

Supporting Information to

Zero Valent Metal Catalyzed Removal of Thiocarbonylthio End Groups from RAFT-Made Polystyrene: Producing Controllable Bimodal Molecular Weight Distribution

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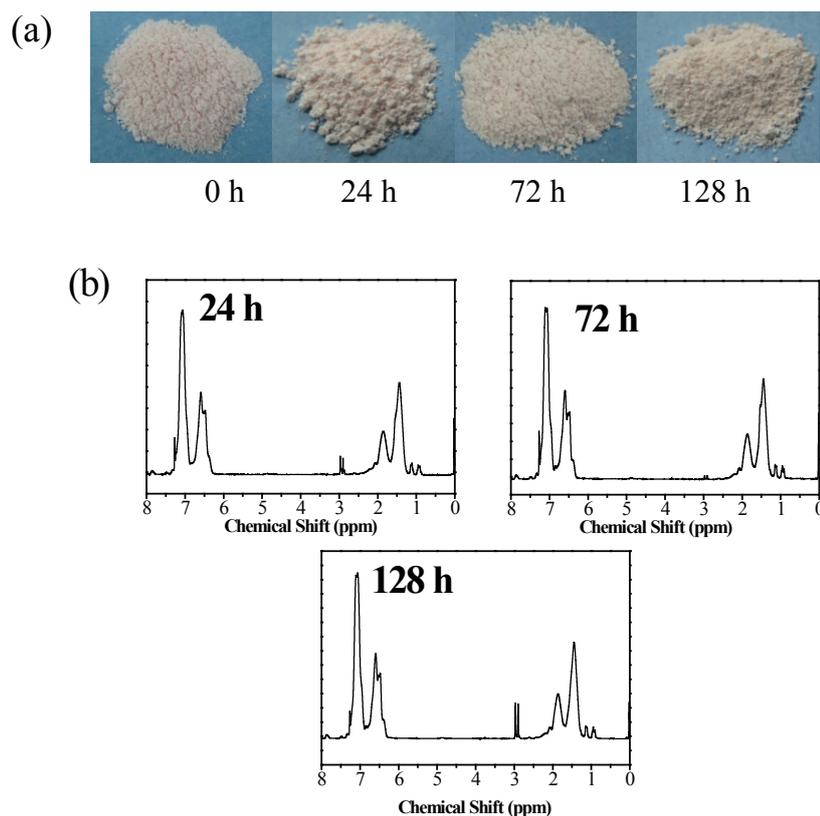
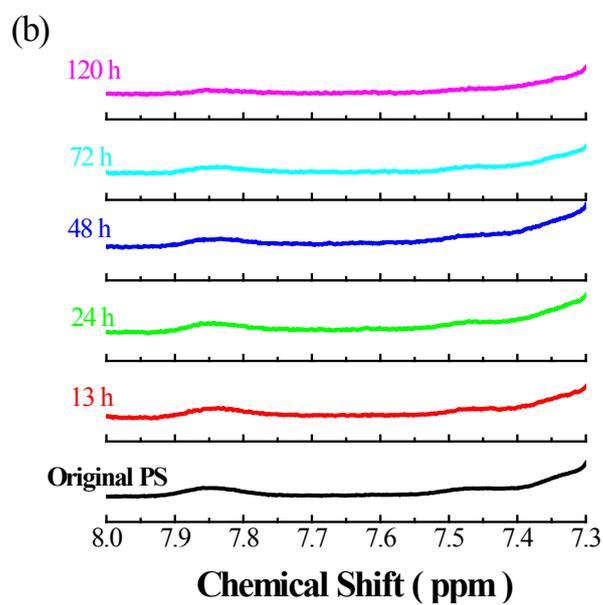
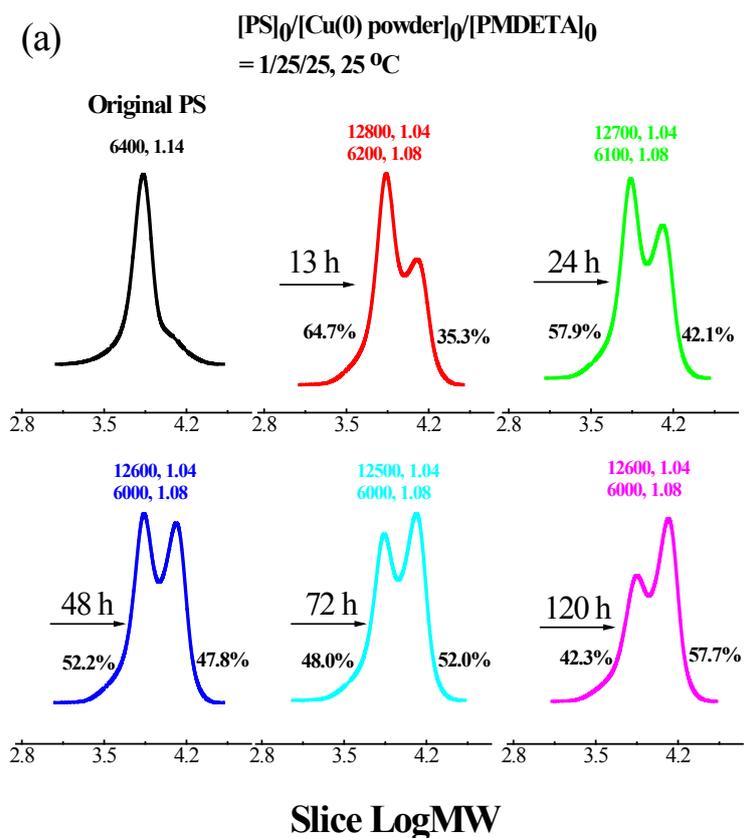


