Sulfonated Poly(phenylene sulfone)s Ionomers

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Abstract. SPPSU(2S) and SPPSU(4S) ionomers with two and four sulfonic acid groups per PPSU unit were synthesized and characterized. SPPSU(2S) ionomers were synthesized and characterized by varying the acid type, sulfonation temperature, and time. Mild sulfuric acid was suitable for sulfonation of PPSU(2S). The IEC, molecular weight, and viscosity of SPPSU(2S) ionomers were 3.42–5.15 meq/g, 150,000–430,000, and 50–80 mPa·s, respectively, depending on the synthesis conditions. The tensile strength of SPPSU(2S) ionomer membranes was higher than that of Nafion membrane, the tensile elongation was lower than that of Nafion membrane, and the elastic modulus was higher than that of Nafion membrane. The conductivity of SPPSU(2S) ionomer membranes was similar to that of Nafion212 membrane. On the other hand, SPPSU(4S) ionomer was synthesized by monomers. The IEC and molecular weight of SPPSU(4S) ionomer were 5.6 meq/g and 303,203. The viscosity of SPPSU(4S) ionomer was higher than that of SPPSU(2S) ionomer. The stress-strain properties of SPPSU(4S) ionomer membrane showed a slightly higher elastic modulus than Nafion membrane, but the tensile strength and tensile elongation were similar to those of Nafion membrane. In addition, the conductivity of SPPSU(4S) ionomer membrane was higher than that of SPPSU(2S) and Nafion membranes. The above characteristics of SPPSU(2S) and SPPSU(4S) ionomer membranes are expected to be used as ionomer electrolytes for energy devices.

Introduction

Ion exchange materials are used in energy devices (fuel cells, water electrolysis, redox flow battery (RFB)), power generation (polishing of condensed water, purification of nuclear waste), water treatment (electrodialysis, ultrapure water generation, water softening, desalination, wastewater treatment), separation technology and chemical technology (chlor-alkali process, ion exchange chromatography, chemical catalysis, metal extraction and purification), food production (sugar production, beverage production) and pharmaceuticals (drug delivery, separation and purification of biochemical substances), and high performance is required [1,2,3]. Currently, perfluoroalkylsulfonic acid-based polymers are widely used as proton exchange electrolytes, and Nafion® is well known for energy devices [3]. On the other hand, hydrocarbon-based proton exchange electrolyte materials are expected to be alternatives to fluorine-based materials in terms of high mechanical strength, high glass transition temperature and low environmental impact. Polyaryl ether ketone (PAEK: polyether ether ketone (PEEK)), polyimide (PI: aromatic polyimide), polysulfone (PSU, polyarylsulfone (PES), polyphenylsulfone (PPSU)), polybenzimidatole (PBI), and polyphenylene oxide (PPO), which are engineering resins with high thermal and chemical stability, have been studied for application as ion exchange materials [4]. However, further research and development is required for practical use in energy devices. The main purpose of proton exchange electrolyte membranes is to conduct protons at a higher rate, and the aromatic rings of hydrocarbon-based resins can be chemically modified, such as by electrophilic or nucleophilic substitution, to improve proton conductivity [4,5]. PPSU is a consist of bisphenol and diphenylsulfone linked by ether groups. The arylene ether segment is a nonpolar, flexible, electron-rich portion. The arylene sulfone segment is a polar, rigid, and electron-poor

portion. PPSU has high chemical, thermal and mechanical stability, and can be sulfonated to a high degree, making it a promising ion exchange material with high proton conductivity [2,4,5-12].

The conductivity of SPPSU ionomers can be improved by increasing the degree of sulfonation. I have been studying ionomers with two or four sulfonic acid groups per PPSU unit. SPPSU(2S) ionomers with two sulfonic acid groups per PPSU unit were obtained by sulfonating Solvay's PPSU. On the other hand, SPPSU(4S) ionomers with four sulfonic acid groups per PPSU unit were synthesized by monomers. In this paper, I report on the synthesis and properties of SPPSU(2S) and SPPSU(4S) ionomers.

