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Metal Alkoxides as Additives for Ruthenium(II)-Catalyzed Living Radical Polymerization[1]

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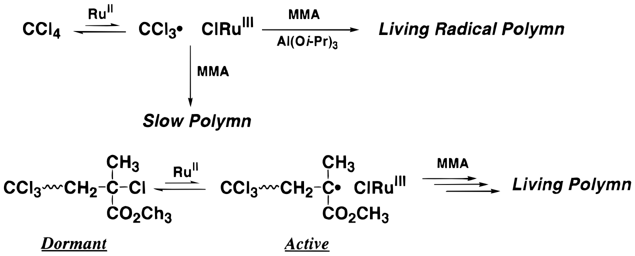
ABSTRACT: Effects of additives (metal alkoxides and halides) were investigated in the $\mathrm{RuCl_2(PPh_3)_3}$-catalyzed living radical polymerization of methyl methacrylate (MMA) in toluene at 80 °C. While the MMA polymerization with the $\mathrm{RuCl_2(PPh_3)_3/CCl_4}$ system ($\mathrm{CCl_4}$: initiator) is very slow and produces polymers with broad molecular weight distributions (MWDs), addition of metal alkoxides, such as Al(O*i*-Pr)$_3$, Ti(O*i*-Pr)$_4$, and Sn(O*i*-Pr)$_4$, accelerated the polymerization to produce polymers with controlled molecular weights and narrow MWDs. Metal chlorides such as $\mathrm{SnCl_4}$ and $\mathrm{TiCl_4}$ were not effective additives. According to NMR and cyclic voltammetric analyses, Al(O*i*-Pr)$_3$ does not interact with monomer or the polymer termini (∼∼∼C−Cl and ∼∼∼C$^\bullet$ radicals) but interacts with the ruthenium complex, or more likely, its higher oxidation state Ru(III) species.

Introduction

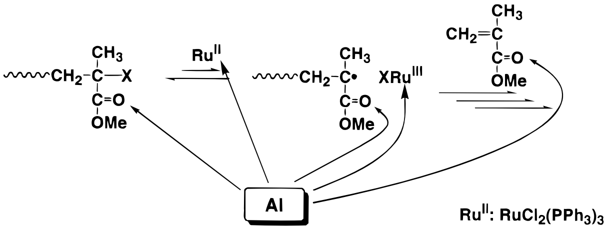
As a prelude to the current rapid development of transition-metal-catalyzed living radical polymerizations,[2−18] we have developed the $\mathrm{RuCl_2(PPh_3)_3}$-catalyzed living radical polymerization of methyl methacrylate (MMA) using $\mathrm{CCl_4}$[3a] and related halogen-containing initiators (Scheme 1).[3−5] In both this reaction and the corresponding radical addition,[19−21] the ruthenium complex promotes cleavage of the carbon−chlorine bond of $\mathrm{CCl_4}$ to generate the trichloromethyl radical ($\mathrm{CCl_3^\bullet}$) via oxidation of Ru(II) into Ru(III), and the $\mathrm{CCl_3^\bullet}$ radical adds to the carbon−carbon double bond of an olefin (monomer), followed by the formation of a new carbon−chlorine bond via reduction of Ru(III) to the original Ru(II) species. Although the $\mathrm{RuCl_2(PPh_3)_3/CCl_4}$ system itself is not effective in MMA polymerization, addition of an aluminum alkoxides such as Al(O*i*-Pr)$_3$ accelerates the reaction and produces polymers with narrow MWDs.[3] The aluminum additive also accelerates living radical polymerizations catalyzed by other transition metals such as Ni,[12−14] Fe,[16] Re,[17] and Cu.[18] However, it is still unknown how these additives function.

