

Supporting Information

Poly(*p*-phenylene)-based membrane materials with excellent cell efficiencies and durability for use in vanadium redox flow batteries

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Monomer synthesis

2,5-Dichlorobenzophenone (2,5-DCBP)

2,5-Dichlorobenzophenone (2,5-DCBP) was synthesized according to a previously reported method. 2,5-Dichlorobenzoyl chloride (120 g, 0.537 mmol) was added to excess benzene and anhydrous aluminum chloride (76.40 g, 0.716 mmol) was continuously added to this solution at 0 °C. After stirring for 3 h, the mixture was maintained at room temperature for 24 h. The reaction mixture was poured into 10% hydrochloric acid in ice water. The product was recrystallized from ethanol and was dried at 35 °C under vacuum for 24 h. (Yield: 85%) ¹H-NMR (300 MHz, DMSO-d₆), d (ppm): 7.77 (s, 1H), 7.74 (m, 2H), 7.73–7.70 (m, 1H), 7.68 (m, 2H), 7.60–7.59 (d, 1H), 7.58–7.55 (d, 1H), ¹³C-NMR (75 MHz, DMSO), d (ppm): 193.00, 139.74, 135.26, 134.45, 132.23, 131.53, 131.41, 129.65, 129.11, 128.51, 128.33.

2,5-Dichloro-4'-fluorobenzophenone (2,5-DCFBP)

2,5-Dichloro-4'-fluorobenzophenone (2,5-DCFBP) was synthesized according to a previously reported method. An excess of fluorobenzene (67.2 mL), nitromethane (150 mL), and anhydrous aluminum chloride was added to a round-bottom flask and stirred at 0 °C. Then, 2,5-dichlorobenzoyl chloride (100 g, 0.477 mmol) was added to the mixture by dropping funnel, and the reaction proceeded at room temperature for 24 h. The reaction mixture was poured into 10% hydrochloric acid in ice water. The product was recrystallized from an aqueous solution of n-hexane/ethyl acetate (4:1,v:v). The crystals were dried at 35 °C under vacuum for 24 h. (Yield: 78%) ¹H-NMR (300 MHz, DMSO-d₆): 7.84 (d, 2H), 7.40 (m, 2H), 7.34 (d, 1H), 7.16 (d 2H), ¹³C-NMR (75 MHz, DMSO): 192.1, 166.3, 139.6, 133.0, 132.8, 132.3, 131.3, 131.2, 129.4, 128.8, 116.0

Mono(4-hydroxy)sexiphenylene (SP)

Mono(4-hydroxy)sexiphenylene (SP) was synthesized according to a previously reported method. The synthesis of mono(4-hydroxy)sexiphenylene was carried out in two steps as described: First, 1-methoxy-4-(2-phenylethynyl)benzene (2.0 g, 9.47 mmol) and 2,3,4,5-tetraphenylcyclopenta-2,4-dien-dien-1-one (3.68 g, 9.47 mmol) were stirred in sulfolane (7 mL) at 260 °C for 7.5 h. The reaction mixture was stirred in distilled water and methanol and dried under vacuum at 40 °C for 12 h. Subsequently, the solid was dissolved in dichloromethane (40 mL) and dropped into a 1-M boron tribromide solution in dichloromethane (5.4 mL, 5.4 mmol) slowly at -78 °C. Then, the reaction mixture was stirred for 3 h, and the temperature was slowly increased to room temperature over 16 h. After the reaction, the mixture was poured into distilled water and the dichloromethane residue was eliminated from the product under vacuum. Subsequently, the final product was stirred in distilled water and dried in a vacuum oven at 40 °C for 24 h. Mono(4-hydroxy)sexiphenylene was used after

purification from acetone. (Yield: 98%) $^1\text{H-NMR}$ (300 MHz, CDCl_3) 6.88–6.79 (m, 25H), 6.65 (d, 2H), 6.30 (d, 2H), 4.27 (s, 1H), $^{13}\text{C-NMR}$ (75 MHz, CDCl_3) 152.7, 140.6, 140.5, 140.4, 139.7, 132.5, 131.31, 131.29, 126.5, 126.4, 125.03, 125.01, 113.6.

Polymer synthesis

Synthesis of PBP-5, PBP-8 and PBP-11

PBP-5

PBP-5 was synthesized by typical synthesis procedure of PBP-z in experimental section.

2,5-DCBP (25 g, 99.56 mmol), 2,5-DCFBP (5.36 g, 19.91 mmol), $(\text{PPh})_2\text{Ni}_2\text{Cl}_2$ (2.34 g, 3.58 mmol), NaI (2.15 g, 14.34 mmol), TPP (11.28 g, 43.01 mmol), Zinc (9.37 g, 143.4 mmol), 4-chlorobenzophenone (0.40023 g), and DMAc (240 mL). $^1\text{H-NMR}$ (300 MHz, DMSO-d_6) 7.70-7.46 (m, 12H), 7.43–7.20 (m, 35H). $^{19}\text{F-NMR}$ (470 MHz, CDCl_3) -105.2 (s, 1F).

PBP-8

PBP-8 was synthesized by typical synthesis procedure of PBP-z in experimental section.

2,5-DCBP (25 g, 99.56 mmol), 2,5-DCFBP (3.35 g, 12.44 mmol), $(\text{PPh})_2\text{Ni}_2\text{Cl}_2$ (2.20 g, 3.36 mmol), NaI (2.01 g, 13.44 mmol), TPP (10.58 g, 40.32 mmol), Zinc (8.79 g, 134.40 mmol), 4-chlorobenzophenone (0.3752 g), and DMAc (225 mL). $^1\text{H-NMR}$ (300 MHz, DMSO-d_6) 7.70-7.47 (m, 18H), 7.42–7.20 (m, 53H). $^{19}\text{F-NMR}$ (500 MHz, CDCl_3) -105.2 (s, 1F).

PBP-11

PBP-11 was synthesized by typical synthesis procedure of PBP-z in experimental section.

