

Effect of thermal crosslinking on the properties of sulfonated poly(phenylene sulfone)s as proton conductive membranes

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ABSTRACT: The synthesis and characterization of crosslinked aromatic polymer membranes with high ion exchange capacity (IEC) values are reported. Through aromatic nucleophilic substitution polycondensation and the subsequent sulfonation reaction, the highly sulfonated polymers SPPSU-2S and SPPSU-4S with high molecular weight ($M_n = 138\text{--}145$ kDa, $M_w = 200\text{--}279$ kDa) and well-defined structures were synthesized. By solution casting and thermal annealing treatment, flexible crosslinked membranes with high solvent insolubility were obtained. The membranes exhibited mechanical and chemical stability as confirmed by dynamic mechanical analysis (DMA) and conductivity measurement. The crosslinked SPPSU-4S membrane with IEC = 3.20 meq/g showed the highest proton conductivity of 0.163 S/cm at 120 °C, 90% RH, and improved thermal stability compared with its precursor (uncrosslinked) membrane. The results show that simple annealing method could improve significantly membranes properties of highly sulfonated aromatic polymers. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 44218.

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INTRODUCTION

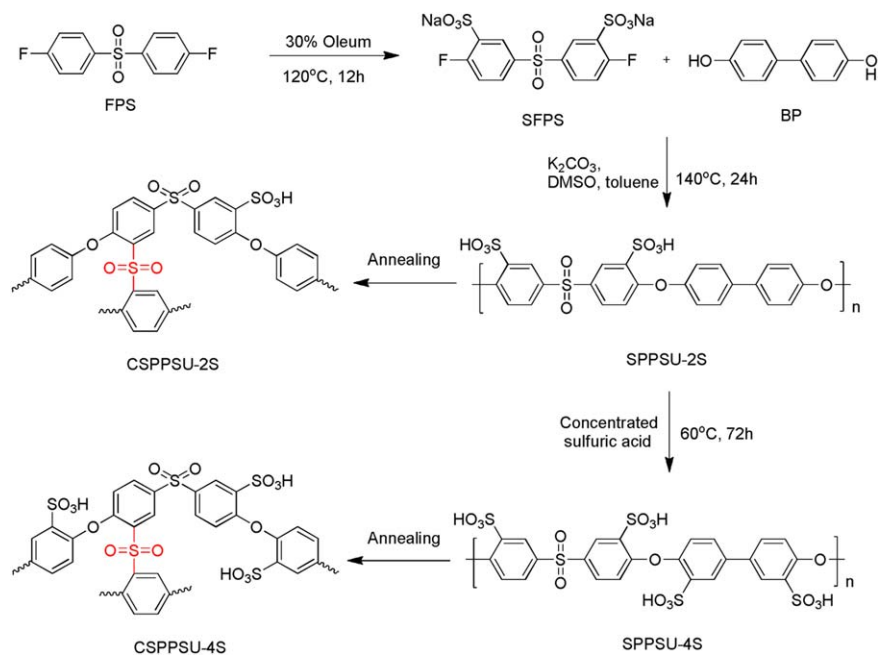
As a promising next-generation power generating device, polymer electrolyte membrane fuel cells (PEMFCs) have gained much attention. Proton exchange membranes (PEMs) are one of the key components of the PEMFCs and strongly influence the device performance.^{1,2} Recent research³ has been devoted to the development of fluorine-free aromatic-type proton exchange membranes as alternatives to state-of-the-art perfluorinated ionomer membranes such as Nafion, since perfluorinated ionomer membranes suffer from high production cost, loss of conductivity at relatively high temperature (>100 °C) and low humidity, hindering their practical applications.^{4,5} A wide variety of aromatic polymers, such as poly(arylene ether sulfone)s,⁶ poly(ether ether ketone)s,^{7–9} polyphenylenes,¹⁰ and polyimides¹¹ have been studied as basic materials for PEMs. Among them, poly(phenylene sulfone)s (PPSU) with excellent thermal stability, low cost, and good membrane forming capability have been applied widely.¹² For sulfonated PPSU, it is one of the crucial topics to balance the ionic exchange capacity (IEC) values and membrane stability. High IEC values are desirable for the proton conductivity;

however, often result in excess swelling to cause mechanical failure and chemical instability. It was reported that the crosslinking could mitigate excess swelling of IEC membranes.¹³ The crosslinking could be generally made by acid–base (electrostatic) interactions^{14–16} or covalent bonds.^{17–19} The ionically crosslinked membranes are not very stable particularly at high temperature and humidity due to the relatively weak electrostatic interactions. The covalent bond crosslinking requires some crosslinkers and should increase the cost.

