Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information to

Zero-Valent Metal Catalyzed Radical-Induced Adjustable Removal/Modification of Thiocarbonylthio End Groups of RAFT Polymer at Ambient Temperature

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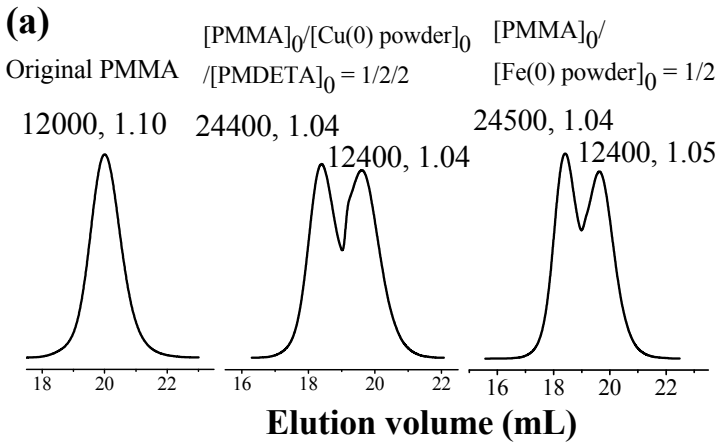


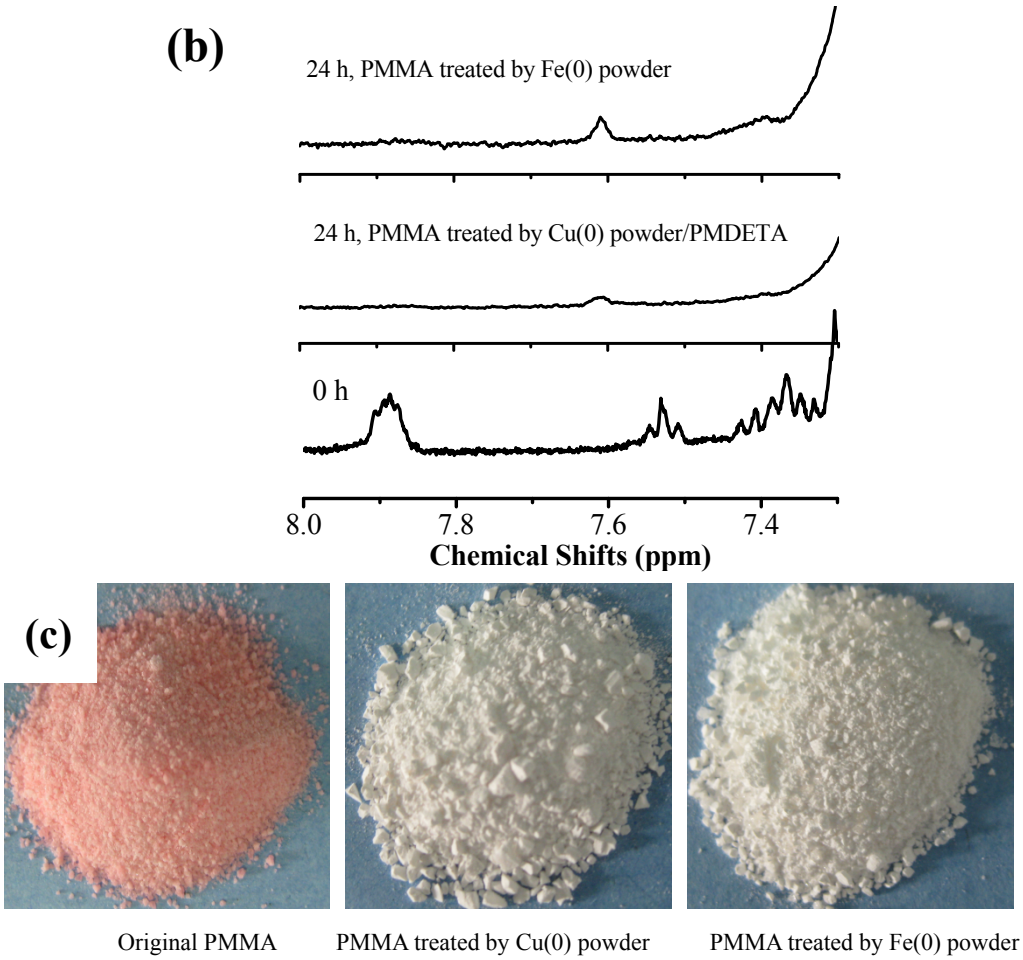


Figure S1. Original PMMA: $[MMA]_0/[CPDB]_0/[AIBN]_0$ = 500/5/1, time = 11 h, Conversion = 90.3 %, temperature = 60 ^oC, MMA = 5 mL, toluene = 2.0 mL; Treated Conditions: $[PMMA]_0/[Cu(0)\ powder]_0/[PMDETA]_0$ = 1/2/2, PMMA = 0.6902 g, DMF = 4.0 mL; 24 h, 25 ^oC; $[PMMA]_0/[Fe(0)\ powder]_0$ = 1/2, PMMA = 0.6902 g, DMF = 4.0 mL, 24 h, 25 ^oC; (a) SEC evolutions of the original PMMA and treated PMMA. (b) Enlarged ^1H NMR spectra of the original PMMA and treated PMMA. (c) Photographs of PMMA before and after treatment.

