-Supporting Information-

Synthesis and in-depth characterization of reactive, uniform, crosslinked microparticles based on free radical copolymerization of 4-vinylbenzyl azide

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Influence of Toluene Addition on Porosity

In order to investigate the influence of toluene porogen on the specific surface area, pore volume, and particle stability, a series of particles with varying volume fractions of toluene in the monomer mixture was prepared. As presented in Table S1, the specific surface area and pore volume increase dramatically at constant particle diameters and uniformity, apparent in the calculated coefficient of variation. Mechanical stability of the microspheres is lowered with increasing amount of toluene in the monomer feed, leading to broken particles, shown in Figure S1c and d.



Figure S1. SEM images of microspheres with 100% DVB and 0% toluene (top images); 150% Toluene (middle images); and 400% toluene (bottom images).

Entry	Code	Seed		Feed		porogen	SEM analysis			
			DVB	VBA	S	Toluene	$d_{ m n}^{ m b}$	CV^{c}	\mathbf{S}^{d}	Ve
			[wt%]	[wt%]	[wt%]	[wt%] ^a	[µm]	[%]	$[m^2/g]$	$[cm^3/g]$
1	HT0	А	100	0	0	0	9.1	8.2	170	0.05
2	HA0	А	100	0	0	67	10.6	9.6	341	0.230
3	HT1	А	100	0	0	150	8.9	7.6	721	1.091
4	HT2	А	100	0	0	250	9.7	6.2	687	0.989
5	HT3	А	100	0	0	400	12.2	7.6	747	1.142
	1 2 3 4 5	I HT0 2 HA0 3 HT1 4 HT2 5 HT3	IHT0A1HA0A3HT1A4HT2A5HT3A	Entry Code Seed DVB [wt%] 1 HT0 A 100 2 HA0 A 100 3 HT1 A 100 4 HT2 A 100 5 HT3 A 100	Entry Code Seed Feed DVB VBA [wt%] [wt%] 1 HT0 A 100 0 2 HA0 A 100 0 3 HT1 A 100 0 4 HT2 A 100 0 5 HT3 A 100 0	Entry Code Seed Feed DVB VBA S [wt%] [wt%] [wt%] 1 HT0 A 100 0 2 HA0 A 100 0 0 3 HT1 A 100 0 0 4 HT2 A 100 0 0 5 HT3 A 100 0 0	Entry Code Seed Feed porogen DVB VBA S Toluene $[wt\%]$ $[wt\%]$ $[wt\%]$ $[wt\%]$ $[wt\%]^a$ 1 HT0 A 100 0 0 0 2 HA0 A 100 0 0 67 3 HT1 A 100 0 0 150 4 HT2 A 100 0 0 250 5 HT3 A 100 0 0 400	Entry Code Seed Feed porogen SEM analysis DVB VBA S Toluene d_n^b $[wt\%]$ $[wt\%]$ $[wt\%]$ $[wt\%]^a$ $[\mu m]$ 1 HT0 A 100 0 0 9.1 2 HA0 A 100 0 67 10.6 3 HT1 A 100 0 250 9.7 4 HT2 A 100 0 400 12.2	EntryCodeSeedFeedporogenSEM analysis DVB VBA SToluene d_n^b CV^c $[wt\%]$ $[wt\%]$ $[wt\%]$ $[wt\%]^a$ $[\mum]$ $[\%]$ 1HT0A1000009.12HA0A100006710.63HT1A100001508.94HT2A100002509.75HT3A1000040012.27.6	EntryCodeSeedFeedporogenSEM analysis DVB VBA SToluene d_n^b CV^c Sd $[wt\%]$ $[wt\%]$ $[wt\%]$ $[wt\%]^a$ $[\mum]$ $[\%]$ $[m^2/g]$ 1HT0A1000009.18.21702HA0A100006710.69.63413HT1A100001508.97.67214HT2A1000040012.27.6747

Table S1. Synthesis of Microspheres: Overview of Porogen Feed Ratio, Diameter, and Specific Surface Area

^a amount of toluene relative to 6 g (=100 wt%) monomer mixture ; ^b number-average particle diameter from SEM; ^c coefficient of variation of the particle diameter; ^d specific surface area; ^e cumulative pore volume

Inside Structure of Particles.



HA1 (DVB:VBA:S = 97.5:2.5:0)



MA3 (DVB:VBA:S = 50:7.5:42.5)



HA2 (DVB:VBA:S = 95:5:0)



LA2 (DVB:VBA:S = 16:5:79)



HA4 (DVB:VBA:S = 85:15:0)

Figure S2. SEM images of particles presumably broken during sample preparation and assumed to provide representative evidence of the inside structures at different comonomer feed ratios.

SEM Analysis of Particles Prepared from lower MW Seeds (B)



Figure S3. SEM images of microparticle sample HB1 (left, DVB:VBA:S = 95:5:0) and HB2 (right, DVB:VBA:S = 80:20:0) showing spherical, porous particles

Seed-Swelling Polymerizations Using Cationic or Neutral Stabilizers



Figure S4. SEM images of microparticles prepared from DVB:VBA:S = 95:5:0 (left) and 80:20:0 (right) using the cationic stabiliser **DTAB**. Qualitatively, the samples are similar to microparticles HA2 and HA5 prepared from the same comonomer ratio using sodium dodecylsulfate.



Figure S5. SEM images of microparticles prepared from DVB:VBA:S = 95:5:0 (left) and 80:20:0 (right) using the neutral stabiliser **NPOE**. Qualitatively, the samples are similar to microparticles HA2 and HA5 prepared from the same comonomer ratio using sodium dodecylsulfate and the above DTAB-stabilised particles, though the right image suggests an apparently lower amount of secondary particles.

Stabiliser	DVB:VBA:S feed ratio	Code Main Text	N ₁ /N ₀	
SDS	95:5:0	HA2	0.64	
NPOE	95:5:0	-	0.38	
DTAB	95:5:0	-	0.43	
SDS	80:20:0	HA5	0.47	
NPOE	80:20:0	-	0.57	
DTAB	80:20:0	-	0.34	

Table S2. Overview of N_1/N_0 values for different stabilisers