

Supporting Information

A Simple Combination of Higher Oxidation State FeX_3 and Phosphine or Amine Ligand for Living Radical Polymerization of Styrene, Methacrylate, and Acrylate

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Contents

Figure S1. Living radical polymerization of styrene with FeCl_3 /ligand

Figure S2. Living Radical Polymerization of MMA with FeCl_3 /ligand

Figure S3. ^1H -NMR spectra of PMMA-Cl and PMMA-*b*-polystyrene block copolymer

Figure S4. Living radical polymerization of MA with FeCl_3 /ligand

Figure S5. UV-Vis spectra of FeCl_3 /*Pn*Bu₃

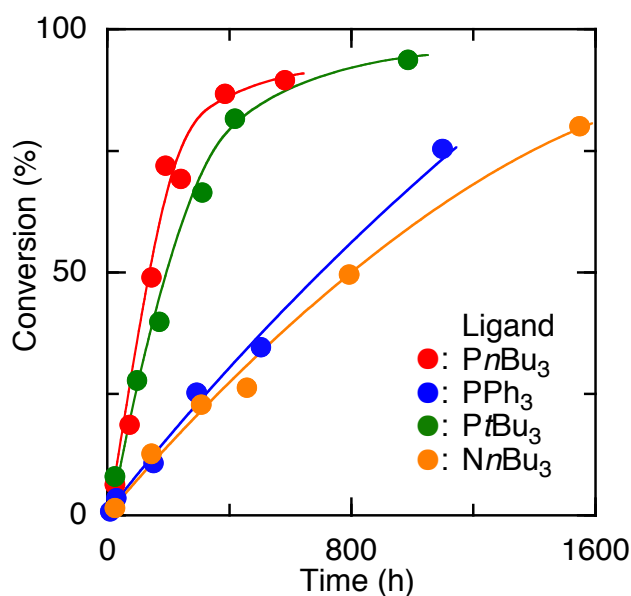


Figure S1. Time-conversion curves of living radical polymerization of styrene with **1**/ FeCl_3 /ligand system: $[\text{styrene}]_0 = 4.0 \text{ M}$, $[\mathbf{1}]_0 = 40 \text{ mM}$, $[\text{FeCl}_3]_0 = 10 \text{ mM}$, $[\text{ligand}]_0 = 20 \text{ mM}$ in toluene at 100°C .

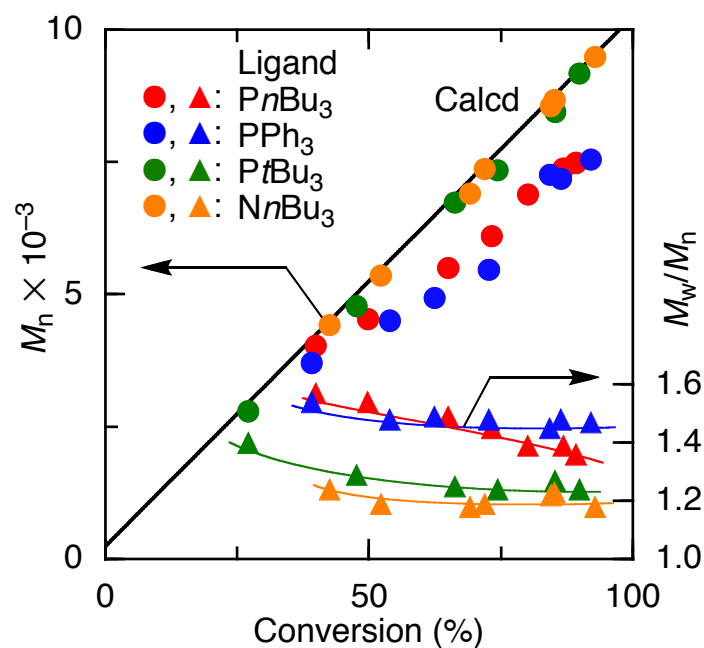


Figure S2. M_n and M_w/M_n of PMMA obtained in the living radical polymerization of MMA with $\text{FeCl}_3/\text{ligand}$: $[\text{MMA}]_0 = 2.0 \text{ M}$, $[\mathbf{1}]_0 = 20 \text{ mM}$, $[\text{FeCl}_3]_0 = 10 \text{ mM}$, $[\text{ligand}]_0 = 20 \text{ mM}$ in toluene at 100°C .

