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Synthesis and characterization of fluorinated ionomer *p*-perfluoro-[1-(2-sulfonic)ethoxy]ethylated polyacrylonitrile-styrene

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Abstract

Fluorinated ionomer *p*-perfluoro[1-(2-sulfonic)ethoxy]ethylated polyacrylonitrile-styrene (SFAS) (**5**) was synthesized via electron transfer reaction between polyacrylonitrile-styrene (AS) (**1**) and perfluoro-di[2-(2-fluorosulfonyl)ethoxy]propionyl peroxide (FAP) (**2**) and followed by alkali hydrolysis and acidification of *p*-perfluoro[1-(2-fluorosulfonyl)ethoxy]ethylated polyacrylonitrile-styrene (**3**). The microstructure of ionomer **5** was well characterized by FTIR and ^{19}F NMR. Its desulfonation occurred above 197 °C was found by TGA, the degree of substitution (DS) and ion exchange capacity (IEC) determined by titration were well controlled through changing the molar ratio of **2**:**1**. The proton exchange membranes made of ionomer **5** have water uptake from 13.4 to 135.3% and conductivity up to 10^{-2} S cm^{-1} at 25 °C.

Keywords: Polyacrylonitrile-styrene; Perfluoro-di[2-(2-fluorosulfonyl)ethoxy]propionyl peroxide; *p*-Perfluoro[1-(2-sulfonic)ethoxy]ethylated polyacrylonitrile-styrene; Ionomer; Proton exchange membrane

1. Introduction

Polymer ionomers have attracted extensive studies duo to their potential application, as fuel cell, sensor, ion exchange resin and so on. In particular, the study of proton exchange membrane for fuel cell has received tremendous attention [1,2]. Specially, the perfluorinated ionomeric membranes, developed by Dupont, Dow and Asahi companies, have been widely applied owning to their excellent chemical and oxidative stability, conductivity and mechanical property [3,4]. However, they are too costly to be applied extensively. In the recent years, much research has peered into low cost polymer membranes, such as sulfonated polystyrene membranes [5], sulfonated triblock copolymer polystyrene-(ethylene-butylene)-styrene [6,7], sulfonated polyphosphazene [8] and sulfonated aromatic polymers [9–11]. There was also a few partial fluorinated proton exchange membranes developed [12,13]. However, there is no literature about partial fluorinated polymer membrane containing perfluoroether sulfonic acid side chain similar to Nafion, before Zhao's new aromatic perfluoroalkylation reaction using perfluorodiacyl peroxides [FAP, $(R_fCOO)_2$] [14] and its application in the synthesis of fluorinated polymers [15] and the innovative synthesis of ω-fluorosulfonyl-perfluorodiacyl peroxides [16] and its polymer modification via ω-sulfonic-perfluoroalkylation bearing perfluoroether sulfonic acid functional group similar to Nafion [17] (Scheme 1).

In this paper, we synthesized a fluorinated ionomers of *p*-perfluoro[1-(2-sulfonic)ethoxy]ethylated polyacrylonitrile-styrene (**5**) via electron transfer reaction between the substrate **1** and perfluoro-di[2-(2-fluorosulfonyl)ethoxy]propionyl peroxide (**2**) at 0 °C in CH_2Cl_2 and followed by alkali hydrolysis and acidification of the intermediate product **3**. The structural analysis of ionomer **5** was performed by FTIR, ^{19}F NMR, TGA and DSC. The properties of membrane made of **5** were tested by water uptake, IEC and proton conductivity determinations.

2. Results and discussion

2.1. Synthesis of ionomer p-perfluoro[1-(2-sulfonic)ethoxy]ethylated polyacrylonitrile-styrene (5)

As shown in Scheme 2, styrene unit in the substrate copolymer **1** reacted just as an alkylbenzene, the reaction looks

