Supplementary information

Fabrication of shape controllable Janus alginate/pNIPAAm microgels via microfluidics technique and off-chip ionic crosslinking

Yuandu Hu[1], Shibo Wang[1], Alireza Abbaspourrad[3], Arezoo M. Ardekani*[1,2]

1 Department of Aerospace and Mechanical Engineering, University of Notre Dame, Notre Dame, Indiana 46556, USA

2 School of Mechanical Engineering, Purdue University, 585 Purdue Mall, West Lafayette, Indiana 47907, USA

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

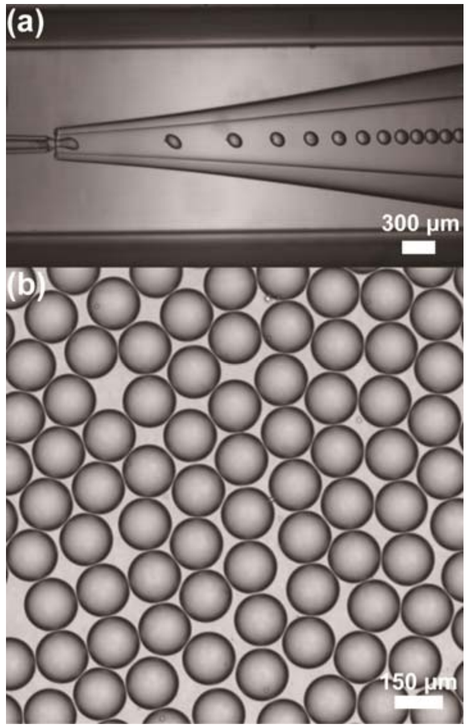

Figure S1. Optical images of (a) the droplet formation process inside the microfluidic device; (b) monodispersed pNIAAm/sodium alginate droplets on a glass slide.

Table S1. Top: Density of 1 wt% sodium alginate solution mixed with 1 wt% pNIPAAm and 2 wt% pNIPAAm. Bottom: Density of the collecting solution with different glycerol concentration.

Droplet density(g/cm^3) — pNIPAAm concentration / Sodium alginate concentration	1 wt%	2 wt%
1 wt%	0.953	0.966

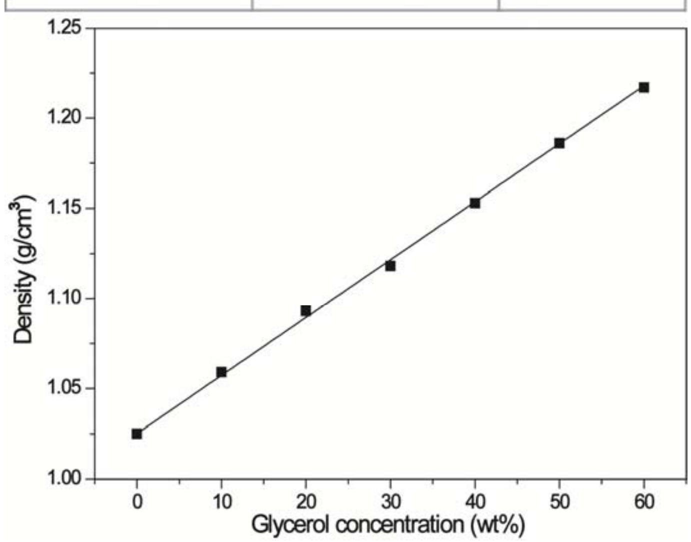

Table S2. pH values of the collecting solution with glycerol concentration ranging from 0 to 40 wt%. Even though the pNIPAAm ends in carboxyl groups, the pH values of the collecting solution are all higher than the pKa value (pKa ~ 4.7) of the carboxyl group [1]. Consequently, pH values of the collecting solutions have no deswelling effects on the pNIPAAm polymer chain.

