Living Radical Polymerization of Para-Substituted Styrenes and Synthesis of Styrene-Based Copolymers with Rhenium and Iron Complex Catalysts[1]

Yuzo Kotani, Masami Kamigaito, and Mitsuo Sawamoto*

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Kyoto 606-8501, Japan

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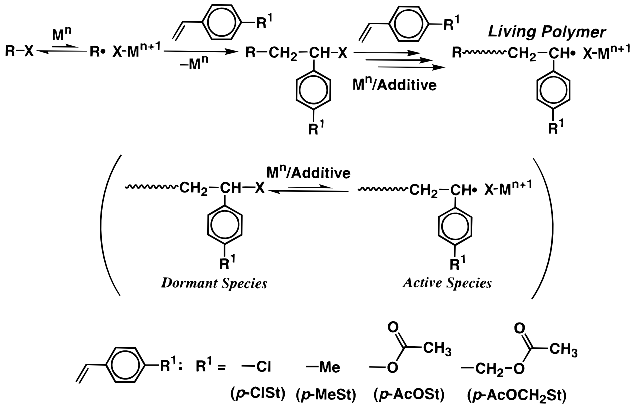
ABSTRACT: Living radical polymerizations of para-substituted styrenes (*p*-chloro, *p*-methyl, *p*-acetoxy, *p*-acetoxymethyl) were examined with the oxo-complex of rhenium(V) [ReO_2I: $ReO_2I(PPh_3)_2$] and half-metallocene carbonyl complexes of iron(II) [FeCpI: FeCpI$(CO)_2$] and iron(I) [Fe_2Cp_2: $Fe_2Cp_2(CO)_4$] (Cp = cyclopentadienyl), all coupled with an iodoester initiator [$(CH_3)_2C(CO_2Et)I$] in the presence of metal alkoxides. Living polymers with narrow molecular weight distributions (MWDs) were obtained from *p*-chlorostyrene (*p*-ClSt) with ReO_2I and FeCpI ($\bar{M}_w/\bar{M}_n = 1.29$ and 1.09, respectively). ReO_2I proved effective also for the living polymerization of *p*-methylstyrene (*p*-MeSt), while FeCpI failed, probably due to the β-H elimination from the ω-end. In the absence of metal alkoxides, Fe_2Cp_2 led to living polymerization of *p*-acetoxystyrene (*p*-AcOSt) with narrow MWDs ($\bar{M}_w/\bar{M}_n \sim 1.2$) and gave long-lived poly[*p*-(acetoxymethyl)styrene]. *p*-MeSt− and *p*-AcOSt−styrene block copolymers were synthesized by sequential polymerizations with ReO_2I and Fe_2Cp_2, respectively. The recovered polystyrene with an iodine ω-end (prepared with ReO_2I) efficiently initiated the living polymerization of methyl acrylate in the presence of $RuCl_2(PPh_3)_3$ to give block copolymers.

Introduction

Ring-substituted styrene derivatives provide interesting monomers, in which the substituents can be widely varied, not only with electron-withdrawing or -donating groups such as halogen or alkyl substituents but also with polar functional groups such as ester, ether, and sulfonate. These styrenes can be polymerized via a variety of mechanisms including radical, anionic, cationic, and coordination. However, in most cases, the electronic nature of substituents strongly affects their reactivity. For example, in cationic polymerization, electron-donating alkyl and alkoxy substituents enhance the reactivity and stabilize the growing carbocations, and vice versa for electron-withdrawing substituents such as chlorine.[2] In contrast, electronic effects are not as critical in radical polymerization because of the neutrality of the propagating species.[3,4] A wide variety of styrene derivatives can therefore be polymerized radically without large difference in rate.[3] Moreover, for substituted styrenes with a polar functional group, radical processes are advantageous because polar substituents often lead to side reactions with ionic propagating species.[5]

In this study, we then aimed at exploiting transition-metal-mediated living radical polymerizations[6] of various styrene derivatives. We also examined various metal-based initiating systems for the polymerization of substituted styrenes, because the correlation between initiating systems and their polymerization behavior would provide further insight into the reaction mechanism. The initiating systems thus far developed have been based on transition-metal complexes of Ru,[7−12] Cu,[13−18] Fe,[19,20] Ni,[21−24] Rh,[25−27] Pd,[28] Re,[29] and Mo[30,31] with phosphine- or nitrogen-based ligands. A plausible polymerization mechanism is illustrated in Scheme 1. The growing radical is reversibly generated from a “dormant species” with a carbon−halogen covalent bond, which is derived from an initiator (R−X) via a single-electron redox cycle like $\sim\!\sim\!\sim$C−X + Ru(II) $\rightleftarrows$ $\sim\!\sim\!\sim$C$^\bullet$X−Ru(III).