Experimental

Synthesis of SPPSU(2S) ionomer. SPPSU (2S) ionomer, which has two sulfonic acid groups per PPSU unit, was obtained by direct sulfonation of PPSU. PPSU (Radel R-5000 NT: Mw = 50,000) was provided by Solvay Specialty Polymers Japan Co., Ltd. Sulfonation was performed using sulfuric acid (98%), oleum (fuming sulfuric) acid (30%), and $ClSO_3H$. After sulfonation of SPPSU, the solution was precipitated in ice and filtered. SPPSU was further washed with ultrapure water to pH 7 using a dialysis membrane (MWCO = 14,000, sigma-aldrich, St. Louis, Missoure (MO), USA). SPPSU was then completely dried using a freeze dryer (FDV-12AS, AS ONE Co., Ltd.) to obtain SPPSU ionomer (Fig. 1).

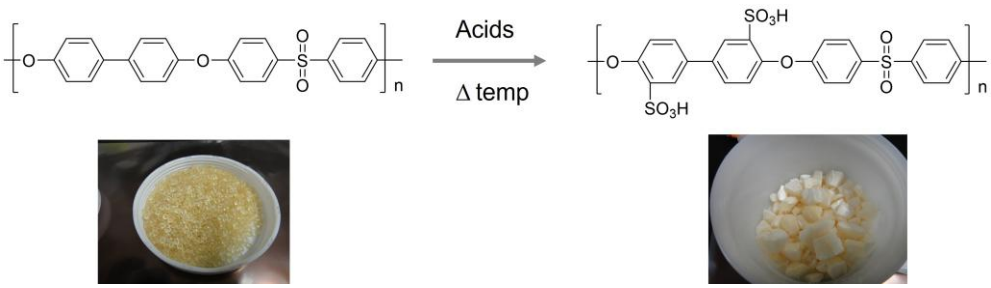

Figure 1. Sulfonation of PPSU (SPPSU(2S)); chemical structure and appearances of PPSU (left) and Sulfonated PPSU (right).

Synthesis of SPPSU(4S) ionomer. The SPPSU(4S) ionomer, which has four sulfonic acid groups per PPSU unit, was obtained by sulfonating the monomer bis(4-fluorophenyl)sulfone (sulfonated bis(4-fluorophenyl)sulfone (SFPS)), followed by a condensation polymerization reaction with 4,4'-biphenol (BP), and then sulfonating these in sulfuric acid (Fig. 2).

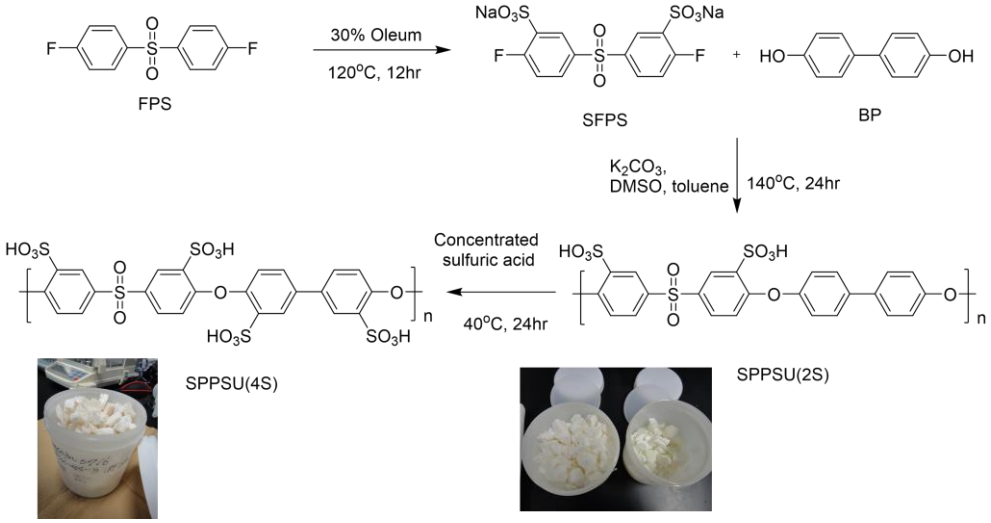

Figure 2. Synthesis of SPPSU(4S); chemical structure and appearances of Sulfonated PPSU.

