Supporting information

Effect of molecular parameters on the architecture and membrane properties of 3D assemblies of amphiphilic copolymers

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Monocarbinol Poly(dimethylsiloxane) (PDMS-OH). Fresh dried hexamethylcyclotrisiloxane (D_3) (69.12 g, 310.71 mmol) was distilled into a dried three necks round flask under vacuum. Fresh dried and distilled cyclohexane (110 mL) and n-buty lithium solution (9.52 mL, 23.91 mmol) were added successively at the room temperature under argon atmosphere. After 4.5 hours, fresh dried and distilled THF (12 mL) was added under argon atmosphere. After 40 hours, dimethylchlorosilane (8.5 mL, 76.57 mmol) was added to quench the reaction. The white LiCl salt was filtrated in 4 hours, then the solvent and unreacted D_3 were distilled under high pressure in order to yield the 1. 1 (5.2 g, 2 mmol) was dissolved in fresh distilled toluene first, then 2-allyloxyethanol (0.25g, 2.1 mmol) and Pt(dvs) (2.28 µL) were added successively. The mixture was stirred overnight at 110 °C under inert atmosphere. After removal of the toluene, dichloromethane and the activated carbon were added and the final product was filtrated to yield the PDMS-OH as colorless oil. ^{1}H NMR (400 MHz, δ, $CDCl_3$): 0 ppm (m, -Si(CH_3)$_2$), 0.54 ppm (m, -SiCH_2), 0.88 ppm (t, -CH_3), 1.31 (m, -CH_2-CH_2-), 1.62 (m, -SiCH$_2$-CH_2-CH$_2$O-), 3.44 ppm (t, -CH_2-O-), 3.54 ppm (t, -O-CH_2-), 3.72 ppm (t, -CH_2-OH).

PDMS-OTf and PDMS-*b*-PMOXA. PDMS-OH (10.71g, 2.142 mmol) was put into a three-neck, round-bottomed flask and dried under stirring over night at 120 °C in high vacuum. Dry toluene was added under argon atmosphere and the solution was dried for 24 hours by reflux in a Soxleth apparatus containing a molecular sieve 4 Å. After cooling to room temperature, fresh dried and distilled triethylamine was added. The solution was cooled to 0 °C and trifluoromethanesulfonic anhydride in 20 mL of dry toluene was added slowly over 30 minutes. The mixture was reacted for another 3 hours at 0 °C. Then the mixture was separated from triflate salt by filtration through a glass frit. After evaporating the toluene, fresh dried and distilled chloroform (65 mL), acetonitrile (28 mL) and 2-methyl-2-oxazoline (4.19 g, 49.27 mmol) were added successively. The reaction mixture was stirred for 60 h at

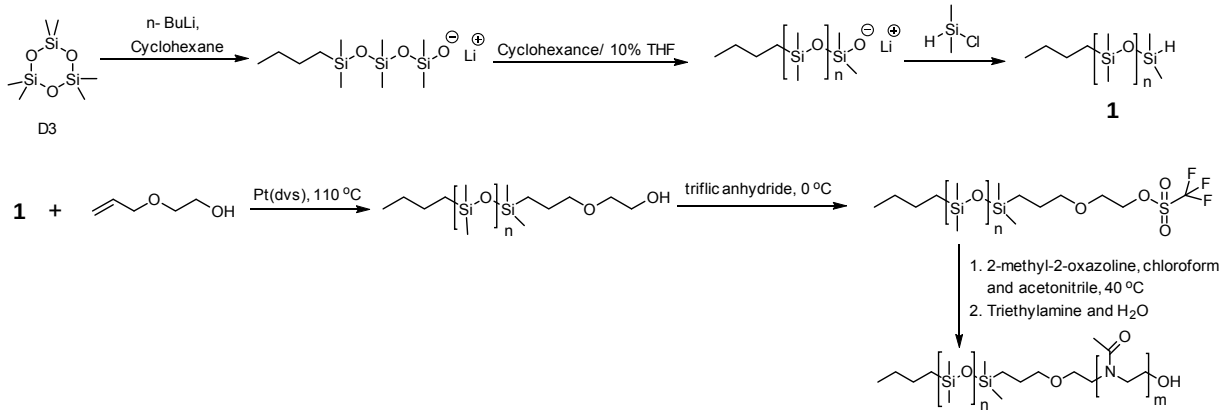
40 °C. Finally, the solution was cooled to room temperature, triethylamine (20 mL) and H_2O (20 mL) were added to quench the reaction. The polymer was dissolved in ethanol, subsequently the ethanol solution was transferred into a solvent-resistant, stirred ultrafiltration device (Millipore, USA) equipped with a 3000 MWCO regenerated cellulose membrane (Millipore, USA) and extensively washed with ethanol and H_2O mixture for six times to yield transparent, rubber-like PDMS-*b*-PMOXA-OH diblock copolymer.

PDMS-OTf: ^{1}H NMR (400 MHz, δ, $CDCl_3$): 0 ppm (m, -Si(C*H*$_3$)$_2$), 0.54 ppm (m, -SiC*H*$_2$), 0.88 ppm (t, -C*H*$_3$), 1.31 (m, CH_3-C*H*$_2$-C*H*$_2$-), 1.62 (m, -Si-CH_2-C*H*$_2$-CH_2-O-), 3.45 ppm (t, -C*H*$_2$-O-), 3.75 ppm (t, -O-C*H*$_2$-), 4.62 ppm (t, -C*H*$_2$-OTrf).

PDMS-*b*-PMOXA: ^{1}H NMR (400 MHz, δ, $CDCl_3$): 0 ppm (m, -Si(C*H*$_3$)$_2$), 0.54 ppm (m, -SiC*H*$_2$), 0.88 ppm (t, -C*H*$_3$), 1.31 ppm (m, -C*H*$_2$-C*H*$_2$-), 1.62 ppm (m, -$SiCH_2$-C*H*$_2$-CH_2O-), 2.08-2.21 ppm (m, C*H*$_3$-C=O), 3.40-3.60 ppm (m, -C*H*$_2$-O-C*H*$_2$-C*H*$_2$-N-C*H*$_2$-C*H*$_2$-), 3.75 ppm (t, -C*H*$_2$-OH).

