

## **Tuning the water intrinsic permeability of PEGDA hydrogel membranes by adding free PEG chains of varying molar masses**

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*S1. Composition of the PEGDA/PEG hydrogel membranes used in this study*

*Table S1. Composition of the PEGDA/PEG samples used in this study with PEG-600 g.mol<sup>-1</sup>.*

m <sub>PEGDA</sub> (g)	m <sub>water</sub> (g)	m <sub>Irgacure</sub> (g)	m <sub>PEG-600</sub> (g)	total mass (g)	%wt PEG	%wt PEGDA	%wt water	%wt Irgacure	PEGDA/water ratio
2	10	2x10 <sup>-3</sup>	1	13.002	7.7	15.4	77.0	1.54x10 <sup>-2</sup>	0.2
2	10	2x10 <sup>-3</sup>	3	15.002	20.0	13.3	66.6	1.33x10 <sup>-2</sup>	0.2
2	10	2x10 <sup>-3</sup>	5	17.002	29.5	11.8	58.8	1.18x10 <sup>-2</sup>	0.2

*Table S2. Composition of the PEGDA/PEG samples used in this study with PEG-3000 g.mol<sup>-1</sup>.*

m <sub>PEGDA</sub> (g)	m <sub>water</sub> (g)	m <sub>Irgacure</sub> (g)	m <sub>PEG-3000</sub> (g)	total mass (g)	%wt PEG	%wt PEGDA	%wt water	%wt Irgacure	PEGDA/water ratio
2	10	2x10 <sup>-3</sup>	0.2	12.202	1.6	16.4	81.9	1.64x10 <sup>-2</sup>	0.2
2	10	2x10 <sup>-3</sup>	0.5	12.502	4.0	16.0	80.0	1.60x10 <sup>-2</sup>	0.2
2	10	2x10 <sup>-3</sup>	1	13.002	7.7	15.4	77.0	1.54x10 <sup>-2</sup>	0.2
2	10	2x10 <sup>-3</sup>	2	14.002	14.3	14.3	71.4	1.43x10 <sup>-2</sup>	0.2
2	10	2x10 <sup>-3</sup>	2.5	14.502	17.2	13.8	68.9	1.38x10 <sup>-2</sup>	0.2
2	10	2x10 <sup>-3</sup>	3	15.002	20.0	13.3	66.6	1.33x10 <sup>-2</sup>	0.2

*Table S3. Composition of the PEGDA/PEG samples used in this study with PEG-10 000 g.mol<sup>-1</sup>.*

m <sub>PEGDA</sub> (g)	m <sub>water</sub> (g)	m <sub>Irgacure</sub> (g)	m <sub>PEG-10 000</sub> (g)	total mass (g)	%wt PEG	%wt PEGDA	%wt water	%wt Irgacure	PEGDA/water ratio
2	10	2x10 <sup>-3</sup>	0.5	12.502	4.0	16.0	80.0	1.60x10 <sup>-2</sup>	0.2
2	10	2x10 <sup>-3</sup>	0.8	12.802	6.2	15.6	78.1	1.56x10 <sup>-2</sup>	0.2
2	10	2x10 <sup>-3</sup>	1.5	13.502	11.1	14.8	74.1	1.48x10 <sup>-2</sup>	0.2
2	10	2x10 <sup>-3</sup>	2	14.002	14.3	14.3	71.4	1.43x10 <sup>-2</sup>	0.2

Table S4. Composition of the PEGDA/PEG samples used in this study with PEG-35 000  $g.mol^{-1}$ .

