Supporting Information

Monodipserse Nanostructured Spheres of Block Copolymers and Nanoparticles via Cross-Flow Membrane Emulsification

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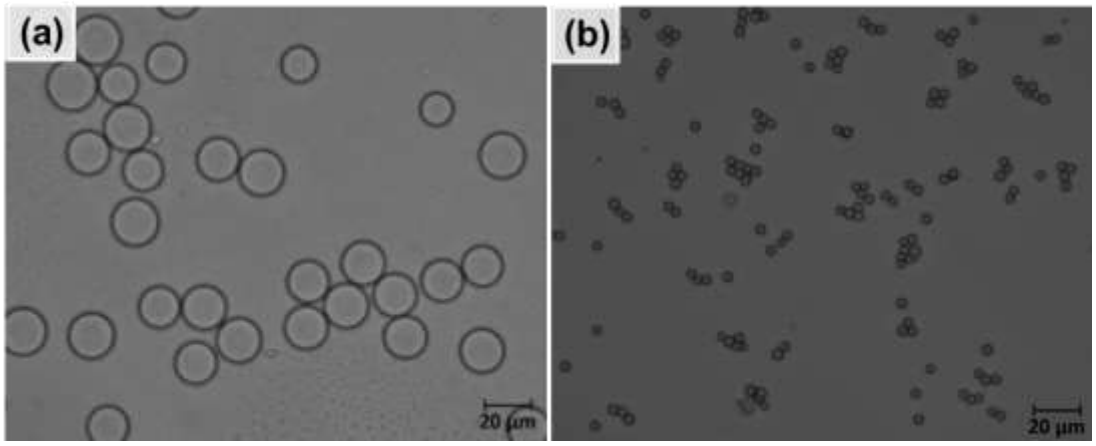


Figure S1. Optical microscope images of (a) emulsion droplets before solvent evaporation and (b) BCP particles after solvent evaporation. The emulsion droplets were produced using 5.1 µm membrane. The average diameters were measured to be (a) 18.365 ± 1.779 µm and (b) 4.086 ± 0.322 µm. The concentration of SDS was 0.5 wt%.

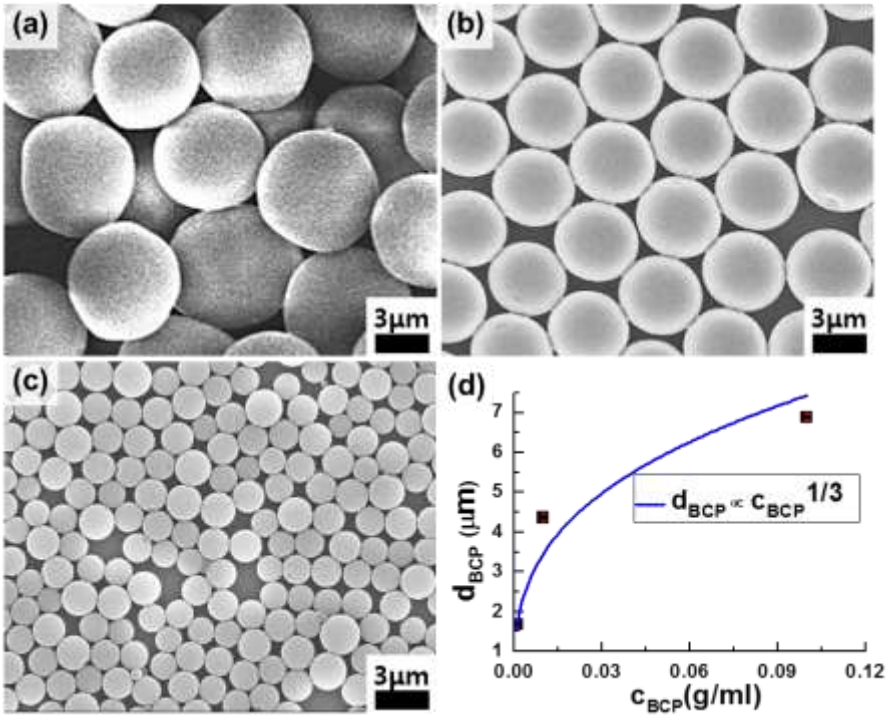


Figure S2. SEM images of BCP particles prepared at different polymer concentrations using 5.1 μm membrane: (a) 0.1 g/mL; (b) 0.01 g/mL; (c) 0.001 g/mL. The average diameters of the BCP particles were determined to be (a) 6.890 ± 0.603 μm, (b) 4.366 ± 0.370 μm, and (c) 1.679 ± 0.172 μm, respectively. (d) Sizes of the BCP particles as a function of the c_{BCP} values; the blue line represents $\boldsymbol{d_{BCP} \propto \sqrt[3]{c_{BCP}}}$. The particles with high c_{BCP} of 0.1 g/mL did not have perfect spherical shapes.

