Electronic Supplementary Material (ESI) for Soft Matter.

Supporting Information for Influence of NaCl on Shape Deformation of Polymersomes

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1 Synthesis of PEG_{14}-$PDMS_{15}$-PEG_{14} Triblock copolymer

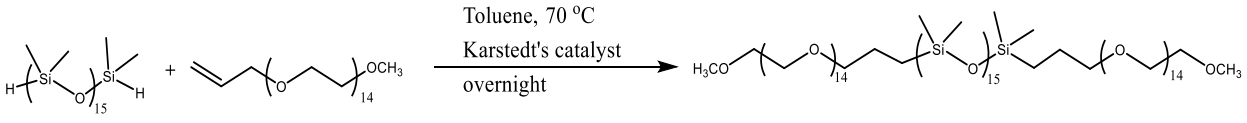

Figure S1. Synthesis scheme of PGE_{14} – $PDMS_{15}$ – PEG_{14} triblock copolymer.

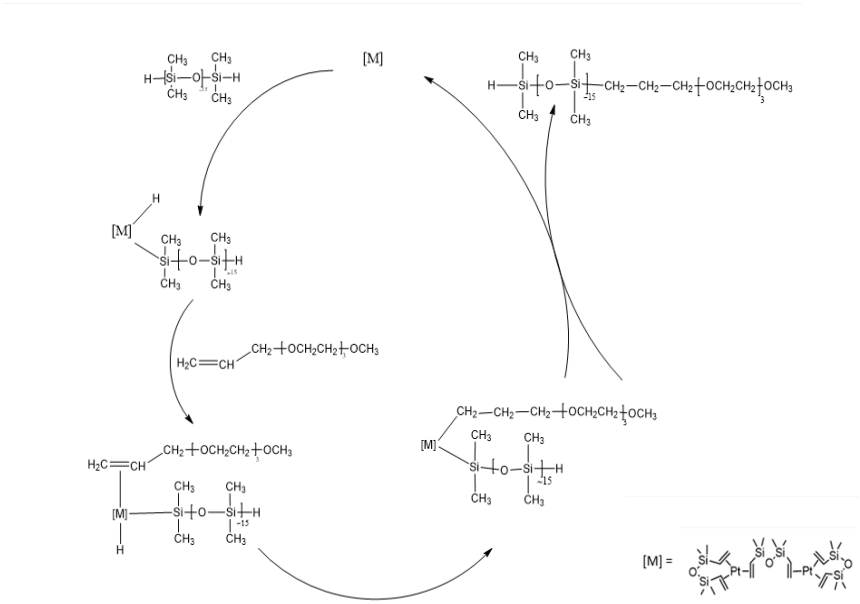

Figure S2. Suggested Chalk-Harrod mechanism for the hydrosilylation between Hydride terminated poly(dimethyl siloxane) and allyloxy (polyethylene oxide), methyl ether.[S1]

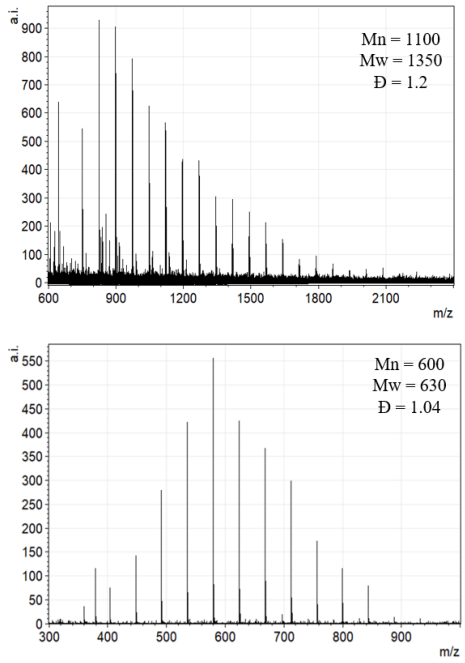

Figure S3: A representative MALDI-TOF MS spectrum of the precursor (a) PDMS, (b) PEG polymers

