

# Electronic Supplementary Information

## CO<sub>2</sub> -Triggered Liquid-Solid Switching through Jamming Mechanism

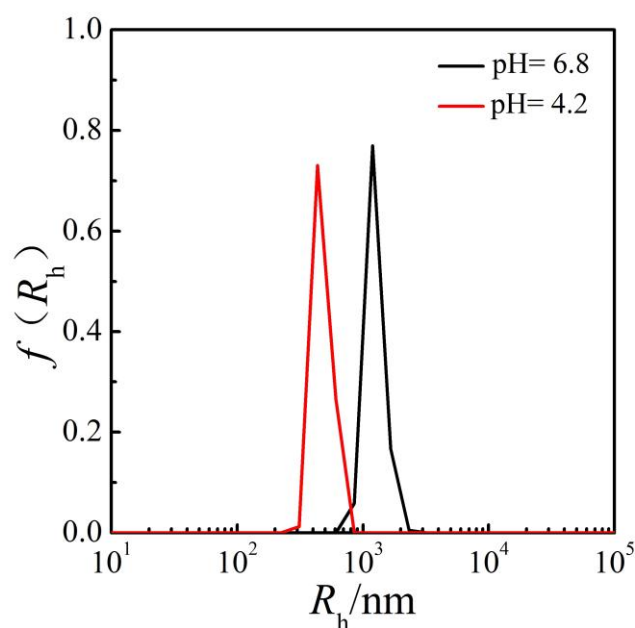
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**Synthesis of PDMAEMA Microgel:** PDMAEMA microgel was synthesized through a dispersion polymerization technique developed by Hu et al.<sup>1</sup> 9.8g DMAEMA (98%, Alfa Aesar, purified by reduced pressure distillation), and 0.05g N,N-Methylenebisacrylamide (MBA, 99%, Alfa Aesar) were dissolved in 10mL methanol. 90mL deionised water (Millipore, Bedford, MA, USA) and 1.0g polyvinylpyrrolidone (PVP,  $M_w = 58,000$  g/mol, Alfa Aesar) were added into a 250 mL three-neck reaction flask equipped with a condenser and a gas inlet. After a homogeneous solution formed at room temperature, the flask was transferred into a 65 °C oil bath and the solution was deoxygenated by bubbling Argon gas for 30min. Then the methanol solution was transferred into the flask. The reaction was continued for 3 hours with the agitating of a magnetic stirrer and bubbling of Argon gas. The resulted microgel suspension was dialyzed for one week to remove the methanol, unreacted monomer and PVP. The size distribution of the microgel was characterized by DLS. As Fig. S1 shows, at pH = 6.8, the microgels have an average hydrodynamic radius at 480nm and polydispersity at 25%; while at pH = 4.2, the microgels have an average hydrodynamic radius at 1250nm and polydispersity at 27%.



**Fig. S1** Distribution of hydrodynamic radius of a PDMAEMA microgel with  $c = 9.7 \times 10^{-7} \text{ g/mL}$  at different pH.

**Instrumentation:**  $\zeta$ -potential measurement was carried out on a Malvern Nano ZS90 zetasizer. Dynamic light scattering (DLS) experiments were performed with an ALV goniometer and an ALV 5000 correlator at a wavelength of 632.8 nm, and a scattering angle at  $20^\circ$ . In DLS, the baseline-normalized intensity-intensity time correlation function  $g^{(2)}(t, q)$  in the self-beating mode was measured. CONTIN program supplied with the correlator was used to calculate the hydrodynamic radius.<sup>2</sup> Oscillatory frequency sweeps were performed in a 50 mm cone-plate geometry and a 25 mm cone-plate geometry on a stress-controlled rheometer (Anton Paar MCR 501). As a standard protocol a high strain dynamic shear rejuvenation ( $\gamma_0 = 1000\%$ ,  $\omega = 1 \text{ rad/s}$ ) was performed followed by a waiting time of typically 100 s before each experiment. Silica oil was coated on the edge of the sample to prevent the water evaporation.

