

Supporting Information: Crowding effects on the structure and rheology of ultrasoft PNIPAM-PEGMA copolymer microgels

Gavino Bassu^{a,b}, Jacopo Vialetto^{a,b}, José Ruiz-Franco^{c,d}, Andrea Scotti^e, Judith E. Houston^f, Jitendra Mata^{g,h}, Emanuela Zaccarelli^{i,1}, and Marco Laurati^{* a,b}

^aDipartimento di Chimica "Ugo Schiff", Università di Firenze, Sesto Fiorentino (FI), 50019 Italy.

^bConsorzio per lo Sviluppo dei Sistemi a Grande Interfase (CSGI), via della Lastruccia 3, Sesto Fiorentino (FI), 50019, Italy

^cDepartment of Condensed Matter Physics, University of Barcelona, 08028, Barcelona, Spain.

^dInstitute for Complex Systems (UBICS), University of Barcelona, 08028, Barcelona, Spain.

^eDivision of Physical Chemistry, Lund University, SE-22100 Lund, Sweden

^fEuropean Spallation Source ERIC, Box 176, SE-221 00 Lund, Sweden

^gAustralian Centre for Neutron Scattering (ACNS), Australian Nuclear Science and Technology Organisation (ANSTO), Lucas Height, New South Wales 2234, Australia

^hSchool of Chemistry, University of New South Wales, NSW, Australia

ⁱDepartment of Physics, Sapienza University of Rome, Piazzale Aldo Moro 2, 00185 Roma, Italy.

¹CNR Institute of Complex Systems, Uos Sapienza, Piazzale Aldo Moro 2, 00185, Roma, Italy.

SI. HYDRODYNAMIC RADIUS AS A FUNCTION OF TEMPERATURE

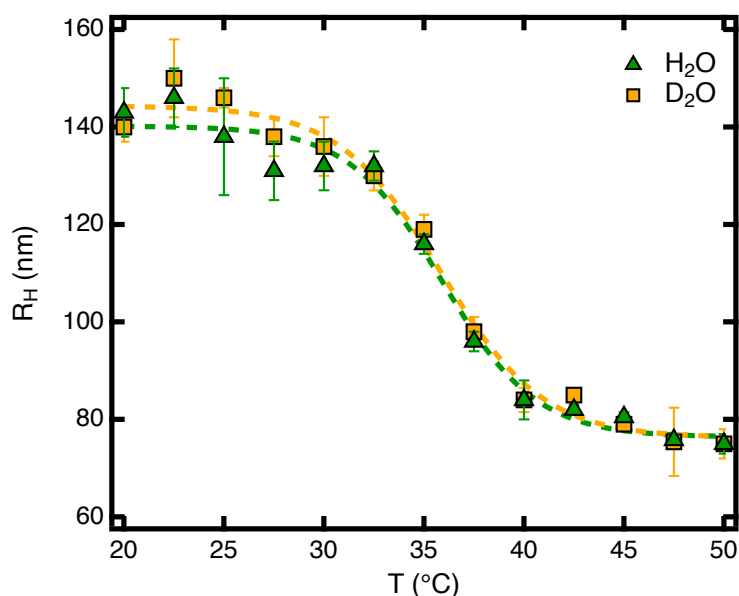


Figure S1: Hydrodynamic radius R_H obtained from DLS measurements at different temperatures for microgels in H_2O (triangles) and D_2O (squares).

Fig. S1 shows the hydrodynamic radius of the particles R_H measured by DLS, as a function of temperature. The line is a fit to a sigmoidal function, used to determine the VPT temperature. There are no significant differences in the size of the particles in H_2O (used for SAXS and rheology) and D_2O (used for SANS).

SII. RADIUS OF GYRATION AS A FUNCTION OF DPEG CONCENTRATION

Fig. S2 reports the values of R_g obtained from the fits of the SANS scattered intensities of Fig.1 of the main article, as a function of the dPEG solution in the mixture, used to control the osmotic pressure.

SIII. EXTENDED R_G/R_G^0 AND ϕ VS ϕ_{EFF} PLOTS

Fig.S3 reports the dependence of R_g/R_g^0 and ϕ on ϕ_{eff} , where it can be clearly seen that most of the variations are observed for $\phi_{eff} < 0.61$.

