Electronic Supplementary Material (ESI) for Soft Matter.

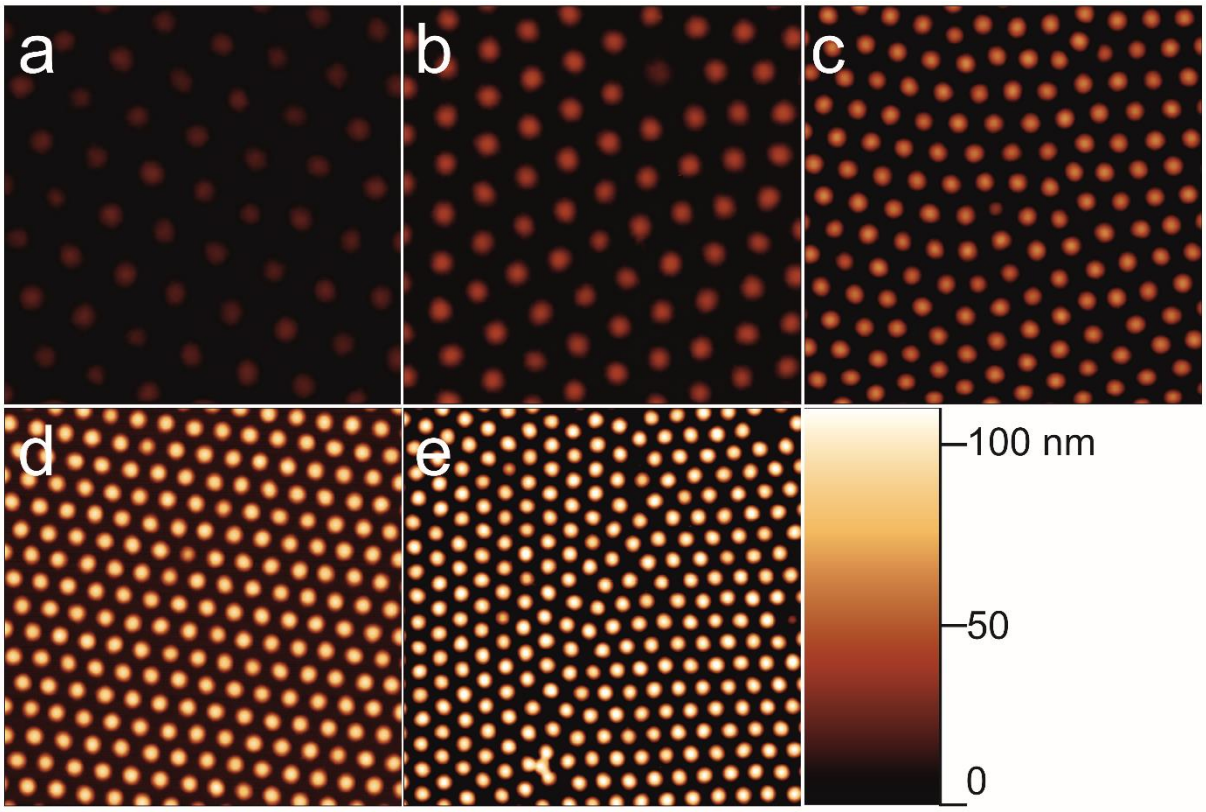
Interfacial arrangement and phase transitions of PNiPAm microgels with different crosslinking density

Marcel Rey[a,b], Xunan Hou[a,b], Jo Sing Julia Tang[a,b], Nicolas Vogel*[a,b]

