Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supplementary Information for Core-shell droplets and microcapsules formed through liquid-liquid phase separation of a colloid-polymer mixture

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This PDF file includes:

Figures S1 – S6
Captions to Movies S1 – S6

Other Supplementary Materials include the following:

Movies S1 – S6

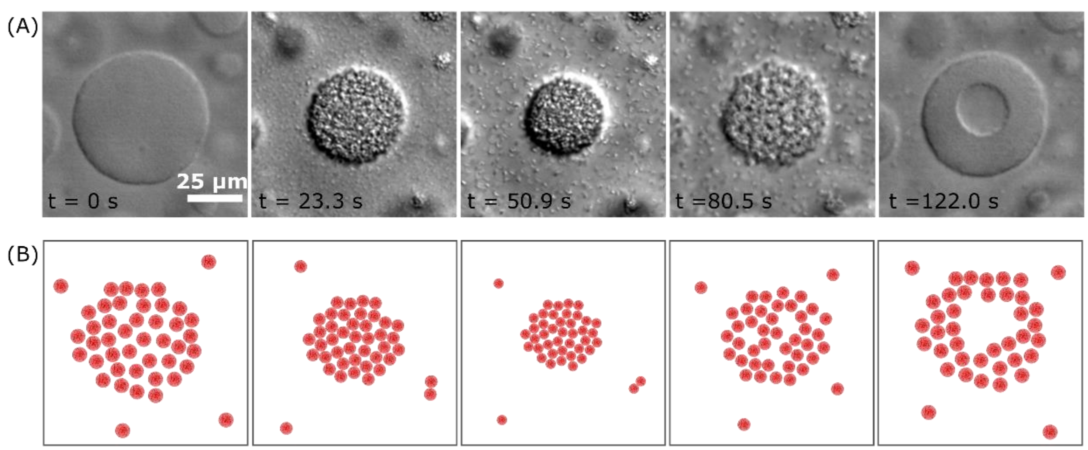

Fig. S1. In (A) we have reproduced Fig. 1B from the main text. We see the formation of a core-shell droplet after heating the sample with a heat gun. The sample was observed using a 20× objective lens with DIC. (B) The cartoon shown illustrates the process of core-shell droplet formation to go along with (A). As the temperature increases (first two panels of (B)), the pNIPAM particles shrink and aggregate together into a gel-like ball. As the temperature cools (last two panels of (B)), the pNIPAM particles swell and the colloid-rich region undergoes a fluid-fluid phase separation which results in multiple colloid-poor regions within the drop. As those colloid-poor regions coalesce together, we are left with a single colloid-poor droplet surrounded by a shell of the colloid-rich phase. Note that this cartoon shows the individual pNIPAM particles which are too small to resolve in our actual micrographs.

