Living Radical Polymerization of Styrene by Half-Metallocene Iron Carbonyl Complexes

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ABSTRACT: A series of half-metallocene Fe(II) complexes [FeLX(CO)2;X = I, Br; L = η5-C5H5 (Cp), η5-C5Me5 (Cp*)] were employed for living radical polymerization of styrene in conjunction with halide initiators [(CH3)2C(CO2Et)X; X = I and Br] in the presence or absence of Ti(Oi-Pr)4. The iron-based systems induced living radical polymerization of styrene to give polymers of narrow molecular weight distributions (MWDs) in the presence of Ti(Oi-Pr)4. The Cp*–iodide complex [FeCp*(CO)2] gave the narrowest MWDs (Mn/Mw = 1.05–1.09) when coupled with the iodoester initiator. The polymerization with FeCp(CO)2 was examined in several ether solvents, where dioxane proved most effective. Dinuclear iron(I) complexes [Fe2Cp2(CO)4] were also employed for living radical polymerization of styrene coupled with the iodoester initiator. Dinuclear half-metallocenes induced faster polymerization even without Ti(Oi-Pr)4. Cyclic voltammetric analysis showed that the redox potential of the dinuclear complex is lower than that of the mononuclear one. Some interactions of Ti(Oi-Pr)4 with the iron complexes were observed by cyclic voltammetric and NMR analysis of the mixtures.

Introduction

Living radical polymerization is now one of the most rapidly developing areas in polymer chemistry in the past several years, still expanding the scope of initiating/catalyst systems, applicable monomers, and novel polymer structures to be obtained thereby. Transition-metal catalysts have been effectively used for living radical polymerization (Scheme 1), where the dormant carbon–halogen bond at a polymer terminal is reversibly and homolytically cleaved by the transition metal complexes, such as ~~~C–X + M(n) ↔ ~~~C–X–M(n−1). Along with the nitroxide-mediated20a,c and RAFT counterparts,21 the metal-mediated living radical polymerization is one of the most efficient systems in terms of versatility and controllability. One of its distinguishable features is that metal catalysts can be designed according to monomers and other conditions, in contrast to the other systems where the dormant covalent bonds are cleaved not by catalysts but by heat or carbon radical species.

The effective transition metal catalysts thus far employed for the living radical polymerizations are mostly halides of metals such as Ru,4–9 Cu,10–15 Fe,16,17 Ni,18–21 Rh,22–24 Pd,25 Re,26 and Mo27,28 with phosphine- or nitrogen-based ligands. These metal complexes most probably undergo reversible one-electron redox reaction by interacting catalytically with organic halides to form radical growing species. Obviously, the design of catalysts by the central metals and the ligands is crucial for the activity and the controllability of the metal-catalyzed polymerization.

Among the metals, iron is especially attractive because of its low cost and harmlessness. Recently, we first developed an iron-mediated living radical polymerization of methyl methacrylate (MMA) with the use of Fe(II) phosphate halides, FeX2(PPh3)2 (X = Cl, Br).16 Similar living polymerizations of MMA and styrene were also achieved by a mixture of FeX2 (X = Cl, Br) and phosphate- or nitrogen-based compounds.16 These showed that, if properly designed, iron complexes can be suitable catalysts for transition metal catalyzed living radical polymerization. Later on, however, studies on iron catalysts have not been extensively done in comparison to copper and ruthenium derivatives.

Quite recently, we have found that a half-metallocene-type iron complex, FeCp(CO)2, led to living radical polymerization of styrene in the presence of an iodide initiator and Ti(Oi-Pr)4 as an additive to give polymers of precisely controlled molecular weights and narrow molecular weight distributions (MWDs) (Mn/Mw ~ 1.1).30 Such a half-metallocene iron carbonyl complex can be directly modified by anionic Cp-based ligands, which coordinate to the iron center more tightly than neutral phosphines or amines, so as to be more active and more efficient in contrast to simple iron complexes such as FeX2(PPh3)2. Cp-based ligands proved also effective in increasing the catalytic activity and the controllability of the polymerization in the Ru(II)-based living radical polymerizations.7

