Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Shape Control of Nanostructured Cone-Shaped Particles by Tuning Blend Structure of A-*b*-B Diblock Copolymer and C-type Copolymer within Emulsion†

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Supplementary Table S1

Supplementary Fig. S1-5

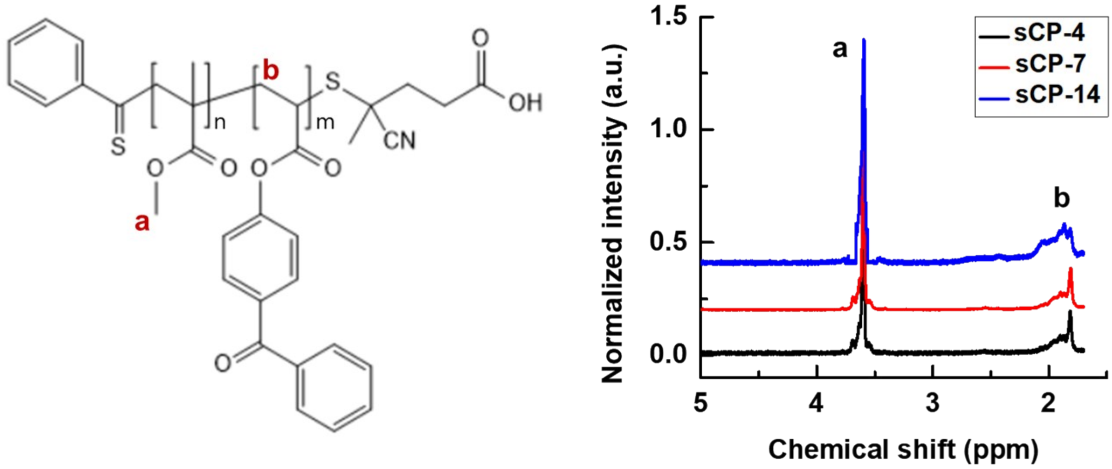

Fig. S1 ^{1}H NMR spectra of for three series of P(MMA-*stat*-4ABP) (sCP-4, sCP-7, and sCP-14 from **Table 1**) with different mole fraction of 4ABP (ϕ_{4ABP}). $CDCl_3$ was used as the NMR solvent.

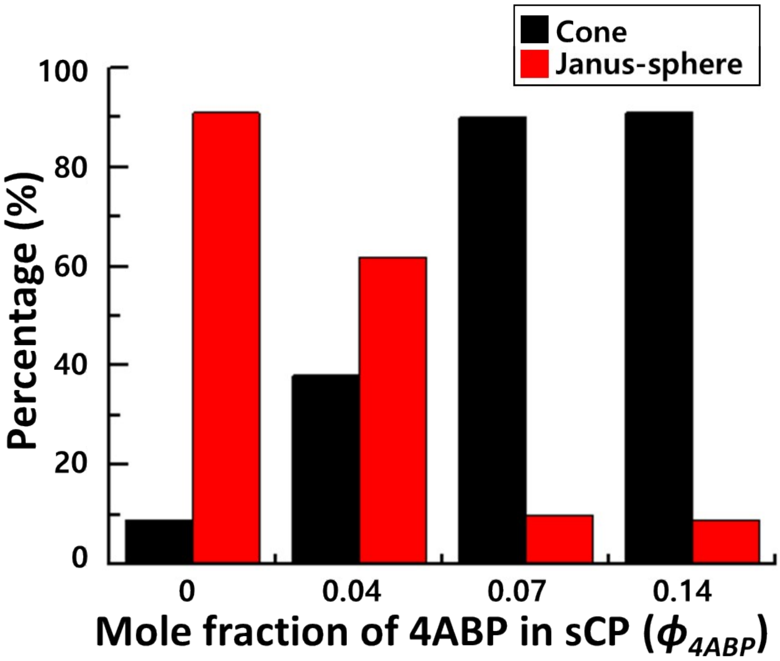

Fig. S2 Histograms showing the percentage of each particle shape as a function of ϕ_{4ABP}: Cone-shaped particle (black) and Janus-sphere (red). The volume fraction of sCP (f_{sCP}) was fixed at 0.45, and the particles were prepared from the SPG membrane with d_{pore} = 2.1 μm.

