Supporting Information

Gold-poly(N-isopropylacrylamide) core-shell colloids with homogeneous density profiles: A small angle scattering study^{\dagger}

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Particle analysis using TEM and AFM

Figure S1 shows low magnification images of the three gold-polymer core-shell particles. All images have the same magnification and the scale bars correspond to 500 nm. The images were used as recorded by the CCD camera of the microscope. Hence, brightness and contrast were not changed after image recording. The gold cores and the increase in polymer shell thickness from A to C is clearly visible. Some empty microgels can be observed. The percentage of particles without gold cores is less than 5% as determined from analysis of different TEM images.



Figure S1: Low-magnification TEM images of Au-PNIPAM-1 (A), Au-PNIPAM-2 (B) and Au-PNIPAM-3 (C) core-shell particles. The scale bars correspond to 500 nm.

In addition to TEM we performed AFM measurements of the core-shell particles adsorbed on Si wafer. Height profiles of particle monolayers can be seen in figure S2.

Densely packed monolayers were obtained for all samples. In case of Au-PNIPAM-1 (A) the shell thickness is thin enough that the gold core can be probed even in tapping mode AFM. In contrast for the thicker polymer shells only the topography of the polymer shell is scanned. All particles are of spherical shape and low polydispersity. In particular for sample Au-PNIPAM-3 hexagonally close-packed domains are visible which underlines the low polydispersity of the colloids.

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Figure S2: AFM images of the core-shell particles with different shell-thicknesses. A: Au-PNIPAM-1. B: Au-PNIPAM-2. C: Au-PNIPAM-3. The AFM images are height profiles recorded in tapping mode of samples adsorbed on Si wafer measured against air. The scale bars correspond to 5 μ m. The insets show higher magnification images with scale bars corresponding to 200 nm.

Molar mass determination from UV-vis absorbance spectroscopy

The optical properties of the core-shell particles were investigated using absorbance spectroscopy. The spectra show features which can be clearly attributed to the gold cores (localized surface plasmon resonance, electronic transitions at lower wavelength) and to the PNIPAM shells (scattering). Hence, in a first assumption the spectra of the core-shell particles are a superposition of a spectrum of the bare gold cores and a spectrum of PNIPAM particles without gold cores (empty microgels). We have found that the scattering contribution of the polymer shell can be simulated by a simple power law $Abs = A\lambda^{-b}$ as published recently¹. This allows to analyze the spectral contribution of the gold cores. Figure S3 shows the spectral analysis we performed for all samples, exemplary for sample Au-PNIPAM-1.



Figure S3: Analysis of UV-vis absorbance spectra of Au-PNIPAM-1. A) Spectra of an aqueous dispersion of Au-PNIPAM-1 (0.03 wt-%) and the respective gold cores prior to encapsulation with PNIPAM. Both measurements were performed at 20°C. The spectra were normalized to the absorbance at the LSPR maximum. B) Spectrum of Au-PNIPAM-1 after subtraction of the gold core contribution. For comparison the spectrum of the initial core-shell particles is plotted as well. C) Double-logarithmic representation of the spectrum after subtraction of the gold cores prior to PNIPAM encapsulation in comparison to the spectrum obtained after subtracting the scattering contribution from the core-shell spectrum shown in A). The spectra were normalized to the absorbance at 400 nm.

The experimental spectra recorded for the core-shell particles Au-PNIPAM-1 and the gold cores prior to PNIPAM encapsulation are presented in figure S3 A). Both spectra were normalized to the absorbance at

Table S1: Parameters for simulated scattering intensities of the three samples obtained from analysis of UV-vis absorbance spectra.

Sample	A [10 ⁵ A.U.]	b
Au-PNIPAM-1	74	-3.3
Au-PNIPAM-2	62	-2.8
Au-PNIPAM-3	16	-2.5

the LSPR position. The difference in both spectra attributed to the scattering contribution of the PNIPAM shell is visible as an increase in absorbance towards lower wavelength. Assuming that the core-shell spectra can be treated as a spectral superposition of the core and shell contribution, the core absorbance spectra $(Abs_C(\lambda))$ can be subtracted from the core-shell spectrum $Abs_{CS}(\lambda)$. Since the core concentration is unknown in the core-shell dispersion measured and only its weight-fraction is known (based on freeze-dried material), a factor *n* has to be used as a multiplier in the subtraction: $Abs_{CS}(\lambda) - n \cdot Abs_C(\lambda)$

