

## Supporting Information

**Nanoporous Block Copolymer Membranes with Enhanced Solvent Resistance via UV-Mediated Cross-Linking Strategies**

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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.<sup>[1]</sup>

Standard size exclusion chromatography (SEC) was performed with a system composed of a 1260 Infinity II (Agilent Technologies) and two eluents. With tetrahydrofuran (THF) as the mobile phase (flow rate 1 mL min<sup>-1</sup>) a PSS SECurity<sup>2</sup> RI/UV detector on a SDV column from polymer standard service (PSS) (SDV 10<sup>3</sup>A, 5 µm) was used. Calibration was carried out using polystyrene (PS) standards from PSS. With dimethylformamide (DMF) as the mobile phase (flow rate 1 mL min<sup>-1</sup>, containing 1 g L<sup>-1</sup> LiBr) a PSS GRAM Analytical column from PSS (10<sup>3</sup> A) was used at 60 °C. Calibration was carried out using poly(methyl methacrylate) (PMMA) standards from PSS.

Scattering electron microscopy (SEM) was carried out with a Zeiss Sigma VP device. The samples were mounted on an aluminum stud using adhesive graphite tape and sputter-coated with platinum using a Turbo-Sputter Coater SCT120. Additionally, a FEI Quanta 400 FEG scanning electron microscope was used, where the samples were sputter-coated with gold/palladium for 30 s at 10 mA. Lastly, a XL30 FEG SEM from FEI/Phillips, where samples were sputtered with 2 nm platinum.

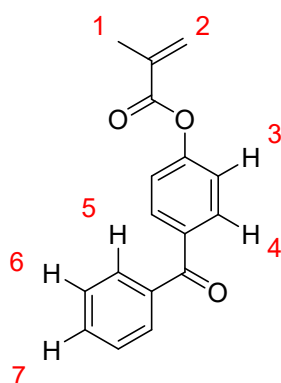
Differential scanning calorimetry (DSC) was carried out on a Netzsch DSC 214 Polyma with a heating rate of 10 K min<sup>-1</sup>.

The chemicals used were purchased from Sigma Aldrich, Acros Organics, Alfa Aesar and Euriso Top GmbH and used as received, unless otherwise stated.

The monomers methyl methacrylate, butyl methacrylate and (Trimethylsiloxy ethyl) methacrylate were passed through basic aluminum oxide before being used.

The Cu<sup>I</sup>Br was suspended in glacial acetic acid for 12 h, before being washed with absolute ethanol and dried in a high vacuum. The purified copper bromide was kept in a glovebox until use. Methacryloyl chloride was distilled before being stored at -20 °C until use.

*Synthesis of benzophenone methacrylate (BPMA) 2:*



The monomer benzophenone methacrylate was synthesized according to the procedure published by Kim et al.<sup>[2]</sup> The purification step was modified to generate the required purity. 4-Hydroxy benzophenone (9.93 g, 50 mmol, 1.00 Eq.) were suspended in dry dichloromethane (150 mL), and dry triethyl amine (7.7 mL, 55 mmol, 1.10 Eq.) was added. Methacryloyl chloride (5.3 mL, 55 mmol, 1.10 Eq.) was added dropwise to the light brown solution at 0 °C and subsequently stirred at ambient temperature. After complete reaction, the ammonium salt was filtrated off and washed with dichloromethane. The combined organic phases were passed through silica before the solvent was evaporated under reduced pressure. After recrystallization

from *n*-hexane, the product was dried under high vacuum at 40 °C. 10.40 g (78 %) colorless white crystals were obtained as product.

<sup>1</sup>H-NMR(400 MHz, CDCl<sub>3</sub>, 300K): δ = 2.09 (1, s, 3H); 5.81 (2, m, 1H); 6.39 (2, m, 1H); 7.23 – 7.29 (3, CDCl<sub>3</sub>, m, 2H); 7.45 – 7.54 (6, m, 2H); 7.56 – 7.64 (7, m, 1H); 7.77 – 7.83 (5, m, 2H); 7.85 – 7.90 (4, m, 2H) ppm.