2,5-DCBP (25 g, 99.56 mmol), 2,5-DCFBP (2.44 g, 9.05 mmol), $(\text{PPh})_2\text{Ni}_2\text{Cl}_2$ (2.13 g, 3.26 mmol), NaI (1.95 g, 13.03 mmol), TPP (10.26 g, 39.10 mmol), Zinc (8.52 g, 130.33 mmol), 4-chlorobenzophenone (0.3638 g), and DMAc (220 mL). $^1\text{H-NMR}$ (300 MHz, DMSO-d_6) 7.69-7.48 (m, 24H), 7.41–7.21 (m, 71H). $^{19}\text{F-NMR}$ (500 MHz, CDCl_3) -105.2 (s, 1F).

Synthesis of PBSP-8 and PBSP-11

PBSP-5

PBSP-5 was synthesized by typical synthesis procedure of PBSP-z in experimental section.

PBP-5 (21.6 g), sexiphenylene (13.02 g, 23.64 mmol), K_2CO_3 (3.92 g, 28.37 mmol), DMAc (303 mL), and toluene (76 mL). $^1\text{H-NMR}$ (300 MHz, DMSO-d_6) 7.69-7.43 (m, 12H), 7.41–

7.00 (m, 33H), 6.97-6.73 (m, 27H), 6.57-6.28 (m, 4H). ¹⁹F-NMR (470 MHz, CDCl₃).

PBPSP-8

PBPSP-8 was synthesized by typical synthesis procedure of PBPSP-z in experimental section.

PBP-8 (20.2 g), sexiphenylene (8.12 g, 14.76 mmol), K₂CO₃ (2.45 g, 17.71 mmol), DMAc (282 mL), and toluene (76 mL).

¹H-NMR (300 MHz, DMSO-d₆) 7.69-7.42 (m, 18H), 7.41–7.01 (m, 51H), 6.98-6.72 (m, 27H), 6.55-6.28 (m, 4H). ¹⁹F-NMR (470 MHz, CDCl₃).

PBPSP-11

PBPSP-11 was synthesized by typical synthesis procedure of PBPSP-z in experimental section.

PBPSP-11 (19.2 g), sexiphenylene (5.84 g, 10.61 mmol), K₂CO₃ (1.76 g, 12.73 mmol), DMAc (385 mL), and toluene (96 mL). ¹H-NMR (300 MHz, DMSO-d₆) 7.68-7.43 (m, 24H), 7.41–6.99 (m, 69H), 6.98-6.71 (m, 27H), 6.56-6.27 (m, 4H). ¹⁹F-NMR (470 MHz, CDCl₃).

Synthesis of sPBPSP-8 and sPBPSP-11

sPBPSP-5

sPBPSP-5 was synthesized by typical synthesis procedure of sPBPSP-z in experimental section.

PBPSP-5 (30.83 g), 1,1,2,2-tetrachloroethane (616.70 mL), chlorosulfonic acid (39.28 mL), and 1,1,2,2-tetrachloroethane (616.70 mL). ¹H-NMR (300 MHz, DMSO-d₆) 7.68-7.47 (m, 12H), 7.42-7.22 (m, 33H), 7.20-7.01 (s, 10H), 6.97-6.76 (s, 12H) 6.55-6.37 (m, 4H). The synthetic procedure of sPBPSP-8 and sPBPSP-11 were shown in ESI.

sPBPSP-8

sPBPSP-8 was synthesized by typical synthesis procedure of sPBPSP-z in experimental section.

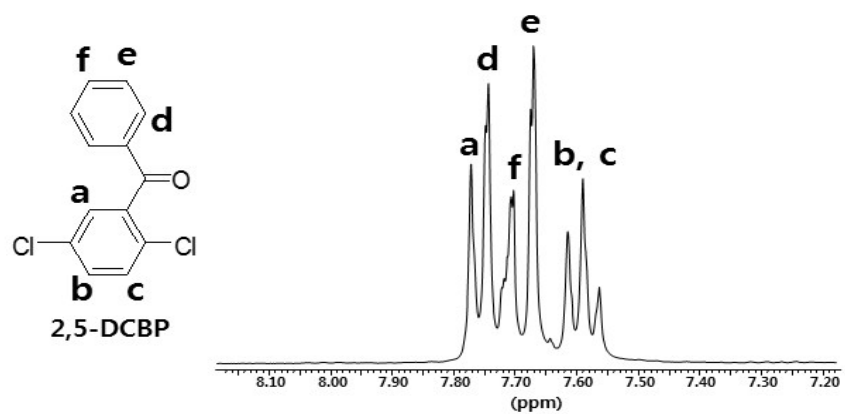
PBPSP-8 (25 g), 1,1,2,2-tetrachloroethane (505 ml), chlorosulfonic acid (24.53 ml, 369 mmol), and 1,1,2,2-tetrachloroethane (505 ml). ¹H-NMR (300 MHz, DMSO-d₆) 7.67-7.48 (m, 18H), 7.43-7.21 (m, 51H), 7.20-7.00 (s, 10H), 6.97-6.75 (s, 12H) 6.56-6.37 (m, 4H).

sPBPSP-11

sPBPSP-11 was synthesized by typical synthesis procedure of sPBPSP-z in experimental section.

PBPSP-11 (23 g), 1,1,2,2-tetrachloroethane (395 ml), chlorosulfonic acid (17.63 ml, 265 mmol), and 1,1,2,2-tetrachloroethane (395 ml). ¹H-NMR (300 MHz, DMSO-d₆) 7.68-7.46 (m, 24H), 7.41-7.20 (m, 69H), 7.20-7.02 (s, 10H), 6.98-6.73 (s, 12H) 6.57-6.38 (m, 4H).

