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

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Thermoresponsive polymer-supporter catalyst consisting of ruthenium (Ru) main catalyst and ferrocene (Fc) cocatalyst were designed to realize both high activity and efficient removal of metal residues. The supported catalyst/cocatalyst was easily prepared via ternary random free radical copolymerization of vinylferrocene (VFc), phosphine-pendant monomer (SDP), and PEG-pendant methacrylate (PEGMA), followed by mixing with a Ru precursor ($[Ru(Cp^*)Cl]_4$). The thermoresponsive feature was confirmed from visual appearance with water/toluene binary solvent: it was preferably soluble in water at room temperature but moved to toluene phase at high temperature for polymerization. The supported catalyst/cocatalyst showed high catalytic activity for living radical polymerization of MMA in toluene to give controlled PMMAs with narrow molecular weight distributions and high halogen end functionality (e.g., M_w/M_n = 1.16 and 96 % Cl-end of PMMA obtained at 89 % conversion in 24h). Metal residues in PMMA can be almost quantitatively removed via water washing of resultant polymerization solution [Residual Ru: 5.7 ppm (99.8% removal), residual Fe: 89 ppm (98.5% removal), characterized by ICP-AES analysis].

Introduction

Transition metal catalyst is now one of the most powerful tools in synthesis of polymers as well as organic molecules because of its high activity and selectivity as well as its extensibility, while the difficulty in removal of metal residue is a serious problem for industrial applications. One classical idea for this problem is using polymer-supported insoluble metal catalysts, such as polystyrene (PSt)-supported catalysts.[1,2] Despite its practical advantage, however, insolubility often incurs loss of reaction efficiency and selectivity. Design of themoresponsive property in catalyst would be one solution to dissolve the dilemma, and for this purpose poly(ethylene glycol) (PEG) have received attention as the supporter for metal catalyst due to that the chemical structure of ether bond is less sensitive to metal catalysis despite high solubility in various solvents.[3-5] The PEG-bound metal catalyst is hydrophilic at ambient temperature but lipophilic at higher temperature, which allows homogeneous catalysis in organic solvent (at higher temperature) and removal after the reaction just through water washing at ambient temperature.

Transition metal-catalyzed living radical polymerization (Mt-LRP) is one of the most widely used among precision polymerization methods, where the carbon-halogen bond as the dormant species is reversibly activated into the carbon-centered radical species (~~~C–X ↔ ~~~C•; ~~~: polymer chain, X: halogen) through the one electron redox reaction of the transition metal catalyst ($Mt^n \leftrightarrow XMt^{n+1}$).[6-12] Herein, there is a limit to efficiency in catalyzing the both reactions (i.e., activation and deactivation) with only one metal complex. Besides, a tiny level of side reactions (coupling and disproportionation), which are unavoidable at later stage in living radical polymerization, incurs accumulation of the high oxidation state complex (i.e., XMt^{n+1}), and thus the reduction to lower state is required to keep the equilibrium balance. Thus, as already demonstrated in some systems, a concomitant use of cocatalyst[13-15] or reducing agent[16-19] is efficient to promote the catalysis for living radical polymerization.

In this context, we have recently reported that a combination of ferrocene ($FeCp_2$; Fc) allows promotion of the catalysis of ruthenium-catalyzed living radical polymerization[20]. Ferrocene is incapable of catalyzing living radical polymerization itself but could assist the ruthenium-based catalysis through two contributions from some mechanical studies: (1) reduction of trivalent ruthenium complex; $XRu^{III} + Fc^{II} \rightarrow Ru^{II} + XFc^{III}$, (2) halogen-capping for growing radical species by resultant XFc^{III}; ~~~C• + $XFc^{III} \rightarrow$ ~~~C–X + Fc^{II}. We coined the ferrocene-combined system as "ferrocene-concerted redox catalysis" (Figure 1), and indeed it allowed the synthesis of high molecular weight PMMA with narrow molecular weight distribution ($M_n \sim 1.0 \times 10^5$; $M_w/M_n \sim$

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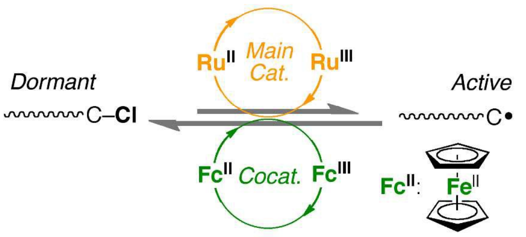


Fig. 1 Ferrocene-concerted redox catalysis in ruthenium catalyzed living radical polymerization.

