Structural changes of poly(*N*-isopropylacrylamide)-based microgels induced by hydrostatic pressure and temperature studied by small angle neutron scattering

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We study the structural properties of microgels made of poly(*N*-isopropylacrylamide) and acrylic acid as a function of hydrostatic pressure and temperature using small angle neutron scattering. Hydrostatic pressure induces particle deswelling by changing the mixing of the microgel with the solvent, similar to temperature. We extend this analogy to the structural properties of the particles and show that the form factor at a certain temperature is equal to the form factor at a certain hydrostatic pressure. We fit the results with an existent model for the microgel structure and carefully analyze the fitting procedure in order to obtain physically meaningful values of the free parameters in the model. © 2010 American Institute of Physics. [doi:10.1063/1.3447386]

I. INTRODUCTION

A gel is a polymeric network immersed in a solvent, which can change its volume in response to changes in its environment.^{1–3} Microgel particles are gels in the colloidal domain.^{4,5} As a result of the different sizes, microgels respond faster to external stimuli than their macroscopic counterparts; this makes them very useful in a wealth of different applications, including artificial muscle fabrication,^{6,7} oil recovery,⁸ water purification,⁹ drug delivery,^{10,11} paints,¹² and optical switching.^{13,14} They have also been extensively used as model hard spheres to address fundamental questions, including crystallization,^{15,16} melting,^{17,18} and the glass transition.^{19,20}

However, there is recent evidence that microgels can also behave very differently from hard spheres. For example, a suspension of small microgels can still crystallize in the presence of larger microgels by deswelling these larger particles and accommodating them inside the lattice.²¹ In addition, microgel suspensions exhibit fundamental changes in phase behavior, depending on the charge or the stiffness of the particles: For highly charged and swollen microgels, the range of volume fractions corresponding to the crystal phase becomes narrower than that of hard spheres.²² From a theoretical point of view, the charge in very soft microgels is also expected to play a major role, with slightly charged microgels lacking a crystal phase and highly charged microgels exhibiting a complex phase behavior, including formation of noncubic crystal phases.^{23,24} This richness in behavior arises from the coupling between charge and softness, which allows for particle deformation, interpenetration, and compressibility. The internal structure of the microgel critically affects the suspension behavior, as it determines to a large measure the stiffness of the particle and the interaction between particles.

Among all microgels, those based on poly(*N*-isopropylacrylamide) (pNIPAM) are the most widely used. pNIPAM is a temperature-sensitive polymer that undergoes a coil-to-globule transition in the proximity of its lower critical solution temperature,^{25,26} which is $\approx 32\text{--}33^\circ\text{C}$ in water, heavy water, or in any of its mixtures.^{27–33} Interestingly, pNIPAM-based microgels also respond to hydrostatic pressure.³⁴ This is achieved through solubility changes, in a way that is analogous to temperature. As a result, both temperature and hydrostatic pressure change the mixing of the polymer in the solvent, as seen also in macroscopic gels.^{35,36}

In this paper, we explore whether these similarities are reflected in the microgel structure by performing small angle neutron scattering (SANS) experiments as a function of hydrostatic pressure and temperature. We find that increasing either of the two variables causes analogous structural changes, emphasizing the similar role played by hydrostatic pressure and temperature in deswelling the particles. The measured form factors are well described by a particle model based on a particle core with a polymer gel structure, coated with a fuzzy surface.³⁷ The fitting procedure, however, must be carefully performed in order to obtain physically meaningful values of the free parameters. This is due to a significant overlap in reciprocal space of the contribution describing the internal gel structure of the particle with that giving the spherical shape. As a result, prior knowledge of the values of some of these parameters is desired for guiding the fitting process. With these considerations, the model correctly describes the structure of the microgel particles, which we show can be tuned externally using hydrostatic pressure, in as much as temperature.

II. EXPERIMENTAL SYSTEM

The particles we use are comprised of pNIPAM and acrylic acid (AAc). They are synthesized by emulsion polymerization³⁸ of NIPAM monomer, AAc (2 mol %), and

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the cross-linker methylene-bis-acrylamide (5 mol %) in water at 70 °C using the surfactant sodium dodecyl sulfate (0.05 wt %) to control the particle size. This precursor solution is stirred and bubbled with nitrogen prior to the initiation of the reaction with potassium persulfate (0.06 wt %). The reaction is allowed to proceed for 4 h under a nitrogen blanket to ensure full reaction of the monomers.³⁹ After cooling the products, the particles are exhaustively dialyzed against ultrapure water until the conductivity of the removed water matches the conductivity of the added water. Finally, we freeze dry the particles and redisperse them in heavy water. The *pD* of the resultant dilute suspension is always 5.5. We use the abbreviation *pD* instead of *pH* since heavy water is used as a solvent.