EPR measurements

16 DSA inserting in preformed polymeric vesicles. In order to test more the hypothesis of a tri-layer composition of PDMS-b-PMOXA polymersomes with a quite dense hydrophobic PDMS in the centre and PMOXA on the inner and outer part of the PDMS are a second spin trap 16 DSA was added to the self-assembled structures of $PDMS_{65}$-b-$PMOXA_{12}$, $PDMS_{65}$-b-$PMOXA_{14}$ and $PDMS_{65}$-b-$PMOXA_{32}$ in solution. 16 DSA was chosen due to its higher ability to go deep inside the hydrophobic layers due to its higher hydrophobicity.[1] For 16 DSA as depicted in Figure S7 in the presence of all three types of polymersomes as also for 5 DSA at temperatures lower than 280 K the spectra in all three polymers vesicles solutions are anisotropic, typical for slowly moving species. The extreme separation, respectively $2A_{zz}$ values in spectra recorded at 150 K are smaller than those recorded in glycerol (71.2 G), respectively 70 G for all three polymersomes solutions. At temperature higher than 280 K the three line spectra characteristic for a nitroxide can be observed, a_N values at 300 K are equal to 15.8 G for all three polymer solutions, similar with that recorded in glycol, indicating the localization of the nitroxide group of the spin probe into a hydrophilic, polar environment, as also observed for 5 DSA. In a similar manner as described for 5 DSA in case of 16 DSA the rotation correlation time also increases from 0.16 nsec (as also reported by Beghein, N., et al.,[2]) to 1.29 ns for $PDMS_{65}$-*b*-$PMOXA_{12}$ polymersomes, 1.26 ns for $PDMS_{65}$-*b*-$PMOXA_{14}$ polymersomes and 1.18 ns for $PDMS_{65}$-*b*-$PMOXA_{32}$ structures indicating the insertion of the spin probe inside a more viscous environment comparable with 20% glycol (1.08 ns). As 16 DSA presents a similar behaviour as 5 DSA can be concluded that the PDMS layer is quite dense preventing the insertion of neither of chosen spin traps.



Scheme S1. Synthesis Route of PDMS-*b*-PMOXA.

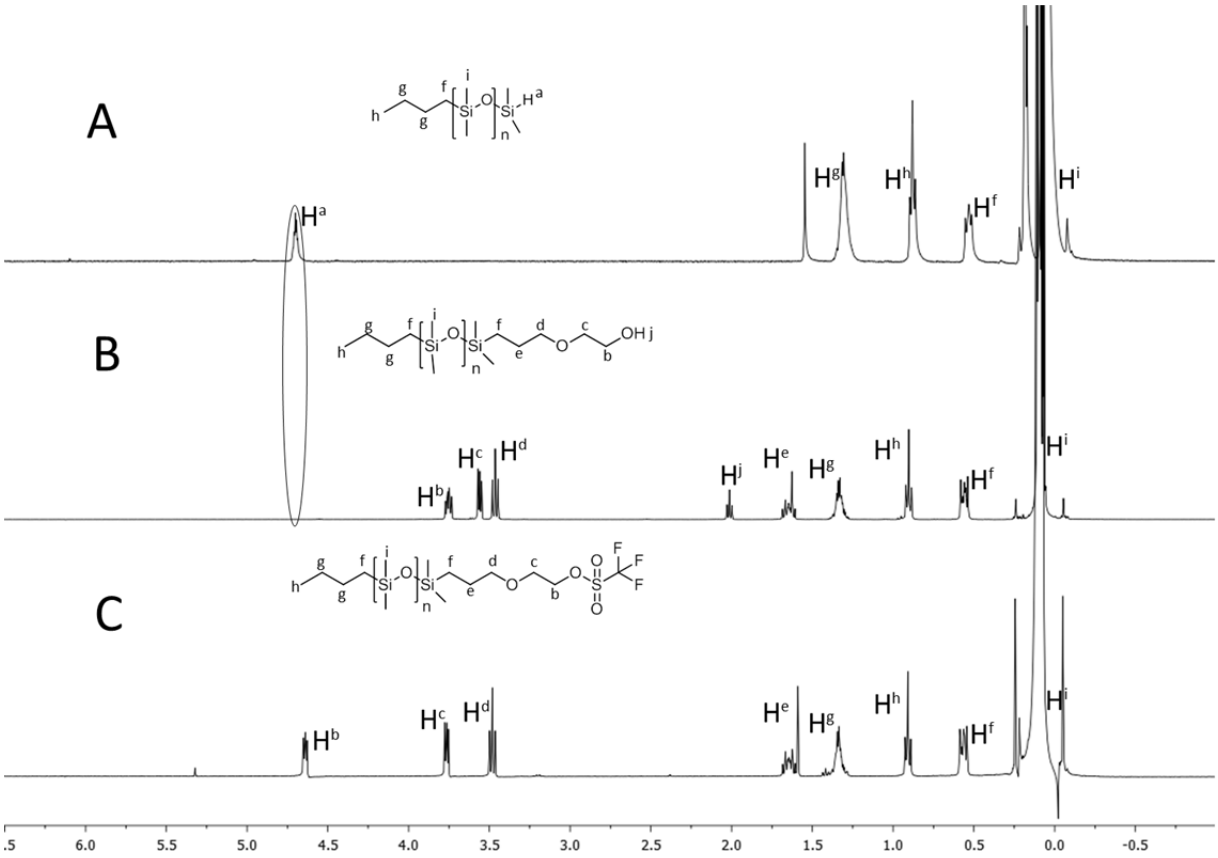


Figure S1. ^{1}H NMR spectrum of PDMS-H, PDMS-OH, and PDMS-OTf.

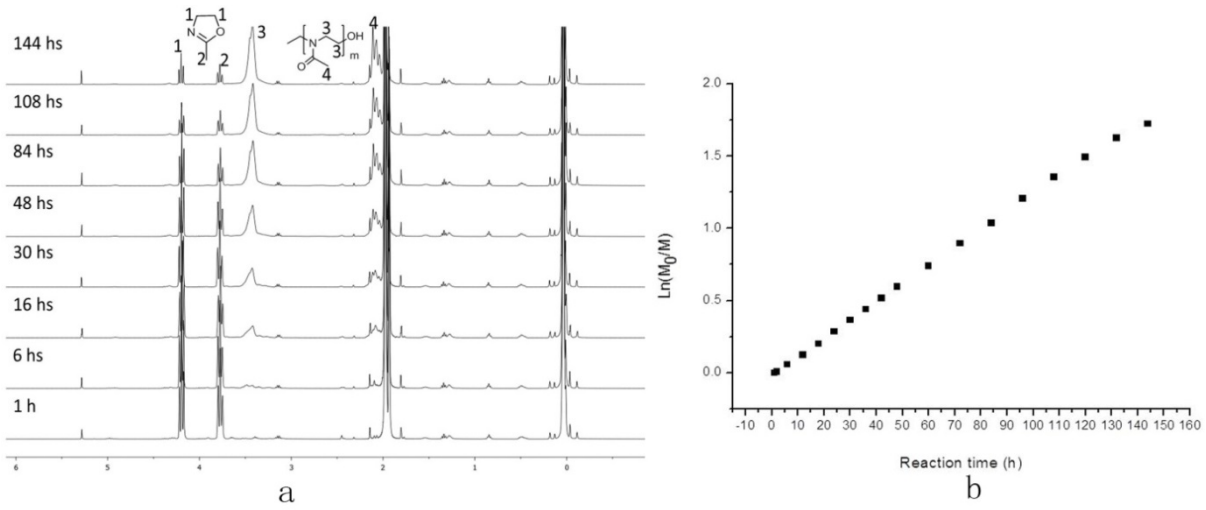


Figure S2. The kinetic result of polymerization of 2-methyl-2-oxazoline initiated by PDMS-OTf in the mixture solvent of chloroform and acetonitrile (v/v= 7:3).