Scheme 1



We have recently found the following metal catalysts effective for living radical polymerization of styrene: $RuCl_2(PPh_3)_3$,[32] Ru(Ind)Cl$(PPh_3)_2$,[10] $ReO_2I(PPh_3)_2$ (ReO_2I),[29] FeCpI$(CO)_2$ (FeCpI),[33] and $Fe_2Cp_2(CO)_4$ (Fe_2Cp_2)[34] (Ph = phenyl; Cp = cyclopentadienyl). All these metal complexes afford well-defined polystyrene with narrow molecular weight distributions (MWDs), especially in conjunction with iodoesters as initiators.[32] The use of these iodides as initiators, relative to the chlorides, most probably facilitates fast initiation and interconversion between dormant and active species.[34] Iodide- or halogen-free complexes are suitable as the catalysts because they cannot generate other halogen terminals via halogen-exchange reaction with a dormant polymer terminal.

This study will define the effective initiating systems (initiators and metal catalysts) for the living radical polymerization of para-substituted styrenes, some of

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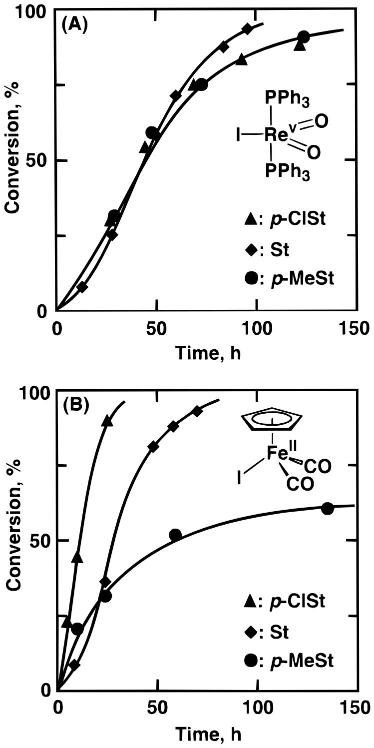
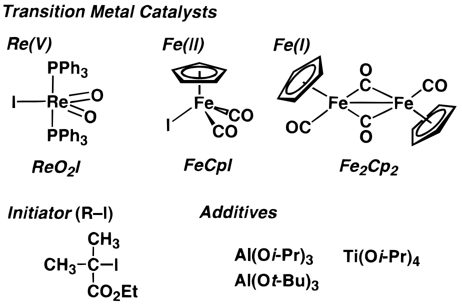


Figure 1. Polymerization of p-ClSt (▲), p-MeSt (●), and styrene (◆): (A) with $(CH_3)_2C(CO_2Et)I/ReO_2I/Al(Oi\text{-}Pr)_3$ (60/10/100 mM) in toluene at 60 °C; $[M]_0 = 6.0$ M. (B) $(CH_3)_2C(CO_2Et)I/FeCpI/Ti(Oi\text{-}Pr)_4$ (60/10/100 mM) in dioxane at 80 °C. $[M]_0 = 6.0$ M.

Scheme 2



which have only been polymerized with copper-based initiating systems.[35,36] The monomers include p-chloro- (p-ClSt), p-methyl- (p-MeSt), p-acetoxy- (p-AcOSt), and p-(acetoxymethyl)styrene (p-AcOCH$_2$St); the metal complexes are ReO$_2$I, FeCpI, or Fe$_2$Cp$_2$, coupled with an iodoester initiator in the presence or absence of metal alkoxides (Scheme 2). These initiating systems were also used to prepare block copolymers of styrene, and para-substituted styrenes were also conducted. AB-block copolymers of styrene and methyl acrylate (MA) were synthesized from a polystyrene macroinitiator with a C−I terminal.

Results and Discussion

1. p-ClSt and p-MeSt. ReO$_2$I and FeCpI were used to polymerize p-ClSt and p-MeSt. Coupled with $(CH_3)_2C(CO_2Et)I$ as an initiator, these catalysts were used under optimal conditions for the living polymerization of styrene: ReO$_2$I in the presence of Al(Oi-Pr)$_3$ in toluene at 60 °C[29] (Figure 1A); FeCpI with Ti(Oi-Pr)$_4$ in dioxane at 80 °C[33] (Figure 1B). With ReO$_2$I, the polymerizations proceeded slower than that of styrene to reach 90% monomer conversion in approximately 120 h. With FeCpI, p-ClSt polymerized much faster than styrene (90% in 25 h), but p-MeSt consumption leveled off around 60%.

