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Supporting Information

Colloidal Particles with Complex Microstructures via Phase Separation in Swelled Polymer Microspheres

Zhang Luo [a,b], Yitong Li [a,b], Bing Liu[a,b,*]

a) State Key Laboratory of Polymer Physics and Chemistry, CAS Research/Education Center for Excellence in Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, China

b) University of Chinese Academy of Sciences, Beijing, 100149, China

E-mail: liubing@iccas.ac.cn

EXPERIMENTAL SECTION

Materials. Styrene (St, 99%, Aladdin) was purified by passing through a column filled with basic alumina (Sinopharm Chemical Reagent Co., Ltd.) to remove inhibitors. Azobis(isobutyronitrile) (AIBN, Shanghai Mountain Pu Chemical Co., Ltd.) was purified by recrystallization with methanol. Sodium styrene sulfonate (NaSS, Sinopharm Chemical Reagent Co., Ltd.), 2-ethylhexyl methacrylate (EHMA, 98%, Sinopharm Chemical Reagent Co., Ltd.), Polyvinylpyrrolidone (PVP, K-30, Aladdin), Cetyltrimethyl Ammonium Bromide (CTAB, 98%, Sinopharm Chemical Reagent Co., Ltd.), Decane (99%, Aladdin), anhydrous ethanol (Beijing Chemical Works), anhydrous methanol (Beijing Chemical Works) were used directly without further purification. Millipore pure water with an electrical resistance of 18.2 MΩ·cm was used.

Poly(St-NaSS) Microspheres. Monodisperse poly(St-NaSS) microspheres were prepared by dispersion polymerization. In brief, 0.53 g of PVP and certain amount of NaSS were dissolved in the mixture of 36 g of anhydrous ethanol and 4 g of water. And then 7.3 g of St containing 0.14 g of AIBN was added. After being purged with nitrogen for 30 min, the system was heated to 70 °C and kept for 24 h. The mass ratio of was chosen to be 99.5/0.5, 99/1, 98/2, 97/3, 95/5 and 90/10, correspongding to mole ratio of 394, 196, 97, 64, 38 and 18, respectively. The obtained poly(St-NaSS) microspheres were named as PSN1 to PSN6 in turn.

Poly(St-NaSS) Colloidal Particles with Complex Structures. Monodisperse poly(St-NaSS) colloidal particles with complex structures were prepared via phase separation route in a seeded dispersion polymerization. In brief, 0.0625 g of poly(St-NaSS) microsphere, 0.125 g of EHMA, 6 mg of AIBN, 0.05 g of PVP were mixed with 10 g of mixed methanol and water (8:2) and deoxygened with nitrogen flow. And then 0.469 g of decane was added. The reactive system was sealed and then heated to 60 °C for 24 h. Afterwards, poly(St-NaSS) particles were washed with butanol and ethanol in turn for three times. The obtained poly(St-NaSS) particles were named as PStNaSS1 to PStNaSS6 in turn.

Characterization.

Scanning Electron Microscopy imaging was performed in a Hitachi s-4800 scanning electron microscope at an operating votage of 15 kv. Before measurement, the samples were sputtered with a thin platinum layer around 10 nm by a JFC-1600 auto fine coater at a current of 20 mA for 2 min.

Transmission Electron Microscopy imaging was perfomed by employing a Hitachi JEM-2200FS transmission electron microscope at an accelerating voltage of 200 kV. The sample was firstly dispersed into a solvent and then droped onto carbon-coated copper grid for measurements.

Focused Ion Beam-Scanning Electron Microscopy (FIB-SEM). A carbon layer (25 × 25 × 1 μm3) was then deposited on the top of the sample by in situ ion beam-induced deposition (IBID) to protect the surface during slicing in order to achieve sharp upper edges and minimize curtaining artifacts. The FIB system (type Nanolab G3 CX) consisted of a dual beam unit equipped with an electron column and an ion column. The ion column operated at accelerating voltages of up to 30 kV, gallium was used as the liquid metal ion source to produce cross-sections of the particles. SEM imaging conditions were kept

low to prevent potential damage of the layer by the beam, typical imaging conditions were 2 kV and 0.21 pA.