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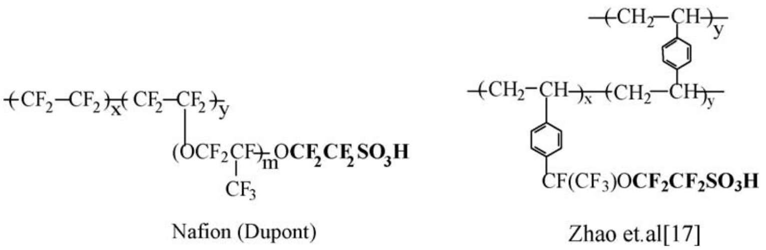
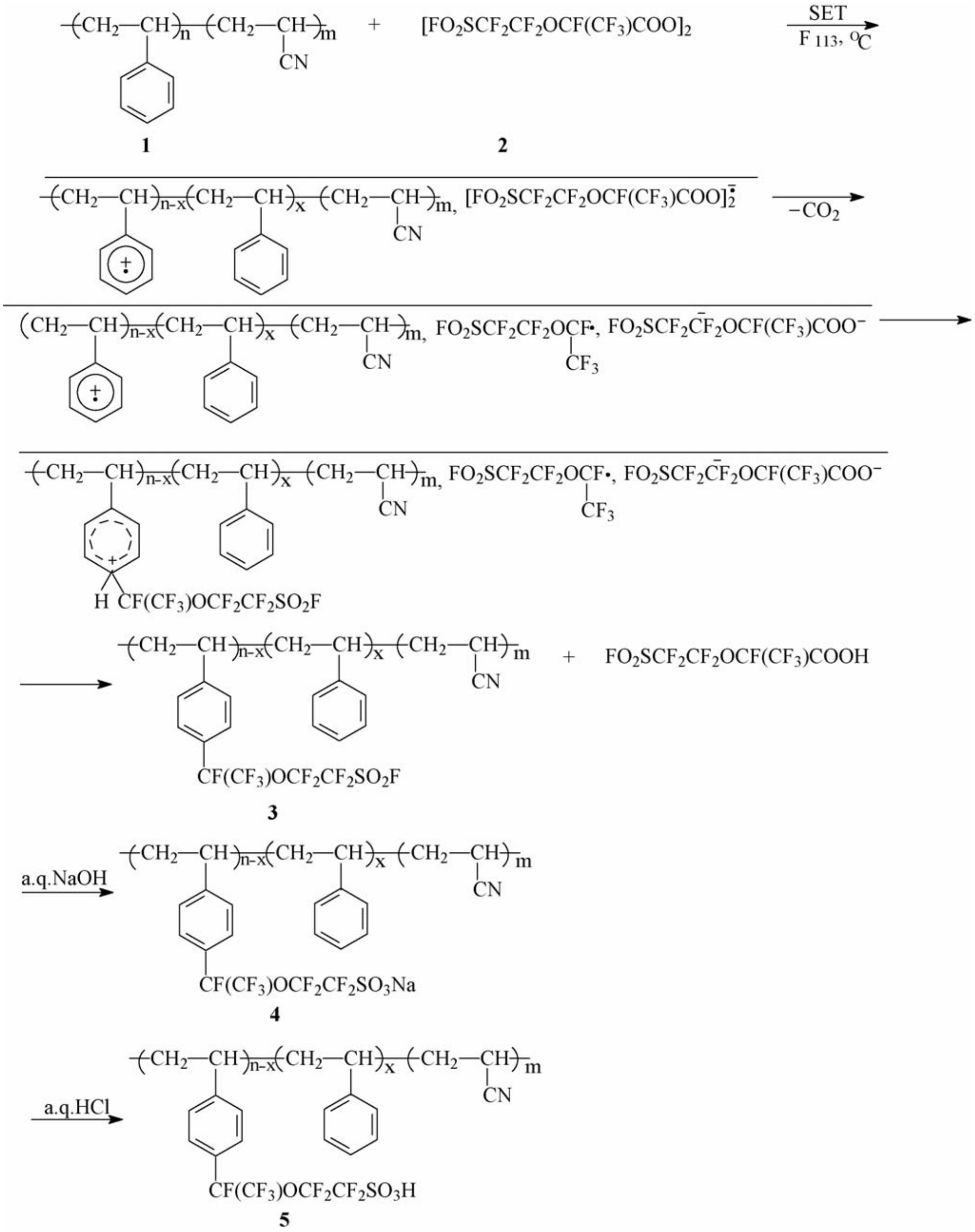


