Sulfonated polybenzimidazoles containing phosphine oxide units as proton exchange membranes

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Figure captions

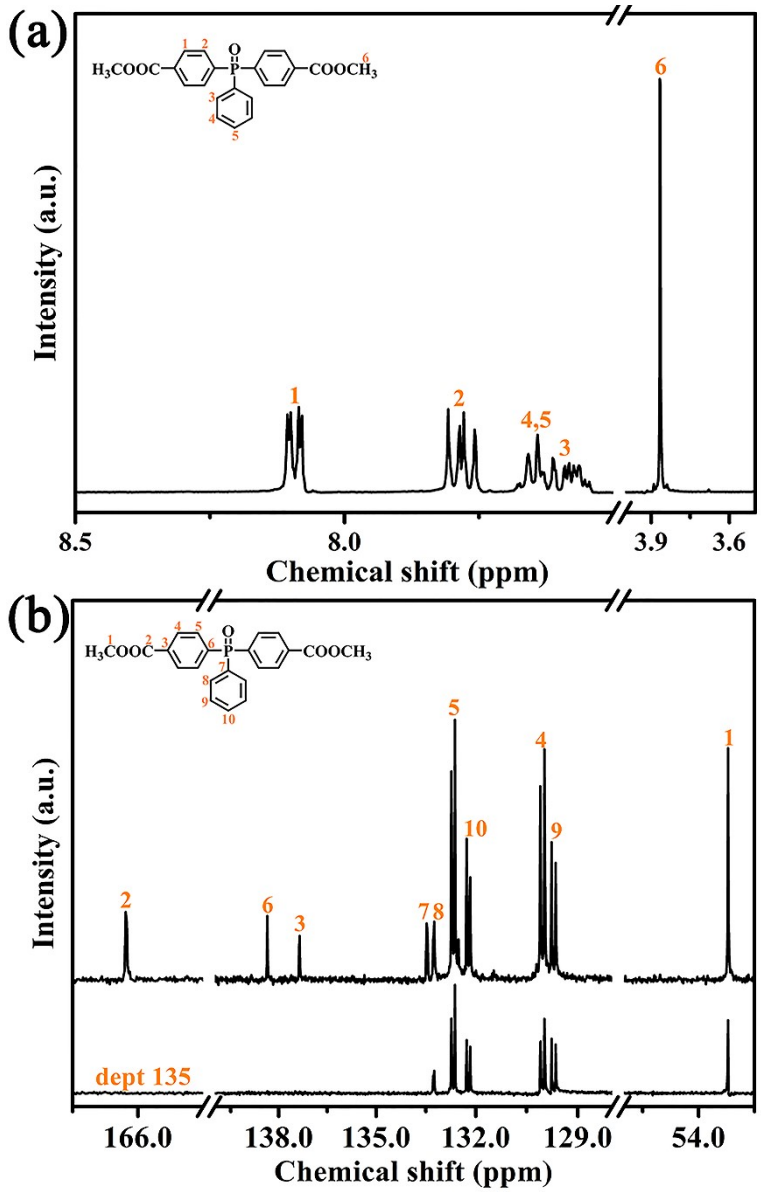

Fig. S1 (a) ^{1}H NMR and (b) ^{13}C NMR spectra of BMPO.

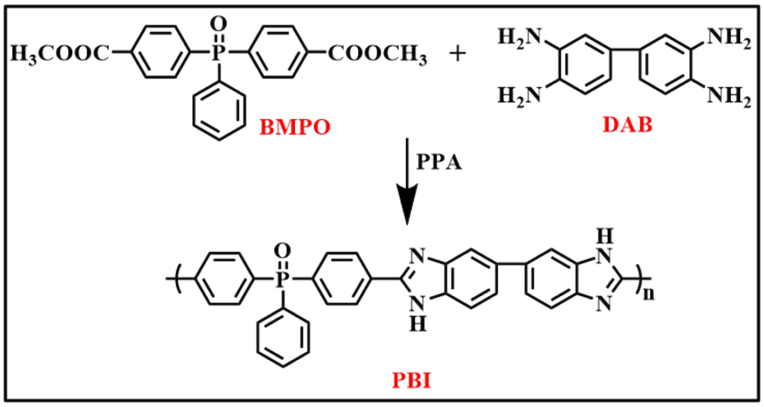

Fig. S2 Scheme for the synthesis of PBI.

