Supplementary Material (ESI) for *Soft Matter*

Electronic Supplementary Information

Thermoresponsive Colloidal Molecules

Martin Hoffmann,[a] Miriam Siebenbürger,[b] Ludger Harnau,[cd] Markus Hund,[e] Christoph Hanske,[e] Yan Lu,[b] Claudia S. Wagner,[a] Markus Drechsler,[f] and Matthias Ballauff*[b]

[a] *Physikalische Chemie I, Universität Bayreuth, Universitätsstraße 30, 95440 Bayreuth, Germany, Fax: +49(0)921 55 2780; Tel:+49(0)921 55 2217; E-mail: martin.hoffmann@uni-bayreuth.de*

[b] *F-I2 Soft Matter and Functional Materials, Helmholtz-Zentrum Berlin, Glienicker Str. 100, 14109 Berlin, Germany. Fax: +49(0)30 8062 2308; Tel:+49(0)30 8062 3071; E-mail: matthias.ballauff@helmholtz-berlin.de*

[c] *Max-Planck-Institut für Metallforschung, Heisenbergstr. 3, D-70569, Stuttgart, Germany,*

[d] *Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Pfaffenwaldring 57, D-70569 Stuttgart, Germany*

[e] *Physikalische Chemie II, Universität Bayreuth, Universitätsstraße 30, 95440 Bayreuth, Germany*

[f] *Macromolecular Chemistry II, University of Bayreuth, Universitätsstraße 30, 95440 Bayreuth, Germany*

ESI 1 MATERIALS

1.1 Synthesis of PMMA seed particles. Conventional emulsion polymerization was performed using methyl methacrylate as monomer (MMA; 96.52 g), potassimum peroxodisulfate as initiator ($K_2S_2O_8$; 0.375 g), sodium dodecylbenzenesulfonate (SDBS; 1.499 g) as surfactant and Millipore water as solvent (370.02 g) according to **Ref. 1**. Ultrafiltration of the diluted suspension (9.126 wt %) was carried out until the conductivity of the eluent was below 4 μS cm^{-1}.

1.2 Seeded growth polymerization with styrene (core particles) proceeded as described in **Ref. 1** using 78.01 g of the PMMA seed latex (7.12 g solid), styrene (12.258 g), $K_2S_2O_8$ (0.239 g in 14 g water) and additional Milliporewater (132.14 g). Monomer and initiator were added under starved conditions (33 μL min^{-1}) at 60 °C and stirring at 300 rpm. A uniform particle fraction was obtained with an ultracentrifuge (Allegra 64R, Beckman Coulter; rotor F0650) by repeated centrifugation and redispersion of the diluted suspensions (ca. 4 wt %). First, the very little amount of coagulum formed (larger particles) was removed from the supernatant in runs of 60 min at 4500 rpm and 45 min at 5000 rpm. As the formation of new particles by secondary nucleation could not be fully suppressed, smaller polystyrene particles had to be removed in the supernatant at runs of 75 min at 12000 rpm and 65 min at 12000 rpm.

1.3 Polymerization of the crosslinked PNIPA shell. The seeded emulsion polymerization was carried out following the lines in **Ref. 2.** The latex of the core particles (94.12 g; 4.781 wt %; 4.501 g solid content),

NIPA monomer (5.035 g; recrystallized from hexane) and *N,N'*-methylenebisacrylamide (BIS) as a crosslinker (0.327 g) were dissolved together with 12.63 g water in a 250 mL three neck flask equipped with a reflux condenser under nitrogen and stirring at 300 rpm at 23 °C for 180 min. After raising the temperature to 80 °C, $K_2S_2O_8$ (0,056 g dissolved in 1.7 g water) was added. The reaction mixture was slowly cooled down to room temperature after 360 min and filtered over glass wool to remove coagulum. The conductivity of the eluent was below 2.4 μS cm^{-1} after ultrafiltration of the latex (ca.4 wt %).

ESI 2 METHODS

2.1 Dynamic light scattering experiments (DLS/DDLS) were done with an ALV/DLS/SLS-5000 compact goniometer system (Peters) equipped with a He-Ne laser (632.8 nm). The concentration was 0.003 wt % for the core and 0.002 wt % for the core-shell particles in 5 mM KCl. The samples were filtered through 1 μm nylon filters in dust free quartz glass cuvettes and tempered 120 min to assure conformational equilibrium of the PNIPA network. The cuvettes were immersed in an index matching *cis*-decaline bath. For DDLS (DLS) we measured three runs between 5 and 10 min (1 min) for scattering angles between 20° and 42.5° (90°) with angular steps of 2.5° (15°), respectively. The scattered light passed through a Glan Thompson polarizer with an extinction ratio better than 10^{-5}. The relaxation frequencies were obtained by CONTIN-analysis of the intensity autocorrelation functions.

