Electronic Supplementary Information (ESI)

Control of ion exchange capacity in block copolymer binders enables high hydroxide conductivity at low swelling and improves catalyst activity for AEM water electrolysis

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Materials and Methods

m-terphenyl (BLD Pharm, 99.5%), biphenyl (Carl Roth GmbH + Co. KG, 99%), *N*-methyl-4-piperidone (MePip, BLD Pharm, 98.27%), 2,2,2-trifluoroacetophenone (ABCR GmbH, 98%), dichloromethane (DCM, Fisher Scientific, 99%), trifluoroacetic acid (TFA, ABCR GmbH, 99.9%), trifluoromethanesulfonic acid (TFSA, ABCR GmbH, 99%), dimethyl sulfoxide (DMSO, Fisher Scientific, 99.9%), DMSO-d_6 (Deuteron GmbH, 99.8%), potassium chloride (Fisher Scientific, 99%), potassium hydroxide (Fisher Scientific, 85%), methyl iodide (MeI, Thermo Scientific, 99%), *N*,*N*-diisopropylethylamine (DIPEA, Carl Roth GmbH, 99%), ethyl acetate (Fisher Scientific), methanol (VWR Chemicals, 98.5%), acetone (VWR Chemicals, 99%), *N*,*N*-dimethylformamide (Fisher Scientific, 99.5%) and ammonium trifluoroacetate (Thermo Scientific, 98%) were all used as received. Nafion was obtained from Sigma-Aldrich.

Synthesis of poly(arylene piperidinium) block copolymers and subsequent quaternization

Polymers of the BCP series were synthesized by stepwise addition of monomer components according to the following procedure.

Synthesis of BCP_26. *N*-methyl-4-piperidone (0.53 g, 4.7 mmol) and biphenyl (0.75 g, 4.9 mmol) were added to a 100 ml round bottom flask equipped with a magnetic stirrer. Subsequently, DCM (2 mL) was added and the mixture was cooled to 0 °C under stirring. At this temperature, TFA (0.4 mL, 5.3 mmol) and TFSA (4.3 mL, 49 mmol) were added. The mixture was stirred at 0 °C for 3 hours. *m*-terphenyl (2.62 g, 11.4 mmol), 2,2,2-trifluoroacetophenone (2.58 g, 14.8 mmol) dissolved in DCM (6 mL) and TFSA (10.1 mL, 114 mmol) were added at 0 °C. The mixture was stirred at 0 °C until the viscosity of the reaction mixture prevented magnetic stirring. The mixture was poured into an excess of methanol at 0 °C, resulting in a white fibrous solid which was filtered and washed with water until the filtrate was neutral. The product gave quantitative yield after drying under ambient conditions. Further purification of the polymer was conducted via Soxhlet extraction with methanol for 3 days and acetone for one day. Subsequently, this precursor polymer was directly methylated by the following procedure. After dissolving the polymer in a mixture of DMSO (200 mL), DIPEA (4.0 mL, 23 mmol) and MeI (1.5 mL, 24 mmol) were added and the mixture was stirred one day at room temperature protected from light. After that, the solution was poured into excess ethyl acetate and the polymer precipitated as colorless powder. The solids were collected by filtration and washed repeatedly with ethyl acetate and subsequently with water to remove organic solvents and residual *N*,*N*-diisopropylethyl ammonium salts. Afterwards the quaternized polymer was dried under ambient conditions to give BCP_26 (3.20 g, yield: 47% in respect to the starting materials).

Synthesis of BCP_55. *N*-methyl-4-piperidone (1.75 g, 15.5 mmol) and biphenyl (2.5 g, 16.2 mmol) were added to a 100 ml round bottom flask equipped with magnetic stirrer. Subsequently, DCM (6 mL) was added and the mixture was cooled to 0 °C under stirring. At this temperature, TFA (1.25 mL, 16.4 mmol) and TFSA (14.5 mL, 164 mmol) were added. The mixture was stirred at 0 °C for 3 hours. *m*-terphenyl (1.40 g, 6.1 mmol), 2,2,2-trifluoroacetophenone (2.38 g, 13.7 mmol) dissolved in DCM (2.7 mL) and TFSA (5.4 mL, 61 mmol) were added at 0 °C. The mixture was stirred at 0 °C until the viscosity of the reaction mixture prevented magnetic stirring. The mixture was poured into an excess of methanol at 0 °C, resulting in a white fibrous solid which was filtered and washed with water until the filtrate was neutral. The product gave quantitative yield after drying under ambient conditions. Further purification of the polymer was conducted via Soxhlet extraction with methanol for 3 days and acetone for one day. Subsequently, this precursor polymer was directly methylated by the following procedure. After dissolving the polymer in a mixture of DMSO (200 mL), DIPEA (14.0 mL, 80 mmol) and MeI (4.8 mL, 77 mmol) were added and the mixture was stirred one day at room temperature protected from light. After that, the solution was poured into excess ethyl acetate and the polymer precipitated as colorless powder. The solids were collected by filtration and washed repeatedly with ethyl acetate and subsequently with water to remove organic solvents and residual *N*,*N*-diisopropylethyl ammonium salts. Afterwards the quaternized polymer was dried under ambient conditions to give BCP_55 (5.10 g, yield: 52% in respect to the starting materials).

Synthesis of BCP_79. *N*-methyl-4-piperidone (2.79 g, 24.7 mmol) and biphenyl (4.00 g, 26.0 mmol) were added to a 100 ml round bottom flask equipped with a magnetic stirrer. Subsequently, DCM (10 mL) was added and the mixture was cooled to 0 °C under stirring. At this temperature, TFA (2.0 mL, 26.3 mmol) and TFSA (23.0 mL, 261 mmol) were added. The mixture was stirred at 0 °C for 3 hours. *m*-terphenyl (0.31 g, 1.3 mmol), 2,2,2-trifluoroacetophenone (1.91 g, 11.0 mmol) dissolved in DCM (0.6 mL) and TFSA (1.2 mL, 13.6 mmol) were added at 0 °C. The mixture was stirred at 0 °C until the viscosity of the reaction mixture prevented magnetic stirring. The mixture was poured into an excess of methanol at 0 °C, resulting in a white fibrous solid which was filtered and washed with water until the filtrate was neutral. The product gave quantitative yield after drying under ambient conditions. Further purification of the polymer was conducted via Soxhlet extraction with methanol for 3 days and acetone for one day. Subsequently, this precursor polymer was directly methylated by the following procedure. After dissolving the polymer in a mixture of DMSO (200 mL), DIPEA (22.0 mL, 127 mmol) and MeI (7.7 mL, 124 mmol) were added and the mixture was stirred one day at room temperature protected from light. After that, the solution was poured into excess ethyl acetate and the polymer precipitated as colorless powder. The solids were collected by filtration and washed repeatedly with ethyl acetate and subsequently with water to remove organic solvents and residual *N*,*N*-diisopropylethyl ammonium salts. Afterwards the quaternized polymer was dried under ambient conditions to give BCP_79 (3.40 g, yield: 29% in respect to the starting materials).

Synthesis of statistical poly(arylene piperidinium) copolymers and subsequent quaternization

Synthesis of stat_22. *N*-methyl-4-piperidone (0.72 g, 6.4 mmol), biphenyl (0.75 g, 4.9 mmol), *m*-terphenyl (1.7 g, 7.4 mmol) and 2,2,2-trifluoroacetophenone (1.65 g, 9.5 mmol) were added to a 100 ml round bottom flask equipped with a magnetic stirrer. Subsequently, DCM (13 mL) was added and the mixture was cooled to 0 °C under stirring. At this temperature, TFA (0.6 mL, 7.9 mmol) and TFSA (10.8 mL, 122 mmol) were added. The mixture was stirred at 0 °C until the viscosity of the reaction mixture prevented magnetic stirring. The mixture was poured into an excess of methanol at

0 °C, resulting in a white fibrous solid which was filtered and washed with water until the filtrate was neutral. The product gave quantitative yield after drying under ambient conditions. Further purification of the polymer was conducted via soxhlet-extraction with methanol for 3 days and acetone for one day. Subsequently, this precursor-polymer was directly methylated by the following procedure. After dissolving the polymer in a mixture of DMSO (200 mL), DIPEA (5.5 mL, 32 mmol) and MeI (2.0 mL, 32 mmol) were added and the mixture was stirred one day at room temperature protected from light. After that, the solution was poured into excess ethyl acetate and the polymer precipitated as colorless powder. The solid was filtered off and washed repeatedly with ethyl acetate and subsequently with water to remove organic solvents and residual *N*,*N*-diisopropylethyl ammonium salts. Afterwards the quaternized polymer was dried under ambient conditions to give stat_22 (3.40 g, yield: 62% in respect to the starting materials).