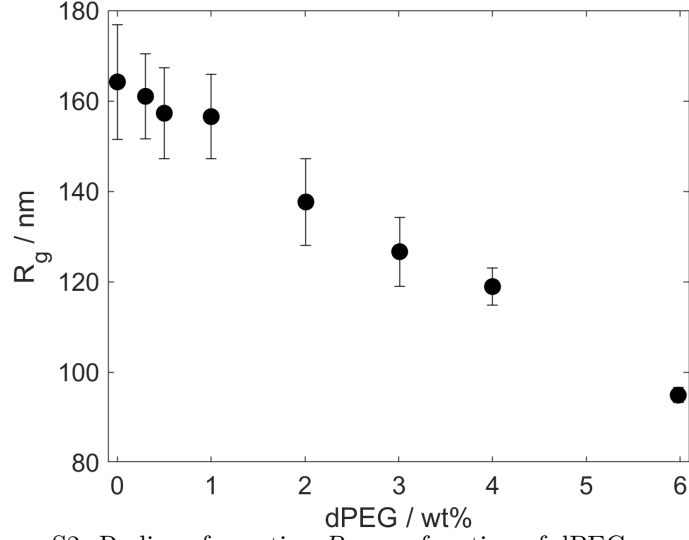


Figure S2: Radius of gyration R_g as a function of dPEG concentration.

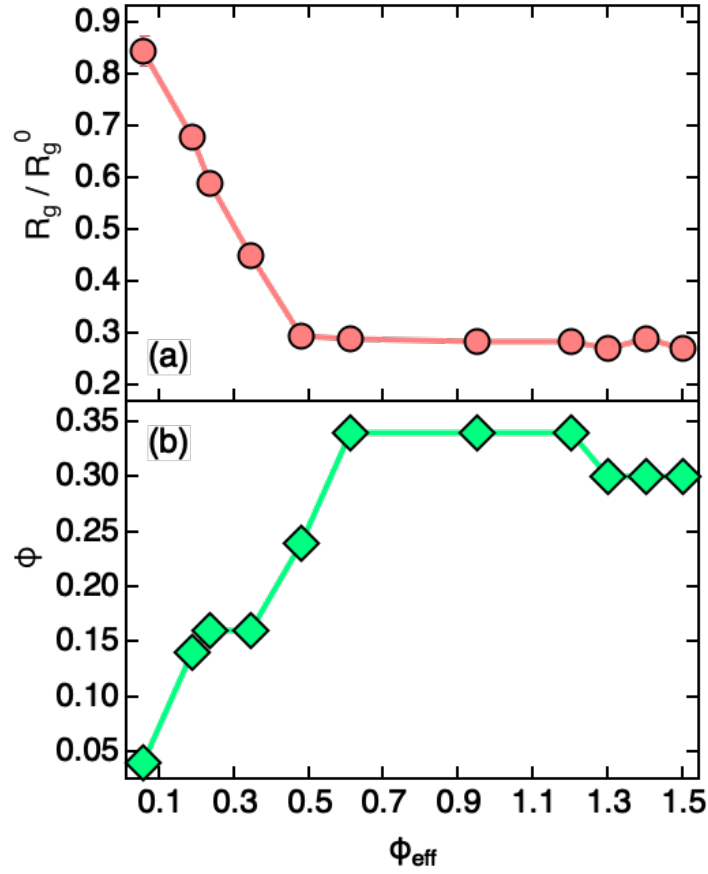


Figure S3: R_g/R_g^0 and ϕ as a function of ϕ_{eff} , including data of previous work.¹

SIV. SAXS FITS FOR $\phi_{\text{EFF}} > 1$ WITH A HYDROGEL NETWORK MODEL

Fig. S4 shows the scattering intensities measured for samples with effective packing fractions $\phi_{\text{eff}} = 1.20, 1.30, 1.40$ and 1.50 at $T = 20$ °C, and fit curves obtained according to the following model,² typically used to describe scattering data from macroscopic hydrogels:

$$I(Q) = I_{\text{OZ}}(Q) + I_{\text{DB}}(Q) + \text{bkg} \quad (\text{S1})$$

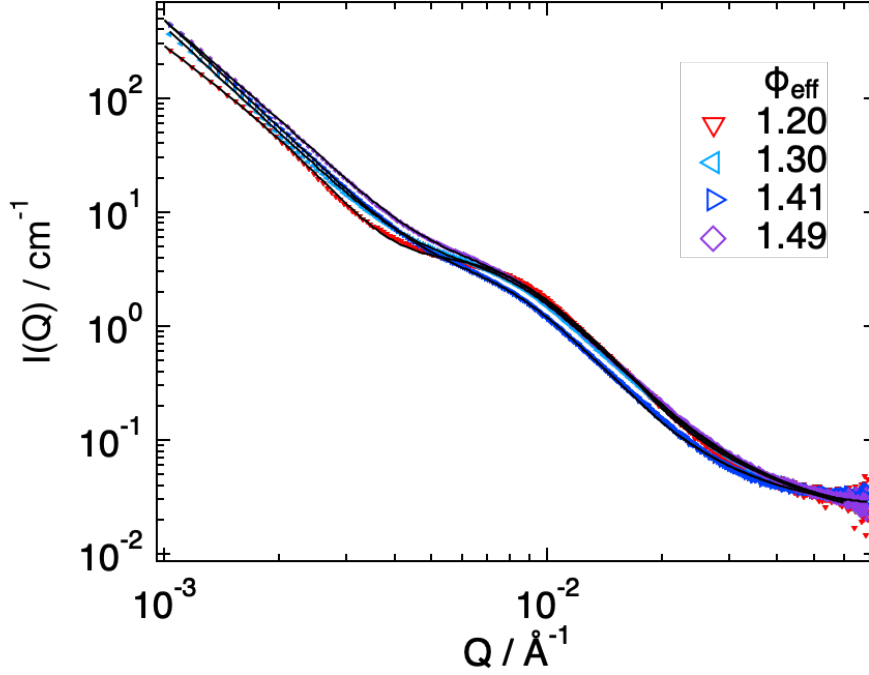


Figure S4: SAXS scattering intensities $I(Q)$ for $\phi_{\text{eff}} = 1.20, 1.30, 1.41$ and 1.49 , as indicated, and fits (lines) obtained using Eqs. S1 to S3.

with³ :

$$I_{\text{Oz}}(Q) = \frac{I_{\text{Oz}}(0)}{1 + (\zeta Q)^m} \quad (\text{S2})$$

in which the quantity $I_{\text{Oz}}(0)$ represents the scattering intensity at $Q = 0$, which is determined by the contrast between the polymer and the solvent, and by the volume fraction of the polymer within the gel. The parameter m is the Porod exponent, reflecting the interactions between the polymer and the solvent. For linear polymer chains in a good solvent, $m = 1.67$, while m progressively increases with the worsening of the solvent conditions and the associated polymer collapse.⁴ The Debye-Bueche function⁵ has the following expression:

$$I_{\text{DB}}(Q) = \frac{I_{\text{DB}}(0)}{(1 + a^2 Q^2)^2} \quad (\text{S3})$$

in which $I_{\text{DB}}(0)$ is the excess scattering at $q = 0$, which is again related to the contrast and the volume fraction of the heterogeneities. Note that the latter term is the same used in the main article to model the contribution of heterogeneities.

REFERENCES

- [1] M. Lara-Peña, A. Licea-Claverie, I. Zapata-González, and M. Laurati, “Colloidal and polymeric contributions to the yielding of dense microgel suspensions,” *J. Coll. Interf. Sci.* **587**, pp. 437–445, 2021.
- [2] G. Bassu, M. Laurati, and E. Fratini, “Microgel dynamics within the 3d porous structure of transparent peg hydrogels,” *Colloids and Surfaces B: Biointerfaces* **221**, p. 112938, 2023.
- [3] M. Shibayama, “Spatial inhomogeneity and dynamic fluctuations of polymer gels,” *Macromolecular Chemistry and Physics* **199**(1), pp. 1–30, 1998.
- [4] E. I. Wisotzki, P. Tempesti, E. Fratini, and S. G. Mayr, “Influence of high energy electron irradiation on the network structure of gelatin hydrogels as investigated by small-angle x-ray scattering (saxs),” *Phys. Chem. Chem. Phys.* **19**, pp. 12064–12074, 2017.
- [5] P. Debye and A. M. Bueche, “Scattering by an inhomogeneous solid,” *Journal of Applied Physics* **20**(6), pp. 518–525, 1949.