Scheme 1.

like an aromatic electrophilic substitution. Actually, the styrene unit undergone electron transfer (ET) to the one-electron oxidant perfluoro diacyl peroxides **2** in inert solvent at temperature no higher than 30 °C [14,15]. In the bimolecular ET-reactions of $(R_fCO_2)_2$ with electron-donors, the spontaneous unimolecular decomposition of the peroxide was unavoidably accompanied [18]. In the *p*-perfluoroalkylation of the moderate reactive polymer like PS, the reaction temperature was better fixed at as lower as possible. Since at lower temperature, the ET step with smaller activation energy



Scheme 2. Synthesis of ionomer **5**.

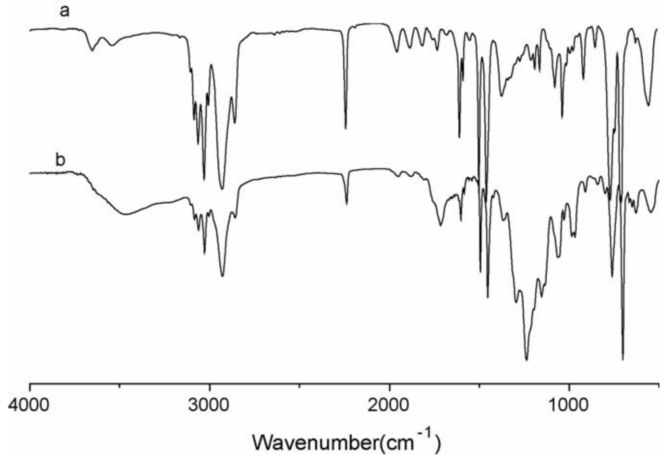


Fig. 1. FTIR spectra of **1** (a) and ionomer **5** (b) (at **2**:**1** = 1:5).

leading to the desired product **3** was not heat sensitive, but the unimolecular decomposition of $(R_fCO_2)_2$ forming useless coupling product R_f–R_f could be largely depressed. After electron was transferred from PS to peroxide **2**, the radical anion $\mathbf{2}^{\bullet-}$ in the original solvent cage collapsed extremely fast (at about 10^{10} S^{-1}) [19], and the free radical $FO_2SCF_2CF_2OCF(CF_3)COO^{\bullet}$ decarboxylated even faster to give $FO_2SCF_2CF_2OCF(CF_3)^{\bullet}$ which reacted with $PS^{\bullet+}$, and formed polymer intermediate **3**. Followed by alkali-hydrolysis and acidification, **3** was converted to the final ionomer **5**.

2.2. Microstructure characterization and tests of ionomer 5

FTIR spectra comparing the ionomer **5** with the substrate **1** is presented in Fig. 1. The FTIR spectrum (Fig. 1b) shows the strong absorption bands between 1100 and 1350 cm^{-1} which are characteristic for the fluorinated groups [15,17]: $\nu(CF_3)$ at 1314 cm^{-1}, $\nu(CF_2)$ at 1244 and 1210 cm^{-1}. The asymmetric stretching absorption of $\nu(S{=}O)$ at 1340 cm^{-1} can be seen. The peak at 1113 and 1138 cm^{-1} is characteristic of ether linkage. The peak at 821 cm^{-1}, which is characteristic of a *para*-disubtituted phenyl ring (860–800 cm^{-1}), provides a strong evidence for *para*-substitution. The peak at about 3600 cm^{-1} indicates characteristic absorption of –OH of $-SO_3H$. The lack of carbonyl absorption discloses the absence of ring-ω-sulfonic-perfluoroacyloxylation.

