

## Supporting Information of

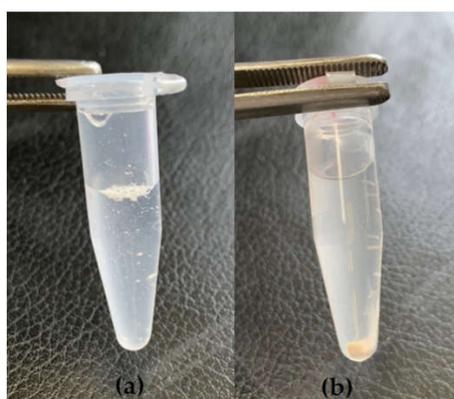
# Effect of Site-Specific Functionalization on the Shape of Nonspherical Block Copolymer Particles

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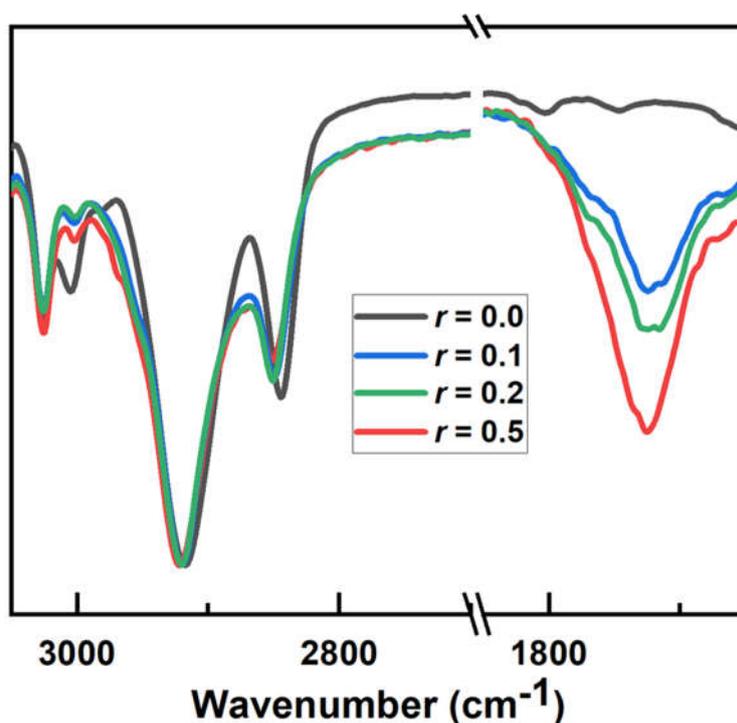
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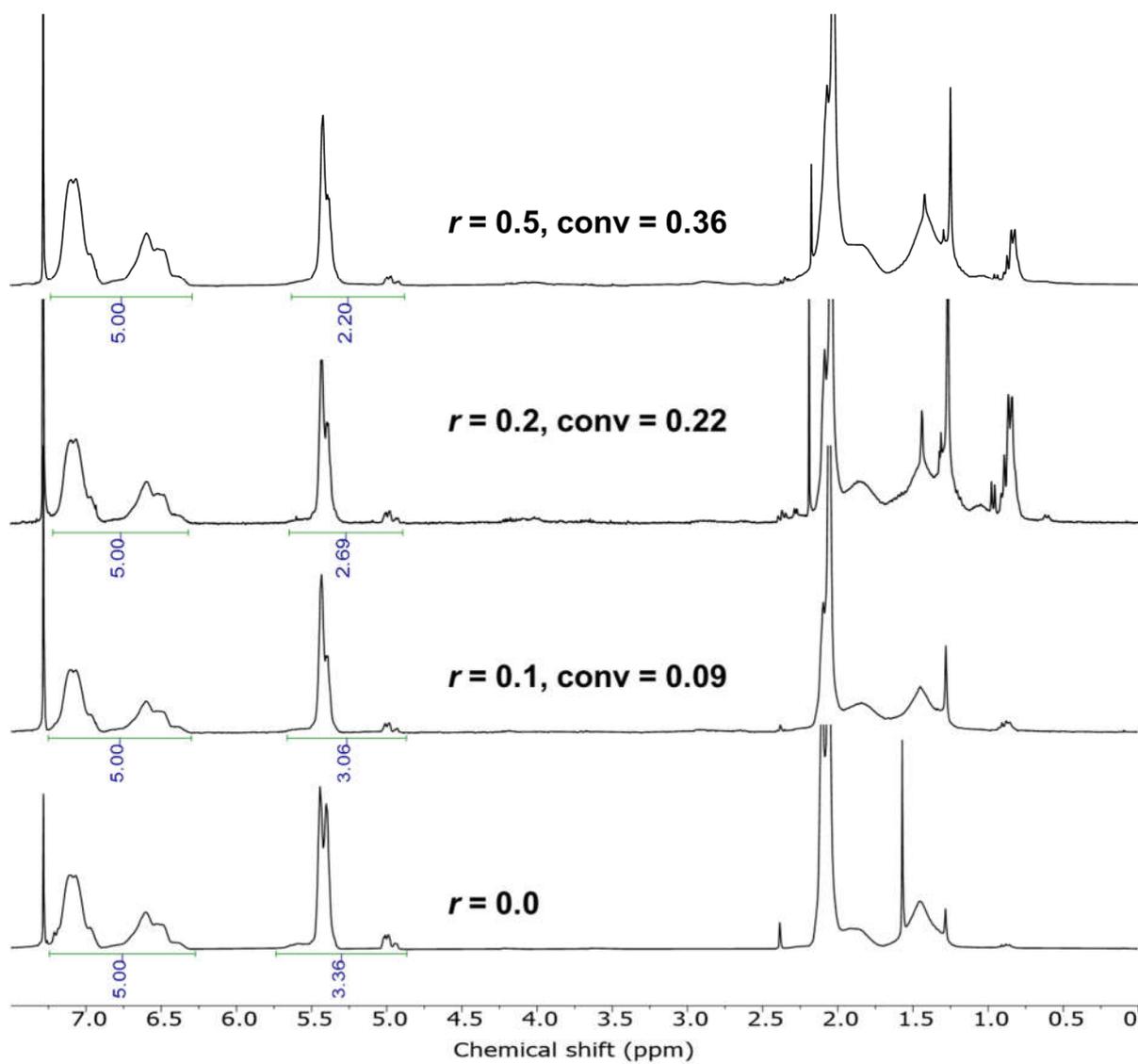