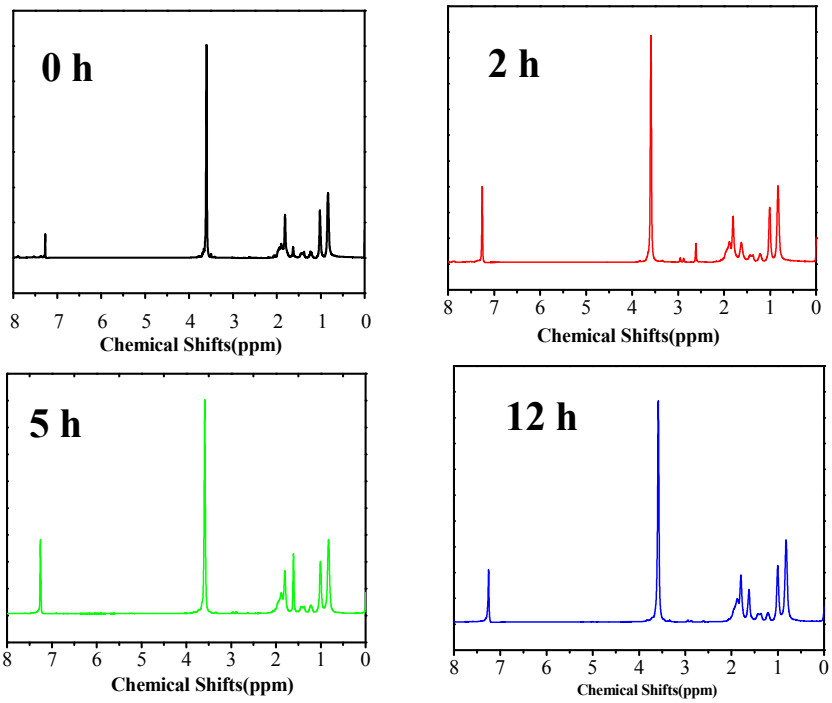


Figure S2. Full ^{1}H NMR Spectra before and after the treatment of PMMA catalyzed by Cu(0) powder/TEMPO (Figure 1 in main text).

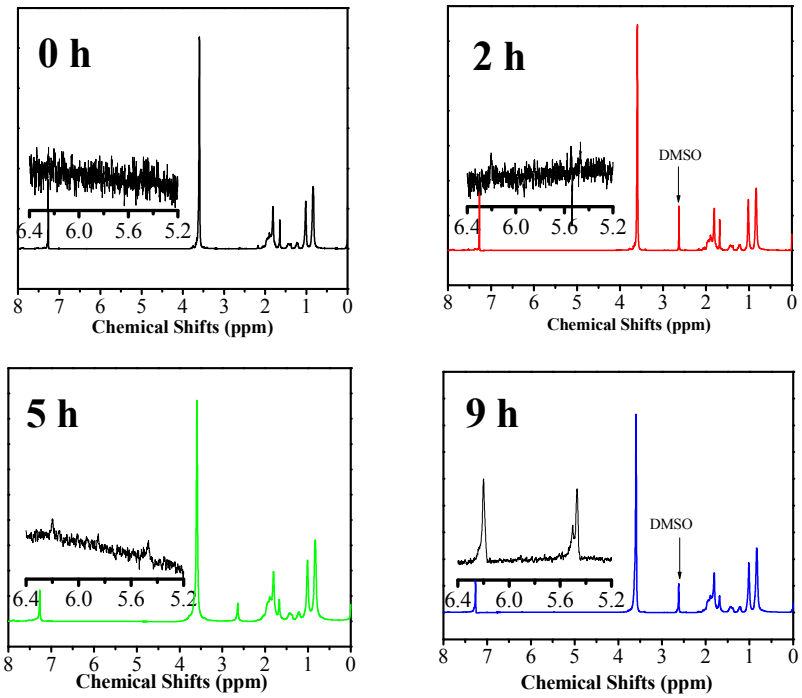


Figure S3. Full ^{1}H NMR Spectra before and after the treatment of PMMA catalyzed by Cu(0) powder/TEMPO (Figure 2 in main text).