Figure S1. Photographs before and after the treatment of PS catalyzed by Cu(0) powder (a) ^1H NMR spectra of resultant PS (b). Original PS: $[\text{St}]_0/[\text{CPDB}]_0/[\text{AIBN}]_0 = 500/5/1$, time = 117 h, conversion = 38.1 %, 60 °C, St = 15.0 mL, toluene = 5.0 mL; Treated conditions: $[\text{PS}]_0/[\text{Cu}(0)]_0/[\text{PMDETA}]_0 = 1/5/5$, PS = 0.2001 g, DMF = 1.0 mL, 25 °C, 24 h, 72 h, 128 h.



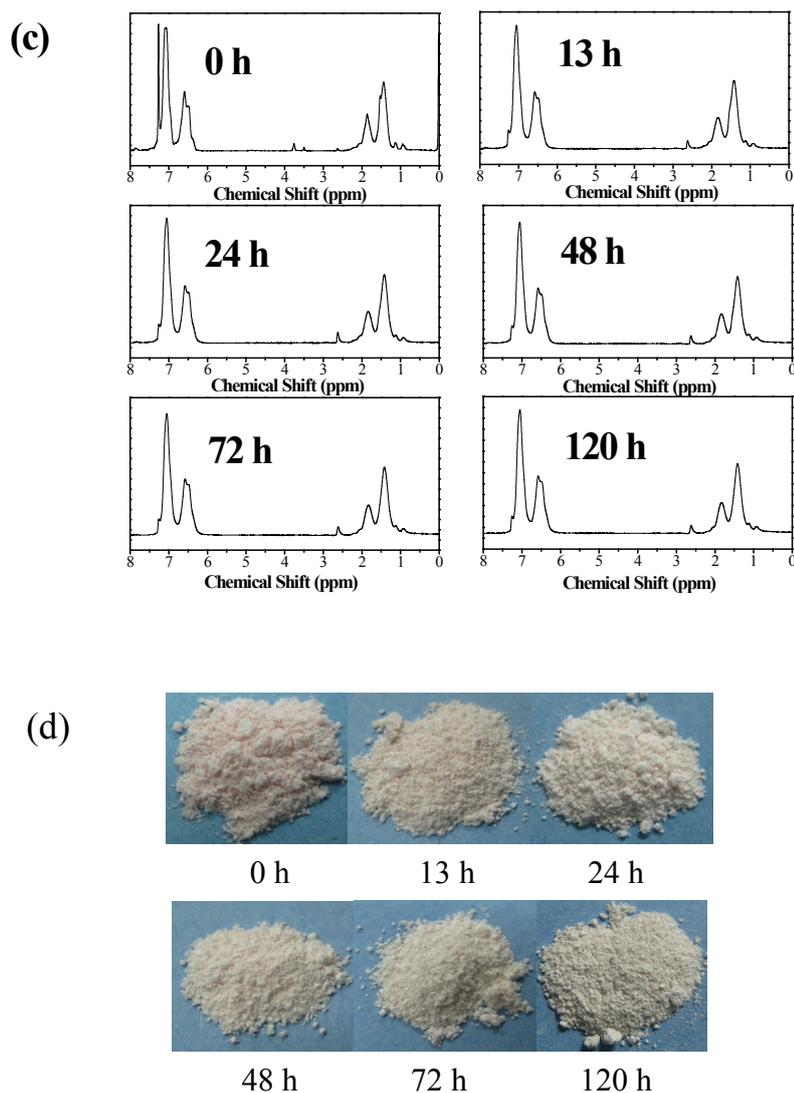


Figure S2. SEC traces (a) enlarged ^1H NMR signals of thiocarbonylthio groups (b) ^1H NMR spectra of original PS and resultant PS (c) and photographs (d) before and after the treatment of PS catalyzed by Cu(0) powder. Original PS: $[\text{St}]_0/[\text{CPDB}]_0/[\text{AIBN}]_0 = 500/5/1$, time = 71 h, conversion = 57.3 %, 60 °C, St = 5.0 mL, toluene = 2.0 mL; Treated conditions: $[\text{PS}]_0/[\text{Cu}(0)]_0/[\text{PMDETA}]_0 = 1/25/25$, PS = 0.2073 g, DMF = 1.8 mL, 25 °C, 13 h, 24 h, 48 h, 72 h, 120 h.

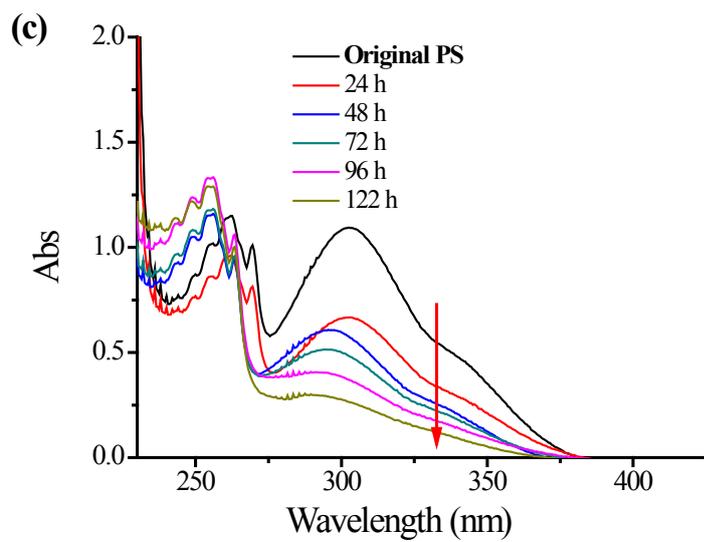
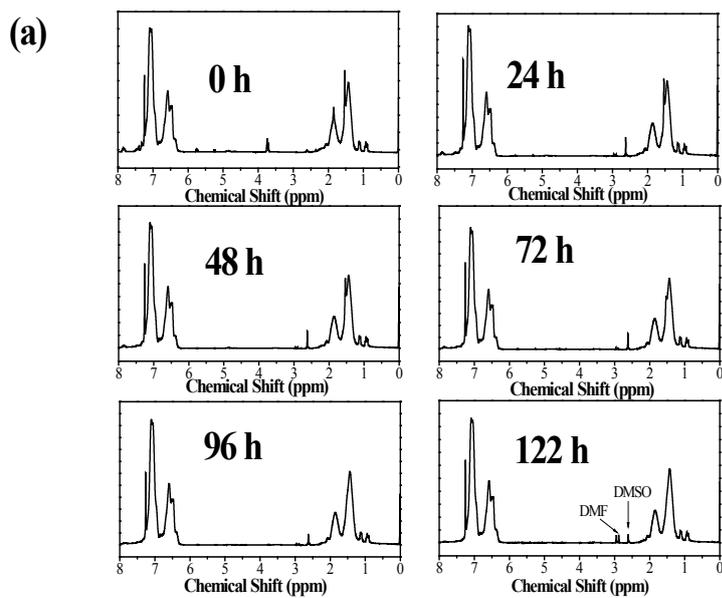


