

Materials and methods

Materials

The polydimethylsiloxane-*block*-polyethylene glycol (PDMS-*b*-PEG) copolymer was synthesized and purified according to a paper previously published by the authors¹. Tetrahydrofuran (THF) stabilizer-free was purchased from VWR () and used for light scattering and CryoTEM experiments. Deuterated THF (99.50 atom% deuterium, <0.05% water) and deuterium oxide (D₂O) (99.90 atom% deuterium) was purchased from Eurisotop (France) and used for the neutron scattering experiments.

Dialysis preparation

As described in the main text, the dialysis device consists of a central measuring cell with a volume of approximately 4.5 mL and two lateral solvent reservoirs with a volume of up to 200 mL each. The measuring cell is formed by the assembly of the main frame with two quartz windows placed at the front and at the back creating a measurement path through the sample. The thickness between the windows can be adjusted to either 1 or 2 mm. Two holes are placed on the top to fill or remove the sample from the cell. The solvent exchange rate between the cell and the lateral reservoirs is controlled by placing a regenerated cellulose membrane with specific pore sizes between them (typically between 1 and 100 kDa molecular weight cut-off). The contents of both the measuring cell and the lateral reservoirs are homogenized under stirring by magnetic stirrers.

The sample solution was prepared by dissolving the copolymer in THF at a concentration of 5 g.L⁻¹. After filtration through 0.22 µm PTFE syringe filter, the solution was poured into the measuring cell of the dialysis device. BC solution was measured as starting point before the solvent was added to the lateral reservoirs.

Dynamic light scattering

In situ and time-resolved DLS experiments were performed with a Vasco Kin device (Cordouan Technologies) equipped with a remote head operating at a wavelength of 638 nm with a detection at 170° (back-scattering). The head was positioned at an incident angle of 30° to the dialysis cell window. The scattering signal was acquired during the whole dialysis period then processed using NanoKin software (Cordouan Technologies). The time-resolved raw data were first sliced into equals periods of time, then the correlation functions were fitted using a continuous multimodal analysis algorithm (SBL) to access the particle size distribution.

Small angle neutron scattering

The time-resolved small angle neutron scattering experiments (Tr-SANS) were performed at the Institut Laue-Langevin (Grenoble, France) on the D22 spectrometer. Neutron beam was collimated through an aperture of 13 mm diameter while the wavelength was selected at 6 Å with a detector distances of 17.6 m to cover a q-range of 2.5 x10⁻³ to 5.8 x10⁻² Å⁻¹. The intensity presented in absolute units is obtained after correction by the empty sample container, the blocked beam, the sample transmission and incoming neutron flux through a direct beam measurement. Data were reduced using Grasp software.

SANS data fitting procedure

In neutron scattering experiment, the scattering intensity of spherically symmetric particles is classically expressed as:

$$I(q) = n \Delta\rho^2 V_{part}^2 P(q) S(q) \quad \text{Eq. 1}$$

where n is the number density of particles, $\Delta\rho$ is the difference in the neutron scattering length density between the particles and the solvent, and V_{part} is the unit volume of the particles. The form factor describes the structure of particles while the structure

factor describes the interaction between particles. In the absence of interactions, $S(q) = 1$. Introducing the volume fraction of particles Φ , the scattering intensity can be written:

$$I(q) = \Phi \Delta\rho^2 V_{part} P(q) \quad \text{Eq. 2}$$

The volume fraction of particles corresponds to the initial volume fraction of copolymer dissolved in solution. The copolymer volume fraction is considered to be equal to its weight fraction (copolymer density ~ 1). The scattering of the PEG block is neglected because of its high solvation as usually done for the hydrophilic block during SANS experiment on the self-assembly of amphiphilic copolymer in water. The volume fraction of particles can then be simplified as:

$$\Phi \sim [copolymer]_{wt.} \cdot (1 - f) \quad \text{Eq. 3}$$

where $[copolymer]_{wt.}$ is the copolymer weight concentration and f is the hydrophilic weight fraction. In the case of the PDMS₂₇-*b*-PEG₁₇ dialysis experiments, $[copolymer]_{wt.} = 0.005$, $f = 0.26$ then $\Phi \sim 0.0037$.

The difference in the neutron scattering length density $\Delta\rho$ is defined as:

$$\Delta\rho = \rho_{solvent} - \rho_{part.} \quad \text{Eq. 4}$$

where $\rho_{solvent}$ is the neutron scattering length density of the solvent mixture and $\rho_{part.}$ is the neutron scattering length density of the particles. In the same way as for the calculation of the volume fraction of particles, only the neutron scattering length density of the PDMS block is considered here for the neutron scattering length density of the particles.

During the dialysis, the scattering length density of the solvent is changing with the solvent composition. It is defined as:

$$\rho = N_A \frac{b_{coh}}{V_{mol}} \quad \text{Eq. 5}$$

where N_A is the Avogadro's number, V_{mol} is the molar volume of the solvent mixture and b_{coh} is the coherent scattering cross section of the solvent mixture which can be calculated as follows:

$$b_{coh} = x_1 b_{coh/D_2O} + (1 - x_1) b_{coh/THF-d8} \quad \text{Eq. 6}$$

with x_1 the D₂O molar ratio and b_{coh/D_2O} and $b_{coh/THF-d8}$ the coherent scattering cross section of D₂O and THF-d₈ respectively. The average molar volume of the solvent mixture can be expressed as:

$$V_{mol} = \frac{M}{D} \quad \text{Eq. 7}$$

where D is the density of the solvent mixture extracted from literature² and M is the average molar mass of the solvent mixture written as:

$$M = x_1 M_{D_2O} + (1 - x_1) M_{THF-d8} \quad \text{Eq. 8}$$

where M_{D_2O} and M_{THF-d8} are the molar mass of D₂O and of THF-d₈ respectively.

The scattering length density of the solvent mixture is calculated over the range of composition covered by the dialysis and is represented in the figure S4. These values will be used during the fitting process of the SANS data.

Fitting of the SANS data aims at extracting the shape and characteristic sizes of the particles. All data fitting was performed on SasView software (<https://www.sasview.org/>). Individual spectrum was fitted independently using a single form factor model or a combination of different form factor models. Simple models were tried to minimize the total number of fitting parameters. This included: sphere, cylinder, ellipsoid and vesicle. However, only cylindrical and vesicular shapes were found to be useful.

The form factor associated with randomly oriented cylinders is defined as:

$$P(q, \alpha) = \frac{\Phi}{V} \int_0^{\pi/2} F^2(q, \alpha) \sin(\alpha) d\alpha + background \quad \text{Eq. 9}$$

with:

$$F(q, \alpha) = 2 \Delta\rho V \frac{\sin(\frac{1}{2} q L \cos(\alpha))}{\frac{1}{2} q L \cos(\alpha)} \frac{j_1(q R \sin(\alpha))}{q R \sin(\alpha)} \quad \text{Eq. 10}$$

where Φ is the volume fraction of the shell material, α is the angle between the axis of the cylinder and the scattering vector q , L is the length of the cylinder, R is the radius of the cylinder, V is the volume of the cylinder, $\Delta\rho$ is the difference in the neutron scattering length density between the particles and the solvent, J_1 is the first order Bessel function, *background* is a flat background level due to incoherent scattering and V is the volume of the cylinder:

$$V = \pi R^2 L \quad \text{Eq. 11}$$

Using Sasview software, this cylinder model can be used to obtain the following parameters: particle scattering length density, radius and cylinder length.

The form factor associated with an unilamellar vesicular morphology is derived from the form factor of a core-shell structure. The scattering is normalized by the volume that is contributing to the scattering, namely the volume of the shell alone, the scattering length density of the core is fixed the same as that of the solvent:

$$P(q) = \frac{\Phi}{V_{shell}} \left[\frac{3 V_{core} (\rho_{solvent} - \rho_{shell}) j_1(q R_{core})}{q R_{core}} + \frac{3 V_{tot} (\rho_{shell} - \rho_{solvent}) j_1(q R_{tot})}{q R_{tot}} \right]^2 + background \quad \text{Eq. 12}$$

where Φ is the volume fraction of the shell material, V_{shell} is the volume of the shell, V_{core} is the volume of the core, V_{tot} is the total volume, R_{core} is the radius of the core, R_{tot} is the outer radius of the shell, $\rho_{solvent}$ is the scattering length density of the solvent, ρ_{shell} is the scattering length density of the shell, *background* is a flat background level due to incoherent scattering, and j_1 is the spherical Bessel function defined as:

$$j_1 = \frac{\sin(x) - x \cos(x)}{x^2} \quad \text{Eq. 13}$$

Using Sasview software, this vesicle model can be used to obtain the following parameters: particle scattering length density, radius (R_{tot}) and vesicle thickness ($R_{tot} - R_{core}$).

The fitting procedure was carried out following some specifications:

- Fitting with a single form factor was preferred before trying any combination of form factor.
- The volume fraction and background level were imposed after being determined using Equation 3 and determined manually, respectively.
- The cylinder length was found to increase greatly during the dialysis. As the instrumental configuration used here limits the range of accessible cylinder lengths (Figure S5), the latter parameter is imposed to 1500 Å when values fall outside the range.
- When a combination of form factors is used, a volume fraction is expressed for each form factor in addition to an overall volume fraction. By imposing that the sum of the volume fraction of each form factor is equal to 1, these parameters are fitted and thus indicate the ratio of each morphology.
- When using the combination of form factors, some fitting parameters were fixed to reduce the number of fitting parameters. The cylinder radius was imposed at the previously found value. This is justified by the fact that the

value of the cylinder radii reaches a plateau before the introduction of the vesicle model. Similarly, the thickness of the vesicle was imposed at twice the cylinder radius.

- When needed, a Gaussian polydispersity function was applied to specific parameters. The polydispersity value was fixed manually.

The scattering length density of the particles determined by the fitting procedure give valuable information on the solvation rate Ψ of the PDMS block, which can be approximated as the volume fraction of solvent in close proximity with the PDMS. The particle scattering length density $\rho_{part.}$ extracted from the fitting procedure, can be expressed as:

$$\rho_{part.} = \Psi \rho_{solvent} + (1 - \Psi) \rho_{PDMS} \quad \text{Eq. 14}$$

where $\rho_{solvent}$ is calculated as previously explained and ρ_{PDMS} is the theoretical value of the PDMS scattering length density ($0.06 \times 10^{-6} \text{ \AA}^{-1}$). The solvation rate can then be expressed as:

$$\Psi = \frac{\rho_{part.} - \rho_{PDMS}}{\rho_{solvent} - \rho_{PDMS}} \quad \text{Eq. 15}$$

Cryo-transmission electron microscopy

Small amount of the dialysis cell content was collected at different dialysis time corresponding to different water fraction. A volume of 5 μl was applied onto a 400 Cu grid for the sample containing 23% water. For samples with higher water content, we used 400 Cu grid covered with a lacey carbon film that was freshly glow discharged to render it hydrophilic (Elmo, Cordouan Technologies). The grid was rapidly plunged into liquid ethane slush by using a homemade freezing machine with a controlled temperature chamber. The grids were then mounted onto a Gatan 626 cryoholder and observed under low dose conditions on a Tecnai G2 microscope (FEI) operating at 200 kV. The images were recorded with a slow scan CCD camera (Eagle 2k2k FEI).