(a)



(b)

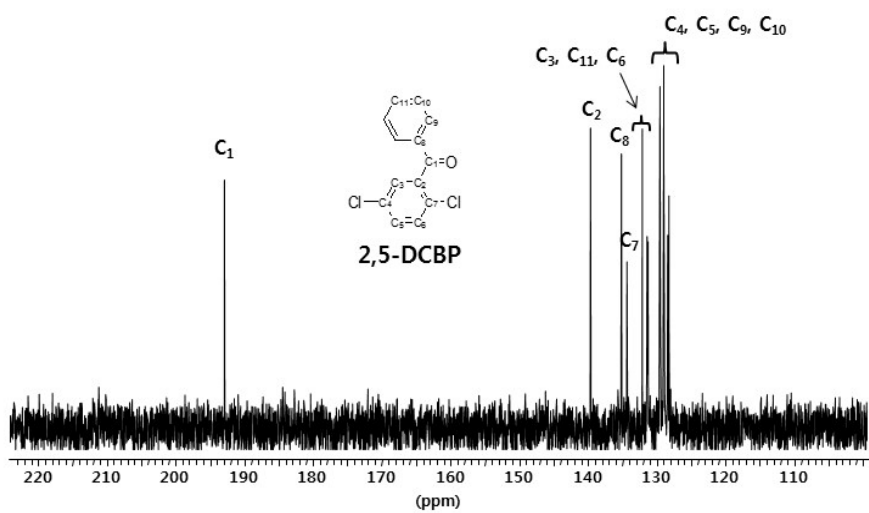
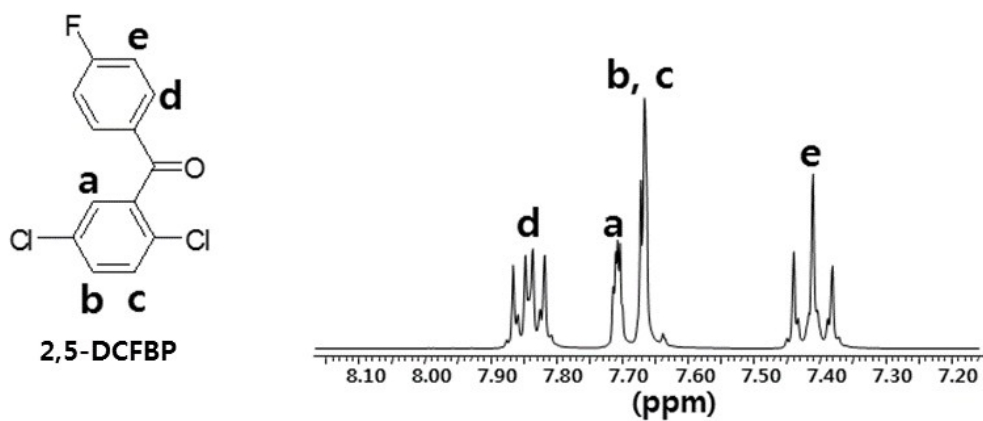


Fig. S1 NMR spectra of 2,5-DCBP: (a) ¹H-NMR and (b) ¹³C-NMR.

(a)



(b)

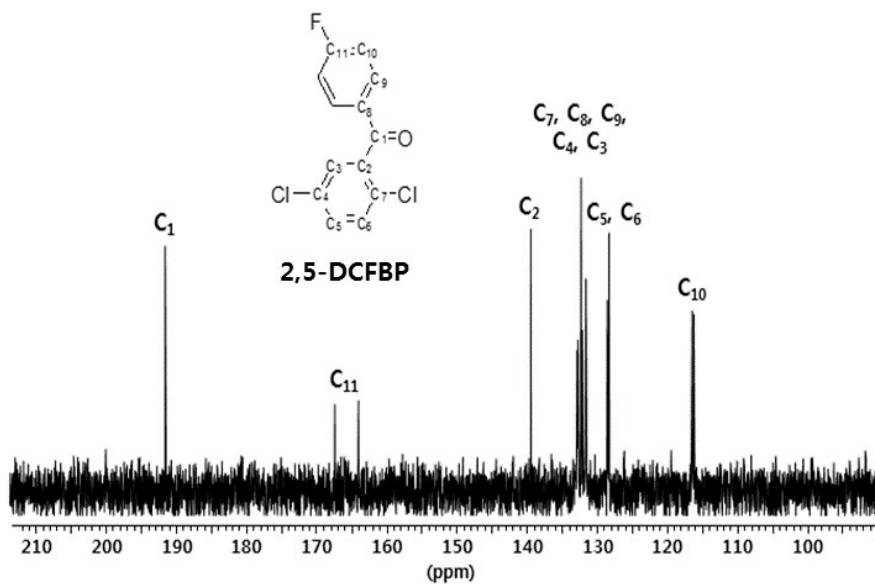
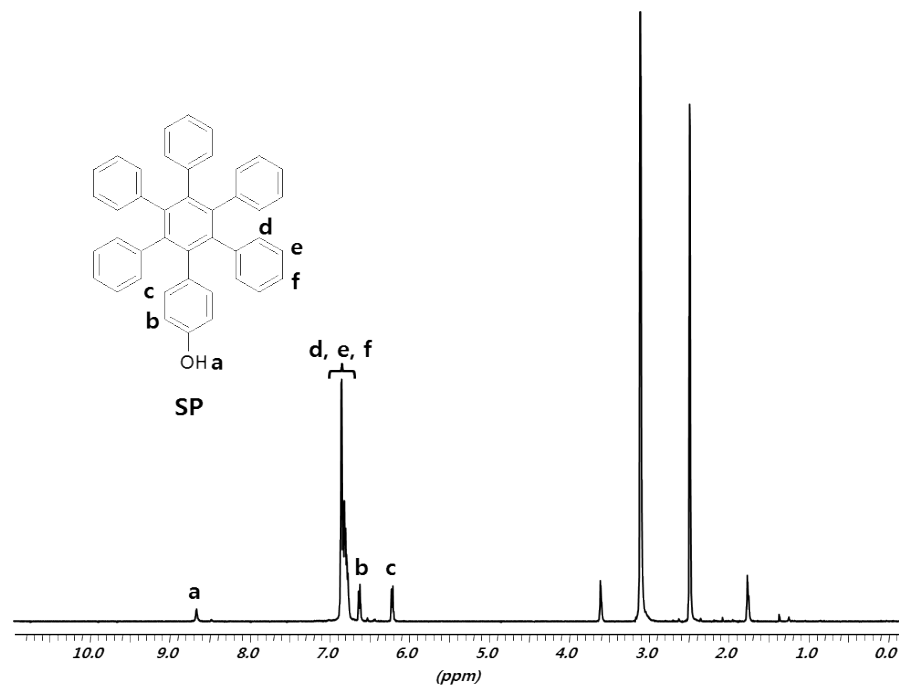


Fig. S2 NMR spectra of 2,5-DCFBP: (a) ¹H-NMR and (b) ¹³C-NMR.

