# Electronic Supplementary information (ESI) for

# Acidic Liquid-Swollen Polymer Membranes Exhibiting Anhydrous Proton Conductivity Higher than 100 mS/cm at Around 100 °C

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## Experimental section

### Synthesis and preparation of polymer membranes.

PBI powder (Hozole® C) was supplied from HOS-Technik. A PBI membrane was prepared using the same method as previously reported (Fig. S1).[1]

The cross-linked poly(4-vinylpyridine), CL-P, was prepared as follows (Fig. 1(a)). First, 2.00 g (19.0 mmol) of 4-vinylpyridine (Sigma-Aldrich) purified with an alumina column (activated, basic, Brockmann I, Sigma-Aldrich), 50.3 mg (0.326 mmol) of *N*,*N'*-methylenebisacrylamide (TCI) as a bifunctional vinyl monomer, and 2.0 mg (0.012 mmol) of 2,2'-azobis(isobutyronitrile) (AIBN, Kishida Chemical) as an initiator were mixed in a glass vial, and the resulting mixture was bubbled with nitrogen gas for 45 minutes to remove oxygen gas in the solution. Then, the free radical copolymerization reaction proceeded by immersing the glass vial in an oil bath at 70 °C and stirring at 500 rpm for about 3.5 hours. The vial was then taken out from the oil bath and put on a hot plate at 50 °C for 2 days. The reaction solution became gel-like and did not flow. The crude product was purified by transferring it to a Teflon®-made beaker and immersing it in methanol (Nacalai tesque) for 1 hour. Then, the methanol was replaced with fresh stuff and the product was again immersed in large amount of methanol for 1 hour. Unreacted monomer, low-molecular-weight oligomer, and solvent were removed by repeating this operation three times. The purified CL-P was prepared after drying in a vacuum oven at room temperature for 12 hours to completely remove the methanol. In a similar manner, cross-linked poly(1-vinylimidazole) (CL-I) was also synthesized (Scheme S1). In addition, a 4-vinylpyridine monomer; a bifunctional reversible addition/fragmentation chain transfer (RAFT)[2] agent (*S*,*S*′-bis(α,α′-dimethyl-α″-acetic acid)trithiocarbonate synthesized on the basis of a previous report[3]); and AIBN were mixed at a weight ratio of 13640/3.5/1, and stirred at 80 °C for about 1.5 hours to synthesize the uncross-linked P ($M_n$ = 42 k, $Đ$ = 1.34) as a control sample (Fig. 1(b)).

The post-cross-linked polymer, Post-CL-P, was prepared by cross-linking a homopolymer P (Scheme S2). First, 99 wt% uncross-linked homopolymer P and 1 wt% 1,4-dibromobutane ($BrC_4Br$, TCI) as a cross-linking agent were homogeneously mixed in methanol, and the solution was transferred to a polymethylpentene petri dish. Then, solution casting was carried out at 50 °C for 2 days to cross-link a homopolymer P, followed by drying in vacuum at 50 °C for about 1 day to completely evaporate methanol. The CL-P and Post-CL-P membranes did not dissolve in a good solvent such as methanol but swelled instead, indicating that these membranes were cross-linked.

