Electronic Supporting Information (ESI)

From spherical compartments to polymer films: exploiting vesicle fusion to generate solid supported thin polymer membranes

Myrto Kyropoulou, Saziye Yorulmaz Avsar, Cora-Ann Schoenenberger, Cornelia G. Palivan* and Wolfgang. P. Meier*

Department of Chemistry, University of Basel, Mattenstrasse 24a, BDR 1096, 4058, Basel, Switzerland

*Email: cornelia.palivan@unibas.ch and wolfgang.meier@unibas.ch

SH %	*PDI* PMOXA$_6$-PDMS$_{34}$-PMOXA$_6$	*PDI* PMOXA$_6$-PDMS$_{65}$-PMOXA$_6$
0	0.14 ± 0.03	0.21 ± 0.08
2.5	0.15 ± 0.11	0.11 ± 0.01
5	0.09 ± 0.07	0.19 ± 0.01
10	0.17 ± 0.09	0.13 ± 0.03
15	0.64 ±0.34	0.75 ± 0.12
20	1.2 ±0.41	1.5 ± 0.31

Table S1: Polydispersity indices of $A_6B_{34}A_6$ and A_6-$B_{65}A_6$ polymersomes with SH modification ranging from 0 – 20%

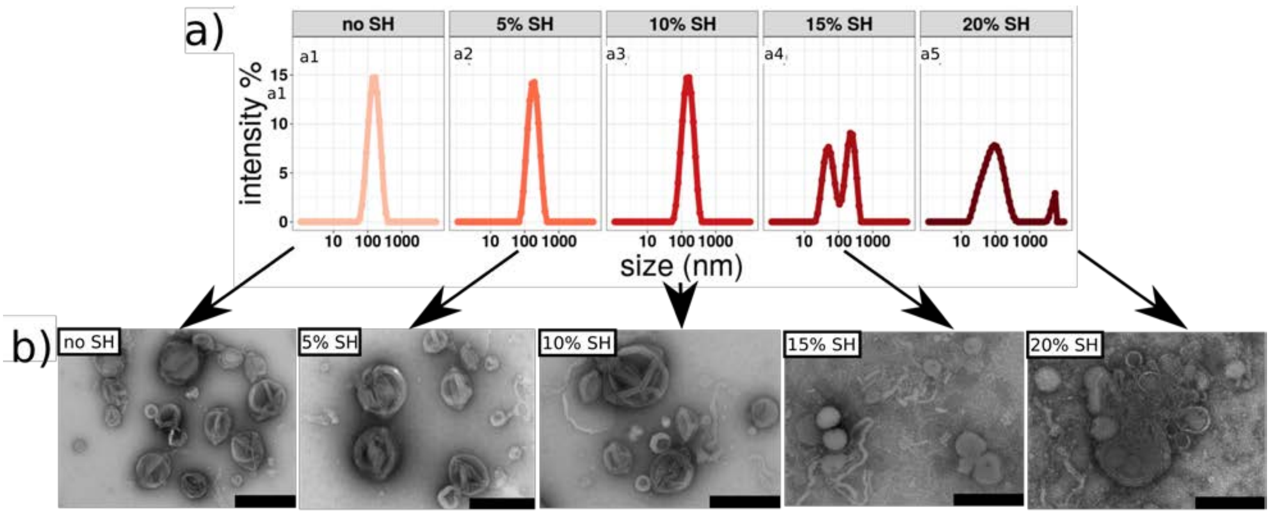

Figure S1: a) DLS graph and b) TEM micrographs of $A_6B_{65}PA_6$ containing: a1) 0 a2) 5% a3) 10% a4) 15% and a5) 20% SH bearing polymer, scale bar 100 nm

Estimation of SH bearing polymer chains per polymersome:

The 10 % ratio which we eventually used to mix PMOXA18-PDMS47-PMOXA18SH with PMOXAx-PDMSy-PMOXAx represents a molar ratio (please see the table below). Based on the molecular weight and concentration of the polymers used for self-assembly, and the concentration of the resulting polymersomes determined by Nanoparticle Tracking Analysis (NTA), we estimate the number of polymer chains per polymersome to be:

$$\text{Npolymerchains} = \frac{c\,N_A}{\text{Mn}\;c_{\,max}} = 5{,}19 \times 10^9 \text{ polymer chains per polymersome}$$

which at a ratio of 10% corresponds to around 5 x 108 thiol groups/polymersome for each type of polymersome.