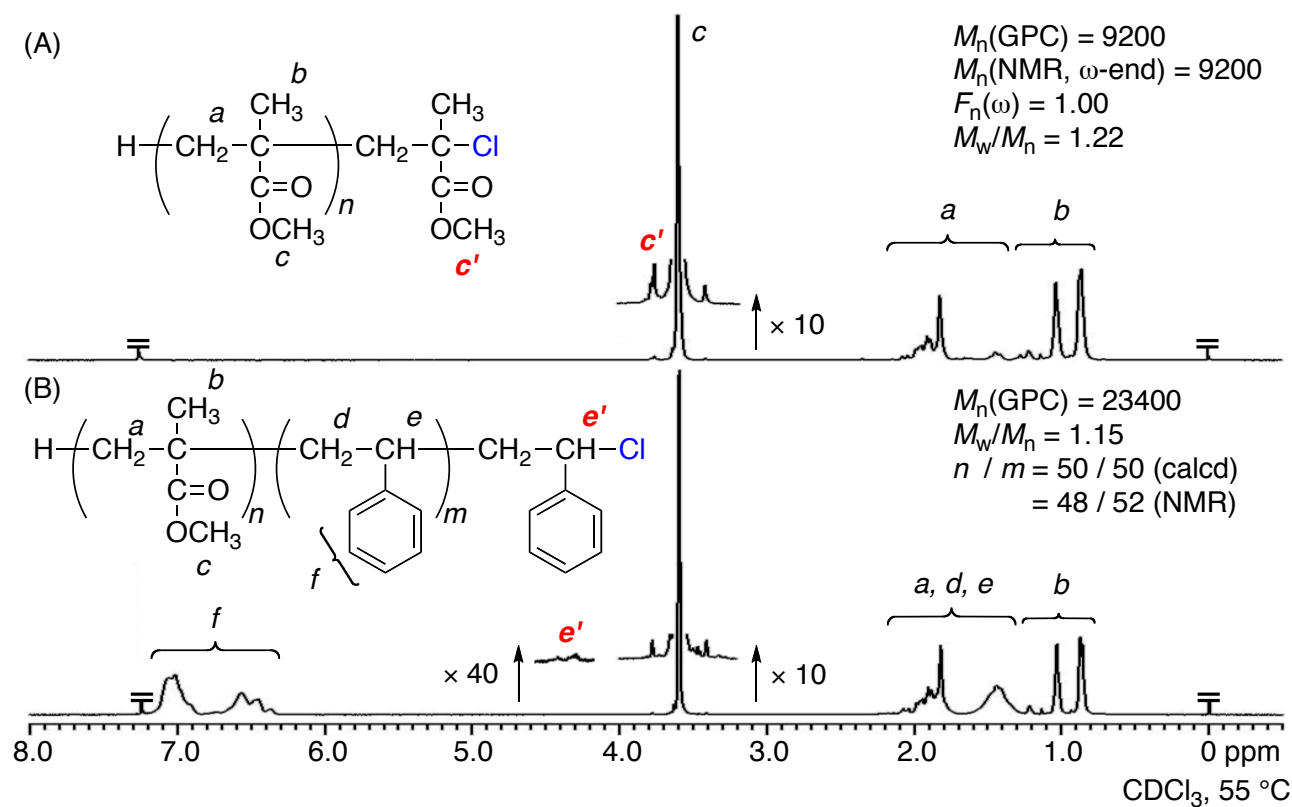


Figure S3. ^1H NMR spectra (CDCl₃, 55 °C) of PMMA-Cl (A) and PMMA-*b*-polystyrene block copolymer (B): (A) was synthesized with **1**/FeCl₃/PtBu₃ (20/10/10 mM) in toluene at 80 °C (MMA Conversion = 63%). Styrene was polymerized with the PMMA-Cl/FeCl₃/PnBu₃ (40/10/20 mM) in toluene at 100 °C: [styrene]₀ = 4.0 M.

