Submitted to small NANO MICRO

Supporting Information

Electrostatic Control of Structure in Self-Assembled Membranes

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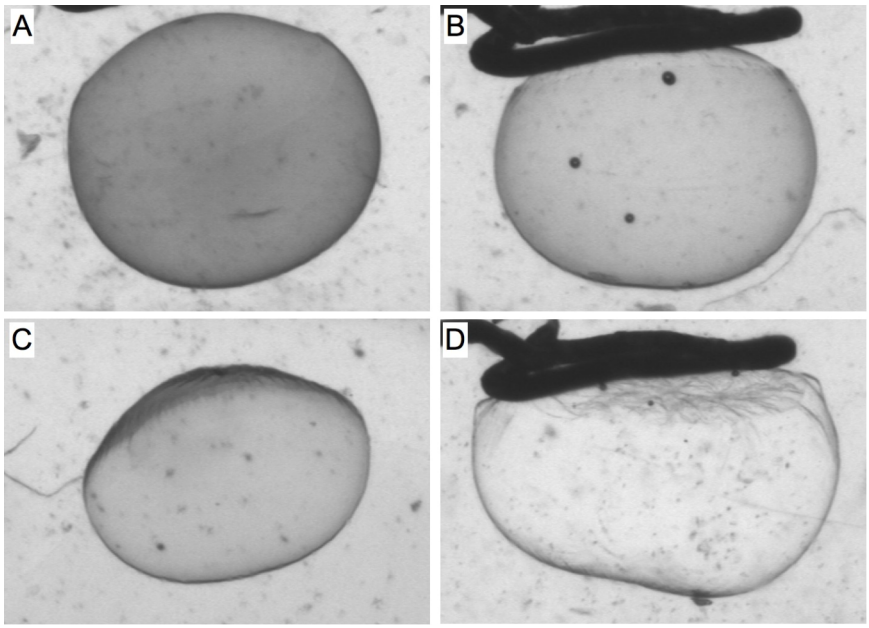

Figure S1. Representative images of HA/HBPA sacs self-assembled with (A) 0 wt% heparin, (B) 0.1 wt% heparin, (C) 0.25 wt% heparin, and (D) 0.5 wt% heparin.

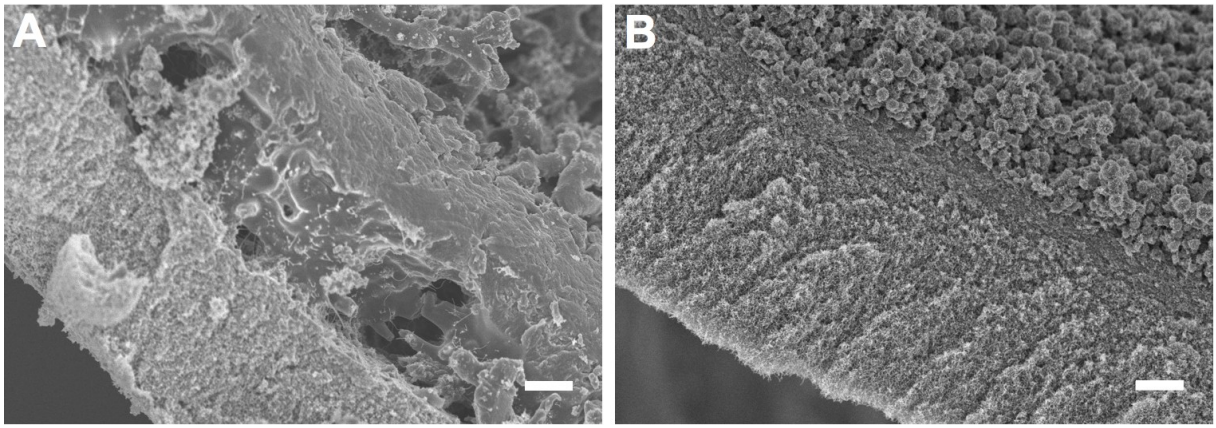

Figure S2. Scanning electron micrographs of membrane cross-sections of HA/HBPA sacs self-assembled with (A) 0.1 wt% heparin and (B) 0.25 wt% heparin (scale bar = 5 μm).