$m_{PEGDA}$ (g)	$m_{water}$ (g)	$m_{Irgacure}$ (g)	$m_{PEG-35\ 000}$ (g)	total mass (g)	%wt PEG	%wt PEGDA	%wt water	%wt Irgacure	PEGDA/water ratio
2	10	$2 \times 10^{-3}$	0.05	12.052	0.4	16.6	83.0	$1.66 \times 10^{-2}$	0.2
2	10	$2 \times 10^{-3}$	0.1	12.102	0.8	16.5	82.6	$1.65 \times 10^{-2}$	0.2
2	10	$2 \times 10^{-3}$	0.2	12.202	1.6	16.4	81.9	$1.64 \times 10^{-2}$	0.2
2	10	$2 \times 10^{-3}$	0.3	12.302	2.4	16.3	81.3	$1.63 \times 10^{-2}$	0.2
2	10	$2 \times 10^{-3}$	0.4	12.402	3.2	16.1	80.6	$1.61 \times 10^{-2}$	0.2
2	10	$2 \times 10^{-3}$	0.5	12.502	4.0	16.0	80.0	$1.60 \times 10^{-2}$	0.2
2	10	$2 \times 10^{-3}$	0.8	12.802	6.2	15.6	78.1	$1.56 \times 10^{-2}$	0.2
2	10	$2 \times 10^{-3}$	1	13.002	7.7	15.4	76.9	$1.54 \times 10^{-2}$	0.2
2	10	$2 \times 10^{-3}$	2	14.002	14.3	14.3	71.4	$1.43 \times 10^{-2}$	0.2
2	10	$2 \times 10^{-3}$	3	15.002	20.0	13.3	66.7	$1.33 \times 10^{-2}$	0.2

Table S5. Composition of the PEGDA/PEG samples used in this study with PEG-300 000  $g.mol^{-1}$ .

$m_{PEGDA}$ (g)	$m_{water}$ (g)	$m_{Irgacure}$ (g)	$m_{PEG-300\ 000}$ (g)	total mass (g)	%wt PEG	%wt PEGDA	%wt water	%wt Irgacure	PEGDA/water ratio
2	10	$2 \times 10^{-3}$	0.05	12.052	0.4	16.6	83.0	$1.66 \times 10^{-2}$	0.2
2	10	$2 \times 10^{-3}$	0.1	12.102	0.8	16.5	82.6	$1.65 \times 10^{-2}$	0.2
2	10	$2 \times 10^{-3}$	0.2	12.202	1.6	16.4	81.9	$1.64 \times 10^{-2}$	0.2
2	10	$2 \times 10^{-3}$	0.5	12.502	4.0	16.0	80.0	$1.60 \times 10^{-2}$	0.2
2	10	$2 \times 10^{-3}$	1	13.002	7.7	15.4	76.9	$1.54 \times 10^{-2}$	0.2

Table S6. Composition of the PEGDA/PEG samples used in this study with PEG-600 000  $\text{g}\cdot\text{mol}^{-1}$ .

$m_{\text{PEGDA}}$ (g)	$m_{\text{water}}$ (g)	$m_{\text{Irgacure}}$ (g)	$m_{\text{PEG-600 000}}$ (g)	total mass (g)	% wt PEG	% wt PEGDA	% wt water	% wt Irgacure	PEGDA/water ratio
2	10	$2 \times 10^{-3}$	0.01	12.012	0.08	16.65	83.3	$1.67 \times 10^{-2}$	0.2
2	10	$2 \times 10^{-3}$	0.05	12.052	0.4	16.6	83.0	$1.66 \times 10^{-2}$	0.2
2	10	$2 \times 10^{-3}$	0.1	12.102	0.8	16.5	82.6	$1.65 \times 10^{-2}$	0.2
2	10	$2 \times 10^{-3}$	0.2	12.202	1.6	16.4	82.0	$1.64 \times 10^{-2}$	0.2
2	10	$2 \times 10^{-3}$	0.3	12.302	2.4	16.2	81.3	$1.63 \times 10^{-2}$	0.2