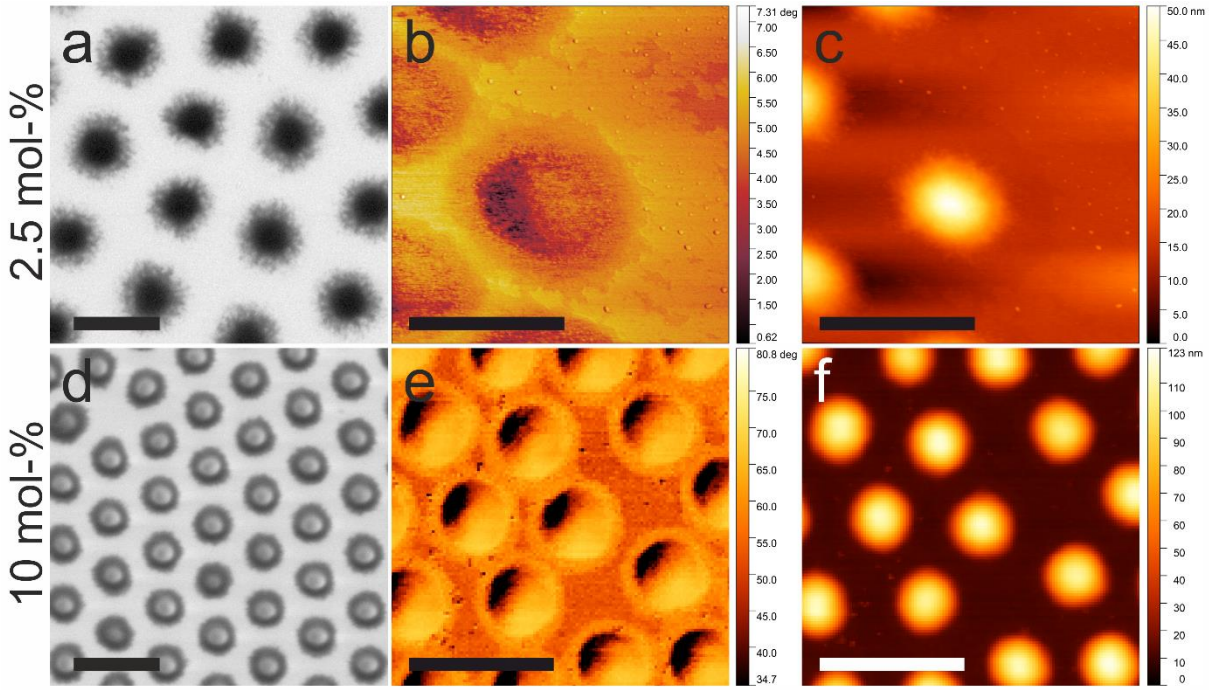
[a] Institute of Particle Technology, Friedrich-Alexander University Erlangen-Nürnberg, Cauerstrasse 4, 91058 Erlangen, Germany

[b] Interdisciplinary Center for Functional Particle Systems, Friedrich-Alexander University Erlangen-Nürnberg, Haberstrasse 9a, 91058 Erlangen, Germany

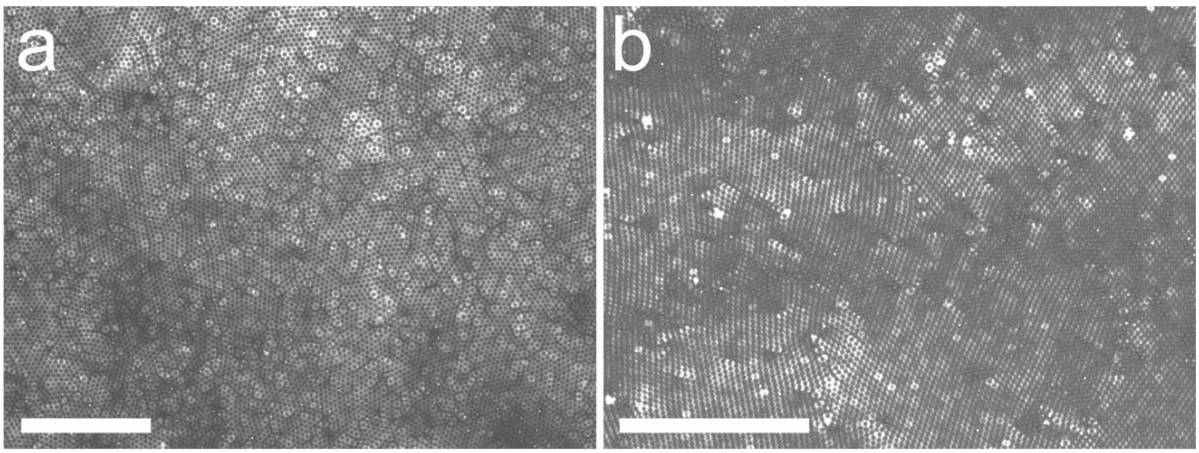
Supplementary Figures:



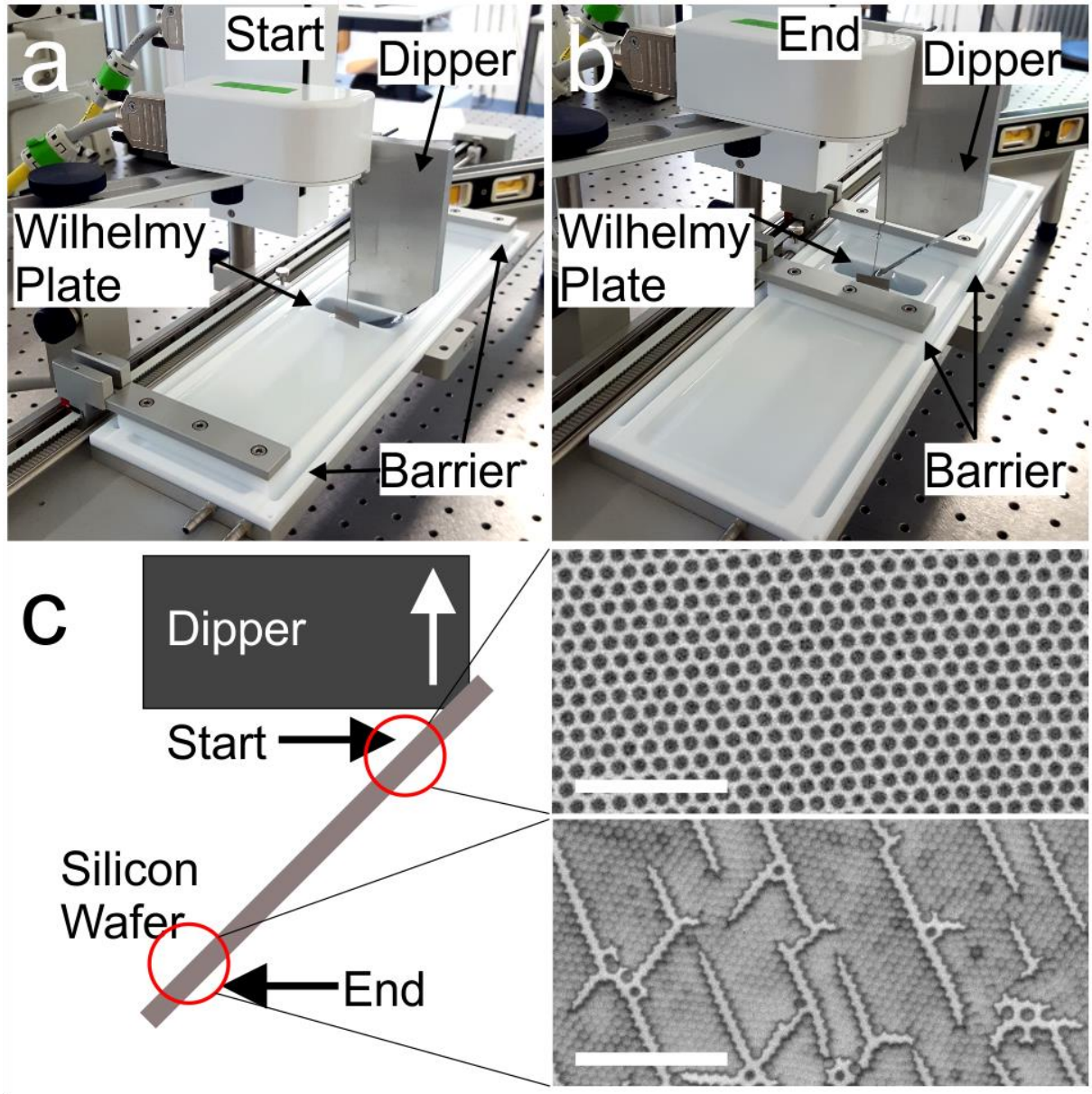
Supplementary Figure 1: Atomic force microscopy (AFM) images of microgels with different crosslinking densities deposited at 5 mN/m: a) 1 mol-%, b) 2.5 mol-%, c) 5 mol-%, d) 7.5 mol-%, e) 10 mol-%). Image size: 10 µm.