This study examines the effects of aluminum additives on the $\mathrm{RuCl_2(PPh_3)_3}$-mediated living radical polymerization of MMA. Because the polymerization most likely proceeds via a ruthenium-catalyzed reversible homolytic cleavage of a carbon−chlorine bond [∼∼∼C−X + Ru(II) ⇌ ∼∼∼C$^\bullet$ X−Ru(III) in Scheme 2], the additive may interact with the propagating radical, its dormant analogue (∼∼∼C−X), the ruthenium complex, or the monomer. This interaction may determine the polymerization rate and the extent of polymer molecular weight control. For example, the additive may interact with monomer by coordinating with its carbonyl oxygen, thereby modifying its reactivity. Alternatively, it may interact with the propagating radical by coordinating with the terminal carbonyl group. Such interactions have been reported in conventional radical polymerizations,[22,23] although the additives employed therein are metal halides, much stronger Lewis acids than the metal alkoxides in our work here. Additives may also activate the carbon−halogen bond at the dormant polymer terminus by coordination with the carbonyl group. Finally, the additive may coordinate the ruthenium complex at the metal center or may abstract its phosphine ligand.

Scheme 1. Living Radical Polymerization Using $\mathrm{CCl_4/RuCl_2(PPh_3)_3}$ in the Presence of Al(O*i*-Pr)$_3$



Scheme 2. Possible Interactions of Al(O*i*-Pr)$_3$ with the Four Components in the $\mathrm{RuCl_2(PPh_3)_3}$-Mediated Living Polymerization of MMA



In this work, we first examined the effects of metal alkoxides [Al(O*i*-Pr)$_3$, Ti(O*i*-Pr)$_4$, and Sn(O*i*-Pr)$_4$] and metal halides ($\mathrm{TiCl_4}$ and $\mathrm{SnCl_4}$), in both $\mathrm{RuCl_2(PPh_3)_3}$-mediated and conventional radical polymerizations of MMA. The possible interactions of Al(O*i*-Pr)$_3$ with the monomer, the dormant polymer terminal (∼∼∼C−X), the growing radical, and/or $\mathrm{RuCl_2(PPh_3)_3}$ were then analyzed by NMR and cyclic voltammetry. These results indicate that the most important interaction of added Al(O*i*-Pr)$_3$ occurs with $\mathrm{RuCl_2(PPh_3)_3}$, which most likely stabilizes its higher oxidation state Ru(III) complex to facilitate the formation of the growing radicals.

Results and Discussion

1. Effects of Additives on Polymerization. (a) Metal Isopropoxides. MMA was polymerized with

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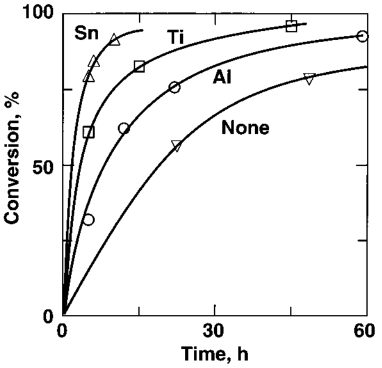


Figure 1. Polymerization of MMA with $CCl_4/RuCl_2(PPh_3)_3/M(Oi\text{-}Pr)_n$ in toluene at 80 °C: $[MMA]_0 = 2.0$ M; $[CCl_4]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[M(Oi\text{-}Pr)_n]_0 = 0$ or 40 mM. $M(Oi\text{-}Pr)_n$: $Sn(Oi\text{-}Pr)_4$ (△); $Ti(Oi\text{-}Pr)_4$ (□); $Al(Oi\text{-}Pr)_3$ (○); none (▽).

