# Supporting Information

## Single-step microfluidic fabrication of soft monodisperse polyelectrolyte microcapsules by interfacial complexation

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### *Materials*

Fluorescently labeled chitosan (KITO-2, MW 50,000 - 190,000, Polyscitech) and Polystyrene-block-poly(ethylene-ran-butylene)-block-polystyrene (s-SEBS,29 wt% styrene,55-56% sulfonated, Sigma Aldrich) were used as polyelectrolytes in the aqueous and organic phase, respectively. Toluene (Sigma Aldrich) served as organic solvent for SEBS.

### *Capillary Microfluidics*

Briefly, two tapered cylindrical capillaries with outer diameter of 1 mm were inserted into opposite ends of a square capillary with an inner diameter of 1.05 mm. Droplets were generated with the dispersed phase injected through one of the tapered capillaries as shown in Figure 1a. In practice, to fabricate aqueous-core capsules, we inject the aqueous phase containing a water soluble polyelectrolytes as the inner dispersed phase and flow the oil phase containing oil soluble polyelectrolytes with opposite charge around through the capillary interstice. Droplets exit through the interior of the opposing capillary.

### *Confocal Imaging*

The sample chamber was assembled as follows: silicone square chambers (Lab-Tek Chamber Slide 177445) were placed onto glass coverslip (Fisher, No. 1.5, 24mm x 60mm) and 20µL of sample with capsules were pipetted in the center of each square. The chamber was then covered with another coverslip (VWR, No. 1.5, 18mm x 18mm) and placed on the microscope for imaging.

Images of capsules were acquired with an Andor Revolution spinning-disk confocal system, Andor Technology, on an inverted Nikon Eclipse Ti microscope. A 40x Plan Fluor oil-immersion objective with a numerical aperture of 1.3 was used. Capsules were imaged with a 491nm laser at 30% power and a 525nm emission filter. Images were acquired with an iXon

EMCCD camera with a 1024x1024 pixel resolution using a 500ms exposure time and a gain of 100.

We measured the diameter of 2.0 μm size carboxylate-modified fluorescently labeled silica beads (Life Science) on a cover slip and in capsules shell as shown in Figure S3

***Confocal images Analysis***

Capsule images were processed with a customized Matlab code. An example of a typical image is shown in Fig. S3A. The user manually selected 25 points along the wall of the capsule of interest (Fig. S3B) and an arc was fitted to the selected points (Fig. S3C). Using the fitted center and radius, radial line segments were drawn, 6.4μm long with the midpoint at the microcapsule wall. The lines were spaced 0.2 degrees apart. Intensity profiles along those lines were plotted and averaged in groups of 15 (Fig. S3D). The resulting profile was then fitted to a Gaussian (Fig. S3E). The thickness of that section of the capsule was taken as the full-width at half-maximum of the Gaussian profile. The arithmetic mean of all of the section thicknesses in the given capsule was taken to be the capsule thickness. For each experimental condition, 7-10 capsules were measured. The mean of the thicknesses of those capsules was reported as the wall thickness for the given condition. The standard deviation of the thicknesses was reported as the uncertainty or error bar for each condition.

To estimate the spatial resolution of our imaging system we acquired 73 images of 100 nm diameter fluorescent particles and fit their images to Gaussian profiles. An example image and fit are shown in Figure S4. A histogram of all FWHM is shown in Figure S5. The tail of the distribution is likely due to aggregated particles. The peak is at 650nm. This confirms that shell thickness measurements do not suffer from diffraction limitations.

***Capsule Micromechanics by Transit Pressure Characterization***

The deformability of SEBS-Chitosan microcapsules was characterized based on pressure driven flow of microcapsules through a tapered capillary. The experimental setup, shown in Figure S4, consists of a capillary tapered to 122 um at a taper angle of 7º, tubing, mineral oil bath, and ultra low pressure regulator (equilibar LPR2). The capillary is connected to the pressure regulator using soft tubing from the untapered side and inserted into a mineral oil bath. The capsules are loaded into the capillary using a micropipete and flow towards the tapered part of the capillary by applying a pressure in the range of 0 to 500 Pa. The pressure was increased in steps of 25 Pa with 90 seconds equilibration time between each step.