Figure S3 B) shows a comparison of the core-shell spectrum and the spectrum obtained after subtraction of the core contribution. The value for *n* was adjusted using a double-logarithmic representation of the subtracted spectrum (figure S3 C). Ideally subtraction of the gold core absorbance provides solely the scattering spectrum of PNIPAM shell, which should give a straight line in this representation due to the power law character of the scattering. However, due to the small offset between the plasmon resonances of the bare gold cores (no PNIPAM) and the core-shell particles, subtraction cannot completely remove the plasmonic contribution. This is visible as the local minimum and maximum at ≈ 2.72 in figure S3 C). Apart from this small deviation the obtained spectrum shows clearly a linear relation in this double logarithmic representation and a linear fit can be applied (red solid line). The value of *n* was adjusted in a way that the area between the linear fit and the spectrum below and above the point of inflection are nearly equal. The obtained fit parameter from the linear fit can now be employed to determine the power law parameters *A* and *b*. The values obtained for all samples are listed in table S1.

A and *b* fully describe the scattering contribution of the PNIPAM shell, which can now be subtracted from the experimental core-shell absorbance spectrum. Figure S3 D) compares the spectrum measured for the gold nanoparticle cores (no PNIPAM) with the spectrum obtained after subtraction of the scattering contribution from the Au-PNIPAM-1 spectrum. The latter spectrum represents the spectrum of the core-shell particles without the scattering contribution of the PNIPAM shell and hence the spectrum of the encapsulated cores only. Both spectra were normalized to the absorbance at 400 nm for better comparison. The nice overlap between both spectra reveals the quality of our approach. The slight difference in LSPR position and intensity between both spectra can be attributed to refractive index effects of the PNIPAM shell. Since the PNIPAM shell has a higher refractive index than water, which is the medium the bare gold nanoparticles are surrounded with, the LSPR of the core-shell particles appears at slightly higher wavelength and is slightly more intense.

The gold core spectra calculated from the spectra of all three core-shell particles were used to determine the molar masses of the particles: Since we know the weight fraction of the core-shell dispersions measured in UV-vis experiments (0.03 wt-%) and the optical density of the gold cores is known, we can calculate the gold core number concentration of each sample based on the gold core size as determined by TEM. Assuming a 100% encapsulation by PNIPAM, i.e. the number concentration of gold cores equals the number concentration of core-shell particles, the molar mass is accessible. Without accounting and subtracting the scattering contribution such an estimation would not have provided reasonable values for the molar mass, since the spectra are strongly affected by the scattering of the PNIPAM shell. This significantly enhances the measured absorbance at wavelength where the gold cores absorb light.

Data analysis from DLS

DLS was used to study the hydrodynamic dimensions and the swelling behavior of the core-shell particles. Representative intensity-time autocorrelation functions for all three core-shell samples measured at $6^{\circ}C$ ($\theta = 60^{\circ}$), which is the lowest possible temperature we could use, are shown in Figure S4.



Figure S4: Intensity-time autocorrelation functions measured at a constant scattering angle of 60° for the swollen state (6° C) and the collapsed state (58° C). The solid lines are fits using cumulant analysis performed according to reference².

This temperature is far below the expected VPTT of the core-shell particles and hence the particles will be in a swollen state. In addition representative autocorrelation functions for $58 \,^\circ C$ ($\theta = 60 \,^\circ$) are shown. Here, the temperature is far above the VPTT and the core-shell particles will be in the collapsed state. All correlation functions show monomodal decays with shorter decay times for measurements at $58 \,^\circ C$ as compared to $6 \,^\circ C$. This illustrates a significant reduction in particle size due to the VPT behavior of the polymer shell. The smaller dimensions of the collapsed particles lead to shorter decay times. All correlation functions could be satisfyingly fitted using the method of cumulants (second order) according to reference² following equation:

$$g_2(\tau) = B + \beta exp\left(-2\overline{\Gamma}\tau\right)\left(1 + \frac{\mu_2}{2!}\tau^2\right)^2$$

The values of $\overline{\Gamma}$ were used to calculate the translational diffusion coefficient $D_T = \overline{\Gamma}/q^2$. In the following we used the Stokes-Einstein relation to calculate R_h according to $R_h = \frac{k_B T}{6\pi\eta D_T}$ with k_B the Boltzmann constant, T the sample temperature and η the viscosity of the dispersion medium (water). In addition to

cumulant analysis, which can provide quantitative values of the intensity-weighted polydispersity, we used CONTIN analysis to determine $\overline{\Gamma}$ from the autocorrelation functions. The values of R_h determined from $\overline{\Gamma}$ obtained by CONTIN were very close to the values from cumulant analysis. In the following we used only CONTIN analysis for our DLS data.