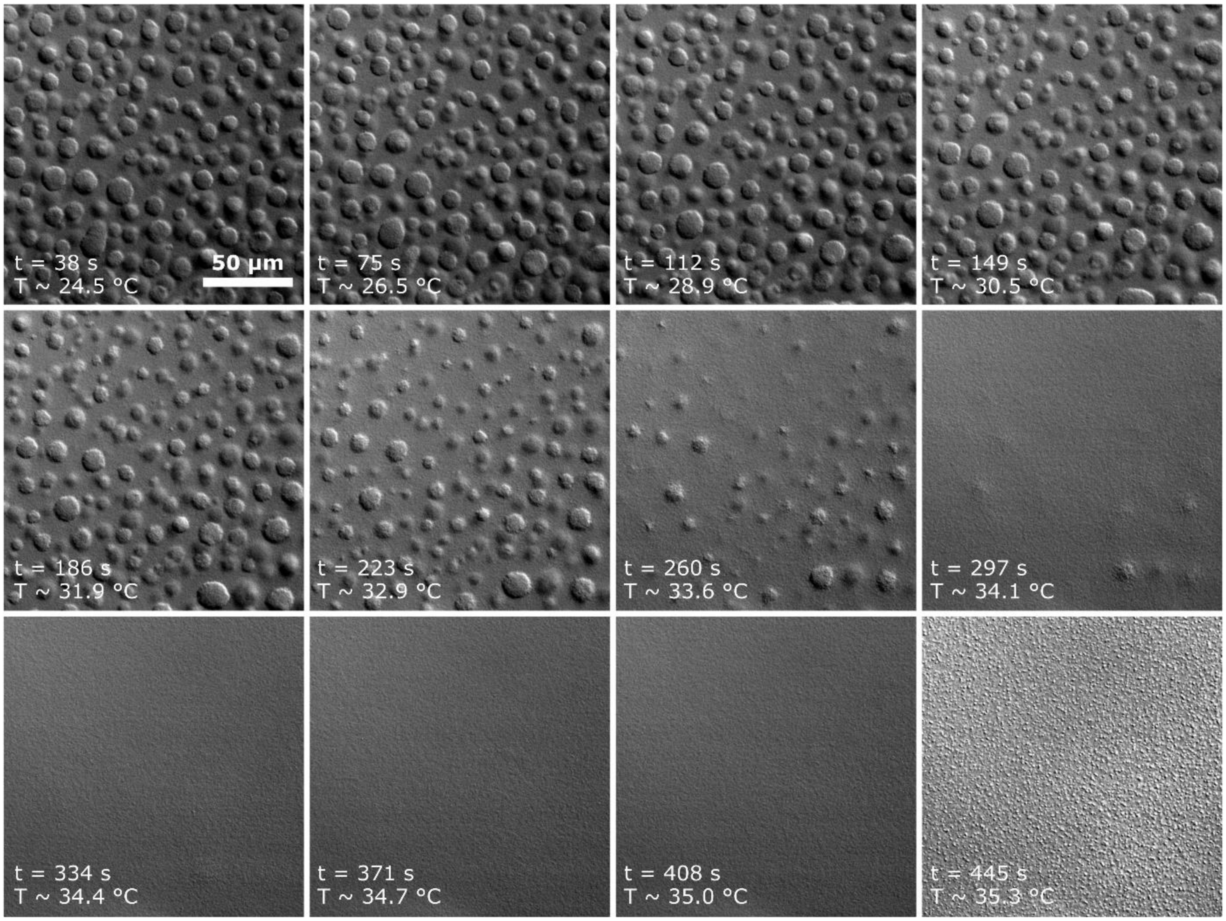

Fig. S2. A gradual increase in temperature results in the phase separated colloid-polymer mixture becoming homogeneous. A pNIPAM-xanthan mixture (0.08 wt% xanthan, 11.4% pNIPAM volume fraction) separates into colloid-rich droplets in a continuous colloid-poor phase at room temperature. Using a stage-top incubator on an inverted light microscope we heat the sample above the LCST of pNIPAM. As the temperature increases, the colloid-rich droplets shrink and disappear until the sample becomes homogeneous. Above the LCST, we see clusters of pNIPAM particles. The temperature indicated in the figure is recorded from a temperature probe placed a couple of centimeters away from the sample but on the glass slide. However, since the objective lens (a 20× air objective) was not heated, we suspect the actual sample temperature to be approximately 1-2 °C lower. See Movie S2.

