# Raspberry structures in microgel-silica nanoparticle composite systems

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**Abstract**

Composite materials consisting of responsive microgels together with additional nanoparticles might provide new and "smart" functionality, e.g. uptake and release of nanoparticles, or special mechanical or rheological properties of a solution. Here, composites consisting of PNIPAM microgels and silica nanoparticles have been investigated by CryoTEM and neutron scattering techniques. The formation of "raspberry" like core-shell structures with a silica nanoparticle layer around the microgel core has been observed.

*Keywords:* Microgels, Neutron Scattering, Neutron Spin Echo, CryoTEM

## Introduction

Microgels (MG) are polymeric nanoparticles consisting of polymer chains, which are crosslinked to form a single particle with a size of the order of 100 nm. In solution, microgels can be designed with a responsiveness to changes in temperature or chemical potential and are therefore interesting materials for smart applications [1, 2, 3]. Organic-inorganic hybrid particles, for example microgel-silica hybrid particles with a silica core, have been investigated and characterized [4, 5]. Microgel particles with a silica surface coating are presented in Ref. [6], nanorods adsorbed onto a microgel surface were investigated in Ref. [7]. When microgels are employed as substrates for coatings, one has to consider the prososity or permeability of the network as polymers or particles - depending on the their size - can be adsorbed to or absorbed by the microgel. Furthermore, both processes can affect the size of the hybrid microgels in a complex matter [8]. Nevertheless, it has been shown that even layer-by-layer adsorption onto microgels is possible [9]. Here, we study poly-N-isopropylacrylamide (PNIPAM) microgels, having a volume phase transition temperature (VPTT) of 32 °C, determined with DLS. For this study, we used a combination of neutron spin echo (NSE) and cryo-TEM investigation connecting the dynamical behavior to the structural properties. The former technique has been used in the past to study internal microgel dynamics [10, 11] while the latter gives a real space view on microgels on nanoscopic length scales.

## Method

Microgels were produced by precipitation polymerisation [12], with the monomer N-isopropylacrylamide (NIPAM), the cross-linker methylenbisacrylamide (BIS, 2 mol%), ammonium peroxodisulphate (APS) as initiator and the surfactant sodium dodecylsulphate (SDS), all purchased from VWR, Germany. Deuterium oxide (D2O) were procured from Deutero, Germany. Plain silica particles (with terminal Si-OH-bonds) as aqueous suspension, sicastar® of 10 nm diameter, was obtained from Micromod, Germany.

Microgel (MG) dispersions (2.5 wt.% in D2O) were prepared. The measured samples with guest particles had a 0.25 wt% concentration of silica nanoparticles. NSE measurements have been performed by using the J-NSE spectrometer at the FRM II research reactor in Garching, Germany [13] at a wavelength of 8 Å.The samples were mounted in a thermostat controlled sample environment. The internal dynamics of the microgel with and without guest particles was then measured at a temperature of 22 °C, below the VPTT (and a short try at 42°C above the VPTT). Scattering from corresponding quartz cells containing the deuterated solvent has been subtracted as background from the NSE data. Cryo-TEM experiments were carried out with a JEM 2200 FS EFTEM instrument (JEOL, Tokyo, Japan) at -180°C with a cryo-transfer holder ((Model 920, Gatan, Munich, Germany). Zero-loss filtered images were taken under reduced dose conditions ($< 10\,000$ e-/nm2). MG dispersions (1 wt.% in D2O) were prepared few days before the experiment. The measured samples with silica guest particles had a 0.1 wt% concentration. A holey carbon-coated copper grid was dipped into the solution and after blotting plunged into liquid ethane, before being transferred to the Cryo-TEM.

