## Core-shell colloidal particles with dynamically tunable scattering properties

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## **Experimental Section**

*Core/Shell Particle Synthesis*: We synthesized the fluoresent polystyrene (PS) seeds by miniemulsion polymerization.<sup>[1-2]</sup> 100 mg of sodium dodecyl sulfate (SDS, 99%, J.T. Baker) were dissolved in 50 mL of deionized (DI) water (Milli-Q grade, Millipore). Then a mixture of 0.4 g of hexadecane (Fluka), 5 g of styrene monomer (99%, Alfa Aesar), and 0.1 mg of fluorescent dye (Nile Red, 99%, Aldrich) was introduced under vigorous stirring. This solution was placed in an ultrasound bath for 10 minutes to create a mini-emulsion. The mixture was purged under nitrogen for 30 minutes and heated to 70°C. The polymerization was initiated by adding 50 mg of potassium persulfate (KPS, 99%, Acros). After 3 hours, the resulting PS latexes were dialyzed against DI water for one week to remove the remaining reactants. The diameter of the PS particles, as measured by dynamic light scattering, was 85 nm. By adding 75 mg of SDS instead of 100 mg we were able to synthesize 175 nm particles.

We synthesized the core-shell particles using seeded precipitation polymerization. 1.29 g of N'-Isopropylacrylamide (NIPAM, monomer, 99%, Acros), 6.5 mg of N,N'-Methylenebisacrylamide (crosslinker, 0.5% w/w to NIPAM monomer, Promega), 50 mg of acrylic acid (AAc, 4% w/w to NIPAM monomer, 99%, Sigma) and PS seed particles (number of seed particles  $N = 7 \times 10^{13}$ ) were mixed in 50 mL of water. The mixture was purged under nitrogen for 30 minutes, and then the polymerization was initiated by adding 50 mg of KPS at 70°C. The reaction time was 4 hours. The yield of the reaction and the optical properties of the resulting core-shell particles were optimized by controlling the size and the concentration of polystyrene seeds, the amount of crosslinker, and acrylic acid.<sup>[Erreur ! Signet non défini.]</sup>

*Static and Dynamic Light Scattering:* We used an ALV DLS/SLS-5000 (ALV-Laser GmbH, Langen, Germany) light scattering instrument to measure the angular scattering properties of the particles.<sup>[3]</sup> The apparatus consists of a diode-pumped solid-state laser source (wavelength  $\lambda = 532$  nm, with incident intensity  $I_i$ ), beam splitter optics, attenuator, temperature controlled

sample vat, and fiber-based detection optics. The scattered light intensity  $I_{SC}$  from a dilute colloidal solution was measured by a photomultiplier tube at an angle  $\theta$ , where  $30 \le \theta \le 150$ . The scattering intensity was calculated from the measured scattering ratio ( $I_{SC}/I_i$ ) and normalized by the number density of the colloidal particles  $\rho$  in the sample. By analyzing the correlation functions at fixed scattering angles, we determined the hydrodynamic diameter  $D_h$  of the colloidal particles in the solvent.

*Turbidimetry and Diffuse-Tranmission Spectroscopy*: To measure the turbidity<sup>[4]</sup> of the colloidal suspensions we used a miniature high-resolution fiber optic spectrometer (HR2000+, Ocean Optics Inc.) with a fiber coupled laser diode (FTEC0658-V60SFN, FiberTec, wavelength  $\lambda = 656$  nm). The cuvette holder (CUV-ALL-UV, Ocean Optics Inc.) was connected to a water circulator (HE-6, Julabo Labortechnik GmbH) to maintain a stable temperature during the measurement. Dilute colloidal samples were held in disposable polystyrene spectrometer cuvettes with fixed optical pathlength L = 10 mm (BRAND GMBH+CO KG). We measured the turbidity  $= -\frac{1}{L} ln \frac{I_t}{I_i}$ , where  $I_t$  is the transmitted light intensity and  $I_i$  the incident light intensity, of dilute colloidal suspensions at a given temperature and for varying number densities  $\rho$ . Then we fit the data to the Beer-Lambert law to determine the scattering cross-section: $\sigma_{sc} = \frac{\tau}{\rho}$ .

We calculated the scattering mean free path  $l_{sc}$  of opaque colloidal samples from the number density and the measured scattering cross-sections, as  $l_{sc} = (\rho\sigma_{sc})^{-1}$ . We measured the transport mean free path  $l_{tr}$  of opaque colloidal samples with diffuse-transmission spectroscopy,<sup>[16]</sup> using the same spectrometer but placing a cosine corrector (CC-3-UV, Ocean Optics Inc.) in front of the detection fiber. We measured the transmission coefficient of the colloidal suspensions in glass cuvettes (VitroCom Inc.) with different optical pathlengths, L = 3, 4, 6 and 10 mm. We also conducted the same transmission measurements on a reference sample (1% v/w, 1.0 µm sulfate polystyrene suspension, Invitrogen Corp.). For this sample we calculated a transport mean free path of  $l_{tr} = 3.54 \times 10^{-4}$  m. Then we fit the transmission data to Ohm's law to calculate the transport mean free path, using the transport mean free path of the reference sample as a calibration,  $l_{tr} = \propto T \cdot L$ . The anisotropy parameter g for the opaque colloidal suspension was determined from the scattering mean free path  $l_{sc}$  and the transport mean free path  $l_{tr}$  as  $g = 1 - \frac{l_{sc}}{l_{tr}}$ .

<sup>[1]</sup> K. Landfester, *Macromolecular Rapid Communications* 2001, 22, 896.

<sup>[2]</sup> S. Lelu, C. Novat, C. Graillat, A. Guyot, E. Bourgeat-Lami, Polymer International 2003, 52, 542.

<sup>[3]</sup> W. Brown, Dynamic light scattering: the method and some applications, Vol. 49, Clarendon Press Oxford 1993.

<sup>[4]</sup> J. D. Ingle, S. R. Crouch, Spectrochemical analysis, Prentice Hall Englewood Cliffs, N. J. 1988.