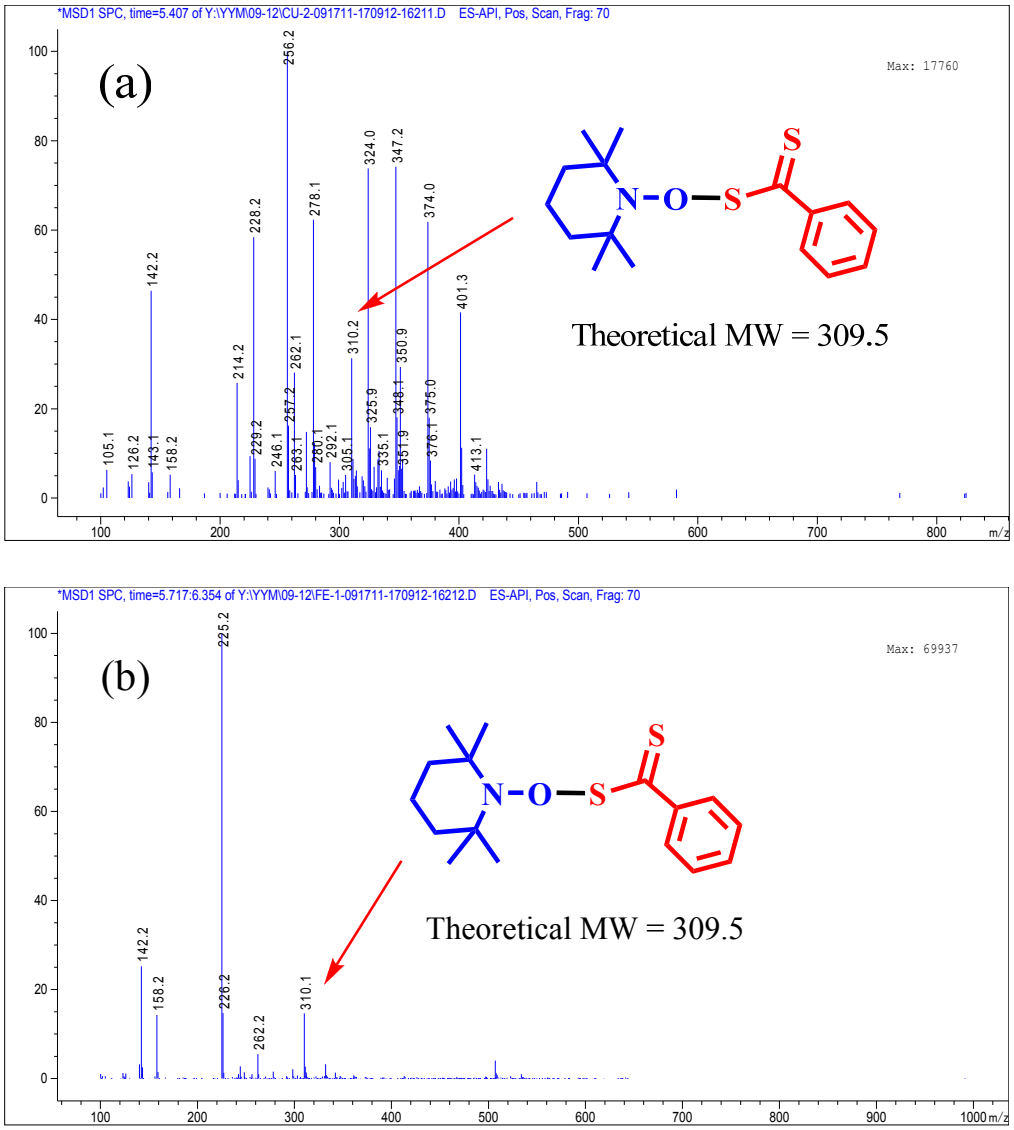


Figure S4. Liquid chromatography-mass spectrometric (LC-MS) analysis of resultants from the control experiments under: (a) $[CPDB]_0/[Cu(0)\ powder]_0/[PMDETA]_0/[TEMPO]_0$ = 1/5/5/5, CPDB = 0.2 g, DMF = 1 mL, 12 h, 25 ^oC; (b) $[CPDB]_0/[Fe(0)\ powder]_0/[TEMPO]_0$ = 1/1/5, CPDB = 0.2 g, DMF = 1 mL, 24 h, 25 ^oC.