Glycerol Concentration (wt%)	0	10	20	30	40
pH Value	7.55	7.67	7.73	7.36	7.26

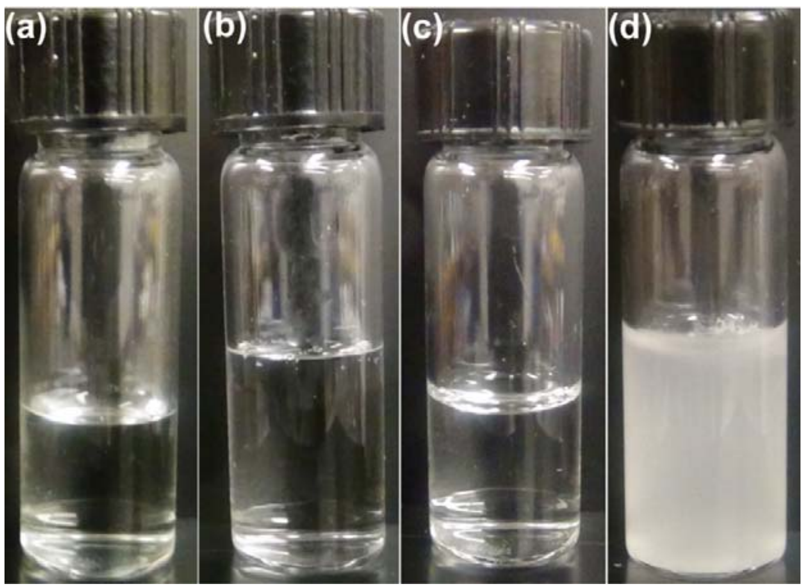

Figure S2. (a-b) Optical images of 1wt% sodium alginate aqueous solution (a) before and (b) after the addition of 20 wt% glycerol. The solutions remain transparent even after the addition of glycerol, indicating that the glycerol has no negative optical effect on the sodium alginate. (c-d) Optical images of 1 wt% pNIPAAm/1wt% sodium alginate aqueous solution (c). before and (d). after the addition of 10 wt% glycerol. The images confirm that addition of glycerol affects the optical properties of the solution. In Figure S2 (b), the final concentration of glycerol and alginate is 5wt% and 0.75wt%, respectively. In Figure S2 (d), the final concentration of glycerol, alginate and pNIPAAm is 5wt%, 0.75wt% and 0.75 wt%, respectively. The experiments are performed in 5 mL glass vials.