Synthesis of stat_46. *N*-methyl-4-piperidone (1.42 g, 12.6 mmol), biphenyl (1.50 g, 9.7 mmol), *m*-terphenyl (1,8 g, 7.8 mmol) and 2,2,2-trifluoroacetophenone (1.79 g, 10.3 mmol) were added to a 100 ml round bottom flask equipped with a magnetic stirrer. Subsequently, DCM (8.5 mL) was added and the mixture was cooled to 0 °C under stirring. At this temperature, TFA (1.2 mL, 17.1 mmol) and TFSA (15.5 mL, 176 mmol) were added. The mixture was stirred at 0 °C until the viscosity of the reaction mixture prevented magnetic stirring. The mixture was poured into an excess of methanol at 0 °C, resulting in a white fibrous solid which was filtered and washed with water until the filtrate was neutral. The product gave quantitative yield after drying under ambient conditions. Further purification of the polymer was conducted via soxhlet-extraction with methanol for 3 days and acetone for one day. Subsequently, this precursor-polymer was directly methylated by the following procedure. After dissolving the polymer in a mixture of DMSO (200 mL), DIPEA (11 mL, 64 mmol) and MeI (4.0 mL, 64 mmol) were added and the mixture was stirred one day at room temperature protected from light. After that, the solution was poured into excess ethyl acetate and the polymer precipitated as colorless powder. The solid was filtered off and washed repeatedly with ethyl acetate and subsequently with water to remove organic solvents and residual *N*,*N*-diisopropylethyl ammonium salts. Afterwards the quaternized polymer was dried under ambient conditions to give stat_22 (5.6 g, yield: 71% in respect to the starting materials).

Synthesis of stat_73. *N*-methyl-4-piperidone (1.43 g, 12.7 mmol), biphenyl (1.50 g, 9.7 mmol), *m*-terphenyl (0.56 g, 2.4 mmol) and 2,2,2-trifluoroacetophenone (0.55 g, 3.2 mmol) were added to a 100 ml round bottom flask equipped with a magnetic stirrer. Subsequently, DCM (8.5 mL) was added and the mixture was cooled to 0 °C under stirring. At this temperature, TFA (1.3 mL, 17.1 mmol) and TFSA (10.8 mL, 122 mmol) were added. The mixture was stirred at 0 °C until the viscosity of the reaction mixture prevented magnetic stirring. The mixture was poured into an excess of methanol at 0 °C, resulting in a white fibrous solid which was filtered and washed with water until the filtrate was neutral. The product gave quantitative yield after drying under ambient conditions. Further purification of the polymer was conducted via soxhlet-extraction with methanol for 3 days and acetone for one day. Subsequently, this precursor-polymer was directly methylated by the following procedure. After dissolving the polymer in a mixture of DMSO (200 mL), DIPEA (11 mL, 64 mmol) and MeI (4.0 mL, 64 mmol) were added and the mixture was stirred one day at room temperature protected from light.

After that, the solution was poured into excess ethyl acetate and the polymer precipitated as colorless powder. The solid was filtered off and washed repeatedly with ethyl acetate and subsequently with water to remove organic solvents and residual *N*,*N*-diisopropylethyl ammonium salts. Afterwards the quaternized polymer was dried under ambient conditions to give stat_73 (4.0 g, yield: 72% in respect to the starting materials).

Synthesis of NiFe as layered double hydroxide (LDH) with molar nickel

Nickel : iron ratio of 5 : 1 was prepared with a microwave assisted one-pot synthesis is conducted using 1200 µL of 0.6 M $Ni(OAc)_2*4H_2O$ and 240 µL of 0.6 M $Fe(NO_3)_3*9\ H_2O$ precursor solution, added to 6 mL DMF and stirred subsequently. 4 mL DMF and 8 mL ultrapure water were added. The resulting solution was transferred to a microwave and reacted with constant stirring for 60 min at 120 °C and 160 °C for 30 min. The product was collected, washed with ethanol and Mili-Q and finally dried in a freeze dryer. NiFe-LDH resulted in a Ni/Fe ratio of 3.25 ± 0.07.

Molecular characterization

NMR spectroscopy. ^1H NMR spectra of the polymers were recorded in DMSO-d_6 (δ ^1H = 2.50 ppm) or $CDCl_3$ (δ ^1H = 7.26 ppm) solutions containing a few drops of trifluoroacetic acid, to protonate any tertiary amines as well as causing a downfield shift of the water signal, using an Avance NEO 600 FT Spectrometer (600 MHz).

Size Exclusion Chromatography (SEC). Molecular weights were measured on a Shimadzu system comprising a 10 µm PSS GRAM guard column and three PSS GRAM columns with pore sizes ranging from 30 to 10^3 Å, connected in series with a RID20A refractive index detector and an SPD-40V UV-vis detector (Shimadzu). Calibration was done with polystyrene standards with peak molecular weights ranging from 682 to 2520000 $g \cdot mol^{-1}$. A 0.1M solution of ammonium trifluoroacetate in DMF was used as eluent at 70 °C with a flow rate of 1.0 $mL \cdot min^{-1}$.

MALDI-ToF mass spectroscopy. Matrix-assisted laser desorption/ionization spectra were taken using BRUKER autoflex MALDI-TOF instrument (smartbeam-II, 355 nm) in positive ion and linear operating modes. Samples were prepared on a standard sample plate (Bruker "MTP 384 target plate polished steel BC"). Sample spot preparation was as follows. 10 µL of trans2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB) matrix solution (20 mg/mL in chloroform), 0.5 µL of sodium trifluoroacetate (NaTFA, 0.1 M in THF) solution, and 1.5 µL of polymer sample (4 mg mL^{-1} in chloroform or in THF depending on solubility) were mixed. Then 1 µL of this matrix/salt/polymer solution mixture was spotted onto a MALDI sample plate and air-dried before analysis. The spectra were calibrated externally using poly-hexylthiophene with H-and Br- end group (H-(P3HT)-Br) as a standard.

Membrane preparation and characterization

Membranes of ~ 100 µm thickness were prepared by doctor-blading DMSO solutions (30 *wt*-%) onto flat glass substrates. After drying the wet films at 60 °C for 20 hours under ambient pressure, they were removed from the substrate by immersion into water. After treatment with 1 M potassium chloride solution and extensive washing with deionized (DI) water at elevated temperature (60 °C) the chloride form of the polymer was obtained, which was kept immersed in DI water until further characterization.

Water uptake (WU) and swelling ratio (SR). The water uptake of the membrane, in hydroxide form, was measured under immersed conditions. Membrane pieces, of each sample, in chloride form were ion-exchanged to hydroxide form by immersion in carbon dioxide free 1 M sodium hydroxide solution during 3 d at room temperature. Then, the membranes were first extensively washed with and then stored in degassed deionized water. After 1 d of storage at room temperature, the membranes were removed from the water, gently wiped with tissue paper, and weighed. This was then repeated after 1 d of storage at 40, 60, and 80 °C, respectively. Subsequently, the membranes were ion-exchanged to chloride form by immersion in an aqueous 1 M KCl solution during 3 d at 60 °C, after which they were extensively washed with deionized water and dried under vacuum at 60 °C during 2 d. The dry membranes, in chloride form, were weighed, and their weight in hydroxide form was calculated by multiplying the noted weights with the ratio of the molar mass of the repeating unit in hydroxide form divided by the molar mass in chloride form. The water uptake was calculated as the mass increase of the wet membranes divided by the dry weight. From these values, the hydration number, defined as the molar concentration of water divided by thy concentration of hydroxide ions, was calculated by dividing the water uptake with the product of the theoretical ion-exchange capacity (IEC, in hydroxide form) times the molar mass of water.
Additionally, the width, length and thickness of the dry membranes, in chloride form, were determined and the in-plane swelling ratio was calculated by the areal increase divided by the dry membrane area; the through-plane swelling ratio was calculated by the thickness increase divided by the dry membrane thickness.

Ion conductivity (σ). Membrane samples, in hydroxide form, were clamped into a four-electrode in-plane conductivity cell (BekkTech BT-110, Scribner) immersed in water which was constantly de-aerated with argon, as previously reported.[1–3] To remove all carbonates from the membranes, a current of 0.1 mA was applied over the inner electrodes. Every 30 min, electrochemical purging was stopped, and several linear voltage sweeps were conducted over the range of 100 mV to −100 mV with a scan rate of 50 mV s^{-1} until the resistance reached a constant value. The membrane resistance (R) was measured at 25, 40, 60 and 80 °C by linear sweep voltammetry over the range of 100 mV to −100 mV with a scan rate of 100 mV s^{-1}.

