Supporting Information

Surfactant-Free Synthesis of Sub-100 nm Poly(styrene-co-divinylbenzene)

Nanoparticles by One-Step Ultrasonic Assisted Emulsification/Polymerization

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Figure S1. Photograph of the reaction apparatus used in the present work for the construction of polymeric nanoparticles *via* an one-pot acoustic emulsification/polymerization method.



Figure S2. Photographs (left) and droplet size distribution (right; diameter, nm) of the emulsions produced over time upon acoustic treatment (20 kHz) of an aqueous solution (35 mL) of St/DVB (200 μ L) at different St/DVB ratio: (a) 95:5, (b) 70:30, (c) 50:50, (d) 30:70, and (e) 5:95.



Figure S3. Effect of the St/DVB relative ratio (95:5 \rightarrow 5:95, v/v) on the mean droplet diameter of acoustically emulsified aqueous solutions (35 mL) of St/DVB (200 µL) over 20 min.



Figure S4. SEM images (left) and particle size histograms (right) of P(St/DVB) NPs prepared *via* polymerization of acoustically emulsified aqueous solutions (35 mL) of St/DVB (1:1, v/v) over 60 min, at varying monomer loading: (a) 1.4×10^{-3} L/L, (b) 2.8×10^{-3} L/L, (c) 5.6×10^{-3} L/L, and (d) to 8.6×10^{-3} L/L. All samples were sputter-coated with a thin layer of gold (approx. 4 nm; for further details see § 2.3 in the main text) prior to SEM imaging. Non-sputtered samples were also imaged for the sake of comparison (see Figure S5).



Figure S5. SEM images of unsputtered P(St/DVB) NPs prepared *via* polymerization of acoustically emulsified aqueous solutions of St/DVB 1:1 (v/v) over 60 min, at varying monomer loading: (a) 1.4×10^{-3} L/L, (b) 2.8×10^{-3} L/L, (c) 5.6×10^{-3} L/L, and (d) to 8.6×10^{-3} L/L. For the corresponding sputter-coated samples (gold, 20 mA, 30sec) see Figure S4.

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Figure S6. SEM image of P(St/DVB) NPs prepared *via* acoustic emulsification of an aqueous solution of an 1:1 mixture of St/DVB (200 μ L; 5.7 × 10⁻³ L/L) in UPW (35 mL) for 10 min, followed by radical polymerization at 80 °C for 24 h, with heat provided by a heating plate and under magnetic stirring conditions. The sample was sputter-coated with a thin layer of gold (approx. 4 nm; for further details see § 2.3) prior to SEM imaging.



Figure S7. SEM images (left) and particle size histogram (right) of P(St/DVB) NPs synthesized at various concentrations of APS initiator: (a) 1.2 mM, (b) 2.9 mM, (c) 6.3 mM, and (d) 12.5 mM. Experimental conditions: St (100 μ L), DVB (100 μ L), UPW (35 mL), reaction time 60 min, and reaction temperature 80 °C. All samples were sputter-coated with a thin layer of gold (approx. 4 nm; for further details see § 2.3 in the main text) prior to SEM imaging.



Figure S8. SEM images and particle size histogram of P(St/DVB) NPs obtained after 20 min of reaction time. The sample was sputter-coated with a thin layer of gold (approx. 4 nm; for further details see § 2.3 in the main text) prior to SEM imaging.



Figure S9. FT-IR spectrum of PNPs prepared *via* polymerization of acoustically emulsified aqueous solutions (35 mL) of St/DVB (1:1, v/v; 200 μ L) in the presence of 2-sulfoethyl methacrylate.



Figure S10. FT-IR spectrum of PNPs prepared *via* polymerization of acoustically emulsified aqueous solutions (35 mL) of St/DVB (1:1, v/v; 200 μ L) in the absence of stabilizers.



Figure S11. SEM image (left) and particle size histogram (right) of P(St/DVB) NPs synthesized in the presence of 2-SEM, upon ultrasonic emulsification of St/DVB 1:1 (200 μ L; 5.7 × 10⁻³ L/L) for 10 min, followed by thermal treatment at 80 °C for 12 h. The sample was sputter-coated with a thin layer of gold (approx. 4 nm; for further details see § 2.3 in the main text) prior to SEM imaging. 2-SEM = 2-sulfoethyl methacrylate.