Recently, we reported that the sulfonated ionomers could be effectively crosslinked through thermal annealing.^{20–22} This method is economically preferable and upscalable, and thus suitable for the practical application. In this article, we report sulfonated PPSU synthesized from sulfonated bis(4-fluorophenyl)sulfone (SFPS) and 4,4'-biphenol (BP). The degree of sulfonation could be increased by further sulfonation of the polymer. The obtained polymers, SPPSU-2S and SPPSU-4S, were then thermally crosslinked under well-controlled conditions. The properties of the polymer membranes were investigated in order to evaluate the effect of the crosslinking on the proton conductivity and the stability.

Additional Supporting Information may be found in the online version of this article.

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Scheme 1. Synthesis of SPPSU-2S, SPPSU-4S, CSPPSU-2S, and CSPPSU-4S membranes. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

EXPERIMENTAL

Materials

Dimethyl sulfoxide (DMSO), toluene (dehydrated), 30% oleum, concentrated sulfuric acid (96%), hydrochloric acid (35%), potassium carbonate (K₂CO₃), calcium carbonate (CaCO₃), lead(II) acetate (Pb(OAc)₂) trihydrate, and sodium chloride (NaCl) were purchased from Kanto Chemical Co. and used as received. Bis(4-fluorophenyl)sulfone (FPS) and 4,4'-biphenol (BP) were obtained from TCI Inc. and used as received. Methyl sulfoxide-*d*₆ [DMSO-*d*₆, for NMR, with 0.03% tetramethylsilane (TMS), 99.9 atom % D] was purchased and used as received.

Measurements

¹H and ¹⁹F NMR spectra were recorded on a JEOL JNM-ECA 500 at room temperature (r.t.) with DMSO-*d*₆ as solvent and TMS as an internal reference. Apparent molecular weights were obtained on gel permeation chromatography (GPC) and calibrated with standard polystyrene samples. IEC of the membranes was measured by titration at r.t. A small piece of dry membrane in acid form was immersed into a large excess of NaCl aqueous solution. Then, the solution was titrated with 0.1M NaOH aqueous solution. For transmission electron microscopic (TEM) observations, the membranes were stained with lead ions by ion exchange of sulfonic acid groups in about 0.5M Pb(OAc)₂ aqueous solution. The samples were sectioned into 50 nm slices with a Leica microtome Ultracut UCT, collected by copper grids, and then examined with a Hitachi H-9500 TEM. Water uptake was measured at 80 °C in a humidity controllable chamber. The weight of the membranes was recorded by magnetic suspension balance. The water uptake was calculated by the following equation.

$$\text{Water uptake (\%)} = 100 \times (W_{\text{wet}} - W_{\text{dry}}) / W_{\text{dry}}$$

The membranes were dried at 80 °C for 3 h under vacuum to obtain the weight of dry membranes (*W*_{dry}) and exposed to the given

humidity for at least 2 h to obtain the weight of hydrated membranes (*W*_{wet}). Through-plane proton conductivity (σ) was calculated using four-point probe impedance spectroscopy under different relative humidities (RH) by a Scribner MTS 740 test system. A frequency range of 1 Hz to 1 MHz and a peak-to-peak voltage of 10 mV were used for the impedance measurements. Ion conducting resistances (*R*) were determined from the impedance plot. The proton conductivity was calculated according to the following equation:

$$\sigma = L / (S \times R)$$

where *L*, *S*, and *R* are the thickness of the membrane, the area of the electrode, and the resistance of the membrane, respectively.

Dynamic mechanical analysis (DMA) of the samples was evaluated via an ITK DVA-225 dynamic viscoelastic analyzer. The storage modulus (*E'*), loss modulus (*E''*), and tan δ (*E''/E'*) of the membranes was measured over a humidity range from 0% to 90% relative humidity (RH) at 80 °C (10 Hz).

The tensile strength was investigated by a Shimadzu AGS-J 500N universal test machine attached with a Toshin Kogyo Bethel-3A temperature and humidity controllable chamber. The measurement was performed with samples cut into dumbbell shape [DIN-53504-S3, 35 mm × 6 mm (total) and 12 mm × 2 mm (test area)] and conducted at 80 °C, 60% RH at a tensile rate of 10 mm/min.

The thermal stabilities of the membranes were recorded using thermogravimetric analysis (TGA) with an SII TG/DTA 6000. The samples were heated from 80 to 800 °C in nitrogen atmosphere at a heating rate of 10 °C/min.

