

Revised Supporting Information of

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

Malak Alaa Eddine^{1,2}, Alain Carvalho³, Marc Schmutz³, Thomas Salez⁴, Sixtine de Chateauneuf-Randon¹, Bruno Bresson¹, Nadège Pantoustier¹, Cécile Monteux^{*1}, Sabrina Belbekhouche^{*2}

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- 3- Université de Strasbourg, CNRS, Institut Charles Sadron, 23 rue du Loess, 67034 Strasbourg Cedex 02, France.
- 4- Univ. Bordeaux, CNRS, LOMA, UMR 5798, F-33400 Talence, France.

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sabrina.belbekhouche@cnrs.fr (S. Belbekhouche).

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⁻¹.

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

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

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

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

m _{PEGDA} (g)	m _{water} (g)	m _{Irgacure} (g)	m _{PEG-10 000} (g)	total mass (g)	%wt PEG	%wt PEGDA	%wt water	%wt Irgacure	PEGDA/water ratio
2	10	2x10 ⁻³	0.5	12.502	4.0	16.0	80.0	1.60x10 ⁻²	0.2
2	10	2x10 ⁻³	0.8	12.802	6.2	15.6	78.1	1.56x10 ⁻²	0.2
2	10	2x10 ⁻³	1.5	13.502	11.1	14.8	74.1	1.48x10 ⁻²	0.2
2	10	2x10 ⁻³	2	14.002	14.3	14.3	71.4	1.43x10 ⁻²	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	2x10 ⁻³	0.05	12.052	0.4	16.6	83.0	1.66x10 ⁻²	0.2
2	10	2x10 ⁻³	0.1	12.102	0.8	16.5	82.6	1.65x10 ⁻²	0.2
2	10	2x10 ⁻³	0.2	12.202	1.6	16.4	81.9	1.64x10 ⁻²	0.2
2	10	2x10 ⁻³	0.3	12.302	2.4	16.3	81.3	1.63x10 ⁻²	0.2
2	10	2x10 ⁻³	0.4	12.402	3.2	16.1	80.6	1.61x10 ⁻²	0.2
2	10	2x10 ⁻³	0.5	12.502	4.0	16.0	80.0	1.60x10 ⁻²	0.2
2	10	2x10 ⁻³	0.8	12.802	6.2	15.6	78.1	1.56x10 ⁻²	0.2
2	10	2x10 ⁻³	1	13.002	7.7	15.4	76.9	1.54x10 ⁻²	0.2
2	10	2x10 ⁻³	2	14.002	14.3	14.3	71.4	1.43x10 ⁻²	0.2
2	10	2x10 ⁻³	3	15.002	20.0	13.3	66.7	1.33x10 ⁻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	2x10 ⁻³	0.05	12.052	0.4	16.6	83.0	1.66x10 ⁻²	0.2
2	10	2x10 ⁻³	0.1	12.102	0.8	16.5	82.6	1.65x10 ⁻²	0.2
2	10	2x10 ⁻³	0.2	12.202	1.6	16.4	81.9	1.64x10 ⁻²	0.2
2	10	2x10 ⁻³	0.5	12.502	4.0	16.0	80.0	1.60x10 ⁻²	0.2
2	10	2x10 ⁻³	1	13.002	7.7	15.4	76.9	1.54x10 ⁻²	0.2

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

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

S2. Chemical composition of hydrogels

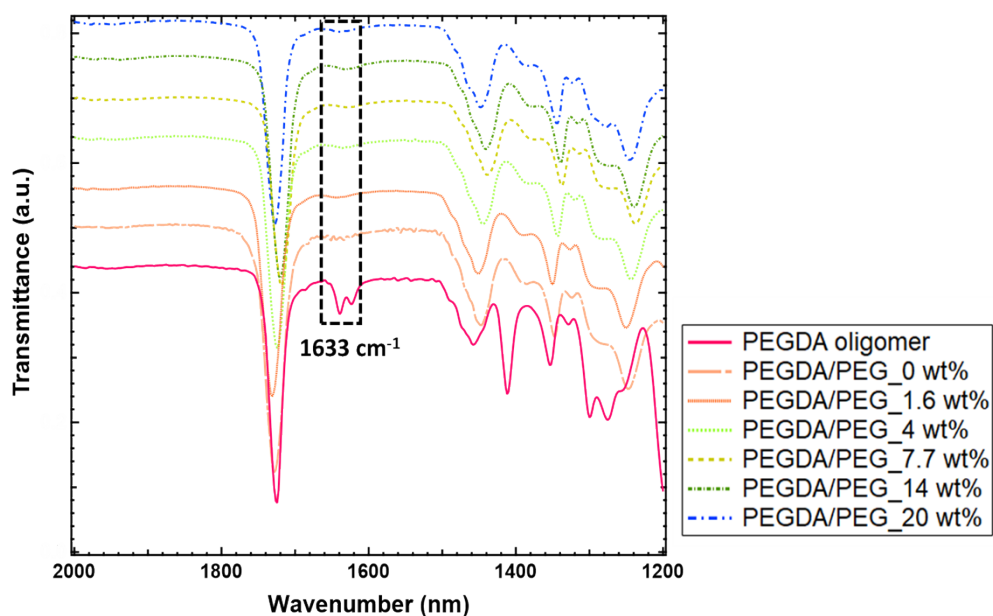


Figure S1. FTIR spectra of dried PEGDA hydrogel membranes prepared with 16 wt% of PEGDA and various PEG-3000 g.mol^{-1} contents in the prepolymerization mixture, compared to the spectrum of the as-received PEGDA oligomer.