Polymer sample solutions were prepared by dissolving the polymer in tetrahydrofuran (THF) to a 1 mg/mL concentration. The matrix solutions were prepared using 2,5-Dihydroxybenzoic acid (DHB; Sigma-Aldrich, St. Louis, MO, USA) by dissolving 50 mg of DHB in 1 mL of methanol (for PDMS) or using alpha-cyano-4-hydroxy-cinnamic acid (CHCA; Sigma-Aldrich, St. Louis, MO, USA) by dissolving 10 mg of CHCA in 1 ml of 50:50 water: methanol mixture (for PEG). A 1 µL aliquot of polymer sample solution was first deposited to the MALDI target plate followed by a 1 µL aliquot of matrix, which was deposited above it and mixed with a micropipette before letting air-dry the resulting mixture. MALDI-TOF/TOF MS measurements were performed on a Bruker UltrafleXtreme (Bruker Scientific, Billerica, MA, USA). Mass spectra were recorded in positive ion reflection mode and analyzed in the mass range 500–2500 Da. The spectra were acquired after calibration of the instrument with a peptide standard (Peptide Calibration Standard II, Bruker Daltonics, MA, USA). A minimum of 500 laser shots per sample was used to generate each mass spectrum.

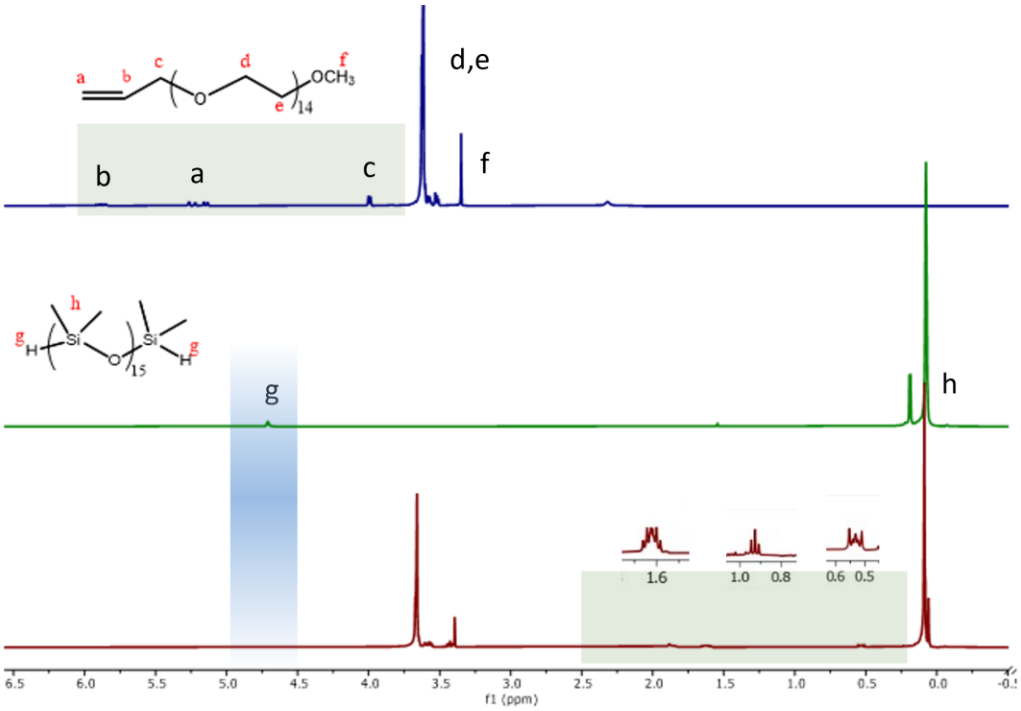

Figure S4. The success of the hydroxylation was monitored via disappearance of proton signal from terminal H of PDMS block and the position shift of the protons of allyl group attached to PEG blocks. From top to bottom: ^{1}H NMR spectrum in $CDCl_3$ of allyloxy poly(ethylene oxide) methyl ether; hydroxy terminated PDMS and PEG_{14} – $PDMS_{15}$ – PEG_{14}. ^{1}H NMR spectra were collected using a Bruker 400 MHz NMR spectrometer.