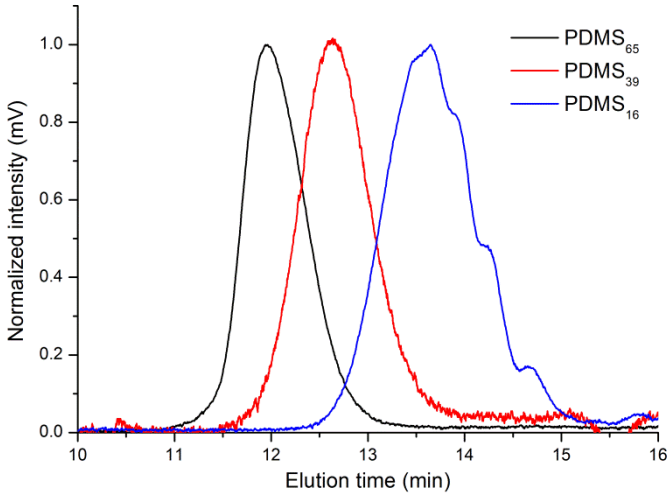


Figure S3. GPC traces of the $PDMS_{65}$ (ABCR), $PDMS_{39}$ and $PDMS_{16}$.

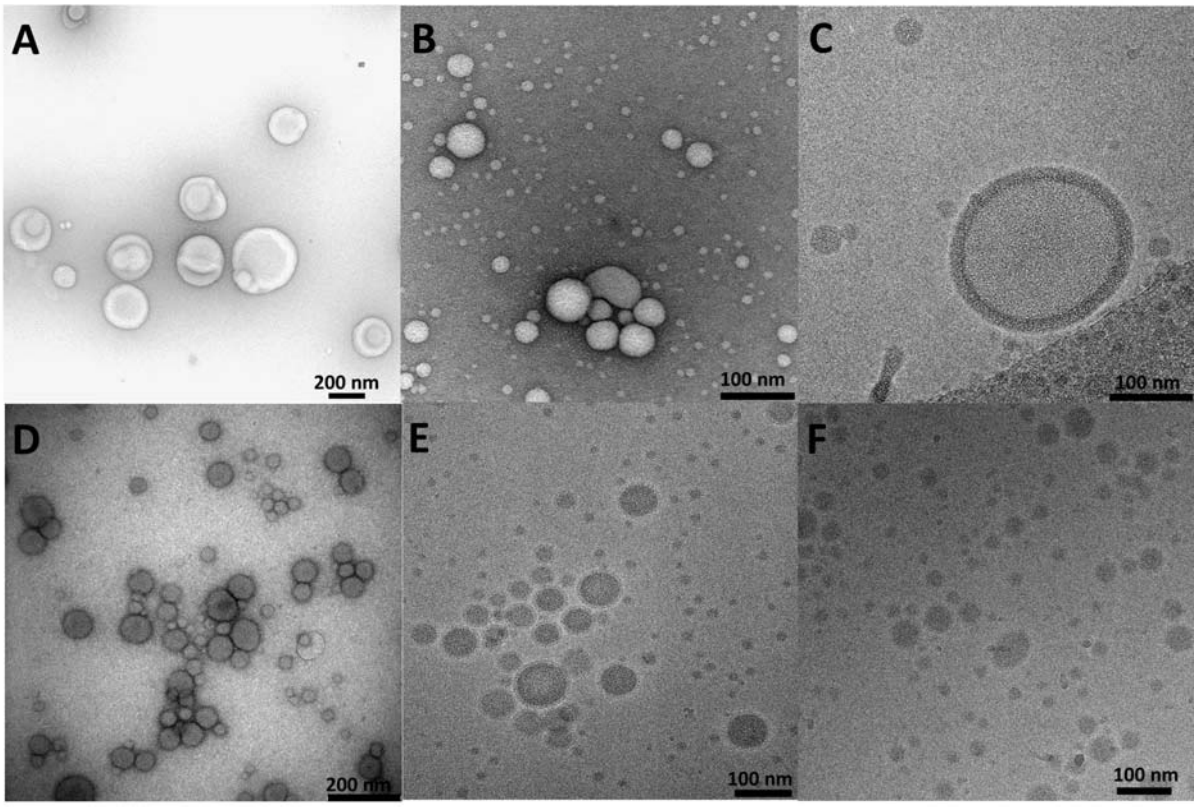


Figure S4. Representative TEM and Cryo-TEM images from the series of $PDMS_{65}$-*b*-$PMOXA_{10-38}$. A: TEM image of vesicular structures ($PDMS_{65}$-*b*-$PMOXA_{10-14}$, $f_{PMOXA} = 16 - 24\%$); B,C: TEM and Cryo-TEM images of micelles and vesicles structures ($PDMS_{65}$-*b*-$PMOXA_{16-19}$, $f_{PMOXA} = 27 - 31$); D, E, F: TEM and Cryo-TEM images of micelles and multicompartment micelles ($PDMS_{65}$-*b*-$PMOXA_{26-38}$,$f_{PMOXA} = 44 - 64\%$).