S3. Filtration experiments

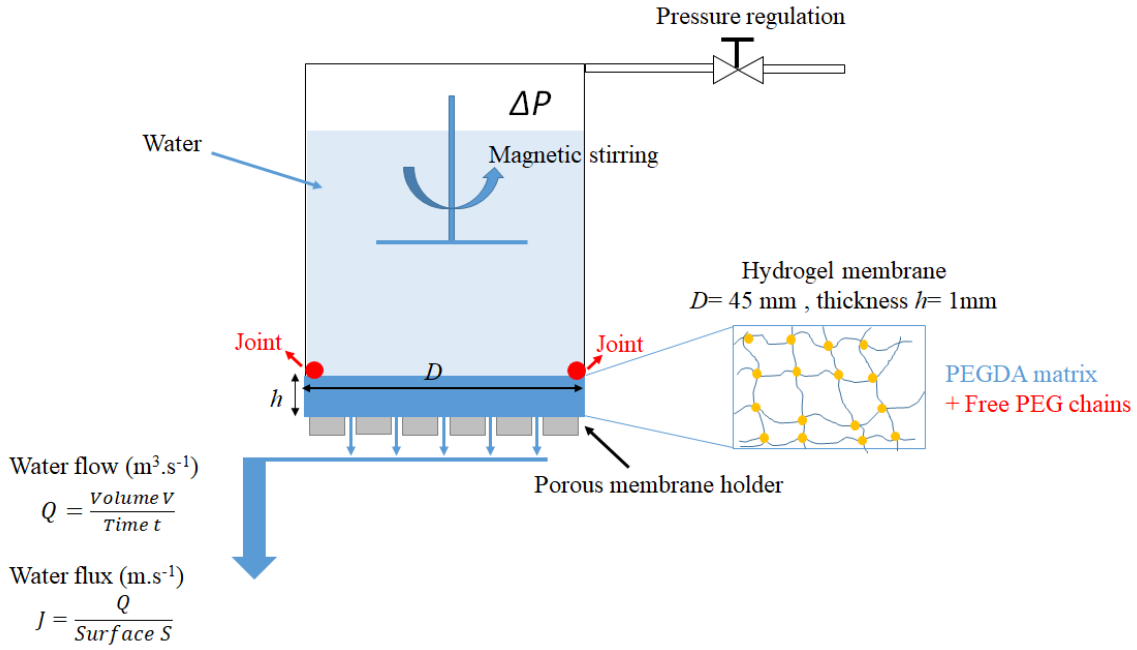


Figure S2. Schematic of the filtration experiment using an ultrafiltration stirred cell ¹.

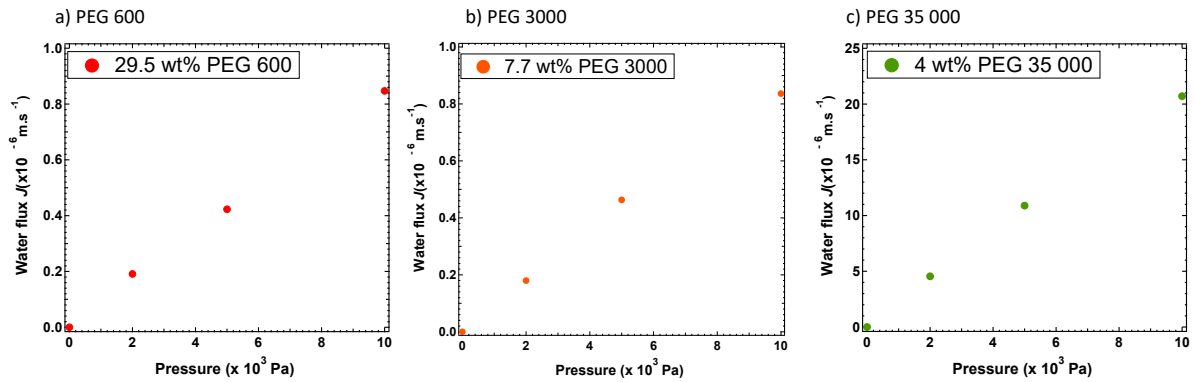


Figure S3. Water flux vs pressure for PEGDA/PEG with a) PEG-600 $\text{g} \cdot \text{mol}^{-1}$, b) PEG-3000 $\text{g} \cdot \text{mol}^{-1}$ and c) PEG-35 000 $\text{g} \cdot \text{mol}^{-1}$.

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 $\text{g} \cdot \text{mol}^{-1}$, from 0.68 to 2.7 for PEG-35 000 $\text{g} \cdot \text{mol}^{-1}$ 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 ~37 wt%, 4 wt%, 1.6 wt% and 1 wt% for PEG-3000, 35 000, 300 000 and 600 000 g.mol⁻¹, respectively.