Gel Permeation Chromatography (GPC) (HLC-8320GPC) fitted with a refractive index detector was used for the characterization of weight-average molecular weight (M_w) and molecular weight distribution (M_w/M_n) of poly(St-NaSS) microspheres. The measurement was carlibrated by polystyrene and performed in tetrahydrofuran at 25 °C.

X-ray photoelectron spectroscopy (XPS) was performed on the Thermo Scientific ESCALab 250Xi using 200 W monochromatic Al Kα radiation. The 500 μm X-ray spot was used for SAXPS analysis. The base pressure in the analysis chamber was about 3×10^{-9} mbar. Typically the hydrocarbon C1s line at 284.8 eV from adventitious carbon is used for energy referencing.

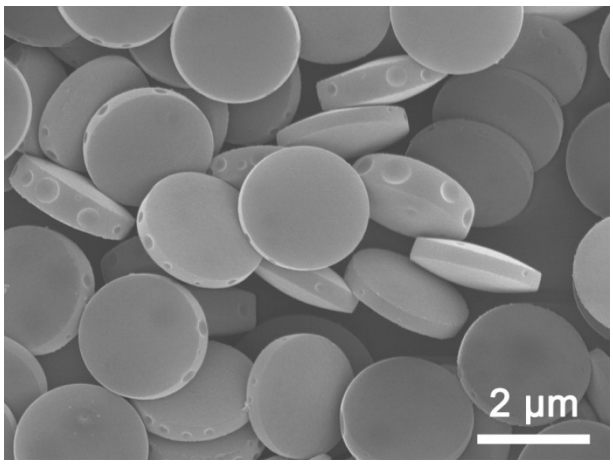

Figure S1. Disc-like particles prepared from PS microspheres without NaSS.

