Electronic Supplementary Information

Proton conducting ABA triblock copolymers with sulfonated poly(phenylene sulfide sulfone) midblock obtained via copper-free thiol-click chemistry

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Experimental section

Materials

Oleum (65 % SO_3 in H_2SO_4, Sigma Aldrich), 4,4'-difluorophenylsulfone (99 % TCI), sodium chloride (Merck), diethyl ether (Analytical grade, Avantor), sodium hydroxide (pellets, Merck), decafluorobiphenyl (DFBP, 99 % Sigma Aldrich), Phosphorous pentachloride (PCl_5, Merck) 1,8-Diazabicyclo(5.4.0)undec-7-ene (DBU, >98 % Acros Organics), toluene (99,5 % Extra Dry stored over molecular sieves, water <50ppm Acros Organics), hydrazine monohydrate (>98%, TCI), tetrahydrofuran (THF, HPLC grade stabilized with BHT, Boom), 2-propanol (analytical grade, Avantor), methanol (analytical grade, Avantor), acetone (analytical grade, Avantor), piperidine (99% Acros Organics), chloroform (analytical grade, Avantor), *N,N*-dimethylacetamide (DMAc, >99 % Acros Organics), *N,N*-dimethylformamide (DMF, > 99 % Acros Organics), 1,2-dichloroethane (DCE, Merck), *N,N*-dimethylformamide (DMF, > 99 % Extra Dry stored over molecular sieves, water <50ppm Acros Organics), 2-Cyano-2-propyl benzodithioate (CPBD, >97%, Sigma-Aldrich), dichloromethane (anhydrous, ≥99.8% Sigma Aldrich), hydrochloric acid (HCl, 35-37 wt% Boom) were used without further purification. *N*-Methyl-2-pyrrolidone (NMP, 99.5 % Acros Organics) was dried over P_2O_5, distilled at reduced pressure, and stored under argon over a molecular sieve (4 Å), 4,4'-thiobisbenzenethiol was recrystallized under inert atmosphere from toluene and dried under vacuum at 50 °C for 24 h before being stored in a nitrogen filled glove-box until used. Styrene (>99 % Sigma Aldrich with 4-tert butylcatechol as inhibitor) was dried over CaH_2 and distilled at reduced pressure, anhydrous potassium carbonate (K_2CO_3, 99 %+ Acros Organics) was dried at 120 °C under vacuum for 24 h before use, 2,2′-Azobis(2-methylpropionitrile) (AIBN, >98 % Sigma Aldrich) was recrystallized twice from methanol before use, piperidine was dried over molecular sieves. Disodium 3,3'-Disulfonate-4,4'-difluorodiphenylsulfone was synthesized according to a reported method[1]

Synthesis of sulfonated poly(phenylene sulfide sulfone) (sPSS)

The sulfonated polysulfone was synthesized according to a step-growth nucleophilic aromatic substitution using a dithiol excess to ensure thiophenol end-groups.
Inside a nitrogen filled glovebox, SDFSPS (12.347 g, 0.0270 mol), TBBT (7.017 g, 0.0280 mol) and K_2CO_3 (6.119 g, 0.0420 mol) were added to a dry 3 neck 250 mL round bottom flask. The flask was sealed, transferred in a fume-hood and equipped with a mechanical stirrer, a

Dean-Stark trap fitted with a condenser and an argon inlet. All connections were performed under argon. After purging the reaction system for 20 min, dry NMP (100 mL) and dry toluene (50 mL) were added to the solids under argon and the reaction mixture was stirred for 30 min at room temperature before heating at 150 °C for 4 h in order to azeotropically remove the water. After the drying step, the toluene was removed from the Dean-Stark, and the temperature was raised to 175 °C for 36 h. After cooling down to RT, the reaction mixture was diluted with NMP (15 mL) and precipitated in 2-propanol (1500 mL) under vigorous stirring. The purple precipitate was filtered and washed on a filter before collecting the solid and removing the remaining salts through dialysis for 3 days (dialysis tubing regenerated cellulose Spectrapor® MWCO 12-14 kDa) against D.I. water. After dialysis, the water was removed using a rotary evaporator at 50 °C and the product dried under vacuum at 65 °C for 24 h yielding 16.450 g of dark purple polymer (Mw= 700.9 g mol^{-1} K-form, 87.1%).

