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Re(V)-Mediated Living Radical Polymerization of Styrene:[1] $ReO_2I(PPh_3)_2$/R−I Initiating Systems

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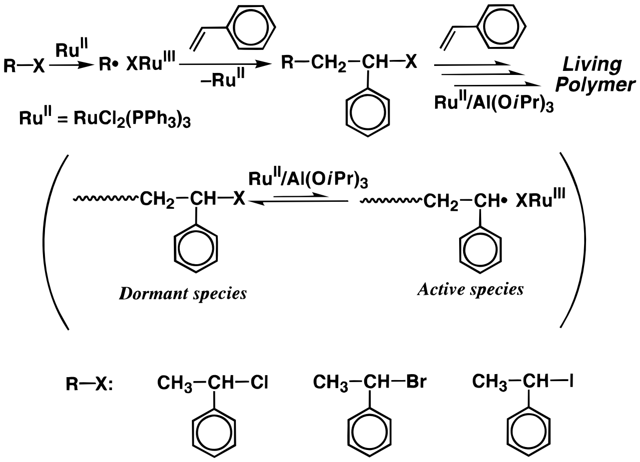
ABSTRACT: Rhenium(V) iododioxobis(triphenylphosphine) [$ReO_2I(PPh_3)_2$] proved an effective metal catalyst for living radical polymerization of styrene in conjunction with alkyl iodide as an initiator [R−I: $CH_3CH(Ph)I$, $(CH_3)_2C(CO_2Et)I$, and $CH_3CH(CO_2Et)I$] in the presence of $Al(O\textit{i}\text{-}Pr)_3$. Compared to $RuCl_2(PPh_3)_3$, the group 7 complex was highly effective for styrene, so as to induce the living polymerization even at 30 °C to yield well-controlled polystyrene, with $\bar{M}_n$ up to $\sim 4 \times 10^4$ and very narrow molecular weight distributions (MWDs) ($\bar{M}_w/\bar{M}_n = 1.19$). The polystyrene thus obtained possessed one initiator moiety (R) at the α-end and one iodine atom at the *ω*-end, both from the initiator R−I, which indicates that the polymerization proceeds via activation of the C−I terminal, derived from R−I, by the Re(V) complex. Addition of methanol or water did not inhibit these polymerizations, while a stable nitroxide radical (TEMPO) immediately and completely quenched them. The quenching experiments thereby supported intervention of radical species in the Re(V)-mediated living polymerization.

Introduction

Transition-metal-mediated living radical polymerizations have rapidly been developed in the past few years.[2] The complexes thus far effective therein are primarily based on late transition metals, such as ruthenium(II),[3−7] iron(II),[8,9] nickel(II),[10,11] copper(I),[12−16] rhodium(I),[17,18] and palladium(II),[19] all of which belong to groups 8−11. Most of the complexes are also known as catalysts for Kharasch or atom-transfer radical addition reactions[20] via reversible and homolytic cleavage of carbon−halogen bonds, similar to the dormant−active species equilibrium proposed for the current living radical polymerizations. An immediate question would therefore be, which range of transition metals can one utilize for living radical polymerizations of various monomers?

We have recently reported living radical polymerization of methacrylates with late transition metal complexes such as $RuCl_2(PPh_3)_3$,[2−6] $FeCl_2(PPh_3)_2$,[7] and $NiBr_2(PR_3)_2$ (R = Ph, *n*Bu)[9,10] in combination with halogen-containing initiators R−X. Also, we found that the Ru(II) complex is effective for living radical polymerization of styrene (Scheme 1), in which the choice of the halogen atom in the initiator [$CH_3CH(Ph)X$; X = Cl, Br, I] proved to be an important key to the control of styrene polymerization.[21] Namely, the iodide initiator (X = I) gave the best results among these; the number-average molecular weights were precisely controlled by the feed ratio of the monomer to the initiator, and the molecular weight distributions (MWDs) were narrow ($\bar{M}_w/\bar{M}_n \sim 1.5$). In contrast, the MWDs were broader with the other halides (X = Cl, Br), with which the $\bar{M}_n$ were higher than the calculated values. However, with the $RuCl_2(PPh_3)_3$/R−I system, or a hetero-halogen combination of the catalyst and the initiator, halogen atom exchange was inevitable between the polymer terminal and $RuCl_2(PPh_3)_3$.[22,23] Our preliminary results also showed that $FeCl_2(PPh_3)_2$ and $NiBr_2(PR_3)_2$, both of which induced living polymerization of methacrylates, were not effective for styrene. For bromide or chloride initiators, only copper (I)-based systems with bipyridines[12−16] and $FeBr_2$-based systems with mixed ligands of phosphine and amines[8] were effective in controlled radical styrene polymerization. These results prompted us to develop more effective systems for living radical polymerization of styrene, particularly focusing on metal complexes beyond the range of late transition metals of group 8−10.

