Supporting Information: Does Flory-Rehner theory quantitatively describe the swelling of thermosensitive microgels?*

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I. CALCULATION OF PRE-FACTOR TO ELASTIC TERM.

The mass in grams of polymer in a microgel at the reference state is $M = V_0\phi_0\rho_p$ and the total number of monomers is given by $N_M = MN_A/M_0$ where M_0 is the mass of the cross-linker. The number of crosslinks in the microgel is then $N_{CL} = N_M f$ and since each cross-linker molecule generates two chains, the number of chains in a microgel particle is $N_c = 2N_{CL}$. The prefactor to the elastic term in equation 4 of the main text is then

$$\frac{N_c}{V_0}\frac{v_s}{N_A} \simeq \frac{2\phi_0\rho_p f}{M_0}\frac{v_s}{N_A}$$

This prefactor to for PNIPAM in water, cross-linked with BIS ($\phi_p = 1.1$ g/mL, $M_0 \times N_A = 113$g and $v_s = 18$ mL) reduces to:

$$\frac{N_c v_s}{V_0 N_A} \simeq 0.35\phi_0 f \qquad (1)$$

A spreadsheet calculating ϕ and R_H as a function ϕ_0, θ, A, C and D is provided.

II. FLORY-RHENER FITS TO LITERATURE DATASETS.

Figure S1 shows Flory-Rehner fits to the datasets considered in Table 1 of the main manuscript. Figure S2 shows fits of the Flory-Rehner model to the two samples with lowest cross-linking densities of reference [1] leaving ϕ_0 as a free parameter. The fit parameter values for these are presented in Table 1 of the main text in brackets. The microgel of Acciaro et al prepared by the feeding method and the sample of Arleth et al are reported to be uniformly cross-linked.

III. FITS WITH VARYING f

Fit results to the datasets by Senff and Richtering[1] were considered in the main manuscript using the cross-link density calculated from synthesis f_{syn}. Figure S3 shows the best fit parameters obtained when f is fixed

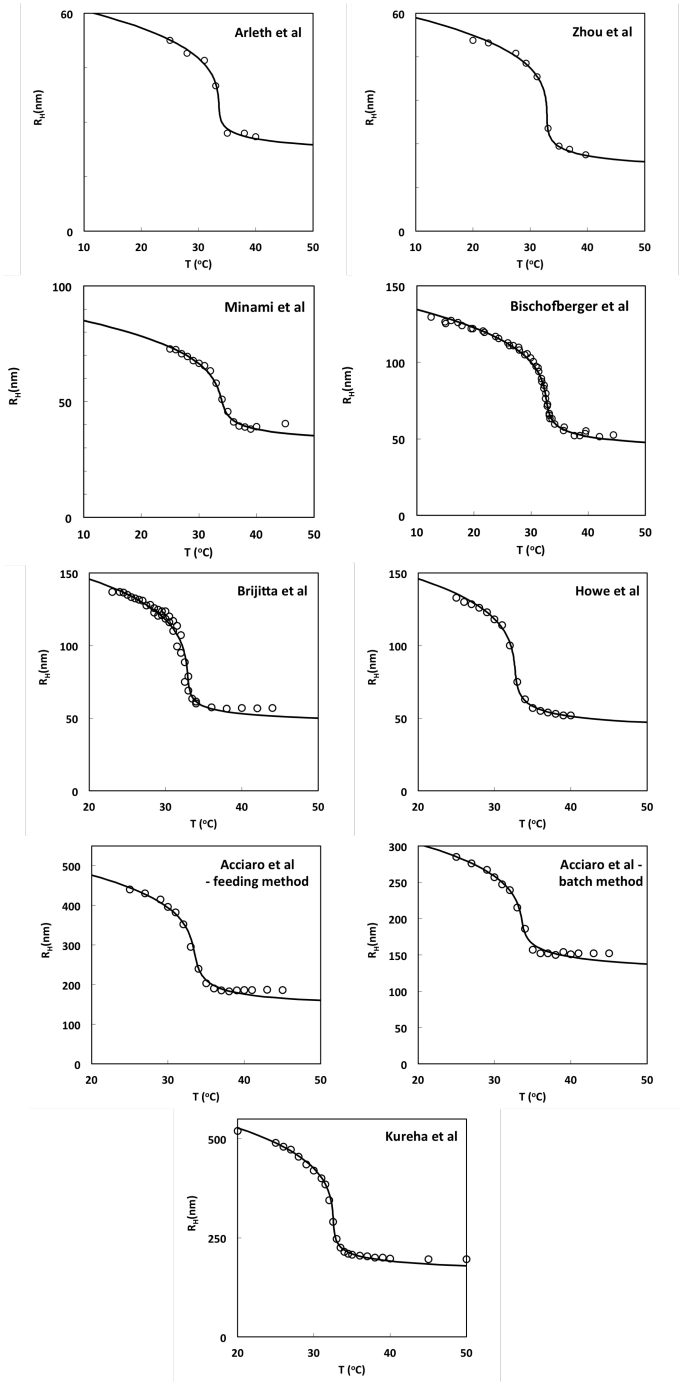

FIG. S1. Fits to different datasets from references [2–9].

