Supplementary Information (SI) for Journal of Materials Chemistry A.

Supporting Information

Polynorbornene Copolymers Combining Flexible Ether Side Chains and Rigid Hydrophobic Segments for AEMWE

Linus Hager,[a, b] Timo Maron,[a, b] Trung Ngo Thanh,[c] Julian Stonawski, [a, b] Andreas Hutzler,[a] Thomas Böhm,[a] Peter Strasser,[c] Simon Thiele, [a, b] Jochen Kerres*[a, d]*

[a] Helmholtz Institute Erlangen-Nürnberg for Renewable Energy (IET-2)

Forschungszentrum Jülich GmbH

Cauerstr. 1, 91058 Erlangen, Germany

E-mail: l.hager@fz-juelich.de, j.kerres@fz-juelich.de

[b] Department of Chemical and Biological Engineering

Friedrich-Alexander-Universität Erlangen-Nürnberg

Egerlandstr. 3, 91058 Erlangen, Germany

[c] Department of Chemistry, Chemical Engineering Division

Technical University of Berlin

Straße des 17. Juni, 19623 Berlin, Germany

[d] Chemical Resource Beneficiation Faculty of Natural Sciences

North-West University

Potchefstroom 2520, South Africa

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1 Materials and methods

1.1 Chemicals

Acetone (99 %, Sigma-Aldrich), allyloxy(diethylene glycol) (*Gelest Inc.*), anthracene (99 %, *Thermo Scientific*), biphenyl (Reagent Plus, 99.5%, *Sigma Aldrich*), 6-bromo-1-hexene (95 %, *TCI Chemicals*), chloroform (99 %, *Sigma-Aldrich*), deuterated chloroform (99 %, 99.8 atom% deuterated, *Sigma-Aldrich*), dichloromethane (99.8 %, amylene as stabilizer, *Sigma-Aldrich*), dicyclopentadiene (for synthesis, *Sigma-Aldrich*), N,N-dimethylacetamide (99.9 %, *Sigma-Aldrich*), deuterated dimethyl sulfoxide (99.9 atom% deuterated, *Sigma-Aldrich*), anhydrous tetrahydrofuran (99.9 %, 250 ppm BHT as inhibitor, *Sigma-Aldrich*), ethyl acetate (99.5 %, *Sigma-Aldrich*), ethyl vinyl ether (99 %, 0.1 % KOH as stabilizer, *Sigma-Aldrich*), extra dry dichloromethane (99.8 %, AcroSeal®, *Thermo Scientific*), extra dry chloroform (99.9 %, AcroSeal®, *Thermo Scientific*), Grubbs Catalyst® M300 (*Sigma-Aldrich*), hydrochloric acid (35 %, *VWR Chemicals*), isatin (97 %, *Sigma Aldrich*), lithium bromide (99 %, *Sigma-Aldrich*), lithium chloride (for analysis, *Sigma-Aldrich*), magnesium sulfate (99.5 %, anhydrous, *Sigma-Aldrich*), methanesulfonyl chloride (98 %, *Sigma-Aldrich*), methanol (99.9 %, *Sigma-Aldrich*), 2,5-norbornadiene (97 % BHT as inhibitor, *TCI Chemicals*), potassium hydroxide (for analysis, *Sigma-Aldrich*), aqueous silver nitrate solution (99.9 %, 0.01 M, *ITW Reagents*), sodium chloride (for analysis, *Sigma-Aldrich*), sodium hydrogen carbonate (for analysis, *Merck*), sodium nitrate (99.7 %, *VWR Chemicals*), sulfuric acid (99.8 %, 2 M, *VWR Chemicals*), toluene (HPLC quality, *Sigma-Aldrich*), tosyl hydrazide (97 %, *Sigma-Aldrich*), trifluoroacetic acid (Reagent Plus, >99%, *Sigma Aldrich*), trifluoromethanesulfonic acid (Reagent Plus, >99%, *Sigma Aldrich*), trimethyl amine in ethanol (4.2 M, 31-35 wt%, toluene as stabiliser, Sigma-Aldrich), tert-butylcatechol (99 %, Sigma-Aldrich) and triethylamine (99 %, for synthesis, Merck) were used as received. AF2-HLF8-25X membranes, obtained from Ionomr Innovations Inc., consist of a polyimidazolium backbone[1,2] with an ion exchange capacity (IEC) ranging from 2.3 to 2.6 mmol g^{-1}. These membranes contain a non-woven reinforcement layer and have a thickness of 25 µm. PBIm+ was synthesized according to our previously published procedure.[3] For the fabrication of the electrodes, ethanol (ACS grade, 99.9 %, *Chemsolute*), DMF (HPLC grade, 99.9 %, *VWR*), iron nitrate nonahydrate (99 %, *Acros Organics*), nickel acetate tetrahydrate (99 %, *Chempur*), cobalt(II, III)-oxide nanopowder (99.5 %, *Sigma-Aldrich*), potassium hydroxide pellets (99.98 % metal basis, *Thermo*

Fisher Scientific), sodium hypophosphite monohydrate (NaH2PO2; 99 %, *Th. Geyer*), thioacetamide (99 %, *Carl Roth*) were used as described. Vulcan XC72 was acquired from *Cabot*. Nickel fiber paper was purchased from *Dioxide Materials*.

1.2 Synthetic procedures

2-(2-((Bicyclo[2.2.1]hept-5-en-2-yl)methoxy)ethoxy)ethan-1-ol:

The synthesis of 2-(2-((Bicyclo[2.2.1]hept-5-en-2-yl)methoxy)ethoxy)ethan-1-ol was performed using an adapted protocol from the literature.[4] A mixture of dicyclopentadiene (16.2 mL, 120 mmol, 1.00 eq.), allyloxy diethylene glycol (43.1 mL, 360 mmol, 3.00 eq.), and tert-butylcatechol (0.080 g, 0.50 mmol, 0.004 eq.) was degassed by bubbling argon through it for 15 min. The mixture was heated to 200 °C under reflux for 16 h. After cooling to room temperature, the excess allyloxy diethylene glycol was distilled off at 0.001 mbar at a vapor phase temperature of 37–48 °C. Afterward, the product was distilled at 50–70 °C in the vapor phase.

Yield: 25.421 g (119.75 mmol, 50.0 %).

Endo/exo ratio (^{1}H NMR) = 81/19.

Endo ^{1}H NMR (500 MHz, $CHCl_3$-d): δ / ppm = 6.12 (dd, J = 5.7, 3.0 Hz, 1H), 5.93 (dd, J = 5.8, 2.9 Hz, 1H), 3.74 (m, 2H), 3.67 (t, 4.8 Hz, 2H), 3.63 (t, 4.8 Hz, 2H), 3.60 – 3.51 (m, 2H), 3.19 (dd, J = 9.3, 6.6 Hz, 1H), 3.10 (t, J = 9.1 Hz, 1H), 2.91 (s, 11H), 2.79 (s, 1H), 2.71 – 2.64 (m, 1H), 2.40 – 2.31 (m, 1H), 1.82 (ddd, J = 11.7, 9.2, 3.8 Hz, 1H), 1.42 (dq, J = 8.2, 2.1 Hz, 1H), 1.24 (dtd, J = 8.1, 1.5, 0.7 Hz, 1H), 0.49 (ddd, J = 11.6, 4.5, 2.6 Hz, 1H).

Exo ^{1}H NMR (500 MHz, $CHCl_3$-d): δ / ppm = 6.09 (dd, J = 5.7, 3.0 Hz, 1H), 6.05 (dd, J = 5.8, 2.9 Hz, 1H).

2-(2-((Bicyclo[2.2.1]hept-5-en-2-yl)methoxy)ethoxy)ethyl methanesulfonate:

2-(2-((Bicyclo[2.2.1]hept-5-en-2-yl)methoxy)ethoxy)ethan-1-ol (25.500 g, 120.10 mmol, 1.00 eq.) and triethylamine (TEA) (14.591 g, 144.20 mmol, 1.20 eq.) were dissolved in dry chloroform (60.1 mL) under argon atmosphere and cooled to 0 °C. Methanesulfonyl chloride (16.512 g, 144.10 mmol, 1.20 eq.) was added dropwise. The reaction proceeded under stirring at 0 °C for 6 h. The mixture was poured into 1 M hydrochloric acid and extracted twice with chloroform. The organic fraction was washed with saturated $NaHCO_3$ solution, dried with $MgSO_4$, and filtered. Chloroform was removed via rotary evaporation, and the product was used without further purification.

Yield: 34.700 g (119.50 mmol, 99.5 %).

Endo ^{1}H NMR (500 MHz, $CHCl_3$-d): δ / ppm = 6.12 (dd, J = 5.7, 3.0 Hz, 1H), 5.91 (dd, J = 5.7, 2.9 Hz, 1H), 4.39 (t, J = 6.1 Hz, 2H), 3.80 – 3.75 (m, 2H), 3.69 – 3.66 (m, 2H), 3.65 (t, J = 3.9 Hz, 2H), 3.62 – 3.49 (m, 2H), 3.16 (dd, J = 9.3, 6.6 Hz, 1H), 3.08 (d, J = 1.7 Hz, 1H), 2.88 (s, 1H), 2.79 (m, 1H), 2.39 – 2.28 (m, 1H), 1.80 (ddd, J = 11.7, 9.2, 3.8 Hz, 1H), 1.60 (d, J = 1.3 Hz, 1H), 1.42 (dq, J = 8.2, 2.1 Hz, 1H), 1.23 (dt, J = 8.1, 1.6 Hz, 1H), 0.48 (ddd, J = 11.6, 4.5, 2.6 Hz, 1H).

Exo ^{1}H NMR (500 MHz, $CHCl_3$-d): δ / ppm = 6.09 (dd, J = 5.7, 3.0 Hz, 0H), 6.05 (dd, J = 5.7, 2.9 Hz, 0H).

5-((2-(2-bromoethoxy)ethoxy)methyl)bicyclo[2.2.1]hept-2-ene (EM):

Lithium bromide (31.136 g, 358.50 mmol, 3.00 eq.) was dissolved in acetone (89.6 mL) under an argon atmosphere and 2-(2-(5-Norbornene-2-methoxy)ethoxy)ethyl methanesulfonate (34.700 g, 119.50 mmol, 1.00 eq.) was added. The reaction proceeded under reflux at 70 °C for 24 h. The solvent was removed via rotary evaporation, and the remaining mixture was taken into water. After extracting twice with ethyl acetate, the organic layer was washed twice with water, dried with magnesium sulfate, and filtered. Ethyl acetate was removed by rotary evaporation to obtain the EM as a product, which was further purified by vacuum distillation.

Yield: 22.900 g (83.27 mmol, 69.7 %).

Endo ^{1}H NMR (500 MHz, $CHCl_3$-d): δ / ppm = 6.11 (dd, J = 5.7, 3.0 Hz, 1H), 5.93 (dd, J = 5.8, 2.9 Hz, 1H), 3.82 (t, J = 6.3 Hz, 2H), 3.69 – 3.60 (m, 4H), 3.59 – 3.51 (m, 2H), 3.48 (t, J = 6.4 Hz, 2H), 3.19 (dd, J = 9.3, 6.6 Hz, 1H), 3.08 (t, J = 9.3 Hz, 1H), 2.90 (dq, J = 3.9, 2.0 Hz, 1H), 2.78 (s, 1H), 2.41 – 2.30 (m, 1H), 1.84 – 1.77 (m, 1H), 1.41 (dq, J = 8.2, 2.1 Hz, 1H), 1.27 – 1.21 (m, 2H), 0.49 (ddd, J = 11.6, 4.6, 2.6 Hz, 1H).

Exo ^{1}H NMR (500 MHz, $CHCl_3$-d): δ / ppm = 6.09 (dd, J = 5.7, 2.9 Hz, 1H), 6.05 (dd, J = 5.7, 2.9 Hz, 1H), 2.74 (s, 1H).

Exo- 1,4,4a,9,9a,10-hexanhydro-9,10-benzeno-1,4-methanoanthracene (AM):

The AM was synthesized using an adapted synthesis from the literature.[5] Anthracene (94.42 g, 0.530 mol, 1.000 eq.), norbornadiene (254.80 g, 2.765 mol, 5.220 eq.), and 4-tert-butyl catechol (0.352 g, 0.002 mol, 0.004 eq.) were added into a 600 mL sealed steel stirred tank reactor. The mixture was degassed by bubbling with argon for 15 min. The reactor was closed, and the reaction mixture was stirred for 24 h at 180 °C. After cooling to room temperature, the white precipitate was separated from the liquor by vacuum filtration and washed with heptane. After drying in a vacuum, the white crystalline product was recrystallized from isopropanol/ethyl acetate (7/3 v/v) to obtain white needle-like crystals.

