# Supporting Information

## An Anchor for Help: A Cross-linking Moiety for Block Copolymer Membrane Stabilization for Ultrafiltration Applications in Water

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## Experimental Section

The monomers allyl methacrylate, butyl methacrylate, methyl methacrylate, (2-hydroxyethyl) methacrylate and 2-(Trimethylsilyloxy)ethyl methacrylate were purchased from Sigma Aldrich and BLDpharm. Before the synthesis the radical stabilizers were removed by passing the monomers through an aluminum oxide column. ALMA, BMA and MMA were degassed via three freeze, pump, thaw cycles and stored in a glovebox at -20 °C. HEMA and HEMA-TMS were stored under argon atmosphere at -7 °C.

The Initiators *tert*-butyl $\alpha$-bromoisobutyrate and ethyl $\alpha$-bromo phenyl acetate were purchased at Sigma Aldrich and ABCR GmbH respectively and used as received.

The solvents, tetrahydro furan, dimethyl formamide and 1,4-dioxane, for the membrane formation process were purchased from Sigma Aldrich in HPLC grade and used as received. All other solvents were bought at reagent grade from various sources.

Copper bromide and chloride salts were purchased from Sigma Aldrich at 99,999% trace metal purity. After stirring of the salt in glacial acetic acid for 24 h, the colorless solid was washed with dry ethanol and dry diethyl ether and dried in high vacuum at 40 °C for another 24 h. The copper salts were stored in a glovebox.

The bipyridyl- and *N,N,N',N'',N''*-Pentamethyl diethylenetriamine ligands were purchase at Sigma Aldrich and purified by vacuum distillation and sublimation, before storage in a glovebox. Before use, a stock solution of the catalyst in anisole was prepared with a concentration of 0.2 M.

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance II 400 spectrometer with a 9.4 T Ultrashield Plus Magnet, a BBFO probe, and referenced by using the solvent signals. For processing Bruker TopSpin 4.2.0 software was used.

Standard size exclusion chromatography (SEC) was performed with a 1260 Infinity II (Agilent Technologies) system and in this work THF was used as the mobile phase (HPLC grade, flow rate 1 mL $min^{-1}$) on an SDV column set from polymer standard service (PSS) (SDV $10^3$ A, SDV $10^5$ A, SDV $10^6$ A, 5 µm) with a PSS SECurity$^2$ RI/UV detector. Calibration was carried out using polystyrene (PS) standards from PSS. With dimethylformamide (DMF) as the mobile phase (flow rate 1mL $min^{-1}$, containing 1 g $L^{-1}$ LiBr) a PSS GRAM Analytical column from PSS ($10^3$ A) is used at 60 °C. Calibration was carried out using poly(methyl methacrylate) (PMMA) standards from PSS.

Scattering electron microscopy (SEM) was carried out on a Zeiss Sigma VP device (GeminiSEM 500) using the software SmartSEM Version 6.07. The samples were mounted on an aluminum stud

using adhesive copper tape and sputter-coated with approximately 6 nm platinum using an Automatic Turbo Coater PLASMATOOL 125 SIN 2020_131 from Ingenieurbüro Peter Liebscher.

UV irradiation for cross-linking was carried out in a Hönle UV-technology UVA-Cube 2000, equipped with a UVAPRINT 100-200 HPV EZ lamp, which operated at 1000 W.

## Synthesis of the macroinitiator P(ALMA-BMA-MMA)Br

In a glovebox, the monomers, anisole and the initiator were placed in a flame-dried Schlenk flask. After heating the reaction solution to the appropriate temperature, the catalyst solution was added via syringe. The reaction was terminated by placing the Schlenk flask in an ice bath and the polymer subsequently passed through an aluminum oxide column, before being precipitated in *n*-hexane. In table S1 the amount of substances, temperatures and reaction times are summarized.