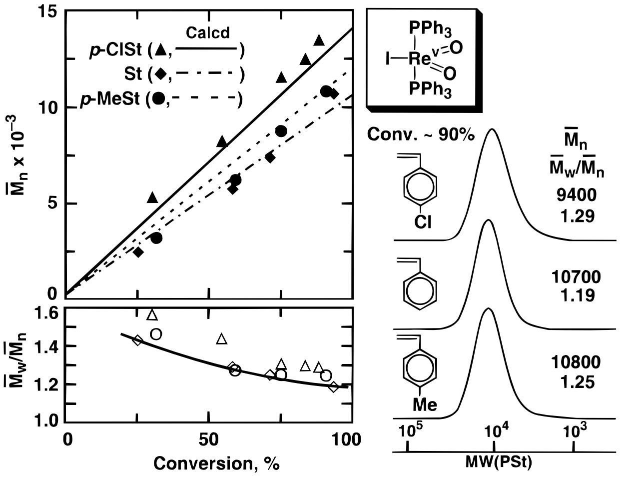


Figure 2. $\bar{M}_n$ (▲, ●, ◆), $\bar{M}_w/\bar{M}_n$ (△, ○, ◇), and SEC curves of p-ClSt (▲, △), p-MeSt (●, ○), and styrene (◆, ◇) obtained with $(CH_3)_2C(CO_2Et)I/ReO_2I/Al(Oi\text{-}Pr)_3$ in toluene at 60 °C: $[M]_0 = 6.0$ M; $[(CH_3)_2C(CO_2Et)I]_0 = 60$ mM; $[ReO_2I]_0 = 10$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 100$ mM. The calibrated $\bar{M}_n$(NMR) of poly(p-ClSt) obtained by the following relationship: $\bar{M}_n(\text{NMR}) = 1.43\bar{M}_n(\text{SEC})$.

Figure 2 shows the number-average molecular weight ($\bar{M}_n$), $\bar{M}_w/\bar{M}_n$, and size exclusion chromatography (SEC) curves of poly(p-ClSt) and poly(p-MeSt) obtained with ReO$_2$I. Throughout this work, $\bar{M}_n$'s of poly(p-MeSt) and poly(p-ClSt) were determined by SEC relative to polystyrene. For p-ClSt, the value by SEC was further calibrated by an equation: $\bar{M}_n = 1.43\bar{M}_n$(NMR).[2] The $\bar{M}_n$ for both polymers increased in direct proportion to monomer conversion and agreed well with the calculated values, assuming that one molecule of the iodoester initiator generated one living chain. The MWDs of both polymers became narrower with monomer conversion and were as narrow as those of the polystyrene obtained with the same system.

The terminal structures of poly(p-ClSt) and poly(p-MeSt) were investigated by ^{1}H NMR spectroscopy. The alkyl group of the initiator moiety (α-end) (0.9 ppm) and the methine proton adjacent to the ω-end iodine (4.5 ppm) were observed for each polymer.[29] The number-average end functionality of the α- and ω-end [$\bar{F}_n(\alpha)$ and $\bar{F}_n(\omega)$] were 0.90 and 0.90 for poly(p-ClSt) ($\bar{M}_n = 6300$), respectively, and 0.92 and 0.80 for poly(p-MeSt) ($\bar{M}_n = 3700$), respectively. Thus, ReO$_2$I proved effective for the living radical polymerization of para-substituted styrenes with either electron-withdrawing (−Cl) or -donating (−Me) group. The polymer terminal structures showed that both polymerizations proceeded via reversible activation of the C−I bond derived from the iodoester initiator.

Figure 3 shows a similar set of data for the polymers with FeCpI. The $\bar{M}_n$ of poly(p-ClSt) increased in direct proportion to monomer conversion and agreed well with the calculated values. The MWDs remained very narrow throughout the polymerization ($\bar{M}_w/\bar{M}_n < 1.1$), similar to the polystyrene obtained with the same catalyst. On the other hand, the $\bar{M}_n$'s of poly(p-MeSt) were almost unchanged with conversion, and the MWDs became broader along with tailing as the polymerization proceeded. As also suggested by the leveling-off conversion

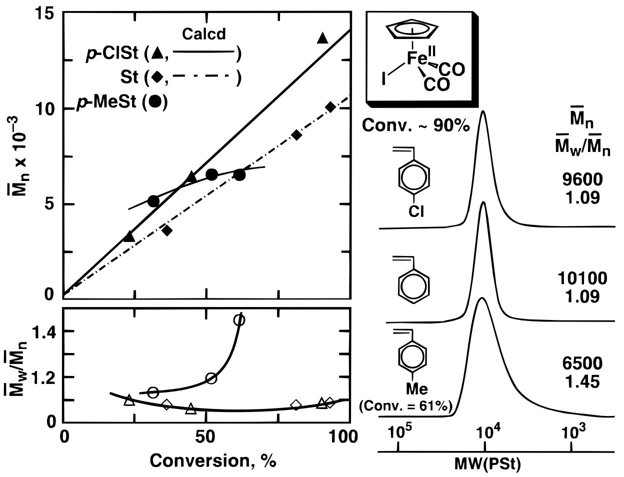


Figure 3. $\bar{M}_n$ (▲, ●, ◆), $\bar{M}_w/\bar{M}_n$ (△, ○, ◇), and SEC curves of *p*-ClSt (▲, △), *p*-MeSt (●, ○), and styrene (◆, ◇) obtained with $(CH_3)_2C(CO_2Et)I/FeCpI/Ti(Oi\text{-}Pr)_4$ in dioxane at 80 °C: $[M]_0 = 6.0$ M; $[(CH_3)_2C(CO_2Et)I]_0 = 60$ mM; $[FeCpI]_0 = 10$ mM; $[Ti(Oi\text{-}Pr)_4]_0 = 100$ mM. The calibrated $\bar{M}_n$(NMR) of poly(*p*-ClSt) obtained by the following relationship: $\bar{M}_n(\text{NMR}) = 1.43\bar{M}_n(\text{SEC})$.