**Figure S1.** Photograph of particles after centrifugation at 10,000 rpm for 5 min for (a) pristine PS<sub>34k</sub>-*b*-PB<sub>25k</sub> particles and (b) MPA-modified particles. While pristine PS<sub>34k</sub>-*b*-PB<sub>25k</sub> particles floated on the top of the aqueous phase, MPA-modified particles were settled to the bottom.

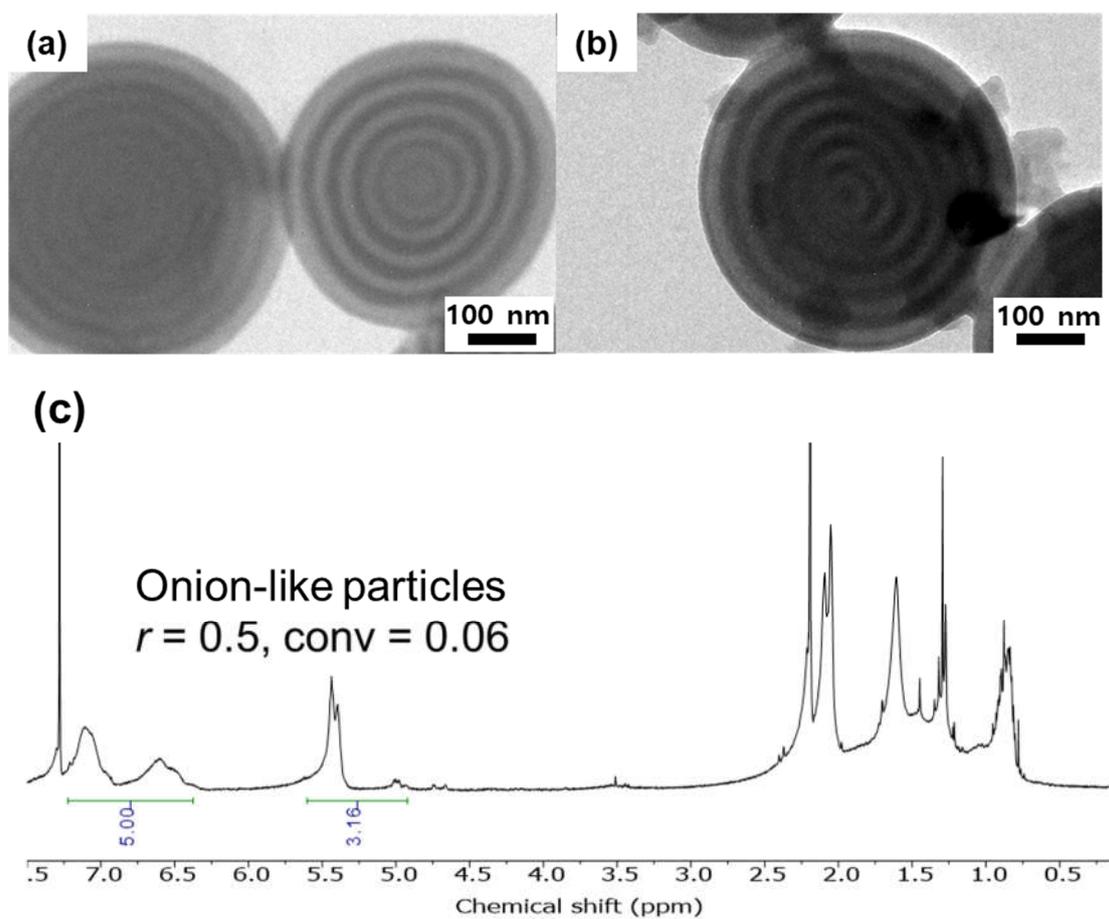


**Figure S2.** Magnified FT-IR spectra of PS<sub>34k</sub>-*b*-PB<sub>25k</sub> particles modified with MPA for a varying degree of  $r = 0, 0.1, 0.2, 0.5$ . Normalization to C–H signal from PS block on 2800–3000 cm<sup>-1</sup> shows a gradual

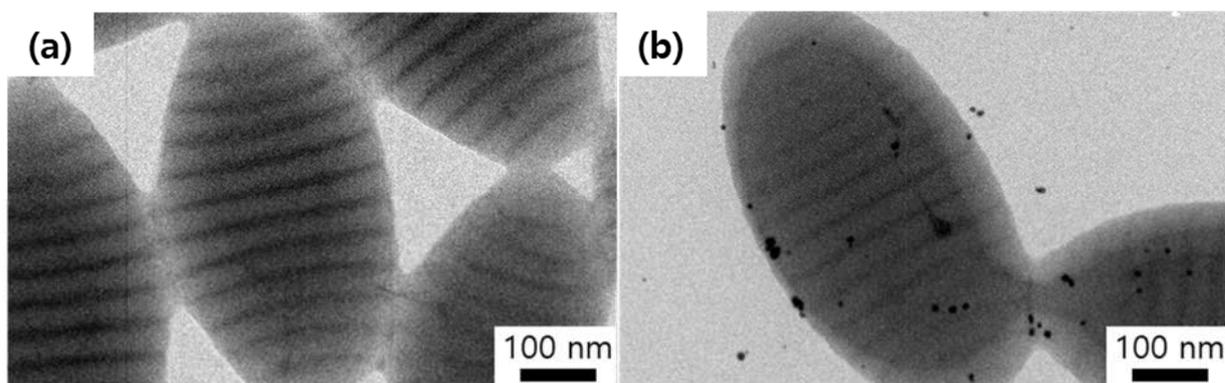
increase in signal intensity near 1722  $\text{cm}^{-1}$  corresponding to the carbonyl (C=O, purple) stretch from the carboxyl acid group.