1.3) even under really catalytic condition with only 50 ppm (for monomer) of Ru main catalysts. However, toward practical applications of this system, we have to remove the ferrocene residue as well as ruthenium from obtained polymers.

One possibility to develop the ferrocene-concerted system is derivatization of the ferrocene cocatalyst. For instance, vinyl ferrocene (VFc) would be suitable for design of polymer-supported ferrocene, since it can be easily polymerized via free radical propagation.[21,22] Combination of suitable comonomers with VFc would allow further functionalization of the polymer for a useful supporter, and herein we designed two comonomers: phosphine-bearing styrene derivative (diphenylphosphino styrene) to support main ruthenium catalyst though the ligation;[23,24] methacrylate carrying PEG chain (PEGMA) to provide a thermoresponsive feature to the supporter. The ternary random copolymer (PPh_3–Fc–PEG) was treated with ruthenium precursor for complexation of ruthenium catalyst (Figure 2). The obtained polymer catalyst (Ru–Fc–PEG) was then used for living radical polymerization of methyl methacrylate (MMA) to evaluate its catalytic activity and removal efficiency by washing with water. As a result, we found that the supported ruthenium and ferrocene can catalyze well-controlled living radical polymerization to give PMMA with narrow molecular weight distribution and high end-functionality. In addition, the metal residues were almost quantitatively removed with the PEG-based supporter by just washing the polymerization solution with water.

Experimental

Materials

MMA (TCI; purity: >99%) was dried overnight over calcium chloride and purified by distillation from calcium hydride before use. PEGMA ($CH_2{=}CMeCO_2(CH_2CH_2O)_n$; Me = CH_3; n = 8.5 on average) (Aldrich) was purified by passing through an inhibitor-removal column (Aldrich) and was subsequently degassed by three-time vacuum-argon bubbling cycle before use. Diphenylphosphinostyrene (SDP; kindly supplied by Hokko Chemical; purity: >99.9%), vinyl ferrocene (Wako; purity: >95%) and 2,2'-azobisisobutyronitrile (AIBN; TCI; purity: >98%) were degassed by reduced pressure and purged by argon before use. The $H\text{-}(MMA)_2\text{-}Cl$ initiator for LRP ($H\text{-}(CH_2CMeCO_2Me)_2\text{-}Cl$; an MMA dimer chloride) was prepared according to the literature.[25] $Ru(Cp^*)Cl(PPh_3)_2$ (Aldrich), Ferrocene ($FeCp_2$; Aldrich; purity >98%), and Triphenylphosphine (PPh_3; Aldrich; purity: 99%) were used as received. A ruthenium precursor complex (chloro(pentamethylcyclopentadienyl) ruthenium(II) tetramer: $[Ru(Cp^*)Cl]_4$) was prepared according to the literature.[26,27] $Ru(Cp^*)Cl(PPh_3)_2$, $FeCp_2$, PPh_3, and $[Ru(Cp^*)Cl]_4$ were handled in a glove box under a moisture- and oxygen-free argon atmosphere (H_2O < 1 ppm, O_2 < 1 ppm). Tetralin (1,2,3,4-tetrahydronaphthalene; Kisida Chemical; purity: >98%) as an internal standard for ^1H NMR was dried over calcium chloride and distilled from calcium hydride before use. Toluene as a solvent of the polymerization was purified by passing through a purification column. (Solvent Dispensing System; glass counter; HANSEN&CO., LTD.). For a solubility test of the polymer, Water (Wako; distilled) was bubbled with dry nitrogen for more than 15 min immediately before use. Hexane (Wako; dehydrated) for

