

Thermoresponsive Polymer Supporter for Concerted Catalysis of Ferrocene with Ruthenium Catalyst in Living Radical Polymerization: High Activity and Efficient Removal of Metal Residues

Kojiro Fujimura, Makoto Ouchi, and Mitsuo Sawamoto**

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura,

Nishikyo-ku, Kyoto 615-8510, Japan

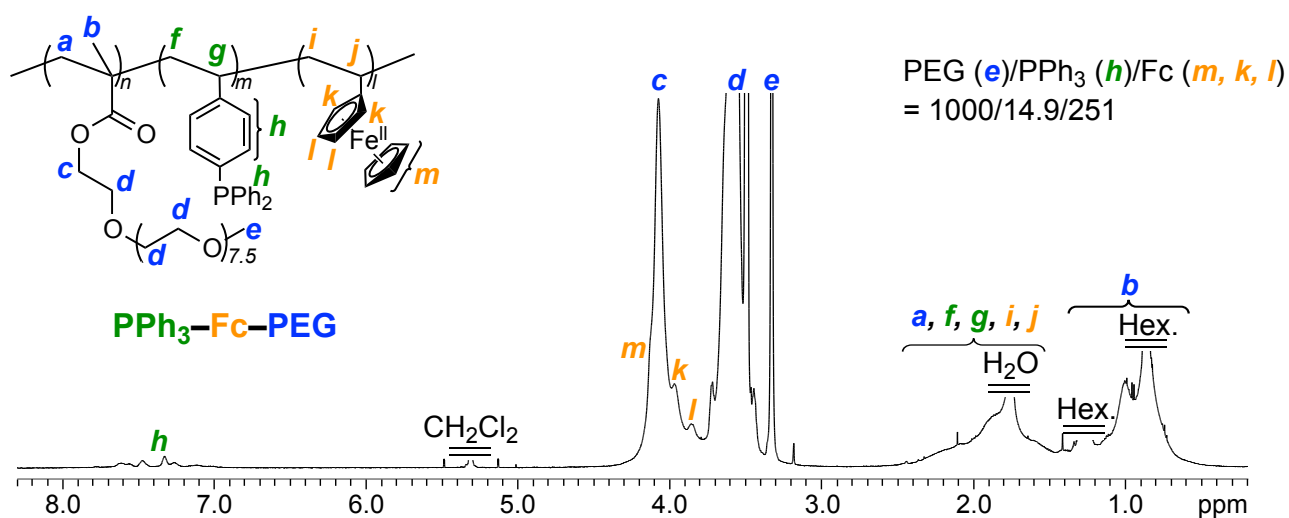


Figure S1. ^1H NMR spectrum of $\text{PPh}_3\text{-Fc-PEG}$ in CD_2Cl_2 at room temperature.