Table S1: Summary of the reaction conditions for the Synthesis of P(ALMA-BMA-MMA)Br

| Polymer | n(ALMA) / mmol | n(BMA) / mol | n(MMA) / mol | V(Anisole) / mL | Initiator | n(initiator) / µmol | Temperature / °C | Time / min |
|---|---|---|---|---|---|---|---|---|
| MI 1 | 2.4 | 42 | 50 | 21.4 | EPBA | 68 | 65 | 460 |
| MI 2 | 2.4 | 42 | 50 | 21.4 | EPBA | 68 | 65 | 300 |
| MI 3 | 2.4 | 42 | 50 | 21.4 | EPBA | 68 | 60 | 300 |
| MI 4 | 2.4 | 42 | 50 | 21.4 | EPBA | 68 | 60 | 300 |
| MI 5 | 3.6 | 64 | 76 | 32.1 | tBib | 100 | 60 | 270 |

## Synthesis of the block copolymer P(ALMA-BMA-MMA)-*b*-P(HEMA)

The macroinitiator P(ALMA-BMA-MMA)Br was dissolved in the respective solvent and placed in a flame-dried Schlenk flask, before the monomer for the second block was added. The reaction mixture was subsequently degassed via three freeze, pump and thaw cycles. After heating the solution to reaction temperature, the catalyst solution was added via a syringe. Following, the reaction was terminated by placing the Schlenk-flask in an ice bath and subsequently the copper catalyst was removed by passing the mixture through an aluminum oxide column. The block copolymer was precipitated in *n*-hexane.

For the TMS protected monomer, the block copolymer was dissolved in THF and a small amount of 1 $molL^{-1}$ hydrochloric acid was added in order to cleave the protecting group, before precipitating the polymer in *n*-hexane.

In Table S2 the amount of substances, solvents, temperatures and reaction times are listed.

Table S2: Summary of the composition of the different block copolymer reactions. Solvent A = 1-Propanole/methyl ethyl ketone (30:70 V/V), B = Anisole

| Polymer | BCP 1 | BCP 2 | BCP 3 | BCP 4 | BCP 5 | BCP 6 | BCP 7 |
|---|---|---|---|---|---|---|---|
| Macroinitiator | MI 1 | MI 1 | MI 3 | MI 2 | MI 2 | MI 4 | MI 5 |
| n(MI) / mol | 1.68e-5 | 1.09e-5 | 2.5e-5 | 1.05e-5 | 1.05e-5 | 7.94e-6 | 1.69e-5 |
| Monomer | HEMA | HEMA | HEMA-TMS | HEMA-TMS | HEMA-TMS | HEMA-TMS | HEMA-TMS |
| n(Monomer) / mol | 9.95e-3 | 6.43e-3 | 1.48e-2 | 1.25e-2 | 1.25e-2 | 6.75e-3 | 1.14e-2 |
| Solvent | A | A | A | A | A | B | B |
| V(Solvent) / mL | 2.43 | 1.57 | 2.61 | 3.04 | 3.04 | 4 | 5 |
| Catalyst | Cu(Bpy)Cl | Cu(Bpy)Cl | Cu(Bpy)Cl | Cu(PMDETA)Br | Cu(PMDETA)Cl | Cu(PMDETA)Cl | Cu(PMDETA)Br |
| n(catalyst) / mol | 1.60e-5 | 1.03e-5 | 2.38e-5 | 1e-5 | 1e-5 | 7.94e-6 | 2.2e-5 |
| Temperature / °C | 50 | 50 | 50 | 50 | 50 | 60 | 60 |
| P / % | 3 | 1 | 2 | 3 | 4 | 8 | 5 |
| Time / h | 1.5 | 4 | 3 | 3 | 3 | 43.5 | 19 |

## Membrane formation using the SNIPS process

0.4532 g of BCP 6 and 1.9 mg $CuCl_2$ as well as 22.9 mg of benzophenone, were dissolved in 1.032 g of a mixture of THF, DMF and 1,4-dioxane (2:1:1 by weight), similar to the conditions used BY SCHÖTTNER ET AL.[1] After the formation of a viscous solution, it was transferred to a polyester/polypropylene nonwoven and cast with a doctor blade (200 µm gap). After 15 s of evaporation time, the polymer membrane was precipitated in deionized water and dried at ambient conditions first, before being placed in a vacuum oven (40 °C, vac.).