Figure S3. ^1H NMR spectra of original PS and resultant PS (a), photographs (b) and UV-Vis spectra of the PS (c) before and after the treatment of PS catalyzed by Cu(0) powder/TEMPO. Original PS: $[\text{St}]_0/[\text{CPDB}]_0/[\text{AIBN}]_0 = 500/5/1$, time = 117 h, conversion = 38.1 %, 60 °C, St = 15.0 mL, toluene = 5.0 mL; Treated conditions: $[\text{PS}]_0/[\text{Cu}(0)]_0/[\text{PMDETA}]_0/[\text{TEMPO}]_0 = 1/5/5/10$, PS = 0.2001 g, DMF = 1.0 mL, 25 °C, 24 h, 48 h, 72 h, 96 h, 122 h.

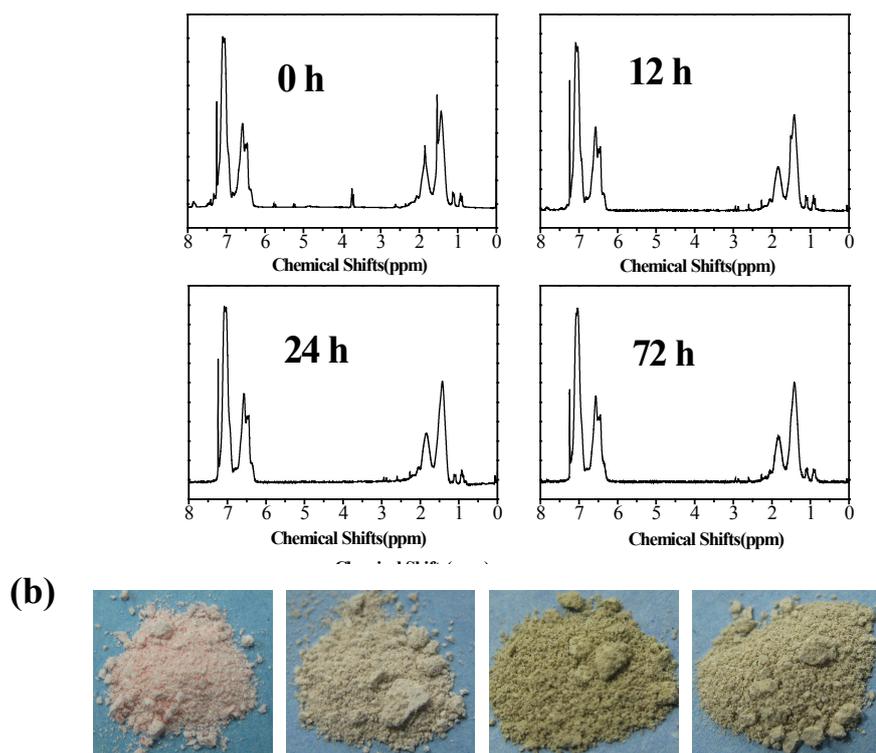


Figure S4. SEC traces (a) and enlarged ^1H NMR signals of thiocarbonylthio groups (b) before and after the treatment of PS catalyzed by Cu(0) powder/TEMPO. Original PS: $[\text{St}]_0/[\text{CPDB}]_0/[\text{AIBN}]_0 = 500/5/1$, time = 117 h, Conversion = 38.1 %, 60 °C, St = 15.0 mL, toluene = 5.0 mL; Treated conditions: $[\text{PS}]_0/[\text{Cu}(0)]_0/[\text{PMDETA}]_0/[\text{TEMPO}]_0 = 1/5/5/50$, PS = 0.2003 g, DMF = 1.0 mL, 60 °C, 12 h, 24 h, 72 h.