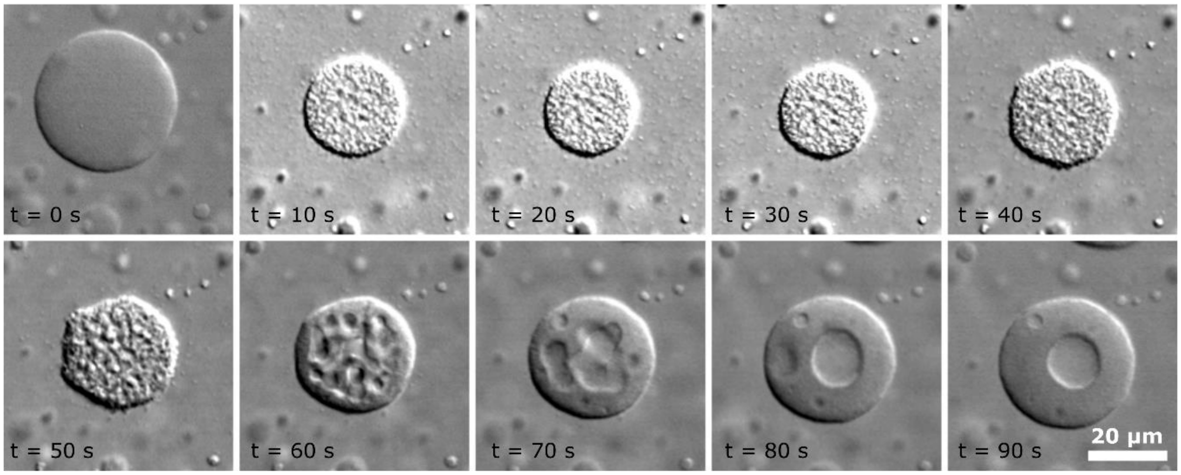

Fig. S3. Formation of a core-shell droplet occurs after a single emulsion droplet is heated and cooled. A droplet of the colloid-rich phase within a colloid-poor phase is shown at t = 0 s. The sample is heated for approximately 10 seconds using a heat gun. The temperature goes above the LCST of pNIPAM since the pNIPAM particles shrink and aggregate. As the sample passively cools, the colloid-rich droplet reliquefies, and numerous colloid-poor droplets can be seen inside (t=60s). As those internal droplets coalesce, a core-shell droplet forms. See Movie S3.

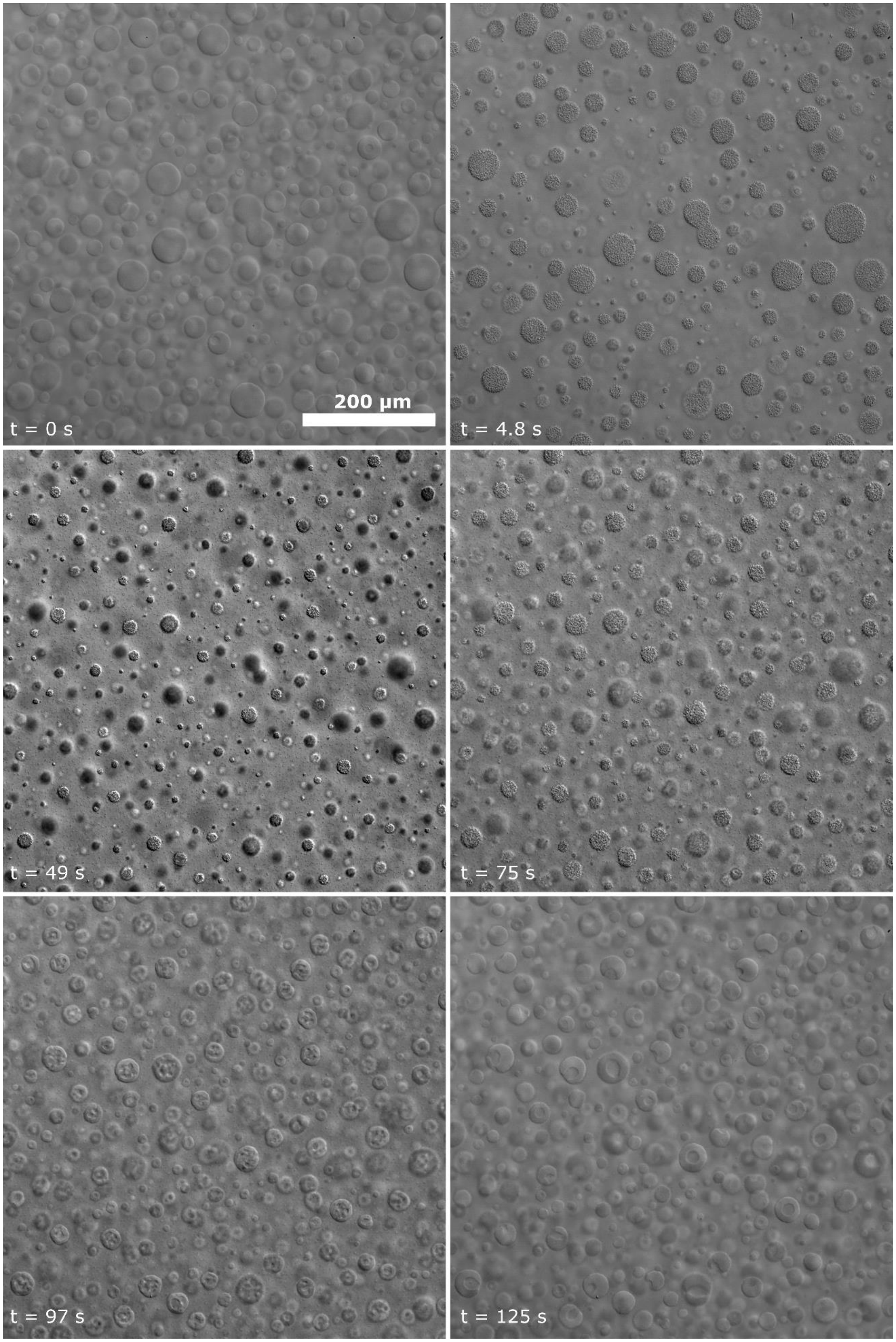
200 µm
t = 0 s
t = 4.8 s
t = 49 s
t = 75 s
t = 97 s
t = 125 s