## Cross-linking procedure

For the cross-linking tests with the polymer P(ALMA-BMA-MMA)Br, 100 mg polymer was dissolved in a solution of benzophenone in THF. The amount of solution was calculated, so the resulting polymer film would have the appropriate amount of benzophenone (1, 2 or 5 wt-%).

After manufacturing the polymer films, or membranes they were placed in the UV-cube for the specified time. Irradiation was carried out in 30 s intervals, with pauses of 15 s. Additionally, the polymer was cooled via placing a water/ice mixture beneath a glass plate.

## Water permeance measurements

Water permeance measurements were carried out using a dead-end filtration cell with a volume of 400 mL. The pressure of 0.2 bar was applied through the clean water feed via an in-house nitrogen line. Round membranes with a diameter of 1 cm were used. Water was collected for 10 minutes in a glass vial and weight was used to calculate permeance.

## Pre-conditioning of the membranes

The permeance of membranes usually drops significantly at the beginning of a measurement (or application) and afterward reaches a plateau when maximum compaction is reached. There appears to be no agreed timeframe for characterizing such membranes, with many different methods used in the literature. In our group, we established a clear protocol for comparing all our membranes with other team players: the technique involves conditioning for 1 h in water before collecting three samples over 30 min to determine pure water permeance. Following this procedure, we collected data for 1.5 h. At the same time, the first hour was also monitored to gain insight into the exact compacting behavior since this is the focus of this research."

