

Supporting Information for:

A new strategy to synthesize well-defined PS brushes on silica particles by combination of lithium-iodine exchange (LIE) and surface-initiated living anionic polymerization (SI-LAP)

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Experimental section

Materials. Styrene (99%), ethanol (99%), ammonium hydroxide solution (28% NH₃), hydrofluoric acid (HF, 40%), tetraethoxysilane (TEOS, 99.9%), acetone, toluene, *n*-hexane, isopropanol, sodium iodide (NaI), diethyl ether and cyclohexane were purchased from China National Medicines Corporation Ltd. 3-Chloropropyltrimethoxysilane (CTS, 94%) was purchased from Aldrich. *tert*-Butyllithium (*tert*-BuLi, 1.6M in pentane) was purchased from Alfa Aesar. Styrene, TEOS, acetone, isopropanol and diethyl ether were dried over CaH₂ or NaH and distilled under reduced pressure prior to use. Toluene, *n*-hexane and cyclohexane were purified by a Braun system. All other reagents were used as received.

Synthesis of 3-Iodopropyltrimethoxysilane (ITS). ITS was prepared by incorporating dry sodium iodide (NaI) into commercially-available 3-chloropropyltrimethoxysilane (CTS, 94%, ¹H NMR (CDCl₃) of CTS: δ 3.65-3.55 (-OCH₃), 3.54-3.48 (-CH₂Cl), 1.9-1.8 (-CH₂), 0.8-0.7 (-Si-CH₂.) as previously reported.¹ The synthesis process was as follows: NaI (4.5 g, 30 mmol) and CTS (4.3 g, 20 mmol) were added to acetone (50 ml) and refluxed for 48 h at 50 °C under nitrogen. Subsequently, the solution was filtered and distilled under reduced pressure to get the

product (ITS). $^1\text{H NMR}$ (CDCl_3) of ITS: δ 3.65-3.55 (-OCH₃), 3.24-3.12 (-CH₂I), 1.9-1.8 (-CH₂), 0.8-0.7 (-Si-CH₂).

Synthesis and Chemical Modification of Silica Particles. The silica particles (SiPs) were synthesized by hydrolysis of TEOS with ammonia in a mixed solvent of ethanol and ultrapure water, according to the typical sol-gel method.² Ultrapure water (50 ml) and ethanol (200 ml) were added into a single-necked round-bottom flask (500 ml) equipped with a magnetic agitator and heated to 30 °C. TEOS (5 ml) was added into the solution under magnetic stirring at a speed of 300 rpm. Ammonia (5 ml) was dropwise added after 10 min to the flask while stirring. Subsequently, the mixture was stirred at a speed of 500 rpm for 6 h, purified by centrifugation and redispersion three times using ethanol to get the SiPs powders with a mean diameter of 200 nm ultimately. The powders were stored in a vacuum drying oven at 60 °C.

The above-obtained SiPs powders (3 g) were redispersed in 50 ml of fresh anhydrous toluene while stirring. 5 ml ITS were quickly injected into the solution at 60 °C for 1 h, and then stirred under dry nitrogen at 110 °C for 12 h and cooled to room temperature.³ The resultant ITS-modified silica particles ($\text{SiO}_2\text{@ITS-12h}$) were separated by centrifugation and redispersion three times with toluene to remove the excess ITS. The above operation was repeated again with reaction time of 24 h to obtain the $\text{SiO}_2\text{@ITS-24h}$. The iodine-functionalized silica particles ($\text{SiO}_2\text{@ITSS}$) were finally stored in a vacuum drying oven at 80 °C.