Two sets of ^{19}F NMR spectra (Fig. 2) comparing the ionomer **5** (Fig. 2B) with intermediate product **3** (Fig. 2A) shows the perfluoro[1-(2-fluorosulfonyl)ethoxy]ethyl group [$-CF^a(CF_3{}^b)OCF_2{}^cCF_2{}^dSO_2F^e$] of **3** (at molar ratio **2**:**1** = 1:3) appears at δ123.1 (1F, f), −51.8 (1F, a), −34.1 (2F, d), −6.37 (3F, b) and −2.186 to −0.192 ppm (2F, c). However, perfluoro[1-(2-sulfonic)ethoxy]ethyl group [$-CF^a(CF_3{}^b)-OCF_2{}^cCF_2{}^{d'}SO_3H$] of ionomer **5** (at molar ratio **2**:**1** = 1:3) appears no signal at δ123.2 ppm, which indicates all $-SO_2F$ groups of **3** have turned into $-SO_3H$ of **5** completely [20], so the peak of $-CF_{2-}{}^{d}$ was changed into $-CF_{2-}{}^{d'}$ from −34.1 ppm (2F, d) to −39.8 ppm (2F, d′) [21].

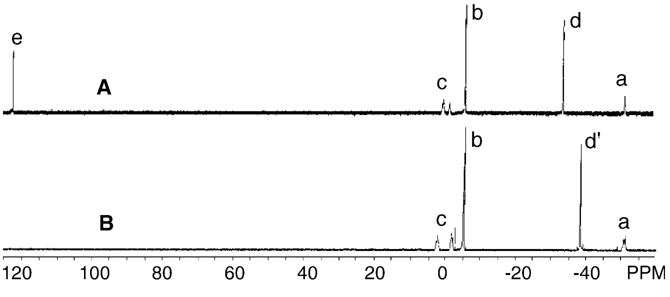


Fig. 2. ^{19}F NMR spectra of polymer **3** (A) and ionomer **5** (B) (at **2**:**1** = 1:3).

Table 1
Solubility of ionomer **5**[a]

Solvents	Polymer					
	AS	SFAS120	SFAS110	SFAS105	SFAS103	SFAS102
Dichloromethane	+	−	−	−	−	−
Toluene	+	−	−	−	−	−
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
DMSO	−	−	+	+	+	+
Acetone	+	+	+	+	+	+

[a] +: soluble; −: not soluble.

2.3. Solubility behaviour and intrinsic viscosity

As shown in Table 1, the ionomer **5** markedly altered its solubility. **5** became insoluble in nonpolar solvents such as dichloromethane and toluene at room temperature. At the same time, ionomer **5** also became dissoluble in strong polar solvents such as dimethyl sulfoxide (DMSO) at room temperature. This behaviour was similar to the solubility of characteristics of other ionomers [22,23]. With the increasing substituted degree, we also found that the ionomer **5** became more soluble in methanol or water and a direct precipitation into water or methanol could not be used to obtain ionomer **5**. So, at higher reactant ratios, the solvent used in acidification was directly evaporated under stirring at ambient temperature to obtain products.

The intrinsic viscosities of the ionomer **5** measured in *N*,*N*-dimethylformamide (DMF) at 30 °C are shown in Fig. 3. The intrinsic viscosity increases with increasing DS. There are possibly two reasons for this increase: first, with the increase of DS, the molecular weight would increase to some extent; second, with the increase of DS, the increasing intermolecular ionic associations will enhance the intrinsic viscosity [22].

2.4. Thermal analysis

The TGA curve of the substrate **1** (Fig. 4a) indicates that the degradation of the substrate **1** into its monomer started at 410 °C The curve of the polymer **5** (at the ratio **2**:**1** = 1:3) (Fig. 4b) shows the similar degradation starting at 358 °C and an important feature weight loss occurred at 197 °C. Apparently, the added weight loss was not caused by the main-chain degradation, but the desulfonic characteristic. The desulfonic temperature (197 °C) of **5** is high enough to be used as proton exchange membrane in fuel cell.

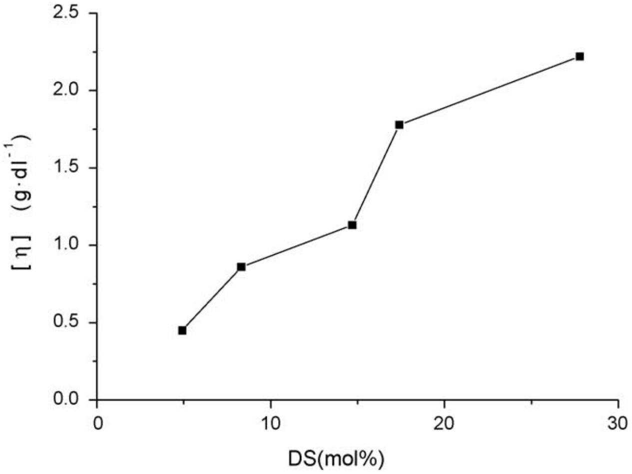


Fig. 3. The relation of intrinsic viscosity and DS of ionomer **5**.

