Experimental Report

04/09/2014

Proposal:	**TEST-2199**	**Council:**	10/2012

Title: Confinement effects of collapsed shell on swollen core of PDEAAM-PNIPAM microgel particles

This proposal is a new proposal

Researh Area:

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Experimental Team: MACCARRONE Simona

Local Contact: SHARP Melissa

Samples: PDEAAM-PNIPAM particles in MeOD/D2O

Instrument	Req. Days	All. Days	From	To
IN15	5	5	22/02/2013	27/02/2013

Abstract:

Introduction

Sensitive microgels are sub-micron sized, cross-linked polymer particles with a unique swelling behavior changing in response to surrounding conditions like temperature, pH and ionic strength. In this experiment, we influence the swelling capability of thermo-sensitive microgels microgel by the composition of the solvent (cononsolvency). In particular, we investigate the effects on the dynamics of poly-N-isopropylacrylamide (PNIPAM) and poly-N,N-diethylacrylamide (PDEAAM) microgels with different degree of swelling in MeOD/D_2O solvent mixture at 10 °C using Neutron Spin Echo (NSE) spectroscopy at nanoseconds scales in the range of several nanometers.

Experiment

Compared to our previous experiments[1] a higher microgel concentration of 1 wt % was used. To achieve maximum contrast and minimum incoherent background resulting from protonated material, we used deuterated solvents D_2O and MeOD. The measured samples with $x_{MeOD} = 0.2$ were mixed from 1 wt% parent dispersions shortly previous to the experiment in order to avoid evaporation of MeOD. Measurements on PNIPAM and PDEAAM microgel particles in the q range between 0.02 and 0.15 $Å^{-1}$ were performed using two wavelengths, 12 and 17 Å, to cover a wide Fourier time range up to 250 ns. The samples were mounted in a thermostat controlled sample environment at 10 °C. Scattering from corresponding quartz cells containing the deuterated solvent mixture has been subtracted as background from the NSE data. The additional $q = 0.18$ $Å^{-1}$ curve was obtained at the J-NSE spectrometer at the FRM II research reactor in Garching (Germany) at a wavelength of 8 Å probing Fourier times up to 40 ns.

Analysis. At higher crosslink-densities, when the observed length scale probes the mesh of the network, collective diffusion (D_c) with a q^2-dependent rate and a simple exponential decay is expected[2-4] as well as the translational diffusion (D_{td}) of the entire microgel accounted for with the multiplicative first exponential function:

$$S(q,t)/S(q,0) = e^{-\Gamma_{td} t} e^{-\Gamma_c t} = e^{-D_{td} q^2 t} e^{-D_c q^2 t} = e^{-(D_{td}+D_c) q^2 t} \tag{1}$$

The Zimm model[5] for the segmental dynamics of polymers in solution is used to fit the data for the highest q-values. It describes the dynamics of a Gaussian chain in terms of a bead spring model adding the hydrodynamic interaction between the chain segments in terms of a simple Oseen tensor approach. The internal motions including rotational diffusion of a finite chain consisting of N beads connected by entropic springs with a uniform bead distance l are described by relaxation modes with mode number p and characteristic times τ_p:

$$\tau_p = \frac{\eta R_e^3}{\sqrt{3\pi}\, k_B T} p^{-3\nu} \tag{2}$$

where R_e corresponds to the mesh size of the polymer network. Inserting $\nu = 0.5$, $S(q,t)$ is computed for a Gaussian chain:

$$S(q,t) = \sum_{m,n}^{N} e^{-q^2 D_{CM} t - (q^2/6) B(m,n,t)} \tag{3}$$

with

$$B(m,n,t) = |n-m|^{2\nu} l^2 + \frac{4R_e^2}{\pi^2} \sum_{p=1}^{p_{max}} \frac{1}{p^{2\nu+1}} cos\left(\frac{\pi p n}{N}\right) cos\left(\frac{\pi p m}{N}\right)\left(1 - e^{-1/\tau_p}\right) \tag{4}$$

The center-of-mass diffusion assuming a Gaussian chain (Θ-solvent) is:[6]

$$D_{CM} = 0.196\frac{k_B T}{R_e \eta} \tag{5}$$

In our special case, since we do not deal with free polymer in solution, the center-of-mass diffusion coefficient will be the one for the entire particle as obtained by Dynamic Light Scattering (DLS). The q-values accessible in DLS are sufficiently low such that internal modes do not contribute to the decay of the correlation function.[7] Moreover, for the same reason that the polymer segments are not free in solution but attached to the cross-linkers, the odd p modes are not possible in the Zimm model and the summation in eq. 4 is made only on even p-values. The maximal number of modes p_{max} was set to 20. Further increase of the number p_{max} did not change the results, higher modes do not contribute to the dynamics.

