Supplementary Information

Acidity Effects of Medium Fluids on Anhydrous Proton Conductivity of Acid-Swollen Block Polymer Electrolyte Membranes

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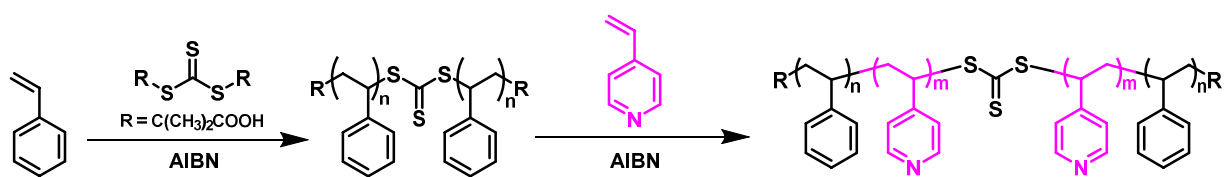
Scheme S1 Synthesis of S-P-S.

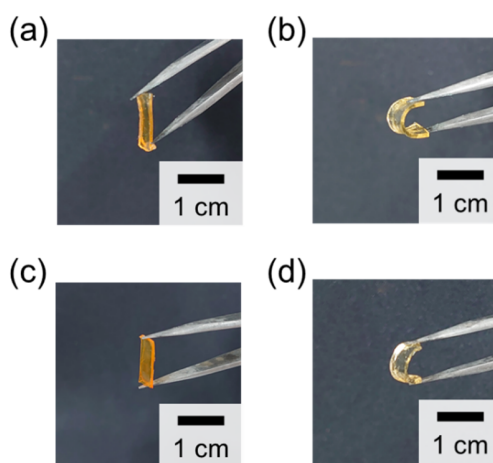**Macroscopic appearance of S-P-S/Sa and S-P-S/Pa membranes.**

Fig. S1 Macroscopic appearance of (a) S-P-S/Sa(40), (b) S-P-S/Sa(80), (c) S-P-S/Pa(40), and (d) S-P-S/Pa(80) membranes.

Blends of S/Sa, P/Sa, S/Pa, and P/Pa.

The blends of S/Sa, P/Sa, S/Pa, and P/Pa were prepared to confirm compatibility of each component.

As shown in Figure S2, S cannot be dissolved in Sa and Pa whereas P is soluble in Sa and Pa within

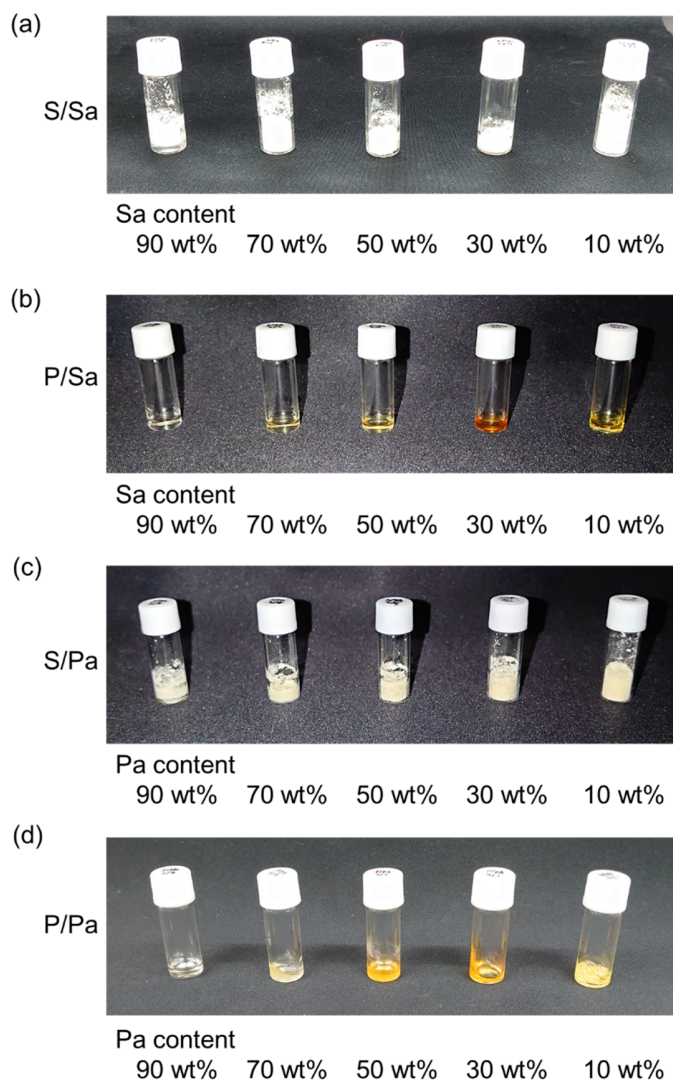an acid-concentration range from 10 wt% to 90 wt%.