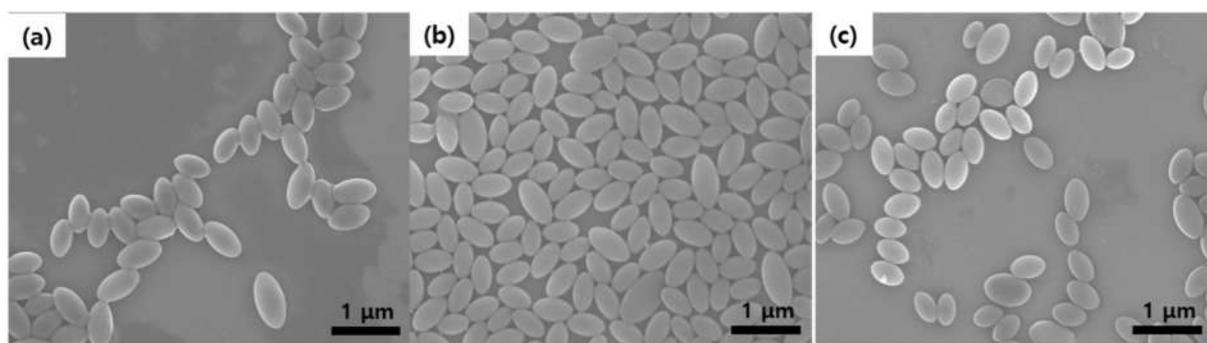
**Figure S3.** Full spectra of  $^1\text{H}$  NMR for MPA-modified  $\text{PS}_{34\text{k}}\text{-}b\text{-PB}_{25\text{k}}$  particles with  $r = 0, 0.1, 0.2,$  and  $0.5$ .



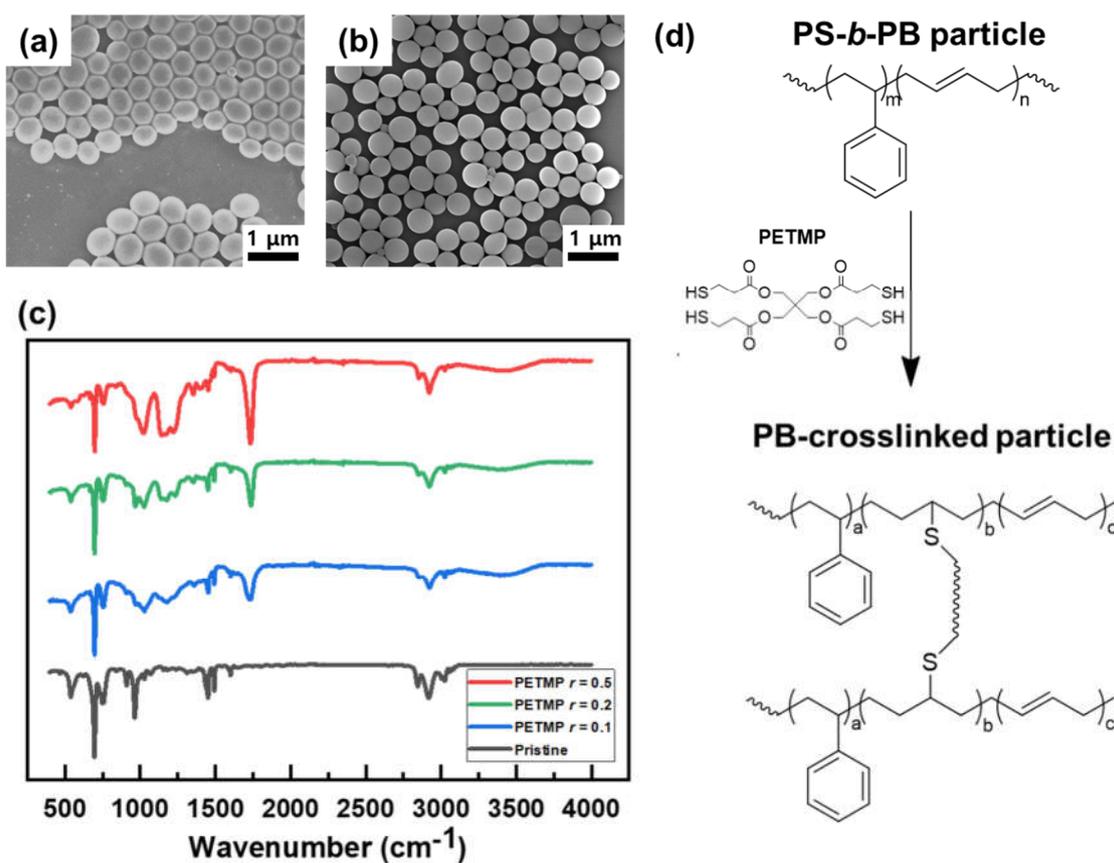
**Figure S4.** TEM images of (a) before and (b) after MPA modification of onion-like PS<sub>34k</sub>-*b*-PB<sub>25k</sub> particles, and (c) 1H NMR spectrum of modified onion-like particles showing minimal modification (low conversion of 0.06) even at high feed ratio of MPAs ( $r = 0.5$ ).