Ion conductivity was determined by the following equation:

$$\sigma = L\cdot(R\cdot W\cdot T)^{-1}$$

where L is distance between the voltage-sensing electrodes (set at 0.425 cm), W is the width of membrane, and T is membrane thickness after immersing in deionized water at room temperature.

Alkaline stability. Membranes in hydroxide form were immersed into 2 M NaOH for 29 days at 90 °C. ^{1}H NMR spectroscopy was used to evaluate the extent of degradation. The membranes were first taken out from the NaOH solution and thoroughly washed with DI water. Then they were ion exchanged to chloride form using 1 M KCl solution and dried for 24 h under vacuum at 60 °C.

Small and wide angle X-ray scattering

WAXS and SAXS patterns were measured with a Retro-F laboratory setup from SAXSLAB (Copenhagen, Denmark) equipped with a microfocus X-ray source from AXO (Dresden, Germany) and an AXO multilayer X-ray optics (ASTIX) as monochromator for Cu Kα radiation (λ = 0.15418 nm). A PILATUS R 300K detector from DECTRIS (Daettwil, Switzerland) was used to record 2D scattering patterns. WAXS and SAXS measurements on dry and wet membranes were performed in transmission geometry under vacuum at room temperature with a sample-detector distance of about 90 mm for WAXS and 440 mm for SAXS. Dry membranes were measured as received. For WAXS and SAXS measurements on wet membranes, thin strips of membranes were cut and placed in standard borosilicate glass capillaries from Hilgenberg (Malsfeld, Germany) with an outer diameter of 1 mm and a wall thickness of 0.01 mm. Water was added to the capillaries to ensure that the membranes were wet, and the capillaries were then sealed vacuum-tight. After the measurements, the capillaries were carefully inspected to ensure that the water was still in contact with the membranes, proving that the capillaries remained vacuum-tight during the measurements. The measured scattering intensities were corrected for absorption in all cases, for both dry and wet samples.

Atomic force microscopy (AFM)

Atomic force microscopy was performed with a NanoWizard II instrument (JPK Instruments AG, Berlin, Germany) using Si cantilevers (Pointprobe-Plus PPP-NCST, NanoWorld AG, Neuchâtel, Switzerland). Samples were prepared from DMSO solution by a procedure similar to doctor blading at 60°C. An approximately 1 x 1 mm^2 piece of a membrane prepared by doctor blading was placed on a polished Si substrate held at 60°C. Using a single-hair brush, a small drop of DMSO was deposited near the piece of polymer. Then, using gentle strokes, some of the DMSO was spread over the polymer, partially spreading the BCP-DMSO solution on the Si substrate. After evaporation of the DMSO, the substrate was cooled to room temperature. This results in tiny BCP droplets and BCP strokes with a thickness ranging from 20 to 100 nm that were imaged with AFM in intermittent contact mode under ambient conditions.

Rotating disk electrode (RDE) experiments

For electrocatalytic activity testing with rotating disk electrode (RDE), a NiFe-LDH suspension was prepared from 4 mg NiFe-LDH, 768 µL de-ionised water, 200 µL *i*-propanol and 32 µL 5 wt. % binder solution. 10 µL of the resulting dispersion was pipetted on the glassy carbon electrode. Electrocatalytic performance was evaluated in N_2-saturated 0.1 M KOH at 1600 rpm using a Biologic SP-200 potentiostat operating in a three-electrode setup with a platinum counter electrode (CE) and a reversible hydrogen (RHE) reference electrode. Reported CVs for evaluation of the electrochemical activity were iR- and capacity-corrected. The reported overpotentials necessary to reach a current density of 10 mA cm^{-2} (OER) are the average of three measurements. Stability measurements of the multi-component system were conducted with the same setup. Here, cycling experiments with 2000 CVs between 1.23 V vs RHE and 1.63 V vs RHE were conducted to periodically evaluate the OER performance.

Preparation of anode catalyst inks

NiFe-LDH (400 mg) was dispersed in a mixture of isopropanol and water (2.0 g, 1:1). After the addition of the previously prepared ionomer solution (0.5 g, 7 wt% PAP (eg. BCP26) in DMSO). The ionomer content in solids was 8%. Each ink was mixed for 2 days on a roller mixer (IKA, Roller 10) using ZrO_2 grinding balls (Retsch 22.455.0009) before bar coating.
For the PiperION-A reference, NiFe-LDH (400 mg) was dispersed in a mixture of isopropanol and water (1.4 g, 1:1), later adding ethanol (0.55 g), and the PiperION-A ionomer solution (0.7 g, 5 wt% in Ethanol) and then treated as described above.

Preparation of catalyst-coated membranes[4]

After attaching a PiperION 40 µm membrane (5 cm x 11cm) carefully to a vacuum table, 800 µL of the anode ink was distributed with a bar coater (Thierry, PG-032-150), using a wet film thickness of 150 µm and a coating speed of 50 mm/s. The catalyst loading measured with an X-ray fluorescence microscope (µXRF, Bruker, M4 Tornado) was determined to be 1.1±0.2 mg_{NiFe}/cm^2.

Preparation of cathode GDEs

Pt/C 50 wt% (300 mg, Umicore Elyst Pt50 0550) was dispersed in water (0.6 g) and ethanol (0.4 g). After adding an ionomer solution (1.0 g, 5 wt% PiperION-A in ethanol), the ink was mixed on a roll mixer with ZrO_2 grinding balls for 2 days. Using bar coating, the ink was casted on a Freudenberg H24C5 GDL with using a bar with 80 µm wet film thickness a coating speed of 80 mm/s. The average Pt-loading was determined with XRF to be 0.5±0.1 mg_{Pt}/cm^2.

Single cell testing

AEMWE single cell measurements were performed according to previously published work by Koch *et al.*[4] unless otherwise noted. Briefly, MEAs were immersed in 1 M KOH for 24 h to perform ion-exchange to the hydroxide form. Nickel fiber felt (Bekaert, 200 µm) and carbon paper (H24C5, Freudenberg) were used as transport layers on the anode and cathode side, respectively. Using a custom-built cell fixture[5] and AEMWE test bench, the MEAs (5 cm²) were measured in 1 M KOH at the indicated temperatures (60 °C and 80 °C). The active area of the anode and cathode was 5 cm². The electrolyte flow rate was set to 40 ml/min using a peristaltic pump and a bath thermostat. A BioLogic VSP-300 potentiostat with two 10 A/5 V boosters was employed to measure polarization curves and electrochemical impedance spectroscopy (to extract the high-frequency resistance (HFR)). The polarization curves were measured holding each current for 40 s plus 30 s of GEIS measurement. The amplitude of the GEIS was 5% of the current but not exceeding 50 mA/cm^2, measured in a frequency range of 500 kHz to 100 Hz. In the region of 0 - 100 mA/cm^2, 30 points were measured using step increments of 1 mA/cm^2 from 0-20 mA/cm^2 and 10 mA/cm^2 increments up to 100 mA/cm^2. Up to 400 mA/cm^2, steps of 50 mA/cm^2 were used, proceeding with 100 mA/cm^2 step size up to 3800 mA/cm^2. For a break-in of the cell, a polarization curve as described above and additional GEIS at currents from 100, 225, 500 and 1000 mA/cm^2 were measured with 5 % amplitude from 100 kHz to 100 mHz. After using this characterization as break-in, a second polarization curve was measured that was used for evaluation.

Additional Figures

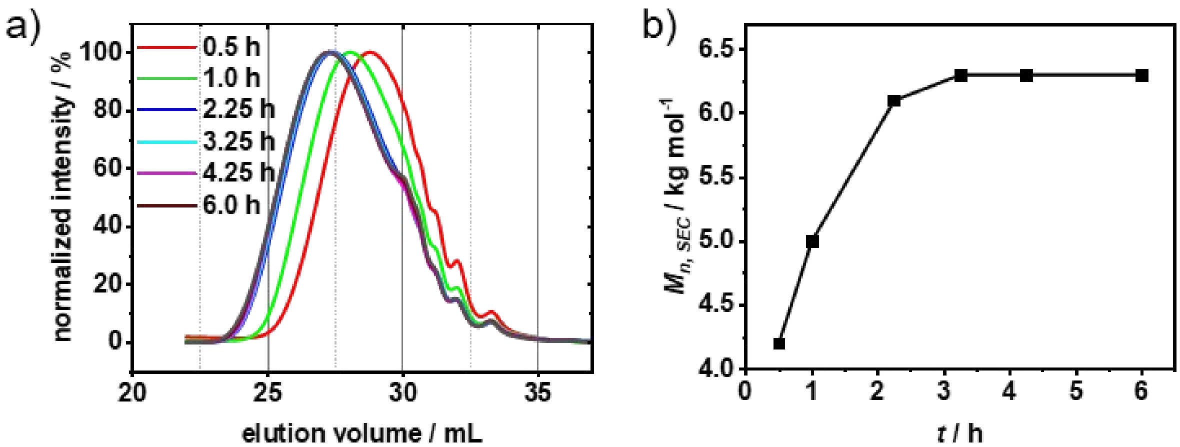

Figure S1. a) Time-dependent SEC curves of the products of the polyhydroxyalkylation reaction between biphenyl and N-methyl piperidone (0.95 equivalents) at 0°C. Partially resolved oligomers are seen at the high elution volume onset. b) Values of $M_{n,SEC}$ as a function of time obtained after calibration with polystyrene standards. The deviation of these values from those mentioned in the manuscript (4.1-4.5 kg/mol) is due to different monomer batches used.