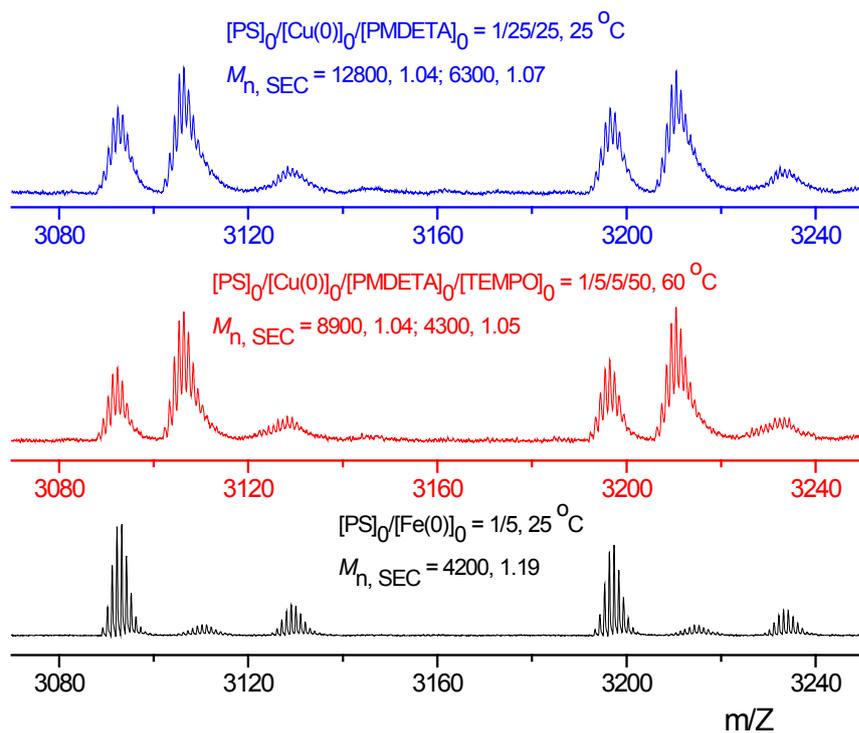


Figure S5. Matrix assisted laser desorption/ionization time of flight (MALDI-TOF) mass spectrometry of PS treated under different conditions.