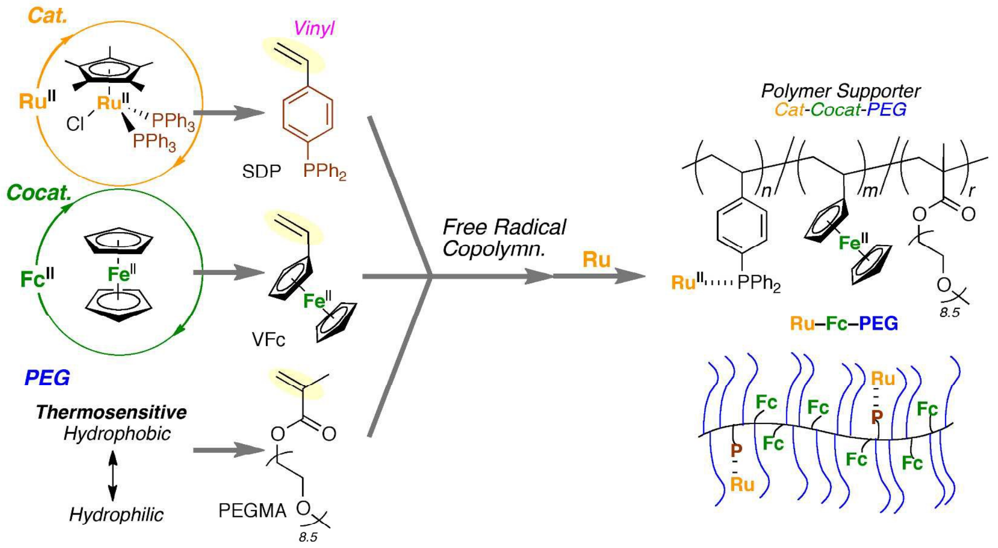


Fig. 2 Design of the thermoresponsive polymer supporter for ferrocene-concerted redox catalysis in ruthenium-catalyzed living radical polymerization.

polymer precipitation was used as received.

Synthesis of PPh_3–Fc–PEG

The polymer supporter (PPh_3–Fc–PEG) was synthesized under argon. In a 50 mL round-bottomed flask were placed SDP (34.6 mg, 0.12 mmol), VFc (424 mg, 2.0 mmol), and AIBN (26.3 mg, 0.16 mmol). Toluene (4.1 mL), tetralin (internal standard: 0.4 mL), and PEGMA (3.5 mL, 8.0 mmol) were added sequentially in this order at room temperature under dry argon. Immediately after mixing, the flask with the reaction solution was placed in an oil bath at 60 ˚C, and stirred for 48 h. After SDP, VFc, and PEGMA were completely consumed (confirmed by ^{1}H NMR with the peak from tetralin), the reaction solution was cooled to room temperature. The mixture was evaporated, and then crude product was purified by precipitation from the dichloromethane solution into hexane three times. The orange colored sticky product, PPh_3–Fc–PEG, was dried under reduced pressure (3.51 g, yield: 82.4%; M_n = 57200, M_w/M_n = 4.25, SEC in DMF, PMMA calibration). ^{1}H and ^{31}P NMR spectra of PPh_3–Fc–PEG are available in Figure S1 and Figure 3A respectively. The mole concentrations of phosphine ligand ([PPh_3]) and ferrocene ([Fc]) per polymer weight were determined to be 0.028 mmol/g ([PPh_3]) and 0.47 mmol/g ([Fc]) respectively from ^{1}H NMR spectrum.

Synthesis of PPh_3–PEG

The ferrocene-free supporter (PPh_3–PEG) was synthesized via free radical polymerization similar to above without using VFc: SDP (17.3 mg, 0.06 mmol), AIBN (13.1 mg, 0.08 mmol), PEGMA (1.8 mL, 4.0 mmol), tetralin (0.4 mL), toluene (5.8 mL). After the re-precipitation procedure, PPh_3–PEG was obtained as the colorless oil (1.51 g, yield: 78.7%; SEC in DMF: M_n = 55100, M_w/M_n = 3.97). ^{1}H and ^{31}P NMR spectra of PPh_3–PEG are available in Figure S2. The mole concentration of phosphine ligand ([PPh_3]) per polymer weight was determined to be 0.031 mmol/g from ^{1}H NMR spectrum.