Lithium-Iodine Exchange (LIE) and Surface-Initiated Living Anionic Polymerization (SI-LAP) of PS from $\text{SiO}_2\text{@ITS}$. Both the LIE and SI-LAP procedure were conducted under an atmosphere of dry, deoxygenated nitrogen. At the first step, $\text{SiO}_2\text{@ITSS}$ (2 g) was added to a mixed solvent of *n*-hexane (18 ml) and diethyl ether (2 ml) by stirring for 2 h at -78 °C. Then the reaction of LIE was conducted by adding 2.1-2.2 molar equivalent (relative to Si-I groups) of commercial tert-butyllithium (*tert*-BuLi, 1.6 M) to the mixture, stirred at a speed of 800 rpm for 6 h when the temperature was stable. At last, the mixture was warmed to room temperature and kept for 2 h to remove the residual *tert*-BuLi which was consumed by rapid proton abstraction from diethyl ether⁴ after the reaction was finished.

The above-obtained suspension (after clearing the supernate) was divided into four parts and added into cyclohexane (100 ml) separately, preparing for anionic polymerization. The SI-LAP was started by adding designed amount of styrene monomer to each reaction system quickly to react for 8 h, 16 h, 24 h and 32 h, respectively. The SI-LAP was quenched by trace amounts of isopropanol at the end. The hybrid particles were purified by centrifugation/redispersion three times using toluene, dried at 60 °C under a vacuum to generate eight

hybrid particles ($\text{SiO}_2@\text{PSs}$) samples with various PS brushes. The resultant products were nominated as $\text{SiO}_2@\text{ITS-xh}@\text{PS-yh}$, here “x” is the reaction time between SiPs and ITS, and “y” is the polymerization time of styrene. For example, $\text{SiO}_2@\text{ITS-24h}@\text{PS-16h}$ means the product synthesized by modified SiPs through the reaction with ITS for 24 h, following by LIE and the polymerization of styrene for 16 h.

Cleavage of $\text{SiO}_2@\text{PSs}$ hybrid particles. All the $\text{SiO}_2@\text{PSs}$ hybrid particles (8.71 g) were put into an aqueous HF solution with 5 vol% HF (a mixed solution of hydrofluoric acid (HF, 10 ml) with ultrapure water (70 ml)) to perform the cleavage of grafted PS brushes. The mixtures were stirred for 4 h at room temperature. The cleaved polymer brushes were obtained through filtration by using a 0.2 μm syringe filter and then dried in the air.

Preparation of PS Film Composites Containing $\text{SiO}_2@\text{PS}$ Hybrid Particles. The raw SiPs (0.263 g) and $\text{SiO}_2@\text{ITS-24h}@\text{PS-32h}$ hybrid particles (0.375 g, the content of PS brush accounts for 28.3 wt %) were implanted in 5 g PS matrixes by dissolving in toluene at room temperature. After stirring well, the mixtures were sonicated for 1 h, cast onto three watch-glass plates, dried in air and dried in a vacuum oven at 80 °C for 24 h to get rid of residual solvents, respectively. At last, the relative smooth and flat films of uniform thickness (1 mm) were cured by hot-pressing at 180 °C for 10 min.

Characterization

Transmission Electron Microscope (TEM). TEM observations were conducted on a JEM-1011 transmission electron microscope at an acceleration voltage of 100 kV. Ultrathin sections were cut using a Leica Ultracut and a glass knife at room temperature. The samples were collected on carbon-coated copper TEM grids.

High-Resolution Transmission Electron Microscope (HRTEM). HRTEM observations were done on a FEI Tecnai G2 S-Twin transmission electron microscope operating at 200 kV.

Nuclear Magnetic Resonance (NMR) Spectra. ^1H NMR spectra were performed on a Bruker AV400 MHz spectrometer using CDCl_3 as the solvent.

X-ray Photoelectron Spectroscopy (XPS). XPS was carried out on a VG ESCALAB MK II spectrometer using an Al K α exciting radiation from an X-ray source operated at 10.0 kV and 10 mA.

Thermal Gravimetric Analysis (TGA). TGA was performed on an SDTQ600 (TA Instruments) in the range from room temperature to 800 °C under air flow at a heating rate of 10 °C /min.