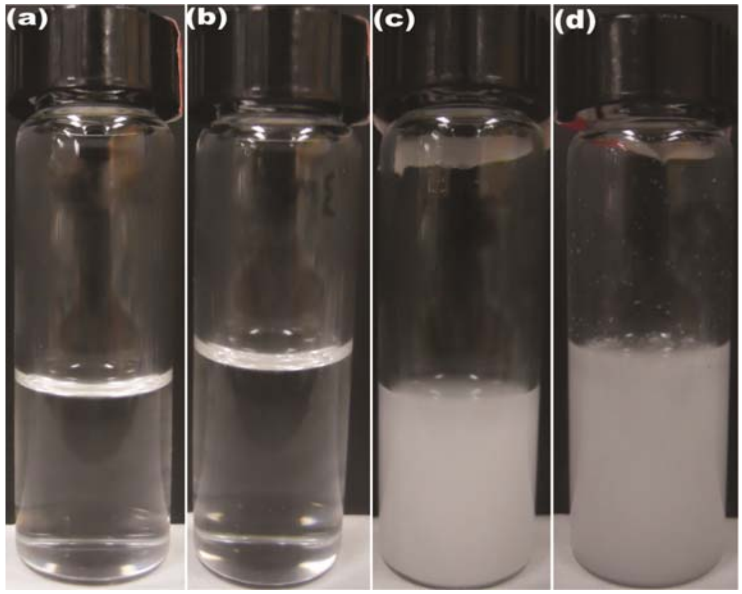

Figure S3. (a-b) Optical images of 1wt% sodium alginate aqueous solution (a) before and (b) after the addition of 20 wt% of glycerol at 45 ℃. The solutions remain transparent even after the addition of glycerol, indicating that the glycerol has no negative optical effect on the sodium alginate at 45℃. (c-d) Optical images of 1 wt% pNIPAAm/1wt% sodium alginate aqueous solution (c) before and (d) after the addition of 10 wt% of glycerol at 45 ℃. The images confirm that both the temperature and addition of glycerol affect the optical properties of the solution. The experiments are performed in 5 mL glass vials. In Figure S3 (b), the final concentration of glycerol and alginate is 5wt% and 0.75wt%, respectively. In Figure S3 (d), the final concentration of glycerol, alginate and pNIPAAm is 5wt%, 0.75wt% and 0.75 wt%, respectively.

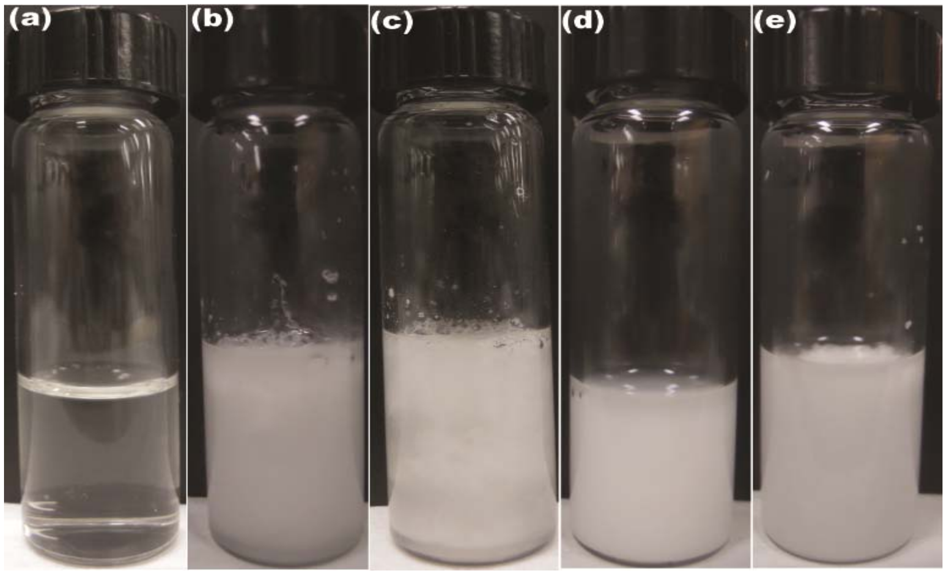

Figure S4. (a-b) Optical images of 1wt% pNIPAAm aqueous solution (a) before and (b) after the addition of 20 wt% glycerol at room temperature. The transparent solution changes into turbid solution after addition of glycerol. (c) Optical image of solution (b) heated to 45 ℃. (d-e) 1 wt% pNIPAAm/1wt% sodium alginate aqueous solution before (d) and after (e) the addition of 10 wt% glycerol at 45℃. These images further confirm that both the temperature and glycerol could affect the solubility of pNIPAAm and thus result in the change in optical properties of the solution. The experiments are performed in 5 mL glass vials. In Figure S4 (b-c), the final concentration of glycerol and pNIPAAm is 5wt% and 0.75wt%, respectively. In Figure S4 (e), the final concentration of glycerol, alginate and pNIPAAm is 5wt%, 0.75wt% and 0.75 wt%, respectively.