Scheme 1. Living Radical Polymerization of Styrene with Ru(II) Complex



In this study, we have employed $ReO_2I(PPh_3)_2$ as a new catalyst for living radical polymerization of styrene (Scheme 2). Rhenium belongs to group 7 which displays the characteristics of early and late transition metals.[24] For example, it can also take a wide range of oxidation states and give stable high-valent complexes as do group 8−10 metals. Among Re(V) derivatives, $ReO_2I(PPh_3)_2$ is a stable dioxo five-valent complex substituted with an iodine atom. The excited-state properties of $ReO_2{}^+$(V) (for the pyridine complex) were studied by Gray et al., and the reversible oxidation and reduction process [$ReO_2{}^+(V) \rightleftarrows ReO_2{}^{2+}(VI)$] has been examined by cyclic voltammetry.[25] Grigg et al. reported radical addition reactions mediated by a rhenium(III) complex [$ReCl_3(PPh_3)_2(MeCN)$].[26] However, there were no reports on the use of rhenium(V) complexes for radical addition

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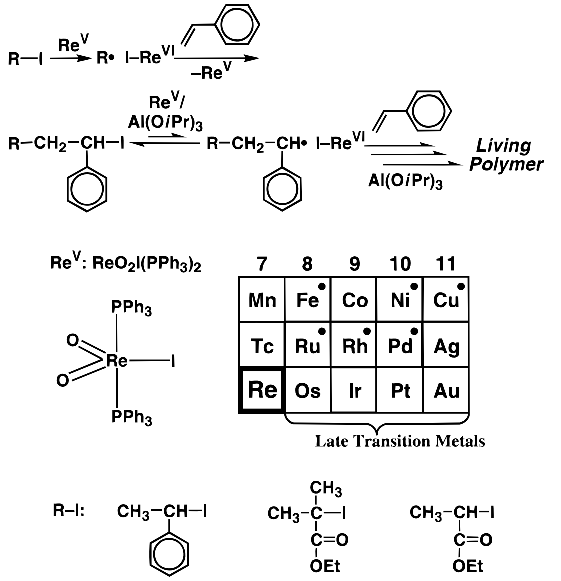
Scheme 2. Living Radical Polymerization of Styrene with Re(V) Complex[a]



[a] The dots in the attached periodic table show the metals whose complexes have thus far been shown effective for living radical polymerization.

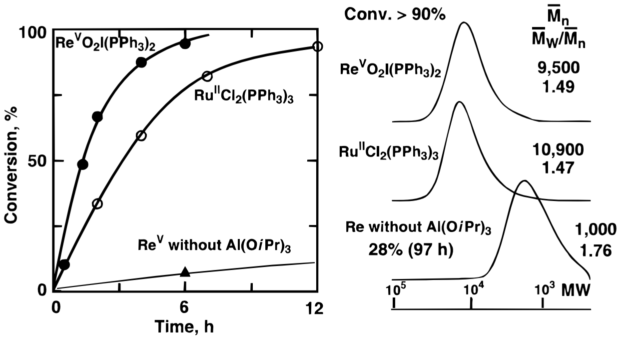


Figure 1. Polymerization of styrene with $CH_3CH(Ph)I/M^n/Al(Oi\text{-}Pr)_3$ at 100 °C: $[styrene]_0 = 6.0$ M; $[CH_3CH(Ph)I]_0 = 60$ mM; $[M^n]_0 = 30$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 100$ (●, ○) or none (▲) mM. M^n: $ReO_2I(PPh_3)_2$ (●); $RuCl_2(PPh_3)_3$ (○).