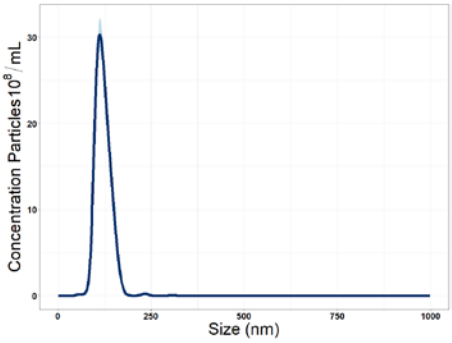

Figure S2: Measured NTA data of a 1:10000 diluted thiol-bearing PDMS-PMOXA-PDMS polymersomes

Polymer	Mn	$A_{18}B_{49}B_{18}SH$ / $A_xB_yA_x$	Estimated thiol-bearing polymer chains / polymersome
$A_3B_{22}B_3$	2274	10% mol	5 x 10^8
$A_6B_{34}B_6$	3672	10% mol	
$A_7B_{42}B_7$	4412	10% mol	
$A_6B_{44}B_6$	5122	10% mol	
$A_6B_{65}B_6$	6922	10% mol	
$A_{18}B_{49}B_{18}SH$	**6674**	-	-

Assuming a statistical incorporation of $PMOXA_{18}$-$PDMS_{47}$-$PMOXA_{18}SH$ during self-assembly, half of the thiols will be facing the polymersome interior and the other half (2.5 x 10^8) are exposed on the surface:

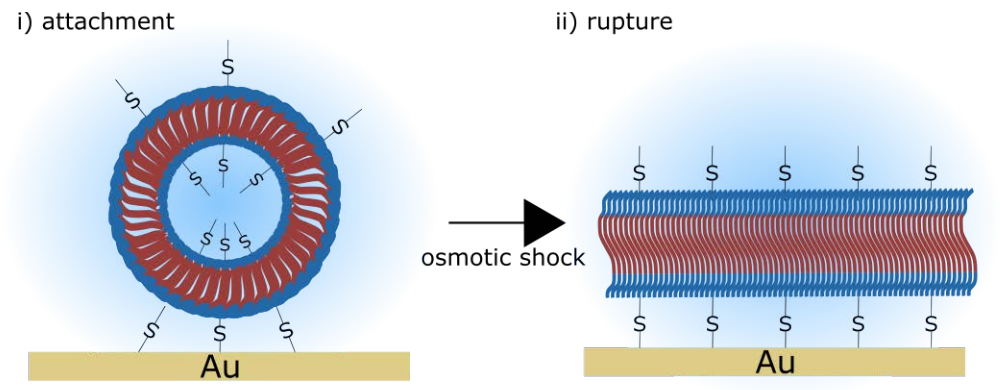

Figure S3: Schematic representation of i) polymersome attachment and ii) rupture on gold coated substrate

Based on the average diameter of the polymersomes (determined by NTA) we calculate the polymersome surface area to be:

$$\text{Polymersome surface area: } A = 4\pi r^2 \approx 0.14 \text{ nm}^2$$

and obtain ≈ 1.8 x 10^9 / nm^2 thiol-bearing chains per polymersome.

