

Synthesis of Hybrid Silica Nanoparticles Densely Grafted with Thermo and pH Dual-Responsive Brushes via Surface-Initiated ATRP

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Scheme S1. Synthetic routine of the functional ATRP initiator, BPME.

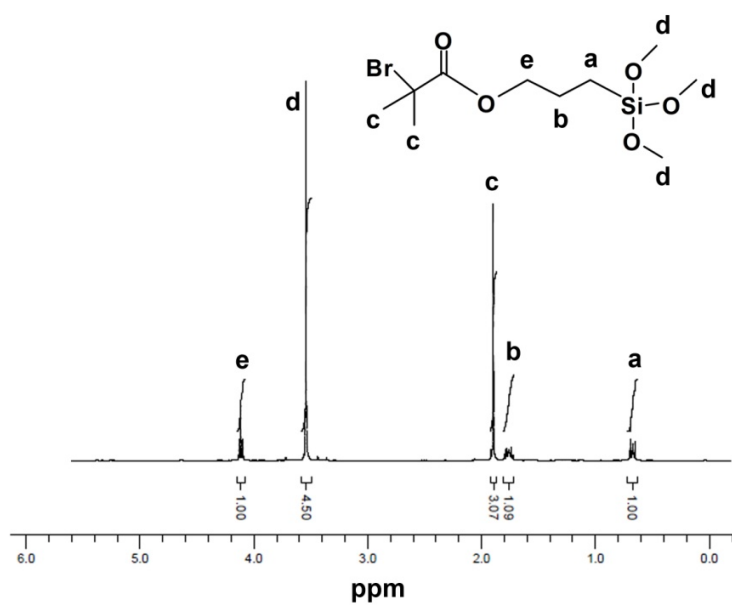
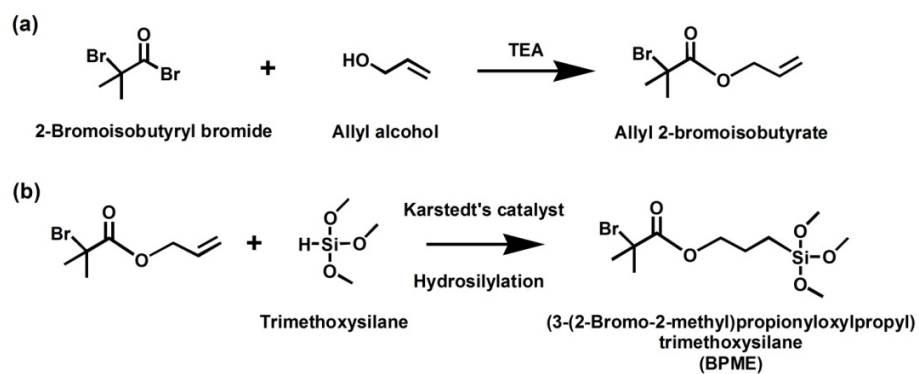


Figure S1. ^1H NMR spectrum of BPME in CDCl_3 .