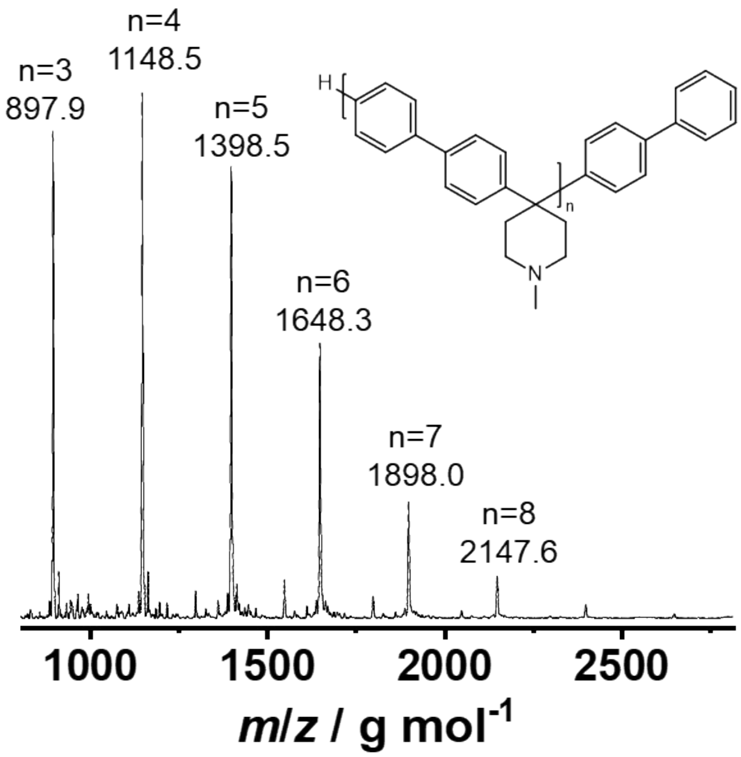

Figure S2. MALDI-ToF mass spectrum of hydrophilic starting block. M+H$^+$ peak series of BP end-capped PBP oligomers.

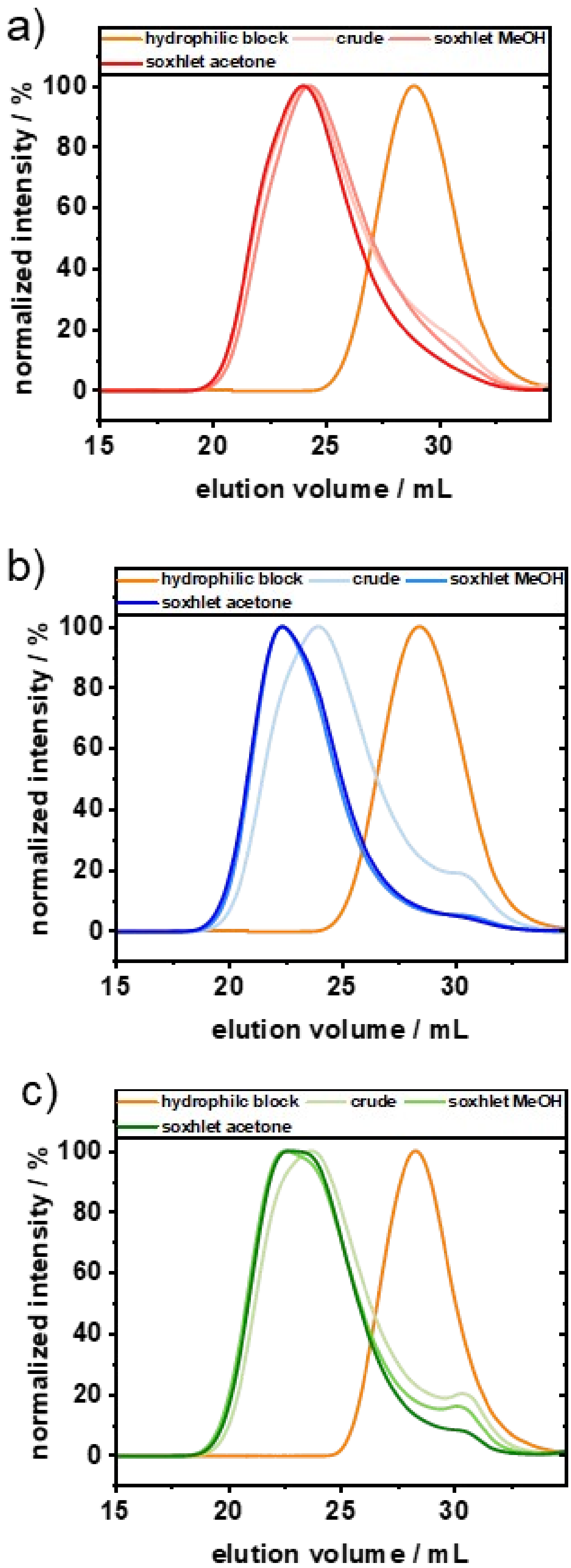

Figure S3. SEC elution volume curves of final block copolymers compared with their corresponding hydrophilic starting blocks, as well as and as-prepared materials: BCP_26 (a), BCP_55 (b), BCP_79 (c).

