

Terminal Groups Control Self-Assembly of Amphiphilic Block Copolymers In Solution

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Supplementary Information

Figure S1: Particle diameters of hydrated NH_2 -ABA- NH_2 polymers with different degree of functionalization;

Figure S2: Cryo-TEM characterization of compound micelles from BA-OH polymer after extrusion;

Figure S3: Cryo-TEM and stopped flow characterization of lipid vesicles;

Figures S4 and S5: NMR spectra for ABA and BA polymers

Figure S6: Large vesicles from carboxylated ABA polymer;

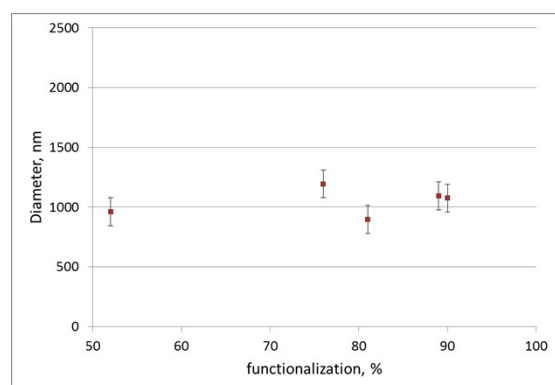
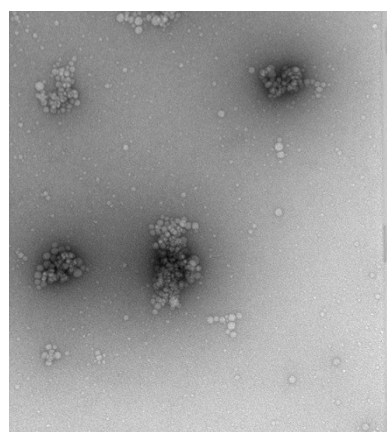


Figure S1. Particle diameters (after hydration, before extrusion) vs. functionalization degree for the NH_2 -ABA- NH_2 polymer at pH 7.



S2677_98d.tiff
S2677.post 0.4 um.40X
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11:55:52.19.15
TEM Mode: Imaging
100 nm
HV=80kV
Direct Mag: 130000x

Figure S2. A TEM image of compound micelles from the BA-OH polymer, after extrusion through a 400 nm membrane. The scale bar is 100 nm.

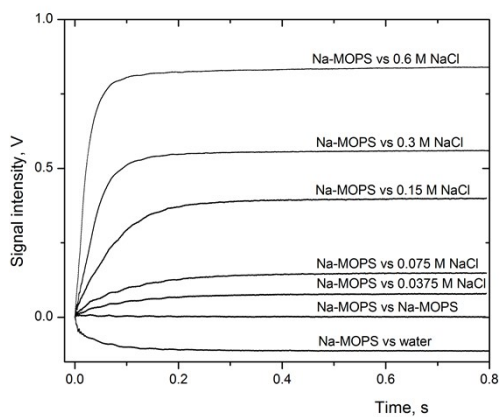
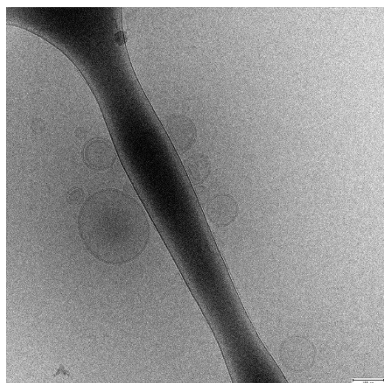


Figure S3. A cryo-TEM image of lipid vesicles (from *E. Coli* extract), scale bar 100 nm, top, and their corresponding stopped-flow traces, bottom, as a response to varied osmotic stress.