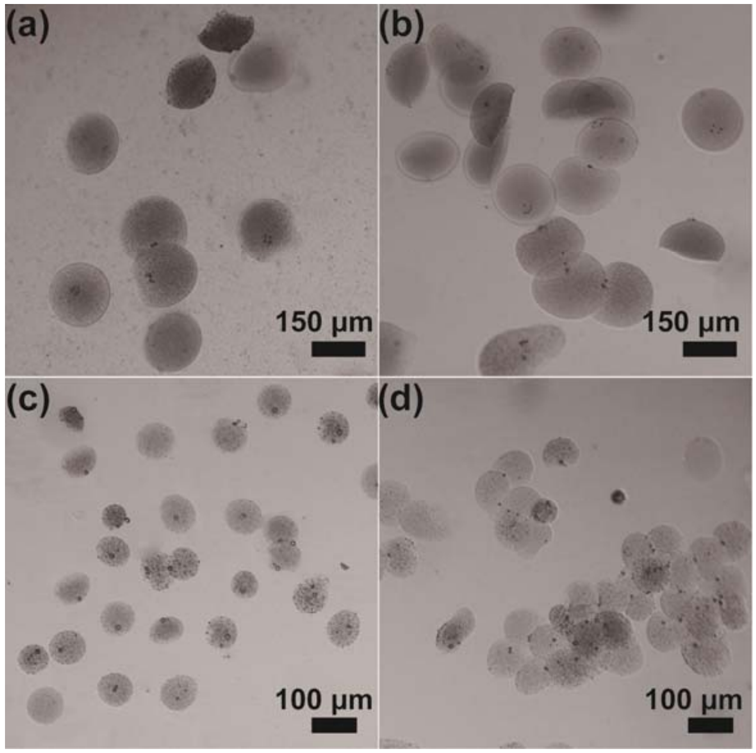

Figure S5. Optical images of 1wt% pNIPAAm/1wt% SA microgels formed using 300 μm (a-b) and 150 μm (c-d) diameter droplets. The droplets were collected in 50 wt% glycerol collecting solutions in (a-c) and in 60 wt% glycerol collecting solutions in (b-d). All the samples were heated to 45°C for 12 hours and then cooled down. All the images were taken at room temperature.

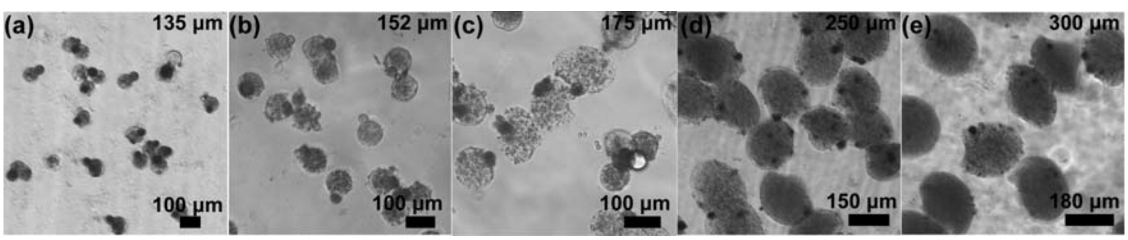

Figure S6. Optical images of microgels formed out of 2wt% pNIPAAm/1wt% SA droplets with different initial diameters (a) 135 μm, (b) 152 μm, (c) 175 μm, (d) 250 μm and (e) 300 μm. All the droplets are collected in 20 wt% glycerol collecting solutions which were heated to 45°C. There exists a critical initial diameter of about 175 μm above which mushroom-like microgels form. Below this critical diameter Janus particles are observed.