In this study, a series of half-metallocene iron(II) carbonyl complexes [FeLX(CO)2; L = Cp, Cp* (Cp* = η5-C5Me5); X = I, Br] were employed for polymerization of styrene coupled with a halide initiator [(CH3)2C(CO2Et)X; X = I, Br] in the presence of Ti(Oi-Pr)4, where effects of Cp-based ligands and halogens were studied (Scheme 2). These iron carbonyl complexes are moisture- and oxygen-tolerant and thus can be prepared under air by halogenation of the corresponding dinuclear iron(I) carbonyl complexes [Fe2L2(CO)4; L = Cp, 

Scheme 1. Living Radical Polymerization of Styrene with Fe(II) Complexes

R–X ⇌ R–FeII ⇌ R–CH2–CH–X

Living Polymer

R–CH2–CH–X + FeII

(Dormant Species)

(R–CH2–CH–X + FeII)

(Active Species)
These dinuclear complexes were also examined herein as possible catalysts for living radical polymerization of styrene. Prior to our work on living radical polymerizations, halogen-free iron carbonyl complexes such as Fe₇Cp₂(CO)₅ and Me₃NFe(CO)₃ have proved effective in metal-mediated radical polymerization such as Fe₂Cp₂(CO)₄, Fe₂(CO)₉, and Me₃NFe(CO)₃. These halogen-free iron carbonyl complexes were also examined and employed for the polymerization of cyclic olefins. This work revealed that Fe₂Cp₂(CO)₄ induced living radical polymerization of styrene without additives such as Ti(O-Pr)₄. Effects of ligands and Ti(O-Pr)₄ along with catalytic activity were investigated by cyclic voltammetry and NMR spectroscopy.

Results and Discussion

1. Half-Metallocene Fe(II) Complexes: FeLX(CO)₂ (X = I, Br; L = Cp, Cp*). As we reported previously, FeCpBr(CO)₂ induced living radical polymerization of styrene, when coupled with [(CH₃)₂C(CO₂Et)I] (initiator) and Ti(O-Pr)₄ (additive) in toluene at 80 °C. A series of half-metallocene complexes [FeLX(CO)₂]: FeCpBr (L = Cp, X = Br), FeCp*Br (L = Cp*, X = Br), FeCpI (L = Cp, X = I), and FeCp*I (L = Cp*, X = I) were synthesized and employed for the polymerization of styrene (Figure 1). For the iodide complexes, an iodostyrene ([CH₃)₂C(CO₂Et)I] was used, and a bromostyrene ([CH₃)₂C(CO₂Et)Br] was used for the bromide complexes to avoid the formation of mixed-halogen terminals and complexes. The polymerization rate depended on the halogen and the ligands of catalysts and increased in the following order: FeCp*I < FeCpBr < FeCp*Br < FeCpBr. Thus, a more electron-donating ligand, Cp*, led to a slower polymerization for both bromide and iodide complexes. The polymerizations with two bromide complexes were faster than those with the iodides.

Figure 2 shows the Mₙ, Mₘ/Mₙ, and MWD curves of polystyrene obtained with (CH₃)₂C(CO₂Et)Br/Fe(II) in the presence of Ti(O-Pr)₄ in toluene at 80 °C: [styrene]₀ = 60 mM; [(CH₃)₂C(CO₂Et)Br]₀ = 60 mM; [Fe(II)]₀ = 10 mM; [Ti(O-Pr)₄]₀ = 100 mM. FeCpI (○, △), FeCp*I (●, ▲).

A similar trend was observed in the polymerization with the bromide complexes (Figure 3). The Mₙ were precisely controlled and agreed well with calculated values with both FeCpBr and FeCp*Br, where the MWDs narrowed as the polymerization proceeded. In these bromine-based initiating systems, the MWDs with the Cp* complex were also narrower than those with the Cp complex.

