

Microgels

A microgel is a cross-linked polymer network in a stable spherical form which has the ability to take up and release large amounts of solvent. The colloidal particles range in a size between tens of nanometers to a few micrometers and are typically formed of hydrophilic polymers which inherit their physiochemical properties to the microgel. The polymer chains are cross-linked via covalent bonds which allows the microgel to retain its physical shape even when taking up extensive amounts of solvent. In its swollen state it can be considered a soft fuzzy sphere with dangling polymer chain ends while in their dry state they may behave like rigid particles of a defined size. In smart microgels, the solvent uptake can be controlled by an external trigger. They are constituted of stimuli-responsive polymers which undergo strong changes in one or more physical properties upon small stimuli from their surroundings. Such a stimulus is for example a change in temperature, humidity, light irradiation, pH-value, or ionic strength and leads to a volume phase transition (VPT) as shown in Figure 1. As the microgel switches between a collapsed and a swollen state its mesh size and thus its permeability change as well. This serves a range of applications where a controlled uptake and release of selected molecules is crucial. Examples are drug delivery systems, where a microgel can be used as transporting agent of the drug, or nanoreactors, where the microgel serves as a micro-container for controlled chemical reactions.

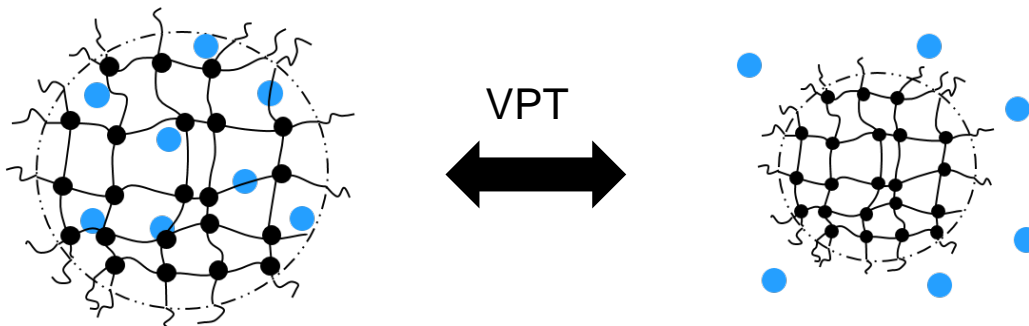


Figure 1: Volume phase transition of microgels. The blue dots indicate solvent molecules.

We make use of the change in permeability to control the breathing ability of fabrics. We investigated the use of a thermo-responsive microgel as textile coating with self-regulating moisture permeability and anti-bacterial properties¹. In a thermo-responsive microgel the VPT is controlled by a change in temperature and shows strong changes in volume around a so-called volume phase transition temperature (VPTT). The thermo-responsive polymer we investigated was copolymerized by the monomers di(ethylene glycol) methyl ether methacrylate (MEO₂MA), (ethylene glycol) methyl ether methacrylate (OEGMA₃₀₀), and ethylene glycol methacrylate (EGMA) with a molar ratio of 10:10:1. It does not have a sharp VPT but shows a mostly linear decline in a temperature range between 20°C and 70°C. Its functionality as a self-regulating fabric coating is illustrated in Figure 2. We covered the cotton fibers in a layer of microgels by crosslinking them to the fibers using 1,2,3,4-butanetetracarboxylic acid (BTCA), leading to an overall weight gain of the fabric of 15 % or 30 %. In their swollen state the microgel clogs up the pores in the fabric, reducing the diffusion of body moisture and thereby also preserving body

temperature. In contrast, at warmer temperatures, for example in summer or while doing sportive activities, the microgel shrinks and opens up the fabric pores for an improved moisture permeability. As shown in our studies the water vapor transmission through the fabric increases linearly by a factor of 7 when increasing the temperature from 20°C to 50°C. Additionally, the coating exhibits anti-bacterial properties and showed that the number of *E. coli* and *S. aureus* bacteria which are able to adhere to the cotton fabric was reduced by up to 94 % and 96 %, respectively.

