# Experimental report

03/03/2016

**Proposal:** **9-12-416** **Council:** 4/2015

**Title:** Deswelling of highly crosslinked polystyrene microgel colloids in colloid-polymer mixtures close to the glass transition lines

**Research area:** Soft condensed matter

**This proposal is a continuation of 9-10-1374**

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**Samples:** polystyrene(PS)/toluene
fully deuterated PS/toluene/toluene-d8

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| D33 | 0 | 0 | | |
| D22 | 0 | 0 | | |
| D11 | 2 | 2 | 20/11/2015 | 22/11/2015 |

## Abstract:

The question of osmotic deswelling of microgel colloids in mixtures with free polymer is of utmost importance for understanding the extraordinarily large shift of the glass transition line to higher volume fractions in these systems. To study the extent of osmotic deswelling we investigate the influence of linear polystyrene (PS) polymer addition to highly concentrated dispersions of PS microgels by measuring the particle form factor of fully deuterated PS tracer particles in an index-matched host of protonated PS microgels and protonated PS chains. In a previous beam time we demonstrated for two free polymer to microgel size ratios that is possible to resolve very small changes of the tracer radius using three detector positions and a doubled detector resolution on D11. Now we want to finish the project by measuring the tracer P(q) for additional state points in order to monitor systematically the variation of the microgel deswelling which will allow for a clear-cut comparison with macrogel deswelling data and to clarify the role of osmotic deswelling for the shift of the glass transition line.

## 9-12-416: Deswelling of highly crosslinked polystyrene microgel colloids in colloid-polymer-mixtures close to the glass transition lines

The behavior of highly crosslinked polystyrene microgels can be mapped onto that of hard spheres with respect to phase behavior, short range order and glass transition dynamics [1]. As a hard sphere system their dynamic properties can be compared to the predictions made by the mode coupling theory and easily observed by dynamic light scattering (DLS). One of the most prominent effects predicted is the re-entrant melting, that is the creation of a fluid pocket at high volume fractions in the phase diagram when an attractive force is introduced by addition of a non-adsorbing (free) polymer. The investigation of the re-entrant glass transition of polystyrene (PS) microgels in a good solvent on addition if PS polymer via DLS indicated an exceptionally large re-entry region with fluid samples up to volume fractions of about 0.74 [2].

As such high fluid volume fractions are hard to rationalize within an amorphous (glass) structure a reduction of the microgel size by osmotic deswelling has been discussed as an obvious explanation [2]. To experimentally test this hypothesis we measured in a first SANS experiment on D11 the particle formfactor of a small amount of fully deuterated tracer PS microgels in a contrast-matched host of protonated PS microgels and PS polymer at a volume fraction of 0.72 using a toluene/toluene-d8 solvent mixture. Even though the q-resolution was significantly increased - allowing to detect particle size changes of about 1 nm - a decrease of the tracer particle size could not be verified [3].

In this continuation experiment we therefore aimed to amplify the hypothetical radius change due to osmotic deswelling by use of a large size of the used microgel particles and by going ot even larger volume fractions. A fully-deuterated 1:50 crosslinked polystyrene microgel with a DLS radius of 180 nm was now used as a tracer in a host consisting of two 1:50 crosslinked polystyrene microgels with a DLS radius of 150 nm and 175 nm. To introduce attractive interactions between the microgels free, nonadsorbing polystyrene with a molecular weight of 79600 g/mol was used yielding a size ratio $\delta = \frac{R_{g,polymer}}{\langle R_{colloid} \rangle} = 0.06$ to make the studied system as closely similar to the colloid-polymer mixture of [2]. A mixture of toluene and d-toluene according to the ZAC measurements in experiment No. TEST-2369 served as a contrast-matching solvent for the protonated host.

For the determination of the radius in a highly concentrated system four samples with different polymer concentrations and a volume fraction $\varphi$ = 0.745 ($\varphi_{host}$ = 0.715 and $\varphi_{tracer}$ = 0.030) near the highest fluid sample in [2] were prepared. The first sample with a polymer concentration of 0 g/L was prepared in order to check whether if the preparation of highly concentrated colloidal dispersions already leads to a particle deswelling. The other three samples represent states in the repulsive glass ($c_P$ = 13.0 g/L), the fluid phase ($c_P$ = 23.5 g/L) and the attractive glass ($c_P$ = 27.9 g/L) according to the phase diagram in [2] which is reproduced in the inset of Fig. 1. All samples were measured at a wavelength of $\lambda$ = 10 Å and three different detector distances of d = 28, 34 and 39 m to get the best resolution around the first two minima.

The measured P(q)-curves of the tracer are shown in figure 1.

