Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information for

Strong Anionic Polyelectrolyte Microgels

by Rahul Tiwari, Andreas Walther*

DWI – Leibniz-Institute for Interactive Materials, Forckenbeckstr. 50, 52074 Aachen, Germany

Experimental Section

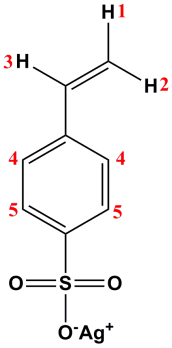
Materials

Ultrapure MilliQ water with a resistivity of 18.2 MΩ/cm was used for all experiments. Sodium 4-styrenesulfonate sodium salt (≥ 90%), bromoethane (≥ 99%), silver nitrate (99%), iodotrimethylsilane (≥ 97%), were used as received from Sigma Aldrich without any further purification. Divinyl benzene (55%) was obtained from Sigma-Aldrich and used after passing through a column of basic alumina to remove the inhibitor. The initiator potassium peroxodisulfate (KPS > 99%, Fluka), surfactant sodium dodecyl sulfate (SDS) from Bio-Rad (Electrophoresis purity reagent) were used without any purification.

Synthesis of 4-styrenesulfonic acid ethyl ester

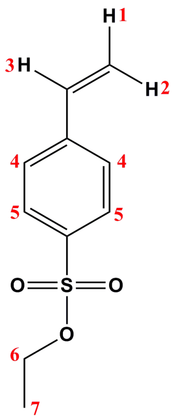
The two step synthesis procedure was adapted from the literature[1] as follow:

Synthesis of 4-styrenesulfonic acid silver salt: 0.05 mol 4-styrenebenzensulfonic acid sodium salt was dissolved in 100 mL distilled water at 4 °C. Under complete light exclusion, 0.05 mol $AgNO_3$ was added to the solution. After stirring for 30 min, the slightly grey product was filtered (suction filtration) and washed several times with ice water and diethyl ether. Then the product was dissolved in acetonitrile and filtered to remove insoluble impurities. Evaporation of the solvent under reduced pressure gave a white powder (50% yield), which was dried under vacuum at 50 °C. ^{1}H-NMR (400 MHz, CD_3CN-d3, δ, ppm): 5.27 (d; H^1), 5.85 (d; H^2), 6.73 (dd; H^3), 7.42 (d; H^4), 7.58 (d; H^5).



4-styrenesulfonic acid silver salt

Synthesis of 4-styrenesulfonic acid ethyl ester: 0.01 mol of 4-styrenesulfonic acid silver salt was dissolved in 25 mL acetonitrile, and subsequently, the double molar amount of bromoethane was added. The reaction was stirred for 5 h at 70 °C. After the reaction, AgBr was removed by filtration and the solvent was removed under reduced pressure. The residual product was extracted with dichloromethane and passed through a silica gel column. Afterwards, the solvent was removed under reduced pressure by rotatory evaporator, to give a slightly yellow and viscous liquid, which was finally dried under vacuum at room temperature. The product (79% yield) was stored at -18 °C. ^{1}H-NMR (400 MHz, CD_3CN-d3, δ, ppm): 1.22 (t; H^7), 4.08 (q; H^6) 5.27 (d; H^1), 5.85 (d; H^2), 6.73 (dd; H^3), 7.42 (d; H^4), 7.58 (d; H^5).



4-styrenesulfonic acid ethyl ester

Emulsion polymerization for the synthesis of cross-linked PSSE latex

The latex particles based on 4-styrenesulfonic acid ethyl ester (SSE) and divinyl benzene (DVB) as a crosslinker were synthesized by simple batch emulsion polymerization at 60 °C. A typical recipe is as follows: A 25 mL glass bottle was charged with 19 g water, SDS (0.5 mM) as surfactant, and a monomer mixture of SSE/DVB with a molar ratio of 25 at 1 wt%. Then the mixture was deoxygenated for 10 min by bubbling with nitrogen gas and placed in an oil bath with constant stirring at 500 rpm. After equilibration for 30 min at 60 °C, 1 mL of a stock solution of KPS initiator was injected into the reaction mixture to give a final KPS concentration of 2 mM. The contents of the bottle turned white within few minutes and the reaction was continued for 24 h. Samples for gravimetry were constantly withdrawn from the reaction mixture to monitor the conversion. The white dispersion was purified by centrifugation and redispersion in MilliQ water for several times to remove the unreacted monomer and excess of surfactant. The suspension was stored with 1 wt% solid content.

Deprotection of charged groups in $PSSE_X$ latex to form $PSSA_X$ microgels

$PSSA_X$ microgels were obtained by adding iodotrimethylsilane (0.33 mL, 1.177 mM) to a dispersion of freeze dried $PSSE_X$ latex (50 mg) in dimethyl sulfoxide (2.5 mg of latex in 1 mL of

DMSO) and the mixture was stirred at 50 °C for 15 h. After the reaction, the solution was treated with a mixture of MeOH/1N HCL (1/1) for 2 h and then neutralized to pH - 7 with aqueous NaOH (1 M). The solution was later dialyzed for 2 days against deionized water to remove excess salt.

Characterization

Dynamic light scattering: The particle size distributions were measured by laser light scattering instrument (ALV/DLS/SLS-5000) equipped with an ALV-5000/EPP multiple digital time correlator and laser goniometry system ALV/CGS-8F S/N 025 with a helium neon laser (Uniphase 1145P, output power of 22 mW and wavelength of 632.8 nm) as a light source, at a fixed scattering angle of 90°. Very dilute samples were used for sample preparation and filtered through 1.2 µm PET syringe filter.