To characterize the temperature dependence of the particle size, we use three-dimensional (3D) dynamic light scattering (DLS).⁴⁰ The source of the equipment consists of a He–Ne laser operating at a wavelength of 632.8 nm. The laser beam is split into two parallel beams that are focused onto the sample. The scattered light is collected and guided using optical fibers toward two avalanche photodiodes (APDs) and the signals of the APDs are cross correlated.⁴¹ By doing so, the resultant correlation function is only sensitive to single-scattering events.⁴⁰ The sample tubes are placed in a temperature controlled, index matched vat filled with decalin. We ensure homogeneous equilibration of the temperature in the samples by waiting ≈ 30 min prior to each measurement.

To obtain the size dependence with hydrostatic pressure, we use a high pressure cell consisting of a sample container located between two parallel sapphire windows designed for a SANS line at Paul Scherrer Institute (PSI).⁴² The pressure is applied using hydraulic oil and a pressure generator. As a result of the particular arrangement of our setup, we use a home-built DLS apparatus with a He–Ne laser operating at a wavelength of 632.8 nm. The scattered light is collected at a scattering angle of 135° and is split into two beams, using a fiber beam splitter, coupled to two APDs. The signal in the two detectors is pseudo-cross-correlated in a two channel correlator to effectively avoid the afterpulsing of the APDs.⁴³

In both cases, we measure the intensity correlation function, $g_2(\tau)$, which is related to the electric field correlation function, $g_1(\tau)$, by means of the Siegert relation^{44,45}

$$g_2(\tau) = 1 + \beta g_1^2(\tau), \quad (1)$$

where β is the so-called coherence factor.^{44,45}

All size measurements are performed with dilute samples and are characterized by an exponential field correlation function $g_1(\tau) \sim e^{-\Gamma\tau}$, where $\Gamma = Dq^2$, with D the diffusion coefficient and q the modulus of the scattering wave vector. We obtain D from a linear fit of Γ versus q^2 and use the Stokes–Einstein equation, $D = \frac{k_b T}{6\pi\eta R_{DLS}}$, with k_b the Boltzmann constant, T the temperature, and η the solvent viscosity at the experimental temperature and hydrostatic pressure, to determine the hydrodynamic radius, R_{DLS} .⁴⁴ We always obtain $\beta \in [0.95, 1.00]$ in conventional DLS measurements, which is close to $\beta=1$ expected for optimum detection of

FIG. 1. Radius R_{DLS} of pNIPAM-AAc microgels in D_2O as a function of (a) temperature T and (b) hydrostatic pressure P measured by DLS. The particles deswell in both cases with increasing T or P .

scattered light fluctuations. However, this theoretical maximum is reduced to $\beta=0.25$ in the 3D-DLS cross-correlation scheme since in this case

$$\begin{aligned} \langle I_1(t)I_2(t+\tau) \rangle &= \langle I_{b1d1}(t)I_{b2d2}(t+\tau) \rangle + \langle I_{b1d1}(t)I_{b1d2}(t+\tau) \rangle \\ &+ \langle I_{b2d1}(t)I_{b2d2}(t+\tau) \rangle + \langle I_{b2d1}(t)I_{b1d2}(t+\tau) \rangle, \end{aligned} \quad (2)$$

where I_1 and I_2 are the intensities collected in detectors 1 and 2, respectively, τ is the correlation time, and $I_{bidj}(t)$ is the intensity collected in detector j at time t coming from beam i . Since there are two incident beams and two detectors, there are four contributions to the cross-correlation function. Among all, only the first term contributes to the correlation;⁴¹ the other three terms correspond to cross correlations corresponding to different q and only contribute to the background. In our experiments, $\beta \approx 0.21$, which is close to the theoretical maximum.