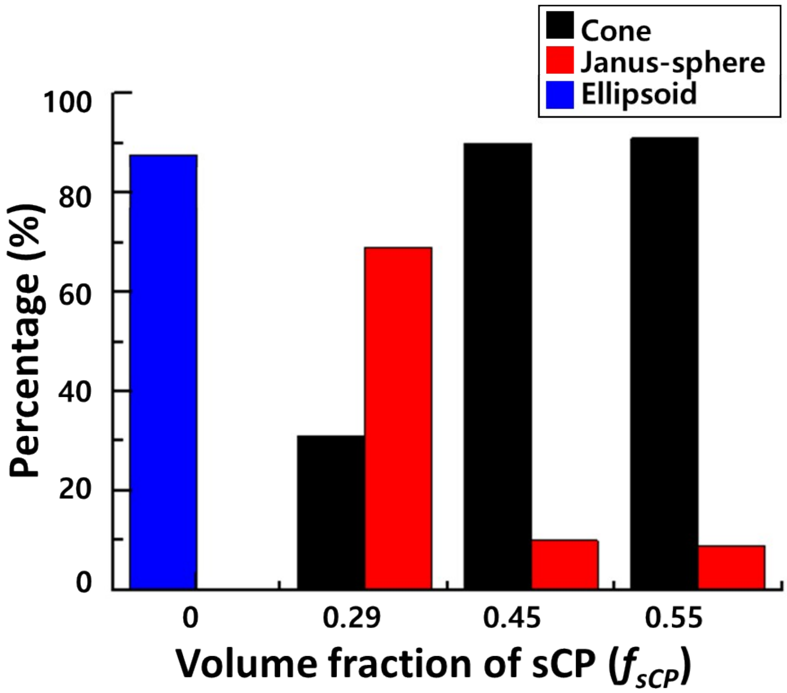

Fig. S3 Histograms showing the percentage of each particle shape as a function of f_{sCP}: Cone-shaped particle (black), Janus-sphere (red), and ellipsoid (blue). The mole fraction of 4ABP in sCP (ϕ_{4ABP}) was fixed at 0.07 for $f_{sCP} > 0$, and the particles were prepared from the SPG membrane with $d_{pore} = 2.1$ µm.

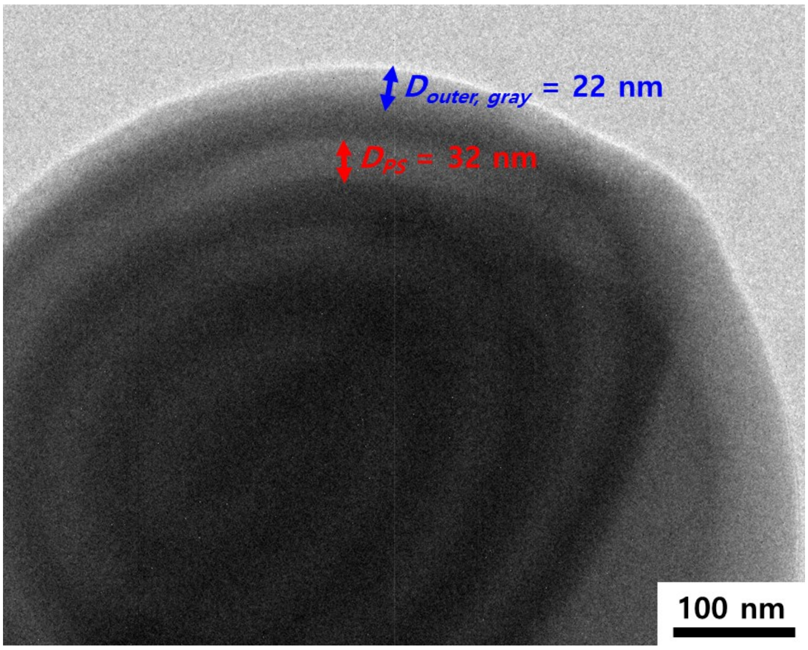

Fig. S4 High-magnification TEM image of Janus-sphere (PS_{112k}-*b*-PB_{104k}/sCP-0, f_{sCP} = 0.45 and ϕ_{4ABP} = 0). The particle was produced from the SPG membrane with d_{pore} = 2.1 μm.

Table S1. Summary of height of the BCP cone (*L*), diameter of the cross-sectional area of the BCP cone (*S*), height or the sCP compartment (*H*), and AR ((*L*+*H*)/*S*)) produced from BCPs and sCP-7 blend with different particle size and Janusity (f_{sCP}).

f_{sCP}	d_{pore} (µm)	*L* (nm)	*S* (nm)	*H* (nm)	AR ((*L*+*H*)/*S*)
0.29	2.1	816 ± 51	703 ± 33	381 ± 25	1.81
0.45	2.1	800 ± 53	764 ± 47	521 ± 34	1.73
0.55	2.1	618 ± 58	730 ± 67	615 ± 47	1.69
0.45	0.5	216 ± 19	264 ± 17	91 ± 11	1.16
0.45	1.1	453 ± 25	471 ± 31	244 ± 22	1.48
0.45	2.1	800 ± 53	764 ± 47	521 ± 34	1.73