The S-P-S triblock copolymer was synthesized by RAFT polymerization (Scheme S3). First, a purified styrene monomer (Kishida chemical); *S*,*S*'-bis(α,α'-dimethyl-α"-acetic acid)trithiocarbonate as a bifunctional RAFT agent; and AIBN as an initiator were mixed at a weight ratio of 2730/19/1, and RAFT polymerization was carried out by stirring for about 6 hours at 130 °C to synthesize precursor polystyrene ($M_n$ = 19 k, $Đ$ = 1.17). Since the RAFT agent residue was located at the center of this precursor polystyrene, it can be called a macro-CTA. Then, a purified 4-vinylpyridine monomer, the macro-CTA, and AIBN were mixed at a weight ratio of 4120/39/1, and stirred at 80 °C for about 1 hour to synthesize the S-P-S triblock copolymer. Molecular characteristics of this copolymer were found to be; $M_n$ = 370 k; $Đ$ = 1.92; $\varphi_S$ = 0.06 ($\varphi_S$ denotes the volume fraction of polystyrene), where $\varphi_S$ was calculated with the density of S and P (S: 1.05 g/cm$^3$; P: 1.17 g/cm$^3$). Here, the molecular weight (or degree of polymerization) and composition of the polymer synthesized were determined by $^1$H NMR measurements (Bruker Ascend 500 MHz; solvent: $CDCl_3$), and the molecular weight distribution $Đ$ was determined by size exclusion chromatography (SEC) measurements (HPLC pump: Shimadzu LC-20AD; column oven: Shimadzu CTO-20A; RI detector: Shimadzu CTO-20A; column: three TSKgel G4000H$_{HR}$; eluent solvent: *N*,*N*-dimethylformamide (DMF); flow rate: 1.0 mL/min; temperature: 40 °C) (Fig. S2). The purified S-P-S block copolymer was dissolved in a solvent of pyridine, and the solution was transferred to a polymethylpentene petri dish. Then, solvent casting was carried out at 50 °C for 2 days, followed by vacuum drying at 50 °C for about 1 day to completely remove pyridine, resulting in preparation of S-P-S membranes. See also details of synthesis and preparation of a similar block copolymer in the previous literature.[4] The S-P-S membranes did not dissolve but swelled in methanol, which is a poor solvent for S and a good solvent for P.

### Preparation of proton-conductive membrane.

A solution of concentrated sulfuric acid dissolved in methanol was prepared in a Teflon beaker, and each polymer membrane was then immersed in the solution. By solvent casting at 50 °C for 2 days followed by vacuum drying at 50 °C for about 1 day, sulfuric acid was homogeneously incorporated into the polymer membrane. The amount of $H_2SO_4$ incorporated into CL-P was varied by changing the weight fraction of $H_2SO_4$. For CL-I, Post-CL-P and S-P-S, a four-fold weight of $H_2SO_4$ to polymers was used to prepare the anhydrous proton-conductive membranes.

**Measurements.**

Differential scanning calorimetry (DSC) was performed to measure $T_g$ of the samples. The measurements were carried out using Q2000 (TA Instruments) with a heating rate of 10 °C/min in the temperature range −95 to 190 °C.

To evaluate the conductivity, AC impedance spectroscopy was taken with Potentio/galvanostat Versa STAT 4-400 (Princeton Applied Research) equipped with the frequency characteristic analysis (FRA) option. By sandwiching a sample membrane (for instance, length, width and thickness were 7.0 mm, 3.2 mm and 1.3 mm, respectively) with two tetrafluoroethylene/perfluoroalkyl vinyl ether copolymer (PFA) plates attached to a platinum electrode, a cell for bulk resistance measurements was prepared for measurements using the two-terminal method. To dry membranes further, the measurement cell was kept at 120 °C for at least 1.5 hours before measurements. The bulk resistance was measured in a natural convection drying oven under nonhumidification (14.5–1.4% RH) in the range 50–120 °C at a frequency of 1–$10^5$ Hz and an applied voltage of 80 mV. The conductivity was estimated from $\sigma_{DC} = l/(A|Z|)$ using the $|Z|$ value of the plateau in the AC impedance spectrum as the bulk resistance, where $\sigma_{DC}$ is the ionic conductivity, $l$ is the distance between the electrodes, $A$ is the cross-sectional area of the sample, and $|Z|$ is the AC impedance ($|Z| = (Z'^2 + Z''^2)^{1/2}$, where $Z'$ and $Z''$ are the real and the imaginary parts of the AC impedance *Z*, respectively).

Tensile tests were conducted to evaluate the mechanical properties of membranes. A membrane specimen was 4 mm wide and about 0.58 mm thick, with a dog-bone shape, which was punched out with a die. The tensile tests were carried out at an initial distance between jigs of about 4.5 mm and an initial strain rate of approximately 0.33 $s^{-1}$ (a tensile rate of 1.5 mm/s) with AGS-X (Shimadzu) equipped with a 50 N load cell and 50 N clip-type gripper.

To confirm that acid-base complexes were formed between base groups on polymer P and sulfuric acid, Fourier transform infrared spectroscopy (FT-IR, Fig. S3) at room temperature was carried out using a spectrophotometer (IR Prestige-21, Shimadzu, 128 accumulations) equipped with an infrared microscope (AIM-8800, Shimadzu). FT-IR measurements were also used to confirm the progress of a quaternization reaction of the pyridyl group by $BrC_4Br$ in preparation of Post-CL-P membranes (Fig. S6).

