

Striped, Ellipsoidal Particles by Controlled Assembly of Diblock Copolymers

Se Gyu Jang,^{a,†} Debra J. Audus,^{a,b} Daniel Klinger,^a Daniel V. Krogstad,^{a,c} Bumjoon J. Kim,^d Alexandre Cameron,^a Sang-Woo Kim,^a Kris T. Delaney,^a Su-Mi Hur,^a Kato L. Killops,^e Glenn H. Fredrickson,^{a,b,c*} Edward J. Kramer,^{a,b,c*} Craig J. Hawker^{a,c,f*}

^a Materials Research Laboratory, University of California, Santa Barbara, CA, 93106, USA. ^b Department of Chemical Engineering, University of California, Santa Barbara, CA, 93106, USA. ^c Department of Materials, University of California, Santa Barbara, CA, 93106, USA. ^d Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology, Daehon 305-701, Republic of Korea. ^e Edgewood Chemical Biological Center, U.S. Army Research, Development, and Engineering Command, Aberdeen Proving Ground, MD, 21010, USA. ^f Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA, 93106, USA. [†] Current address: Korea Electric Power Research Institute, Daejeon 305-701, Republic of Korea

Supporting Information:

Synthesis of Surfactant Nanoparticles. Surfactant nanoparticles (SNPs) were synthesized by previously reported methods¹⁻² and based on Au nanoparticles coated with PS-*b*-PI-SH ligands (PS-*b*-PI-SAu). The thiol-terminated poly(styrene-*b*-1,2&3,4 isoprene) (PS-*b*-PI-SH) ligands were synthesized by sequential anionic polymerization using tetrahydrofuran (THF) as a solvent at -78°C with the number average molecular weight M_n values of the PS block, 3 kg/mol, and the PI block, 1.4 kg/mol (by end-group analysis using proton nuclear magnetic resonance spectroscopy, ¹H NMR, Bruker, 500 MHz). Au nanoparticles coated with PS-*b*-PI-SH ligands (PS-*b*-PI-SAu) were synthesized via a two-phase toluene/water method using tetraoctylammonium bromide (TOAB, Sigma-Aldrich) as a phase transfer agent and sodium borohydride (Sigma-Aldrich) as a reducing agent. The Au nanoparticles were precipitated in methanol at least three times to remove TOAB. The unbound polymer ligands were removed from the Au nanoparticles by precipitating the nanoparticles in hexane at least five times. The average diameter of SNP (D_{av}) was 2.5 ± 0.8 nm as determined by image analysis of TEM micrographs. The areal chain density of ligands on the Au-core surface, which was estimated from thermal gravimetric analysis (TGA) and D_{av} , was 1.7 chains/nm². Pendant double bonds within the PI block were cross-linked by a hydrosilylation reaction using 1,1,3,3-tetramethyldisiloxane (TMDS, Gelest Inc.) in the presence of chloroplatinic acid hexahydrate (CPA, Sigma-Aldrich).¹ First, the dry PS-*b*-PI-SAu nanoparticles were dispersed in dry THF under argon. Subsequently, the Pt catalyst (100 mol %) and TMDS

(150 mol % of SiH groups) relative to pendant double bonds on the PI block dissolved in dry THF was added under magnetic stirring at room temperature. The dark red color of the Au nanoparticle dispersion turned dark brown after 30 min. The reaction continued for 2 days under argon. After the reaction was completed, nanoparticles were precipitated in a hexane and methanol mixture (1:1 v/v) at least three times.

Synthesis of PS-*b*-P2VP Block Copolymer Colloidal Particles. Block copolymer colloidal particles were created by an emulsification strategy involving dissolution of PS-*b*-P2VP block copolymer (199 kg/mol, Polymer Source Inc.) in 2 mL chloroform (1 wt %, 30 mg of PS-*b*-P2VP). Various amounts of SNPs from 2.1 to 7.5 mg were added to the chloroform solution to prepare composite colloidal particles with different volume fractions of SNPs (ϕ_p) ranging from 2.2 to 13.5 wt%, respectively. This solution with block copolymer and SNPs was emulsified by ultrasonication in 15 mL deionized water containing CTAB (Sigma-Aldrich, 0.1 wt %) as a surfactant. Then, the emulsion was poured into a 100 mL beaker containing an aqueous CTAB solution (0.1 wt %, 10 mL) and stirred for a day (100 rpm). To allow chloroform to slowly evaporate, the beaker was covered with a glass lid. After complete evaporation of chloroform, the solid block copolymer colloidal particles were washed by centrifugation at 10,000 rpm for 10 min followed by re-dispersion in deionized water. It is noteworthy that the centrifugation speed and duration above are not optimized values to settle down all the colloidal particles. Some tiny colloidal particles without any meaning internal morphologies of block copolymer (less than 50 nm in diameter) generated during the emulsification were hardly settled down at the above centrifugation condition. Therefore, the yield of composite colloidal particles was about 80~90% by mass. Centrifugation at 15,000 rpm for one hour was successful to settle down almost all the colloidal particles (yield > 95 %).