2 Cryo-TEM Images and Analysis

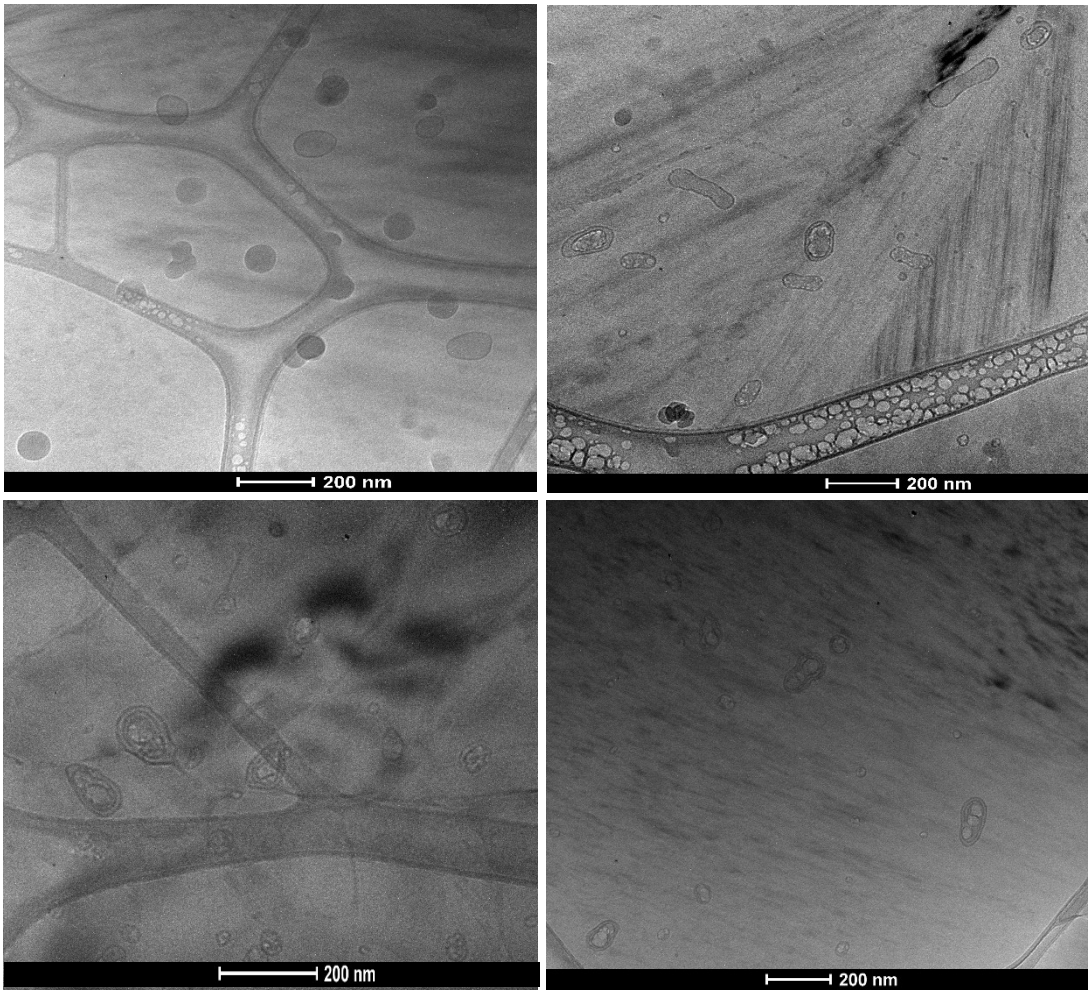

Figure S5: Cryo - TEM images of polymersomes (a) in their original state, under (b) 5 mM (c) 100 mM. (d) 250 mM NaCl concentrations. Scale bar represents 200 nm.

Aspect ratio distribution analysis (Figure S6) gave a wider picture of the changes of vesicle morphology than expected from SANS. Polymersome systems under 5 mM NaCl, showed the widest range and high values for aspect ratios probably due to the presence of elongated tubular shaped vesicles. Other systems did not have a wide range of aspect ratio distributions and the low values indicates that most of the vesicles are spherical or spheroidal structures.