**Deduction of  $\Phi_{\text{eff}}$ :** The volume fraction ( $\Phi$ ) of a hard sphere suspension is proportional to number density ( $n$ ) and hence its weight concentration ( $c$ ):

$$\Phi = nV_p = kc \quad (1)$$

where  $V_p$  is the volume of a hard sphere.

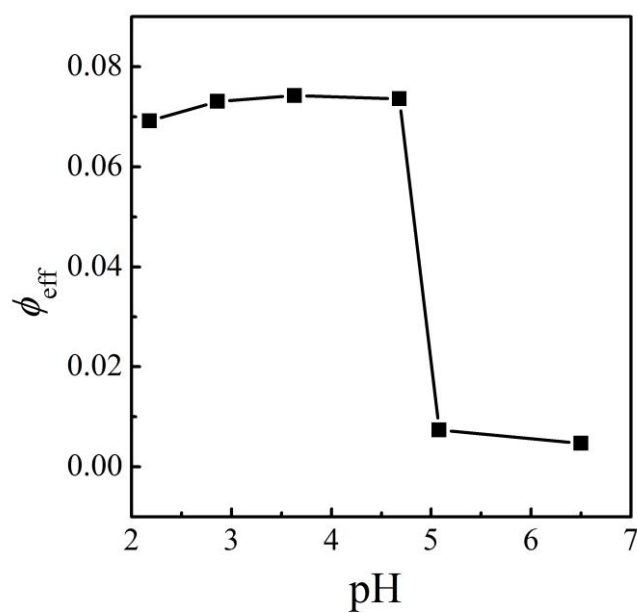
According to Batchelor's theory<sup>3</sup>, in dilute regime of the hard sphere suspension, the relative viscosity of the suspension is related to the  $\Phi$  in the following equation:

$$\eta_r = 1 + 2.5\Phi + 5.9\Phi^2 \quad (2)$$

The repulsive potential between microgel particles is a slow rising function as interparticle distance is decreasing. Thus the volume of microgels decreases with  $c$  due to their mutual compression and the draining of solvent. However, at dilute regime ( $\Phi < 0.30$ ) where the compression can be neglected, the microgel can be treated as hard sphere<sup>4</sup>. In our work, the viscosity measurement was conducted at dilute regime within the whole pH range, so equation (1) and equation (2) can be applied to deduce  $k$ . For example, the  $k$  turns to be 0.39 at  $\text{pH} < 5.0$ .

When the microgel suspension is more concentrated,  $\Phi$  is not a good measure to the concentration. Instead, we used  $\Phi_{\text{eff}} = kc$ , which illustrate the hydrodynamically non-draining volume fraction of the microgel. Only at dilute regime, the value of  $\Phi_{\text{eff}}$  is close to the "true" volume fraction of the microgel. At high concentration,  $\Phi_{\text{eff}}$  is not equal to the "true" volume fraction of the microgel, but still meaningful to tell how dense the system is.

Fig.S2 shows the  $\Phi_{\text{eff}}$  of a dilute microgel suspension at different pH. As for a microgel suspension with  $c = 1.94 \times 10^{-3}$  g/mL,  $\Phi_{\text{eff}}$  is 0.023 at pH6.9, and 0.37 at pH4.7, indicating  $k \approx 39$  at  $\text{pH} < 5.0$ ,  $k \approx 2.5$  at  $\text{pH} > 5.0$  and a volume swelling ration of 16.



**Fig. S2** Effective volume fraction of a PDMAEMA microgel with  $c = 1.9 \times 10^{-3} \text{ g/mL}$  at different pH.

### References

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- (4) M. Stieger, J. S. Pedersen, P. Lindner, W. Richtering, *Langmuir* 2004, **20**, 7283.