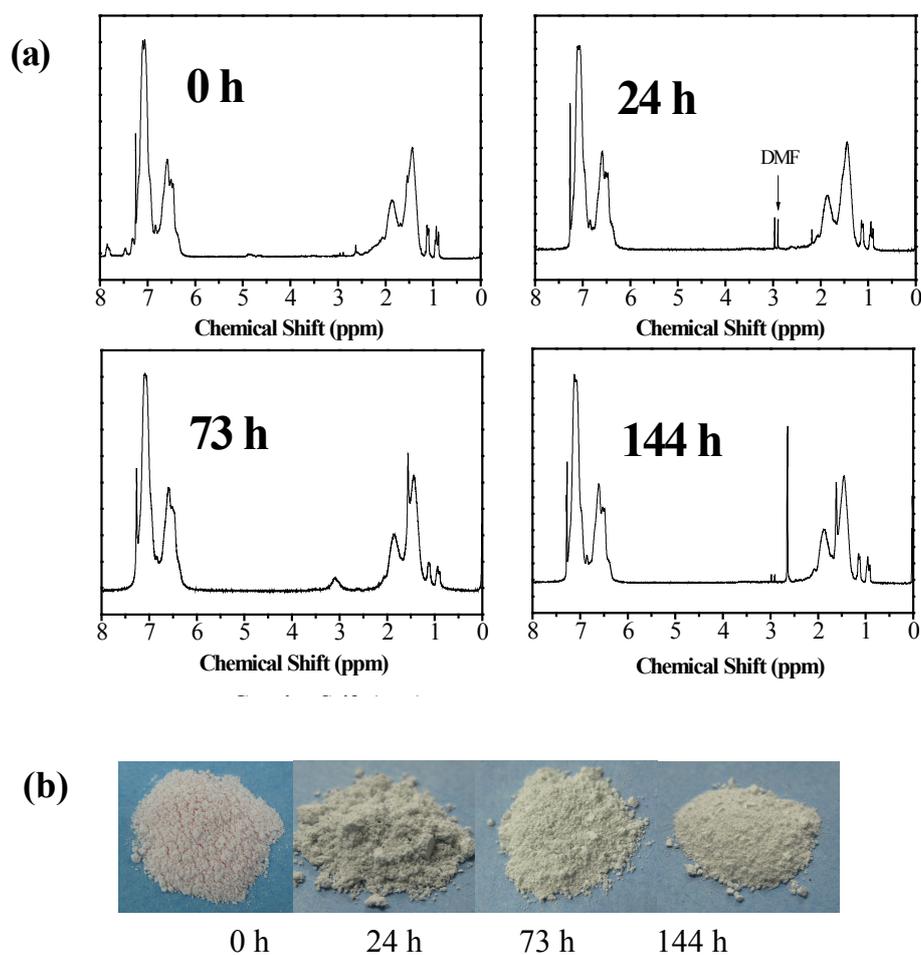


Figure S6. ^1H NMR spectra of original PS and resultant PS (a) and photographs (b) before and after the treatment of PS catalyzed by Fe(0) powder. Original PS: $[\text{St}]_0/[\text{CPDB}]_0/[\text{AIBN}]_0 = 500/5/1$, time = 71 h, Conversion = 68.5 %, 