Immobilization of Polymer-Decorated Liquid Crystal Droplets on Chemically Tailored Surfaces

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Supporting Information

Time Dependent Ordering Configurations of LC Droplets During Incubation with Polymer 1

The preradial and radial configurations discussed in the second section of the main text were the predominant configurations observed after exposure to polymer concentrations of 0.1 mg/mL or 1.0 mg/mL for two hours. For experiments conducted at lower polymer concentrations, approximately 86% of the droplets exhibited preradial configurations after two hours of incubation [the remaining droplets exhibited the radial (11%) or bipolar configurations (3%)], and this configuration remained the predominant topological state over an additional 23 hours. For experiments conducted at higher concentrations, approximately 68% of the droplets exhibited radial configurations after two hours of incubation (the remaining 32% of droplets exhibited the preradial configuration). However, the relative number of LC droplets with radial configurations continued to increase over an additional 23 hours, suggesting that, under these conditions, polymer 1 continued to adsorb to the surfaces of the droplets over this period (as shown in Figure S1). To eliminate the influence of this time dependence on the configuration of the droplets, all of the observations in this current study were restricted to the characterization of droplets after two hours of incubation. In addition, centrifugation and washing procedures were used to remove any excess polymer from solution in the subsequent experiments described in the text (see Materials and Methods for additional details). The removal of excess polymer and other

mechanical manipulation of the droplets did not significantly change the observed configurations of these droplets described above (e.g., as shown in Figure 1 of the main text).



Figure S1: Orientational configurations of LC droplets incubated in solutions of polymer **1** at A) 1.0 mg/mL or B) 0.1 mg/mL as a function of time. The LC ordering was categorized into bipolar (hatched bars), preradial (black bars), or radial (gray bars) configurations on the basis of bright-field and polarized light micrographs captured from the emulsions at the indicated times.



Figure S2: Polarization-modulation infrared reflectance-absorbance spectra (PM-IRRAS) of BPEI/PVDMA multilayered films fabricated on gold-coated silicon. A) Spectra of a film before (black line) and after (green line) exposure to saturated water vapor for 48 hours at 37 °C. The complete disappearance of the characteristic peak at 1828 cm⁻¹ (carbonyl stretch of the azlactone group in PVDMA) and the appearance of a peak at 1729 cm⁻¹ (C=O stretch of the carboxylic acid) indicates that the azlactone functionality in the films was hydrolyzed. B) Spectra of a film as a function of time immersed in HEPES buffer (pH = 7.0). No significant decrease in the carbonyl peak at 1828 cm⁻¹ is observed for at least 30 minutes, indicating that the film does not hydrolyze to a significant extent over this period of time.



Figure S3: Confocal fluorescence micrographs of a glass bead resting on the surface of a PVDMA/BPEI multilayered film surrounded by an aqueous solution containing FITC-dextran. Images were collected using the same conditions as described in the capture of the images shown in Figure 6 of the main text: A) x-y plane and B) x-z plane.



Figure S2: Confocal fluorescence micrographs of LC droplets immobilized on surface **3** in the (A, B) *x-y* plane (bottom-up view) and the (C, D) *x-z* plane (side-on view). Images were captured by collecting the red channel (A, C; polymer 1_{TMR} adsorbed to the surface of the LC droplets) or the green channel (B, D; FITC-dextran dispersed in the aqueous solution). Scale bar = 5 µm.