Synthesis of SFPS

SFPS was prepared by the sulfonation of FPS using 30% oleum according to the literature.²³ The typical procedure is as follows. FPS (5.00 g) and 30% oleum (10 mL) were added into a 100 mL round-bottom flask equipped with a magnetic stirring

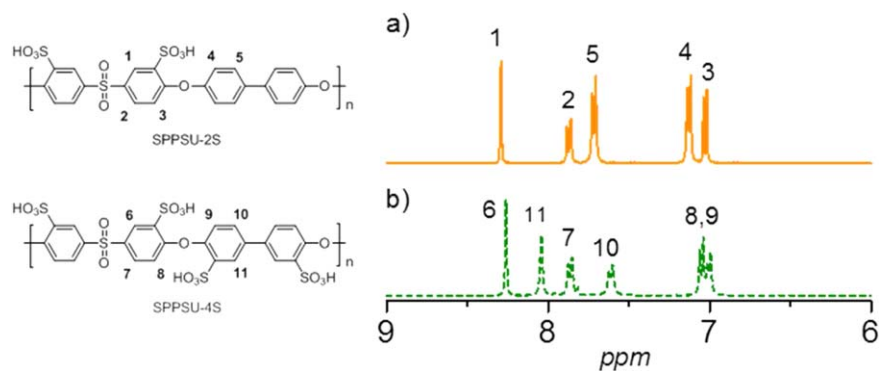


Figure 1. ^1H NMR spectra of SPPSU-2S and SPPSU-4S in $\text{DMSO}-d_6$ at r.t. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

bar. After stirred at 120°C for 12 h, the mixture was poured into a large excess of cold brine. After filtration, the precipitate was dissolved in water, basified with NaOH aqueous solution, reprecipitated with additional NaCl. The crude product was purified by recrystallization three times and dried in vacuum oven at 120°C overnight to obtain SFPS in 35% yield.

Synthesis of SPPSU-2S

A typical procedure is as follows. SFPS (0.70 g, 1.52 mmol), BP (0.28 g, 1.52 mmol), K_2CO_3 (0.53 g, 3.80 mmol), DMSO (5 mL), and toluene (3 mL) were added into a 100 mL three-neck flask equipped with a magnetic stirring bar, Dean-Stack trap, condenser, and nitrogen inlet/outlet. After heated at 140°C for 24 h, the mixture was cooled to room temperature, diluted with DMSO and poured into a large excess of 1M H_2SO_4 to precipitate a solid product. After filtration, the crude product was dissolved in water and dialyzed. After drying in a vacuum oven at 80°C for 12 h, SPPSU-2S was obtained in 87% yield.

Synthesis of SPPSU-4S

A typical procedure is as follows. SPPSU-2S (0.25 g) and concentrated sulfuric acid (25 mL) were added into a 100 mL round-bottom flask. After heated at 60°C for 3 days, the mixture was poured into ice water to precipitate a solid product. After filtration, the crude product was dissolved in water and dialyzed. After drying in a vacuum oven at 80°C for 12 h, SPPSU-4S was obtained in 91% yield.

Membrane Preparation and Thermal Crosslinking

Casting from DMSO solution (3 wt %) and drying at 80°C for overnight gave yellow and flexible membranes of SPPSU-2S and SPPSU-4S. The resulting membranes were annealed in the air at 120°C for 24 h, at 160°C for 24 h, and at 180°C for 6 h, to obtain the crosslinked CSPPSU-2S and CSPPSU-4S membranes.

RESULTS AND DISCUSSION

Synthesis of SPPSU-2S and SPPSU-4S

Scheme 1 shows the overall synthetic route for the target polymers (SPPSU-2S and SPPSU-4S). SFPS was prepared by the sulfonation reaction of FPS with 30% oleum at 120°C for 12 h. The chemical structure of SFPS was characterized by ^1H and ^{19}F NMR spectra, in which all peaks were well-assigned to the supposed chemical structure (Supporting Information Figure S1). SPPSU-2S was prepared by nucleophilic substitution polycondensation of SFPS and BP under the basic conditions. The equimolar amount of the monomers was used to obtain high molecular weight polymer. The chemical structure of SPPSU-2S was characterized by NMR spectra [Figure 1(a) and Supporting Information Figure S2]. The progress of the polymerization was confirmed by the absence of the terminal fluorine groups of the starting monomer SFPS. GPC analyses (Supporting Information Figure S3) suggested the formation of high molecular weight ($M_n = 138$ kDa and $M_w = 200$ kDa) polymer (SPPSU-2S).