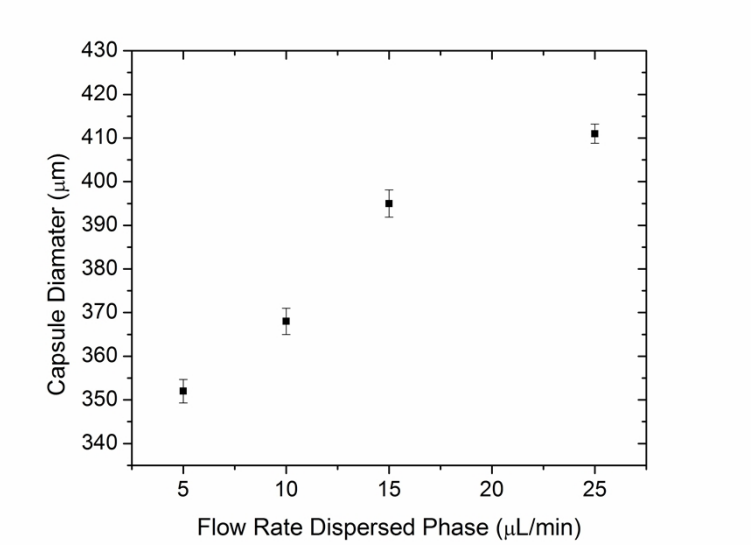


**Figure S1.** (a) The effect of dispersed fluid rate flow rate on capsule diameter. The outer fluid flow rate was held constant at 80 μl/min.

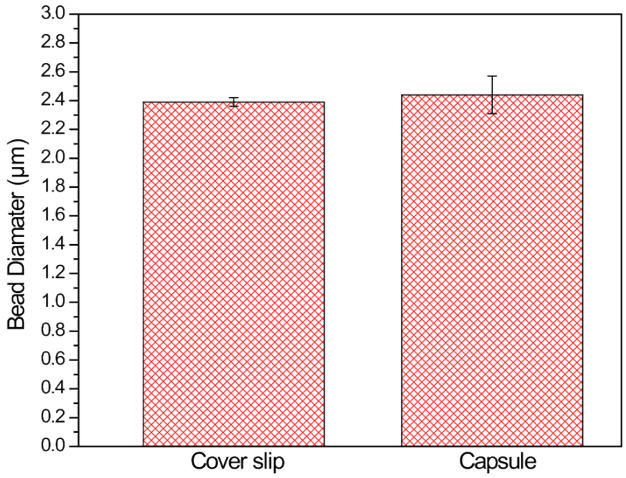


**Figure S2**. Size of Carboxylate-modified fluorescently labeled silica beads imaged on a cover slip and in the capsule shell. Capsules prepeared using 0.1 wt.% polymer solution, aqueous ph 2.7, and 0.04 wt.% beads in the aqueous phase.

