

## Supporting Information

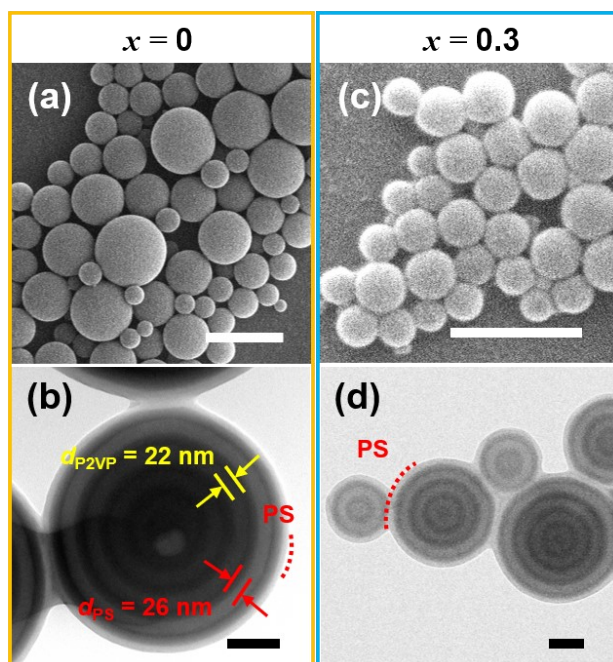
# **Bifunctional Additive-Driven Shape Transitions of Block Copolymer Particles through Synergistic Quaternization and Protonation**

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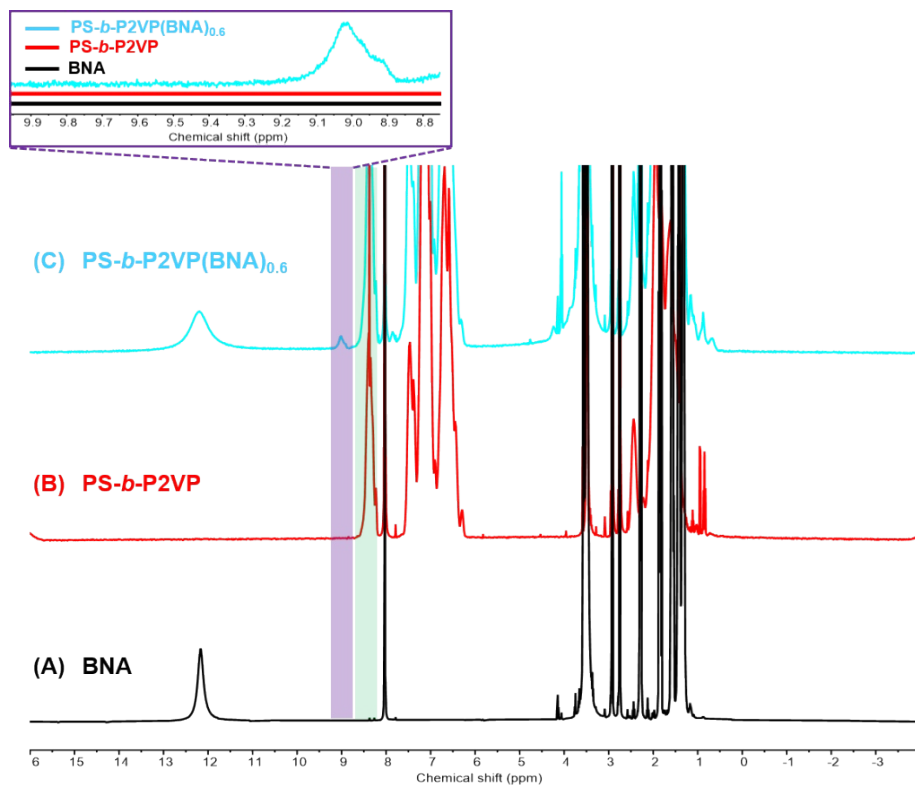
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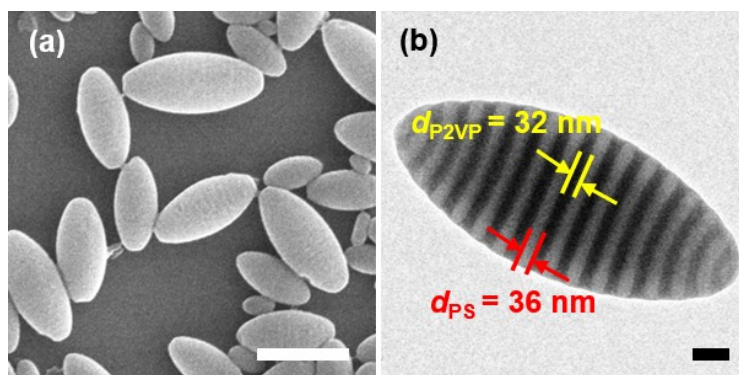
**Figure S1.** SEM and TEM images of PS-*b*-P2VP(BNA)<sub>*x*</sub> particles at (a, b)  $x = 0$  and (c, d)  $x = 0.3$ . Scale bars are 1  $\mu\text{m}$  in the SEM images and 100 nm in the TEM images.