*Synthesis of Poly(butyl methacrylate-co-benzophenone methacrylate-co-methyl methacrylate) (P(BMA-co-BPMA-co-MMA)) P1:*

Benzophenone methacrylate (2.00 g, 7.51 mmol, 55 Eq.) was dissolved in anisole (44 mL) and placed in a baked-out, and argon-purged Schlenk flask, followed by butyl methacrylate (8.2 mL, 515 mmol, 378 Eq.) and methyl methacrylate (7.1 mL, 667 mmol, 489 Eq.). After adding tert-Butyl 2-bromoisobutyrate (20 μL, 0.136 mmol, 1 Eq.) the reaction mixture was degassed via three cycles of the freeze, pump, thaw technique and heated to 60 °C. Following the addition of 0.1 mol L<sup>-1</sup> Cu<sup>II</sup>(PMDETA)Br solution in anisole (2 μL), the reaction was started with 0.1 mol L<sup>-1</sup> Cu<sup>I</sup>(PMDETA)Br solution in anisole (0.11 mL). The reaction was terminated after 2.5 h, and after passing the reaction mixture through a neutral aluminum oxide column, 4.29 g polymer was precipitated in *n*-hexane.

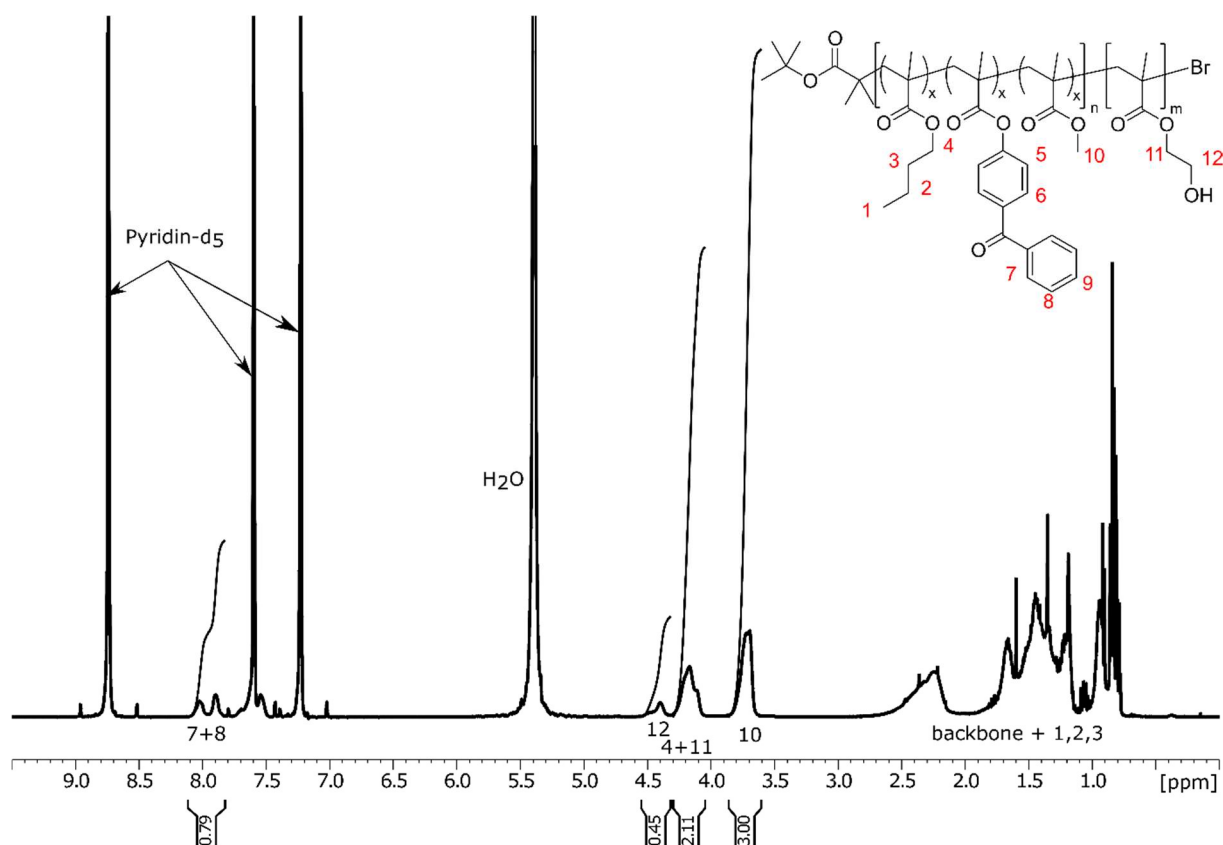
<sup>1</sup>H-NMR(400 MHz, 300 K, Pyridin-d<sub>5</sub>): δ = 0.94 (1, s, 3H); 1.11 – 2.80 (backbone + 2,3, m); 3.70 (1, s, 3H); 4.18 (4, s, 2H); 7.47 – 7.73 (Pyridin-d<sub>5</sub> + 5,8, m); 7.82 – 8.13 (6,7,9, m, 5H) ppm.