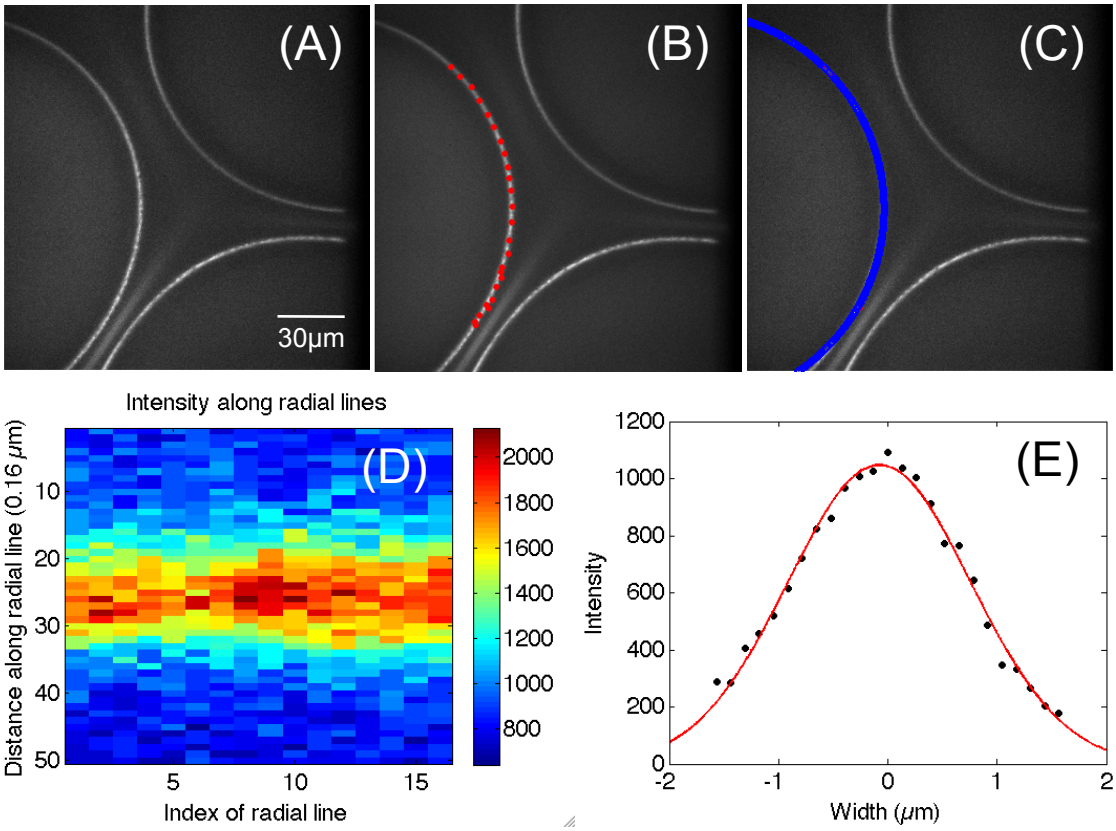


**Figure S3**. An example of analysis of confocal image of microcapsules to determine shell thickness. A) Confocal Image of Microcapsules. B) 25 Points are chosen along the capsule wall. C) Fitting an Arc to selected points D) Intensity profiles of average of radial lines drawn along the arc. E) Gaussian fitted to intensity profile.

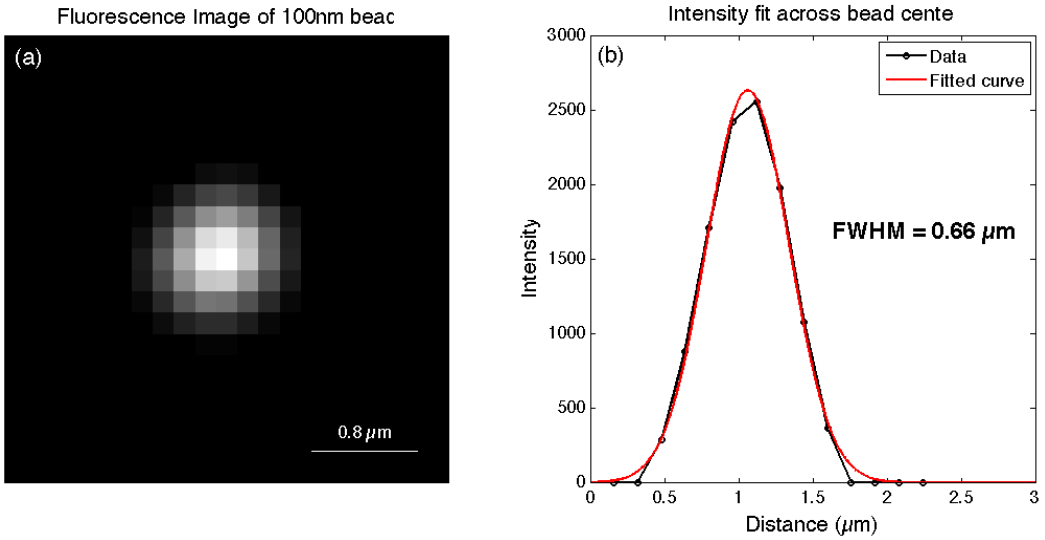


**Figure S4.** (a) Example image of a 100nm diameter bead acquired under the same imaging conditions as microcapsules. (b) Intensity profile along a line across the diameter of the bead fitted with a Gaussian.

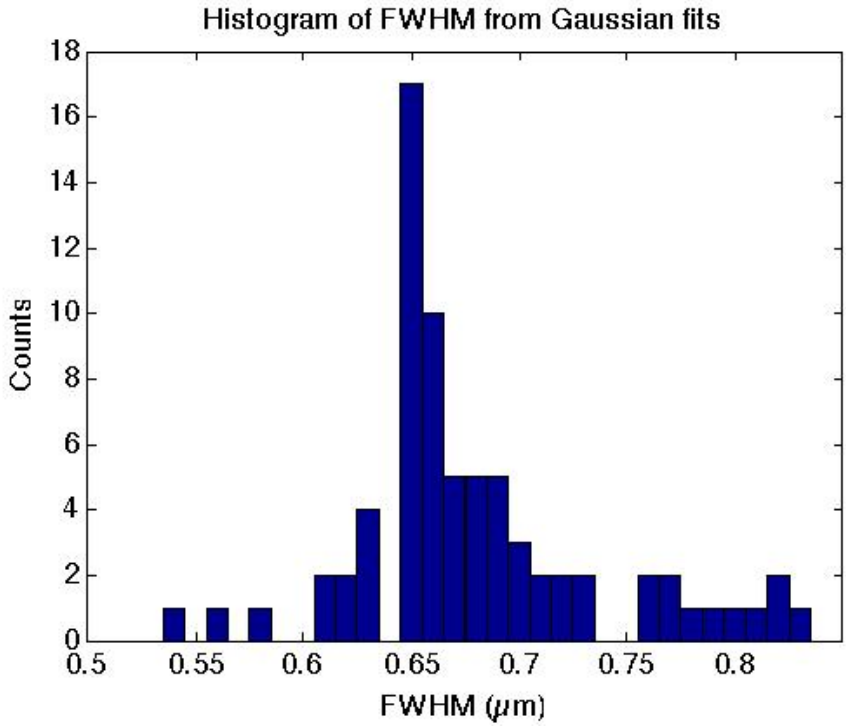


**Figure S5.** Histogram of full width at half maximum (FWHM) from Gaussian fits to profiles as in the example image (Fig. S4). Histogram includes FWHM from 73 beads.

