Supplementary Information

Quantitative X-ray microscopic analysis of individual thermoresponsive microgel particles in aqueous solution

Andreas Späth[1], Birgit A. Graf-Zeiler[1], Gaio Paradossi[2], Shivkumar Ghugare[2,3], George Tzvetkov[4], Rainer H. Fink[*,1,5]

[1] Physikalische Chemie II and ICMM, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Egerlandstraße 3, 91058 Erlangen, Germany

[2] Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica, 00133 Roma, Italy

[3] present address: Solvay Research & Innovation Centre, Plot no. 72/73/74, Alindra Extention, G.I.D.C. Estate, Sailing, Dist. Vadadora, 391770 Gujarat, India

[4] Department of Inorganic Chemistry, Faculty of Chemistry, University of Sofia, James Bourchier 1, 1164 Sofia, Bulgaria

[5] CENEM, Friedrich-Alexander Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen, Germany

1) Effect of NIPAM/MA ratio on the swelling degree of PVA/P(MA-co-NIPAM) microgel particles

Definition of swelling degree:

$$SD = \frac{\text{weight of swollen gel - weight of dry gel}}{\text{weight of dry gel}} \qquad \text{(S1)}$$

Microgel Type	Cross deg (%)	NIPAM/MA	SD (%)	Size by CLSM (μm)
PM-I	5±1	0	79±2	
PMN-I	5±1	0.8	82±3	4.0±1.0
PMN-II	5±1	2.4	83±3	1.6±0.5

Table S1: *Swelling degree of PVA/P(MA-co-NIPAM) microgel particles with different NIPAM/MA ratios. The crosslinking degree is 5% for all particles according to elemental analysis. SD is almost independent from the NIPAM content.*

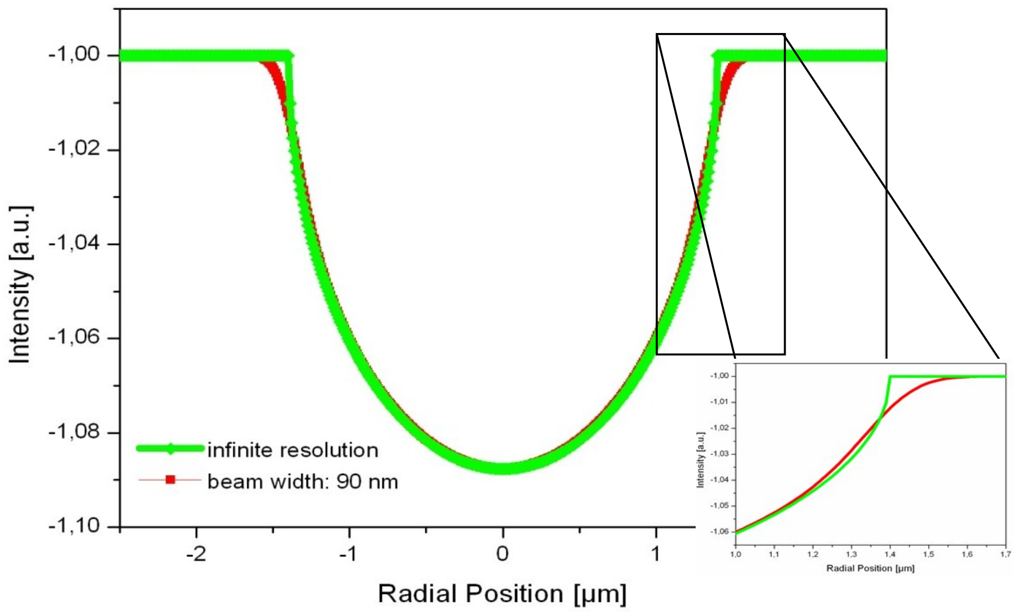
2) Beam size effects

Within the presented model it is assumed that the X-ray beam is infinitesimally small in diameter (infinite resolution). The STXM beam size, however, is determined by the parameters of the applied zone plate and the quality of focusing. The finite dimension of the beam is considered by a discrete convolution (eqn. S2) of the modeled transmission profiles in all regimes with a Gaussian distribution (eqn. S3) with a Full Width at Half Maximum (FWHM) given by ~2.35 σ [50].