## S2. Chemical composition of hydrogels

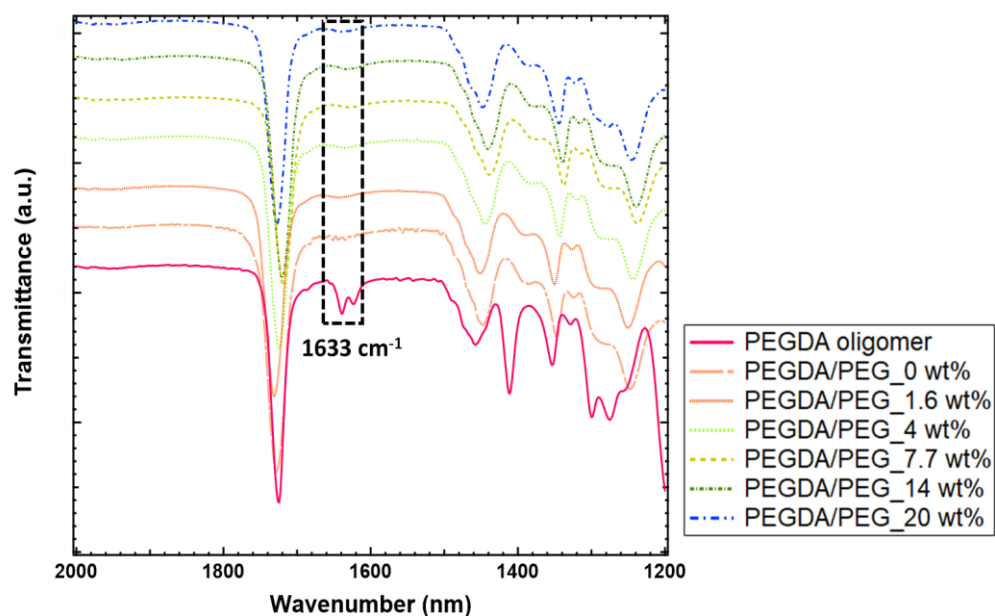


Figure S1. FTIR spectra of dried PEGDA hydrogel membranes prepared with 16 wt% of PEGDA and various PEG-3000  $\text{g}\cdot\text{mol}^{-1}$  contents in the prepolymerization mixture, compared to the spectrum of the as-received PEGDA oligomer.

### S3. Filtration experiments

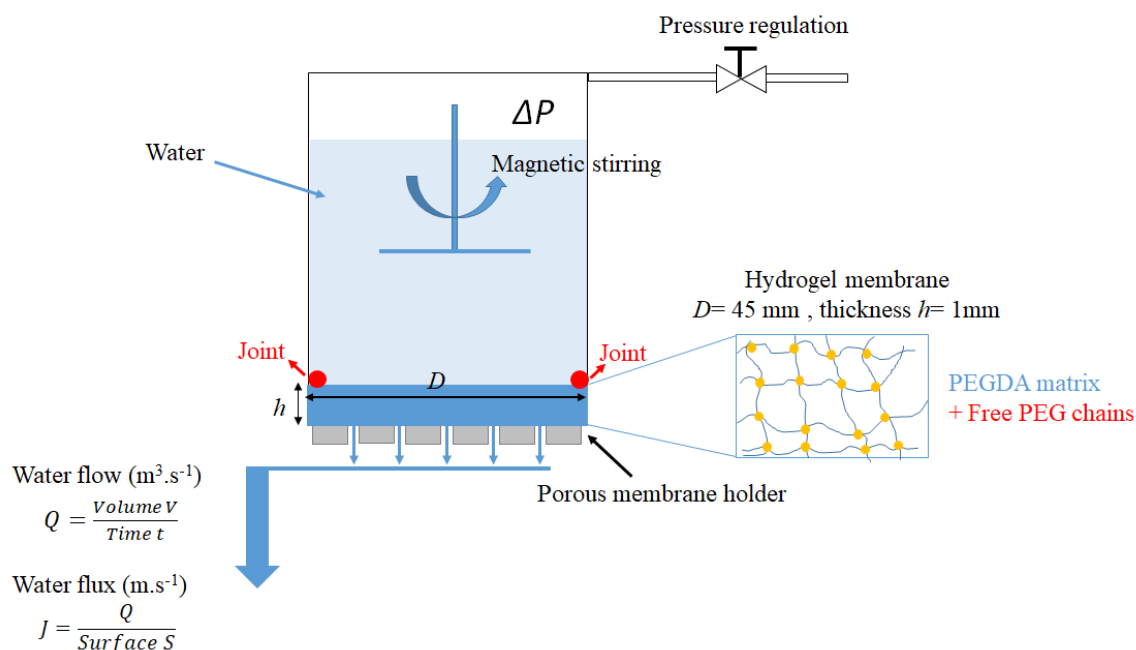


Figure S2. Schematic of the filtration experiment using an ultrafiltration stirred cell<sup>1</sup>.