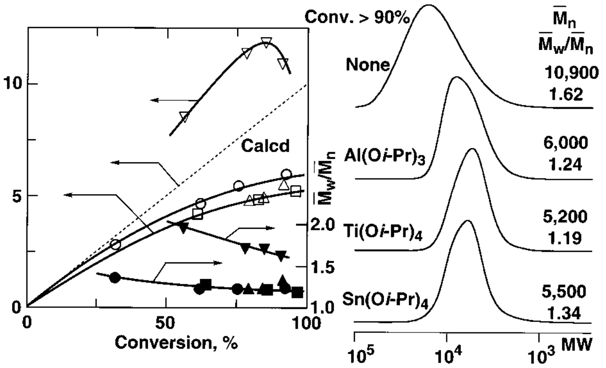


Figure 2. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD chromatogram curves of poly(MMA) obtained with $CCl_4/RuCl_2(PPh_3)_3/M(Oi\text{-}Pr)_n$ in toluene at 80 °C: $[MMA]_0 = 2.0$ M; $[CCl_4]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[M(Oi\text{-}Pr)_n]_0 = 0$ or 40 mM. $M(Oi\text{-}Pr)_n$: $Sn(Oi\text{-}Pr)_4$ (△, ▲); $Ti(Oi\text{-}Pr)_4$ (□, ■); $Al(Oi\text{-}Pr)_3$ (○, ●); none (▽, ▼).

CCl_4 and $RuCl_2(PPh_3)_3$ in toluene at 80 °C in the presence or absence of the three metal isopropoxides. As shown in Figure 1, polymerization occurred without additives but slowly, and a clear acceleration was observed on addition of the additives. The polymerization rate increased in the order $Al(Oi\text{-}Pr)_3 < Ti(Oi\text{-}Pr)_4 < Sn(Oi\text{-}Pr)_4$, where the conversion reached 90% in 10 h with $Sn(Oi\text{-}Pr)_4$.

Figure 2 shows the $\bar{M}_n$ and MWD curves of the obtained polymers. Without additives, the MWD was broad, and the $\bar{M}_n$ was higher than the calculated value assuming that one initiator produces one polymer chain. In the presence of the additives, the $\bar{M}_n$ increased with monomer conversion, and the MWDs were relatively narrow ($\bar{M}_w/\bar{M}_n = 1.2-1.3$). As already reported for $Al(Oi\text{-}Pr)_3$,[3b] these metal alkoxides thus proved effective in controlling and accelerating the $RuCl_2(PPh_3)_3$-catalyzed polymerization. However, the $\bar{M}_n$ were lower than the calculated values, which indicates a chain transfer reaction, most likely via the CCl_3 group at the α-end.[24] As discussed below, the use of a monofunctional initiator, $(CH_3)_2C(CO_2CH_3)CH_2C(CH_3)(CO_2CH_3)Cl$ [$(MMA)_2-Cl$], gives polymers the $\bar{M}_n$ of which agreed well with the calculated values in the presence of $Al(Oi\text{-}Pr)_3$.

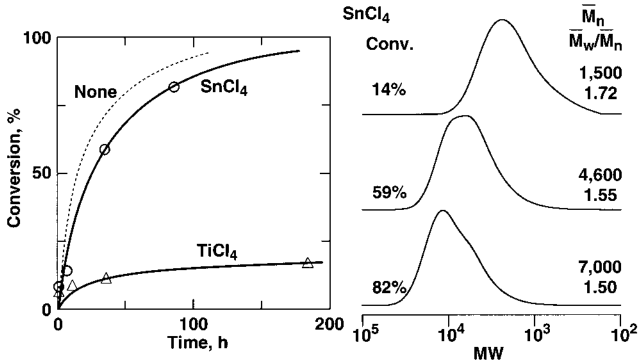


Figure 3. Time−conversion curves for the polymerization of MMA with $CCl_4/RuCl_2(PPh_3)_3/MCl_4$ and MWD chromatogram curves of poly(MMA) in toluene at 80 °C: $[MMA]_0 = 2.0$ M; $[CCl_4]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[MCl_4]_0 = 40$ mM. MCl_4: $SnCl_4$ (○); $TiCl_4$ (△).

(b) Metal Chlorides. Lewis acids are known to accelerate conventional radical polymerization via complexation with monomer or propagating radicals.[22,23] Two metal halides, $SnCl_4$ and $TiCl_4$, were then examined as additives for the ruthenium-mediated polymerization. Polymerization proceeded but was slower than without additives (Figure 3). On addition of $SnCl_4$, the reaction solution changed from brown to reddish brown, suggesting that $SnCl_4$ reacts with $RuCl_2(PPh_3)_3$ to result in another complex. Addition of $TiCl_4$ also turned the reaction mixture from brown to dark blue, and the polymerization was significantly retarded.