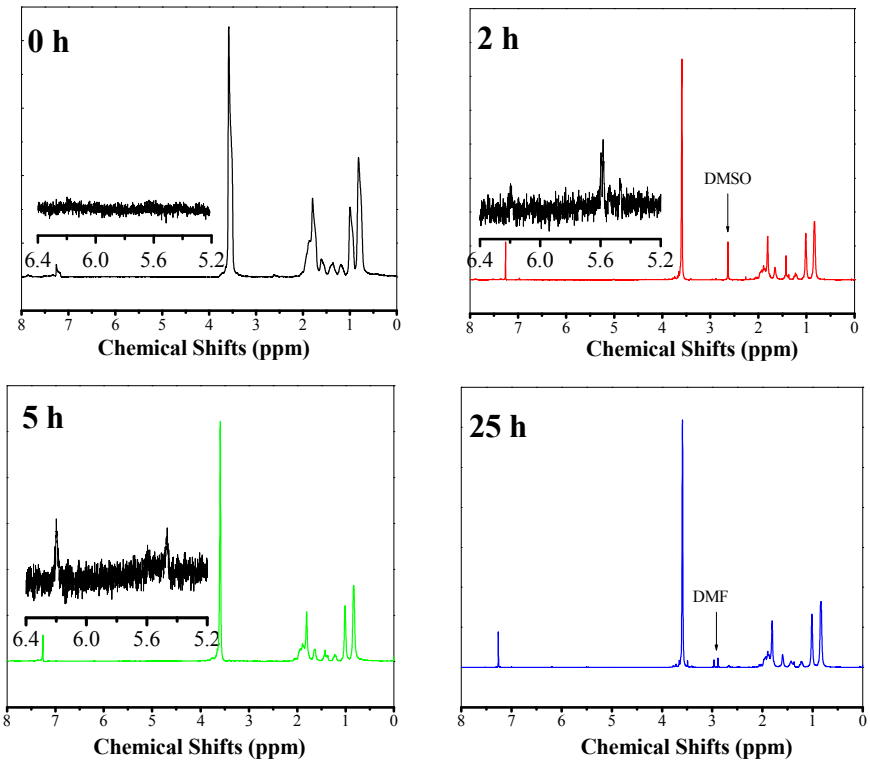


Figure S5. Full ^{1}H NMR Spectra before and after the treatment of PMMA catalyzed by Cu(0) wire/TEMPO (Figure 3 in main text).

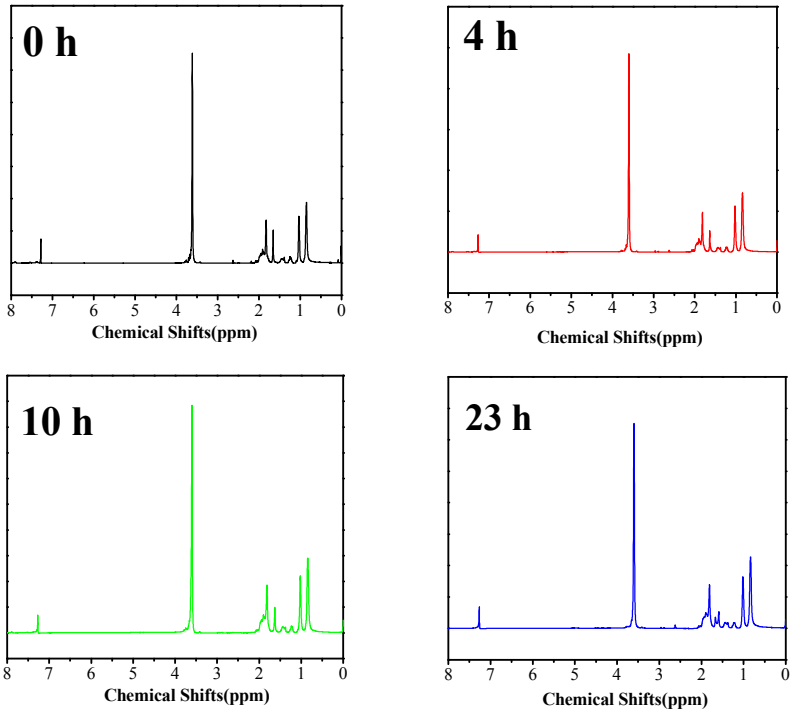


Figure S6. Full ^{1}H NMR Spectra before and after the treatment of PMMA catalyzed by Fe(0) powder/TEMPO (Figure 6 in main text).

