Electronic Supplementary Information

One-pot Synthesis of Nanomaterials via RAFT Polymerization Induced Self-assembly and Morphology Transition

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Experimental

Materials : Styrene (St) (Shanghai Chem. Co.) was washed with an aqueous solution of sodium hydroxide (5 wt %) three times, and then washed with water until neutralization. After dried with anhydrous magnesium sulfate, St was distilled under reduced pressure. 4-Vinylpyridine (4VP, Acros, 96%) was dried over CaH_2, and then was distilled under reduced pressure prior to use. The 2,2'-azobisisobutyronitrile (AIBN) was purified by recrystallization from ethanol. All other reagents with analytical grade were used as received.

Synthesis of S-1-dodecyl-S-(α,α'-dimethyl-α''-acetic acid) trithiocarbonate (TC): TC was synthesized in yield of 78.4% according to reference 1. ^{1}HNMR, δ(TMS, ppm): 0.90 (t, 3H, $-C\boldsymbol{H}_3$), 1.37-1.47 (m, 20H, $-(C\boldsymbol{H}_2)_{10}-$), 1.75 (s, 6H, $2-C\boldsymbol{H}_3$), 3.42 (t, 2H, $-C\boldsymbol{H}_2S$), 13.05 (s, 1H, $-COO\boldsymbol{H}$).

Preparation of TC-terminated poly(4-vinylpyridine) (P4VP-TC): The general procedure is as follows. 4VP (2.12 g, 20 mmol), TC (36 mg, 0.1 mmol), isopropanol (2 mL) and AIBN (2 mg, 0.01 mmol) with the molar ratio of 4VP: TC: AIBN= 2000: 10: 1, were added into a 10 mL polymerization tube with a magnetic bar. After three freeze-evacuate-thaw cycles, the tube was sealed under high vacuum, and then the sealed tube was placed in an oil bath at 80 °C while stirring. After 6 h of polymerization, the tube was cooled to room temperature with ice-water, and then the tube was opened. The polymer was precipitated by pouring a polymer solution in isopropanol into excess diethyl ether while stirring. The precipitate obtained by filtration was dried in a vacuum oven at room temperature overnight, 1.08 g of the product was obtained, and the conversion measured by ^{1}H NMR method was 50%. Its ^{1}H NMR spectrum is shown in **Figure S7B**.

RAFT polymerization of St using P4VP-TC as macro chain transfer agent: A typical procedure is as follows. The P4VP-TC (0.106 g, 0.01 mmol), St (1.05 g, 10 mmol), AIBN (0.2 mg, 1 μmol) and methanol (1 mL) were successively added into a 5 mL glass tube with a magnetic bar, and then the system was degassed by three freeze-pump-thaw cycles. The tube was sealed under vacuum, and then the sealed tube was placed in an oil bath at 80^{o}C while stirring. After polymerization was carried out for 6 h, the reaction mixture was cooled to room temperature with ice-water and then the tube was opened. The polymer was precipitated by pouring a polymer solution in isopropanol into excess petroleum ether while stirring. The precipitate was collected by filtration, and then dried in a vacuum oven at room temperature overnight, 0.65 g of the product was obtained, and the conversion was 52%.

For preparation of nanorods, St (5.20 g, 50 mmol), P4VP (106 mg, 1 × 10^{-2} mmol) and AIBN (0.20 mg, 1 × 10^{-3} mmol) were dissolved in 3.5 g methanol, the resultant solution was equally divided into 5 portion and every portion was placed in a 5 mL polymerization tube. The same procedure described above was carried out, and the polymerizations were performed at 80^{o}C for 2 h, 4 h, 12 h, 24 h and 48 h, respectively.

