Supplementary Information (SI) for Chemical Communications.

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Preparation of barium sulfate/polymer hybrid nanoparticles from Bunte salt precursors

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Experimental section

Materials

4-Vinylbenzyl chloride (VBC, 90%, Acros Organics), sodium thiosulfate pentahydrate ($Na_2S_2O_3 \cdot 5H_2O$, 99.5%, Merck), methyl methacrylate (99%, Merck), hexadecane (99%, Acros Organics), potassium persulfate (KPS, 99%, Carlo Erba), 1,1′-azobis(cyclohexanecarbonitrile) (ABCN, 98%, Sigma-Aldrich), Lutensol AT-50 (BASF), barium chloride (99%, Carlo Erba), ethanol (99.9%, Daejung), and hydrochloric acid (HCl, 37%, Carlo Erba) were used as received. Deionized water was used throughout all experiments.

Synthesis of vinyl benzyl thiosulfate

The synthesis was carried out following a previously reported method.[32] A solution of 4-vinyl benzyl chloride (1.01 g, 6.64 mol) in ethanol (0.5 mL) was added to a solution of sodium thiosulfate pentahydrate (1.23 g, 4.97 mol) in water (1.5 mL) and the mixture was stirred for 12 h at 27 °C. The resulting white precipitate was then filtered and washed with methanol. Afterward, the solvent was removed with a rotary evaporator and the product was dried under vacuum at 40 °C for 12 h to provide a white solid. ^{1}H-NMR spectroscopy (DMSO-d_6, 600 MHz) δ [ppm]: 4.07-4.10 (s, 2H), 5.20-5.25 (d, 1H), 5.77-5.83 (d, 1H), 6.66-6.75 (m, 1H), 7.29-7.41 (m, 4H). ^{13}C-NMR spectroscopy (600 MHz, DMSO-d_6): δ 138.9, 136.9, 136.0, 129.6, 126.5, 114.3, 38.54.

Synthesis of thiosulfate-functionalized nanoparticles

A mixture of methyl methacrylate (800 mg, 500 mg or 200 mg) and hexadecane (31.6 mg) was added into a continuous phase prepared by dissolving vinyl benzyl thiosulfate (200 mg, 500 mg or 800 mg), KPS or ABCN (22.6 mg) and Lutensol AT-50 (72.7 mg) in water (24.0 g). Both mixtures were stirred at 1000 rpm for 1 h to obtain emulsions, which were then ultrasonicated (Branson Digital Sonifier SFX 550) with a pulsed regime for 3 min (1 s on, 1 s off) at 40% amplitude while cooling in an ice–water bath to avoid polymerization due to heating. Copolymerization occurred at 80 ° C for 24 h in N_2 atmosphere with a stirring rate at 400 rpm. Afterward, the dispersion was filtered using centrifuge filter tube (centrifuge tube with modified PES membrane filter, 10 kDa, PALL) and dried nanoparticles were collected by freeze-drying the dispersion under vacuum for 24 h.

Preparation of $BaSO_4$/polymer nanoparticles

Dried thiosulfate-functionalized nanoparticles (20 mg) were dispersed in 20 mL of barium chloride aqueous solutions (9.28 mg/L, 23.2 mg/L and 46.4 mg/L). The mixtures were stirred at 27 ° C for 24 h with a stirring rate at 400 and then at 70 °C at 400 rpm for another 24 h. Then, 50 μL of an 1 M aqueous HCl solution was added to the different barium thiosulfate-functionalized nanoparticles dispersions at 70 °C while stirring at 400 rpm. After 48 h, 100 μL of an 1 M aqueous HCl solution was further added to the dispersions at 70 °C while stirring at 400 rpm. Finally, the dispersions were filtered using nylon syringe filter (diameter 13 mm, pore size 0.45 μm, FilterBio), followed by freeze-drying.