Characterization. Images of the block copolymer colloidal particles and their cross-sections were taken by transmission electron microscopy (TEM, FEI Tecnai G2 microscope, 200 kV). The block copolymer nanoparticle samples were prepared on carbon-coated TEM grids by drop casting the aqueous block copolymer nanoparticle dispersion. For cross-sectional TEM micrographs, aqueous dispersions of block copolymer colloidal particles were drop cast on pre-cured epoxy resin (Embed-812, Electron Microscopy Sciences). After evaporation of water, the epoxy-resin with block copolymer colloidal particles was embedded into additional epoxy resin on top.

Then, the cured resin (60°C for 12 hrs) was sliced to a thickness of about 100 nm by ultra-microtoming (Leica). The samples for cryogenic transmission electron microscopy (cryo-TEM) were prepared by pipetting a 3.5 mL droplet of emulsion onto a glow discharged lacey carbon coated copper grid. The samples were vitrified in liquid nitrogen cooled liquid ethane using the environmentally controlled FEI Vitrobot Mark IV (24°C, 100% humidity). After vitrification, the grid was placed in a Gatan cryoholder and was kept below -165°C throughout imaging. Imaging was performed using low dose mode and the images were recorded digitally with a Gatan Ultrascan 1000 CCD camera and analyzed using the Gatan Digital Micrograph software.

Morphology change versus SNP loading

Morphology change was also found to be dependent on the block copolymer particles size for a given SNPs feed volume ratio. This effect of SNP volume fraction on particle shape depending on the colloids' size was evaluated qualitatively.

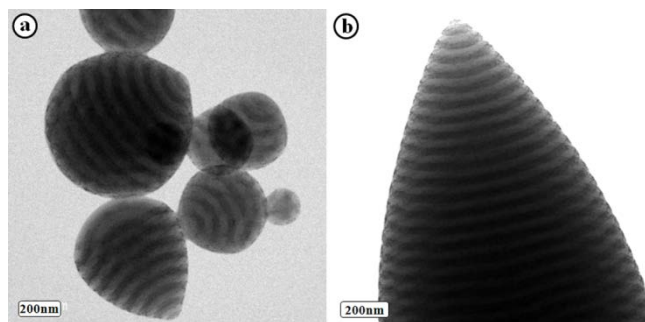


Figure SI-1. TEM micrographs of PS-*b*-P2VP block copolymer colloidal particles mixed with SNPs with feed volume fractions of a) 4.3 % and b) 7.3 %, which were found to be insufficient to induce the morphology transition from radial to stacked lamella in the relatively small particles shown in Figure 3.

Figures SI-1a and SI-1b show TEM micrographs of PS-*b*-P2VP block copolymer colloidal particles mixed with SNPs at different feed volume fractions (ϕ_p), 4.3 % and 7.3 %, respectively. Comparing these images with the ones shown in Figure 3b and Figure 3c, it can be seen that these SNP feed ratios were too low to induce the formation of stacked lamellae in small particles with diameters about 250 nm. However, in the same samples, cone-shaped (Figure SI-1a) and stacked lamellae (Figure SI-1b) block copolymer colloidal particles could be observed for much larger particles.

This morphology variation according to the size (or volume) of block copolymer colloidal particles suggests that the SNPs were adsorbed at the emulsion/CTAB interface during evaporation of chloroform solvent and a morphological transition from radial to stacked lamellae took place once the areal density of nanoparticles was sufficiently high to effectively neutralize the CTAB interface towards PS and P2VP. By assuming an equal SNP concentration in each emulsion droplet (assuming no inter-droplet diffusion) and the complete segregation of all SNP to the droplet surface, it is obvious that this surface areal density depends on the droplet size. In other words, for constant SNP concentrations, the surface coverage is higher for larger droplets due to the decreased surface/volume ratio:

