Supporting Information to the Article

Magneto-responsive hydrogels based on maghemite/triblock terpolymer hybrid micelles

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Fourier transform infrared spectroscopy (FT-IR)

FT-IR spectra were recorded on a Bruker Equinox 55/S FT-IR spectrometer using the software OPUS Viewer™ 4.2. The measurements were performed with KBr pellets, prepared after grinding a mixture of KBr (Merck) with a small amount of the sample.

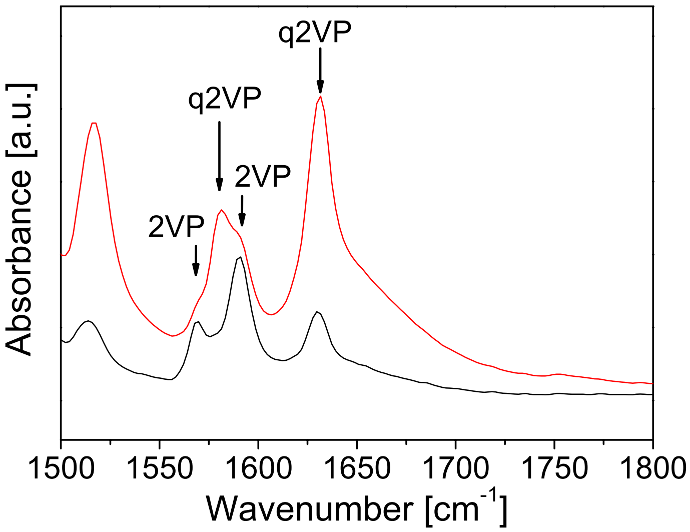

Figure S1 FT-IR spectra of Pq2VP$_{60}$-*b*-PEO$_{398}$-*b*-P(GME$_{26}$-*co*-EGE$_{26}$) quaternized with MeI (—) and Me_2SO_4 (—); KBr pellets.

The extracted wavenumber region shows four bands of interest (Figure S1). The bands at 1630 and 1578 cm^{-1} correspond to quaternized 2VP (q2VP) units, whereas the bands at 1590 and 1568 cm^{-1} are caused by the remaining non-quaternized 2VP units in the P2VP$_{60}$-*b*-PEO$_{398}$-*b*-P(GME$_{26}$-*co*-EGE$_{26}$) triblock terpolymer. The band from the q2VP units at 1630 cm^{-1} is clearly visible for both triblock terpolymers, however, the absorbance at the peak maximum is much higher for the triblock terpolymer being quaternized with Me_2SO_4, indicating a much higher degree of quaternization. In addition, the peak at 1578 cm^{-1} is only detectable when Me_2SO_4 was used for quaternization. Having in mind that the degree of quaternization of the P2VP block being quaternized with MeI was calculated to 20 mol%, by determining the amount of iodide counterions via titration with $AgNO_3$, we estimate from the FT-NIR spectrum that quaternization with Me_2SO_4 resulted in a degree of quaternization of about 60 mol%.

TEM

For the evaluation of the maghemite nanoparticle size, the software Image Tool^{TM} 3.00 (UTHSCSA) was used. The diameter of 150 individual particles was measured and the obtained values were averaged. The mean diameter of the nanoparticles is 8.2 nm with a standard deviation of 2.5.

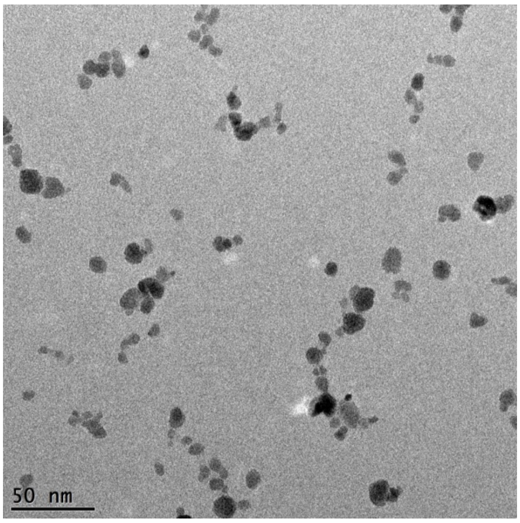

Figure S2 TEM image of the pure γ-Fe_2O_3 nanoparticles (c = 1 g/L).

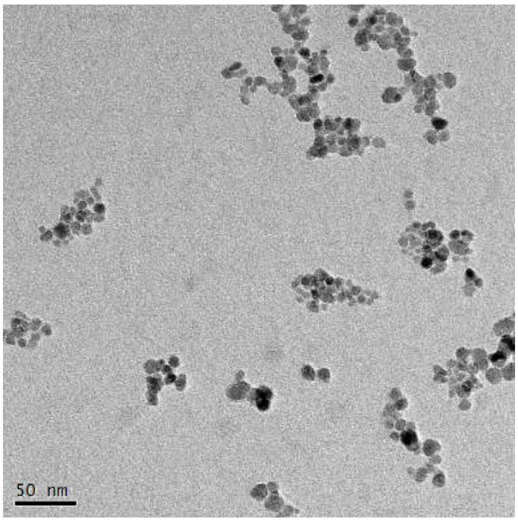

Figure S3 TEM image of γ-Fe_2O_3/$Pq2VP_{95}$-*b*-PEO_{337}-*b*-P(GME_{21}-*co*-EGE_{21}) hybrid clusters; degree of quaternization of the P2VP-block: 60 mol% (c = 1 g/L; γ-Fe_2O_3/polymer = 65/35 w/w).