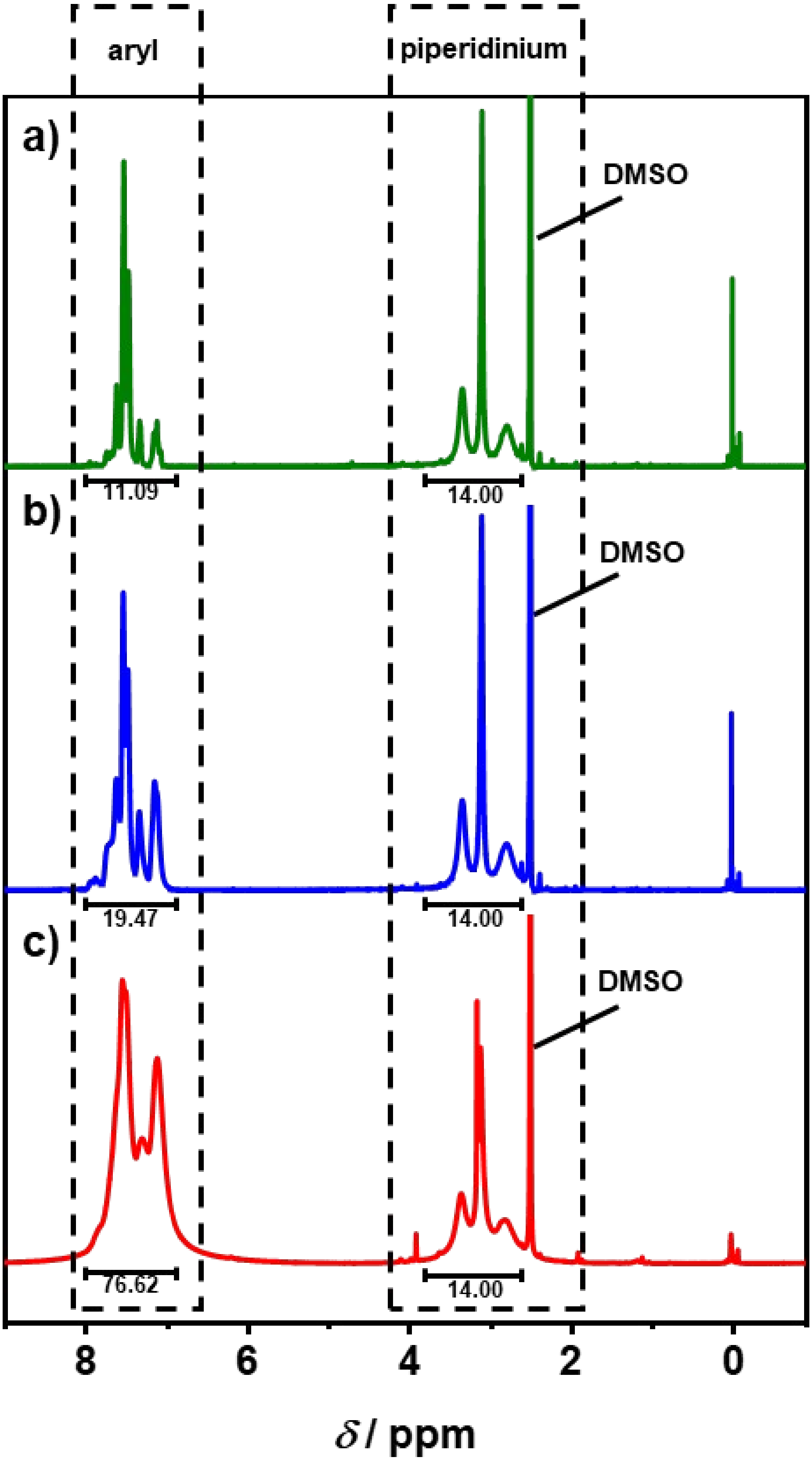

Figure S4. ^{1}H NMR spectra of block copolymers: a) BCP_79, b) BCP_55, c) BCP_26.

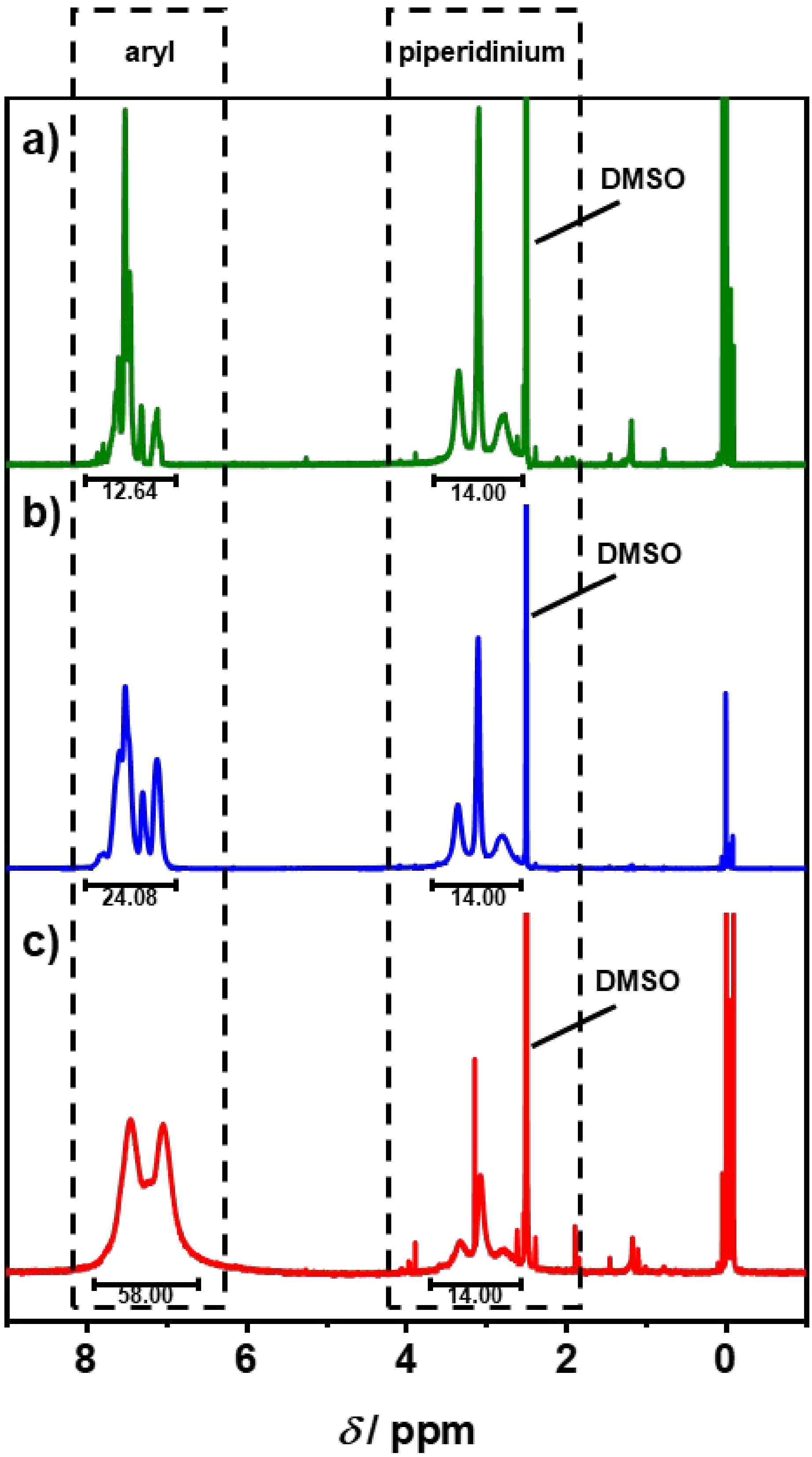

Figure S5. ^{1}H NMR spectra of statistical copolymers: a) stat_73, b) stat_46, c) stat_22.

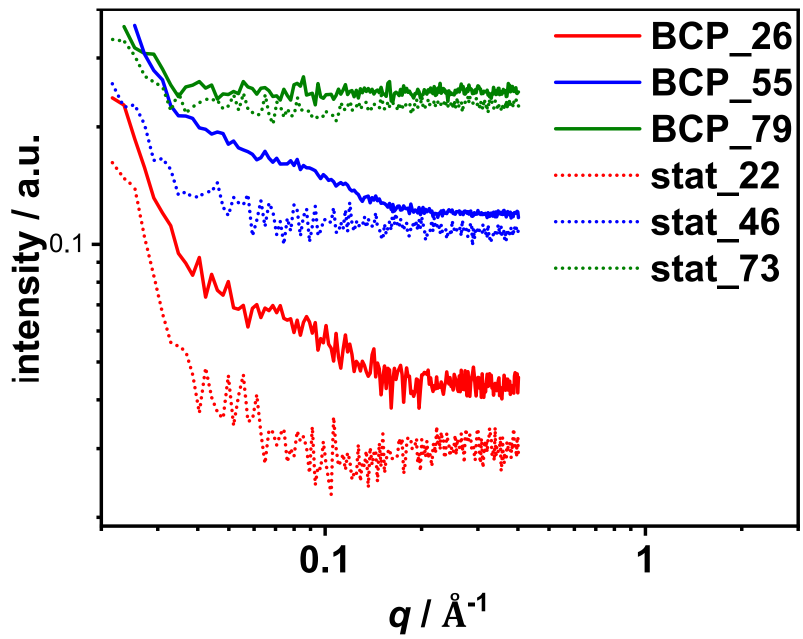

Figure S6. Double log plot of the SAXS curves of dry BCP and stat samples showing increased intensity of BCP_26 and BCP_55 in the 0.03 Å^{-1} < q < 0.2 Å^{-1} region.

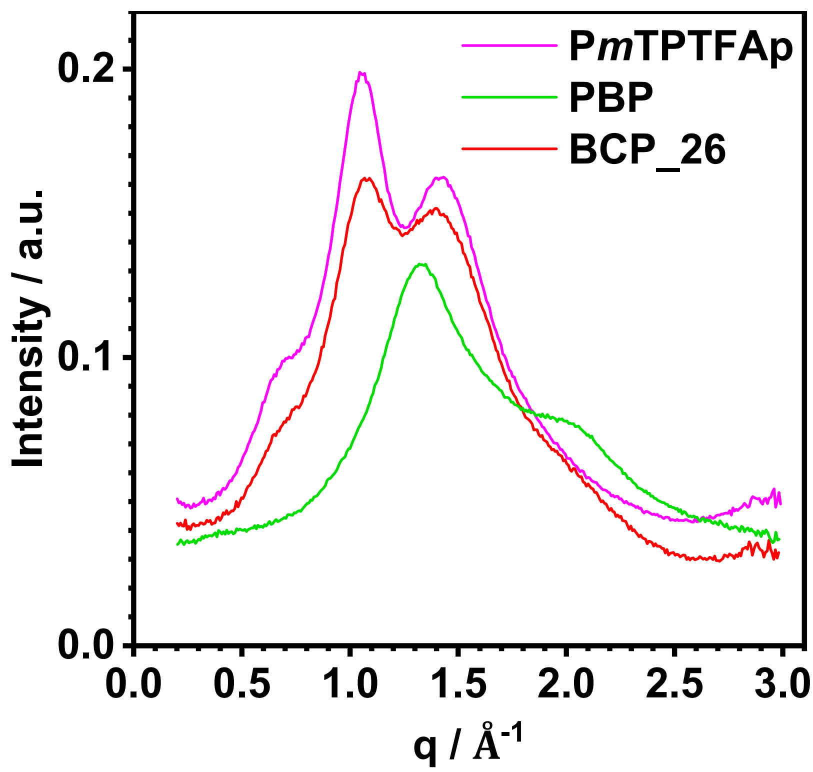

Figure S7. WAXS profiles of the homopolymers P*m*TPTFAp and PBP in comparison to BCP_26.

