## Supporting Information: Experimental determination of the bulk moduli of hollow nanogels

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## S1. GOODNESS OF THE FITS



FIG. S1. Values of the  $\chi^2$  of the fits as a function of the exerted osmotic stress,  $\pi$ . Squares and circles correspond to HN1 and HN2, respectively. Residual fro HN1 (b) and HN2 (c). The different symbols corresponds to the different applied  $\pi$ .

We have computed the final values of the  $\chi^2$  for the fits at different compression and they are plotted in Figure S1(a). In panels S1(b) and S1(c), we show the residuals. The oscillation of the residuals at low q might indicate overfitting. The model we choose - Eqs. 2 and 3 in the main text - is the one that can represent the data with the lowest number of fitting parameters. For instance, fits of the data of dilute solution of the hollow nanogels with an hard sphere model or with a model for a simple fuzzy sphere were not able to reproduce the I(q) and lead to values of the total radius and size polydispersity consistent with multi angle dynamic light scattering measurements.

However, to see if the data changes with increasing the applied osmotic stress, and if the evolution of the characteristic lengths are not due to bias during the fitting procedure, we plot the measured intensities normalized by the intensity measured for a suspension of nanogels without  $d_{83\%}$ PEG, Figure S2. As can be seen the curves shows significant differences in the low and middle *q*-range for both the HN1 and HN2, panel (a) and (b), respectively.

To verify the goodness of the fits for the hollow nanogels at high  $\pi$ , we also used a model that does not assume any radial distribution *a priori*. The nanogel is divided in *i*-shells with the same length. This multi-shell model is used to find the best radial profile that generates the best fit of the experimental data. We use i = 20 for the number of shells. Using an



FIG. S2. Intensities measured at  $\pi > 0$  divided by the intensity of samples measured in dilute conditions at  $\pi = 0$  fro HN1 (a) and HN2 (b).

iterative process, the density of the *i*-th shell is changed and the theoretical scattering profile is obtained from the Fourier transform density profile. The resulting scattering profile is compared to the experimental data. If the agreement between them is better than in the previous step the density profile is kept; otherwise it is rejected. Then a new profile is computed by changing the density of another shell. The iterations end when the difference in the goodness between the fit at step n and at the step n-1 is lower than a threshold. At the end of the iterations, the radial profile of the relative polymer volume fraction that generates the best fit of the data is obtained. Virtanen *et al.* [2] have shown that this multi-shell model is able to reproduce the scattering data of nanogels with different internal architectures.

Here, we fit the form factor of the hollow nanogels nanogels at  $\pi = 0$  kPa, (1.040  $\pm$  0.002) kPa, and (93.9  $\pm$  0.1) with the 20-shell model (dashed line in Figure S3(a)). As can be seen by the comparison with the fit with of the model in Eqs. 2 and 3 (solid line), there is agreement between the results for the three sets of data shown. Also the ratio between the  $\chi^2$  of the original model divided by the  $\chi^2_{20 shell}$  of the 20-shell model is slightly smaller or equal to one. This indicates that the original model is as good as, if not slightly better than the 20-shell model.



FIG. S3. (a) SANS intensity, I(q), as a function of the scattering vector, q, for the hollow nanogels HN1 (squares), obtained from the core-shell particles with sacrificial 105 nm silica core (a). The osmotic pressure exerted by the  $d_{83\%}$ PEG are from bottom to top 0,  $(1.040 \pm 0.002)$ , and  $(93.9 \pm 0.1)$  kPa. The solid lines are fits of the data with the model in Eqs. 2 and 3 introduced by Berndt *et al.* [1]. The dashed red lines are fits with the 20-shell model. Data are shifted in the y-direction for clarity. Radial profiles obtained fitting the data with the the model in Eqs. 2 and 3 (solid red line) and te 20-shell model black lines for osmotic pressure exerted by the  $d_{83\%}$ PEG equal to 0 kPa in (b),  $(1.040 \pm 0.002)$  kPa in (c), and  $(93.9 \pm 0.1)$  kPa in (d).

Figures S3(b) to (c) show the radial distributions as obtained from the original model (solid lines) and from the iterations of the 20-shell model (black lines). The radial distributions are virtually identical and the characteristic lengths - shell thickness and cavity size - are correctly predicted. The total radius of the nanogels, as obtained from the two models, are listed in Table S1. As can be seen, the difference between the obtained values

is comparable with the experimental errors we state in the manuscripts.

TABLE S1. Osmotic pressure,  $\pi$ , total nanogel radius, R, total nanogel radius as determined from the 20 shell model,  $R_{20 \ shell}$ , and ratio between the  $\chi^2$  of the model in Eqs. 2 and 3 divided by the  $\chi^2_{20 \ shell}$  obtained from teh 20 shells model.

Name	$\pi$ (kPa)	$R \ (nm)$	$R_{20shell}$ (nm)	$\chi^2/\chi^2_{20shell}$
	0	$206\pm4$	$205\pm25$	1.6750
HN1	$1.040\pm0.002$	$166\pm3$	$163\pm2$	0.2659
	$93.9\pm0.1$	$140\pm3$	$143\pm5$	0.3326

## S2. VARIATION OF $\xi$ WITH COMPRESSION



FIG. S4. Radius and mesh size normalised for their values at  $\pi = 0$ ,  $R/R_0$  and  $\xi/\xi_0$ , respectively, as a function of the exerted osmotic stress,  $\pi$ . Squares and diamonds correspond to  $R/R_0$  and  $\xi/\xi_0$ for HN1. Circles and triangle correspond to  $R/R_0$  and  $\xi/\xi_0$  for HN2.

In Figure S4, we show the variation of the particle radius and mesh size, normalized to their values at  $\pi = 0$ . We cannot find a clear relation between the changes in  $R/R_0$  and  $\xi/\xi_0$  for any of the hollow microgel studied. What can be observed is that for the HS1, both the particle radius and the mesh size changes abruptly already for  $\pi \leq 4$  kPa. In contrast, a pronounced change of R and  $\xi$  can be observed at  $\approx 30$  kPa for HN2. The evolution of  $\xi$  with  $\pi$  is qualitatively consistent with the reported behavior of R vs.  $\pi$  and shows a difference between HN1 and HN2. A more quantitative analysis is limited also by the large errors on the values of  $\xi$ . The determination of  $\xi$  from scattering data is not trivial.

Indeed the multi-dimensional space of the fitting parameters contains many local minima of the  $\chi^2$ . The high incoherent background for  $q > 0.1 \text{ nm}^{-1}$ , mainly due to hydrogen atoms, affects the uncertainty on the values of  $\xi$  and the associated multiplicative prefactor, that is the zero-q intensity contribution to the scattering signal of the internal mesh. In this q-region, the quality of the fit depends strongly on  $\xi$  and its prefactor. Therefore, it is easy for the minimization process to get trapped locally in any of these minima. It has been shown by Lietor-Santos *et al.* [3] that, for fixed values of R, the size polydispersity, and of the characteristic lengths of the nanogels, such as core radius and length of the fuzzy shell,  $\xi$  and its prefactor can vary largely from some to hundreds of nanometer and still lead to good fits according to the  $\chi^2$  value.

- [1] I. Berndt, J. S. Pedersen and W. Richtering, Angewandte Chemie, 2006, 118, 1769–1773.
- [2] O. Virtanen, A. Mourran, P. Pinard and W. Richtering, Soft matter, 2016, 12, 3919–3928.
- [3] J. Lietor-Santos, U. Gasser, R. Vavrin, Z. Hu and A. Fernandez-Nieves, The Journal of chemical physics, 2010, 133, 034901.