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.20 (s, 2H), 7.66 (d, 2H), 7.55 (d, 4H), 7.48 (d, 4H), 6.91 (d, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.8, 144.0, 136.5, 136.1, 135.8, 132.0, 130.8, 127.6, 126.0. (**Figure S1**)

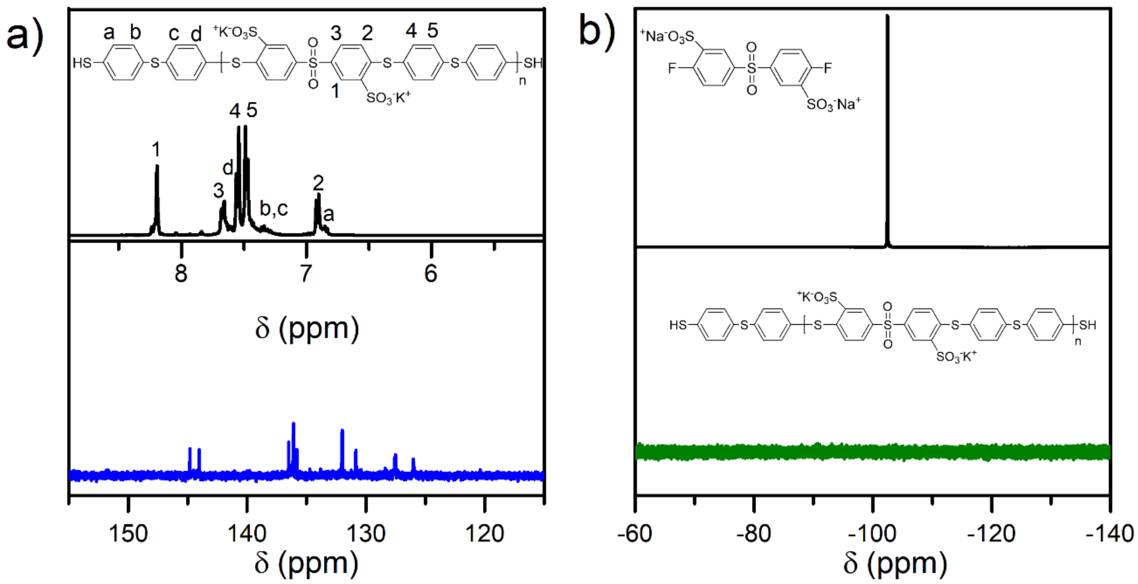

Figure S1 Reaction scheme of the sPSS synthesis with a) ^{1}H NMR (black line) and ^{13}C NMR (blue line) confirming the chemical structure and b) ^{19}F NMR confirming full conversion of the sulfonated monomer and absence of fluorine end-groups in the sPSS.

Synthesis of sPSS-piperidine

Molecular weight determination of charged sPSS block is crucial for the click reaction stoichiometry. To ensure accurate GPC analysis a derivatization step was performed converting the sulfonic groups into sulfonamides functionalities adapting a procedure reported elsewhere[2] and using piperidine as amine (**Figure S2**).

In a pre-dried three neck flask equipped with a condenser and a nitrogen inlet, sPSS (0.200 g, 1 eq) were suspended in DCE (8 mL) under an inert atmosphere. Subsequently PCl_5 (0.356 g, 6 eq) and a catalytic amount of DMF (0.1 mL) were added under nitrogen flow and the mixture was heated at 50 °C for 24 h. The polymer dissolved over time confirming the successful formation of the sulfonyl chloride groups (sPSS-SO_2Cl). The turbid solution was filtered to remove the salts and precipitated in excess diethyl ether before washing thoroughly with fresh diethyl ether. The polymer was dried under vacuum at room temperature before proceeding with the second step of the reaction.

In a three neck flask equipped with a condenser and a nitrogen inlet, sPSS-SO_2Cl (0.200 g, 1 eq) was suspended in anhydrous DCM (2 mL) before adding excess of piperidine (0.224 mL, 8 eq.). The mixture was stirred for 24 h at room temperature. The mixture was precipitated in methanol and washed thoroughly on the filter. Subsequently, the obtained polymer was dried under vacuum at 60 °C for 24 h.

