Electronic Supplementary Material (ESI) for Polymer Chemistry

Supplementary Information

Properties and degradation of hydrocarbon fuel cell membranes:

a comparative study of sulfonated poly(arylene ether sulfone)s with different positions of the acid groups

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Preparation of the *ms*SPAES and *os*SPAES series

Materials

4,4'-Dichlorodiphenylsulfone (DCDPS, Acros, 97%) and 4,4'-dihydroxybiphenyl (BP, Acros, 97%) were recrystallized from toluene and 2-propanol, respectively. *N*,*N*-dimethylacetamide (DMAc, Acros, 99%), 1-methyl-2-pyrrolidinone (NMP, Acros, 99%), toluene (Fisher Scientific, HPLC grade), 2-propanol (Fisher Scientific, HPLC grade), methanol (Fisher Scientific, HLPC grade), trimethylsilyl chlorosulfonate (TMSCS, Sigma-Aldrich, 99%), chloroform (Fisher Scientific, HPLC grade), sodium methoxide (Acros, anhydrous), hydrogen peroxide (Acros, 35% solution in water), sodium hydroxide (Acros, extra-pure) and calcium chloride (Acros, 96%, anhydrous) were all used as received. Potassium carbonate (Acros, 99+%) was dried at 120 ˚C overnight. Radel® polymer (R-5500-NT, Solvay Advanced Polymer) was dried at room temperature overnight before use. The disulfonated monomer *ms*SDCDPS was prepared by disulfonation of DCDPS using fuming sulfuric acid at 110 ˚C, followed by neutralization, salt-out by NaCl and recrystallization by water/2-propanol. It was then dried at 80 ˚C overnight before use.

Synthesis of the msSPAES copolymer series

The copolymer with the lowest degree of sulfonation (*ms*SPAES*l*) was prepared as follows. DCDPS (0.5141 g, 1.7904 mmol), *ms*SDCDPS (0.2447 g, 0.4981 mmol), biphenol (0.4261 g, 2.2885 mmol), K_2CO_3 (0.380 g, 2.746 mmol), DMAc (5.0 mL) and toluene (5.0 mL) were placed in a two-neck flask (50 mL) equipped with a magnetic stirrer, a N_2 inlet, a Dean-Stark trap filled with toluene and a condenser fit with a $CaCl_2$ trap. The solution was first kept at 160 ˚C for 4 h to dehydrate and remove the toluene. The temperature was then increased to 175 ˚C for 24 h to complete the polycondensation. The product was recovered by precipitation in isopropanol, followed by a wash in deionized water. The product was filtered and dried at 60 ˚C in a vacuum oven for 24 h (yield: 0.88 g, 88%).

Synthesis of the oeSPAES copolymer series

The polymer with the lowest degree of sulfonation (*oe*SPAES*l*) was prepared as follows. Radel® polymer (10.0 g, 25.0 mmol) and chloroform (100 mL) were added to a two-neck flask (250 mL) equipped with a magnetic stirrer, a N_2 inlet and a condenser fitted with a $CaCl_2$ filter. After dissolving the polymer at room temperature (~1 h), TMSCS (3.1 mL, 20.1 mmol) was slowly added, and the solution was heated at 60 ˚C for 17 h. MeONa (1.3 g, 24.0 mmol) was gradually added after cooling to room temperature, followed by stirring for 3 h. The product was then precipitated in MeOH, and kept in fresh MeOH containing MeONa (1.3 g) during stirring overnight to complete the hydrolysis of the trimethylsilyl ester groups. The precipitate was collected by filtration and dried on the glass filter before it was dissolved in NMP for precipitation in isopropanol. The final product was dried under vacuum at 60 ˚C overnight (yield: 9.75 g, 84%).