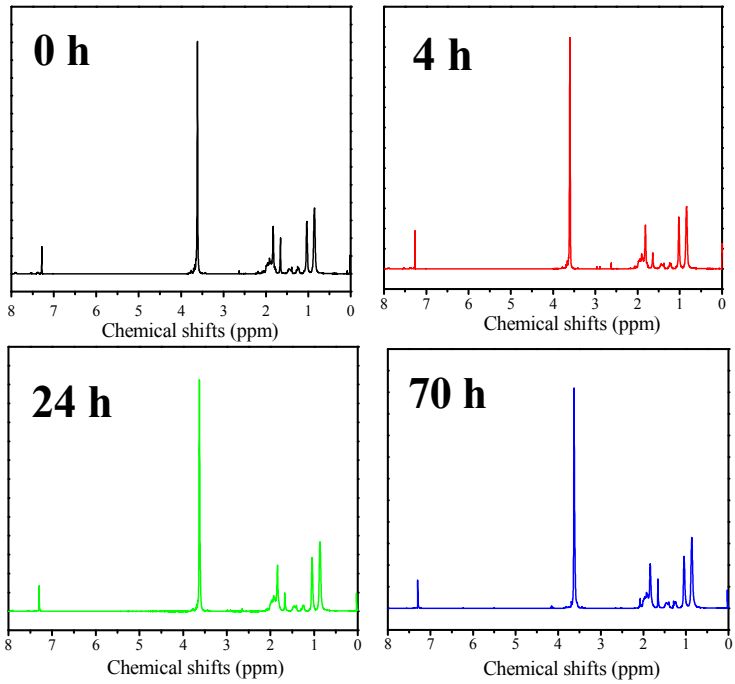


Figure S7. Full ^{1}H NMR Spectra before and after the treatment of PMMA catalyzed by Fe(0) powder/TEMPO (Figure 7 in main text).

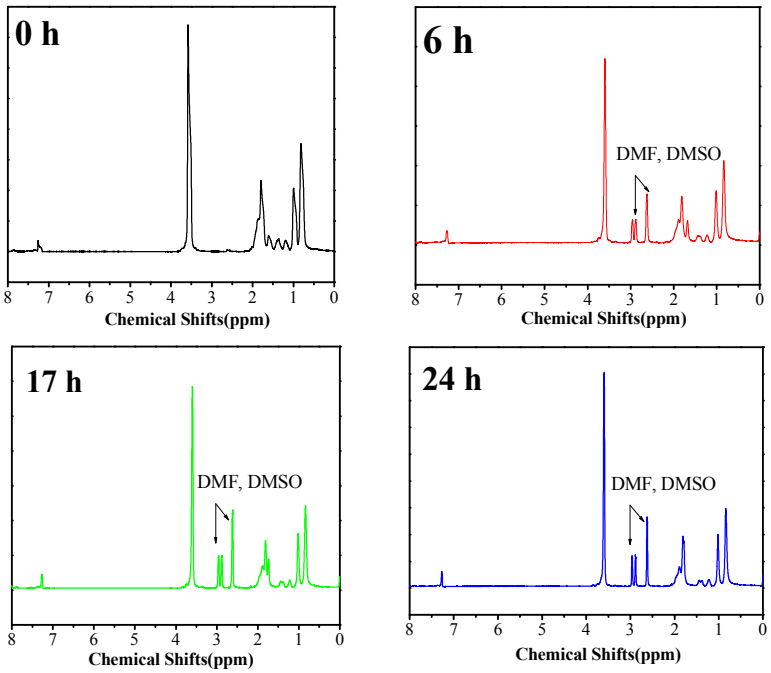


Figure S8. Full ^{1}H NMR Spectra before and after the treatment of PMMA catalyzed by Fe(0) powder/TEMPO (Figure 8 in main text).