Synthesis of Fc–PEG

The phosphine-free supporter (Fc–PEG) was synthesized via free radical polymerization similar to above without using SDP: VFc (424 mg, 2.0 mmol), PEGMA (3.5 mL, 8.0 mmol), AIBN (26.3 mg, 0.16 mmol), tetralin (0.4 mL), toluene (4.1 mL). After the re-precipitation procedure, PPh_3–PEG was obtained as the orange colored oil (3.16 g, yield: 74.8%; SEC in DMF: M_n = 60600, M_w/M_n = 4.49). ^{1}H NMR spectrum of Fc–PEG is available in Figure S3. The concentration of ferrocene ([Fc]) per polymer weight was determined to be 0.47 mmol/g from ^{1}H NMR spectrum.

Procedures for Living Radical Polymerization

The polymerization was carried out by syringe technique under dry argon in baked glass tubes equipped with a three-way stopcock. A typical procedure for MMA polymerization with H–$(MMA)_2$–Cl/Ru–Fc–PEG is given below. $[Ru(Cp^*)Cl]_4$ (1.7 mg, 0.002 mmol), a 400 × 10^{-3} g/mL toluene solution of PPh_3–Fc–PEG (1.7 mL, 0.019 mmol of PPh_3 ligand and 0.32 mmol of ferrocene cocatalyst), and toluene (0.98 mL) were added into a schlenk tube. The mixture was placed in an oil bath at 80 ˚C for 12 h to give Ru–Fc–PEG. Into the in situ formed Ru–Fc–PEG solution, tetralin (0.3 mL), MMA (2.57 mL, 24 mmol), and a 540 × 10^{-3} M toluene solution of H-$(MMA)_2$-Cl (0.45 mL, 0.24 mmol) were added at room temperature under argon (total volume: 6.0 mL). Six aliquots (1.0 mL each) of the mother solution were distributed into backed glass tubes that were subsequently sealed and placed in an oil bath at 100 ˚C. After predetermined periods, the reaction was terminated by cooling the solutions to –78 ˚C. The conversion of MMA was determined from the concentration of residual monomer measured by ^{1}H NMR from the integrated peak area of the olefinic protons of the monomer with tetralin as an internal standard. The terminated reaction solutions were diluted with toluene, washed with water three times, and evaporated to dryness to give the polymers, which were subsequently dried overnight under vacuum at room temperature.

Measurement

M_n and M_w/M_n of PMMA were measured by size exclusion chromatography at 40 ˚C in THF as an eluent on three polystyrene-gel columns (Shodex LF-404; exclusion limit = 2 × 10^6; particle size = 6 μm; pore size = 3000 Å; 0.46 cm i.d. × 25 cm; flow rate, 0.3 mL min^{-1}) connected to a DU-H2000 pump, a RI-74 refractive-index detector and a UV-41 ultraviolet detector (all from Shodex). The columns were calibrated against 13 standard poly(MMA) samples (Polymer Laboratories; M_n = 620–1 200 000; M_w/M_n = 1.06–1.22) as well as the monomer. For PPh_3–Fc–PEG, PPh_3–PEG, and Fc–PEG, M_n and M_w/M_n were measured by size exclusion chromatography at 40 ˚C in DMF containing 10 mM LiBr as an eluent on three polystyrene-gel columns (Shodex KF-805 L; exclusion limit = 4 × 10^6; particle size = 5000 Å; 0.8 cm i.d. × 30 cm; flow rate, 1.0 mL min^{-1}) connected to a PU-2080 pump and a RI-1530 refractive-index detector, and a UV-1570 ultraviolet detector (all from Jasco). The columns were calibrated against 13 standard poly(MMA) samples (Polymer Laboratories; M_n = 630–1 200 000; M_w/M_n = 1.02-1.30) as well as the monomer. ^{1}H and ^{31}P NMR spectra were recorded in CD_2Cl_2 and $CDCl_3$ at room temperature on a JEOL JNM-ECA500 spectrometer, operating at 500.16 MHz and 202.47 MHz, respectively. For the ^{31}P NMR analysis, a capillary of $(C_2H_5O)_2POH$ solution (50 mM in toluene-d_8) was used as an internal chemical shift standard (12 ppm for the phosphite). The residual ruthenium and iron amount in the obtained PMMA were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES: IRIS Intrepid II XDL Radial; Thermo Fisher Scientific).