Supporting information

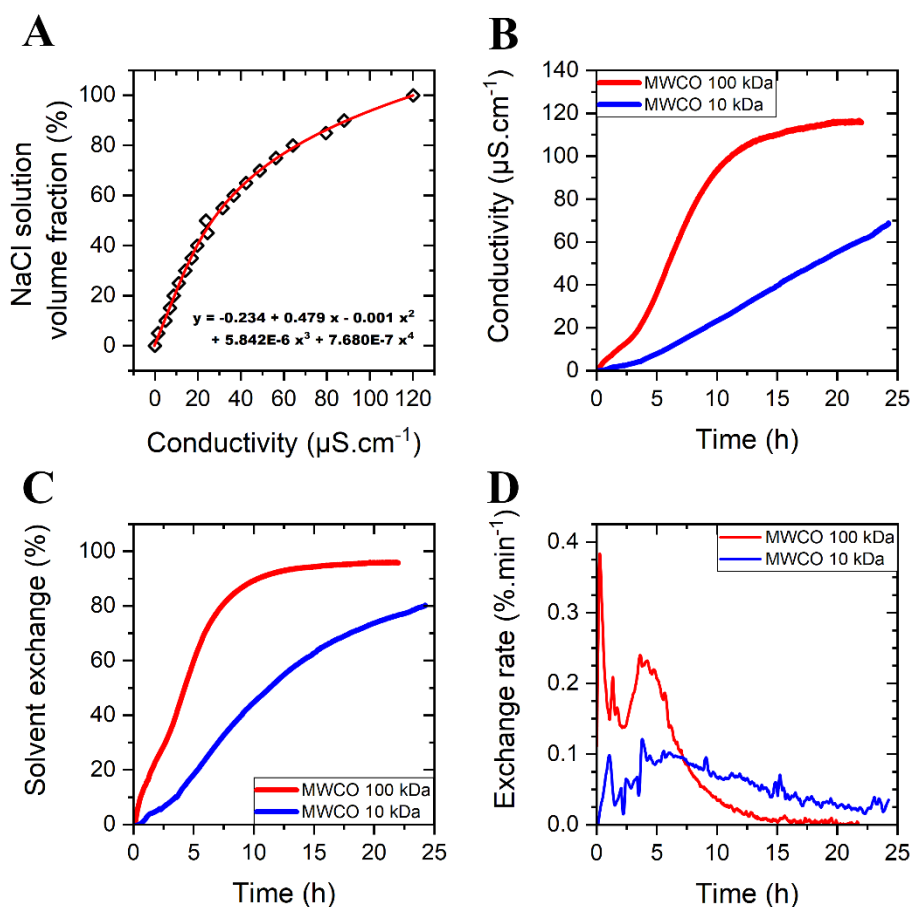


Figure S1. Solvent exchange kinetic during the dialysis measured by conductimetry. (A) Calibration curve made by measuring the conductivity of different mixtures of THF with a 1 mM NaCl water solution. (B) Conductivity measured inside the cell during the dialysis using two different dialysis membranes. (C) Solvent exchange kinetic determined by the conductivity measurements using the calibration curve. A faster dialysis is performed using a 100 kDa MWCO membrane while a slower solvent exchange is achieved using a 10 kDa MWCO membrane. (D) Solvent exchange rate determined by derivation of the solvent exchange kinetic curves.

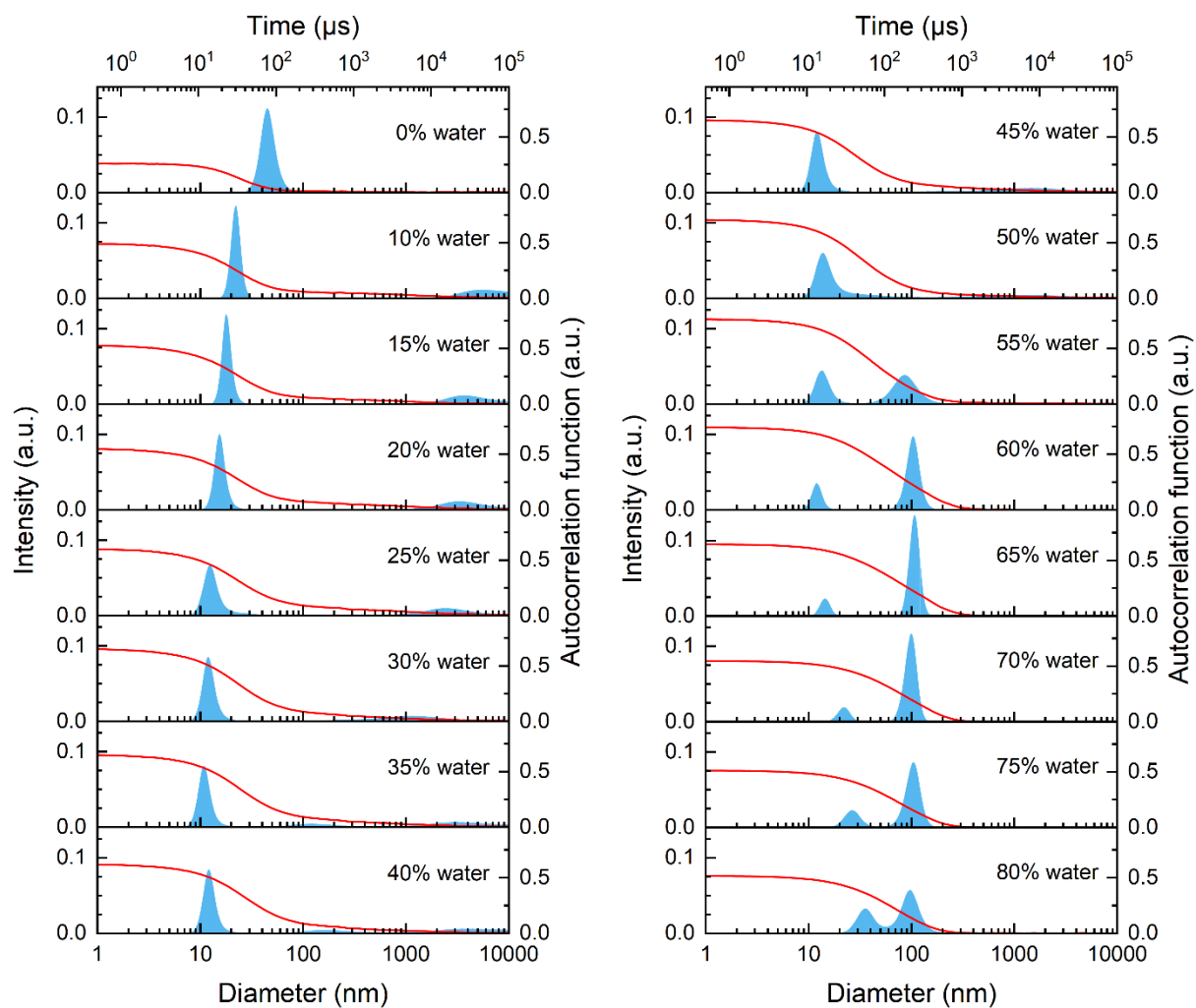
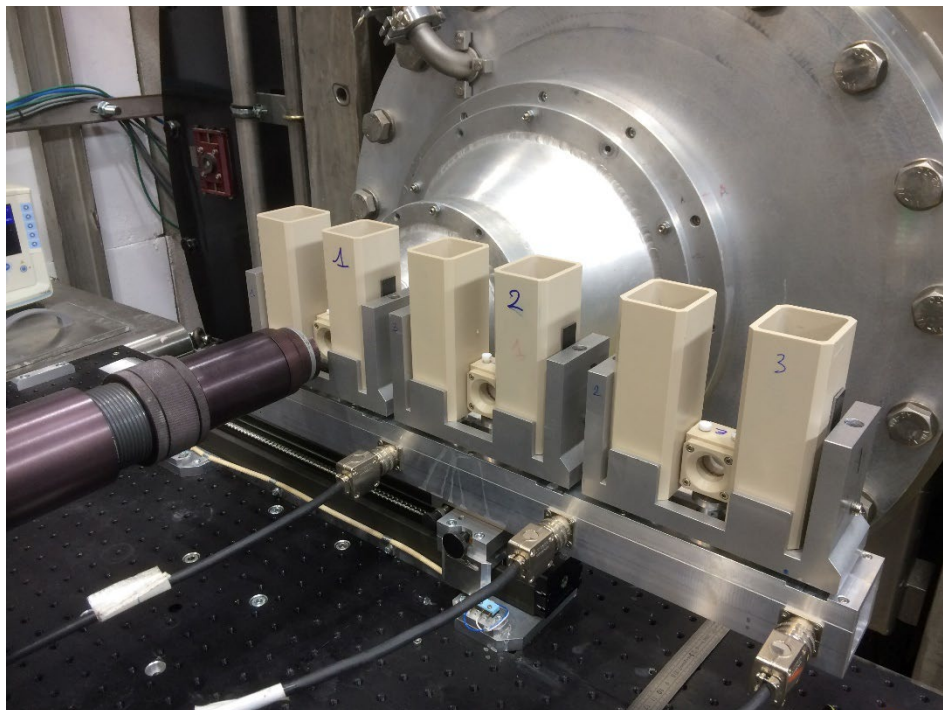


Figure S2. Tr-DLS mapping performed in situ during the dialysis of PDMS₂₇-*b*-PEG₁₇ using a 10 kDa dialysis membrane cut-off. Particle size distributions (blue peaks) and auto-correlation functions (red lines) are shown for different water fractions.



Picture S1. Pictures showing three dialysis cells placed on the sampler of the D22 SANS spectrometer at the Institut Laue Langevin (Grenoble, France).

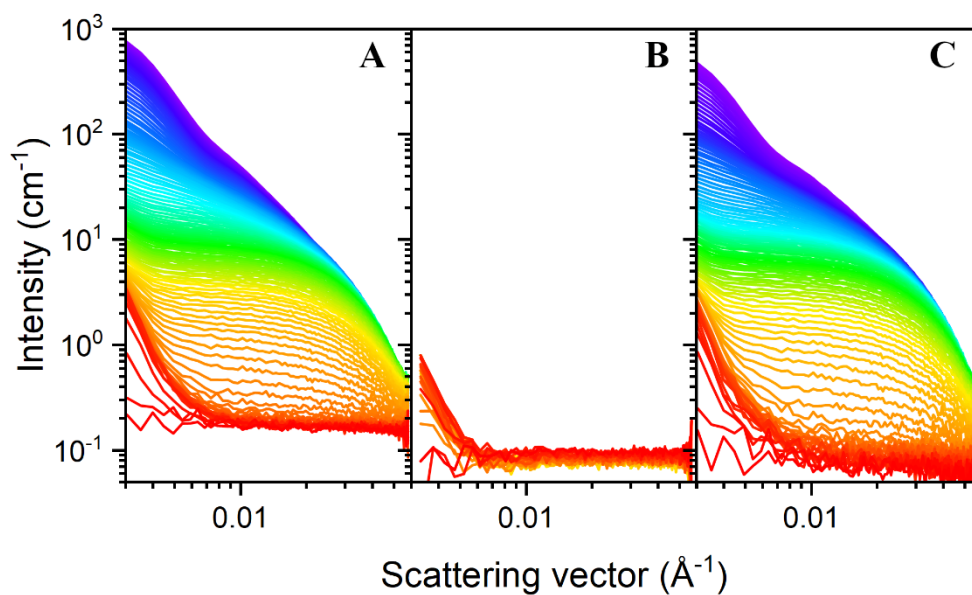


Figure S3. SANS curves showing the scattering profile of the copolymer dialysis (A), the dialysis of only THF-d8 against D_2O (B) and the subtraction of the former by the latter. Both pure THF-d8 and copolymer dialysis exhibit an up-turn at low q values. This phenomenon is probably due to local solvent fluctuations which contrast is exacerbated by the presence of the copolymer.

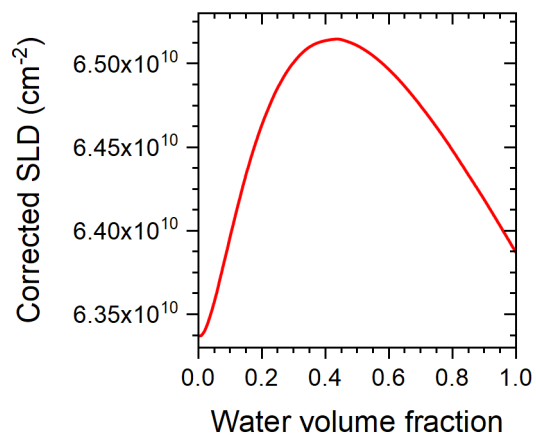


Figure S4. Calculated scattering length densities of THF-d8/D₂O at different D₂O volume fraction.

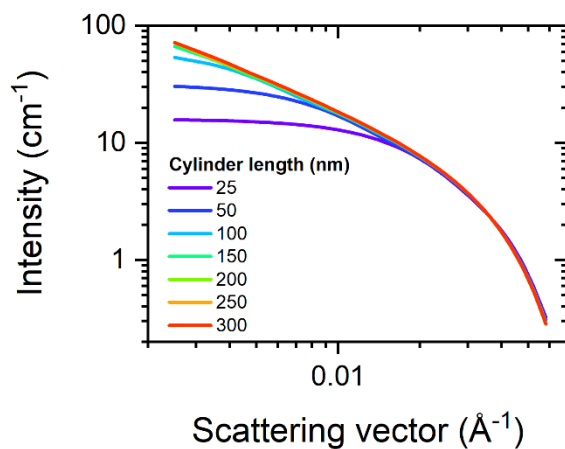


Figure S5. Simulated SANS data corresponding to scattering patterns of cylinder form factors with constant radius (5 nm) and various length in the q-range used for this study. This specific SANS configuration allows to be sensible to the cylinder's length up to 150 nm.