Consistent with previous measurements,^{27–33} we find that the particle size decreases with increasing temperature, as shown in Fig. 1(a); this shrinkage results from the temperature dependence of the polymer/solvent miscibility.^{46,47} Since the experiments are performed at $pD=5.5$ and the pK_a for polyacrylic acid is 5.6,⁴⁸ the AAc is partially ionized. As a result, there is a contribution to the total osmotic pressure arising from the counterions that are electrostatically trapped inside the microgel particle. This ionic concentration broadens and shifts the temperature range associated to the size transition to higher temperatures compared to most pNIPAM microgels.³³ We find a final deswollen radius of $R_{DLS}=60$ nm at $T=60$ °C, and an overall behavior that agrees with what is also observed with charged gels^{49,50} and other ionic pNIPAM microgels.^{51,52}

A similar particle shrinkage is observed with hydrostatic pressure, as shown in Fig. 1(b). As the hydrostatic pressure increases, it is increasingly unfavorable for the polymer to mix with the solvent leading to particle deswelling. Consistent with the temperature measurements, we find a deswollen size of $R_{DLS}=60$ nm at high pressures and a broad deswelling transition due to the presence of AAc.

III. RESULTS AND DISCUSSION

A. Experimental measurements of the particle form factor

SANS measurements are performed using the SANS-I beamline at SINQ, PSI, Switzerland. We use a velocity se-

lector to select a wavelength of $\lambda=8.8$ Å for the temperature experiments and a wavelength of $\lambda=12$ Å for the hydrostatic pressure experiments, with a resolution of $\Delta\lambda/\lambda=0.1$. The resolution in the magnitude of the scattering wave vector, $q=(4\pi/\lambda)\sin(\theta/2)$, with θ the scattering angle, is determined by this wavelength spread and by the scattering angle resolution, $\Delta\theta$:

$$\frac{\Delta q}{q} = \frac{\Delta\lambda}{\lambda} + \frac{\Delta\theta}{\theta}. \quad (3)$$

The experiments are performed at sample-detector distances of 18 and 8 m, with collimation lengths of 18 and 8 m, respectively. We also employ neutron lenses^{53,54} to focus the beam and reduce $\Delta\theta/\theta$. As a result, $\Delta q/q \approx \Delta\lambda/\lambda$. The data are collected in a two-dimensional detector with 128×128 pixels with an area of $7.5 \times 7.5 \times \text{mm}^2$ each. The scattering from the solvent and from the sample cell is corrected using standard procedures. The neutron path length of the cells we use is 2 mm.

For spherically symmetric particles, the scattered intensity can be approximated as⁵⁵

$$I(q) \approx (\Delta\rho_v)^2 n V_{\text{polymer}}^2 P(q) S(q), \quad (4)$$

where $\Delta\rho_v$ is the difference in the scattering length density between the polymer and the solvent, n is the number density of particles, and V_{polymer} is the volume of polymer in one particle. The form factor $P(q)$ accounts for interference of radiation from polymer segments within the same particle, while the structure factor $S(q)$ accounts for interference of radiation from polymer segments in different particles. The form factor is thus related to the internal structure of the particles, while the structure factor is related to the structural properties of the suspension. In our experiment, we use dilute suspensions and thus can safely assume that $S(q)=1$. Therefore, the q dependence of the scattered intensity directly results from the internal structure of the particles.

We find that the q dependence of the form factor is characterized by an initial decay at low q , followed by a shoulder at intermediate q , as shown in Fig. 2. At even higher q , the scattered intensity plateaus due to the presence of incoherent scattering.⁵⁵ The form factors measured as a function of hydrostatic pressure at a fixed temperature of $T=25$ °C, exhibit similar q behavior. However, we only clearly observe the decay at low q , as shown in Fig. 3. At higher q , the scattered intensity is very noisy due to insufficient counting time; this does not allow the interpretation of the data in this q region. We note that an increase in temperature and hydrostatic pressure causes an overall shift of the form factor to higher q , consistent with particle deswelling.