Results and discussion

Synthesis of PPh_3–Fc–PEG

We synthesized the ligand polymer (PPh_3–Fc–PEG) by free radical copolymerization of SDP, VFc, and PEGMA in conjunction with AIBN as the radical initiator in toluene at 60˚C ($[SDP]_0/[VFc]_0/[PEGMA]_0/[AIBN]_0$ = 15/250/1000/20 mM: the feed ratio of SDP and VFc was set according to the previous report about Ru/ferrocene concerted redox catalysis).[20] Three monomers were all consumed quantitatively in 48 h to give PPh_3–Fc–PEG (M_n = 57200), and the ratio of PPh_3 (from SDP), $FeCp_2$ (from VFc), and PEG chain (from PEGMA) in the obtained polymer was determined to be [PPh_3]/[$FeCp_2$]/[PEG chain] = 14.9/251/1000 from ^{1}H NMR spectrum (Figure S1), which was well fitted to the monomer feed ratio.

Ru–Fc–PEG: thermoresponsive polymer catalyst

A tetrameric Cp*-ligated ruthenium complex [Ru(Cp*)Cl]$_4$ can accept phosphine based ligands (PR$_3$) by just mixing to give coordinatively saturated (18e) or unsaturated (16e) complexes (Ru(Cp*)Cl(PR$_3$)$_n$; n = 1, 2), which are well known to be useful for living radical polymerization.[15] A mixture solution of [Ru(Cp*)Cl]$_4$ and PPh$_3$–Fc–PEG in toluene ([Ru]$_0$/[PPh$_3$ in PPh$_3$–Fc–PEG]$_0$ = 1/2.4; a little excess PPh$_3$ was mixed to perfectly promote complexation) was stirred at 80 ˚C for 12 h. From ^{31}P NMR spectra, the signal at –1 ppm originating from PPh$_3$ pendant on polymer was clearly decreased upon mixing with [Ru(Cp*)Cl]$_4$ (Figure 3A), implying Ru introduction to the polymer by phosphine ligation. The new signal originating from Ru ligation was not observed because of low mobility of ligating PPh$_3$ on polymer supporter, which was also reported with other polymer-supported Ru catalysts.[23,24,28]

The obtained Ru–Fc–PEG was soluble in toluene at room temperature to give yellowish-orange colored homogeneous solution. When a same volume of water was added to prepare a bilayer solution, the color was transferred from upper (toluene) to lower phase (water: Figure 3B), indicating the preference of the polymer for water rather than hydrophobic solvent at room temperature. Once the bilayer was heated up to 95˚C that is higher than reported LCST of PEGMA homopolymer (~ 90˚C),[29] the color moved to upper phase, whereas the color was back to lower upon cooling to room temperature. These results indicate the supported Ru/Fc, Ru–Fc–PEG showed thermo-responsibility fitted to both of catalysis and removal for polymerizations of hydrophobic monomers, i.e., it prefers hydrophobic solvent to water at higher temperature for polymerization, but the preference is reversed at room temperature for workup process. As another demonstration for thermo-responsibility of Ru–Fc–PEG, the polymer gave a transparent solution in water at room temperature but it became cloudy at around 90 ˚C (Figure 3C). Rather unsurprisingly, such thermoresponsive behaviors were not observed with the corresponding unsupported complexes (Ru(Cp*)Cl(PPh$_3$)$_2$: Figure S4A; FeCp$_2$: Figure S4B).