Analytical tools

^{1}H NMR spectra were recorded with a Bruker 600 MHz nuclear magnetic resonance spectrometer were obtained on an Avance III HD, Bruker at room temperature with DMSO-d_6. Hydrodynamic diameters and ζ potentials of nanoparticles were measured by dynamic light scattering (Zetasizer Lab, Malvern). Morphology of nanoparticles was observed by scanning electron microscopy (SEM, JEOL, JSM-7610F) operating at 1.0−2.0 kV on a gentle-beam mode. Samples for SEM were prepared by drop-casting diluted nanoparticles dispersions on silicon wafers that were sputtered with platinum at 10 mA for 10 s to increase surface conductivity before measurements. The morphology of nanoparticles was further investigated with a transmission electron microscope (TEM, JEOL, JEM-ARM200F) with an accelerating voltage of 200 kV. Samples for TEM were prepared by drop-casting diluted nanoparticle dispersions on copper grids, degassing with a dry pumping station, and cleaning with anion cleaner. X-ray powder diffraction was performed using a BRUKER (NEW D8 Advance) with a monochromatic Cu Kα radiation (λ = 1.54 A°) at 40 kV with a current of 40 mA. Before measurements, the dispersions were dried in an oven for 1 day. A scan of 2θ angle between 5° and 40° and a time step of 0.75 s per 2θ of 0.02° were set. The Ba content in samples was measured by inductively coupled plasma – optical emission spectrometry (ICP-OES, Agilent Technologies, 710 Series). Nanoparticles were digested in 2 mL of aqua regia and heated at 80° C for 1 h. A calibration curve in the range of barium concentration between 0 and 0.5 mg/L determined by ICP-OES was prepared with barium nitrate (ICP grade, Agilent). X-ray attenuation of $BaSO_4$/polymer hybrid nanoparticles was measured with a X-ray computed tomography (micro-CT, Bruker, Skyscan 1173) at 70 kV, 114 μA, 500 ms integration time for 326 slices and 1.0 mm Al filter. The measured linear attenuation coefficient was converted to Hounsfield units (HU) using an internal linear calibration against air (-1000 HU) and water (0 HU). $BaSO_4$/polymer nanoparticles were dispersed in water and placed in 0.01 mL Eppendorf tubes at a concentration of 0.01 g/mL.

