More than ever polymer science focus on complex molecular structures and supramolecular assemblies. Beyond this, responsive polymer materials are structures, which can be manipulated in e.g. charge or size change by external parameters like pH or temperature variation. This leads to Microgels. Microgels are soft particulate polymer networks that can be dispersed in a aqueous medium. They reveal unique features providing new opportunities to develop smart bio-inspired materials. In contrast to rigid colloidal particles, which lack the possibility to adapt their size and shape to environmental requirements, microgels have switchable properties of form and function that makes them very useful in a wide range of e.g. biological sciences and medical applications. They combine properties of dissolved macromolecules with those of colloidal particles.

In the present work, thermoresponsive microgels were studied in their ambient environment by in situ-experiments in TEM/STEM. The microgels are made from N-isopropylacrylamide (NiPAAm) as is described in [1].

In order to stain the microgel complexes with gold nanoparticles, they were redispersed in water (1mg per 1ml water). HCl (aq) is used to set a defined pH. By adding chloroauric acid (HAuCl₄·3H₂O), centrifuging, redispersing in HCl (aq) and reducing with NaBH₄ (aq) the stained microgels in aqueous solution are obtained.

In our studies, these microgels were observed by in situ-TEM in liquid environment. In the experiments, a thin layer of liquid was embedded between two hermetically sealed, electron transparent Si₃N₄-windows. The used holder is an in situ-liquid cell holder manufactured by Hummingbird Company and the microscope is a Zeiss Libra 200FE with an acceleration voltage of 200 kV. The resolution is mainly limited by the thickness of the liquid. To increase the contrast, an energy filter window of about 100 eV is inserted at the most probable energy loss, which reduces the background scattering of the solvent. A big challenge is to focus and get sufficient resolution because of the high mobility of the almost freely moving particles through the liquid.

Figure 1 shows an energy-filtered TEM-image of single microgel particle moving through the liquid, Figure 2 a energy-filtered TEM-image of a cluster of agglomerated microgel particles and Figure 3 a STEM image of a particle that adhere on the surface of the Si₃N₄-membrane with an additional EDX-spectra that shows the presence of gold, a EELS-Spectra to prove the presence of water and an intensity profile through the particle.

References:

Acknowledgement: The authors kindly acknowledge the financial support through the SFB 985 through the DFG.
Fig. 1: Single microgel particle observed by a TEM-magnification of 20,000x. The right corner shows a part of a second particle moving through the liquid.

Fig. 2: Aggregation of several microgel particles observed by a TEM-magnification of 8000x.

Fig. 3: STEM image of a microgel particle adhering on the surface (top left). The EDX-Spectra (top right) shows the presence of gold and the EELS-spectra (bottom right) the presence of water. An intensity profile (bottom left) shows the structure of the microgel.