Electronic supplementary information (ESI)

Multiblock-copolymerisation-derived sulfonated-poly(p-phenylene)-based polymer electrolyte membranes with simultaneously enhanced proton conductivity and mechanical strength

Mizu Yoshida-Hirahara,ab Masahiro Yoshizawa-Fujita,a Yuko Takeoka a and Masahiro Rikukawa *a

a Department of Materials and Life Sciences, Sophia University, 7-1 Kioi-cho, Chiyoda-ku, Tokyo 102-8554, Japan

b Research and Development Bureau, Saitama University, Shimo-Okubo 255, Saitama-shi 338-8570, Japan

* Corresponding author. E-mail: m-rikuka@sophia.ac.jp
**Synthesis of S-6H (14) 3:1**

NS-6H (14) 3:1 was prepared using NS-DPBP (2.500 g, 5.067 mmol), PAEK6H-Cl (14) (0.717 g, 1.69 mmol), PPh₃ (0.555 g, 2.11 mmol), NaI (0.103 g, 0.684 mmol), Zn (0.830 g, 12.7 mmol), NiCl₂(PPh₃)₂ (0.104 g, 0.159 mmol), and NMP (13.0 mL) following the general procedure described in the Experimental section. Yield: 72% (1.84 g). ¹H NMR (300 MHz, CDCl₃): δ 6.84–7.98 (m), 3.69 (s), 1.71 (s), 0.90 (s) ppm. IR (KBr): 3043, 2966, 1658, 1592, 1496, 1415, 1363, 1240, 1186, 1164, 871–676 cm⁻¹. Elemental analysis: Calcd. for (CHN)ₙ C, 71.53%; H, 5.31%. Found C, 71.53%; H, 5.16%.

**Synthesis of S-6H (14) 2:1**

S-6H (14) 3:1 was prepared using NS-6H (14) 3:1 (2.212 g), (C₂H₅)₂NH·HBr (3.039 g, 19.72 mmol), and NMP (25.0 mL) following the general procedure described in the Experimental section. Yield: 58% (1.12 g). ¹H NMR (500 MHz, DMSO-d₆): δ 6.68–7.83 (m, peaks at 7.66, 7.51, 7.39, 7.20, 6.96) ppm. IR (ATR): 3400, 3966, 1656, 1585, 1490, 1415, 1380, 1360, 12435, 1160, 1120, 1031, 1005, 872–690 cm⁻¹. Elemental analysis: Calcd. for (CHNS)ₙ C, 69.64%; H, 3.99%; S, 6.63%. Found C, 65.45%; H, 4.13%; S, 6.21%. Molecular weight (GPC): Mₙ = 70,600 g·mol⁻¹, Mₘ = 176,000 g·mol⁻¹, Mₘ/Mₙ = 2.50.

**Synthesis of S-6H (14) 2:1**
NS-6H (14) 2:1 was prepared using NS-DPBP (2.000 g, 4.054 mmol), PAEK6H-Cl (14) (0.717 g, 1.69 mmol), PPh₃ (0.555 g, 2.11 mmol), NaI (0.103 g, 0.684 mmol), Zn (0.830 g, 12.7 mmol), NiCl₂(PPh₃)₂ (0.104 g, 0.159 mmol), and NMP (13.0 mL). Yield: 90% (2.00 g). ¹H NMR (300 MHz, CDCl₃): δ 6.84–7.98 (m), 3.69 (s), 1.71 (s), 0.90 (s) ppm. IR (KBr): 3043, 2966, 1658, 1592, 1496, 1415, 1363, 1240, 1186, 1164, 871–676 cm⁻¹. Elemental analysis: Calcd. for (CHN)n C, 72.75%; H, 5.32%. Found C, 72.75%; H, 5.35%.

S-6H (14) 2:1 was prepared using NS-6H (14) 2:1 (1.708 g), (C₂H₅)₂NH·HBr (21.42 g, 13.90 mmol), and NMP (20.0 mL). Yield: 49% (0.74 g). ¹H NMR (500 MHz, DMSO-d₆): δ 6.68–7.83 (m, peaks at 7.66, 7.51, 7.39, 7.20, 6.96) ppm. IR (ATR): 3400, 3966, 1656, 1585, 1490, 1415, 1380, 1360, 12435, 1160, 1120, 1031, 1005, 872–690 cm⁻¹. Elemental analysis: Calcd. for (CHNS)n C, 71.25%; H, 4.17%; S, 5.81%. Found C, 67.92%; H, 4.25%; S, 6.09%. Molecular weight (GPC): $M_n = 58,000$ g·mol⁻¹, $M_w = 124,000$ g·mol⁻¹, $M_w/M_n = 2.13$.