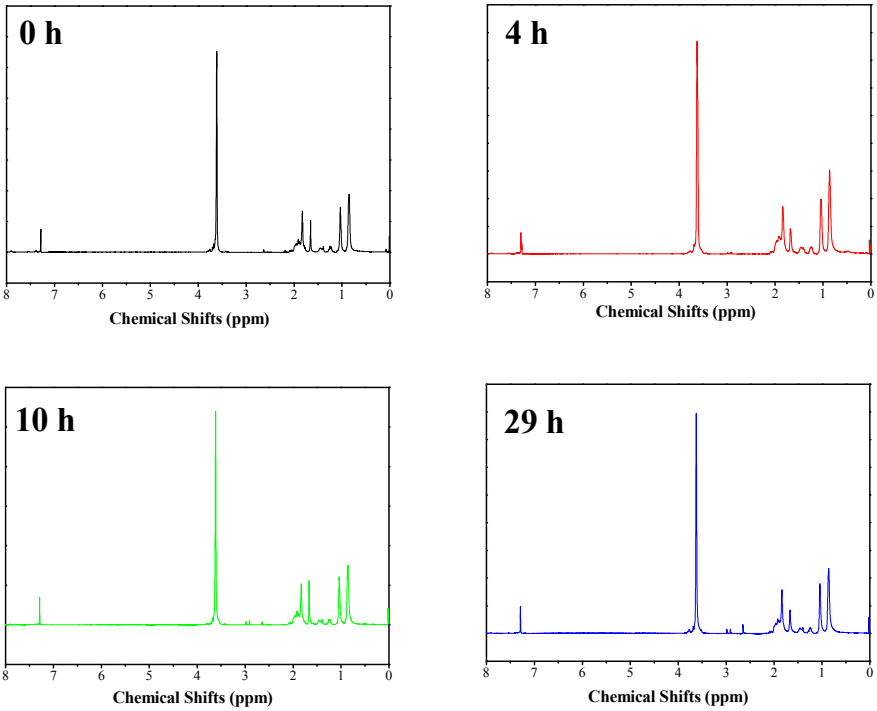
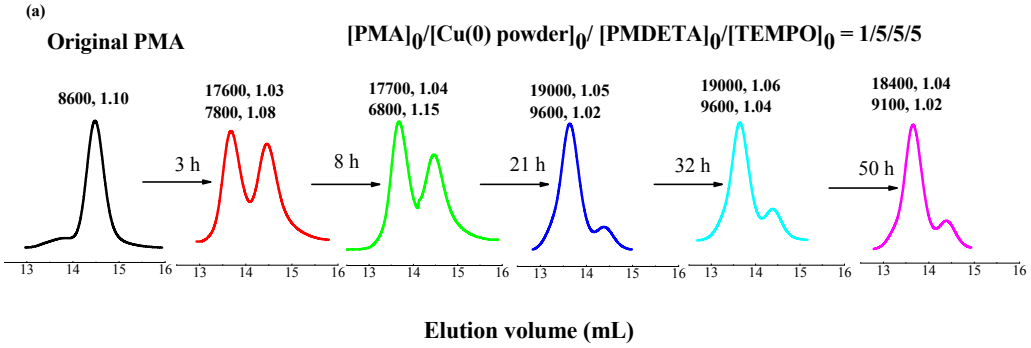
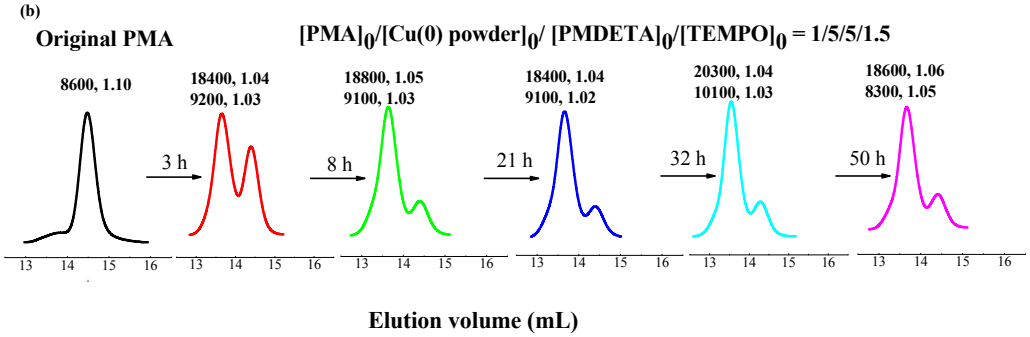
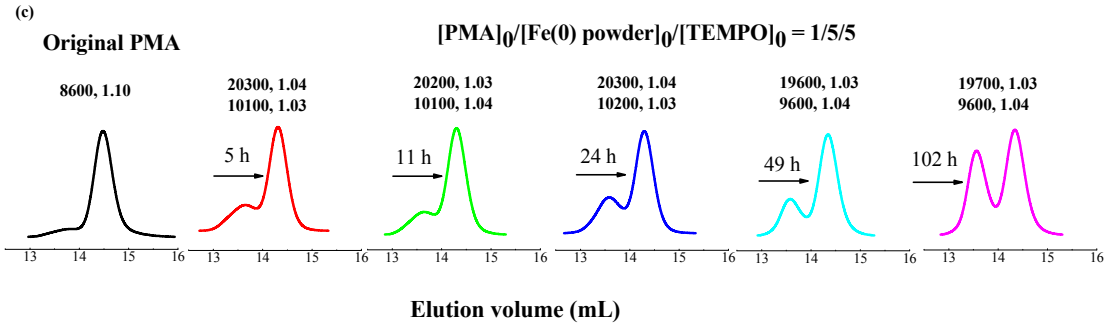
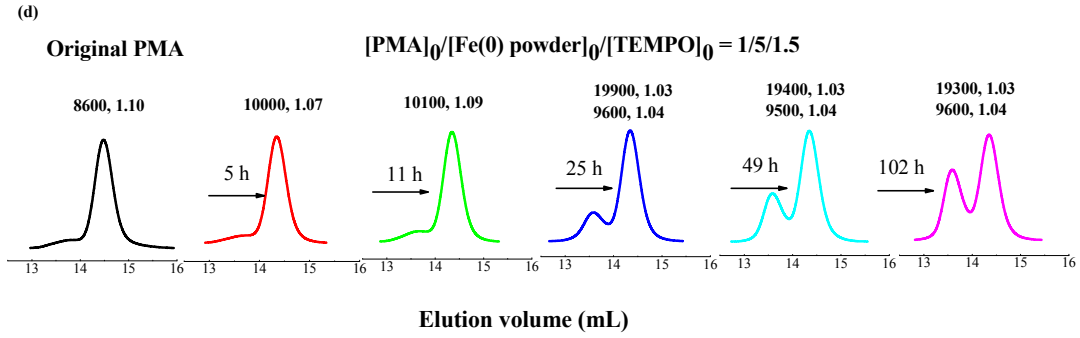