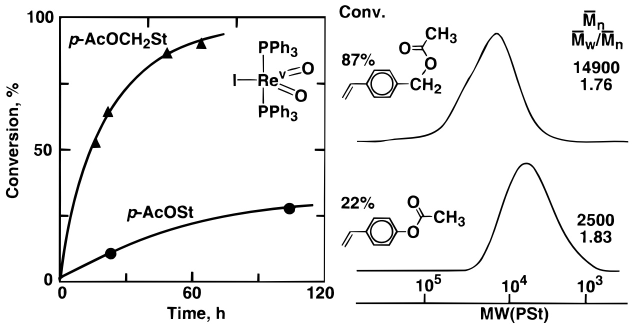


Figure 4. Polymerization of *p*-AcOCH$_2$St (▲) and *p*-AcOSt (●) with $(CH_3)_2C(CO_2Et)I/ReO_2I/Al(Ot\text{-}Bu)_3$ in toluene at 60 °C: $[M]_0 = 4.0$ M; $[(CH_3)_2C(CO_2Et)I]_0 = 40$ mM; $[ReO_2I]_0 = 10$ mM; $[Al(Ot\text{-}Bu)_3]_0 = 40$ mM.

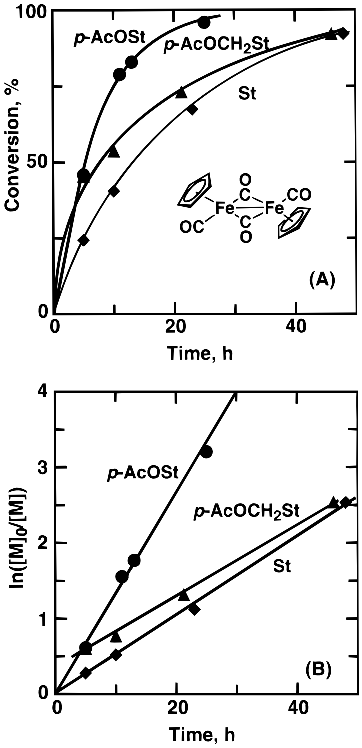


Figure 5. Time–conversion curves (A) and first-order plots (B) for the polymerization of *p*-AcOCH$_2$St (▲), *p*-AcOSt (●), and styrene (◆) with monomers/$(CH_3)_2C(CO_2Et)I/Fe_2Cp_2$ (300/3/1) in dioxane at 60 °C: $[p\text{-AcOCH}_2\text{St}]_0 = [p\text{-AcOSt}]_0 = 5.0$ M; $[\text{styrene}]_0 = 6.0$ M.

curve (Figure 1), termination and/or chain transfer reaction occurs in the *p*-MeSt polymerization with FeCpI. ^{1}H NMR analysis indicated that part of the *p*-MeSt polymers carried a terminal olefin (a broad signal at 6.0 ppm; dead polymer chain), while no peak attributable to the C–I end was observed. The olefinic terminal was most likely produced via *β*-H elimination from the *ω*-end. Because of the electron-donating *p*-methyl substituent, the terminal C–I bond of poly(*p*-MeSt) would dissociate ionically more easily than those in polystyrene or poly(*p*-ClSt). In addition, FeCpI potentially acts as a weak Lewis acid to induce the *β*-H elimination. At the later stage of the polymerization, oily black compounds appeared in the reaction mixture, which are presumably decomposed byproducts from FeCpI and the hydrogen iodide eliminated from the polymer end.

Thus, the FeCpI-based initiating system induced living radical polymerization of *p*-ClSt faster than that of styrene, to give narrow MWDs, whereas it was not effective for *p*-MeSt. In contrast, ReO$_2$I proved effective for living radical polymerization of both *p*-ClSt and *p*-MeSt. This suggests that complexes of less acidic metals such as Re(V) are required for the living radical polymerization of styrenes with electron-donating substituents, especially when coupled with an iodide initiator.

2. *p*-AcOSt and *p*-AcOCH$_2$St. Besides the simple alkyl- or halogen-substituted styrenes, *p*-AcOSt and *p*-AcOCH$_2$St were examined. First, $ReO_2I(PPh_3)_2$ was employed with $(CH_3)_2C(CO_2Et)I$ in the presence of $Al(Ot\text{-}Bu)_3$ (Figure 4); the *tert*-butoxide was an additive to replace $Al(Oi\text{-}Pr)_3$, not to induce the ester exchange reaction with the acetoxy pendant group.[37] An insoluble reddish precipitate appeared during the polymerization of *p*-AcOSt, and the conversion leveled off around 30% to yield low molecular weight polymers with broad MWDs. In contrast, *p*-AcOCH$_2$St reached 87% conversion in 73 h. The $\bar{M}_n$ of the resulting poly(*p*-AcOCH$_2$St) increased with monomer conversion, although the MWDs became broader ($\bar{M}_w/\bar{M}_n \sim 1.8$).