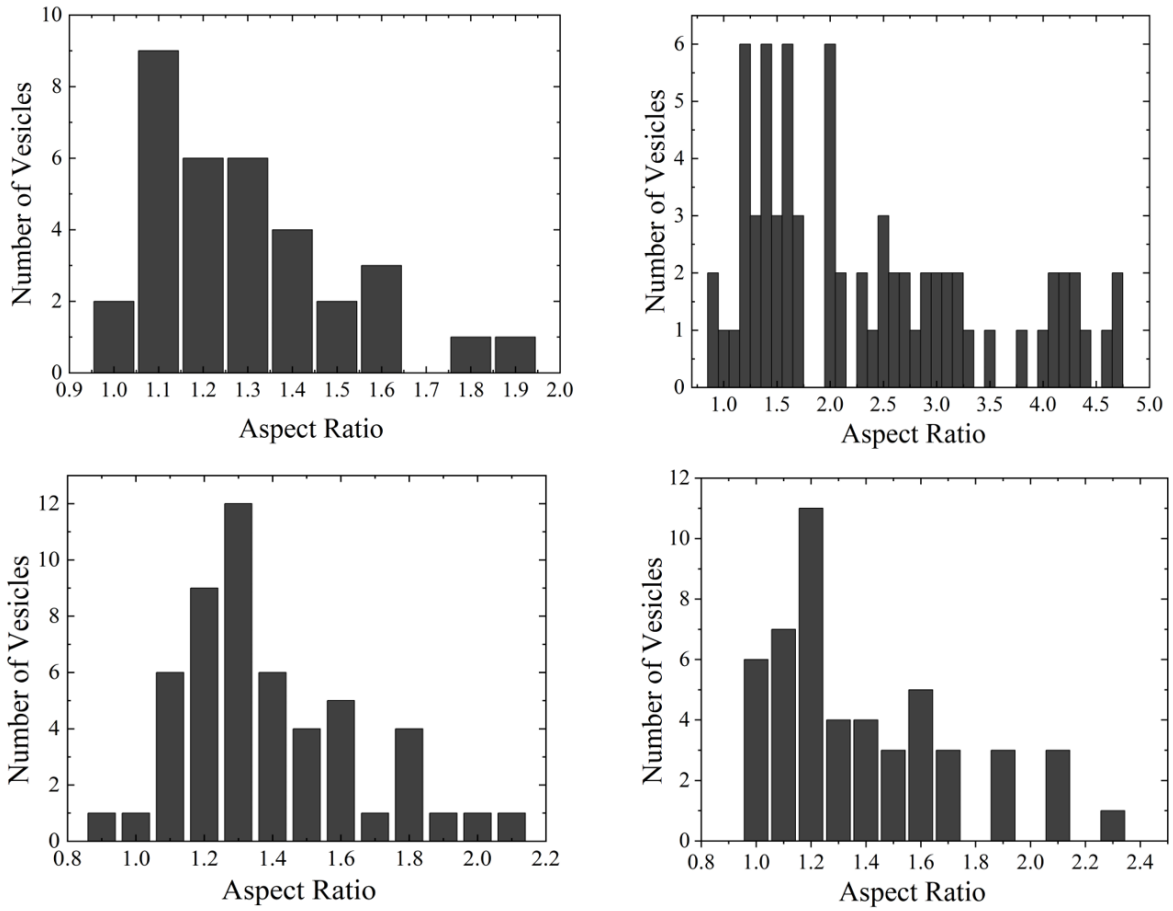

Figure S6: Aspect ratio distribution of polymersomes (a) in their original state (b) under 5 mM (c) 100 mM, and (d) 250 mM NaCl concentrations.