The block copolymer emulsion droplets at intermediate stages were spherical in shape and their surface areas proportional to the square of the time dependent emulsion droplet size ($\sim R_e(t)^2$). Since the vast majority of the SNPs were adsorbed at the emulsion/CTAB interface, the areal density Σ of these SNPs at the interface was given by the number of SNPs in the initial emulsion droplet, which is given by $(\phi_p \phi_{bcp+SNP,i}/v_p)(4\pi/3)(R_{e,i})^3$, where $\phi_{bcp+SNP,i}$ is the initial volume fraction of block copolymer and SNPs in chloroform, v_p is the volume of an SNP and $R_{e,i}$ is the initial radius of an emulsion droplet, divided by the area of droplet interface ($4\pi R_e^2$). If the SNPs segregate exclusively to the P2VP/CTAB interface, the areal density there is 2Σ ; for the symmetric block copolymer case. The final areal density is given by $2\Sigma = (2\phi_p/3v_p)R_{e,f}$, where $R_{e,f}$ is the radius of a sphere with the same volume as the final block copolymer colloidal particle. Therefore, a higher initial concentration of SNPs is required to induce the morphology transition of the smaller block copolymer colloidal particles since the areal density scales as $R_{e,f}$.

This observation explains why morphology transitions were only observed in the smallest block copolymer colloidal particles, containing three layers of lamellar domains, when the feed ϕ_p was higher than 13.5 %. Consequently, for feed volumes of $\phi_p \sim 14$ %, even the smallest colloidal particles formed an asymmetric stacked lamellar morphology (Figure SI-2 and SI-3).

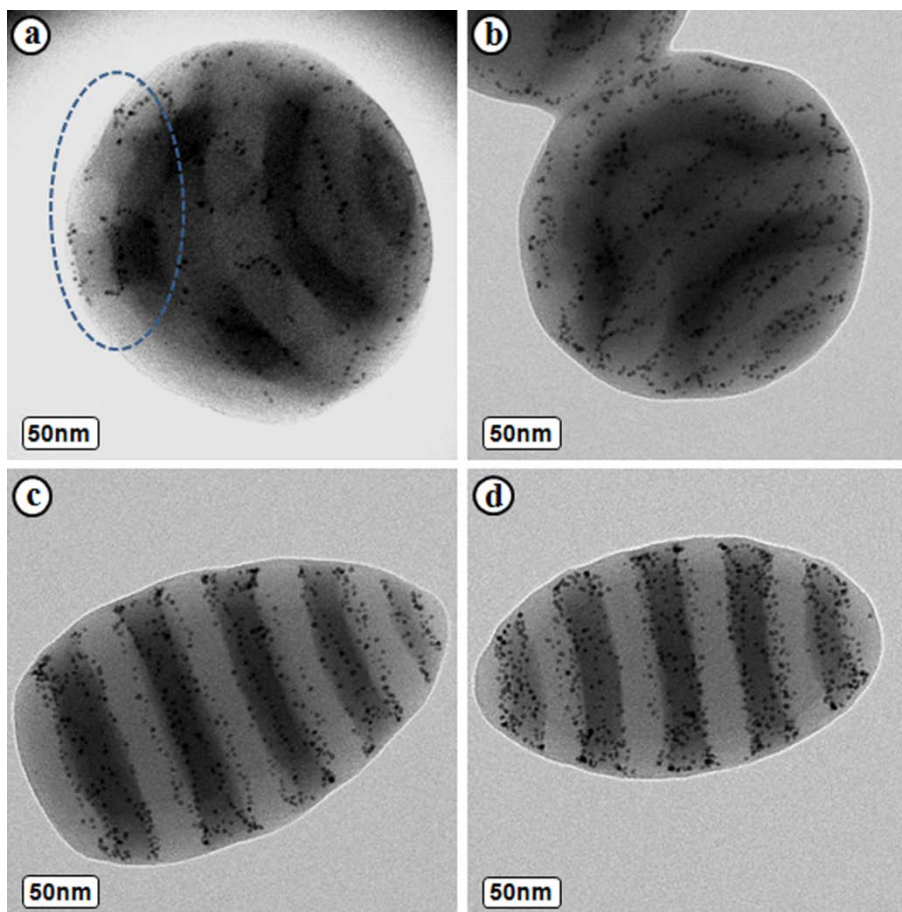


Figure SI-2. TEM micrograph of a PS-*b*-P2VP block copolymer colloidal particle with mixed morphologies of RL and ASL observed from the feed volume fraction of SNPs (ϕ_p) was a) 2.2 %; b) 4.3%, c) 7.3% and d) 13.5%.