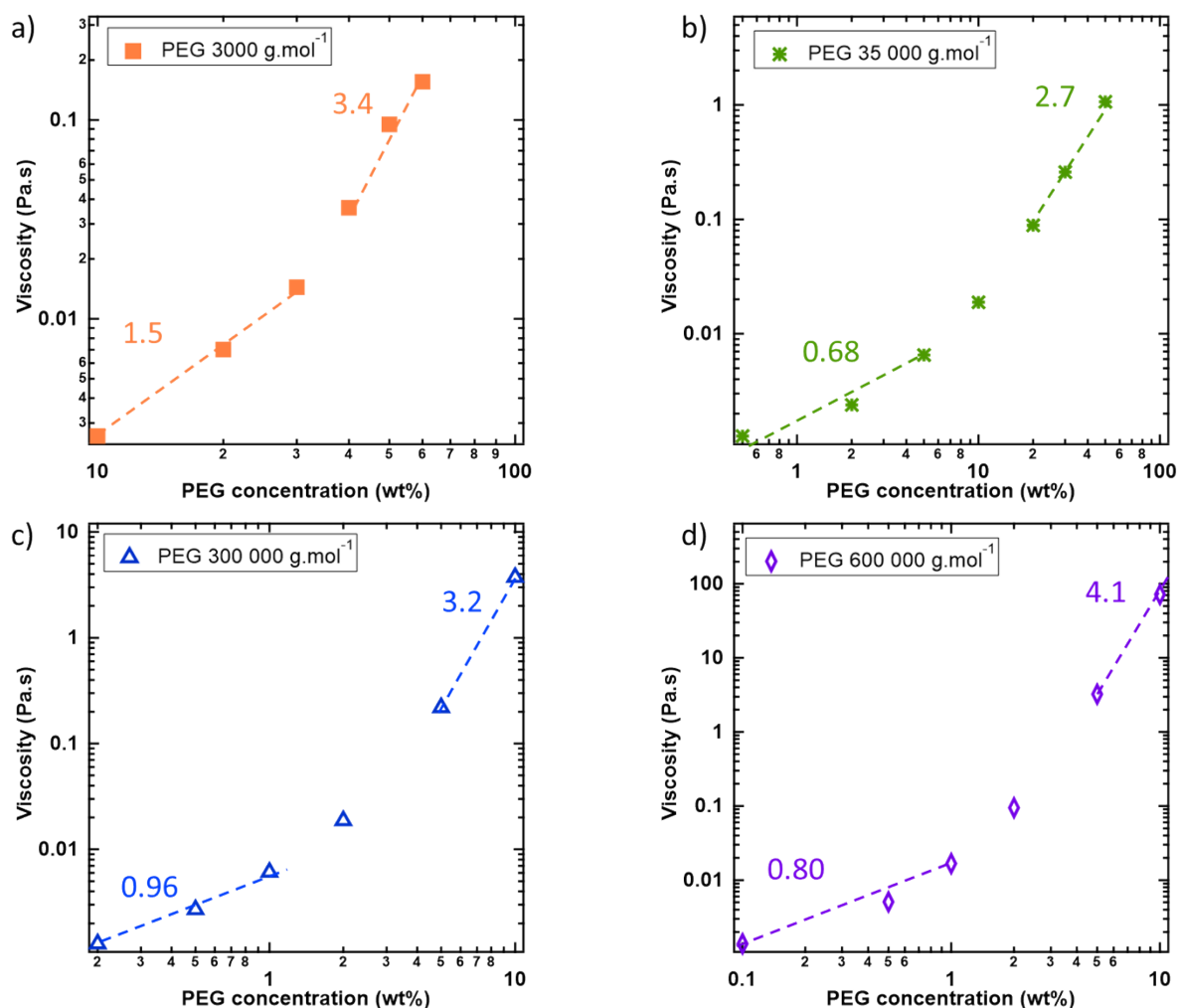


Figure S3 S4. Viscosity as a function of PEG concentration for various PEG molar masses: a) PEG-3000, b) PEG-35 000, c) PEG-300 000 and d) PEG-600 000 g.mol⁻¹.

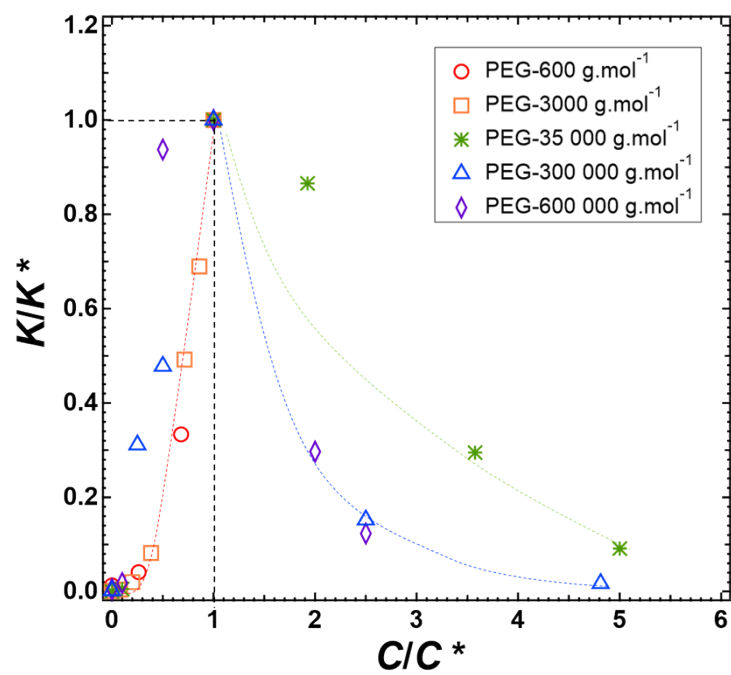


Figure S5. K/K^* as a function of C/C^* as a function of PEG concentration for various molar masses.

