(1) Device design

Monodisperse o/w microdroplets were generated by injecting oil and water phases into a microfluidic device with a channel height of 25 μm. The chip design is shown in Fig. S1.

![Diagram of device design](image)

**Fig. S1** Design of the device used for the controlled formation of o/w microdroplets as shown in Fig. 2(a) and Fig. 2(b).

(2) Movies

(a) **M1 – Formation of functional o/w droplets**

This movie depicted in Fig. 2(a) shows the formation of dodecane-in-water droplets stabilized by a pH responsive MAA/PEGMA surfactant at an oil flow rate of 100 μl h\(^{-1}\) and a water flow rate of 300 μl h\(^{-1}\).

(b) **M2 – Injection of the emulsion sample into basic water**

In this movie depicted in Fig. 2(e) the injection of the emulsion sample into an open reservoir containing basic water (pH 10) at a constant flow rate of 70 μl h\(^{-1}\) is illustrated. Due to the absence of inter-droplet hydrogen bonding a dispersion of non-interacting droplets is generated.

(c) **M3 – Injection of the emulsion sample into acidic water**

The injection of the emulsion sample into an open reservoir containing acidic water (pH 2) at a constant flow rate of 70 μl h\(^{-1}\), as depicted in Fig. 2(f), is shown in this movie. As inter-droplet hydrogen bonding occurs a droplet aggregate is formed at the end of the tubing.

(d) **M4 – Quantitative analysis of droplet-droplet interactions via optical tweezers**

This movie illustrates the computer-controlled 3D manipulation of a droplet pair using optical tweezers. While the left microdroplet is kept quasi-stationary the right droplet is slowly...
retracted. Within 120 s the trap distance is steadily increased from 20 μm to 25 μm. Displacements of the left droplet are measured and used to quantify droplet-droplet adhesion. Pictures taken from the movie are displayed in Fig. 4(a).