Yield: 94.6 g (349.88 mmol, 66.0 %).

^{1}H NMR (500 MHz, CHCl$_3$-d): δ / ppm = 7.21 (ddd, J = 11.8, 5.3, 3.2 Hz, 4H), 7.10 (dd, J = 5.3, 3.2 Hz, 2H), 7.02 (dd, J = 5.3, 3.2 Hz, 2H), 6.12 (t, J = 1.5 Hz, 2H), 4.14 (t, J = 1.5 Hz, 2H), 2.46 (m, 2H), 2.04 (m, 2H), 0.71 (dt, J = 9.3, 1.4 Hz, 1H), -0.16 ((dt, J = 9.3, 1.8 Hz, 1H).

5-(4-bromobutyl)bicyclo[2.2.1]hept-2-ene (BM):

The synthesis was performed with a slightly adapted procedure from the literature.[6] Dicyclopentadiene (6.611 g, 50.00 mmol, 1.000 eq.), 6-bromo-1-hexene (16.306 g, 100.00 mmol, 2.000 eq.) and 4-tert-butylcatechol (0.010 g, 0.90 mmol, 0.018 eq.) were added with a microwave absorbing boiling stone into a Pyrex® glass vessel. Argon was bubbled through the mixture for 10 minutes. The mixture was stirred and heated to 200 °C in a Discover 2.0 microwave from *CEM Corporation* for 72 h. After cooling to room temperature, the mixture was distilled under reduced pressure (0.001 mbar). The product evaporated at 50–60 °C in the vapor. The crude product was further purified in a flash chromatographic column (Pure C-815 Flash from *Büchi*) with heptane as eluent.

Yield: 3.088 g, (13.48 mmol, 13.5 %).

Endo/exo ratio (1H NMR) = 78/22.

Endo ^{1}H NMR (500 MHz, CHCl$_3$-d): δ / ppm = 6.11 (dd, J = 5.7, 3.0 Hz, 1H), 5.91 (dd, J = 5.7, 2.9 Hz, 1H), 3.40 (t, J = 0.5 Hz, 2H), 2.77 – 2.73 (m, 2H), 2.01 – 1.93 (m, 1H), 1.90 – 1.78 (m, 3H), 1.43 – 1.36 (m, 3H), 1.21 (d, J = 0.7 Hz, 1H), 1.15 – 1.00 (m, 2H), 0.48 (ddd, J = 11.2, 4.3, 2.6 Hz, 1H).

Exo ^{1}H NMR (500 MHz, $CHCl_3$-d): δ / ppm = 6.08 (dd, J = 5.5, 3.2 Hz, 1H), 6.01 (dd, J = 5.7, 0.7 Hz, 1H), 3.44 – 3.40 (m, 2H), 2.50 (m, 1H).

Statistical copolymerisation of EM and AM:

The following procedure targeted an EM-AM copolymer with an IEC of 2.00 meq./g and M_n of 50 000 g/mol. EM (9.630 g, 34.996 mmol, 1.18 eq.) and AM (8.000 g, 29.588 mmol, 1.00 eq.) were dissolved in extra dry DCM (646 mL) under an argon atmosphere obtaining a 0.1 M solution. The monomer solution was degassed by three subsequent freeze-pump thaw cycles. Grubbs M300 catalyst (0.3122 g, 0.353 mmol) was dissolved in extra dry DCM (31.2 mL) and added to the monomer solution in one shot to start the polymerization. The reaction was stirred for 5 minutes at room temperature. Afterward, ethyl vinyl ether (32.3 mL) was added to deactivate the catalyst and remove it from the chain ends. The solution was stirred again for 30 min. The crude polymer was precipitated in excess methanol and dried under a vacuum at 60 °C.

Yield: 16.90 g (95.9 %).

GPC: 49 100 g mol^{-1}, Đ = 1.07

Built-in ratio (^{1}H NMR): x_{EM} = 54.6 %.

^{1}H NMR (500 MHz, $CHCl_3$-d): δ / ppm = 7.45 – 6.92 (m, EM: 0H, AM: 8H), 5.66 – 5.06 (m, EM: 2H, AM: 2H), 4.29 – 3.97 (m, EM: 0H, AM: 2H), 3.90 – 3. 20 (m, EM: 10H, AM: 0H), 3.11 – 2.62 (m, EM: 1H, AM: 0H), 2.58 – 2.39 (m, EM: 1H, AM: 0H), 2.35 – 1.49 (m, EM: 3H, AM: 4H), 1.49 – 1.01 (m, EM: 2H, AM: 2H).

Statistical copolymerisation of BM and AM:

The following procedure targeted an BM-AM copolymer with an IEC of 2.00 meq./g and M_n of 50 000 g/mol. BM (1.660 g, 7.250 mmol, 0.98 eq.) and AM (2.000 g, 7.400 mmol, 1.00 eq.) were dissolved in extra dry DCM (147 mL) under an argon atmosphere obtaining a 0.1 M solution. The monomer solution was degassed by three subsequent freeze-pump thaw cycles. Grubbs M300 catalyst (65.500 mg, 0.074 mmol) was dissolved in extra dry DCM (8 mL) and added to the monomer solution in one shot to start the polymerization. The reaction was stirred for 5 minutes at room temperature. Afterward, ethyl vinyl ether (7.8 mL) was added to deactivate the catalyst and remove it from the chain ends. The solution was stirred again for 30 min. The crude polymer was precipitated in excess methanol and dried under a vacuum at 60 °C.

Yield: 3.535 g (96.6 %).

GPC: 49 000 g mol^{-1}, Đ = 1.79

Built-in ratio (^1H NMR): x_{BM} = 45.0 %.

^1H NMR (500 MHz, $CHCl_3$-d): δ / ppm = 7.45 – 6.92 (m, BM: 0H, AM: 8H), 5.41 – 5.30 (m, BM: 2H, AM: 2H), 4.17 – 4.07 (m, BM: 0H, AM: 2H), 3.53 – 3.39 (m, BM: 2H, AM: 0H), 2.22 – 1.15 (m, BM: 13H, AM: 6H)

Sequential polymerization of EM and AM:

The following procedure targeted an EM-AM block copolymer with an IEC of 2.00 meq./g and M_n of 50 000 g/mol. EM (9.630 g, 34.996 mmol, 1.18 eq.) was dissolved in extra dry DCM (351 mL), and AM (8.000 g, 29.588 mmol, 1.00 eq.) was dissolved separately in extra dry DCM (295 mL) under argon atmosphere obtaining a 0.1 M solution for each monomer. Both monomer solutions were degassed by three subsequent freeze-pump thaw cycles. Grubbs M300 catalyst (0.3122 g, 0.353 mmol) was dissolved in extra dry DCM (31.2 mL) and added to the AM solution in one shot to start the polymerization of the AM block. After 5 minutes of reaction, a sample was withdrawn and quenched with ethyl vinyl ether for GPC and NMR analysis to verify complete monomer conversion. Then, the EM solution was added in one shot under strong argon reverse flow utilizing a funnel. After 5 minutes of reaction time, another sample was taken and quenched with ethyl vinyl ether to prove the complete consumption of the second monomer. Then, ethyl vinyl ether (32.3 mL) was added to deactivate the catalyst and remove it from the chain ends. The solution was stirred again for 30 min. The crude polymer was precipitated in excess methanol and dried under a vacuum at 60 °C.

Yield: 17.20 g (97.6 %).

GPC: 50 500 g mol^{-1}, Đ = 1.26

Built-in ratio (^1H NMR): x_{EM} = 54.6 %.

^1H NMR (500 MHz, $CHCl_3$-d): δ / ppm = 7.45 – 6.92 (m, EM: 0H, AM: 8H), 5.66 – 5.06 (m, EM: 2H, AM: 2H), 4.29 – 3.97 (m, EM: 0H, AM: 2H), 3.90 – 3. 20 (m, EM: 10H, AM:

0H), 3.11 – 2.62 (m, EM: 1H, AM: 0H), 2.58 – 2.39 (m, EM: 1H, AM: 0H), 2.35 – 1.49 (m, EM: 3H, AM: 4H), 1.49 – 1.01 (m, EM: 2H, AM: 2H).

Hydrogenation of the double bonds:

The following procedure was identical for the statistical (EM and BM) and the block copolymer and is exemplary described for the statistical EM-copolymer. The EM-co-AM copolymer (16.90 g, 61.908 mmol, 1.000 eq.) was dissolved in toluene (2.112 L) in a two-necked round-bottom flask with a reflux condenser. After the polymer was dissolved, tosyl hydrazide (69.175 g, 0.3714 mol, 6.000 eq.) was added to the polymer solution. The solution was purged with argon gas for 30 min and then stirred under reflux for 24 h under an argon atmosphere. After cooling to room temperature, the mixture was cooled with an ice bath for 1 h to allow the decomposition product of the tosyl hydrazide (p-toluene sulfinic acid) to precipitate. Afterward, the precipitated solid was removed by filtration over a short alox column. The polymer solution was concentrated and then precipitated in excess methanol. Finally, the pure white fiber-like polymer was dried under vacuum at 60 °C.

Yield: 14.97 g (87.9 %)

^{1}H NMR (500 MHz, CHCl$_3$-d): δ / ppm = 7.45 – 6.92 (m, EM: 0H, AM: 8H), 4.29 – 3.97 (m, EM: 0H, AM: 2H), 3.90 – 3. 20 (m, EM: 10H, AM: 0H), 3.11 – 2.62 (m, EM: 1H, AM: 0H), 2.58 – 2.39 (m, EM: 1H, AM: 0H), 2.35 – 1.49 (m, EM: 3H, AM: 4H), 1.49 – 1.01 (m, EM: 2H, AM: 2H).

Quaternisation of the statistical EM-AM copolymer and block-copolymer:

The following procedure was identical for the statistical (EM and AM) and the block copolymer. The hydrogenated copolymer or block-copolymer (14.97 g, 54.437 mmol, 1.00 eq.) was dissolved in THF (336 mL) by stirring at 40 °C. Then, trimethylamine (129.6 mL, 0.5443 mol, 4.2 mol L^{-1} in ethanol, 10 eq.) was added. The mixture was stirred at 40 °C for 48 h. The precipitated polymer was filtrated and dried at 60 °C in a vacuum.

Yield: 16.10 g (98.1 %).

^{1}H NMR (500 MHz, CHCl$_3$-d): δ / ppm = 7.49 – 6.89 (m, EM: 0H, AM: 8H), 4.28 – 3.95 (m, EM: 0H, AM: 2H), 3.91 – 3.38 (m, EM: 10H, AM: 0H), 3.13 (s, EM: 9H, AM: 0H), 3.00 – 2.55 (m, EM: 2H, AM: 0H), 2.30 – 1.36 (m, EM: 3H, AM: 4H), 1.35 – 0.85 (m, EM: 2H, AM: 2H).

Synthesis of poly(oxindolebiphenylene) (POB)

POB was synthesized according to a procedure adapted from the literature.[7] Trifluoromethanesulfonic acid (52.00 mL, 588.0 mmol, 45.31 eq.) was added dropwise to a mixture of isatin (2.100 g, 14.26 mmol, 1.100 eq.) and biphenyl (2.000 g, 12.97 mmol, 1.000 eq.) in TFA (35 mL, 449.0 mmol, 34.62 eq.). The reaction mixture was stirred at room temperature for 16 h and precipitated into methanol. The nearly white fiber formed was filtered off and washed via Soxhlet extraction with methanol. After drying, a white, fiber-like polymer was obtained.

Yield: 3.40 g (92.5 %)

GPC: 165 000 g mol^{-1}, Đ = 1.92

Preparation of pure block copolymer membranes:

The hydrogenated and quaternized block copolymer EM$_{0.54}$-q-block-AM$_{0.46}$-h (0.500 g) was dissolved in NMP (3.50 g) to form a 12.5 wt% solution. The solution was cast onto a glass plate with a doctor blade (ZAA2300.H from Screening Eagle Technologies AG) with a gap height of 560 µm. The solvent was evaporated slowly at 80 °C for 24 h. Afterward, the glass plate was immersed in distilled water, and the membrane was detached. Subsequently, the membrane was immersed in 1 M NaCl at 85 °C for 24 h, followed by immersion in distilled water at 85 °C two times. The dry thickness of the membranes obtained by this procedure was 50 µm.

