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Supplementary Material

Phase Separated Block Copolymer Particles with Tuneable Morphologies: Striped, Onion and Patchy Particles

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The detailed composition of surfactant mixtures and weight of BCP solutions to prepare nanoparticles are tabulated in below tables. Table S-4 shows details of the three BCPs purchased from Polymer Source, Inc. including thermal analysis results and chemical structure.

Table S-1. Composition of continuous phases for different values of mass fraction of CTAB in the respective sample.

mass fraction of CTAB (*x*)	CONTINUOUS PHASE			DISPERSED PHASE
	stock solution CTAB (1mg/ml)	stock solution HO-CTAB (1mg/ml)	deionized water	stock solution PS-*b*-P2VP (1 wt%)
	ml	ml	ml	g
0.0	0.0	5.0	5.0	1.5
0.1	0.5	4.5	5.0	1.5
0.7	3.5	1.5	5.0	1.5
0.8	4.0	1.0	5.0	1.5
1.0	5.0	0.0	5.0	1.5

Table S-2: Composition of continuous and dispersed phases for different surfactant concentration in the respective sample.

mass fraction of CTAB (*x*)	CONTINUOUS PHASE			DISPERSED PHASE
	stock solution CTAB (1mg/ml)	stock solution HO-CTAB (1mg/ml)	deionized water	stock solution PS-*b*-P2VP (1 wt%)
	ml	ml	ml	g
1.0	5.0	0.0	5.0	0.50
1.0	5.0	0.0	5.0	0.75
1.0	5.0	0.0	5.0	1.00
1.0	5.0	0.0	5.0	1.25
1.0	5.0	0.0	5.0	1.50
1.0	5.0	0.0	5.0	1.75

Table S-3: Composition of continuous and dispersed phases for different surfactant concentration in the respective sample (surfactant concentrations varied in the continuous phase).

Surfactant Concentration (%)	CONTINUOUS PHASE			DISPERSED PHASE
	stock solution CTAB (1mg/ml)	stock solution HO-CTAB (1mg/ml)	deionized water	stock solution PS-*b*-P2VP (1 wt%)
	ml	ml	ml	g
0.04	4.0	0.0	6.0	1.0
0.05	5.0	0.0	5.0	1.0
0.06	6.0	0.0	4.0	1.0
0.07	7.0	0.0	3.0	1.0

Table S-4: BCPs specifications and details.

Sample	Block Copolymers			PDI	Structure
1	$P2VP_{8.5k}$-*b*-$PDMS_{10k}$			1.20	
2	$P2VP_{12.5k}$-*b*-$PDMS_{10k}$			1.28	
3	$P2VP_{17k}$-*b*-$PDMS_{10k}$			1.28	
Thermal Analysis Result					
Sample	Blocks	T_m (℃)	T_c (℃)	T_g (℃)	
1	2VP	-	-	20	
	DMS	-48	-58	-127	
2	2VP	-	-	90	
	DMS	-44	-	-62	
3	2VP	-	-	90	
	DMS	-44	-	-62	

Examples of optical images of nanoparticle prepared at different mass fraction of HO-CTAB are shown in Figure S-1. Images were taken by optical microscopy (Eclipse Ci, Nikon).