For studying the kinetics of RAFT dispersion polymerization, the P4VP-TC, St, AIBN with their feed molar ratio = 10: 50000: 1 were added into methanol in six 5 mL glass tubes respectively. The polymerizations were carried out at the same conditions mentioned above, and then stopped at 0.5 h, 1 h, 2 h, 4 h, 6 h and 8 h respectively. After the polymerization, the solution was treated with the same procedure mentioned above; the white powder products were obtained. The relationship of molecular weights with polymerization time, and GPC traces of the block copolymers obtained at different times are shown in **Figure S6**. Their ^{1}H NMR spectra were measured for calculation of St conversion. Conversion = (104/105) × (W_{P4VP}/W_{St}) × $[(I_{6.3}-I_{8.34})/I_{8.34}]$, where 104 and 105 are the molecular weights of 4VP and St, W_{P4VP} and W_{St} are the weights of P4VP and St added, $I_{6.3}$ and $I_{8.34}$ are the integral values of the proton signals at δ=6.18~6.82 ppm and at 8.34 ppm, respectively, and then conversion was plotted against polymerization time for estimation of critical chain length degree of PS at phase separation.

For preparation of vesicles, the same procedure and conditions with preparation of nanorods were adopted. Every polymerization tube contained St (2.08 g, 20 mmol), P4VP (21.2 mg, 2 × 10^{-3} mmol), AIBN (0.033 mg, 2 × 10^{-4} mmol) and methanol (1.1 g), and the polymerizations with the same procedure were performed at 80^{o}C for 2 h, 4 h, 12 h and 24 h, respectively.

Characterization

Nuclear Magnetic Resonance (NMR) Spectra. The ^{1}H NMR (300 MHz) measurements were performed on Bruker DMX300 spectrometer in D_2O or in $CDCl_3$ using tetramethylsilane as an internal reference.

Gel permeation chromatography (GPC). The molecular weight and molecular weight distribution were determined on a Waters 150C gel permeation chromatography (GPC) equipped with three ultrastyragel columns (500, 10^3, 10^4Å) in series and RI 2414 detector at 30 °C, and THF was used as eluent at a flow rate of 1.0 mL/min. Monodispersed polystyrene standards were used in the calibration of molecular weight and molecular weight distribution.

Field Emission Scanning Electron Microscopy. The field-emission scanning electron microscope (FESEM) images were measured on a JEOL JSM-6700F. The samples were prepared by placing a drop of the polymer solution in ethanol on copper grids, and gilding a shell of Pt nano-particle.

Transmission Electron Microscopy. The transmission electron microscope (TEM) observations were performed on a Hitachi H-800 TEM at an accelerating voltage of 200 kV. The samples for TEM observations were prepared by depositing a drop of the polymer solution in methanol on copper grids.

Laser light scattering. The Laser light scattering (LLS) studies were conducted with a modified commercial LLS spectrometer (ALV/SP-125) equipped with an ALV-5000 multi-τ digital time correlator and a solid-state laser (ADLAS DPY42511, out power was ~400 mW at λ= 532 nm) at a fixed scattering angle (θ) of 15° with both cumulants and CONTIN software. Static light scattering (SLS) studies were conducted at 25 °C using the same instrument at scattering angles ranging from 15° to 135°. The radius of gyration (R_g) data was obtained using standard Zimm plot analyses.

