Supporting Information

Synthesis of non-spherical microcapsules through controlled polyelectrolyte coating of hydrogel templates

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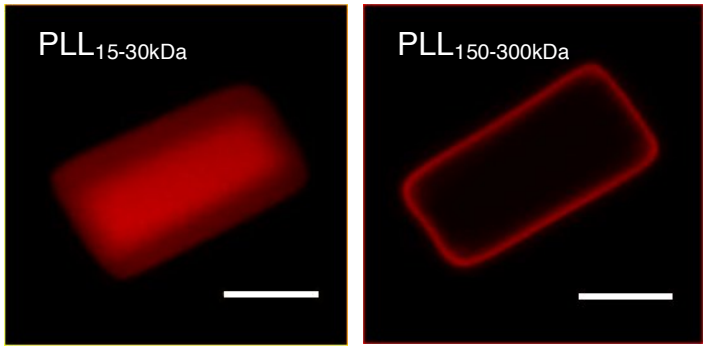

Figure S1. Effect of PLL molecular weight on diffusion into PEGDA-AAc particle. Low molecular weight Cy5-PLL (M_v = 15-30 kDa) diffuses through the hydrogel particle, while high molecular weight Cy5-PLL (M_v = 150-300 kDa) forms a thin shell of uniform thickness on the outer edge of the particle (pH = 7, ionic strength = 0.5 M NaCl) Scale bars are 20 μm.

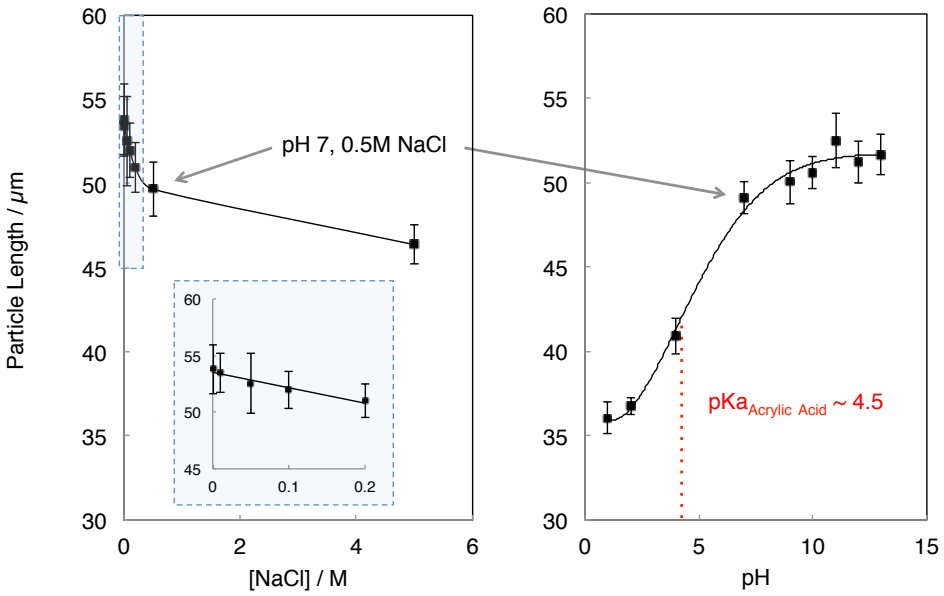

Figure S2. Swelling of PEGDA-AAc particles under different pH and ionic strength conditions. PEGDA-AAc particles with expected length of ~30 μm (approximate channel height) are immersed in different solutions for 1.5 hours before imaging. Particles show a variation in length of up to 44% in different pH and ionic strength solutions, N=10 (error bars show standard deviation). Particle size decreases with increasing ionic strength due to increased charge screening of negative charges. Particle size increases as pH increases due to increasing charge density. The black line is a fit to the data and shows the largest slope around the pKa of acrylic acid (~4.5), plateauing at high pH values.