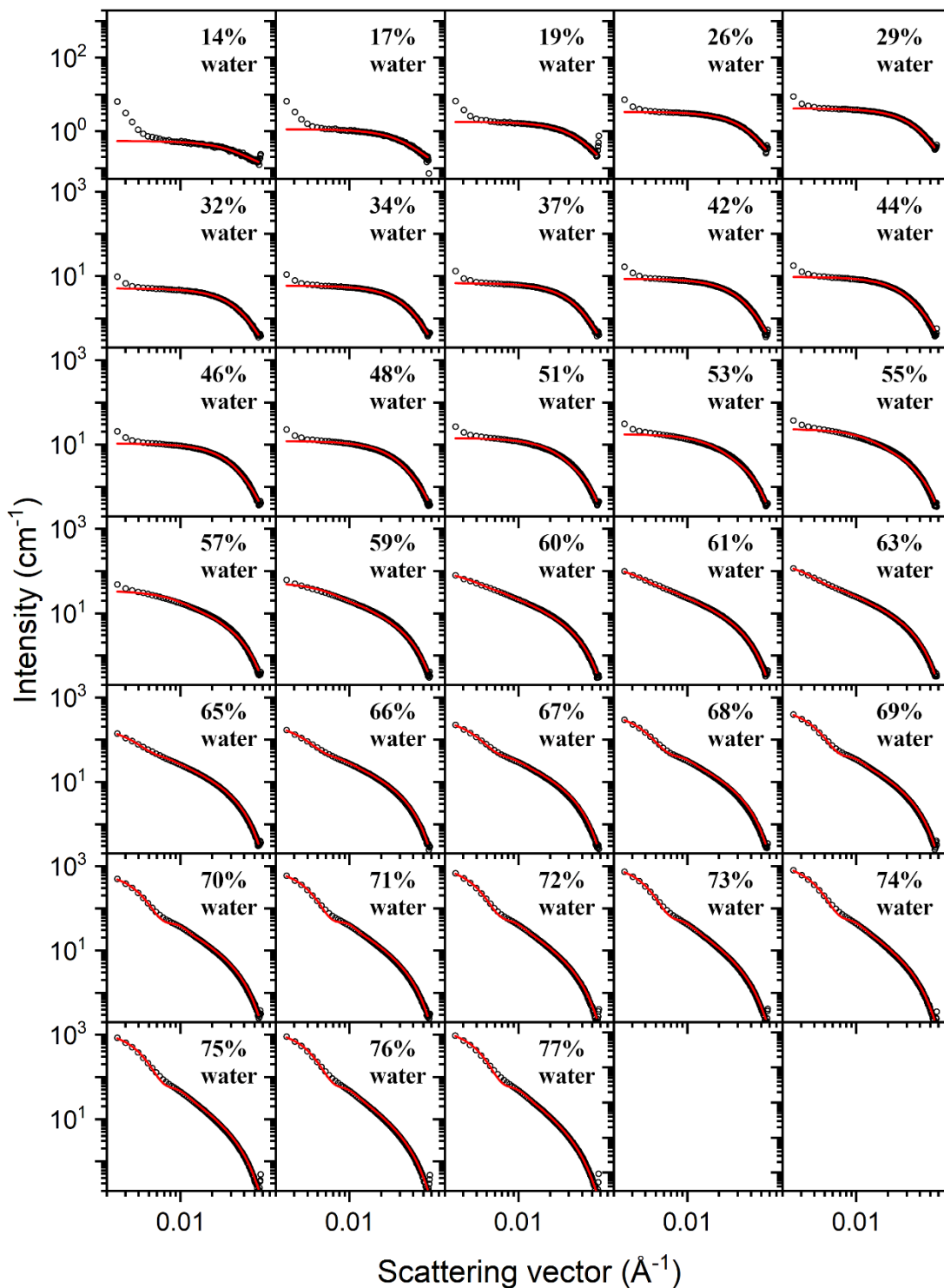


Figure S6. Tr-SANS curves acquired during the dialysis of PDMS₂₇-*b*-PEG₁₇ at 5 g/L in THF-*d*8 against D₂O using a 10 kDa dialysis membrane cut-off. The scattering profile (black sign) and the fit result (red line) are represented at different water fraction. Fitted parameters are summarized in Tables S1 and S2.

Time Water content	Background (cm ⁻¹)	Scale	Solvent SLD (10 ⁻⁶ Å ⁻¹)	Sample SLD (10 ⁻⁶ Å ⁻¹)	Cylinder fraction	Cylinder radius (Å)	Cylinder radius distribution	Cylinder length (Å)	Vesicle fraction	Vesicle radius (Å)	Vesicle radius distribution	Vesicle thickness (Å)
4.2 h 14 %	* 0.05	* 0.0037	6.42	4.47458	* 1	27.056 ± 41.547	/	158.22 ± 172.65	* 0	/	/	/
4.7 h 17 %			6.44	4.17721		34.595 ± 36.726		160.9 ± 144.1				
5.2 h 19 %			6.45	3.8408		39.609 ± 17.637		148.21 ± 85.758				
6.3 h 26 %			6.49	3.13634		42.673 ± 10.118		149.61 ± 55.058				
6.8 h 29 %			6.50	2.86942		44.089 ± 8.5575		149.28 ± 47.088				
7.3 h 32 %			6.51	2.61375		44.803 ± 8.4832		151.85 ± 45.545				
7.8 h 34 %			6.51	2.42424		46.004 ± 7.4853		151.57 ± 30.731				
8.3 h 37 %			6.51	2.24193		46.362 ± 5.1261		156.85 ± 32.918				
9.4 h 42 %			6.52	1.96714		47.489 ± 4.5058		167.06 ± 19.578				
9.9 h 44 %			6.52	1.87018		47.487 ± 4.1738		177.66 ± 18.353				
10.4 h 46 %			6.52	1.83803		50.237 ± 4.1414		174.34 ± 29.016				
10.9 h 48 %			6.52	1.73385		50.223 ± 4.0321		190.67 ± 30.67				
11.5 h 51 %			6.51	1.71097		50.553 ± 3.5389		219.86 ± 33.595				
12.0 h 53 %			6.51	1.6502		50.255 ± 3.2534		268.33 ± 39.204				
12.5 h 55 %			6.51	1.61511		50.057 ± 2.7212		354.46 ± 48.869				
13.0 h 57 %			6.50	1.57982		50.231 ± 2.4228		500.3 ± 68.844				
13.5 h 59 %	6.50	1.54043	50.869 ± 2.2353	757.49 ± 117.03								
14.1 h 60 %	6.49	1.4926	51.818 ± 2.0834	1443.6 ± 429.32								

Table S1. Values extracted from the fitting procedure on the SANS data at different time/water fraction during the dialysis of PDMS₂₇-*b*-PEG₁₇ using a 10 kDa dialysis membrane cut-off. Parameters for which the value has been fixed during the fitting procedure are preceded by a star.

Time water content	Background (cm ⁻¹)	Scale	Solvent SLD (10 ⁻⁶ Å ⁻¹)	Sample SLD (10 ⁻⁶ Å ⁻¹)	Cylinder fraction	Cylinder radius (Å)	Cylinder radius distribution	Cylinder length (Å)	Vesicle fraction	Vesicle radius (Å)	Vesicle radius distribution	Vesicle thickness (Å)
14.6 h 61 %	* 0.05	* 0.0037	6.49	1.42969	0.99191 ± 0.0057264	53.175 ± 2.0958	/	* 1500	* 0.0080891	400.85 ± 232.75	* 0.3	* 106.35
15.1 h 63 %			6.49	1.28343	0.9843 ± 0.0008268	* 53		* 1500	* 0.0157	391.57 ± 14.654	* 0.3	* 106
15.6 h 65 %			6.48	1.26489	0.9732 ± 0.0009043	* 54		* 1500	* 0.026799	379.72 ± 8.1971	* 0.3	* 108
16.1 h 66 %			6.48	1.19805	0.95633 ± 0.0010671	* 54		* 1500	* 0.043668	356.05 ± 4.7077	* 0.3	* 108
16.7 h 67 %			6.48	1.0786	0.92623 ± 0.0012872	* 54		* 1500	* 0.073774	340.07 ± 2.5978	* 0.3	* 108
17.2 h 68 %			6.48	1.0164	0.88428 ± 0.001575	* 54	* 0.1	* 1500	* 0.11572	334.96 ± 1.6066	* 0.3	* 108
17.7 h 69 %			6.47	1.12144	0.81135 ± 0.012724	* 54		* 1500	* 0.18865	324.82 ± 11.194	* 0.3	* 108
18.2 h 70 %			6.47	1.07728	0.7522 ± 0.014899	* 54		* 1500	* 0.2478	328.52 ± 9.1884	* 0.3	* 108
18.8 h 71 %			6.47	1.04168	0.69914 ± 0.016834	* 54		* 1500	* 0.30086	328.85 ± 7.9754	* 0.3	* 108
19.3 h 72 %			6.47	1.12443	0.62611 ± 0.020345	* 54		* 1500	* 0.37389	300.38 ± 7.5233	* 0.3	* 108
19.8 h 73 %			6.46	1.11322	0.58322 ± 0.021991	* 54		* 1500	* 0.41678	297.23 ± 6.9149	* 0.4	* 108
20.3 h 74 %			6.46	1.09046	0.54402 ± 0.023419	* 54		* 1500	* 0.45598	293.76 ± 6.4155	* 0.4	* 108
20.8 h 75 %			6.46	1.06433	0.51422 ± 0.024443	* 54		* 1500	* 0.48578	290.5 ± 6.0664	* 0.4	* 108
21.4 h 76 %			6.46	1.03266	0.48426 ± 0.02542	* 54		* 1500	* 0.51574	288.64 ± 5.7643	* 0.4	* 108
21.9 h 77 %			6.45	1.10542	0.41941 ± 0.10023	* 54		* 1500	* 0.58059	286.97 ± 76.982	* 0.4	* 108

Table S2. Following values extracted from the fitting procedure on the SANS data at different time/water fraction during the dialysis of PDMS₂₇-*b*-PEG₁₇ using a 10 kDa dialysis membrane cut-off. Parameters for which the value has been fixed during the fitting procedure are preceded by a star.

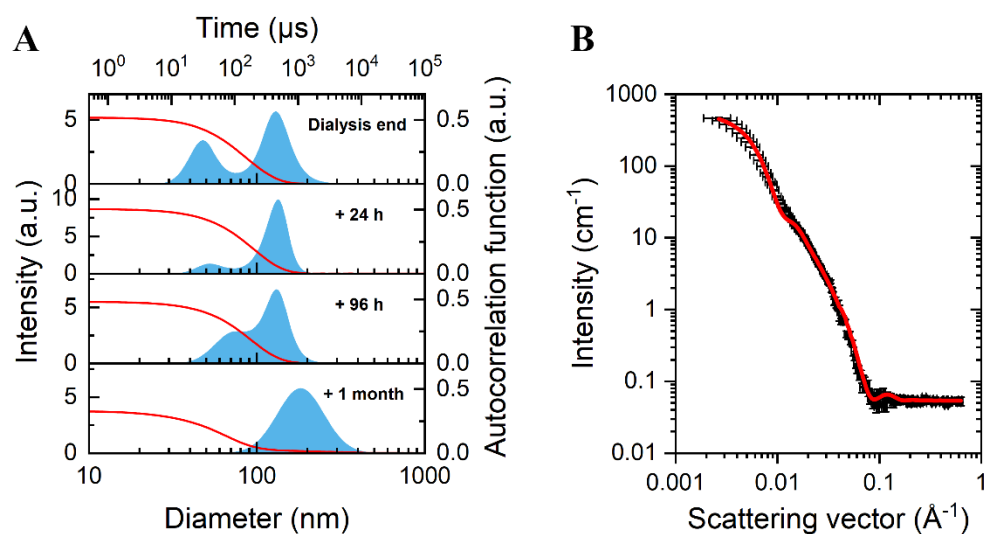


Figure S7. Maturation effect observed after the dialysis. (A) Evolution with time of the size distribution by DLS for the sample collected at the end of the dialysis. Results show a merge of the two population into a monomodal distribution corresponding to the vesicular morphology. (B) SANS results measured on a sample after 40 days of maturation. Data were fitted by a single vesicle form factor (red line). Fitted parameters are summarized in Table S3.

Time Water content	Background (cm ⁻¹)	Scale	Sample SLD (10 ⁻⁶ Å ⁻¹)	Solvent SLD (10 ⁻⁶ Å ⁻¹)	Vesicle radius (Å)	Vesicle radius distribution	Vesicle thickness (Å)
40 days 100 %	* 0.05	* 0.0037	1.7213	6.38	190.18 ± 0.6982	* 0.4	72.863 ± 0.47748

Table S3. Values extracted from the fitting procedure on the SANS data at the end of the dialysis of PDMS₂₇-*b*-PEG₁₇ using a 10 kDa dialysis membrane cut-off after 40 days of maturation. Parameters for which the value has been fixed during the fitting procedure are preceded by a star.