reactions and related polymerizations. This paper is to show that $ReO_2I(PPh_3)_2$ induces living radical polymerization of styrene in conjunction with organic iodides [$CH_3CH(Ph)I$, $(CH_3)_2C(CO_2Et)I$, and $CH_3CH(CO_2Et)I$] in the presence of $Al(Oi\text{-}Pr)_3$. The Re(V)-mediated polymerization was faster and gave narrower MWDs than those with $RuCl_2(PPh_3)_3$, perhaps giving the first example of the use of metal complexes outside the late transition metal group.

Results and Discussion

1. Living Polymerization of Styrene with $ReO_2I(PPh_3)_2$. The Re(V) complex was employed for styrene polymerization, coupled with $CH_3CH(Ph)I$ in the presence of $Al(Oi\text{-}Pr)_3$ in toluene at 100 °C (Figure 1). The polymerization proceeded faster than that with $RuCl_2(PPh_3)_3$ to reach 94% conversion in 6 h. Without $Al(Oi\text{-}Pr)_3$, however, the polymerization proceeded very slowly to yield oligomers only.[27] The polystyrene thus obtained in the presence of $Al(Oi\text{-}Pr)_3$ showed unimodal MWDs very similar to that with $RuCl_2(PPh_3)_3$ ($\bar{M}_w/\bar{M}_n \sim 1.5$).[28] $\bar{M}_n$ increased in direct proportion to monomer conversion and agreed well with the calculated values assuming that one molecule of $CH_3CH(Ph)I$ generates one living polymer chain.

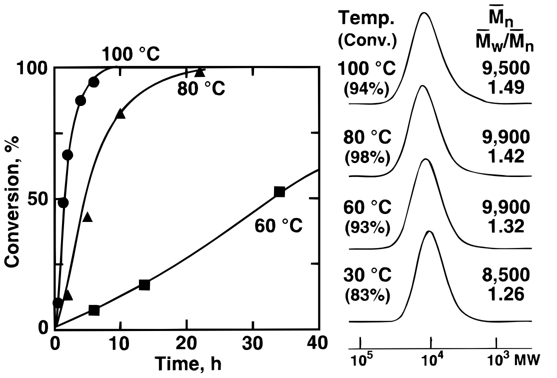


Figure 2. Polymerization of styrene with $CH_3CH(Ph)I/ReO_2I(PPh_3)_2/Al(Oi\text{-}Pr)_3$ at varing temperature: (●) 100 °C; (▲) 80 °C; (■) 60 °C [$[styrene]_0 = 6.0$ M; $[CH_3CH(Ph)I]_0 = 60$ mM; $[ReO_2I(PPh_3)_2]_0 = 30$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 100$ mM]. The reaction at 30 °C reached 83% conversion in 27 days; thus, no data point is shown in the conversion−time profile.