These results show that the MWDs became narrower in the following order of Mₘ/Mₙ ratio: FeCpBr (≥1.25); FeCp*Br (≥1.14); FeCpI (1.06–1.11); FeCp*I (1.05–1.09). In a polymerization involving the equilibrium between dormant and active species, in general, the MWD of polymers is determined by the rates of propagation and dormant-active species interconversion: a faster interconversion and/or a slower polymerization results in a narrower MWD. As denoted in Scheme 1, a single electron must be transferred from Fe(II) to the dormant polymer terminal. Among our four iron complexes, the electron density of the Fe(II) center is considered the highest for FeCp*I due to the more electron-donating Cp* ligand and the less electron-withdrawing iodo group. Such an electron-rich complex

\[ \text{FeCpI} \]
facilitates electron release to induce faster interconversion. The lower bond energy of the C–I terminal is also effective in narrowing MWD.\(^{36}\) The polymerization with \(\text{FeCp}^+\) was slowest among them, which also produces the narrowest MWDs. The slower the polymerization, the narrower the MWD. Thus, a series of half-metalloocene Fe(II) complexes induced living radical polymerization of styrene, and an electron-donating \(\text{Cp}^*\) ligand provided more precise polymerization control.

2. Solvent Effects on Living Radical Polymerization of Styrene with FeCpI

Apart from toluene, various ethers [anisole (PhOMe), dioxane, and tetrahydrofuran (THF)] were examined as a solvent for living radical polymerization of styrene with \((\text{CH}_3)_2\text{C} (\text{CO}_2\text{Et})\text{I}\) and FeCpI in the presence of Ti(O–Pr)\(_4\) in dioxane at \(80 ^\circ \text{C}\). [Styrene] = 60 M; [(CH\(_3\))\(_2\text{C} (\text{CO}_2\text{Et})\text{I}] = 60 mM; [FeCpI] = 10 mM; [Ti(O–Pr)\(_4\)] = 100 mM.

Figure 5 shows \(M_n\), \(M_w/M_n\), and MWD curves of polystyrene obtained with \((\text{CH}_3)_2\text{C} (\text{CO}_2\text{Et})\text{I}/\text{FeCpI}/\text{ThF}^\text{+}\) in toluene (●, ○), PhOMe (●, △), dioxane (●, △), and THF (◆, ◐) at \(80 ^\circ \text{C}\). [Styrene] = 60 M; [(CH\(_3\))\(_2\text{C} (\text{CO}_2\text{Et})\text{I}] = 60 mM; [FeCpI] = 10 mM; [Ti(O–Pr)\(_4\)] = 100 mM.

Monomer-addition experiments were carried out in dioxane with \((\text{CH}_3)_2\text{C} (\text{CO}_2\text{Et})\text{I}/\text{FeCpI} (\text{CO})_2/\text{ThF}^\text{+}\) at \(80 ^\circ \text{C}\) (Figure 6). A fresh feed of styrene was added to the reaction mixture after the polymerization was virtually completed. The second-phase polymerization further proceeded to reach 194\% monomer conversion in an additional 144 h. The \(M_n\) increased in direct proportion to monomer conversion and agreed well with the calculated values, where the MWDs remained still narrow (\(M_w/M_n = 1.18\)). In similar monomer-addition experiments in toluene, however, a little shoulder was observed in SEC curve of the polystyrene obtained after monomer addition, along with slightly broader main MWDs (174\% in additional 116 h; \(M_n = 25300\); \(M_w/M_n = 1.38\)). These results confirm the living nature of the FeCpI(CO)\(_2\)-based system in dioxane solvent.

3. Dinuclear Half-Metallocene Iron Complexes: \(\text{Fe}_2\text{Cp}_2(\text{CO})_4\) and \(\text{Fe}_2\text{Cp}^*_2(\text{CO})_4\)

As mentioned in the Introduction, the dinuclear iron half-metallocene complex \(\text{Fe}_2\text{Cp}_2(\text{CO})_4\) (\(\text{Fe}_2\text{Cp}_2\)) is an effective catalyst for homogeneous Kharasch addition reaction (Scheme 3). An active catalyst is supposed to be an Fe(I) dinuclear complex, \(\text{Fe}_2\text{Cp}_2(\text{CO})_3\), which is formed via elimination of one of the carbonyl ligands from the tetrakis precursor.