Calculation Details for the AR of the Cone-Shaped Particles

$$\frac{F}{k_bT} = \underbrace{\frac{\pi}{6b^2}(2n-1)\sqrt{\frac{\chi}{6}}S^2}_{\text{Interfacial tension btw two blocks}} + \underbrace{\frac{\pi^2 L^3 S^2}{48N^2b^5(2n-1)^2}}_{\text{Chain stretching energy of BCP}} + \underbrace{\frac{\pi(\gamma_{PS}+\gamma_{PB})}{8(1+\beta\Sigma)^{\alpha}}S^2\left[1+\frac{2L\sin^{-1}\sqrt{1-S^2/4L^2}}{S\sqrt{1-S^2/4L^2}}\right]}_{\text{Surface energy between BCP and surrounding}}$$

$$+ \underbrace{\frac{\pi^2 {L_0}^2}{1024N^2b^5}C^2V_c}_{\text{Bending energy}} + \underbrace{\frac{\chi_{PS/sCP}}{4b^2}\pi S^2}_{\text{Interfacial tension between BCP(PS) \& sCP}} + \underbrace{\frac{\pi}{4}(S^2+4H^2)\frac{\gamma_{sCP}}{(1+\beta\Sigma_{sCP})^{\alpha}}}_{\text{Surface energy between sCP and surrounding}}$$

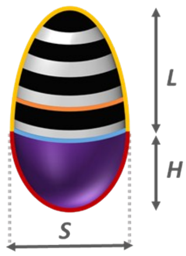

Fig. S5 Total free energy of cone-shaped particle and the schematic illustration that represents the corresponding energy term.

The total free energy of cone-shaped particles (F), consisting of n-layered PS_{112k}-*b*-PB_{104k} BCP half-ellipsoid having height of L and diameter of S, and sCP cap having height of H can be expressed as the equation above, by modifying previous theoretical model[1–5], where k_b is the Boltzmann constant, T is the temperature, χ is the interaction parameter between two blocks of BCP (PS and PB), $\chi_{PS/sCP}$ is the interaction parameter of the PS block and sCP, b is the monomer length of BCP, N is the degree of polymerization of BCP, γ_{PS} , γ_{PB}, and γ_{sCP} are the interfacial tensions between each polymer and its surroundings (aqueous media), $\sum$ and $\sum_{sCP}$ are the ratios of volume to surface area of BCP ellipsoid cone (half-ellipsoid) and sCP sphere cap, respectively, and α and β are the fitting parameters for the surface energy term between the cone-shaped particles and the surrounding. C and V_c are the curvature and the volume of curved layer at the end of ellipsoid, respectively. In this system, we assumed that the effects of surface (aqueous media) energy reduction from the addition of surfactant are the same for BCP ellipsoid cone and sCP sphere cap. For this system, χ and $\chi_{PS/sCP}$ were both set to 0.04, and the surface tension values between the polymer and its surrounding were set to γ_{PS} = 9.76, γ_{PB} = 8.57, and χ_{sCP} = 7.19 mN m^{-1}, respectively, based on the contact angle measurements of each polymer film upon surfactant solution. The monomer length of BCP is set to (b = 0.5 nm). C and V_c were numerically calculated from the given geometry of the prolate particle. When the size of the BCP half-ellipsoid is determined with L and S values, the height of sCP cap (H) can be calculated by the following equation:

$$V_{sCP} = \frac{1}{6}\pi H\left(\frac{3S^2}{4} + H^2\right) \qquad (S1)$$

With known value of volume of the sCP cap (V_{sCP}) (*i.e.* by the relationship between the volume of BCP (function of L and S) and the volume ratio between BCP part and sCP part (f_{sCP})), H can be calculated by solving eqn (S1), which result in a single real-value solution as expressed in eqn (S2):

$$H = \left(\frac{3V_{sCP}}{\pi} + \sqrt{\frac{9V_{sCP}}{\pi^2} + \frac{S^6}{64}}\right)^{\frac{1}{3}} + \left(\frac{3V_{sCP}}{\pi} - \sqrt{\frac{9V_{sCP}}{\pi^2} + \frac{S^6}{64}}\right)^{\frac{1}{3}} \qquad (S2)$$

Finally, the total free energy of cone-shaped particles were calculated as a function of n, L, S, H, α, and β. For given total volume of BCP and sCP, set of L, S, and H was numerically calculated which minimize the total free energy of the system. As a result, we can plot aspect ratio (L+H)/S as a function of length of cone-shaped particle (L+H) as shown in **Fig. 4** which are matched to the experimental results. The fitting parameters in this particular system were optimized to α = 0.97 and β = 0.9 nm.

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