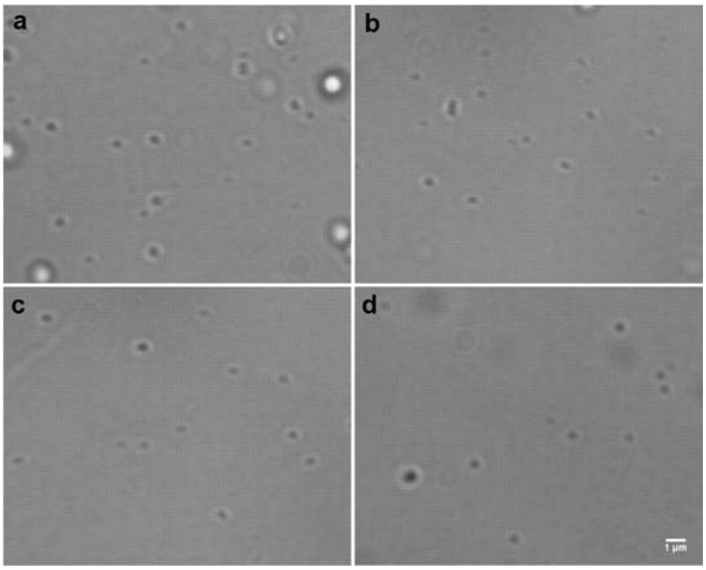

Figure S-1. Optical images of nanoparticles prepared by different mass fraction of HO-CTAB in CTAB/HO-CTAB surfactant mixtures (a) 100% of HO-CTAB; (b) 90% of HO-CTAB; (c) 70% of HO-CTAB; (d) 0% of HO-CTAB. Scale bar: 1 μm.

The size of nanoparticles (shown in Figure S-2) is characterized using dynamic light scattering (Zetasizer Nano ZS, Malvern). The increasing weight of BCP solutions (denoted by "m") corresponds to decreasing relative surfactant concentration. Although the size of nanoparticles is generally inversely proportional to the surfactant concentration, there is a number of samples deviate the trend. The deviation in nanoparticles size may be attributed to the non-linear correlation and change in sensitivities of size to surfactant concentration.

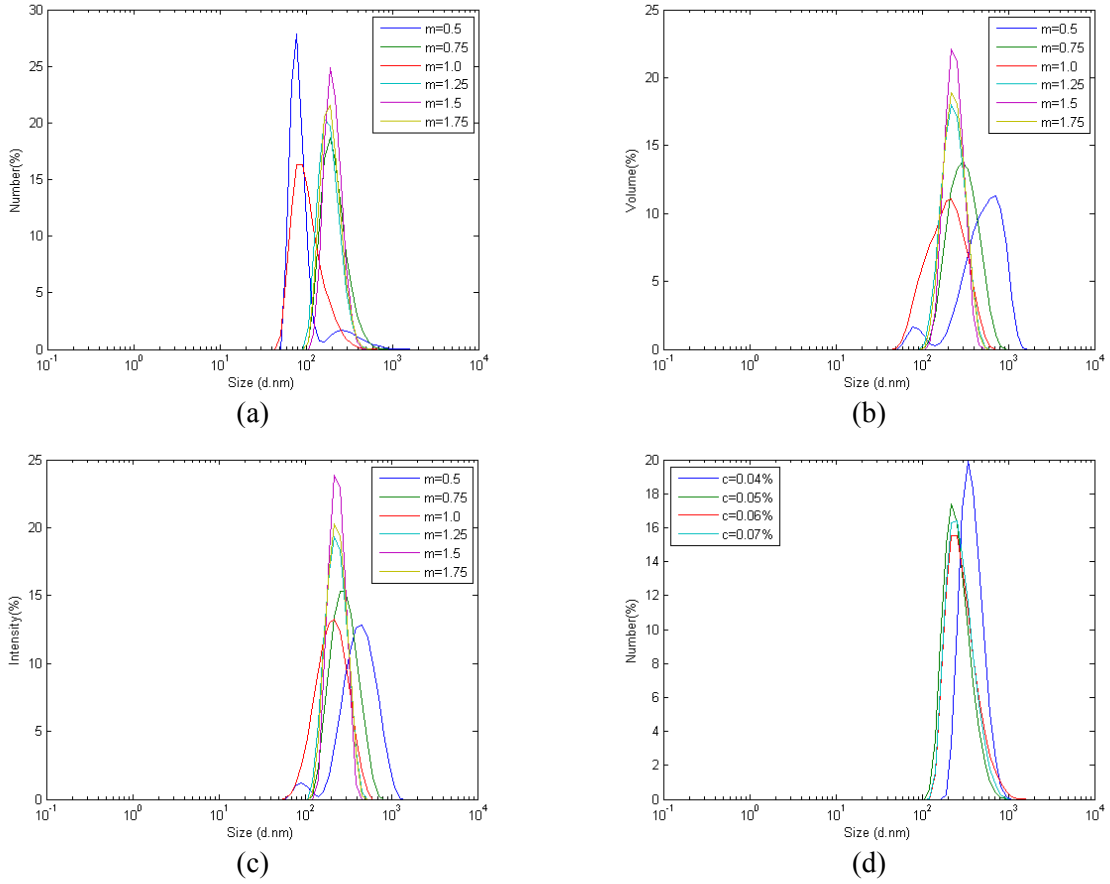

Figure S-2. Size distribution (a) by number, (b) by volume, (c) by intensity of nanoparticles prepared by different weight of dispersed phase, where "m" denotes the weight of BCP solution in gram. (d) Size distribution by number of nanoparticles prepared by different surfactant concentration in the continuous phase, "c" denotes surfactant concentration in continuous phase.