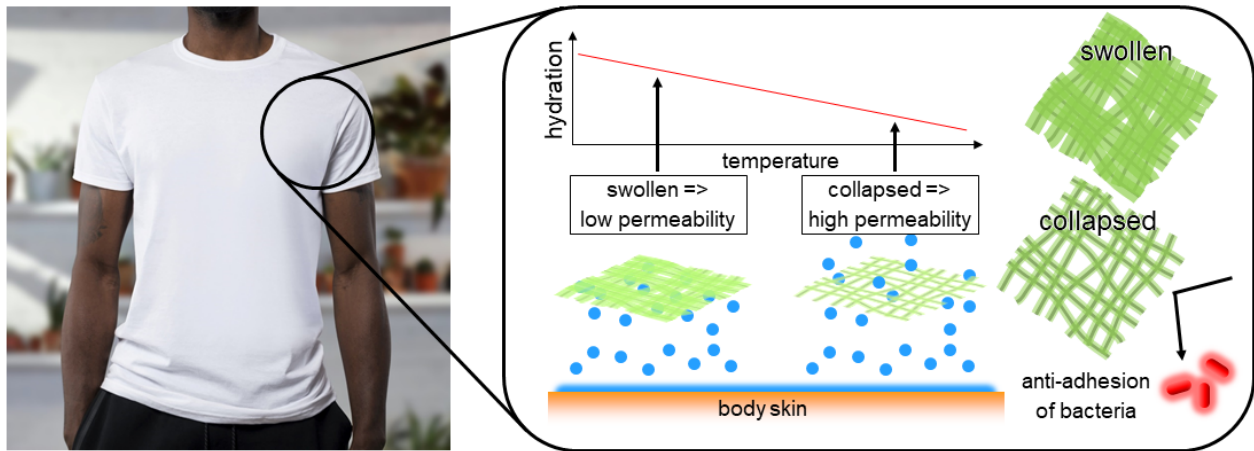


Figure 2: Microgel coated cotton fabrics for self-regulating moisture permeability

For the coating of cotton fabrics, but also for many other applications like thin film biosensors, thermomechanical devices or functional surface coatings, a thorough understanding of the microgel adhesion properties is crucial. For that purpose we compared the thermo-responsive microgel poly(NIPAM-co-acrylic acid) in solution and adsorbed on a silicon substrate with an poly(allylamine hydrochloride) (PAH) coating². We tested two different acrylic acid contents (2.2 and 18.2 mol%) and compared the microgel VPT and inner structure in dependence on a change in temperature. We made use of dynamic light scattering (DLS) and small-angle neutron scattering (SANS) to study the bulk microgel in colloidal dispersion and atomic force microscopy (AFM) and grazing-incidence small-angle neutron scattering (GISANS) to study microgel monolayers on a solid support (see Figure 3). The DLS and AFM measurements showed a temperature-dependent deswelling of the microgel at a VPTT of around 45°C in both the bulk suspension and the monolayer. Additionally, a higher microgel volume is observed in solution compared to its adsorbed state, due to the confinement and deformation of the microgel against a solid support. The SANS measurements revealed that the correlation length of the microgel in solution shows a similar temperature-dependence as the pure PNIPAM homopolymer. Contrary to that, the GISANS measurements showed that for different temperatures the correlation length remains constant in the adsorbed microgel monolayer. This showed the significant influence of the substrate on the temperature dependence and is an important basis on which further applications can build.

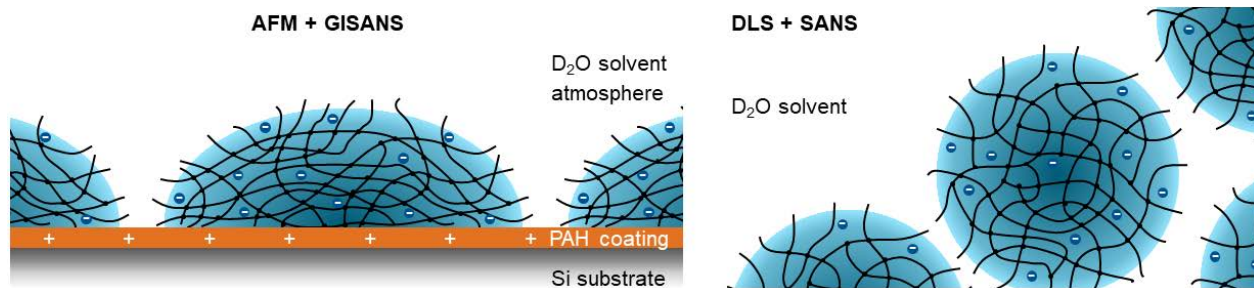


Figure 3: microgel monolayer on a solid support studied with AFM and GISANS (left) is compared to a microgel dispersion studied with DLS and SANS (right)