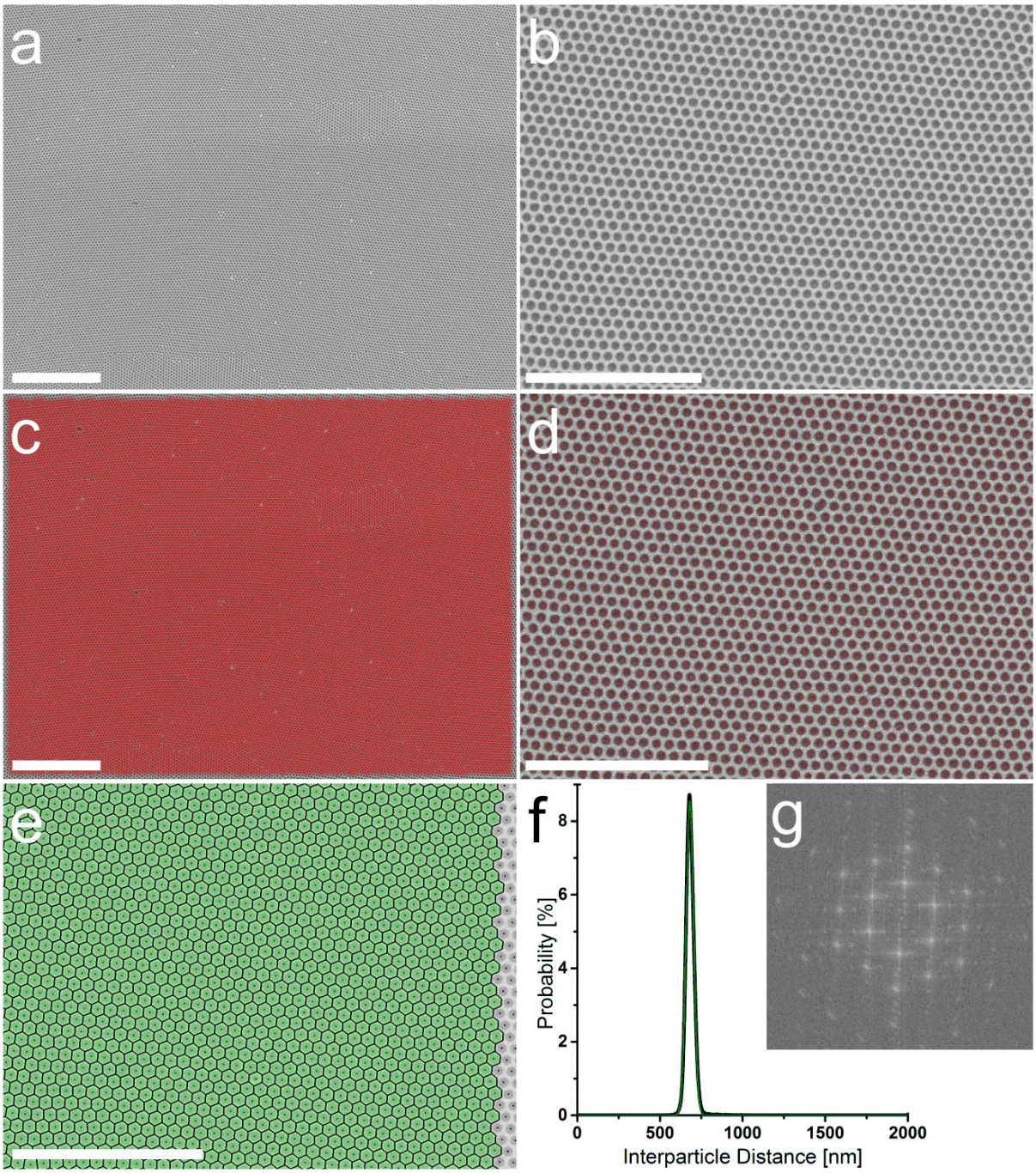
Supplementary Figure 2: “Core-shell” structure of microgel with 2.5 mol-% crosslinking density (a-c) and 10 mol-% crosslinking density (d-f) deposited on a substrate: a,d) SEM images. b,e) AFM phase image. c,f) AFM height image. Scale bar: 1 µm