References

1. Lai, J. T.; Filla, D.; Shea, R. *Macromolecules* **2002**, *35*, 6754-6756.

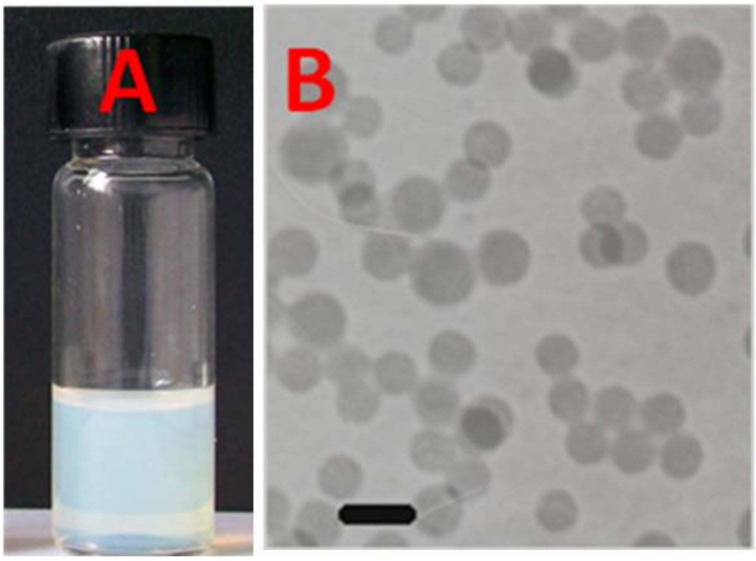

Figure S1. The optical digital photo (A) of the polymerization system and TEM image (B) of the aggregates formed from RAFT polymerization in methanol with a feed molar ratio of P4VP-TC/St/2,2’-azobisisobutyronitrile (AIBN) =10:5000: 1 and a St concentration of 9 wt% at 80 ^{o}C for 24 h.

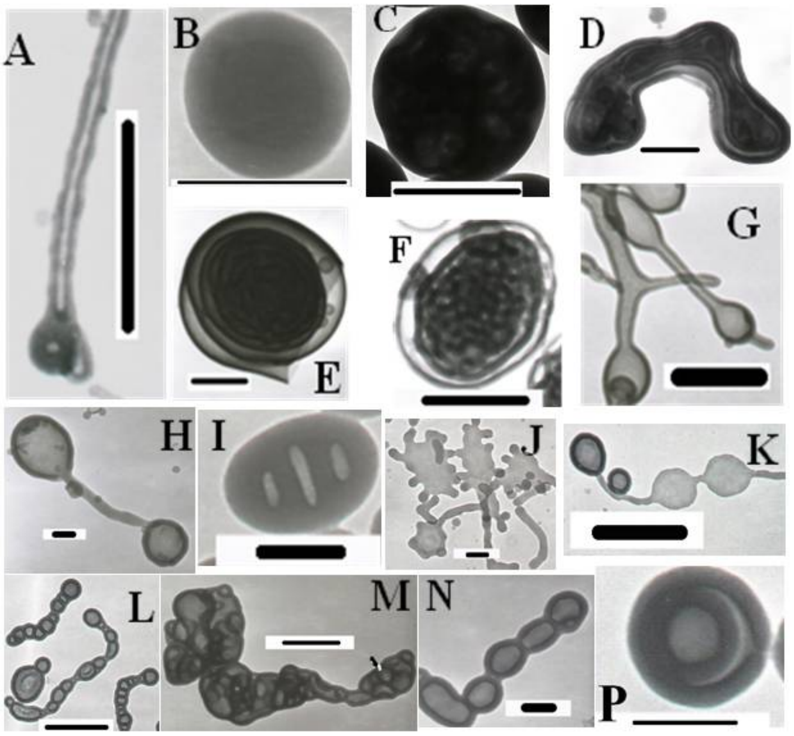

Figure S2. TEM images of multiple morphologies were prepared by RAFT polymerization at 80 ^{o}C for 24 h, A-D: the feed molar ratio of P4VP-TC/St/AIBN= 10/200000/1 in methanol (P4VP-TC: 5 mg; methanol: 0.5~1g); E-H: the feed molar ratio of P4VP-TC/St/AIBN = 10/100000~200000/1 in methanol (P4VP: 10 mg; methanol: 0.5~1g); I-P: P4VP-TC/St/AIBN= 10/50000-150000/1 in methanol (P4VP-TC: 20 mg; methanol: 0.5~1g); The scale bar is 1000 nm, except 200 nm for B, H, J, L, N and P.

