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Supporting Information

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Control of Vesicular Morphologies via Hydrophobic Block Length

Tony Azzam and Adi Eisenberg

Department of Chemistry – McGill University
801 Sherbrooke St. West
Montreal PQ H3A2K6 Canada
Tel: (+1)-514-3986934
Fax: (+1) 514-3983797
E-mail: adi.eisenberg@mcgill.ca

Experimental Section

Materials

Styrene and tert-butyl acrylate (tBA) obtained from Aldrich were passed through a short column of Alumina to remove the inhibitor, dried over CaH_2 for 24 h and distilled under vacuum just before use. N,N,N',N',N''-Pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%) was dried with small amount of CaH_2 for 24 h and distilled under reduced pressure. CuBr (98%, Aldrich) was suspended overnight with an excess of glacial acetic acid, filtered and washed with copious amounts of absolute ethyl alcohol followed by anhydrous ethyl ether. The purified copper bromide was dried in vacuum at 80 ^{o}C for three days and stored under nitrogen at 4 ^{o}C. All other chemicals and solvents were of analytical grade and were used as received.

Synthesis of PAA-b-PS block copolymer

PtBA-Br macroinitiators were prepared as described elsewhere.[1] PtBA-Br along with CuBr (1.5 eq.) were placed in a Schlenck-flask equipped with a septum and evacuated and purged with nitrogen several times to remove oxygen. To this flask and under nitrogen, deoxygenated styrene was added (200-600 mol ratio, [styrene]/PtBA) and the content of the flask was deoxygenated by three freeze and thaw cycles. Deoxygenated PMDETA (1 eq. to CuBr) was added and the mixture was stirred at RT for 15 min to ensure the formation of the CuBr-ligand complex (light green color). The mixture was further deoxygenated and placed under nitrogen in an oil-bath thermostated at 110 ^{o}C. The polymerization was allowed to proceed for 6 h and quenched by cooling to room temperature and exposing to air. The viscous crude product was dissolved in THF and passed through a short column of basic alumina in order to remove the catalyst. Finally, the product was precipitated in excess of methanol, filtered and dried in vacuum at 50 ^{o}C.

The average conversion of styrene monomer was 80% in all runs as determined ^{1}H-NMR. Hydrolysis of the t-butyl esters was accomplished by treating the block for 12 h and at RT with an excess of trifluoroacetic acid in dichloromethane. The solvent was removed under reduced pressure, redissolved in a small amount of THF and recovered by precipitation in excess of water and filtered. Finally, it was dried under vacuum at 50 ^{o}C for three days.

Morphological studies

The corresponding block copolymer was dissolved in dioxane (1 wt%) or THF/Dioxane (1/3) mixture and stirred overnight at ambient temperature. To induce self assembly, water was added at a rate of 0.1 wt% per minute until a water content of 50 wt% was reached. The colloidal suspension was then quenched by water and dialyzed for few days against water to remove the organic solvent.

