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Molecular motions in low cross-linked poly(*N*-isopropylacrylamide) microgels

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Abstract

Non-ionic *N*-isopropylacrylamide (PNIPAM) microgel is employed to investigate the molecular motion of polymer chains in the swollen and collapsed states. This study is performed using incoherent elastic (IES) and quasielastic neutron scattering (IQNS). IES measurements show an increase of both, the elastic intensity and the oscillations of the polymer network vibrational amplitude at the transition temperature. IQNS was measured at two different selected temperatures 290 K and 327 K corresponding to the swollen and collapsed states, respectively. The diffusion constant from IQNS experiments decreases nearly two orders of magnitude when the microgel de-swells and finally collapses.

Keywords: Microgels; Molecular dynamics; Neutron scattering; Volume phase transition; PNIPAM

1. Introduction

Polymer microgels constitute an interesting group of gels with promising applications in nanotechnology [1–6] due to their fast response to external stimuli. It is well known that PNIPAM microgels present a continuous volume transition from swollen to collapsed states at 307 K [7–9]. The internal structure of PNIPAM microgels was investigated in previous papers using small angle neutron scattering and dynamic light scattering, leading to a core–shell model for highly cross-linked particles [10–12]. Structural changes associated to the microgel swelling in D_2O were also investigated by light and neutron scattering [10]. However, the dynamics of the polymer network along the swelling process has not been tackled yet. In this work we present preliminary results, obtained by quasielastic neutron scattering, of the polymer dynamics in swollen and collapsed microgels.

2. Samples

Poly(*N*-isopropylacrylamide) microgel dispersions with 0.25% cross-linking content were prepared by surfactant-free emulsion polymerization, following the original recipe by Pelton et al. [13]. *N*,*N*′-Methylenebis (acrylamide) (BA) and potassium persulfate (Sigma–Aldrich) were used as the cross-linking monomer and the initiator, respectively. NIPAM $(12 - x)$ grams and BA (x) grams were placed in a three-necked, round-bottomed flask equipped with a stirred paddle and a water-cooled condenser. The reaction vessel was filled to 800 mL using deionized ultrapure water (Millipore). The solution was stirred at 70 °C for 20 min at 350 rpm, under a nitrogen atmosphere. Potassium persulfate (0.54 g), dissolved in water, was then added in order to initiate the polymerization reaction. The reaction was maintained for 16 h before cooling (but with continued stirring). The dispersion was then filtered through glass wool and extensively dialyzed against deionized

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water, using 14,000 Da dialysis tubing (Medicell International), until the conductivity of the dialysate was reduced to 1 μS/cm. For neutron scattering experiments, samples were prepared by dispersing the microgels in D_2O to guarantee good polymer-solvent contrast. The polymer concentration was low enough (3 wt%) to diminish colloidal interactions as well as to reduce multiple scattering. Technical aspects about sample preparation are extensively reported in Ref. [10].

3. Methods

Microgel particles were characterized using scanning electron microscopy (SEM), JEOL 2000FX operating at 200 kV. Gold sputtering was performed using a Balzer Sputter Coater (SCD-004). Particle size changes were monitored using dynamic light scattering (DLS). A Malvern 4700 system, equipped with a 5 mW helium–neon laser (632.8 nm) was employed, with the scattering angle set at 40°. The temperature was controlled to a precision of 0.1 °C, using simultaneously a Peltier thermocouple located inside the water bath surrounding the sample cell and by circulating temperature-controlled water through an external aluminum bath chamber. The dispersions were diluted sufficiently to diminish any colloidal interactions (and hence any structure factor contributions), as well as any multiple scattering. The mean diffusion coefficient was derived from the intensity autocorrelation function using cumulant analysis and converted into mean particle size via the Stokes–Einstein equation for spherical particles ($R_H = k_B T q^2/6\pi\eta\Gamma$ where η is the solvent viscosity, k_B the Boltzmann's constant, T the temperature, Γ the decay rate of the intensity autocorrelation function, and q is the transfer vector). The mean hydrodynamic diameter was averaged over five single measurements. The molecular dynamics was studied using elastic and quasielastic incoherent neutron scattering. The experiments were carried out at the Institute Laue Langevin (ILL) in Grenoble (France) using the cold neutron backscattering spectrometer IN10 [14]. The analyzed neutron wavelength was kept always fixed at 6.271 Å using Si(1 1 1) crystals, whilst the incident neutron wavelength was set using two different monochromators. For "fixed energy window" scans were centered at zero energy transfer (elastic scans). The incident wavelength was equally set to 6.271 Å by an equivalent Si(1 1 1) crystal. Thereby, an energy resolution of 1 μeV FWHM was achieved. The quasielastic measurements were performed by varying the lattice spacing of a KCl(2 0 0) monochromator crystal through controlled heating and cooling [15] and adjusted to cover an experimental energy transfer range of $-6\ \mu\text{eV} < E < 16\ \mu\text{eV}$. An energy resolution of about 2 μeV FWHM was thus achieved. Measurements were performed at seven different scattering vectors, with momentum transfer Q ranged between 0.5 and 2 Å^{-1} ($Q = (4\pi/\lambda)\sin(\theta)$, 2θ being the scattering angle). Quasielastic spectra were recorded at 290 K and 327 K for every Q. Double wall hollow cylinder was chosen as holder in order to avoid D_2O evaporation during measurements. The thickness and sample concentration was selected to yield a transmission of about 85%. Standard ILL procedures and programs were used for corrections (empty cell), normalization and quasielastic peak fit.