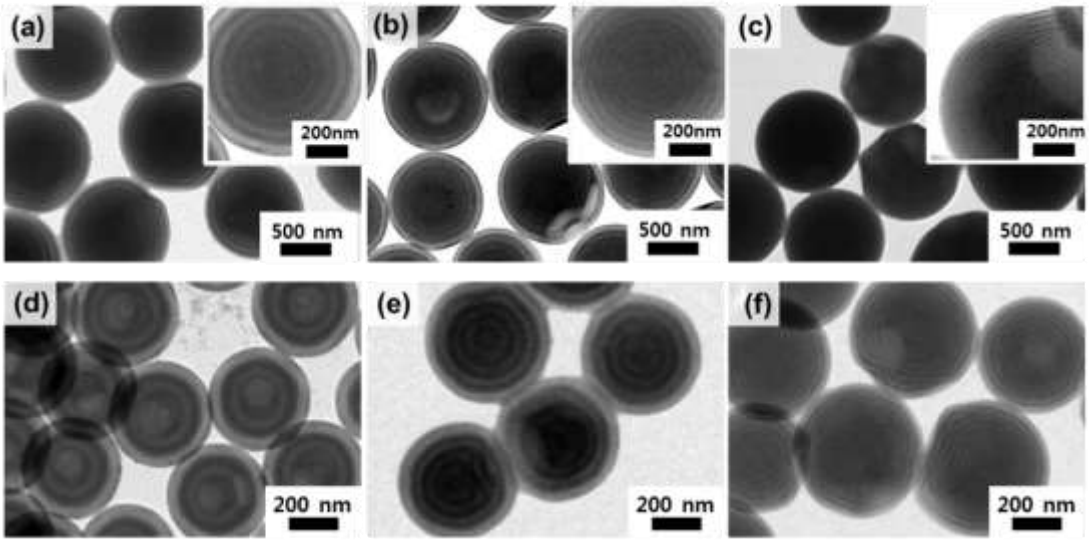


Figure S3. TEM images of BCP particles consisting of three different PS-*b*-PB BCPs with M_n= (a, d) 112k-104k; (b, e) 67k-75k; (c, f) 20k-22k. The BCP particles were produced from 1.1 μm membrane ((a), (b), (c)) and 0.5 μm membrane ((d), (e), (f)), respectively. The inset images are magnified ones corresponding to each of (a-c). The PB domain appears dark due to OsO_4 staining.