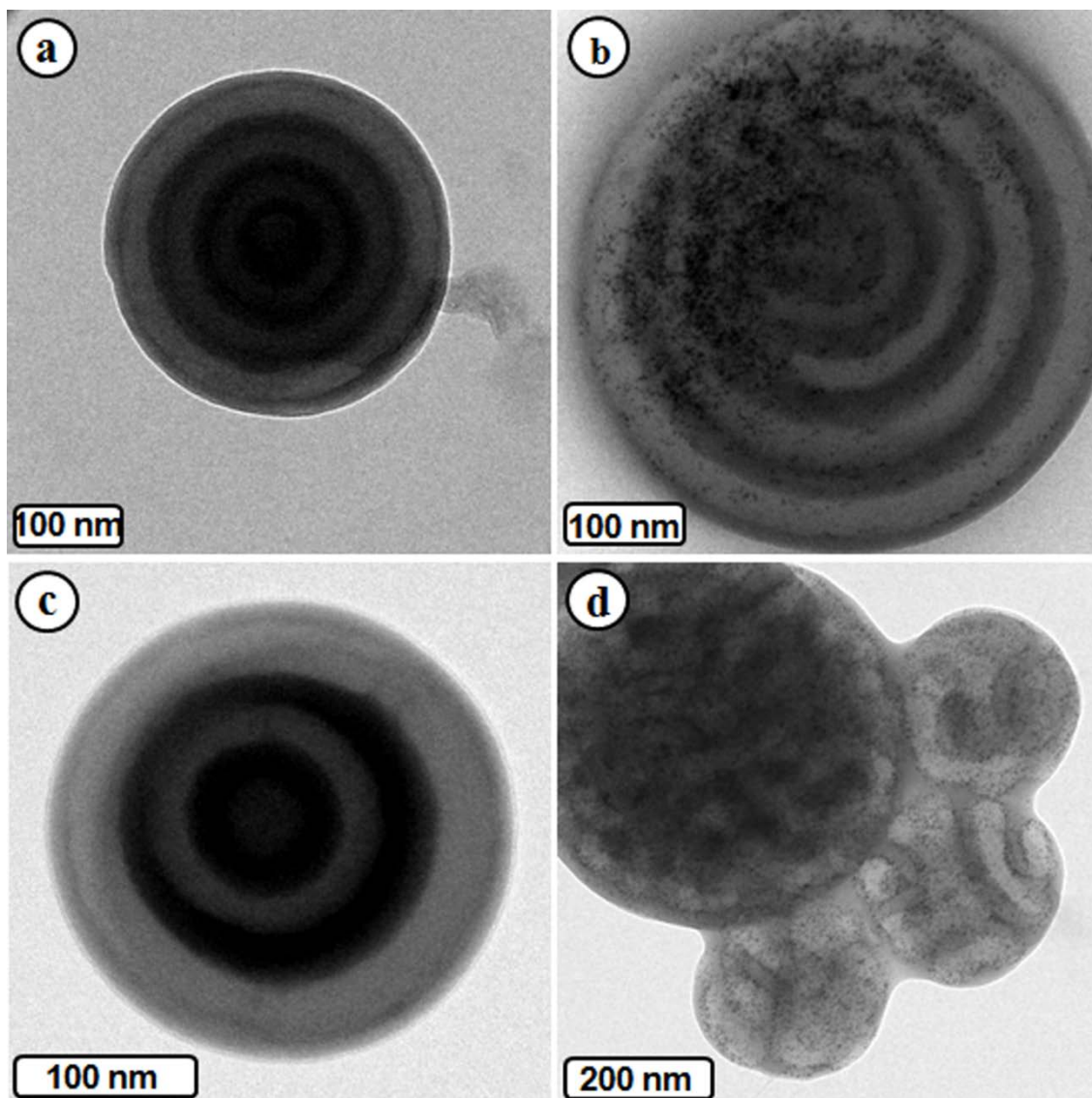


Figure SI-3. TEM micrographs of PS-*b*-P2VP block copolymer colloidal particles obtained with a-b) anionic sodium dodecyl sulfate and c-d) non-ionic Pluronic F108 surfactants. a) a colloid without SNPs. Outer layer is covered by P2VP. b) a colloid with SNPs at $\phi_p \sim 12.5\%$. SNPs were not evenly distributed inside the colloid. c) a colloid without SNPs. Outer layer is covered by P2VP. d) colloids with SNPs at $\phi_p \sim 16.2\%$. Colloidal particles with distorted bicontinuous internal morphology of block copolymer, which has been observed from previous report, was obtained (Jang *et al. Macromolecules* 2011, 44, 9366-9373).