^{1}H NMR (400 MHz, $CDCl_3$) $\delta = 8.35$ (s, 1H), 7.78 (d, 2H), 7.75 (d, 2H), 7.74 (d, 1H), 6.99 (d, 1H), 3.29 (t, 4H), 1.65 (s, 4H), 1.57 (s, 2H). FTIR (ATR): $v = 2935$ (m; v (-C-H *aliph*)), 1320 cm^{-1} (s; v_{str} (-SO_2-)), 936 cm^{-1} (s; v (-S-N-)), 537 cm^{-1} (s; v_{wagg}(-SO_2-)). (see **Figure S2**)

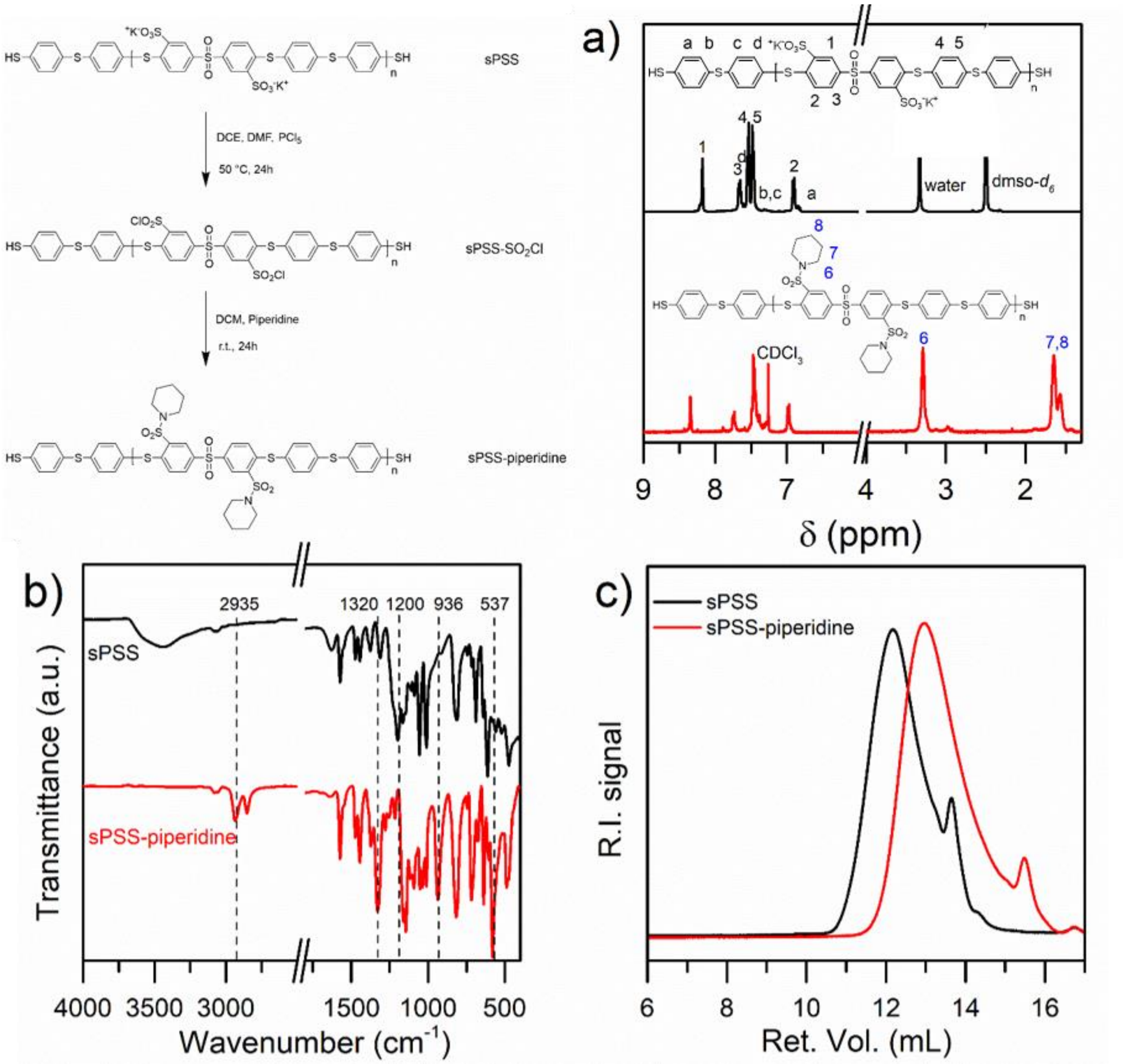

Figure S2 Derivatization reaction scheme and a) ^{1}H NMR spectra of the sPSS and the sPSS-piperidine with the corresponding assignment of the peaks (residual signal of water and DMSO-d_6 have been partially masked for graphical reasons) b) FTIR spectra of the sPSS and sPSS-piperidine highlighting the appearance of the sulfonamide peaks (dashed lines are guides) c) GPC traces of the neat sPSS and sPSS-piperidine in DMF 0.01 M LiBr at 50 °C showing the effect of charge removal on the elution time (and the molecular weight determination).

Table S1 Molecular weight characterization of the sPSS homopolymer. GPC analysis was performed in DMF with 0.01 M LiBr at 50 °C.

	M_n^{GPC} (kg mol^{-1})	M_w (kg mol^{-1})	Đ
sPSS (K-form)	27.9	39.1	1.4
sPSS-piperidine	8.9[a)]	20.0	2.2

[a)] From the M_n in the piperidine form, the related values in the K-form (7.9 kg mol^{-1}) and H-form (7.1 kg mol^{-1}) were calculated and used for the reaction and weight fraction evaluations, respectively.

RAFT polymerization of Styrene with 2-Cyano-2-propyl benzodithioate (CPDB) (PS-CPDB)

A typical procedure of the RAFT polymerization of styrene is as follows.
Freshly distilled styrene (35 mL, 87 mmol), CPBD and AIBN in molar ration 400:1:0.1 were added to a pre-dried Schlenk tube vacuum/purged three times with argon. The mixture was degassed via three freeze/pump/thaw cycles before being immersed in a pre-heated oil bath at 65 °C. After 15 h the reaction was stopped by quenching in liquid nitrogen, the solution was diluted with toluene (3 mL) and the polymer was precipitated in methanol (300 mL). The polymer was collected via filtration and reprecipitated two more times in methanol from THF. The resulting polymer was dried under vacuum at 50 °C for 24 h. Different molecular weights were obtained by varying the [monomer]:[CTA] ratio (see Table S1).