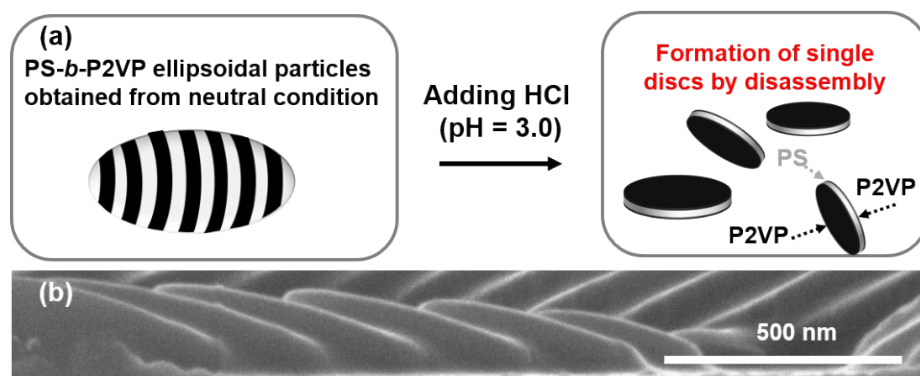
**Figure S2.**  $^1\text{H}$  NMR spectra of solution containing BNA, PS-*b*-P2VP, PS-*b*-P2VP(BNA) $_{0.6}$ . The new proton peaks highlighted by light purple framework between 8.8 ppm and 9.5 ppm in (C) indicate the reacted pyridine group of PS-*b*-P2VP while the light green framework in (B) or (C) indicate the non-reacted pyridine group of PS-*b*-P2VP. Inset above (C) is the magnified NMR between 8.8 ppm and 9.5 ppm for BNA, PS-*b*-P2VP, PS-*b*-P2VP(BNA) $_{0.6}$ .

**Table S1.** Interfacial tension ( $\gamma$ , mN m<sup>-1</sup>) between the polymer solution (i.e., PS<sub>50k</sub> or P2VP<sub>50k</sub> or P2VP<sub>50k</sub>(BNA)<sub>x</sub> in chloroform, 10 mg mL<sup>-1</sup>) and the aqueous surfactant solution (i.e., CTAB in water, 10 mg mL<sup>-1</sup>)

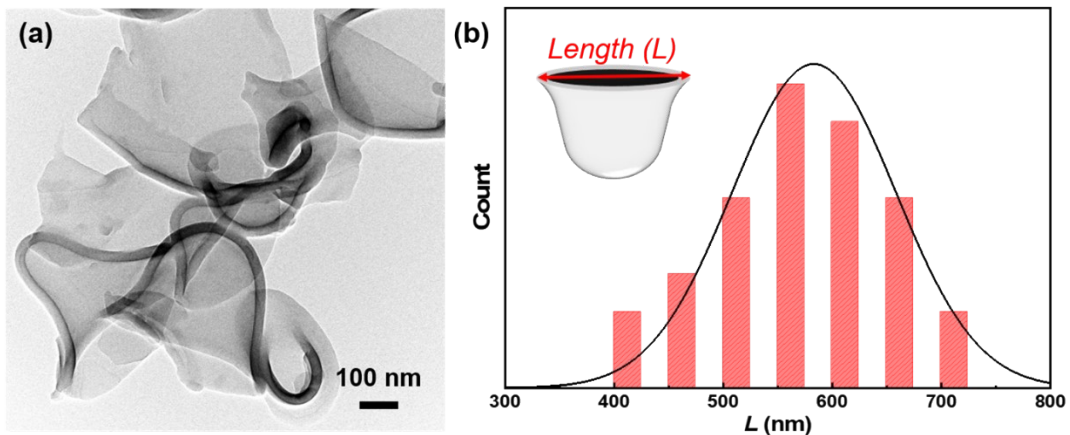
PS	P2VP	P2VP(BNA) <sub>x</sub>						
		<i>x</i> = 0.1	<i>x</i> = 0.3	<i>x</i> = 0.5	<i>x</i> = 0.6	<i>x</i> = 0.8	<i>x</i> = 1.2	<i>x</i> = 1.5
3.99 ± 0.25	4.66 ± 0.18	4.62 ± 0.28	4.51 ± 0.58	4.38 ± 0.13	4.26 ± 0.17	3.93 ± 0.24	3.48 ± 0.41	3.32 ± 0.31