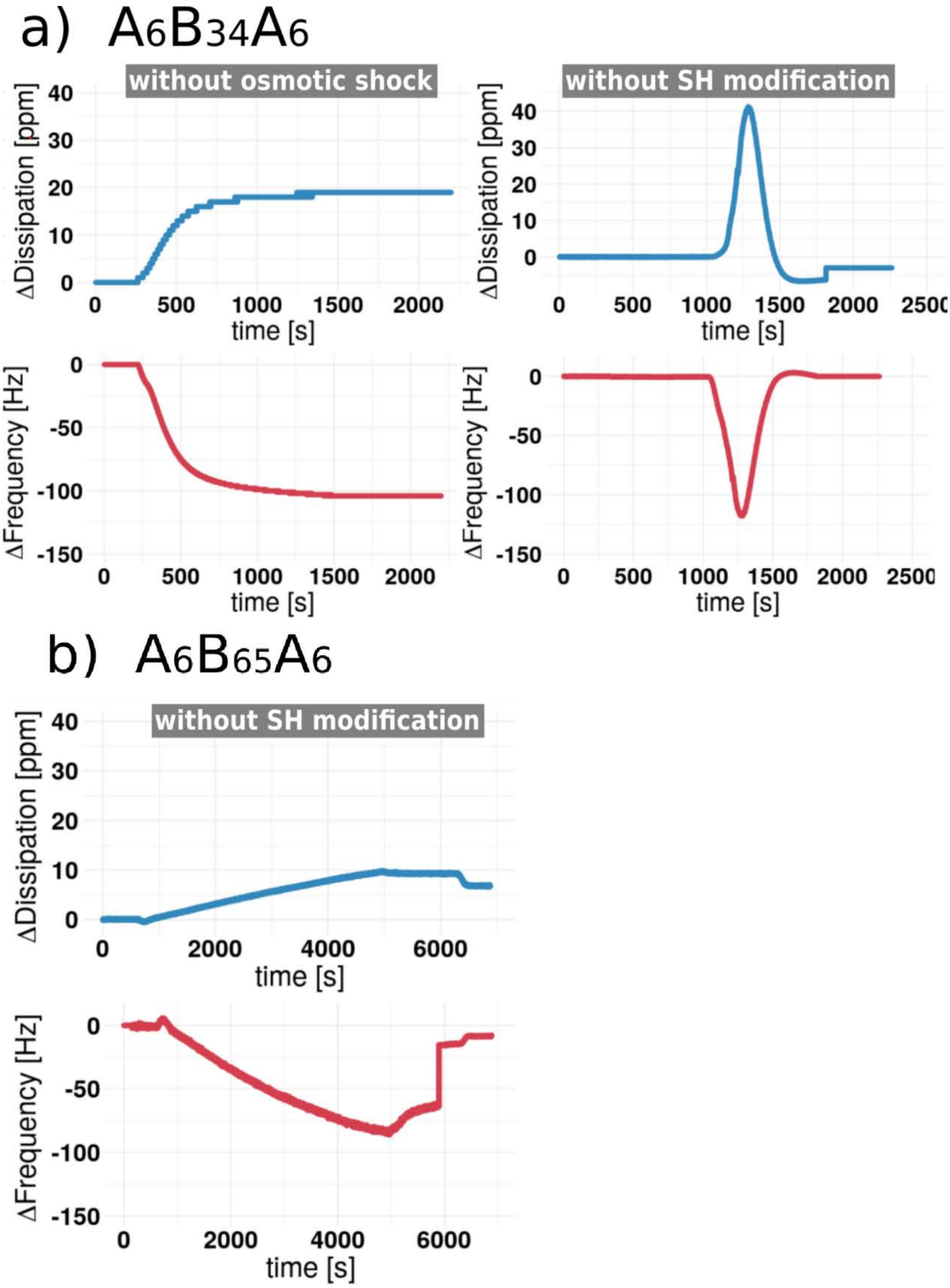

Figure S4: QCM-D frequency and dissipation shifts for a) $A_6B_{34}A_6$ polymersomes containing thiol-modification without osmotic shock (left) and without thiol-modification (right) and b) for $A_6B_{65}A_6$ without thiol-modification