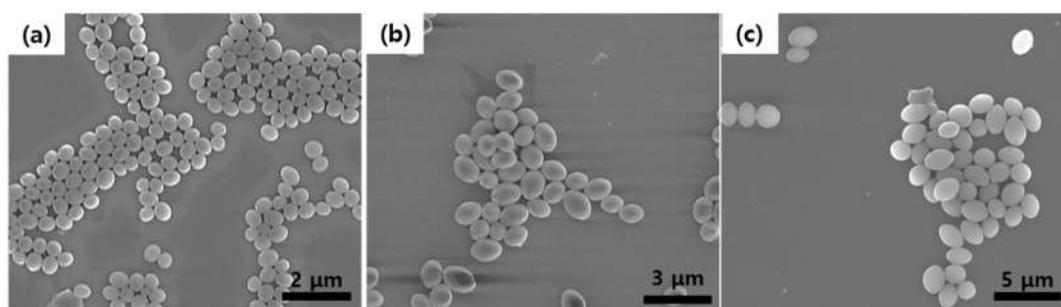
**Figure S5.** TEM image of MPA-modified PS<sub>34k</sub>-*b*-PB<sub>25k</sub> particles treated with (a) OsO<sub>4</sub> and (b) Au precursor (HAuCl<sub>4</sub>·3H<sub>2</sub>O) before TEM imaging.



**Figure S6.** SEM images of PS<sub>34k</sub>-*b*-PB<sub>25k</sub> particles after reacting with MPA under UV irradiation for (a) 1 h, (b) 2 h, (c) 3 h.



**Figure S7.** SEM image of (a) pristine PS<sub>34k</sub>-*b*-PB<sub>25k</sub> particle and (b) PETMP-modified particle ( $r = 0.5$ ). (c) FT-IR spectra comparing the pristine PS<sub>34k</sub>-*b*-PB<sub>25k</sub> particle (black) and PETMP-modified particle (blue). (d) Schematic showing the crosslinking of PB domains via PETMP having branched tetrathiol groups.



**Figure S8.** SEM images of PS<sub>34k</sub>-*b*-PB<sub>25k</sub> particles produced by membrane emulsification using different  $d_{pore}$ , where (a) 0.5, (b) 1.1 and (c) 2.1  $\mu\text{m}$  of pore size were used, respectively.