SPPSU-4S was prepared by the sulfonation reaction of SPPSU-2S at 60°C for 72 h. It should be noted that, compared with the sulfonation of FPS with 30 wt % oleum, concentrated

Table I. Solubility and IEC of the Membranes

Sample	Solubility ^a					IEC ^b (meq/g)	IEC ^c (meq/g)	IEC ^d (meq/g)
	Water	DMSO	NMP	DMAc	DMF			
SPPSU-2S	○	○	○	○	○	3.47	3.56	3.57
SPPSU-4S	○	○	○	○	○	5.35	5.57	5.52
CSPPSU-2S	×	×	×	×	×	2.13	na	na
CSPPSU-4S	×	×	×	×	×	3.20	na	na

^a ○: Soluble. ×: Insoluble.

^b Obtained by titration.

^c Calculated from the polymer structure.

^d Obtained by the ^1H NMR spectra.

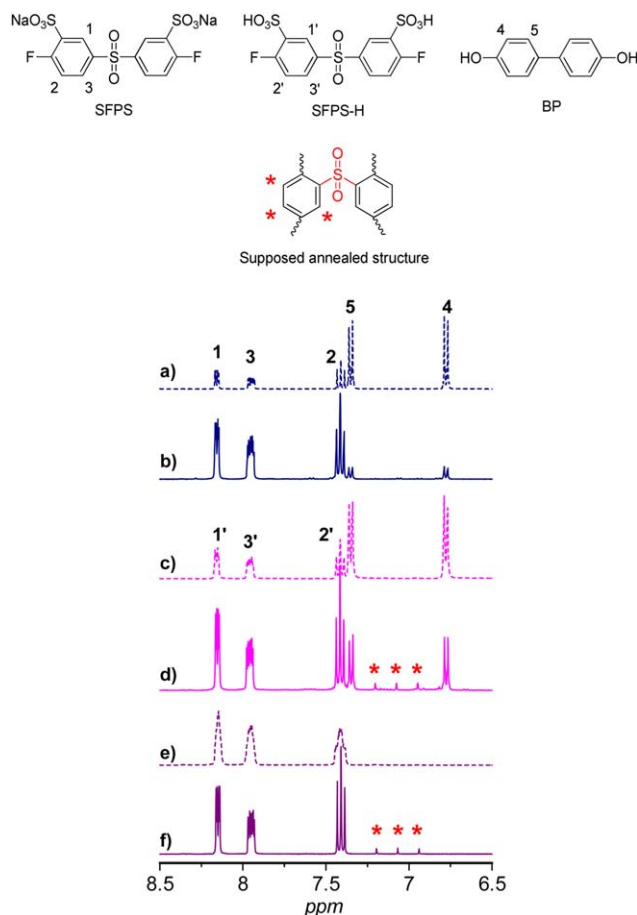


Figure 2. ^1H NMR spectra of (a) mixture of SFPS/BP, (b) annealed mixture of SFPS/BP, (c) mixture of SFPS-H/BP, (d) annealed mixture of SFPS-H/BP, (e) SFPS-H, and (f) annealed SFPS-H in $\text{DMSO}-d_6$ at r.t. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

sulfuric acid was enough for the reaction due to the existence of electron-donating ether groups in place of electron-withdrawing fluorine groups for FPS. The chemical structure of SPPSU-4S was characterized by ^1H NMR spectrum [Figure 1(b)]. Comparison of the ^1H NMR spectra between SPPSU-2S and SPPSU-4S revealed that the sulfonation reaction was quantitative and selective on the biphenylene unit, in which one sulfonic acid group was introduced at the specific position of each phenylene group; the protons 1, 2, and 3 on the sulfonated biphenyl sulfone groups did not change and the new peaks (protons 9, 10, and 11) were assignable to bis(sulfophenylene) groups. The integral ratios of these peaks were in good accordance with the structure of SPPSU-4S. Furthermore, the IEC values of SPPSU-2S and SPPSU-4S obtained by titration, calculation and ^1H NMR spectra were in good agreement within acceptable errors proving that the target structures were obtained (Table I). Due to the introduction of the sulfonic acid groups, the molecular of SPPSU-4S ($M_w = 279$ kDa, $M_n = 145$ kDa, Supporting Information Table S1) was higher than that of SPPSU-2S ($M_w = 200$ kDa, $M_n = 138$ kDa, Supporting Information Table S1).