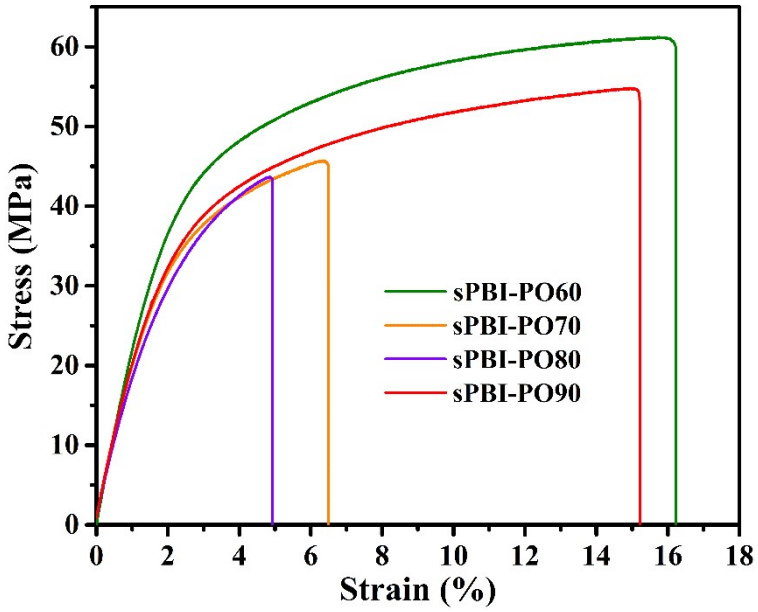

Fig. S3 Stress-strain curves of sPBI-PO60, 70, 80, and 90.

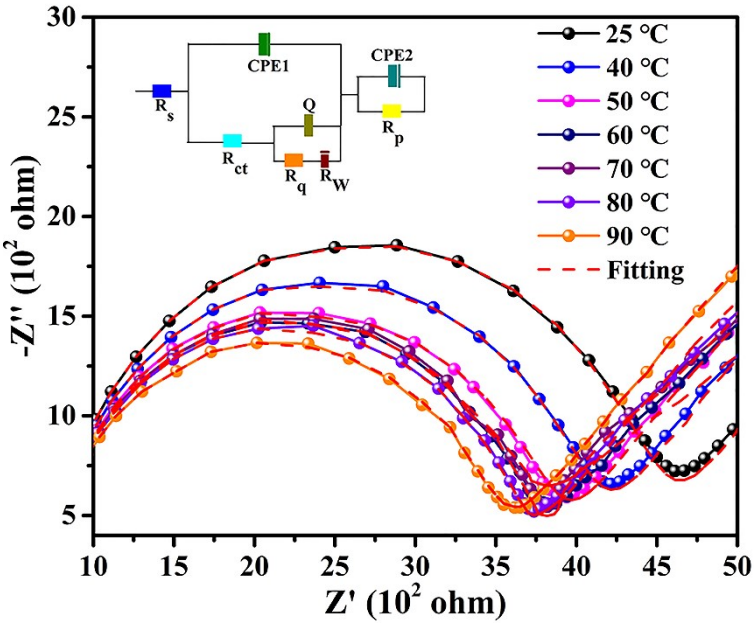

Fig. S4 Nyquist plots and corresponding fit curves of sPBI-PO90-PPA membranes at different temperature and simulated equivalent circuit diagram.