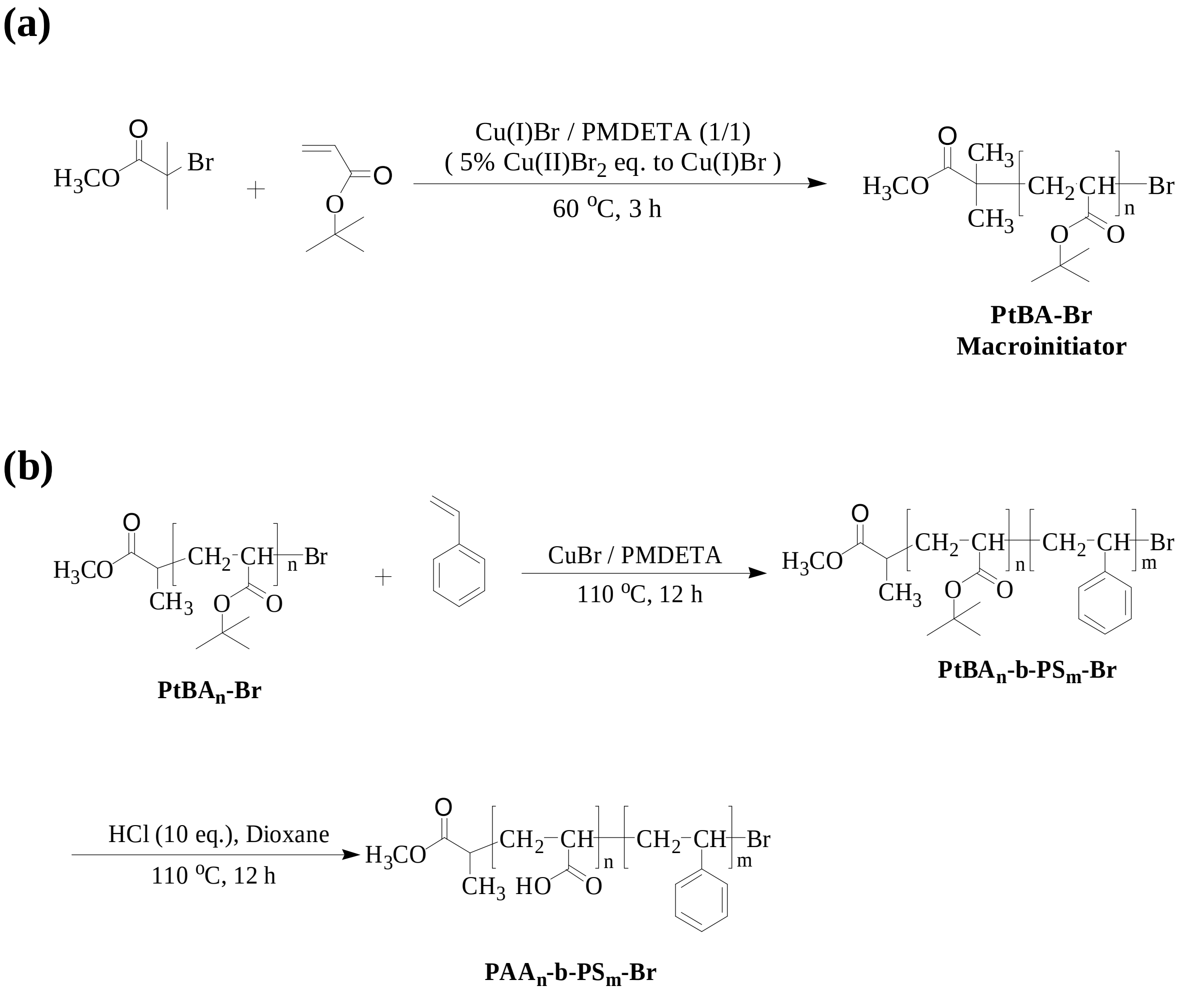
Characterization

Size exclusion chromatography (SEC) was used to measure the degree of polymerization and the polydispersity of the PtBA macroinitiators and the PtBA-b-PS block copolymers. Waters 510 liquid chromatography pump equipped with two (HR1 and HR4) Styragel columns connected in series, and a refractive index detector (Varian RI-4) were used at room temperature. Polystyrene and poly(t-butyl acrylate) standards (Scientific Polymer Products Inc., NY, USA) with narrow molecular weight distribution were used for calibration.

^{1}H-NMR spectra were recorded on a Varian XL-300 spectrometer using $CDCl_3$ as solvent with TMS as internal reference.

Transmission electron microscopy was performed on a JEOL microscope equipped with a CCD camera and operating at an acceleration voltage of 80 kV. Copper EM grids were precoated with a thin film of Formvar and then coated with carbon. A drop of solution containing 0.05 wt% of polymer was deposited on the resulting grids. Samples were dried in air overnight.

Dynamic light scattering (DLS) measurements were performed on a Brookhaven Instruments goniomeer system equipped with a Compass 315M-150 laser (Coherent technologies) which provides a wavelength of 532 nm, and a BI9000 AT digital correlator. Auto correlation functions were recorded at 60^o, 75^o, 90^o, 105^o and 120^o. Radii were obtained by cumulant analysis from the correlation functions. Extrapolation of the inverse radii to a scattering angle of 0^o led to the hydrodynamic radius R_H of the self-assembled morphologies.