The $(CH_3)_2C(CO_2Et)I/FeCpI/Ti(Oi\text{-}Pr)_4$ initiating system was then employed for the polymerization of *p*-AcOSt. The monomer solution turned orange upon addition of $Ti(Oi\text{-}Pr)_4$, suggesting formation of titanium phenoxides produced via ester exchange reaction between $Ti(Oi\text{-}Pr)_4$ and *p*-AcOSt. Subsequently, insoluble solids resulted, probably due to cross-linked polymers of titanium *p*-vinylphenoxides. Thus, a controlled *p*-AcOSt polymerization may require a metal alkoxide-free system.

Very recently, we have developed such a system based on a dinuclear half-metallocene iron(I) complex, $Fe_2Cp_2(CO)_4$ (Fe_2Cp_2).[34] *p*-AcOSt and *p*-AcOCH$_2$St were thus polymerized with this catalyst in conjunction with $(CH_3)_2C(CO_2Et)I$ (initiator) in dioxane at 60 °C (Figure 5). The polymerizations proceeded smoothly without any color change and precipitation. *p*-AcOSt was consumed faster than styrene, to reach 96% conversion in 25 h, while *p*-AcOCH$_2$St nearly at the same rate as styrene (Figure 5A). The first-order plot for the *p*-AcOSt polym-

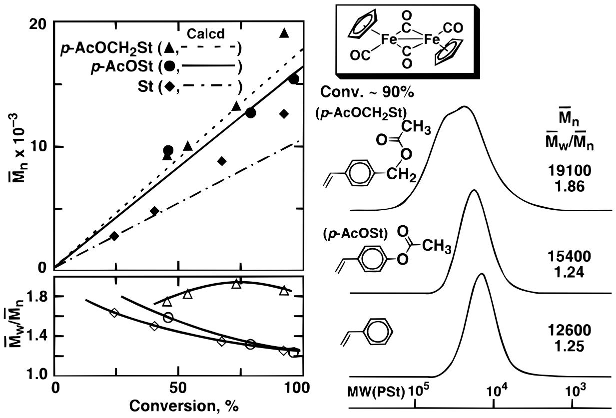
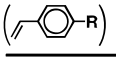


Figure 6. $\bar{M}_n$ (▲, ●, ◆), $\bar{M}_w/\bar{M}_n$ (△, ○, ◇), and SEC curves of *p*-AcOCH$_2$St (▲, △), *p*-AcOSt (●, ○), and styrene (◆, ◇) obtained with monomers/(CH$_3$)$_2$C(CO$_2$Et)I/Fe$_2$Cp$_2$ (300/3/1) in dioxane at 60 °C: [*p*-AcOCH$_2$St]$_0$ = [*p*-AcOSt]$_0$ = 5.0 M; [styrene]$_0$ = 6.0 M.

Table 1. Re(V)- and Fe(II)-Catalyzed Radical Polymerizations of Para-Substituted Styrenes

R	H	Cl	CH_3	$CH_3\overset{\overset{O}{\|}}{C}O$	$CH_3\overset{\overset{O}{\|}}{C}OCH_2$
	Styrene	*p*-ClSt	*p*-MeSt	*p*-AcOSt	*p*-AcOCH$_2$St
ReO$_2$I	○	○	○	✕	△
FeCpI	◎	◎	✕	✕	—
Fe$_2$Cp$_2$	○	—	—	○	△

○ : *Living* △ : *Long-Lived* ✕ : *Not Living*

◎ : *Living and Very Narrow MWDs* ($\bar{M}_w/\bar{M}_n \leq 1.1$)

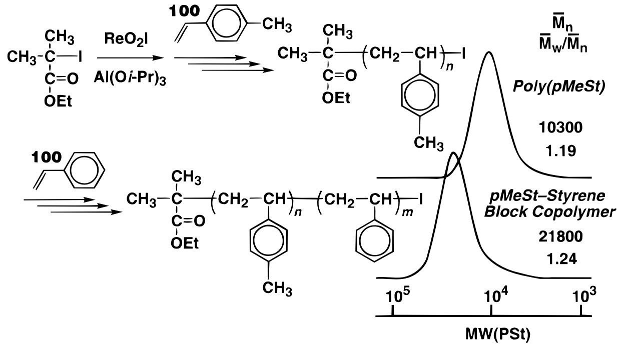


Figure 7. SEC curves of poly(*p*-MeSt) and *p*-MeSt−styrene block copolymer obtained with (CH$_3$)$_2$C(CO$_2$Et)I/ReO$_2$I/Al(O*i*-Pr)$_3$ in toluene at 60 °C: [*p*-MeSt]$_0$ = [styrene]$_{add}$ = 6.0 M; [(CH$_3$)$_2$C(CO$_2$Et)I]$_0$ = 60 mM; [ReO$_2$I]$_0$ = 10 mM; [Al(O*i*-Pr)$_3$]$_0$ = 100 mM.