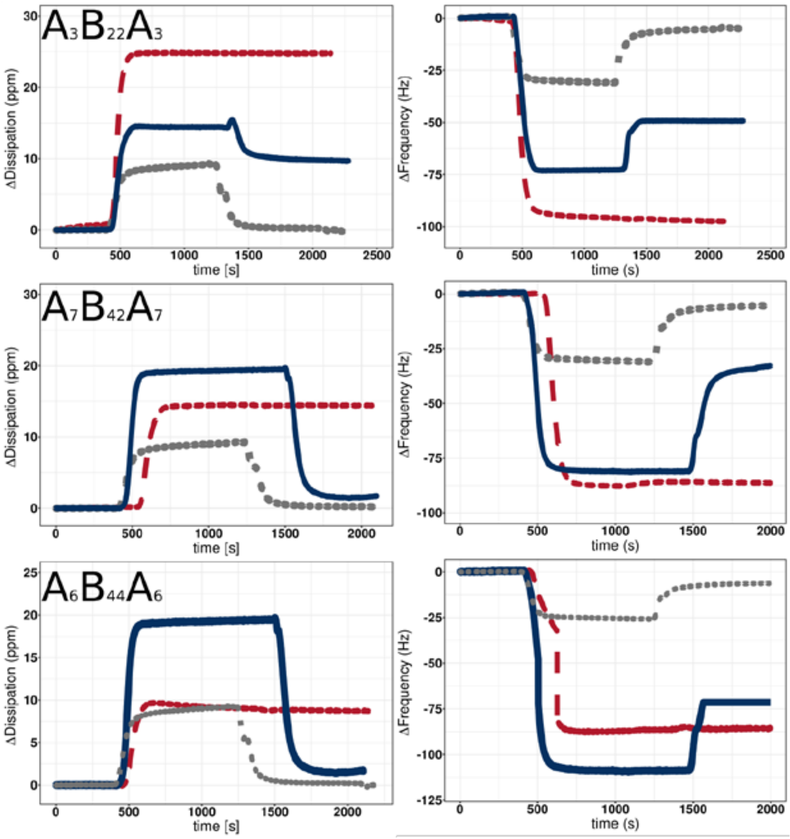

Figure S5:QCM-D measurement (5th overtone) of ABA polymersomes deposition on Au sensor: thiol modified polymersomes exposed on osmotic shock (blue solid line), thiol modified polymersomes without osmotic shock (red dashed line) and polymersomes without thiol modification (gray dotted line),

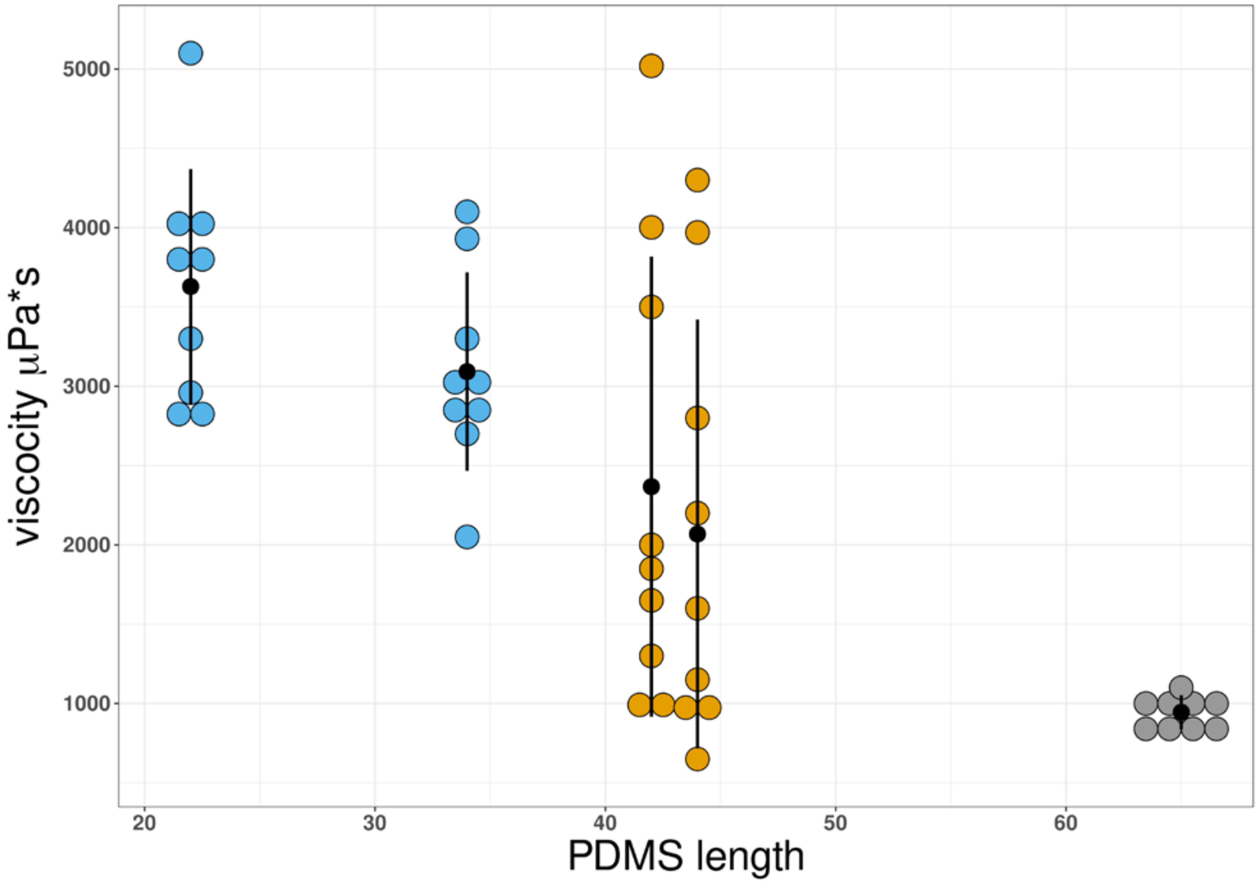

Figure S6: Viscosity of the thiol modified ABA polymersomes deposited on a Au QCM-D sensor after osmotic shock plotted as a function of PDMS length.

