Electronic Supplementary Material (ESI) for Chemical Communications

Temperature mediated generation of armoured bubbles

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1. Schematic of the microfluidic device

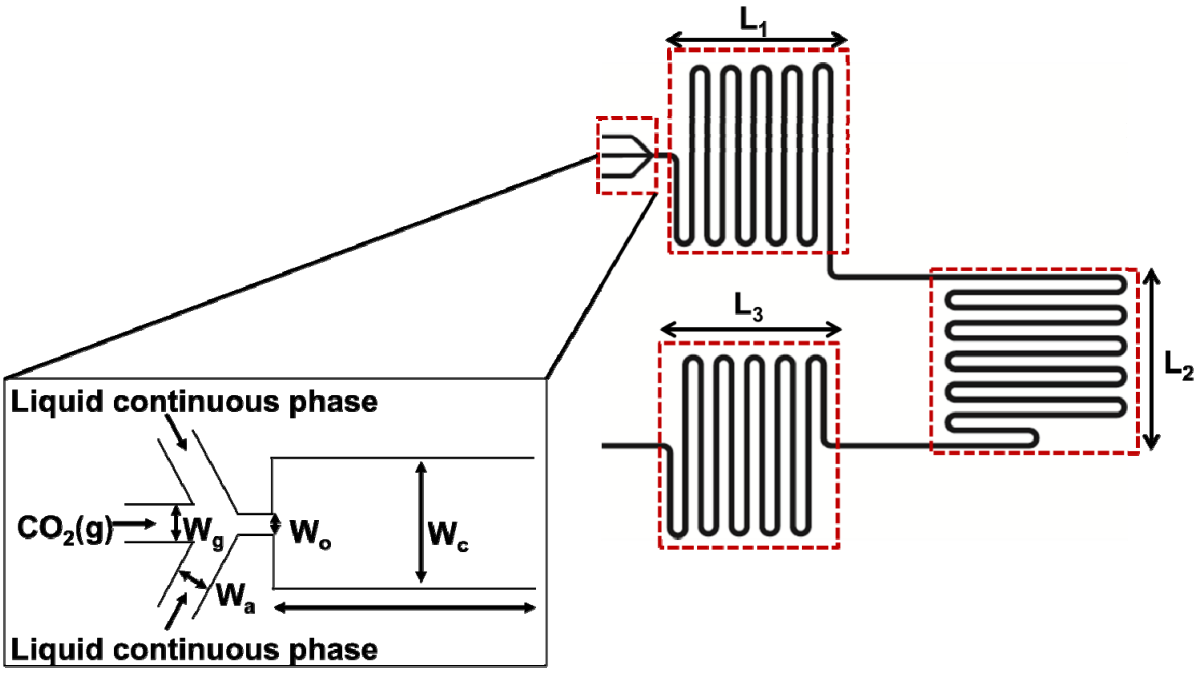

Figure S1. Schematic of the MF bubble generator. W_g=50 μm, W_a=100 μm, W_o=20 μm, W_c=200 μm. $L_1 = L_2 = L_3$= 135 mm. The total channel length of the device (from the orifice to the outlet is 450 mm). The height of the MF device is 120 μm.

2. Control of temperature in the microfluidic device

Zones 1 and 3 of the channel were cooled by placing underneath them a hollow copper block and purging through it a glycerol/water mixture (1:4 v/v) at a temperature of 0 ^{o}C. The temperature

of the mixture was controlled using a water circulator (Neslab RTE-040). Zone 2 of the microchannel was heated by placing beneath it a 1.5 cm^2-area heating module (TE Technology). The temperature in the module was controlled using an electronic temperature controller (TE Technology) at 28, 68, and 98 ^oC, which corresponded to the maximum temperatures of the continuous phase of 23, 56, and 77 ^oC, respectively. The temperature of the continuous liquid phase along the MF device was measured using a thermocouple (VWR, Canada). Prior to the generation of bubbles, the system was equilibrated for 30 min.

3. Materials and Methods

Gaseous CO_2 (purity 99.8%) was purchased from BOC Canada. Impurities included N_2, O_2, and inert gases such as He and Ne. Poly(dimethylsiloxane) (PDMS) elastomer (Sylgard 184) was supplied by Dow Corning. Carbon dioxide (CO_2) was purchased from BOC Canada. Sodium hydroxide (NaOH) was purchased from EMD Canada. Methyl methacrylate (MMA, 99%) was purchased from Fluka, Canada and used without further purification. Triton X-100 (TX-100), was purchased from Sigma-Aldrich, Canada and used as received. The synthesis of 2.8 μm-diameter poly(styrene-co-acrylic acid) (PS-co-PAA) particles was carried out as described elsewhere.[1,2]

4. Characterization of Bubble Dimensions

The dimensions of the bubbles were examined immediately after their formation (next to the orifice) and during their flow in the downstream channel. An Olympus BX51 microscope, a high-speed camera (Photometrics Cool SNAP ES, 150 ms per frame), and an Image Pro (Media Cybernetics) software were used to image the bubbles and determine their dimensions and

polydispersity (defined as standard deviation in bubble diameter divided by mean diameter of the bubbles). The volume, V, of bubbles was calculated as $V=(4/3)\pi(D/2)^3$, where D is the diameter of the undeformed bubble. When the value of D exceeded the height, h, of the microchannels, the volume of the bubbles forming plugs was approximated as: $V=(\pi/12)[2D^3-(D-h)^2(2D+h)]^3$

References:

1 J. S. Song, L. Chagal, M. A. Winnik, *Macromolecules,* 2006, **39**, 5729-5737.
2 J. S. Song, F. Tronc, M. A. Winnik, *Polymer*, 2006, **47**, 817-825
3 Z. H. Nie, M. S. Seo, S. Q. Xu, P. C. Lewis, M. Mok, E. Kumacheva, G. M. Whitesides, P. Garstecki and H. A. Stone, Microfluid. Nanofluid., 2008, 5, 585-594.