



On the scattered light by dilute aqueous dispersions of nanogel particles



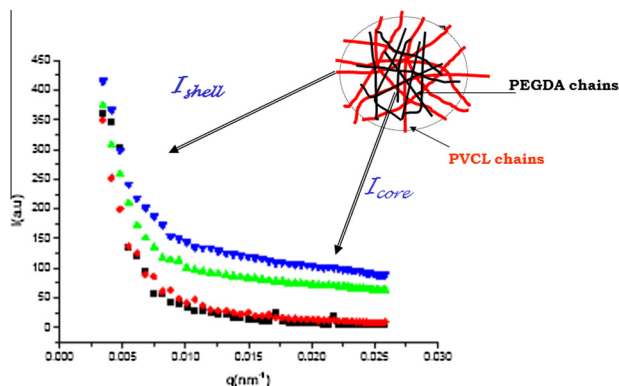
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GRAPHICAL ABSTRACT



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ABSTRACT

This work deals with the scattered light by nanoparticles formed by a temperature sensitive polymer networks, namely nanogel particles. The scattered light is measured as a function of the scattering angle at temperatures below and above the volume phase transition temperature (VPPT) of nanogel particles. Our experimental results indicate that nanogel particles have a core-shell structure, formed by a uniform highly cross-linked core surrounded by a fuzzy shell where the polymer density decays to zero gradually for swollen configurations and sharply for shrunken states. The theoretical fitting of the experimental curves shows that the scattered light at low angle obeys a decreasing power law with the scattering vector, $q^{-\alpha}$. The value of exponent α provides information about the radial dependence of the polymer density at the external shell of the particles for swollen nanogels, and about the degree of roughness of the surface for the case of shrunken nanogels. On the one hand, at low temperatures (below the VPPT), the nanogel particle is in the swollen state and the light scattering data show that its shell structure follows a fractal behaviour, with a polymer density that decays as r^{-3} , where r is the distance to the particle centre. On the other hand, above the VPPT the results indicate that nanogel collapses into a core of uniform polymer density and a rough shell, with a fractal surface dimension of 2.5.

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1. Introduction

The structure and characteristics of new particles for potential use in Materials Science or Biomedicine turns to be of increasing

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complexity and its knowledge is a challenge of outstanding interest. Scattering methods using neutrons, X-rays or light are able to explore individual properties of particles such as size, shape or internal structure. All this information is contained in the form factor, $P(q)$, where q is the scattering vector. The form factor may be obtained from the measured scattered intensity $I(q)$ of a very diluted sample as a function of the scattering vector, q . Physically, $P(q)$ considers the interference between the beams from all the points inside the particle [1]. On the one hand, neutrons or X-rays allow exploring the internal structure due to their high q -values. On the other hand, light scattering is able to explore the low q -region and it is well suited for studying global properties of the particles such as size and shape. However, the structures of some ideal morphologies as hard spheres or hard rods are also well captured with light scattering experiments. Our interest here is to discuss what kind of information can be obtained using light scattering when particles have internal degrees of freedom that may lead to complex internal architectures. We focus on polymer microneetwork colloids, i.e., particles mainly formed by networks of polymers [2]. Micro-nanogels particles, pH or temperature dependent, belong to this class of particles [2,3].

In this work, we report on the scattered light intensity for a class of temperature sensible nanogels based on Poly (N-vinylcaprolactam) (PVCL) nanogels dispersed in water [4].

In literature, most of the experimental work regarding the determination of the microgel form factor has been performed using particles based on Poly (N-isopropylacrylamide) (PNIPAM) polymer by means of neutrons [5–12]. Nevertheless, the use of PNIPAM nanogels in Biomedicine is restricted due to its toxicity. On the contrary, nanogels based on Poly (N-vinylcaprolactam) polymer are more promising in this field due to its biocompatibility. To our knowledge, the literature concerning PVCL-based nanogels is scarce, excluding the work of Boyko et al. [13]. These authors use Poly (N-vinylcaprolactam)/Poly(N-vinylpyrrolidone) based nanogels with N,N'-methylenebisacrylamide as cross-linker. The particle size ranged from 370 nm in average hydrodynamic radius (swollen state) to 200 nm (shrunken state). Using a combination of static–dynamic light scattering (SLS, DLS) and Small Angle Neutron Scattering (SANS) methods, they were able to explore the internal structure of the nanogels. They fitted successfully the experimental results using a model containing 5 adjustable parameters, concluding that the nanogel particle consists in an inhomogeneous structure, a dense core surrounded by a diffuse corona, in a similar way to the previous works with PNIPAM [9,11,12].