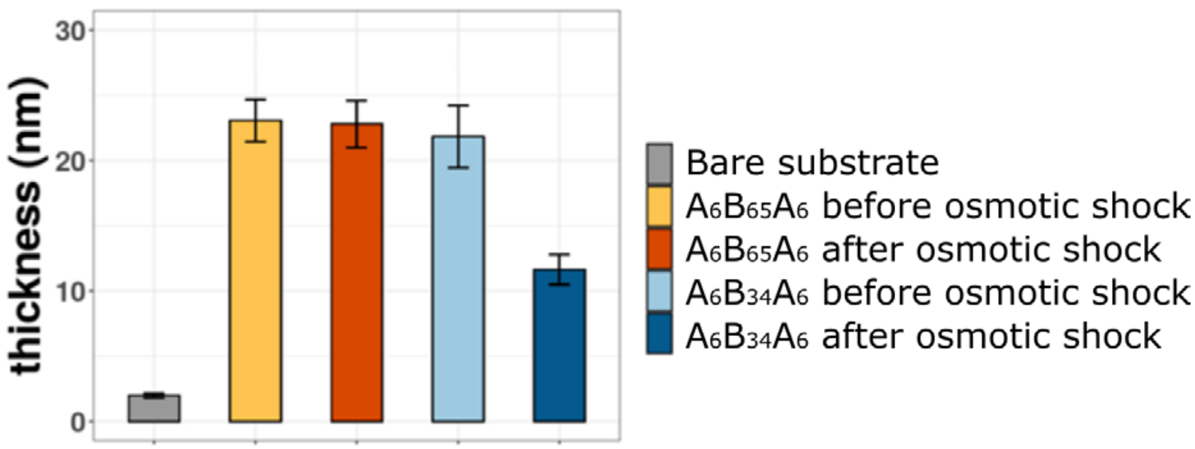

Figure S7: Thickness of the upper layer (nm) determined by spectroscopic ellipsometry for: empty gold coated silica(gray bar), $A_6B_{65}A_6$ polymersomes attached on the substrate before (yellow bar) and after (orange bar) the osmotic shock and $A_6B_{34}A_6$ polymersomes attached on the substrate before (light blue bar) and after (dark blue bar) the osmotic shock