Transmission electron microscopy and cryo-TEM: For morphological observation, zero-loss energy-filtered transmission electron microscopy (TEM) images were recorded with a LIBRA 120 operating at 120 kV using a bottom mounted CCD camera. For sample preparation, one drop of colloidal solution (0.1 wt.% solid content) was placed on a plasma-treated 300-mesh carbon-coated copper grid (EMS) and excess solution was soaked by dust-free tissue paper. No additional staining was applied. Particle diameters and distribution were determined from micrographs using “ImageJ” software with at least 100 particles being counted. Cryogenic TEM samples were prepared by rapid vitrification from aqueous dispersion (0.1 wt%) using plasma-treated lacey grids and a vitrobot system.

^{1}H NMR spectra were recorded on a Bruker AC400 FT NMR spectrometer operating at 400 MHz.

Zeta-potential measurements: Zeta potentials the microgels were measured using a NanoZS Zetasizer (Malvern), connected to a MPT-2 titrator and degasser. Titration process was performed from pH 3 to pH 10 using 0.1 M NaOH and 0.1 M HCl. Measurements were performed in disposable capillary cells (Malvern, DTS1060C) at 25 °C.

Fourier Transform Infrared Spectroscopy (FTIR): FTIR spectra of dried samples were recorded using Thermo Nicolet Nexus 470 spectrometer with a resolution of 4 cm^{-1}.

Table SI 1. Tuning the size as a function of the surfactant concentration at monomer/crosslinker = 25.[a]

Sample[b]	**c(SDS) [mM]**	**$\langle R\rangle_{n,TEM}$ ± STD (Đ_{TEM})[c] [nm]**	**$\langle R_h\rangle_{z,DLS}$ (Đ_{DLS}) [nm]**[d]
PSSE$_{25}$1	0.1	n.a.	92 (1.05)
PSSE$_{25}$2	0.5	62 ± 8 (1.09)	80 (1.02)
PSSE$_{25}$3	1.0	57 ± 7 (1.06)	74 (1.01)
PSSE$_{25}$4	2.0	45 ± 5 (1.06)	54 (1.01)

[a] Emulsion polymerization using c($K_2S_2O_8$) = 2 mM at 60 °C. [b] The subscript denotes the ratio of monomer/crosslinker. [c] Dispersity, Đ_{TEM}, is defined as R_w/R_n. n.a. = not acquired. [d] $\langle R_h\rangle_z$ from CONTIN analysis and dispersity, Đ_{DLS}, from 2nd Cumulant.

Table SI 2. Influence of the ratio of monomer/crosslinker on the particle size.[a]

Sample	**SSE/DVB**	**$\langle R\rangle_{n,TEM}$ ± STD ($Đ_{\text{TEM}}$)[b] [nm]**	**$\langle R_h\rangle_{z,DLS}$ ($Đ_{\text{DLS}}$) [nm]**[c]
PSSE$_{25}$	25	62 ± 8 (1.09)	80 (1.02)
PSSE$_{150}$	150	52 ± 6 (1.06)	74 (1.06)
PSSE$_{500}$	500	55 ± 8 (1.08)	79 (1.05)
PSSE$_{\infty}$	No DVB	57 ± 9 (1.07)	81 (1.02)

[a] Emulsion polymerization using the indicated ratios of monomer/crosslinker at constant surfactant concentration (c(SDS) = 0.5 mM) and c($K_2S_2O_8$) = 2 mM at 60 °C. [b] Dispersity, $Đ_{\text{TEM}}$ is defined as R_w/R_n. [c] $\langle R_h\rangle_z$ from CONTIN analysis and $Đ_{\text{DLS}}$ from 2nd Cumulant.

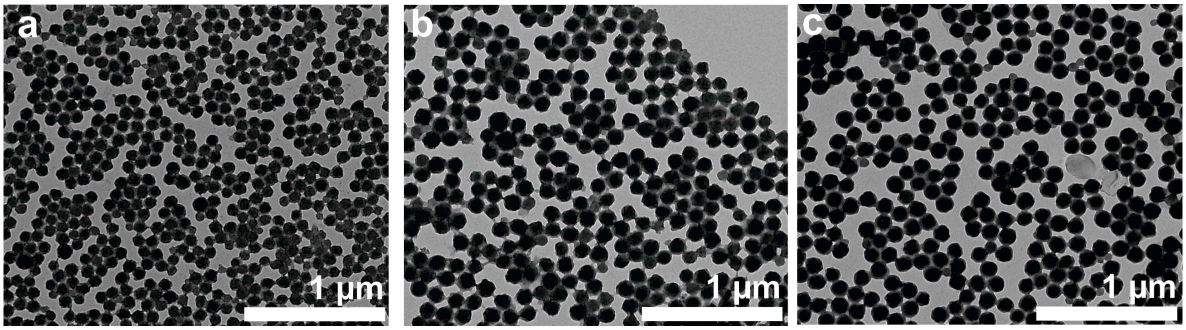


Figure SI 1. Characterization of PSSE$_x$ latex by transmission electron microscopy (TEM). (a) TEM images of PSSE$_{25}$4 obtained at c(SDS) = 2 mM, and TEM images of (b) PSSE$_{500}$ and (c) PSSE$_\infty$ obtained at c(SDS) = 0.5 mM, respectively.

1. G. Woeste, Dissertation, Universität Mainz, 1993.