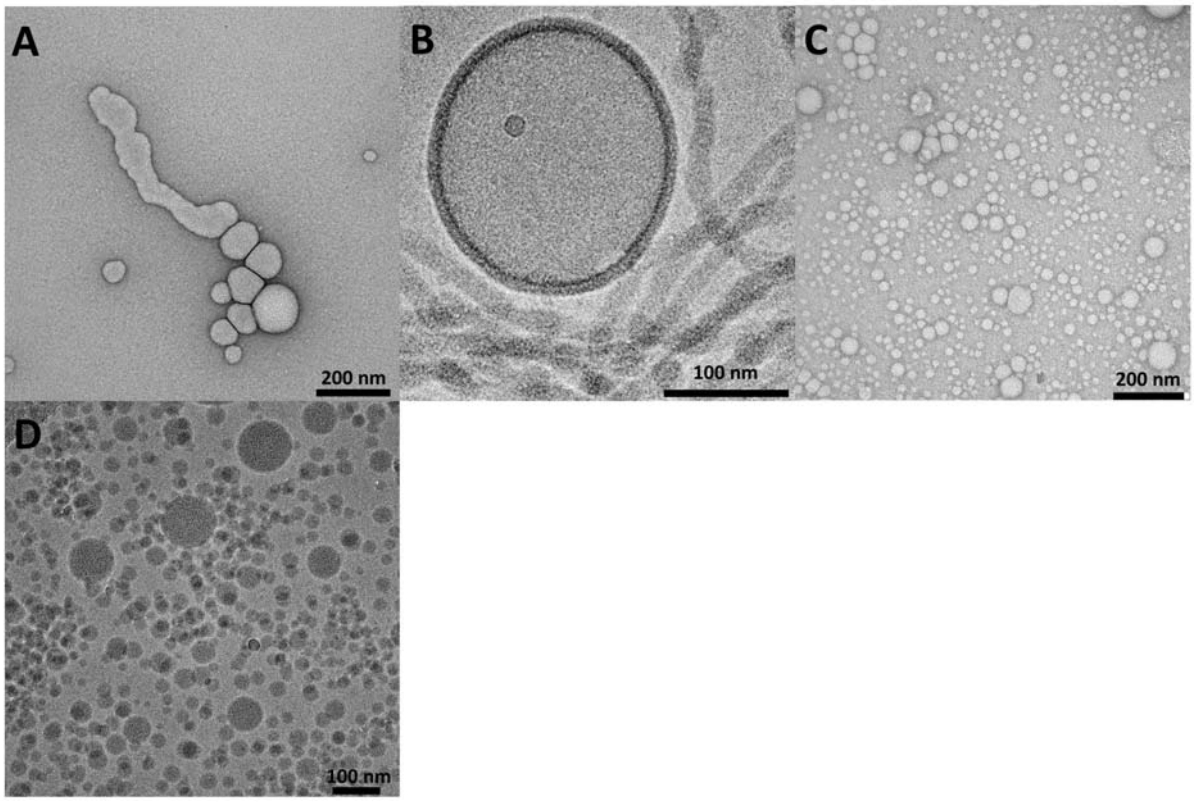


Figure S5. Representative TEM and Cryo-TEM images from the series of $PDMS_{39}$-*b*-$PMOXA_{6-22}$. A, B: TEM and Cryo-TEM images of worm-like micelles, small polymersomes and micelles ($PDMS_{39}$-*b*-$PMOXA_{6-10}$,$f_{PMOXA} = 16 - 27\%$); b: TEM and cryo-TEM images of micelles and multicompartment micelles ($PDMS_{39}$-*b*-$PMOXA_{10-22}$,$f_{PMOXA} = 30 - 60\%$).

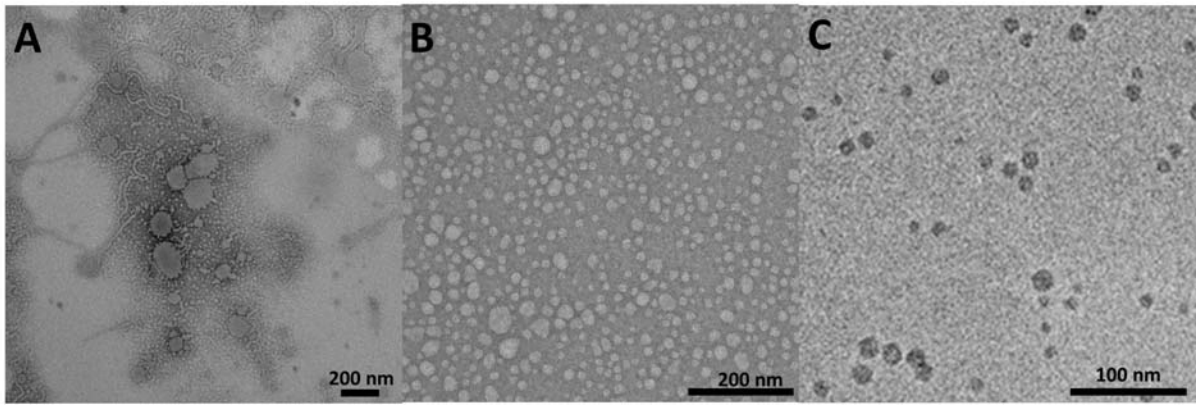


Figure S6. Representative TEM and Cryo-TEM images from the series of $PDMS_{16}$-*b*-$PMOXA_{3-10}$ forming micelles ($f_{PMOXA} = 18 - 60\%$). A: TEM image of worm-like micelles, micelles ($PDMS_{16}$-*b*-$PMOXA_{3-4}$,$f_{PMOXA} = 18 - 24\%$); B, C: TEM and Cryo-TEM images of micelles ($PDMS_{16}$-*b*-$PMOXA_{5-10}$,$f_{PMOXA} = 30 - 60\%$).