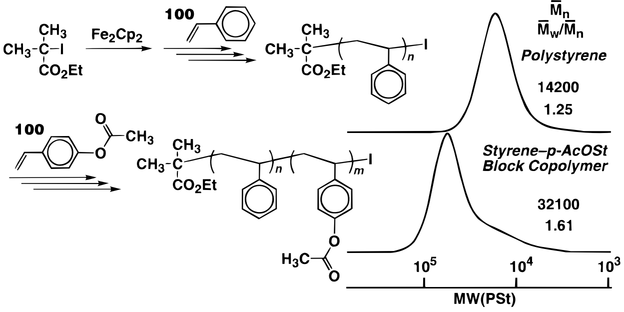


Figure 8. SEC curves of polystyrene and styrene−*p*-AcOSt block copolymer obtained with (CH$_3$)$_2$C(CO$_2$Et)I/Fe$_2$Cp$_2$ in dioxane at 60 °C: [styrene]$_0$ = [*p*-AcOSt]$_{add}$ = 6.0 M; [(CH$_3$)$_2$C(CO$_2$Et)I]$_0$ = 60 mM; [Fe$_2$Cp$_2$]$_0$ = 20 mM.

erization was linear, passing through the origin as for styrene, whereas there seems an intercept in the *p*-AcOCH$_2$St polymerization (Figure 5B).

The $\bar{M}_n$ of the polymers increased along with monomer conversion (Figure 6). The $\bar{M}_n$ of poly(*p*-AcOSt) agreed well with the calculated values, and the MWDs were unimodal and narrowed with conversion ($\bar{M}_w/\bar{M}_n$ = 1.24 at 96% conversion). In contrast, those of poly(*p*-AcOCH$_2$St) were broad with a shoulder in higher molecular weight region. This may be due to the chain transfer reaction to the pendant benzyl ester group, although ^{1}H NMR analysis of the poly(*p*-AcOCH$_2$St) revealed that almost quantitative benzylic protons and methyl protons in the pendant ester group remained even after complete polymerization. Thus, the iodoester initiator/Fe$_2$Cp$_2$ system induced living radical polymerization of *p*-AcOSt, with fairly narrow MWDs, and long-lived polymer of *p*-AcOCH$_2$St.

Table 1 summarizes the results of the metal-catalyzed radical polymerizations of para-substituted styrenes. The ReO$_2$I-based system induced a living radical polymerization of *p*-MeSt, with an electron-donating substituent, which was previously difficult with transition-metal-mediated systems such as Cu(I),[35] where the polymerization was slow and gave broader MWDs ($\bar{M}_w/\bar{M}_n$ ~ 1.5). In this study, living polymerization of *p*-AcOSt has been achieved with the Fe$_2$Cp$_2$-based initiating system in the absence of any additives such as Ti(O*i*-Pr)$_4$, similar to the Cu(I)-based systems that also do not need additives for reaction control.[36] Considering effectiveness of metal complexes for each monomer, we then investigated block copolymerization of para-substituted styrenes by employing suitable catalyst systems.

3. Synthesis of Block Copolymers. Sequential block copolymerization of *p*-MeSt and styrene was examined with the ReO$_2$I-based initiating system. *p*-MeSt was first polymerized with ReO$_2$I and (CH$_3$)$_2$C(CO$_2$Et)I in the presence of Al(O*i*-Pr)$_3$ in toluene at 60 °C. After the conversion exceeded 90%, styrene (equimolar to *p*-MeSt) was added to the reaction mixture (Figure 7). The poly(*p*-MeSt) prepolymer showed a narrow MWD ($\bar{M}_w/\bar{M}_n$ = 1.19), and $\bar{M}_n$ agreed well with the calculated value. After the styrene addition, the overall molecular weight increased, and the MWDs stayed narrow without any trace of *p*-MeSt prepolymer. Thus, *p*-MeSt−styrene block copolymers were obtained with ReO$_2$I, which confirms the living nature of the *p*-MeSt polymerization with ReO$_2$I.

A block copolymer of styrene and *p*-AcOSt was also synthesized via sequential polymerization using the Fe$_2$Cp$_2$-based system. Styrene was polymerized first with Fe$_2$Cp$_2$ and (CH$_3$)$_2$C(CO$_2$Et)I in dioxane at 60 °C, and then *p*-AcOSt was added. The $\bar{M}_n$ of the copolymers increased, and the SEC curve shifted to high molecular weight (Figure 8). The number-average degrees of polymerization (DP$_n$) of styrene and *p*-AcOSt segments (by ^{1}H NMR) agreed well with the values calculated from the gas chromatographic conversions: styrene/*p*-AcOSt = 97/88 (NMR) and 98/84 (GC). However, the copolymer showed a broad MWD ($\bar{M}_w/\bar{M}_n$ = 1.61) with a small shoulder in the low molecular weight region, probably due to dead polymer chains. ^{1}H NMR analysis of the homopolystyrene synthesized with Fe$_2$Cp$_2$ showed that $\bar{F}_n(\alpha)$ and $\bar{F}_n(\omega)$ were 1.28 and 0.64, respectively.