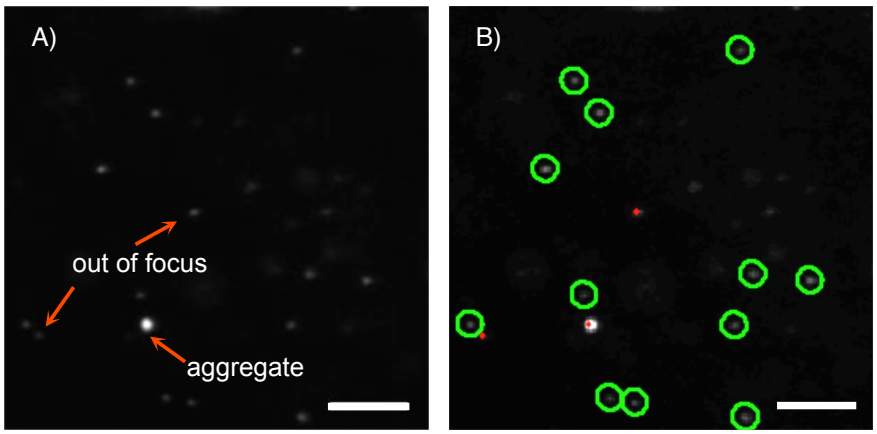

Figure S3. Particle tracking of 200nm YG carboxy polystyrene beads embedded in hydrogel matrix. A representative still image from a video used for particle tracking (12 hour time point) (A). Tracking was performed using a public-domain MATLAB algorithm written by Kilfoil and coworkers. The algorithm identifies appropriate particles in each video frame, disregarding aggregated or out of focus beads (B) and averages the particle trajectories to obtain mean-square displacements, which are plotted in Figure 5. Green circles indicate selected in-focus particles, while red dots indicate particles that are not counted due to failure to meet intensity, shape or size criteria set in the MATLAB program. Scale bars are 5 μm.