S5. CryoSEM and AFM images

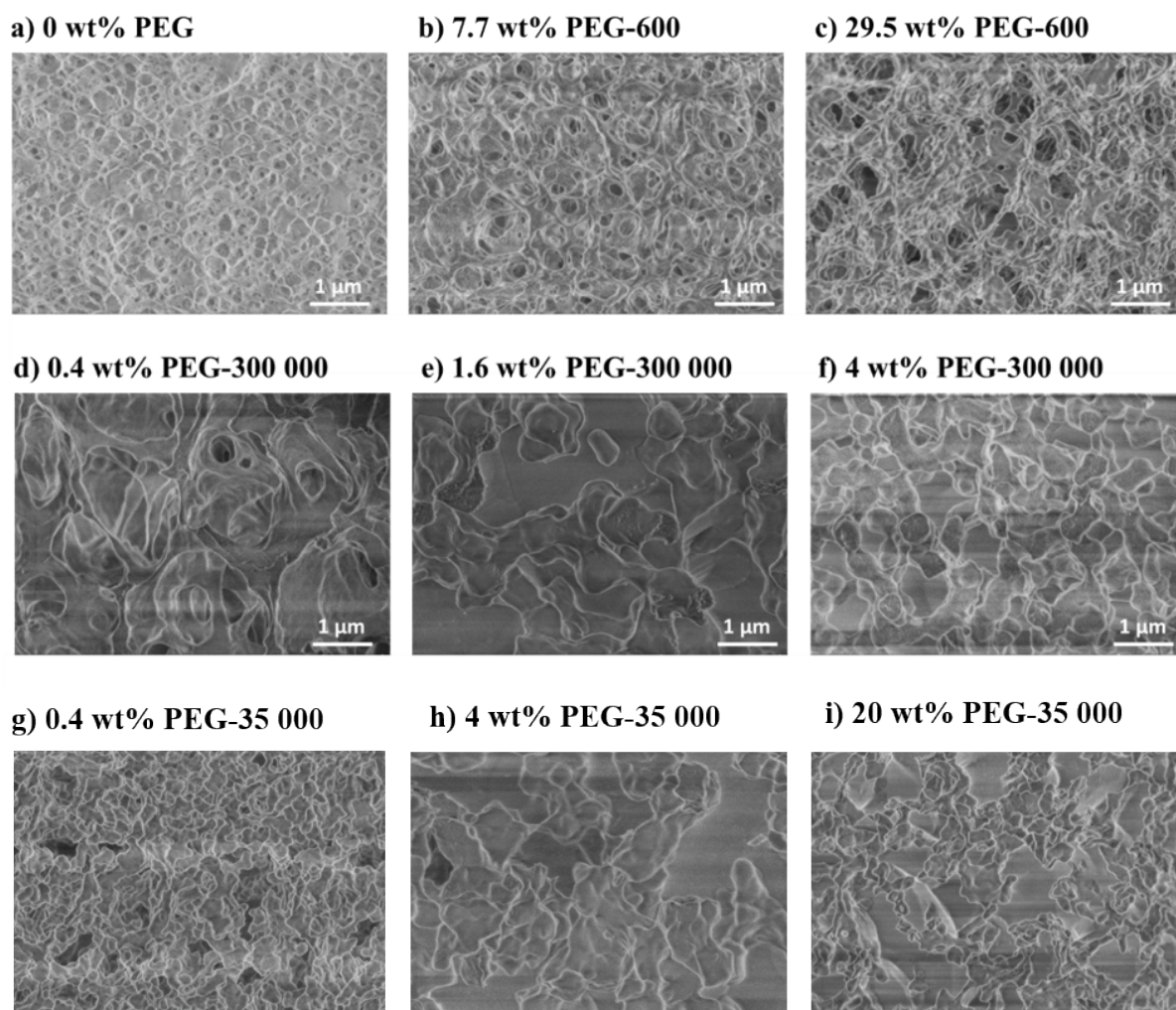


Figure S4 S6. CryoSEM images of hydrogel membranes prepared with PEGDA and various contents of PEG-600 g.mol⁻¹: a) 0, b) 7.7 and c) 29.5 wt%; PEG-300 000 g.mol⁻¹: d) 0.4, e) 1.6 and f) 4 wt% and PEG-35 000 g.mol⁻¹ g) 0.4, h) 4 and i) 20 wt%.