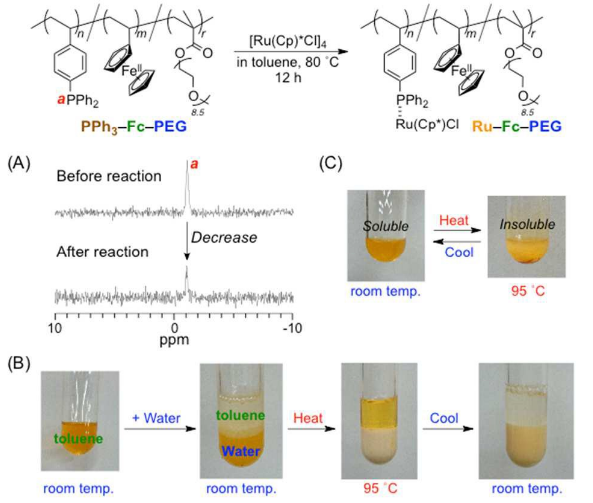
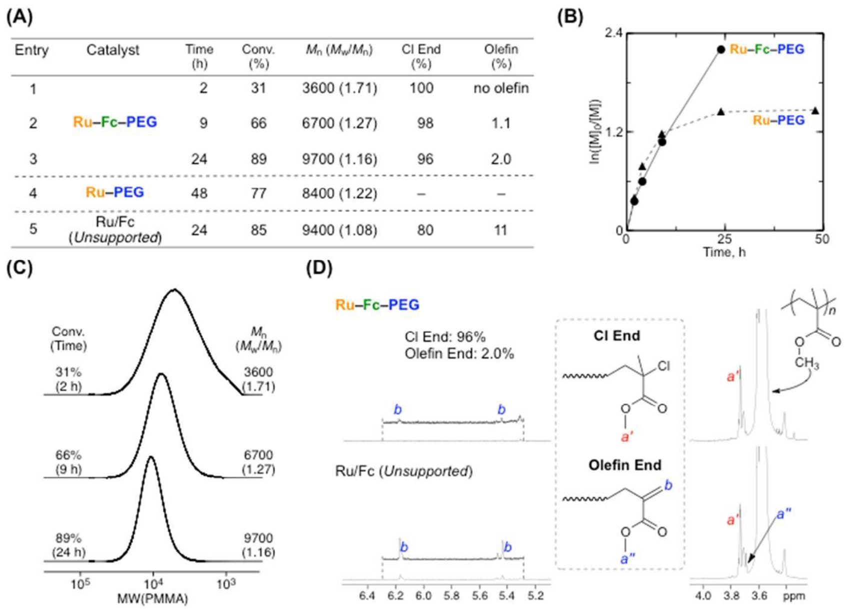


Fig. 3 Synthesis of Ru–Fc–PEG ([[Ru(Cp*)Cl]$_4$]$_0$/[PPh$_3$ in polymer]$_0$ = 0.25/2.4 mM in toluene at 80 ˚C) and its thermoresponsive solubility: (A) ^{31}P NMR spectra (in CDCl$_3$) for Ru introduction reaction (upper: before reaction (PPh$_3$–Fc–PEG); lower: after reaction (Ru–Fc–PEG)); (B) thermoresponsive phase transfer behavior of Ru–Fc–PEG in a toluene/water biphasic solution; (C) thermoresponsive solubility of Ru–Fc–PEG in water.

Living radical polymerization via polymer-supported metal catalysts

The polymer-supported binary metal catalysts (Ru–Fc–PEG) was then applied to a living radical polymerization of MMA in conjunction with a chlorine initiator [H–(MMA)$_2$–Cl] in toluene at 100 ˚C: [MMA]$_0$ = 4.0 M, [H–(MMA)$_2$–Cl]$_0$ = 40 mM, [Ru]$_0$ = 1.0 mM, [FeCp$_2$ (Fc) in polymer]$_0$ = 40 mM (Figure 4A, Entry 1-3). The polymerization proceeded smoothly to reach around 90% conversion in 24 h and showed an almost linear first-order kinetic



(A)