We have thus employed \(\text{Fe}_2\text{Cp}_2(\text{CO})_4\) for living radical polymerization of styrene under the same condition performed with FeCpI: styrene was polymerized with \(\text{Fe}_2\text{Cp}_2\) and \((\text{CH}_3)_2\text{C} (\text{CO}_2\text{Et})\text{I}\) in the presence of Ti(O–Pr)\(_4\) in dioxane at 80 or 60\ C (Figure 7). At both temperatures, polymerizations occurred smoothly to near
The completion in 33 h (80 °C) or 67 h (60 °C), which were much faster than the polymerizations with FeCp2 otherwise under the same conditions (cf. Figure 4). The $M_n$ of the obtained polystyrene increased in direct proportion to monomer conversion and almost agreed with the calculated values, where the MWDs were fairly narrow ($M_w/M_n \sim 1.2$). Thus, living polymerization can also be achieved with the dinuclear iron complex in the presence of Ti(O-i-Pr)$_4$.

We have also employed Fe$_2$Cp$_2$ in the absence of Ti(O-i-Pr)$_4$: styrene was polymerized with Fe$_2$Cp$_2$ and (CH$_3$)$_2$C(CO$_2$Et)I in dioxane at 60 °C (Figure 8). A smooth polymerization proceeded to reach 94% conversion in 23 h at a high initial concentration of the iron complex, [Fe$_2$Cp$_2$]$_0 = 60$ mM. The lower the [Fe$_2$Cp$_2$]$_0$ concentration, the slower the polymerization; e.g., at [Fe$_2$Cp$_2$]$_0 = 10$ mM, monomer conversion leveled off around 75%. The SEC curves obtained at [Fe$_2$Cp$_2$]$_0 = 60$ mM showed bimodal distributions, where the $M_n$ were much higher than the calculated values, although they were narrow and unimodal at lower conversions ($\leq 60\%$). The SEC peak molecular weight for the higher molecular weight fraction was 55 000, almost twice the lower (28 800) which was most likely due to the coupling reaction of polystyryl radicals at such high conversions of styrene. At [Fe$_2$Cp$_2$]$_0 = 20$ mM, on the other hand, the MWDs were unimodal and relatively narrow ($M_w/M_n \sim 1.2$), and the $M_n$ increased in direct proportion to monomer conversion and almost agreed with the calculated values. Another dinuclear iron(I) complex, Fe$_2$Cp$_2$(CO)$_2$I, also gave relatively narrow MWDs ($M_w/M_n = 1.25$). Thus, half-metalloocene-type dinuclear complexes induced living polymerization of styrene without any additives, although the polymerization conditions were carefully selected.

4. Cyclic Voltammetry of Fe Complexes. The electrochemical behavior of the Fe complexes was then examined by cyclic voltammetry, which should give information about the redox processes of the complexes. All the measurements were conducted in CH$_2$CICH$_2$Cl containing n-Bu$_4$NPF$_6$ (0.1 M) at a platinum working electrode with a scan rate of 0.1 V s$^{-1}$. Cyclic voltammograms of FeCp and Fe$_2$Cp$_2$ are shown in Figure 9A. FeCp showed an oxidation wave around 1.4 V but almost no reduction wave (solid line in Figure 9A). Such a high oxidation potential (~1.4 V) of FeCp suggests that FeCp alone is not a good catalyst for the living polymerization as reported.$^{30}$