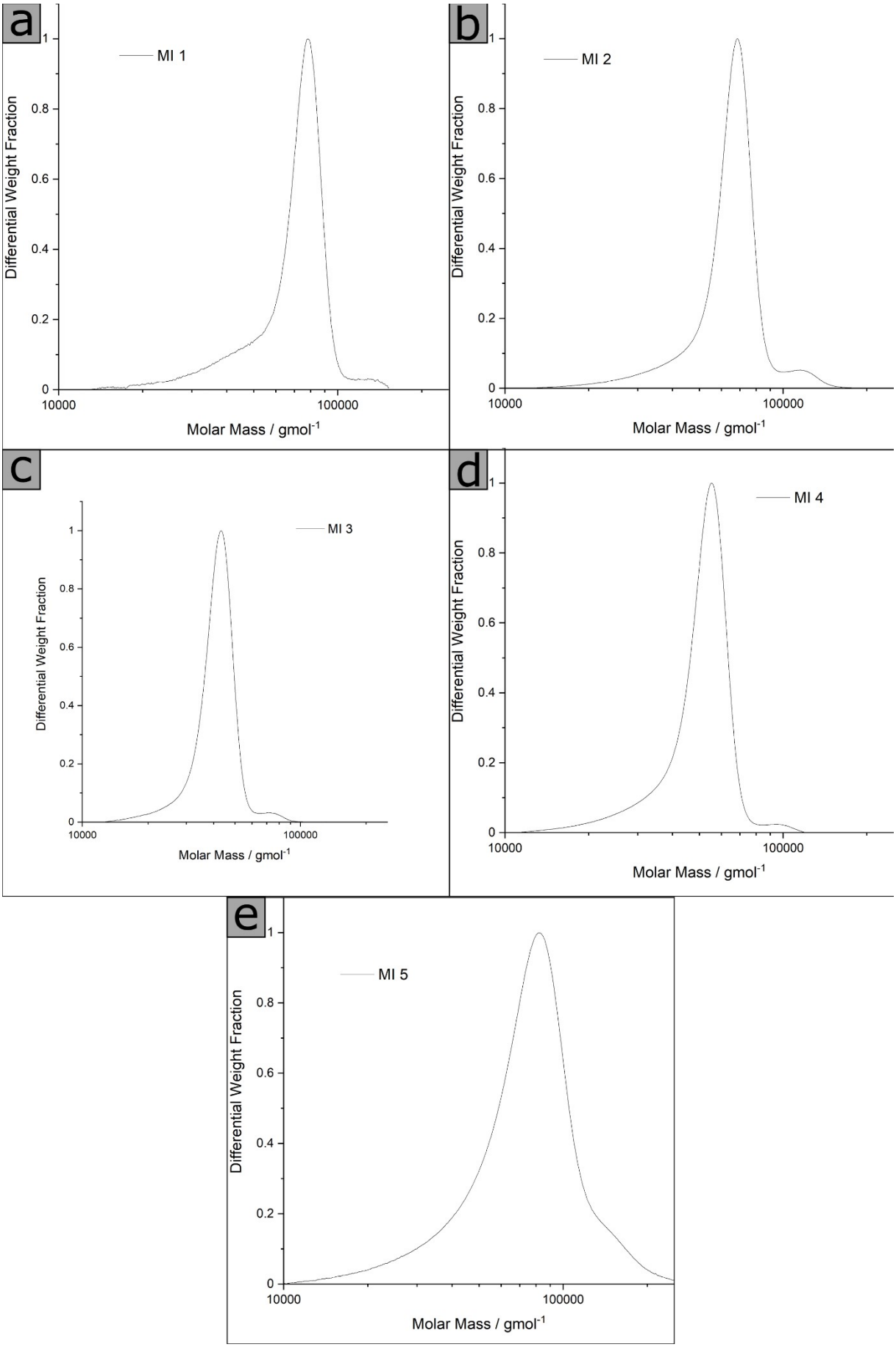