3 SANS Modeling of Unilamellar Polymersome

The 1D scattering pattern for a unilamellar PEG-PDMS-PEG Polymersome is described by:

$$P(Q,R,t,\Delta\rho) = \frac{\phi A^2(Q)}{V(r_3)-V(R_c)} \quad \text{(S1)}$$

Here ϕ is the block copolymer volume fraction. The scattering contribution from three different shells consisting of PEG, PDMS and PEG are given by

$$A^2(Q) = A_1^2 + A_2^2 + A_3^2 + A_{12} + A_{23} + A_{13} \quad \text{(S2)}$$

with $A_{12} = A_1 A_2,\ A_{12} = A_2 A_3$, and $A_{13} = A_1 A_3$ are the cross terms for PEG-PDMS, PDMS-PEG and the two outer PEG-PEG layers, respectively.

For a spherical Bessel's function $j_1(x) = \frac{\sin(x) - x\cos(x)}{x^2}$, and volume $V(r) = \frac{4}{3}\pi r^3$ we have

$$A_1^2 = \left(\rho_{\mathrm{PEG}} - \rho_{\mathrm{solv}}\right)^2 \left[3V(r_1)\frac{j_1(Qr_1)}{Qr_1} - 3V(R_c)\frac{j_1(QR_c)}{QR_c}\right]^2$$

$$A_2^2 = \left(\rho_{\mathrm{PDMS}} - \rho_{\mathrm{solv}}\right)^2 \left[3V(r_2)\frac{j_1(Qr_2)}{Qr_2} - 3V(r_1)\frac{j_1(Qr_1)}{Qr_1}\right]^2$$

$$A_3^2 = \left(\rho_{\mathrm{PEG}} - \rho_{\mathrm{solv}}\right)^2 \left[3V(r_3)\frac{j_1(Qr_3)}{Qr_3} - 3V(r_2)\frac{j_1(Qr_2)}{Qr_2}\right]^2$$

$$A_{12} = 2(\rho_{\mathrm{PEG}} - \rho_{\mathrm{solv}})(\rho_{\mathrm{PDMS}} - \rho_{\mathrm{solv}})\left[3V(r_1)\frac{j_1(Qr_1)}{Qr_1} - 3V(R_c)\frac{j_1(QR_c)}{QR_c}\right]\left[3V(r_2)\frac{j_1(Qr_2)}{Qr_2} - 3V(r_1)\frac{j_1(Qr_1)}{Qr_1}\right]$$

$$A_{23} = 2(\rho_{\mathrm{PEG}} - \rho_{\mathrm{solv}})(\rho_{\mathrm{PDMS}} - \rho_{\mathrm{solv}})\left[3V(r_2)\frac{j_1(Qr_2)}{Qr_2} - 3V(r_1)\frac{j_1(Qr_1)}{Qr_1}\right]\left[3V(r_3)\frac{j_1(Qr_3)}{Qr_3} - 3V(r_2)\frac{j_1(Qr_2)}{Qr_2}\right]$$

$$A_{13} = 2(\rho_{\mathrm{PEG}} - \rho_{\mathrm{solv}})(\rho_{\mathrm{PEG}} - \rho_{\mathrm{solv}})\left[3V(r_1)\frac{j_1(Qr_1)}{Qr_1} - 3V(R_c)\frac{j_1(QR_c)}{QR_c}\right]\left[3V(r_3)\frac{j_1(Qr_3)}{Qr_3} - 3V(r_2)\frac{j_1(Qr_2)}{Qr_2}\right]$$

Here $r_1 = R_c + t_{PEG}$, $r_2 = R_c + t_{PEG} + t_{PDMS}$, $r_3 = R_c + 2t_{PEG} + t_{PDMS}$. The parameters are explained in the main text. Now if we insert $A^2(Q) = A_1^2$ or A_2^2, and so on in equation S1 we get the scattering contribution from each term, which is presented in Figure S6. The scattering amplitude from one inner and outer layer of PEG is given by A_1^2 and A_3^2, respectively. Whereas the combined scattering amplitudes from both inner and outer layers are given by $A_1^2 + A_3^2 + A_{13}$, which give rise to a correlation peak at Q = 0.1 Å^{-1}. The scattering amplitude from the PDMS layer is given by A_2^2. The corresponding scattering length densities (SLD) for neutrons and X-rays are reported in Table S1.