## Results and Discussion

The interaction of PNIPAM microgels with silica nanoparticles has been investigated in solution with neu-

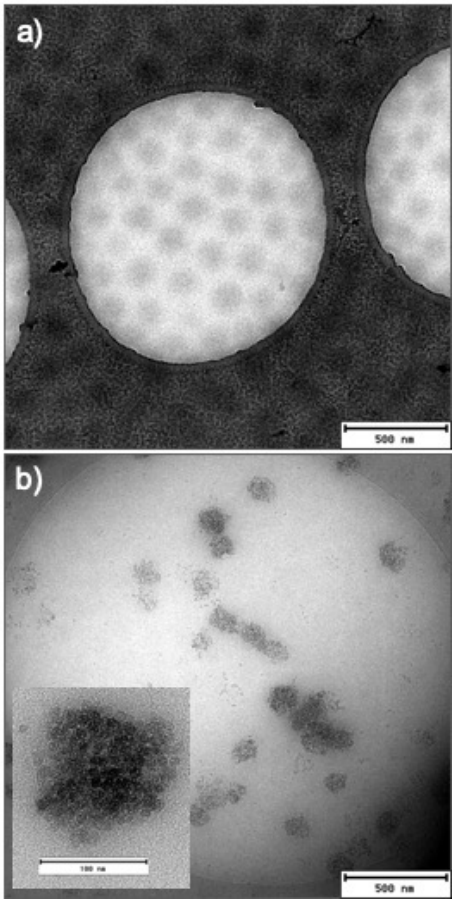


Figure 1: Cryo-TEM images of a) the pure microgel and b) the microgel with added silicon nanoparticles into the solution. The inset in b) shows such a Si nanoparticle decorated microgel at higher magnification.

tron spin echo spectroscopy and compared to Cryo-TEM images of the respective samples.

Cryo TEM images of the frozen microgel suspension showed the typical smooth spherical microgel particle in Fig. 1 a). The silica particles added to the suspension arranged around the microgel particles, as shown in Fig. 1 b).

The Silica particle distribution of such a 2D projection is not straighforward. A reconstruction of the 3D density profile of such microgels has been done in Ref. [14]. Here we checked in a simplified procedure the radial average of single particles, showing a flat absorption with a slight increase in grayscale towards the border. We interprete the arrangement of nanoparticles thus as a multilayer shell around the core of the PNIPAM particle (or at least the core is less densely filled with nanoparticles). A self assembled hybrid particle has been formed. With NSE, the local thermally driven fluctuations are observed. A first experiment at 22°C is presented in Fig. 2. At large Q, the segmental chain dynamics of the microgel particles is observed. The pure microgel shows a strechted exponential relaxation ($S(Q,t/S(Q,0) = exp(-(\Gamma t)^{\beta})$ with $\beta = 0.78 \pm 0.07$, indicating Zimm-dynamics of the segments. The influence of the Si nanoparticles on the segmental chain dynamics is a change in line shape to an exponential decay with $\beta = 1.06 \pm 0.08$, characteristic for density fluctuations imposed by the additional Si particle shell, which suppress the segmental dynamics on these length scales of $2\pi/Q = 4$ nm. At larger length scales (Q=0.05 $\AA^{-1}$) no significant difference between the microgel with and without Si particles has been observed within the time range of observation. A similar suppression of Zimm dynamics has been observed recently by electrolytes added to the microgels [15].

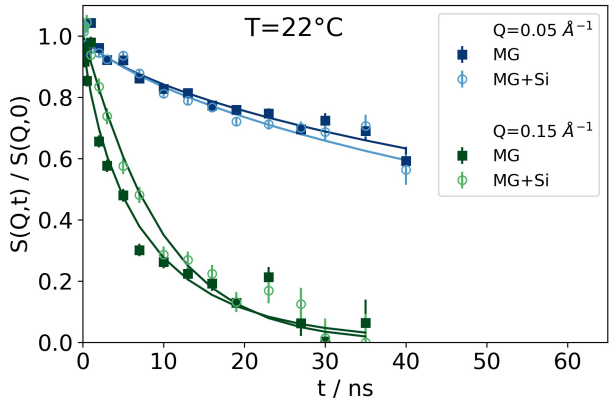


Figure 2: Intermediate scattering function at 22 °C. The segmental chain dynamics dominant at high Q is altered by the Si particles from Zimm like behaviour (with a stretched exponential decay) to diffusive behaviour (simple exponential decay).

Electrostatic interactions of the Silicon nanoparticles with the microgels might be the origin of this "raspberry" like structure, more investigations of the interactions such as $\zeta$-potential measurements would be required to analyse this in more depth. Surface modification of the Si nanparticles and modifications of the microgel by introducing chaged groups may shed a more detailed light on the interaction between Si nanoparticles and microgels. Further studies in this direction are planned for the future.

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