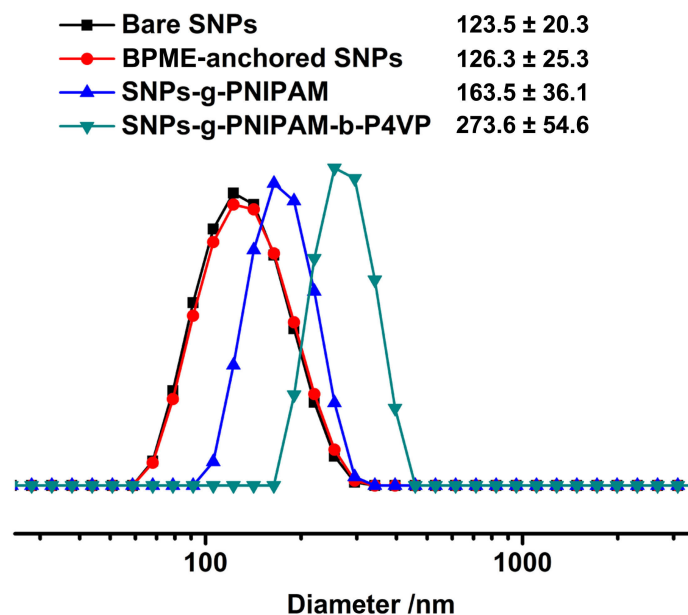


Figure S2. Particle size distribution from DLS analysis of bare SNPs, BPME-anchored SNPs, SNPs-g-PNIPAM, and SNPs-g-PNIPAM-b-P4VP. For SNPs-g-PNIPAM-b-P4VP, the chain extension time for the P4VP block is 10 h. The DLS measurements were conducted in isopropanol.

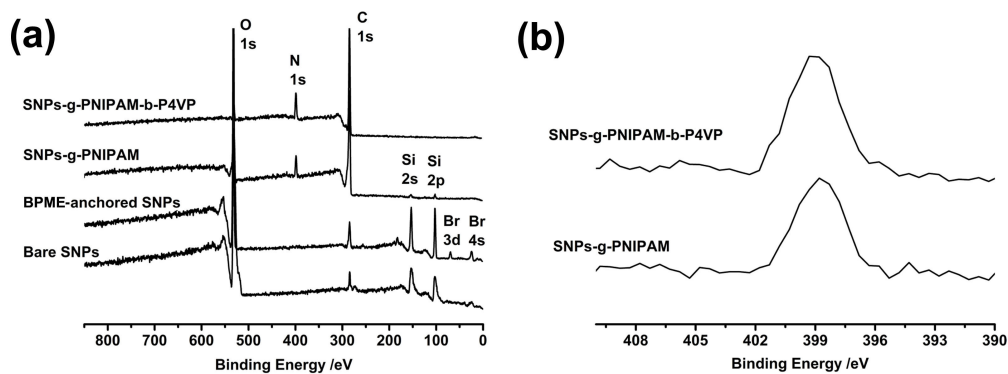


Figure S3. (a) Wide scan XPS spectra of bare SNPs, BPME-anchored SNPs, SNPs-g-PNIPAM, and SNPs-g-PNIPAM-b-P4VP. (b) N 1s XPS spectra of SNPs-g-PNIPAM and SNPs-g-PNIPAM-b-P4VP. For the SNPs-g-PNIPAM-b-P4VP, the chain extension time with 4VP is 10 h.

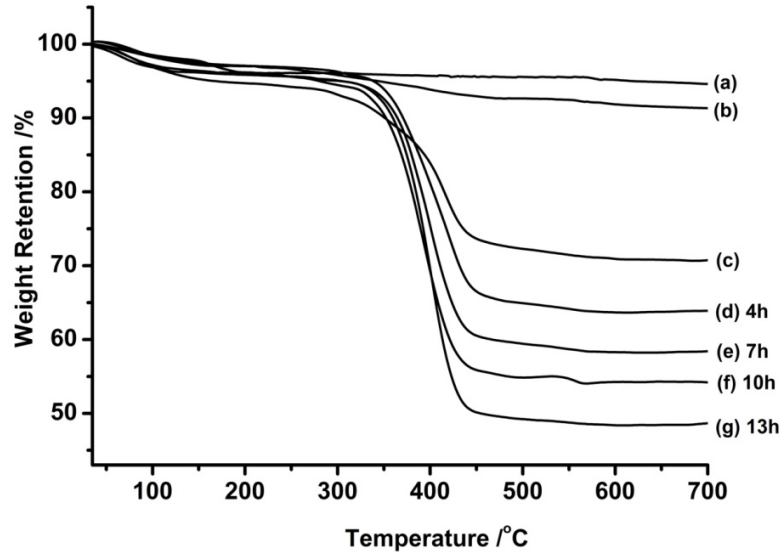


Figure S4. TGA analysis of (a) bare SNPs, (b) BPME-anchored SNPs, (c) SNPs-g-PNIPAM, and (d–g) SNPs-g-PNIPAM-b-P4VP at different chain extension times.