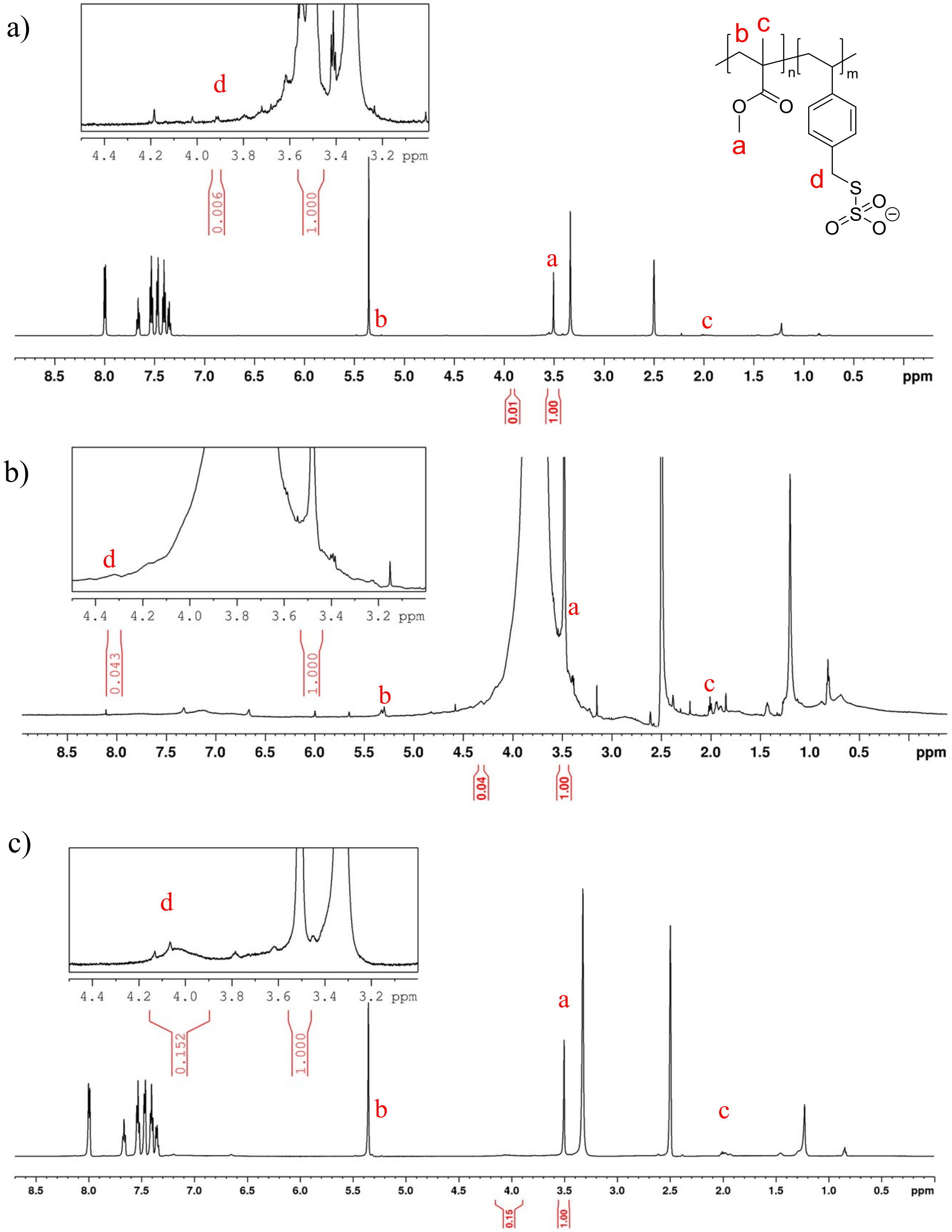

Fig. S1 ^{1}H NMR spectra of copolymer nanoparticles after freeze-drying and purification: a) VL134-9, P(MMA$_{0.99}$-*co*-VBT$_{0.01}$) b) VL131-1, P(MMA$_{0.96}$-*co*-VBT$_{0.04}$) c) VL134-6, P(MMA$_{0.87}$-*co*-VBT$_{0.13}$) in DMSO-d$_{6}$.