$$T_{R(x)} = \left(T * G\right)_{(x)} = \sum_{n} T_{(t)} \cdot G_{(t-x)} \qquad \text{(S2)}$$

$$G_{(x)} = \frac{1}{\sigma\sqrt{2\pi}} \cdot e^{-\frac{x^2}{2\sigma^2}} \qquad \text{(S3)}$$

A minimization procedure is be employed to find the particle radius, shell thickness and absorption coefficients $k_i(x)$ that produce the best correlation with the experimental data. Fig. S1 shows the effects of the convolution on the transmission profiles as calculated for a beam width of 90 nm (for better visualization).



<u>Fig. S1:</u> Radial transmission profile according to eqn. (2a) – (2c) taking into account infinite STXM resolution and finite beam size. Variations become most obvious at the outermost rim (R_1).

3) Size distribution and selection of the microgel particles for the present STXM study

Fig. S2 illustrates the size distribution of the investigated PMN-II microgel particles. The exemplary particles investigated within the present study have been chosen with respect to characteristic sizes. The "large" particle represents the average and also most prominent particle size, while the "small" particle has a diameter close to the lower size limit (neglecting a very small portion of the size distribution). The largest available particles (diameter > 3.5 µm) are difficult to be analyzed by the presented STXM approach due to absorption saturation effects.

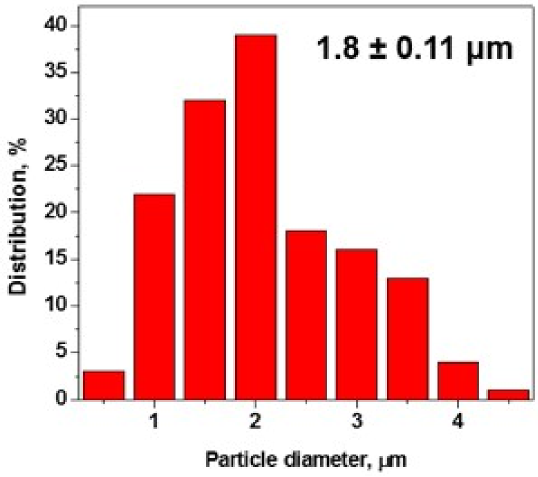


Fig. S2: Size distribution of the investigated batch of PMN-II microgel particles as determined by SEM in dry state and DLS in solution.

4) Detailed results of fit analysis for the investigated PMN-II particles

large particle	**25 °C**	std. dev.	**45 °C**	std. dev.	**55 °C**	std. dev.
R_0 [µm]	1.25	0.021	1.05	0.019	0.881	0.035
R_1 [µm]	1.70	< 0.001	1.51	0.001	1.44	< 0.001
k_{H_2O} [μm^{-1}]	0.110	fixed	0.110	fixed	0.110	fixed
k_{shell} [μm^{-1}]	0.500	0.005	0.638	0.007	0.727	0.007
k_{core} [μm^{-1}]	0.928	0.006	1.18	0.009	1.33	0.013
small particle	**25 °C**	std. dev.	**45 °C**	std. dev.	**55 °C**	std. dev.
R_0 [µm]	0.426	0.001	0.329	< 0.001	0.244	0.001
R_1 [µm]	0.869	0.001	0.732	< 0.001	0.708	0.002
k_{H_2O} [μm^{-1}]	0.110	fixed	0.110	fixed	0.110	fixed
k_{shell} [μm^{-1}]	0.482	0.005	0.647	0.008	0.771	0.008
k_{core} [μm^{-1}]	0.901	0.018	1.24	0.030	1.48	0.048

Table S2: Summary of the least-square fit results depicted in Fig. 3, including the standard deviations for the investigated particles at temperatures 25°C, 45°C and 55 °C.