Fig. S4. Formation of core-shell droplets occurs after the sample is heated and cooled. Images show the same process as in Fig. S3 over a wider field of view. See Movie S4.

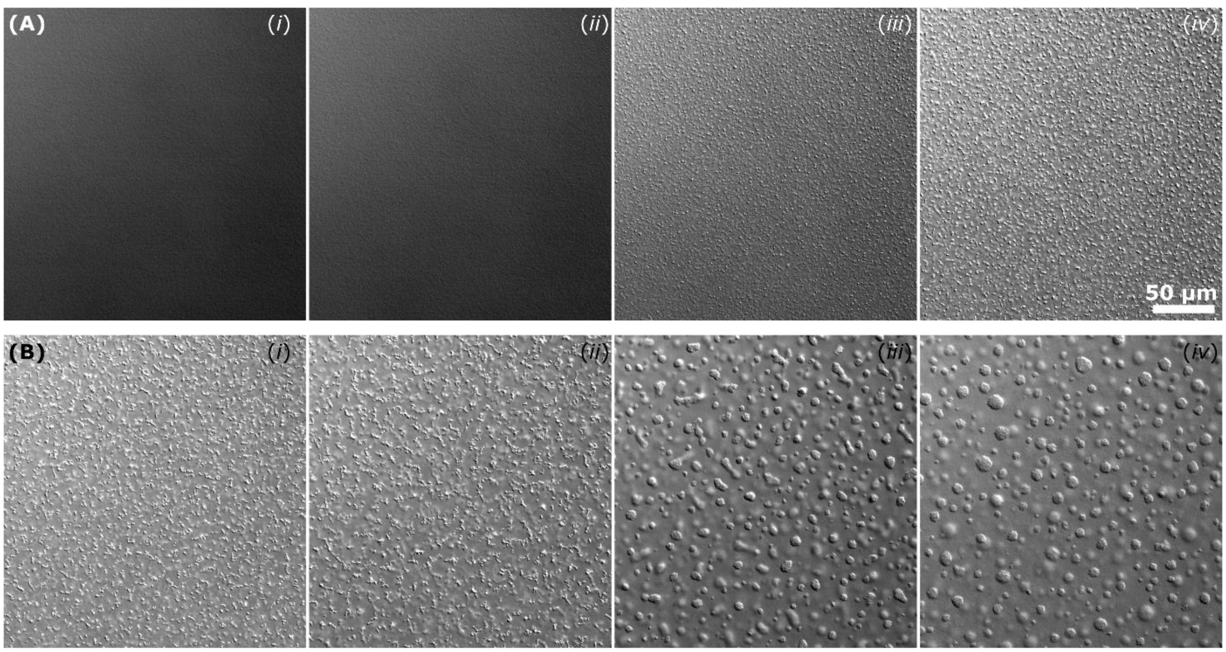

Fig. S5. A pNIPAM-xanthan mixture which is homogeneous at room temperature shows liquid-liquid phase separation at just below the LCST as it cools from above the LCST. (A) A sample that is mixed at room temperature (0.04 wt% xanthan, 11.4%) is slowly heated using a stage top incubator on an inverted light microscope. The frames shown as (*i*) through (*iv*) are each separated by 30 s and the temperature measured near the sample over this entire time span goes from approximately 34 to 34.2 °C. Clusters of pNIPAM particles are observed in (*iii*) and (*iv*). (B) Following the slow heating in (A), the sample is then cooled. The frames shown as (*i*) through (*iv*) are each separated by 120 s and the temperature measured near the sample over this entire time span goes from approximately 34.2 to 33.2 °C. We observe the pNIPAM particle clusters forming colloid-rich fluid droplets. As the sample cools back to room temperature, these droplets disappear, and the sample becomes homogeneous. We note that the temperature of the sample is slightly less than that measured by the probe as explained in the caption to Fig. S2. See Movie S5.

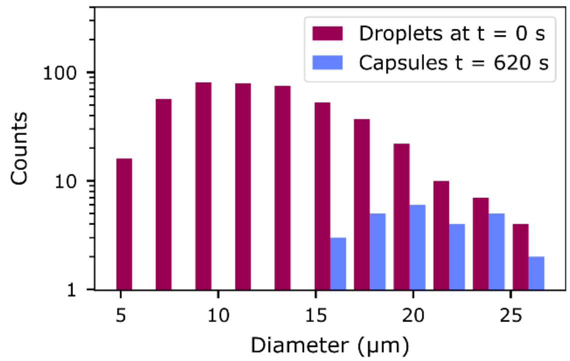

Fig. S6. The size distribution of droplets within a volume of 290×269×100 μm^3 is shown at room temperature before the sample is heated (at t = 0 s) in red. About 10 minutes after heating the sample to generate capsules, about 7.5% of droplets contain an inner droplet (as shown in Fig. 5). The size distribution of those capsules which remain is shown in blue.