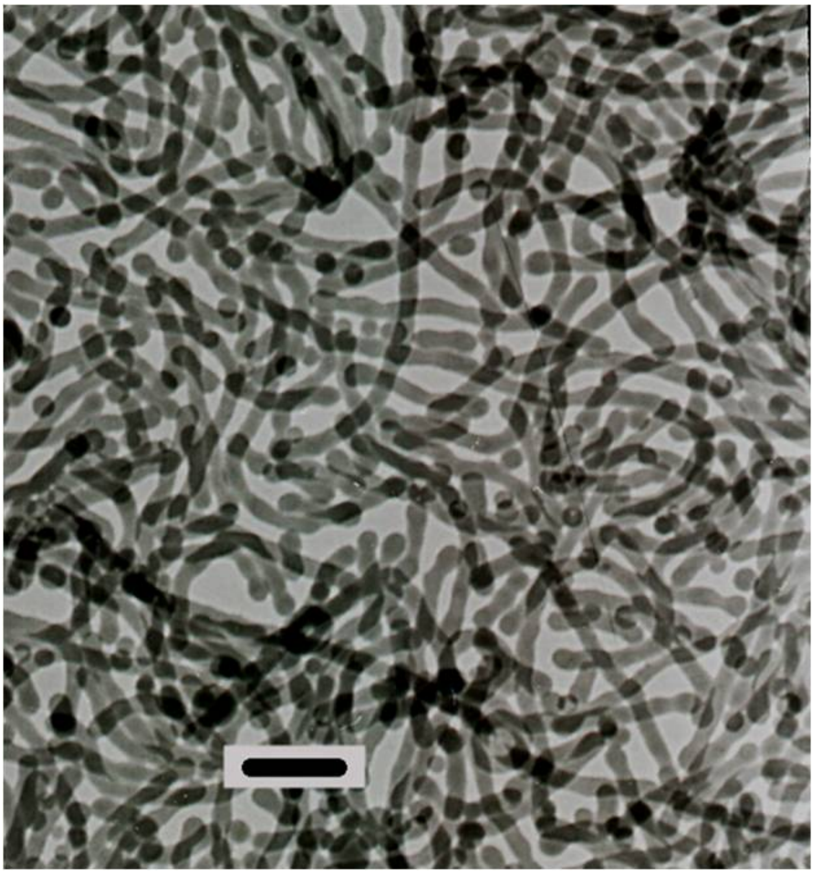

Figure S3. TEM image of the polymer nanorods prepared by RAFT polymerization with a feed molar ratio of P4VP/St (1 g) /AIBN= 10: 50000: 1 in methanol (0.7 g) at 80 ^{o}C for 24 h of polymerization. The scale bar is 500 nm.

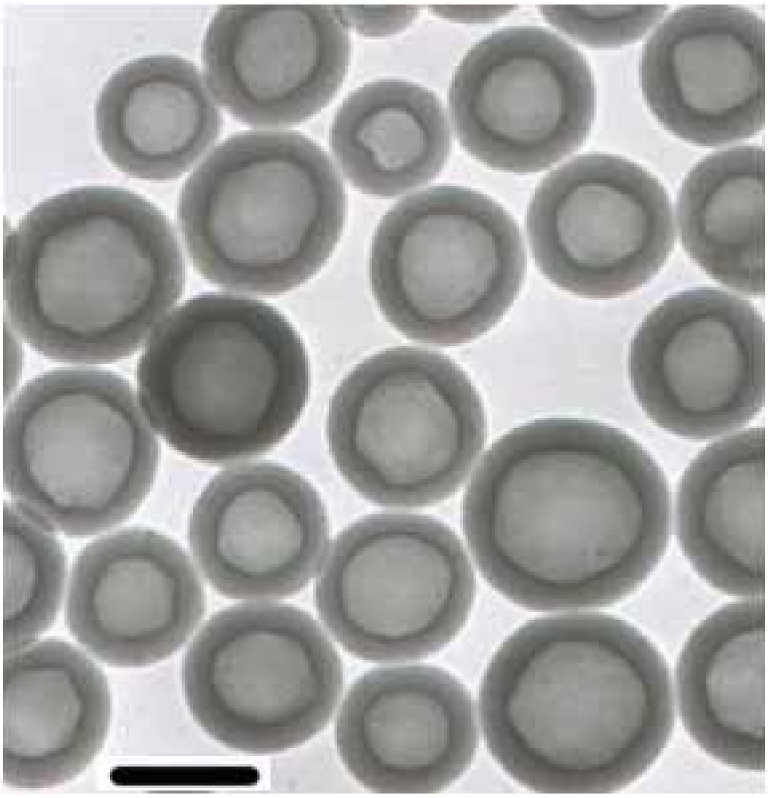

Figure S4. FETEM image of the polymer vesicles prepared by RAFT polymerization with a feed molar ratio of P4VP/St (2 g) /AIBN= 10: 100000: 1 in methanol (1.1 g) at 80 ^{o}C for 24 h. The scale bar is 400 nm.