Scheme S1. Synthesis of $PtBA_n$-Br macroinitiator (a) and PAA_n-b-PS_m block copolymer (b) by ATRP.

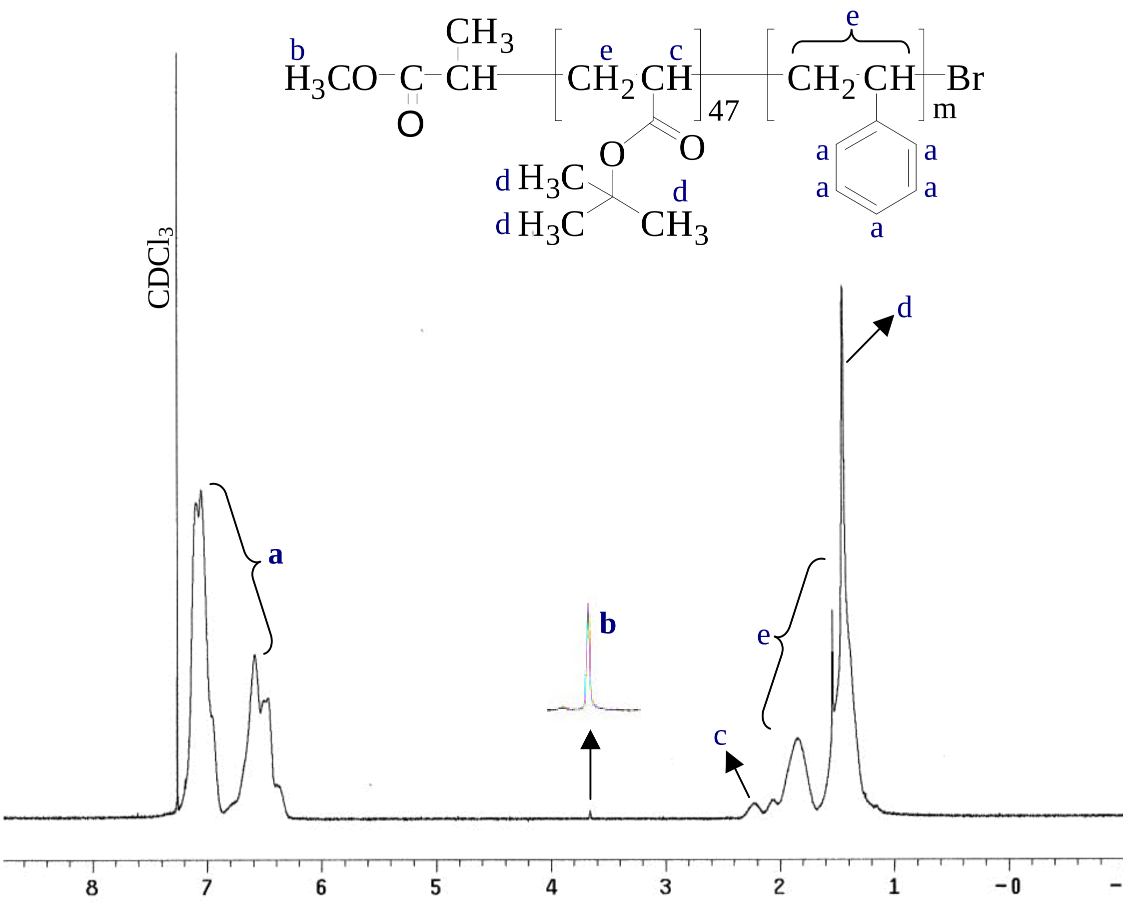


Figure S1. Typical ^{1}H-NMR of $PtBA_{47}$-b-PS_n in $CDCl_3$.