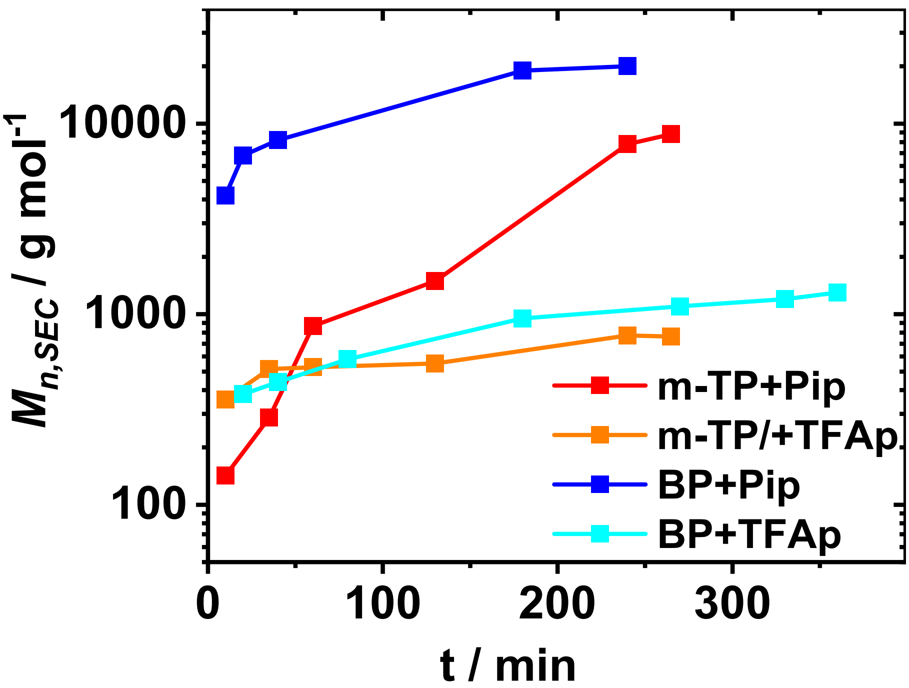

Figure S8. Number-average molar mass as function of time for polyhydroxyalkylations with different monomer combinations monitored via SEC. Values for $M_{n,SEC}$ were obtained after calibration with polystyrene standards.

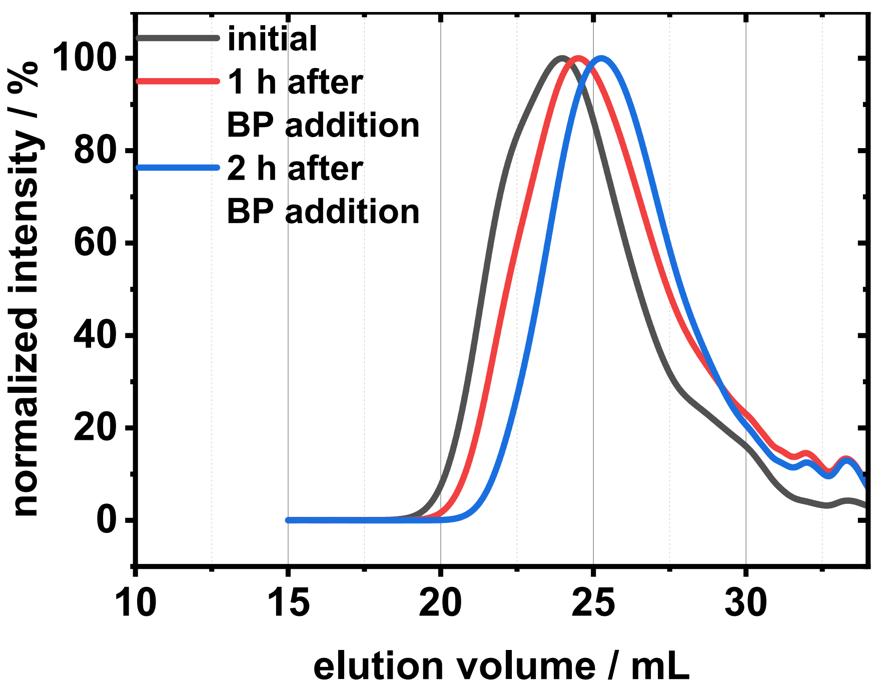

Figure S9. Effect of adding excessive BP during a polyhydroxyalkylation of BP and Pip.

Table S1. Activation energy (E_a) values for ionic transport of the investigated polymers.

Polymer	E_a / kJ mol^{-1}
BCP_79	10.40
stat_73	10.45
BCP_55	14.23
stat_46	13.00
BCP_26	11.36
stat_ 22	15.90

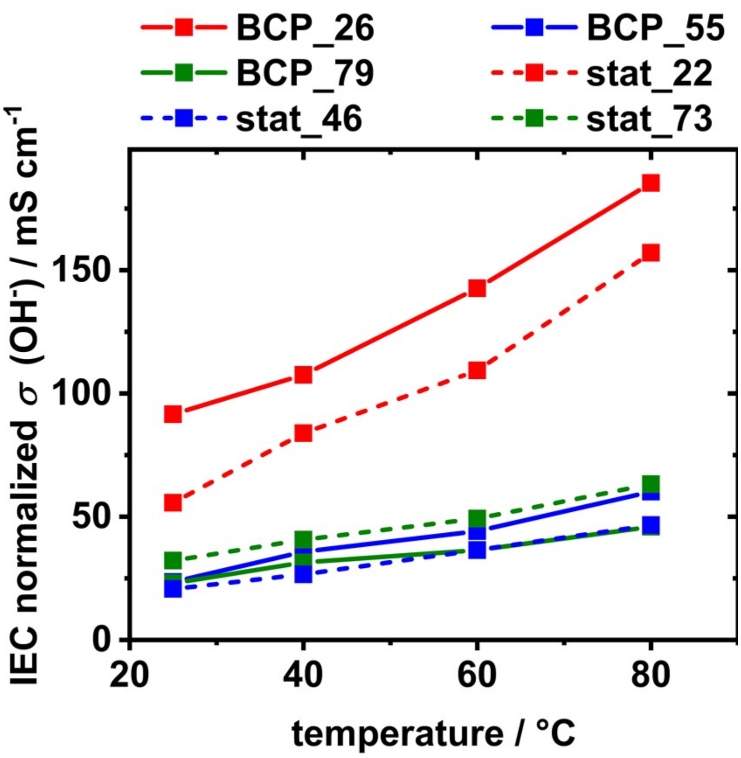

Figure S10. IEC normalized hydroxide conductivity of the investigated polymers depending on the temperature.