**Synthesis of S-6H (14) 1:1**

NS-6H (14) 1:1 was prepared using NS-DPBP (1.630 g, 3.304 mmol), PAEK6H-Cl (14) (1.402 g, 3.304 mmol), PPh₃ (0.555 g, 2.11 mmol), NaI (0.103 g, 0.684 mmol), Zn (0.830 g, 12.7 mmol), NiCl₂(PPh₃)₂ (0.104 g, 0.159 mmol), and NMP (12.0 mL). Yield: 92% (2.53 g). ¹H NMR (300 MHz, CDCl₃): δ 6.84–7.98 (m), 3.69 (s), 1.71 (s), 0.90 (s) ppm. IR (KBr): 3043, 2966, 1658, 1592, 1496,
1415, 1363, 1240, 1186, 1164, 871–676 cm\(^{-1}\). Elemental analysis: Calcd. for (CHN)\(_n\) C, 74.53%; H, 5.35%. Found C, 74.52%; H, 5.13%.

S-6H (14) 1:1 was prepared using NS-6H (14) 1:1 (2.300 g), (C\(_2\)H\(_5\))\(_2\)NH·HBr (2.105 g, 13.7 mmol), and NMP (25.0 mL). Yield: 96% (2.024 g). \(^1\)H NMR (500 MHz, DMSO-\(d_6\)): \(\delta\) 6.68–7.83 (m, peaks at 7.66, 7.51, 7.39, 7.20, 6.96) ppm. IR (ATR): 3400, 3966, 1656, 1585, 1490, 1415, 1380, 1360, 12435, 1160, 1120, 1031, 1005, 872–690 cm\(^{-1}\). Elemental analysis: Calcd. for (CHNS)\(_n\) C, 74.66%; H, 4.56%; S, 4.09%. Found C, 72.94%; H, 4.64%; S, 4.63%. Molecular weight (GPC): \(M_n = 22,000\) g·mol\(^{-1}\), \(M_w = 69,200\) g·mol\(^{-1}\), \(M_w/M_n = 3.16\).

■ Synthesis of S-6F (10) 3:1

NS-6F (10) 3:1 was prepared using NS-DPBP (3.000 g, 6.080 mmol), PAEK6F-Cl (10) (1.093 g, 2.027 mmol), PPh\(_3\) (0.985 g, 3.75 mmol), NaI (0.182 g, 1.22 mmol), Zn (1.000 g, 15.29 mmol), NiCl\(_2\)(PPh\(_3\))\(_2\) (0.184 g, 0.281 mmol), and NMP (14.0 mL) following the general procedure described in the Experimental section. Yield: 72% (1.84g). \(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta\) 6.83–7.96 (m), 3.67 (s), 0.87 (s) ppm. IR (KBr): 3068, 2966, 1660, 1591, 1490, 1415, 1363, 1240, 1207, 1186, 1164, 875–690 cm\(^{-1}\). Elemental analysis: Calcd. for (CHNS)\(_n\) C, 67.26%; H, 4.55%; S, 5.05%. Found C, 67.05%; H, 4.48%; S, 5.05%.
S-6F (10) 3:1 was prepared using NS-6F (10) 3:1 (2.510 g), (C₂H₅)₂NH·HBr (3.270 g, 21.22 mmol), and NMP (30.0 mL) following the general procedure described in the Experimental section. Yield: 48% (1.06 g). IR (ATR): 3400, 3067, 1660, 1585, 1490, 1415, 1235, 1205, 1120, 1031, 1005, 872–690 cm⁻¹. Elemental analysis: Calcd. for (CHNS)n C, 64.99%; H, 3.33%; S, 5.68%. Found C, 60.06%; H, 3.84%; S, 5.93%. Molecular weight (GPC): $M_n = 50,800$ g·mol⁻¹, $M_w = 118,000$ g·mol⁻¹, $M_w/M_n = 2.31$.

**Synthesis of S-6F (10) 2:1**

NS-6F (10) 2:1 was prepared using NS-DPBP (3.000 g, 6.080 mmol), PAEK6F-Cl (10) (1.640 g, 3.040 mmol), PPh₃ (0.957 g, 3.65 mmol), NaI (0.177 g, 1.18 mmol), Zn (1.432 g, 21.90 mmol), NiCl₂(PPh₃)₂ (0.179 g, 0.274 mmol), and NMP (14.0 mL). Yield: 86% (3.57 g). ¹H NMR (300 MHz, CDCl₃): $\delta$ 6.83–7.96 (m), 3.67 (s), 0.87 (s) ppm. IR (KBr): 3068, 2966, 1660, 1591, 1490, 1415, 1363, 1240, 1207, 1186, 1164, 875–690 cm⁻¹. Elemental analysis: Calcd. for (CHNS)n C, 67.13%; H, 4.45%; S, 4.68%. Found C, 67.29%; H, 4.34%; S, 4.68%.