4. Theory and previous calculations

From neutron scattering measurements we obtain the double differential scattering cross section $d^2\sigma/d\Omega dE$ which is proportional to the coherent $S_{coh}(Q,\omega)$ and the incoherent $S_{inc}(Q,\omega)$ scattering functions [16]. The incoherent scattering cross section of hydrogen is large in comparison to the coherent and incoherent scattering cross sections of the rest of atoms in the sample such as carbon, oxygen and nitrogen. For PNIPAM the ratio $\sigma_{inc}(H)/\sigma_{inc}$ (total) is 0.9997. $S_{inc}(Q,\omega)$ is measured for the H atoms and hence, we can infer the dynamics of the polymeric chain to which the H atoms are attached. The incoherent cross section of ^2H is low (2.05 barn) as compared to ^1H (80.26 barn). However, this effect is not relevant for diluted samples since the amount of incoherent scattering coming from the heavy water used as solvent is of the same order of magnitude than the signal arising from the PNIPAM gel. Fortunately, the dynamics of the heavy water molecules is faster than the polymer chains and both contributions can be separated.

Dynamics in polymeric systems result from the superposition of vibrations, rotations and translational motions [16–18]. We assume that the time scales are sufficiently different to be uncoupled, such that in IQNS spectra features characteristic of these different motions show at separate ω-regions. Furthermore, any rotational motion is normally very fast on the translational motions time scale, forming a low intensity flat background that can be separated when using a high resolution spectrometer like IN10. For data analysis we have considered that molecular motion in the experimental energy range is composed by the combination of vibrational and translational diffusive processes. Vibrational motions for polymers are uncoupled from other motions and the incoherent scattering function $S_{inc}(Q,\omega)$ can be described by

$$S_{inc}(Q,\omega) = S_{inc}^{vib}(Q,\omega) \otimes S_{inc}^{trans}(Q,\omega) \tag{1}$$

where $\otimes$ means the convolution product in ω (provided that the inelastic contribution is well separated from the quasielastic one). $S_{inc}^{vib}(Q,\omega)$ is the incoherent scattering function for vibrational motion, corresponding to the elastic Debye–Waller factor. It can be approximated to

$$S_{inc}^{vib}(Q,\omega = 0) = \exp\left(-\langle u\rangle^2 \frac{Q^2}{3}\right)\delta\omega \tag{2}$$

where $\langle u\rangle^2$ is the mean square amplitude of the proton vibration, Q the scattering vector, and $\delta\omega$ is the Dirac's delta function. For diffusive processes $S_{inc}^{trans}(Q,\omega)$ is given by a quasielastic contribution:

$$S_{inc}^{trans}(Q,\omega) = L(\omega,\Gamma(Q)) \tag{3}$$

where $L(\omega,\Gamma(Q))$ is a Lorentzian function with half-width at half-maximum $\Gamma(Q)$. Since $\Gamma(Q) = D_c Q^2$ for Fickian diffusion (D_c is the diffusion constant) [19], the incoherent scattering function can be finally written as

$$S_{inc}(Q,\omega) = \exp\left(-\langle u^2\rangle \frac{Q^2}{3}\right)\delta\omega \otimes \frac{1}{\pi}\frac{D_c Q^2}{(D_c Q^2)^2 + \omega^2} \tag{4}$$