Determination of the degree of polymerization (DP) of the PS block by ^{1}H-NMR

Known value: $DP_{PtBA} = 47$ (from SEC calibrated against PtBA standards)

$$I_{PtBA} = I_{aliphatic} - 0.6\ x\ I_a$$

Where:

- I_{PtBA} is the integration of all PtBA protons (12H) in the aliphatic region (i.e. 1-2.5 ppm)
- $I_{aliphatic}$ is the total integration of all protons in the aliphatic region (i.e. 3 protons in the PS block and 12 protons in the PtBA block).
- I_a is the total integration value in the aromatic region (i.e. 6.2-7.4 ppm).

Therefore: $DP_{PS} = \frac{I_a}{I_{PtBA}}\ x\ \frac{12}{5}\ x\ DP_{PtBA}$

The factor 12/5 is due to the ratio between PtBA protons (12 H) and the PS protons in the aromatic region (5H).

Table S1. Compositions and molecular weight distributions of PAA-b-PS block copolymers used in this study.

Polymer [a]	*Mn*[b]	*Mw/Mn*[b]	mol% PAA[c]
PAA_{47}-b-PS_{670}	78,500	1.33	7
PAA_{47}-b-PS_{435}	72,600	1.18	9.8
PAA_{47}-b-PS_{370}	58,800	1.16	11.3
PAA_{47}-b-PS_{355}	51,000	1.18	11.7
PAA_{47}-b-PS_{310}	46,000	1.17	13.3
PAA_{47}-b-PS_{275}	42,200	1.19	14.6
PAA_{47}-b-PS_{250}	36,300	1.12	15.9
PAA_{47}-b-PS_{200}	28,900	1.10	19.3
PAA_{34}-b-PS_{325}	44,800	1.14	9.5
PAA_{34}-b-PS_{240}	31,200	1.10	12.5
PAA_{34}-b-PS_{190}	24,500	1.10	15.3

[a] Composition of block copolymers as determined by ^{1}H-NMR (Figure S1).[2] The PAA block length was estimated before hydrolysis (i.e. PtBA-Br macroinitiator) using size exclusion chromatography (SEC) calibrated by poly(t-butyl acrylate) standards. The subscripts refer to the average degree of polymerization (DP) of each block. [b] *Mn* and *Mw/Mn* of the blocks before hydrolysis (i.e. PtBA-b-PS) were determined by SEC against polystyrene standards (Figures S2 and S3). [c] Calculated by the following equation: mol% PAA=DP_{PtBA}/DP_{tot} x 100, where DP_{PtBA} is the average degree of polymerization of the PtBA block, and DP_{tot} is the average total degree of polymerization of both blocks together.