Preparation of CSPPSU-2S and CSPPSU-4S Membranes

The thermal crosslinking reaction was carried out at three steps as described in the experimental section in order to avoid immediate decomposition of the sulfonic acid groups. The obtained membranes, CSPPSU-2S and CSPPSU-4S, were brown colored (Supporting Information Figure S4) compared with yellow color of the parent SPPSU-2S and SPPSU-4S membranes, suggesting the changes in the electronic structure of the aromatic rings. While SPPSU-2S and SPPSU-4S were soluble in water and several polar organic solvents, the heat treated CSPPSU-2S and CSPPSU-4S were insoluble in any solvents (Table I). The results were indicative of the interpolymer crosslinking reaction. The IECs of CSPPSU-2S and CSPPSU-4S were 2.13 and 3.20 meq/g, respectively, and were lower than those of the parent polymer membranes. The results suggest sulfone bond formation from the sulfonic acid groups.²¹ The losses of the sulfonic acid groups calculated from the IEC values were 39% and 40% for CSPPSU-2S and CSPPSU-4S, respectively, implying similar degree of crosslinking for the membranes. It is considered that the annealing induced interpolymer sulfone bond formation in addition to the decomposition (removal) of the sulfonic acid groups. Detailed structural analyses with NMR spectra were unavailable due to the insolubility of the CSPPSU membranes.

Crosslinking Mechanism

Since NMR analyses were not available because of the insolubility of the crosslinked products, some model reactions were performed using monomeric compounds. The same annealing processes were used for three samples including SFPS-H (SFPS in H^+ form, Supporting Information Scheme S1 and Supporting Information Figure S5), mixture of SFPS/BP, and mixture of SFPS-H/BP. The annealed mixture of SFPS/BP showed no new peaks but a decrease in the intensity of BP. The result indicates that the chemical reaction did not take place but the evaporation of BP occurred [Figure 2(a,b)]. For the mixture of SFPS-H/BP, three new peaks labeled with * were observed at about 7.20, 7.07, and 6.94 ppm [Figure 2(c,d)]. The same set of the peaks were also observed for annealed

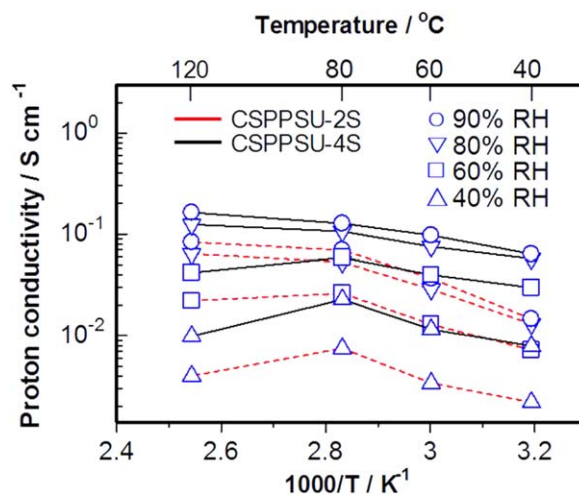


Figure 3. Temperature dependence of the proton conductivity of CSPPSU-2S and CSPPSU-4S membranes at different RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table II. Apparent Activation Energy of the Proton Conduction at Different RH and Mechanical Properties at 80 °C, 60% RH of the Crosslinked Membranes

Sample	E_a (kJ/mol)				Initial Young's modulus (GPa)	Yield stress (MPa)	Maximum strain (%)
	40% RH	60% RH	80% RH	90% RH			
CSPPSU-2S	28	30	32	22	0.54	31.3	20
CSPPSU-4S	24	16	14	12	0.40	22.1	92

SFPS-H [Figure 2(e,f)]. It is suggested that the sulfonic acid groups (in H^+ forms) take part in the thermal reaction. The new peaks could be assignable to the chemical structure as shown Figure 2.

