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Microarticle

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.

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 [1–3]. 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 porosity 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 behaviour 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 polymerization [12], with the monomer N-isopropylacrylamide (NIPAM), the cross-linker methylenebisacrylamide (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 neutron spin echo spectroscopy and compared to Cryo-TEM images of the respective samples.

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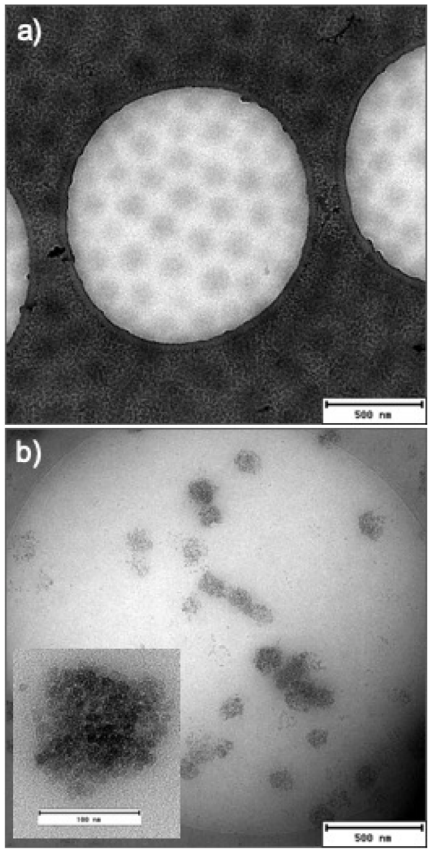

Fig. 1. Cryo-TEM images of (a) the pure microgel and (b) the microgel with added silicon nanoparticles into the solution. The inset in (b) shows such a Si nanoparticle decorated microgel at higher magnification.

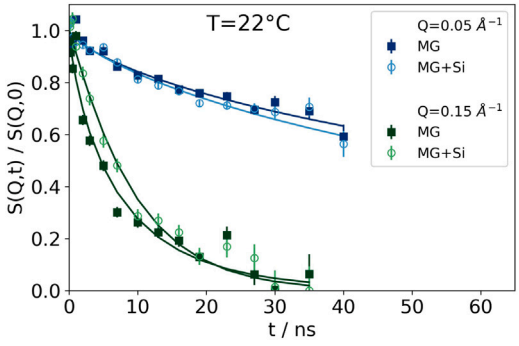

Fig. 2. Intermediate scattering function at 22 °C. The segmental chain dynamics dominant at high Q is altered by the Si particles from Zimm like behaviour (with a stretched exponential decay) to diffusive behaviour (simple exponential decay).

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 straightforward. 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 greyscale towards the border. We interpret 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 stretched 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 $\forall^{-1}$) 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].

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 ζ-potential measurements would be required to analyse this in more depth. Surface modification of the Si nanoparticles and modifications of the microgel by introducing charged 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.

CRediT authorship contribution statement

O. Holderer: Conceptualization, Writing - original draft, Writing - review & editing, Formal analysis. **S. Maccarrone:** Conceptualization, Writing - original draft, Formal analysis. **S. Pasini:** Writing - review & editing. **M.-S. Appavou:** Resources, Investigation. **A. Gelissen:** Resources, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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