

Supporting Information

A robust platform for functional microgels via thiol-ene chemistry with reactive polyether-based nanoparticles

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Particle characterization by dynamic light scattering (DLS)

Angle dependent dynamic light scattering experiments were carried out at 25 °C on a BI-200SM (Brookhaven Instruments) multi-angle detector system with a 632.8 nm (HeNe continuous wave) laser. Cumulant analysis of the intensity autocorrelation functions at different scattering angles between 50° and 110° gave the corresponding hydrodynamic diameters. From these values the apparent diffusion coefficients D_{app} were calculated and plotted against the quadratic scattering vector q^2 . The z-averaged diffusion coefficient D_s was obtained by extrapolation (linear fit in Origin 8.0) to the y-intercept and used to calculate the actual hydrodynamic radius R_h of the microgels. Obvious outliers were not included in the linear fit. The experimental error for the hydrodynamic diameters is influenced by the deviation between multiple measurements for each angle and the quality of the linear regression. Taking both factors into account, a relative error of 5 % was estimated for the obtained values of D_h . The influence of this error on the values of the swelling degree Q was then calculated via Gaussian error propagation.

For the degradation experiments, DLS measurements at a fixed detection angle of 173° were recorded in backscattering mode on a Malvern Zetasizer Nano ZS ZEN 3600 at a temperature of 25 °C with a laser wavelength of 633 nm. The solutions were placed in a glass cuvette with a layer thickness of 1 cm. The non-negative-least-squares algorithm in general-purpose mode was used for interpretation. For analysis, the number weighted size distributions were taken into account and mean values of at least five measurements were calculated.

Additional characterization of native microgels

For reaction times longer than 4 hours, the average size of native microgels in water was found to be independent of the irradiation time (see Fig. S-1a). Particle size distributions of these samples were obtained by cumulant analysis at fixed angles and showed monomodal distributions of the hydrodynamic diameters (see Fig. S-1b).

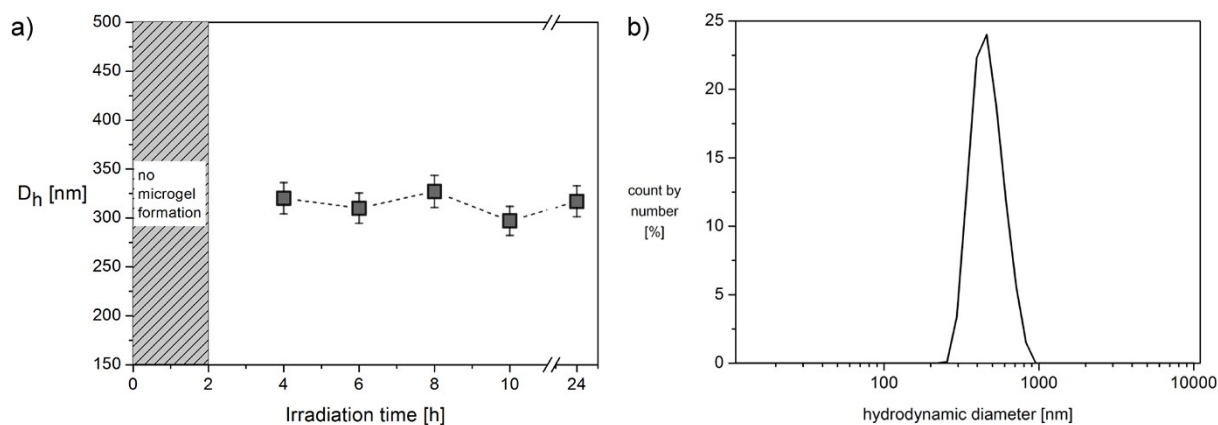


Figure S-1. Characterization of reactive precursor particles in aqueous dispersion. a) Hydrodynamic diameters of particles with 2 mol-% crosslinker: **MG-A4**, **-A6**, **-A8**, **-A10**, and **-A24**. b) Representative number weighted size distribution of **MG-A24** determined by DLS at a fixed detection angle of 173° .

Upon decreasing the crosslinker concentration, the size of the native microgels in water slightly increases. The observed size range spans from 320 to 375 nm and from 290 to 350 nm for reaction times of 8 and 10 hours respectively (see Fig. S-2).

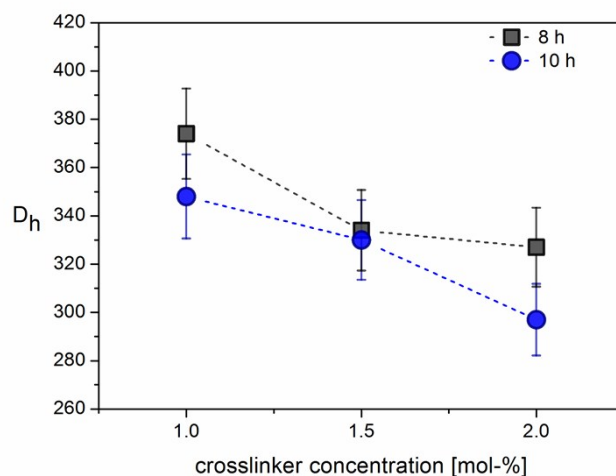


Figure S-2. Hydrodynamic diameters of native microgels in water (reaction times of 8 and 10 hours) as a function of the crosslinker feed ratio.