Properties and Morphology of CSPPSU-2S and CSPPSU-4S Membranes

The proton conductivities of the crosslinked CSPPSU-2S and CSPPSU-4S membranes were measured at different RH and temperature (T) and are plotted as a function of $1000/T$ in Figure 3. The proton conductivity of CSPPSU-2S and CSPPSU-4S membranes increased as increasing RH and temperature (lower than 120 °C). As expected, CSPPSU-4S with higher IEC showed higher proton conductivity than that of CSPPSU-2S. At 80 °C, 90% RH, its conductivity reached 128 mS/cm, about 1.4 times higher than that of Nafion (94 mS/cm) (not shown). The highest conductivity of CSPPSU-4S reached 0.163 S/cm at 120 °C, 90% RH. At any RH, the proton conductivity showed approximate Arrhenius-type temperature dependence up to 80 °C, however, decreased at 120 °C when RH was lower than 80% RH. It is considered that the morphological changes might have occurred at such high temperature to cause a decrease in the proton conductivity. The apparent activation energies (E_a) were calculated from the slopes in the linear region, from 40 to 80 °C at 40%–80% RH, and from 40 to 120 °C at 90% RH and are included in Table II. The activation energies of CSPPSU-4S membrane were lower than those of CSPPSU-2S membrane due

to the former's higher IEC resulting in high density and high mobility of the protons.

The proton conductivity of the CSPPSU-2S and CSPPSU-4S membranes at 80 °C, 90% RH was recorded as a function of time (Supporting Information Figure S6) to evaluate the stability of the membranes. The membranes exhibited good stability under the testing conditions without no changes in the conductivity for several tens of hours.

Figure 4 shows the cross-sectional TEM images of the CSPPSU-2S and CSPPSU-4S membranes stained with Pb^{2+} ions, in which the dark areas represent ionic clusters composed of the sulfonic acid groups. Both membranes showed phase-separated morphology, in which small hydrophilic clusters were distributed uniformly. Due to the higher IEC value, CSPPSU-4S showed slightly larger ionic clusters (ca., 3 nm in diameter) than that (ca., 1.5 nm in diameter) of CSPPSU-2S. It is well-known that such distinct phase-separated morphology promotes proton conductivity,^{24,25} which is accountable for higher proton conductivity of CSPPSU-4S than that of CSPPSU-2S. Relatively small ionic clusters could cause some dead-end channels at low RH to cause the low conductivity as discussed above (Figure 3).

Water uptake of CSPPSU-2S and CSPPSU-4S membranes was measured at 80 °C and plotted as a function of RH [Figure 5(a)]. The water uptake increased with increasing IEC and RH values as expected. The highest water uptake of CSPPSU-4S was

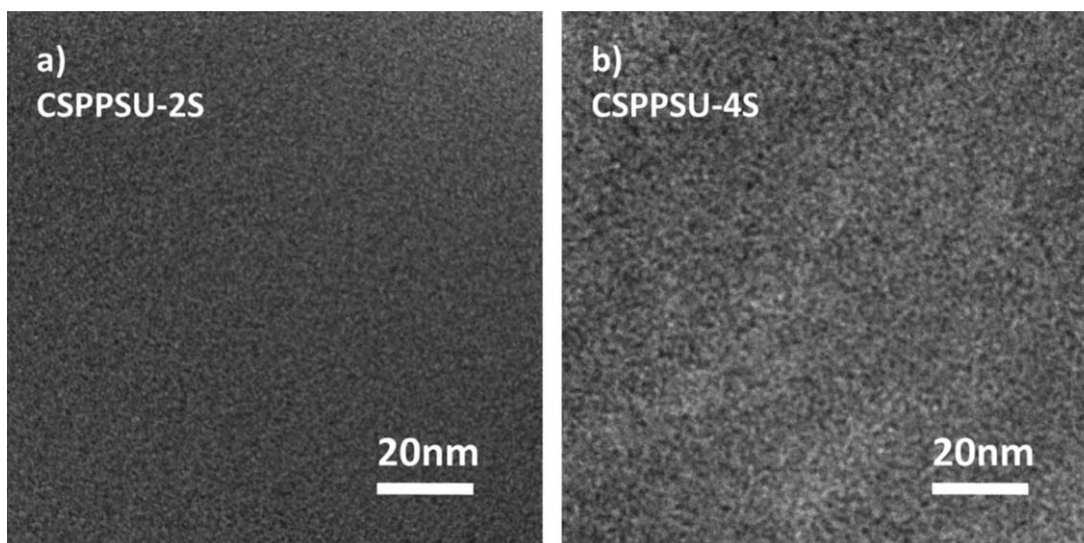


Figure 4. TEM images of crosslinked membranes in lead ion (Pb^{2+}) form: (a) CSPPSU-2S, (b) CSPPSU-4S.