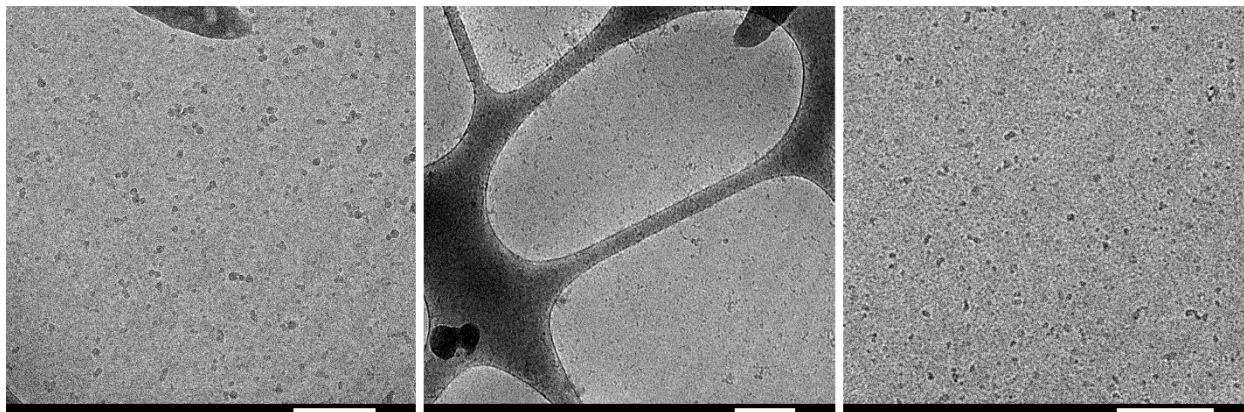


Figure S8. Cryo-TEM analysis of sample collected after 6 hours of dialysis corresponding to 24% of water. Scale bar = 200 nm.

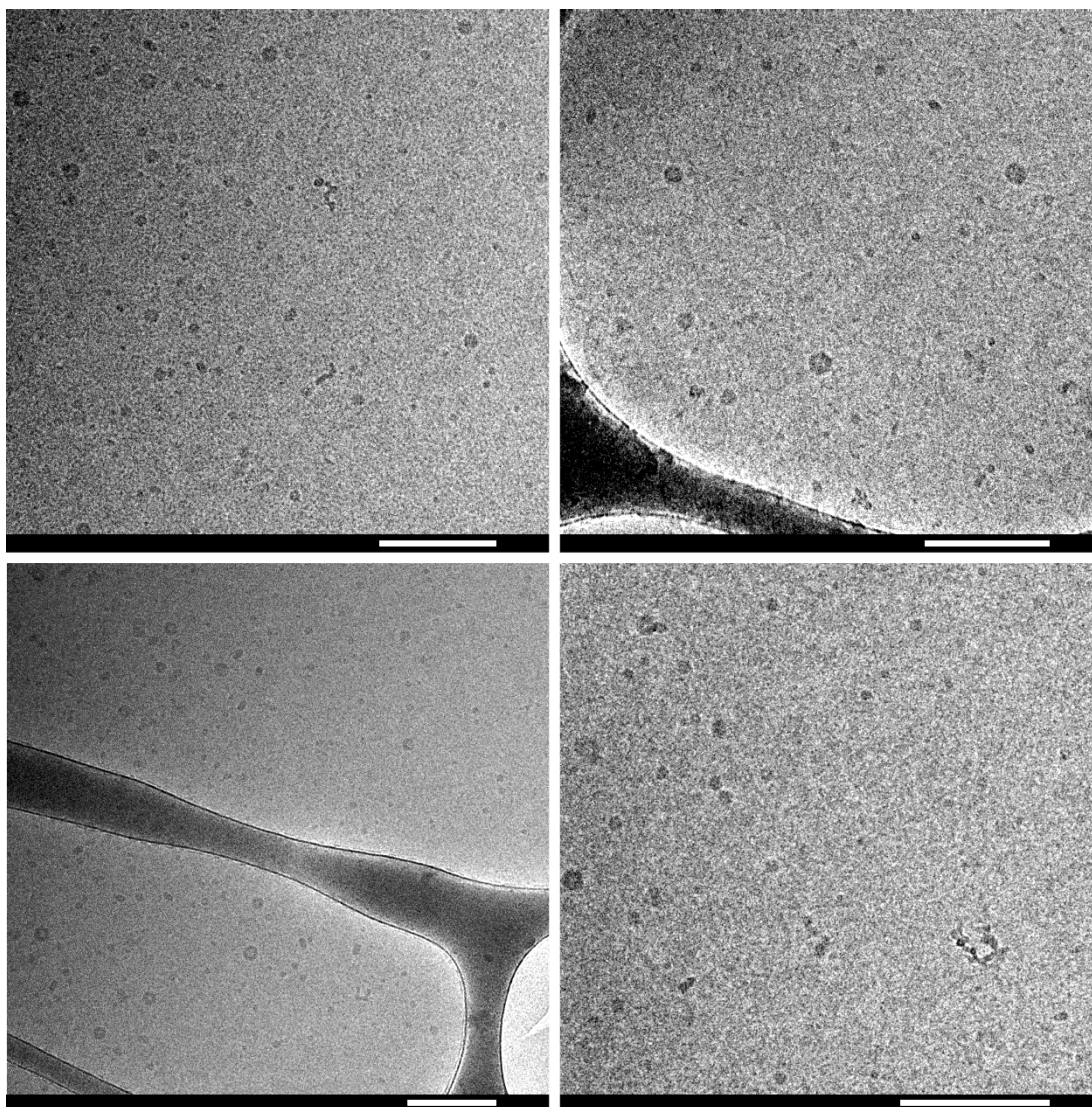


Figure S9. Cryo-TEM analysis of sample collected after 12 hours of dialysis corresponding to 53% of water. Scale bar = 200 nm.

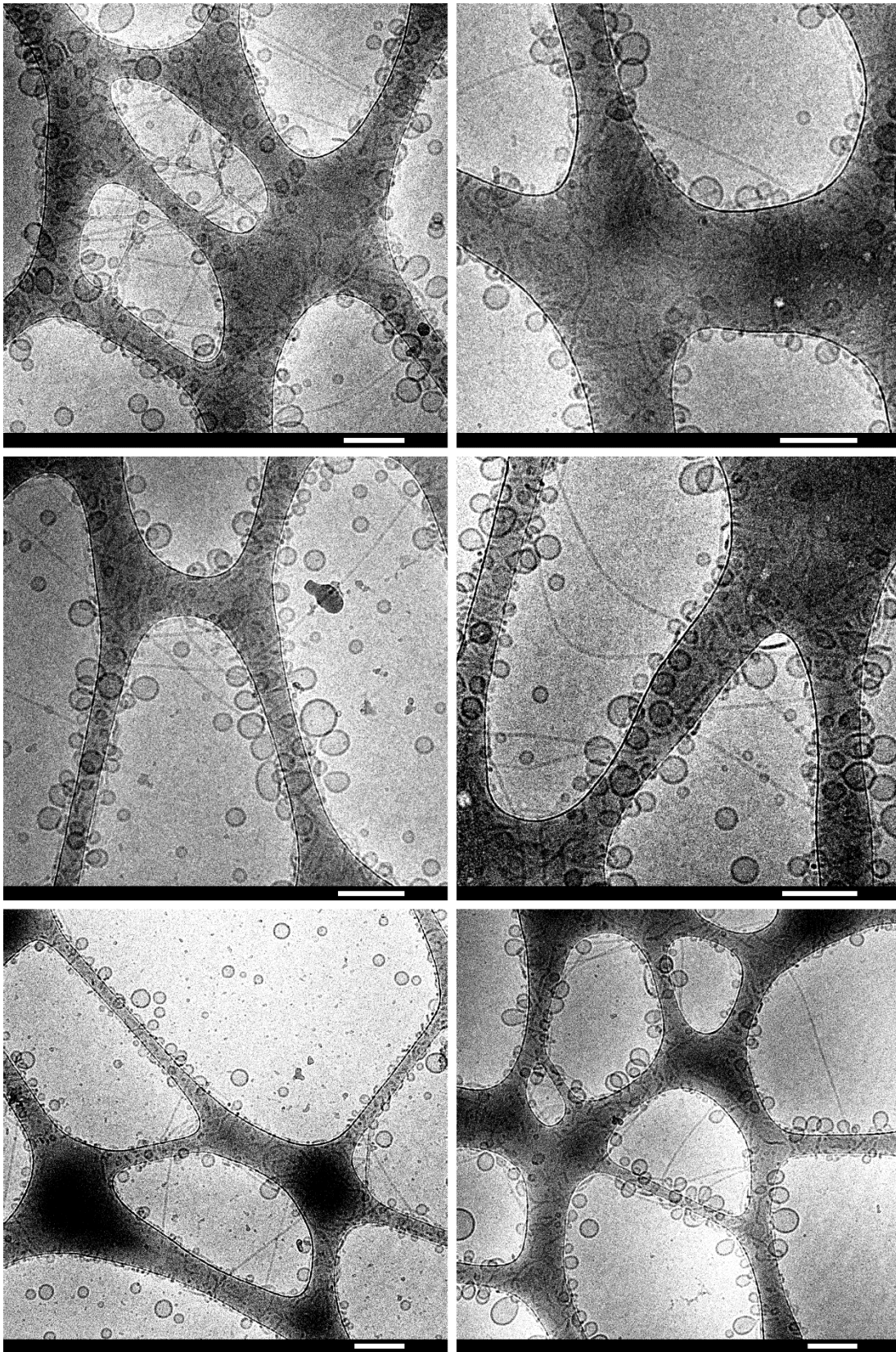


Figure S10. Cryo-TEM analysis of sample collected after 17 hours of dialysis corresponding to 68% of water. Scale bar = 200 nm.

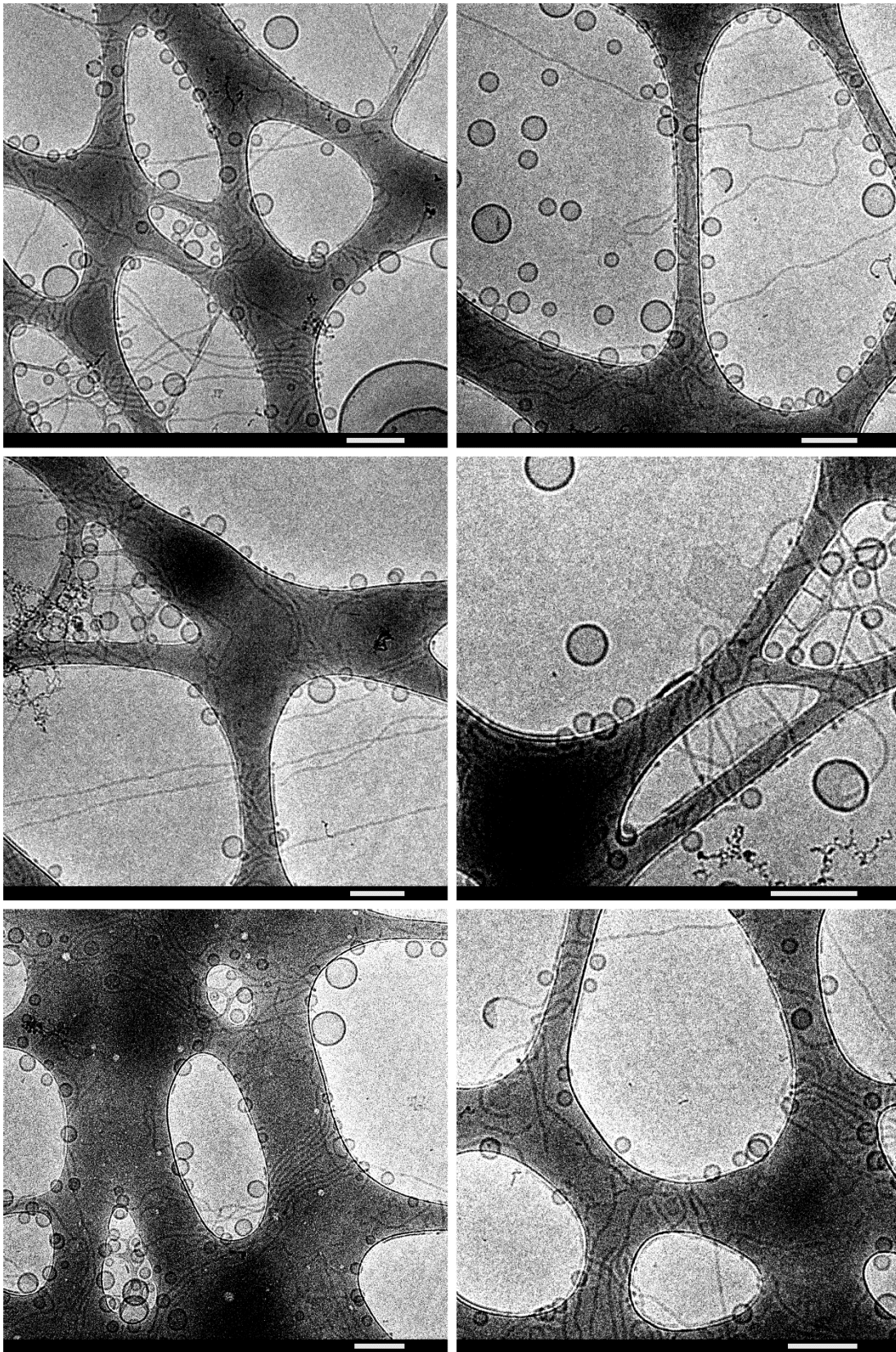


Figure S11. Cryo-TEM analysis of sample collected after 24 hours of dialysis corresponding to 80% of water. Scale bar = 200 nm.

