Investigations of the internal structure of hollow charged microgels by SANS

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Hollow microgels have the potential to meet one of the key challenges in biomedical research: The design of nano-carriers allowing for triggered uptake, storage and release of drugs [1]. Small-angle neutron scattering (SANS) was already used to study the internal structure of hollow doubly temperature-sensitive microgels. Based on the temperature-dependent swelling behavior of poly(*N*-isopropylacrylamide) (PNIPAM) based microgels, the size of the void changes when changing the temperature [2]. Introduction of charges into the polymeric network improves the swelling properties of microgels due to the repulsion of similar charges and the increased osmotic pressure within the gel network [3].

In this work, we address the synthesis of hollow charged microgels and the investigation of their properties as a function of charge density and ionic strength of the solvent. NIPAM is copolymerized with dimethylitaconate (DMI) onto sacrificial silica cores in a seed and feed precipitation polymerization. Sodium hydroxide is used to etch the silica and to saponify the DMI to itaconic acid introducing negative charges into the shell. Potentiometric titrations, electrophoretic mobility and different scattering techniques are used to analyze the pH-dependent behavior of charge density and microgel size. Furthermore, SANS is used to prove the persistence of the void below and above the volume phase transition temperature (Fig. 1). Additionally, the suppression of the temperature-sensitive collapse of the shell due to the presence of charges is demonstrated.

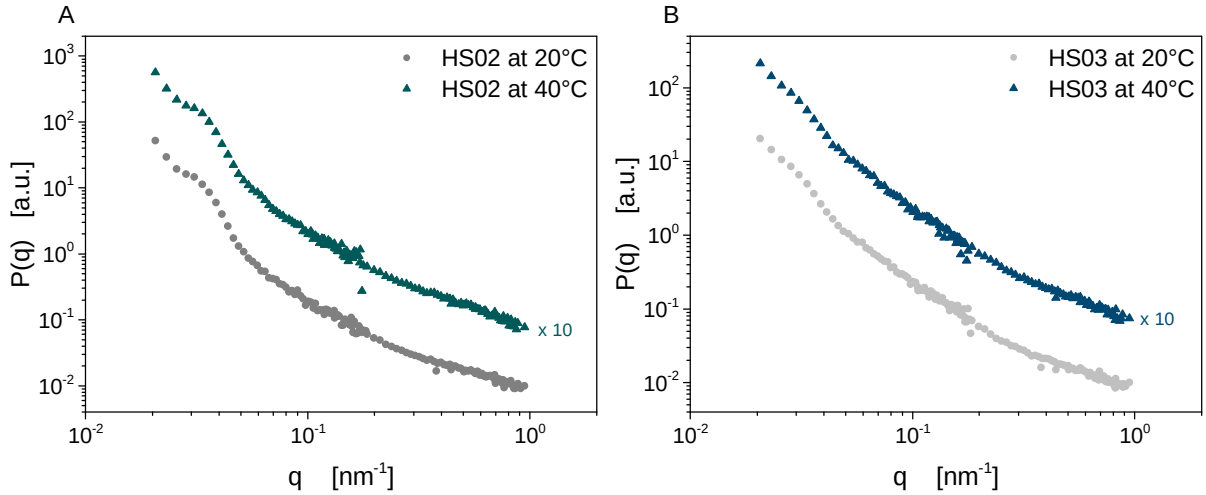

Figure 1. (A) SANS form factor for the hollow microgel HS02, with a DMI content of 10 mol% at two different temperatures below and above the VPTT at pH 9 and 10 mM ionic strength. Data are shifted up for clarity. (B) SANS form factor for the hollow microgel HS03 with a DMI content of 25 mol% at two different temperatures below and above the VPTT at pH 9 and 10 mM ionic strength. Data are shifted up for clarity.

[1] W. Richtering et al., *Nanomedicine* **11** (2016), 2879.
[2] A. J. Schmid et al., *Scientific Reports* **6** (2016), 22736.
[3] A. Pich et al., "*Chemical Design of Responsive Microgels"*, (Springer Berlin Heidelberg, 2010).

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