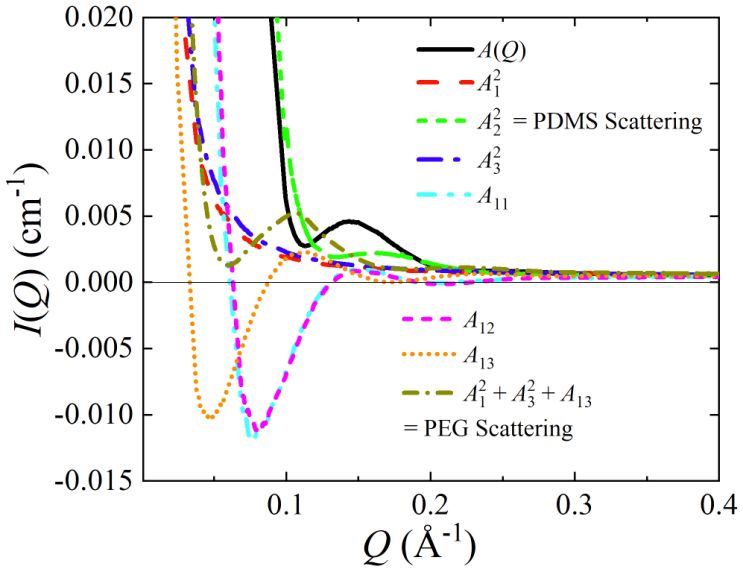

Figure S7: Calculated SANS scattering contribution presented in linear scales from each scattering amplitudes obtained by pugging A_1^2 , A_2^2 , A_3^2, etc. in equation S1, normalized by their corresponding volumes.

4 Log-normal Distribution

For the analysis of the data from SANS, cryo-TEM Data, we used a log-normal distribution given by:

$$s(r) = \frac{1}{\sigma_{LN} r\sqrt{2\pi}} exp\left(-\frac{[\ln(r/R_{median})]^2}{2{\sigma_{LN}}^2}\right) \quad \text{(S3)}$$

where R_{median} refers to the radius of the particle and, σ_{LN} is the standard deviation representing the polydispersity, $PD_{LN} = \sigma_{LN}$.

5 Gaussian Distribution

The Gaussian distribution used in SAXS and SANS is given by:

$$G(r) = \frac{1}{\sigma_G\sqrt{2\pi}} exp\left(-\frac{[\mathrm{r} - R_{mean}]^2}{2{\sigma_G}^2}\right) \quad \text{(S4)}$$

where R_{mean} is the mean radius of the particle and the polydispersity is given by $PD_G = \sigma_G/R_{mean}$, with σ_G the width of the distribution function.