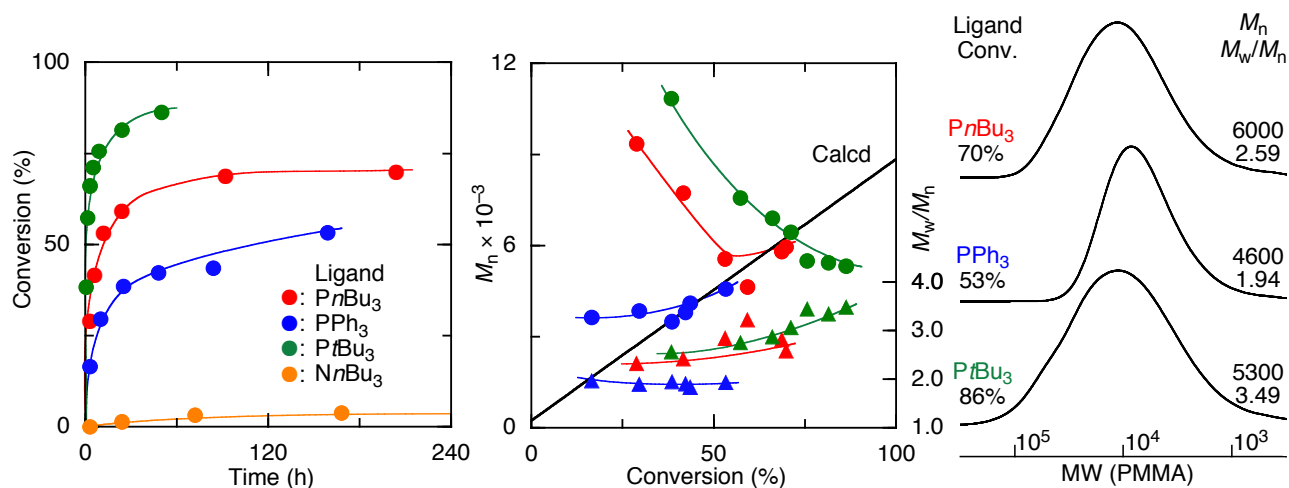


Figure S4. Time-conversion, M_n , M_w/M_n , and SEC curves of living radical polymerization of MA with $\text{FeCl}_3/\text{ligand}$: $[\text{MA}]_0 = 2.0 \text{ M}$, $[\mathbf{1}]_0 = 20 \text{ mM}$, $[\text{FeCl}_3]_0 = 10 \text{ mM}$, $[\text{ligand}]_0 = 20 \text{ mM}$ in toluene at 100°C .

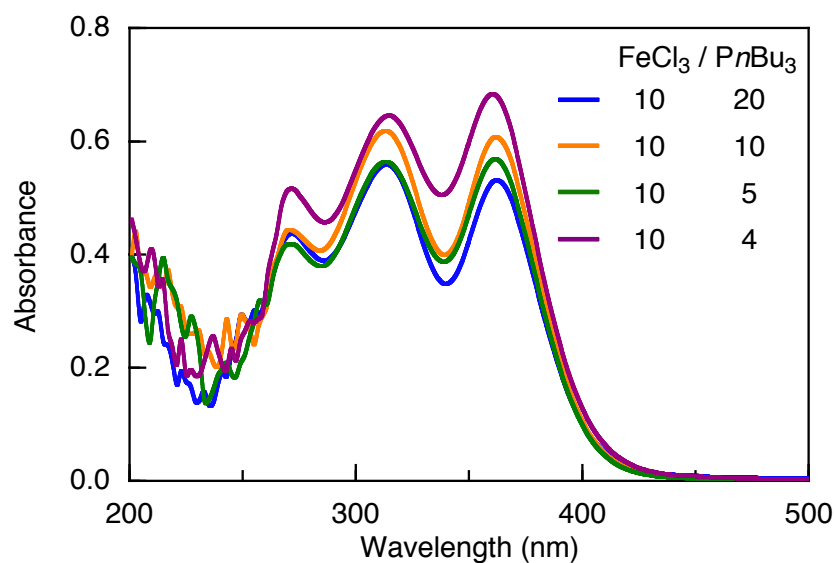


Figure S5. UV-Vis spectra of $\text{FeCl}_3/\text{PnBu}_3$: $[\text{FeCl}_3]_0 = 0.10 \text{ mM}$, $[\text{PnBu}_3]_0 = 0.04\text{--}0.20 \text{ mM}$ in EtOAc at 25°C .