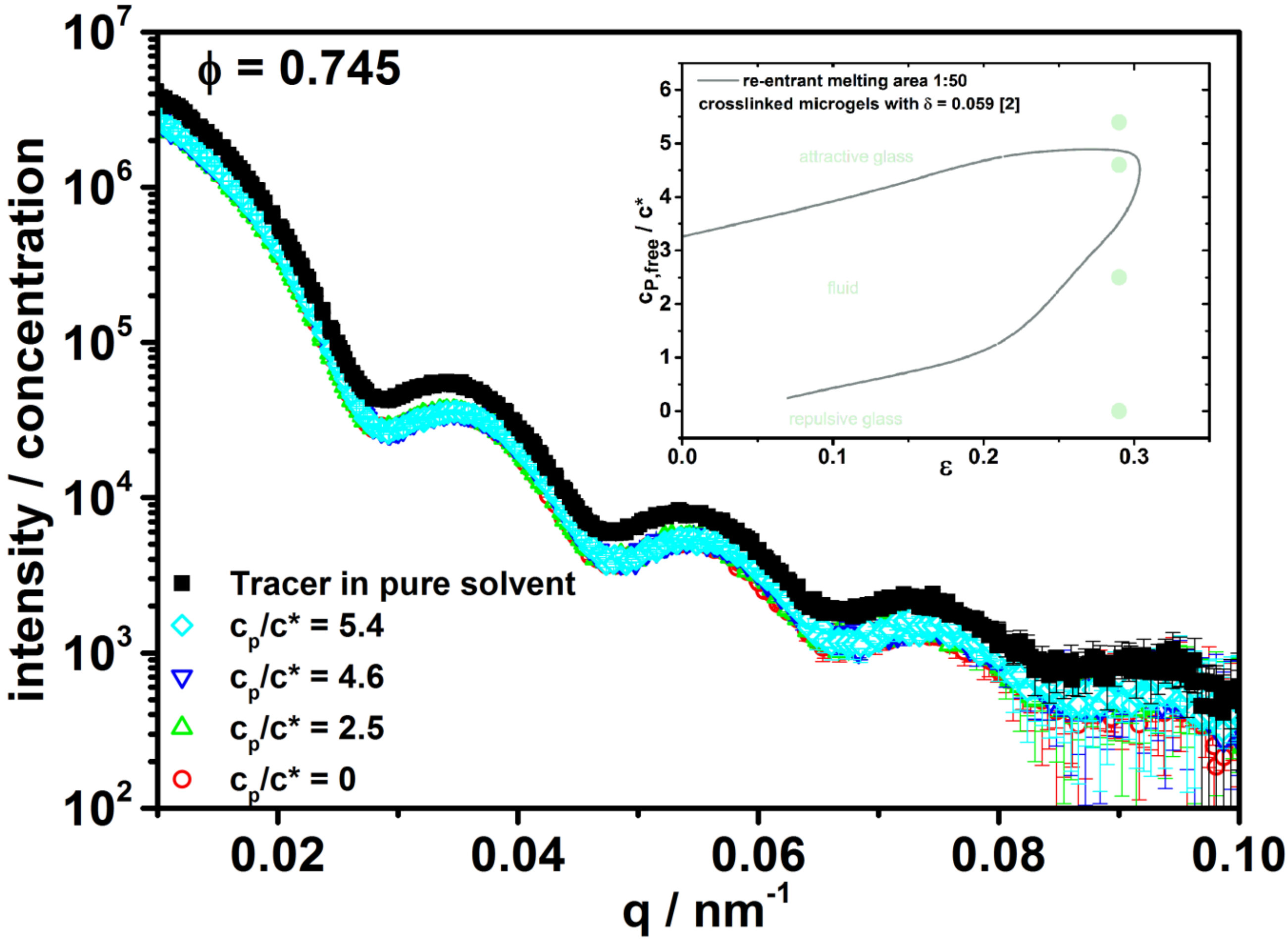

Fig. 1: Measured P(q)-curves of four different highly concentrated host-tracer-dispersions in comparison with the pure tracer microgel. The inset reproduces the phase diagram of [2] with the state points measured in the experiment indicated by solid circles.

All four curves fit perfectly on top of each other and even with the obtained high resolution no difference in the radius of the four samples was found. For comparison the pure tracer in toluene was also measured and except for a slight shift in absolute intensities the particle form factor was identical to that of the tracer in the host systems. A quantitative analysis of the form factor curves provided a difference of radius of 0.7 nm - a value well within experimental uncertainty.

From these experimental results we must conclude that osmotic deswelling of the microgels particles - if it occurs at all in this system - amounts to a particle radius reduction of significantly less than 1%. Thus, this effect cannot be responsible for the extraordinarily large re-entry region observed in [2].

[1] T. Eckert, E. Bartsch, Faraday Disc. **123**, 51 (2003)

[2] S. Burger, E. Bartsch, Colloids Surf. A: Physicochem. Eng. Aspects **442**, 6 (2013)

[3] BARTSCH Eckhard; BURGER Stefanie; LINDNER Peter; SCHAERTL Nicole; SCHNEIDER Jochen and WERNER Marcel. (2014). Deswelling of highly crosslinked polystyrene microgel colloids in colloid-polymer mixtures close to the glass transition lines. Institut Laue-Langevin (ILL) doi:10.5291/ILL-DATA.9-10-1374