Fig. S2 Photographs of blends of (a) S/Sa, (b) P/Sa, (c) S/Pa, and (d) P/Pa.
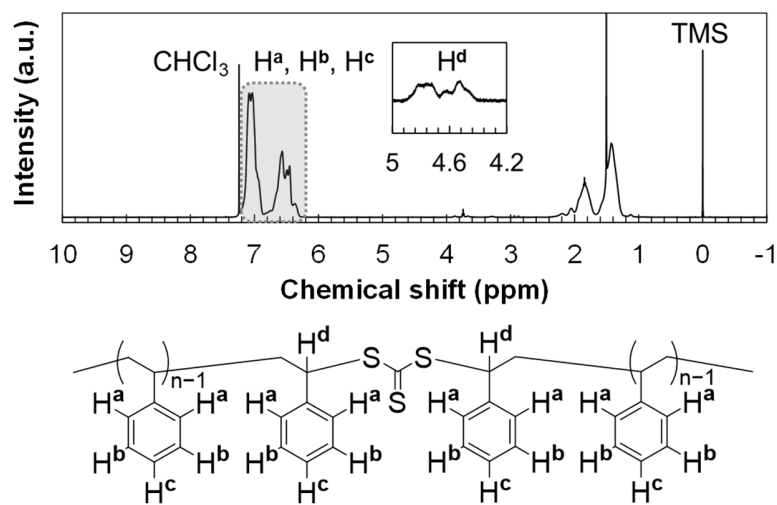
^{1}H NMR spectrum of S.

Fig. S3 ^{1}H NMR spectrum and the chemical structure of precursor S, where the inset shows an enlarged view of the range from 4.2 to 5.0 ppm. The molecular weight of the precursor S was determined by comparing the integral of peaks from 4.2 to 5.0 ppm originating from two protons (H^d) adjacent to the RAFT agent residue (S-C(=S)-S) with that of peaks from 6.0 to 7.2 ppm originating from five protons (H^a, H^b and H^c) on the phenyl groups of the precursor S.

Small angle X-ray scattering (SAXS) measurement of neat S-P-S.

A SAXS measurement was performed at room temperature to acquire the nanostructural information of neat S-P-S membrane by Nano-Viewer (Rigaku). A wavelength of X-ray and a camera length were 0.1542 nm and 760 mm, respectively. A scattering pattern was detected with an imaging plate. Figure S4 shows a SAXS profile for neat S-P-S membrane.
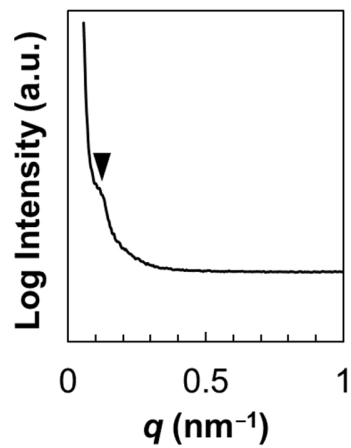

Fig. S4 A SAXS profile for the neat S-P-S membrane.

Anhydrous conductivity after keeping at 95°C.