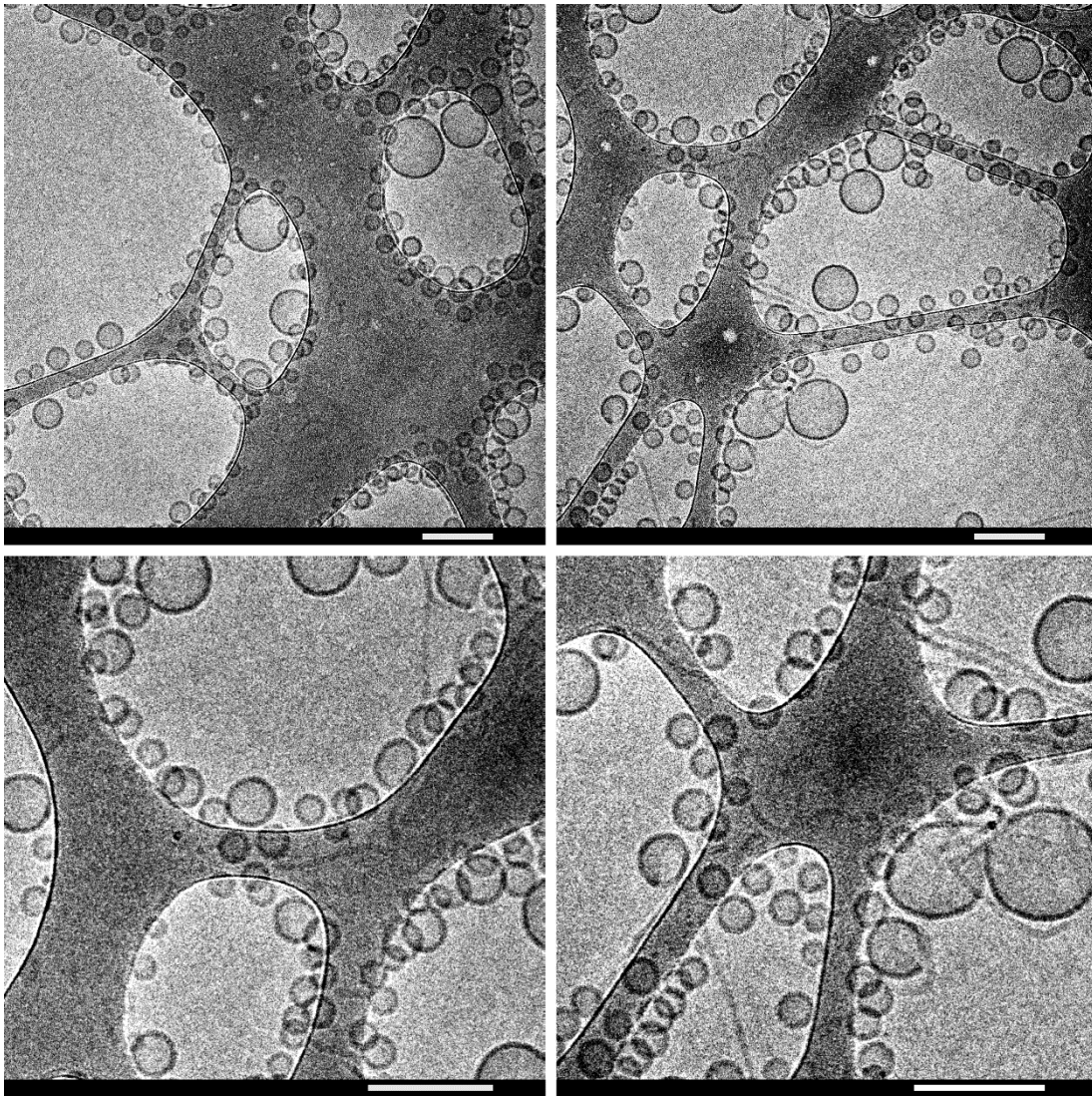


Figure S12. Cryo-TEM analysis of sample collected at the end of the dialysis (24 hours/80% of water) and let to mature for an extra period of time of one month. Scale bar = 200 nm.

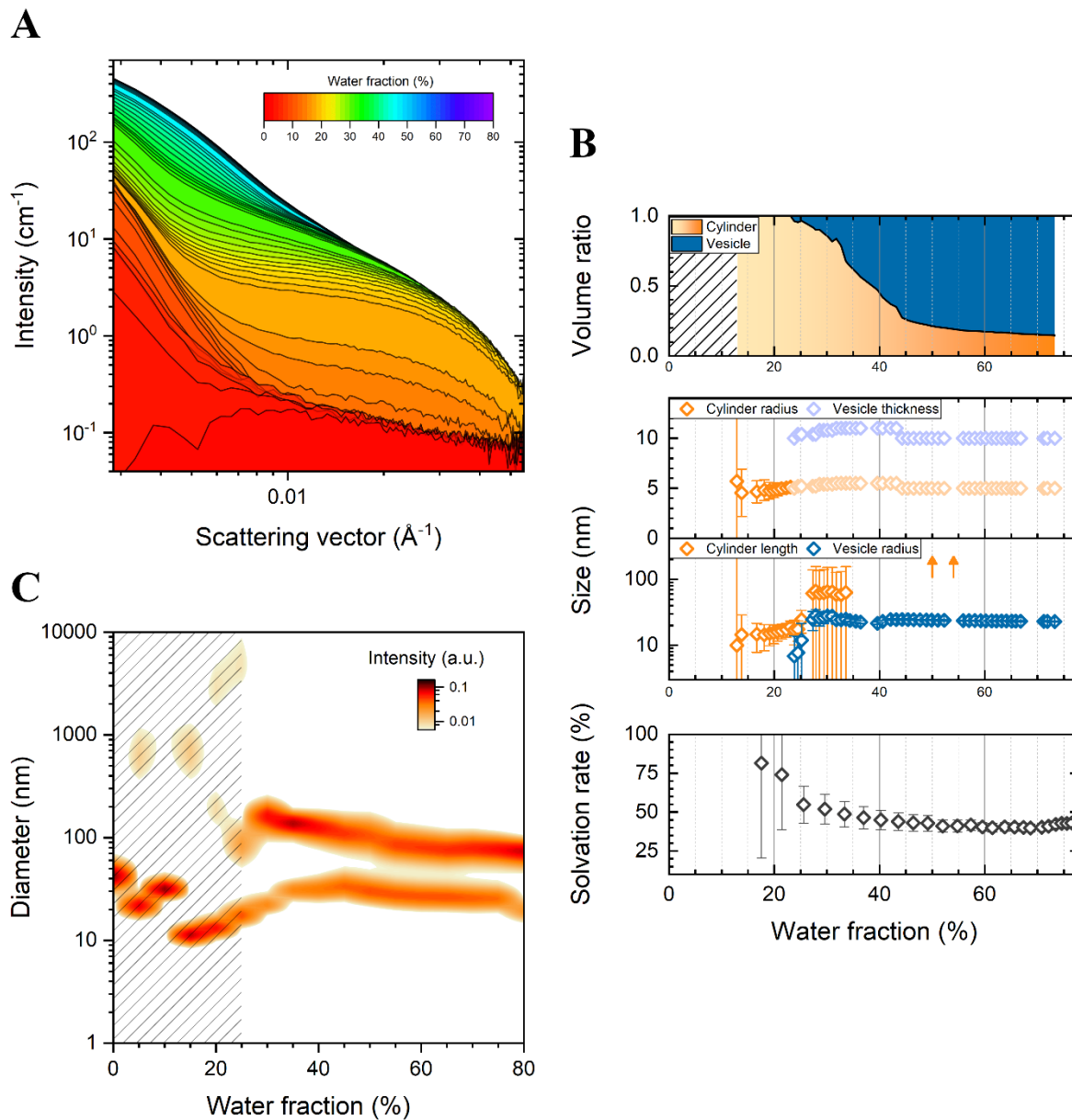


Figure S13. Tr-SANS and Tr-DLS mapping of the dialysis of PDMS₂₇-*b*-PEG₁₇ at 5 g/L in (deuterated) THF against (deuterated) water using a 100 kDa dialysis membrane cut-off. (A) SANS spectra at different water fraction. The scattering contribution due to solvent fluctuations alone was subtracted from the SANS spectra. (B) Main results derived from SANS spectra fitting plotted as function of the water volume fraction: i) volume ratios of the aggregate morphologies, ii) characteristic sizes of BC aggregates, iii) Solvation rate of PDMS blocks in BC assemblies, expressed as the volume fraction of THF-d₈ remaining in the core of aggregates. (C) hydrodynamic sizes from Tr-DLS measurements as function of the water fraction.

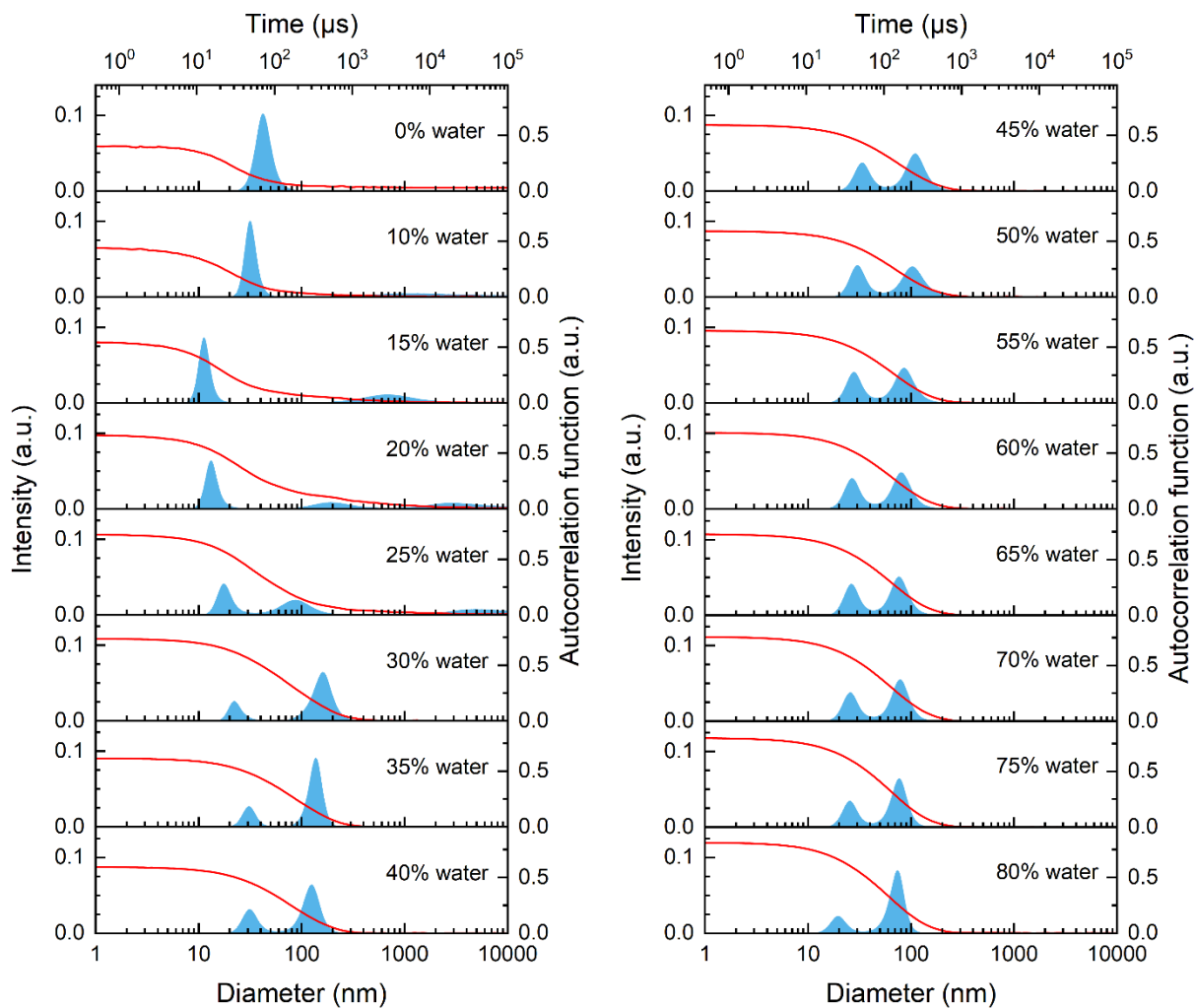


Figure S14. Tr-DLS mapping performed in situ during the dialysis of PDMS₂₇-*b*-PEG₁₇ using a 100 kDa dialysis membrane cut-off. Particle size distributions (blue peaks) and auto-correlation functions (red lines) are shown for different water fractions.