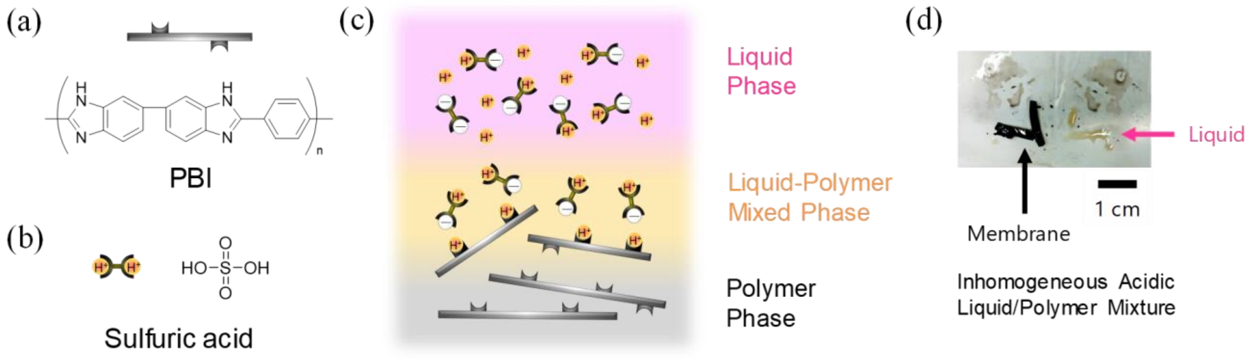


**Fig. S1.** Chemical structures and schematic illustration. (a) Polybenzimidazole (PBI), (b) sulfuric acid ($H_2SO_4$). (c) Schematic representation and (d) a photo of $H_2SO_4$-doped PBI membrane (weight ratio $H_2SO_4$/PBI: 76/24). Leaching out of $H_2SO_4$ was observed over several days after the preparation of $H_2SO_4$-doped PBI.

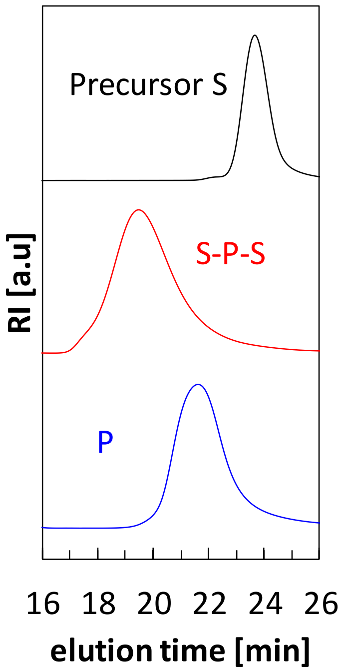


**Fig. S2.** SEC chromatograms of precursor S for S-P-S, S-P-S triblock copolymer, and uncross-linked homopolymer P. SEC measurements were conducted with three TSK gel columns G4000H$_{HR}$ (Tosoh Corp.), combined with an HPLC pump (LC-20AD, Shimadzu), a column oven (40 °C, CTO-20A, Shimadzu), and a refractive index detector (RID-10A, Shimadzu). *N*,*N*-Dimethylformamide (DMF) was used as an eluent, and the flow rate was 1 mL/min. The elution volume was calibrated with polystyrene standards.