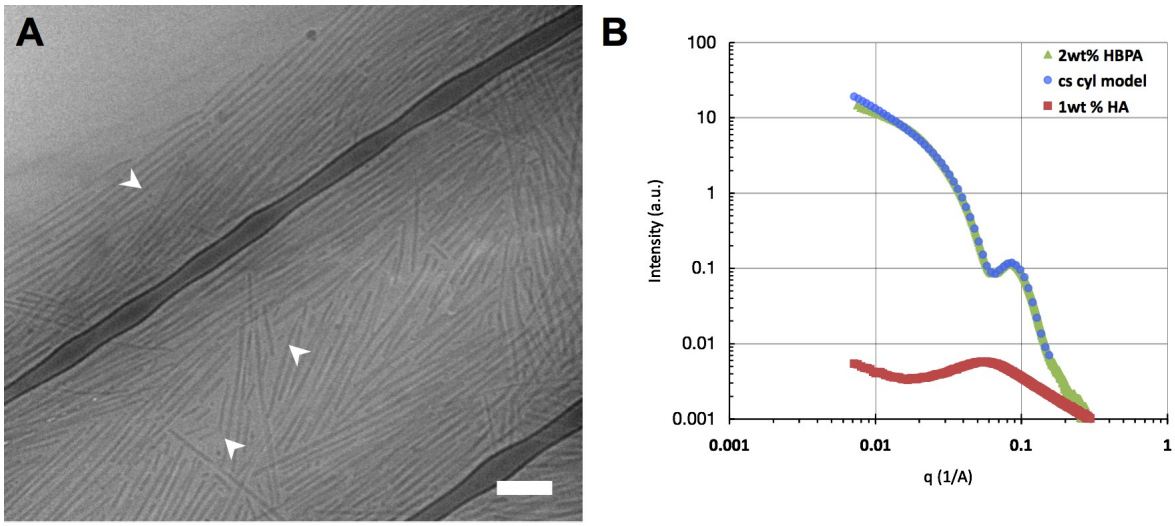

Figure S3. (A) Cryogenic transmission electron micrograph of an aqueous solution of 2 wt% HBPA. Arrows indicate spherical micelles and smaller aggregates found with the expected cylindrical micelle morphology. Scale bar = 100 nm. (B) Fitting of polydisperse core-shell cylinder model to HBPA scattering profile indicates a core radius of 16.3 Å, shell thickness of 44.5 Å, polydispersity of 0.3, and scattering length density of $8.6e^{-6}$ $Å^{-2}$ and $1.2e^{-5}$ $Å^{-2}$ for the core and shell respectively. The cylinder dimensions are in line with cryo-TEM results and previously reported PA SAXS data.[23] The SLDs obtained are reasonable for a palmitic acid tail and amino acids. However, it should be noted that a cylindrical core-shell model with a gradient in the electron density of the shell should be ideally be used, but the electron density of the highly hydrated outer PA headgroup is similar to that of the solvent. Therefore, a simpler core-shell model was used, and thus the shell thickness and SLD values obtain should not be considered completely accurate.

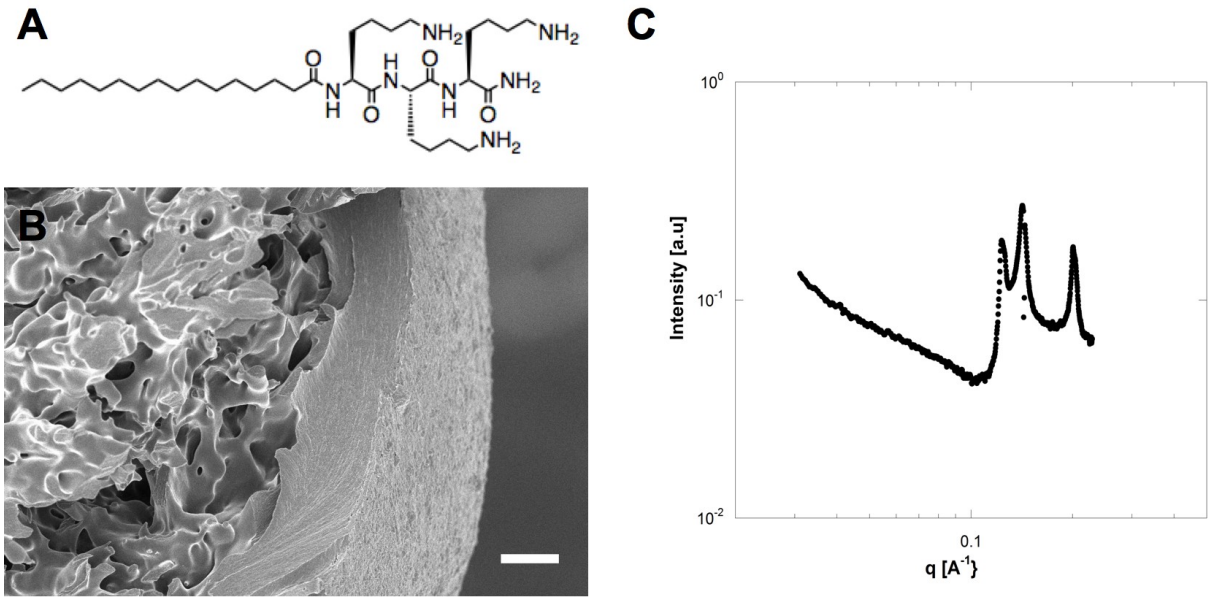

Figure S4. (A) Schematic of a PA with the sequence C16KKK, and (B) the scanning electron micrograph of the cross-section of a membrane made with HA and this KKK PA (scale bar = 5 μm). (C) SAXS scattering of this KKK PA/HA membrane.