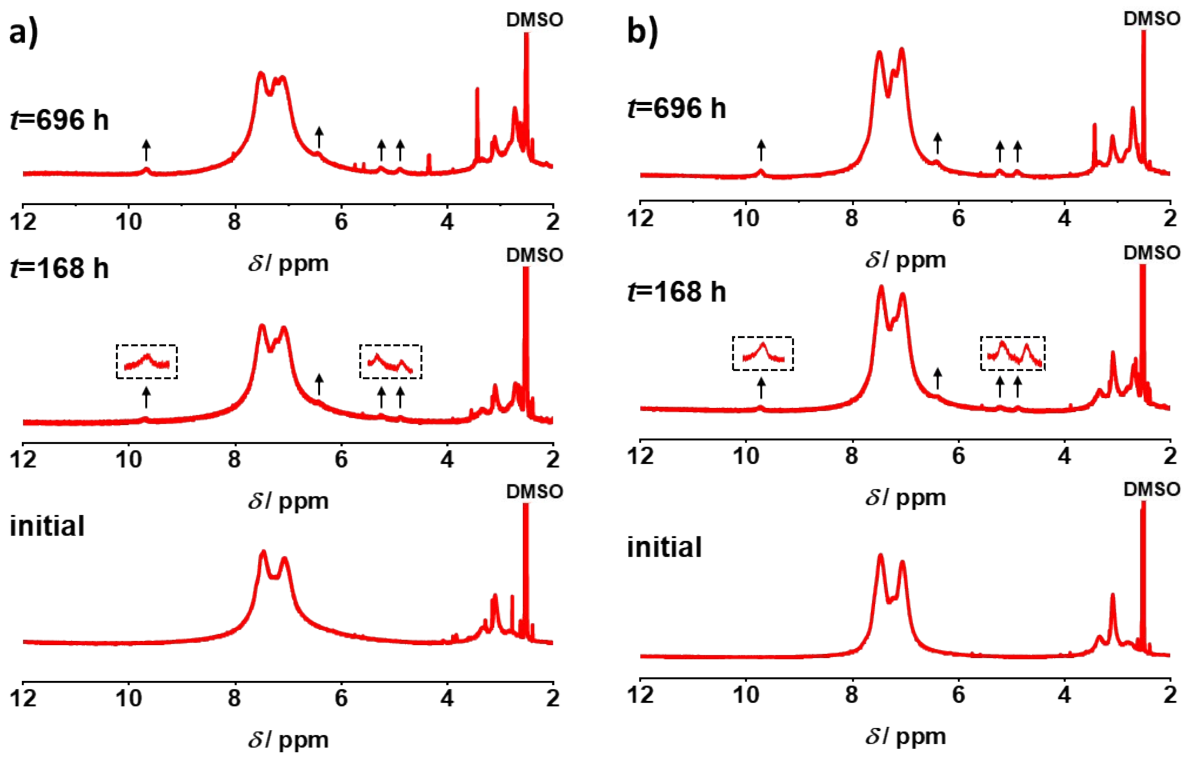

Figure S11. [1]H NMR spectra of a) BCP_26 and b) stat_22 after alkaline treatment in 2 M NaOH at 90 °C.

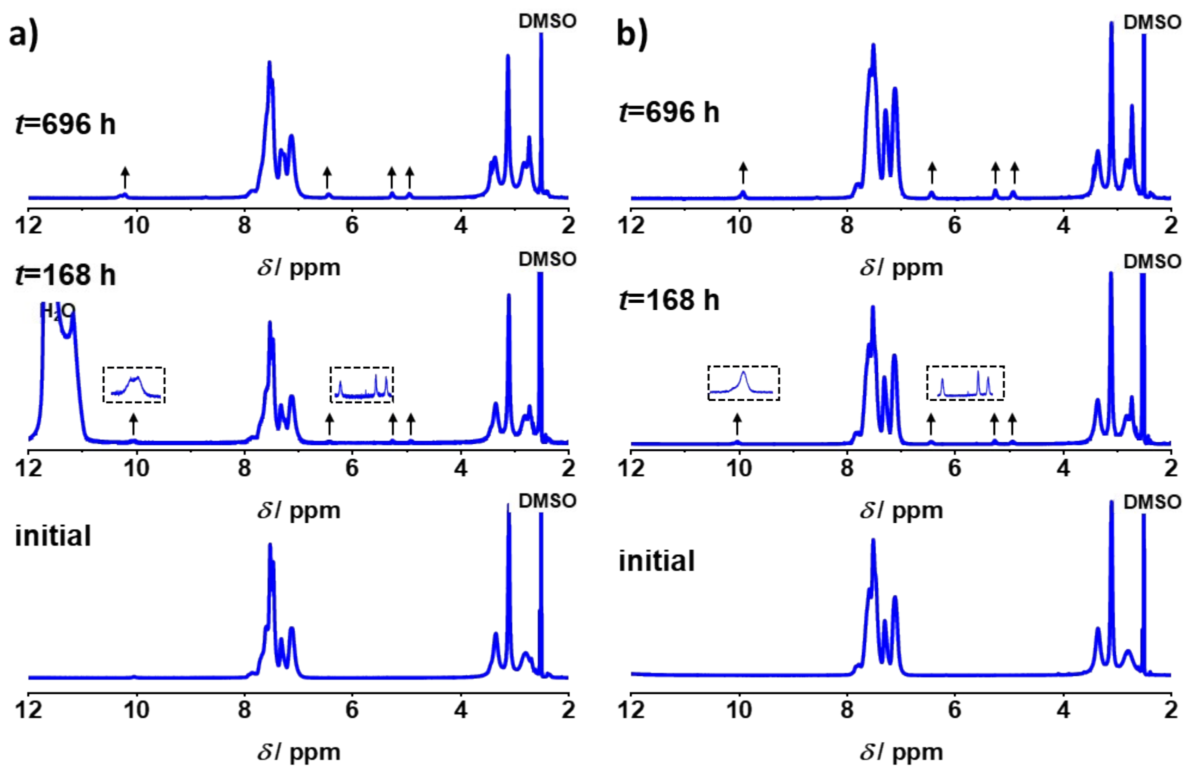

Figure S12. [1]H NMR spectra of a) BCP_55 and b) stat_46 after alkaline treatment in 2 M NaOH at 90 °C.

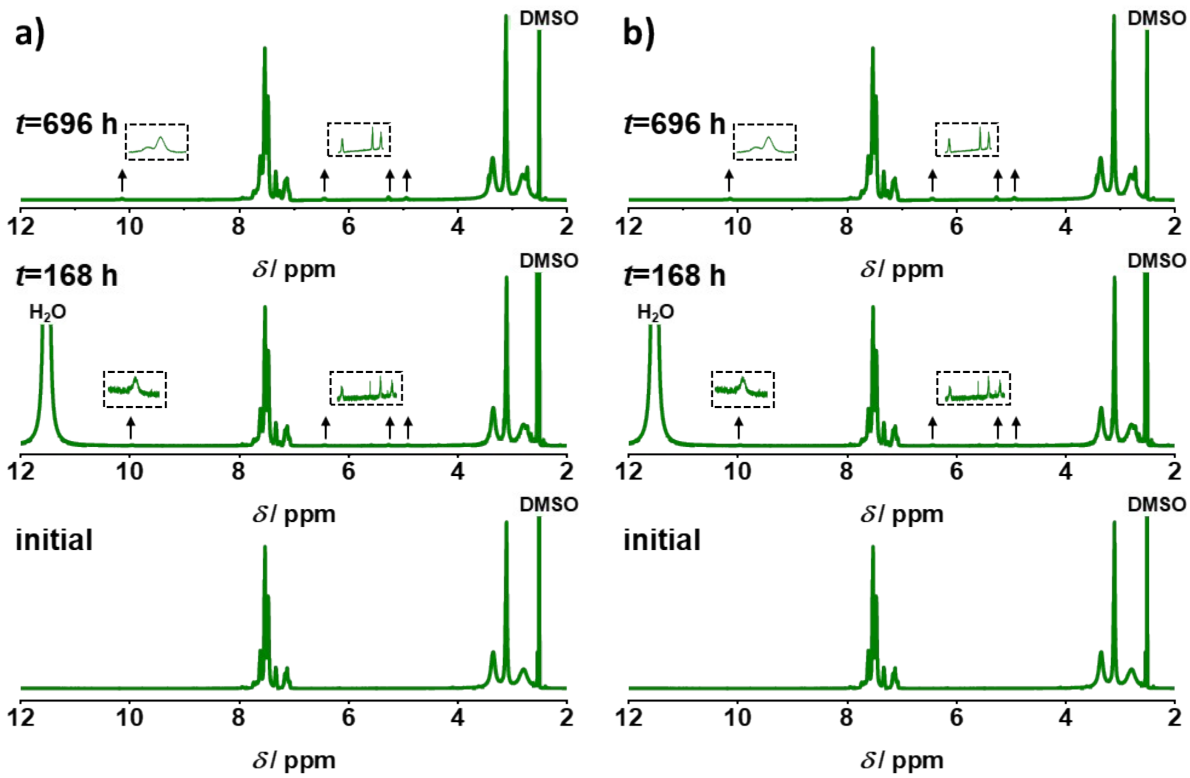

Figure S13. [1]H NMR spectra of a) BCP_79 and b) stat_73 after alkaline treatment in 2 M NaOH at 90 °C.

