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SYNTHESIS OF SULFONATED POLY(ARYL ETHER KETONE)S WITH PENDANT FLUORINATED GROUPS (SPAEK-6FP) FOR PROTON EXCHANGE MEMBRANES

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Introduction

Proton exchange membrane fuel cells (PEMFC)s are promising clean power sources for automotive and portable applications.[1] Nafion, with a perfluorosulfonic acid structure, has been successfully employed as a PEM because of its high proton conductivity and other outstanding properties. However, high cost, low operation temperature, and high methanol crossover of Nafion and other perfluorinated membranes have limited their further commercial application. Inexpensive fluorine-free and partially fluorinated polymers with improved performance are being investigated as alternative PEMs. Aromatic polymers such as sulfonated derivatives of poly(ether ether ketone) (SPEEK), poly(ether sulfone) (SPES), and polyimide (SPI) are regarded as promising materials for PEMs because of their stable structures and high performance.[2,3]

Recently, our group reported a series of SPAEEKs based on 4,4'-(hexafluoroisopropylidene)diphenol as an approach to increase the hydrophobicity and length of nonsulfonated segments and to improve the mechanical properties and hot water stability of the films, which showed some ideal properties as PEMs.[4] In the present work, sulfonated poly(aryl ether ketone)s (SPAEKs), specifically sulfonated poly(aryl ether ether ketone)s (SPAEEKs) and sulfonated poly(aryl ether ether ketone ketone)s (SPAEEKKs) with partially fluorinated pendant moieties were synthesized by direct copolymerization. The structures and selected properties such as thermal stability, water uptakes and proton conductivity, are discussed.

Experimental

Materials. (3,5-Ditrifluoromethyl)phenylhydroquinone was synthesized according to a reported synthetic procedure.[5] 1,4-Bis(4-fluorobenzoyl)benzene was received from Jilin University (China) and recrystallized from 1,2-dichlorobenzene before use. 4,4'-Difluorobenzophenone was obtained from Sigma-Aldrich Ltd. and purified by sublimation before use. 1,4-Bis(3-sodium sulfonate-4-fluorobenzoyl)benzene and sodium 5,5'-carbonylbis(2-fluorobenzenesulfonate) were synthesized according to a reported procedure.[6,7] Solvents were obtained commercially and used without purification.

Polymerization. The synthesis of SPAEEKK-6FP-50 is given as an example. To a 100-mL three-necked flask equipped with a magnetic stirrer, a nitrogen inlet and a Dean-Stark trap, were added 1,4-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene (0.5264g, 1mmol), 1,4-bis(4-fluorobenzoyl)benzene (0.3223g, 1mmol), 6F-PH (0.6444g, 2mmol), anhydrous K_2CO_3 (0.3594g, 2.6mmol), DMAc (6ml) and toluene (12ml). The system was allowed to reflux for 3h while water was removed, and then the toluene was distilled off. The reaction mixture was heated to 160ºC. After 10h, another 4-5ml of DMAc was added into the viscous reaction mixture. The polymerization was complete after another 2h. The viscous solution was then poured into ethanol. The polymer was thoroughly washed with hot deionized water to remove the salts and solvents, and dried at 100ºC for 48h.

Characterization. FTIR spectra were measured on a Nicolet 520 Fourier transform spectrometer. ^{1}H NMR spectra were recorded on a Varian Unity Inova NMR spectrometer. Differential scanning calorimetry (DSC) measurements were performed on a TA Instrument 2920 DSC at a heating rate of 10°C/min under nitrogen. Thermogravimetric analysis (TGA) was performed on a TA Hi-Res TGA 2950 thermal analyzer system at a heating rate of 10 ^{o}C/min under N_2. Viscosities of the copolymers in sodium form were measured in DMAc (0.5g/dL) at 30°C using an Ubbelohde viscometer. The proton conductivities of the membranes were obtained on by AC impedance spectroscopy with a Solartron 1260 gain phase analyzer. The membranes were clamped between two electrodes and then placed in an open temperature-controlled chamber with water vapor at 100% relative humidity. Samples were hydrated in water at room temperature for at least one week before measurements. The water uptakes and swelling ratios of the polymers were measured by immersion of the polymer films (5mm × 50mm) in deionized water at 25°C and 80°C for 24h. The water uptakes and swelling ratios were calculated from the differences in weight and length.