2.2 Cryogenic-Transmission Electron Microscopy (cryo-TEM) specimens were prepared by vitrification of thin liquid films (0.2 wt % in Millipore water) supported on a TEM copper grid (Agar G 600HH Cu, Polyscience) in liquid ethane at its freezing point. Examinations were carried out at a Zeiss EM 922Omega EFTEM (Zeiss NTS GmbH, Oberkochen, Germany) at a temperature around 90 K operating at 200 kV. The image was recorded digitally by a bottom-mounted CCD camera system (UltraScan 1000, Gatan) and processed with a digital imaging processing system (Digital Micrograph 3.10 for GMS 1.5, Gatan).

2.3 Field Emission Scanning Electron Microscopy (FESEM) was done with a LEO 1530 Gemini microscope equipped with a field emission cathode (acceleration voltage 2000 V). The diluted samples (ca. 0.003 wt %) were dried on a Si-wafer in air and sputtered with Pt (Cressington Sputter Coater 208 HR).

2.4 Scanning Force Microscopy (SFM) measurements were performed with the same samples on glass slides cleaned with the RCA method (see **Ref. 3**) with a NanoScope Dimension 3100 equipped with a Nanoscope 5 controller and a XYZ hybrid closed-loop scanner. Height and phase images were obtained under ambient conditions (23 °C) by imaging the particles in Tapping™ mode at a frequency of 0.3 Hz (512 samples per line) using an Olympus microcantilever (OMCL-AC160TS).

2.5 Electrophoretic mobilities (μ) of the particles were measured on a Malvern Zeta-Sizer Nano ZS and converted into the ζ-potential *via* the Smoluchowski equation ($\zeta = \mu\eta\varepsilon_0^{-1}\varepsilon^{-1}$), where η denotes the viscosity and $\varepsilon_0^{-1}\varepsilon^{-1}$ the relative permittivity of the solution.

ESI 3 DLS / DDLS ANALYSIS

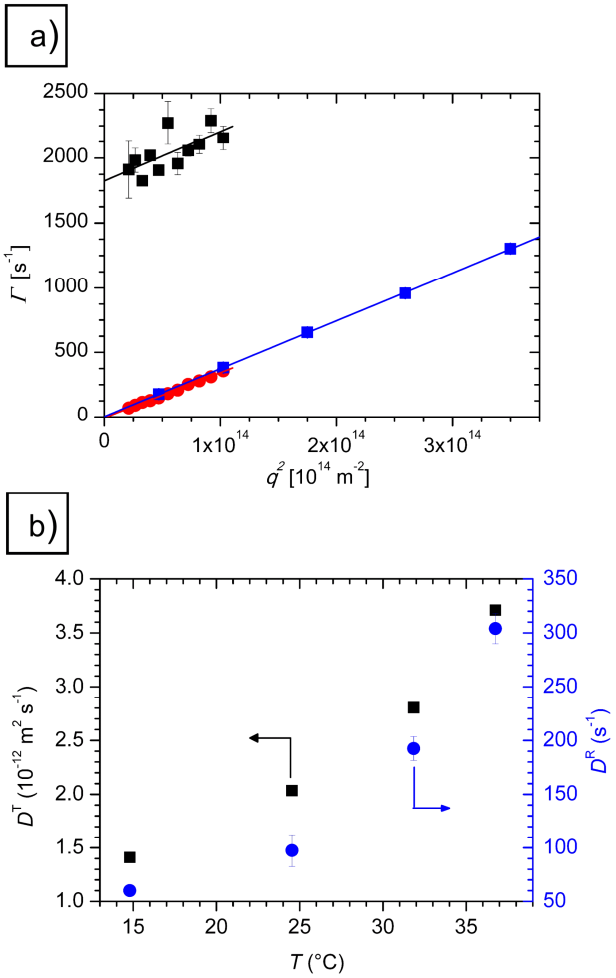

Fig. ESI 1 a) Relaxation rates as a function of the square of the scattering vector q^2 for the DMP particles (0.002 wt % in 5 mM NaCl at 36.8 °C). Both the rotational relaxation together with the q-dependent translational term (fast mode) and the pure translational term (slow mode) were detected in the DLS and the DDLS experiment. DDLS fast mode: black squares, DDLS slow mode: red circles, and DLS slow mode: blue squares. b) Translational (D^T; black squares, left ordinate) and rotational diffusion coefficients (D^R; blue circles) for the DMP core-shell particles (0.002 wt % in 5 mM KCl) at different temperatures as obtained from the DLS/DDLS measurements.

References

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