In analogy to the particles obtained from 8 hours irradiation, particles prepared within 10 hours reaction time were also investigated with respect to their swelling behavior in methanol and THF (see Fig. S-3). In THF a significant increase in the swelling degree was observed with decreasing crosslinking density. In contrast, reducing the crosslinking density causes only a slight increase in swelling of the particles in methanol.

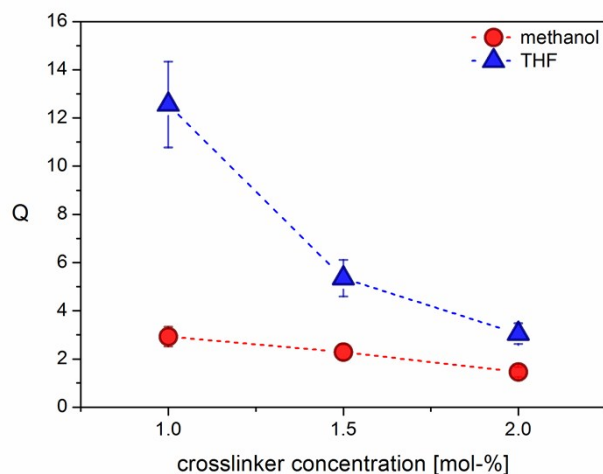


Figure S-3: Investigations on the swelling degree of microgels obtained from 10 hours irradiation: Dependency of swelling degree Q in THF and methanol on the crosslinker feed ratio.

Functionalized microgels – additional characterization

MAA-functionalized microgels **MG-A8-MAA**, **-B8-MAA**, and **-C8-MAA** were investigated with regards to their pH-dependent swelling behavior. The swelling degrees as functions of the pH are shown in Figure S-4a. In aqueous dispersion of $\text{pH} > 8$ the particles are fully swollen and - analogous to the swelling behavior of native microgels in THF - the corresponding maximum degree of swelling ($\text{pH} 10$) decreases with increasing crosslinker feed ratio. At lower pH values ($\text{pH} < 6$), the particles are collapsed with hydrodynamic diameters similar to the non-swollen precursor particles in water (see Figure S-4b).

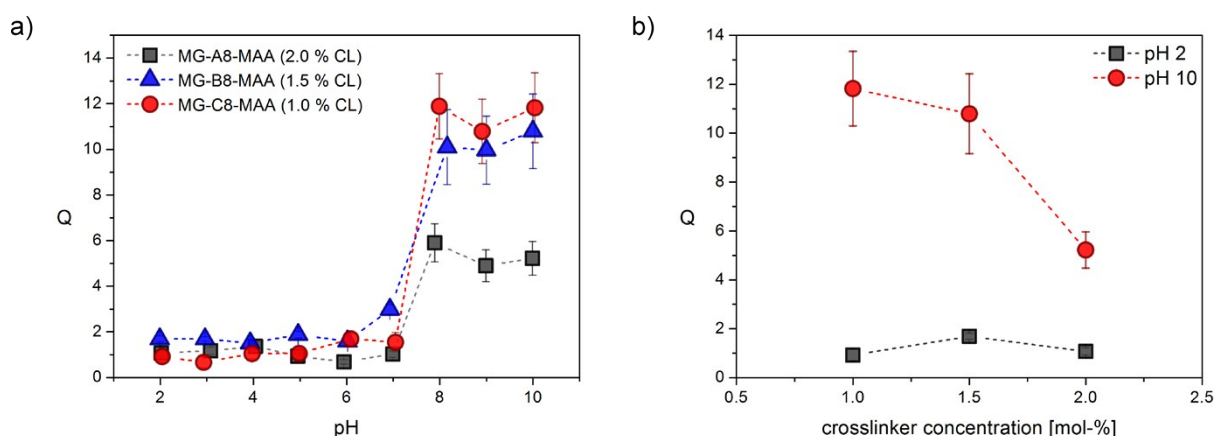


Figure S-4: Swelling degrees of microgels **MG-A8-MAA**, **-B8-MAA** and **-C8-MAA** as a function of pH: a) Swelling degrees Q calculated from DLS measurements. b) Swelling degrees at pH 10 and pH 2 as function of the crosslinker concentration.

In an analogous procedure, the pH-dependent swelling behavior of the His-functionalized microgels **MG-A8-His** and **MG-C8-His** was examined. The dependency of swelling degree on pH is shown in Figure S-5. Both particles exhibit an increased degree of swelling in acidic medium (pH < 5). Comparing the maximum swelling degree of both particles, it can be seen that a decreased crosslinker feed ratio results in an increased maximum degree of swelling.