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.84 (m, -C(=S)-Ph *o-H*), 7.66 (m, -C(=S)-Ph *p-H*), 7.48 (m, -C(=S)-Ph *m-H*), 7.07 (m, -CHPh- *m-* and *p- H*), 6.56 (m, -CHPh -*o-H*), 4.86 (m, -CPh*H*-S-), 1.91 (m, -CPh*H*-CH_2-), 1.45 (m, -CPhH-CH_2-), 1.02 (m,-C(CH_3)$_2$-CN).

"One-pot" synthesis of decafluorobiphenyl-terminated polystyrene (PS-DFBP)

PS-DFBP was synthesized in a "one-pot" sequential reaction by cleaving the RAFT agent by aminolysis with hydrazine.[3]The thiol-terminated polystyrene was subsequently functionalized with DFBP. Here we report a typical reaction condition for PS-CPBD_1.
In a 100 mL Schlenk tube a solution of PS-CPBD_1 in dry DMF (35 mL 4.0 mM) was degassed by three freeze-pump-thaw cycles before 5 times molar excess of hydrazine monohydrate was added through a degassed pipette. The solution was stirred for 30 min at room temperature in the dark before being cooled down at 0 °C in an ice bath. The cleavage of the CTA end-group was monitored via UV-Vis checking the disappearance of the characteristic peak of the benzodithioate group at 306 nm. An ice-cold solution containing DFBP (2.334 g, 50 eq), TEA (0.030 mL, 1.5 eq) in dry DMF (35 mL), previously degassed by three freeze-pump-thaw cycles, was added all at once through a degassed needle to the PS solution and the reaction mixture stirred at 0 °C. After 30 min the reaction mixture was equilibrated at room temperature and stirred for additional 15 h. The polymer was precipitated in excess volume of acidified methanol and collected by filtration. The functionalized polymer was reprecipitated in methanol from THF. The white polymer was finally dried in vacuum oven at 50 °C for 24 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.07 (m, -CHPh- *m-* and *p- H*), 6.57 (m, -CHPh -*o-H*), 4.00 (m, -CPh*H*-S-), 1.91 (m, -CPh*H*-CH_2-), 1.46 (m, -CPhH-CH_2-), 1.04 (m,-C(CH_3)$_2$-CN).