Blend membrane preparation:

The following procedure describes the preparation of a blend membrane with 10 wt% POB in the blend. Membranes with other POB contents were prepared accordingly. A quaternized copolymer (0.150 g) was dissolved in NMP (1.350 mL) and mixed with a POB solution (0.300 g, 5 wt% in NMP). The solution was cast onto a glass plate with a doctor blade (ZAA2300.H from Screening Eagle Technologies AG) with a gap height of 650 µm. The solvent was evaporated slowly at 80 °C for 24 h. Afterward, the glass plate was immersed in distilled water, and the membrane was detached. Afterwards, the membrane was immersed in 1 M NaCl at 85 °C for 24 h, followed by immersion in distilled water at 85 °C two times. The dry thickness of the membranes obtained by this procedure was 44 µm.

Synthesis of electrodes:

The several electrode components were synthesized as described in our previous work.[3] Briefly, NiFe-LDH was obtained *via* a solvothermal method. $Ni(OAc)_2{\cdot}4H_2O$ (62.5 mL, 0.6 M) and $Fe(NO_3)_3{\cdot}9H_2O$ (12.5 mL, 0.6 M) were mixed in a MilliQ-H_20 and DMF solution. The mixture was transferred into a Teflon autoclave reactor and put into a microwave (*Anton Paar,* 1 h at 120 °C, then 1 h at 160 °C). The obtained powder was centrifuged, washed with ethanol and water, and freeze-dried. Co_xP_y supported on Vulcan XC72 (CoP/C) was synthesized *via* wetness impregnation followed by phosphor chemical vapor deposition (P-CVD). A dispersion of Co_xO_y-NPs in ethanol and water was added to carbon. The mixture was dried under stirring at room temperature. The obtained Co_xO_y/C was treated *via* P-CVD by placing two ceramic boats with NaH_2PO_2 at the upstream and the cobalt-carbon precursor at the downstream of the furnace using a 5:1 weight ratio. The heat treatment was conducted at 350 °C for 2 h with a heating ramp of 2 K min^{-1}. Ni@Ni_xP_y fiber felts were prepared using a similar approach to Co_xP_y/C powders and adjusting the temperature to 400 °C. Ni@Ni_xS_y fiber felts were obtained through a hydrothermal method. A precut Ni felt was immersed in a 0.05 M thioacetamide solution (40.0 mL) and transferred to a glass-lined stainless-steel autoclave. The mixture was heat treated for 4 h at 120 °C. Subsequently, the obtained Ni@Ni_xS_y fiber felts were washed with ethanol and water and dried at 60°C overnight.

1.3 Methods

Nuclear magnetic resonance spectroscopy (NMR) – NMR spectra were measured at room temperature with a JEOL JNM-ECZ-500R with a proton resonance frequency of 500 MHz. For the different NMR measurements, samples were dissolved in $CDCl_3$ (unsaturated precursor polymers and hydrogenated polymers), DMSO-d_6 (quaternized statistical copolymer), or in a 7/3 v/v mixture of benzene-d_6/DMSO-d_6 (quaternized block-copolymer). The signal of the residual protons in the deuterated solvent was selected as the internal standard with a shift of 7.26 ppm for $CHCl_3$-d and 2.50 ppm for DMSO-d_6.

Gel permeation chromatography (GPC) – GPC measurements were performed using a SECcurity2 1260 from *PSS*. For measurements with THF as eluent, a PSS SDV LUX GUARD was used as a guard column, and three separation columns (2x PSS SDV LUX 3 µm 1000 Å and 1x PSS SDV LUX 3 µm 10000 Å) were applied for sample analysis. The eluent was THF with a 1.0 ml/min flow rate at 35 °C. A dual variable wavelength UV-Vis (P/N 404-2107, *PSS*) and a refractive index detector (P/N 404-2106, *PSS*) were used as detectors. The relative molecular weight was obtained by calibration with narrowly distributed polystyrene standards from PSS. For NMP as eluent, a *PSS* GRAM GUARD was used *as a* guard column, and three separation columns (1x *PSS* GRAM 10 µm 100 Å and 2x *PSS* GRAM 10 µm 3000 Å) were applied for sample analysis. A dual variable wavelength UV-Vis (P/N 404-2107, PSS) and a refractive index detector (P/N 404-2106, PSS) were used as detectors. The relative molecular weight was obtained by calibration with narrowly distributed polystyrene standards from *PSS.* The eluent was NMP containing 0.1 M LiBr with a 1.0 mL min^{-1} flow rate at 70 °C.

Thermogravimetrically analysis (TGA) – The thermal stability of the polymers and membranes was analyzed using a TGA 8000 from PerkinElmer with a heating rate of 10 K min^{-1} from 30 °C to 800 °C under a synthetic air atmosphere.

Differential Scanning calorimetry (DSC) – DSC curves were obtained using a Mettler Toledo DSC 3+. Analyses were performed under nitrogen flow (50 mL/min) at a 10 K/min heating rate. The method consisted of three measurement steps with stationary phases of 5 min in between: (1) heating from -50 °C until 250 °C, (2) cooling down to -50 °C, and (3) repeating step 1. The glass transition temperature (Tg) was calculated using the ISO standard method on the last heating curve.

Tensile testing – The mechanical properties were investigated utilizing an EZ Test EZ-SX from *Shimadzu* equipped with the SM-100N-168 100 N force transducer from *Interface Inc*. Seven dry 1.5 cm x 4.0 cm samples were measured for each membrane at a test speed of 10 mm min^{-1}. A preload of 0.1 N was applied before the test. The gauge length corresponding to the preload was subtracted from the previously measured gauge length. The Young's Modulus was calculated from a linear fit between 0.05% and 0.25% strain. The tensile strength was set as the stress at the maximum of the stress-strain curve. The measurements were performed at 23°C and 25% RH.

Tensile testing – Dynamic mechanical analysis in tension mode was conducted with a DMA 1 from *Mettler Toledo*. Samples with a size of (0.5x2) cm were analyzed with an oscillating frequency of 1 Hz and a heating rate of 2 K min^{-1}.

Conductivity measurement – Membrane pieces with the thickness, d, and the width, w, were immersed in 1 M KOH for 24 h to convert the membranes into their mixed hydroxide form. Afterward, the membranes were washed three times with DI water to remove excess KOH. The membranes were loaded into an MTS 740 (*Scribner Associates*) four-point probe conductivity cell and immersed in DI water. For temperature-dependent measurements, the cell was first equilibrated at 30 °C for 1 h, and then the resistance of the membrane was measured. Then, the temperature was raised by 10 °C, and the cell was equilibrated at the respective temperature for 1 h. After equilibration, the resistance was measured again. All measurements were repeated three times. The conductivity was calculated with equation (1), whereby L is the distance between the two sensing electrodes (l = 0.425 cm), R is the measured resistance, w is the width, and d is the thickness of the membrane:

$$\sigma = \frac{L}{R \cdot w \cdot d} \tag{1}$$

Chloride conductivities were measured analogously with the membranes obtained after converting them into the chloride form by the abovementioned procedure.

Mohr's Titration – A membrane in Cl- form was immersed in 1 M aqueous $NaNO_3$ solution for 24 h at room temperature three times each, and the combined solutions were titrated. The membrane was withdrawn, and sulfuric acid (250 µL, 2 mol L-1) was added to the combined solutions. The solution was titrated at room temperature with 0.01 M aqueous $AgNO_3$ solution in an OMNIS Titrator with an OMNIS Dosing Module from *Metrohm*. The IEC was calculated by the following equation, with V_{AgNO3} as the consumed volume of $AgNO_3$, c_{AgNO3} the concentration, and $m_{dry,OH-}$ as the dry mass of the membrane in hydroxide form:

$$\mathrm{IEC}_{titrated} = \frac{V_{\mathrm{AgNO_3}} \cdot c_{\mathrm{AgNO_3}}}{m_{\mathrm{dry,OH^-}}} \tag{2}$$

Swelling Ratio (SR) and Water Uptake (WU) – A wet piece of the membrane was gently swabbed with a dry paper towel, then weighed, and its thickness, d, and length, L, were measured. After drying in a vacuum at 60 °C for 24 h, the membrane was weighed and measured again. The SR_L and WU were calculated with the following formulas:

$$\mathrm{SR}_L = \frac{L_{wet} - L_{dry}}{m_{dry}} \cdot 100\% \tag{3}$$

$$\mathrm{WU} = \frac{m_{wet} - m_{dry}}{m_{dry}} \cdot 100\% \tag{4}$$

Transmission electron microscopy (TEM) – Before TEM analysis, the membranes were immersed in 0.5 M Na_2WO_4 for 72 h, followed by immersion in ultrapure water for 24 h three times each. The $WO4^{2-}$ staining increases the contrast since the image contrasts with a high-angle annular dark field (HAADF) detector scales approximately with the square of the atomic number (Rutherford scattering). The membranes were embedded in epoxy resin (Araldite 502) and cut at room temperature with a Diatome ultra 45 diamond knife with water as a floating liquid on an RMC Boeckeler PowerTome. Nanostructure analysis was performed using a Talos F200i (*ThermoFisher Scientific*). The microscope was operated at an acceleration voltage of 200 kV to reduce beam damage. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was utilized to exploit the mass-thickness contrast within ultrathin sections (60 nm) of the tungstate-stained blend-polymer material. Therefore, a beam current of 40 pA and a convergence angle of 10.5 mrad were adjusted.

Anion exchange membrane water electrolysis (AEMWE) with non-PGM electrodes – For the electrochemical characterization of the membrane in dry-cathode mode AEMWE, the same conditions as in our previous work were applied.[3] Ti-bipolar plates with parallel flow fields for the cathode and anode were used. The active area of the cell was 5 cm^{-2}. As a cathode catalyst, 4 mg cm^{-2} CoP/C with 10 wt% PBIm+ ionomer was used on a custom-made nickelphosphide felt (Ni@NiP-felt). 2 mg cm^{-2} NiFe with 10 wt% PBIm+ ionomer on a custom-made nickel sulfide felt (Ni@NiS-felt) was used as anode catalyst. On the anode side, 1 M KOH with a flow rate of 50 mL min^{-1} was applied. On the cathode side, dry N_2 gas with a flow rate of 100 mL min^{-1} was used. The cell temperature was 60 °C for all measurements. The membranes (commercial AF2-HLF8-25X and the custom-made blend membrane

90 wt% $EM_{0.54}$-q-co-$AM_{0.46}$-h/10 wt% POB) were pre-conditioned by immersion in 1 M KOH for 24 h twice, with refreshment of the solution in between. A *Reference 3000* potentiostat (*Gamry*) with a 30k Booster was used for electrochemical testing. The measurement protocol involved cell conditioning from 0.1 A cm^{-2} to 2 A cm^{-2} followed by potentiostatic electrochemical impedance spectroscopy (PEIS) at 1.5 V and a constant current hold at 2 A cm^{-2} for 2 min followed by the measurement of the polarization curve from 2 A cm^{-2} to 0.1 A cm^{-2} and again a PEIS measurement. A constant current hold at 1 A cm^{-2} for 20 h was performed for stability testing, and polarization curves and PEIS measurements were recorded before the current hold. The sequence was repeated six times, reaching 120 h of testing.

2 Additional Figures: Monomer synthesis

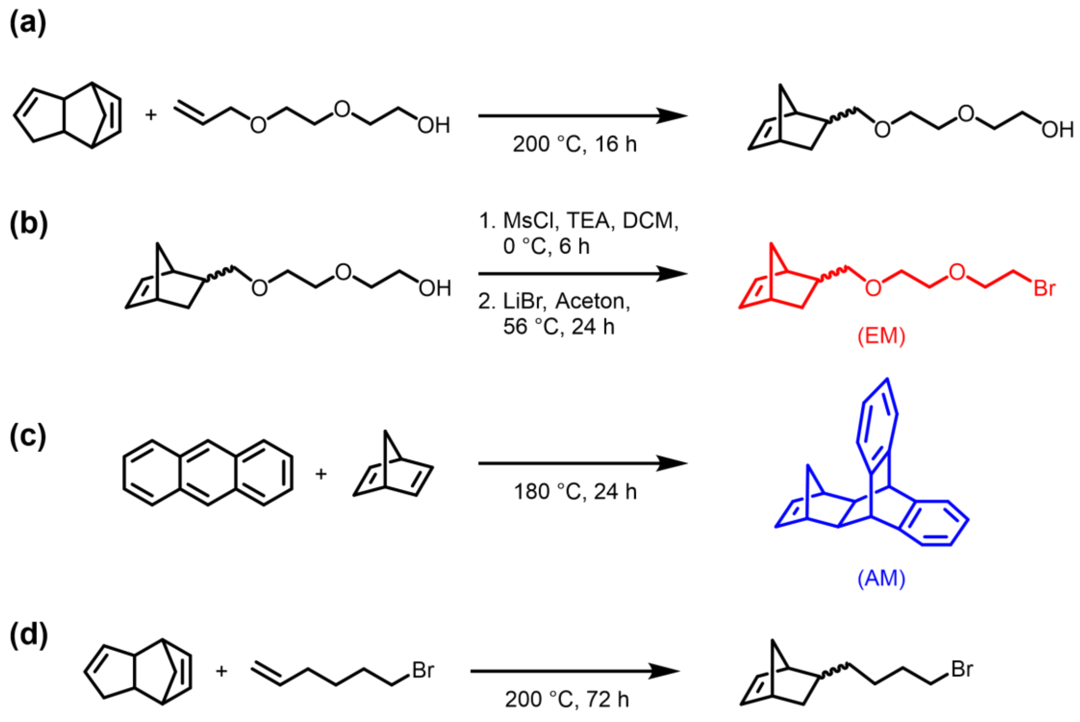

Figure S 1: (a) Synthesis of 2-(2-((Bicyclo[2.2.1]hept-5-en-2-yl)methoxy)ethoxy)ethan-1-ol via a Diels-Alder reaction (b) Mesylation and subsequent nucleophilic substitution with bromine to yield 5-((2-(2-bromoethoxy)ethoxy)methyl)bicyclo[2.2.1]hept-2-ene (EM). (c) Exo- 1,4,4a,9,9a,10-hexanhydro-9,10-benzeno-1,4-methanoanthracene (AM) (d) Synthesis of 5-(4-bromobutyl)bicyclo[2.2.1]hept-2-ene (BM).