The MWD curves for the polymers obtained in the presence of $SnCl_4$ shifted to higher molecular weight with monomer conversion. The $\bar{M}_n$ increased with monomer conversion and were close to the calculated values. However, the products with $TiCl_4$ were only oligomers.

Thus, metal chlorides are ineffective in accelerating the ruthenium-mediated living radical polymerization. Because metal alkoxides are weaker Lewis acids than metal chlorides, the observed rate enhancement by the former does not result from the Lewis acid-promoted activation of monomer or the propagating radicals proposed for conventional radical polymerizations.

2. Roles of $Al(Oi\text{-}Pr)_3$. To clarify the impact of the metal alkoxides on the polymerization, we investigated further the effects of $Al(Oi\text{-}Pr)_3$ on the $RuCl_2$-mediated polymerization, along with its possible interaction with MMA, the dormant species, and the ruthenium complex by ^1H NMR and CV.

(a) Effects of $Al(Oi\text{-}Pr)_3$ on Polymerization. In the presence or absence of $Al(Oi\text{-}Pr)_3$, MMA was polymerized with initiation by 2,2′-azobis(isobutyronitrile) (AIBN) or by $RuCl_2(PPh_3)_3$ coupled with the MMA-dimer initiator [$(MMA)_2-Cl$] in toluene at 80 °C (Figure 4). The added aluminum compound accelerated the polymerization with $(MMA)_2-Cl$ as with CCl_4 (cf. Figure 1), whereas the AIBN-initiated polymerization was not affected.

Figure 5 shows the $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves for the polymers obtained in these systems. The polymers obtained with AIBN/$Al(Oi\text{-}Pr)_3$ had almost the same molecular weights and distributions in both the presence and the absence of the additives. In the Ru(II)-mediated polymerization with $Al(Oi\text{-}Pr)_3$, however, the $\bar{M}_n$ of the polymers increased in direct proportion to monomer conversion and agreed well with the calculated values. The MWDs became much narrower than those for $Al(Oi\text{-}Pr)_3$-free systems. These results indicate that $Al(Oi\text{-}Pr)_3$ does not interact with monomer nor the growing radical species.

(b) NMR Analysis. Figure 6A−C shows the ^{13}C NMR spectra for the carbonyl absorption of MMA in the

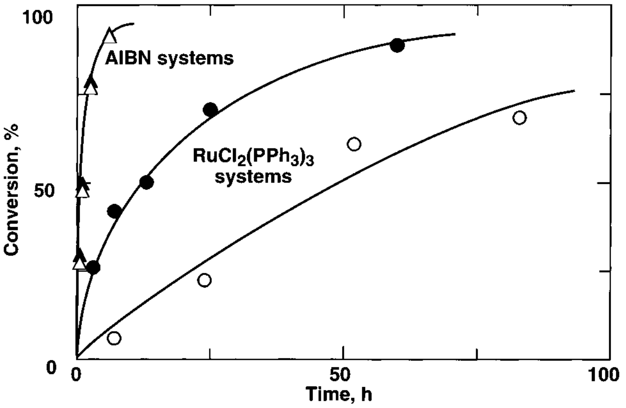


Figure 4. Time–conversion curves for the polymerization of MMA with AIBN or $(MMA)_2$–Cl/$RuCl_2(PPh_3)_3$ in the presence or absence of $Al(O\textit{i}\text{-}Pr)_3$ and MWD chromatogram curves of poly(MMA) in toluene at 80 °C: $[MMA]_0 = 2.0$ M; $[AIBN]_0 = 20$ mM; $[(MMA)_2\text{–}Cl]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(O\textit{i}\text{-}Pr)_3]_0 = 40$ mM. Symbols mean AIBN/$Al(O\textit{i}\text{-}Pr)_3$ (▲), AIBN (△), $(MMA)_2$–Cl/$RuCl_2(PPh_3)_3$/$Al(O\textit{i}\text{-}Pr)_3$ (●), and $(MMA)_2$–Cl/$RuCl_2(PPh_3)_3$ (○).