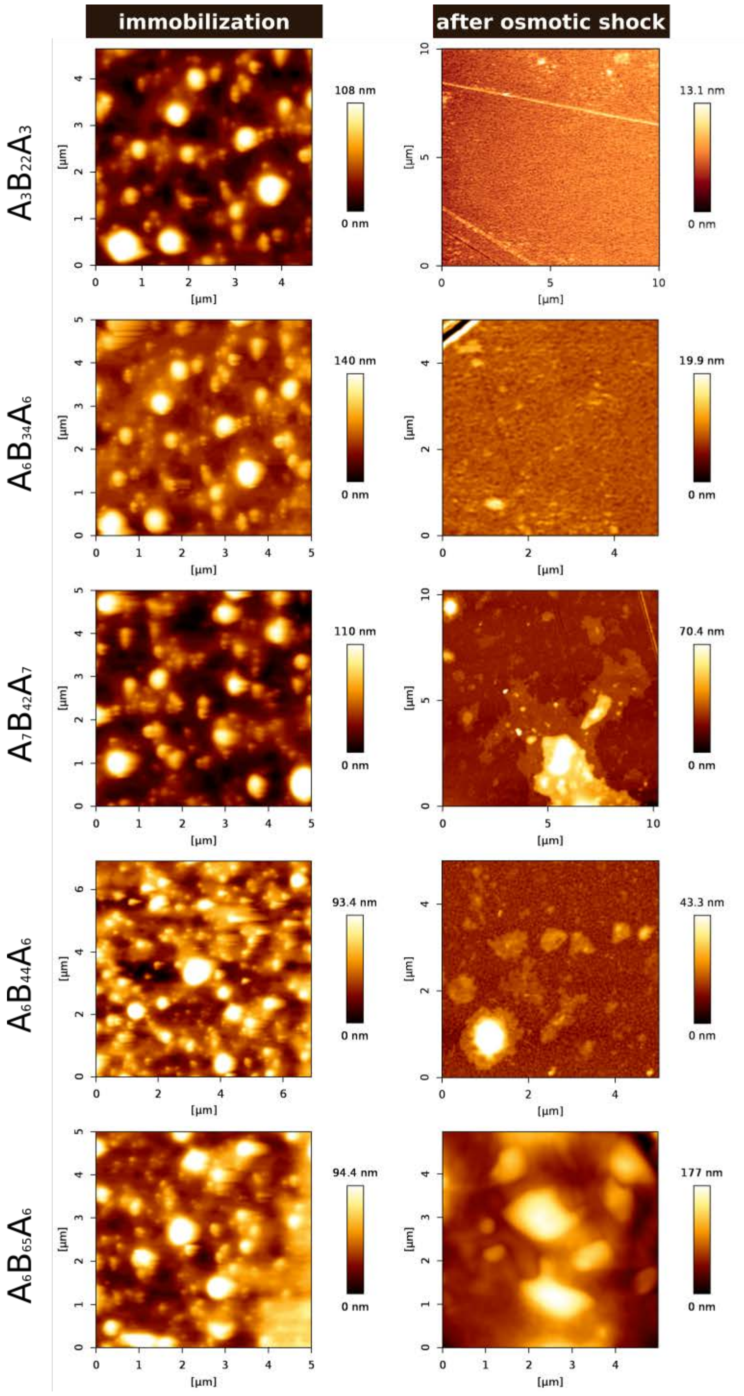

Figure S8 : Height channel AFM micrographs of thiol-modified ABA polymersomes immobilized on Au solid support (left) and after osmotic shock (right)

