



Supporting Information

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Controllable Monodisperse Multiple Emulsions

Liang-Yin Chu^{1,2*}, Andrew S. Utada¹, Rhutesh K. Shah¹, Jin-Woong Kim^{1,3} and David A. Weitz^{1,4*}

¹School of Engineering and Applied Sciences, Harvard University, Cambridge, Massachusetts 02138, USA

²School of Chemical Engineering, Sichuan University, Chengdu, Sichuan 610065, China

³Amore-Pacific R&D Center, 314-1, Bora-dong, Giheung-gu, Yongin-si, Gyeonggi-Do, 446-729, Korea

⁴Department of Physics, Harvard University, Cambridge, Massachusetts 02138, USA

*e-mail: chuly@scu.edu.cn; weitz@seas.harvard.edu

Experimental Section

Materials: The outermost fluid for all the multiple emulsions was poly(dimethylsiloxane) oil (PDMS) (Sigma-Aldrich) with a viscosity of 100 cSt, containing 2 %wt Dow Corning 749 fluid (Dow Corning) as a surfactant. The next inner fluid for both the double and triple emulsions was an aqueous solution containing 10 %wt glycerol (Sigma-Aldrich) and 2% (w/v) poly(vinyl alcohol) (PVA, 87-89% hydrolyzed, Sigma-Aldrich). The innermost fluid for the double emulsions was PDMS oil with a viscosity of 10 cSt (Sigma-Aldrich). The inner oil phase for the triple emulsions was kerosene (Sigma-Aldrich) containing 10% (w/v) polyglycerol polyricinoleate (PGPR 90, Danisco) and 15%wt Dow Corning 749 fluid. The innermost fluid for the triple emulsions was the same aqueous solution containing 10 %wt glycerol and 2% (w/v) PVA. For the thermo-sensitive microcapsules, we used the same

outermost and innermost fluids as for the triple emulsions. The outer middle fluid (II) was an aqueous solution containing 10%wt glycerol, 2% (w/v) PVA, 11.3% (w/v) of the monomer *N*-isopropylacrylamide (NIPAM, 99%, Acros), 0.8% (w/v) of the co-monomer sodium acrylate (Sigma-Aldrich), 0.77% (w/v) of the crosslinker *N,N'*-methylenebisacryamide (BIS, Sigma-Aldrich), and 0.6% (w/v) of the initiator, ammonium persulfate (APS, Acros). The inner middle fluid (I) was 10 cSt PDMS oil containing 5 %wt Dow Corning 749 fluid and 8% (v/v) of the accelerator *N,N,N',N'*-tetramethylethylenediamine (TEMED, 99%, Acros).

Capillary Microfluidic Devices: The outer diameter of cylindrical capillaries was 1 mm. The square capillary tubes had an inner dimension of 1 mm (Vitrocom). The inner diameter (ID) of the transition tube used for the double emulsions was 200 μm (AIT glass). For the triple emulsions, the IDs of the first (I) and second (II) transition capillaries were 100 μm and 250 μm , respectively. The ID of the collection tube was 580 μm . We used a transparent epoxy resin to seal the tubes where required. Solutions were supplied to the microfluidic device through polyethylene tubing (Scientific Commodities) attached to syringes (Hamilton Gastight). We drove the fluid flow with positive displacement syringe pumps (Harvard Apparatus, PHD 2000 series). The drop formation was imaged with a high-speed camera (Vision Research) attached to a microscope.

Polymerization and Characterization of Thermo-sensitive Microcapsules: The accelerator TEMED is both oil- and water-soluble. When TEMED is dissolved in the middle fluid (I), it diffuses into the outer middle fluid (II) where it meets the initiator APS; this starts a redox reaction that polymerizes the monomers. The polymerized microcapsules together with the surrounding fluids were contained in a transparent holder on a slide glass, which was placed on a microscope-mounted heating and cooling stage (Physitemp Instruments, TS-4ER) to measure the thermo-sensitive behavior. A digital camera (Hamamatsu, C4742-95) recorded the behavior and the release process.