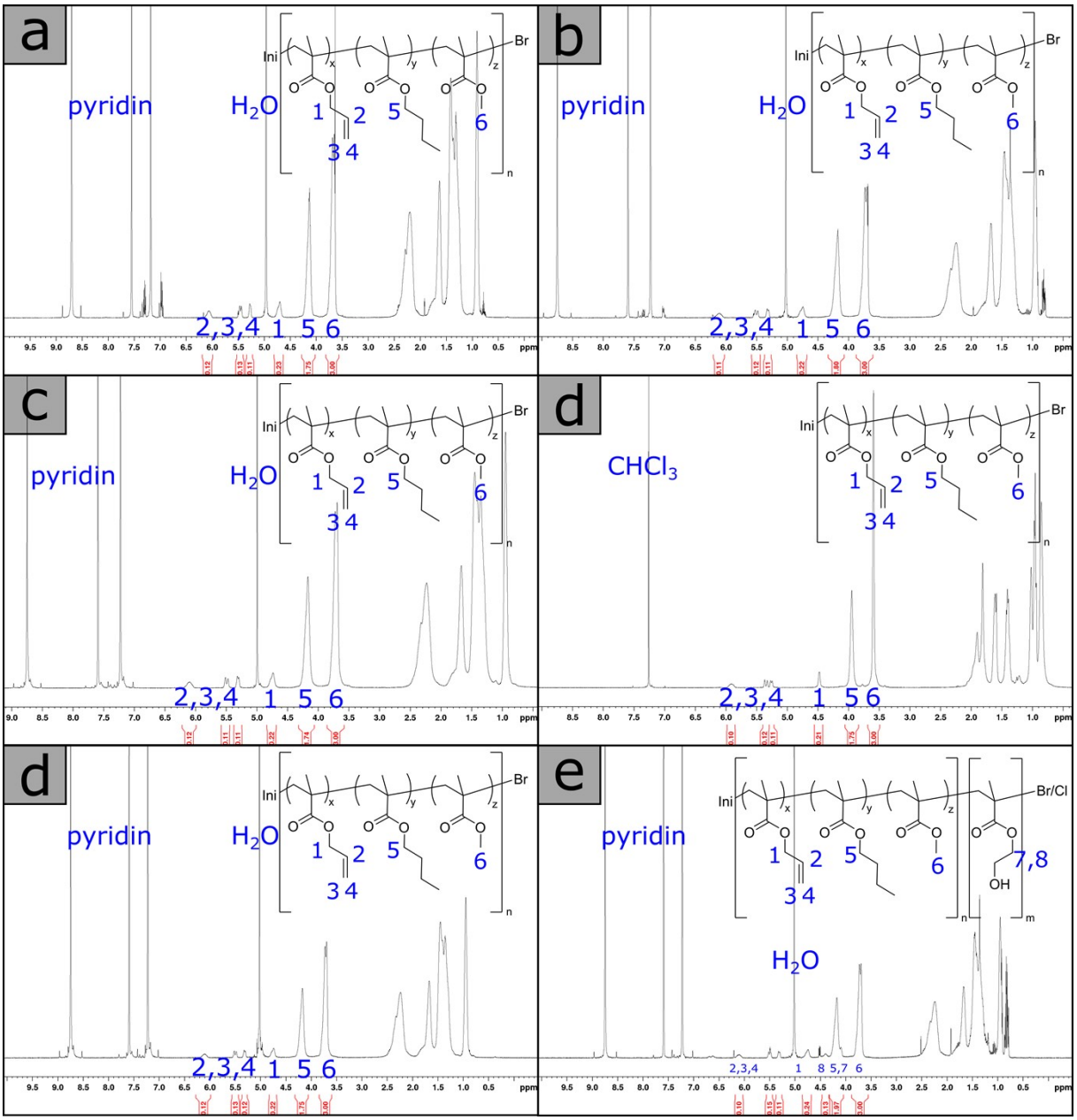