B. Model for the form factor

The intensity profiles show the intrinsic structural richness of these particles. At high pressures, the resultant form factor is reasonably well described by what is expected for hard spheres with a size similar to our microgel size, as shown in Fig. 3 for $P=350$ MPa. As a result, at high pressures, the structure of our microgel particles is reminiscent of the structure of hard spheres. However, at low hydrostatic

FIG. 2. Experimental profiles for four different temperatures and their corresponding fits according to Eq. (8): ($\square$) $T=25$ °C and $R_{\text{av}}=83$ nm, $\sigma=21$ nm, $\sigma_{\text{pol}}=0.13$, $I_{\text{chain}}(0)=2.0 \times 10^{-4}$, $\xi=10.4$ nm; ($\circ$) $T=27$ °C and $R_{\text{av}}=82$ nm, $\sigma=21$ nm, $\sigma_{\text{pol}}=0.11$, $I_{\text{chain}}(0)=9.0 \times 10^{-5}$, $\xi=10.2$ nm; ($\triangle$) $T=30$ °C and $R_{\text{av}}=77$ nm, $\sigma=23$ nm, $\sigma_{\text{pol}}=0.13$, $I_{\text{chain}}(0)=5.9 \times 10^{-4}$, $\xi=9.8$ nm; and (∇) $T=35$ °C and $R_{\text{av}}=73$ nm, $\sigma=18$ nm, $\sigma_{\text{pol}}=0.12$, $I_{\text{chain}}(0)=1.3 \times 10^{-4}$, $\xi=9.2$ nm; The data are vertically shifted by a factor of 10 with increasing temperature.

pressures, this hard sphere model is unable to capture the experimental results, as also shown in Fig. 3 for $P=0$. The hard sphere analogy no longer holds, highlighting the intrinsic inhomogeneous structure of the particle in its swollen state. One source for this inhomogeneity resides in the uneven distribution of crosslinker molecules within the particle.^{38,56,57} As a result, in order to fully describe the form factor of these particles, a more sophisticated model must be considered.

Here we follow the model first proposed by Stieger *et al.*,^{37,58} who considered the microgel particle as a core with a certain fuzziness at its periphery, essentially arising from the inhomogeneous distribution of cross-linker within the particle. This is modeled in real space as a convolution of a compact sphere with a Gaussian generating the fuzzy shell. In reciprocal space:

$$P_1(q) = \left[\frac{3(\sin qR - qR \cos qR)}{(qR)^3} e^{-[(\sigma q)^2/2]} \right]^2, \quad (5)$$

where R is the radius of the core and σ is the width of the fuzzy surface. A similar model was proposed by Pedersen

FIG. 3. Experimental profiles for different hydrostatic pressure: ($\square$) $P=0$, ($\blacksquare$) $P=100$ MPa, ($\circ$) $P=150$ MPa, ($\bullet$) $P=175$ MPa, ($\triangle$) $P=200$ MPa, ($\blacktriangle$) $P=250$ MPa, (∇) $P=300$ MPa, and ($\blacktriangledown$) $P=350$ MPa. The data are vertically shifted by a factor of 10 with increasing hydrostatic pressure. The lines represent the expected form factor for hard spheres with radii of $R=145$ nm (lower line) and $R=70$ nm (upper line).

FIG. 4. Intensity profile for $T=25$ °C and $P=0$. The two fits to the data are essentially inappreciable and result in identical χ^2 values for the parameters shown in Table I.

*et al.*⁵⁹ to account for the scattering of block copolymer micelles.

The particle is further considered inhomogeneous at length scales much smaller than the particle size, as they are made from cross-linked polymer chains. These inhomogeneities are taken into account by incorporating an additional contribution associated to polymer chain correlations³⁰

$$I_{\text{chain}}(q) = \frac{I_{\text{chain}}(0)}{1 + (\xi q)^2}, \quad (6)$$

where $I_{\text{chain}}(0)$ is the zero- q intensity associated to this contribution and ξ is the correlation length or mesh size of the network. We note that this expression can also describe the scattering intensity from certain semidilute polyelectrolyte solutions;⁶⁰ it can thus be considered a reasonable approximation for the internal structure of our ionic microgel particles.

As a refinement of the model, we also consider polydispersity in the core

$$D(R) = \frac{1}{\sqrt{2\pi}\sigma_{\text{pol}}R_{\text{av}}} e^{-[(R - R_{\text{av}})^2/(2\sigma_{\text{pol}}^2 R_{\text{av}}^2)]} \quad (7)$$

with R_{av} the average core radius and σ_{pol} the relative particle polydispersity.