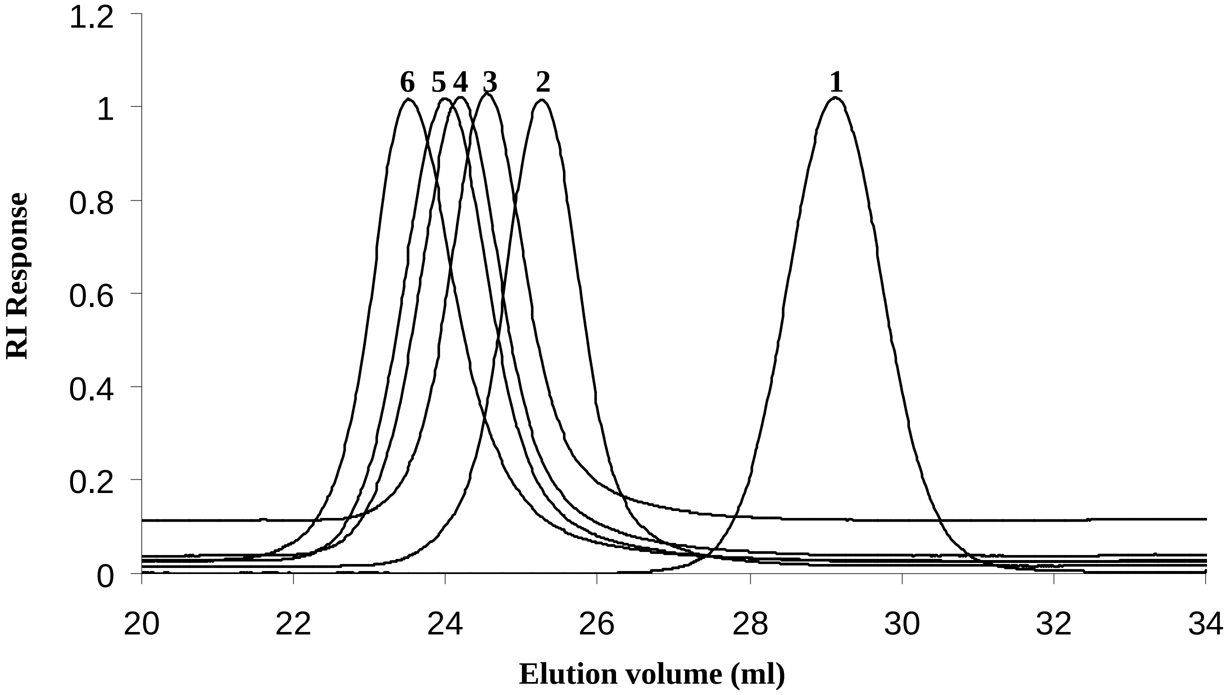


Figure S2. SEC traces of $PtBA_{47}$-Br macroinitiator (1), $PtBA_{47}$-b-PS_{200} (2), $PtBA_{47}$-b-PS_{250} (3) and $PtBA_{47}$-b-PS_{310} (4), $PtBA_{47}$-b-PS_{370} (5) and $PtBA_{47}$-b-PS_{435} (6) copolymers.