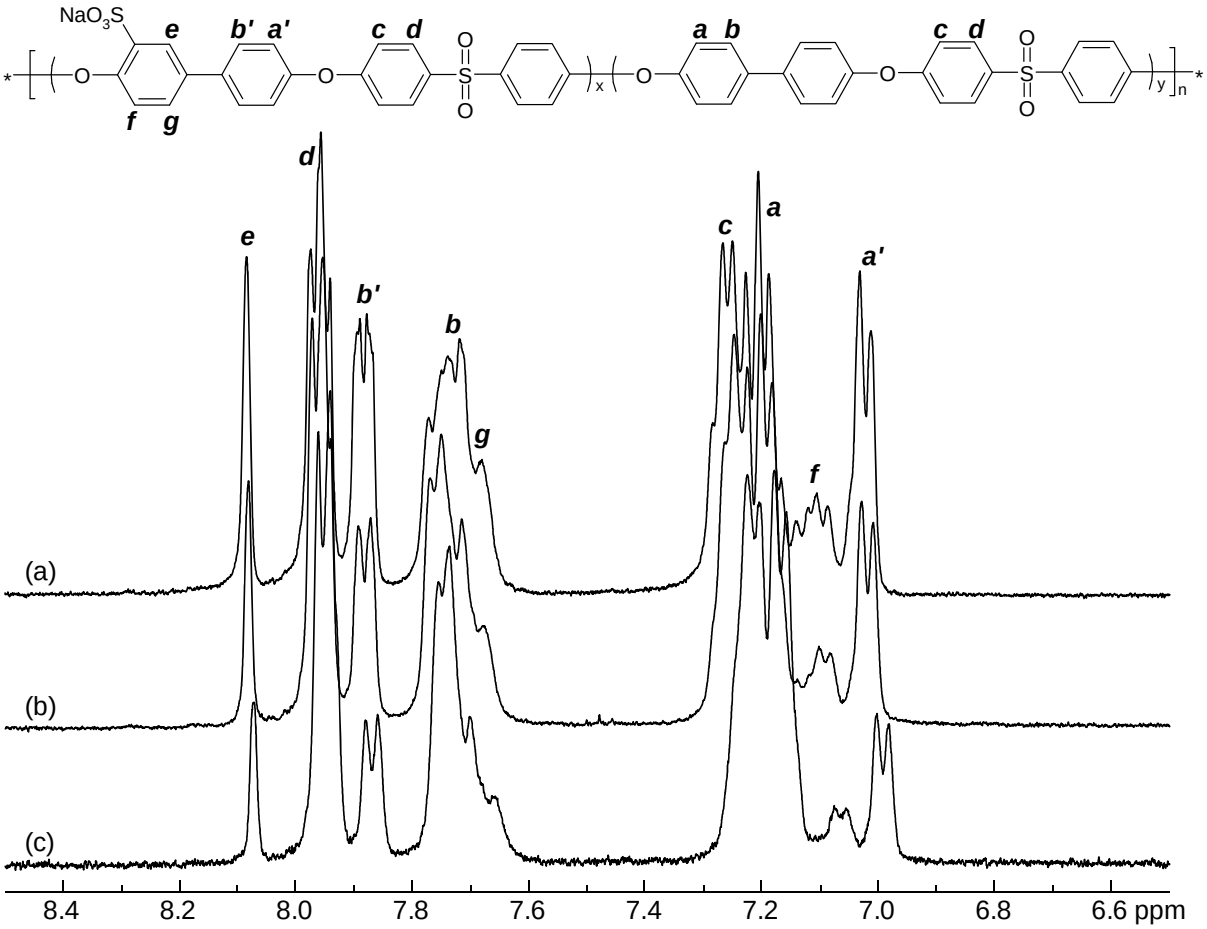

Figure S1. ^{1}H NMR spectra of (a) *oe*SPAES*h*, (b) *oe*SPAES*m*, and (c) *oe*SPAES*l*. The polymers were obtained by sulfonation of Radel® using trimethylsilyl chlorosulfonate.