(a)



(b)

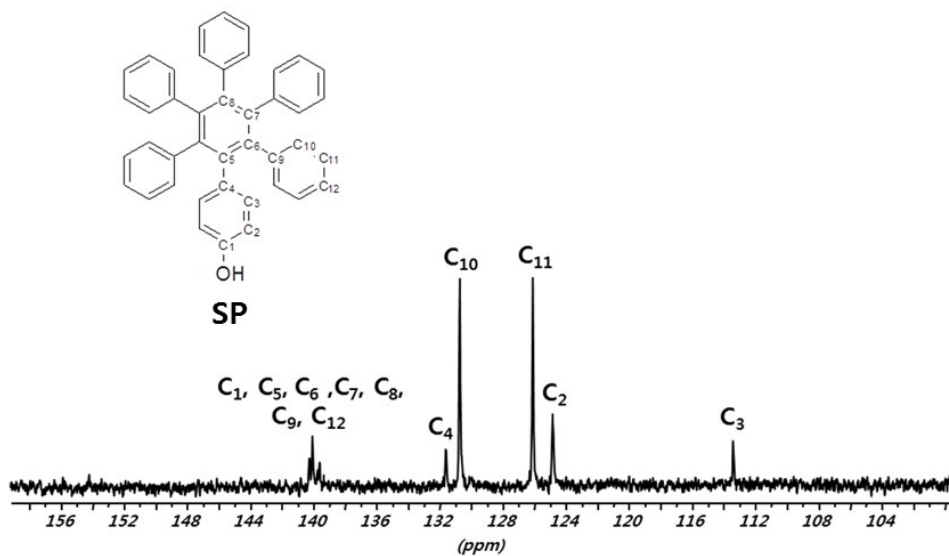


Fig. S3 NMR spectra of SP: (a) ^1H -NMR and (b) ^{13}C -NMR.

Table S1 Inherent viscosity changes of the polymers depending on molecular weight.

Molar percentages of 4-chlorobenzophenone compared to the sum of 2,5-DCBP and 2,5-DCFBP	PBP-7- ω	PBPSP- 7- ω	sPBPSP-7- ω
0	4.7	3.0	2.1
0.7	2.7	2.0	2.7
1.6	1.7	1.7	1.9
4.2	0.7	0.7	0.9

- ◆ The polymerization of PBP-7- ω was studied by varying the molar percentage of 4-chlorobenzophenone to the sum of 2, 5-DCBP and 2, 5-DCFBP to estimate the effect of molecular weight on the VRFB properties.
- ◆ The polymerization of PBP-7- ω was conducted by setting the molar ratio of 2, 5-DCBP and 2, 5-DCFBP to 7:1.
- ◆ We measured the inherent viscosities of PBP-7- ω and PBPSP-7- ω at 25 °C in NMP and in DMSO + 0.05 M LiBr (0.5 g dL⁻¹) in the case of sPBPSP-7- ω .
- ◆ sPBPSP-7-4.7 did not dissolve completely, resulting in the inherent viscosity of sPBPSP-7-4.7, 2.1 being much lower than the actual value as shown in Table S1.

Table S2 Molecular weight changes of the PBP-7- ω and PBPSP-7- ω polymers.

polymer	Molecular weight [kDa]	
	M_n	M_w
PBP-7-4.7	29.6	141.4
PBP-7-2.7	26.3	115.9
PBP-7-1.7	16.2	83.9
PBP-7-0.7	9.7	38.9
PBPSP-7-4.7	103.8	566.1
PBPSP-7-2.7	55.3	325.1
PBPSP-7-1.7	31.2	133.7
PBPSP-7-0.7	15.1	54.5

◆ The more the amount of end-capper used, the smaller the molecular weight of polymers.

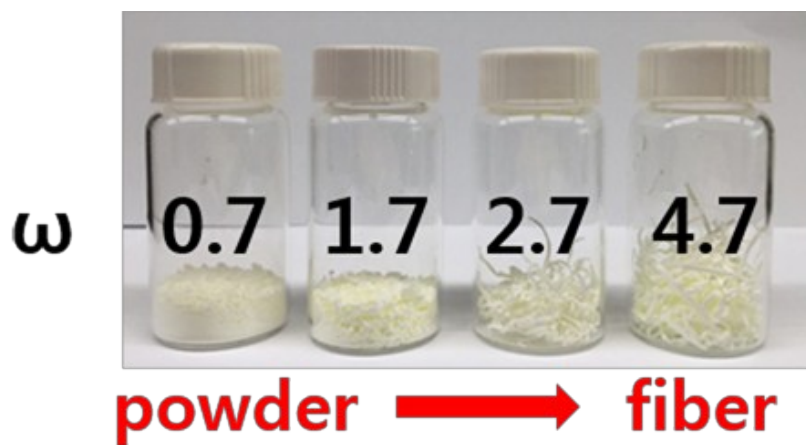


Fig. S4 PBP-7- ω with different molecular weights.

Table S3 Properties of sPBSP-7- ω polymers.