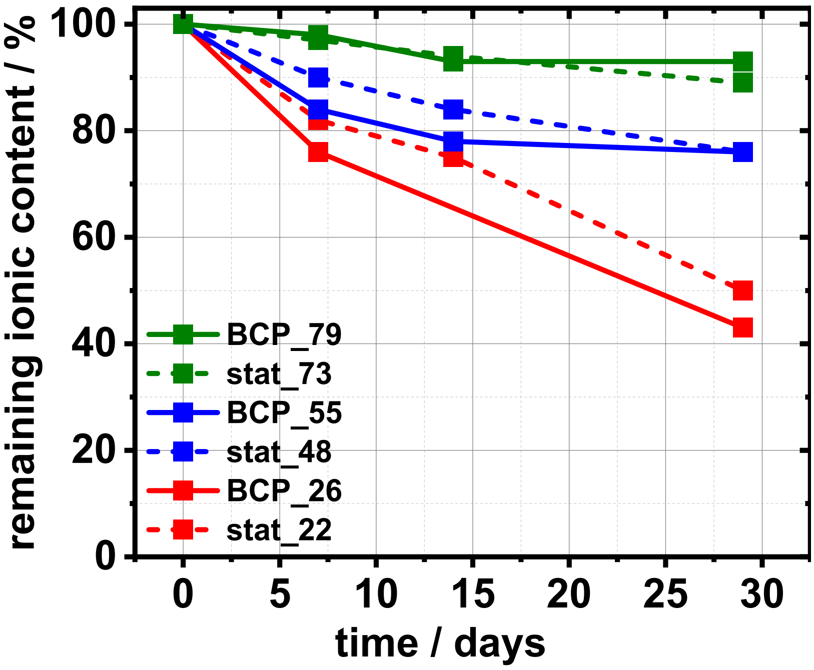

Figure S14. Degradation of BCP and statistical copolymer ionomers under alkaline conditions (2 M NaOH at 90 °C) as a function of time.

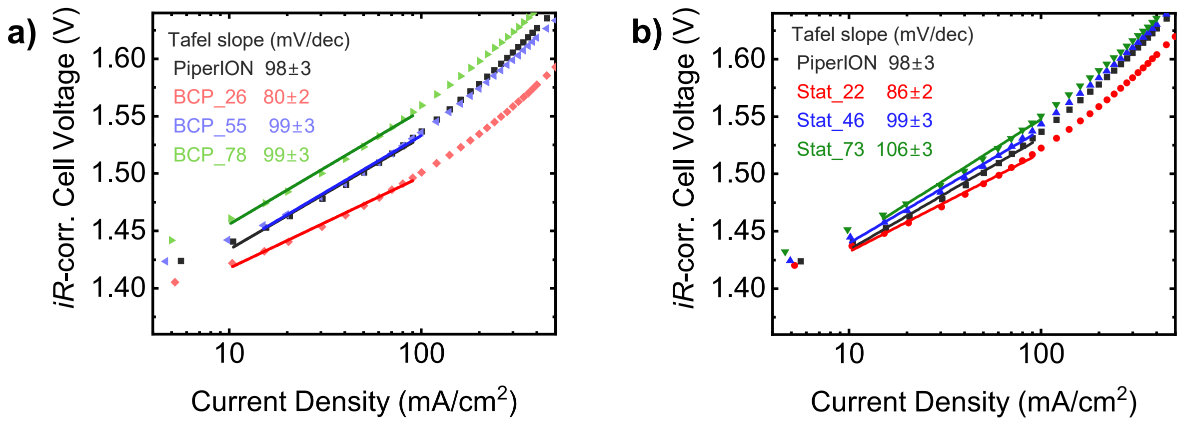

Figure S15. Tafel plots of the *iR*-corrected polarization curves from Fig. 7. showing the Tafel slopes of a) BCP_x and b) stat_x in the range of 10-100 mA cm^{-2}. Tested in 1.0 M KOH at 60 °C, NiFe-LDH Anode and Pt/C cathode.

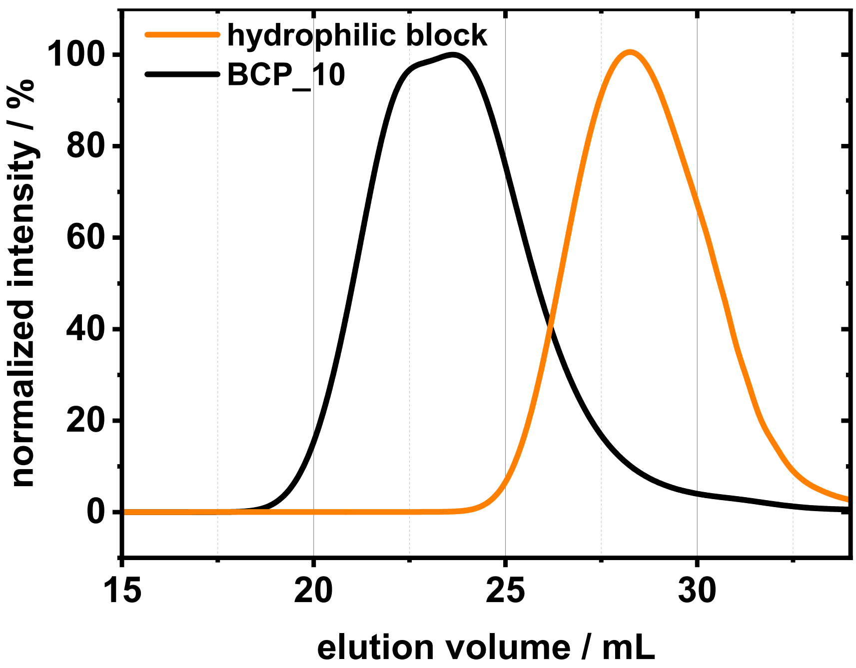

Figure S16. SEC curves of hydrophilic starting block and final block copolymer BCP_10 after purification and quaternization. SEC curves were measured at 70 °C in DMF containing ammonium trifluoroacetate (0.1 M) at a flow rate of 1 mL min^{-1} and calibrated against PS standards.

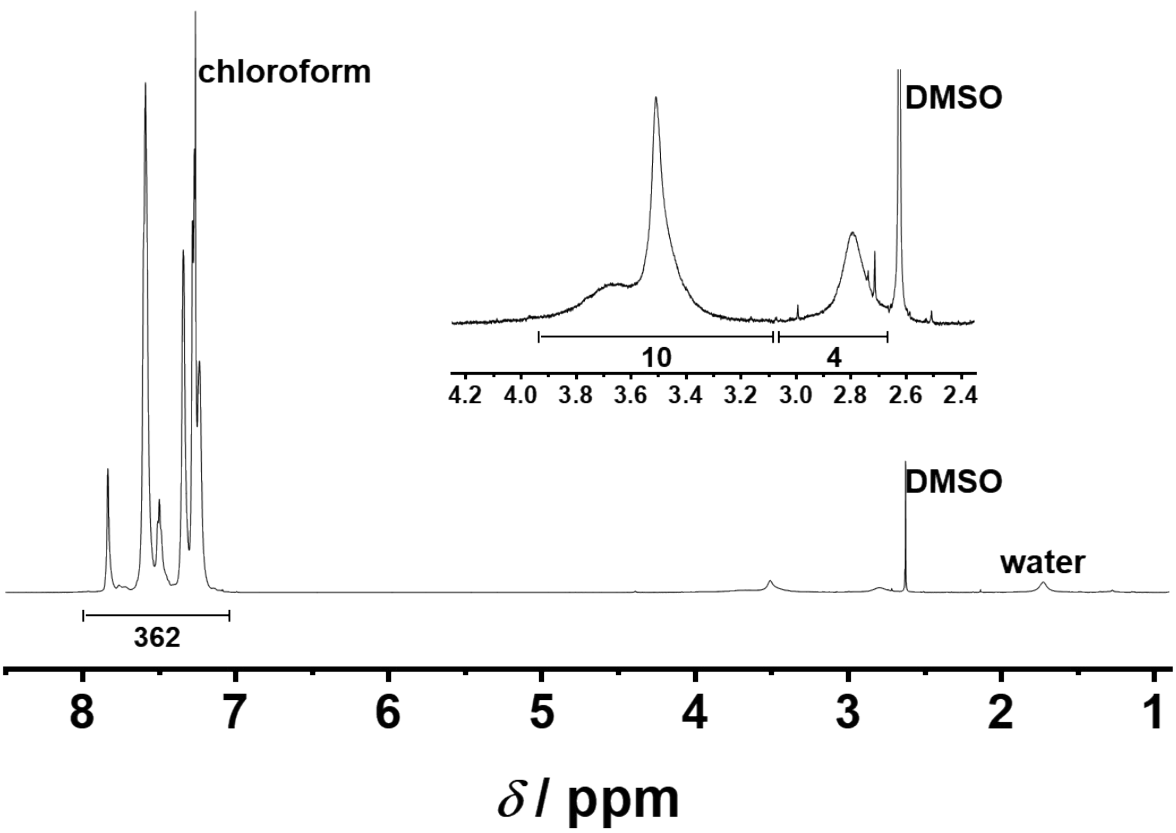

Figure S17. ^1H NMR spectrum of block copolymer BCP_10 in $CDCl_3$.

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