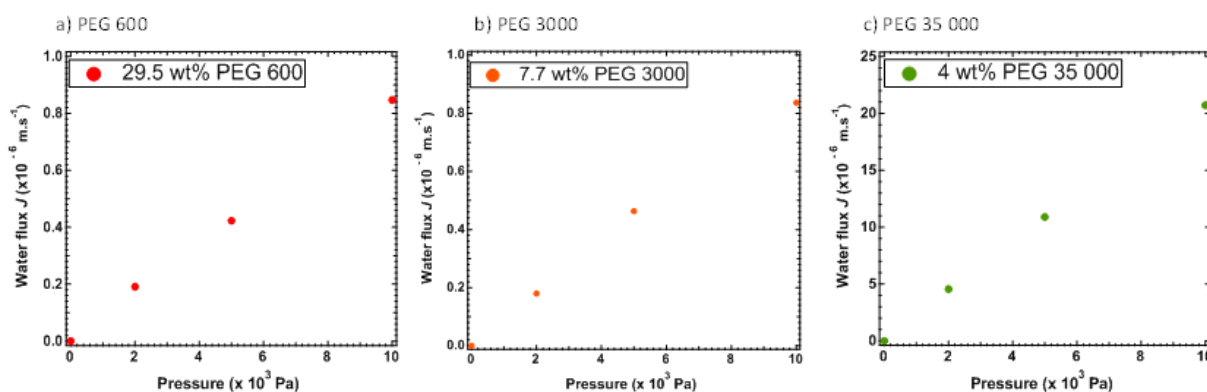


Figure S3. Water flux vs pressure for PEGDA/PEG with a) PEG-600 g.mol<sup>-1</sup>, b) PEG-3000 g.mol<sup>-1</sup> and c) PEG-35 000 g.mol<sup>-1</sup>.

### S4. Rheological experiments

Rheological experiments are performed using an ARG-2 rheometer from TA, in order to obtain the critical overlap concentration  $C^*$  of the PEG chains with different molar masses.

As shown in Figure S4, and as expected, the viscosity increases when the PEG concentration increases. For different PEG molar masses, we notice a variation of the slope from 1.5 to 3.4 for PEG-3000 g.mol<sup>-1</sup>, from 0.68 to 2.7 for PEG-35 000 g.mol<sup>-1</sup> and from 0.9 to 3 and above,

for the very high PEG molar masses (i.e. 300 000 and 600 000  $\text{g}\cdot\text{mol}^{-1}$ ). This variation can be correlated to the transition between the dilute and semi-dilute regimes. At this stage, there is contact between the PEG coils due to the decrease of the distance between them. The associated concentration is called the critical overlap concentration  $C^*$  and is determined to be  $\sim 37$  wt%, 4 wt%, 1.6 wt% and 1 wt% for PEG-3000, 35 000, 300 000 and 600 000  $\text{g}\cdot\text{mol}^{-1}$ , respectively.

