

Conformational changes upon high pressure-induced hydration of poly(*N*-isopropylacrylamide) microgels

Supplementary information

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1. Materials and sample preparation

Poly(*N*-isopropylacrylamide) (PNiPAm) was synthesized as described earlier.¹ Owing to the large overlap of an H₂O infrared band with the amide band, the microgel was dissolved in D₂O (Merck, Darmstadt, Germany), yielding a total concentration of 3 % (w/w) for the high pressure FTIR and 0.5 % (w/w) for the high pressure SAXS measurements.

2. Experimental details of SAXS measurements

The scattering curves were recorded with a CCD-detector with a sample to detector distance of 10 m, covering a range of momentum transfer Q from 0.02-0.94 nm⁻¹. The exposure time was

between 0.05 and 0.5 s. The measurements were carried out in a home-built high-pressure X-ray cell, which is equipped with two flat diamond windows of 1 mm thickness (type IIa quality, Drukker, Cuijk, The Netherlands). Further technical details are described by Woenckhaus *et al.*² High hydrostatic pressures up to 300 MPa—with an accuracy of 2 MPa—at steps of 10 MPa were applied in a temperature range from 10 °C to 50 °C using water as pressurising medium. Temperature control (with an accuracy of ± 0.2 °C) was achieved by a computer-controlled water circulation system from a thermostat through the temperature controlled jacket of the pressure cell. The time for thermal equilibration before each measurement was set to 15 min. For the SAXS measurements, a total of 1 mL of the sample was filled into the pressure cell, yielding a concentration of 0.5 % (w/w). The intensity of the diffraction pattern was plotted against the magnitude of the scattering vector Q ($Q = (4\pi/\lambda) \sin\theta$, with 2θ being the scattering angle) by a MATLAB based software, provided by the ESRF. The scattering curves were corrected for background using the pure solvent and taking into account the different absorption factors.

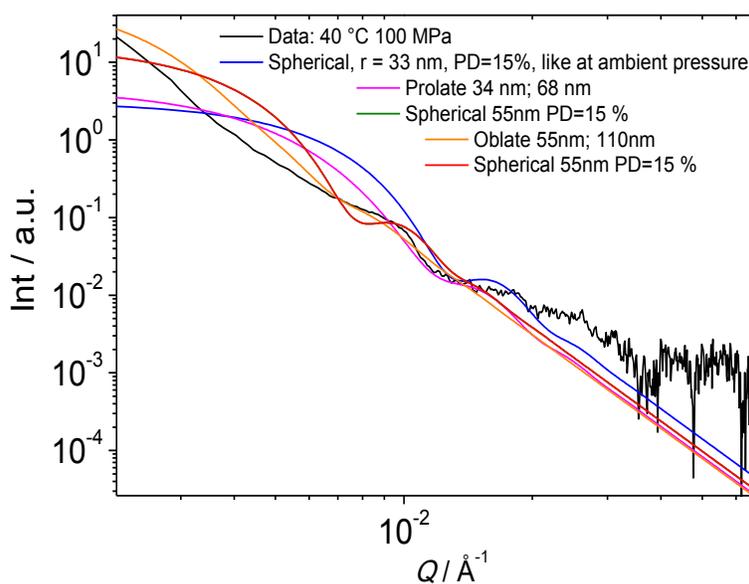


Figure S - 1: Scattering curve measured at 40 °C and 100 MPa (black) with different model curves

1. Fits assuming spherical particles: Fit for a spherical particle of radius 34 nm with 15 % polydispersity (similar to fit at ambient pressure; cf. Fig. 2 in main article; blue); same shape and polydispersity but increased radius of 55 nm (red).
2. Fits assuming ellipsoidal particles: Prolate with semiaxes of 34 nm and 68 nm, respectively (magenta); oblate with semiaxes of 55 nm and 110 nm, respectively.

3. Details on SAXS data fitting

The deviation from a spherical form factor of scattering curves at 40 °C and higher pressures is further illustrated in Figure S - 1. The fitting results for a sphere with inhomogeneous density distribution at 20 °C and ambient pressure is presented together with the data in Figure S - 2. The parameters of the fit and those found at increased pressure are given in Table S - 1.