60 °C, St = 10.0 mL, toluene = 4.0 mL; Treated conditions: $[\text{PS}]_0/[\text{Fe}(0) \text{ powder}]_0 = 1/5$, PS = 0.2001 g, DMF = 1.0 mL, 25 °C, 24 h, 73 h, 144 h.

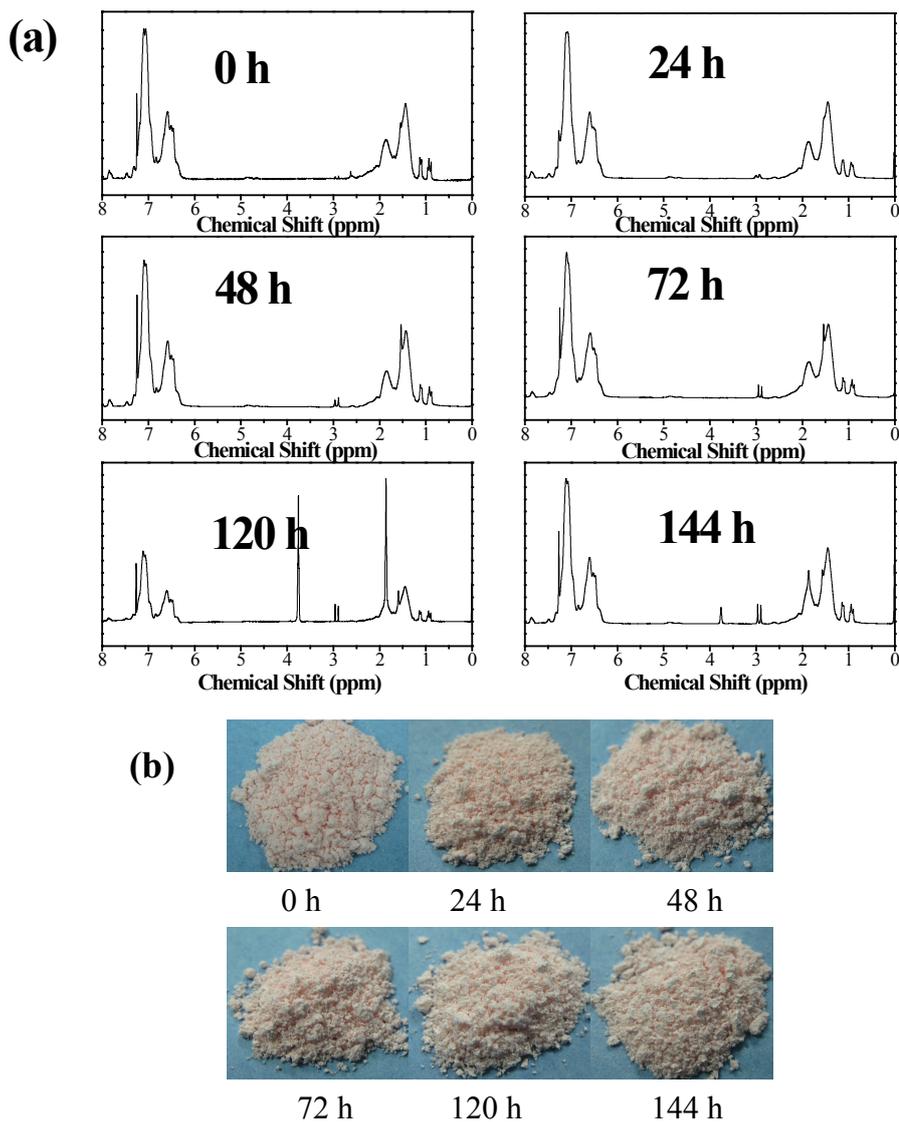
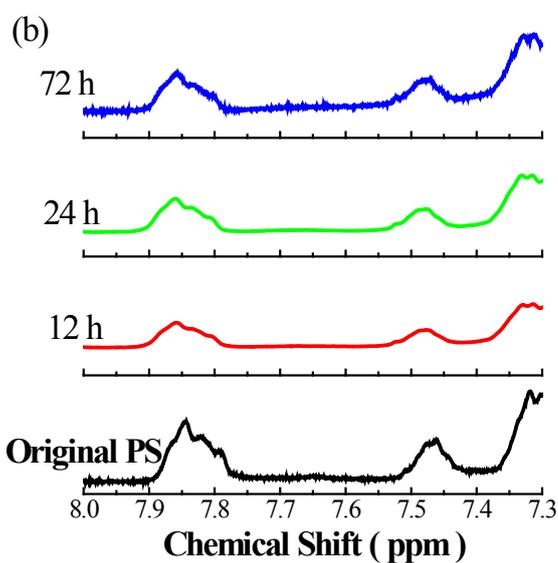
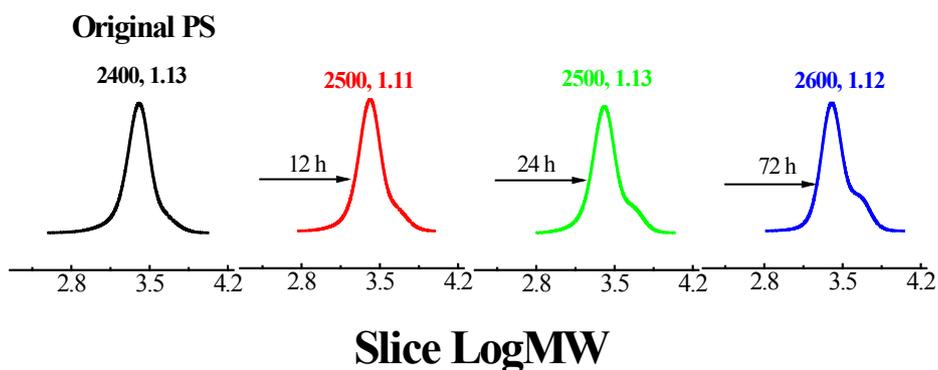