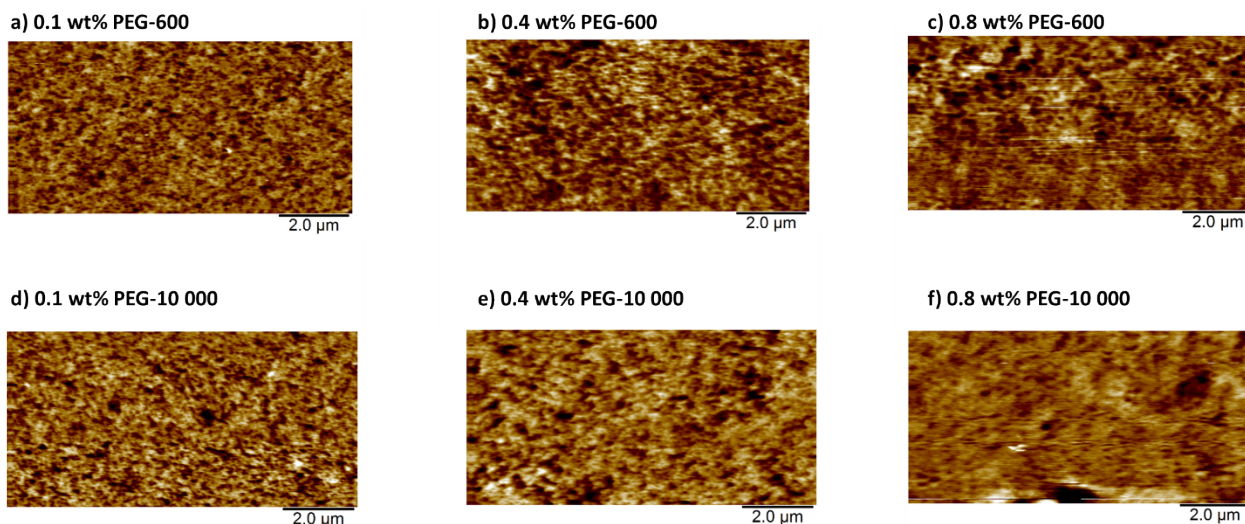


Figure S5 S7. Surface AFM images of PEGDA hydrogel membranes prepared with 16 wt % of PEGDA and various contents of PEG-600 (a, b and c) and PEG-10 000 g.mol⁻¹ (d, e and f). The typical z-scale is 50 nm.

Reference :

1. Eddine, M. A.; Belbekhouche, S.; de Chateauneuf-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.

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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⁻¹.

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

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

m _{PEGDA} (g)	m _{water} (g)	m _{Irgacure} (g)	m _{PEG-3000} (g)	total mass (g)	%wt PEG	%wt PEGDA	%wt water	%wt Irgacure	PEGDA/water ratio
2	10	2x10 ⁻³	0.2	12.202	1.6	16.4	81.9	1.64x10 ⁻²	0.2
2	10	2x10 ⁻³	0.5	12.502	4.0	16.0	80.0	1.60x10 ⁻²	0.2
2	10	2x10 ⁻³	1	13.002	7.7	15.4	77.0	1.54x10 ⁻²	0.2
2	10	2x10 ⁻³	2	14.002	14.3	14.3	71.4	1.43x10 ⁻²	0.2
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Table S3. Composition of the PEGDA/PEG samples used in this study with PEG-10 000 g.mol⁻¹.

m _{PEGDA} (g)	m _{water} (g)	m _{Irgacure} (g)	m _{PEG-10 000} (g)	total mass (g)	%wt PEG	%wt PEGDA	%wt water	%wt Irgacure	PEGDA/water ratio
2	10	2x10 ⁻³	0.5	12.502	4.0	16.0	80.0	1.60x10 ⁻²	0.2
2	10	2x10 ⁻³	0.8	12.802	6.2	15.6	78.1	1.56x10 ⁻²	0.2
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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	2x10 ⁻³	0.05	12.052	0.4	16.6	83.0	1.66x10 ⁻²	0.2
2	10	2x10 ⁻³	0.1	12.102	0.8	16.5	82.6	1.65x10 ⁻²	0.2
2	10	2x10 ⁻³	0.2	12.202	1.6	16.4	81.9	1.64x10 ⁻²	0.2
2	10	2x10 ⁻³	0.3	12.302	2.4	16.3	81.3	1.63x10 ⁻²	0.2
2	10	2x10 ⁻³	0.4	12.402	3.2	16.1	80.6	1.61x10 ⁻²	0.2
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Table S6. Composition of the PEGDA/PEG samples used in this study with PEG-600 000 g.mol^{-1} .

m_{PEGDA} (g)	m_{water} (g)	m_{Irgacure} (g)	$m_{\text{PEG-600 000}}$ (g)	total mass (g)	%wt PEG	%wt PEGDA	%wt water	%wt Irgacure	PEGDA/water ratio
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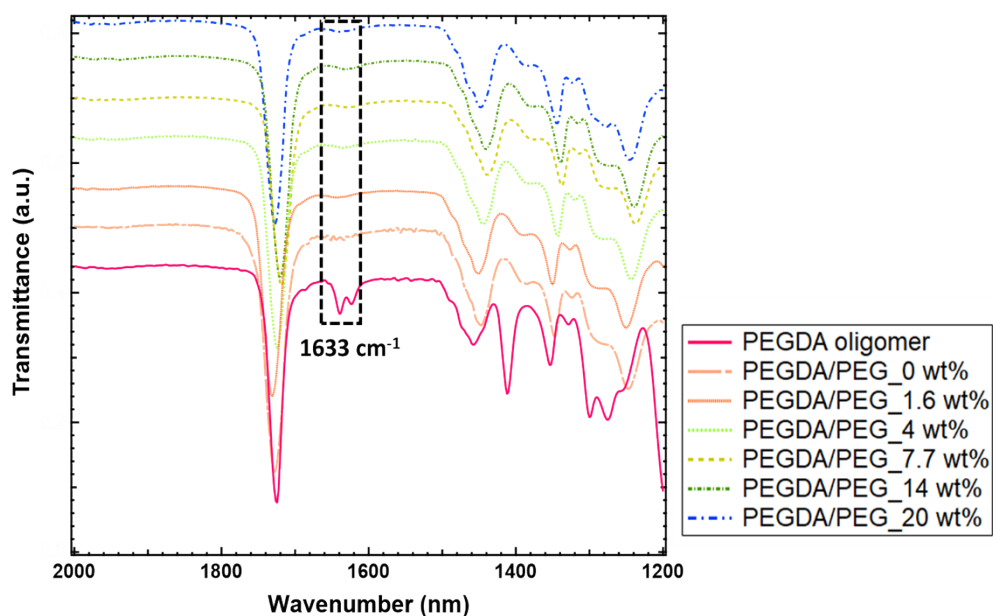