6 SANS Scattering Profile

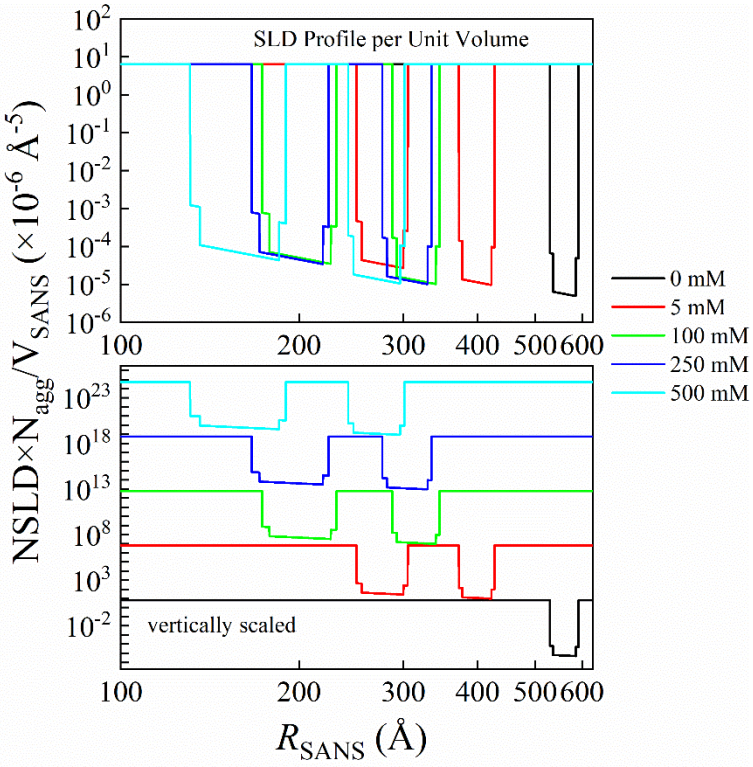

Figure S8. The neutron scattering length density, NSLD, times polymer number density (N_{agg}/V_{SANS}) as a function of particle radius, R_{SANS}. Here, N_{agg}, refers to the aggregation number and, V_{SANS}, to the particle volume. The data in the lower panel is vertically shifted in log scale for proper visualization.

7 SAXS Scattering Profile

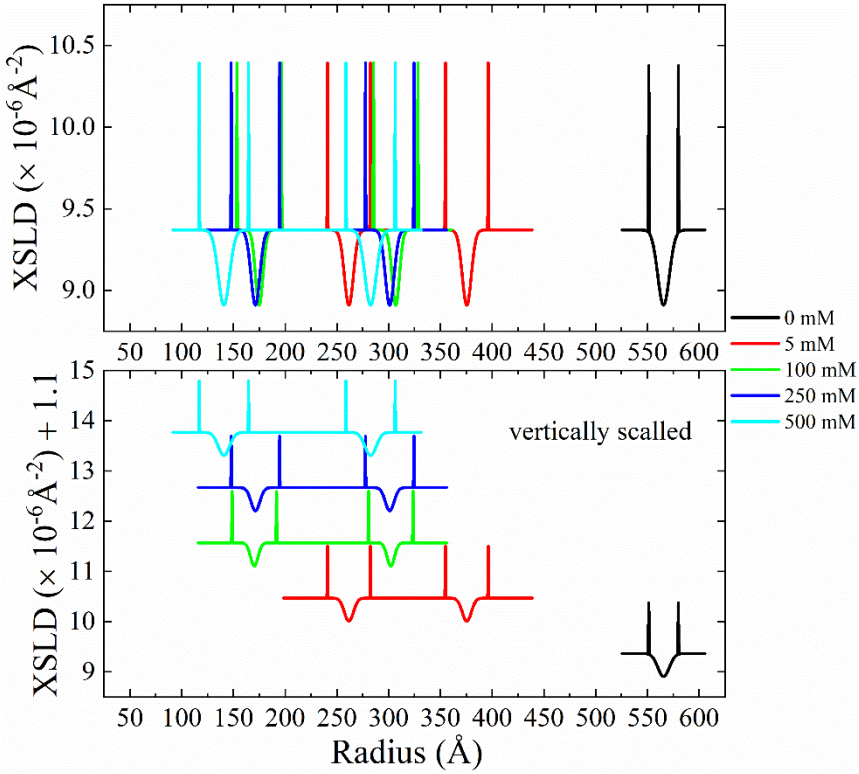

Figure S9. The X-ray scattering length density (XSLD) profile along the particle radius (= $R_c + \delta_M + (N-1)t_w$*) calculated from the water core radius,* R_c*, from SANS whereas, the membrane thickness,* δ_M*, and water thickness,* t_w*, calculated from SAXS. The data in the lower panel is vertically shifted by 1.1 for proper visualization.*

Table S1. Scattering Length Densities (ρ) of Sample Components. Data Obtained from NIST Neutron Activation and Scattering Calculator.[2] The Average Value for XSLD has been Calculated for the Energy 11 keV, used in SLAC.