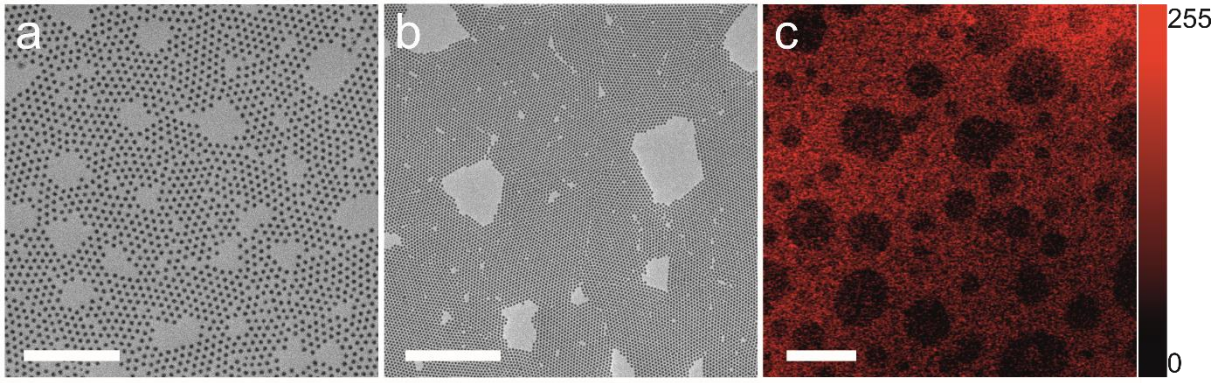
Supplementary Figure 3: Buckling of the microgel monolayer at high pressure: a) 2.5 mol-% crosslinking density microgels at 32.7 mN/m. b) 7.5 mol-% crosslinking density microgels at 34.2 mN/m. Scale bar: 10 µm.