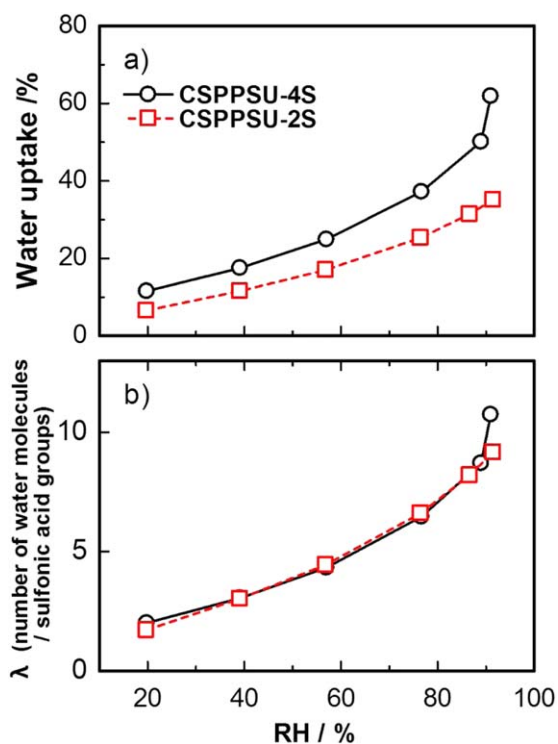


Figure 5. (a) Water uptake and (b) λ [calculated from the data in Figure 5(a) and IEC values] of CSPPSU-2S and CSPPSU-4S membranes at 80 °C, different RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

62 wt %, about two times higher than that of CSPPSU-2S (35 wt %) at 95% RH. The high water uptake contributes to the high proton conductivity due to developed ion conducting pathway in the membrane. However, CSPPSU-4S membrane showed several times higher swelling ratio than that of CSPPSU-2S membrane (Supporting Information Table S2). For more detailed discussion, the number of water molecules absorbed per sulfonic acid group (λ) is plotted as a function of IEC in Figure 5(b). The λ value increased with RH. It should be noticed that the two membranes exhibited very similar λ values and the humidity dependence. The results suggest that the water molecules were absorbed selectively to the sulfonic acid groups and that the excess swelling was suppressed for these crosslinked membranes.

Then, we measured the mechanical properties of CSPPSU-2S and CSPPSU-4S membranes. In the DMA analyses, humidity dependence of storage modulus (E'), loss modulus (E''), and $\tan \delta$ of the membranes were measured at 80 °C (Figure 6). CSPPSU-2S membrane with lower IEC exhibited excellent DMA properties, with slight losses in E' and E'' and no transition peak in $\tan \delta$ curve. In contrast, CSPPSU-4S with higher IEC showed larger losses in E' and E'' at greater than 80% RH and a transition peak in $\tan \delta$ curve at about 88% RH. The water molecules absorbed by the sulfonic acid groups in the membrane would act as a plasticizer, resulting in a gradual decrease in E' and E'' with increasing the humidity. The mechanical properties of the CSPPSU-2S and CSPPSU-4S membranes were further investigated by the tensile test at 80 °C and 60% RH (Figure 7, Table II). Both membranes showed moderate

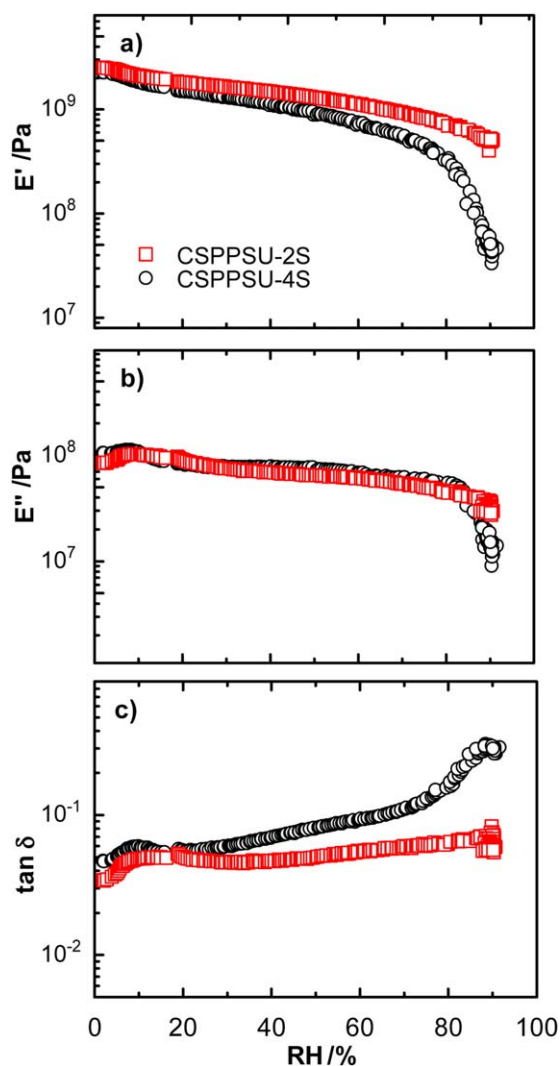


Figure 6. DMA properties of CSPPSU-2S and CSPPSU-4S membranes: (a) E' , (b) E'' , (c) $\tan \delta$ at 80 °C as a function of RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