Preparation of ionomer membranes. The PPSU(2S) and PPSU(4S) ionomer membranes were obtained by dissolving the PPSU(2S) and PPSU(4S) ionomers in water, respectively, and heating them in a petri dish at 40°C (12hr), 60°C (12hr), and 120°C (12hr) to evaporate the water.

Characterization. The molecular weight of the ionomers was analyzed using gel permeation chromatography (GPC, Toso, HLC-8220GPC). Ion exchange capacity (IEC) was defined as the milli-equivalent value of sulfonic acid groups per gram of dry sample. The thermal stability of the SPPSU ionomers was evaluated using Shimazu's DTG-60AH. The rheology of the membrane was measured using a Rheometer (Anton Paar_MCR102). The stress-strain test of the ionomer membranes was performed at room temperature using a tensile testing machine (Shimadzu Corporation, EZ-S). The sample was cut using Super Dumbbell Cutter SDMP-100 (manufactured by Dumbbell Co., Ltd.). The conductivity in the thickness direction of the SPPSU ionomer membranes was obtained by impedance measurement using the MTS740 membrane test system (MTS, Scribner Associates, Inc.) using the four-probe method at a frequency range of 1 Hz to 1 MHz and a peak-to-peak voltage of 10 mV. The ionomer membrane was sandwiched between carbon paper electrodes (electrode area = 0.9 cm^2) dedicated to the MTS740 device, and measurements were taken while changing the temperature and humidity.

Results and discussion

Properties of SPPSU(2S) ionomers. SPPSU(2S) ionomer was obtained by sulfonating PPSU polymer with H_2SO_4, $ClSO_3H$, and Oleum acid at different temperatures and times. From the H and C-NMR analysis results, an SPPSU(2S) ionomer with two sulfonic acid groups was obtained. On the other hand, when sulfonation was performed with Oleum at 23°C for 24hr, the main chain of PPSU polymer was broken. Table 1 summarizes the ion exchange capacity, molecular weight, and polymer structure stability by H-NMR of the synthesized SPPSU ionomers. The theoretical IEC of 2 sulfonic acid groups per PPSU unit (DS=2) is 3.56 meq/g. The IEC higher than the theoretical value is thought to be due to the acid used during synthesis not being completely removed. On the other hand, the molecular weight of the SPPSU (2S) ionomer increased by 2 to 8 times that of PPSU. It is thought that crosslinking between polymers also occurred during the sulfonation of PPSU, resulting in an increase in molecular weight. The H-NMR analysis results of SPPSU using oleum acid suggested that the PPSU structure may have been destroyed. These results indicate that H_2SO_4 is more suitable for the sulfonation of PPSU than $ClSO_3H$ or oleum acid. The thermal stability (TGA) of the synthesized SPPSU(2S) polymer was measured using air (N_2/O_2=7/3) gas. The weight loss behavior of the SPPSU ionomers does not show a significant difference depending on the synthesis conditions. The weight loss occurs in three stages, such as a decrease due to the evaporation of water molecules below 100°C, desorption of -SO_3H groups above 250°C, and decomposition of the polymer backbone above 400°C.

Table 1. Properties of sulfonated PPSU (2S) using different acids and at temperatures.

	PPSU	Sulfonation of PPSU							
Acids		H_2SO_4						$ClSO_3H$	Oleum
T(°C)/hr	-	40 / 24	40 / 48	60 / 24	60 / 48	80 / 6	80 / 24	23 / 20	23 / 24
IEC (meq/g)	-	3.42	3.76	3.91	4.1	3.60	3.58	3.88	5.15
DS	-	1.89	2.16	2.29	2.47	2.03	2.02	2.3	3.5
Mw	50,000	395,692	426,222	360,182	295,886	165,314	202,909	151,143	211,110
Stability (NMR)	○	○	○	○	○	○	○	○	×