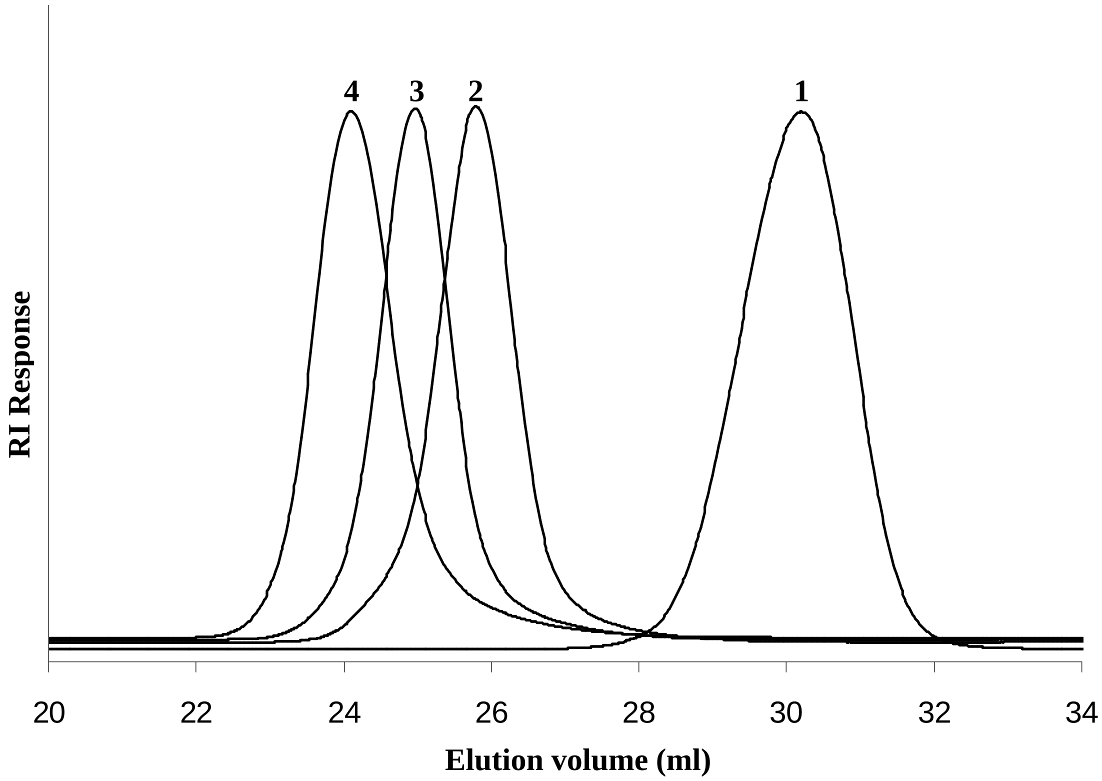
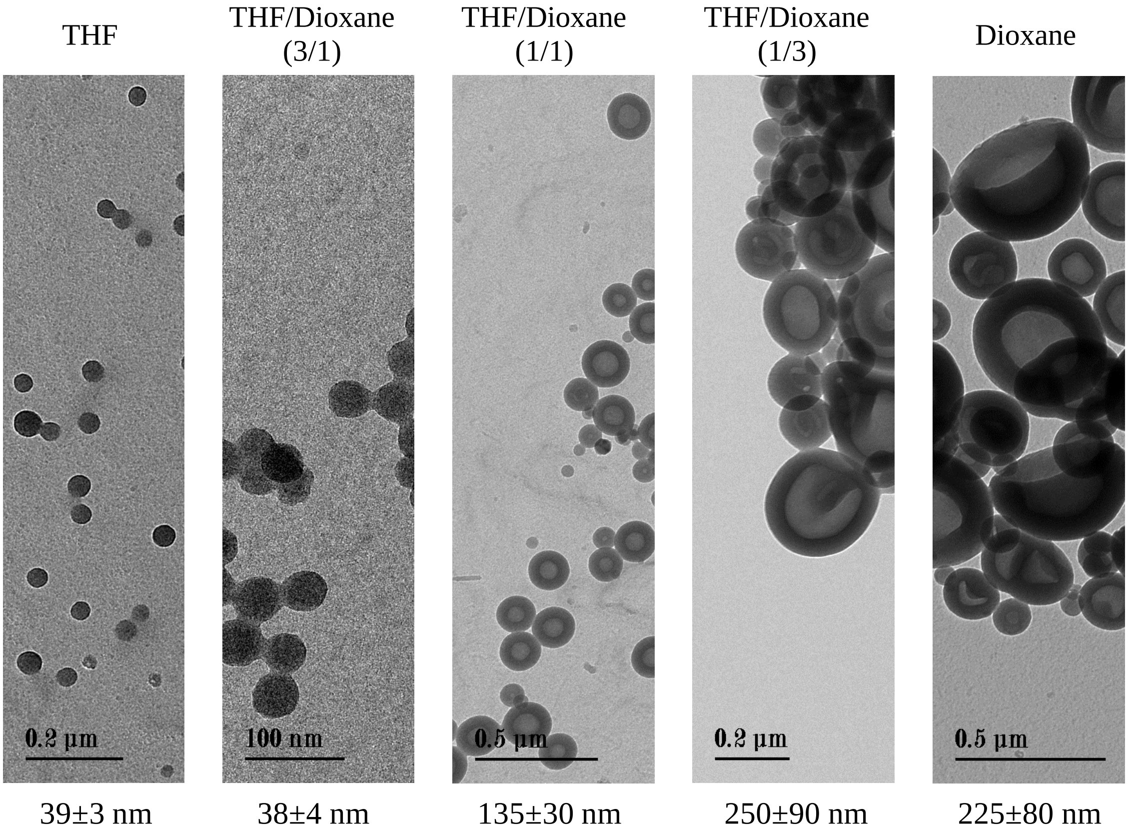


Figure S3. SEC traces of $PtBA_{34}$-Br macroinitiator (1), $PtBA_{34}$-b-PS_{190} (2), $PtBA_{34}$-b-PS_{240} (3) and $PtBA_{34}$-b-PS_{325} (4) copolymers.



THF | THF/Dioxane (3/1) | THF/Dioxane (1/1) | THF/Dioxane (1/3) | Dioxane

39±3 nm | 38±4 nm | 135±30 nm | 250±90 nm | 225±80 nm

Figure S4. TEM Images and average diameters of micelles/vesicles made from PAA_{47}-b-PS_{435} in various THF/dioxane solvent mixtures. The Self-assembled morphologies were prepared from a solution containing 1 wt% copolymer at a final water content of 50 wt%.