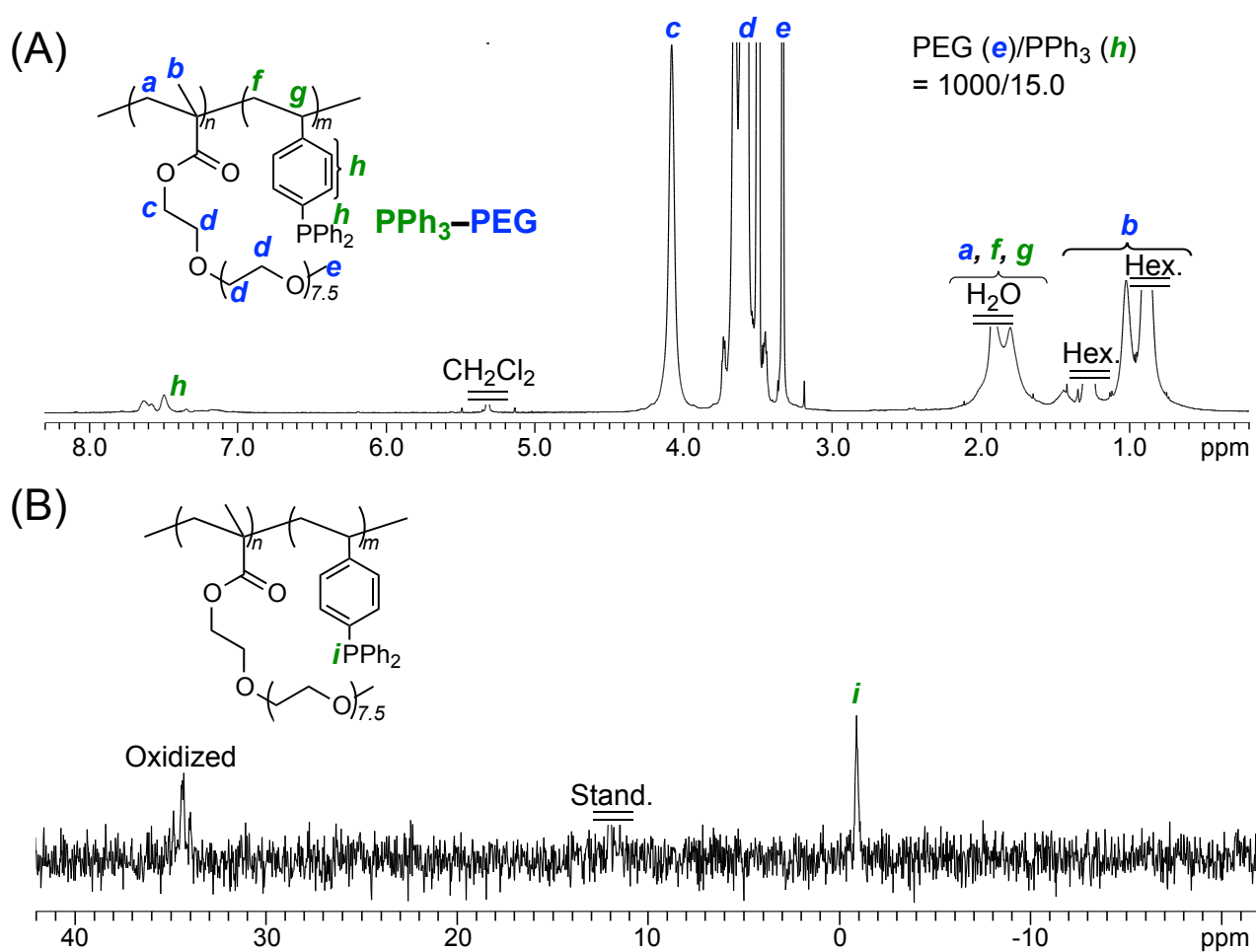


Figure S2. (A) ^1H (in CD_2Cl_2), and (B) ^{31}P NMR (in CDCl_3) spectrum of $\text{PPh}_3\text{-PEG}$ at room temperature.

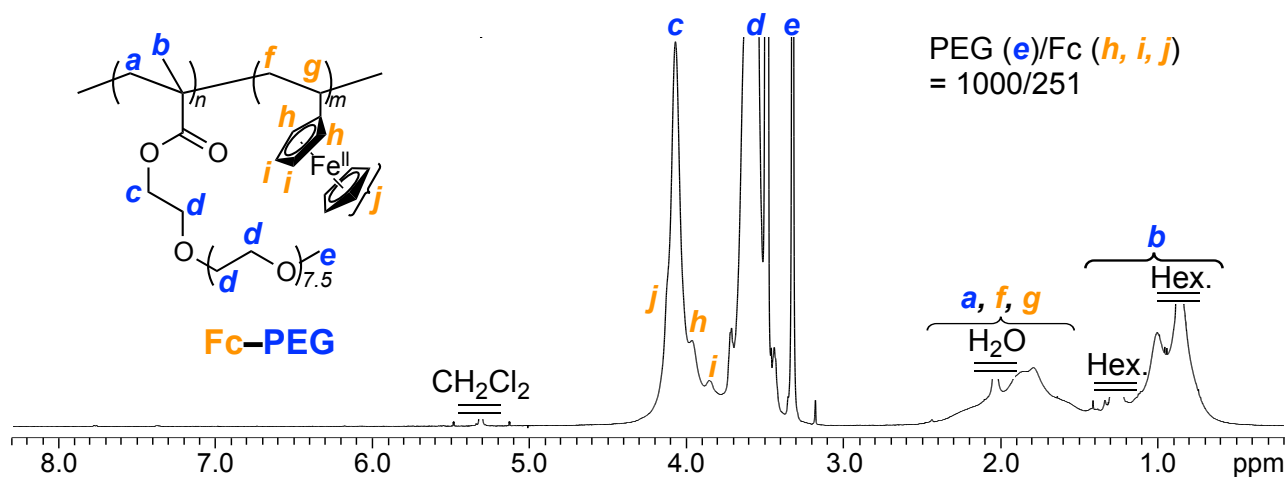
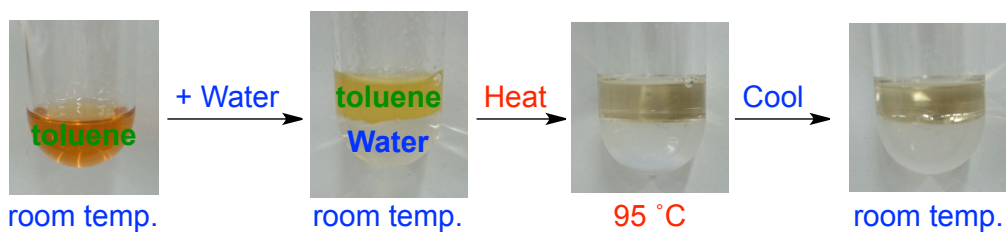


