Electronic Supplementary Material (ESI) for Soft Matter.

Smart membranes by electron beam cross-linking of copolymer microgels

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Supporting Information

SEM results

In addition to the AFM measurements also SEM images were recorded (Fig. S.1). These images support the information gathered through the AFM measurements and also show that the synthesized microgel particles have a circular cross-section and are most likely spherical in shape and have a narrow size distribution. Scanning electron microscopy (SEM) investigations were performed on an ESEM-FEG (Philips XL30, Philips, Eindhoven, Netherlands) with an acceleration voltage of 3 kV and a working distance of 10 mm. For the sample preparation 25 μL of microgel solution ($c \leq 0.0001$ wt%) were deposited on cleaned silicon wafers and dried at ambient temperature in air. The wafers were cleaned as described in the section "atomic force microscopy" and sputtered with palladium. Particle diameters were analyzed to support the AFM Images using the program ImageJ (Wayne Rasband, National Institutes of Health, USA).

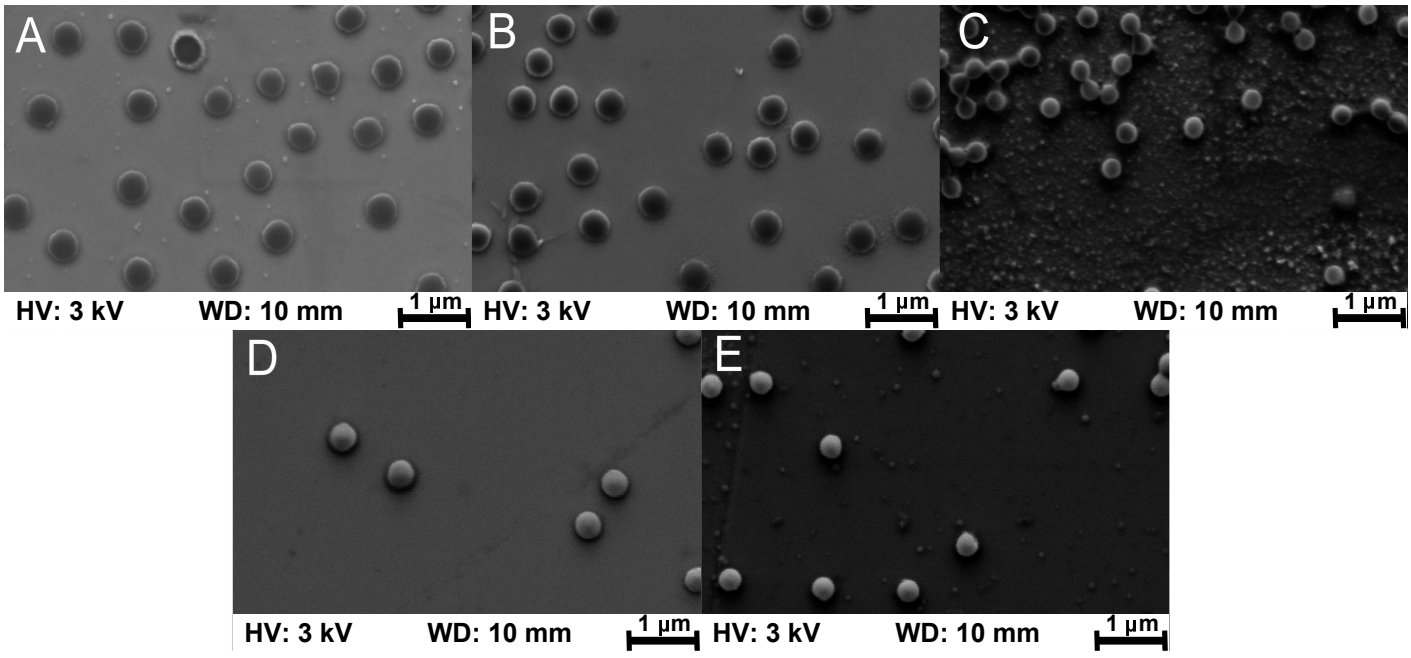

Fig. S. 1: SEM images of the copolymer microgels (A) NcBH5, (B) NcBH10, (C) NcBH15, (D) NcBH20, (E) NcBH30. The microgel particles were deposited on silicone wafers by drying of the solution at ambient conditions. The wafers with the deposited microgels were sputtered with palladium before measurement.