*Synthesis of Poly(butyl methacrylate-co-benzophenon methacrylate-co-methyl methacrylate)-block-poly(hydroxy ethyl) methacrylate (P(BMA-co-BPMA-co-MMA)-b-P(HEMA)) P2:*

Macroinitiator **P1** (1.70 g, 0.052 mmol, 1 Eq.) was dissolved in anisole (13 mL) and placed in a baked-out, and argon-purged Schlenk flask, and (Trimethylsiloxy ethyl) methacrylate

(4.80 mL, 22 mmol, 425 Eq.) was added. After degassing the reaction mixture via three freeze, pump, thaw cycles, 0.02 mol L<sup>-1</sup> Cu<sup>II</sup>PMDETABr solution in anisole (8  $\mu$ L) was added and the reaction was started with 0.2 mol L<sup>-1</sup> Cu<sup>I</sup>(PMDETA)Br solution in anisole (0.21 mL). After 17 h the polymer solution was passed through a neutral aluminum oxide column and 1.37 g polymer were precipitated in *n*-hexane. The HEMA-TMS block was deprotected by treatment with 2 mol L<sup>-1</sup> hydrochloric acid in a solution of THF.

<sup>1</sup>H-NMR(400 MHz, 300 K, Pyridin-d<sub>5</sub>): 0.94 – 2.80 (backbone + 1,2,3, m); 3.70 (10, s, 3H); 4.04 – 4.30 (4, 11, s, 2H+2H); 4.33 – 4.54 (12, s, 2H); 7.47 – 7.73 (Pyridin-d<sub>5</sub> + 5,8, m); 7.82 – 8.13 (6,7,9, m, 5H)



**Figure S1:** <sup>1</sup>H-NMR-spectrum of **P2**, measured in pyridine-d<sub>5</sub> at 300 K with 400 MHz.

The amount of substance fraction of HEMA is calculated from the signals **12** of the poly(HEMA) block and the signals **10**, **4** and **6+7** of the macroinitiator. The signal of the protons **4** (BMA) is superimposed by the protons **11** of HEMA. Since both proton groups consist of two protons each, the integral of **12** is subtracted from **4+11** to yield the integral for BMA. The factor 1 over N accounts for the number of protons present in each respective group.

$$x(\text{HEMA}) = \frac{I(\mathbf{11}) \cdot \frac{1}{N}}{I(\mathbf{11}) \cdot \frac{1}{N} + (I(\mathbf{10}) - I(\mathbf{11})) \frac{1}{N} + I(\mathbf{1}) \cdot \frac{1}{N} + I(\mathbf{7} + \mathbf{8}) \cdot \frac{1}{N}}$$