Table 2
The properties of the membranes made of ionomer **5**

Sample	**2**:**1**[a]	T_g (°C)	IEC (mmol/g)	DS[b] (mol%)	Water uptake (wt.%)[c]	σ ($\times 10^3$ S cm^{-1})[c]
SFAS120	1:20	106.7	0.32	4.9	13.4	0.40
SFAS110	1:10	95.3	0.51	8.3	20.2	1.01
SFAS105	1:5	125.3	0.81	14.7	38.6	1.87
SFAS103	1:3	–	0.92	17.2	57.6	5.66
SFAS102	1:2	–	1.25	27.8	135.3	13.2
Nafion117	–	–	0.91	–	30.0	100

[a] Reactant molar ratio.
[b] $\mathrm{DS} = \frac{100\mathrm{IEC}}{720-213\mathrm{IEC}}$.
[c] Measured at 25 °C.

As shown in Table 2, the DSC determinations disclosed that the glass-transition temperatures (T_g) of ionomer **5** at different reactant ratios changed irregularly. At molar ratio 1:20 T_g increases from 104.8 °C (parent polymer **1**) to about 106.7 °C, and at molar ratio 1:10 the polymeric T_g decreases to 95.3 °C which is lower than that of parent polymer. Moreover, when the molar ratio is higher (>1/5), there is no apparent glass-transition temperature. This irregular result is owing to two contrary factors: on the one hand, the introduction of perfluoroalkylation into polymer brought incompatibility of perfluoro[1-(2-sulfonic)ethoxy]ethyl groups with the main chains and a disordering of the molecular arrangement caused by the phenyl ring-substitution, which will decrease T_g of **5**; on the other hand, hydrogen bond and ionic crossing intro and inter polymeric chains of **5** will increase T_g. As a result, the change of T_g is caused by the balance of two factors.

2.5. DS and IEC

As shown in Table 2, the degree of substitution (DS) were determined by titration. The DS can be controlled easily by changing the reactant molar ratio. With the increase of reactant molar ratio from 1:20 to 1:2, DS increases from 4.9 to 27.8% (mol%). The IEC of the membranes made of ionomer **5** can be well controlled in the range of 0.32 and 1.25 mmol/g. The ion exchange capacity (IEC) of the membranes made of ionomer **5** reaches up to 1.25 mmol/g when molar ratio is 1:2 (**2**:**1**). The high IEC showed the membranes made of ionomer **5** could be a promising alternative proton exchange membrane.

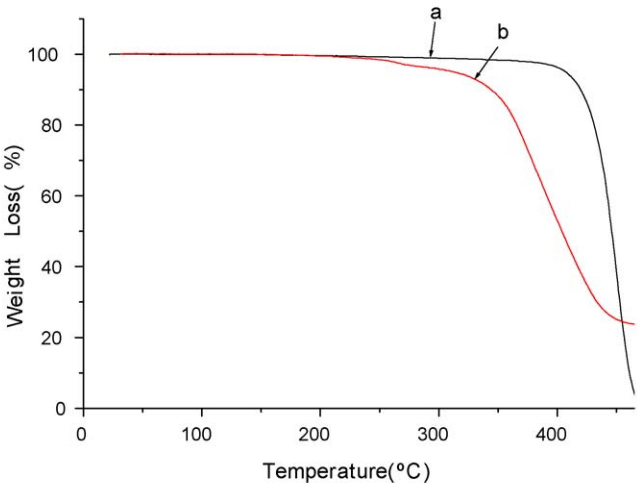


Fig. 4. TGA curves of **1** (a) and **5** (b) (at **2**:**1** = 1:3).

