Supporting Information

Preparation of Silica Nanoparticles: The preparation was conducted by addition reaction of aminopropyltriethoxysilane and glycidol, followed by acidic condensation of the addition product. To 44.55 g (120.6 mmol) of the adduct dissolved in 200 ml methanol was added 6.727 g of aqueous HF solution (3.225 %) under stirring. The reaction mixture was stirred for additional 2 h at ambient temperature. Then water, ethanol, and methanol were removed in vacuum and the nanoparticles were dried at 40 °C at 8 mbar. Yield: 3.514 g (100 % of th.), T_g = 32.2 °C, η (23 °C) = 12.4 MPa*s. FT-IR (NaCl plate): 3346 (OH), 2932, 2876 (CH), 1119, 1045 (Si-O) cm^{-1}. ^1H NMR (CD_3OD): δ (ppm) 0.3-0.8 (2H, br s, SiC*H*$_2$), 1.3-1.7 (2H, br s, SiCH$_2$C*H*$_2$), 2.2-3.0 (6H, br m, NC*H*$_2$), 3.3-4.0 (6H, br m, OC*H*$_2$, OC*H*). The atomic composition of the silica nanoparticles was: C, 43,75; H, 7.86; Si, 10.98; N, 4.76. The relative atomic composition of the organic part (C, 77.6 : H, 13.9 : N, 8.4) of the nanoparticles is in agreement with the value (C, 76.1 : H, 14.1 : N, 9.9) calculated from the structure. The silica nanoparticles form transparent colloidal solution in water, methanol, DMF, and DMSO, while insoluble in most organic solvents, such as dichloromethane, acetone, etc.

Linear poly(acrylic acid) (PAA) was obtained by atom transfer radical polymerization of *tert*-butyl acrylate with CuBr/N,N,N',N",N"-pentamethyldiethylenetriamine, followed by hydrolysis with an excess of trifluoroacetic acid. M_n = 7700 (DP = 107); M_w/M_n = 1.15 (calculated from the molecular weights of poly(*tert*-butyl acrylate), before hydrolysis).

Complex Formation: Linear PAA having low polydispersity and the silica nanoparticles were employed for the complex formation. A representative example is as follows: To 4 mL of an aqueous solution of the silica nanoparticles (60 mg), 4 mL of an aqueous solution of PAA (60

mg) was added at room temperature. The mixed solution became turbid immediately. The product was isolated via centrifugation (4000 rpm, 20 min, 20 °C), and dried in vacuo at room temperature overnight to a give glassy material (Yield = 68 %). The product was characterized by FT-IR, ^{1}H NMR in DMSO-d_6. Elemental analysis indicated that the complexes contain 44.25 % C, 6.55 % H, 5.54 % Si, 2.27 % N. The pH value of the solution was adjusted by adding the appropriate amount of an aqueous solution of NaOH or HCl. All experiments were conducted without adding salt.

Instrumentation. ^{1}H NMR spectra were recorded with a Bruker AC-250 spectrometer. FT-IR spectra were recorded on a Bruker Equinox 55 spectrometer. The elemental analyses were performed by Ilse Beetz Mikroanalytisches Laboratorium (Kulmbach). Potentiometric titration was conducted using a Schott CG840 pH meter equipped with a glass electrode. A 20 mL aqueous solution of the sample (1mg/mL) was titrated with a 0.01 M NaOH standard solution at room temperature, maintained nearly constant at 25 C°. The effective pK of each sample was estimated as the pH at 50% ionization from the titration curves of the PAA and the silica, respectively. The degree of ionization was calculated using Henderson-Hasselbach equation. The turbidity measurement was conducted using a Perkin-Elmer Lambda 15 UV/VIS spectrophotometer at 450 nm. Bright field transmission electron microscopy (TEM) was performed using a Zeiss electron microscope (CEM 902) operated at 80 kV. The samples for TEM observation were prepared by applying a drop of a diluted DMF solution (10 mg/L) on carbon-coated Cu grids and allowed to dry in air. Scanning force microscopy (SFM) height and phase images were taken on a Digital Instruments Dimension 3100 microscope operated in Tapping Mode (free amplitude of the cantilever ≈ 30 nm, set point ratio ≈ 0.98). The samples were prepared on polished silicon wafers by dip-coating or spin-coating from DMF and aqueous solutions.

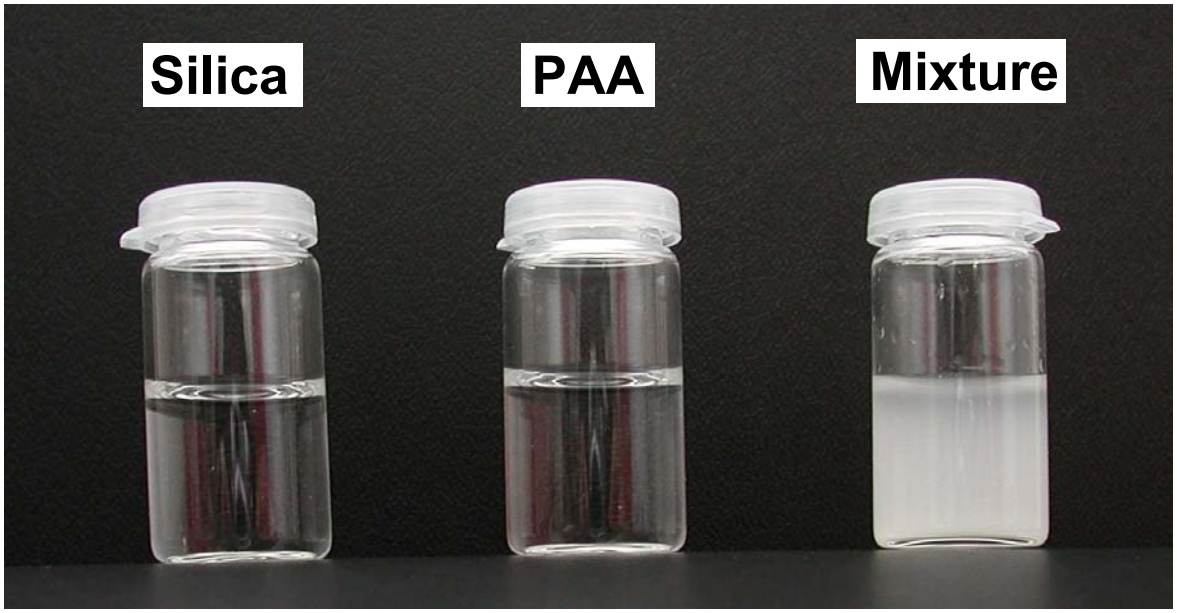

Figure. Photographic demonstration of the complex formation ([silica] = [PAA] = 7.5 mg/mL) by simple mixing the silica nanoparticle and poly(acrylic acid) (PAA) in water at room temperature.