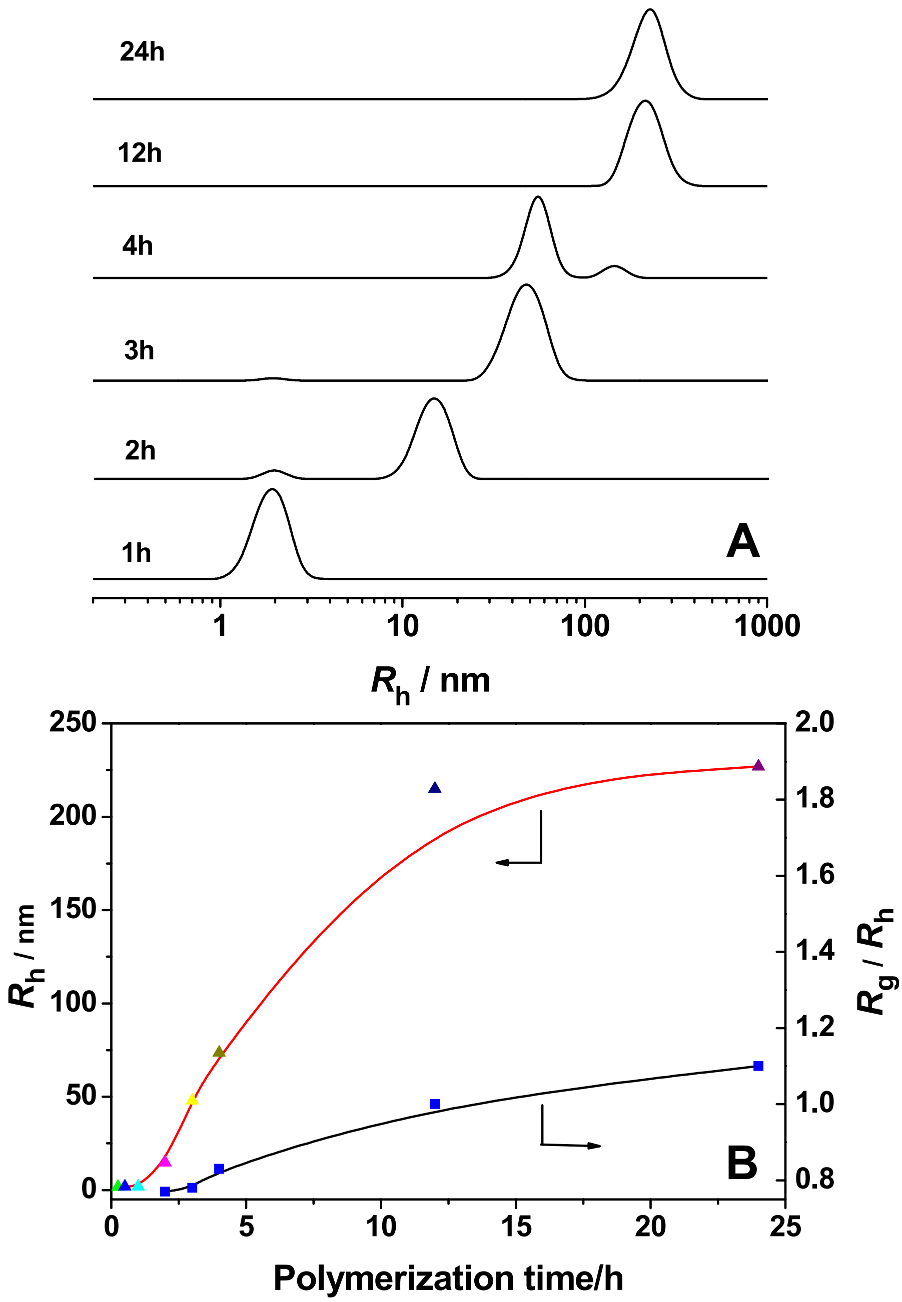

Figure S5. A: The LLS results at different polymerization time; B: The relationship of hydrodynamic radius (R_h) and the ratio of gyration radius to hydrodynamic radius (R_g/R_h) with the polymerization time at a feed molar ratio of P4VP/St/AIBN= 10: 100000: 1 in methanol (St: 2 g; methanol: 1.1 g) at 80 ^{o}C for different polymerization time.

