Colloids and Surfaces A: Physicochem. Eng. Aspects 482 (2015) 724–727

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

# Interplay between internal structure and optical properties of thermosensitive nanogels

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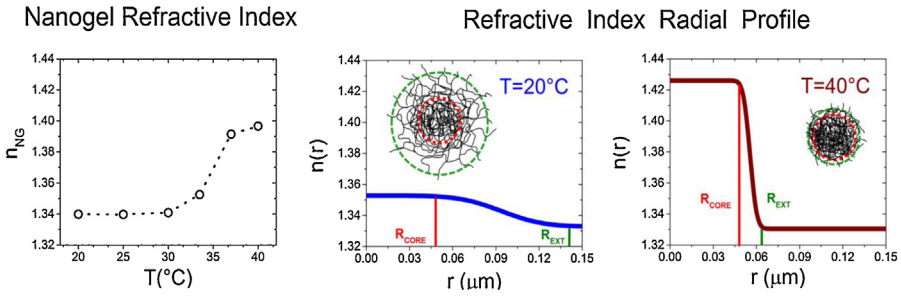
## HIGHLIGHTS

- We study the internal structure of PNIPAM microgels as a function of temperature.
- Core and external radius of PNIPAM particles is determined by light scattering.
- The microgel refactive index, measured by refractometry, increases with temperature.
- We propose a radial profile for the particle refractive index to describe the experiments.
- From the analysis, we determine the refractive index of the microgel core.

## GRAPHICAL ABSTRACT




## ARTICLE INFO

*Article history:*
Received 19 February 2015
Received in revised form 6 July 2015
Accepted 8 July 2015
Available online 18 July 2015

*Keywords:*
Poly-NIPAM nanogels
Particle form factor
Refractive index
Light scattering

## ABSTRACT

The structural and optical properties of thermosensitive particles, nanogels, are studied by light scattering and refractometry as a function of temperature. Nanogels are composed of poly- *N*-Isopropopylacrylamide, a polymer that shrinks at temperatures higher than its lower critical solution temperature, 33 °C. The internal nanogel structure obtained by light scattering is well modeled by assuming a constant radial mass density profile convoluted with a Gaussian function. Moreover, we introduce a simple method that allows us to describe the measured temperature-dependent index of refraction of these complex nanoparticles by using their structural information, core dimension and external radius.


## 1. Introduction

In the last decades, nanogels have been subject of numerous studies due to their numerous technological applications [1–4] and their use as model systems to investigate fundamental phenomena in soft materials [5–8]. One of the interesting properties of these particles is their capacity of reducing their size as the temperature increases due to a change in the interactions between water and polymer chains. Above a certain temperature, the lower critical solution temperature (LCST), Poly-NIPAM becomes hydrophobic causing the collapse of the particle and the subsequent expulsion of water from the nanogel interior [9]. At this transition, that occurs at around 33 °C for this polymer, not only the particle size changes abruptly, but also does the polymer mass density distribution inside

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http://dx.doi.org/10.1016/j.colsurfa.2015.07.020
0927-7757/

the particle, which induces a sudden variation of its optical properties. For example, the refractive index of nanogel particles strongly depends on temperature and exhibits an abrupt increase around the LCST [10]. The temperature dependence of the internal structure of Poly-NIPAM particles has been analyzed by measuring the particle form factor by means of neutron [11–13] and light scattering [14]. In all cases, the authors find that a non-constant mass density profile accounts for the heterogeneous structure of the PNIPAM particles due to an uneven distribution of crosslinker inside the particle. This profile describes an inner denser region, named core, and a shell with a non-constant mass density that decreases gradually from the edge of the core toward the particle surface.

In this paper we assume a mass density profile defined by a convolution of a box with a Gaussian function to describe the particle form factor measured by light scattering [11]. From the analysis of the scattering vector behavior of the scattered light as a function of temperature, we obtain the temperature dependence of the structural parameters, core and overall particle dimensions. The structural information is used to describe the effective refractive index of PNIPAM particles by assuming a radial dependence for the particle refractive index similar to that of the mass density profile. The validity of this model has been confirmed on two different nanogels systems with different degree of crosslinking. The approach used in this study could be useful for the engineering of nanogel systems with potential applications in optics as tunable photonic materials [15,16] and optical tagging [17], among others.

## 2. Experimental system

In this work PNiPAM particles are synthesized in emulsion-polymerization as described in Ref. [6]. The monomer *N*-isopropylacrylamide, NiPAM (7.9 g), the crosslinker *N,N*-methylenbisacrylamide, BIS (0.15 g), and the stabilizer sodium dodecylsulfate, SDS (0.15 g), are dissolved in 450 ml of pure water. In parallel, a solution of the initiator potassium peroxodisulfate, KPS (0.6 g), in 50 ml of pure water is prepared in a separate flask. After bubbling both solutions with nitrogen for 30 min, the initiator is injected in the mixture that contains the monomer, which has been previously heated to 70 °C. The polymerization process is terminated after 5 h and, finally, the dispersion is cooled down to room temperature and purified by dialysis and several centrifugation steps. The solid content of our final stock solution is ~3.1%w/w, and the particle number density is ~ 54 particles/$\mu m^3$. We should mention that our system at quasideionized conditions exhibits a liquid-crystal transition as a function of concentration at 25 °C. This feature indicates a low size polydispersity of our nanogels and allows us to unambiguously determine the particle number density of the crystalline samples from the Bragg peak positions [18], measured by static light scattering with a 3D-DLS scattering device (LS Instruments AG, Fribourg, Switzerland). The device is provided with a multitau digital correlator (Flex) and uses a He–Ne laser as a light source, wavelength $\lambda = 632.8$ nm. As a result, from both the dry solid content and the particle number concentration we obtain the polymer mass per particle being ~5.78 $10^{-16}$ g.