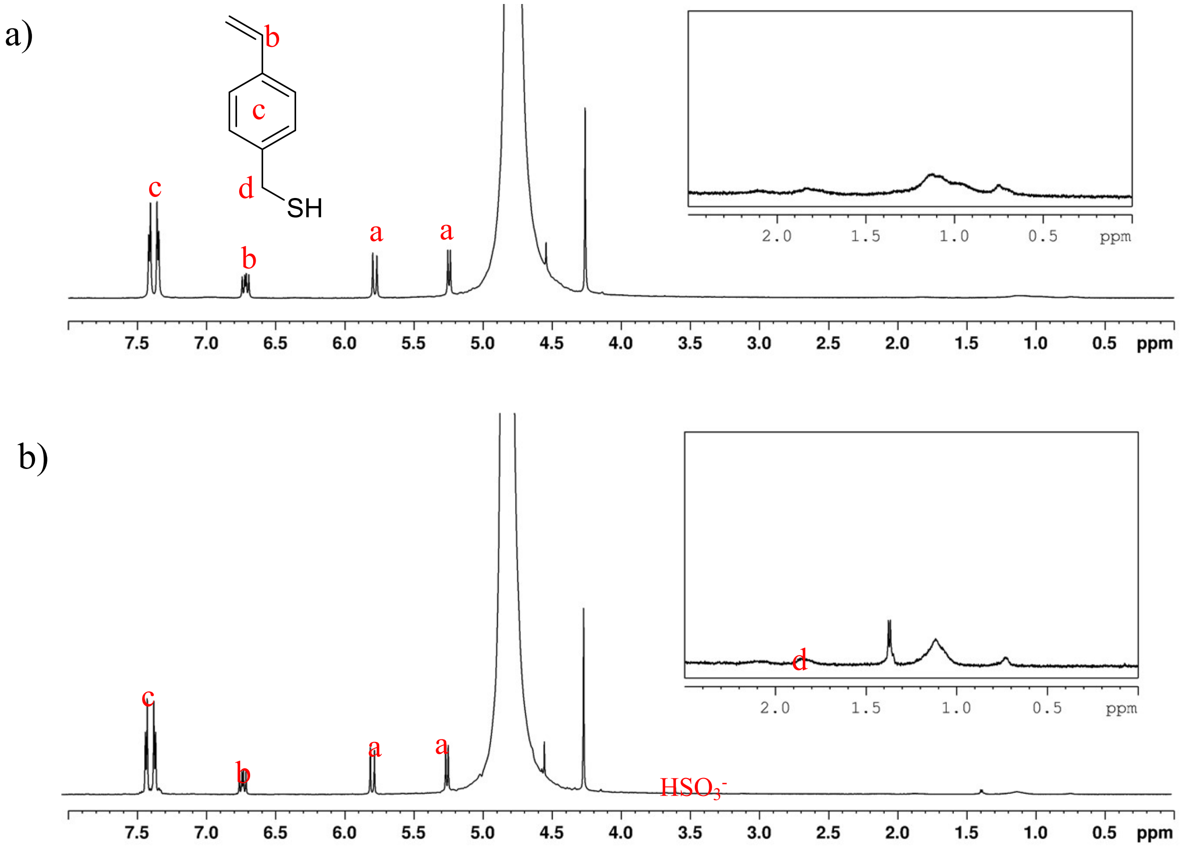

Fig. S2 ^{1}H NMR spectra of the vinyl benzyl thiosulfate a) before b) after hydrolysis in a DCl aqueous solution at 70 °C in D_2O.

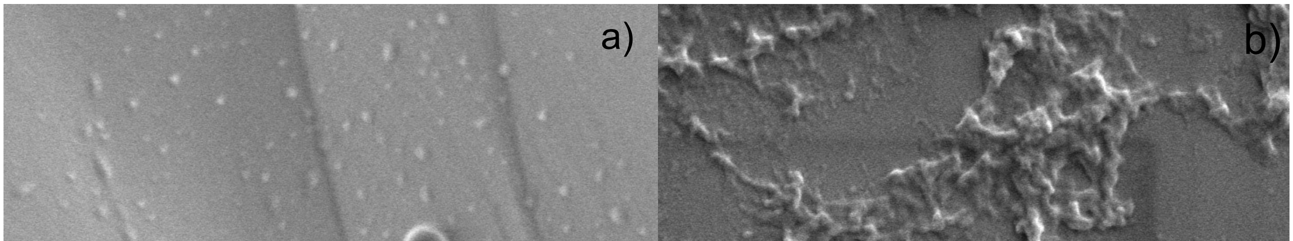

Fig. S3 SEM (a-b) micrographs of $BaSO_4$/polymer nanoparticles after purification (filtration) prepared with VBT units to $BaCl_2$ ratios of 1.0:0.2 (VL134-0.2Ba) and 1.0:1.0 (VL134-1.0Ba).

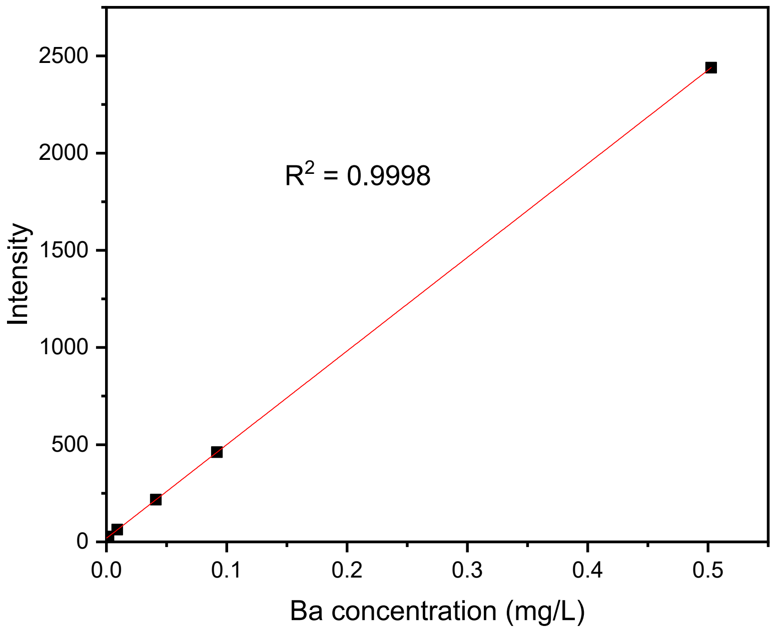

Fig. S4 Evolution of the intensity versus concentration of barium as calibration curve for inductively coupled plasma–optical emission spectrometry (ICP-OES).