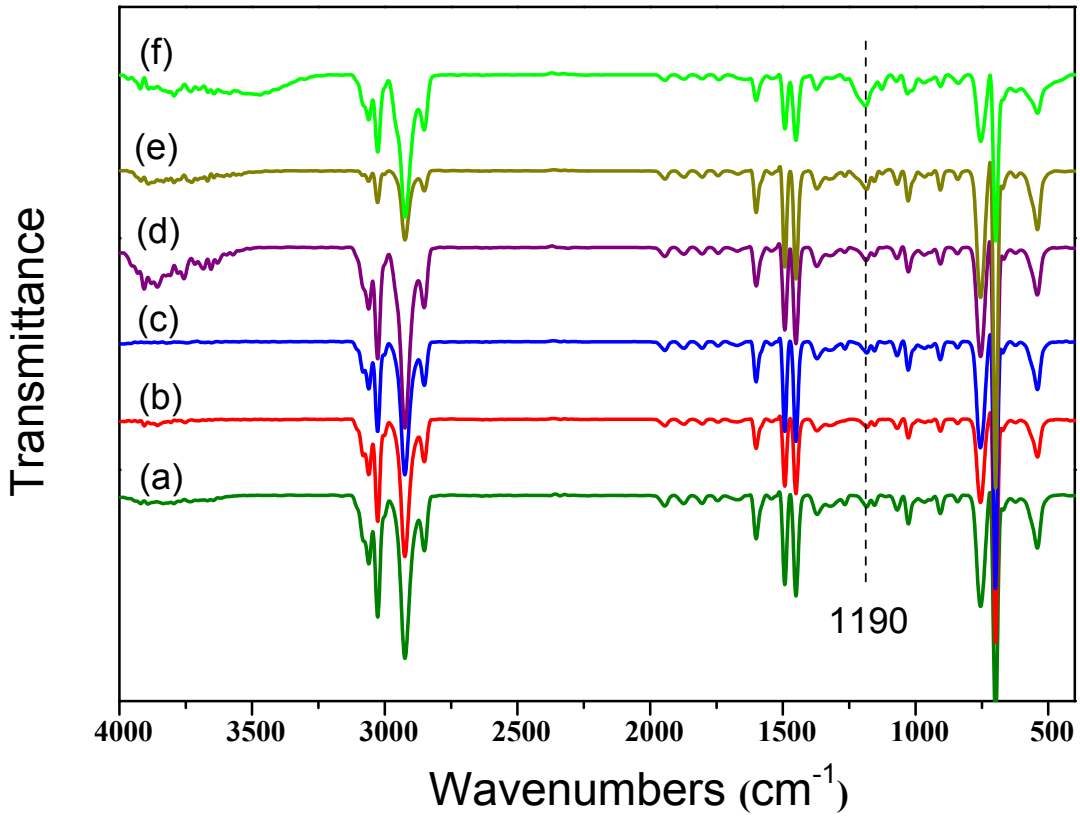

Figure S2. FT-IR spectra of poly(St-NaSS) microspheres. The characteristic peaks at 1190 cm^{-1} corresponding to $-SO_3^-$ group indicate the inconporation of NaSS. (a) PSN1; (b) PSN2; (c) PSN3; (d) PSN4; (e) PSN5; (f) PSN6.

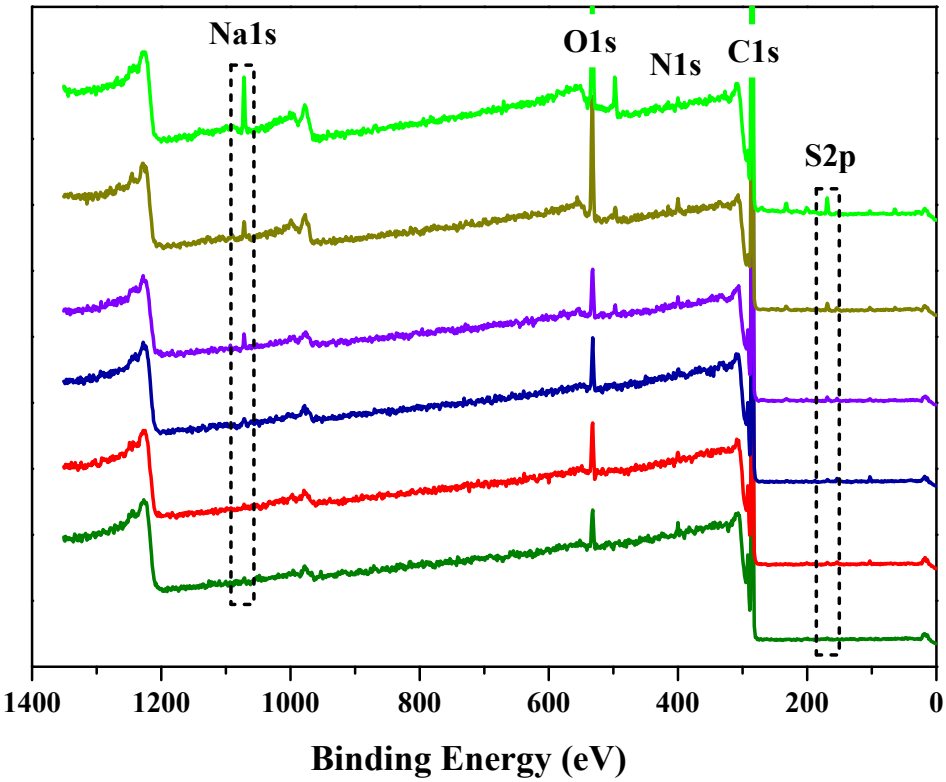

Figure S3. XPS spectra of poly(St-NaSS) microspheres. The curves are PSN1 to PSN6 in turn from the bottom to the top.

Table S1. Elemental analysis data of poly(St-NaSS) microspheres

No.	Feeding Ratio (St/NaSS, w/w)	C1s (%)	O1s (%)	N1s (%)	S2p (%)	Na1s (%)
PSN1	99.5/0.5	96.67	2.02	0.82	0.09	0.1
PSN2	99/1	96.21	2.85	0.7	0.14	0.1
PSN3	98/2	96.44	2.35	0.86	0.18	0.17
PSN4	97/3	95.53	3.06	0.74	0.3	0.37
PSN5	95/5	89.99	7.88	1.18	0.48	0.47
PSN6	90/10	89.78	7.66	0.46	0.93	1.17