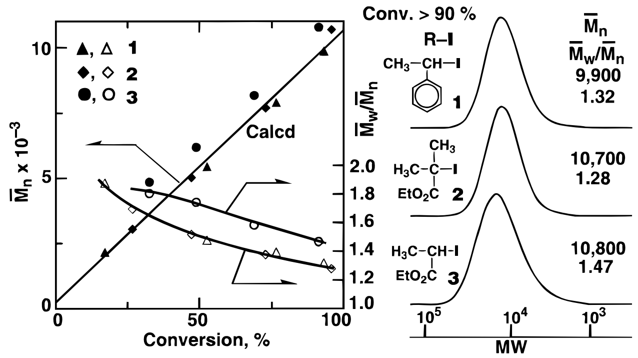


Figure 3. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and SEC curves of polystyrene obtained with $R{-}I/ReO_2I(PPh_3)_2/Al(Oi\text{-}Pr)_3$ at 60 °C: $[styrene]_0 = 6.0$ M; $[R{-}I]_0 = 60$ mM; $[ReO_2I(PPh_3)_2]_0 = 30$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 100$ mM. R−I [(▲, △) $CH_3CH(Ph)I$; (◆, ◇) $(CH_3)_2C(CO_2Et)I$; (●, ○) $CH_3CH(CO_2Et)I$]. The diagonal solid line indicates the calculated M_n assuming the formation of one living polymer per R−I molecule.

Noting the high catalytic activity of the Re(V) complex, we examined polymerizations at lower temperatures with the $CH_3CH(Ph)I/ReO_2I(PPh_3)_2/Al(Oi\text{-}Pr)_3$ initiating system (Figure 2). As expected, the lower the temperature, the slower the polymerization, but the MWDs of the polystyrene became narrower, where the $\bar{M}_w/\bar{M}_n$ ratio was 1.26 at 30 °C.

To search more effective initiators, several iodine compounds were employed with $ReO_2I(PPh_3)_2/Al(Oi\text{-}Pr)_3$ at 60 °C. These iodides include $CH_3CH(Ph)I$, $(CH_3)_2C(CO_2Et)I$, and $CH_3CH(CO_2Et)I$, which possess structures analogous to iodine terminals of polystyrene, poly(ethyl methacrylate), and poly(ethyl acrylate), respectively. All the iodine compounds induced styrene polymerization at nearly the same rate to reach over 90% conversion in ∼70 h. As shown in Figure 3, $\bar{M}_n$ increased in direct proportion to monomer conversion and agreed with the calculated values throughout the polymerization. However, some differences were seen in MWDs. For instance, the distributions with $CH_3CH(Ph)I$ and $(CH_3)_2C(CO_2Et)I$ ($\bar{M}_w/\bar{M}_n \sim 1.3$) were narrower than those with $CH_3CH(CO_2Et)I$. In fact the third one led to $\bar{M}_n$ slightly higher than the calculated values during the early stage of the polymerizaition, suggesting the slow initiation from the acrylate-type initiator. Thus, styrene- and methacrylate-type initiators proved effective for the living polymerization of styrene with $ReO_2I(PPh_3)_2$.

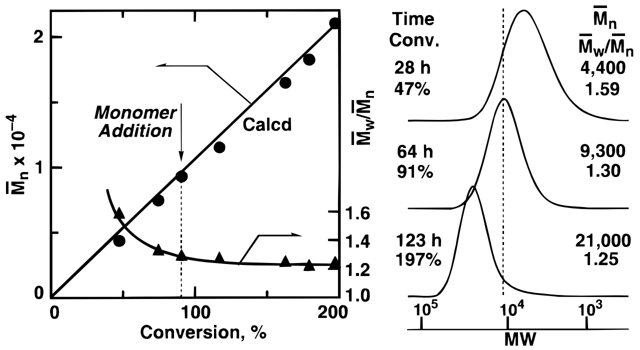


Figure 4. $\bar{M}_n$ (●), $\bar{M}_w/\bar{M}_n$ (▲), and SEC curves of polystyrene obtained in a monomer-addition experiment with $(CH_3)_2C(CO_2Et)I/ReO_2I(PPh_3)_2/Al(Oi\text{-}Pr)_3$ at 60 °C: $[styrene]_0 = [styrene]_{add} = 6.0$ M; $[(CH_3)_2C(CO_2Et)I]_0 = 60$ mM; $[ReO_2I(PPh_3)_2]_0 = 30$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 100$ mM. The diagonal solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per $(CH_3)_2C(CO_2Et)I$ molecule.