Fe$_2$Cp$_2$ showed two oxidation waves when the potential was raised to 2.0 V (dashed line in Figure 9A). The lower potential peak is assigned to one-electron oxidation of one of the two Fe(I) centers in the dinuclear complex [Fe(l, i) → Fe(li, II)], and the second peak is due to the oxidation of the other nucleus [Fe(l, II) → Fe(ii, II)]. The cyclic voltammogram for the first scan showed small reduction wave around 0.7 V, which corresponds to the reduction of Fe(l, II) to Fe(l, I), although the second scan gave no waves. These show that the oxidation of Fe(l, II) to Fe(ii, II) is chemically irreversible, probably due to decomposition of the compound after the second electrochemical oxidation. However, a quasi-reversible wave for Fe(li/II) couple ($\Delta E = E_{p,a} - E_{p,c} = 176$ mV; $E_{p,a}$ and $E_{p,c}$ are peak potential of the oxidation and reduction waves, respectively) was observed at $E_{1/2} = (E_{p,a} + E_{p,c})/2 = 749$ mV when the...
scanning was turned to reduction direction at 1.1 V, where the first oxidation [Fe(I, I) → Fe(I, II)] was observed (dashed line in Figure 9B). This redox cycle was highly reproducible in several scans in the range 0 to 1.1 V vs Ag/AgCl. This shows that Fe2Cp2 undergoes a chemically reversible redox reaction between Fe(I, I) and Fe(I, II). It follows that the dinuclear complex induces living radical polymerization via such a redox cycle even in the absence of Ti(O-Pr)4. Fe2Cp2 was also analyzed to give similar quasi-reversible cycle at E1/2 = 451 mV (ΔE = 130 mV), lower than that of Fe2Cp2 (solid line in Figure 9B). This indicates that a more electron-donating ligand, Cp*, lowers the oxidation potential of the Fe complex.

Cyclic voltammograms of FeCpI and Fe2Cp2 in conjunction with Ti(O-Pr)4 were then measured. In these experiments the Fe complex was mixed with Ti(O-Pr)4 in CH2Cl2/CH2Cl2. The solution was heated to 80 °C, kept at the temperature for 24 h, and cooled to 30 °C. Finally, an n-Bu4NPF6 solution of CH2Cl2/CH2Cl2 was added to the mixture. The solid line in Figure 10A shows the voltammogram of an FeCpI/Ti(O-Pr)4 (5/15 mM) mixture, while the dashed line for Fe2Cp2/Ti(O-Pr)4 (5/15 mM). FeCpI/Ti(O-Pr)4 showed small oxidation and reduction waves at 0.56 and 0.50 V (E1/2 = 530 mV), respectively, in addition to the oxidation wave at 1.35 V which was also observed for FeCpI alone (cf. Figure 9). The peaks are probably due to the new redox potential of FeCpI modified with Ti(O-Pr)4. Fe2Cp2/Ti(O-Pr)4 also exhibited a new redox wave at nearly the same potential (E1/2 = 534 mV), in addition to the peaks observed for the complex alone (Figure 9A). It is also noteworthy that the redox cycle for Fe2Cp2 was reproducible after several scans even in such a wide voltage range (0 to ~1.7 V), in contrast to the results for in the absence of Ti(O-Pr)4 (d. Figure 9A). This may indicate that the Fe center can undergo chemically reversible redox reactions due to the stabilization of higher oxidation states by Ti(O-Pr)4. Similar stabilizing effects of alkoxide additives were observed with RuCl2(PPh3)3 in the presence of Al-i-Pr3 [23]. This is consistent with the polymerization results where FeCp2 resulted to a fast living polymerization at its lower concentration in the presence of Ti(O-Pr)4. Thus, added Ti(O-Pr)4 probably forms a new complex with FeCpI and Fe2Cp2 and/or stabilizes iron species at higher oxidation states.

Figure 10B shows the voltammograms of the mixtures in a narrower scan range (0 to 1.1 or 1.2 V). FeCpI/Ti(O-Pr)4 gave the redox cycles at E1/2 = 537 and 750 mV (ΔE = 97 and 157 mV, respectively), one of which was very similar to that of FeCpI/Ti(O-Pr)4 (E1/2 = 534 mV, ΔE = 75 mV). Both redox cycles were reproducible. In the presence of Ti(O-Pr)4, FeCpI is most probably transformed into an effective catalyst that involves a new redox cycle with a low oxidation/reduction potential. However, the peak intensity was very small, which resulted in a slower polymerization with FeCpI/Ti(O-Pr)4. Thus, cyclic voltammetric analysis gave us valuable information on the complexes, although the interaction between the Fe complexes and Ti(O-Pr)4 was not fully clarified yet.