Table S - 1: Fit parameters at 20 °C assuming an inhomogeneous density.

pressure / MPa	r / nm	σ_{Surf} / nm	R / nm
0	45.0	16.0	77.0
50	44.0	16.0	76.0
100	44.0	12.5	69.0
150	44.0	11.0	66.0
250	44.0	9.0	62.0

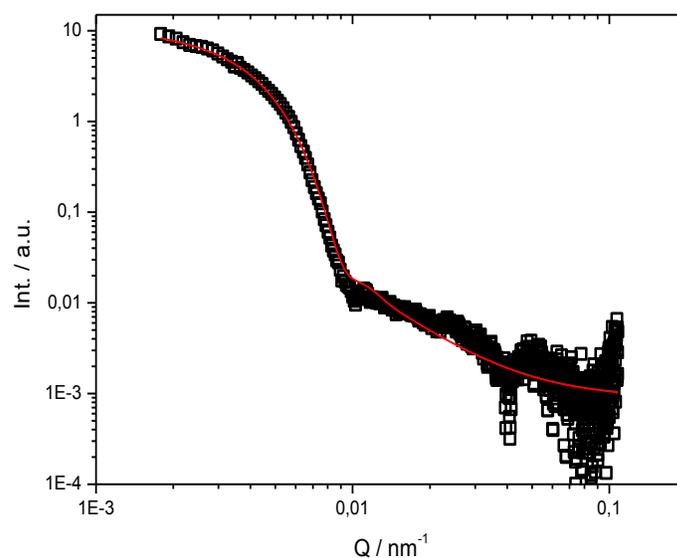


Figure S - 2: SAXS results at 20 °C and ambient pressure, the red line is a fit according to Stieger *et al.*³

4. Fourier-transform infrared spectroscopy

The pressure dependent measurements were carried out with a MAGNA 550 spectrometer from Nicolet (Offenbach, Germany) equipped with a liquid nitrogen-cooled MCT (HgCdTe) detector at 20, 30 and 40 °C, covering a pressure range up to 1000 MPa. As a pressure cell, a P-series diamond anvil cell (DAC) with type IIa diamonds (High Pressure Diamond Optics Inc., Tucson, USA) was used. A 50 μm thick gasket of stainless steel with a 0.45 mm drilling was placed between the two diamonds holding 10 μl of the sample. The final volume in the closed diamond cell was ~ 10 nl. Pressure was determined with co-added BaSO_4 powder, which shows the characteristic pressure sensitive symmetric sulphate stretching mode around 983 cm^{-1} that increases linearly with pressure (accuracy: ± 20 MPa).⁴ Temperature control was achieved with an external water bath, measuring the temperature internally with a digital thermometer (accuracy: ± 0.5 °C). The temperature equilibration time took 15 min. The sample chamber was purged constantly with dry air. Typically, 256 spectra were recorded from 4000 to 650 cm^{-1} with a spectral resolution of 2 cm^{-1} . Apodisation was done with a Happ-Genzel function. Peak positions were determined with two significant digits with OMNIC 7.2 spectral processing software. Further spectral processing and deconvolution of the amide-I'-band was performed with the GRAMS/AI 9.1 software package (Thermo Fisher Scientific Inc., Waltham, USA). After subtraction of noise and background (solvent), all spectra were normalized to the same area.

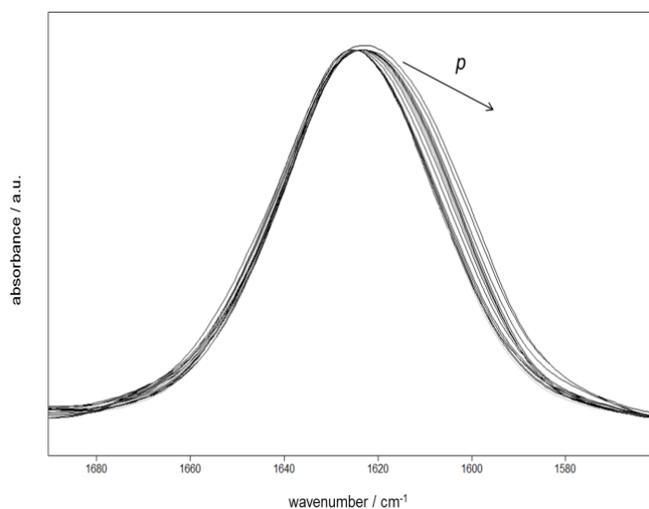


Figure S - 3: Normalized amide-I' FTIR-spectra of PNIPAAm microgel in a pressure range from 1 – 10600 bar (0.1 – 1060 MPa) at 20 °C. The time course of the recorded spectra with increasing pressure is indicated by the black arrow.