The living nature of the polymerization with $ReO_2I(PPh_3)_2$ was then examined in monomer-addition experiments (Figure 4); thus styrene (100 equiv to the initiator) was polymerized with the $(CH_3)_2C(CO_2Et)I/ReO_2I(PPh_3)_2/Al(Oi\text{-}Pr)_3$ system at 60 °C, and a fresh feed of styrene (again 100 equiv) was added to the reaction mixture when the initial charge had almost been consumed. A second-phase polymerization immediately ensued almost at the same rate as in the first phase, and conversion reached an additional 97% in 123 h. Even after the monomer addition, the $\bar{M}_n$ of the polystyrene increased linearly and agreed fairly well with the calculated values based on the monomer/initiator feed ratio. Furthermore, the polymer MWDs showed no shoulder and narrowed to give $\bar{M}_w/\bar{M}_n = 1.25$ as the second phase proceeded. These results demonstrate that living polymerization of styrene was achieved with the $R{-}I/ReO_2I(PPh_3)_2/Al(Oi\text{-}Pr)_3$ initiating system.

Higher molecular weight polystyrenes were also synthesized with the same initiating system based on Re(V). Thus, styrene, 400 equiv to $(CH_3)_2C(CO_2Et)I$, was polymerized with $ReO_2I(PPh_3)_2$ and $RuCl_2(PPh_3)_3$ in the presence of $Al(Oi\text{-}Pr)_3$ in bulk at 80 °C (Figure 5). Monomer conversion exceeded 95% in 21 h with Re(V) and in 60 h with Ru(II). In both cases $\bar{M}_n$ increased linearly with conversion and almost agreed with the calculated values. With $ReO_2I(PPh_3)_2$, in particular, the MWDs were very narrow throughout the polymerization and finally reached $\bar{M}_w/\bar{M}_n = 1.19$; the number-average degree of polymerization > 350. Thus, the Re(V) complex led to a better controlled polymerization of styrene than $RuCl_2(PPh_3)_3$ does, to give living polystyrene with $\bar{M}_n$ up to $\sim 4 \times 10^4$ and narrow MWDs ($\bar{M}_w/\bar{M}_n = 1.1{-}1.2$).

2. End-Group Analysis. The polystyrene obtained with the iodo ester $[(CH_3)_2C(CO_2Et)I]$ and the Re(V) complex was analyzed by ^1H NMR spectroscopy (Figure 6). In addition to the large absorptions of the main chain repeat units (*c*, *d*, and *f*), the enlarged spectrum (inset) exhibits the characteristic signals of the initiator moiety and the ω-end iodide, namely, peaks *a* and *b* around 0.9 ppm for the protons of the ester group and the geminal methyl groups, respectively. The small absorption around 4.6 ppm (peak *e*, split due to a steric difference) is attributed to the methine proton adjacent to the ω-end iodine.[29] The $\bar{M}_n$ obtained from the α-end signals $[9f/5(a + b)]$ was 6200, in good agreement with that by SEC $[\bar{M}_n = 5900]$ calibrated against polystyrene standard samples. The number-average end functionality was close to unity for both α- and ω-terminals: $\bar{F}_n(\alpha) = 0.96$; $\bar{F}_n(\omega) = 0.92$; $\bar{F}_n = \bar{M}_n(SEC)/\bar{M}_n(NMR)$. These data indicate that the $(CH_3)_2C(CO_2Et)I$ served as the initiator that forms one living polystyrene chain per molecule and that the polymerization proceeded via activation of the terminal C−I bond derived from the initiator. Interestingly, the terminal benzyl iodide herein seems rather stable, surviving our workup procedures at room temperature (see below also).

3. Quenching Experiments. To clarify the nature of the Re(V)-mediated living polymerization, the effects of potential terminators [methanol, water, and TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy)] were added to the reaction system with $(CH_3)_2C(CO_2Et)I/ReO_2I(PPh_3)_2/Al(Oi\text{-}Pr)_3$ at 60 °C. Thus, the polymerization was first run without additives, where conversion reached 51% in 44 h and 94% in 97 h (open circles in Figure 7). Under these conditions, the living polymerization gave polystyrenes with very narrow MWDs ($\bar{M}_w/\bar{M}_n = 1.18$).