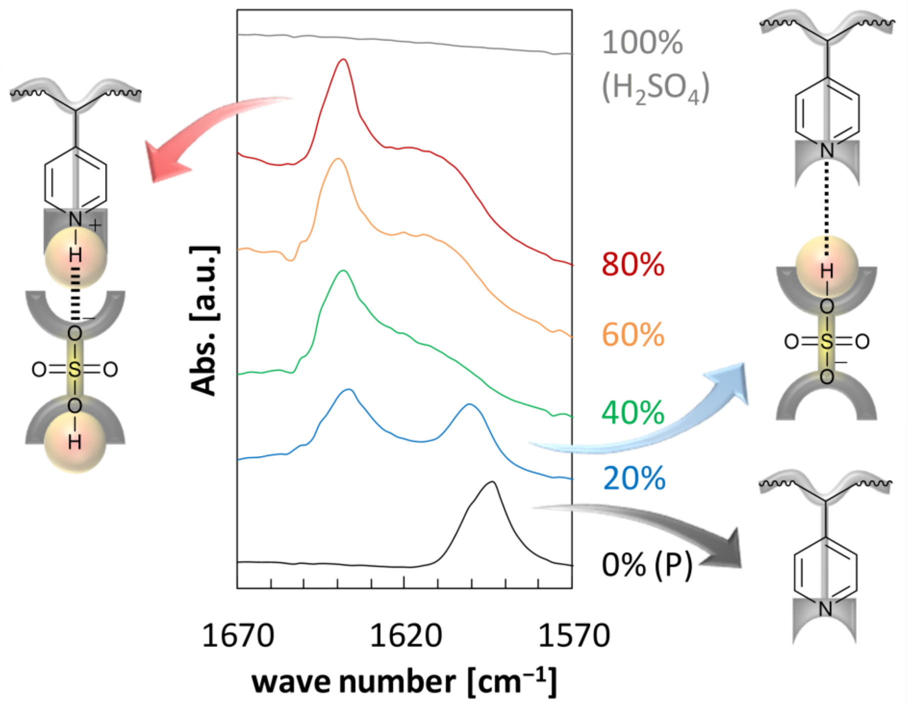


**Fig. S3.** FT-IR spectra of $H_2SO_4$, polymer P, and P/$H_2SO_4$. Absorption at 1595 $cm^{-1}$ derives from stretching vibration of C-C on the pyridyl group. By infiltrating $H_2SO_4$ into polymer P, absorption at 1640 $cm^{-1}$ appeared, which is due to formation of acid-base complex between the pyridyl group and $H_2SO_4$.[5,6] The absorption at 1600 $cm^{-1}$ probably derives from hydrogen bond between the pyridyl group and $H_2SO_4$. As the amount of $H_2SO_4$ increases, the absorption at 1595 $cm^{-1}$ decreases, while the absorption at 1640 $cm^{-1}$ increases.