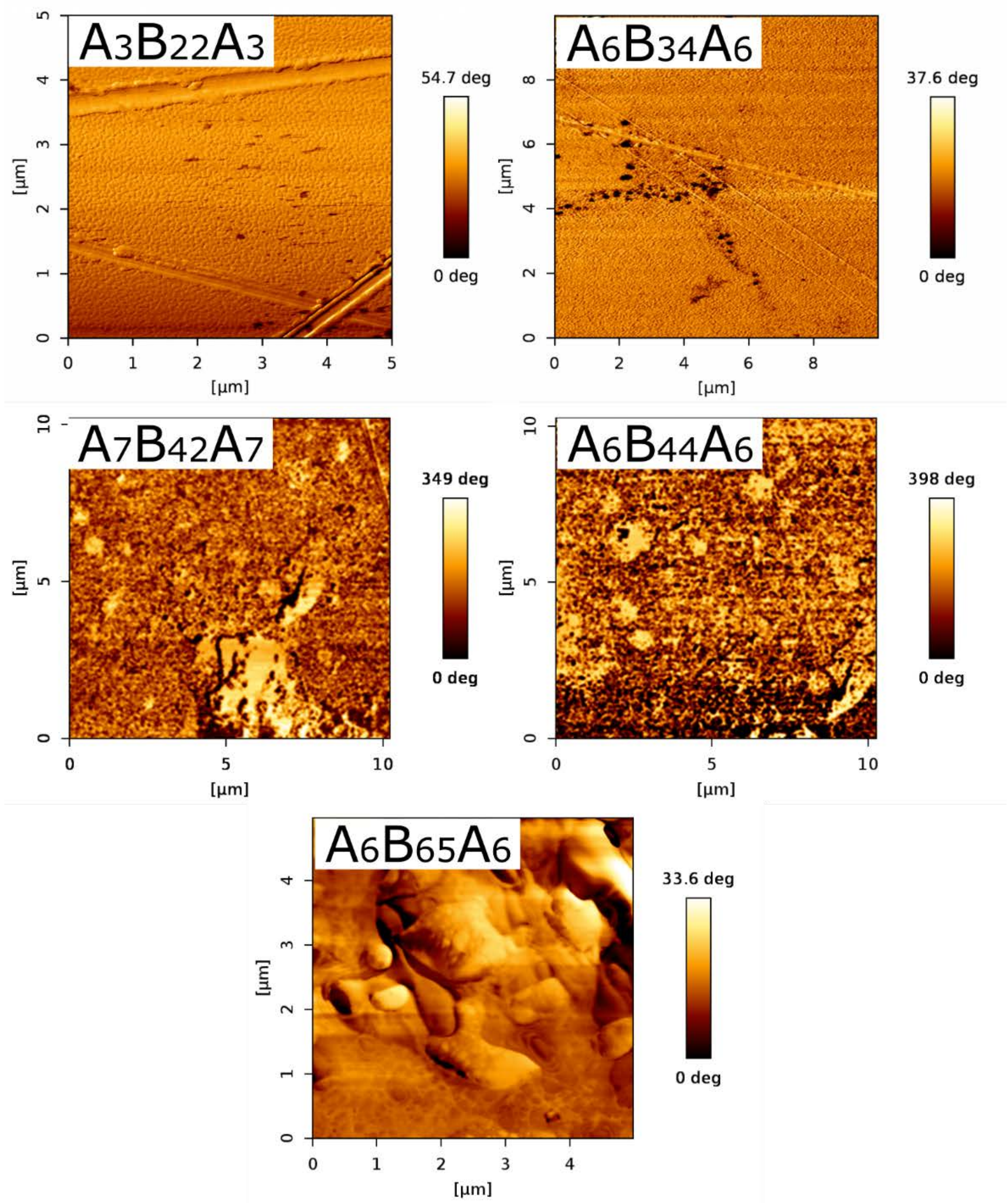

Figure S9: Phase channel AFM micrographs of thiol-modified ABA polymersomes after osmotic shock

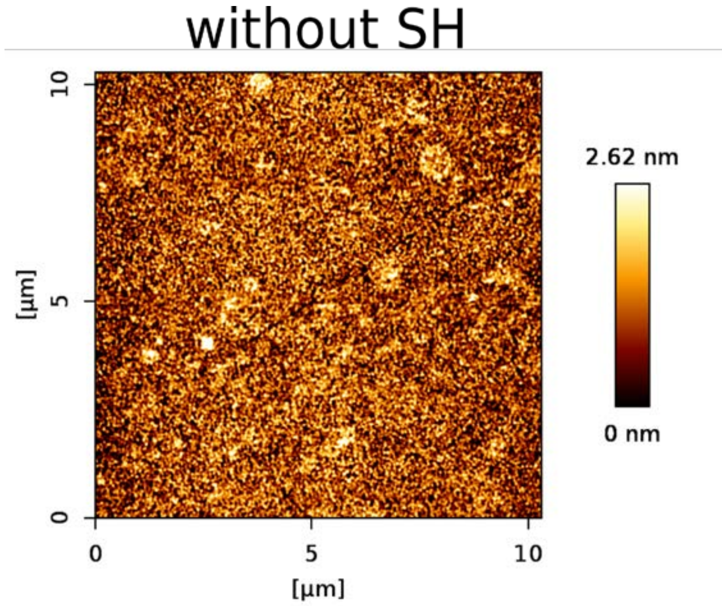

Figure S10: AFM micrograph of $A_6B_{34}A_6$ polymersomes without thiol-modification on Au solid support

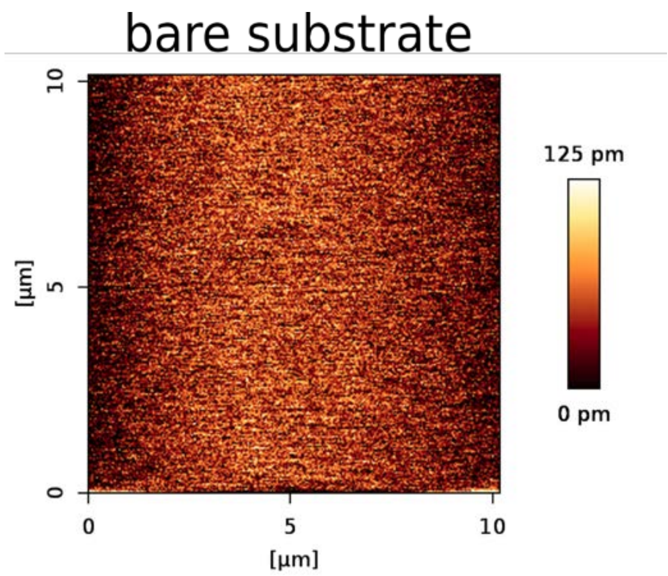

Figure S11: AFM micrograph of the bare Au solid support