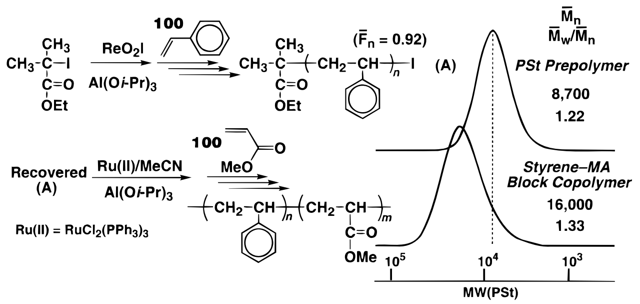


Figure 9. SEC curves of polystyrene and styrene−MA block copolymer: prepolymer (A) was synthesized with $(CH_3)_2C(CO_2Et)I/ReO_2I/Al(Oi\text{-}Pr)_3$ (60/10/100 mM) in toluene at 60 °C. MA was polymerized with (A)/$RuCl_2(PPh_3)_3$/ MeCN/$Al(Oi\text{-}Pr)_3$ (30/15/15/60 mM) in toluene at 60 °C: $[MA]_0 = 3.0$ M.

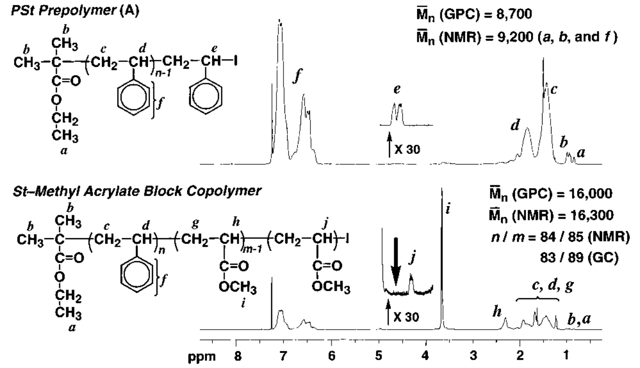


Figure 10. ^{1}H NMR spectra of styrene−MA block copolymer obtained with (A)/$RuCl_2(PPh_3)_3$/MeCN/$Al(Oi\text{-}Pr)_3$ (30/15/15/60 mM) in toluene at 60 °C: $[MA]_0 = 3.0$ M. The ^{1}H NMR spectrum denoted as (A) is for the sample in Figure 9.

This indicates that a small part of the polymer chain had been dead via recombination during the later stage of the first step.

Besides the sequential block copolymerizations, block copolymer was synthesized from an isolated polystyrene macroinitiator (Figure 9). The iodine-terminated polystyrene was synthesized with $(CH_3)_2C(CO_2Et)I$ and ReO_2I in the presence of $Al(Oi\text{-}Pr)_3$ in toluene at 60 °C.[29] The obtained polystyrene possessed the alkyl group and the iodine derived from the iodoester initiator at the α- and ω-end terminals, respectively, with $\bar{F}_n(\alpha) = 0.98$ and $\bar{F}_n(\omega) = 0.90$. The iodine-terminated polystyrene was then employed as the initiator for the polymerization of methyl acrylate (MA) with $RuCl_2(PPh_3)_3$/MeCN (1/1) in the presence of $Al(Oi\text{-}Pr)_3$ in toluene at 60 °C.[38] The homopolymerization of MA at 60 °C completed in 11 days, where the $\bar{M}_n$ increased with MA conversion and agreed with the calculated values assuming that one molecule of polystyrene prepolymer forms one living poly(MA). The MWDs stayed narrow throughout the polymerization of MA ($\bar{M}_w/\bar{M}_n = 1.33$).

The block copolymer was analyzed by ^{1}H NMR spectroscopy (Figure 10). The characteristic signals included the MA repeat units, i.e., the pendant ester group (*i*), and the alkyl group of the main chain (*g* and *h*), in addition to those of the polystyrene prepolymer. The DP_n of styrene and MA units were calculated from the relative peak intensities of initiator alkyl group (*a* and *b*) to their pendant aromatic group (*f*) and the ester group (*i*). The observed styrene/MA ratio was 84/85, in good agreement with the calculated ratio (83/89). The terminal methine proton (*e*), adjacent to the ω-end iodine of polystyrene, disappeared in the spectrum of the styrene−MA block copolymer. Instead, a small signal *j* appeared at 4.3 ppm, which was assigned to the terminal methine proton of poly(MA). This spectral change indicates that the iodine terminal of polystyrene was completely converted into the poly(MA) growing terminal. Also, the terminal C−I bond of polystyrene, which is usually unstable, survived the workup processes and induced further living polymerization of MA in the presence of the catalysts.

In conclusion, living radical polymerizations of various para-substituted styrenes were accomplished with the transition-metal complexes of rhenium or iron. ReO_2I proved effective for both *p*-ClSt and *p*-MeSt, as well as for styrene. FeCpI-induced living polymerization of *p*-ClSt to give very narrow MWDs but was not effective for *p*-MeSt. Living radical polymerization of *p*-AcOSt was achieved with the dinuclear complex, Fe_2Cp_2, in the absence of metal additives to give poly(*p*-AcOSt) with fairly narrow MWDs. AB block copolymers of *p*-MeSt−styrene and styrene−*p*-AcOSt were synthesized with ReO_2I and Fe_2Cp_2, respectively. A styrene−MA block copolymer was also obtained from the polystyrene macroinitiator with an iodine ω-end.