2.6. Water uptake

From Table 2, water uptake of membranes made of ionomer **5** increased continually with the increasing DS. The water uptake of membranes could vary from 13.4 to 135.3%, which is enough good to be used as proton exchange membrane. Higher is the DS (namely, higher is the density of –SO_3H groups of **5**), higher is water uptake, which may suggest that there may be ion-rich regions where proton transfer is particularly fast similar to Nafion. This result may be due to the similar perfluorinated side chain of ionomer **5** and Nafion.

2.7. Proton conductivity

Proton conductivities of the membranes were measured at different temperature in deionized water in Table 2 and Fig. 5. The effect of the DS on the conductivity of the membranes was shown in Table 1, with increasing DS proton conductivities were increasing at 25 °C, which was due to the increasing concentration of sulfonic acid groups. The conductivity value of SFAS103 and SFAS102 is even up to 1.45×10^{-2}, 2.31×10^{-2} S cm^{-1}, respectively, at 80 °C, which was able to be used as proton exchange membrane. Fig. 5 shows the temperature dependence of proton conductivity of the membranes in deionized water. Proton conductivities increased with temperature increasing, which was consistent with other sulfonated polymer systems [24]. Temperature had also a similar effect on the conductivity of the membranes made of polymer **5** to the membranes of Nafion117 [25].

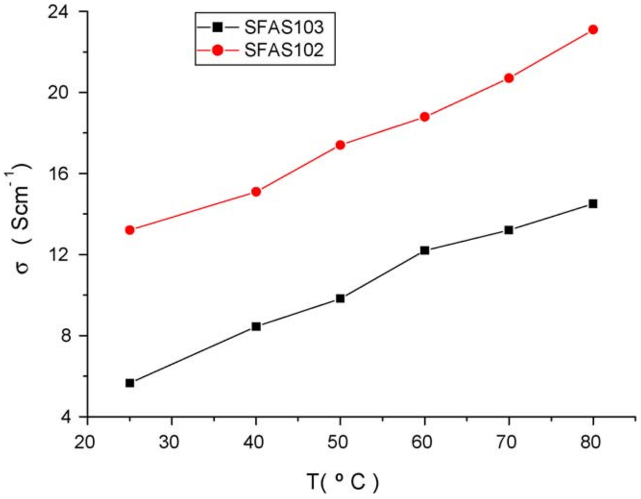


Fig. 5. Proton conductivity of the membranes made of polymer **5** with fixed DS as a function of temperature.

3. Conclusion

New fluorinated ionomer *p*-perfluoro[1-(2-sulfonic)ethoxy]ethylated polyacrylonitrile-styrene (**5**) was synthesized via electron transfer reaction between polyacrylonitrile-styrene (**1**) and perfluoro-di[2-(2-fluorosulfonyl)ethoxy]propionyl peroxide (**2**) and followed by alkali hydrolysis and acidification of the intermediate product **3**. This new synthesis endows proton exchange membranes made of ionomer **5** obtained at molar ratios (**2**:**1**) have suitable thermal stability, good water uptake and fairly high proton conductivity. These preliminary results forecast that our new *p*-perfluoroalkanesulfonation reaction and the partial fluorinated sulfonic ionomers may have extensively potential application in polyelectrolyte membranes.

4. Experimental

4.1. Materials

Perfluoro[2-(2-fluorosulfonyl)ethoxy]propionyl fluoride $FO_2SCF_2CF_2OCFCF_3COF$ used for the preparation of perfluoro-di[2-(2-fluorosulfonyl)ethoxy]propionyl peroxide (**2**) was purchased from 3F Co. Ltd., Shanghai, China. Polyacrylonitrile-styrene (AS) (**1**) (117C) was from CHI MEI Plastic Co. Ltd. and purified before use.

*4.2. Preparation of p-perfluoro[1-(2-sulfonic)ethoxy]ethylated polyacrylonitrile-styrene (**5**)*

*4.2.1. Preparation of perfluoro-di[2-(2-fluorosulfonyl)ethoxy]propionyl peroxide (**2**)*

The F113 solution of the peroxide **2** was prepared according to the reported procedure [16], and kept under freezing condition before use. The concentration was determined by standard iodimetry.