Nanoparticles Prepared by Solvent Exchange:

For copolymer micelles prepared *via* THF solvent exchange, $P2VP_{12.5k}$-*b*-$PDMS_{10k}$ was firstly dissolved into 50 ml of THF giving a polymer concentration of 0.1wt%. Water was then added to the THF solution at a constant rate of 1 ml/min up to 10 ml. The water/THF mixture was well-mixed before evaporating THF at ambient conditions for 3 days. The resulted polymer dispersions were used to prepare TEM grids by drop-casting.

Regarding polymer micelles made *via* DMF dialysis, $P2VP_{12.5k}$-*b*-$PDMS_{10k}$ was firstly dissolved into DMF at a concentration of 0.1 wt %. DMF was then exchanged by water *via* dialysis. The resulted polymer dispersions were then used to prepare TEM grids for morphology characterization.

TEM images of nanoparticles prepared *via* THF solvent exchange and DMF dialysis are shown in Figure S-3a and b respectively.

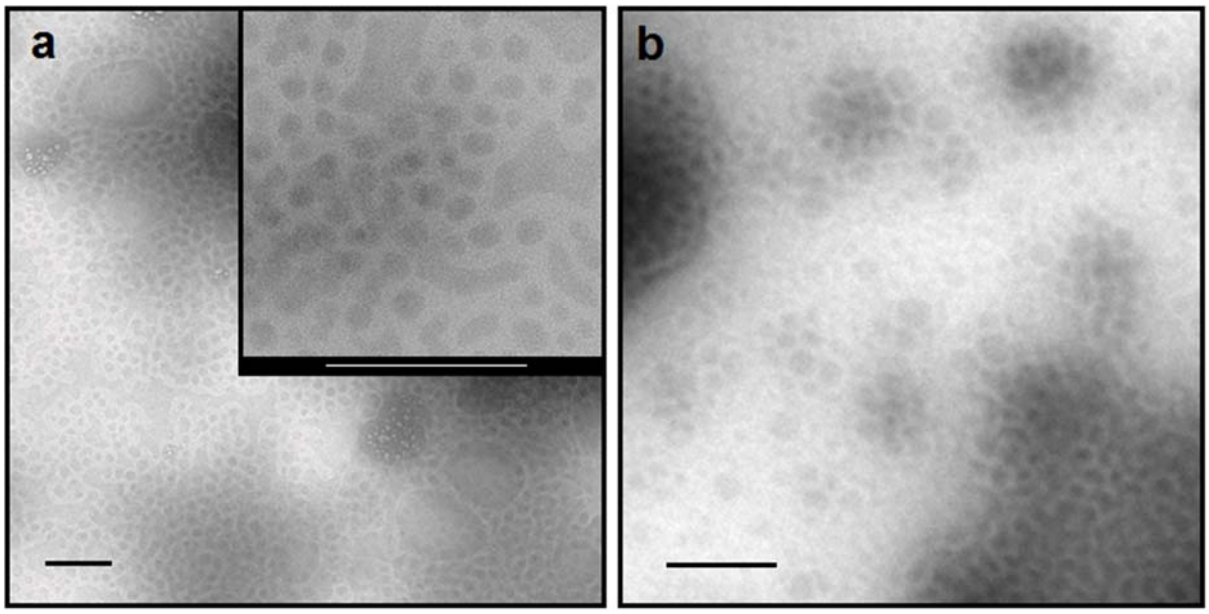

Figure S-3. TEM images of P2VP-*b*-PDMS (M_n=12.5k-10k) assemblies obtained from (a) THF evaporation from THF/water mixture and (b) DMF dialysis. P2VP block is stained by iodine. All scale bars are 200 nm.