S-6F (10) 2:1 was prepared using NS-6F (10) 2:1 (3.571 g), (C₂H₅)₂NH·HBr (4.051 g, 26.29 mmol), and NMP (30.0 mL). Yield: 81% (1.83 g). IR (ATR): 3400, 3067, 1660, 1585, 1490, 1415, 1235, 1205, 1120, 1031, 1005, 872–690 cm⁻¹. Elemental analysis: Calcd. for (CHNS)n C, 65.02%; H,
3.31%; S, 5.22%. Found C, 56.00%; H, 6.30%; S, 4.86%. Molecular weight (GPC): $M_n = 61,400$ g·mol$^{-1}$, $M_w = 239,000$ g·mol$^{-1}$, $M_w/M_n = 3.89$.

**Synthesis of S-6F (10) 1:1**

NS-6F (10) 1:1 was prepared using NS-DPBP (2.200 g, 4.459 mmol), PAEK6F-Cl (10) (2.406 g, 4.458 mmol), PPh$_3$ (0.957 g, 3.65 mmol), NaI (0.177 g, 1.18 mmol), Zn (1.432 g, 21.90 mmol), NiCl$_2$(PPh$_3$)$_2$ (0.179 g, 0.274 mmol), and NMP (14.0 mL). Yield: 91% (3.80 g). $^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 6.83–7.96 (m), 3.67 (s), 0.87 (s) ppm. IR (KBr): 3068, 2966, 1660, 1591, 1490, 1415, 1363, 1240, 1207, 1186, 1164, 875–690 cm$^{-1}$. Elemental analysis: Calcd. for (CHNS)$_n$ C, 66.59%; H, 4.05%; S, 3.27%. Found C, 66.38%; H, 4.00%; S, 3.26%.

S-6F (10) 1:1 was prepared using NS-6F (10) 1:1 (3.798 g), (C$_2$H$_5$)$_2$NH·HBr (3.123 g, 20.27 mmol), and NMP (30.0 mL). Yield: 39% (0.90 g). IR (ATR): 3400, 3067, 1660, 1585, 1490, 1415, 1235, 1205, 1120, 1031, 1005, 872–690 cm$^{-1}$. Elemental analysis: Calcd. for (CHNS)$_n$ C, 65.13%; H, 3.26%; S, 3.52%. Found C, 60.70%; H, 3.67%; S, 3.91%. Molecular weight (GPC): $M_n = 29,900$ g·mol$^{-1}$, $M_w = 47,300$ g·mol$^{-1}$, $M_w/M_n = 2.02$. 
Fig. S1 FT-IR spectra of DCBP, bisphenol A, and PAEK6H-Cl (14).

Fig. S2 FT-IR spectra of DCBP, bisphenol AF, and PAEK6F-Cl (10).
Fig. S3 $^1$H NMR spectrum of PAEK6H-Cl (14) in CDCl$_3$.

Fig. S4 $^1$H NMR spectrum of PAEK6F-Cl (10) in CDCl$_3$. 
Fig. S5 FT-IR spectra of NS-6H-series samples.

Fig. S6 FT-IR spectra of NS-6F-series specimens.
Fig. S7 $^1$H NMR spectra of (a) NS-6H (14) 3:1, (b) NS-6H (14) 2:1, and (c) NS-6H (14) 1:1 in CDCl$_3$. 

11
Fig. S8 $^1$H NMR spectra of (a) NS-6F (10) 3:1, (b) NS-6F (10) 2:1, and (c) NS-6F (10) 1:1 in CDCl$_3$. 
Fig. S9 FT-IR spectra of S-6H-series samples.

Fig. S10 FT-IR spectra of S-6F-series specimens.
Fig. S11 $^1$H NMR spectra of (a) S-6H (14) 3:1, (b) S-6H (14) 2:1, and (c) S-6H (14) 1:1 in DMSO-$d_6$. 
Fig. S12 TGA curves of S-6H- and S-6F-series specimens.
Fig. S13 Stress–strain curves of S-6F membranes under (a) ambient conditions (RT, no extra humidification) and (b) at an elevated temperature and humidity (80 °C, 90% RH).
**Fig. S14** AFM images of S-6H membranes under (a) ambient (RT, 30%–50% RH) and (b) humid conditions (RT, 85% RH). Left, middle, and right columns: topography, phase, and current mapping, respectively; scan size, $1000 \times 1000 \text{ nm}^2$. 
**Fig. S15** AFM images of S-6F membranes under (a) ambient (RT, 30%–50% RH) and (b) humid conditions (RT, 85% RH). Left, middle, and right columns: topography, phase, and current mapping, respectively; scan size, 1000 × 1000 nm².
**Fig. S16** SAXS profiles of S-6F and S-PPBP membranes. Dotted lines indicate the interdomain spacing calculated using Bragg’s law.