initial young's modulus (0.54 GPa for CSPPSU-2S and 0.40 GPa for CSPPSU-4S) and yield stress (31.3 MPa for CSPPSU-2S and 22.1 MPa for CSPPSU-4S). It should be noted that,

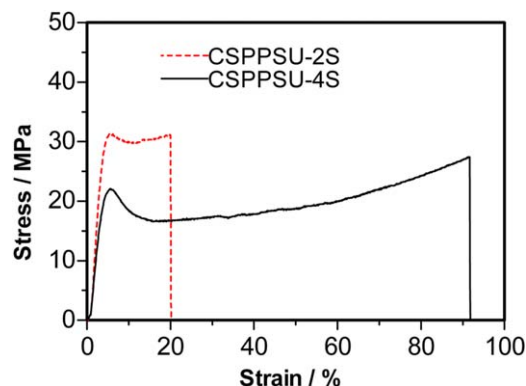


Figure 7. Stress versus strain curves of CSPPSU-2S and CSPPSU-4S membranes at 80 °C, 60% RH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

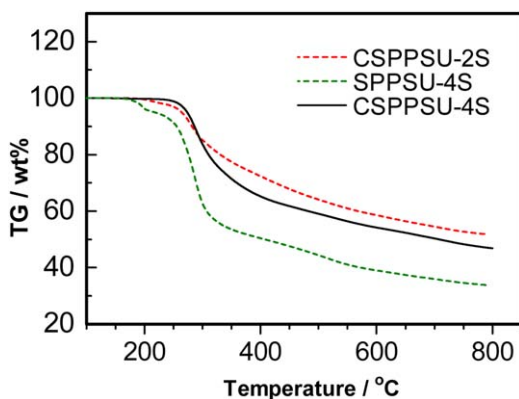


Figure 8. TGA curves of CSPPSU-2S, SPPSU-4S, and CSPPSU-4S membranes in nitrogen. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table III. Thermal Properties of CSPPSU-2S, SPPSU-4S, and CSPPSU-4S Membranes

Sample	T_d^a (°C)	T_d^b (°C)
CSPPSU-2S	261	na
SPPSU-4S	180	254
CSPPSU-4S	256	na

^aTemperature of the first weight loss.

^bTemperature of the second weight loss.

unlike the typical crosslinked membranes with brittle properties, CSPPSU-2S and CSPPSU-4S membranes showed plastic deformation region. This behavior was more pronounced for CSPPSU-4S membrane with a yield strain higher than 90% strain.

The TGA curves of CSPPSU-2S, SPPSU-4S and CSPPSU-4S membranes are shown in Figure 8, and the weight loss temperatures are listed in Table III. The weight loss below 100 °C was assigned to the absorbed water and therefore is not displayed in the diagram. The uncrosslinked SPPSU-4S membrane started to lose weight at about 180 °C probably due to the evaporation of the remaining casting solvent (DMSO). All membrane samples showed a weight loss from about 250 °C which was attributed to the decomposition of the sulfonic acid groups.²² The weight loss at higher temperature starting at ca. 300 °C would be due to the decomposition of the polymer main chain. The residual weights at 800 °C were 52 wt % for CSPPSU-2S, 34 wt % for SPPSU-4S, and 47 wt % for CSPPSU-4S, respectively. The lower IEC value and interpolymer crosslinked structure should be responsible for the larger remaining weight of CSPPSU-2S and CSPPSU-4S.

CONCLUSIONS

We developed a novel series of crosslinked aromatic ionomers with high IEC values. The CSPPSU-2S and CSPPSU-4S membranes were obtained through well-controlled annealing treatment of the precursor SPPSU-2S and SPPSU-4S membranes with high molecular weight and high IEC. Due to the

crosslinking effect, the produced membranes showed high insolubility in water and other organic solvents, good chemical, thermal, and mechanical stability. The high IEC values endowed the crosslinking membranes with high proton conductivity at high temperature and good mechanical stability. While the annealing was turned out to be effective for highly sulfonated PPSU, it may be applicable to the other sulfonated aromatic polymers.

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