Kinetic Studies of Assembled Nanoparticles:

In this work, all nanoparticles prepared from emulsion were examined immediately after self-assembly. To prove the nanoparticles have reached equilibrium, samples were aged for 2-week and examined again. Figure S-4 shows images of nanoparticles taken (a) immediately after self-assembly and (b) after aging. There is no structure evolution observed during the time-scale of study.

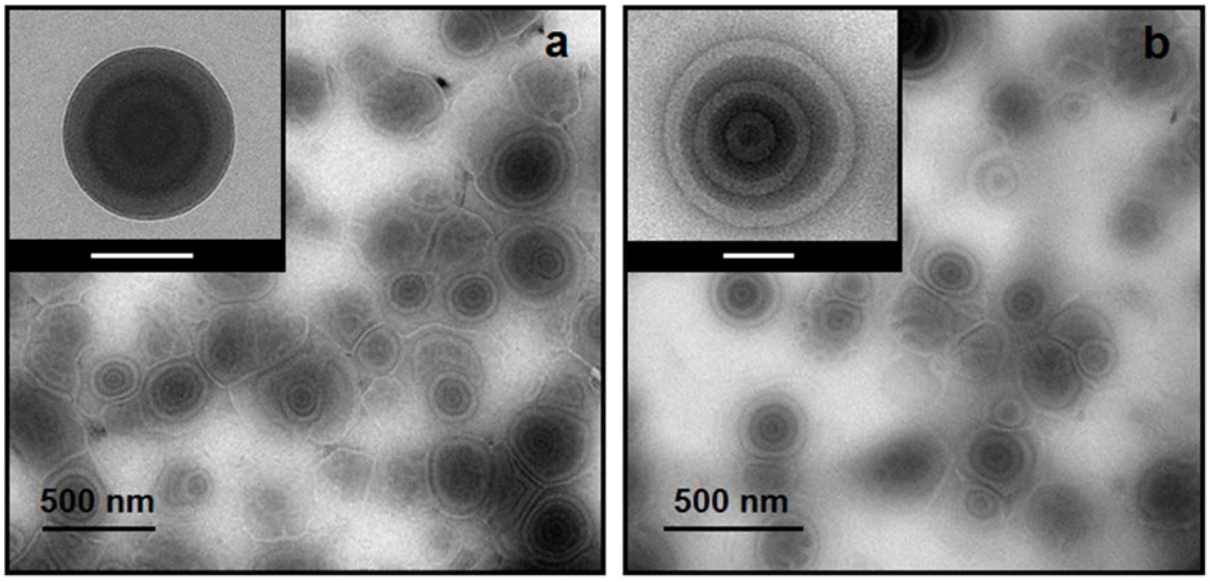

Figure S-4. TEM images of nanoparticles prepared by P2VP-*b*-PDMS (M_n=12.5k-10k) at 100% of HO-CTAB. (a) Image taken right after self-assembly. (b) Sample aged for 2-week before taking a picture. P2VP domain is stained by iodine. Scale bars: 500 nm; inset scale bars:100 nm.

Ill-defined Particles:

There are a number of ill-defined particles observed in some samples especially the ones emulsified by higher mass fraction of HO-CTAB in the surfactant mixtures. It is believed that the defects in nanoparticles are related to the defects in emulsion droplets as the stability of HO-CATB in water is very low. Examples of ill-defined nanoparticles are shown in Figure S-5.