Combining all these contributions, the form factor of the particle becomes

$$P(q) = \sum_R P_1(q, R) D(R) + I_{\text{chain}}(q) + I_0, \quad (8)$$

where I_0 is a constant associated to the amount of incoherent scattering from the samples.

Using this model, we fit the experimental results by minimizing $\chi^2 = \sum [P_{\text{exp}}(q) - P_{\text{theor}}(q)]^2$,⁶¹ leaving as free parameters the average core radius, R_{av} , its polydispersity, σ_{pol} , the size of the fuzzy region, σ , the mesh size of the polymer network, ξ , and $I_{\text{chain}}(0)$. We see that the model successfully captures the various features of the experimental form factor, as shown in Fig. 4 for $T=25$ °C and $P=0$. In this case, we obtain $R_{\text{av}}=83$ nm and $\sigma=21$ nm, giving an overall microgel radius of $R_{\text{SANS}}=R_{\text{av}}+2\sigma=125$ nm, which is similar but slightly smaller than the radius measured by DLS. The origin of the slight discrepancy could be due to the presence of a

FIG. 5. χ^2 as a function of $I_{\text{chain}}(0)$ and ξ for the sample at $T=25$ °C and $P=0$.

very small but non-negligible number of chains in the periphery of the particles, which would only contribute to the hydrodynamic radius, thus, rendering R_{DLS} larger than R_{SANS} .⁵⁷ For the suspension polydispersity, we obtain $\sigma_{\text{pol}}=0.13$, which is reasonable given the method employed for the particle synthesis.⁶² Surprisingly, the value obtained for the mesh size, $\xi=52$ nm, seems unreasonably large given the particle size. Indeed, from the particle synthesis we can estimate the average distance between crosslink points within one particle, $\hat{\xi}=(N_p V_p / N_{\text{x-link}})^{1/3}$, with $N_{\text{x-link}}$ the number of cross-link molecules employed in the synthesis, and N_p and V_p the number of particles and their volume, respectively.⁶³ We obtain $\hat{\xi}\approx 5$ nm, which is an order of magnitude smaller than the value of ξ obtained from the fit.

We note, however, that the free parameter space contains many local minima, as shown in Fig. 5. This uncertainty for ξ and $I_{\text{chain}}(0)$ is linked to the narrow q range, $0.05 < q < 0.1$ nm⁻¹, where the quality of the fit depends strongly on ξ and $I_{\text{chain}}(0)$. It is thus very easy to get trapped locally in any of these minima, all having very similar values of χ^2 . In fact, by fixing the values of R_{av} , σ , and σ_{pol} , the selection of $I_{\text{chain}}(0)$ and ξ becomes degenerate. This corresponds to the narrow line of black points in Fig. 5 corresponding to very similar low values of χ^2 . The ξ - $I_{\text{chain}}(0)$ landscape thus limits the use of our fit to estimate either of these two parameters. However, sensible values can be obtained by carefully spanning the parameter space. To show this, we also show in Fig. 4 an alternative, but equally good fit of the experimental data. In this case, R_{av} , σ , and σ_{pol} all have identical values, but $\xi=10.4$ nm, as shown in Table I. The value of the mesh size is in this case within a factor of 2 with respect to the average distance $\hat{\xi}$ between cross-links, which is reasonable. The selection of the best fit thus not only relies on the value

TABLE I. Values of the free parameters obtained from the fits shown in Fig. 4. R_{av} is the radius of the core, σ is the width of the fuzzy region of the particle, $R_{\text{SANS}}=R+2\sigma$, R_{DLS} is the particle radius as determined by DLS, σ_{pol} is the core polydispersity, $I_{\text{chain}}(0)$ is the amplitude of the polymer chain correlations at zero q , and ξ is the correlation length or mesh size of the network.

R_{av} (nm)	σ (nm)	R_{SANS} (nm)	R_{DLS} (nm)	σ_{pol}	$I_{\text{chain}}(0)$	ξ (nm)	χ^2
83	21	125	142	0.13	2.2×10^{-3}	52	10^{-3}
83	21	125	142	0.13	2.0×10^{-4}	10	10^{-3}

FIG. 6. Analogy between temperature and hydrostatic pressure: (a) ($\circ$) $T=25$ °C, ($\square$) $P=0$; (b) ($\circ$) $T=27$ °C, ($\square$) $P=100$ MPa; (c) ($\circ$) $T=30$ °C, ($\square$) $P=200$ MPa; and (d) ($\circ$) $T=35$ °C, ($\square$) $P=250$ MPa.

of χ^2 , but also on the known value for ξ obtained from the particle synthesis. With this knowledge of ξ we can also fit the experimental data for other temperatures with reasonable values of all the free parameters, as shown in Fig. 2.