## 3. Results and discussion

The structural characterization of the resulting nanoparticles is made by measuring the particle form factor, $P(q)$, by static light scattering (SLS) as a function of temperature. The $q$ -dependence of the scattered light, shown as symbols in Fig. 1(a), becomes less pronounced as the temperature increases as a consequence of the collapse of the poly-NIPAM particles. In order to obtain information about particle dimensions we use a model that assumes

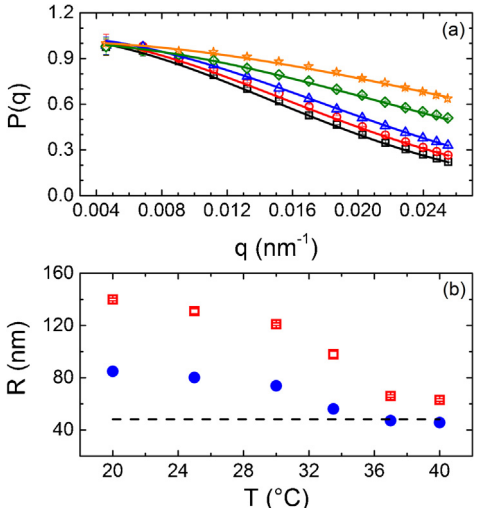


**Fig. 1.** (a) Particle form factor measured by static light scattering at 20 °C (black squares), 25 °C (red circles), 30 °C (blue triangles), 33.5 °C (green diamonds) and 37 °C (orange stars). Lines are fits to the data by assuming a non-constant mass density profile [11]. (b) Temperature dependence of the external (hydrodynamic) radius (open squares), the Guinier radius (solid circles) and the core radius (dashed line) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

a non-constant radial particle density, which is valid under the Rayleigh-Gans-Debye approximation (RGD) [11]. In this model the radial density decreases from the edge of the core toward the surface of the particle and is calculated as a convolution of a radial box of dimension $R$ and a Gaussian function. In this way, the form factor is given by $P(q) = \left[\frac{3[\sin(qR)-qR\cos(qR)]}{(qR)^3}\exp(-\frac{(\sigma q)^2}{2})\right]^2$, where σ accounts for the width of the smeared particle surface and it is defined as $\sigma = 0.25\,(R_{Ext} - R_C)$, $R_{Ext}$ is the overall radius of the particle and $R_C$ is the core radius. $R$ represents the distance from the particle center to the point where the density has decreased to half of the core density and it can be expressed as $R = 0.5\,(R_{Ext} + R_C)$ [11]. The fit to the experimental data, shown as lines in Fig. 1(a), indicates that this model describes well our experiments. Since we have observed crystallization of the deionized suspensions, which is only possible for enough monodisperse dispersions, in the analysis we have omitted size polydispersity effects. We perform a global fit to the form factors measured at all temperatures considering that the core radius does not depend on temperature, as reported previously [12], and using the hydrodynamic radius, $R_H$, measured by dynamic light scattering as an estimate of the external radius, $R_{Ext} = R_H$. The core radius obtained from this fitting procedure is $R_C = (48.1 \pm 0.5)$ nm. The temperature dependent values of the external radius are shown as open squares in Fig. 1(b), where we can observe that $R_{Ext}$ slightly decreases until the temperature reaches the LCST. Around the transition temperature, the external radius decreases abruptly due to the sudden shrink of the particle and remains almost constant for higher temperatures. We find that our results are similar to those reported for a similar system [11]. Additionally, the radius of gyration $R_g$ obtained from the Guinier analysis of ln $[I(q)]$ vs $q^2$ depicts a similar behavior with temperature, as shown in Fig. 1(b) as solid circles. We should note that in the collapsed state of the particle, at 40 °C, the ratio between the radius of gyration and the external radius is $R_g(40\,°C)/R_{Ext}(40\,°C) = 46\,nm/63\,nm = 0.73$, a value compatible with the ratio $R_g/R_{Ext}$ for a compact sphere $R_g/R_{Ext} = (3/5)^{0.5} = 0.774$. By contrast, in the globular state, at 20 °C, the ratio $R_g(20\,°C)/R_{Ext}(20\,°C) = 85\,nm/141\,nm = 0.61$, value that is below the ratio expected for compact spheres indicating a less dense structure of the nanogel in the globular state. These results suggest a non-constant radial profile of the mass inside the particle