**Figure S3.** (a) SEM and (b) TEM images of ellipsoidal  $\text{PS}_{102\text{k}}\text{-}b\text{-P2VP}_{97\text{k}}$  particles prepared using a mixture of polyvinyl alcohol (PVA) and CTAB in a 4:1 weight ratio, creating a neutral preference of PS-*b*-P2VP to the surrounding aqueous medium. Scale bars are 1  $\mu\text{m}$  in the SEM image and 100 nm in the TEM image.



**Figure S4.** (a) Schematic illustration showing the production of PS-*b*-P2VP discs through disassembly of conventional ellipsoidal particles in acidic solution (pH = 3.0). (b) Side-view SEM images of PS<sub>102k</sub>-*b*-P2VP<sub>97k</sub> disc-like particles.



**Figure S5.** (a) TEM image of Janus cups. (b) Statistical distribution of  $L$  values for Janus cups, determined by analyzing 100 particles from TEM images.

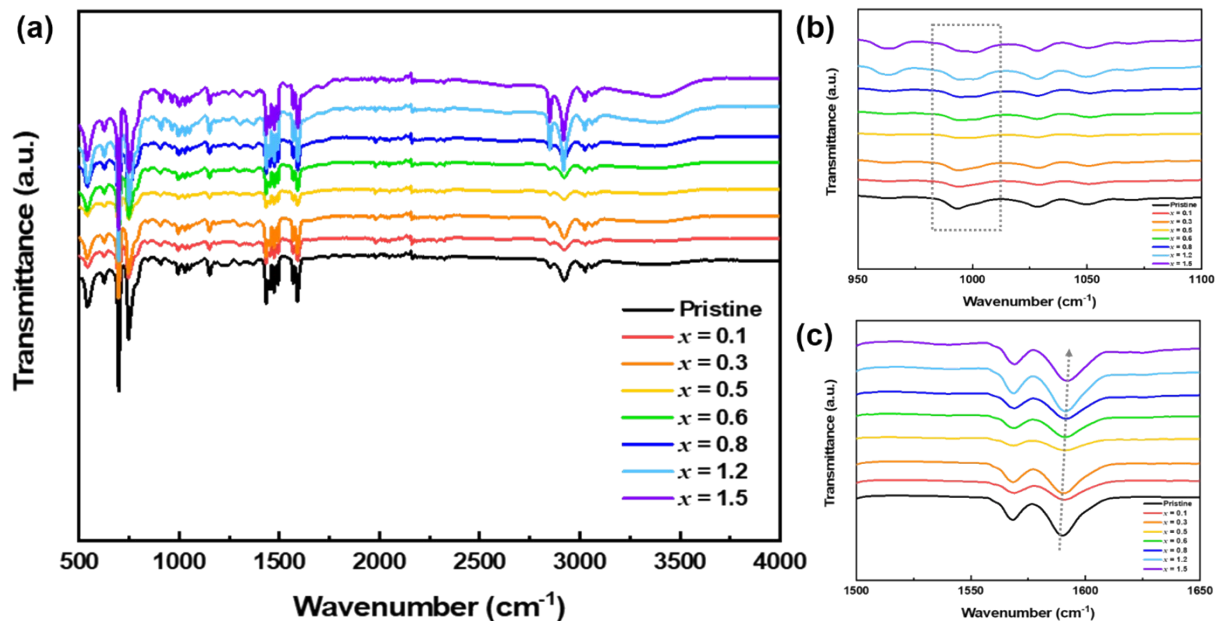
**Table S2.** Degree of reaction of P2VP ( $\alpha$ , %) by BNA at different feed molar ratios ( $x$ ), which was determined by the molar fraction of reacted 2VP units in the reacted P2VP block [reacted  $n_{2VP}/(\text{reacted } n_{2VP} + n_{2VP})$ ].