Experimental Section

Materials. Styrene (Wako Chemicals, >99%), *p*-methylstyrene (Aldrich, 96%), *p*-chlorostyrene (Hokko Chemicals, 99%), and *p*-acetoxystyrene (Honsyu Chemicals, 99%) were dried overnight over anhydrous sodium sulfate and distilled twice from calcium hydride under reduced pressure before use. *p*-(Acetoxymethyl)styrene was prepared by the method of Kanaoka et al.[2] $ReO_2I(PPh_3)_2$ (Aldrich, >99%), $FeCpI(CO)_2$ (Aldrich, >97%), and $Fe_2Cp_2(CO)_4$ (Aldrich, >99%) were used as received. All transition metal complexes were handled in a glovebox (M. Braun) under dry (<1.0 ppm) and oxygen-free (<1.0 ppm) argon. $Al(Oi\text{-}Pr)_3$ (Aldrich, >99.99%), $Al(Ot\text{-}Bu)_3$ (Tokyo Kasei, >99%), and $Ti(Oi\text{-}Pr)_4$ (Kanto Chemicals, >97%) were used as received. Toluene, dioxane (solvents), tetralin (internal standard for gas chromatographic analysis of *p*-substituted styrene), and chlorobenzene (internal standard for *p*-ClSt) were dried overnight over calcium chloride, distilled twice from sodium benzophenone ketyl (toluene and dioxane) or calcium hydride (tetralin and chlorobenzene), and bubbled with dry nitrogen for more than 15 min immediately before use. Ethyl 2-iodoisobutyrate $[(CH_3)_2C(CO_2C_2H_5)I]$ was prepared by the method of Curran et al.;[39] bp 50 °C/9 Torr; identified by 500 MHz ^{1}H NMR. Anal. Calcd for $C_6H_{11}O_2I$: C, 29.8; H, 4.58; I, 52.4. Found: C, 29.7; H 4.59; I, 52.3.

Polymerization Procedures. Polymerization was carried out in glass tubes using syringe technique for reagent transfer under dry nitrogen. A typical example for the polymerization of *p*-ClSt with $(CH_3)_2C(CO_2Et)I/FeCpI(CO)_2/Ti(Oi\text{-}Pr)_4$ is given below: $FeCpI(CO)_2$ (0.040 mmol, 0.0122 g) was mixed with *p*-ClSt (24.0 mmol, 2.88 mL), chlorobenzene (0.222 mL), dioxane (0.50 mL), $Ti(Oi\text{-}Pr)_4$ (0.40 mmol, 0.118 mL), and a solution of $(CH_3)_2C(CO_2Et)I$ (0.240 mmol, 0.268 mL of 894 mM in toluene) sequentially in this order; the total volume of the reaction mixture was thus 4.00 mL. Immediately after mixing, aliquots (0.4 mL each) of the solution were distributed via a syringe into baked glass tubes (0.4 mL), which were then sealed and placed in an oil bath kept at 80 °C. In predetermined intervals, the 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 chlorobenzene as the internal standard. The quenched reaction solutions were diluted with toluene (∼20 mL) and rigorously shaken with an absorbent [Kyowaad-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); 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 $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ ratios of the polymers were measured by size-exclusion chromatography (SEC) in chloroform at 40 °C on three polystyrene gel columns [Shodex K-805L (pore size: 20−1000 Å; 8.0 mm i.d. × 30 cm) × 3; flow rate 1.0 mL/min] that were connected to a Jasco PU-980 precision pump and a Jasco 930-RI refractive index and 970-UV ultraviolet detectors. The columns were calibrated against 11 standard polystyrene samples (Pressure Chemical; $\bar{M}_n$ = 580−1 547 000; $\bar{M}_w/\bar{M}_n \leq 1.1$) as well as the monomer. ^{1}H NMR spectra were recorded in $CDCl_3$ at 25 °C on a JEOL JNM-LA500 spectrometer, operating at 500.16 MHz. Polymers for ^{1}H NMR analysis were fractionated by preparative SEC (column: Shodex K-2002).

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References and Notes

(1) This work was presented in part at the following meetings: (a) The 47th Symposium on Macromolecules, the Society of Polymer Science, Nagoya, Japan, Sept 1998; paper IIPa005: Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1998**, *47* (7), 1277. (b) The 48th Symposium on Macromolecules, the Society of Polymer Science, Niigata, Japan, Sept 1999; paper IIIB06: Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1999**, *48* (8), 1725.

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(38) According to our unpublished results, addition of MeCN to the $RuCl_2(PPh_3)_3$-based initiating system narrows the MWDs of polystyrene and is also effective for the polymerization of MA. The isolated Ru(II) complex with MeCN as a ligand $[RuCl_2(MeCN)_2(PPh_3)_2]$ also gave narrow MWDs ($\bar{M}_w/\bar{M}_n$ = 1.2) of polystyrene. Thus, the added MeCN most probably interacts with the Ru center to modify the catalyst. See: Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1998**, *47* (2), 150; to be submitted.

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