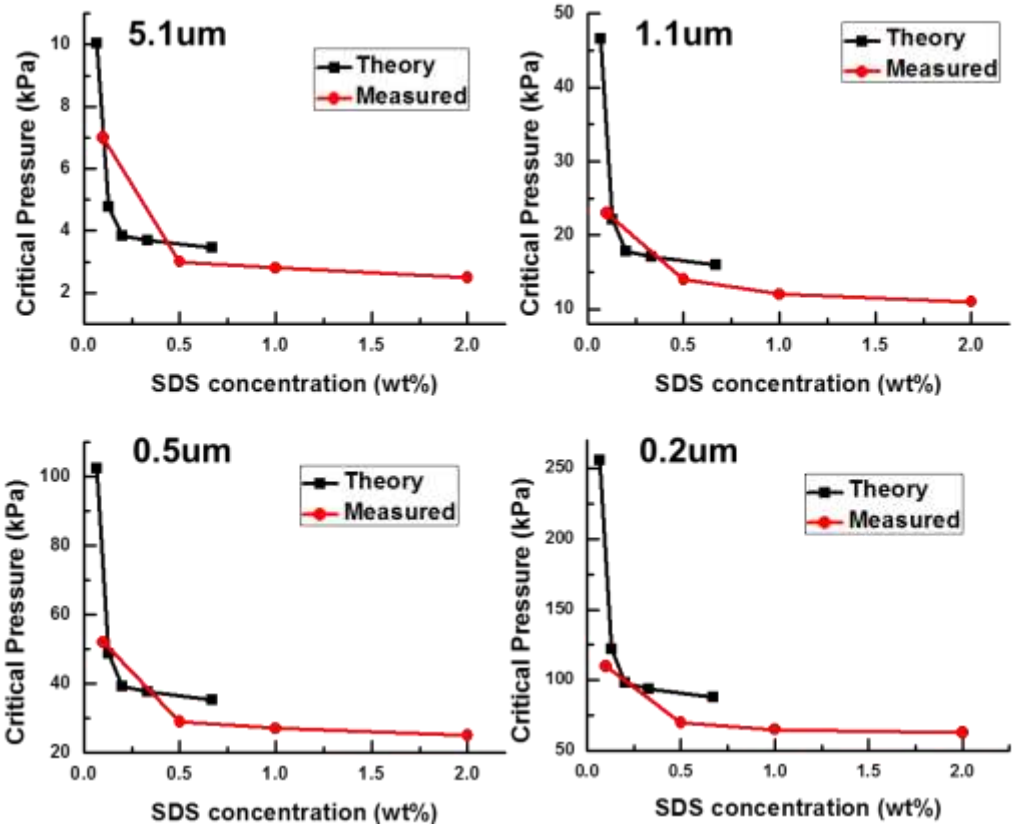


Figure S4. Comparison of calculated and measured P_c values. The calculated values were obtained using Equation (2). The interfacial tensions (γ) at the (PS-toluene)/(water-SDS) interface were estimated depending on SDS concentrations.[1] We used the following assumptions for the estimate: (1) γ for PS-*b*-PB particles was the same as that of the PS particles; (2) the γ value was independent of the BCP concentration; (3) $cos\ \theta = 1$.[2,3]

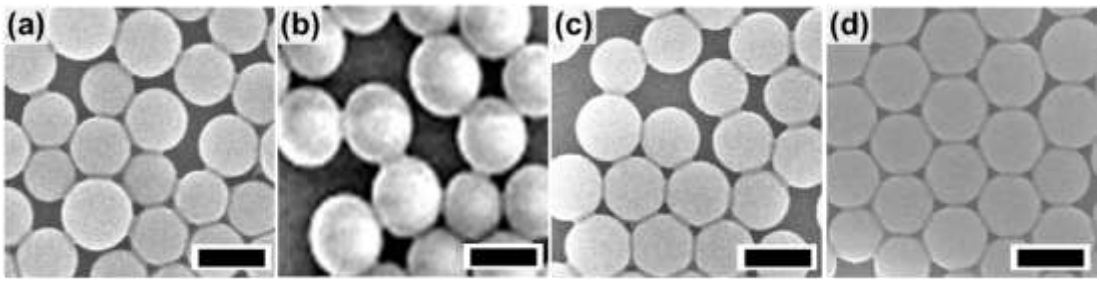


Figure S5. SEM images of BCP particles produced from the 1.1 μm membrane at different stirring speeds. (a) 100 rpm; (b) 280 rpm; (c) 360 rpm; (d) 420 rpm. Scale bars are 1 μm. The SDS concentration was fixed at 0.1 wt%.

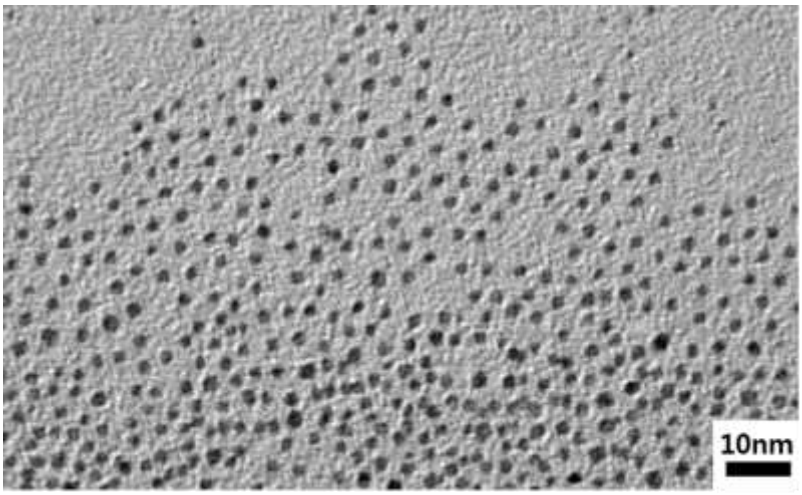
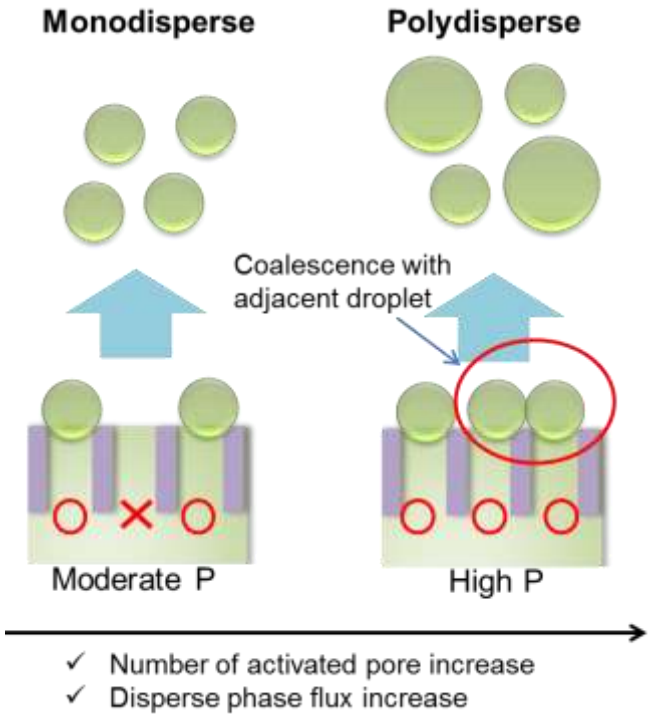