*4.2.2. Preparation of p-perfluoro[1-(2-fluorosulfonyl)ethoxy]ethylated polyacrylonitrile-styrene (**3**)*

3.47 g (25 mmol) polyacrylonitrile-styrene was dissolved in 75 mL of dichloromethane in a flask with magnetic stirring. After flushing with nitrogen, 5 mmol of peroxide solution in F113 (reactant molar ratio **2**:**1** = 1:5) was dropped into polymer solution quickly, and then the reaction mixture was stirred for additional 24 h at 0 °C. The polymeric product **3** was precipitated by methanol, collected and purified by reprecipitation from dichloromethane/methanol binary solvent. After filtration, the product was dried under vacuum at 65 °C overnight. The reaction at different molar ratios were conducted by the same procedure.

*4.2.3. Preparation of p-perfluoro[1-(2-sulfonic)ethoxy]ethylated polyacrylonitrile-styrene (**5**)*

Two grams of the polymer **3** was dissolved in 40 mL of dichloromethane in flask with magnetic stirring. Then the polymeric solution were hydrolyzed in excess 6 mol/L NaOH at room temperature for 24 h. After washed with water to neutral pH, the polymeric solution was acidified in excess 1 M aq. HCl at room temperature for 24 h, and washed with water to neutral. Finally, the product **5** was precipitated by methanol or water and dried at 65 °C under vacuum to constant mass.

4.3. Preparation of the membranes

A solution (50 g/L) of the polymer **5** in a toluene/*n*-ethanol mixture (7:3, v/v) was prepared and filtered. The solution was poured into a smooth glass flat and placed in a vacuum oven at room temperature until complete evaporation of the solvent. Then, the temperature was increased to 50 °C and the polymer was vacuum-dried further for 24 h. Finally, the membranes were removed from the glass plates by submersing them in water and then were vacuum-dried at 50 °C for at least 24 h. The membranes were soaked in deionized water at 80 °C for 3 h, before being tested. The membrane thickness was measured in the dry state by means of a digital micrometer.

4.4. Measurements

A 983-Perkin Elmer FTIR spectrometer was used to record the infrared spectra of polymers. ^{19}F NMR spectra were recorded on a Mercury Plus 400 MHz spectrometer in CD_3Cl and acetone-d_6. Approximately 0.1 g of polymer **5** was dissolved in 25 mL of DMF and filtered, then intrinsic viscosities of the samples were measured in DMF at 30 °C using an Ubbelohde viscometer.

The glass-transition temperatures were determined on Perkin-Elmer DSC-7 under a protective nitrogen atmosphere. Samples were firstly heated to 100 °C, held at that temperature for 30 min to remove water, and then cooled to 20 °C, followed by reheating to 140 °C at heating rate of 20 °C/min. Thermal stability analysis of the membranes was performed with a Perkin-Elmer TG analyzer (model TGA7) under a protective nitrogen atmosphere at heating rate of 20 °C/min from 30 to 550 °C.

Ion exchange capacity was determined by titration. Membrane samples were soaked in 50 mL of 0.05 M NaOH solution for 24 h, and then titrated with 0.05 M HCl solution.

The membranes were soaked in deionized water for a day at 25 °C to determine the water uptake content. Weight of a dried membrane was measure after drying the sample overnight in vacuum at 80 °C. The uptake content was calculated by

$$\text{uptake content}\,(\%) = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\%$$

where W_{dry} is the mass of dried sample and W_{wet} the mass of wet sample.

Proton conductivity of membranes was determined by following a reported procedure [26]. The ac impedance of samples was carried out in the frequency range 100 Hz to 1 MHz with amplitude of 10 mV using Solartron SI 1260 Impedance/Gain-phase analyzer. All membrane samples were immersed in deionized water (room temperature) at least 1 h before being measured. The conductivity of the samples with different degree of sulfonation (DS) immersed in deionized water were measured between 20 and 80 °C. The proton conductivity was calculated using $\sigma = l/(Z'dw)$, where l is the distance between the electrodes, d and w are the thickness and width of the films, respectively, and Z' was determined from the low intersect of the high frequency semi-circle on a complex impedance plane with the axis of abscissas.

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