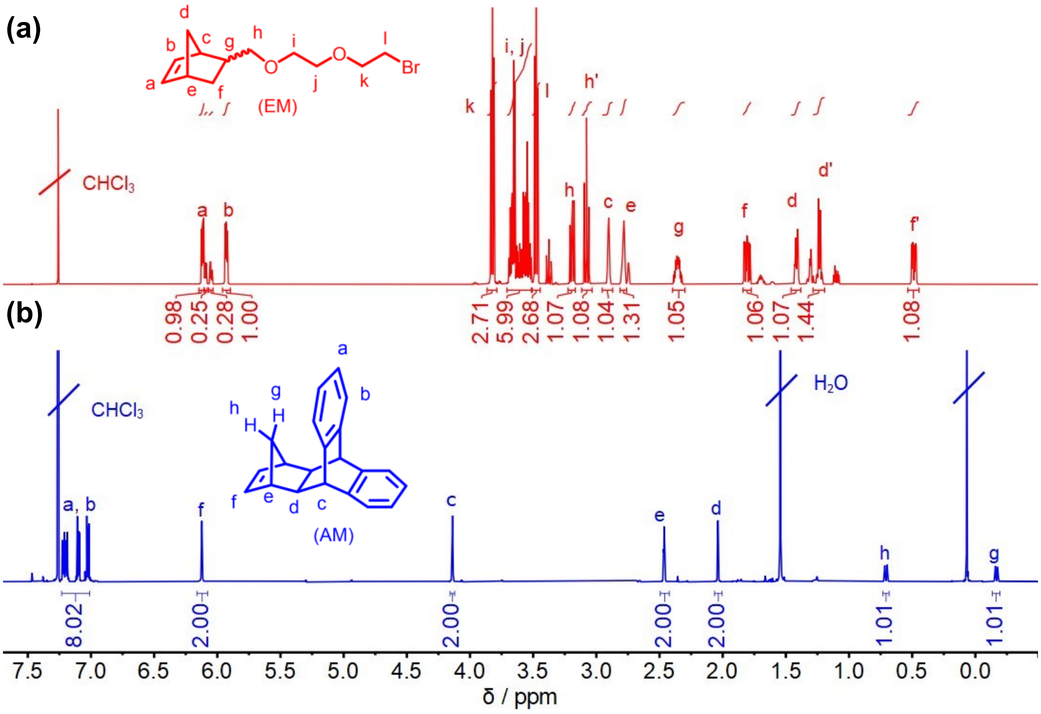

Figure S 2: ^{1}H NMR spectra of the EM and the AM measured in $CDCl_3$ with assignment of all signals.

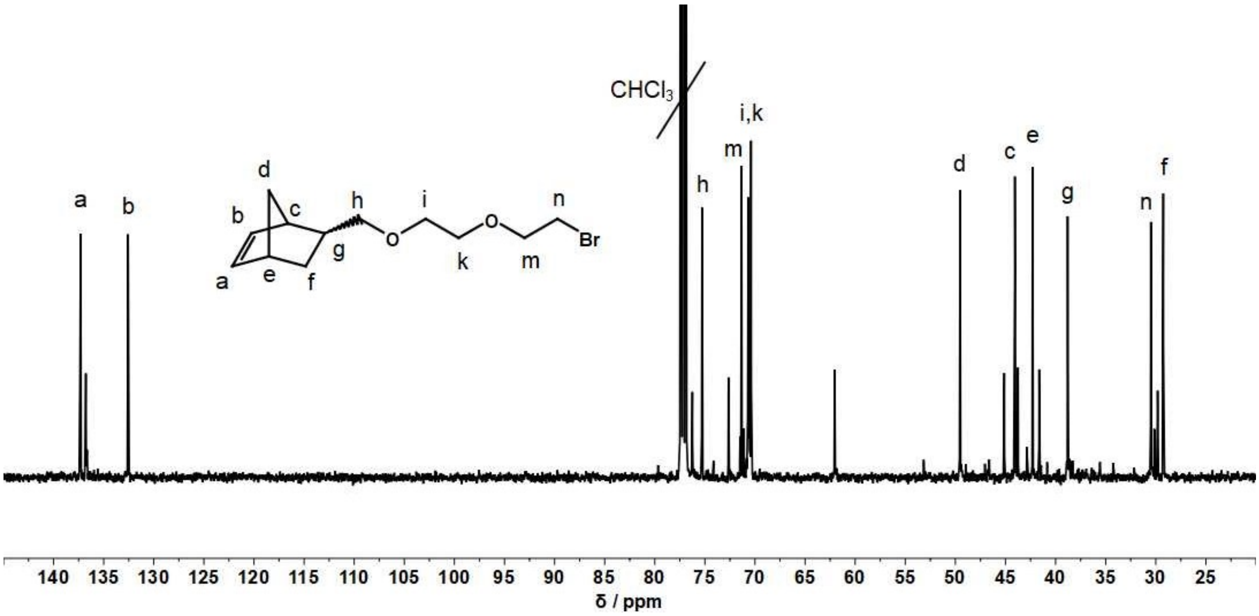

Figure S 3: ^{13}C NMR spectrum of the EM with assignment of all signals.

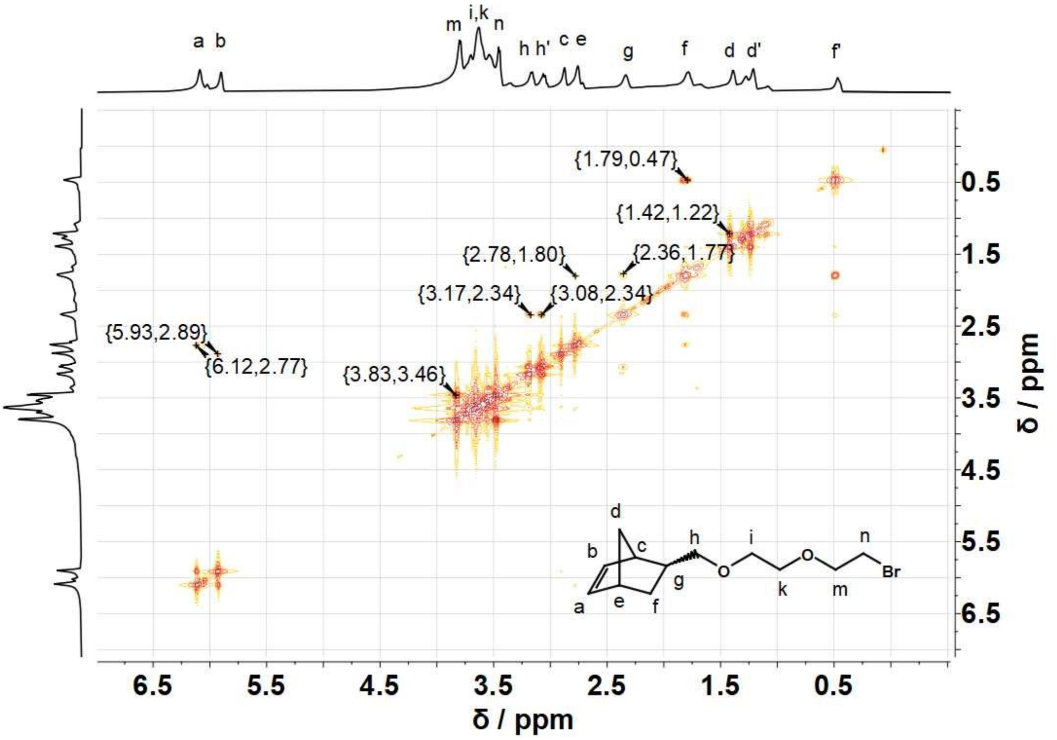

Figure S 4: ^{1}H-^{1}H-COSY spectrum of EM in $CDCl_3$ with assigned peaks and marked couplings for the endo isomer.

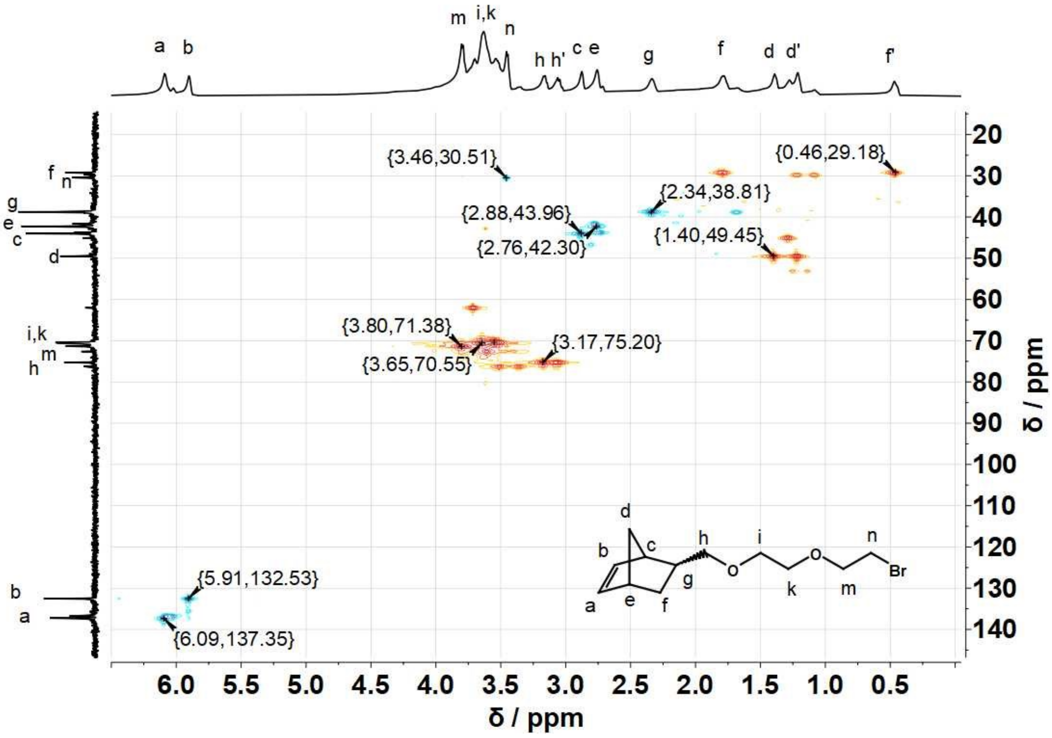

Figure S 5: ^{1}H-^{13}C HSQC spectrum of EM in $CDCl_3$ with assigned signals**.**