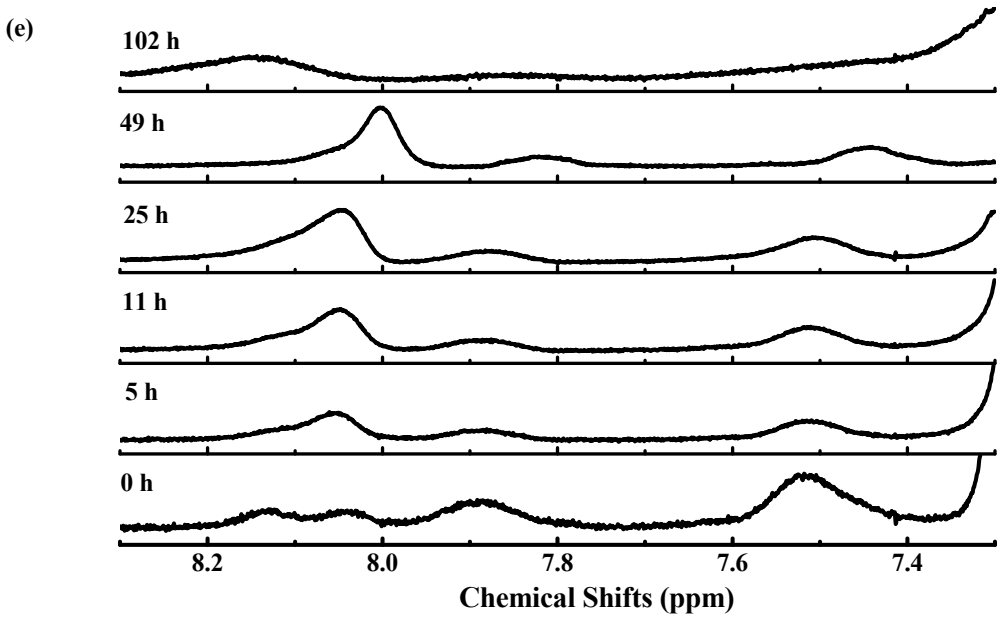
Figure S9. Full ^{1}H NMR Spectra before and after the treatment of PMMA catalyzed by Fe(0) wire/TEMPO (Figure 9 in main text).











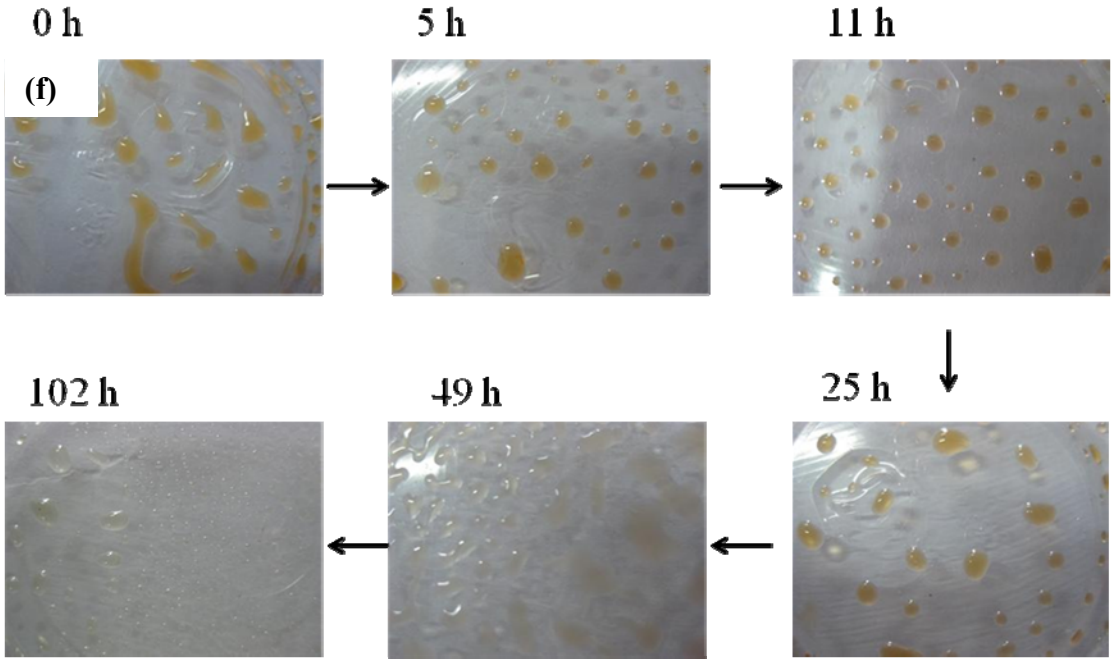
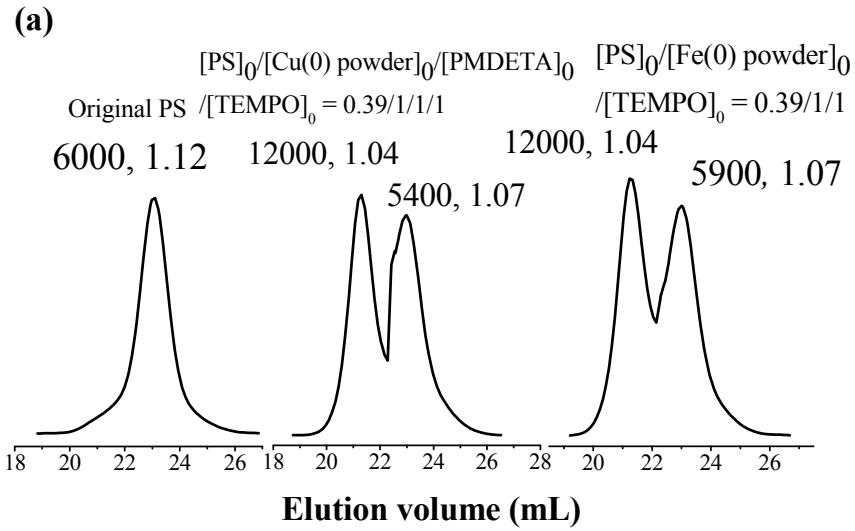