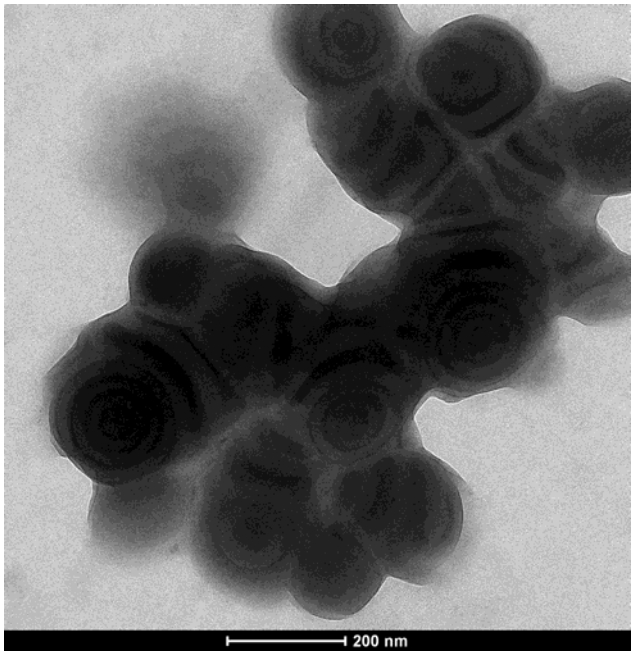

Figure S-5. Example of ill-defined nanoparticles prepared by P2VP-*b*-PDMS (M_n=12.5k-10k) at 80% of HO-CTAB. P2VP domain is stained by iodine. Scale bar is 200 nm.

The synthesized HO-CTAB is characterized using NMR spectrometer at 400 MHz (MR400, Varian). The spectrum is shown in Figure S-6.

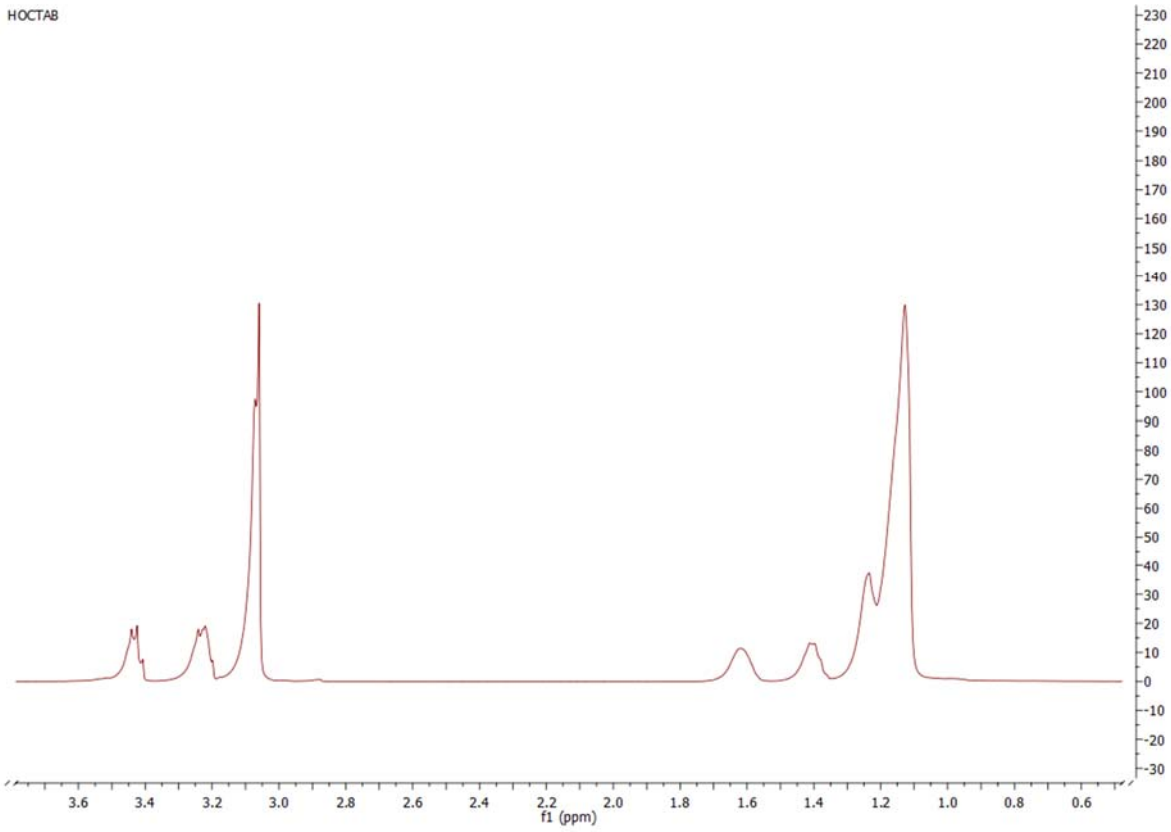

Figure S-6. ^{1}H NMR spectrum of synthesized HO-CTAB.