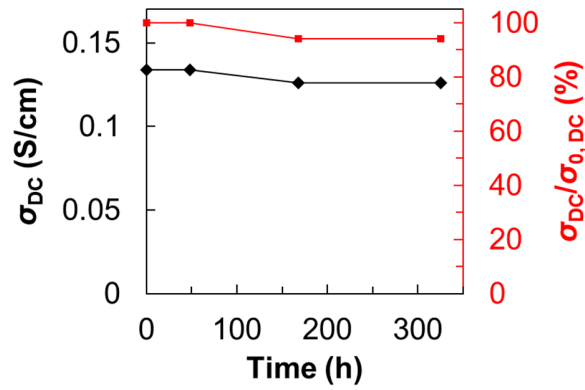**Fig. S5** Anhydrous conductivities for the S-P-S/Sa(80) membrane after keeping at 95°C. Left axis is the anhydrous conductivity of the S-P-S/Sa(80) membrane. Right axis is the ratio of the anhydrous conductivity to the initial conductivity ($\sigma_{0,\,DC}$). Black diamonds and red squares represent σ_{DC} and $\sigma_{DC}/\sigma_{0,\,DC}$, respectively. Solid lines are drawn as guide for eyes

Fourier transform infrared (FT-IR) spectroscopy for S-P-S/Sa and S-P-S/Pa.

FT-IR spectroscopy was carried out using a spectrophotometer FT/IR-6600 (JASCO) at room temperature to confirm the formation of the acid-base complexes between pyridyl groups and the acids (Figure S5). Absorption at 1595 cm^{-1} derives from stretching vibration of C-C on the pyridyl group. By infiltrating Sa or Pa into S-P-S, absorption at around 1640 cm^{-1} appeared, suggesting formation of acid-base complex between the pyridyl group and the acids.[1] The absorption at 1600 cm^{-1} probably derives from hydrogen bond between the pyridyl group and the acids. As the amount of the acids increases, the absorption at 1595 cm^{-1} decreases, while the absorption at 1640 cm^{-1} increases.
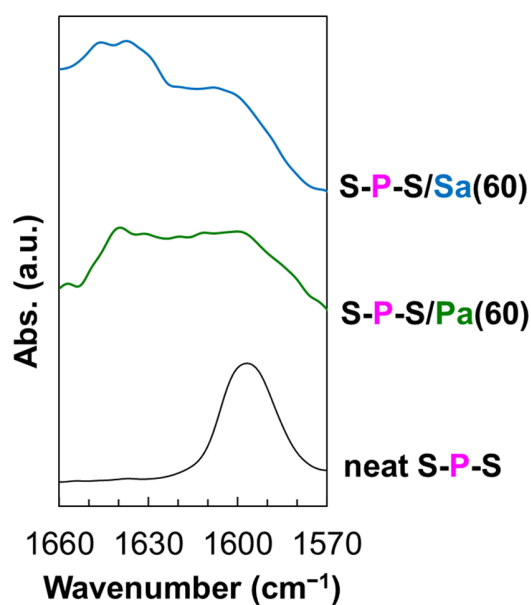

Fig. S6 FT-IR spectra of neat S-P-S, S-P-S/Sa(60), and S-P-S/Pa(60) within a wavenumber range from 1570 to 1660 cm^{-1}.

T_g of S-P-S/Sa and S-P-S/Pa expected by Fox equation.

A T_g of blends composed of a polymer and a solvent (plasticizer) depends on the composition, which are often given by Fox equation (Equation S1).[2]

$$\frac{1}{T_{g,\text{blend}}} = \frac{w_{\text{polymer}}}{T_{g,\text{polymer}}} + \frac{w_{\text{solvent}}}{T_{g,\text{solvent}}} \qquad (\text{S1})$$

where $T_{g,\text{blend}}$, $T_{g,\text{polymer}}$, and $T_{g,\text{solvent}}$ are T_g of the blend composed of a polymer and a solvent, the polymer, and the solvent, respectively, while w_{polymer}, and w_{solvent} are weight fraction of the polymer, and the solvent in the mixture, respectively. Figure S6 shows T_g of P/acid mixed phase in S-P-S/Sa and S-P-S/Pa estimated from Equation S1, where T_g of Sa and Pa was assumed to be $\sim 2T_m/3$.[3,4] However, the calculated T_gs disagree with the experimental T_gs, especially, at ADL < 1 due to forming the acid-base complexes between the pyridyl groups and the acids in the membranes
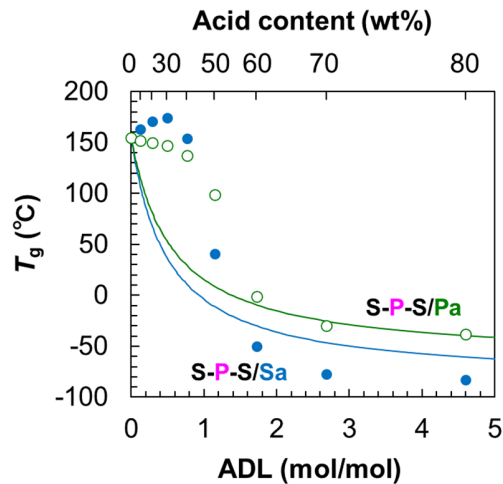