^{19}FNMR (376 MHz, $CDCl_3$) δ = -134.64 (F-**e**), -140.59 (F-**d**), -141.74 (F-**c**), -153.38 (F-**a**), -163.73 (F-**b**). (see **Fig. 1**).

Synthesis of PS-b-sPSS-b-PS using metal-free thiol-fluoro "click" chemistry

A general procedure for one of the BCP with a volume fraction of sPSS $f_{sPSS} =$ 33.9% (named BCP3 in the following paragraphs) is reported here.
In a dried 50 mL Schlenk tube sPSS (1.000 g, 0.127 mmol) was dissolved in anhydrous DMF (20 mL). After complete dissolution of the polymer a 3 times molar excess of PS-DFBP_3 (2.848 g, 0.380 mmol) was added and the solution was degassed via three freeze-pump-thaw cycles, before adding K_2CO_3 (0.070 g, 0.506 mmol). The reaction mixture was heated at 50 °C for 4 days before precipitating the polymer in 2-propanol.
In order to remove the unreacted homopolymers, several sequential washings with selective solvents for each block, namely water and acetone, were performed on the block copolymers. The final product was dried under vacuum for 24 h at 110 °C.
By varying the M_n of the PS blocks, a small family of block copolymer was synthesized.

The weight fraction of the sPSS block in the BCP was evaluated by ^{1}H NMR in DMF-d_7 and elemental analysis.
By ^{1}H NMR the sPSS weight fraction (wt%) was obtained evaluating the ratio between the proton in *o*- to the sulfonic groups of sPSS and the peak corresponding to the aromatic protons of PS moiety according to **Equation S1**:

$$f_{sPSS}^{NMR} = \frac{\frac{1}{2}\int_{8.4}^{8.55} BCP \times M_{sPSS}}{\left[\frac{1}{5}\left(\int_{6.1}^{7.8} BCP - 6 \times \int_{8.4}^{8.55} BCP\right) \times M_{PS}\right] + \frac{1}{2}\int_{8.4}^{8.55} BCP \times M_{sPSS}} \times 100 \qquad \text{(S1)}$$

where M_{sPSS} is the molecular weight of the repeating unit of the sPSS, and M_{PS} is the molecular weight of the styrene unit and *BCP* refers to the ^{1}H NMR intensity of the BCP. From the elemental analysis the sulfur content was evaluated considering sPSS as the only source of sulfur according to **Equation S2**:

$$f_{sPSS}^{El.An.} = \frac{S_{wt\%}^{BCP}}{S_{wt\%}^{sPSS}} \times 100 \qquad \text{(S2)}$$

where $S_{wt\%}^{BCP}$ is the sulfur content as wt% determined by elemental analysis in the block copolymer and the $S_{wt\%}^{sPSS}$ is the sulfur content as wt% determined by elemental analysis in the pure sPSS. Note that the contribution of the single sulfur atom of the RAFT agent at the end of the PS block was neglected here.

Membrane formation

An 8 wt% solution of the block copolymer in DMAc was cast on acid-washed Petri dishes. The solution was slowly dried at 40 °C over 3 days in a solvent saturated chamber before being annealed at 120 °C for 2 h under vacuum. The resulting membranes were peeled off by immersion in HCl 2.5 M and then acidified by heating the solution at 50 °C and changing several times the HCl solution over 24 h. After ion exchange, the membranes were thoroughly washed with deionized water (18.2 MΩ) and then dried at 70 °C in vacuo for 24 h.