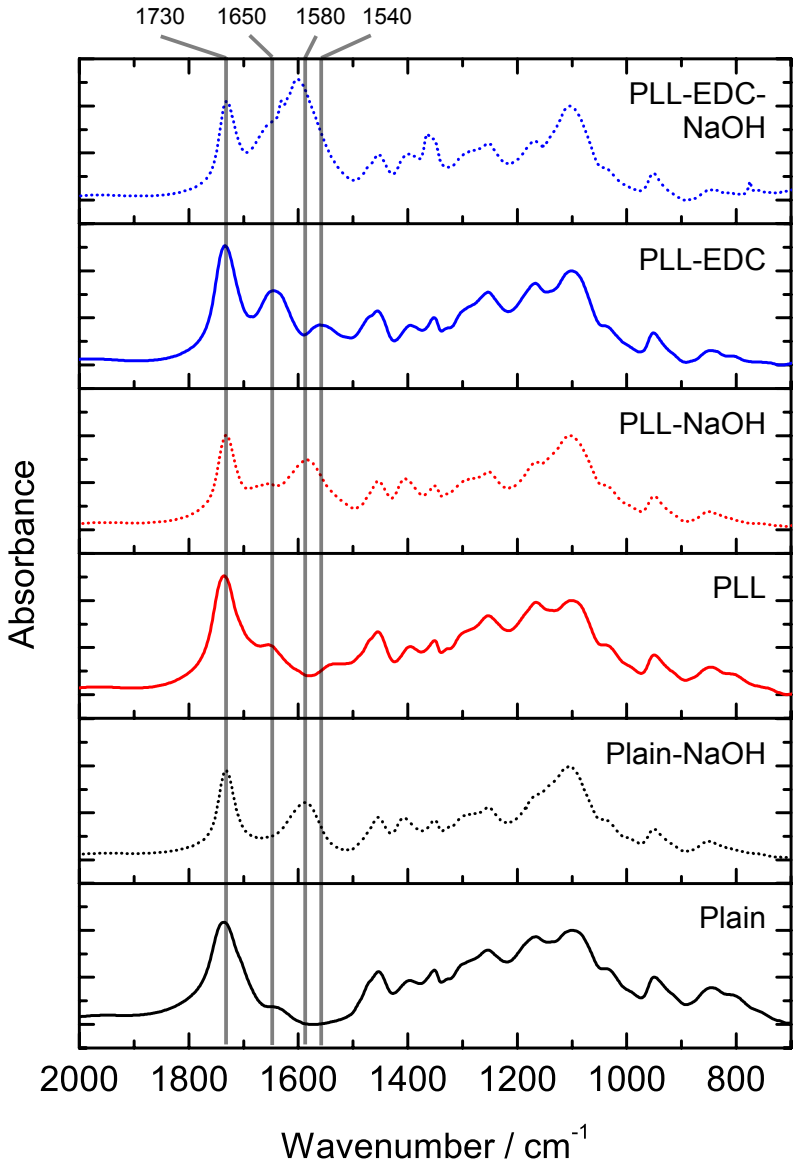

Figure S4. FTIR of bulk hydrogel samples. All samples show characteristic C=O stretch at 1730 cm^{-1} of carboxylic acid/ester groups present in PEGDA-AAc before hydrolysis. After immersion in 0.9 M NaOH overnight (all samples labeled with –NaOH), this peak shrinks, and a peak corresponding to the COO^- asymmetric stretch appears at 1580 cm^{-1}, due to hydrolysis of ester bonds in the PEGDA-AAc hydrogel. Characteristic amide I and II peaks at 1650 cm^{-1} and 1540 cm^{-1}, respectively, are most obvious in the sample containing PLL with EDC activation, indicating significant formation of amide bonds for samples that have undergone EDC activation. The FTIR spectra are consistent with the proposed mechanism that a very small amount of amide linkages are formed when PLL-containing PEGDA-AAc hydrogels are incubated in very basic environments. All plots have been normalized to the peak at 1100 cm^{-1} corresponding to the C-O-C stretch from the poly(ethylene glycol) backbone.

Table S1. Particle/capsule dimensions during and after template removal. The length and width of particles are compared to the photomask during template removal (immersion in 0.9 M NaOH) from image analysis. Particles are swollen in PBS due to their negative charge. Particles increase in size after 15 hours in 0.9 M NaOH due to osmotic pressure during particle degradation. The particles start to decrease in size when degradation products diffuse through the capsule and reach the original mask size after 6 days in 0.9 M NaOH. N = 9, indicated widths and lengths are averages ± standard deviation.

	Width (μm)	**Length (μm)**	**Area (μm^2)**	**Particle Area/ Mask Area (rounded to nearest tenth)**
Mask	63	89	5600	--
PBS	73 ± 4	110 ± 3	8000	1.4
NaOH 15 hrs	86 ± 6	130 ± 9	11200	2.0
NaOH 4 days	67 ± 3	100 ± 4	6700	1.2
NaOH 6 days	60 ± 4	90 ± 7	5400	1.0

Video S1. Diffusing polystyrene beads in microcapsule. 200nm diameter carboxylate polystyrene beads diffuse within the microcapsule after degradation of the hydrogel in 0.9 M NaOH. Beads are initially static within the intact particle (10 min NaOH). Capsules remain intact and hold beads for more than 16 days in 0.9 M NaOH. Videos were taken using an Andor Clara camera at 3 fps, played back at 6 fps and looped four times.

Video S2. Microcapsules deform and recover shape. A rectangular capsule (after 9 days in 0.9 M NaOH; dimensions: 63 μm wide x 83 μm long x 58 μm tall) flows through a microfluidic contraction (dimensions: 30 μm wide x 300 μm long x 60 μm tall). Flow is driven by a small hydrostatic pressure and flow rate is less than 10 μl/min. Video was taken using a Nikon D7000 camera at 30 fps, played back at 3 fps.