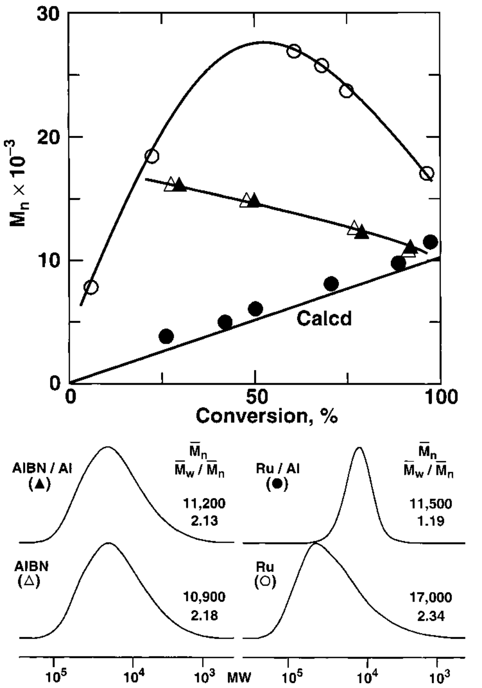


Figure 5. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD chromatogram curves of poly(MMA) obtained with AIBN or $(MMA)_2$–Cl/$RuCl_2(PPh_3)_3$ in the presence or absence of $Al(O\textit{i}\text{-}Pr)_3$ in toluene at 80 °C: $[MMA]_0 = 2.0$ M; $[AIBN]_0 = 20$ mM; $[(MMA)_2\text{–}Cl]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(O\textit{i}\text{-}Pr)_3]_0 = 40$ mM. Symbols mean AIBN/$Al(O\textit{i}\text{-}Pr)_3$ (▲), AIBN (△), $(MMA)_2$–Cl/$RuCl_2$-$(PPh_3)_3$/$Al(O\textit{i}\text{-}Pr)_3$ (●), and $(MMA)_2$–Cl/$RuCl_2(PPh_3)_3$ (○).

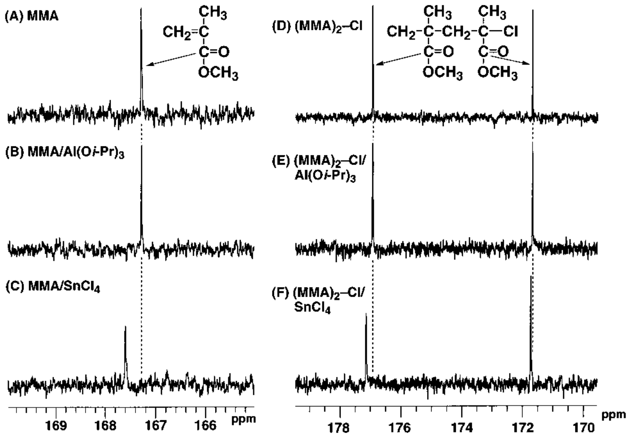


Figure 6. ^{13}C NMR spectra of MMA and $(MMA)_2$–Cl in the presence or absence of $Al(O\textit{i}\text{-}Pr)_3$ or $SnCl_4$ in C_6D_6 at 70 °C: $[MMA]_0 = 80$ mM; $[Al(O\textit{i}\text{-}Pr)_3]_0 = 80$ mM; $[SnCl_4]_0 = 80$ mM.