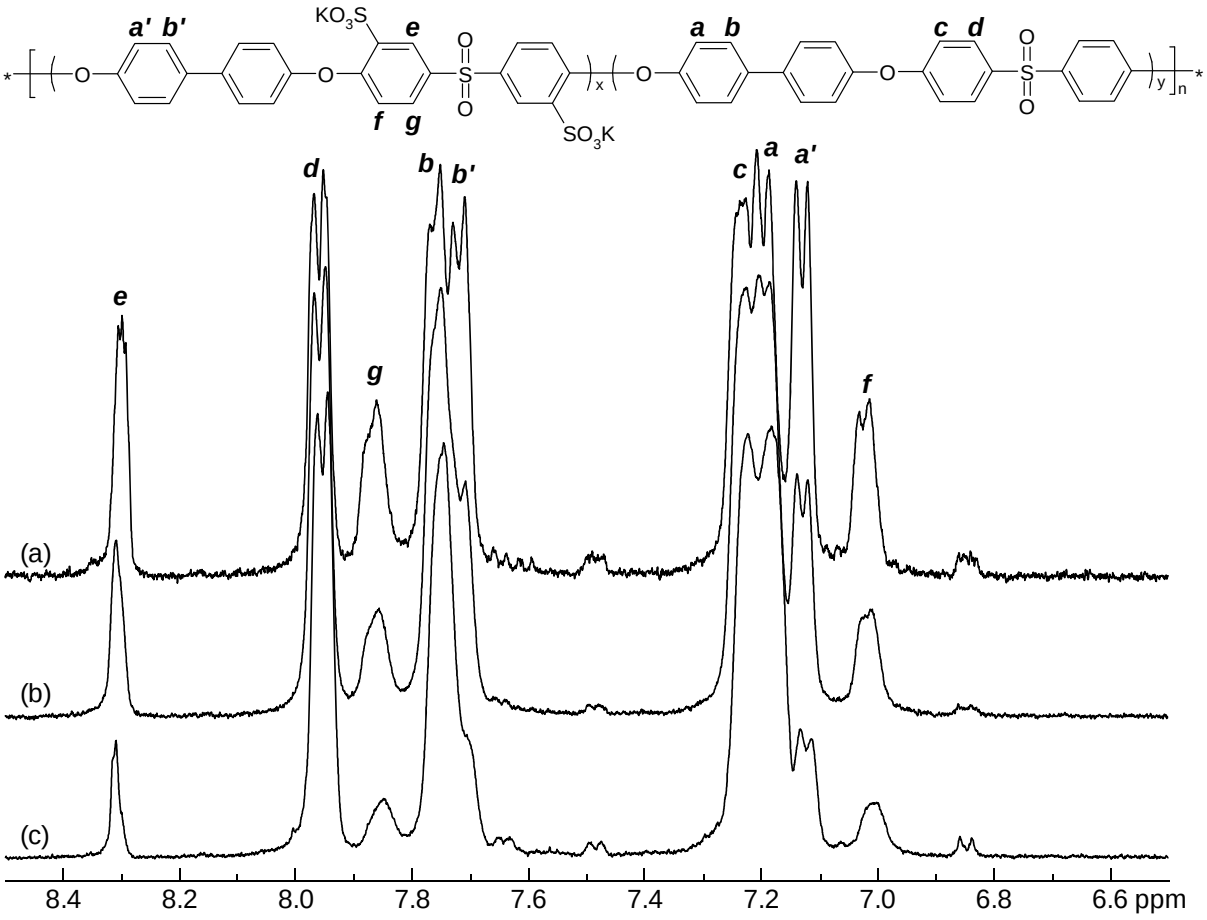

Figure S2. ^{1}H NMR spectra of the (a) *ms*SPAES*h*, (b) *ms*SPAES*m*, and (c) *ms*SPAES*l* polymers obtained by polycondensations using the *ms*SDCPS monomer.

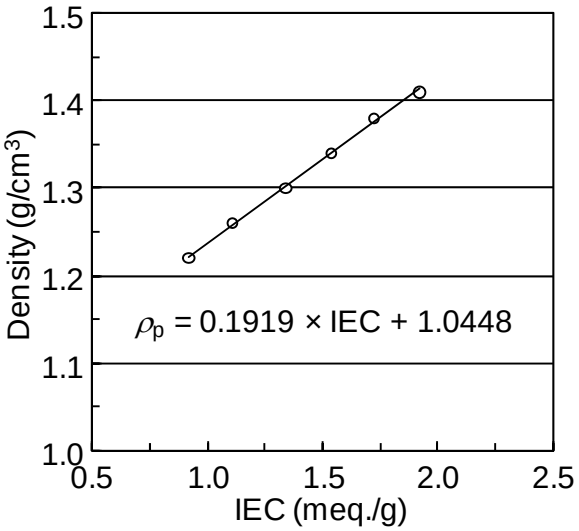

Figure S3. Density of *ms*PAES copolymers as a function of IEC. Data taken from ref.[30].