Table S - 2: Assignment of the amide-I'-subbands to the different hydrogen bonding patterns of PNiPAAm.⁵

Band assignment	Wavenumber / cm^{-1}
Intramolecular H-bonds from carbonyl groups to amide-deuterons	1642 – 1652
Carbonyl groups in mixed hydrophobic / hydrophilic environments ^a	1617 – 1628
Intermolecular H-bonds from carbonyl groups to D_2O (two bands owing to different levels of hydration)	1580 – 1612

^a i.e., where both hydrophobic and hydrophilic groups are present in the direct neighbourhood of the $\text{C}=\text{O}$ groups.

to ensure comparability. The amide-I'-region was fitted with four subbands, which were detected by Fourier Self Deconvolution (FSD) and the second derivative using a Voigt-function. The subbands are characteristic for distinctive hydrogen bonding patterns and were assigned as shown in Table S - 2.⁶ The slightly different intensities of the amide-I' subbands at ambient pressure observed for different sample cells may be due to less accurate background subtraction in the diamond anvil cell and different surface properties and surface-to-volume ratio of the sample cell materials. These minor differences are irrelevant here, as relative changes of conformational states are discussed, only. The amide I' band in dependence of pressure is shown in Figure S - 3. A clear shift of the maximum is visible. The relative area of the different subbands from the fit is given in Figure S -4.

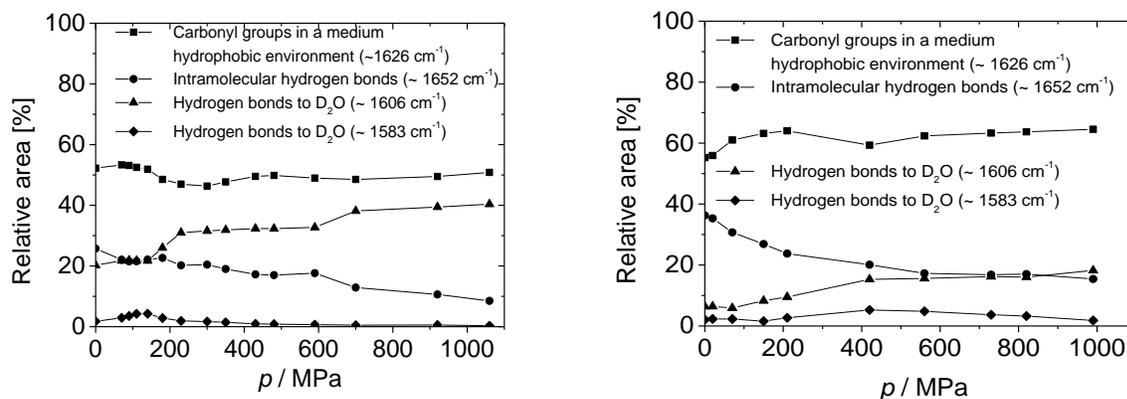


Figure S -4: Pressure dependence of the relative areas of diagnostic amide-I'-bands of PNiPAm microgels in D_2O at 20 °C (left) and 40 °C (right).

5. Dynamic light scattering

The hydrodynamic radius has been determined under atmospheric pressure by DLS. These data are shown in Figure S - 5. The results show the typical shrinking upon temperature increase. In order to avoid multiple scattering and interactions between the particles, the concentration of the microgel is much smaller than that used in the SAXS and FTIR experiments.

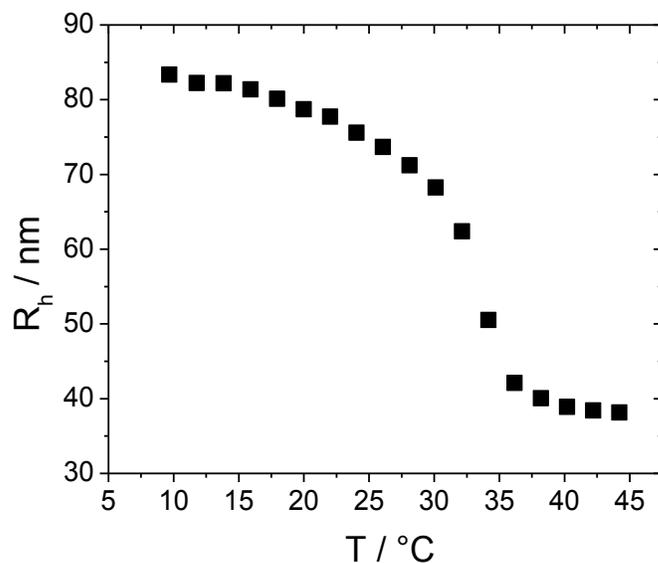


Figure S - 5: Hydrodynamic radius of the microgel under atmospheric pressure as determined by dynamic light scattering.

References

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