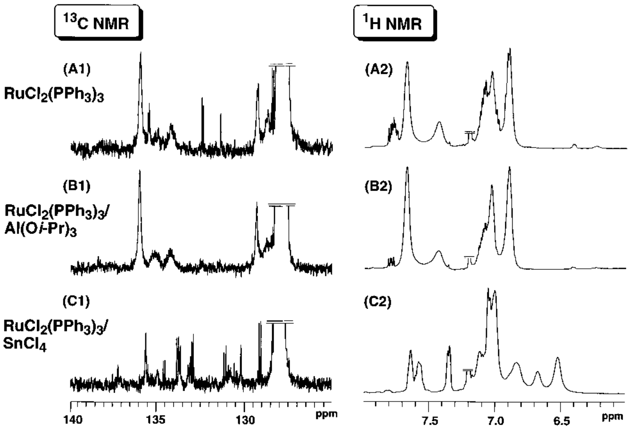


Figure 7. ^{13}C and ^{1}H NMR spectra of $RuCl_2(PPh_3)_3$ in the presence or absence of $Al(O\textit{i}\text{-}Pr)_3$ or $SnCl_4$ in C_6D_6 at 70 °C: $[RuCl_2(PPh_3)_3]_0 = 20$ mM; $[Al(O\textit{i}\text{-}Pr)_3]_0 = 80$ mM; $[SnCl_4]_0 = 80$ mM.

presence or absence of $Al(O\textit{i}\text{-}Pr)_3$ and $SnCl_4$. With or without $Al(O\textit{i}\text{-}Pr)_3$, the absorption appeared at the same position (167.29 ppm) (Figure 6A,B). However, on addition of $SnCl_4$ to MMA, it shifted to lower magnetic field to 167.60 ppm with a peak broadening (Figure 6C), which indicates coordination of $SnCl_4$ to the carbonyl group. Thus, $Al(O\textit{i}\text{-}Pr)_3$ does not work as a Lewis acid that activates the monomer via coordination.

The interaction between the additives and the dormant end was examined, with the chlorine-capped MMA dimer [$(MMA)_2$–Cl] as the model compound of the dormant species. The two carbonyl carbons at the dimer absorb at 171.69 and 176.93 ppm (Figure 6D). There were no changes in the chemical shifts on addition of $Al(O\textit{i}\text{-}Pr)_3$ (Figure 6E), but $SnCl_4$ led to a lower field shifts to 171.73 and 177.14 ppm with peak broadening. This also indicates that interaction between $Al(O\textit{i}\text{-}Pr)_3$ and the dormant polymer terminal is absent or negligible.

Those results showed that $Al(O\textit{i}\text{-}Pr)_3$ does not activate (or interact) monomer, the growing radical species, or the dormant species. We therefore investigated the interaction between $RuCl_2(PPh_3)_3$ and the additives by ^{13}C and ^{1}H NMR (Figure 7). On addition of $Al(O\textit{i}\text{-}Pr)_3$, some peaks of the Ru(II) complex became larger and some became smaller, but the changes were very small. In contrast, mixtures of $RuCl_2(PPh_3)_3$ and $SnCl_4$ showed apparently different spectra (C1 and C2) from those of $RuCl_2(PPh_3)_3$ alone (A1 and A2), which indicates the formation of another complex. These NMR analyses indicate that the added metal alkoxide most probably interacts with the ruthenium complex, rather than with monomer and polymer terminal, although the interaction is very small.

(c) Cyclic Voltammetric Analysis. In the ruthenium-mediated living radical polymerization, the redox potential of Ru(II)/Ru(III) is an important factor that affects the polymerization, because the ruthenium complex is oxidized from Ru(II) to Ru(III) (cf. Scheme 1) when the carbon–halogen bond at the dormant terminal is converted into the active radical species. The