Following, the calculation is shown for **P2**, with values taken from the spectrum above.

$$x(\text{HEMA}) = \frac{0.45 \cdot \frac{1}{2}}{0.45 \cdot \frac{1}{2} + (2.11 - 0.45) \cdot \frac{1}{2} + 3 \cdot \frac{1}{3} + 0.79 \cdot \frac{1}{4}} = 0.10$$

The molar fractions of BMA, BPMA and MMA are calculated within the hydrophobic block **P1** from the same spectrum. Following, the calculations for BMA, BPMA and MMA are shown.

$$x(\text{BMA}) = \frac{2.11 - 0.45 \cdot \frac{1}{2}}{(2.11 - 0.45) \cdot \frac{1}{2} + 3 \cdot \frac{1}{3} + 0.79 \cdot \frac{1}{4}} = 0.41$$

$$x(\text{MMA}) = \frac{3 \cdot \frac{1}{3}}{(2.11 - 0.45) \cdot \frac{1}{2} + 3 \cdot \frac{1}{3} + 0.79 \cdot \frac{1}{4}} = 0.49$$

$$x(\text{BPMA}) = \frac{0.79 \cdot \frac{1}{4}}{(2.11 - 0.45) \cdot \frac{1}{2} + 3 \cdot \frac{1}{3} + 0.79 \cdot \frac{1}{4}} = 0.10$$

From these molar fractions, a mean molecular weight for a repeating unit of the hydrophobic block is calculated in order to determine the molar mass of the poly(HEMA) block.

$$\bar{M}(\mathbf{P1}) = M(\text{BMA}) \cdot x(\text{BMA}) + M(\text{BPMA}) \cdot x(\text{BPMA}) + M(\text{MMA}) \cdot x(\text{MMA})$$

$$\begin{aligned} \bar{M}(\mathbf{P1}) &= 142.20 \text{ g mol}^{-1} \cdot 0.41 + 266.30 \text{ g mol}^{-1} \cdot 0.10 + 100.12 \text{ g mol}^{-1} \cdot 0.49 \\ &= 133.75 \text{ g mol}^{-1} \end{aligned}$$

The degree of polymerization, disregarding the initiator, of the hydrophobic block is then calculated from the number average molecular weight, determined by SEC in THF against PS, and this average weight of a repeating unit.

$$N(\mathbf{P1}) = \frac{49800 \text{ g mol}^{-1}}{133.75 \text{ g mol}^{-1}} = 372$$

Using this degree of polymerization and the molar fraction of HEMA, a degree of polymerization is calculated for the poly(HEMA) block.

$$N(\text{poly(HEMA)}) = \frac{x(\text{poly(HEMA)}) \cdot N(\mathbf{P1})}{1 - x(\text{poly(HEMA)})}$$