Fig. S7 The experimental T_g of P/acid mixed phase in S-P-S/Sa (filled symbols) and S-P-S/Pa (open symbols). Solid blue (S-P-S/Sa) and green (S-P-S/Pa) lines are T_g calculated by from Fox equation.

Table S1 T_g of P/acid mixed phase in S-P-S/Sa and S-P-S/Pa estimated by the DSC measurements

Sample code	ADL [a] (mol/mol)	T_g (°C)
neat S-P-S	0	155
S-P-S/Sa(10)	0.13	163
S-P-S/Sa(20)	0.29	171
S-P-S/Sa(30)	0.49	174
S-P-S/Sa(40)	0.77	154
S-P-S/Sa(50)	1.1	41
S-P-S/Sa(60)	1.7	−50
S-P-S/Sa(70)	2.7	−77
S-P-S/Sa(80)	4.6	−83
S-P-S/Pa(10)	0.13	152
S-P-S/Pa(20)	0.29	150
S-P-S/Pa(30)	0.49	147
S-P-S/Pa(40)	0.77	137
S-P-S/Pa(50)	1.1	99
S-P-S/Pa(60)	1.7	−1
S-P-S/Pa(70)	2.7	−30
S-P-S/Pa(80)	4.6	−38

(a) Acid doping level that is the molar ratio of Sa or Pa to the pyridyl group on the polymer.

Table S2 Anhydrous conductivity for a series of S-P-S/H$_2$SO$_4$ and S-P-S/H$_3$PO$_4$

Sample code	ADL [a] (mol/mol)	σ_{DC} [b] (S cm^{-1})					
		20 °C	35 °C	50 °C	65 °C	80 °C	95 °C
S-P-S/Sa(50)	1.1	1.9×10^{-6}	6.2×10^{-6}	1.7×10^{-5}	4.5×10^{-5}	9.9×10^{-5}	2.0×10^{-4}
S-P-S/Sa(60)	1.7	7.0×10^{-4}	1.5×10^{-3}	2.9×10^{-3}	5.0×10^{-3}	7.9×10^{-3}	1.2×10^{-2}
S-P-S/Sa(70)	2.7	6.7×10^{-3}	1.2×10^{-2}	1.6×10^{-2}	3.2×10^{-2}	4.5×10^{-2}	6.2×10^{-2}
S-P-S/Sa(80)	4.6	2.3×10^{-2}	3.8×10^{-2}	5.2×10^{-2}	7.6×10^{-2}	1.1×10^{-1}	1.4×10^{-1}
S-P-S/Pa(50)	1.1	n.d. [c]	1.5×10^{-6}	6.7×10^{-6}	2.6×10^{-5}	8.3×10^{-5}	2.4×10^{-4}
S-P-S/Pa(60)	1.7	n.d. [c]	5.4×10^{-6}	2.5×10^{-5}	9.1×10^{-5}	2.6×10^{-4}	6.5×10^{-4}
S-P-S/Pa(70)	2.7	8.6×10^{-5}	3.3×10^{-4}	9.8×10^{-4}	2.3×10^{-3}	4.5×10^{-3}	8.1×10^{-3}
S-P-S/Pa(80)	4.6	2.9×10^{-3}	7.0×10^{-3}	1.4×10^{-2}	2.6×10^{-2}	4.1×10^{-2}	6.1×10^{-2}

(a) Acid doping level that is the molar ratio of Sa or Pa to the pyridyl group on the polymer. (b) The conductivity estimated from electrochemical impedance spectroscopy. (c) The conductivity cannot be determined because it is very low.

References

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