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S3. Filtration experiments

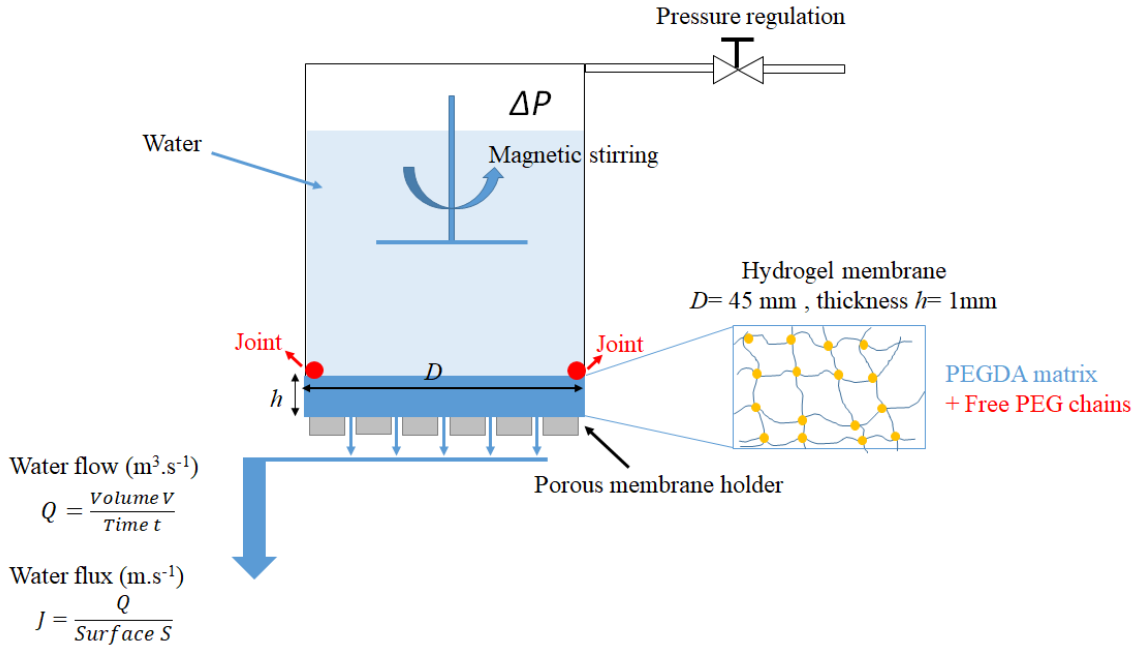


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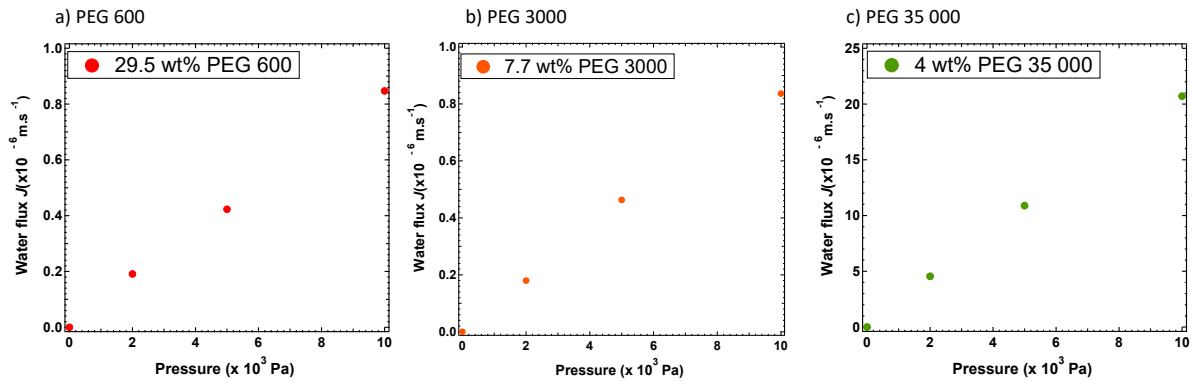