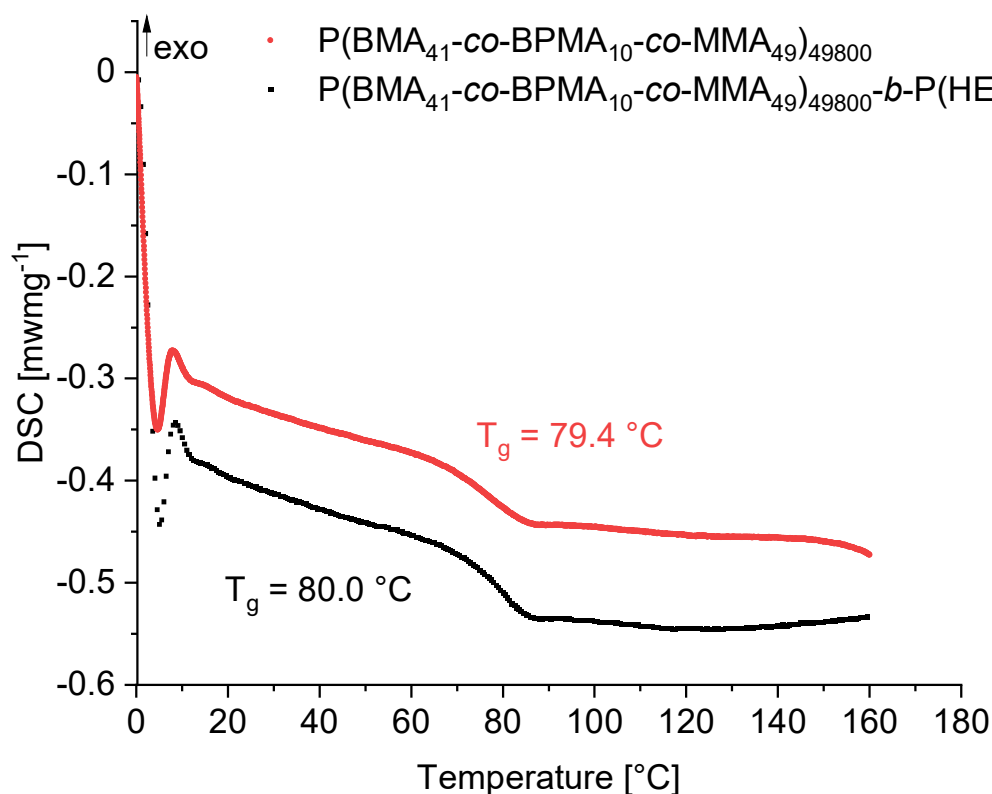
$$N(\text{poly(HEMA)}) = \frac{0.10 \cdot 372}{1 - 0.10} = 41$$

Following the number average molecular weights of the poly(HEMA), poly(HEMA-TMS) and poly(HEMA-benz) can be calculated, for example, for poly(HEMA).

$$M(\text{poly(HEMA)}) = 26 \cdot 130,14 \text{ g mol}^{-1} = 5300 \text{ g mol}^{-1}$$

**Table S1:** Summary of the calculations regarding the number average molecular weights and molar fractions of the block copolymer **P2**.

Polymer	$M_n$ (GPC)	$M_n$ (NMR)	$\bar{D}$	$x(\text{HEMA-TMS})$
	[g mol <sup>-1</sup> ]	[g mol <sup>-1</sup> ]		
P(BMA <sub>41-co</sub> -BPMA <sub>10-co</sub> -MMA <sub>49</sub> ) <sub>49800</sub> - <i>b</i> -P(HEMA-TMS) <sub>8300</sub>	52400	58100	1,29	0,10
P(BMA <sub>41-co</sub> -BPMA <sub>10-co</sub> -MMA <sub>49</sub> ) <sub>49800</sub> - <i>b</i> -P(HEMA) <sub>5300</sub>	35700	55000	1,48	0,10
P(BMA <sub>41-co</sub> -BPMA <sub>10-co</sub> -MMA <sub>49</sub> ) <sub>49800</sub> - <i>b</i> -P(HEMA-Benz) <sub>9600</sub>	59600	59400	1,33	0,10



**Figure S2:** DSC diagram of the macroinitiator **P1** (red) and BCP **P2** (black), measured between 0 °C and 160 °C at a rate of 10 K min<sup>-1</sup> in nitrogen atmosphere. The  $T_g$  of poly(HEMA) is not visible in the second graph, as it only is present as 10 mol-% and the expected  $T_g$  matches closely the one of **P1**.<sup>[3]</sup>