5. NMR Analysis. Possible interaction between the Fe complexes and Ti(O-Pr)4 was analyzed by 13C and 1H NMR spectroscopy. The analyses were carried out in toluene-d8 at 80 °C, where mixtures of the complex and Ti(O-Pr)4 were preheated at 80 °C for 24 h. Figure 11 shows 13C and 1H NMR spectra of FeCpI (A1, A2), FeCp2/Ti(O-Pr)4 (B1, B2), FeCp2 (C1, C2), and FeCp2/Ti(O-Pr)4 (D1, D2). The 13C signal at 83.89 ppm (Figure 11A) is attributed to the aromatic carbon of the Cp ring in FeCpI, and its proton b was observed at 4.14 ppm (A2). On addition of Ti(O-Pr)4 peak a split into two sharp signals (B1) and peak b shifted downfield (4.16 ppm in B2). Apparently, Ti(O-Pr)4 interacted with FeCpI, though the 13C chemical shift of the carbonyl group did not change (213.8 ppm). On the other hand, almost no change was observed for Fe2Cp2 on addition of Ti(O-Pr)4. The Cp carbon was observed at 88.49 ppm as a sharp singlet both in the absence and in the
presence of Ti(O-Pr)₄ (Figure 9-C1 and D1). A very slight downfield shift was observed on ¹H NMR spectra (C2 and D2).

These results are consistent with the polymerization behavior. The FeCp₁-based system induced a slow living polymerization in the presence of Ti(O-Pr)₄, but fast and uncontrolled oligomerization occurred without Ti(O-Pr)₄. The NMR analysis indicates that Ti(O-Pr)₄ changes FeCp into another iron species that is active for living polymerization. On the other hand, the Fe₂Cp₂-based system induced living polymerization with and without Ti(O-Pr)₄. Significant changes in NMR spectra by addition of Ti(O-Pr)₄ were not observed for Fe₂Cp₂. This probably suggests that the dinuclear complex seems as an active catalyst without significant changes in its structure via interaction with Ti(O-Pr)₄. However, Ti(O-Pr)₄ may prevent the decomposition of Fe₂Cp₂, because the polymerization at low concentration of Fe₂Cp₂ became slower without Ti(O-Pr)₄ as the polymerization proceeded.

In conclusion, living radical polymerization of styrene was achieved with a series of half-metallocene iron complexes, FeCpBr, FeCp*Br, FeCp, and FeCp* in the presence of Ti(O-Pr)₄. The FeCp* seems the best among the four. Polymerization rate and MWDs depend on the structure of the iron complexes, where an electron-donating ligand such as Cp* slows the polymerization and narrows the MWDs. FeCp* gave the narrowest MWDs (Mₙ/Mₘ = 1.05–1.09) coupled with iodo initiator. As solvent, dioxane proved better than toluene in controlling the polymerization. Dinuclear iron complexes, Fe₂Cp₂ and Fe₂Cp₂*, induced faster living radical polymerization even in the absence of Ti(O-Pr)₄. Cyclic voltammetric studies revealed that the dinuclear complex has a lower redox potential than the mononuclear halide complex and that Ti(O-Pr)₄ probably stabilizes iron species at higher oxidation states. These iron-based initiating systems recently proved equally active for acrylates, and block and random copolymerizations of styrene and acrylates were successful.³⁰

Experimental Section

Materials. Styrene (Wako Chemicals; purity ≥ 99%) was dried overnight over anhydrous sodium sulfate and distilled twice over calcium hydride under reduced pressure before use. All transition metal complexes were handled in a glovebox (M. Braun) under dry (<1.0 ppm) and oxygen-free (<1.0 ppm) argon. Ti(O-Pr)₄ (Kanto Chemicals, >97%) was used as received. Toluene, dioxane (solvent), and tetralin (internal standard) were received. Toluene, dioxane (solvent), and tetralin (internal standard) were used.