Figure S3. ^1H NMR spectrum of Fc-PEG in CD_2Cl_2 at room temperature.

(A) $\text{Ru}(\text{Cp}^*)\text{Cl}(\text{PPh}_3)_2$



(B) FeCp_2

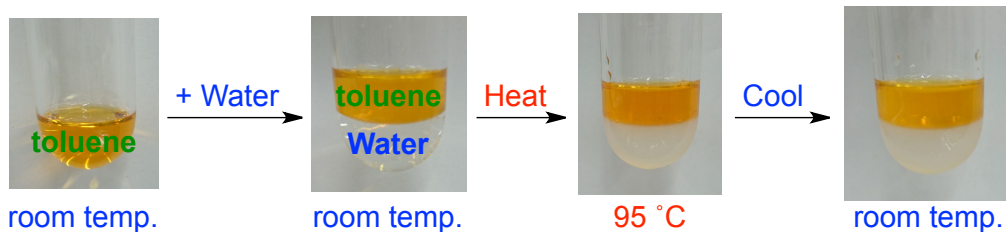


Figure S4. Solubility of $\text{Ru}(\text{Cp}^*)\text{Cl}(\text{PPh}_3)_2$ (A) and FeCp_2 (B) in a toluene/water biphasic solution: $[\text{Ru}(\text{Cp}^*)\text{Cl}(\text{PPh}_3)_2]_0 = 1.0 \text{ mM}$; $[\text{FeCp}_2]_0 = 40 \text{ mM}$.