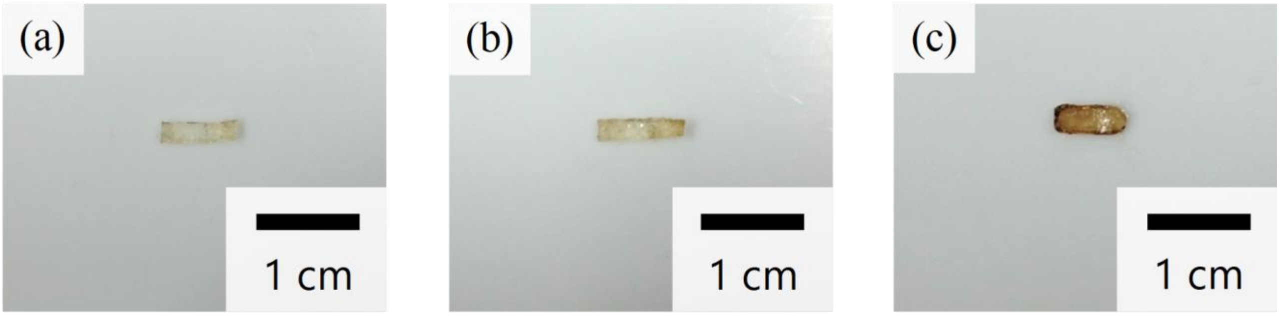


**Fig. S4.** Photos of membranes of CL-P/$H_2SO_4$: (a) $H_2SO_4$ = 55 wt%; (b) 60 wt%; (c) 70 wt%.

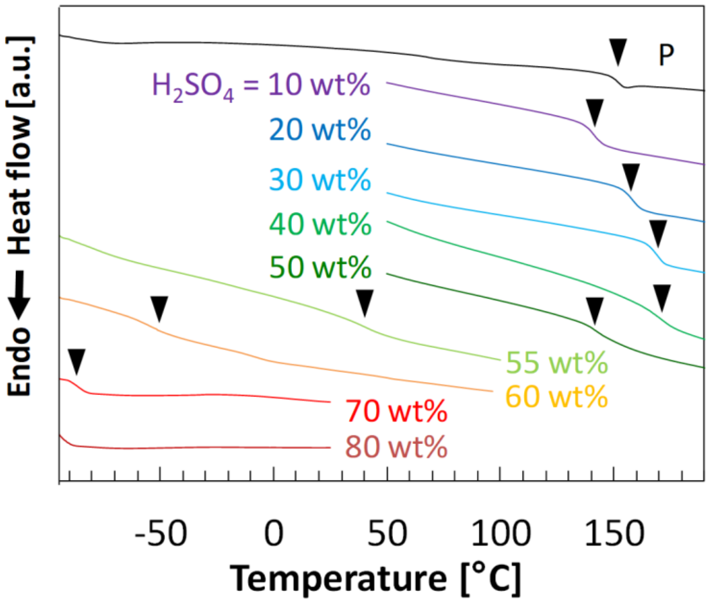


**Fig. S5.** DSC thermograms of polymer P and P/$H_2SO_4$.

**Table S1.** Glass transition temperature for a series of P/$H_2SO_4$.

| $H_2SO_4$ weight content [a] [wt%] | $n_{\mathrm{Acid}}/n_{\mathrm{Base}}$ [b] [mol/mol] | $H_2SO_4$ mole content [c] [mol%] | Glass transition temperature [d] ($T_g$) [°C] |
|---|---|---|---|
| 0 | 0 | 0 | 152 |
| 10 | 0.12 | 11 | 141 |
| 20 | 0.27 | 21 | 158 |
| 30 | 0.46 | 31 | 170 |
| 40 | 0.71 | 42 | 171 |
| 50 | 1.1 | 52 | 142 |
| 55 | 1.3 | 57 | 40 |
| 60 | 1.6 | 62 | −52 |
| 70 | 2.5 | 71 | −86 |
| 80 | 4.3 | 81 | −95 |

(a) The weight content of $H_2SO_4$ in mixtures. (b) The molar ratio of $H_2SO_4$ to the pyridyl group on the polymer. (c) The mole content of $H_2SO_4$, which can be calculated according to $(1 + n_{\mathrm{Base}}/n_{\mathrm{Acid}})^{-1} \times 100$. (d) The glass transition temperature estimated by the DSC measurements.

**Scheme S1.** Synthesis of chemically cross-linked poly(1-vinylimidazole) (CL-I).

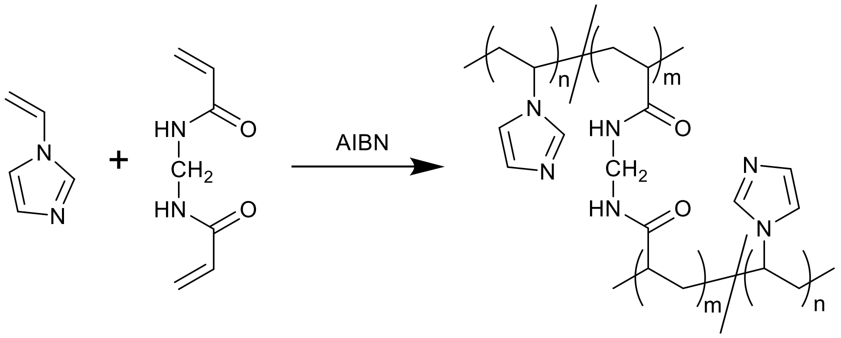


**Table S2.** Anhydrous conductivity for CL-I/$H_2SO_4$.

| Polymer | $H_2SO_4$ weight content [a] [wt%] | $n_{Acid}/n_{Base}$ [b] [mol/mol] | $H_2SO_4$ mole content [c] [mol%] | $\sigma_{DC}$ [d] [mS/cm] | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 50 °C | 80 °C | 95 °C | 110 °C | 120 °C |
| CL-I | 80 | 3.9 | 80 | 75 | 110 | 130 | 150 | 170 |

(a) The weight content of $H_2SO_4$ in polymer membranes. (b) The molar ratio of $H_2SO_4$ to the imidazole group on the polymer. (c) The mole content of $H_2SO_4$, which can be calculated according to $(1 + n_{Base}/n_{Acid})^{-1} \times 100$. (d) The DC conductivity estimated from the $|Z|$ value of the plateau in the AC impedance spectrum, i.e., the bulk resistance. Here, the proton transference number is assumed to be unity. Therefore, the overall ionic conductivity is regarded as the proton conductivity.