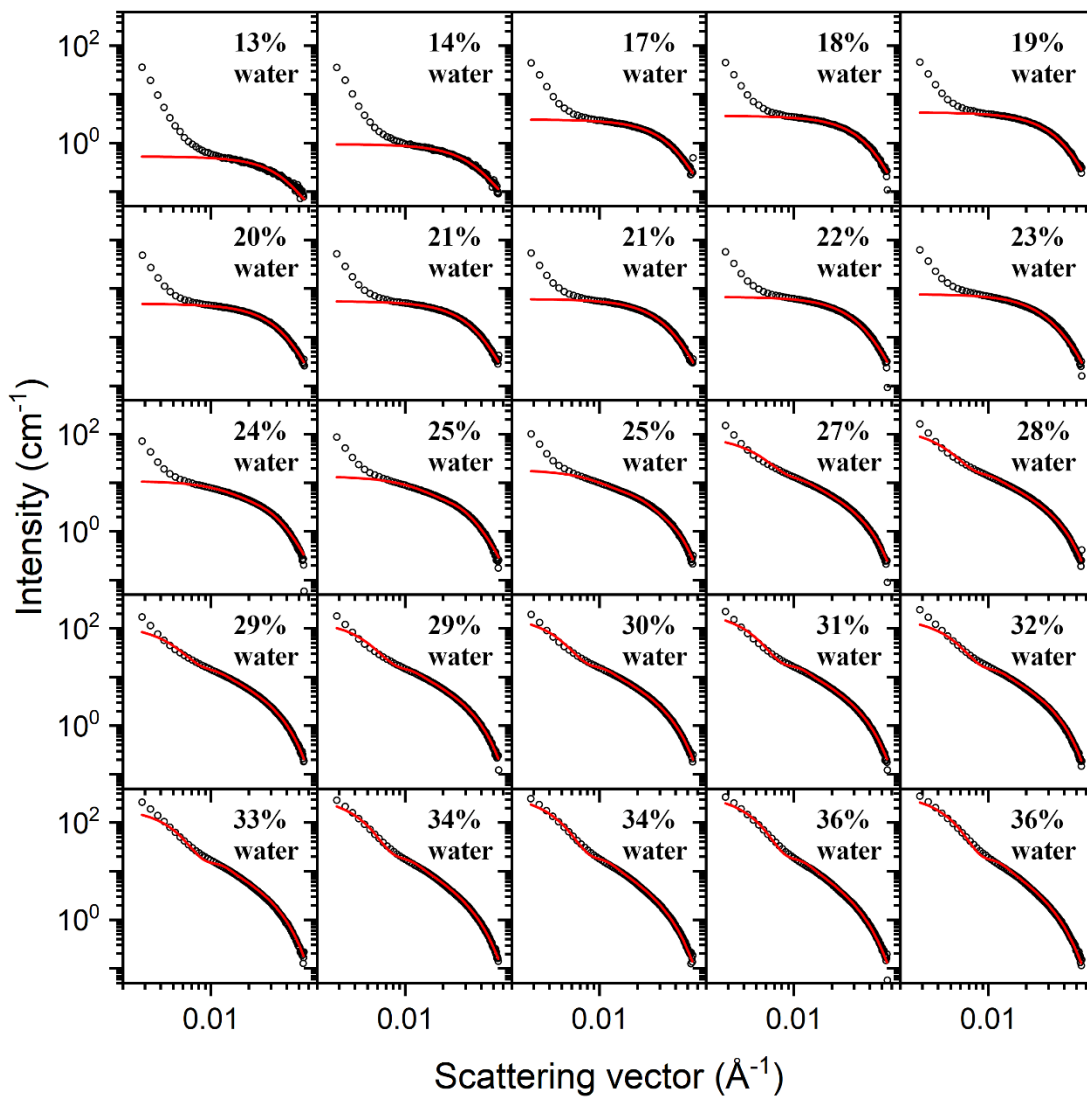


Figure S15. Tr-SANS curves acquired during the dialysis of PDMS₂₇-*b*-PEG₁₇ at 5 g/L in THF-*d*8 against D₂O using a 100 kDa dialysis membrane cut-off. The scattering profile (black sign) and the fit result (red line) are represented at different water fraction. Fitted parameters are summarized in Tables S4, S5 and S6.

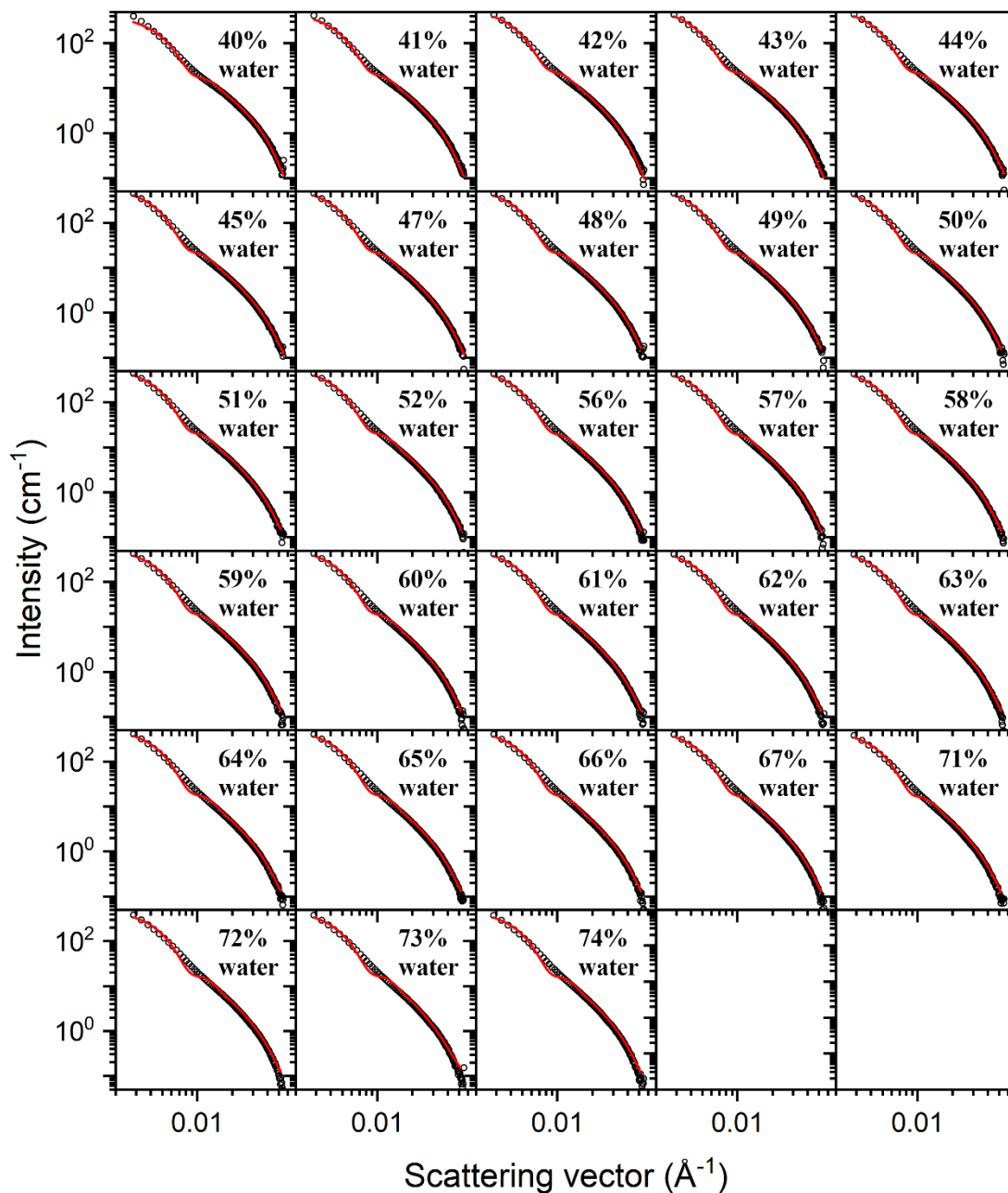


Figure S16. Tr-SANS curves acquired during the dialysis of PDMS₂₇-*b*-PEG₁₇ at 5 g/L in THF-*d*8 against D₂O using a 100 kDa dialysis membrane cut-off. The scattering profile (black sign) and the fit result (red line) are represented at different water fraction. Fitted parameters are summarized in Tables S4, S5 and S6.

Time water content	Background (cm ⁻¹)	Scale	Solvent SLD (10 ⁻⁶ Å ⁻¹)	Sample SLD (10 ⁻⁶ Å ⁻¹)	Cylinder fraction	Cylinder radius (Å)	Cylinder radius distribution	Cylinder length (Å)	Vesicle fraction	Vesicle radius (Å)	Vesicle radius distribution	Vesicle thickness (Å)			
0.8 h 12.9 %	* 0.05	*0.0037	6.42	5.29	1.0	57.03 ± 2342	/	99.63 ± 8292.70	* 0	/	/	/			
0.9 h 13.8 %			6.42	4.81	1.0	45.44 ± 23.60		144.83 ± 142.21	* 0						
1.3 h 16.7 %			6.44	3.58	1.0	46.48 ± 10.93		147.14 ± 68.92	* 0						
1.3 h 18.1 %			6.45	3.41	1.0	48.15 ± 10.24		143.96 ± 60.79	* 0						
1.4 h 19.1 %			6.45	3.20	1.0	47.61 ± 8.34		151.31 ± 53.14	* 0						
1.5 h 19.9 %			6.46	3.05	1.0	48.14 ± 7.38		154.92 ± 49.11	* 0						
1.6 h 20.6 %			6.46	2.96	1.0	48.84 ± 6.45		160.52 ± 43.93	* 0						
1.7 h 21.4 %			6.47	2.90	1.0	49.77 ± 5.71		165.50 ± 41.42	* 0						
1.8 h 22.3 %			6.47	2.84	1.0	50.43 ± 5.28		173.06 ± 41.54	* 0						
1.8 h 23.1 %			6.47	2.83	1.0	51.20 ± 4.74		189.11 ± 43.67	* 0						
1.9 h 23.8 %			6.48	2.71	0.9626 ± 0.0517	* 50		170.26 ± 68.95	* 0.0374				68.46 ± 70.14	* 0.3	* 100
2.0 h 24.5 %			6.48	2.72	0.9551 ± 0.0398	* 52		174.34 ± 59.64	* 0.0449				77.25 ± 56.53		* 104
2.1 h 25.2 %			6.48	2.77	0.9657 ± 0.0366	* 52		245.29 ± 93.42	* 0.0343				119.33 ± 95.47		* 104
2.3 h 27.3 %			6.49	2.69	0.9194 ± 0.0993	* 52		611.90 ± 772.01	* 0.0806				246.33 ± 78.29		* 104
2.4 h 27.9 %			6.49	2.65	0.9012 ± 0.0730	* 52		665.54 ± 894.93	* 0.0988				284.89 ± 64.95		* 104
2.5 h 28.6 %			6.50	2.69	0.9020 ± 0.0811	* 54		609.28 ± 735.68	* 0.0980				258.76 ± 63.97		* 108
2.6 h 29.4 %			6.50	2.68	0.8753 ± 0.0823	* 54		624.48 ± 789.21	* 0.1247				262.93 ± 50.27		* 108
2.7 h 30.1 %			6.50	2.66	0.8565 ± 0.0745	* 54		653.02 ± 857.86	* 0.1435				278.56 ± 44.45		* 108

Table S4. Values extracted from the fitting procedure on the SANS data at different time/water fraction during the dialysis of PDMS₂₇-*b*-PEG₁₇ using a 100 kDa dialysis membrane cut-off. Parameters for which the value has been fixed during the fitting procedure are preceded by a star.