Figure S1: SEC traces of MI 1 – 5, measured with THF eluent vs. PS standard.


a
pyridin
H2O
2,3,4 1 5 6
b
pyridin
H2O
2,3,4 1 5 6
c
pyridin
H2O
2,3,4 1 5 6
d
CHCl3
2,3,4 1 5 6
d
pyridin
H2O
2,3,4 1 5 6
e
pyridin
H2O
2,3,4 1 8 5,7 6
Ini
Br
Br/Cl
OH

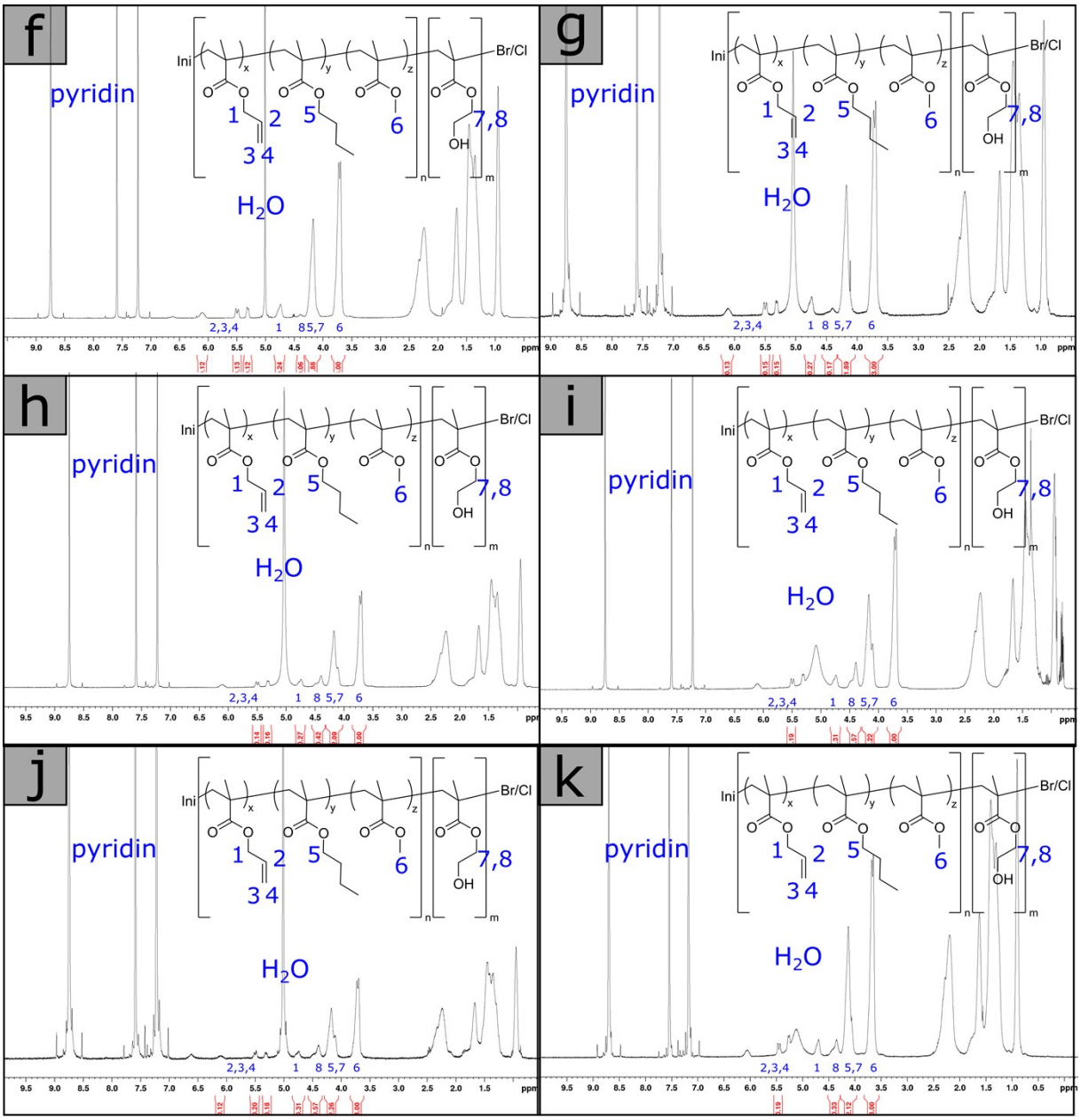



Figure S2: $^{1}$H-NMR spectra of MI 1 (a) to MI 5 (d) and BCP 1 (e) to BCP 7 (k), measured in pyridine-$d_5$ at 400 MHz and 300 K. d) $^{1}$H-NMR spectrum of MI 4, measured in $CDCl_3$ at 400 MHz and 300 K.