Knowing that for the two extreme cases of swelling, i.e. the lowest temperature measurable with the used setup and a temperature far above the volume phase transition temperature, monomodal decays are observed, the *q*-dependence of this dynamic mode can be studied. To analyze whether DLS probes purely translational motion for the studied systems, we performed angle dependent measurements at 15 °C where the particles are swollen. Figure S5 A) shows results from the CONTIN analysis of the recorded correlation functions using the software AfterALV from Dullware. In A) the obtained average relaxation rates $\overline{\Gamma}$ are plotted as a function of the square of the scattering vector *q*. A linear relationship with intercepts near 0 is found for all samples (solid lines are linear fits). This linear behavior confirms that purely translational motion is detected. Consequently the translational diffusion coefficients D_T are accessible through the slope of the linear fits according to $\overline{\Gamma} = D_T q^2$.



Figure S5: Results from CONTIN analysis of angular dependent DLS measurements performed at 15°C. A) Mean relaxation rate $\overline{\Gamma}$ as a function of the squared momentum transfer. Solid lines are linear fits. B) Apparent diffusion coefficient $D_{T,app} = \overline{\Gamma}/q^2$ as a function of the squared momentum transfer. The solid lines are linear fits with slope 0.

Figure S5 B) shows the values of D_T calculated at each measured detection angle versus the square of the momentum transfer. A linear relation with a slope close to 0 is observed for each sample. The solid lines are linear fits with slope 0. This analysis reveals that *q*-dependent effects due to the dispersion concentration and the particle form factor are not significant in the covered *q*-range.

The results from angular dependent DLS measurements confirm on the one hand that purely translational motion is probed and on the other hand that measurements at single scattering angles can be performed to analyze the swelling behavior of the samples, i.e. for temperature dependent runs. Based on this preanalysis of the DLS data, a detailed temperature dependent study of the VPT behavior was performed at a single scattering angle and using the Stokes-Einstein relation to calculate R_h . Figure S6 shows the temperature evolution of the hydrodynamic diameter R_h for all samples.

The typical volume phase transition of PNIPAM in water is observed for all samples. Furthermore it can be clearly seen that the size of the particles increases from Au-PNIPAM-1 to Au-PNIPAM-3.



Figure S6: Results from CONTIN analysis of temperature dependent DLS measurements performed at a constant scattering angle of 60° . Evolution of the hydrodynamic radius R_h as a function of temperature T.

IFT analysis of SAXS data

IFT analysis was used to analyze the SAXS profiles measured in the swollen state (20°C). This method provided the pair-distance distribution function for each sample. Figure S7 shows the distribution functions normalized to the maxima $p_{max}(r)$. The grey area indicates the contribution of the gold cores. The difference in overall particle dimensions is clearly visible since the profiles reach values of zero at different values of *r*. All profiles are nearly symmetrical, which manifests the spherical density distribution of the particles.



Figure S7: Pair-distance distribution functions from IFT analysis of SAXS profiles measured at 20 °C. The distribution functions were normalized to the maximum $p_{max}(r)$. The grey area highlights the profiles attributed to scattering from the gold cores.

Form factor analysis of SANS data using SASfit

Based on the results for the pair-distance distribution functions from IFT analysis of SAXS and SANS data, we applied form factor fitting of the SANS curves using the software SASfit. The SANS profile of sample Au-PNIPAM-1 could be satisfactory fitted using an Ornstein-Zernicke contribution (equation 3) for the high and medium q-range and a core-shell form factor with an exponentially decaying shell (equation 10) for the low q-range. The fitting procedure was performed using the method of minimizing χ^2 . Due to the large number of fit parameters it was not possible to perform the fitting with all parameters set as free fit parameters after parameter initialization. Hence reasonable start parameters were initialized (based on results from SAXS and SLS) and iterations were performed until χ^2 reached a minimum for each fit parameter. Finally all critical fit parameters for each contribution were set as free fit parameters and again iterations were performed until χ^2 reached a minimum. This procedure was continued until no changes of the fit parameters were observed. The quality of fit was mainly judged by the residuals.