At 51% conversion, the inhibitors (10 equiv each to the initiator) were added to the polymerization mixtures. Methanol and water failed to affect the polymerization, which proceeded without changes in rate, $\bar{M}_n$, and MWDs relative to the additive-free system. In contrast, upon addition of TEMPO, no further polymerization occurred beyond 51% conversion even when it was run beyond 97 h, where the system without the inhibitors reached nearly quantitative conversion. The $\bar{M}_n$ did not increase thereafter, and the MWDs stayed unchanged. Definitely, the polymerization was immediately inhibited with the added nitroxide radical.

The terminal structures of the polystyrene obtained with and without the inhibitors were analyzed by ^1H NMR spectroscopy. The spectra of the polymers with added methanol or water are virtually identical to that for the additive-free sample (Figure 6); the iodine terminal still remained intact. $\bar{F}_n(\omega)$ for the iodine: with H_2O, 0.86; with methanol, 0.87; with TEMPO, 0.91; additive free, 0.92. Unexpectedly, the polystyrene quenched with TEMPO did not show any changes nor TEMPO-related peaks that are expected around 0.3 and 4.2 ppm (see the arrows H_t and T in Figure 8).[30] This indicates that the added TEMPO did not react with the dormant C−I bond even in the presence of $ReO_2I(PPh_3)_2$ and $Al(Oi\text{-}Pr)_3$, in contrast to the fact that the nitroxide radical effectively combines with free radicals.[30] We assume that with the Re(V) system the concentration of the growing radical is kept very low via reversible activation of the C−I bond and, therefore, that TEMPO mainly reacts with the Re(V) complex to deactivate it.[31] These results suggest, though not enough to prove, a radical pathway of the polymerization, and it was clarified that the R−I/Re(V)-based initiating system was tolerant toward protic additives such as alcohol or water and that the polymerization does not proceed via ionic mechanism.

In conclusion, the rhenium(V) complex, $ReO_2I(PPh_3)_2$, has been shown to induce living radical polymerization of styrene in conjunction with an alkyl iodide [R−I: $CH_3CH(Ph)I$, $(CH_3)_2C(CO_2Et)I$, $CH_3CH(CO_2Et)I$] as the initiator in the presence of $Al(Oi\text{-}Pr)_3$. Compared to $RuCl_2(PPh_3)_3$, the Re(V) version was so effective as to maintain its activity even at 30 °C to yield well-controlled polystyrene of relatively high molecular weights and narrow MWDs. The polymer end-group analysis and the effects of additives supported that the polymerization proceeds via a nonionic, perhaps radical,