SEC-MALLS. Weight-average molecular weights (M_w) and polydispersity indices (PDI) were measured by size exclusion chromatography (SEC). The SEC-MALLS consisted of a Model 1500 Digital HPLC pump, a DAWN

HELEOS II (Wyatt multi-angle LS detector, GaAs 662.0 nm), an Optilab T-rEX (Wyatt RI detector, LED light 658.0 nm) and a viscosity detector (ViscoStar, Wyatt Technology). This instrument had a protected MZ-Gel SD *plus* 50×0.8 mm column (10²Å pore size) and two MZ-Gel SD *plus* 300×8.0 mm columns (10³ and 10⁵Å pore size). For all SEC analyses, HPLC grade tetrahydrofuran was used as the mobile phase at 25 °C (flow rate: 1 mL min⁻¹). The increments (dn/dc) of samples were measured based on the calibration constant of the RI detector and the concentration of samples. Data acquisition was performed using Wyatt Technology WinAstra6 software.

Graft Density Calculations (D_s). The graft density (D_s , chains/nm²) of PS brushes may be calculated according to eq 1 from the molecular weight (M_n , g/mol), graft amount (W), surface area (S), and Avogadro's number (N_a , molecules/mol).

$$D_s = (W \phi N_a) / (M_n \phi S) \quad \text{eq (1)}$$

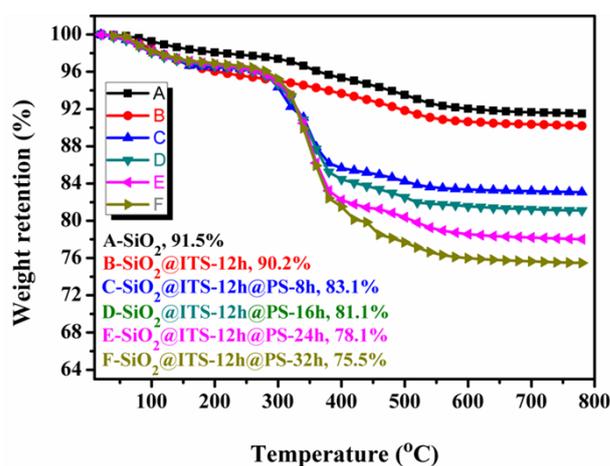


Figure S1. TGA curves: A-SiO₂, B-SiO₂@ITS-12h, (C, D, E, F)-SiO₂@ITS-12h@PSs hybrid particles.

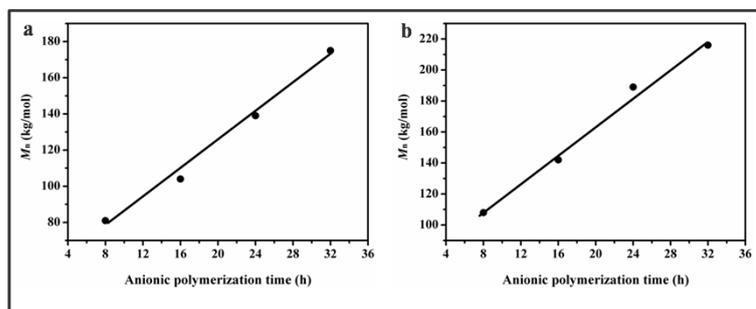


Figure S2. Number-average molecular weights (M_n) of grafted PS brushes of (a) SiO₂@ITS-12h@PSs, (b) SiO₂@ITS-24h@PSs as a function of anionic polymerization time.