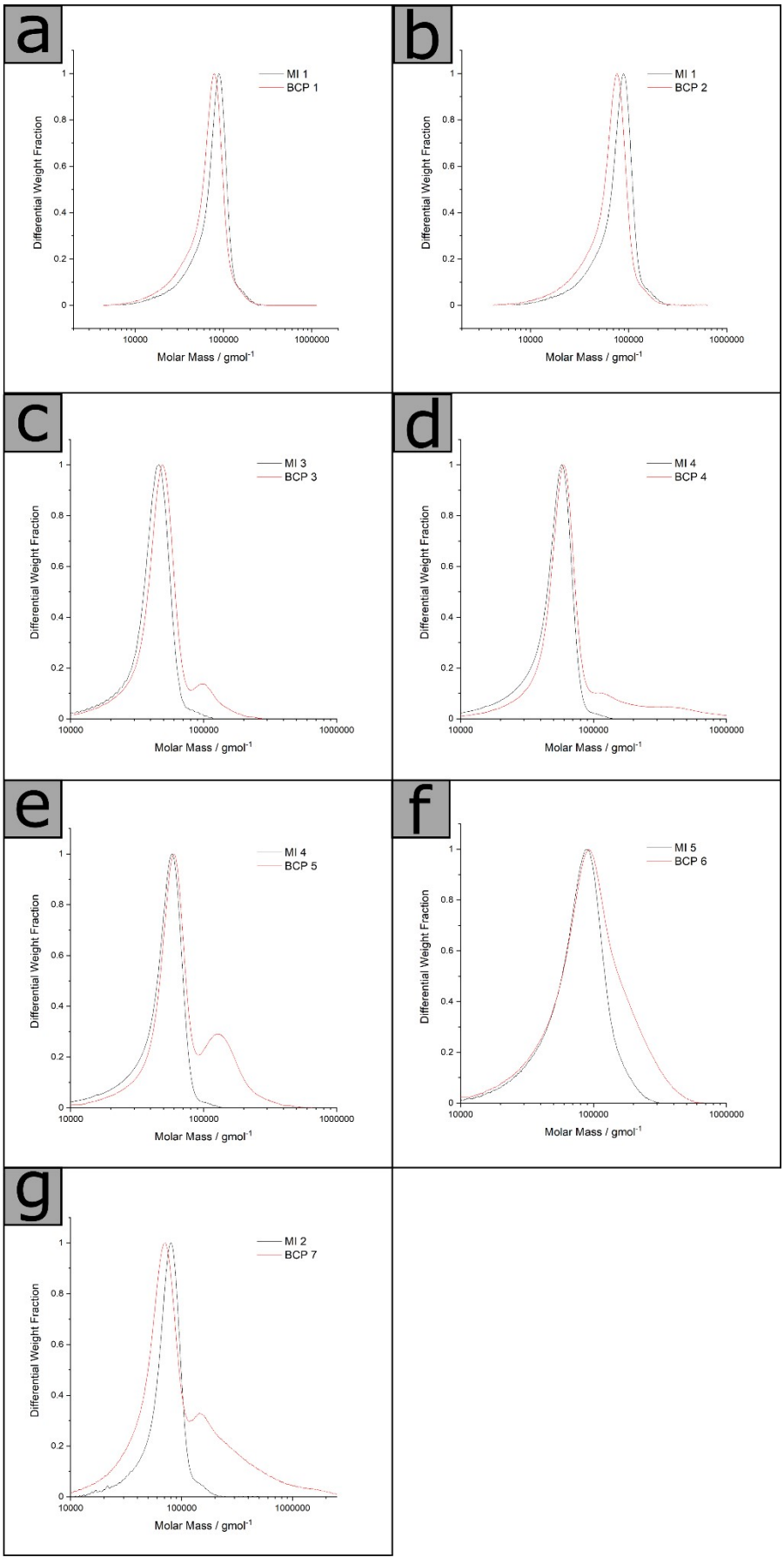



Figure S3: SEC Traces of BCP 1 – 7, overlaid with their corresponding macroinitiator, measured with DMF eluent vs. PMMA standard.

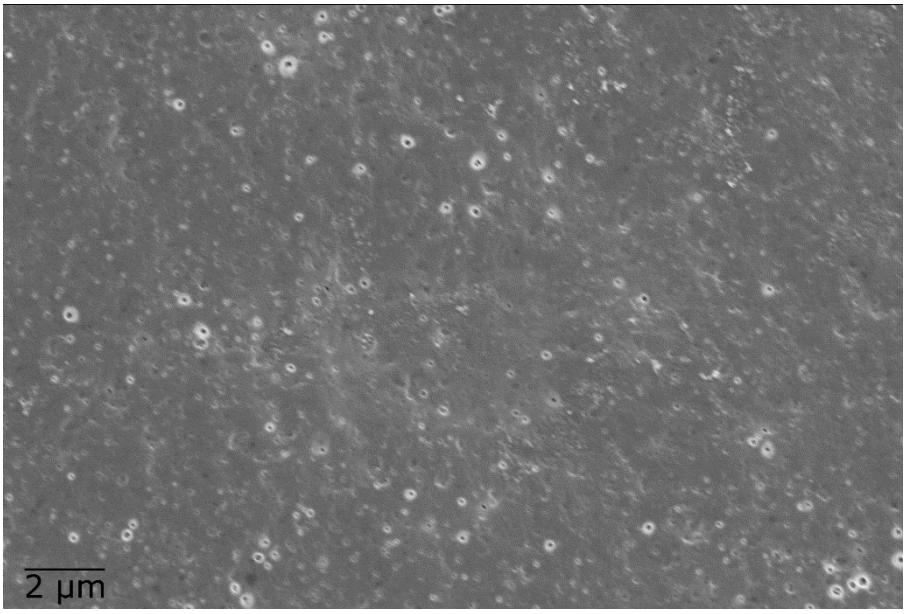



Figure S4: SEM image of the membrane of BCP 6, after 10 min of UV exposure.

[1] S. Schöttner, H.-J. Schaffrath, M. Gallei, *Macromolecules* **2016**, *49*, 7286.