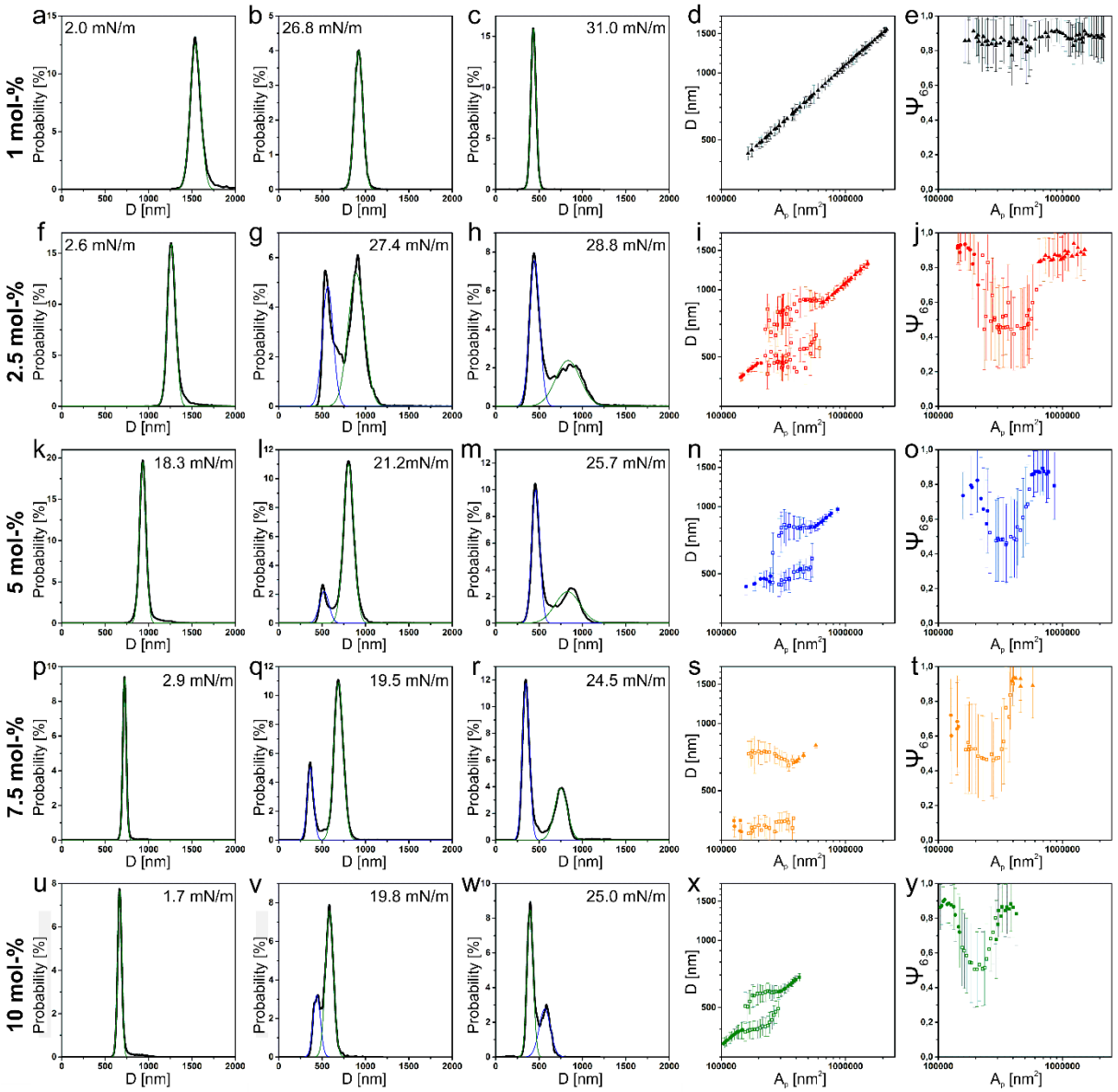
Supplementary Figure 4: Simultaneous compression and deposition Langmuir trough set-up: a) The silicon wafer substrate is fixed to the dipper under a 45 ° angle and lowered into the water reservoir. The substrate is lifted upwards with simultaneous synchronized compression of the barriers. Each position of the wafer can be correlated to its surface pressure measured with a Wilhelmy plate. c) The full compression isotherm can be transferred onto a wafer. Scale bar: 5 µm.



Supplementary Figure 5: Exemplar image analysis of deposited mircogels with 7.5 mol-% crosslinking density at a surface pressure of 10 mN/m.: Original SEM image (a) and zoom-in (b). Microgels tracked by custom-written Matlab software based on the publicly available Matlab code from Crocker and Grier[1] and marked with a red circle in the original SEM image (c) and zoom-in (d); the image contains 22101 microgels. e) Voronoi tessalation of the zoom-in. f) Interparticle distance distribution. g) Fourier transform. Scale bar: 20 µm.



Supplementary Figure 6: SEM images of microgels deposited at zero surface pressure (a,b): a) 1 mol-% crosslinking density, b) 10 mol-% crosslinking density. The microgels assemble into hexagonal non-close packed crystal that forms a network structure around areas without any particles. Scale bar: 20 µm. c) Confocal microscopy image of fluorescently labelled microgels with 10 mol-% crosslinking density taken directly at the air/water interface. Similar to the deposited microgels we observe a holey network. Scale bar: 100 µm.



Supplementary Figure 7: Statistical analysis of the phase transition for microgels with different crosslinking densities: 1 mol-% (a-e), 2.5 mol-% (f-j), 5 mol-% (k-o), 7.5 mol-% (p-t) and 10 mol-% (u-y). The interparticle distance D distribution shows a split-up for 2.5 mol-% to 10 mol-% (g, h, l, m, q, r, v, w) and a single peak for 1 mol-% (b,c). The fits for the interparticle distance were plotted against the area per particle Ap (d, i, n, s, x), where we notice a split-up during the phase transition. Similarly, the 2D hexagonal order parameter Ψ6 drops during the phase transition (j, o, t, y) and remains constant at high order for 1 mol-% crosslinking density (e).

References

1 J. C. Crocker and D. G. Grier, *Phys. Rev. Lett.*, 1996, **77**, 1897–1900.