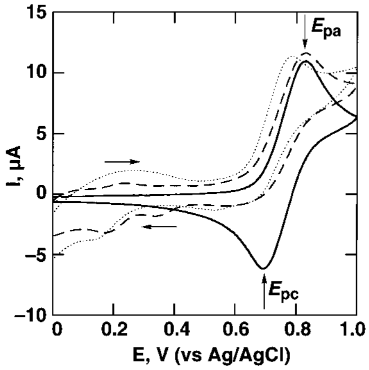


Figure 8. Cyclic voltammograms of $RuCl_2(PPh_3)_3$ in the presence or absence of Al(O*i*-Pr)$_3$ or $SnCl_4$ in $ClCH_2CH_2Cl$ at 30 °C: (- - -) $RuCl_2(PPh_3)_3$; (—) $RuCl_2(PPh_3)_3$ + Al(O*i*-Pr)$_3$; (· · ·) $RuCl_2(PPh_3)_3$ + $SnCl_4$. $[RuCl_2(PPh_3)_3]_0 = 5.0$ mM; [Al(O*i*-Pr)$_3$]$_0$ = 5.0 mM; $[SnCl_4]_0 = 5.0$ mM; [*n*-Bu_4NPF_6]$_0$ = 100 mM (supporting electrolyte). Scan rate = 0.10 V s^{-1}.

effects of Al(O*i*-Pr)$_3$ on the polymerization rate, as well as on the molecular weights of the polymers, suggest that the additive probably works on the ruthenium complex to affect the redox cycle of Ru(II)/Ru(III). This led us to measure cyclic voltammograms of $RuCl_2(PPh_3)_3$ in the presence and absence of Al(O*i*-Pr)$_3$. The CV measurement was carried out in the potential range of 0 to +1.0 V (vs Ag/AgCl) in 1,2-dichloroethane at 30 °C under argon.

$RuCl_2(PPh_3)_3$ alone showed the oxidation wave corresponding to the Ru(II)/Ru(III) conversion at $E_{pa} = 0.83$ V, but in most cases, no reduction wave was detected (the broken line in Figure 8); sometimes a reduction wave appeared at $E_{pc} = 0.70$ V. Although the Ru(II)/Ru(III) redox cycle of $RuCl_2(PPh_3)_3$ seems chemically irreversible during the electrochemical redox process, the absence of any reduction cycle peaks indicates that the Ru(III) species is not stable and immediately decomposes into other species that cannot regenerate the Ru(II) species.

In contrast, addition of Al(O*i*-Pr)$_3$ changed the irreversible redox cycle into a quasi-reversible redox couple where the oxidation and reduction waves were now clearly observed at $E_{pa} = 0.83$ V and $E_{pc} = 0.70$ V, respectively (the solid line). Though the redox cycle was highly reproducible after several scans, the redox potential (E_{pa}) was unchanged by the addition of Al(O*i*-Pr)$_3$. This suggests that Al(O*i*-Pr)$_3$ stabilizes the Ru(III) species via some weak interaction so that the Ru(III) species can be reversibly converted into the Ru(II) species. However, the mixture with $SnCl_4$, which is ineffective for the Ru-mediated polymerization, did not show reduction waves (dotted line) similar to $RuCl_2(PPh_3)_3$ alone.

The stabilization of the Ru(III) species by Al(O*i*-Pr)$_3$ was also confirmed by an anodic polarization (Figure 9). The cyclic voltammogram of $RuCl_2(PPh_3)_3$/Al(O*i*-Pr)$_3$ showed a quasi-reversible Ru(II)/Ru(III) redox couple on repeatedly applying a potential of 1.0 V to the solution for 5 min. This shows that the ruthenium complex is stable even after being kept at a higher oxidation state for such long time.

Thus, the metal alkoxide additives do not affect monomer and polymer terminal but on the ruthenium complex especially on the Ru(III) species.