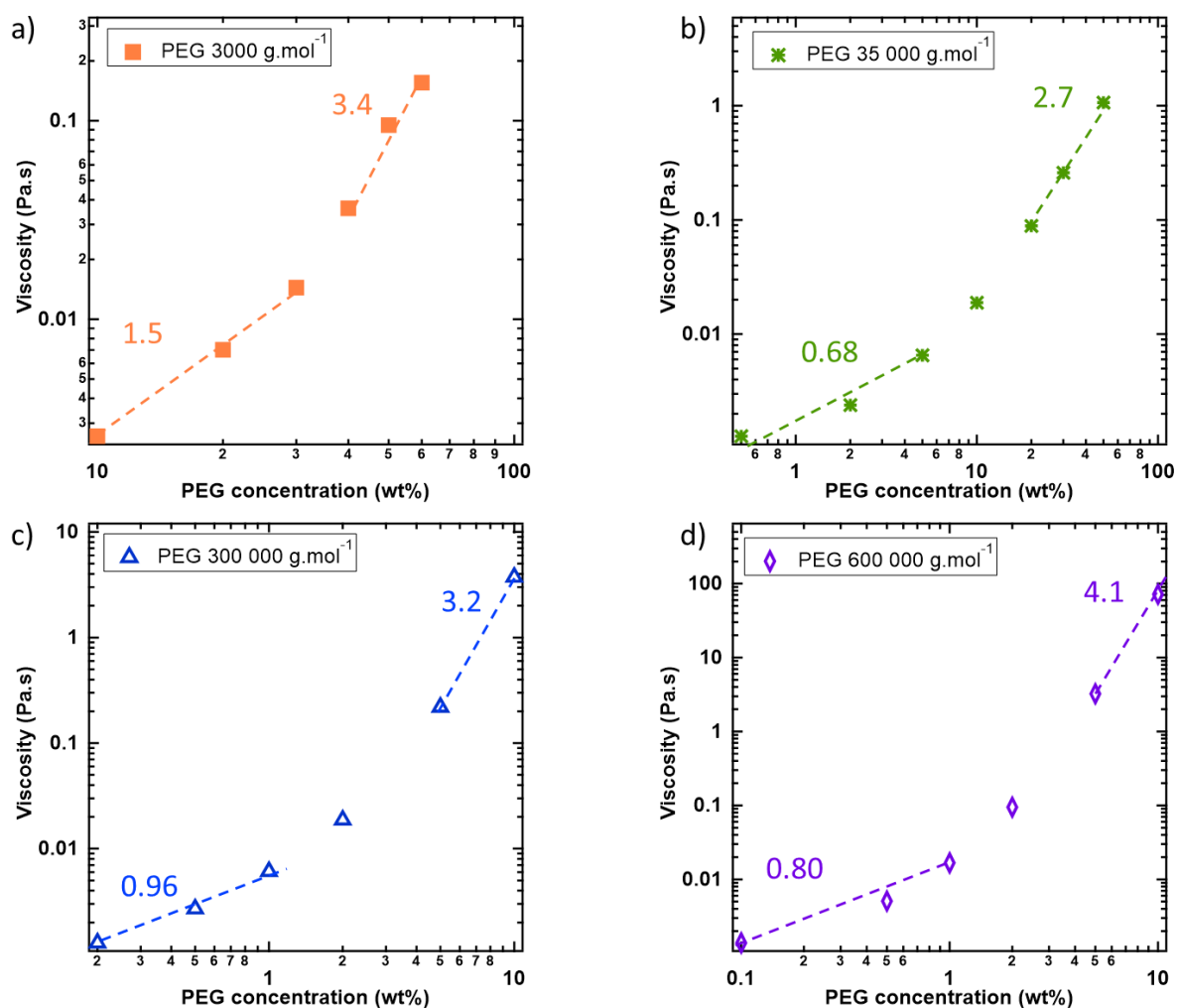


Figure S4. Viscosity as a function of PEG concentration for various PEG molar masses: a) PEG-3000, b) PEG-35 000, c) PEG-300 000 and d) PEG-600 000  $\text{g}\cdot\text{mol}^{-1}$ .