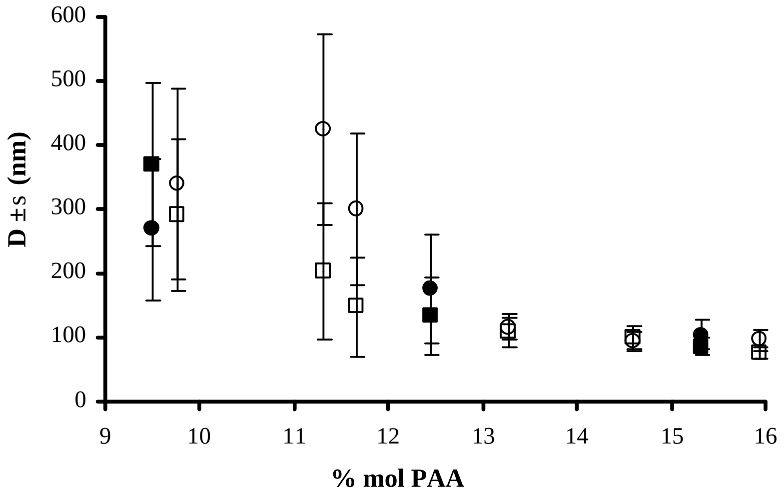


Figure S5. Average vesicle diameter ± SD (D±σ) made from dioxane (? and ¦) and dioxane/THF (3/1) (? and ?) as a function of %mol PAA in the PAA-b-PS block copolymer. Open squares and circles (? and ?) refer to vesicles made from PAA_{47}-b-PS_n series, and filled squares and circles (¦ and ?) refer to vesicles made from PAA_{34}-b-PS_n series. The average vesicle diameter was calculated from at least 600 measurements of each block sample. Samples forming either LCVs (i.e. PAA_{47}-b-PS_{670}) and pure micelles (i.e. PAA_{47}-b-PS_{190}) were excluded.