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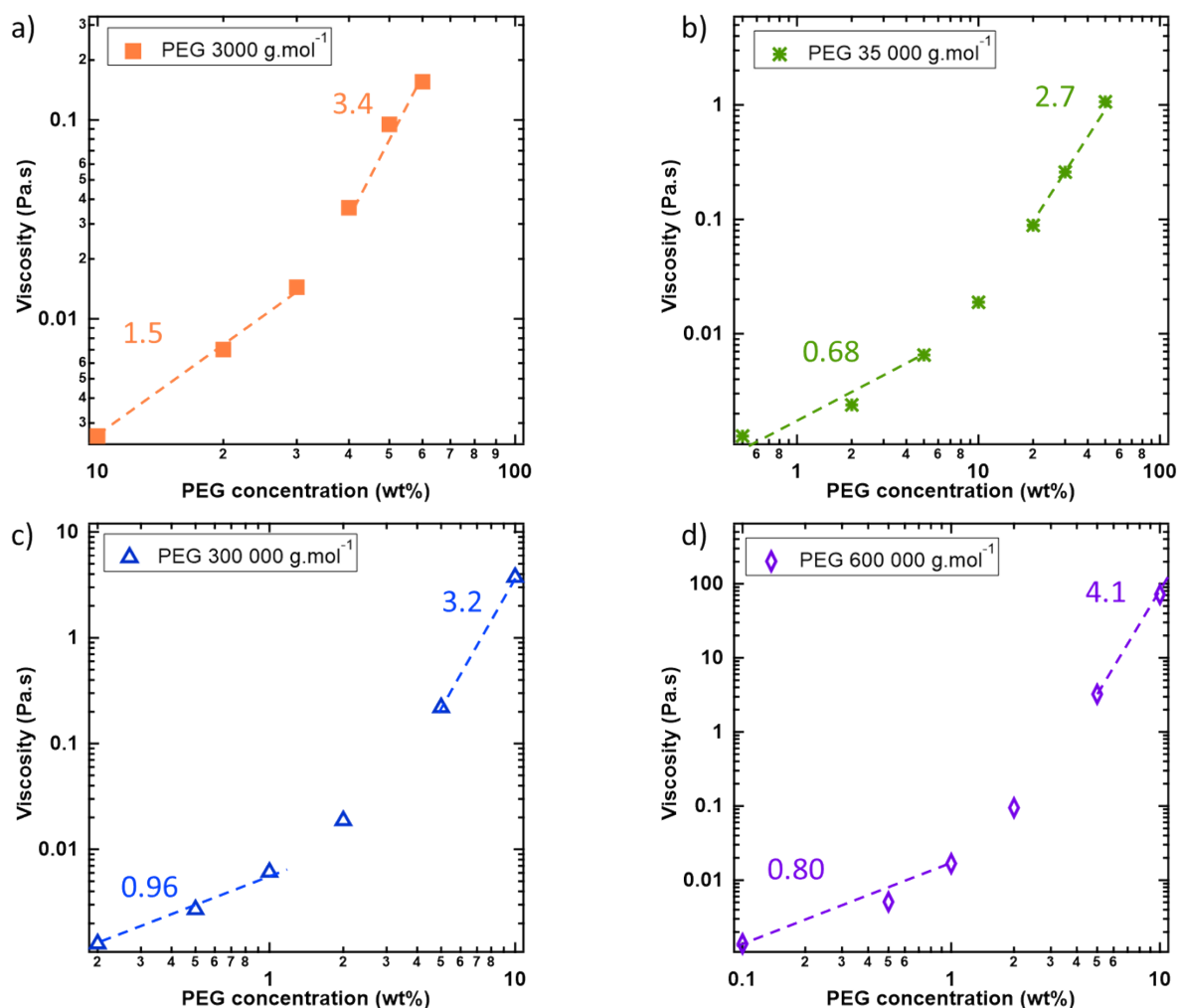


Figure S4. Viscosity as a function of PEG concentration for various PEG molar masses: a) PEG-3000, b) PEG-35 000, c) PEG-300 000 and d) PEG-600 000 g.mol⁻¹.