Table S2. Molecular weight of poly(St-NaSS) microspheres

No.	Feeding Ratio (St/NaSS, w/w)	M_n	M_w	Polydispersity (=M_w/M_n)
PSN1	99.5/0.5	41656	149997	3.60
PSN2	99/1	39106	135904	3.48
PSN3	98/2	31264	98596	3.15
PSN4	97/3	32903	120051	3.65
PSN5	95/5	40452	183874	4.55
PSN6	90/10	-	-	-

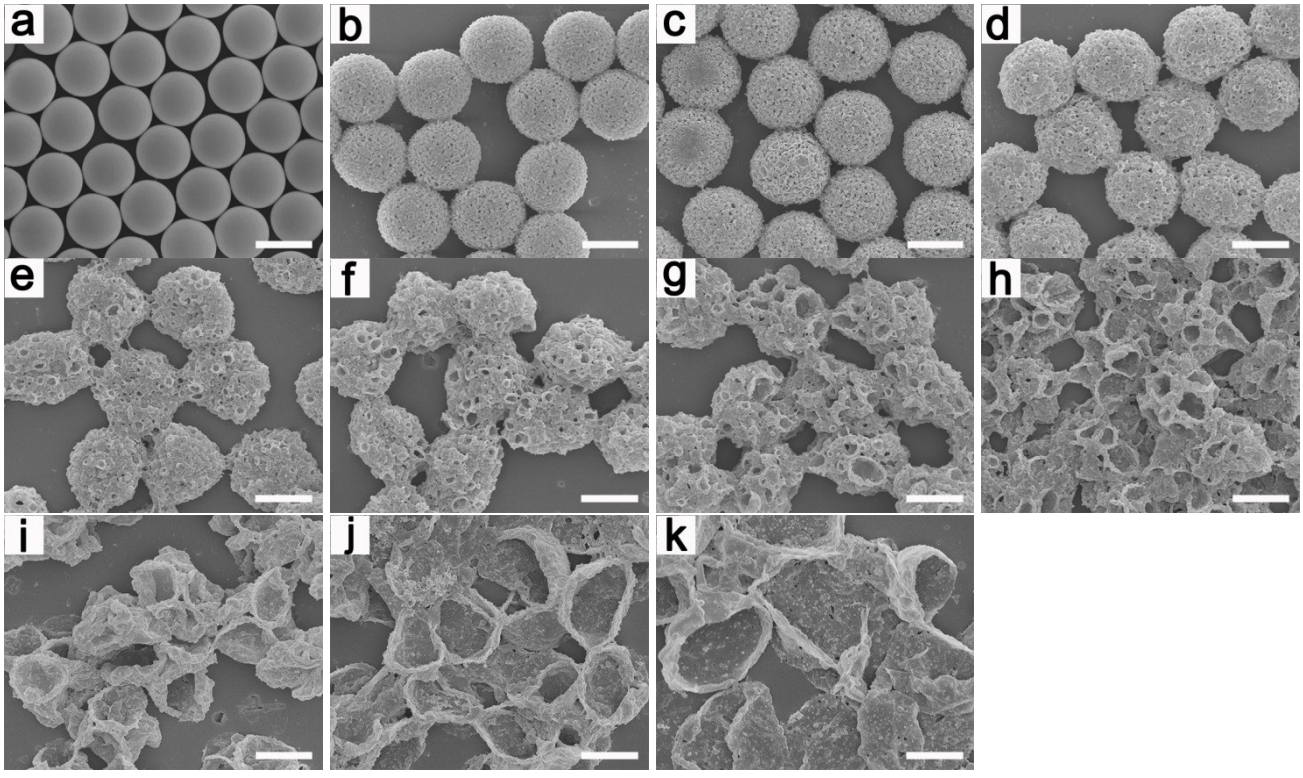

Figure S4. The morphology evolution of poly(St-NaSS) microspheres PSN6 with the time. (a) 0 h; (b) 0.5 h; (c) 1.0 h; (d) 2.0 h; (e) 3.0 h; (f) 4.0 h; (g) 5.0 h; (h) 6.0 h; (i) 9.0 h; (j) 12.0 h; (K) 24.0 h.