Time water content	Background (cm ⁻¹)	Scale	Solvent SLD (10 ⁻⁶ Å ⁻¹)	Sample SLD (10 ⁻⁶ Å ⁻¹)	Cylinder fraction	Cylinder radius (Å)	Cylinder radius distribution	Cylinder length (Å)	Vesicle fraction	Vesicle radius (Å)	Vesicle radius distribution	Vesicle thickness (Å)
2.8 h 31 %	* 0.05	*0.0037	6.50	2.64	0.8173 ± 0.0750	* 54	/	645.28 ± 868.39	* 0.1827	275.68 ± 34.95	* 0.3	* 108
2.8 h 31.8 %			6.51	2.67	0.8372 ± 0.0554	* 55		585.74 ± 689.27	* 0.1628	243.79 ± 34.14		* 110
2.9 h 32.7 %			6.51	2.72	0.7867 ± 0.0523	* 55		584.44 ± 728.27	* 0.2133	243.25 ± 24.84		* 110
3.0 h 33.6 %			6.51	2.80	0.6763 ± 0.0497	* 55		633.46 ± 927.26	* 0.3237	248.40 ± 18.45	* 0.4	* 110
3.1 h 34.4 %			6.51	2.84	0.6418 ± 0.0352	* 55		* 1500	* 0.3582	238.07 ± 12.80		* 110
3.2 h 35.5 %			6.51	2.84	0.6002 ± 0.0371	* 55		* 1500	* 0.3998	230.75 ± 11.34		* 110
3.3 h 36.4 %			6.51	2.86	0.5636 ± 0.0389	* 55		* 1500	* 0.4364	224.21 ± 10.29		* 110
3.5 h 39.6 %			6.52	2.83	0.4724 ± 0.0428	* 55		* 1500	* 0.5276	215.01 ± 8.45		* 110
3.6 h 40.6 %			6.52	2.84	0.4184 ± 0.0438	* 55		* 1500	* 0.5816	229.74 ± 7.60		* 110
3.7 h 42.1 %			6.52	2.84	0.3708 ± 0.0446	* 55		* 1500	* 0.6292	246.46 ± 6.89		* 110
3.8 h 43.2 %			6.52	2.83	0.3503 ± 0.0457	* 55		* 1500	* 0.6497	244.94 ± 6.70		* 110
3.8 h 44.3 %			6.52	2.80	0.2732 ± 0.0528	* 50		* 1500	* 0.7268	245.90 ± 6.46		* 100
3.9 h 45.4 %			6.52	2.81	0.2546 ± 0.0540	* 50		* 1500	* 0.7454	244.70 ± 6.34		* 100
4.0 h 46.5 %			6.52	2.82	0.2430 ± 0.0549	* 50		* 1500	* 0.7571	243.44 ± 6.28	* 100	
4.1 h 47.7 %			6.52	2.84	0.2316 ±	* 50		* 1500	* 0.7684	241.93 ± 6.20	* 100	
4.2 h 48.9 %			6.51	2.85	0.2225 ±	* 50		* 1500	* 0.7776	241.44 ± 6.17	* 100	
4.3 h 49.9 %			6.51	2.88	0.2142 ±	* 50		* 1500	* 0.7858	240.43 ± 6.15	* 100	

Table S5. Following values extracted from the fitting procedure on the SANS data at different time/water fraction during the dialysis of PDMS₂₇-*b*-PEG₁₇ using a 100 kDa dialysis membrane cut-off. Parameters for which the value has been fixed during the fitting procedure are preceded by a star.

Time water content	Background (cm ⁻¹)	Scale	Solvent SLD (10 ⁻⁶ Å ⁻¹)	Sample SLD (10 ⁻⁶ Å ⁻¹)	Cylinder fraction	Cylinder radius (Å)	Cylinder radius distribution	Cylinder length (Å)	Vesicle fraction	Vesicle radius (Å)	Vesicle radius distribution	Vesicle thickness (Å)
4.3 h 51.1 %	* 0.05	*0.0037	6.51	2.89	0.2058 ± 0.0585	* 50		* 1500	* 0.7942	239.32 ± 6.11		* 100
4.4 h 52.3 %			6.51	2.90	0.2016 ± 0.0590	* 50		* 1500	* 0.7984	238.55 ± 6.10		* 100
4.7 h 55.9 %			6.50	2.97	0.1823 ± 0.0612	* 50		* 1500	* 0.8177	236.65 ± 6.09		* 100
4.8 h 57 %			6.50	2.96	0.1799 ± 0.0612	* 50		* 1500	* 0.8202	236.22 ± 6.06		* 100
4.9 h 58.1 %			6.50	2.98	0.1785 ± 0.0615	* 50		* 1500	* 0.8215	236.72 ± 6.09		* 100
5.0 h 59.2 %			6.50	2.98	0.1767 ± 0.0617	* 50		* 1500	* 0.8233	235.29 ± 6.06		* 100
5.0 h 60.2 %			6.49	2.99	0.1721 ± 0.0622	* 50		* 1500	* 0.8279	234.76 ± 6.05		* 100
5.1 h 61.3 %			6.49	3.01	0.1728 ± 0.0625	* 50		* 1500	* 0.8272	234.65 ± 6.09		* 100
5.2 h 62.2 %			6.49	3.03	0.1679 ± 0.0631	* 50		* 1500	* 0.8321	233.68 ± 6.08		* 100
5.3 h 63.2 %			6.49	3.03	0.1690 ± 0.0632	* 50		* 1500	* 0.8310	233.19 ± 6.08		* 100
5.4 h 64.1 %			6.49	3.05	0.1659 ± 0.0637	* 50		* 1500	* 0.8341	233.49 ± 6.10		* 100
5.5 h 65.1 %			6.48	3.06	0.1651 ± 0.0640	* 50		* 1500	* 0.8349	232.56 ± 6.10		* 100
5.5 h 65.9 %			6.48	3.07	0.1605 ± 0.0645	* 50		* 1500	* 0.8395	232.06 ± 6.10		* 100
5.6 h 66.8 %			6.48	3.10	0.1590 ± 0.0650	* 50		* 1500	* 0.8410	231.25 ± 6.11		* 100
6.1 h 71.2 %			6.47	3.16	0.1507 ± 0.0669	* 50		* 1500	* 0.8493	229.96 ± 6.18		* 100
6.1 h 71.9 %			6.47	3.16	0.1497 ± 0.0670	* 50		* 1500	* 0.8503	229.63 ± 6.18		* 100
6.3 h 73.3 %			6.46	3.20	0.1473 ± 0.0678	* 50		* 1500	* 0.8527	229.13 ± 6.22		* 100
4.3 h 51.1 %			6.51	2.89	0.2058 ± 0.0585	* 50		* 1500	* 0.7942	239.32 ± 6.11		* 100

Table S6. Following values extracted from the fitting procedure on the SANS data at different time/water fraction during the dialysis of PDMS₂₇-*b*-PEG₁₇ using a 100 kDa dialysis membrane cut-off. Parameters for which the value has been fixed during the fitting procedure are preceded by a star.

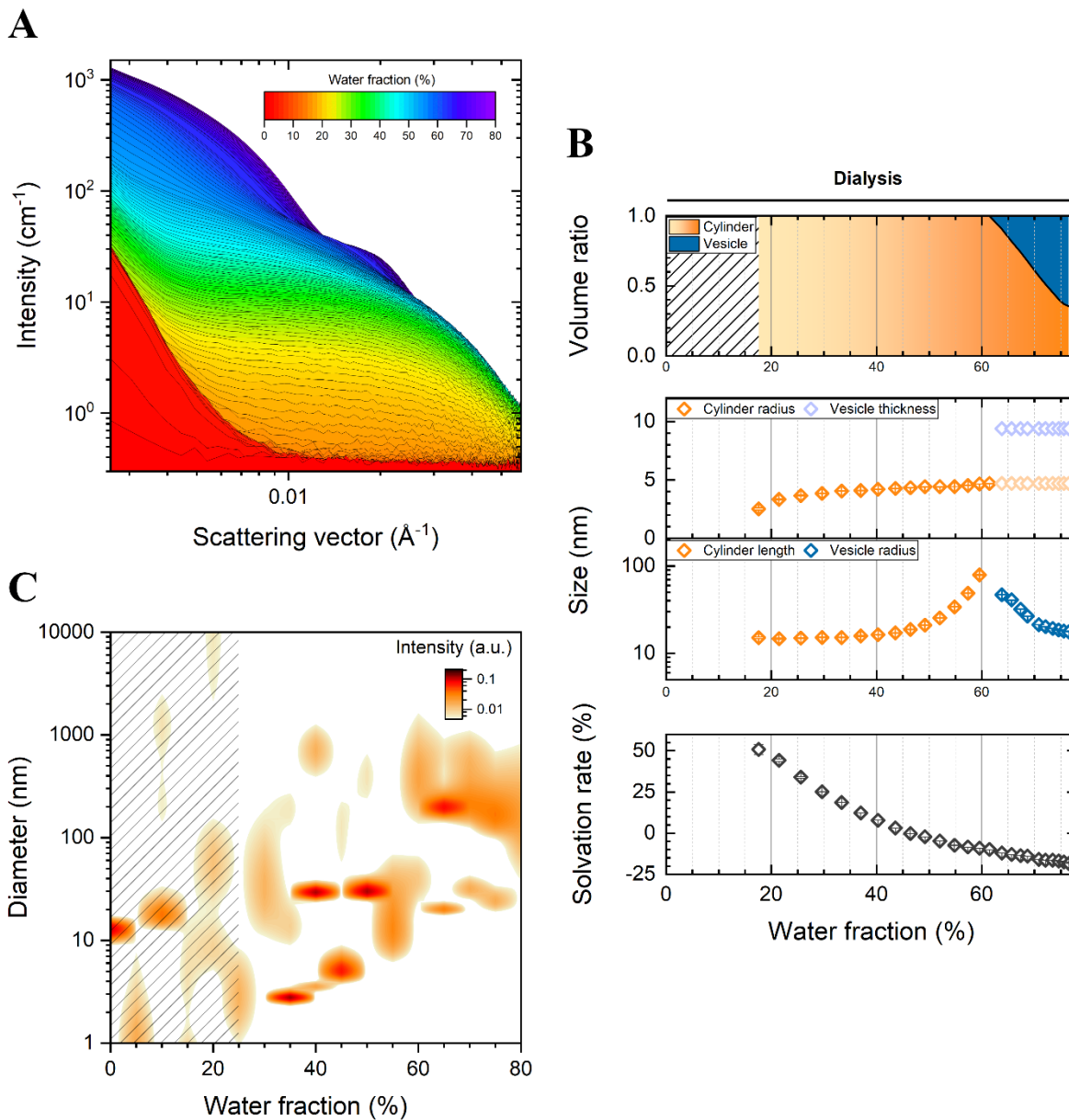


Figure S17. Tr-SANS and Tr-DLS mapping of the dialysis of PDMS₂₃-*b*-PEG₁₃ at 5 g/L in (deuterated) THF against (deuterated) water using a 10 kDa dialysis membrane cut-off. (A) SANS spectra at different water fraction. (B) Main results derived from SANS spectra fitting plotted as function of the water volume fraction: i) volume ratios of the aggregate morphologies, ii) characteristic sizes of BC aggregates, iii) Solvation rate of PDMS blocks in BC assemblies, expressed as the volume fraction of THF-d8 remaining in the core of aggregates. (C) hydrodynamic sizes from Tr-DLS measurements as function of the water fraction.