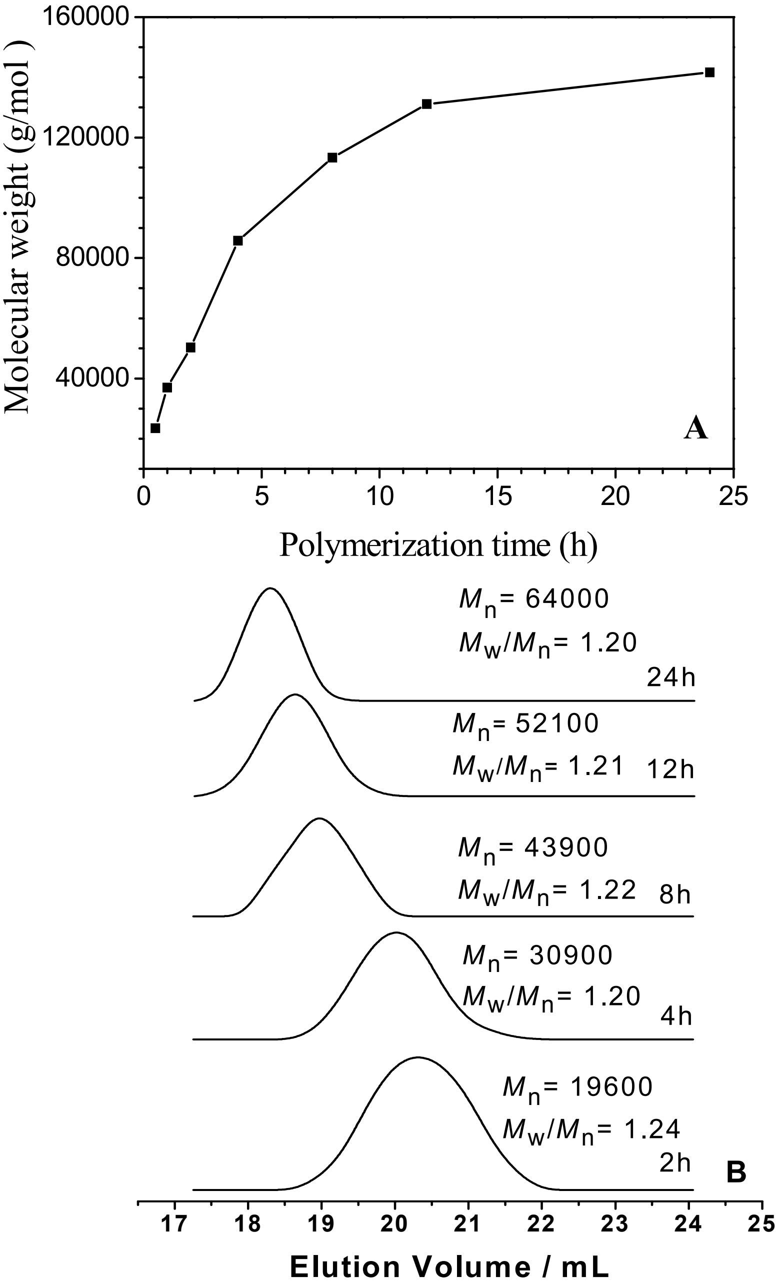

Figure S6. A: The relationship of molecular weights with the polymerization time and B: GPC traces of the block copolymers obtained from RAFT polymerization with a feed molar ratio of P4VP/St/AIBN= 10: 50000: 1 in methanol (St: 1 g; methanol: 0.7 g) at 80 °C for different polymerization time.s