$x$	$\alpha$ (%)
0.1	10.5
0.3	12.5
0.5	14.6
0.6	15.7
0.8	17.8
1.2	19.2
1.5	21.2

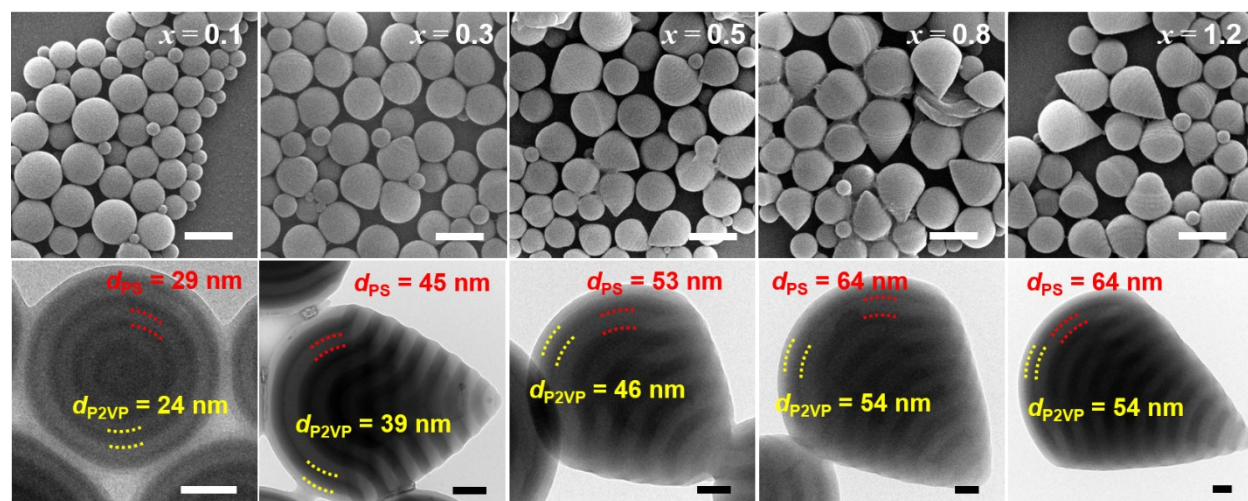


**Table S3.** The pH values of the PS-*b*-P2VP(BN)<sub>*x*</sub>, PS-*b*-P2VP(NA)<sub>*x*</sub>, PS-*b*-P2VP(BNA)<sub>*x*</sub> particle suspension at different feed molar ratios (*x*). The pH values were measured by pH meter (Ohaus ST3100 pH Bench).