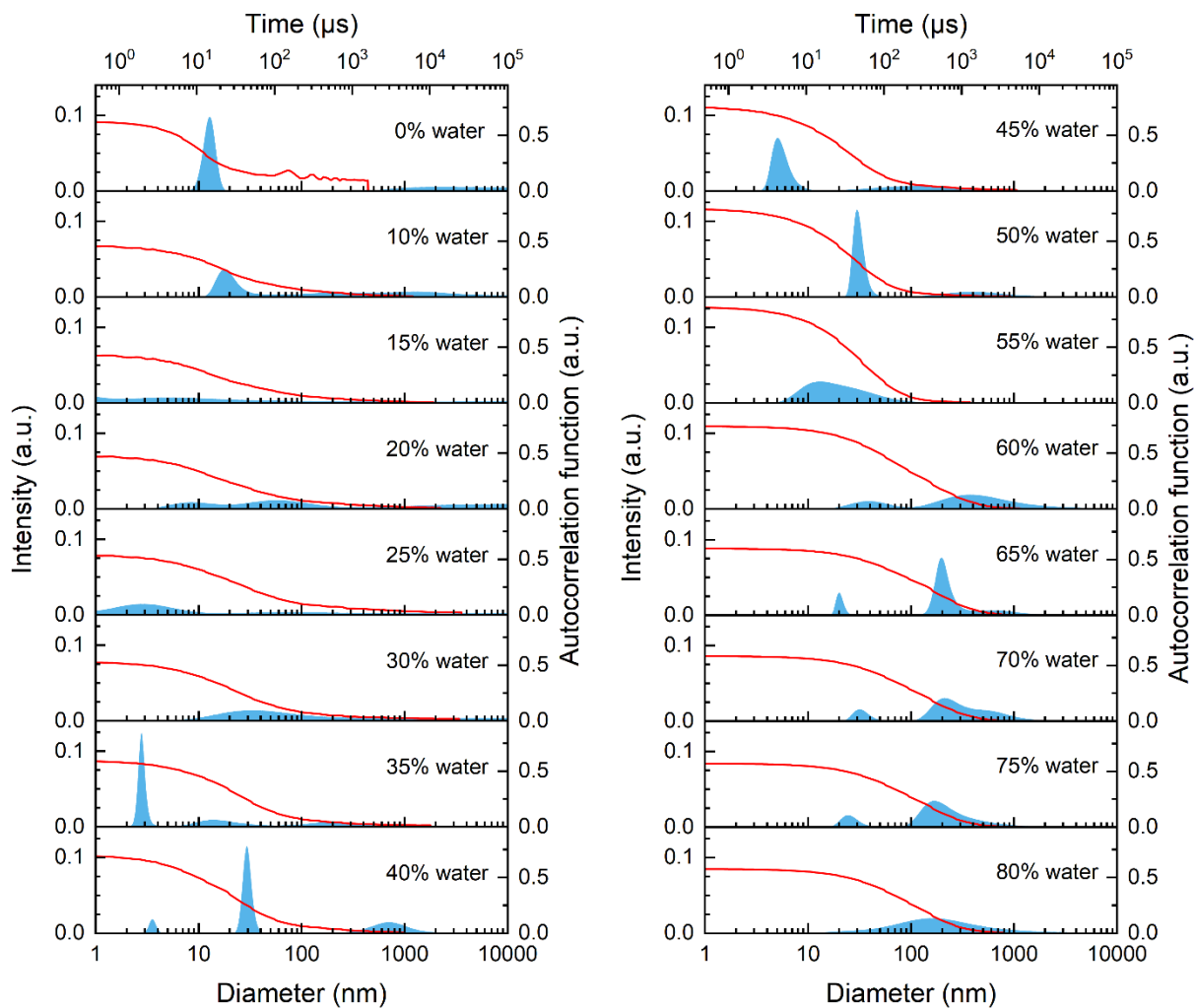


Figure S18. Tr-DLS mapping performed in situ during the dialysis of PDMS₂₃-*b*-PEG₁₃ using a 10 kDa dialysis membrane cut-off. Particle size distributions (blue peaks) and auto-correlation functions (red lines) are shown for different water fractions.

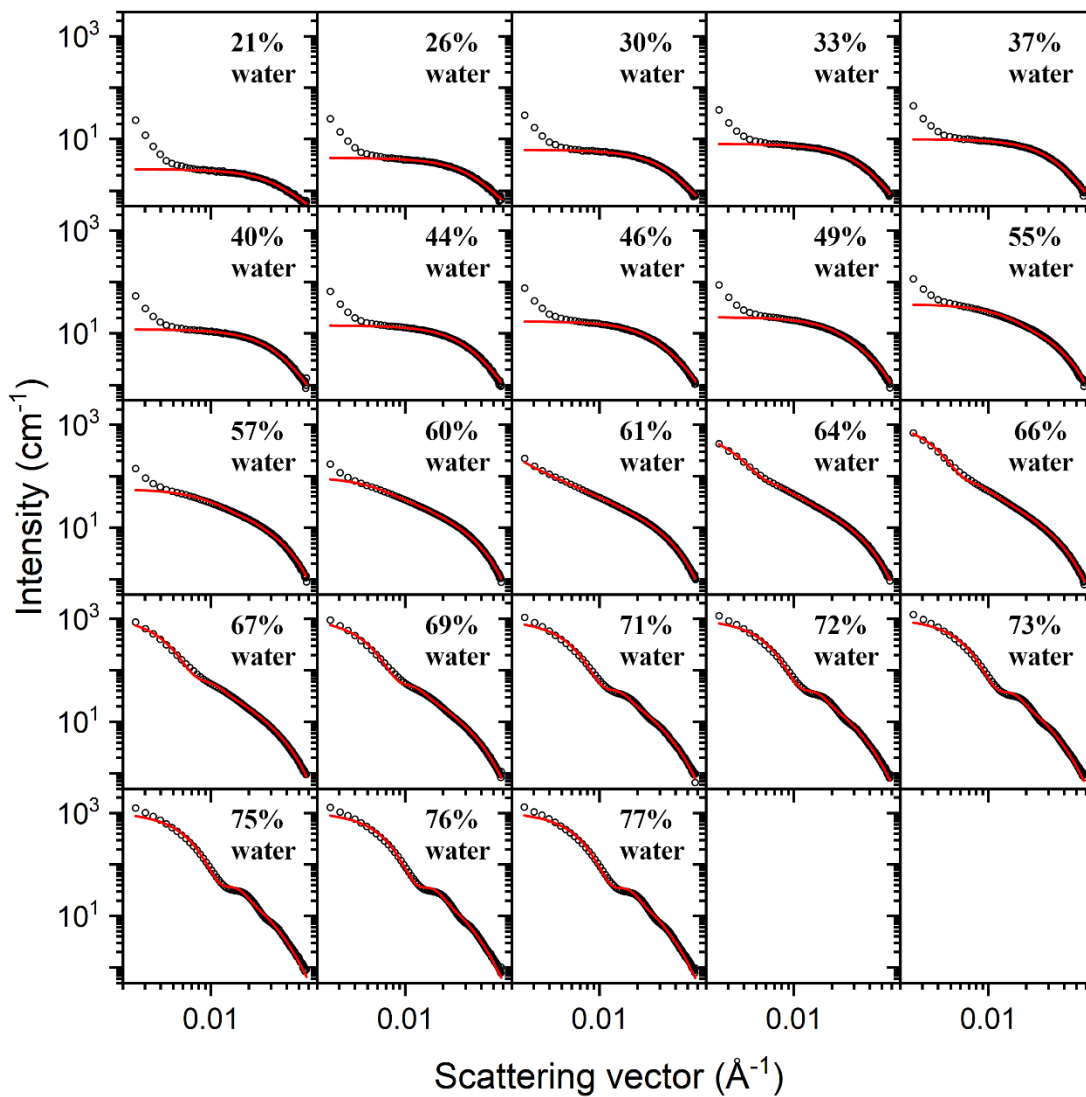


Figure S19. Tr-SANS curves acquired during the dialysis of PDMS₂₃-*b*-PEG₁₃ at 5 g/L in THF-d₈ against D₂O using a 10 kDa dialysis membrane cut-off. The scattering profile (black sign) and the fit result (red line) are represented at different water fraction. Fitted parameters are summarized in Tables S7 and S8.

Time water content	Background (cm ⁻¹)	Scale	Solvent SLD (10 ⁻⁶ Å ⁻¹)	Sample SLD (10 ⁻⁶ Å ⁻¹)	Cylinder fraction	Cylinder radius (Å)	Cylinder radius distribution	Cylinder length (Å)	Vesicle fraction	Vesicle radius (Å)	Vesicle radius distribution	Vesicle thickness (Å)
4.9 h 17.6 %	* 0.24	*0.0037	6.45	50.75	* 1.0	25.15 ± 0.93	/	151.22 ± 3.33	* 0	/	/	/
5.6 h 21.4 %			6.47	44.17	* 1.0	33.38 ± 0.47		147.10 ± 2.04	* 0			
6.3 h 25.6 %			6.49	33.89	* 1.0	36.56 ± 0.31		149.25 ± 1.46	* 0			
6.9 h 29.6 %			6.50	25.14	* 1.0	38.45 ± 0.23		152.25 ± 1.14	* 0			
7.6 h 33.3 %			6.51	18.61	* 1.0	40.51 ± 0.19		151.85 ± 0.97	* 0			
8.3 h 37.0 %			6.51	12.19	* 1.0	40.94 ± 0.16		158.39 ± 0.85	* 0			
9.0 h 40.3 %			6.52	7.77	* 1.0	42.00 ± 0.13		163.57 ± 0.75	* 0			
9.7 h 43.6 %			6.52	3.11	* 1.0	42.70 ± 0.11		171.45 ± 0.70	* 0			
10.4 h 46.4 %			6.52	-0.23	* 1.0	43.26 ± 0.10		188.00 ± 0.67	* 0			
11.1 h 49.2 %			6.51	-2.17	* 1.0	44.09 ± 0.08		210.52 ± 0.70	* 0			
11.8 h 52.0 %			6.51	-4.78	* 1.0	44.22 ± 0.08		253.95 ± 0.86	* 0			
12.5 h 54.8 %			6.51	-7.36	* 1.0	44.31 ± 0.07		340.24 ± 1.19	* 0			
13.2 h 57.3 %			6.50	-8.43	* 1.0	45.22 ± 0.06		487.60 ± 2.13	* 0			

Table S7. Values extracted from the fitting procedure on the SANS data at different time/water fraction during the dialysis of PDMS₂₃-*b*-PEG₁₃ using a 10 kDa dialysis membrane cut-off. Parameters for which the value has been fixed during the fitting procedure are preceded by a star.

Time water content	Background (cm ⁻¹)	Scale	Solvent SLD (10 ⁻⁶ Å ⁻¹)	Sample SLD (10 ⁻⁶ Å ⁻¹)	Cylinder fraction	Cylinder radius (Å)	Cylinder radius distribution	Cylinder length (Å)	Vesicle fraction	Vesicle radius (Å)	Vesicle radius distribution	Vesicle thickness (Å)
13.9 h 59.6 %	* 0.24	*0.0037	6.50	-9.19	* 1.0	46.50 ± 0.06	/	791.18 ± 6.41	* 0	/	/	/
14.6 h 61.4 %			6.49	-9.95	* 1.0	46.98 ± 0.05		1000	* 0	/	/	/
15.3 h 63.8 %			6.49	-12.07	0.9065 ± 0.0003	* 47		1000	* 0.0935	468.31 ± 1.80	* 0.3	* 94
16.0 h 65.7 %			6.48	-12.93	0.8177 ± 0.0004	* 47		1000	* 0.1823	408.72 ± 0.79		* 94
16.7 h 67.4 %			6.48	-13.69	0.7414 ± 0.0004	* 47		1000	* 0.2586	319.64 ± 0.37		* 94
17.4 h 68.7 %			6.47	-13.92	0.6774 ± 0.0005	* 47		1000	* 0.3226	266.74 ± 0.24		* 94
18.4 h 70.8 %			6.47	-15.92	0.5714 ± 0.0006	* 47		1000	* 0.4286	212.90 ± 0.14		* 94
19.1 h 72.1 %			6.47	-16.46	0.5117 ± 0.0005	* 47		1000	* 0.4883	201.94 ± 0.12		* 94
19.8 h 73.5 %			6.46	-16.44	0.4536 ± 0.0006	* 47		1000	* 0.5465	192.60 ± 0.11		* 94
20.5 h 74.6 %			6.46	-16.93	0.4056 ± 0.0006	* 47		1000	* 0.5944	185.43 ± 0.09		* 94
21.2 h 75.6 %			6.46	-17.57	0.3709 ± 0.0007	* 47		1000	* 0.6291	179.97 ± 0.09		* 94
21.9 h 76.5 %			6.46	-18.42	0.3554 ± 0.0007	* 47		1000	* 0.6446	176.00 ± 0.08		* 94

Table S8. Following values extracted from the fitting procedure on the SANS data at different time/water fraction during the dialysis of PDMS₂₃-*b*-PEG₁₃ using a 10 kDa dialysis membrane cut-off. Parameters for which the value has been fixed during the fitting procedure are preceded by a star.

- (1) Fauquignon, M.; Ibarboure, E.; Carlotti, S.; Brûlet, A.; Schmutz, M.; Le Meins, J.-F. Large and Giant Unilamellar Vesicle(s) Obtained by Self-Assembly of Poly(Dimethylsiloxane)-b-Poly(Ethylene Oxide) Diblock Copolymers, Membrane Properties and Preliminary Investigation of Their Ability to Form Hybrid Polymer/Lipid Vesicles. *Polymers* **2019**, *11* (12), 2013. <https://doi.org/10.3390/polym11122013>.
- (2) Aminabhavi, T. M.; Gopalakrishna, B. Density, Viscosity, Refractive Index, and Speed of Sound in Aqueous Mixtures of N,N-Dimethylformamide, Dimethyl Sulfoxide, N,N-Dimethylacetamide, Acetonitrile, Ethylene Glycol, Diethylene Glycol, 1,4-Dioxane, Tetrahydrofuran, 2-Methoxyethanol, and 2-Ethoxyethanol at 298.15 K. *J. Chem. Eng. Data* **1995**, *40* (4), 856–861. <https://doi.org/10.1021/je00020a026>.