Calculation of the grafting density of BPME or polymers. The calculation of the grafting density of anchored BPME or polymers is shown below.

$$\frac{\left(\frac{W_{org}}{M_{org}}\right)N_A}{\left(\frac{W_{Inorg}}{\rho V_{particle}}\right)S_{particle}} \quad (S1)$$

Here, W_{org} and W_{Inorg} represent the weight loss percentage of the decomposed BPME or polymer and the residual weight percentage of the inorganic SNPs. N_A is the Avogadro's number. ρ is the density of bulk silica (2.0 g/cm³). $V_{particle}$ and $S_{particle}$ are the volume and the surface area of a single silica nanoparticle with an average diameter of 100 nm. For the calculation of the grafted density of the attached initiator, M_{org} is the molecular weight of the (3-(2-bromo-2-methyl)propionyloxypropyl) group from the anchored BPME. When calculating the grafting density of polymers, M_{org} is the molecular weight of the grown polymers obtained from MALDI-ToF mass analysis.

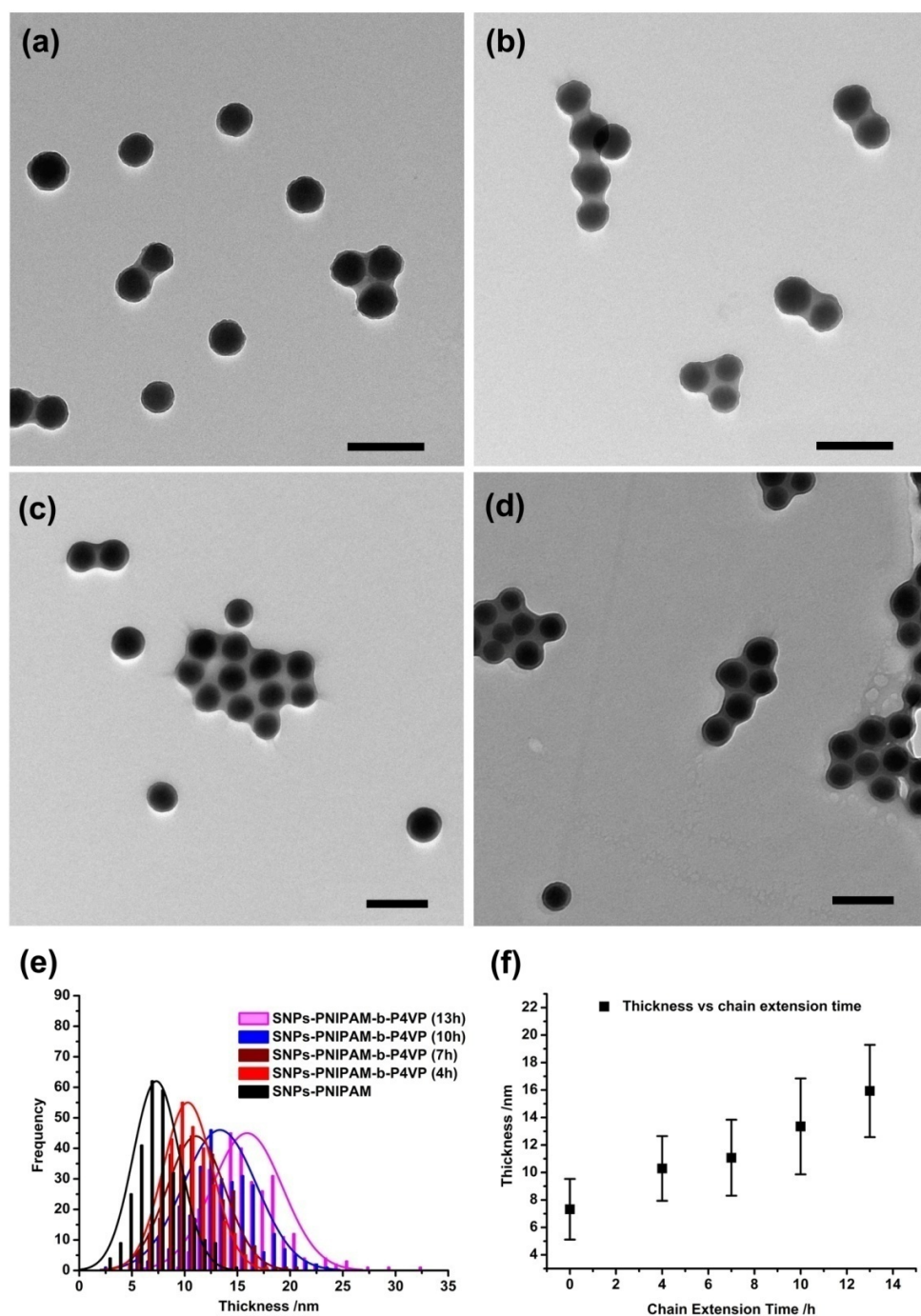


Figure S5. (a–d) TEM images of SNPs-g-PNIPAM-b-P4VP at different chain extension times with 4VP, (a) 4 h, (b) 7 h, (c) 10 h, and (d) 13 h. (e, f) Statistic data of the polymer shell thicknesses of SNPs-g-PNIPAM-b-P4VP according to different chain extension times in dry state. The thickness at 0 h refers to the PNIPAM shell thickness of SNPs-g-PNIPAM. All the scale bars are 250 nm.

