

Preparation and Morphology Control of Block Copolymer/Metal Salt Hybrids via Solvent-Casting by Using a Solvent with Coordination Ability

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Synthesis of polystyrene-*b*-poly(4-vinylpyridine) (PS-P4VP)

PS-P4VP was synthesized via RAFT polymerization by using the monofunctional chain transfer agent (S-1-dodecyl-S'-(α,α' -dimethyl- α' -acetic acid) trithiocarbonate) (Scheme 1). Both styrene and 4-vinylpyridine were purified by passing through an aluminum oxide column before use. Styrene (50.0g, 0.481 mol) was polymerized with a monofunctional CTA (0.351 g, 0.962 mmol) in bulk at 130 °C for 345 min as the first step. After deactivation of the macro-CTA with liquid nitrogen, PS-macro-CTA was purified with reprecipitation into methanol three times (M_n = 28000, PDI = 1.17). Then, 4-vinylpyridine (4VP) (19.7 g, 0.187 mol) was polymerized with AIBN (8.8 mg, 0.054 mmol) from the PS-macro-CTA (5.0 g, 0.178 mmol) at 70 °C in bulk for 80 min. After deactivation with liquid nitrogen, PS-P4VP was purified with reprecipitation into hexane multiple times (M_n = 37000, PDI = 1.24).

Size Exclusion Chromatography (SEC)

SEC was performed to measure polydispersity of a PS precursor and a PS-P4VP block copolymer by using three TSK-GEL G4000H_{HR} columns combined with a DP-8020 dual pump and a UV detector (Tosoh Corp.). The eluent was dimethylformamide (DMF) and the flow rate was 1 ml/min. A calibration curve by polystyrene standards was basically used for all the measurements to estimate the PDIs.

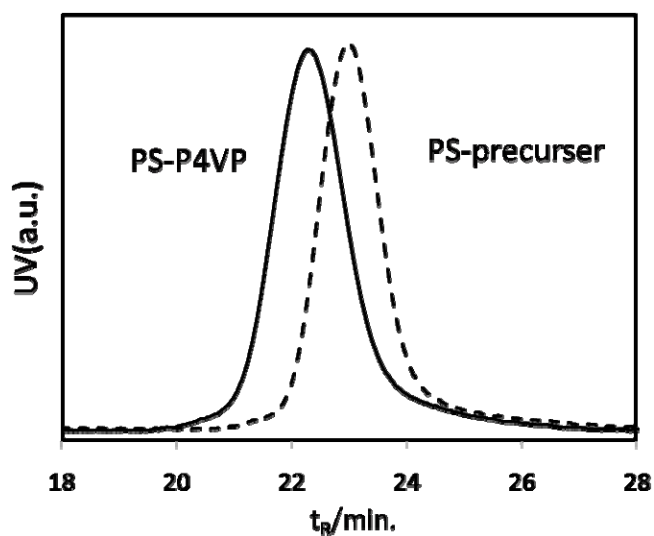


Figure S1. SEC chromatograms of a PS-P4VP block copolymer (solid line) and a PS precursor (dashed line).

¹H NMR

The molecular weight of a PS precursor was determined by ¹H NMR spectroscopy (Varian), by comparing the integral of peaks at 3.2 ppm from two protons at the end of the polymer adjacent to the CTA residue (S-C(=S)-S) with the integral of the peaks for the backbone (Figure S2). ¹H NMR was also used to measure the mole ratio of PS-P4VP (Figure S3). The solvent used for these experiments was deuterated chloroform (CDCl₃).