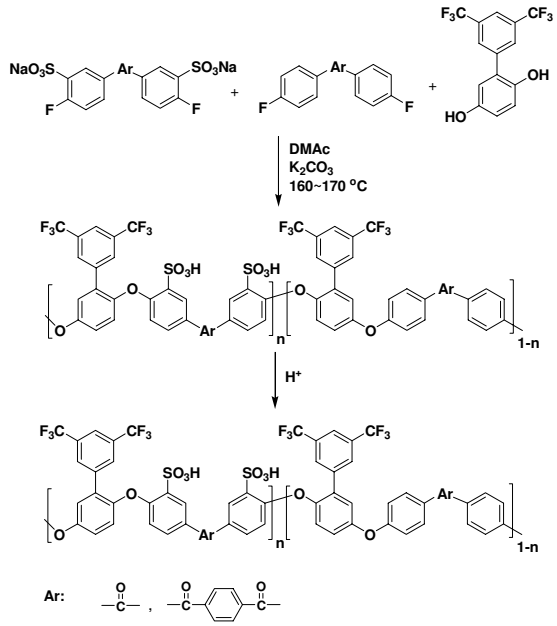

Figure 1. Synthesis of sulfonated poly(aryl ether ketone)s.

Membrane preparation. The films of the copolymers in sodium form were prepared by casting their DMAc solution (0.5g/12ml) onto glass plates and dried at 50°C for 72h. The membranes in proton form were obtained by soaking the above films in 2N H_2SO_4 aqueous solution at room temperature for 24h. The films were thoroughly washed with water to remove excessive acid, and then dried at 120°C for 12h. The thickness of the membranes was in the range of 30-60μm.

Results and Discussion

Copolymerization of 6F-PH with activated difluorinated aromatic ketones, 1,4-bis(3-sodium sulfonate-4-fluorobenzoyl)benzene/1,4-bis(4-fluorobenzoyl)benzene or sodium 5,5'-carbonylbis(2-fluorobenzenesulfonate)/4,4'-difluorobenzophenone was carried out in the presence of K_2CO_3 in DMAc as the solvent at 160-170°C, as shown in **Figure 1**. The sulfonation content (SC) of the polymers

was controlled by the feed ratios of monomers. The inherent viscosities of the resulting polymers were above 0.96dL/g in DMAc at 30°C (**Table 1**).

^{1}H NMR spectra were used to confirm the structures and evaluate the sulfonation contents of the resulting polymers. All the results agreed with the expected structures. A typical ^{1}H NMR spectrum is illustrated in **Figure 2**. As expected, the SC values based on NMR experimental were in agreement with the values derived from monomer feed ratios.

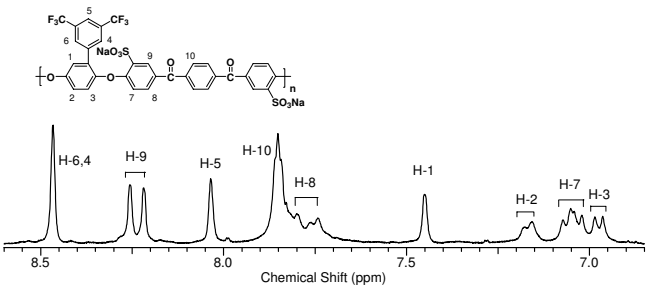

Figure 2. ^{1}H NMR spectrum of SPEEKK-6FP-100.

The thermal properties of the polymers in acid form (-H) and sodium form (-Na) were evaluated by DSC and TGA, as summarized in **Table 1**. The T_gs of the polymers in acid form were above 203°C. The polymers with high SC showed higher T_g values.