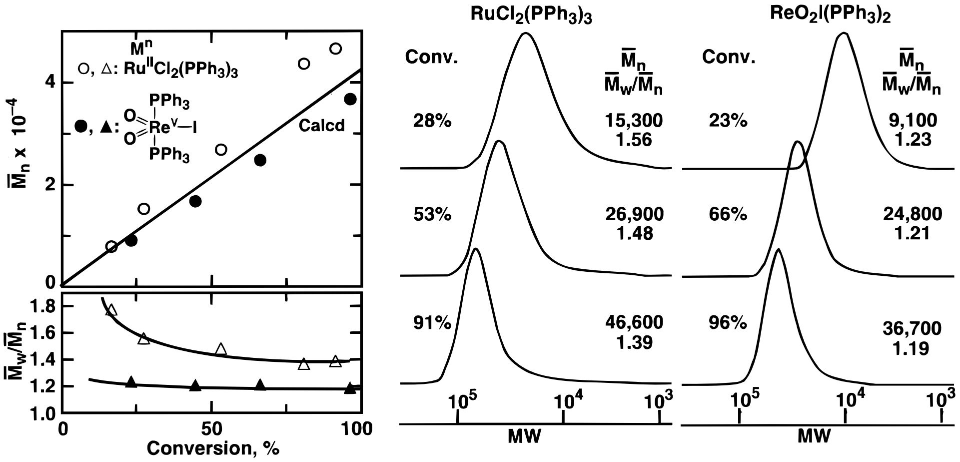


Figure 5. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and SEC curves of polystyrene obtained with $(CH_3)_2C(CO_2Et)I/M^n/Al(O\textit{i}\text{-}Pr)_3$ at 80 °C: $[styrene]_0 = 8.0$ M; $[(CH_3)_2C(CO_2Et)I]_0 = 20$ mM; $[M^n]_0 = 10$ mM; $[Al(O\textit{i}\text{-}Pr)_3]_0 = 40$ mM. $M^n = ReO_2I(PPh_3)_2$ (●, ▲); $RuCl_2(PPh_3)_3$ (○, △). The diagonal solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per $(CH_3)_2C(CO_2Et)I$ molecule.

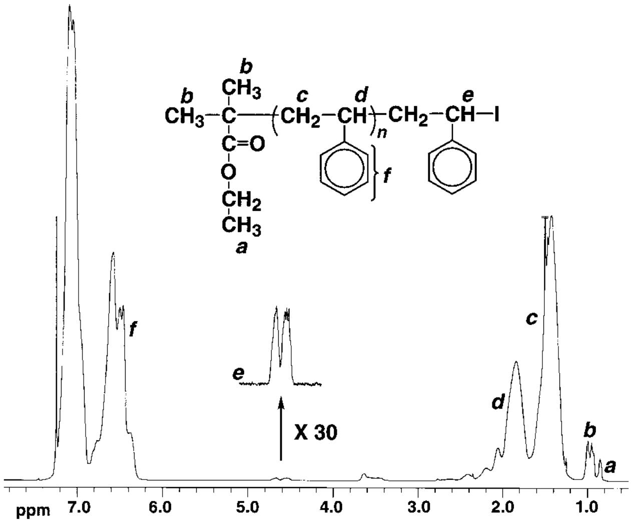


Figure 6. ^1H NMR spectrum (500 MHz) of the polystyrene obtained with $(CH_3)_2C(CO_2Et)I/ReO_2I(PPh_3)_2/Al(O\textit{i}\text{-}Pr)_3$ at 60 °C: $\bar{M}_n$ (SEC) = 5900; $\bar{M}_w/\bar{M}_n = 1.22$. $\bar{F}_n(\alpha) = 0.96$; $\bar{F}_n(\omega) = 0.92$ (see text).

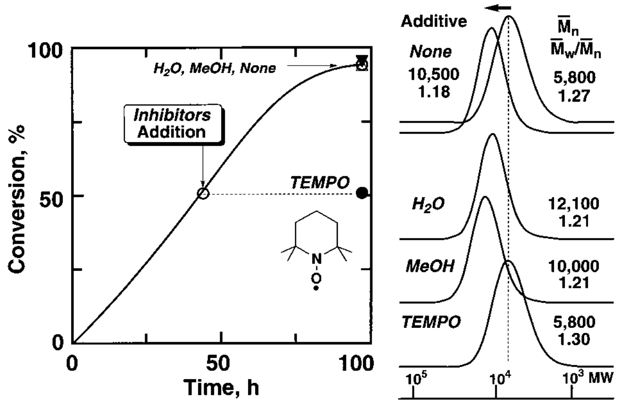


Figure 7. Effect of additives (600 mM) on the living polymerization of styrene with $(CH_3)_2C(CO_2Et)I/ReO_2I(PPh_3)_2/Al(O\textit{i}\text{-}Pr)_3$ at 60 °C: $[styrene]_0 = 6.0$ M; $[(CH_3)_2C(CO_2Et)I]_0 = 60$ mM; $[ReO_2I(PPh_3)_2]_0 = 10$ mM; $[Al(O\textit{i}\text{-}Pr)_3]_0 = 100$ mM. Additives: (●) TEMPO; (▼) MeOH; (△) H_2O; (○) none. Each additive was added to the polymerization mixture when conversion reached 51% in 47 h.

reversible dissociation of a C–I terminal by the Re(V) complex. The radical pathway is also suggested by the tolerance to water and alcohol. This is the first example of living polymerization mediated by rhenium, which does not belong to the late transition metals.