Figure S6. TEM image of oleylamine-capped Au nanoparticles: 3.0±0.32 nm in diameter



Scheme S1. Illustration of the droplet coalescence at higher operation pressure (P).

Table S1. Domain spacing (*L*), commensurability (*D/L*), and number of PB layers in onion-like BCP particles consisting of different molecular weights (M_n) of PS-*b*-PB polymers.

Membrane pore size (μm)	***M_n* of PS-*b*-PB (kg/mol)**	***L* (nm)**	***D/L***	**Number of PB layers**
1.1	112-104	70	14.1	7.5
	67-75	54	17.2	8.5
	20-22	28	36.6	17.5
0.5	112-104	70	6.0	3.5
	67-75	54	9.3	4.5
	20-22	28	16.6	7.5

Table S2. Particle diameters and their distributions produced at different *P* values. The BCP particles were produced at 0.1 wt% SDS for 1.1 μm, 0.5 μm, and 0.2 μm membranes, and 0.5 wt% SDS for 5.1 μm membrane.

Membrane pore size (μm)	P (kPa)	P/Pc	Diameter (μm)	C.V. (%)
5.1	4	1.33	4.366	8.48
	7	2.33	4.596	11.01
	10	3.33	3.673	11.25
	13	4.33	3.226	45.00
1.1	30	1.33	0.986	9.25
	53	2.33	0.994	11.49
	76	3.33	1.025	9.00
	99	4.33	0.984	24.88
0.5	69	1.33	0.429	9.99
	121	2.33	0.433	8.12
	173	3.33	0.492	24.16
	225	4.33	0.476	23.06
0.2	145	1.31	0.201	10.11
	256	2.33	0.197	13.70
	366	3.33	0.263	32.01
	476	4.33	0.247	19.23

Table S3. Particle diameters and their distributions produced at different SDS concentrations.

Membrane pore size (μm)	SDS	P(kPa)	P_c	P/P_c	Diameter (μm)	C.V. (%)
5.1um	0.1wt%	9	7	1.28	3.317	33.67
	0.5wt%	4	3	1.33	4.366	8.48
	1wt%	3.3	2.8	1.17	3.690	9.46
	2wt%	2.8	2.5	1.12	3.655	8.56
1.1um	0.1wt%	30	23	1.33	0.986	9.25
	0.5wt%	19	14	1.36	1.004	9.11
	1wt%	17	12	1.42	1.013	10.16
	2wt%	14	11	1.27	0.961	8.96
0.5um	0.1wt%	69	52	1.33	0.429	9.99
	0.5wt%	38	29	1.31	0.334	10.77
	1wt%	35	27	1.30	0.355	9.99
	2wt%	32	25	1.28	0.374	9.91
0.2um	0.1wt%	145	110	1.31	0.201	10.11
	0.5wt%	90	70	1.28	0.203	12.31
	1wt%	85	65	1.30	0.207	9.68
	2wt%	85	63	1.34	0.204	8.33

Table S4. Particle diameters and their distributions produced at different stirring speeds from 100 to 420 rpm. SDS concentration was fixed at 0.1 wt%, and P/P_c was fixed at 1.33. Diameter and CV value decreased slightly as stirring speed increased, but the differences were small.

Membrane pore size (μm)	Stirring Speed (rpm)	Diameter (μm)	C.V. (%)
1.1	100	0.938	9.38
	280	0.986	9.25
	360	0.913	8.65
	420	0.892	7.40

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(2) Gijsbertsen-Abrahamse, A. J.; Van Der Padt, A.; Boom, R. M. Influence of Membrane Morphology on Pore Activation in Membrane Emulsification. *J. Membr. Sci.* **2003**, 217, 141–150.

(3) Gijsbertsen-Abrahamse, A. J.; Van Der Padt, A.; Boom, R. M. Status of Cross-Flow Membrane Emulsification and Outlook for Industrial Application. *J. Membr. Sci.* **2004**, 230, 149–159.