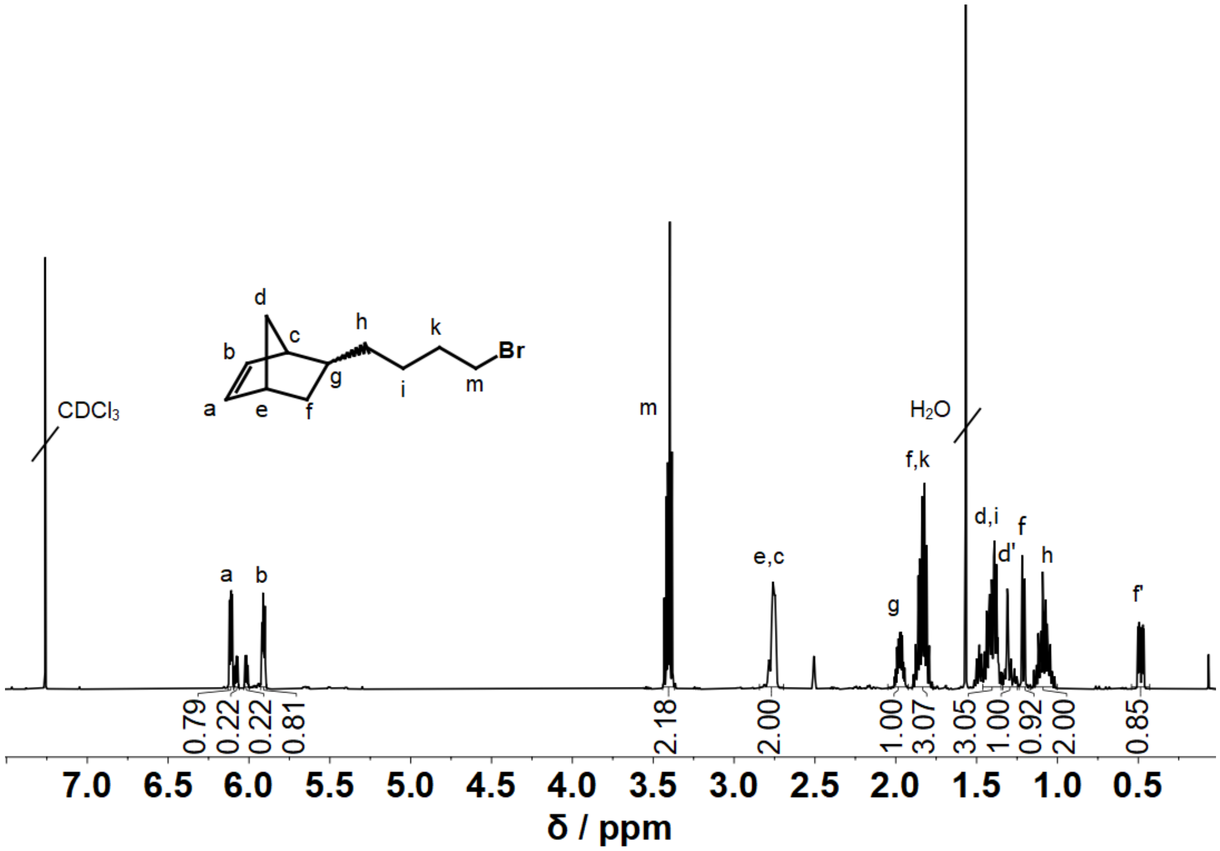

Figure S 6: ^{1}H- spectrum of 5-(4-bromobutyl)bicyclo[2.2.1]hept-2-ene (BM) in $CDCl_3$ with assigned signals.

3 Additional Figures: Polymer synthesis

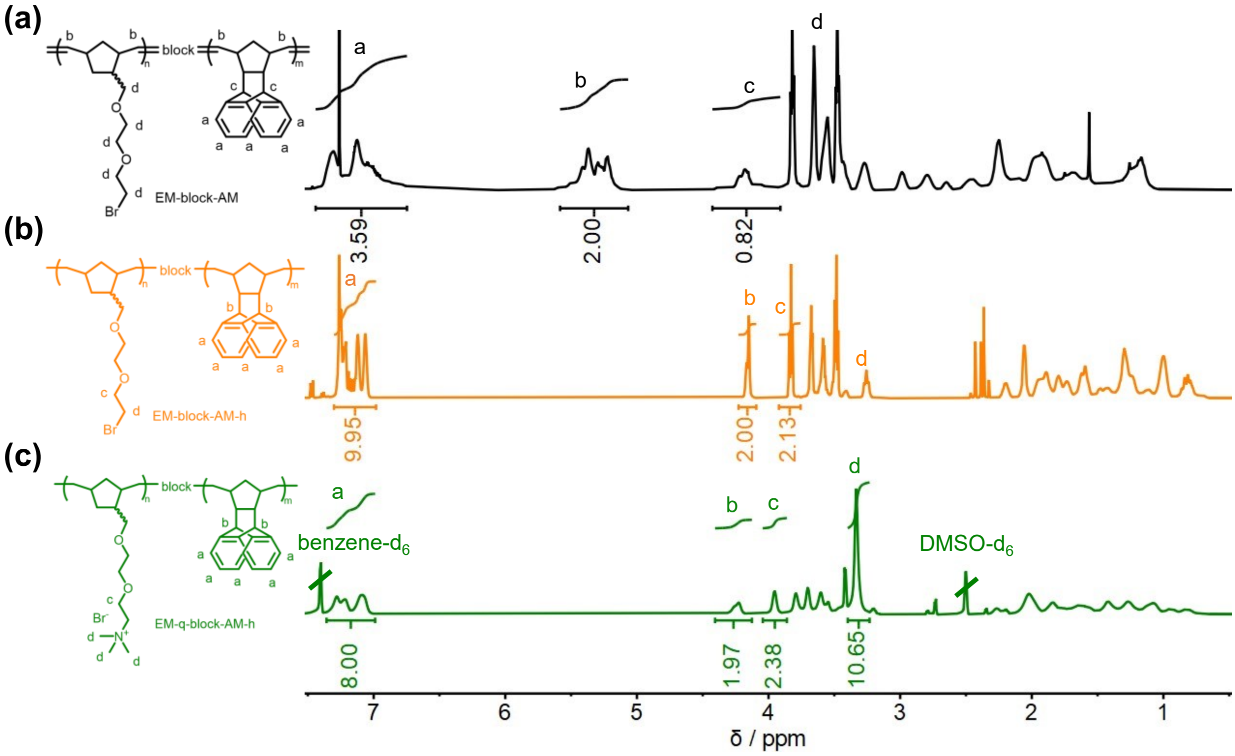

Figure S 7: (a) ^{1}H-NMR spectrum of the unsaturated EM$_{0.54}$-block-AM$_{0.46}$ measured in CDCl$_3$ (b) ^{1}H-NMR spectrum after the hydrogenation reaction (EM$_{0.54}$-block-AM$_{0.46}$-h) with tosyl hydrazide showcasing significant peak sharping due to the loss of cis/trans isomerism measured in CDCl$_3$ (c) ^{1}H-NMR spectrum of the quaternized EM$_{0.54}$-q-block-AM$_{0.46}$-h measured in benzene-d$_6$/DMSO-d$_6$ 7/3 v/v.

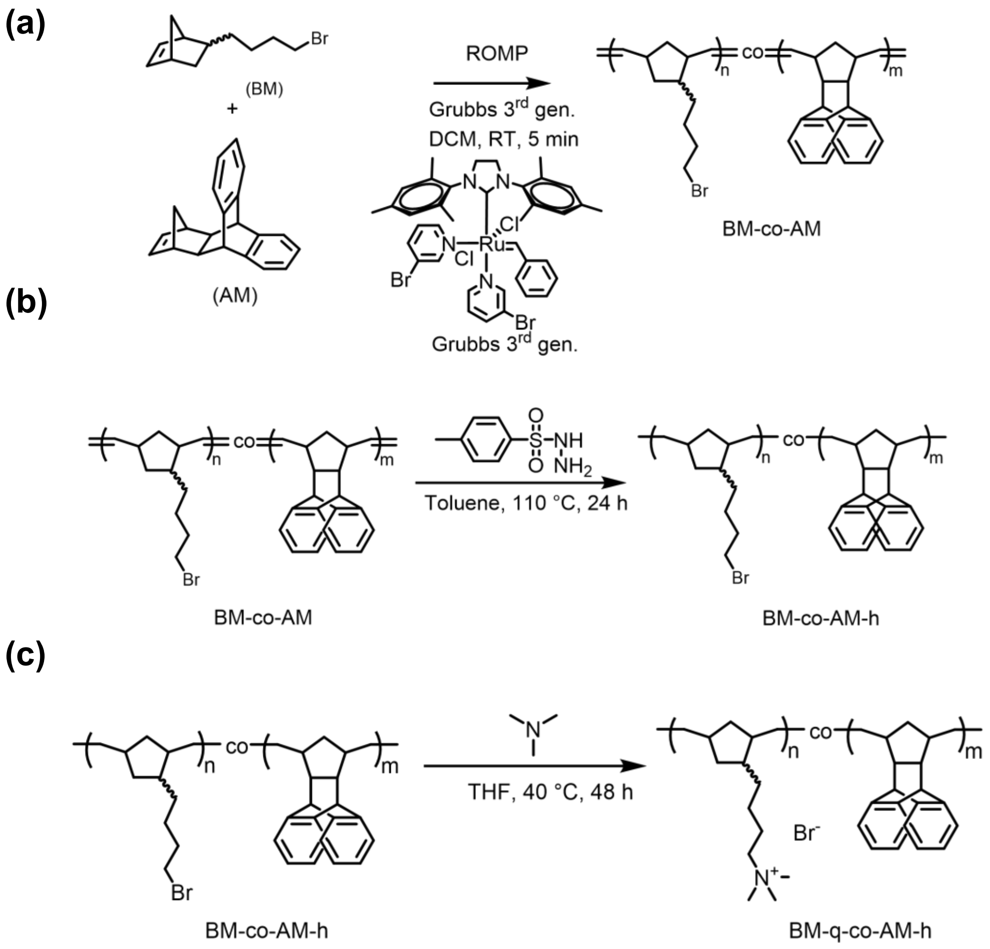

Figure S 8: (a) Synthesis of the precursor polymer (BM-co-AM) via ROMP utilizing the 3rd generation Grubbs catalyst with a 49:51 molar ratio of EM/AM in the feed (IEC_{theo} = 2.00 mmol g^{-1}) (b) Hydrogenation of the double bonds with p-toluenesulfonyl hydrazide and (c) Quaternization of bromo moieties with trimethylamine.

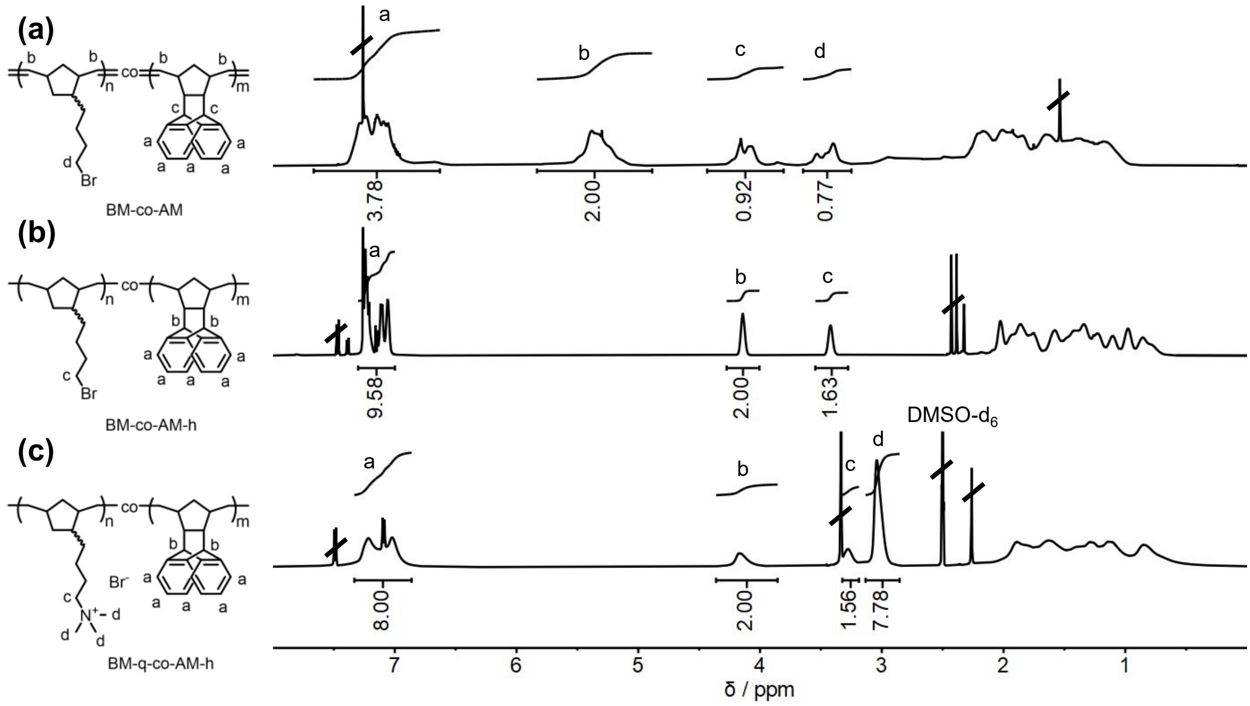

Figure S 9: (a) ^{1}H-NMR spectrum of the unsaturated BM$_{0.45}$-co-AM$_{0.55}$ measured in CDCl$_3$ (b) ^{1}H-NMR spectrum after the hydrogenation reaction (BM$_{0.45}$-co-AM$_{0.55}$-h) with tosyl hydrazide showcasing significant peak sharping due to the loss of cis/trans isomerism measured in CDCl$_3$ (c) ^{1}H-NMR spectrum of the quaternized BM$_{0.45}$-q-block-AM$_{0.55}$-h measured in DMSO-d$_6$.