Results. The expected behavior for a completely collapsed microgel particle should be similar to a hard sphere and therefore the scattered signal should be dominated by translational diffusion.[1] In the partially collapsed PNIPAM sample, hydrodynamic interactions are found to play a role and cannot be neglected in the description of the internal dynamics. Realistically, a significant amount of solvent is still present in the microgel particle. In the left-handed plot of fig. 1, we show the intermediate scattering functions $S(q,t)/S(q,0)$ of partially collapsed PNIPAM for different q-values between 0.02 and 0.18 Å^{-1}. The dynamics for the two smallest q-values (0.02 and 0.05 Å^{-1}) are best fitted by eq. 1. From the fit with a simple exponential decay we obtained a total diffusion coefficient $(D_{td}+ D_c)$ of 0.42±0.05 and 0.44±0.02 Å^2/ns respectively. Substracting D_{td} =1.8×10^{-12} m^2/s as obtained by DLS,[1] we are left with a collective diffusion coefficient D_c around 2,2×10^{-12} m^2/s. This value compares quite well with 0.86×10^{-12} m^2/s obtained by Cabarcos and coworkers considering a five times higher temperature and a two times smaller cross-linking density than our samples.[8] For q-vectors between 0.08 and 0.18 Å^{-1}, the data are well described by the Zimm dynamics with polymer segments with fixed ends. R_e is set to 5.5 nm as mesh size extracted from fit of SANS intensity.[9] The diffusion coefficient was set to 1.8×10^{-12} m^2/s as obtained from DLS measurements.[1] The only free parameter is then the viscosity η of the solvent mixture MeOD/D$_2$O. From a simultaneous fit of the data, we obtained 0.0252±0.0004 Pa·s, seven times higher than the one measured by capillary viscosimetry (0.0032±0.0001 Pa·s). We can explain this as an effective increase of the viscosity. In a collapsed particle, all polymer chains are very close compacted and rather move in a medium made up of "solvent + other chains".

The right-handed plot of fig. 1 displays the intermediate scattering functions $S(q,t)/S(q,0)$ of swollen PDEAAM for different q-values between 0.02 and 0.18 Å^{-1}. The entire set of the curves was fitted with the Zimm model. R_e is set to 8.5 nm as mesh size extracted from fit of SANS intensity (see table 1). The free parameters are the center-of-mass diffusion coefficient D_{CM} and the viscosity η. On the contrary to the partially collapsed microgel, fixing the value of D_{CM} as obtained from DLS measurements did not produce good fitting results. From a simultaneous fit of the data, we obtained 1.029±0.008×10^{-11} m^2/s and 0.0077±0.0002 Pa·s respectively. This value is about three times smaller compared to the D_{CM} for a free chain of 10 nm length calculated via eq. 5 (2.9×10^{-11} m^2/s) and the viscosity is about twice the one measured for the solvent mixture. The smaller diffusion coefficient suggests that an additional contribution to the dynamics has to be taken into account. It is plausible that we see the translational diffusion of cross-linkers that in the swollen state have enough space to move compared to the collapsed state. On the other hand, the higher viscosity could be a signature of static inhomogeneities as observed previously.[1] Since our microgels are synthesized in the collapsed state, the swelling causes stretching of the polymer chains with some polydispersity in length.[10]

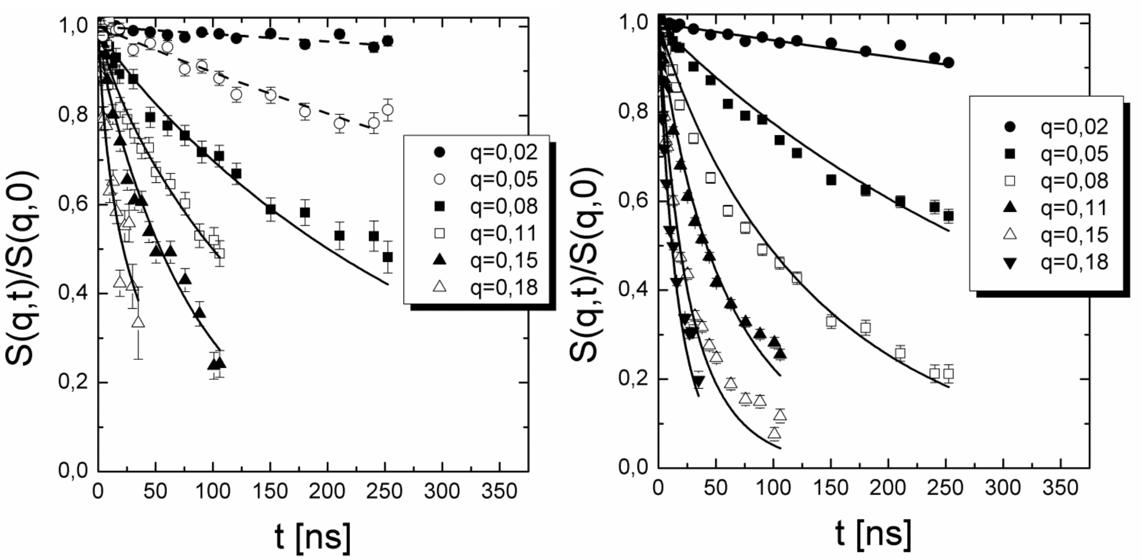

Figure 1. Intermediate scattering functions of partially collapsed PNIPAM (left) and swollen PDEAAM (right) in the solvent mixture with $x_{MeOD} = 0.2$ at 10 °C for different *q*-values. The solid lines are the fitting curves with the Zimm model and the dashed lines with eq. 1.

References

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