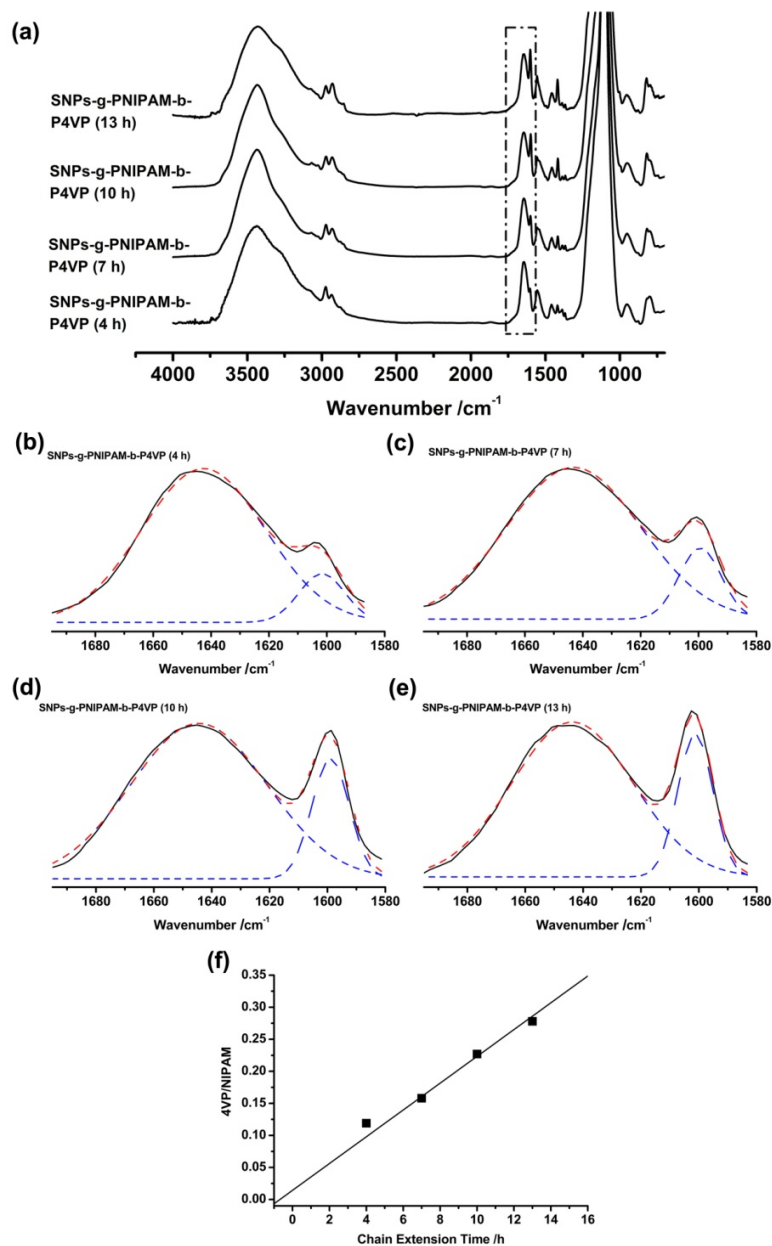


Figure S6. (a) FT-IR spectra of SNPs-g-PNIPAM-b-P4VP at different chain extension times with 4VP and (b–e) corresponding curve fittings in the range of 1690–1580 cm^{-1} . In (b–e), the black curves show the experimental data, while the fitted and split peaks are present in red and blue. The FT-IR band at 1690–1580 cm^{-1} belongs to the stretching vibration of the carbonyl group in NIPAM, while the band at 1620–1580 cm^{-1} is ascribed to the vibration of the pyridine ring in 4VP. (f) The integrated intensity ratio of the two characteristic bands from 4VP and NIPAM units at different chain extension times, which is propor-