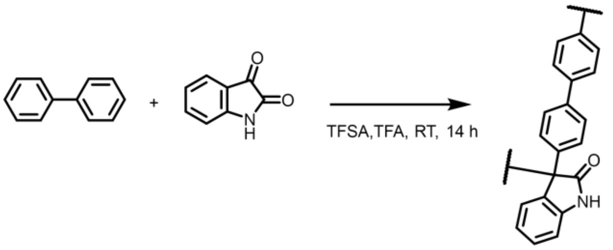

Figure S 10: Synthesis of POB via a super-acid catalyzed polycondensation of biphenyl and isatin**.**

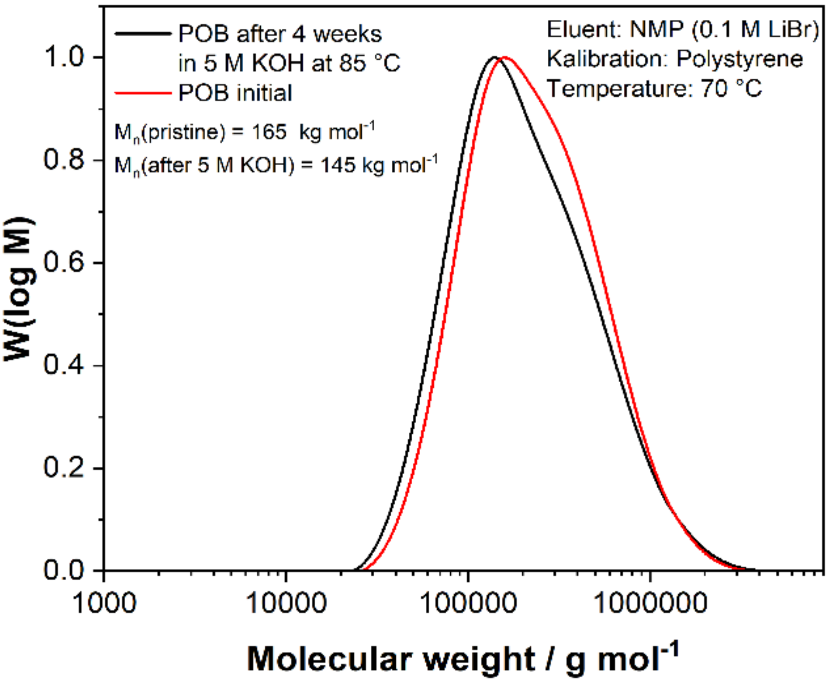

Figure S 11: GPC measurements of POB before and after treatment with 5 M KOH for 4 weeks at 85 °C. The measurements were performed with NMP as eluent at 70 °C against polystyrene standards.

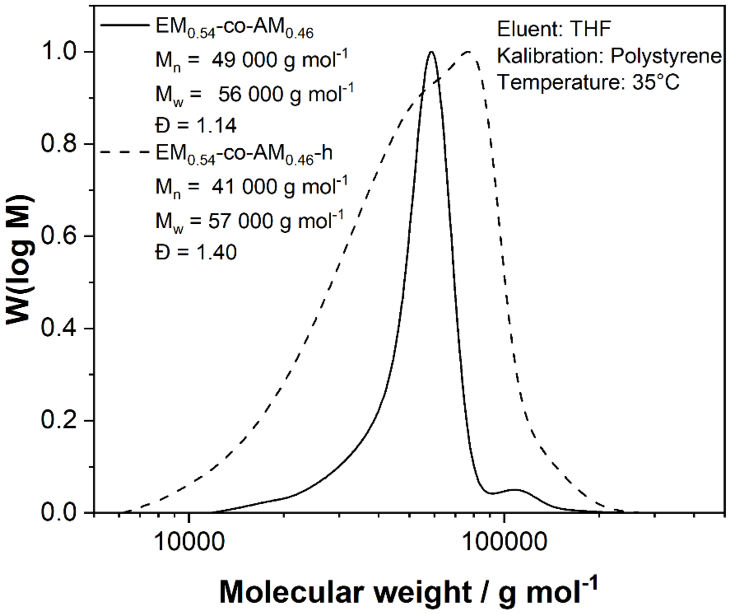

Figure S 12: Comparison of the GPC curves before and after hydrogenation of the double bonds with para-tosyl hydrazide.

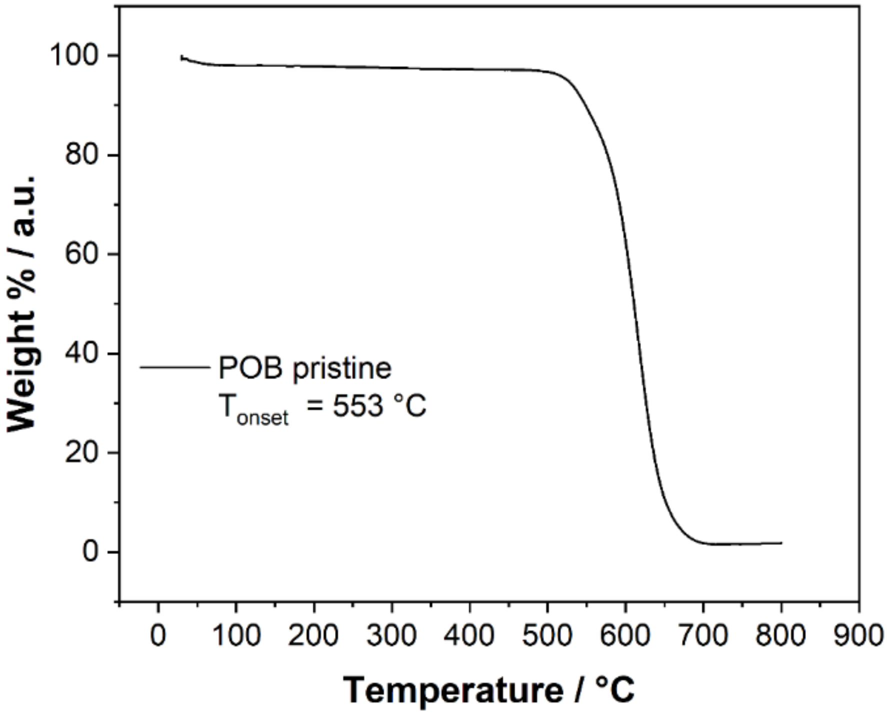

Figure S 13: TGA measurement of POB under synthetic air atmosphere with a heating rate of 10 K/min.

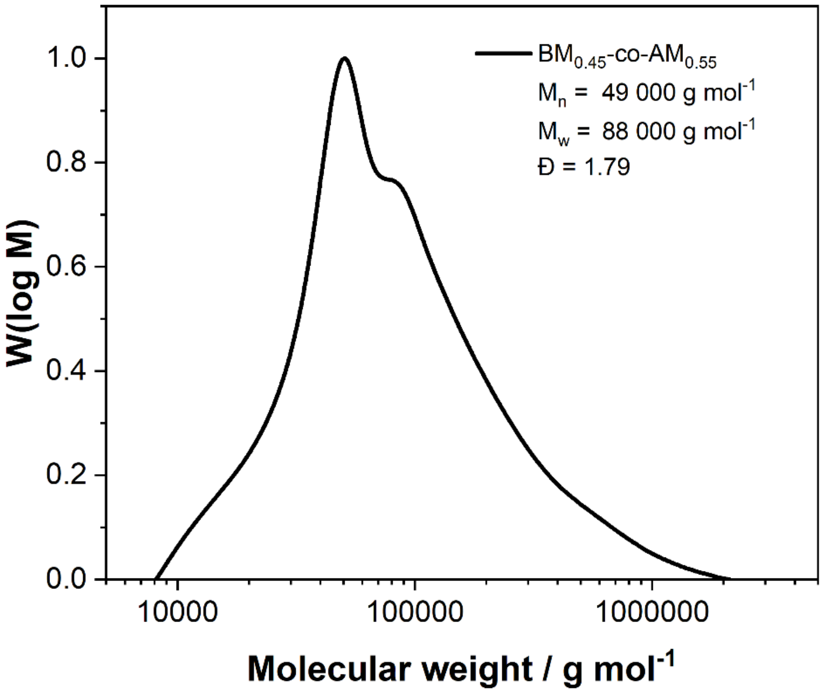

Figure S 14: GPC measurements of $BM_{0.45}$-co-$AM_{0.55}$ with THF as eluent against polystyrene standards.

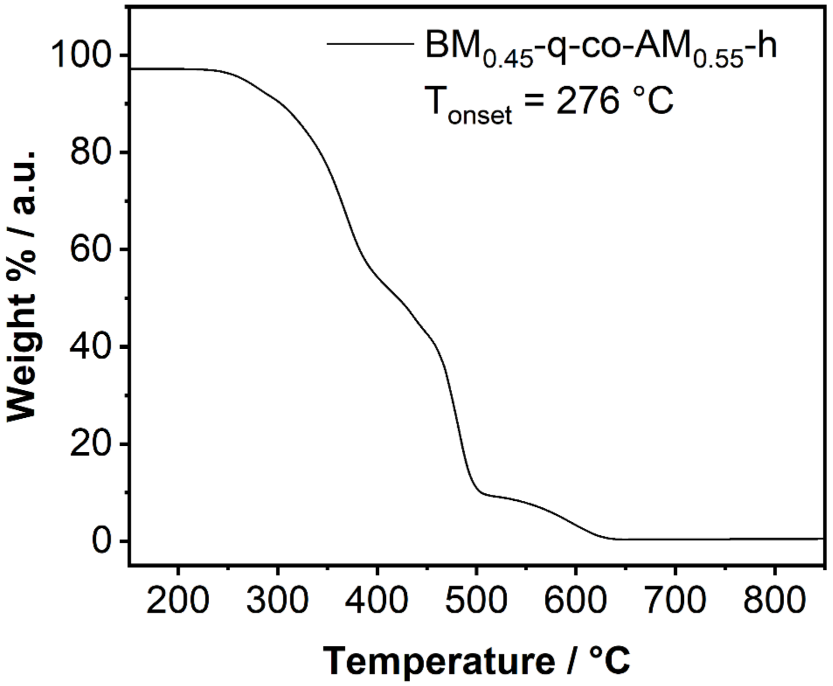

Figure S 15: TGA measurement of $BM_{0.45}$q-co-$AM_{0.55}$-h under synthetic air atmosphere with a heating rate of 10 K/min.

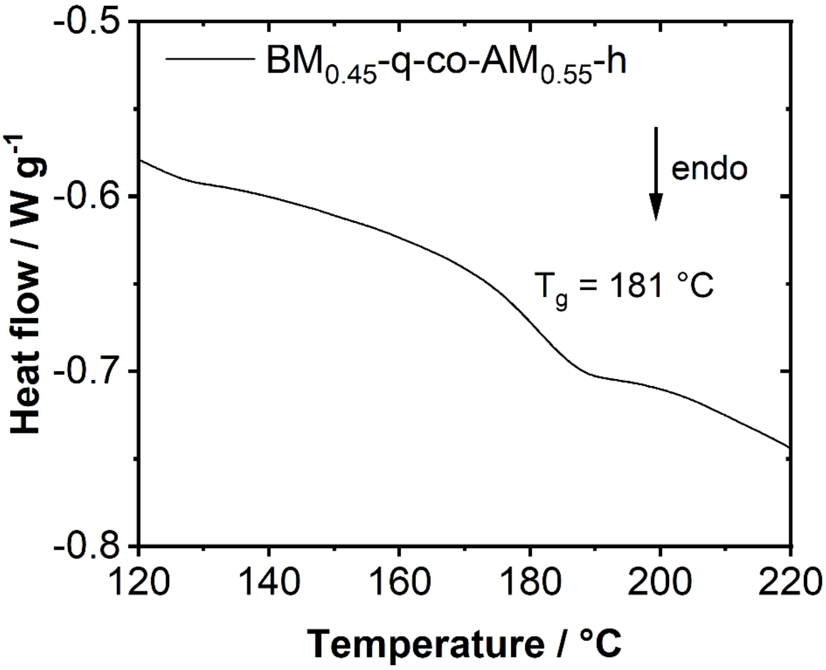

Figure S 16: DSC analysis (2nd heating curve, 10 K min^{-1} heating rate) of $BM_{0.45}$q-co-$AM_{0.55}$-h.