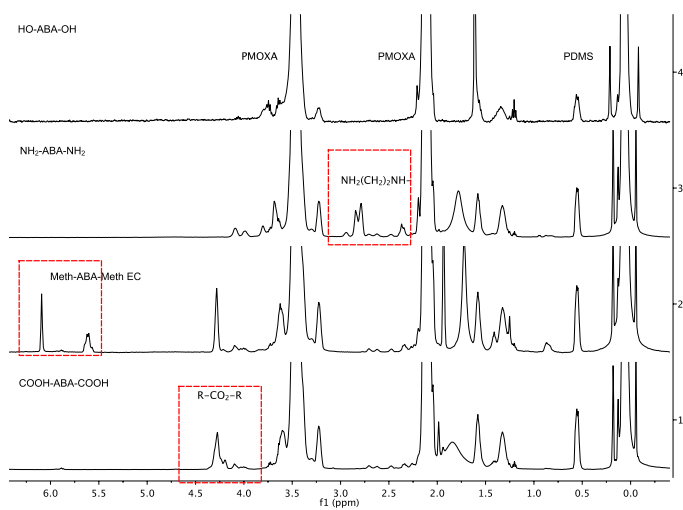


Figure S4. Proton (^1H) NMR of ABA polymers. PDMS: $\text{CH}_3\text{-Si}$ – 0 ppm, $\text{Si-CH}_2\text{-CH}_2$ - 0.5 ppm, $\text{Si-CH}_2\text{-CH}_2$ - 1.4 ppm, PMOXA - $\text{N-CH}_2\text{-CH}_2$ - 3.6 ppm, $-\text{CO-CH}_3$ - 2.1 ppm. End groups: $-\text{NH-CH}_2\text{-CH}_2\text{-NH}_2$ - 2.8 ppm, methacrylate - 5.5, 6.0 ppm, $\text{R-CO}_2\text{-R}$ - 4.2 ppm.

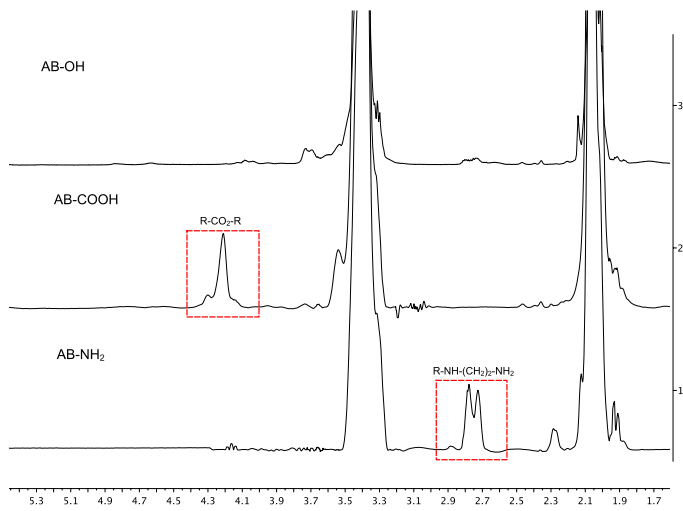


Figure S5. Proton (^1H) NMR of AB polymers. PDMS: $\text{CH}_3\text{-Si}$ - 0 ppm, $\text{Si-CH}_2\text{-CH}_2$ - 0.5 ppm, $\text{Si-CH}_2\text{-CH}_2$ - 1.4 ppm, PMOXA - $\text{N-CH}_2\text{-CH}_2$ - 3.6 ppm, -CO-CH_3 - 2.1 ppm. End groups: $\text{-NH-CH}_2\text{-CH}_2\text{-NH}_2$ - 2.8 ppm, $\text{R-CO}_2\text{-R}$ - 4.2 ppm.

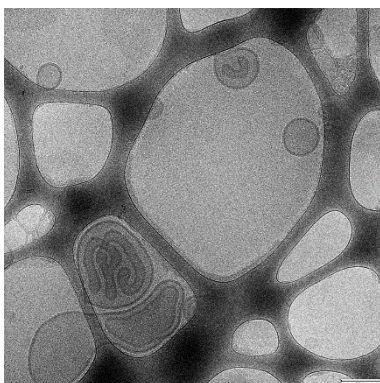
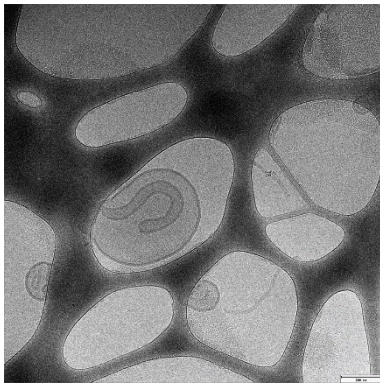


Figure S6. cryo-TEM images of carboxylated ABA polymer. Top: before extrusion, bottom: after extrusion through an 800 nm membrane. Both images show the membranes folding over on themselves due to the large size of aggregates and the measurement conditions of cryo-TEM (scale bars: 200 nm).