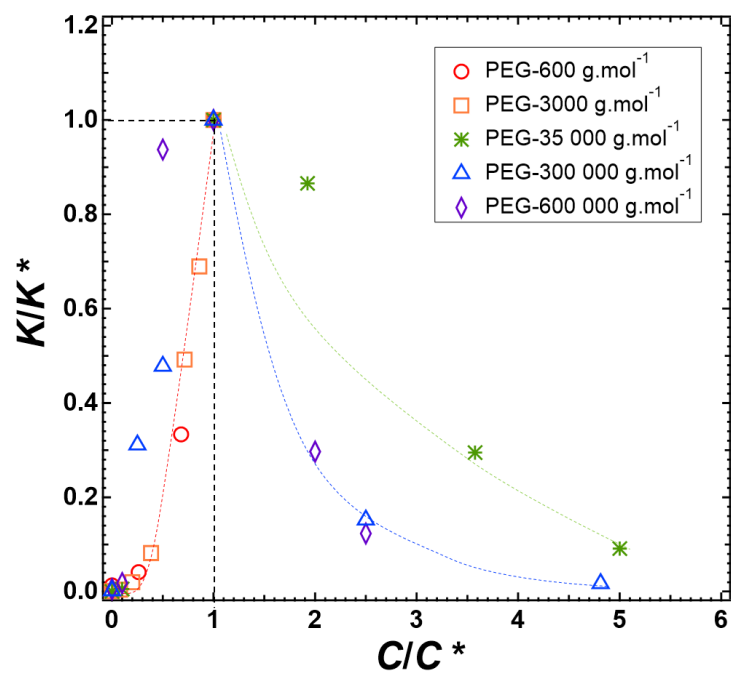
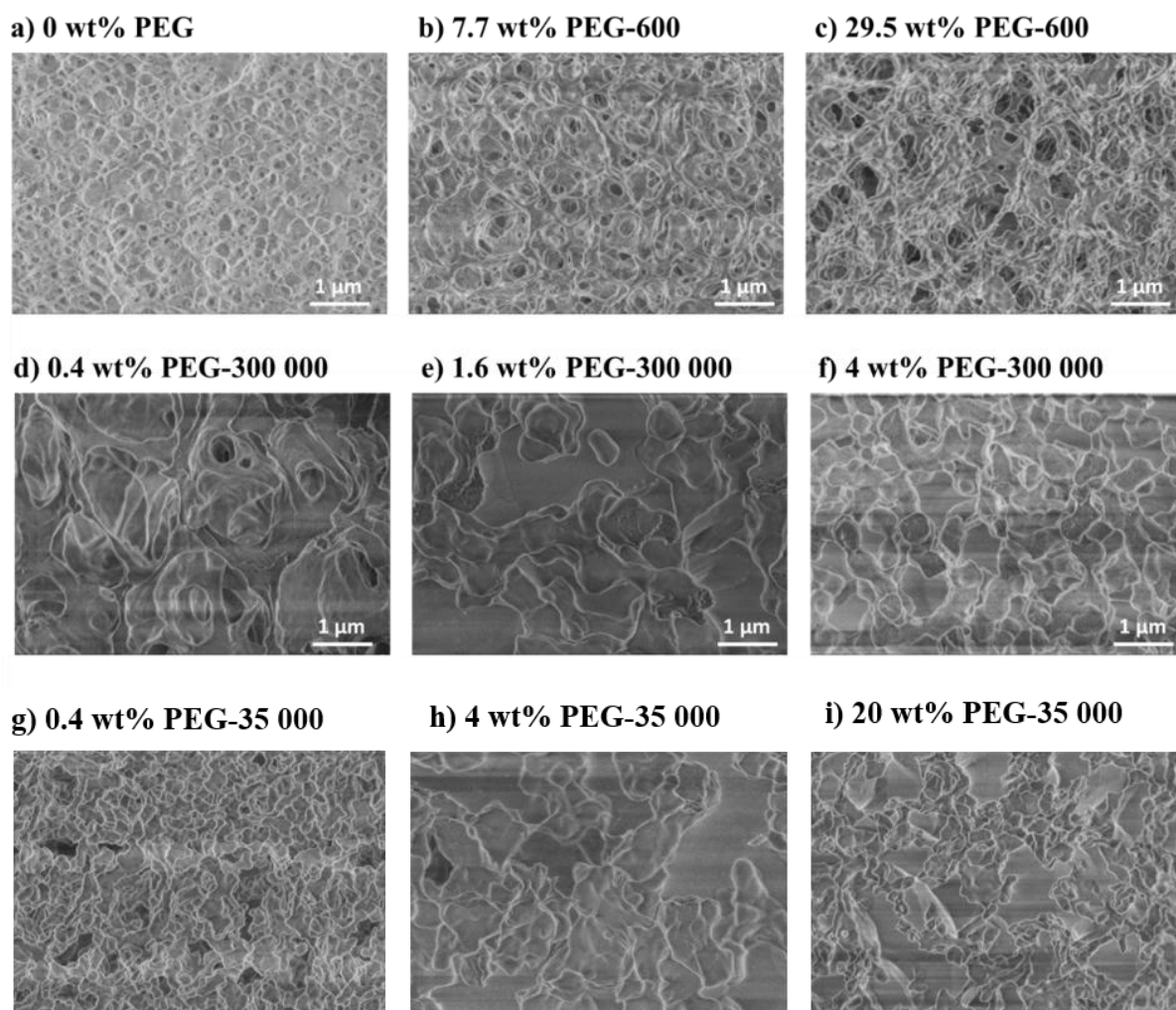