Fig. 1 shows the rheology characteristics of SPPSU solutions using 10wt% SPPSU(2S) in 90wt% DMSO solution. The viscosity of the SPPSU(2S) polymer changed depending on the synthesis temperature and time and showed values of 49 – 77 mPa·s at a shear rate (1/s) of 1000. On the other

hand, the viscosity of each SPPSU solution dropped sharply at shear rates below 100 but remained constant at shear rates above 100. The viscosity of the SPPSU polymer was highly dependent on the synthesis temperature, with little dependence on time. The high viscosity of 77 mPa·s was obtained at a sulfonation temperature of 40°C. This value was higher than the viscosity of Nafion (D520CS, D521CS) (25°C, 10 – 40 mPa·s). Fig. 2 shows the stress-strain characteristics of the SPPSU(2S) ionomer membrane, and Table 2 shows the results. The stress-strain characteristics of the SPPSU(2S) ionomer membrane synthesized at 40°C showed higher values for stress, strain, and flexural modulus than the SPPSU(2S) ionomer membranes synthesized at 60°C and 80°C. In addition, the SPPSU(2S) ionomer membranes had lower stress and flexural modulus than PPSU, and higher strain (plasticity). On the other hand, the plasticity of the SPPSU(2S) ionomer membrane was smaller than that of the Nafion membrane, but its flexural modulus was highter.

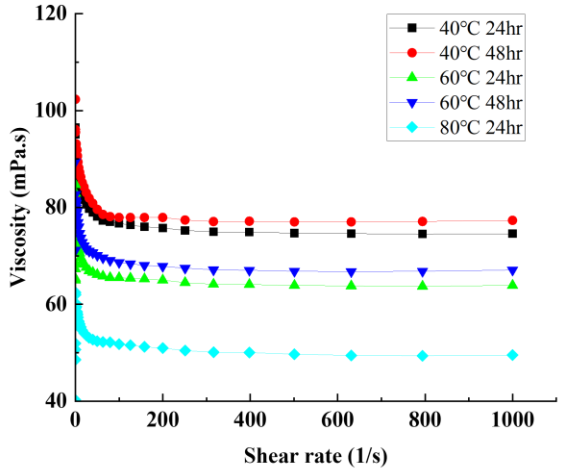

Figure 1. Rheology properties of SPPSU(2S) ionomers sulfonated at the different temperature and time using H_2SO_4.

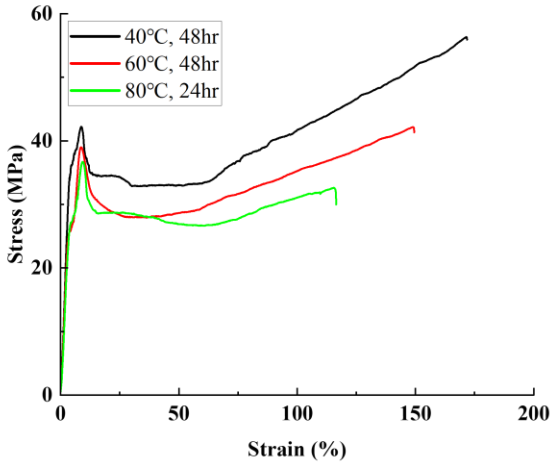

Figure 2. Stress-strain properties of SPPSU(2S) ionomers sulfonated at the different temperature and time using H_2SO_4.

Table 2. Stress-strain results of SPPSU(2S) ionomers sulfonated at the different temperature and times using H_2SO_4.

	SPPSU (2S) ionomer membranes		
Sulfonation conditions	Stress (MPa)	Strain (%)	Flexural modulus* (MPa)
H_2SO_4, 40°C, 48hr	56.4	172	1001
H_2SO_4, 60°C, 48hr	42.3	150	950
H_2SO_4, 80°C, 24hr	32.7	116	886
PPSU**	69.6	60 – 120	2410
Nafion212	18.5	>200	130

*Young's modulus (Flexural modulus) = Dstress/Dstrain

**From Solvay PPSU R-5000_Datasheet

Table 3. The conductivity results at the cell temperature of 100°C and 120°C of SPPSU(2S) ionemer membranes sulfonated at the different temperature and times using H_2SO_4.

	SPPSU ionomer membranes			
Sulfonation conditions	100°C (mS/cm)		120°C (mS/cm)	
	10% RH	40% RH	10% RH	40% RH
40°C, 48hr	0.3	5.6	1.7	13.1
60°C, 48hr	0.4	6.0	1.4	9.1
80°C, 24hr	2.4	10.0	3.5	13.8
Nafion212	1.2	10.6	2.9	12.3

The conductivity characteristics of the SPPSU(2S) ionomer membranes are summarized in Table 3. The conductivity of the SPPSU(2S) ionomer membranes increases with increasing temperature and RH%. In addition, the SPPSU(2S) ionomer synthesized at 80°C had a higher conductivity than those synthesized at 40°C and 60°C. The high conductivity of the SPPSU ionomer synthesized at 80°C is thought to be due to its lower molecular weight and viscosity than those synthesized at 40°C and 60°C (Table 1). On the other hand, the maximum conductivity of the SPPSU(2S) ionomer membrane was 3.5 mS/cm at 120°C and 10% RH.