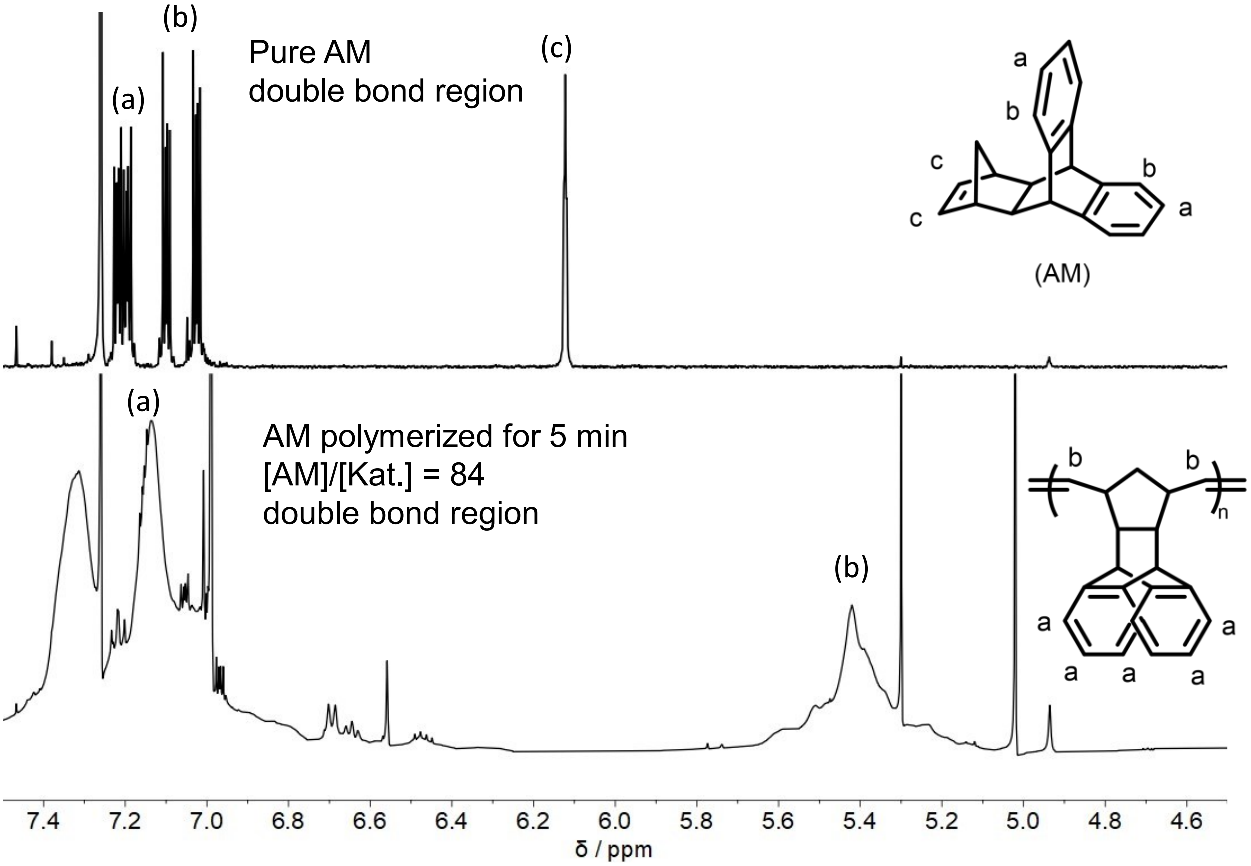

Figure S 17: Magnification of the double bond region for a ^{1}H NMR spectrum of an AM sample after 5 min polymerization time with [AM]/[Kat.] = 84 compared to the NMR spectrum of the monomer, showcasing the complete absence of the characteristic peak of the norbornene double bond signal in the sample after a polymerization time of 5 min and the appearance of the double bond signal in the polymer backbone, which is significantly shifted compared to the monomer.

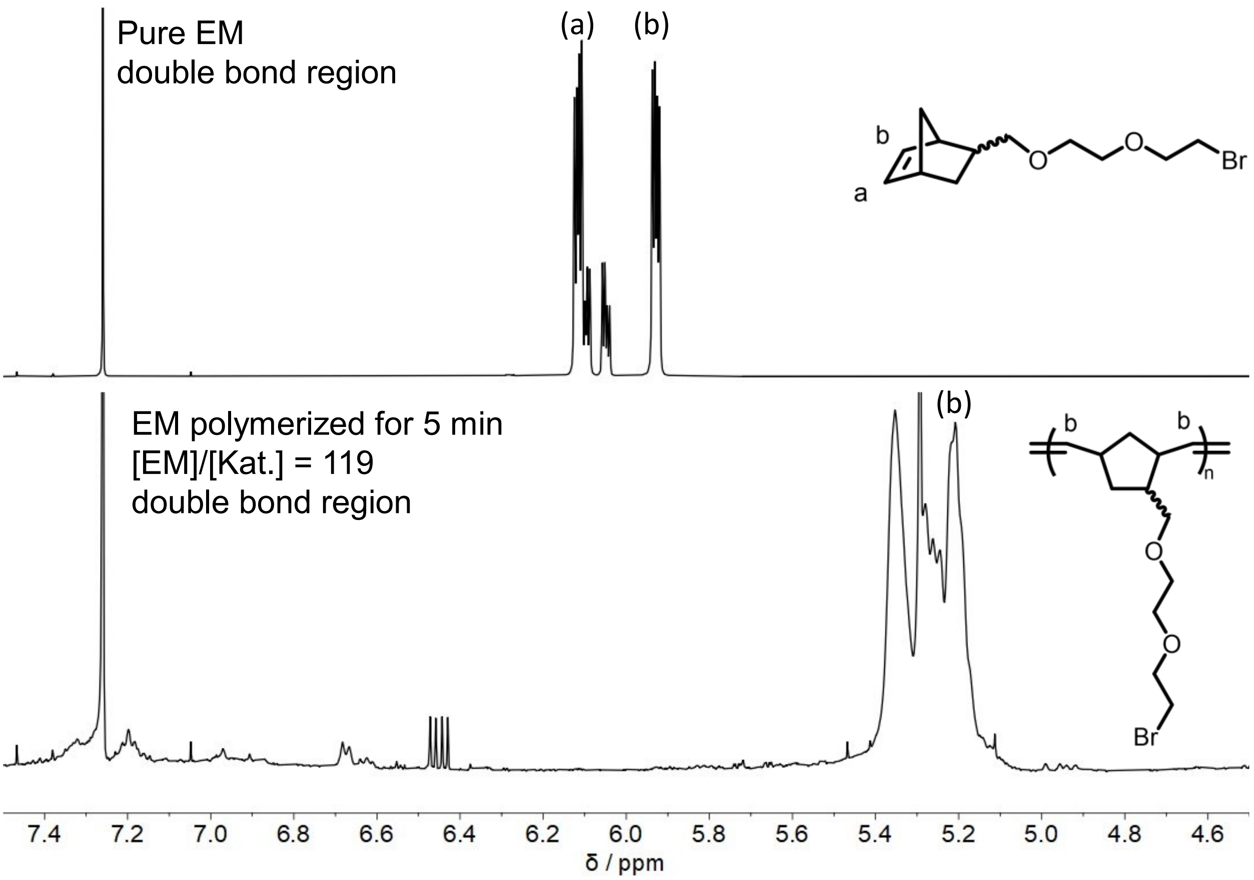

Figure S 18: Magnification of the double bond region for a ^{1}H NMR spectrum of an EM sample after 5 min polymerization time with [EM]/[Kat.] = 119 compared to the NMR spectrum of the monomer, showcasing the complete absence of the characteristic peak of the norbornene double bond signal in the sample after a polymerization time of 5 min and the appearance of the double bond signal in the polymer backbone, which is significantly shifted compared to the monomer.

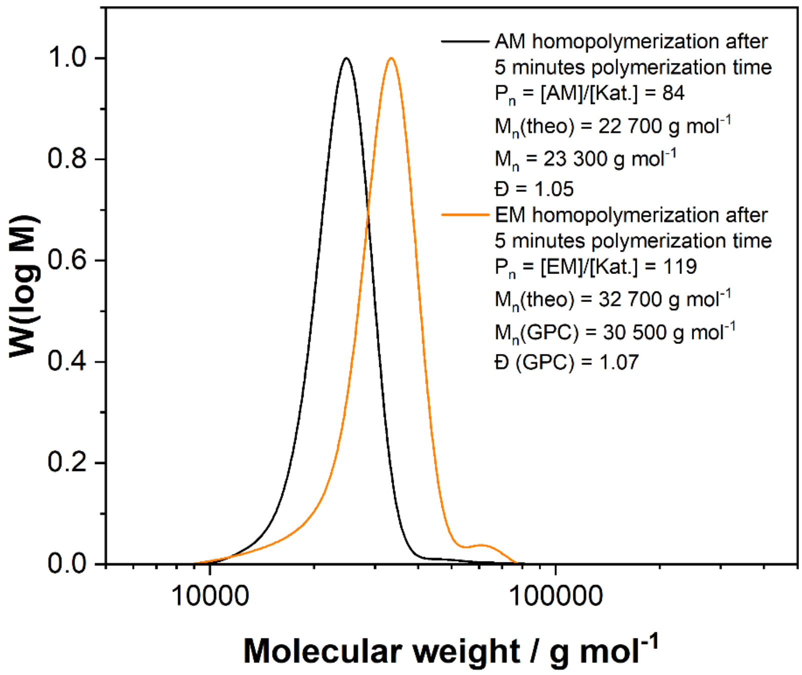

Figure S 19: GPC samples measured in THF and calibrated against polystyrene standards for separate polymerizations of the AM and EM after 5 minutes and with different [M]/[Kat.] ratios referring to the desired build-in-ratio in the block copolymer (54:46 EM:AM) demonstrating that the target molecular weight is reached after 5 minutes and both monomers could be controlled polymerized with ROMP which is a prerequisite for the preparation of block-copolymers.

4 Additional Figures: Membrane characterization

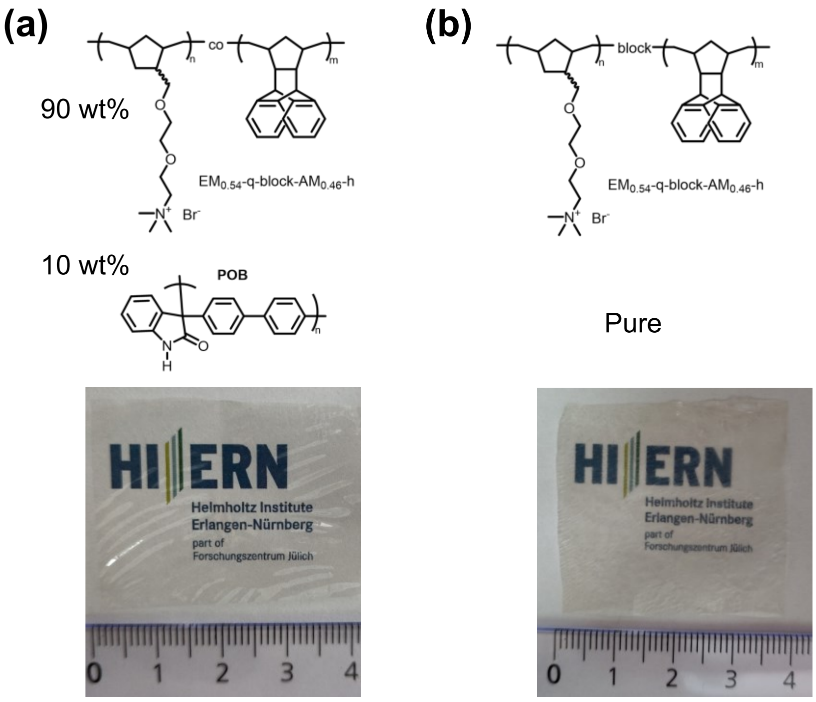

Figure S20: (a) Structures and optical image of a blend membrane consisting of 90 wt% EM$_{0.54}$-q-co-AM$_{0.46}$-h and 10 wt% POB (b) Structure of EM$_{0.54}$-q-block-AM$_{0.46}$-h and optical image of membrane obtained thereof showcasing slight opacity.