In the current research, we use a temperature sensitive PVCL-based nanogel of small size, ranging from 110 nm to 50 nm in average hydrodynamic radius (swollen and shrunken states, respectively) having Poly(ethylene glycol) diacrylate (PEGDA) as cross-linker. In aqueous dilute dispersions, the experimental scattered light obtained from the nanogel dispersion, $I(q)$, has been measured at temperatures smaller and higher than 33 °C, the volume phase transition temperature (VPPT) of nanogel particles. For the physical interpretation of $I(q)$, SLS has a serious drawback: the reduced q -range in comparison with SANS. Specifically, in our experimental device q ranges from 0.005 to 0.025 nm⁻¹, which corresponds to length scales from 50 to 200 nm. Hence, SLS cannot properly solve the internal structure of PVCL nanogels which internal distances are less than 50 nm. Nevertheless, by exploring these length scales (50–200 nm) with light, we have found that the scattered light can still provide valuable information. In fact, we found that $I(q)$ can be interpreted in terms of two additive contributions. The first term (corresponding to low q) arises from the scattering of the surface (shell) of the nanogel particle, and follows a power law dependence, $I(q) \sim q^{-\alpha}$. The second contribution has exponential q -dependence, and accounts for the scattering coming from the

central core of the nanogel particles. In literature, the use of two components has been widely employed to explain the experimental $I(q)$ curves reported with neutrons for PNIPAM particles of large size [5–7,9–12], but is scarce its use with nanogels of small size and using light as experimental tool. What is more, the use of light for such small q -vectors allows in our opinion, to emphasize the noticeable contribution that the particle's surface plays in the final resultant scattered light from the nanogels.

As we will show later on, light scattering techniques are able to characterize the changes of the internal structure of the nanogel particle when varying the swelling ratio. In fact, the measured form factors indicate that the nanogel particle may be regarded as a uniform core enclosed by a fractal shell. In the swollen state, the polymer density at the external shell decays with a power law as a function of the distance to the centre of the particle, $\rho(r) \sim r^{\alpha-3}$, where $\alpha < 3$. This behaviour is typical of a mass fractal object, with a mass fractal dimensions given by $d_m = \alpha$. In the shrunken state the nanogel shows a very narrow interface. This external surface is not smooth, but it shows a high degree of roughness which can be characterized by a surface fractal dimension, given by $d_s = 6 - \alpha$, where $\alpha > 3$.

2. Background

The size, shape and the internal structure of a colloidal particle can be deduced from the experimental $I(q)$ obtained in a diluted (non-interacting) suspension within an adequate q -range. Concerning to nanogel particles, the theoretical models usually employed are the ones used in the framework of scattering of macrogels containing inhomogeneities, i.e. network of polymers having points of bond due to the presence of the cross-linker molecules [14,15]. In the absence of a theory able to fit successfully the experimental results using only one analytical terms, Geissler group [14,15] and Shibayama et al. [16] have proposed some years ago that the $I(q)$ dispersed by macrogels should contain at least two contributions:

$$I(q) \approx I_C(q) + I_L(q) \quad (1)$$

The first component is due to the presence of heterogeneities. These non-uniformities in the concentration of polymer are caused by the elastic constrains generated by the cross-linker molecules. It is called the “Gaussian” term $I_C(q)$ because, originally, Hecht et al. and Mallam et al. supposed that the inhomogeneous regions whose movement is restricted by the cross-linker varies randomly in space following a Gaussian distribution [14,15]. Generally, the expression for the so-called Gaussian term is

$$I_C(q) \approx Ae^{-\Lambda^2 q^2} \quad (2)$$

where A is a constant and Λ is related to the typical size of the heterogeneities inside the gel. Some authors connected Λ with the radius of gyration of the cross-linker zone [15,16]. In fact, Eq. (2) is commonly used in the Guinier regime ($qR_g \ll 1$), being $\Lambda = R_g/\sqrt{3}$, where R_g is here the radius of gyration of the particle.

The second contribution is the Lorentzian term. It considers the thermal fluctuations of the network, i.e., the thermodynamic temporal fluctuation of chain polymers. This term includes, apart from a normalization constant, B , a correlation length, ξ which can be related to the blob size or correlation length of the thermal fluctuations inside the network [12,16],

$$I_L(q) \approx \frac{B}{1 + q^2 \xi^2} \quad (3)$$

Some years later, Bristol's group used SANS to study the structural changes of PNIPAM nanogels during the swelling process applying this macrogel interpretation of $I(q)$ to the context of

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