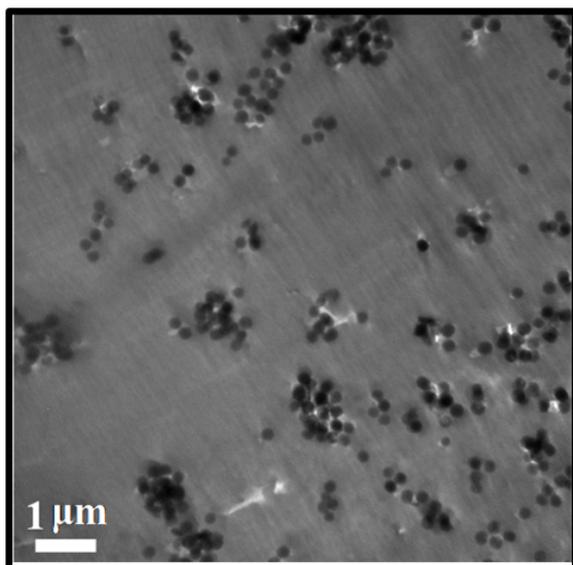


Figure S3. TEM images of PS/SiPs composite containing 5 wt% raw SiPs.

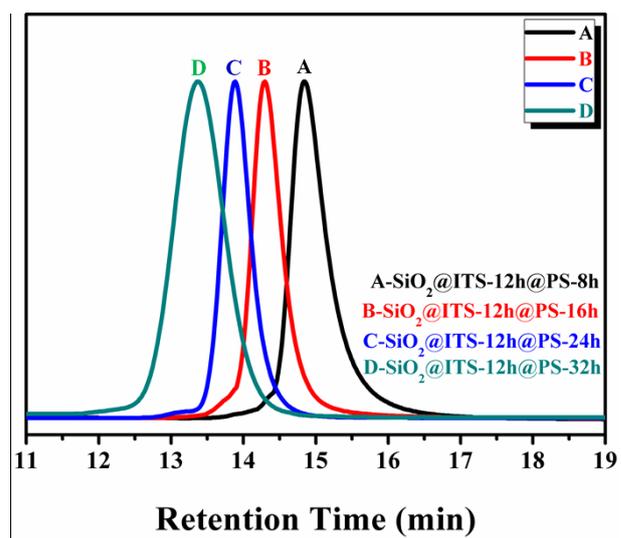


Figure S4. SEC-MALLS curves of grafted PS brushes of SiO₂@ITS-12h@PSs.

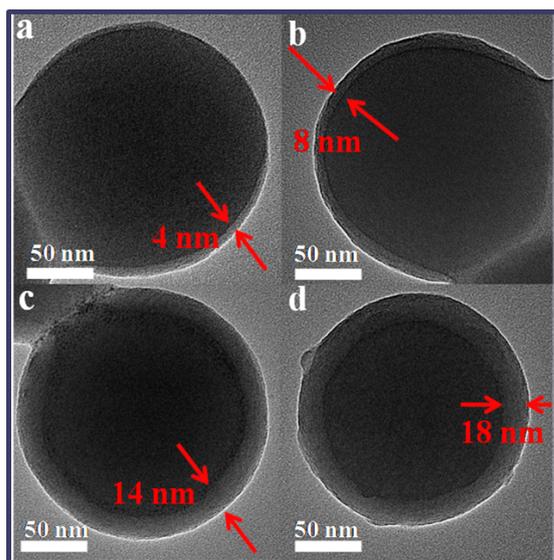


Figure S5. HRTEM images of hybrid particles: (a) $\text{SiO}_2@ITS-12h@PS-8h$, (b) $\text{SiO}_2@ITS-12h@PS-24h$, (c) $\text{SiO}_2@ITS-24h@PS-16h$, (d) $\text{SiO}_2@ITS-24h@PS-24h$.

References:

- 1 B.L. Booth, G.C. Ofunne, C. Stacey, P.J.T. Tait, *J. Org. Chem.*, **1986**, *315*, 143.
- 2 W. Stöber, A. Fink, Bohn, A. J. *Colloid Interface Sci.*, **1968**, *26*, 62.
- 3 M. Wählander, F. Nilsson, E. Larsson, W. Tsai, H. Hillborg, A. Carlmark, U. W. Gedde, E. Malmström, *Polymer*, 2014, *55*, 2125.
- 4 T. F. Bates, M. T. Clarke, R. D. Thomas, *J. Am. Chem. Soc.*, 1988, *110*, 5109.