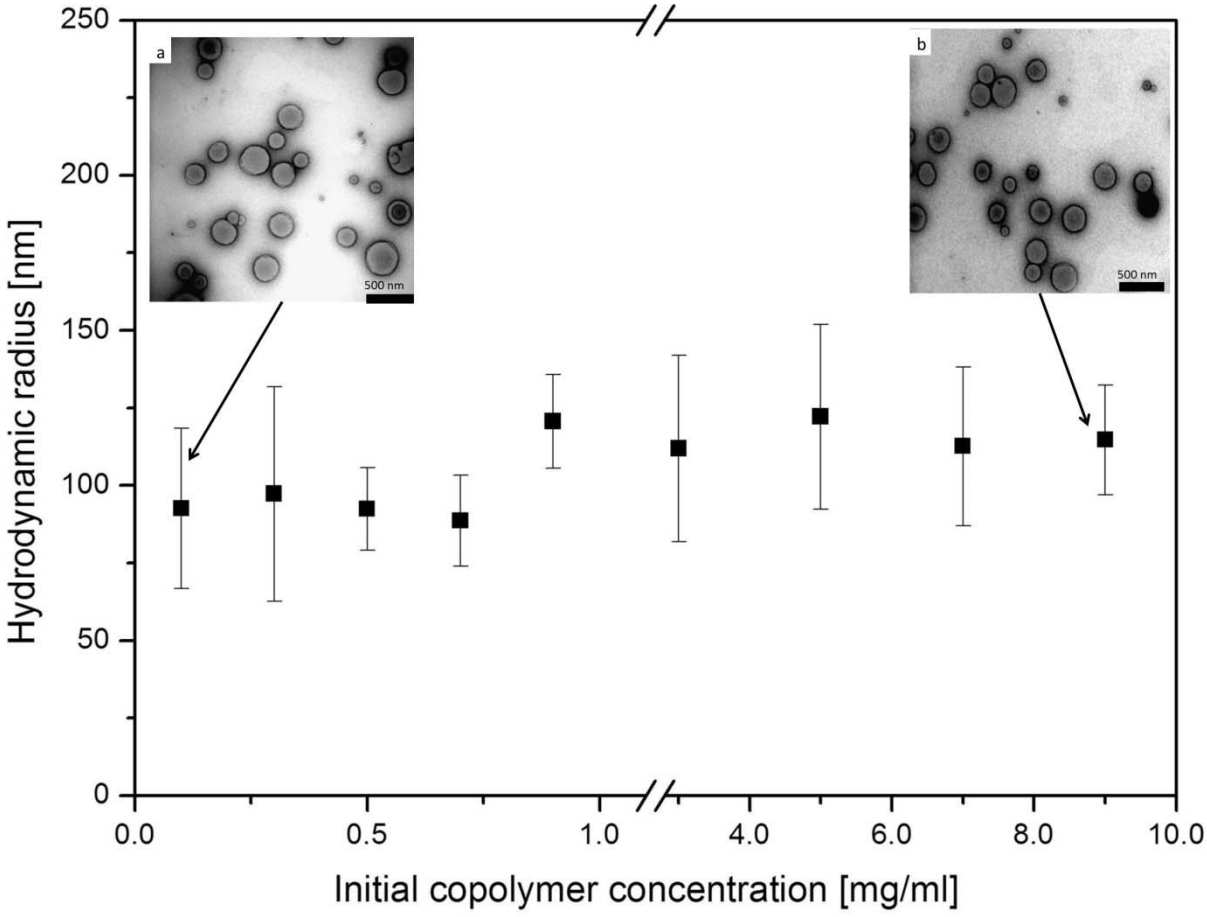


Figure S7. The influence of initial diblock copolymer concentration on self-assembly behaviour of $PDMS_{65}$-*b*-$PMOXA_{14}$. a. 0.1 mg/mL; b. 9.0 mg/mL.

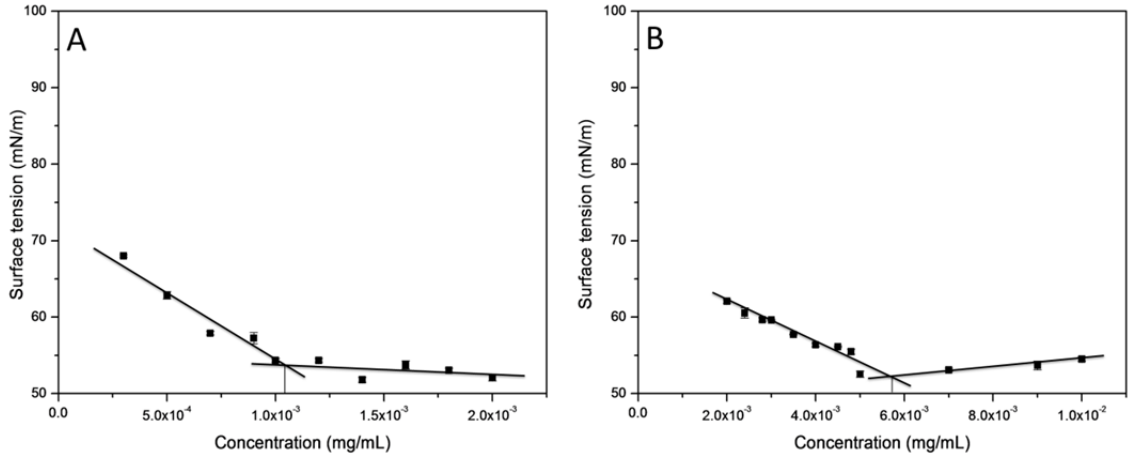


Figure S8. Surface tension experiments of (A) $PDMS_{65}$-*b*-$PMOXA_{14}$ and (B) $PDMS_{65}$-*b*-$PMOXA_{32}$ aqueous solution in different concentration.

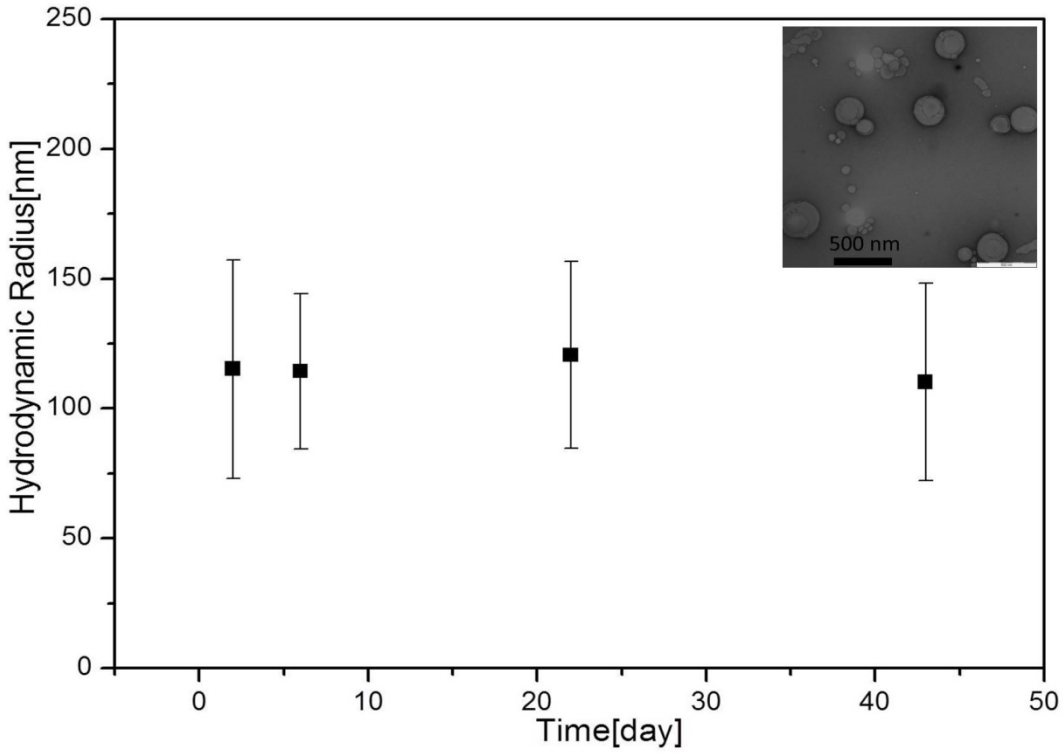


Figure S9. Hydrodynamic radius and stability of $PDMS_{65}$-*b*-$PMOXA_{14}$ polymersomes in Tris/HCl buffer (pH 8.0). Inset: representative TEM image of polymersomes.