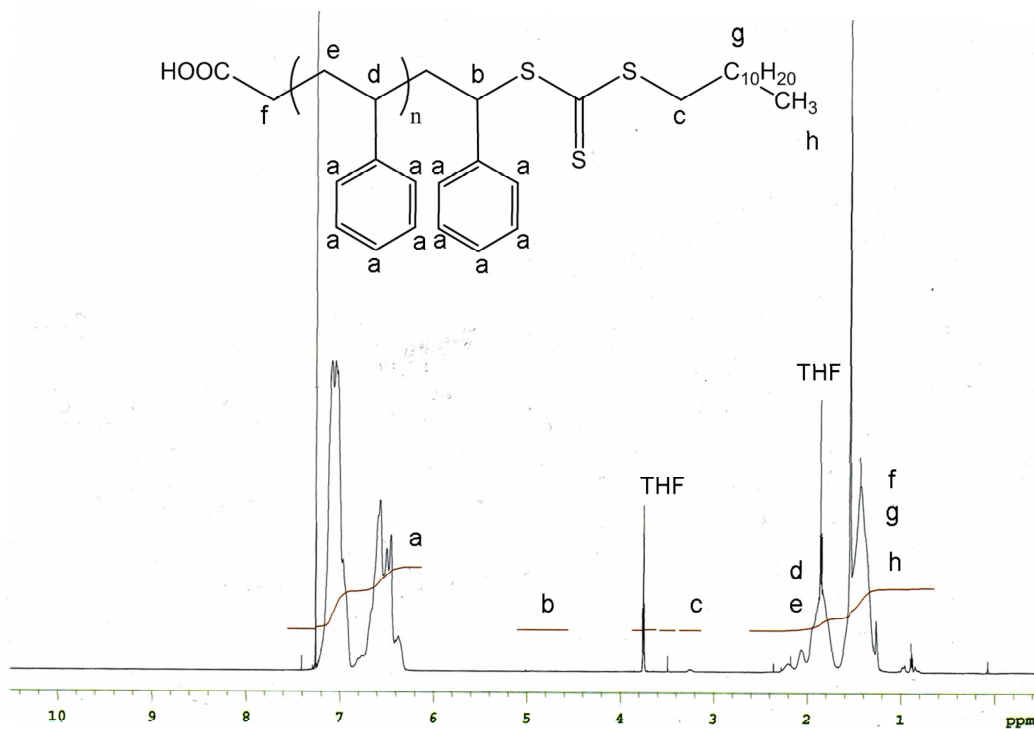


Figure S2. ¹H NMR spectrum of a PS precursor.

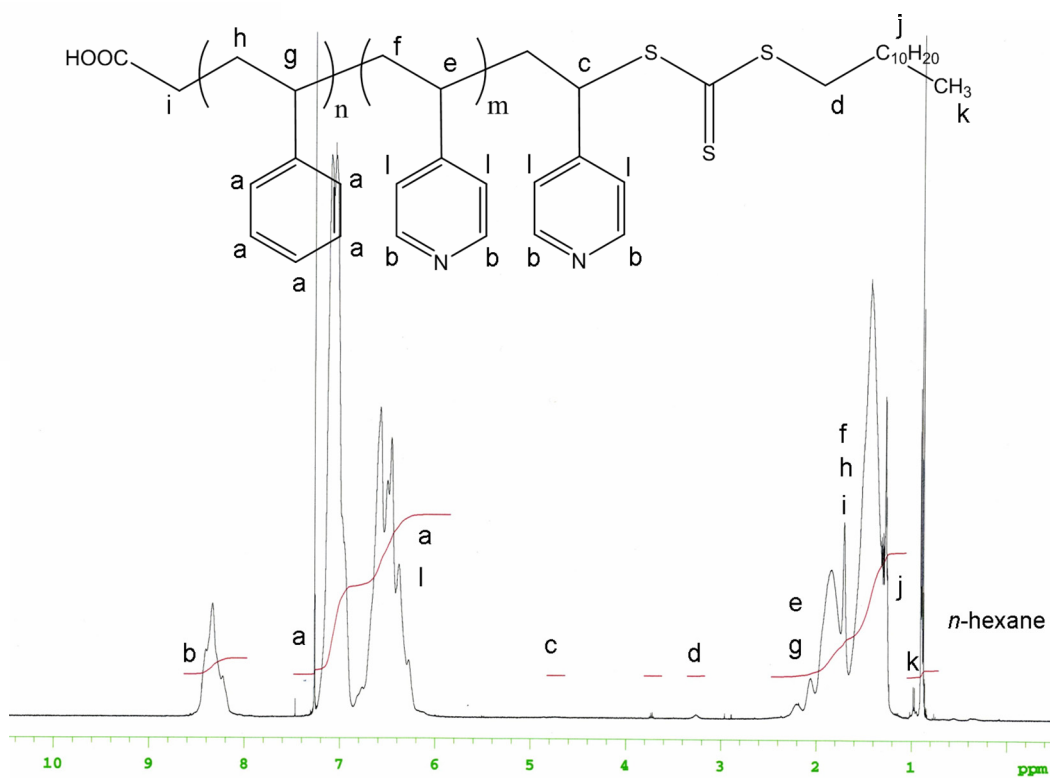


Figure S3. ^1H NMR spectrum of a PS-P4VP block copolymer.