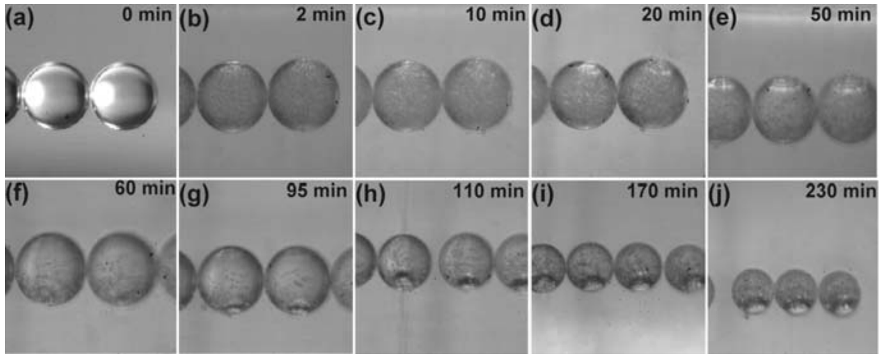

Figure S7. The droplets evolution process (150 μm diameter droplets of 2 wt% pNIPAAm/1 wt% sodium alginate) at the interface of hexadecane/20 wt% glycerol collecting solution. Initial transparent droplets quickly changed to turbid state due to the phase separation of pNIPAAm in a hot glycerol collecting solution. The droplet diameter gradually decreases due to the crosslinking process. The experiment was performed at 45°C and captured using a high speed camera.

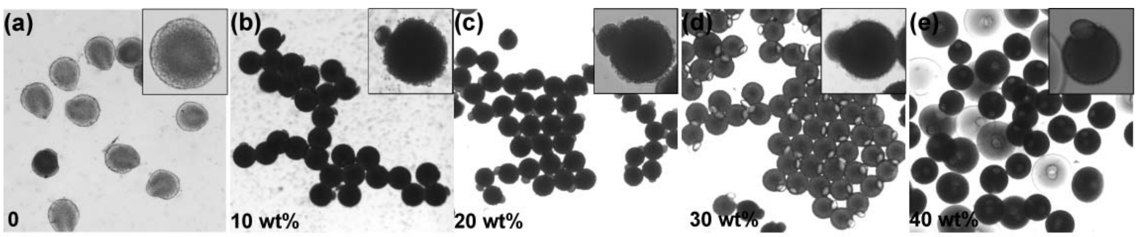

Figure S8. Droplets of 2wt% pNIPAAm/1wt% sodium alginate collected in different collecting solutions with glycerol concentration ranging from 0 to 40 wt%. The temperature of the collecting solution is kept at room temperature (~25°C). Microgels are formed out of 150 μm diameter droplets.

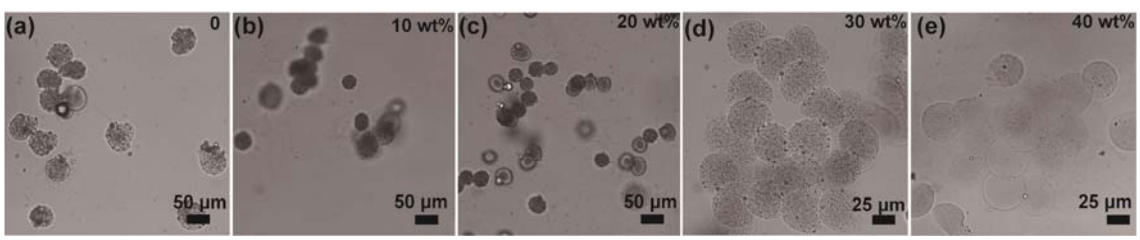

Figure S9. Optical images of microgels formed out of 1wt% pNIPAAm/1.5 wt% SA 150 μm diameter droplets. (a-b) represent microgels formed in collecting solutions with glycerol concentration ranging from 0 to 40 wt%. The droplets were all collected in a 45°C collecting solution. Very few microgels show Janus morphology, indicating that the increase in the concentration of sodium alginate hinders the phase separation process during the droplet deformation. All the pictures were captured after 12 hours, when the microgels were fully settled at the bottom of the glass vial.

[1] Lovett J. R., Warren N. J., Ratcliffe L. P. D., Kocik M. K., and Armes S. P. pH-responsive non-ionic diblock copolymers: ionization of carboxylic acid end-groups induces an order–order morphological transition. *Angew. Chem. Int. Ed.* **2015**, 54, 1279 –1283.