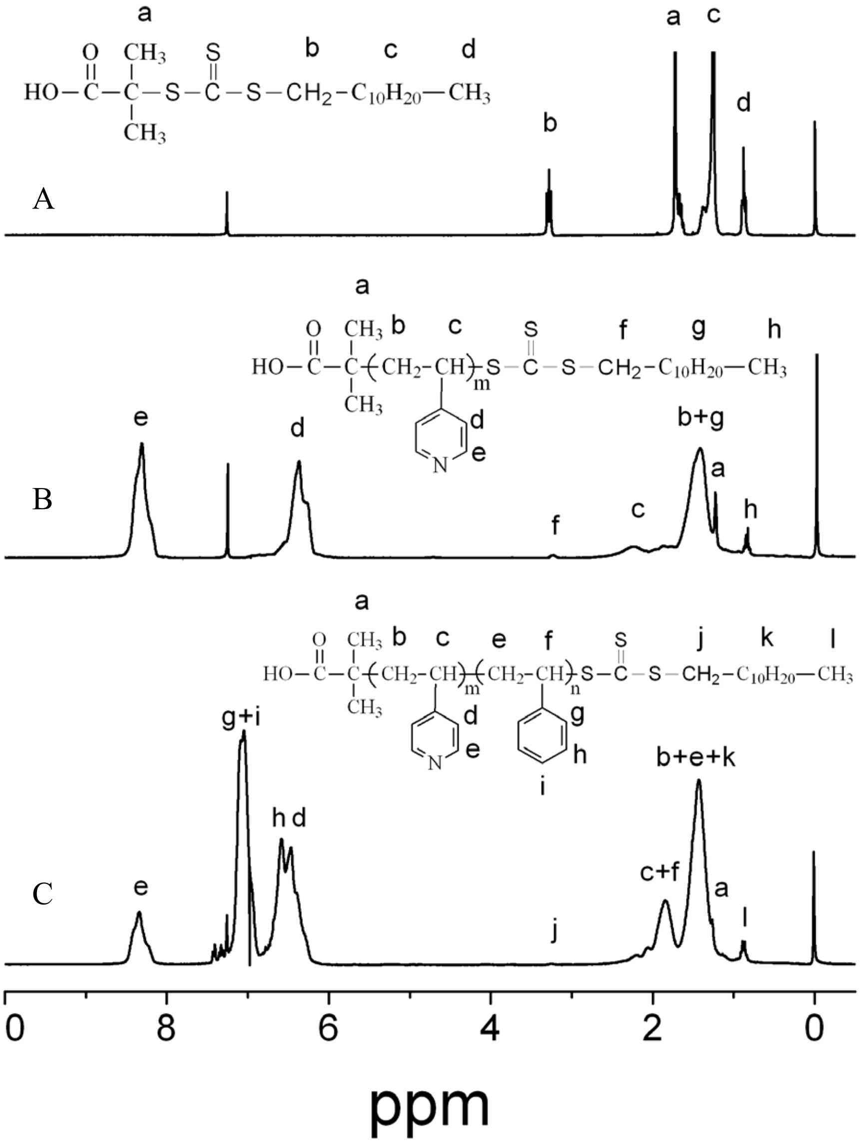

Figure S7. ^{1}H NMR spectra of A: S-1-dodecyl-S-(α,α’-dimethyl-α’’-acetic acid)trithiocarbonate (TC); B: TC-terminated poly(4-vinylpyridine) (P4VP-TC); C: Block copolymer, P4VP-*b*-PS prepared by RAFT polymerization of styrene (St) with a feed molar ratio of P4VP-TC/St (1 g) /AIBN=10/50000/1 in methanol (0.7 g) at 80°C for 2 h.