Caption to Movie S1. The process of core-shell droplet formation is shown. This movie corresponds to the images shown in Fig. 1B. The sample (0.08 wt% xanthan, 11.4% volume fraction pNIPAM) was heated with a heat gun for approximately 20 seconds. As the sample cools, phase separation within the droplet is seen which results in a single colloid-poor droplet within the colloid-rich droplet. The scale bar is 25 μm. Playback speed is 10× real speed.

Caption to Movie S2. A slow temperature increase causes a demixed to mixed transition. This movie shows a sample with the same composition as the sample imaged in Fig. 1 and Movie S1 (0.08 wt% xanthan, 11.4% volume fraction pNIPAM). However, unlike in Movie S1, the sample is slowly heated using a stage top incubator. Individual frames from this movie are shown in Fig. S2. The scale bar is 50 μm. Playback speed is 100× real speed.

Caption to Movie S3. The process of core-shell droplet formation is shown. This movie corresponds to the images shown in Fig. S3. The scale bar is 20 μm. Playback speed is 2× real speed.

Caption to Movie S4. The process of core-shell droplet formation is shown. This movie corresponds to the images shown in Fig. S4. The scale bar is 200 μm. Playback speed is 10× real speed.

Caption to Movie S5. Fluid-fluid phase separation observed after a decrease in temperature from above the LCST in a sample homogeneous at room temperature. This movie corresponds to the images shown in Fig. S5. The scale bar is 50 μm. Playback speed is 100× real speed.

Caption to Movie S6. Solidification of the colloid-rich shell. This movie corresponds to the image shown in Fig. 6. A core-shell droplet was formed in the same way as shown in Movies S1, S3, and S4. The concentration of NaCl in the neighborhood of the droplet then increased which caused the colloid-rich shell to solidify. The colloid-rich shell is fluid in the beginning of this movie, but is rigid by the end. The scale bar is 10 μm. Playback speed is 4× real speed.