was performed using a Perkin-Elmer instrument TGA 7 at a heating rate of 20 °C min^{-1} under a nitrogen atmosphere (50 mL min^{-1}).

Results and discussion

Structure analysis

Chloromethylation provides PESEKK with active group, –CH_2Cl, for the subsequent reaction. The chloromethylation of aromatic polymers is an electrophilic Friedel–Crafts substitution reaction, and the substitution position depends on the type of activating substituents linked to the phenyl ring. In the chemical structure of PESEKK, the ether bond is an electron-donating substituent leading to selective *ortho*- and *para*-substitution, while phthalazinyl and sulfone groups are electron-withdrawing substituents which favor the meta-substitution. Thus, the chloromethyl substitution occurs at the carbon atom adjacent to the ether bond, as shown in Scheme 1. The corresponding structure analysis of CMSPESEKK is shown in Fig. 1. The peak at 8.08 ppm is assigned to the proton adjacent to the C=O group of phthalazinone. Since its relative intensity remains unchanged after chloromethylation, the peak is selected as the reference peak. The peak at 4.8 ppm is attributed to the protons of –CH_2Cl group. The number of chloromethyl group per PESEKK repeat unit (DS, degree of substitution)

Fig. 1 ^{1}H NMR spectrum of CMPESEKK



was calculated based on the intensity of the 4.8 ppm versus the 8.08 pm peak. Consequently, the DS value is calculated to be about 1.18, showing that there are about 1.18 chloromethyl groups in one PESEKK repeat unit.

After the incorporation of chloromethyl groups, which serve as the initiator for the subsequent atom transfer radical polymerization, the monomer of SPMA is grafted onto the PESEKK backbones. The synthetic process of the PESEKK-*g*-PSPMA is illustrated in Scheme 2, and the successful grafting of PSPMA onto PESEKK is confirmed by the ^{1}HNMR analysis as shown in Fig. 2. It is noted that the peak at 3.4 ppm is attributed to the absorbed water, and the peak at 2.5 ppm is assigned to the DMSO solvent. The peak at 4.4 ppm is ascribed to the protons in chloromethyl groups, showing that not all the chloromethyl groups initiate the polymerization of SPMA monomer. The peaks at 2.5, 2.9, and 4.1 ppm are assigned to the protons of –CH_2 groups in the side chains of PSPMA. The peaks at 1.0 and 1.9 ppm are attributed to the methyl and ethylene groups in the PSPMA segments. Furthermore, the peaks located at the regions between 7.2 and 8.0 ppm are attributed to the protons of the phenyl rings in PESEKK main chains.

Membrane properties

Table 1 shows the water uptake, proton conductivity, methanol permeability and IEC values of PESEKK-*g*-PSPMA copolymer membranes. The water uptake, as well as the swelling ratio of PEMs, is closely related to IEC, proton conductivity, dimensional stability, and mechanical strength. The water within the membrane provides a carrier for the proton and maintains high proton conductivity. However, excessive water uptake in a PEM leads to unacceptable dimensional change or loss of dimensional shape, leading to weakness or dimensional mismatch when incorporated into a membrane electrode assembly. It is observed from Table 1 that the water uptake increased as the polymerization time increasing due to the incorporation of more content of sulfonic acid groups. However, the water uptake of the membranes is lower than that of Nafion 117 even after polymerization of 12 h.

It is generally accepted that high value of IEC is desirable to achieve higher proton conductivity in polymer electrolyte membranes. However, the continuous increase in the content of sulfonic acid group may result in the

Fig. 2 ^{1}H NMR spectrum of PESEKK-*g*-PSPMA

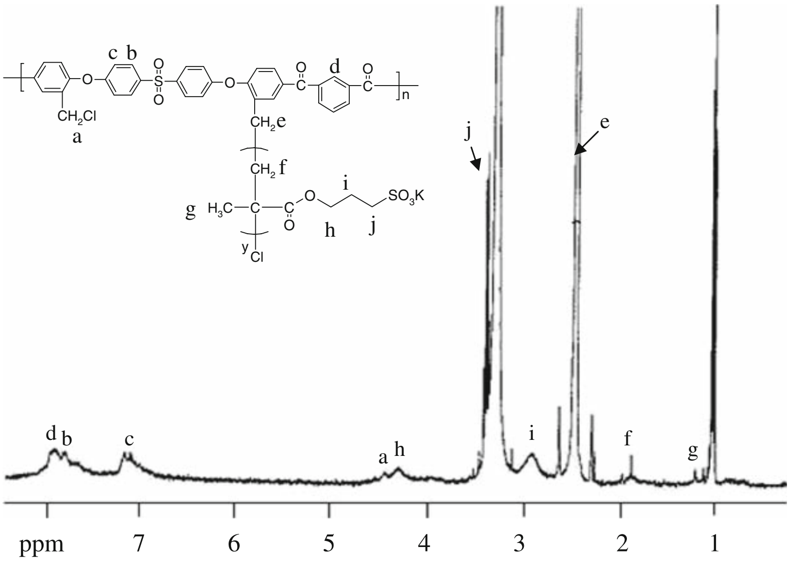


Table 1 Water uptake, proton conductivity, methanol permeability, and IEC values of PESEKK-*g*-PSPMA copolymers membranes