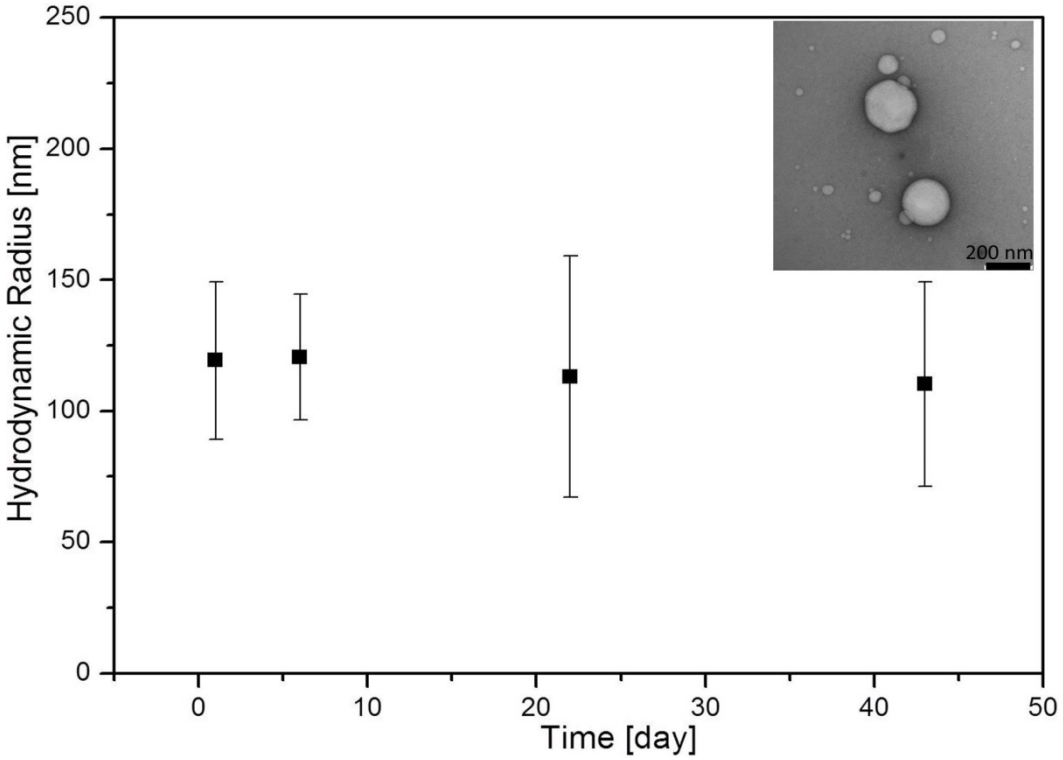


Figure S10. Hydrodynamic radius and stability of $PDMS_{65}$-*b*-$PMOXA_{14}$ polymersomes in PBS buffer (pH 7.2). Inset: representative TEM image of polymersomes.

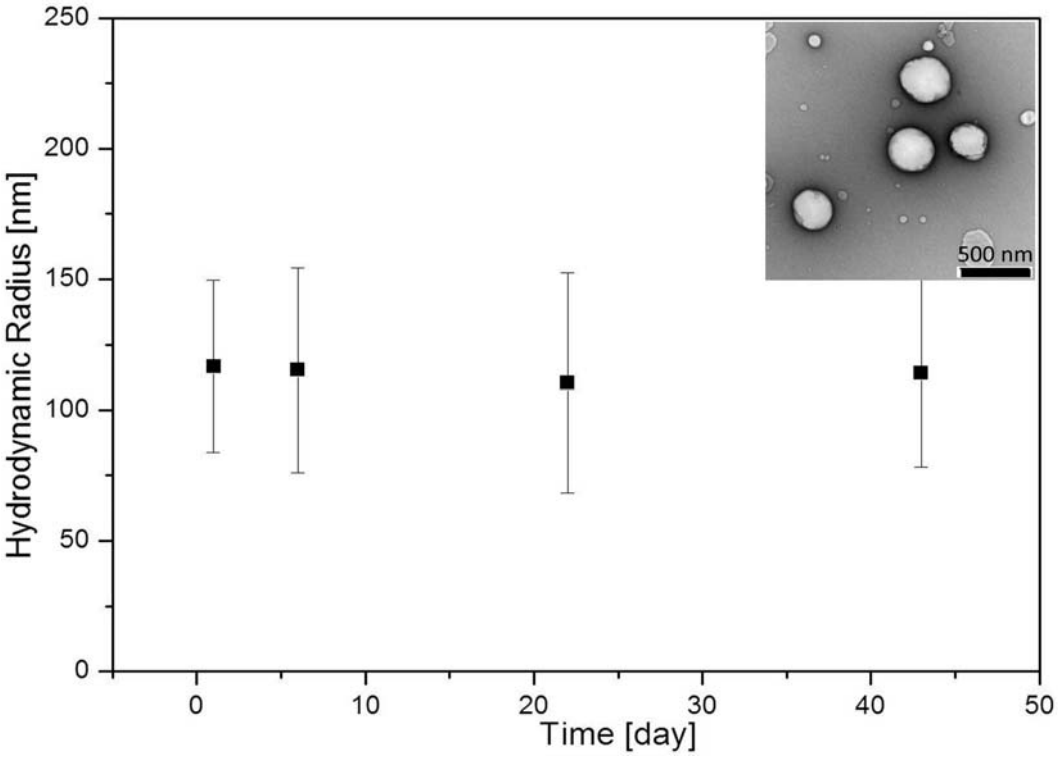


Figure S11. Hydrodynamic radius and stability of $PDMS_{65}$-*b*-$PMOXA_{14}$ polymersomes in acetate buffer (pH 5.0). Inset: representative TEM image of polymersomes.

Table S1. Gyration, hydrodynamic radii and resulting ρ-value ($\rho = \frac{Rg}{Rh}$) of self-assemblies of selected diblock polymers.

Sample	R_g (nm)	R_h (nm)	ρ ($\rho = \frac{Rg}{Rh}$)
$PDMS_{65}$-*b*-$PMOXA_{10}$	131	132	0.99
$PDMS_{65}$-*b*-$PMOXA_{12}$	132	123	1.07
$PDMS_{65}$-*b*-$PMOXA_{14}$	104	115	0.91
$PDMS_{65}$-*b*-$PMOXA_{19}$	71	75	0.94
$PDMS_{65}$-*b*-$PMOXA_{32}$	80	98	0.82