tional to the content ratio of the two monomers in the polymer shell. The content ratio of 4VP to NIPAM unit gradually increases with the chain extension time, matching well with the consumption of 4VP monomer.

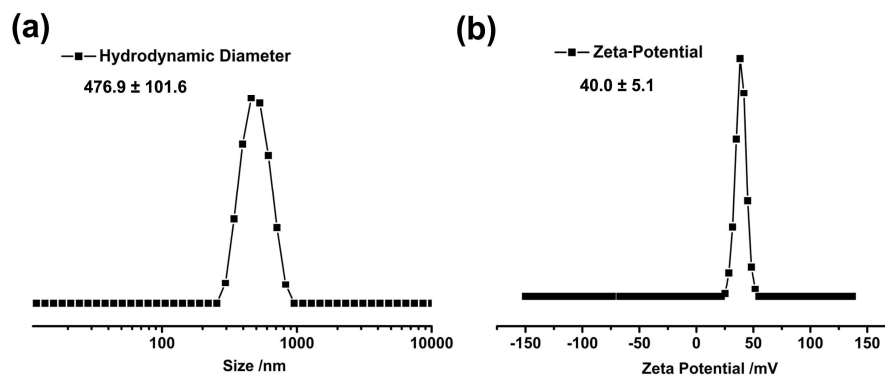


Figure S7. (a) Hydrodynamic diameter and (b) zeta-potential of SNPs-g-PNIPAM-b-QP4VP, demonstrating that the quaternized nanoparticles are well-dispersed in aqueous solution.

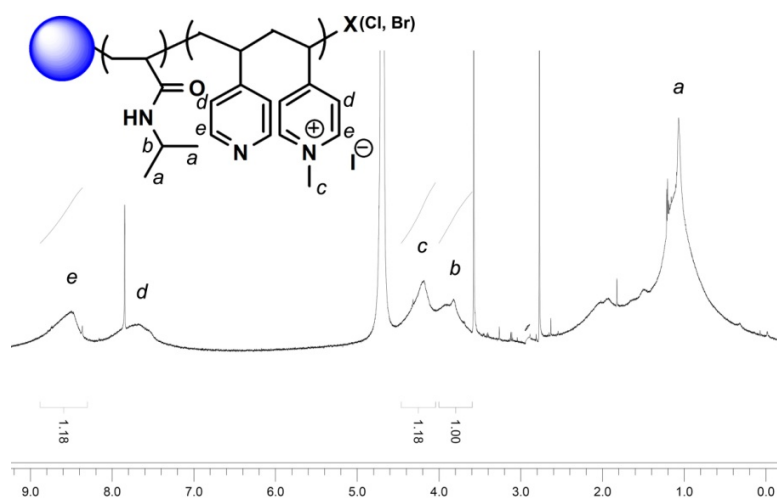


Figure S8. ^1H NMR spectrum of the synthesized SNPs-g-PNIPAM-b-QP4VP collected in D_2O . The quaternization of 4VP units was calculated as 66% by comparing the integral intensities of peak c and e.