#### *Membrane fabrication through SNIPS process:*

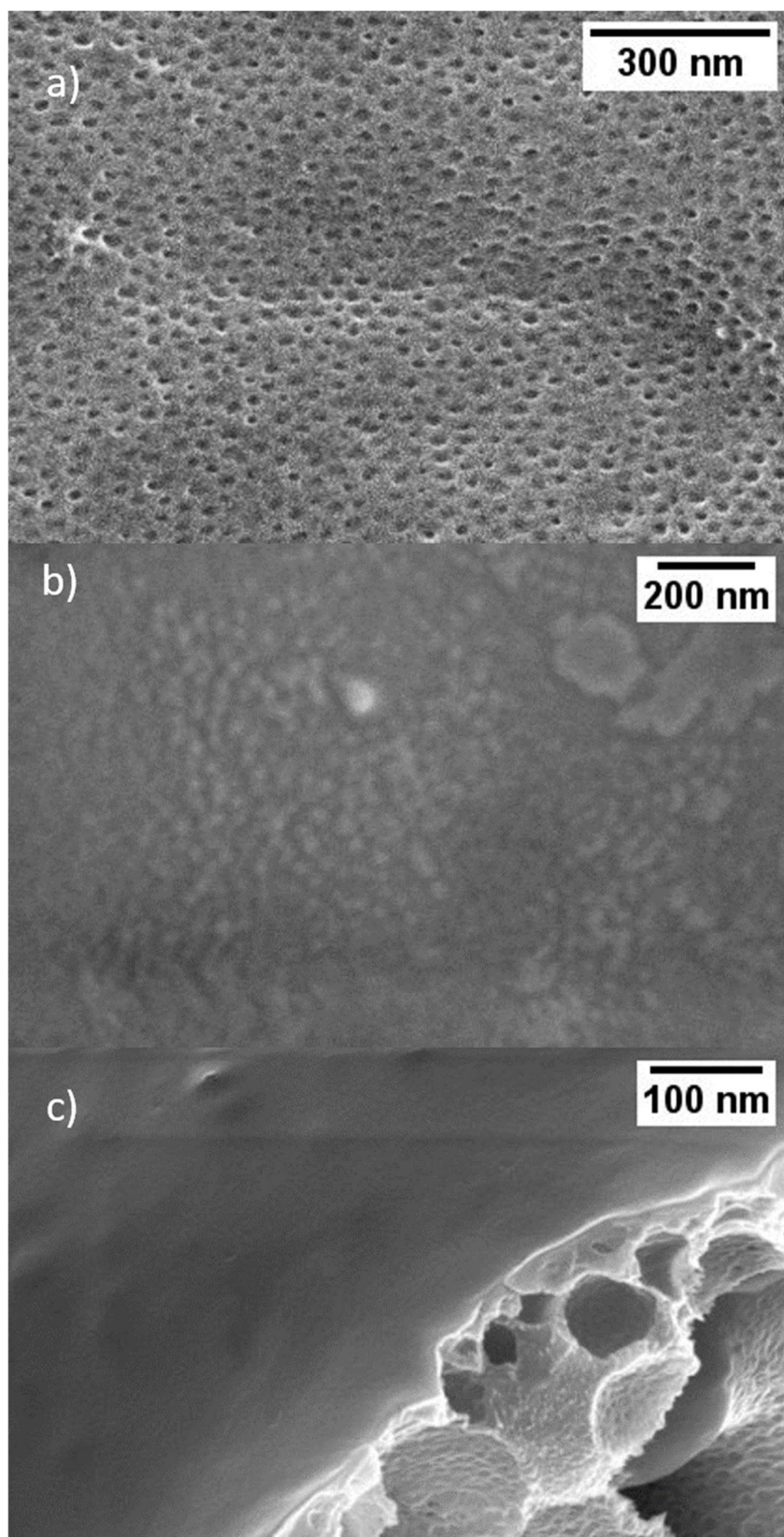
0.862 g block copolymer **P2** are dissolved in a ternary solvent mixture consisting of THF, DMF, and 1,4-dioxane (2:1:1 by mass) and 0.43 w-% CuCl<sub>2</sub> was added to achieve a 30 w-% polymer solution. This solution was cast on a polyester nonwoven (type FLPD 85, Freudenberg Performance Materials) or cellulose paper discs (either commercially available filter discs (grade 3 hw, Munktell, Ahlstrom) or cellulose substrates featuring diameters of 90 mm and a density of 65 g m<sup>-2</sup>. The paper discs are composed of bleached alpha cellulose consisting of pine and spruce fibers featuring a porosity of 8-12 µm. The membrane casting solution was cast on the respective supports via doctor blading (200 µm gap, 3.5 cm width) and evaporation times

of 10 s and 15 s were used prior to precipitation in a water bath. The typical length of a block copolymer membrane is 5 to 10 cm. After 30 min the membranes were dried for 12 h under ambient conditions, before further drying in a vacuum oven at 40 °C for two days.