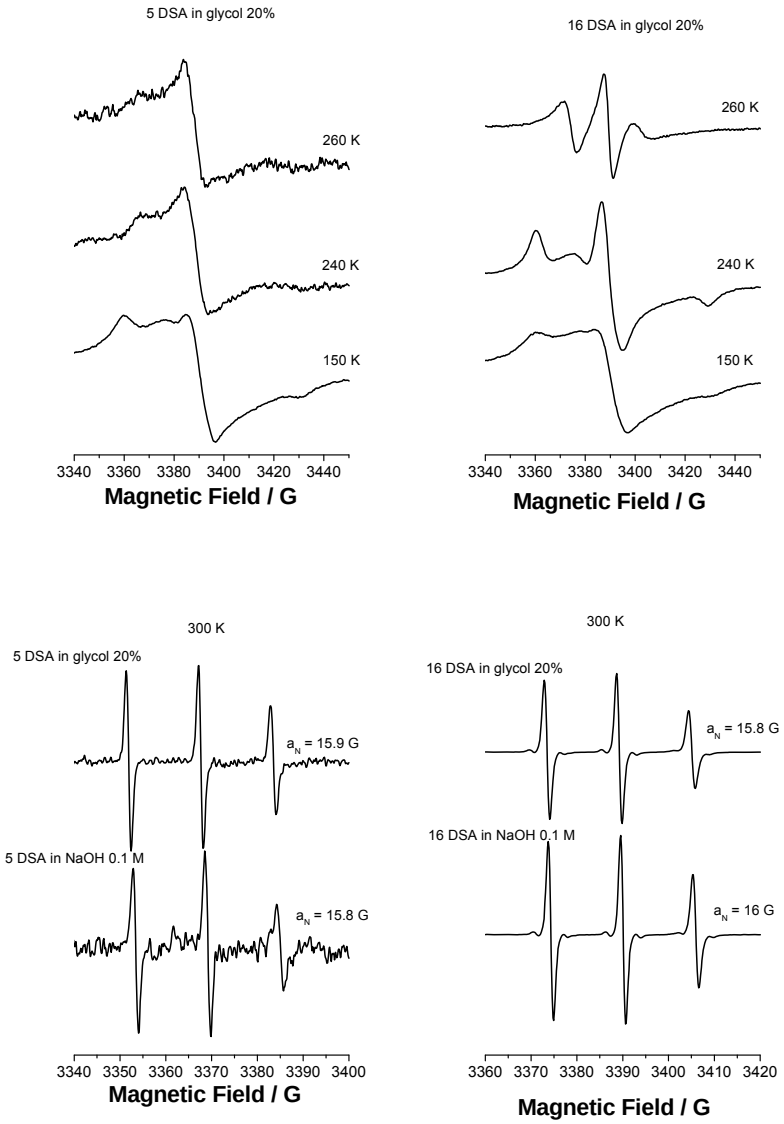
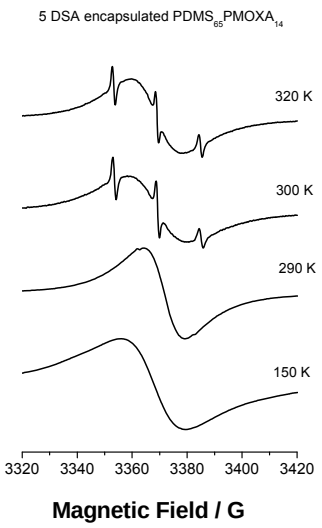
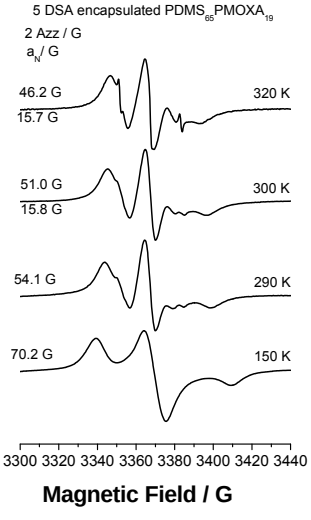
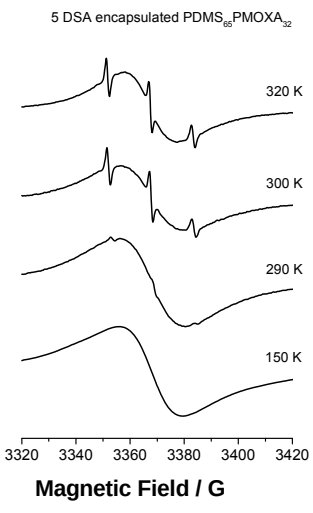
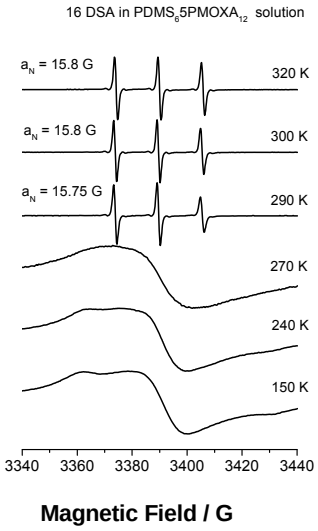


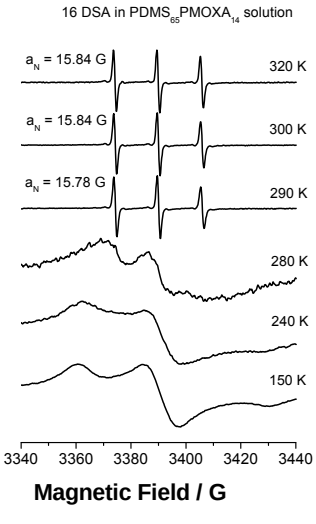
Figure S12. Rigid limit and fast motional spectra of 5 DSA and 16 DSA spectra in 0.1 M NaOH (300 K) and 20% glycol at temperatures ranging from 150 K to 260 K and 300 K, respectively.

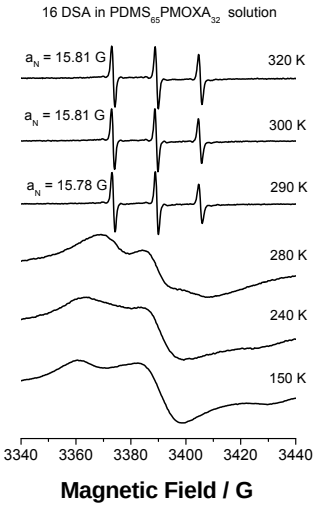

5 DSA encapsulated PDMS65PMOXA14
320 K
300 K
290 K
150 K
3320 3340 3360 3380 3400 3420
Magnetic Field / G

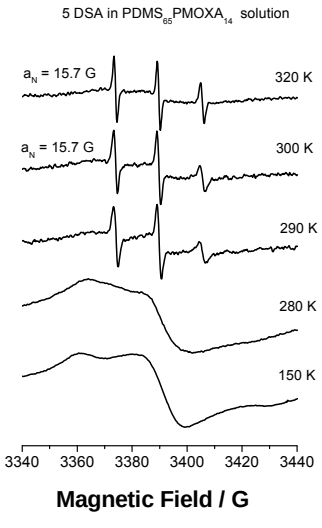

5 DSA encapsulated PDMS65PMOXA19
2 Azz / G
aN / G
46.2 G
15.7 G
320 K
51.0 G
15.8 G
300 K
54.1 G
290 K
70.2 G
150 K
3300 3320 3340 3360 3380 3400 3420 3440
Magnetic Field / G