C. Comparison between hydrostatic pressure and temperature effects

Given that hydrostatic pressure and temperature affect the particle size in similar ways by changing the mixing of the polymer and the solvent,³⁴ we inquire on whether there are also similarities in how they affect the structure of the particles. We plot the form factors obtained at different temperatures and constant hydrostatic pressure, together with those obtained at different hydrostatic pressures and constant temperature, as shown in Fig. 6. There is excellent agreement between certain pairs of temperature and hydrostatic pressure, emphasizing the analogous role of these variables in deswelling and modifying the form factor of our pNIPAM microgel particles.

Employing this analogy, we can model the scattered intensity profiles at different hydrostatic pressures even for the intermediate and high q regions, where the data were noisy due to the increased background in the pressure setup and limited counting time. In this way, we can obtain how R_{SANS} and ξ change with particle deswelling. We find that R_{SANS} decreases with P , as shown in Fig. 7(a); this is consistent

FIG. 7. (a) R_{SANS} vs hydrostatic pressure. (b) ξ as a function of polymer volume fraction ϕ_{polymer} .

with the DLS data. The values of R_{SANS} , however, are slightly smaller than those obtained by DLS, reflecting the influence of the peripheric chains, which contribute to R_{DLS} but not to R_{SANS} . Consistent with this interpretation, the agreement between the two sets of data improves at higher hydrostatic pressures since these chains are expected to collapse as the particles deswell.

The polymer mesh size also decreases with particle deswelling, as expected. To quantify this decrease in ξ , we estimate the polymer volume fraction within a single microgel, ϕ_{polymer} , using $\phi_{\text{polymer}}/\phi_{\text{polymer},0}=(R_{\text{DLS},0}/R_{\text{DLS}})^3$, where $\phi_{\text{polymer},0}=0.8$ (Refs. 5, 34, and 64–66) and $R_{\text{DLS},0}$ are the polymer volume fraction and particle radius in the deswollen state. We plot ξ versus ϕ_{polymer} in Fig. 7(b). We find $\xi \sim \phi_{\text{polymer}}^{-0.15}$, which is similar to the scaling exponent that has already been found in temperature experiments with pNIPAM microgels.⁵⁸ However, it is different from the scaling found for polymer gels, $\xi \sim \phi_{\text{polymer}}^{\nu_{\phi}}$, where $\nu_{\phi} = \nu/(1-3\nu)$, with $\nu=3/5$ for a good solvent or $\nu=1/2$ for a θ solvent. In our experiments, we change ϕ_{polymer} by changing the quality of the solvent, and thus there is no reason to expect any of these behaviors. Moreover, our particles consist of polyelectrolyte rather than polymer chains. As a result, a different scaling is expected for ξ .⁶⁰ Nevertheless, we emphasize the sensitivity of $I_{\text{chain}}(0)$ and ξ to the χ^2 landscape, which results in a large uncertainty for the ξ estimate and, as a result, for the scaling exponent. This in the end is related to the overlap in q of the particle and internal structure contributions to $P(q)$. Despite this fact, we obtain, using hydrostatic pressure, a similar ξ – ϕ_{polymer} relation to that obtained using temperature, providing additional support to the analogous role played by these variables in changing the structural properties of the particles.

IV. CONCLUSIONS

We have measured how the form factor of pNIPAM-AAc microgels changes with hydrostatic pressure and temperature by using SANS. By modeling the particle as a compact core with a fuzzy surface and with internal inhomogeneities associated with the polymer chains, we have described the experimental measurements with reasonable values of the free parameters. However, since χ^2 exhibits a large number of local minima of similar depth depending on the value of the mesh size, the fitting process must be performed with care. Provided this is the case, the values of all free parameters that result are reasonable and the SANS data are well described. Our results provide additional evidence of the analogous role played by temperature and hydrostatic pressure; they both modify the mixing of the polymer in the solvent inducing similar shrinkage and structural changes of the particles.

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