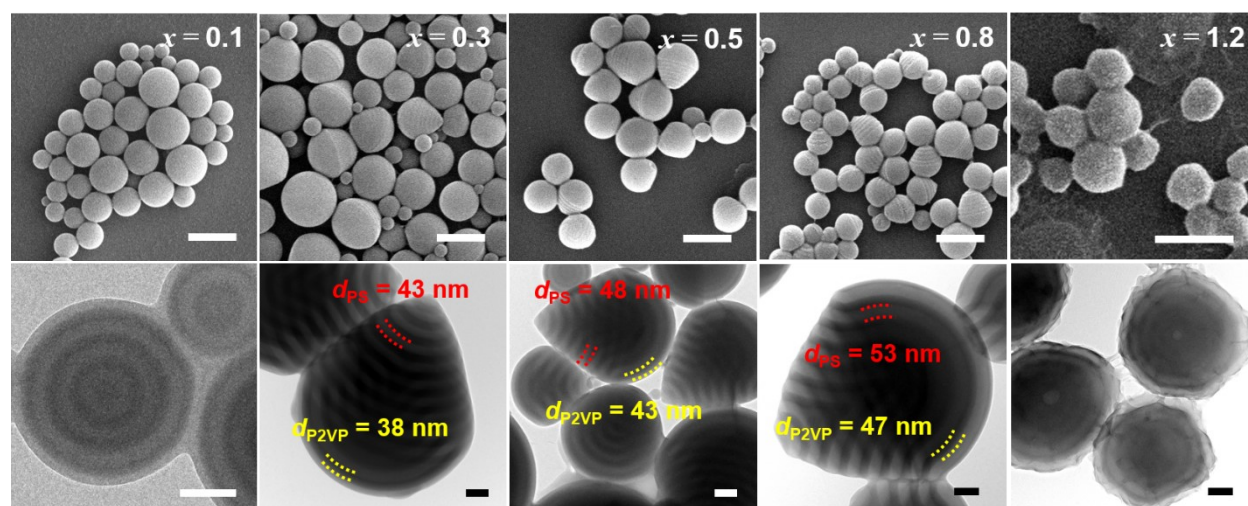
Particle suspension	pH value with		
	BN	NA	BNA
PS- <i>b</i> -P2VP (pristine)	6.96 ± 0.35	6.96 ± 0.35	6.96 ± 0.35
PS- <i>b</i> -P2VP(additive) <sub>0.1</sub>	6.86 ± 0.42	6.81 ± 0.33	6.86 ± 0.44
PS- <i>b</i> -P2VP(additive) <sub>0.3</sub>	6.82 ± 0.15	5.72 ± 0.27	5.57 ± 0.19
PS- <i>b</i> -P2VP(additive) <sub>0.5</sub>	6.89 ± 0.26	5.12 ± 0.38	4.89 ± 0.32
PS- <i>b</i> -P2VP(additive) <sub>0.6</sub>	6.91 ± 0.47	4.85 ± 0.19	4.61 ± 0.27
PS- <i>b</i> -P2VP(additive) <sub>0.8</sub>	6.85 ± 0.29	4.73 ± 0.22	4.52 ± 0.35
PS- <i>b</i> -P2VP(additive) <sub>1.2</sub>	6.94 ± 0.32	3.89 ± 0.43	3.68 ± 0.34
PS- <i>b</i> -P2VP(additive) <sub>1.5</sub>	6.83 ± 0.18	3.45 ± 0.21	3.25 ± 0.21



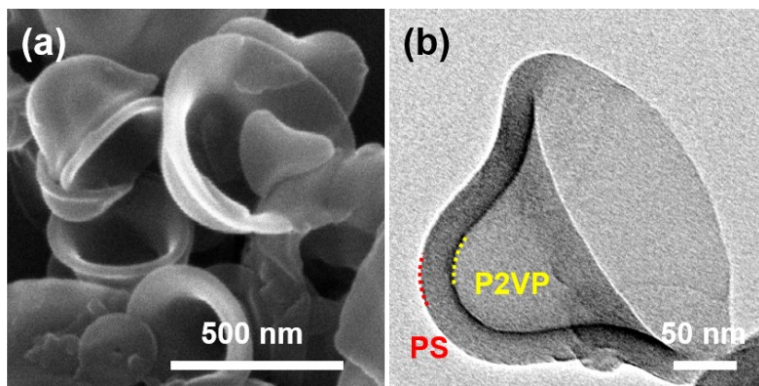
**Figure S6.** FTIR spectra of  $\text{PS}_{102\text{k}}\text{-}b\text{-P2VP}_{97\text{k}}(\text{BNA})_x$  particles obtained at different  $x$  values. (a) The full FTIR spectra and (b, c) amplified FTIR spectra of  $\text{PS}_{102\text{k}}\text{-}b\text{-P2VP}_{97\text{k}}(\text{BNA})_x$  particles obtained at different  $x$  values (b) from  $950\text{ cm}^{-1}$  to  $1100\text{ cm}^{-1}$  and (c) from  $1500\text{ cm}^{-1}$  to  $1650\text{ cm}^{-1}$ . Framework in (b) indicates the broadened spectra around  $1000\text{ cm}^{-1}$  after quaternization while the arrow in (c) indicates the shift after protonation.



**Figure S7.** SEM and TEM images of PS-*b*-P2VP(BN)<sub>x</sub> particles at different *x* values. Scale bars are 1  $\mu$ m in the SEM image and 100 nm in the TEM image.



**Figure S8.** SEM and TEM images of PS-*b*-P2VP(NA)<sub>x</sub> particles at different *x* values. Scale bars are 1  $\mu$ m in the SEM image and 100 nm in the TEM image.



**Figure S9.** (a) SEM and (b) TEM images of Janus cups after crosslinked with dibromobutane for 24 h.