Properties of SPPSU(4S) ionomer. The molecular weight of SPPSU(4S) was 303,203, and the IEC by titration was 5.9 meq/g (D.S.=4.57). The H and C-NMR results indicate that the SPPSU(4S) ionomer was successfully synthesized. The viscosity of the SPPSU(4S) ionomer is higher than that of SPPSU(2S) and Nafion ionomers (Table 4). Table 5 shows the stress-strain property data in comparison with SPPSU(4S), SPPSU(2S), Nafion, and PPSU. The stress-strain properties of the SPPPSU(4S) ionomer membrane tended to be similar to those of the Nafion membrane, unlike the SPPSU(2S) ionomer membrane. On the other hand, the Young's modulus (flexural modulus) was more than three times smaller than that of the SPPSU (2S) ionomer membrane and more than two times higher than that of the Nafion membrane. By sulfonating the PPSU polymer, the tensile strength decreased, the tensile elongation increased, and the flexural modulus decreased, resulting in a flexible ionomer.

Table 4. Viscosity comparison of SPPSU (2S), SPPSU (4S), and Nafion ionomer.

Sample	mPa·s
10wt% SPPSU (2S) / 90wt% DMSO	50 – 80
10wt% SPPSU (4S) / 90wt% DMSO	268
5wt% Nafion / 45wt% water, 50wt% 1-propanol	10 – 40

Table 5. Stress-strain comparison of SPPSU (2S), SPPSU (4S), and Nafion ionomer membranes

	Stress (MPa)	Strain (%)	Flexural modulus* (MPa)
SPPSU (2S)	56.4	172	1001
SPPSU (4S)	22	251	296
Nafion212	18.5	>200	130

Table 6. Conductivity comparison of SPPSU (2S), SPPSU (4S), and Nafion ionomer.

Ionomer membranes	100ºC (mS/cm)		120ºC (mS/cm)		Ea (eV)
	10% RH	40% RH	10% RH	40% RH	
SPPSU (2S)	0.3	5.6	1.7	13.1	0.30
SPPSU (4S)	4.2	33.3	11.3	46.7	0.10
Nafion212	1.2	10.6	2.9	12.3	0.15

The thickness direction conductivity characteristics of SPPSU(4S) ionomer membranes were evaluated while changing the temperature and RH%. A comparison of the conductivity of SPPSU(2S) and Nafion212 membranes is shown in Table 6. The conductivity of SPPSU(4S) ionomer membranes increases with increasing temperature and RH%. The conductivity of the SPPSU (4S) ionomer membrane was higher than those of the SPPSU (2S) and Naion membranes, and the activation energy was lower than that of the Nafion membrane. The high conductivity of the SPPSU(4S) ionomer membrane is attributed to its high IEC and flexibility.

Summary

SPPSU(2S) ionomers with two sulfonic acid groups (IEC=3.5meq/g) and SPPSU(4S) ionomers with four sulfonic acid groups (IEC=3.5meq/g) per PPSU repeat unit were synthesized. The

molecular weights of SPPSU(2S) and SPPSU(4S) ionomers were 150,000–430,000 and 303,203, and the viscosities were 50–80 mPa·s and 268 mPa·s. The tensile strength, tensile elongation, and flexural modulus of SPPSU(2S) and SPPSU(4S) ionomers were 33–56 MPa, 116–172%, 886–1001 MPa, 22 MPa, 251%, and 296 MPa, respectively. The conductivities of the SPPSU(2S) and SPPSU(4S) ionomers at 120°C and RH 10% were 1.4–3.5 mS/cm and 11.3 mS/cm, respectively, which were higher than the conductivity of the Nafion212 membrane (3.2 mS/cm). These results suggest that the SPPSU ionomers can be used as electrolytes for energy devices.

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