pH dependent DLS

pH dependent light scattering experiments were conducted using the DLS device (see manuscript, *Experimental Part*) in combination with a titrator (Titrando 809, Metrohm, Herisau, Switzerland). NaOH (1M, Titrisol, Merck) was added in small portions of 2 µL. The equilibration time after each titration step was 3 min. The scattering intensity data presented in Figure S4 correspond to a time average of one measurement, conducted for 1 min each. The non-quaternized $P2VP_{62}$-*b*-PEO_{452}-*b*-P(GME_{36}-*co*-EGE_{36}) triblock terpolymer shows a strong increase of the scattering intensity at a pH of 5. Below pH = 5, the P2VP block is protonated and therefore hydrophilic, the polymer chains are unimolecularly dissolved. However at a pH higher than 5, P2VP is deprotonated and becomes hydrophobic which causes a formation of core-shell-corona micelles with P2VP in the core[1]. In the case of the analogue quaternized polymer (degree of quaternization of 20 mol%), no increase in count rate is observed up to a pH of almost 10. In conclusion, a degree of quaternization of 20 mol% is already high enough to render the P2VP block water soluble at any pH.

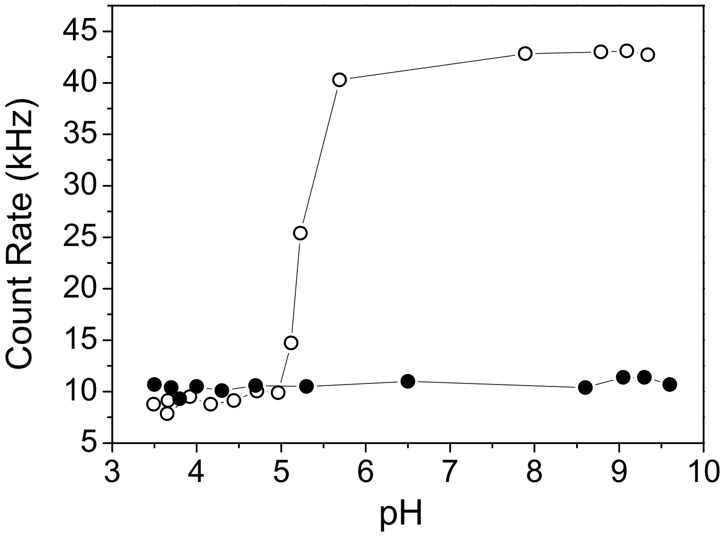

Figure S4 pH-dependent scattering intensity of non-quaternized (open symbols)[1] and quaternized (closed symbols, 20 mol% quaternized q2VP units) $P2VP_{62}$-*b*-PEO_{452}-*b*-P(GME_{36}-co-EGE_{36}) at room temperature (1 g/L, θ = 90°, titer 1M NaOH: stepwise addition of 2 µL with an equilibration time of 3 min).

Test tube inversion

The phase diagram (Figure S5) was constructed applying the test tube inversion method. The samples were heated stepwise (1 °C per step) using a MKR 13 thermomixer (HLC Biotech). After an equilibration time of 2 min per step, the test tubes were taken out of the mixing block, and tilted in order to check whether the samples flow or not. For the highest concentrations, the accuracy of the determined sol-gel transition temperatures is limited due to the already very high viscosity in the fluid state. At temperatures above ca. 70 °C, the samples show a slow phase separation (syneresis) with time (several hours). This is attributed to water getting a bad solvent for PEO at elevated temperatures, and is in accordance with observations on Pluronic^{TM} based hydrogels.

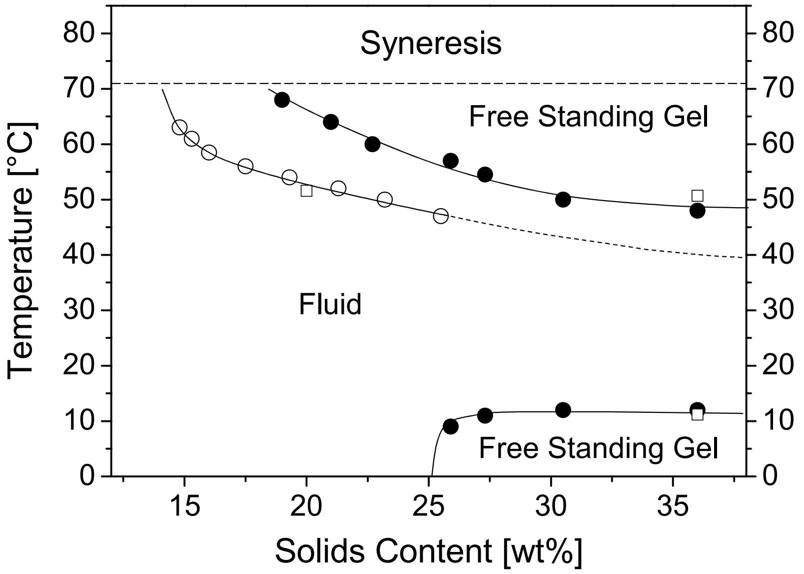

Figure S5. Phase diagram of γ-Fe_2O_3/TB1 (45/55 w/w, closed circles) and γ-Fe_2O_3/TB2 (30/70 w/w, open circles) mixtures, determined by the test tube inversion method. The open squares correspond to transition temperatures extracted from rheology (temperature at which G' = G'').

References

1. S. Reinicke, J. Schmelz, A. Lapp, M. Karg, T. Hellweg and H. Schmalz, *Soft Matter*, 2009, **5**, 2648 - 2657.