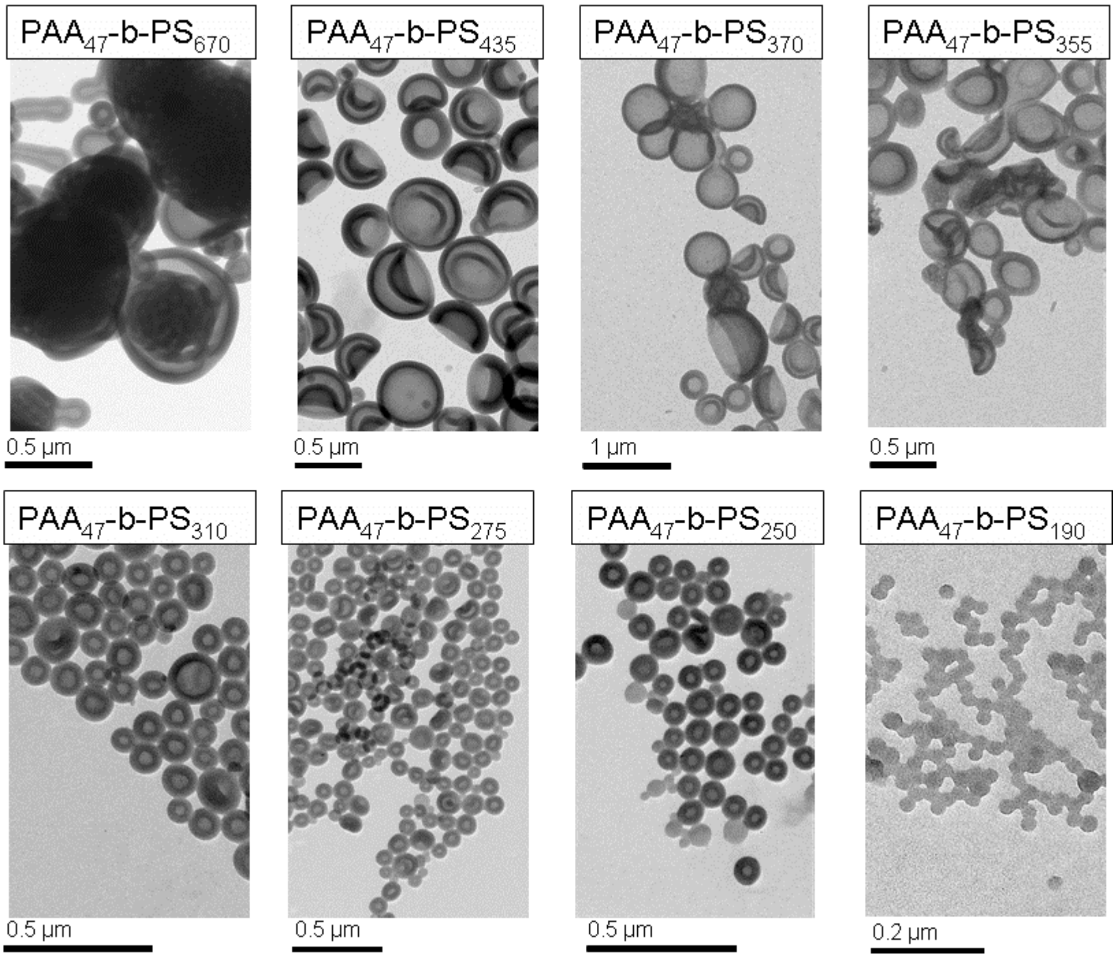


Figure S6. Transmission electron micrographs of vesicles prepared from PAA_{47}-b-PS_n block copolymer series. Vesicles were made from 1 wt% copolymer concentration in dioxane with 50 wt% final water content (Experimental Section).

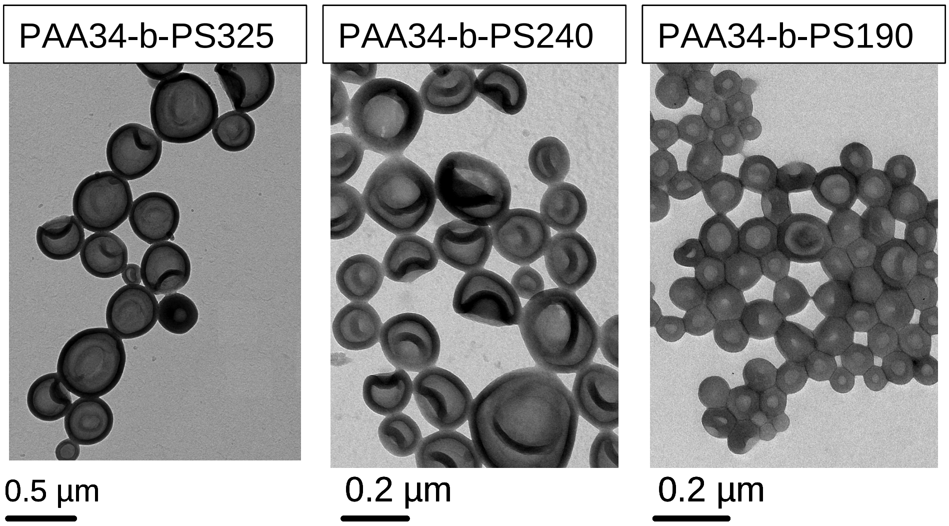


Figure S7. Transmission electron micrographs of vesicles prepared from PAA$_{34}$-b-PS$_n$ block copolymer series. Vesicles were made from 1 wt% copolymer concentration in dioxane with 50 wt% final water content (Experimental Section).

References

[1] Q. Ma, K. L. Wooley, *Journal of Polymer Science, Part A: Polymer Chemistry* **2000**, *38*, 4805; X. Zhang, J. Xia, K. Matyjaszewski, *Macromolecules* **2000**, *33*, 2340.

[2] J. P. Hautekeer, S. K. Varshney, R. Fayt, C. Jacobs, R. Jerome, P. Teyssie, *Macromolecules* **1990**, *23*, 3893.