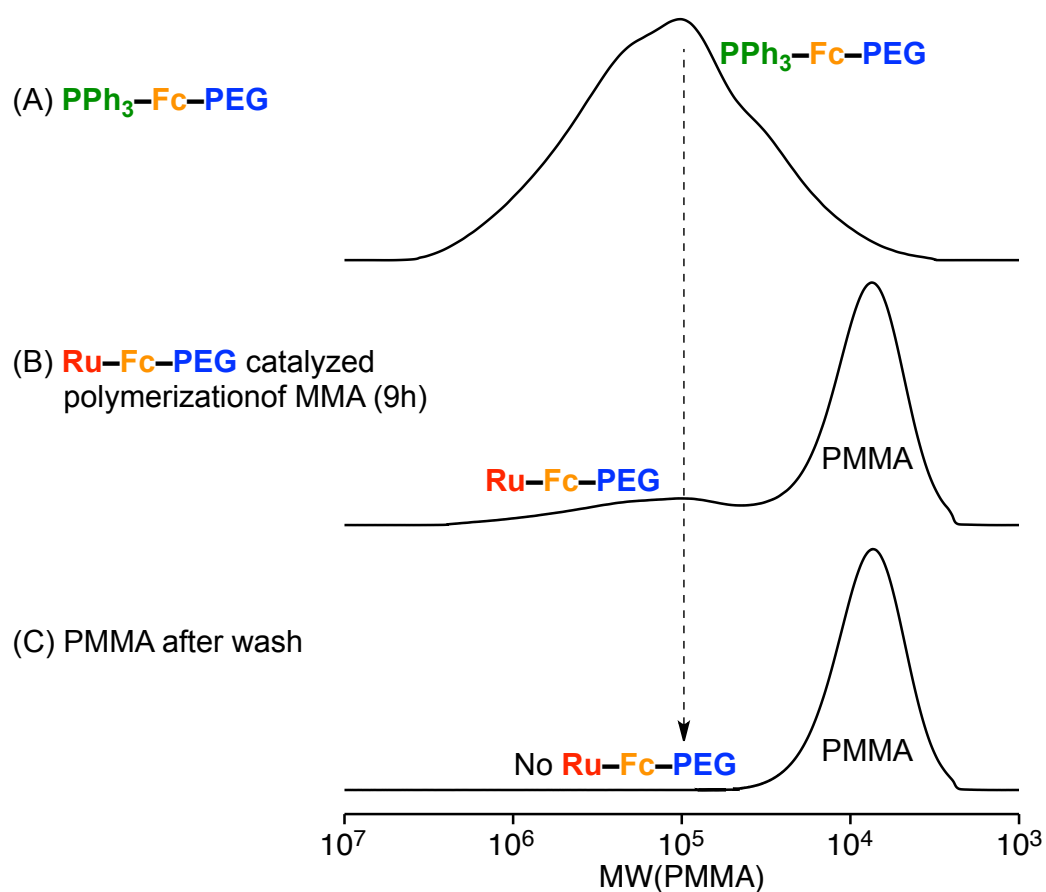


Figure S5. Removal of Ru-Fc-PEG polymer catalyst from obtained PMMA by washing with water: SEC curves of PPh_3 -Fc-PEG (A), the solution of Ru-Fc-PEG catalyzed polymerization of MMA for 9h (see Figure 4A, entry 2 in the main text; B), and the obtained PMMA after washing with water (C).

$$\text{Removability of Ru (Ru}_{\text{remov}}) = 1 - \frac{\text{Residual Ru from ICP-AES}}{\text{Weight of the initially added Ru in 1g of PMMA (Ru}_{\text{init}})}$$

$$\text{Removability of Fe (Fe}_{\text{remov}}) = 1 - \frac{\text{Residual Fe from ICP-AES}}{\text{Weight of the initially added Fe in 1g of PMMA (Fe}_{\text{init}})}$$

$$\left(\begin{array}{l} \text{Ru}_{\text{init}} = \frac{(\text{Atomic weight of the Ru, g/mol}) \times (\text{Ru feed on polymerization, mM})}{(\text{Molecular weight of MMA, g/mol}) \times (\text{MMA feed on polymerization, mM}) \times \text{Conv.}} \\ \text{Fe}_{\text{init}} = \frac{(\text{Atomic weight of the Fe, g/mol}) \times (\text{Fe feed on polymerization, mM})}{(\text{Molecular weight of MMA, g/mol}) \times (\text{MMA feed on polymerization, mM}) \times \text{Conv.}} \end{array} \right)$$

ex) PMMA obtained with **Ru-Fc-PEG** (Conv. = 92%; $M_n = 10700$; $M_w/M_n = 1.17$; see Figure 5A in the main text)

$$\text{Ru}_{\text{init}} = \frac{(101.07 \text{ g/mol}) \times (0.25 \times 4 \text{ mM})}{(100.12 \text{ g/mol}) \times (4000 \text{ mM}) \times 0.92} = 2.72 \times 10^{-3} \quad \text{Fe}_{\text{init}} = \frac{(55.845 \text{ g/mol}) \times (40 \text{ mM})}{(100.12 \text{ g/mol}) \times (4000 \text{ mM}) \times 0.92} = 6.06 \times 10^{-3}$$

$$\text{Ru}_{\text{remov}} = 1 - \frac{5.7 \times 10^{-6}}{2.72 \times 10^{-3}} = 0.998 \text{ (99.8\%)} \quad \text{Fe}_{\text{remov}} = 1 - \frac{89 \times 10^{-6}}{6.06 \times 10^{-3}} = 0.985 \text{ (98.5\%)}$$

Figure S6. The calculation methods for the removability of Ru (Ru_{remov}) and Fe (Fe_{remov}) in PMMA after washing with water (see Figure 5 in the main text).