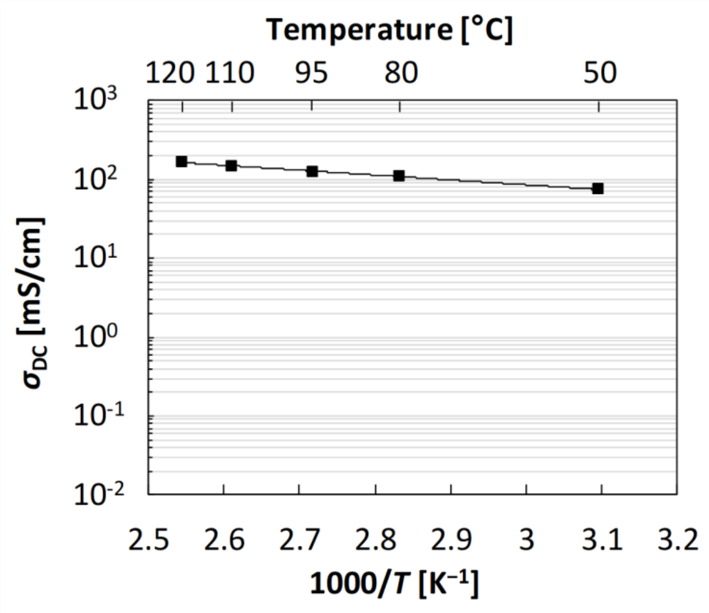
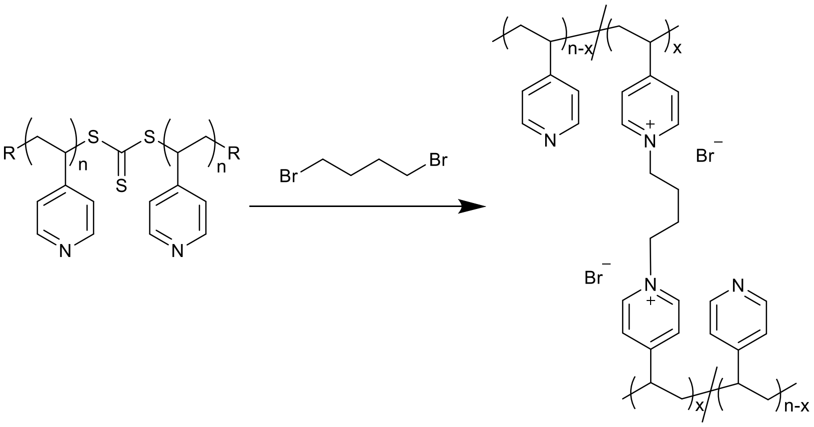


**Fig. S6.** Anhydrous conductivity versus reciprocal absolute temperature for CL-I/$H_2SO_4$ membranes containing 80 wt% $H_2SO_4$. Solid line is drawn as guide for eyes.

**Scheme S2.** Synthesis of chemically post-cross-linked polymer P (Post-CL-P). Note that the RAFT agent residue was omitted in the chemical structure for simplification.



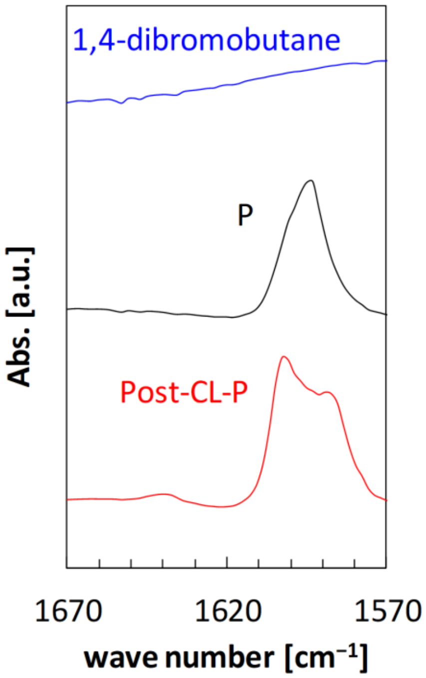


**Fig. S7.** FT-IR spectra of 1,4-dibromobutane, polymer P, and Post-CL-P. Absorption at 1595 cm$^{-1}$ is owing to the stretching vibration of C-N on the pyridyl group. After a quaternization reaction of the pyridyl group by $BrC_4Br$, a small absorption at 1640 cm$^{-1}$ appeared, which is due to the progress of the quaternization reaction on the pyridyl group.