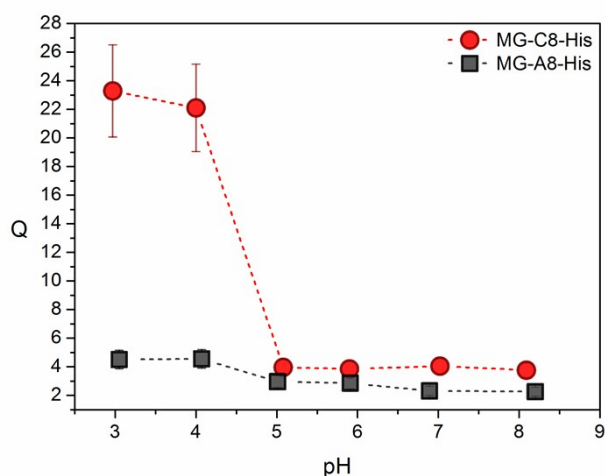


Figure S-5. Swelling degrees of microgels **MG-A8-His** and **MG-C8-His** as a function of pH.

Investigations on Network Functionalization by Infrared Spectroscopy.

Due to the crosslinked nature of the microgels, accurate analysis of the samples via $^1\text{H-NMR}$ spectroscopy of the dispersions is hindered and only broad peaks are observed in the respective spectra. Alternatively, IR spectroscopy represents a facile technique that allows determining microgel functionalization and demonstrating the existence of functional groups in the network interior. Therefore, IR spectra of the native precursor particles and the corresponding MAA-, His-, and MAA+His-functionalized particles were collected from the corresponding freeze dried microgel dispersions. The resulting spectra are shown in Figure S-6.

The IR spectrum of the native microgels clearly exhibits C=C stretching vibrations at 1646, 922, and 843 cm^{-1} due to the unreacted alkenes of AGE moieties. In direct contrast, these bands cannot be detected in either spectrum of the respective functionalized microgels, thus pointing towards full conversion of AGE units.

Additionally, new absorption bands were detected in the spectra of the functionalized microgels. For the MAA-functionalized microgels, a very strong band at 1720 cm^{-1} was found and indicates the presence of carboxylic acids. The spectrum of His-functionalized microgels exhibits two bands at 1643 and 1551 cm^{-1} that derive from a C=N stretching vibration caused by the introduction of the imidazole ring. As expected, all of these three characteristic bands can be observed in the IR spectrum of the microgel functionalized with both moieties (MAA+His). This strongly supports the successful addition of the corresponding thiols and thereby the network functionalization.

However, due to the overlapping of latent low intensity bands from potential remaining AGE units with the strong signals from the introduced functional groups, the quantitative determination of a degree of functionalization was hindered.

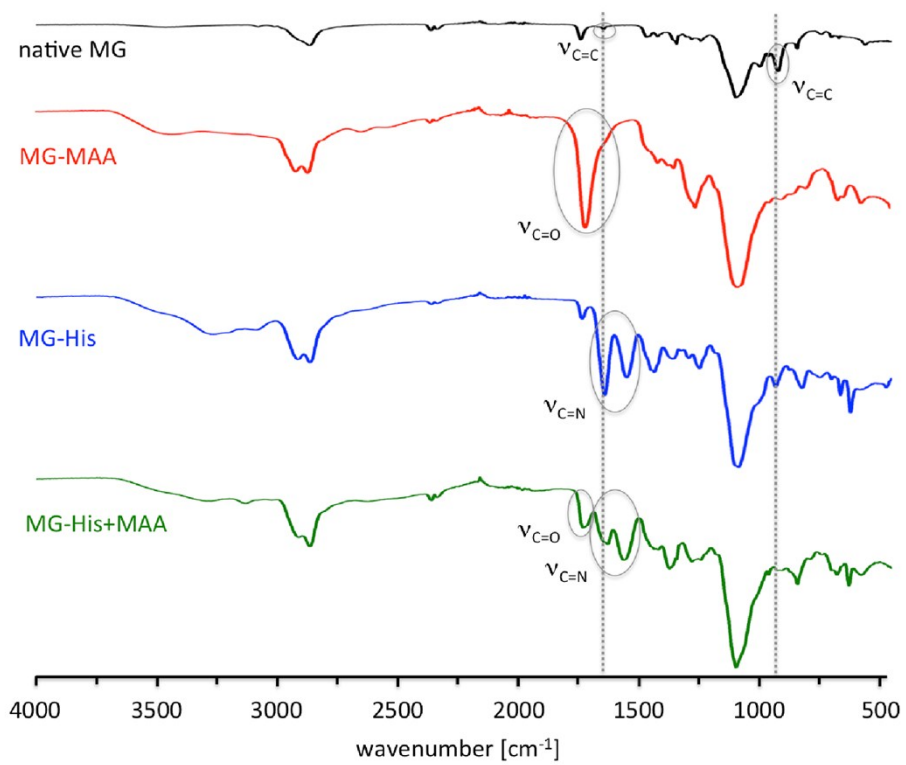


Figure S-6. IR spectra of freeze dried microgels before and after functionalization with MAA-, His-, and MAA+His-thiols.