Angular dependent PCS results

The hydrodynamic radii of the copolymer microgels were calculated using the Stokes-Einstein equation (eq.1) from the data obtained in angular dependent PCS measurements (Fig. S.2). The measurements were performed using photon correlation spectroscopy (PCS)[1] on highly diluted samples (c $\leq$ 0.0001 wt%). The experimental setup is as described in the materials and methods section. The microgel solution was measured at two temperatures, in the swollen state at 10 °C and in the collapsed state at 50 °C. The diffusion coefficient is obtained from linear fits according to $\bar{\Gamma} = D \cdot q^2$. Additionally the maximum swelling ratio α_{max} was determined from this data via (eq.2) and is shown in Tab 2.

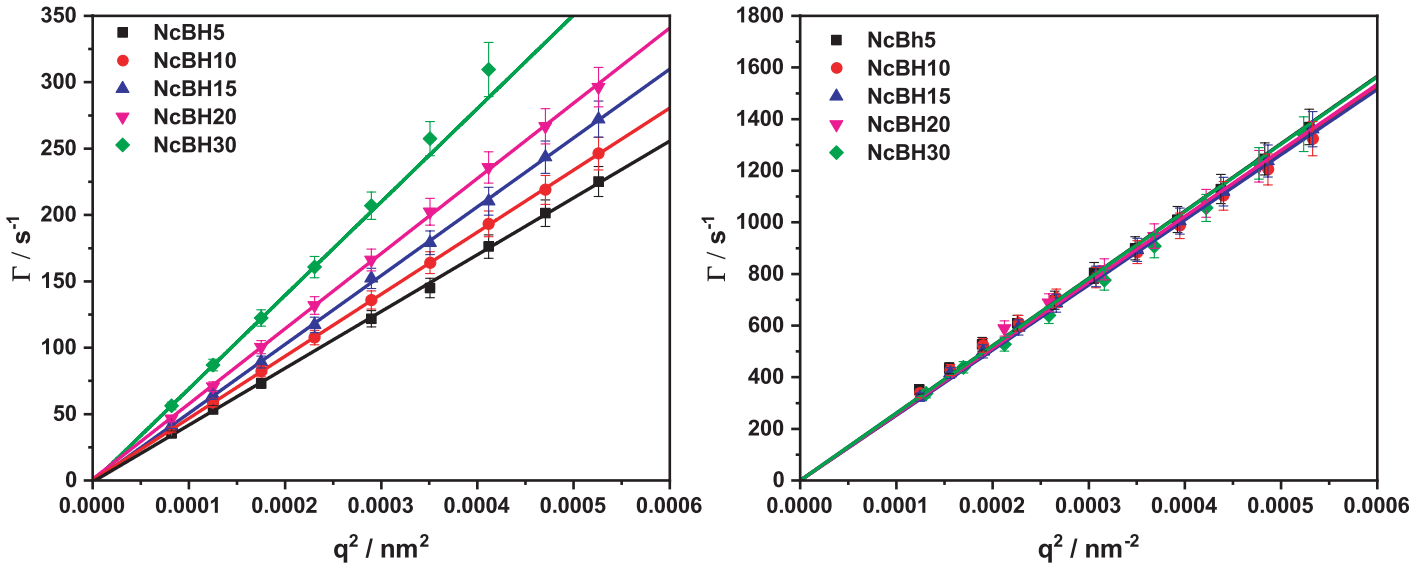

Fig. S. 2: Angular dependent PCS measurements at 10 °C in the swollen state of the copolymer microgels. From the Γ versus q^2 plots the hydrodynamic radii can be calculated via the Stokes-Einstein equation (eq.1).