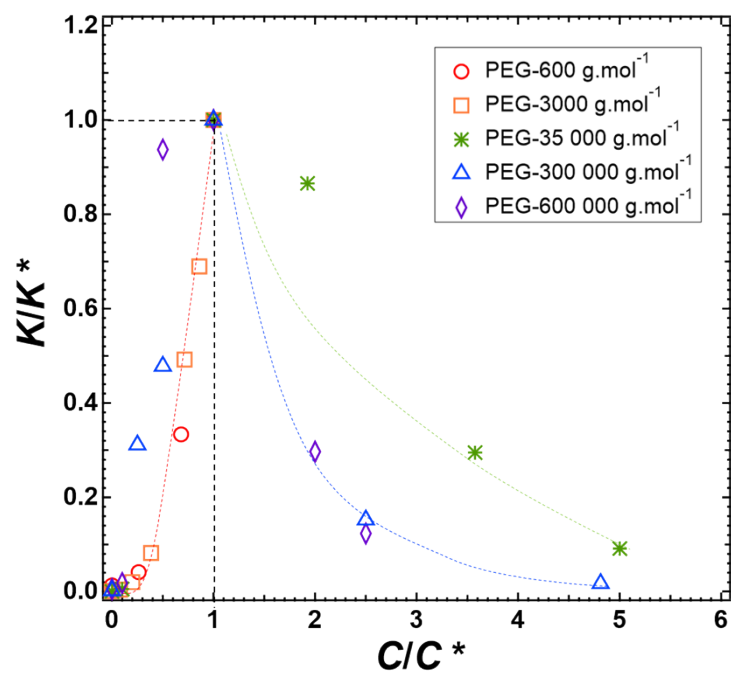


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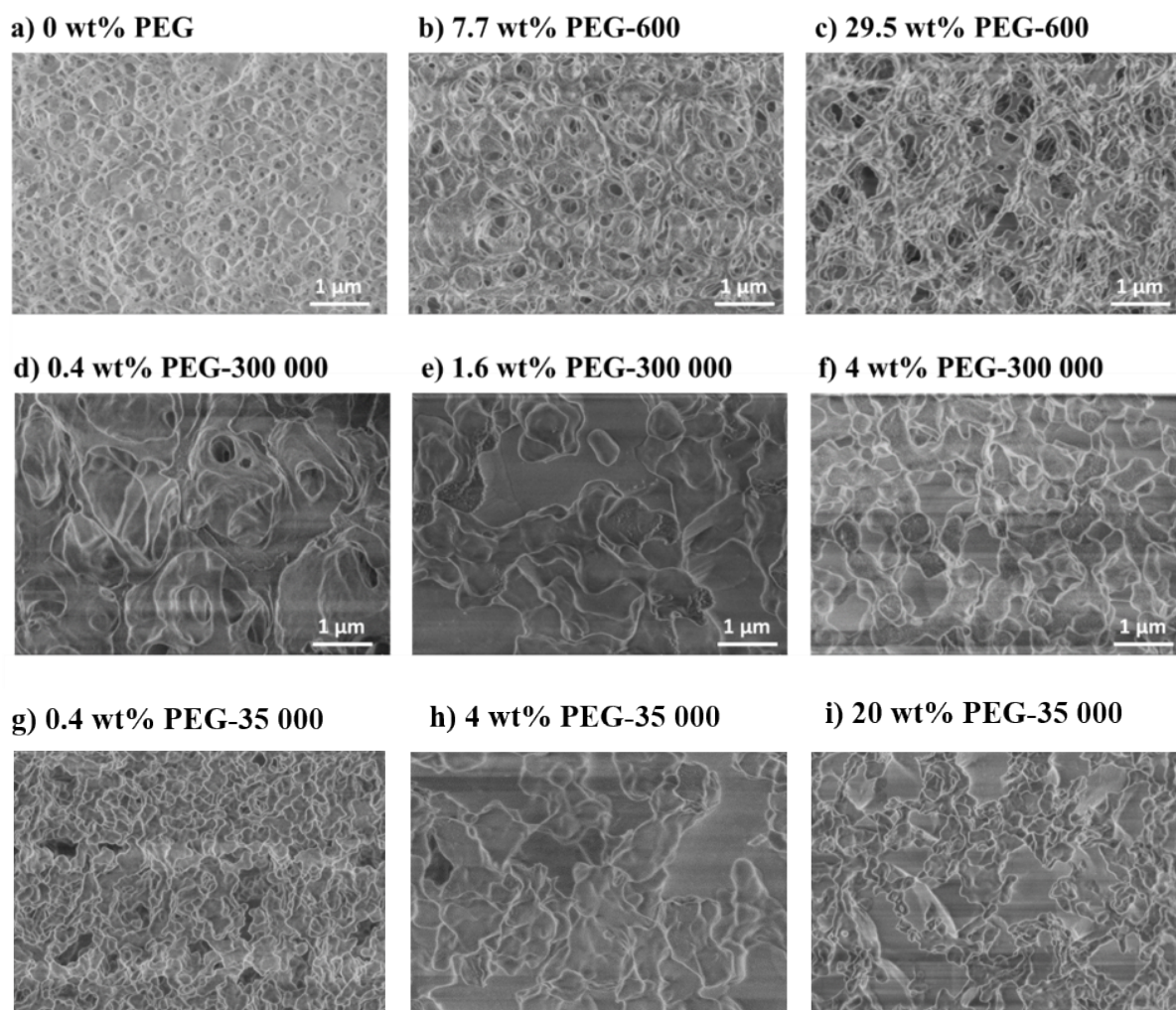


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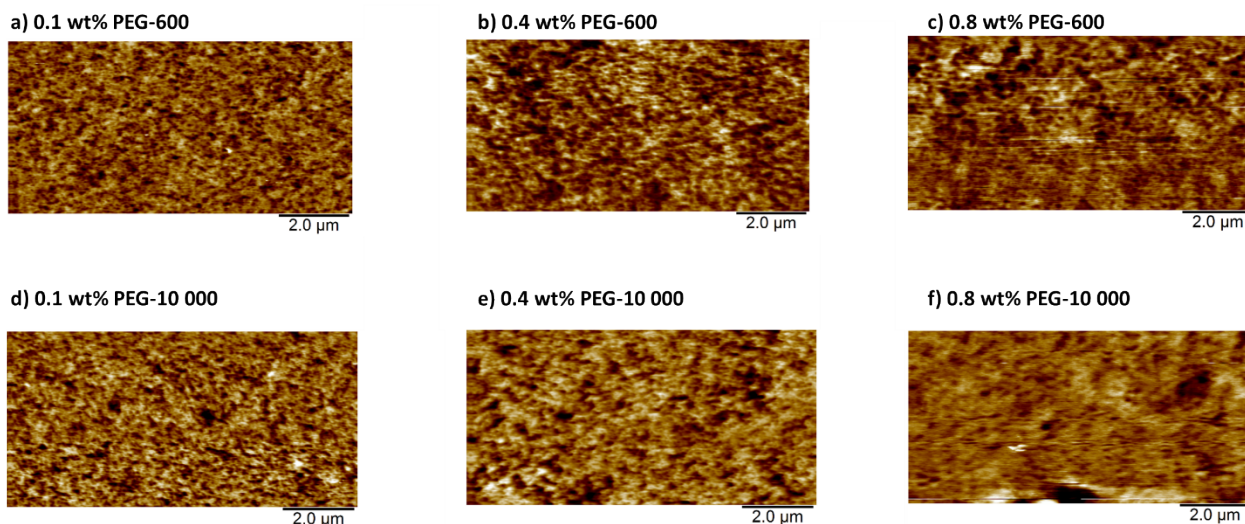


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