Entry	Catalyst	Time (h)	Conv. (%)	M_n (M_w/M_n)	Cl End (%)	Olefin (%)
1		2	31	3600 (1.71)	100	no olefin
2	Ru–Fc–PEG	9	66	6700 (1.27)	98	1.1
3		24	89	9700 (1.16)	96	2.0
4	Ru–PEG	48	77	8400 (1.22)	–	–
5	Ru/Fc (*Unsupported*)	24	85	9400 (1.08)	80	11

Fig. 4 Ru–Fc–PEG catalyzed living radical polymerization of MMA and comparison with Ru–PEG and unsupported system (Ru/Fc) ([MMA]$_0$/[H-(MMA)$_2$-Cl]$_0$/[Ru]$_0$/[Fc]$_0$ = 4000/40/1.0/40 mM in toluene at 100 ˚C): A) fundamental data of polymerizations; B) kinetic plots of ln([M]$_0$/[M]) vs time; C) SEC curves of PMMAs obtained with Ru–Fc–PEG; D) ^{1}H NMR spectra (in CDCl$_3$) of PMMAs obtained with Ru–Fc–PEG (upper) and Ru/Fc unsupported system (lower).

plot (Figure 4B), indicating the catalytic activity was almost kept during polymerization. On the other hand, similar polymer supported catalyst bearing only ruthenium catalyst (Ru–PEG) resulted in slower and retarded polymerization. Thus, an acceleration effect in conjunction with ferrocene is also demonstrated even on polymer supporter. The resultant polymerization solution with Ru–Fc–PEG was washed with water at room temperature to remove polymer catalysts (Figure S5), followed by SEC analyses. Molecular weights of obtained PMMAs were well fitted to the calculated values and narrow molecular weight distribution was observed (Figure 4C). The MWD was relatively broad at earlier stage, which is similar to the polymerization with star polymer-supported ruthenium catalysts.[23,24]

By comparison, unsupported catalyst was also examined under the same condition. The ruthenium catalyst was prepared through mixing $[Ru(Cp^*)Cl]_4$ with PPh_3 at the same ratio as with PPh_3–Fc–PEG ($[Ru]_0/[PPh_3]_0 = 1/2.4$). It was employed in conjunction with $FeCp_2$ for the MMA polymerization. The polymerization smoothly occurred to give narrow MWDs, as we reported before ($M_n = 9400$, $M_w/M_n = 1.08$, conv. = 85% in 24 h: Figure 4A Entry 5), and little significant advantage of Ru–Fc–PEG was observed over the unsupported system.

However, ^{1}H NMR analyses of terminal structure showed a difference between the two systems. For the Ru–Fc–PEG catalyzed polymerization, quite high Cl–end functionalities were observed during polymerization, and the high functionality was kept even at later polymerization stage (96% of Cl-end in 89% conversion: Figure 4D). On the other hand, with the unsupported binary catalyst, 20% of Cl–end was lost at 85% conversion. Some neighboring effects may work in halogen capping for propagating radical species by XFc^{III} and/or XRu^{III} on the supporter. More detailed study is required to clarify it, but it is interesting that polymer-support showed a positive effect in addition to the expected function as described below.

Catalyst Removability

The toluene solution of obtained PMMA (Conv. = 92% in 48 h; $M_n = 10700$, $M_w/M_n = 1.17$) with Ru–Fc–PEG was washed with water at room temperature three times to remove the polymer catalyst. After the washing process, THF solution of PMMA (2 wt%) was colorless (Figure 5A), indicating removal of metal residues. For a quantitative analysis, the metal residues (Ru, Fe) in the PMMA sample were determined with the inductively coupled plasma-atomic emission spectrometry (ICP-AES) analysis. The weight ratio of ruthenium (Ru) and iron (Fe) was 5.7 ppm and 89 ppm respectively, meaning 99.8% (Ru) and 98.5% (Fe) were removed for the initially added metal catalysts (Figure S6 for the calculation).