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* Not really

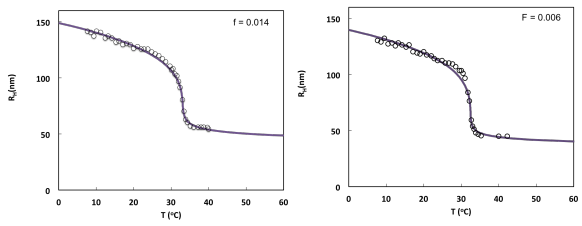

FIG. S2. Fits to datasets of Senff and Richtering, degree of cross-linking indicated on the graphs. The value of ϕ_0 (see Table I of the main text) corresponds to the best fit value for each dataset.

at different values.

If $f \simeq 0.3 f_{syn}$ is used, C and D are approximately independent of cross linking density and A approaches the range expected from equation 5 (although its still $\simeq \times 5$ larger). The effective value of f may be expected to be lower than the nominal one, as explained in the main manuscript due to non-uniform cross-linking. However, analysing the data of Arleth et al, for which the cross-linking is approximately uniform, we again find $f \simeq 0.05 f_{syn}$ is required to obtain a value of $A \simeq -0.3$. Given that in this case cross-linking is homogeneous, this would require that some 95% of the cross-linker remain unreacted. It seems more likely that the affine network model overestimates the elastic contribution of network strands, which therefore leads to reasonable fit parameters for χ when an artificially low value of f is used.

Acciaro's data show that homogeneously cross-linked samples swelll to a greater degree than heterogeneously cross-linked ones, which would therefore require a higher value of f to be used for the data considered in the main text, resulting in greater disagreement between fit values of A and independent estimates from equation 5. The fit to the homogeneously a cross-linked sample prepared by Acciaro et al confirms this with a value of $A \simeq -5$.

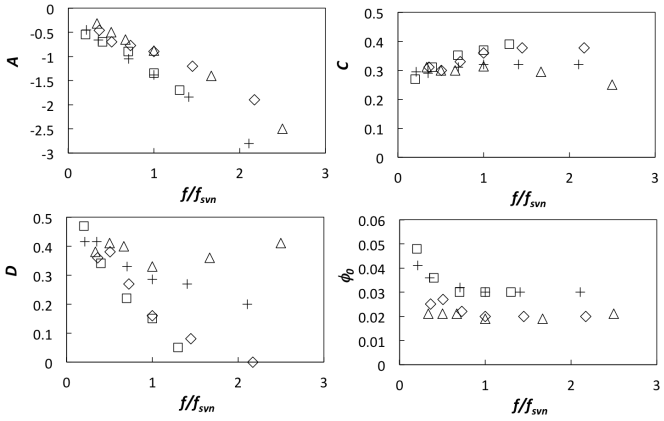

FIG. S3. Fit results to dataset by Senff and Richtering. Best fit values of A, C, D and ϕ_0 as a function of chosen value of f divided by the nominal value of f. Different symbols correspond to the different nominal cross-linking values: $f = 0.05$ (□), $f = 0.029$ (+), $f = 0.014$ (◇), $f = 0.006$ (△).

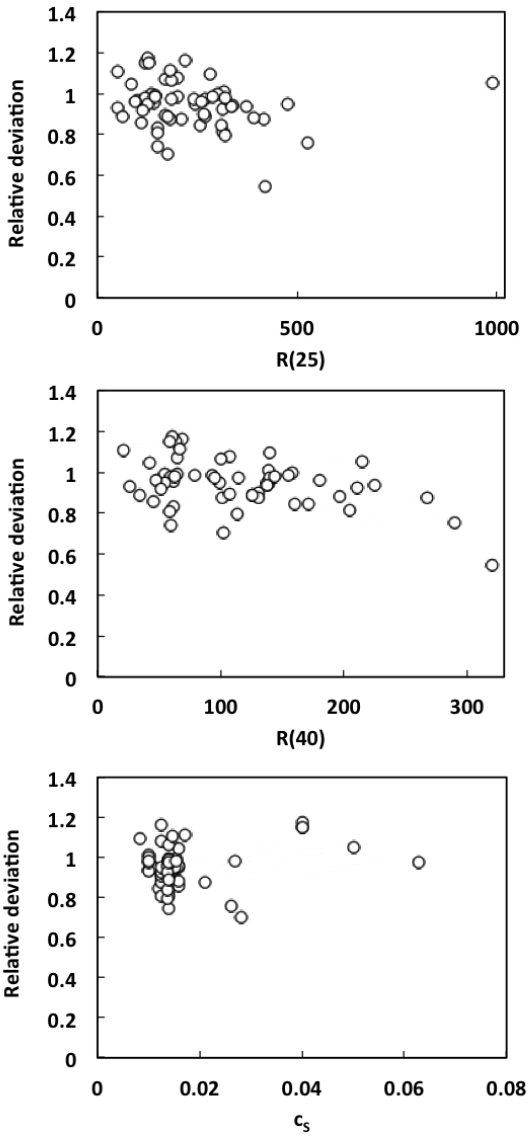

FIG. S4. $[R_H(25°\text{ C})/R_H(40°\text{ C})]/(0.966 f^{-0.2})$ as a function of different parameters. c_S is the total monomer concentration at synthesis in wt/wt. Note this is not the same as the polymer concentration inside a microgel particle.

IV. EFFECT OF SYNTHESIS ON SWELLING PROPERTIES

Figure S4 shows the relative deviation between $R_H(25)/R_H(40)$ data and the best fit equation $R_H(25)/R_H(40) = 0.966 f^{-0.2}$, as a function of different parameters. No systematic deviations are found with any of the parameters considered.

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