Figure S7. ^1H NMR spectra of original PS and resultant PS (a) and photographs (b) before and after the treatment of PS catalyzed by Fe(0) powder/TEMPO. Original PS: $[\text{St}]_0/[\text{CPDB}]_0/[\text{AIBN}]_0 = 500/5/1$, time = 71 h, conversion = 68.5 %, 60 °C, St = 10.0 mL, toluene = 4.0 mL; Treated conditions: $[\text{PS}]_0/[\text{Fe}(0) \text{ powder}]_0/[\text{TEMPO}]_0 = 1/5/5$, PS = 0.2002 g, DMF = 1.0 mL, 25 °C, 24 h, 48 h, 72 h, 120 h, 144 h.

(a) $[\text{PS}]_0/[\text{Fe}(0) \text{ powder}]_0/[\text{TEMPO}]_0 = 1/5/5, 60^\circ\text{C}$



(c)



Figure S8. SEC traces (a) enlarged ^1H NMR signals of thiocarbonylthio groups (b) and photographs (c) before and after the treatment of PS catalyzed by Fe(0) powder/TEMPO. Original PS: $[\text{St}]_0/[\text{CPDB}]_0/[\text{AIBN}]_0 = 500/5/1$, time = 71 h, conversion = 68.5 %, 60°C , St = 10.0 mL, toluene = 4.0 mL; Treated conditions: $[\text{PS}]_0/[\text{Fe}(0) \text{ powder}]_0/[\text{TEMPO}]_0 = 1/5/5$, PS = 0.2000 g, DMF = 1.0 mL, 60°C , 12 h, 24 h, 72 h.