**Table S3.** Anhydrous conductivity for Post-CL-P/$H_2SO_4$ ($H_2SO_4$ content: 80 wt%) at high temperatures.

| Polymer | $H_2SO_4$ weight content [a] [wt%] | $n_{Acid}/n_{Base}$ [b] [mol/mol] | $H_2SO_4$ mole content [c] [mol%] | $\sigma_{DC}$ [d] [mS/cm] | |
|---|---|---|---|---|---|
| | | | | 140 °C | 160 °C |
| Post-CL-P | 80 | 4.3 | 81 | 190 | 220 |

(a) The weight content of $H_2SO_4$ in polymer membranes. (b) The molar ratio of $H_2SO_4$ to the pyridyl group on the polymer. (c) The mole content of $H_2SO_4$, which can be calculated according to $(1 + n_{Base}/n_{Acid})^{-1} \times 100$. (d) The DC conductivity estimated from the $|Z|$ value of the plateau in the AC impedance spectrum, i.e., the bulk resistance. Here, the proton transference number is assumed to be unity. Therefore, the overall ionic conductivity is regarded as the proton conductivity.

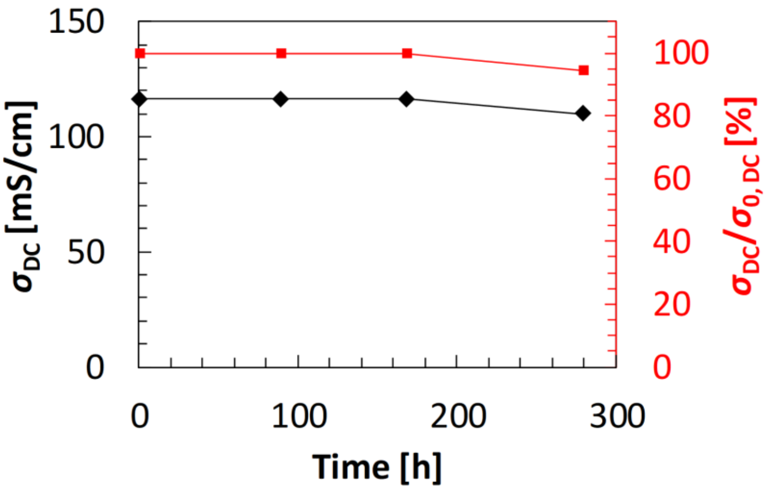
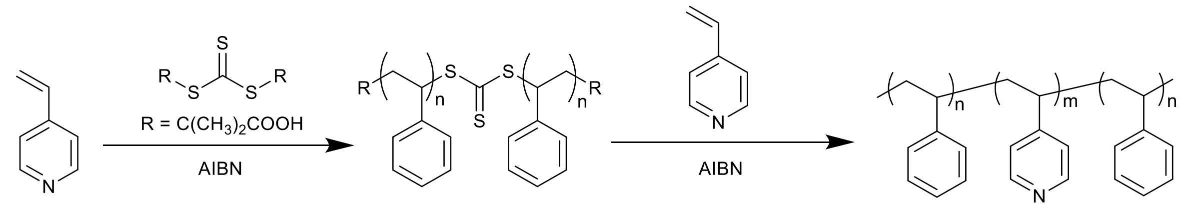


**Fig. S8.** Change of anhydrous conductivity for the Post-CL-P/$H_2SO_4$ membrane after keeping at 95°C. Left axis is the anhydrous conductivity of the Post-CL-P/$H_2SO_4$ membrane. Right axis is the ratio of theanhydrous conductivity to the initial conductivity ($\sigma_{0,\ DC}$). Black diamonds and red squares represent $\sigma_{DC}$ and $\sigma_{DC}/\sigma_{0,\ DC}$, respectively. Solid lines are drawn as guide for eyes.

**Scheme S3.** Synthesis of S-P-S triblock copolymer. Note that the RAFT agent residue was omitted in the chemical structure for simplification.