Polymer	IV ^[a]	IEC ^[b] [meqg ⁻¹]	Molecular weight [kDa]		WU [%]	Dimension change [%]			Conductivity [mS/cm]		Mechanical properties		
			M _n	M _w		Δt	Δl	Δv	25 °C	80 °C	Tensile strength [MPa]	Elongation at break [%]	Young's Modulus [GPa]
sPBSP-7-4.7	1.35	-	-	-	-	-	-	-	-	-	-	-	-
sPBSP-7-2.7	2.67	2.05	-	-	47	26.3	2.1	31.5	45	148	42.7	3.3	2.0
sPBSP-7-1.7	1.93	2.15	36.3	152.0	51	30	2.4	37	43	148	33.8	3.1	1.7
sPBSP-7-0.7	0.97	2.07	18.0	63.1	44	24.6	6.7	43	54	190	30.3	3.3	1.5

[a] Measured at 25 °C in DMSO+ 0.05 M LiBr (0.5 g dL⁻¹).

[b] Determined by acid-base titration.

✘ We could not cast membranes of sPBSP-7-4.7 and could not measure any the material properties owing to its extremely high molecular weight.

◆ sPBSP-7-4.7 was completely insoluble in the solvents tested.

◆ sPBSP-7-2.7 was partially insoluble in the solvents tested because of its high molecular weight.

◆ sPBSP-7-1.7 shows reasonable dimensional changes and good mechanical stability compared to the other polymers in the sPBSP-7- ω series.

◆ sPBSP-7-0.8 has good solubility, but its mechanical properties and dimensional stability are poor.

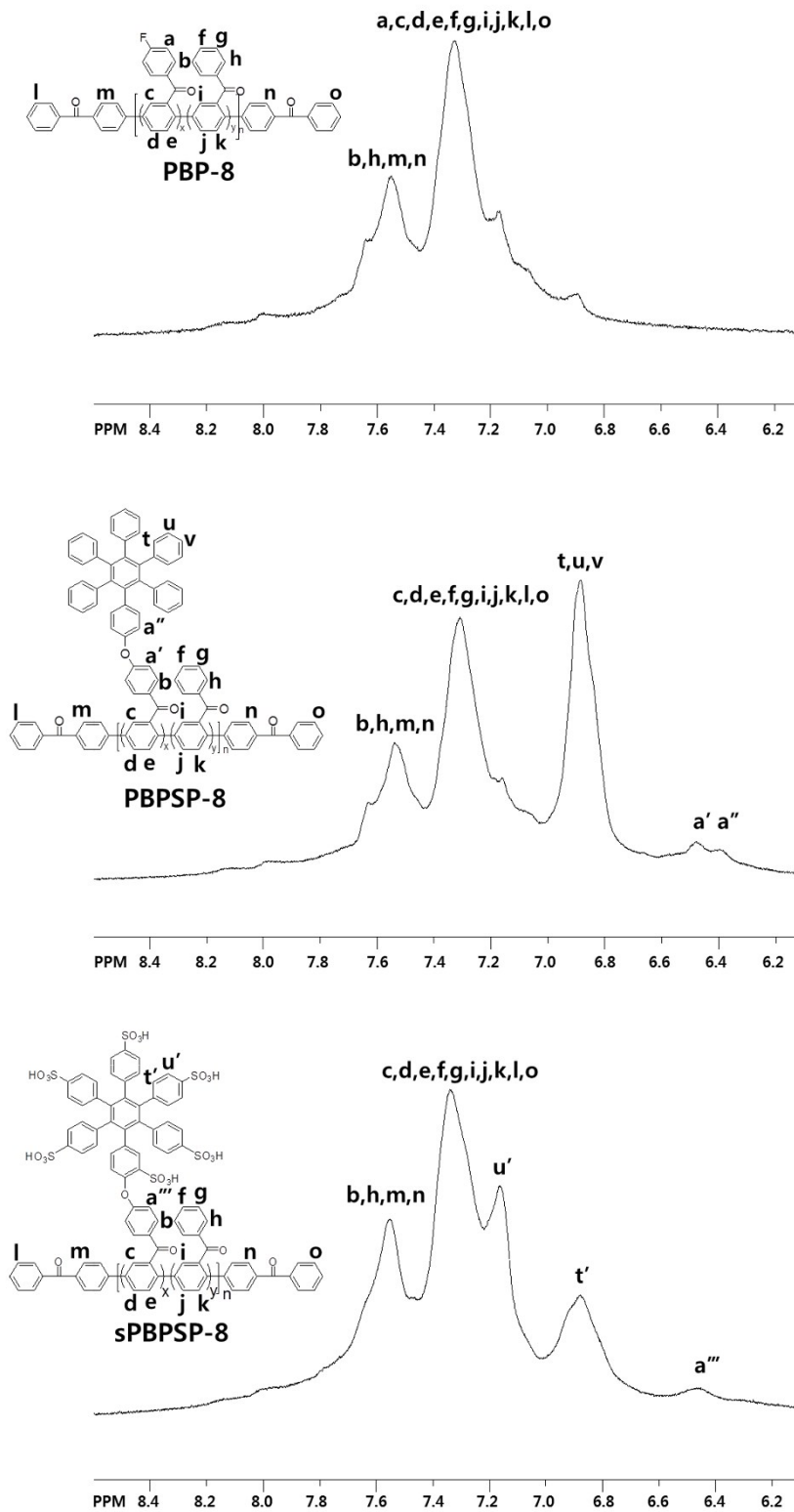


Fig. S5 ¹H-NMR spectra of PBP-8, PBPSP-8, and sPBSP-8.