To see effects of polymer support on removability of the two metal complexes, similar binary catalyst systems without either ruthenium or ferrocene on the chains (Ru–PEG + Fc, or Ru + Fc–PEG) were also used for the polymerization of MMA as well as the both-unsupported (Ru + Fc: see above), and resultant PMMAs were measured with ICP-AES to evaluate the weight ratio of Ru and Fe. Both catalyst systems allowed the controlled polymerizations (Ru–PEG + Fc system: conv. = 88% in 48 h: $M_n = 10500$, $M_w/M_n = 1.20$; Ru + Fc–PEG system: conv. = 91% in 48 h: $M_n = 11100$, $M_w/M_n = 1.18$). However, solutions of these obtained PMMA samples after water-washing treatment obviously colored to yellow. Rather naturally, the weight ratio of unsupported metal was higher, indicating difficulty in removal without polymer support.

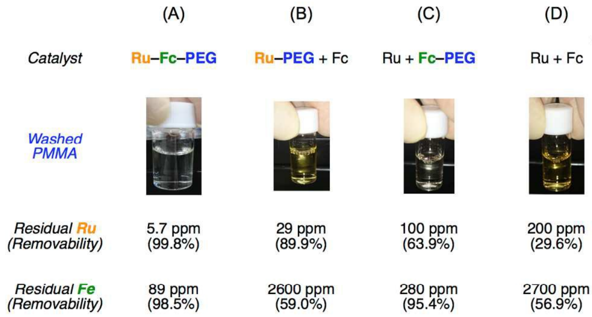


Fig. 5 Removal of metal catalysts from PMMA obtained with Ru–Fc–PEG (A), Ru–PEG + Fc (B), Ru + Fc–PEG (C), and Ru + Fc (D): photographs of THF solutions of the washed PMMA (2 wt%) and residual amounts of Ru and Fe from ICP-AES analysis.

Conclusions

To approach the efficient removal of metal residues for ruthenium-ferrocene concerted catalysis in living radical polymerization, the binary metal catalysts were embedded on the thermoresponsive polymer-supporter. Thus obtained PEG-based polymer, Ru–Fc–PEG, showed a thermoresponsive feature, i.e., hydrophilic at room temperature but hydrophobic at higher temperature as well as high activity in metal-catalyzed living radical polymerization. Importantly, the halogen functionality of polymer terminal was quite higher even at later polymerization stage, likely due to concerted catalysis on condensed polymer backbone. Water washing process of obtained polymer allowed almost quantitative removal of the metal residues (~ 99%), which was supported by ICP-AES analyses.

For industrial processes, compatibility of high activity in the polymerization and easy purification of the product free from metal residues is required. In this context, the design of concerted catalysis on thermoresponsive polymer supporter is promising for practical applications with metal-catalyzed living radical polymerization. Now, our interests are directed to further lowering catalyst load, the recycling, and applying to other types of monomers (acrylates, styrenes, etc.).

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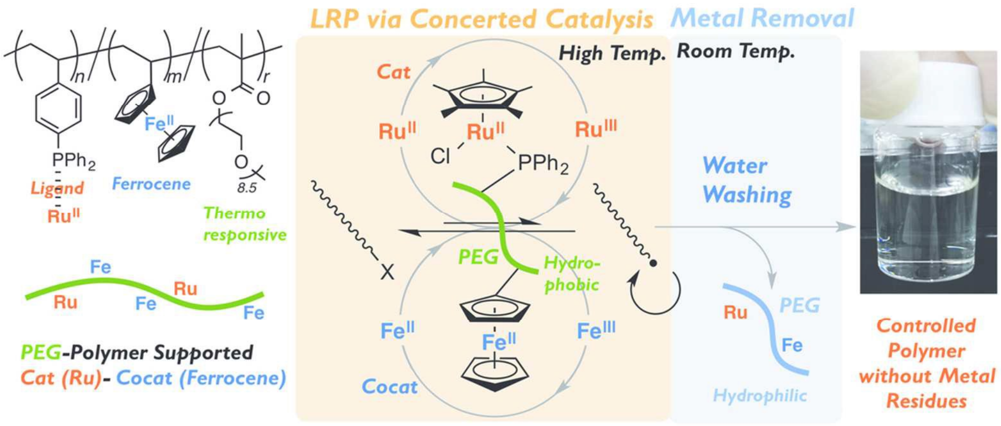

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