The SASfit analysis of the different core-shell samples was performed without accounting for a contribution of the gold cores. This is justified by the very small volume fraction of gold cores as compared to the total particle volume as well as the rather low scattering contrast for gold in heavy water in case of neutron scattering. Figure S8 A) shows the experimental scattering data for Au-PNIPAM-1 and the the applied fit as previously discussed.



Figure S8: Different contributions used for fitting of the SANS profiles using SASfit. A) Experimental data (symbols) and full form factor fit for sample Au-PNIPAM-1. The grey solid line shows the expected gold core contribution to the scattering intensity. This was simulated on the basis of the scattering length density of gold and the number concentration obtained for the core-shell particles. B) - D) Experimental scattering data for all samples (symbols) with different contributions used to perform fittings of the whole scattering profiles. B) Core-shell model with an exponentially decaying shell (dashed line) + Ornstein-Zernicke contribution. C) and D) Porod law + Ornstein-Zernicke contribution. In each case a constant offset was used for the background.

The grey line shown in this graph is the simulated scattering profile of the gold cores based on the

scattering length density of gold, the particle size and size distribution obtained from SAXS and the number density obtained for the core-shell particles. The scattering intensity of the gold cores is by a factor of 10 smaller than the core-shell scattering in the relevant q-range. Implementing the gold core contribution with free fit parameters in the full fit model did not result in reasonable results. However keeping the parameters for the gold cores constant led to only slight changes in the Ornstein-Zernicke contribution. Here the value of ξ changed only in the order of 8%. Figure S8 B) - D) show the different contributions to the scattering profiles for all three samples used in the fitting procedure. The residuals are shown as well. For Au-PNIPAM-2 and Au-PNIPAM-3 the residuals are significantly larger at small values of q since for this data analysis only Porod's law was used to describe the low q-part. Hence the deviations between fit and experimental data are due to the form factor of the overall core-shell particles. This form factor was not taken into account in the fitting procedure due to the rather poorly resolved form factor and data resolution at very low q.

The fit parameters from SASfit analysis of the SANS profiles for all three samples are listed in table S2.

Table S2: Fit parameters from SASfit analysis of the SANS profiles.

Parameter	Au-PNIPAM-1	Au-PNIPAM-2	Au-PNIPAM-3
$\overline{I_0(background)}$	0.0072 cm^{-1}	0.0032 cm^{-1}	0.0045 cm^{-1}
ξ	2.4 nm	1.7 nm	1.6 nm
$I_L(0)$	0.12 cm^{-1}	0.09 cm^{-1}	$0.08~{ m cm}^{-1}$
R _{hom}	28 nm	-	_
ΔR	33 nm	_	_
α	-2.4	-	_
$\eta_{solvent}$	0.00064 nm^{-2}	0.00064 nm^{-2}	0.00064 nm^{-2}
η_{shell}	0.00014 nm^{-2}	0.00014 nm^{-2}	0.00014 nm^{-2}
ϕ_{out}	0.99	-	_
ϕ_{in}	0.81	-	_
A/V	-	0.00007	0.00007
Porod exponent	-	4.6	4.6

DECON analysis of SANS data

DECON analysis was used to derive density profiles on the basis of pair-distance distribution functions as obtained from IFT analysis of the SANS data. Figure S9 shows a representative DECON fit of the pair-distance distribution function for sample Au-PNIPAM-1. The fit describes the data in nearly perfect agreement. The error bars of the data and the fit are in the order of the symbol size.



Figure S9: DECON fit of pair-distance distribution function obtained from IFT analysis of the SANS profile of Au-PNIPAM-1. Note that the graph includes error bars for the pair distance distribution function as well as for the DECON fit.

References

- [1] M. Karg, S. Jaber, T. Hellweg and P. Mulvaney, Langmuir, 2011, 27, 820-827.
- [2] B. Frisken, Applied Optics, 2001, 40, 4087–4091.