Experimental Section

1. Materials. Styrene (Wako Chemicals; purity >99%) was dried overnight over calcium chloride and distilled twice over calcium hydride under reduced pressure before use. 1-(Iodoethyl)benzene was prepared by adding a solution of anhydrous hydrogen iodide[32] (1.0 M in *n*-hexane, 0.5 mL) into styrene (250 mM in toluene, 1.58 mL) at −20 °C. $ReO_2I(PPh_3)_2$ (Aldrich), $RuCl_2(PPh_3)_3$ (Merck; purity >99%), and $Al(O\textit{i}\text{-}Pr)_3$ (Aldrich; purity >99.99%) were used as received and handled in a glovebox (M. Braun) under dry (<1.0 ppm) and oxygen-free (<1.0 ppm) argon. Toluene (solvent), *n*-hexane (solvent for hydrogen iodide solution), and tetralin (internal standard for gas chromatographic analysis of styrene) were dried overnight over calcium chloride, distilled twice over calcium hydride, and bubbled with dry nitrogen for more than 15 min immediately before use.

2. Synthesis of Initiators. Ethyl 2-iodoisobutyrate $[(CH_3)_2C(CO_2C_2H_5)I]$ was prepared by the method of Curran et al.:[33] bp 50 °C/9 Torr; identified by 500 MHz ^1H 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. $CH_3CH(CO_2Et)I$ was prepared by a similar method.

3. 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 $(CH_3)_2C(CO_2Et)I/ReO_2I(PPh_3)_2/Al(O\textit{i}\text{-}Pr)_3$ is given below: $Al(O\textit{i}\text{-}Pr)_3$ (0.1248 g) was mixed with styrene (4.20 mL) and tetralin (1.18 mL). This mixture (4.50 mL) and a toluene solution of $(CH_3)_2C(CO_2Et)I$ (0.365 mL) were added into $ReO_2I(PPh_3)_2$ (0.1305 g), sequentially in this order. Immediately after mixing, the solution was placed in an oil bath at 60 °C. 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 tetralin 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.

4. Measurements. The MWD, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ 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 detectors. The columns were

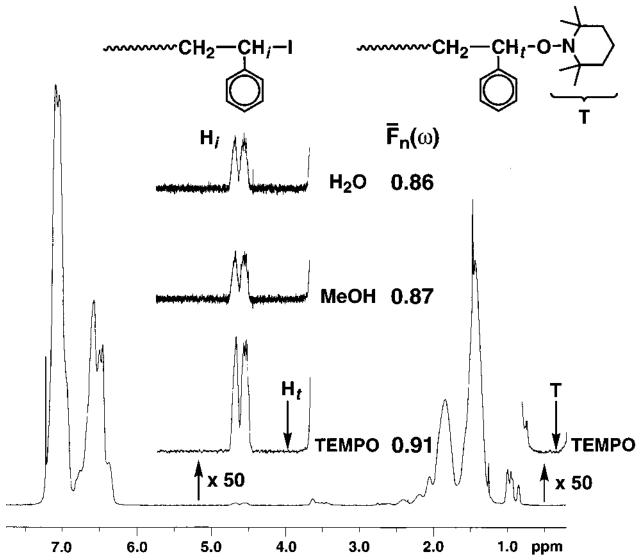


Figure 8. ^{1}H NMR spectra (500 MHz) of the polystyrene samples obtained with $(CH_3)_2C(CO_2Et)I/ReO_2I(PPh_3)_2/Al(Oi\text{-}Pr)_3$ at 60 °C in the presence of added water, methanol, or TEMPO: samples from the experiments shown in Figure 7.

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 of Macromolecules, the Society of Polymer Science, Kyoto, Japan, May 1998; paper II-3-15 (Kotani, Y.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1998**, *47*, 150). (b) The 37th IUPAC International Symposium on Macromolecules, Gold Coast, Australia, July 1998 (Kamigaito, M.; Sawamoto, M. MACRO 98 *Preprints*, p 138).
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