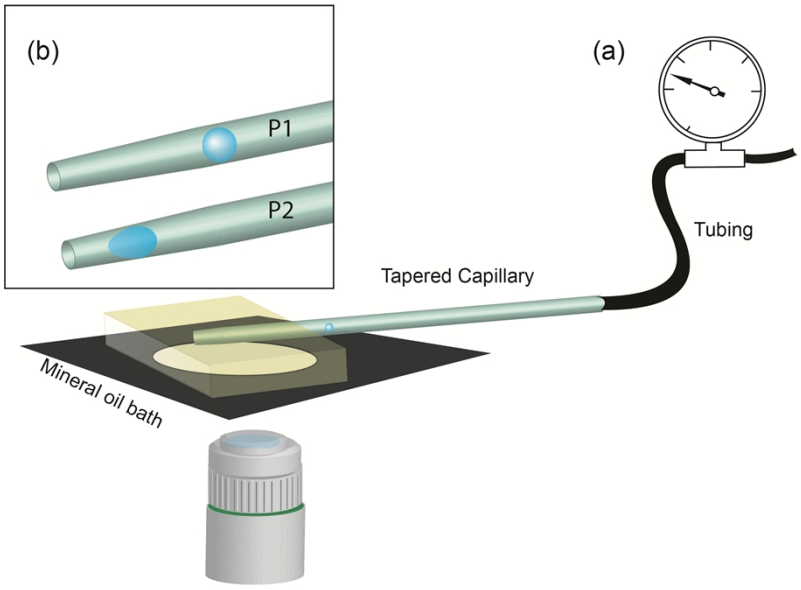


**Figure S6.** (a) Experimental setup for micromechanics experiments. (b) The microcapsule deforms in the tapered capillary as the pressure is increased from P1 to P2.

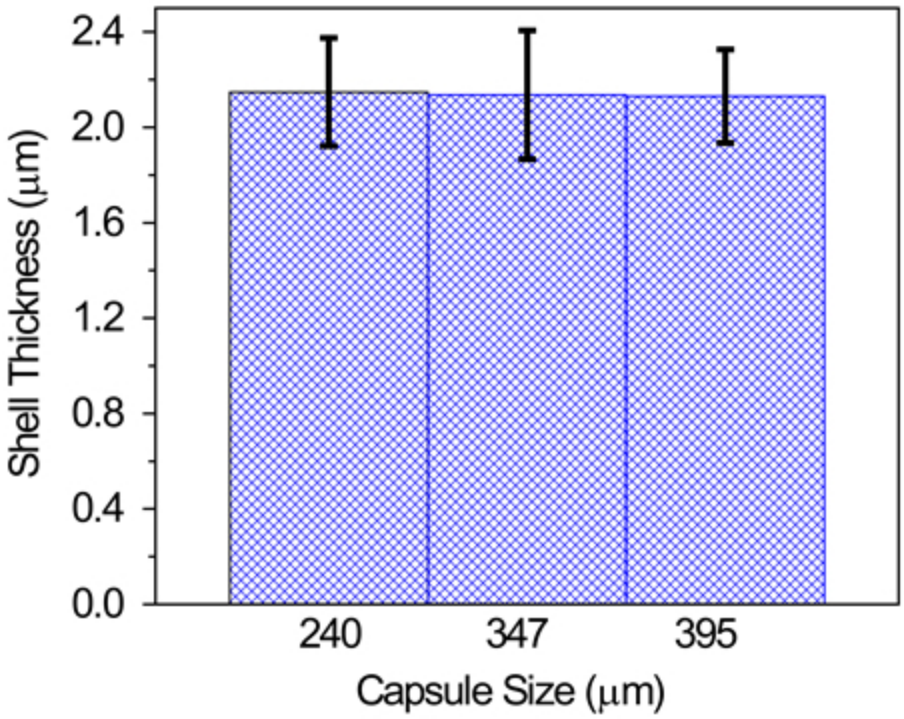


**Figure S7.** Capsule shell thickness as a function of capsule size. Capsules were prepared using 0.1 wt.% solutions at aqueous pH of 2.7 ,and in the absence of salt.