

Smart Colloidosomes with a Dissolution Trigger

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Electronic Supplementary Information:

Experimental Methods

Materials: Eudragit-S was a gift from Evonik. Reagent alcohol (94-96% ethanol/methanol) was purchased from VWR. Dichloromethane, NaCl, NaOH and FITC-Dextran (500 kDa) were obtained from Sigma-Aldrich. Purified water (18.2 MΩcm) was obtained with a Barnstead Easy PureII System. All chemicals were used as received.

Particle Preparation: pH-responsive nanoparticles were prepared from Eudragit-S powder via nanoprecipitation.^[15] Briefly, Eudragit-S (2 g) was dissolved in alcohol (100 ml). This solution was abruptly added to deionized water (200 ml) and stirred at 400 rpm with a magnetic stirrer. The mixture showed turbidity immediately upon mixing. The temperature was then raised to 70° C for 2 hr while continuing mixing to evaporate the solvent. After the solvent was removed, additional water was evaporated to a final volume of 50 ml in order to increase the particle concentration. This dispersion was filtered through a Whatman Grade 6 qualitative filter paper to remove particle aggregates.

Particle Characterization: The suspension pH was found to be 3.1. Gravimetric analysis showed a particle concentration of 3.2% (w/v). The particle size distribution was characterized with dynamic light scattering (DLS) using a goniometer setup (ALV/DLS/SLS-5022F). The zeta potentials of the diluted particle dispersions were measured by electrophoresis (Malvern Zetasizer Nano ZS-90). The particle state at different pH and ionic strengths (aggregated, dispersed or dissolved) was determined by DLS.

Contact Angle Measurement: The contact angle was measured with a Ramé-Hart goniometer for contact angle measurement. A Eudragit-S solution in ethanol at 2% (wt/v) was prepared and a film was cast from this solution onto a propylene substrate. The substrate was then placed in the bottom of a 1 in x 1 in x 2 in quartz cuvette. The cuvette was filled with aqueous solution of the desired pH and ionic strength. A 5 µL drop of dichloromethane was then deposited on the film and the contact angle was measured. The reported data for each aqueous solution is the average obtained from analyzing both sides of 4 different droplets deposited on different Eudragit films. The polymer film, just like the capsule forming particles, are first exposed to the aqueous medium and then the dichloromethane. We therefore expect that these measurements are representative of the true contact angle for particles in the oil-water interface. *Double Emulsion Preparation:* The ionic strength of the dispersion was adjusted before emulsification by adding concentrated 3 M NaCl to reach the final NaCl concentration. The particle concentration of the dispersion was adjusted to 1.6% (w/v) by dilution with water. For the inner w/o emulsion, the aqueous particle dispersion (1 ml) was added dropwise to dichloromethane (2 ml) and homogenized at 30,000 rpm (IKA-T10 Ultraturrax) for 1 minute. The emulsion was left to rest for 1 minute and then rehomogenized for 30 seconds. The w/o emulsion (0.5 ml) was added to the outer particle dispersion (1.5 ml) and shaken by hand for 1 minute.

Microcapsule preparation: The double emulsions were diluted in deionized water (10 ml) and stirred with an IKA-RW20 digital stirrer at 150 rpm for 20 min until the solvent evaporated. Resulting microcapsules were evaluated by observation in a Nikon Eclipse-50i Microscope.

Fluorescence Recovery after Photobleaching (FRAP): 500 kDa FITC-dextran was added to the microcapsule dispersion (0.25 mg/ml) and analyzed in a cell with a no. 1.5 coverglass spacer. FRAP was performed in a Zeiss LM510 Confocal Microscope with an Ar laser ($\lambda=488$ nm, 10x 0.3 NA). Samples were bleached at a laser intensity of 100% and the recovery observed at 0.3%. Images were acquired at 3 sec intervals. Corrections for background bleaching during the experiment were made.

Dissolution: 0.2 M ammonium chloride / ammonium hydroxide buffer solution was prepared at pH 8. The microcapsule dispersion (~10 µL) was added to this buffer solution (~200 µL) in a glass cell.