*Cross-linking the membranes via UV-irradiation:*

The membranes are placed in a Hönle UV-technology UVA-Cube 2000, equipped with a UVAPRINT 100-200 HPV EZ lamp, which was operated at 1000 W for 4 min in 30 s intervals.

*Membrane fabricated of P(BMA-co-(4-ethacryloxy-2-hydroxybenzophenone) (2-OHBP)-co-MMA)-b-P(HEMA) before and after UV irradiation of 10 min*

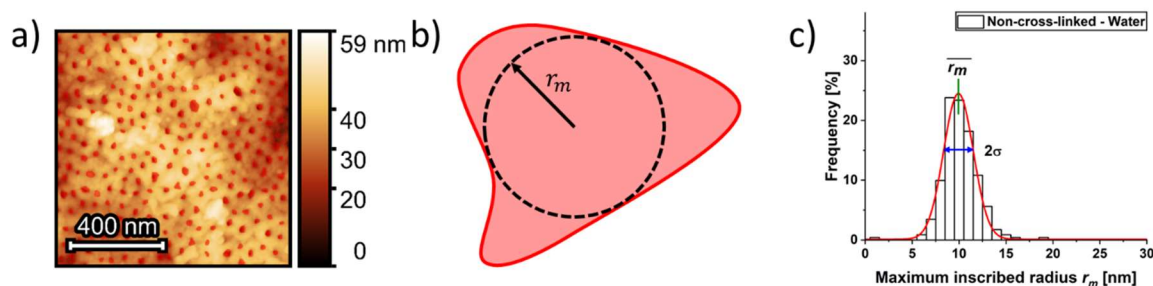


**Figure S3:** SEM images of  $\text{P}(\text{BMA}_{39}\text{-co-}(\text{OHBP})_{11}\text{-co-MMA}_{50})_{35200}\text{-b-P(HEMA)}_{6300}$  before (a) and after 10 min (b and c) of 1000 W UV irradiation.

*AFM imaging of the P2 BCP membranes*

Atomic force microscopy (AFM) imaging was performed on a Cypher ES (Asylum Research, an Oxford Instruments Company) in ultrapure water (Elga, with a conductivity of 0.055  $\mu\text{S}$ ), ethanol (VWR, absolute with >99.7%) and 1:1 by volume water-ethanol mixture, respectively. Before AFM imaging, samples were immersed in the respective solution for 30 minutes to let the polymers swell. The samples were scanned with AC40TS cantilevers (Olympus) with a tip radius of approx. 7 nm. Meanwhile, these two samples were also measured in air as control experiments with AC240TS cantilevers (Olympus) with a tip radius of approx. 7 nm. Imaging was conducted in the intermittent-contact mode. The following parameters were chosen for all measurements: pixel number of  $1024 \times 1024$ , scan area of  $1 \times 1 \mu\text{m}^2$ , scan rate of 1.95 Hz, and scan angle of  $90^\circ$ .