Samples	X-ray Scattering Length Density ρ (XSLD) (× 10^{-6}Å^{-2})	SANS Scattering Length Density ρ (NSLD) (× 10^{-6}Å^{-2})
D_2O	9.34	6.364
PEG	10.45	0.634
PDMS	8.92	0.063

8 SAXS scattering contributions

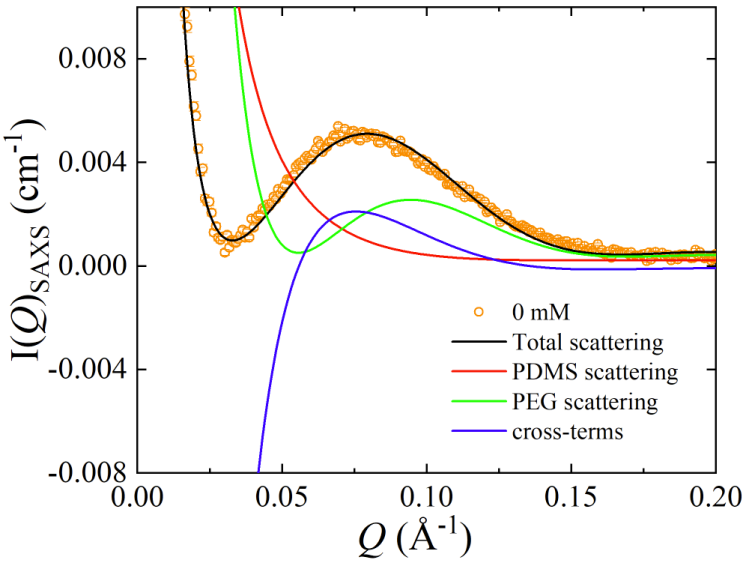

Figure S10: Calculated SAXS scattering contribution presented in linear scales from each scattering amplitudes presented in equations 4 and 5 in the manuscript.

9 SANS-DLS Comparison

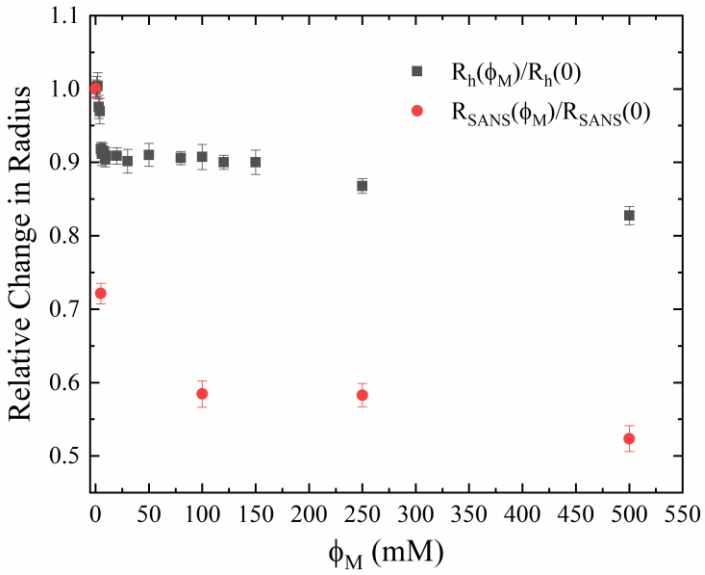

Figure S11. Comparison between relative change in radius with respect to 0 mM NaCl concentration between SANS and DLS. The normalized hydrodynamic and SANS radius, $R(\phi_M)/R(0)$, is plotted as a function of NaCl concentration.

Table S2. Vesicle Parameters Obtained from DLS and SANS.

Φm (mM)	R_h (nm)	R_{SANS} (nm)
0	69.6 ± 0.6	59 ± 2
5	63.9 ± 0.3	43 ± 1
100	63.1 ± 1	35 ± 1
250	60.4 ± 0.4	35 ± 1
500	57.6 ± 0.7	31 ± 1

10 References

S1. Hofmann, R. J.; Vlatkovic, M.; Wiesbrock, F., Fifty Years of Hydrosilylation in Polymer Science: A Review of Current Trends of Low-Cost Transition-Metal and Metal-Free Catalysts, Non-Thermally Triggered Hydrosilylation Reactions, and Industrial Applications. *Polymers (Basel)* **2017,** *9* (10).

S2. NIST Center for Neutron Research: Neutron Activation and Scattering Calculator. https://www.ncnr.nist.gov/resources/activation/.