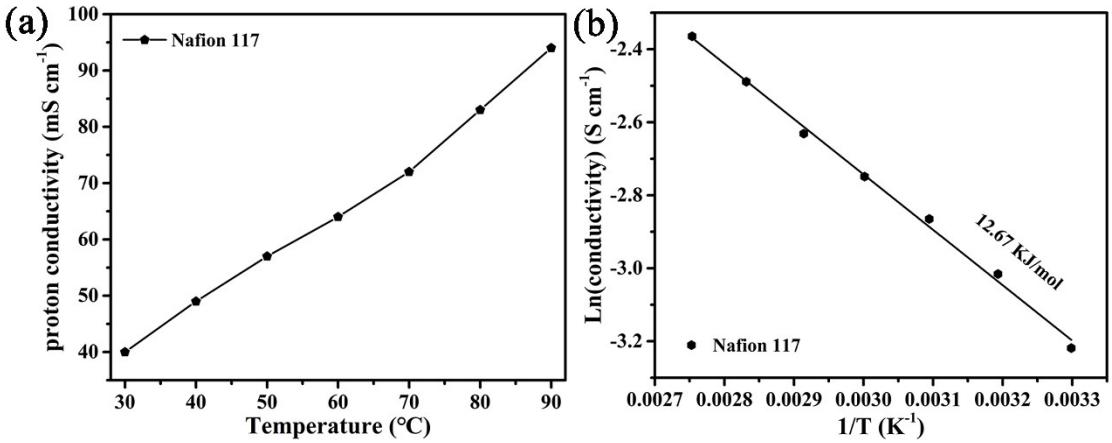

Fig. S5 (a) Proton conductivity and (b) Arrhenius plot of Nafion 117.

Table captions

Table S1 Feed ratios, intrinsic viscosity, and yields of polycondensation

Ionomers	sBMPO/ BMPO / DAB (molar ratio)	[η][a] (dL/g)	Yield (%)
PBI	0/100/100	1.51	95
sPBI-PO60	60/40/100	1.79	94
sPBI-PO70	70/30/100	2.03	96
sPBI-PO80	80/20/100	2.35	94
sPBI-PO90	90/10/100	2.41	94
sPBI-PO100	100/0/100	-[b]	94

[a] The intrinsic viscosity of polymers in DMSO with 0.05 mol L^{-1} LiBr at 30 °C.

[b] Poor solubility in DMSO cannot test exact intrinsic viscosity.

Table S2 T_{d5}, IEC, and oxidative stability of sPBI-PO membranes.

Ionomers	T_{d5} (°C)	IEC (meq/g)		Thickness (μm)	Residue [a] (%)	τ_1 [b] (h)
		calculated	measured			
sPBI-PO60	491	1.10	1.06	55	98	>48
sPBI-PO70	490	1.27	1.24	50	97	>48
sPBI-PO80	488	1.43	1.40	58	96	>48
sPBI-PO90	485	1.58	1.52	50	95	>48
sPBI-PO100	480	-[c]	-[c]	-[c]	-[c]	-[c]

[a] Residual weight after 1 h soak in Fenton's reagent at 80 °C.

[b] τ1 means the time when dissolving the membrane completely at 80 °C.

[c] Poor solubility in DMSO.

Table S3 Solubility of the PBI and sPBI-PO ionomers.

Ionomers	DMSO	DMAC	NMP	DMF	Sulfolane	Methanol	water
PBI	+	±	±	±	±	–	–
sPBI-PO60	+	±	±	±	±	–	–
sPBI-PO70	+	±	±	±	±	–	–
sPBI-PO80	+	±	±	±	±	–	–
sPBI-PO90	+	±	±	±	±	–	–
sPBI-PO100	±	±	±	±	±	–	–

+: soluble when heated; ±: partially dissolved or swollen when heated; –: insoluble when heated.

Table S4 Proton conductivity and mechanical properties of sPBI-PO membranes.

Membranes	Proton conductivity mS/cm		Mechanical properties		
	30 °C	80 °C	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)
sPBI-PO60	0.9	4.6	60.01	1.56	16.22
sPBI-PO70	1.0	4.9	45.10	1.87	6.57
sPBI-PO80	1.1	6.5	43.31	1.81	4.93
sPBI-PO90	1.7	7.1	53.25	1.39	15.21

Table S5 PA uptake and Volume swelling ratio of membrane.

Membrane	PA doping level (mol/mol)	PA uptake (%)	Volume swelling ratio (%)
sPBI-PO60-PA	25.4	153.7	184.1
sPBI-PO70-PA	29.7	162.2	190.7
sPBI-PO80-PA	32.3	175.9	178.3
sPBI-PO90-PA	34.9	187.3	170.6