AFM images were processed with the Gwyddion Free SPM analysis software (Petr Klapetek, version 2.56). To correct the recorded images (using the retrace images for all evaluation), the data was leveled by mean plane subtraction, the rows were aligned to the median of differences, and the minimum data value was set to zero. Using the *Mask Editor* tool, each pore was masked, and each pore size was characterized by the maximum inscribed radius  $r_m$ , based on the masked area. **Figure S4** shows an example of masking an AFM image with the *Mask Editor* tool and the determination of mean and error values of the maximum inscribed radius  $r_m$ : using the tool *Distribution of Various Grain Characteristics*. Distribution histograms were generated and taken to calculate the frequency of each characteristic maximum inscribed radius  $r_m$ . The obtained grain data were further processed in Origin (Version 2020, OriginLab) using Gaussian fitting, where the mean value  $\overline{r_m}$  is given by the maximum of the fit and the error value  $\sigma$  is obtained by the half of the width of the fit.



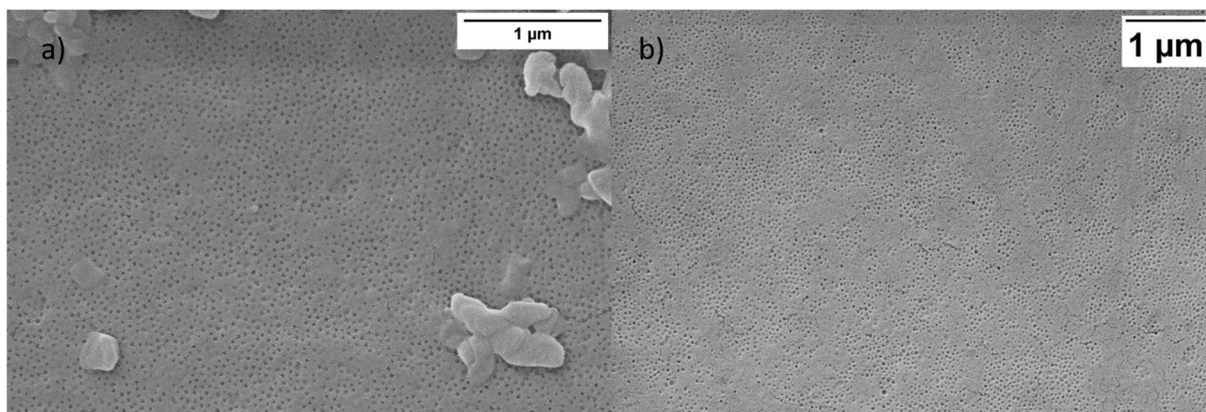
**Figure S4:** Exemplary determination of the mean maximum inscribed radius  $\bar{r}_m$  and the error  $\sigma$  with a) the AFM image where each pore is masked, b) the definition of the maximum inscribed radius  $r_m$ , c) a Gaussian fit (red line) of the histogram where the mean of the maximum inscribed radius  $\bar{r}_m$  is given by the maximum and the error  $\sigma$  is obtained by half of the width.

### *Water-flux measurements:*

The water-flux measurements were carried out in a dead-end cell with 400 mL volume and a membrane diameter of 1 cm, at pressures in the range of 0.2 to 0.6 bar and over a time of 16 - 17 min.

**Table S2:** Summary of the water flux measurements.

	V(water) [10 <sup>-4</sup> L]	time [h]	pressure [bar]	water flux [lbar <sup>-1</sup> h <sup>-1</sup> m <sup>-2</sup> ]
untreated	13.5	0.27	0.2	322
	1.49	0.27	0.4	18
	0.581	0.27	0.6	5
cross-linked	56.9	0.27	0.2	1358
	17.7	0.27	0.4	211
	3.67	0.28	0.6	27



**Figure S5:** SEM-images of the membranes after water-flux measurements with pressure variation. a) untreated membrane, b) cross-linked membrane.

## References:

- [1] G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw, K. I. Goldberg, *Organometallics* **2010**, *29*, 2176.
- [2] H. Kim, N. Hight-Huf, J. H. Kang, P. Bisnoff, S. Sundararajan, T. Thompson, M. Barnes, R. C. Hayward, T. Emrick, *Angewandte Chemie International Edition* **2020**, *59*, 10802.
- [3] B. A. Rozenberg, *Macromolecular Symposia* **2003**, *199*, 443.