Applications like biosensors and micromechanical devices need fast response times, while drug delivery systems require a good understanding of the diffusion mechanics of molecules inside the microgel mesh. For both, a thorough knowledge about the mechanisms of the swelling and deswelling kinetics is crucial. Therefore, we studied the swelling and exchange mechanics of H_2O and D_2O in thin films of PNIPAM microgel cross-linked with *N,N'*-methylenebisacrylamide.³ AFM measurements of our prepared films revealed an exceptional homogeneity of the microgel monolayer. The individual microgel particles are no longer distinguishable and have formed a compact layer of around 25 nm thickness as can be seen in Figure 4 on the left. As schematically shown in Figure 4 on the right, these layers are swollen in solvent atmospheres of H_2O (A, orange) and D_2O (B, blue) before the solvent is exchanged with D_2O and H_2O , respectively (A, blue and B, orange). This procedure was probed with Fourier-transform infrared (FTIR) spectroscopy and time-of-flight neutron reflectometry (TOF NR) which allowed us to distinguish and follow H_2O and D_2O molecules diffusing through the microgel film. The results showed differences in the hydration and exchange kinetics and efficiency for H_2O or D_2O . The microgel film showed a higher affinity towards H_2O reflected by a stronger swelling in H_2O solvent atmosphere and a high amount of residual H_2O after exchanging it with D_2O . Additionally, we could follow the different steps in hydration and exchange process that occur on a molecular level in the films: As the fastest process water molecules quickly diffuse into the microgel and aggregate into a water shell around the polar amide group, as a slightly slower process the whole film is hydrated and swells, and as the slowest process the hydrogen of the amide is exchanged by an D atom in a deuteration process. These findings help to gain a better understanding of the diffusion mechanics of water species through a hydrophilic microgel in thin film conformation.

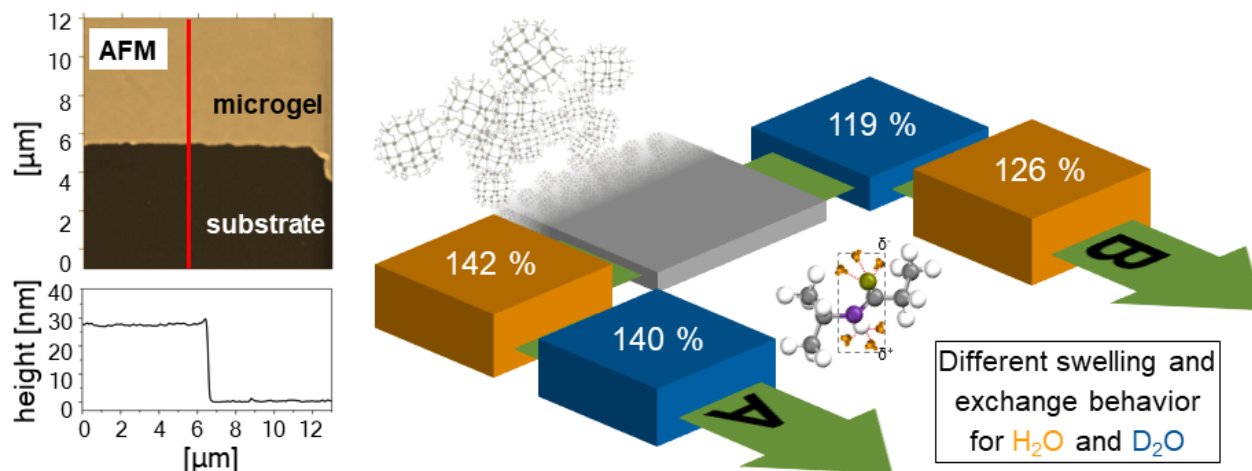


Figure 4: homogeneous microgel monolayers (left) subjected to differing solvent atmospheres of H₂O (orange) and D₂O (blue)

These studies help to further develop the fundamental understanding of microgels in the framework of functional materials. Combining surface sensitive techniques with bulk sensitive scattering techniques we are able to draw a complete picture of the microgel structure and structural changes during dynamic processes. By investigating their dynamics and morphologies we are able to explore their functionality for uses in new applications or designs. For that purpose, we aim to further study novel microgel systems and develop sample environments and measuring procedures to deepen our knowledge on these smart materials.

Selected Publications:

1. **P.Gu, N.Fan, Y.Wang, J.Wang, P.Müller-Buschbaum, Q.Zhong**

Linear control of moisture permeability and anti-adhesion of bacteria in a broad temperature region realized by cross-linking thermo-responsive microgels onto cotton fabrics
 ACS Appl. Mater. Interfaces **11**, 30269-30277 (2019) [link](#)

2. **S.Wellert, Y.Hertle, M.Richter, M.Medebach, D.Magerl, W.Wang, B.Deme, A.Radulescu, P.Müller-Buschbaum, T.Hellweg, R.von Klitzing**

Inner structure of adsorbed ionic microgel particles;
 Langmuir **30**, 7168-7176 (2014) [link](#)

3. **T.Widmann, L.P.Kreuzer, N.Hohn, L.Bießmann, K.Wang, S.Rinner, J.-F.Moulin, A.J. Schmid, Y.Hannappel, O.Wrede, M.Kühnhammer, T.Hellweg, R.von Klitzing, P.Müller-Buschbaum**

Hydration and solvent exchange induced swelling and deswelling of homogeneous poly(N-isopropylacrylamide) microgel thin films
 Langmuir **35**, 16341-16352 (2019) [link](#)