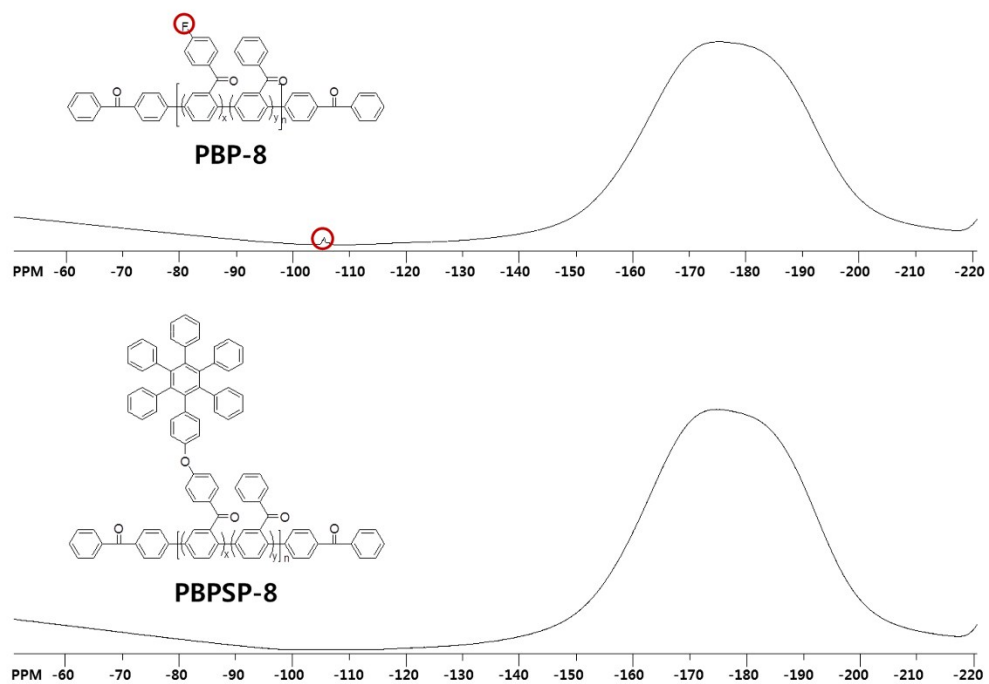


Fig. S6 F-NMR spectra of PBP-8 and PBSP-8.

Table S4 Molecular weight changes of the PBP-z and PBPSP-z polymers.

Polymer	Molecular weight [kDa]	
	M_n	M_w
PBP-5	30.4	118.1
PBP-8	16.4	79.1
PBP-11	20.2	94.1
PBPSP-5	30.1	122.5
PBPSP-8	25.4	108.3
PBPSP-11	26.7	111.6

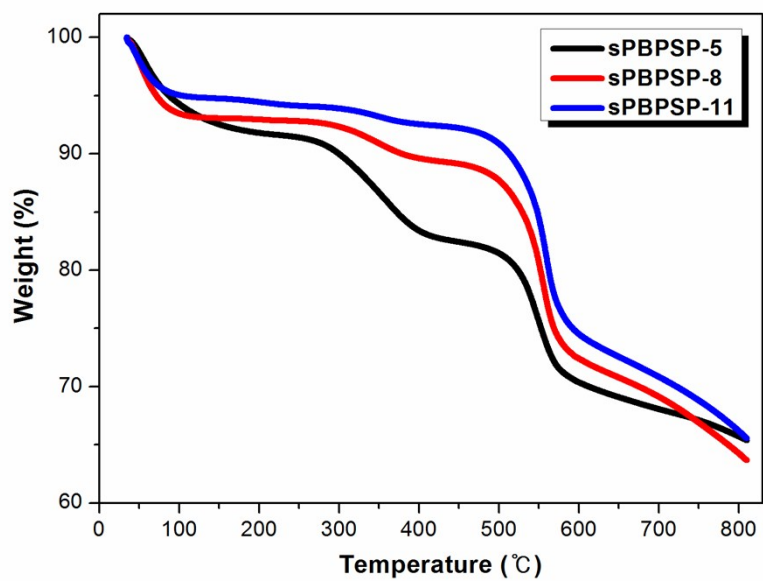


Fig. S7 Thermogravimetric analysis curves of the sPBPSP-z membranes.

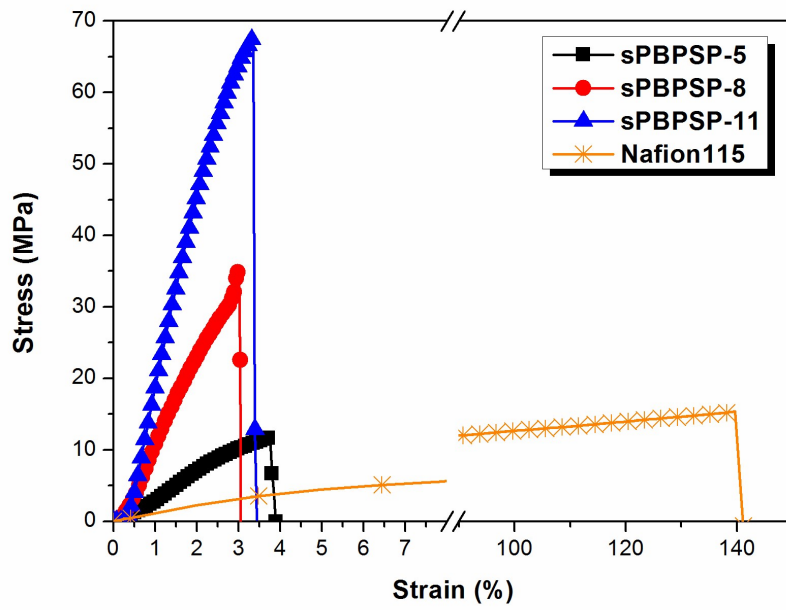


Fig. S8 Stress-strain curves of sPBSP-z and Nafion 115 membranes in the dried state.