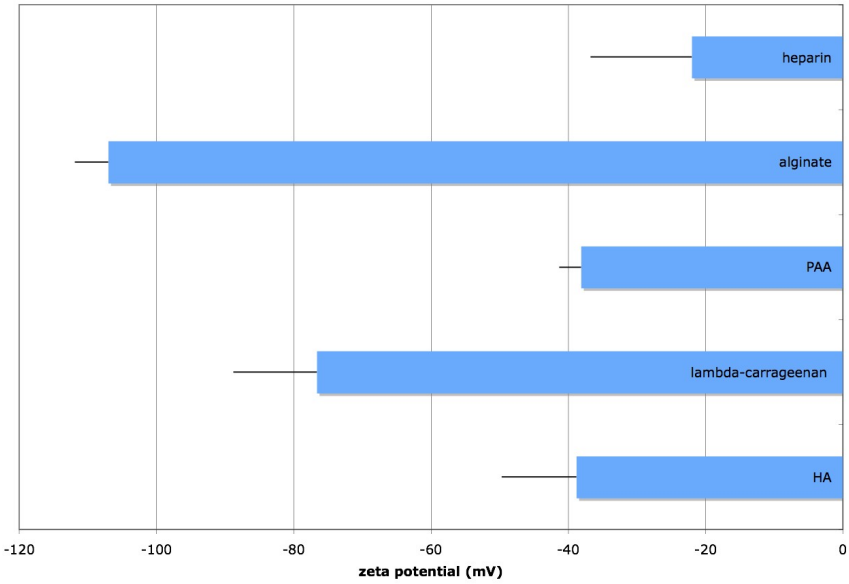

Figure S5. Zeta potential measurements of poly(acrylic acid), alginate, λ-carrageenan, hyaluronic acid, and heparin in milliQ water.

Modeling of small angle scattering patterns

The scattering intensity of a monodispersed system of particles of identical shape can be described by equation S1:

$$I(q) = NP(q)S(q)$$

where N is the number of particles per unit volume, P(q) is the form factor revealing the specific size and shape of the scatterers and S(q) is the structure factor that accounts for the interparticle interactions. In dilute solutions, where the interactions between the objects can be neglected, S(q) is equivalent to 1. In a polydisperse system of particles having identical shapes, the total intensity scattered can be described by equation S2:

$$I(q) = N\int_0^\infty D_n(R)P(q,R)dR$$

where $D_n(R)$ is a distribution function and $D_n(R)dR$ is the number of particles, the size of which is between R and R + dR, per unit volume of sample.

A form factor for a simple polydisperse core-shell cylinder where the core and the shell have a uniform electron density is given by equation S3:

$$P(q) = \int_0^{\pi/2} \sin\theta \cdot d\theta \cdot \left[V_l(\rho_l - \rho_{solv}) \frac{\sin\left(\frac{qH_l\cos\theta}{2}\right)}{\frac{qH_l\cos\theta}{2}} \frac{2J_1(qR_l\sin\theta)}{qR_l\sin\theta} + V_p(\rho_p - \rho_l) \frac{\sin\left(\frac{qH_p\cos\theta}{2}\right)}{\frac{qH_p\cos\theta}{2}} \frac{2J_1(qR_p\sin\theta)}{qR_p\sin\theta} \right]^2$$

$$V_x = \pi R_x^2 H_x$$

where $J_1(x)$ is the first order Bessel function. Theta is defined as the angle between the cylinder axis and the scattering vector, q. R_p and R_l are the core and shell radii respectively, H_p and H_l are the core and shell lengths, and r is electron density.

The polydispersity of the core radius is modeled using a log-normal distribution given by equation S4:

$$D_n(R_p) = \frac{\exp\left(-\frac{1}{2}\left[\frac{\ln\left((R_p/R_0)\right)}{\sigma_p}\right]^2\right)}{\sqrt{(2\pi)}\sigma_p R_p}$$

where R_0 is the mean core radius and σ is equivalent to the standard deviation of the log-normal distribution.

The crystallite size is calculated according to equation S4:

$$L = \frac{\lambda}{\beta_\theta \cos\theta}$$

where β_s is the full width at the half-maximum intensity of a peak (in radians) observed at a mean scattering angle of 2θ (E.V. Shtykova, et. al, *J. Appl. Crystallogr.* **2003**, *36,* 669).