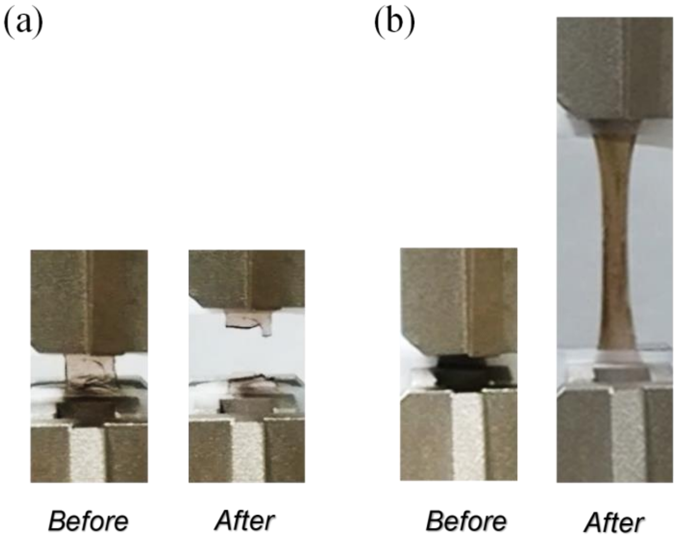


**Fig. S9.** Photos before and after/during elongation for (a) Post-CL-P/$H_2SO_4$ membrane and for (b) S-P-S/$H_2SO_4$ membrane. S-P-S/$H_2SO_4$ can be elongated with a strain larger than 800%, whereas Post-CL-P/$H_2SO_4$ fractured with a strain of only 60%.

**Table S4.** Mechanical characteristics of Post-CL-P/$H_2SO_4$ and S-P-S/$H_2SO_4$ by tensile tests.

| Sample | $E$ [a] [MPa] | $\varepsilon_b$ [b] [%] | $\sigma_{max}$ [c] [MPa] | $S$ [d] [MJ/m$^3$] |
|---|---|---|---|---|
| S-P-S/$H_2SO_4$ | 0.10 | 880 | 0.56 | 2.1 |
| Post-CL-P/$H_2SO_4$ | 0.10 | 60 | 0.054 | 0.021 |

(a) Young's modulus estimated from the slope of stress-strain curves in the low strain region between 0 and 10%. (b) Elongation at break. (c) The maximum tensile stress. (d) The inner area under stress-strain curves, which is an indicator of the robustness of the material.

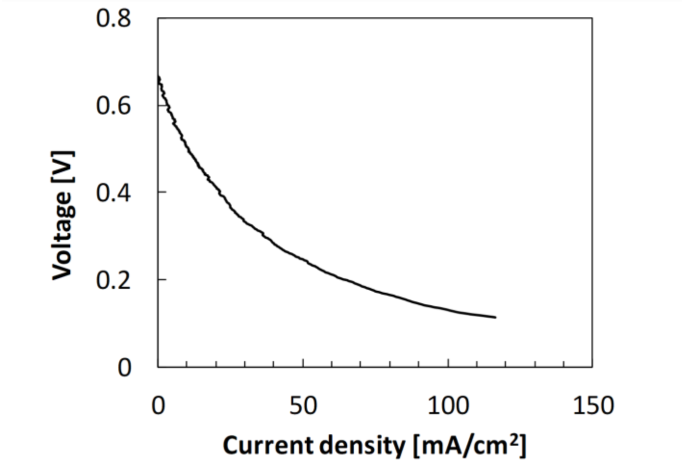


**Fig. S10.** Performance (*i*-*V* curve) of a fuel cell assembled with an S-P-S/$H_2SO_4$ ($H_2SO_4$ content: 75 wt%) membrane and Pt/C electrode catalyst (TEC10E50E) of TANAKA Holdings Co., Ltd. at 60 °C under anhydrous conditions (0% RH). The area of the membrane electrode assembly (MEA) was 0.81 cm$^2$ (0.9 cm × 0.9 cm). Flow rates of $H_2$ gas at an anode and air at a cathode were 0.1 and 0.2 NL/min, respectively. The open circuit voltage was 0.67 V. The maximum power was 10.8 mW, where the current density and the voltage were 81.7 mA/cm$^2$ and 0.163 V, respectively. At the same anhydrous conditions, the Nafion-based fuel cell does not work; therefore, the data of the Nafion-based fuel cell was not shown here.

## References

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