Characterization

Nuclear magnetic resonance spectroscopy (NMR).

NMR spectra were recorded at room temperature on a Varian VXR 400 MHz (^{1}H: 400 MHz; ^{13}C: 101 MHz, ^{19}F: 376 MHz) spectrometer using deuterated solvents. Chemical shifts (δ) are reported in ppm, whereas the chemical shifts are calibrated to the solvent residual peaks. The chemical composition and the purity of the compounds were determined using DMSO-d_6, DMF-d_7 and $CDCl_3$ as solvents. The theoretical number average molecular weight (M_n) was calculated, where possible, from phase and baseline-corrected spectra.

Gel permeation chromatography (GPC)

The molecular weights (M_n number and M_w weight average molecular weights) and the dispersity (Đ) of the samples were determined by GPC using DMF (containing 0.01 M LiBr) as solvent in a Viscotek GPCmax equipped with model 302 TDA detectors and two columns (Agilent Technologies-PolarGel-L and M, 8 μm 30 cm) at a flow rate of 1.0 mL·min^{-1} and 50 °C. The molecular weight dispersity of the polymer samples was calculated via the universal calibration curve constructed using narrow dispersity polymethylmethacrylate (PMMA) standards (Polymer Laboratories). For sample preparation, the purified dry samples were dissolved in DMF (containing 0.01 M LiBr). Once the samples were completely dissolved, they were filtered through a PTFE syringe filter (Minisart SRP 15, Sartorius Stedim Biotech, PTFE-membrane filter; pore size: 0.2 μm, filter diameter: 15 mm) and analyzed by GPC using a 100 μL injection volume. The collected spectra were analyzed with the use of OmniSEC (v5.0) (Malvern).

For the Polystyrene samples, an additional determination of the molecular weights was performed using THF, stabilized with BHT, as solvent and narrow dispersity polystyrene standards (Polymer Laboratories). The separation was performed by utilizing two PLgel 5 μm MIXED-C, 300 mm columns from Agilent Technologies at 35 °C calibrated with narrow disperse polystyrene standards (Agilent Technologies and Polymer Laboratories). The GPC system was a Viscotek GPCmax equipped with triple detection system or Viscotek RALLS detector, a Viscotek viscometer model H502, and a Schambeck RI2012 refractive index detector. Conventional calibration was used to determine the molecular weights and the dispersity of the samples.

Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR)

Background corrected IR spectra were recorded on a Bruker Vertex 70 spectrophotometer in the range of 4000–400 cm^{-1}, using 64 scans at a nominal resolution of 4 cm^{-1} using a diamond single reflection attenuated total reflectance (ATR). Atmospheric compensation and offset-correction were applied on the collected spectra with the use of OPUS spectroscopy software (v7.0) (Bruker Optics).

Differential scanning calorimetry (DSC)

Calorimetric measurements were made on a TA-Instruments Q1000 differential scanning calorimeter under a dry nitrogen atmosphere (50 mL min^{-1}). The samples were scanned in a temperature range from 0 to 250 °C by heating–cooling–heating scans at a rate of 10 °C min^{-1}. The glass transition temperature (T_g) was determined as the inflection point of the specific heat increase in the second heating curve. The thermograms were evaluated with the use of Trios (v5.1) software (TA Instruments).

Thermogravimetric analysis (TGA)

To determine the thermal stability and decomposition behavior, measurements were performed on a TA-Instruments D2500. Programmed heating from 30 to 700 °C was used for TG analysis at a heating rate of 10 °C min^{-1} under nitrogen purge gas (50 mL min^{-1}). The decomposition temperature (T_d) of the samples was assigned to the temperature corresponding to the 5% weight loss of the initial mass. TRIOS software (v5.1) (TA Instruments) was used to analyze the TGA curves.

Ion Exchange Capacity (IEC), Water Uptake (WU) and hydration number (λ)

Ion exchange capacity (IEC, meq g^{-1} dry polymer) of the synthesized polymers was analyzed by titration. Polymers and block copolymers in their acid form were dissolved or stirred at 50 °C in 1 M NaCl solution for 1 day and the released H^+ ions were back-titrated with 0.01 M NaOH in the presence of phenolphthalein as indicator.

