Electronic Supplementary Information for Soft Matter manuscript:

## Synthesis and functionalization of poly(ethylene glycol) microparticles as soft colloidal probes for adhesion energy measurements

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Figure S1: Turbidimetric measurements of PEG-dAAm in sodium sulphate solutions at different concentrations.



**Figure S2:** PEG-dAAm particles ( $M_n = 8000$  Da) fully swollen in water (light microscope).



**Figure S3:** Typical force-deformation curves for unmodified PEG 8000 and PEG 4600 (top panels) and aminefunctionalized PEG 8000 in different media (bottom panels). The curves were analyzed to obtain the elastic modulus *E* using the Hertz model ( $F=4/3 \cdot R^{1/2} \cdot E \cdot D/(1 - v^2)$ , with *F* the force, *D* the deformation, *v* the passion ratio and *R* the effective radius the PEG particle and the colloidal AFM probe. The resulting Hertz fits with *E* as free parameter are represented as dashed lines. Note that the force-deformation curves of the PEG 8000 samples showed Hertzian behavior while the fitting the PEG 4600 curves with the Hertz model was not successful. Depending on the force imposed on PEG 4600 the elastic modulus appeared to range between 40 and 80 kPa as indicated by the two Hertz plots. This suggests that PEG 4600 did not behave like a linear elastic material which could be due to material inhomogeneities. Therefore this material was not used to study surface interactions. On the other hand the PEG 8000 samples are very well represented by the Hertz theory and the average elastic modulus for these particles was  $32\pm5$ kPa. Furthermore the elastic modulus did not change significantly after functionalization with charged groups (see PEG-EDA curve). This could be explained by a relatively low degree of functionalization of the PEG backbone. The TNBS test showed that only one functional (charged) group was introduced to a single polymer chain. Therefore the elastic properties of the network were not altered. Consequently, addition of NaCl and screening of the charges did not affect the elastic properties either.



**Figure S4:** RICM was used to measure the contact radius formed by the PEG particle resting on the glass coverslip (Gingell and Todd, Biophys. J. 26:507–526, 1979). Polarized light waves reflected from the upper glass surface ( $I_1$ ) and the surface of the bead ( $I_2$ ) interact to create an interference image. The intensity at a given position in the image depends on the separation h(x) between the two surfaces:  $I(x) = I_1 + I_2 + 2 \cdot \operatorname{sqrt}(I_1 \cdot I_2) \cos[2k \cdot h(x) + \pi]$ , where  $k = 2\pi n/\lambda$ , and n and  $\lambda$  are the index of refraction of water and the wavelength of the monochromatic light, respectively. In order to detect the interference pattern, stray light was reduced by an antiflex technique. This is accomplished with a  $\lambda/4$ -plate placed between the sample and the objective lens, and crossed polarizers in the illumination and observation paths of light. In the region of contact, corresponding to h(x) = 0 and  $I(x) = I_1 + I_2 - 2 \cdot \operatorname{sqrt}(I_1 \cdot I_2)$  the intensity distribution over the distance d from raw data (bottom left). The intensity distribution was averaged over the entire circumference of the Newton rings to obtain the interference pattern (bottom right). As criteria for the contact radius we chose the half height of the first maximum as indicated.



Figure S5: Confocal microscope pictures of a) FITC labeled PEG-EDA particles and b) unfunctionalized PEG-dAAm particles.



**Figure S6:** Surface topography image of a PEG-dAAm particle measured *via* AFM showing a smooth surface with a root mean square surface roughness of 2.5 nm.



Figure S7: Unmodified PEG-dAAm particles show no adhesion on the coverslip. Instead the particle migrates over the surface.



**Figure S10:** Contact radius versus particle radius of carboxylate functionalized microparticles (PEG-AA and PEG-SUC) on a PDADMAC coated glass surface in water. The contact radii of these particles were determined *via* RICM.



**Figure S11:** Contact radius versus particle radius of benzophenone functionalized microparticles (PEGbenzophenone) on a FOTS covered glass surface in water. The contact radii of these particles were determined *via* RICM.