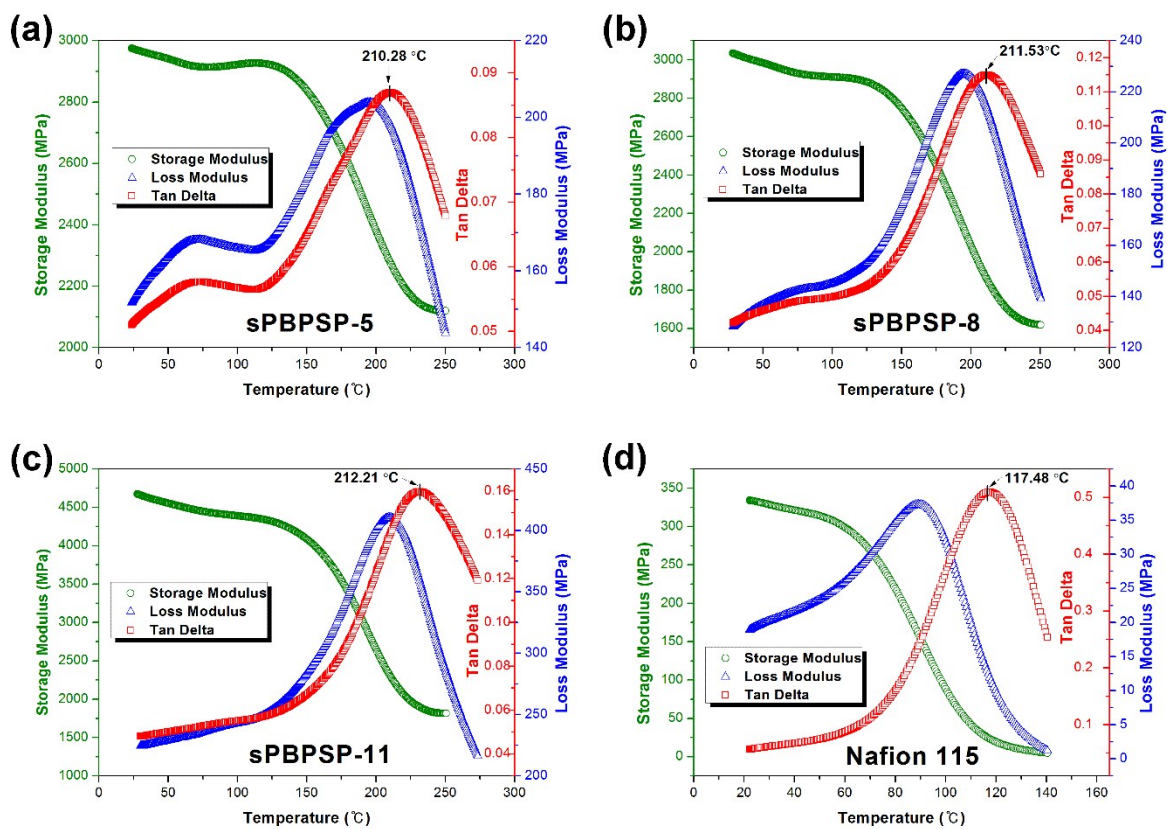


Fig. S9 Dynamic mechanical analysis traces of (a) sPBPSP-5, (b) sPBPSP-7, (c) sPBPSP-11, (d) Nafion 115 (storage modulus (E'), loss modulus (E''), and loss tangent ($\tan\delta$)).

Table S5 IEC values before and after the 1.6 M VO₂⁺ soaking test for the sPBSP-z membranes.

Polymer	before	after
sPBSP-5	2.35	2.30
sPBSP-8	1.83	1.96
sPBSP-11	1.47	1.44

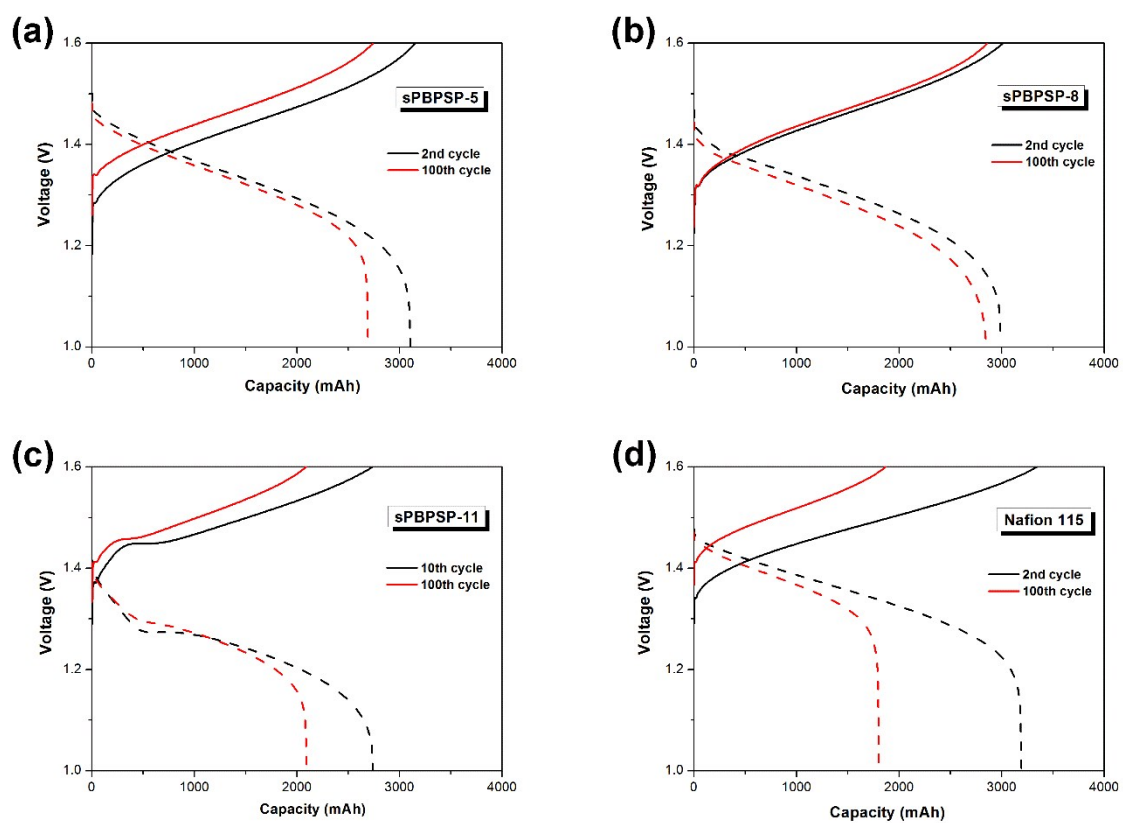


Fig. S10 Charge-discharge curves at the initial cycle and 100th cycle of the sPBSP-z and Nafion 115 membranes at a current density of 50 mAcm⁻².