Figure S10. Original PMA: $[MA]_0/[CPDN]_0/[AIBN]_0$ = 500/5/1, Time =24 h, Conversion = 72.5 %, temperature = 60 °C, MA = 12 mL, toluene = 4.0 mL; Treated conditions, PMA = 0.2 g, DMF = 1.0 mL, 25 oC;: (a) $[PMA]_0/[Cu(0)\ powder]_0/[PMDETA]_0/[TEMPO]_0$ = 1/5/5/5, PMA = 0.2 g, DMF = 1.0 mL; (b) $[PMA]_0/[Cu(0)\ powder]_0/[PMDETA]_0/[TEMPO]_0$ = 1/5/5/1.5; (c) $[PMA]_0/[Fe(0)\ powder]_0/[TEMPO]_0$ = 1/5/5; (d) $[PMA]_0/[Fe(0)\ powder]_0/[TEMPO]_0$ = 1/5/1.5; (e) Enlarged ^1H NMR spectra of the original PMA and treated PMA as (d); (f) Photographs of PMA before and after treatment as (d).



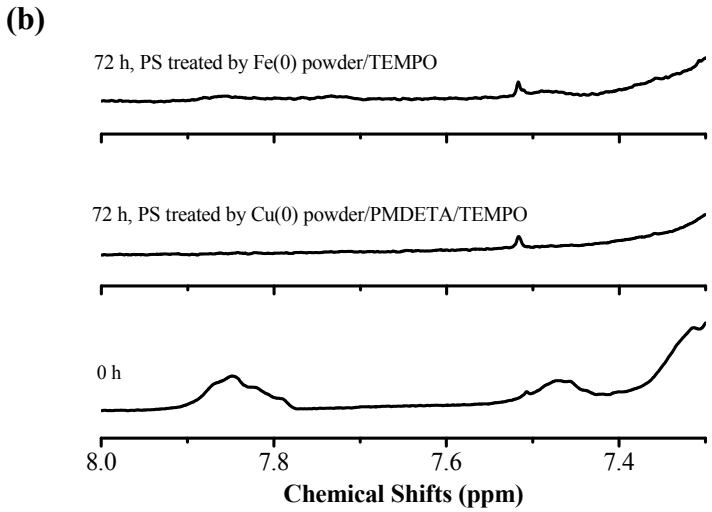


Figure S11. Original PS: $[St]_0/[CPDB]_0/[AIBN]_0$ = 500/5/1, time = 71 h, Conversion = 56.7 %, temperature = 60 ^oC, St = 2.0 mL, toluene = 1.0 mL; Treated conditions: PS treated by Cu(0) powder/PMDETA: $[PS]_0/[Cu(0)\ powder]_0/[PMDETA]_0/[TEMPO]_0$ = 0.39/1/1/1, time = 72 h, PS = 0.2334 g, DMF = 5 mL, 25 ^oC; PS treated by Fe(0) powder: $[PS]_0/[Fe(0)\ powder]_0/[TEMPO]_0$= 0.39/1/1, time = 72 h, PS = 0.2334 g, DMF = 5.0 mL, 25 ^oC; (a) SEC evolutions of the original PS and treated PS. (b) Enlarged ^1H NMR spectra of the original PS and treated PS. (c) Photographs of PS before and after treatment.