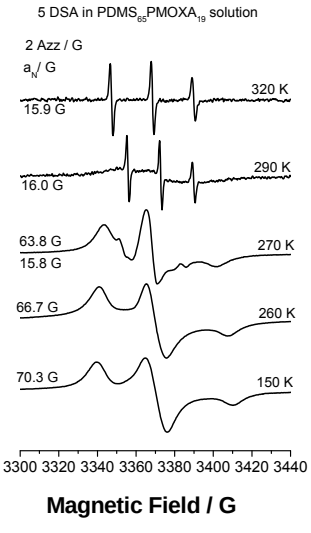

5 DSA encapsulated PDMS65PMOXA32
320 K
300 K
290 K
150 K
3320 3340 3360 3380 3400 3420
Magnetic Field / G


16 DSA in PDMS65PMOXA12 solution
aN = 15.8 G
320 K
aN = 15.8 G
300 K
aN = 15.75 G
290 K
270 K
240 K
150 K
3340 3360 3380 3400 3420 3440
Magnetic Field / G


16 DSA in PDMS65PMOXA14 solution
aN = 15.84 G
320 K
aN = 15.84 G
300 K
aN = 15.78 G
290 K
280 K
240 K
150 K
3340 3360 3380 3400 3420 3440
Magnetic Field / G


16 DSA in PDMS65PMOXA32 solution
aN = 15.81 G
320 K
aN = 15.81 G
300 K
aN = 15.78 G
290 K
280 K
240 K
150 K
3340 3360 3380 3400 3420 3440
Magnetic Field / G


5 DSA in PDMS65PMOXA14 solution
aN = 15.7 G
320 K
aN = 15.7 G
300 K
290 K
280 K
150 K
3340 3360 3380 3400 3420 3440
Magnetic Field / G


5 DSA in PDMS65PMOXA19 solution
2 Azz / G
aN / G
15.9 G
320 K
16.0 G
290 K
63.8 G
15.8 G
270 K
66.7 G
260 K
70.3 G
150 K
3300 3320 3340 3360 3380 3400 3420 3440
Magnetic Field / G

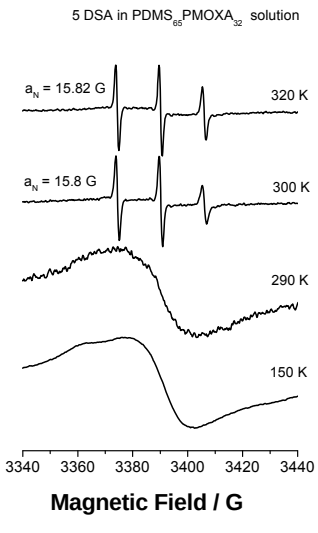

5 DSA in PDMS65PMOXA32 solution
aN = 15.82 G
320 K
aN = 15.8 G
300 K
290 K
150 K
3340 3360 3380 3400 3420 3440
Magnetic Field / G

Figure S13. Rigid limit and fast motional spectra of 5 DSA encapsulated in $PDMS_{65}$-*b*-$PMOXA_{14,}$ $PDMS_{65}$-*b*-$PMOXA_{19}$, $PDMS_{65}$-*b*-$PMOXA_{32}$ and 5 DSA and 16 DSA inserted in preformed structures.

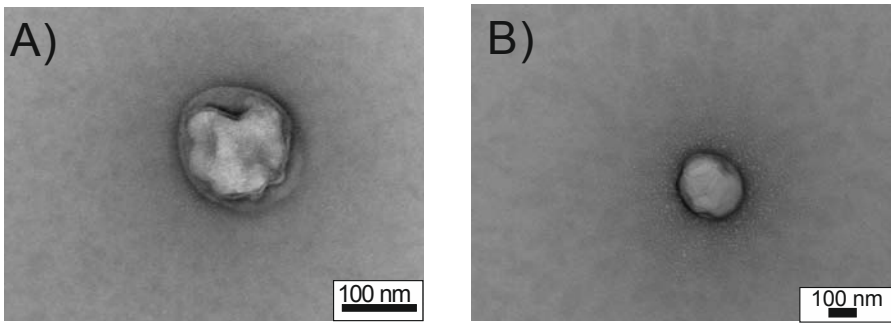


Figure S14. TEM micrographs of (A) $PDMS_{65}$-*b*-$PMOXA_{12}$ and (B) $PDMS_{65}$-*b*-$PMOXA_{14}$ polymersomes formed by self-assembly of block copolymers in PBS in presence of 5 DSA and 1% Triton X-100.

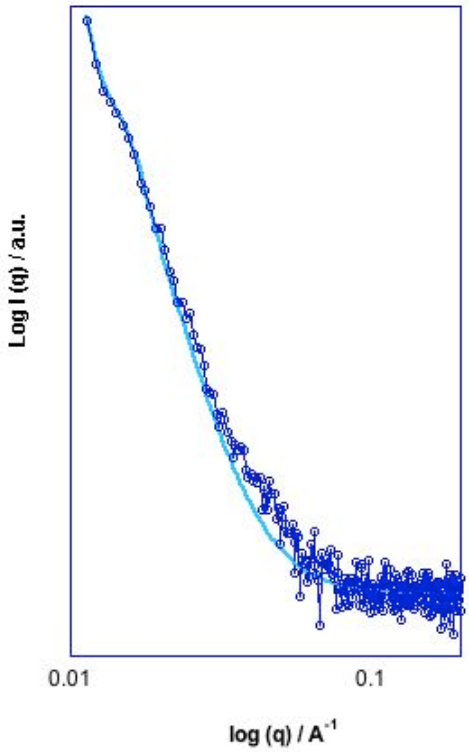


Figure S15. SAXS patterns (dark blue) and data fits (lighter blue) obtained for the respective $PDMS_{65}$-*b*-$PMOXA_{32}$ self-assembles solution (5 mg/mL). The figure shows the scattering curve (dark blue) of "CH4-micelles" (intensity *I* vs momentum transfer *q*). The lighter blue line is a fit taking into account a spherical particle with a radius of *r* = (315 ± 68) Å. An additional scattering feature from 0.03 - 0.06 Å can be seen. However it is difficult to interpret it in more detail.

1. Zhou, L.; Schlick, S., Electron spin resonance (ESR) spectra of amphiphilic spin probes in the triblock copolymer EO13PO30EO13 (Pluronic L64): hydration, dynamics and order in the polymer aggregates. *Polymer* **2000,** *41* (12), 4679-4689.
2. Beghein, N.; Rouxhet, L.; Dinguizli, M.; Brewster, M. E.; Ariën, A.; Préat, V.; Habib, J. L.; Gallez, B., Characterization of self-assembling copolymers in aqueous solutions using Electron Paramagnetic Resonance and Fluorescence spectroscopy. *Journal of Controlled Release* **2007,** *117* (2), 196-203.