Membrane	Polymerization time (h)	Water uptake (%)	IEC[a] (mEq g^{-1})	Proton conductivity[b] (s/cm)	Methanol permeability[c] ($\times 10^{-7}$ cm^2/s)
PESEKK-*g*-PSPMA	3	5.36	0.12	1.40×10^{-4}	1.53
	7	16.73	0.80	4.72×10^{-3}	2.21
	12	25.75	1.05	6.53×10^{-2}	5.23
Nafion 117	–	33.4	0.90	7.0×10^{-2}	24

[a] IEC measured with titration at room temperature

[b] Measured at 28 °C

[c] Measured at 20 °C

deterioration of mechanical properties of the membranes because of highly hydrophilic property of the polymer. Therefore, it is essential to control the amount of sulfonic acid groups. The IEC value of the membranes increased from 0.12 to 1.05 mEq g^{-1} with the increase of polymerization time, which is comparable to that of Nafion 117 of 0.90 mEq g^{-1}. It is concluded that the IEC values could be modulated simply by the control of ATRP time.

In general, proton exchange membrane fuel cells of high performance require the high value of proton conductivity. Nafion 117 was commercialized due to its high proton conductivity, as well as the superior chemical and electrochemical stability. It is observed form Table 1 that the proton conductivity showed the similar behavior with that of water uptake and IEC values as the polymerization time increasing. However, the proton conductivity of the membranes is much lower than that of Nafion 117 except for the samples with polymerization of 12 h.

Methanol permeability is another important parameter determining the performance of the proton exchange membranes. Low methanol permeability as well as the high proton conductivity is required for the direct methanol fuel cells. It is observed that the membranes showed lower value of methanol permeability in comparison with the Nafion 117, indicating that much lower content of methanol passing through the membranes. It is noted that the mechanical property of the membrane began to deteriorate after polymerization for 12 h, and the formation of membrane became difficult.

Thermal properties

The thermal stabilities of the PESEKK, CMPESEKK, and PESEKK-*g*-PSPMAs were investigated by the thermal gravimetric analysis as shown in Fig. 3. It is noted that the pristine PESEKK exhibits two distinct steps. The first weight loss step is mainly associated with the loss of residual solvents in the range of 150–250 °C. The second weight loss step is related to the decomposition of the main chain of PESEKK in the range of 500–650 °C. In contrast, the CMPESEKK exhibited a different decomposition behavior after the incorporation of chloromethyl groups. Another degradation stage ranging from 230 to 320 °C is discerned, which should be related with the decomposition of chloromethyl groups. As far as the PESEKK-*g*-PSPMA copolymers are concerned, the copolymers exhibit an additional degradation step similar to that of CMPESEKK, attributable to the decomposition of the PSPMA grafting segments. Increase of the polymerization time leads to the more weight loss as observed in the degradation curves. It is concluded that the incorporation of PSPMA segments makes the PESEKK less stable.

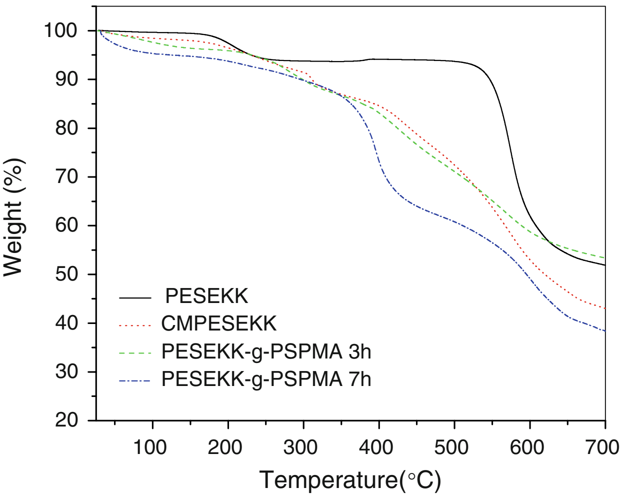


Fig. 3 Thermogravimetric curves of PESEKK, CMPESEKK, and PESEKK-*g*-PSPMA after grafting for 3 and 7 h, respectively

Conclusions

A series of PESEKK-*g*-PSPMA copolymers were successfully synthesized via the chloromethylation of the PESEKK main chain, followed by the ATRP of SPMA monomers onto the backbone of PESEKK. The chemical structures of the polymers were carefully investigated by the ^{1}HNMR analysis, showing that not all the chloromethyl groups initiated the graft polymerization of SPMA. The copolymers with different degree of sulfonation could be modulated simply by the control of ATRP time. The water uptake, IEC values, and proton conductivity of the copolymers depend on the grafting polymerization time, and the increase of ATRP time lead to the value increase of the above parameters. However, these values are comparable to those of Nafion 117. The methanol permeability of the copolymers increases as the polymerization time increasing, which is much lower than that of Nafion 117. The incorporation of chloromethyl groups and the PSPMA segments makes the PESEKK backbone less stable.

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