Initiators. Ethyl 2-bromoisobutyrate ([CH₃]₂C(CO₂H)Br) (Tokyo Kasei, purity ≥ 98%) was distilled twice over calcium hydride under reduced pressure before use. Ethyl 2-iodoisobutyrate ([CH₃]₂C(CO₂H)I) was prepared by the method of Curran et al.,³⁹ bp 50 °C/9 Torr; identified by 500 MHz ¹H NMR. Anal. Calcd for C₇H₈O₂I: C, 29.8; H, 4.58; I, 52.4. Found: C, 29.7; H, 4.59; I, 52.3.

Fe Complexes. FeCp(CO)₂ (Aldrich; purity ≥ 97%), Fe₂Cp₂(CO)₄ (Aldrich; purity ≥ 99%), and Fe₃Cp₃(CO)₁₅ (Azmax; purity ≥ 95%) were used as received. FeCp*Br(CO)₂ and FeCpBr(CO)₄ were synthesized by the method of Fisher et al.³² Anal. Calcd for C₅H₅BrO₂Fe: C, 38.54; H, 4.05; I, 33.93. Found: C, 38.32; H, 3.95; I, 33.92. FeCp*Br(CO)₂ and FeCpBr(CO)₄ were synthesized by the method of Fisher et al.³² Anal. Calcd for C₅H₅BrO₂Fe: C, 44.08; H, 4.62; Br, 24.44. Found: C, 43.98; H, 4.57; Br, 24.57. Calcd for C₅H₅BrO₂Fe: C, 32.73; H, 1.96; Br, 31.11. Found: C, 32.66; H, 1.86; Br, 31.05.

Polymerization Procedures. Polymerization was carried out by the syringe technique under dry nitrogen in sealed glass tubes. A typical example for the polymerization of styrene with (CH₃)₂C(CO₂Et)I/FeCp*Br(CO)₂/Ti(O-Pr)₄ is given below: FeCp*Br(CO)₂ (0.0122 g) was mixed with styrene (2.75 mL), dioxane (0.83 mL), and Ti(O-Pr)₄ (0.118 mL), sequentially in this order. Immediately after adding toluene solution of (CH₃)₂C(CO₂Et)I (0.289 mL) into the reaction mixture, the solution was placed in an oil bath at 80 °C. Polymerization was terminated by cooling the reaction mixtures to ~78 °C. Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with tetralin as the internal standard. The quenched reaction solutions were diluted with toluene (~20 mL) and rigorously shaken with an absorbent [Kyowa-2000G-7 (Mg₂+ Al3+ O13); Kyowa Chemical] (~5 g) to remove the metal-containing residues. After the absorbent was separated by filtration (Whatman 113V), the filtrate was washed with water and evaporated to dryness to give the products, which were subsequently dried overnight.

Measurements. The MWD, Mₙ, and Mₘ/Mₙ ratios of the polymers were measured by size-exclusion chromatography (SEC) in chloroform at room temperature on three polystyrene gel columns (Shodex K-805L × 3) that were connected to a Jasco PU-980 precision pump and a Jasco 930 RI refractive index and 970-UV ultraviolet detector. The columns were calibrated against 11 standard polystyrene samples (Pressure Chemical; Mₙ = 580–1 547 000; Mₘ/Mₙ < 1.1) as well as the monomer. Cyclic voltammograms were recorded by using a Hokuto Denko HZ-3000 apparatus. Measurements were carried out at 0.10 V s⁻¹ in a CH₂Cl₂/CHCl₃ solution (5.0 mM) containing n-Bu₄NPF₆ (100 mM) as the supporting electrolyte under argon. A three-electrode cell was used which was equipped with a platinum disk as a working electrode, a platinum wire as a counter electrode, and an Ag/AgCl electrode as a reference. ¹H NMR spectra were recorded in CDCl₃ at 25 °C on a JEOL J N M-LAS00 spectrometer, operating at 300.16 MHz. Polymers for ¹H NMR analysis were fractionated by preparative SEC (column: Shodex K-2002).

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