Figure S5.  $K/K^*$  as a function of  $C/C^*$  as a function of PEG concentration for various molar masses.

*S5. CryoSEM and AFM images*



*Figure S6. CryoSEM images of hydrogel membranes prepared with PEGDA and various contents of PEG-600 g.mol<sup>-1</sup>: a) 0, b) 7.7 and c) 29.5 wt%; PEG-300 000 g.mol<sup>-1</sup>: d) 0.4, e) 1.6 and f) 4 wt% and PEG-35 000 g.mol<sup>-1</sup> g) 0.4, h) 4 and i) 20 wt%.*



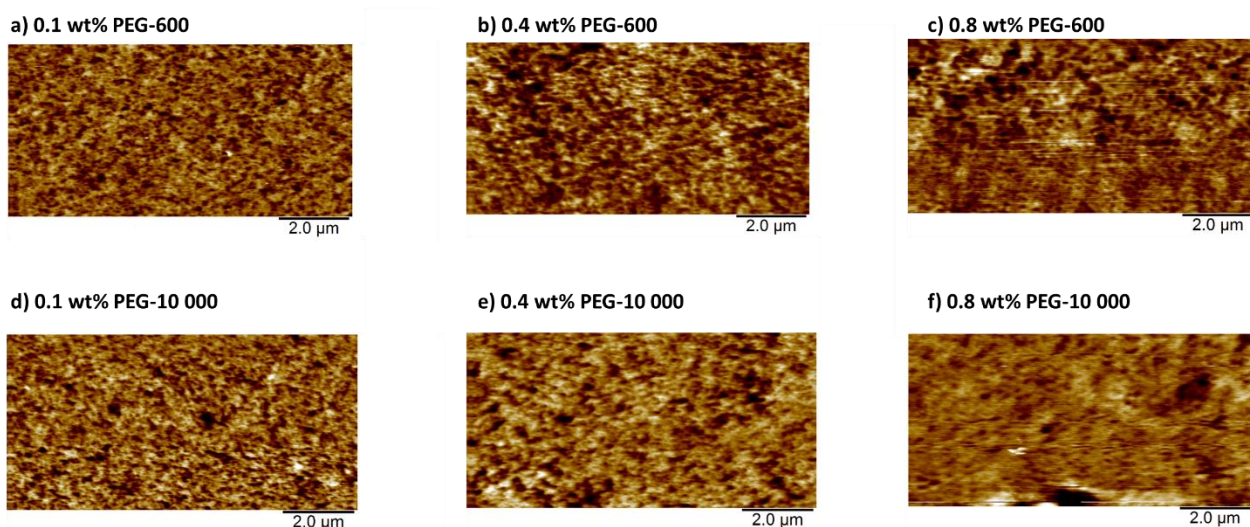


Figure S7. Surface AFM images of PEGDA hydrogel membranes prepared with 16 wt % of PEGDA and various contents of PEG-600 (a, b and c) and PEG-10 000  $\text{g}\cdot\text{mol}^{-1}$  (d, e and f). The typical  $z$ -scale is 50 nm.

#### Reference :

1. Eddine, M. A.; Belbekhouche, S.; de Chateaufneuf-Randon, S.; Salez, T.; Kovalenko, A.; Bresson, B.; Monteux, C., Large and nonlinear permeability amplification with polymeric additives in hydrogel membranes. *Macromolecules* **2022**, *55* (21), 9841-9850, DOI: 10.1021/acs.macromol.2c01462.