FT-IR measurements on films

The microgels were applied to a gold wafer by spin-coating (Fig. S3). Subsequently, the microgels were cross-linked by irradiation with electrons (70 mC / cm^2) and examined. The gold-coated wafers with cross-linked microgels were immersed in aqua regia (6:1) for 20 minutes. The gold layer dissolved and the cross-linked microgel film floated to the surface. The free-standing microgel-layer was transferred to a gold-sputtered wafer. To obtain FTIR spectra of the microgel films the coated wafers were put with the film side down onto the crystal of a single reflection diamond ATR cell (Specac Golden Gate) and pressed down by a diamond anvil. FTIR measurements were performed using a Bruker IFS 66/s with air as the background (1024 scans). Three measurements of each sample were performed, averaged and normalized to the amide band at 1545 cm^{-1}. The comparison of the FTIR spectra of the microgel films before and after electron beam cross-linking do not show any significant change in the molecular structure of the microgel film for both samples containing 5 mol% and 10 mol% BHAM. This analysis clearly shows that the electron beam does not damage the microgels during cross-linking.

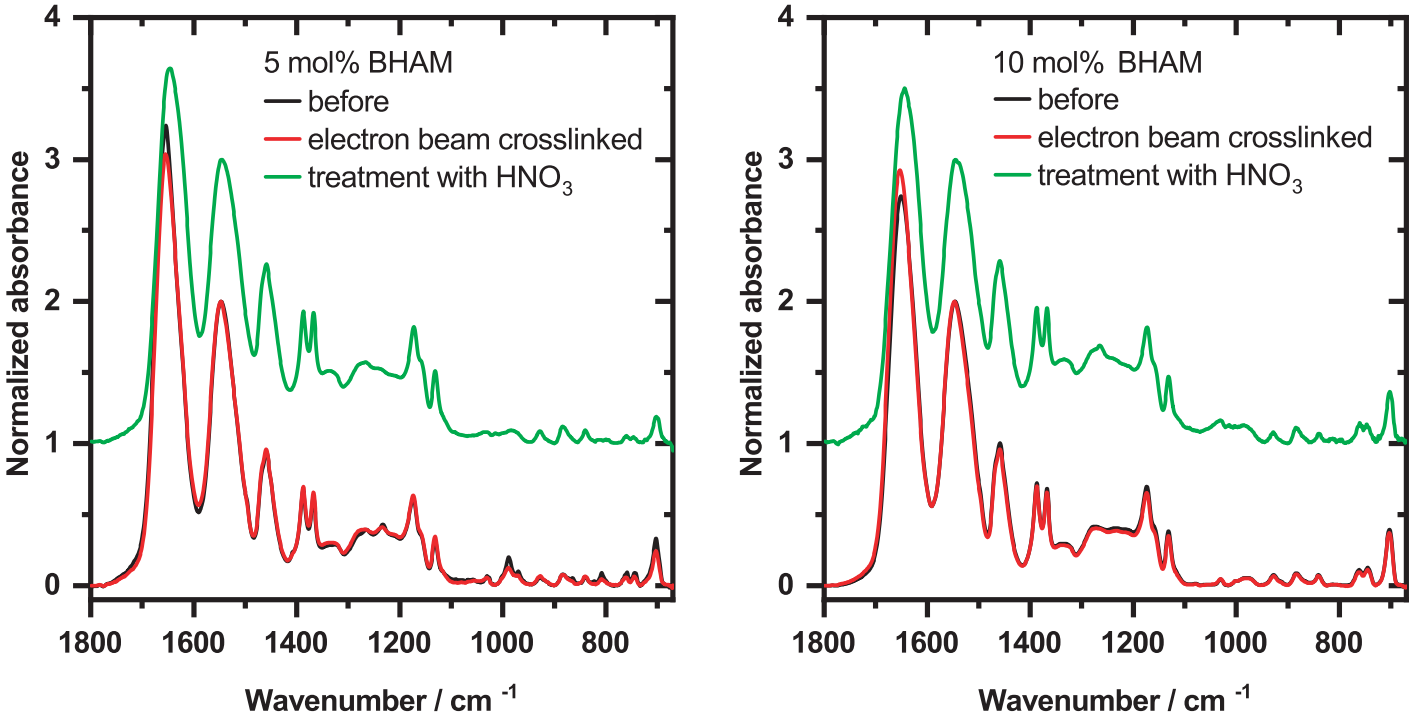

Fig. S. 3: FT-IR spectra of microgel films containing 5 mol% (left) and 10 mol% (right) NBHAM before cross-linking (black), after cross-linking (red) and after subsequent treatment with aqua regia to release the film from the gold-coated silicon wafer.

References

[1] B. J. Berne and R. Pecora, *Dynamic Light Scattering*, John Wiley & sons, Inc., 1976.