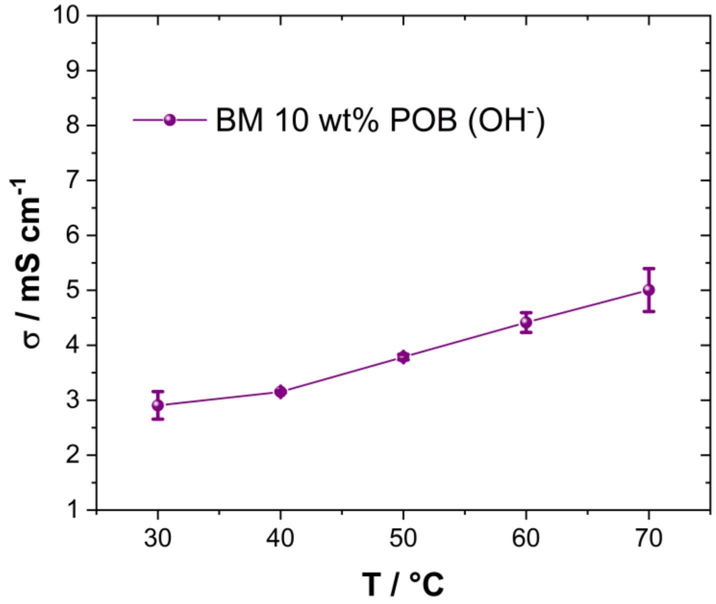

Figure S 21: Ionic conductivity of a blend membrane consisting of 90% $BM_{0.45}q$-co-$AM_{0.55}$-h and 10 % POB.

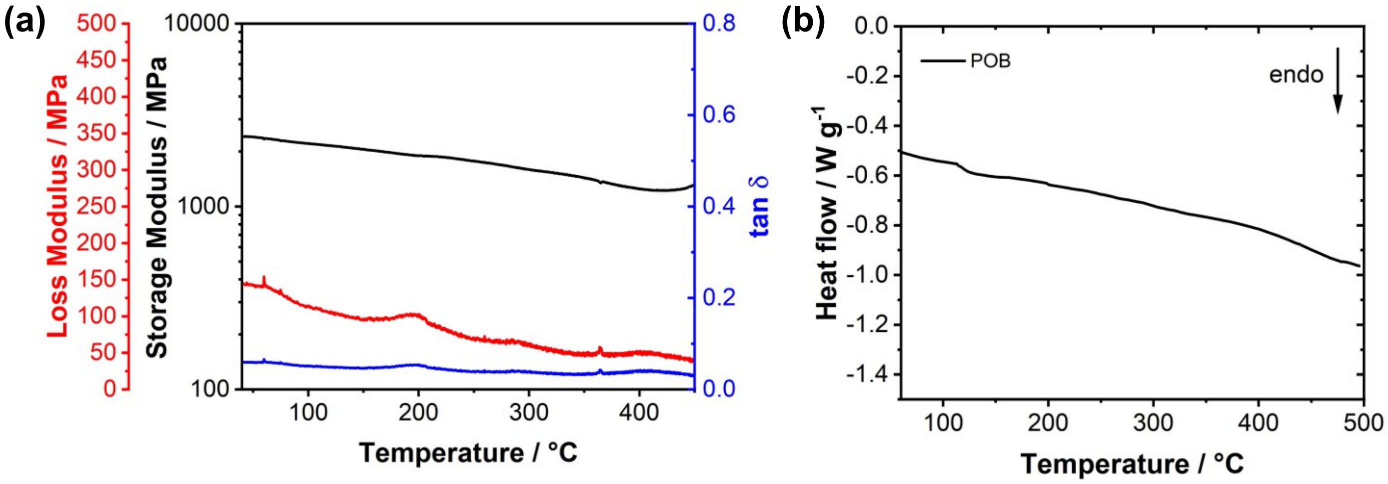

Figure S22: (a) Dynamic mechanical analysis of POB (2 K min^{-1} heating rate, 1 Hz oscillation frequency) (b) DSC measurement of POB (2nd heating curve, 10 K min^{-1} heating rate).

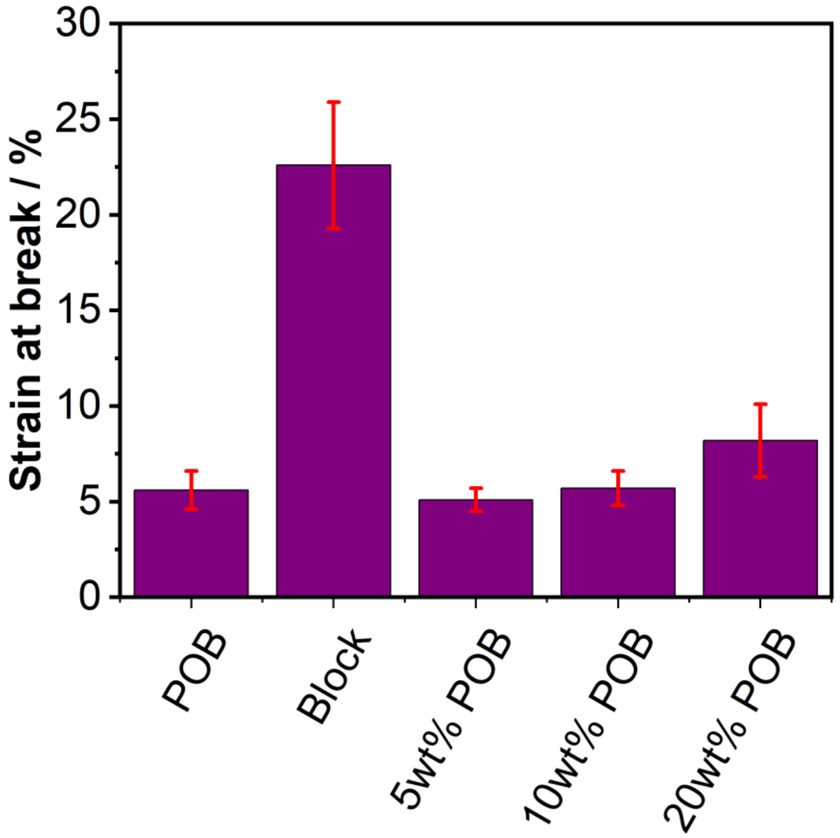

Figure S23: Tensile properties (strain at break) of exemplary blend membranes, the pure block-copolymer and pure POB.

Table S1: Tensile properties of the ether-free $BM_{0.45}q$-co-$AM_{0.55}$-h blended with 10 wt% POB.

Membrane	Youngs Modulus [MPa]	Tensile Strength [MPa]	Strain at break [%]
10 wt% POB/90wt%$BM_{0.45}q$-co-$AM_{0.55}$-h	1670 ± 1.5	38.2 ± 0.6	2.3 ± 0.1
10 wt% POB/90wt%$EM_{0.54}q$-co-$AM_{0.45}$-h	1074 ± 80	33.7 ± 2.6	5.7 ± 0.9

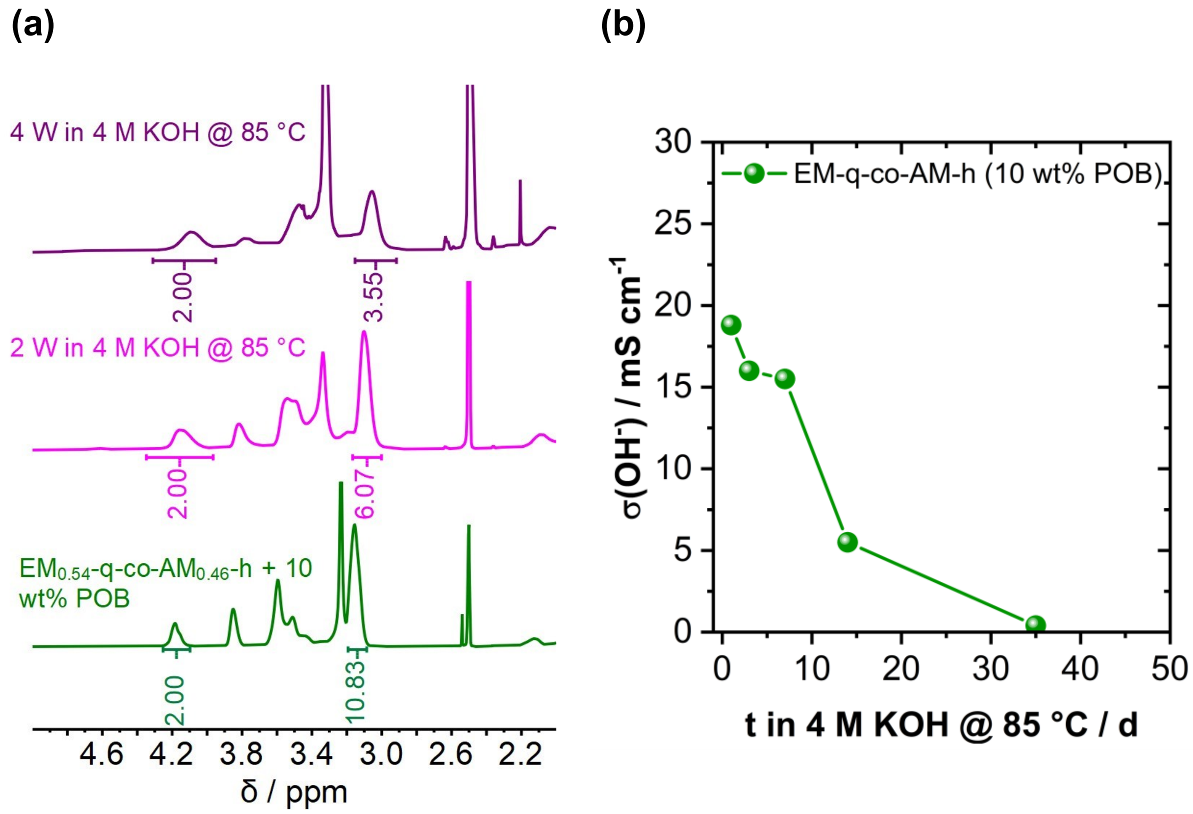

Figure S24: (a) ^{1}H NMR spectra of the pristine blend consisting of 10 wt% POB and 90 wt% $EM_{0.54}$-q-co-$AM_{0.46}$-h (green) and after treating the respective membrane with 4 M KOH at 85 °C for 2 weeks (magenta) and for 4 weeks (purple) (b) Ionic conductivity after certain time intervals in 4 M KOH at 85 °C.

5 Additional Figures: AEMWE tests

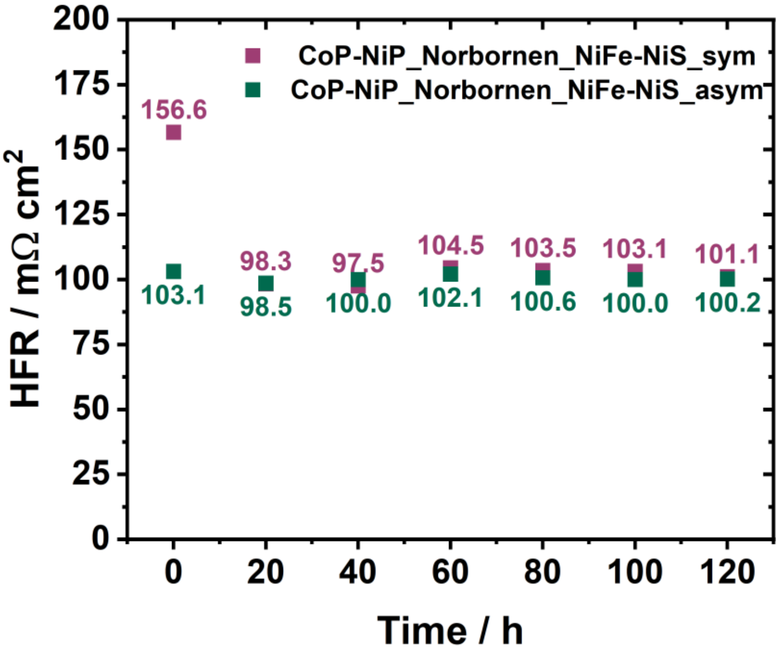

Figure S25: HFR values for a constant current hold at 1 A cm^{-2} and 60 °C for 120 h after 20 h each for a membrane with 10 wt% POB and 90 wt% $EM_{0.54}$-q-co-$AM_{0.46}$-h in the blend under asymmetric conditions (1 M KOH on anode, dry cathode, green curve) and symmetric operation conditions (1 M KOH circulating on cathode and anode, purple curve).

6 References

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