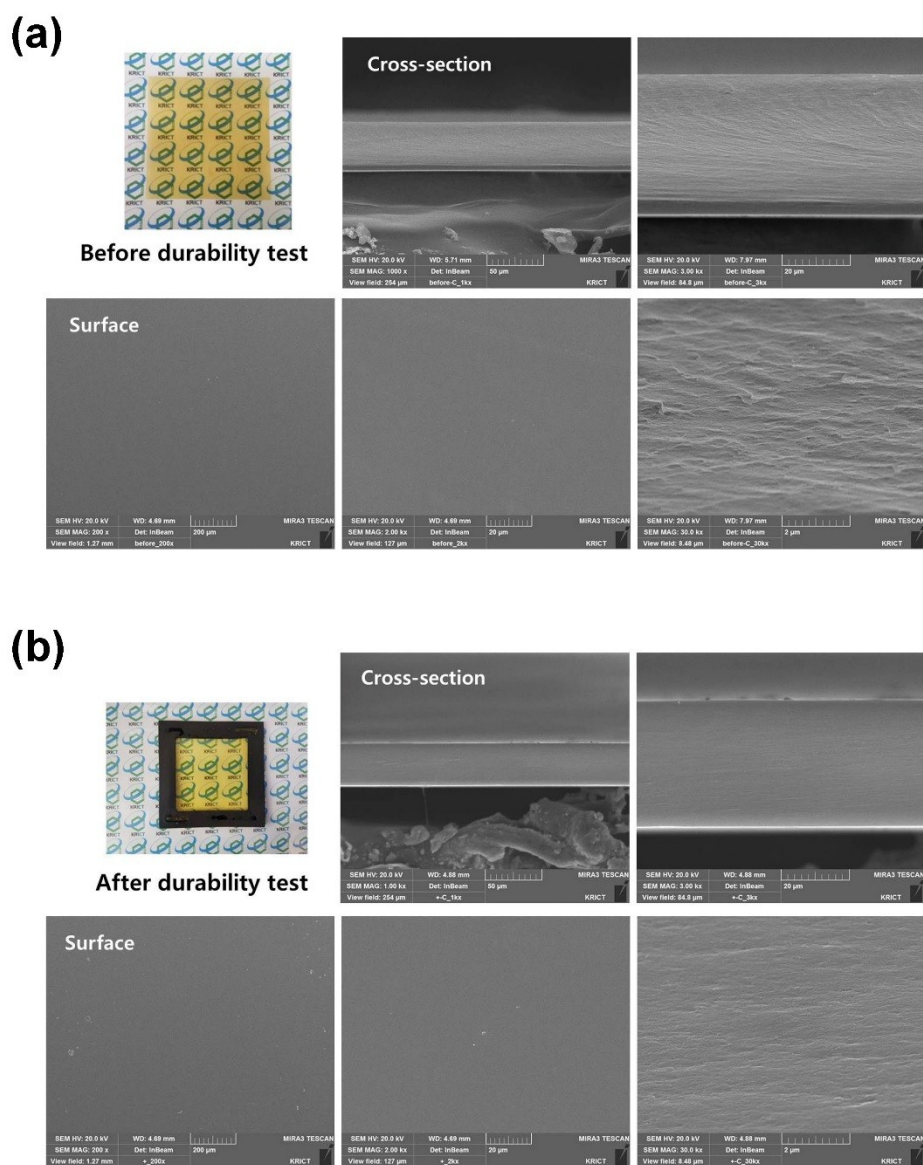


Fig. S11 The surface and cross-sectional SEM images of the sPBSP-8 membrane (a) before and (b) after 1000 cycles.

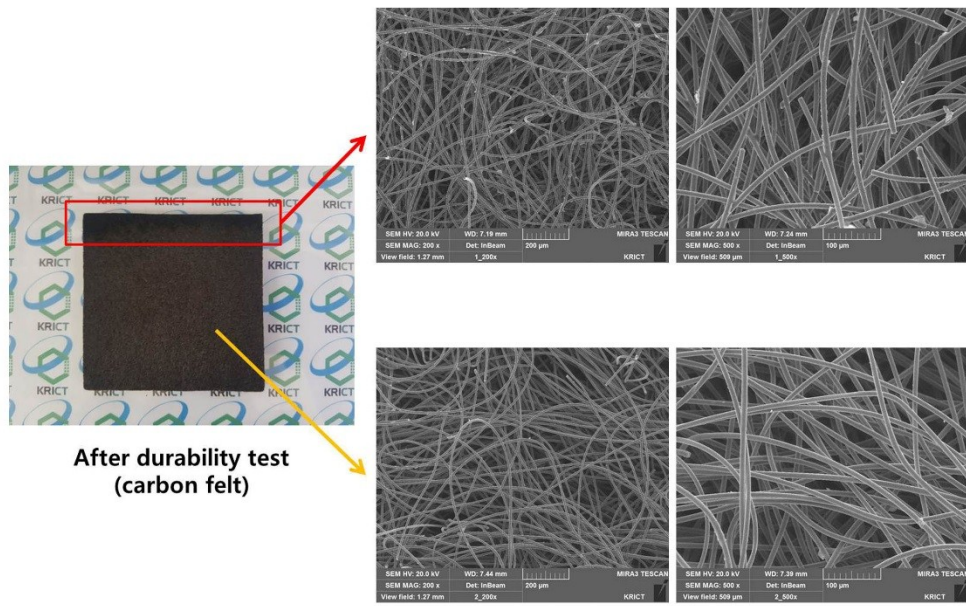


Fig. S12 SEM images of the carbon felt after 1000 cycles.