The water uptake (W.U.) of the block copolymers was evaluated by immersion of the BCP membrane in deionized water. The samples, in the protonated form, were dried at 115 °C under vacuum for 24 h before determining the dry weight (W_{dry}). The dry membranes were then immersed in deionized water for 24 h at 25 °C before weighting the mass of the wet membrane (W_{wet}). The WU (%) was calculated according to **Equation S3**:

$$WU = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \qquad \text{(S3)}$$

The hydration number (λ), i.e. the number of water molecules per sulfonic group ($[H_2O]/[SO_3H]$), was obtained by the **Equation S4**:

$$\lambda = \frac{10 \times WU}{IEC \times 18} \qquad \text{(S4)}$$

Transmission Electron Microscopy (TEM)

The membrane morphology was also investigated via electron microscopy (TEM). Prior to imaging, the membranes were stained with Cs^+ ions by soaking the H-form membranes of the block copolymers in 1 M solution of CsCl. The solution was changed several times over 24 h before washing thoroughly with water and drying the sample at 115 °C under vacuum for at least 6 h. Fragments of the obtained films were embedded in epoxy resin (Epofix, Electron Microscopy Science) and subsequently sectioned at room temperature with a Leica Ultracut UCT-ultramicrotome equipped with a Diatome 35° diamond knife to a nominal thickness of approximately 80 nm. The sections were transferred to a Cu TEM grid and inspected with a Philips CM12 transmission electron microscope without further treatment at an acceleration voltage of 120 kV.

Small and Medium Angle X-ray Scattering (SAXS/MAXS)

SAXS and MAXS analysis was performed at the Multipurpose Instrument for Nanostructure Analysis (MINA) beamline at the University of Groningen. The diffractometer was equipped with Cu rotating anode (λ = 1.5413 Å) using a sample-to-detector distance of 3 m for SAXS and 27.6 cm (MAXS). The scattering patterns were collected using a Bruker Vantec2000 detector (SAXS) and a Bruker Vantec500 detector (MAXS). The scattering angle scale was calibrated using the known position of diffraction rings from a silver behenate standard sample. The scattering intensity curves are reported as a function of the modules of the scattering vector $q = 4\pi \sin\theta / \lambda$, with 2θ being the scattering angle and λ the wavelength of the X-rays. The samples were contained in sealed brass containers equipped with thin Mylar windows. For the humidified measurements, samples were equilibrated for one day or more. Background subtraction was performed for each sample in order to obtain the neat scattering signal from the samples.

Oxidative stability

BCP's membrane in the H-form previously dried at 105 °C under vacuum for 15 h were weighted and then immersed in Fenton's reagent (H_2O_2 3%, Fe^{2+} 2 ppm) for 1 h at 80 °C. The membranes were rinsed with deionized water and dried at 105 °C under vacuum for 15 h before being weighted again.

Electrochemical impedance spectroscopy (EIS)

Ion conductivity of the BCPs was measured by two-electrode through-plane AC electrochemical impedance spectroscopy using an SP300 Potentiostat (Bio-Logic ™) equipped with a controlled environment sample holder (CESH®, Bio-Logic™). The measurement was performed at 95% RH as a function of temperature from 30 to 90 °C with 15 °C steps, in the frequency range from 7 MHz to 10 Hz with an AC voltage amplitude of 50 mV against a 0 V bias DC. The temperature was controlled by the Intermediate Temperature System (ITS, Bio-Logic ™) with an accuracy of ± 1 °C. Inside the CESH, stacks of membrane slices of acidified polymers were placed between two gold electrodes and tightened by a screw in order to ensure optimum contact. The pellets were equilibrated in full-water vapour atmosphere for at least 24 h before being sealed inside the CESH in the presence of additional humidification elements and equilibrated at each temperature for 2 h before measuring the sample resistance.

The proton conductivity was calculated from the high-frequency intercept of the complex impedance with the real axis and the dimensions of the sample according to **Equation S5**:

$$\sigma = \frac{l}{R_b\, A} \tag{S5}$$

Where l is the thickness of the stack, R_b is the bulk resistance, and A active area of the electrodes

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