Table 1. Viscosities and thermal properties of the polymers

Polymer	T_g (°C) [a]	TD_5 (°C) [b]	T_d (°C) [c]	η_{inh} (dL/g) [d]
	-H	-Na/-H	-Na/-H	-Na
SPAEEK-6FP-40	203	473/330	470/267	1.01
SPAEEK-6FP-50	229	467/328	455/258	0.96
SPAEEK-6FP-60	231	468/319	465/252	0.98
SPAEEKK-6FP-40	212	487/341	487/270	2.40
SPAEEKK-6FP-50	219	478/358	473/279	2.09
SPAEEKK-6FP-60	235	479/358	481/279	2.79
SPAEEKK-6FP-70	239	477/324	470/261	1.70

[a] Glass transition temperature from the second heating cycle of DSC.
[b] 5% weight loss temperature measured by TGA.
[c] Onset temperature of decomposition.
[d] Measured at a polymer concentration of 0.5g/dL in DMAc at 30°C.

An obvious two-stage decomposition was observed from the TGA curves of SPAEEK-6FP-H and SPAEEKK-6FP-H. The initial decomposition was likely associated with the loss of the sulfonic acid groups in the range of 252-279°C, and the second loss was caused by the decomposition of the main chains of the polymers in the range of 479-489°C. Compared with the sulfonated PAEK-6FPs in acid form, the polymers in sodium form had high thermal stabilities against thermal decomposition. The temperatures at a 5% weight loss (TD_5) are above 467ºC and the decomposition temperatures are above 455ºC in N_2.

The water uptakes and dimensional swelling ratios of SPAEEK-6FP and SPAEEKK-6FP membranes were tested at 25°C and 80°C, and the results were listed in **Table 2**. After keeping the films in water at 25°C for 24h, all the polymers had swelling ratios below 30%, and water uptakes less than 30%. At 80°C, SPAEEK-6FP-40, SPAEEK-6FP-50, SPAEEKK-6FP-40, 50, 60 maintained their dimensional shape.

The proton conductivities of the membranes at 25 and 80°C are listed in **Table 2**. The conductivities of all the samples increased with increasing temperature. At the same temperature, high SC samples had higher conductivities. All of the samples exhibited proton conductivities > 1×10^{-2} S/cm at room temperature, which was regarded as the lowest value for PEM application in fuel cells. Some copolymers showed comparable proton conductivities to Nafion 117. At 80°C, proton conductivity values of SPAEEK-6FP-50, SPAEEKK-6FP-50 and SPAEEKK-6FP-60 were 1.1×10^{-1}, 1.0×10^{-1} and 1.6×10^{-1} S/cm, which are comparable to that of Nafion 117.

Table 2. Water uptakes, swelling ratios and proton conductivities of the SPAEK-6FPs at different temperatures

Polymer	Water Uptake (%) [a]	Swelling Ratio (%) [b]	σ (S/cm) [c]
	25/80 °C	25/80 °C	25/80 °C
SPAEEK-6FP-40	6/19	6 /18	2.0×10^{-2}/ 9.1×10^{-2}
SPAEEK-6FP-50	12/215	11/72	3.3×10^{-2}/ 1.1×10^{-1}
SPAEEK-6FP-60	29/--	29/--	8.4×10^{-2}/ --
SPAEEKK-6FP-40	5/7	5/12	1.3×10^{-2}/5.4×10^{-2}
SPAEEKK-6FP-50	10/15	6/15	3.2×10^{-2}/1.0×10^{-1}
SPAEEKK-6FP-60	12/54	10/35	4.6×10^{-2}/1.6×10^{-1}
SPAEEKK-6FP-70	21/2563	16/252	6.3×10^{-2}/ --
Nafion 117 [d]	19/30	13/20	7.5×10^{-2}/ 9.6×10^{-2}

[a] Calculated from the weight differences of the membranes before and after treatment in water for 24h.
[b] Calculated from the length differences of the membranes before and after treatment in water for 24h.
[c] Proton conductivities of the membranes at 100% R.H..
[d] Data from Ref. [4] .

Conclusions

A class of poly(aryl ether ketone)s, SPAEEK-6FP and SPAEEKK-6FP series, were synthesized using a nucleophilic substitution polycondensation. Flexible films in sodium form were obtained via solution casting, and then transformed to their acid forms by immersing them in 2N H_2SO_4. The resulting polymers in acid form showed high T_g values above 203°C. The water uptakes and swelling ratios of the 6FP-40 and -50 films were reasonably low, and increased with increasing SC and measurement temperature. All of the polymers possessed proton conductivities higher than 1×10^{-2} S/cm at room temperature, some of the 6FP copolymers being comparable to conductivity values of Nafion 117.

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