Development of Model

The free energy of the droplet F can be written as

$$\beta F = \left(\frac{3L^2}{2Nb^2(n-1)^2} \right) \left(\frac{V}{b^3N} \right) + \left(\frac{\sqrt{\chi_{PS-P2VP}N}}{b^2\sqrt{6N}} \right) \left(\frac{\pi S^2}{12} \left(\frac{3-4n+2n^2}{n-1} \right) \right) \\ + \left(\frac{\beta\gamma_0}{(1+\Sigma/\Sigma_0)^\alpha} \right) \left(\frac{\pi S^2}{2} \left(\frac{L \sin^{-1}(\sqrt{1-(S/L)^2})}{S\sqrt{1-(S/L)^2}} \right) \right)$$

where N and b are the degree of polymerization and statistical segment length of PS- b -P2VP, respectively, V is the volume of the droplet, L is the major axis of the droplet, S is the minor axis of the droplet, n is the number of layers in the droplet, and β is $1/(k_B T)$. The first term is the stretching of the PS- b -P2VP polymer assuming that the polymers are uniformly stretched, that they behave like entropic springs³ and that all of the layers are the same thickness except the end caps, which are half as thick. The second term is the interfacial energy of the PS in contact with P2VP and is the Helfand-Tagami expression for the surface tension⁴ multiplied by the total interfacial area of PS and P2VP assuming an even number of layers. For the surface tension, we have assumed that $\chi_{PS-P2VP}N$ is 200 because the interactions between PS and P2VP were mediated by the chloroform when the diblock droplets became glassy and thus the room temperature estimate of 350 was too large. A $\chi_{PS-P2VP}N$ of 200, would correspond to neat PS- b -P2VP at roughly 200°C.⁵ The third term in the free energy is the interfacial energy of the diblock with the surrounding medium and is written as the interfacial tension multiplied by the surface area of the droplet. The expression for the surface tension between the diblock and surrounding medium contains the surface tension of the diblock with CTAB γ_0 , the areal density of the SNPs Σ , and two fitting parameters Σ_0 and α . Although the SNPs tend to migrate to the three phase interface and the P2VP/CTAB interface, for simplicity, we have assumed that the surface tension of PS and P2VP with the CTAB and the SNPs can be approximated by a single surface tension for both PS and P2VP with the surrounding medium. For γ_0 , we used 3.5 mN/m, which is the surface tension of CTAB in water and hexane⁶ at the critical micelle concentration (cmc) of CTAB⁷ with a small amount of added salt. The surface tension at the cmc was used since the amount of CTAB in our system (0.1 wt %) was well above the cmc.

In order to calculate the aspect ratio for a given droplet volume and set of fitting parameters, the following three relations are used to write the free energy in terms of known quantities, the aspect ratio A and the number of layers n . The unperturbed radius of gyration squared R_g^2 is $Nb^2/6$, A is

L/S , and V is $\pi S^2 L/6$. The unperturbed radius of gyration R_g was calculated using the degree of polymerization and an average value of the statistical segment length b^8 and was determined to be roughly 12.3 nm. Additionally, the areal density was written as the density of SNPs ρ_{SNP} multiplied by the ellipsoid volume divided by the ellipsoid surface area. Since the density represented the SNP density after partial chloroform evaporation and was unknown, it was combined with Σ_o to form a new fitting parameter $\rho_{\text{SNP}}/\Sigma_o$. The free energy, which is a function of only the fitting parameters, the droplet volume, the aspect ratio and the number of layers, was minimized with respect to both the aspect ratio and the number of layers for fixed droplet volumes in order to compute a shape and optimum number of lamellar layers (along the long axis) of the droplets for fixed fitting parameters. To optimize the fitting parameters, the aspect ratio was plotted vs. the droplet volume, and the sum of the square of the difference in aspect ratio between experimental data points and the theoretical envelope for experimental data points that lay outside the theoretical envelope was minimized.

References

1. Jang, S. G.; Dimitriou, M. D.; Kim, B. J.; Lynd, N. A.; Kramer, E. J.; Hawker C. J. *Soft Matter* **2011**, 7, 6255-6263.
2. Jang, S. G.; Kim, B. J.; Hawker, C. J.; Kramer, E. J. *Macromolecules* **2011**, 44 (23), 9366-9373.
3. Bates, F. S.; Fredrickson, G. H. *Phys. Today* **1999**, 52, 32-38.
4. Helfand, E.; Tagami, Y. J. *Polym. Sci., Part B: Polym. Lett.* **1971**, 9, 741-746.
5. Dai, K. H.; Kramer, E. J. *Polymer* **1994**, 35, 157-161.
6. Ravera, F.; Santini, E.; Loglio, G.; Ferrari, M.; Liggieri, L. *J. Phys. Chem. B* **2006**, 110, 19543-19551.
7. Neugebauer, J. M. *Methods Enzymol.* **1990**, 182, 239-253.
8. Dondos, A.; Benoit, H. *Eur. Polym. J.* **1968**, 4, 561-570.