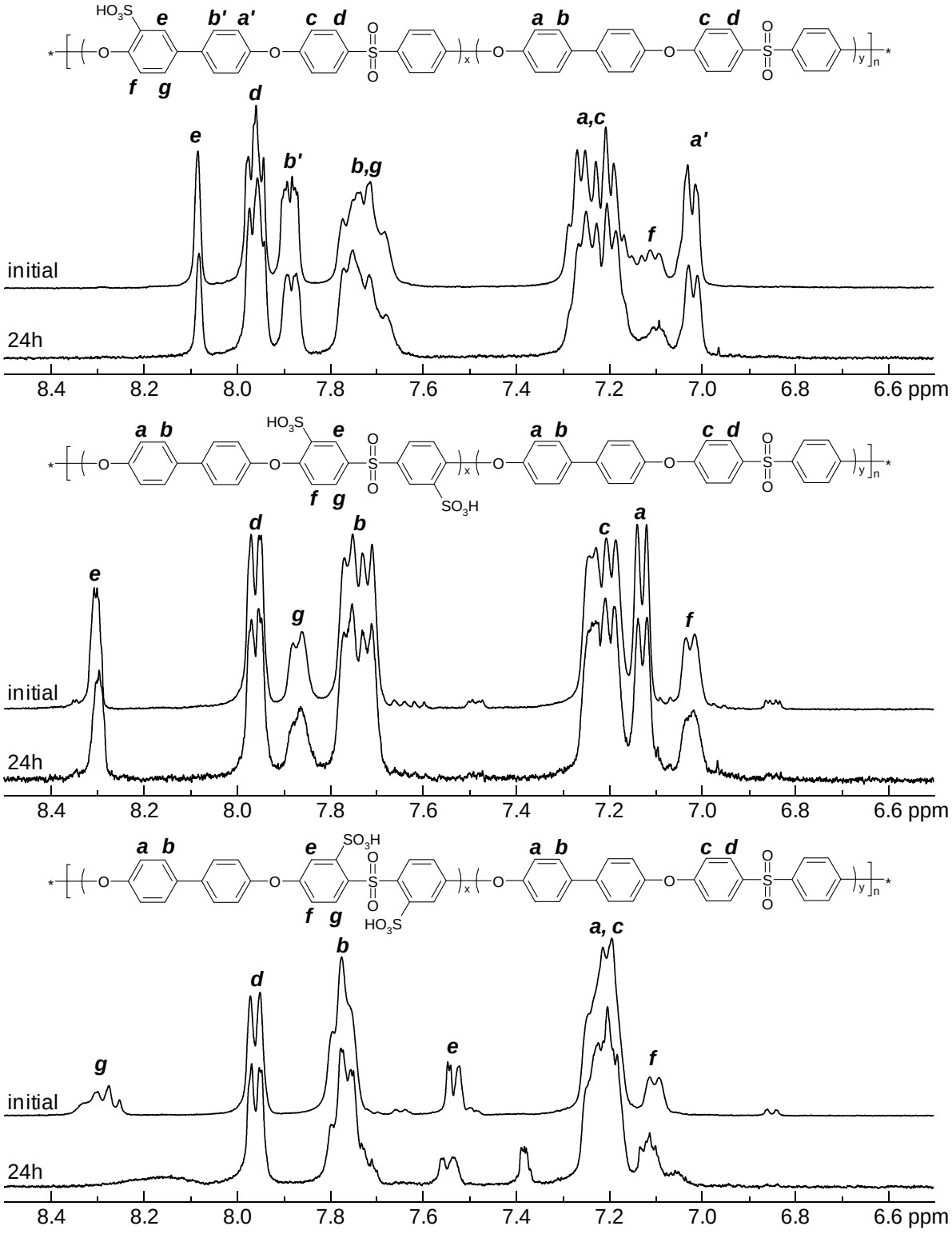

Figure S4. [1]H NMR spectra of (a) the *oe*SPAES*m*, (b) the *ms*SPAES*m*, and (c) the *os*SPAES*m* copolymers before and after a hydrolysis test where the membranes were treated in neutral deionized water at 200 ˚C for 24 h in a sealed vessel.