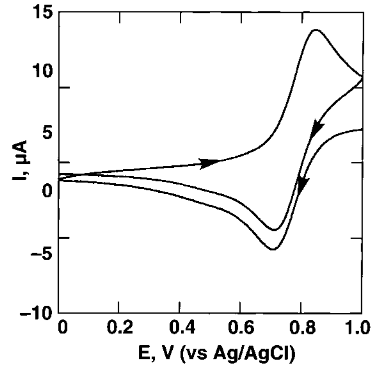
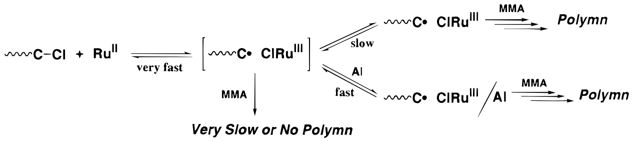


Figure 9. Cyclic voltammograms of $RuCl_2(PPh_3)_3$ in the presence of Al(O*i*-Pr)$_3$ after applying a potential of 1.0 V for 5 min in $ClCH_2CH_2Cl$ at 30 °C: $[RuCl_2(PPh_3)_3]_0 = 5.0$ mM; [Al(O*i*-Pr)$_3$]$_0$ = 5.0 mM; [*n*-Bu_4NPF_6]$_0$ = 100 mM (supporting electrolyte). Scan rate = 0.10 V s^{-1}.

Scheme 3. A Proposed Pathway of the $RuCl_2$-Catalyzed Polymerization in Relations to the Effects of Al(O*i*-Pr)$_3$ Additive



3. Role of Additives. The effects of metal alkoxide additives thus discussed are summarized as follows: (1) accelerate the polymerization; (2) control polymer molecular weight and MWD; (3) do not interact with monomer or with the polymer terminal (dormant or active) but do interact with the ruthenium complex weakly; (4) stabilize the Ru(III) species. Recently, we have reported that a very fast halogen exchange reaction occurs between the dormant polymer terminal (∼∼∼C−Br) and the ruthenium complex [$RuCl_2(PPh_3)_3$] via radical species, in comparison to the polymerization. We have also found that there were no effects of added Al(O*i*-Pr)$_3$ on the rate of the halogen exchange.[25] Thus, Al(O*i*-Pr)$_3$ accelerates only the polymerization without affecting the rate of halogen-exchange or the redox potential of the complex.

Taking these results into consideration, we propose that the polymerization with $RuCl_2(PPh_3)_3$ proceeds as in Scheme 3. The ruthenium(II) complex reversibly activates the carbon−halogen bond of the dormant end to produce a radical species in the coordination sphere involving a radical and a higher oxidation state, Ru(III) [∼∼∼C−X + Ru(II) $\rightleftharpoons$ ∼∼∼C$^•$ XRu(III)]. Such an inner-sphere radical species is proposed for the Kharasch addition reactions with Ru[21] and Ni[26] complexes. Similar to these, the halogen exchange reaction may also occur via an inner-sphere species. The activation (radical dissociation) and the deactivation (halogen-capping) processes are very fast as indicated by the fast halogen-exchange reaction.

The propagation may also take place via the inner-sphere radical, although the reaction proceeds very slowly. The inner-sphere radical species can reversibly go out of the coordination sphere to become a free radical species (outer-sphere radical). The polymerization proceeds faster via the outer-sphere radical than via the inner-sphere radical. In the absence of Al(O*i*-Pr)$_3$, the exchange between the inner- and the outer-sphere radicals is slow, and the equilibrium is shifted to the former. The aluminum additive probably shifts the equilibrium slightly to the outer-sphere radical via the stabilization of the Ru(III) species and also accelerates the exchange reaction. The former effect leads to a higher concentration of the more reactive outer-sphere radicals, which in turn accelerates the polymerization; the latter acceleration of exchange evidently leads to narrower MWDs and controlled molecular weights of polymers.

The halogen-exchange reaction is not affected by Al(O*i*-Pr)$_3$, because it can occur via the inner-sphere radical species. Possibly, the outer-sphere radical species does not exist in the absence of Al(O*i*-Pr)$_3$, and the polymerization proceeds only via the inner-sphere radical species. However, this scenario is less probable because the steric structure of the polymers in the presence of Al(O*i*-Pr)$_3$ is almost the same as that in the absence.

Conclusions

A series of metal alkoxides [Al(O*i*-Pr)$_3$, Ti(O*i*-Pr)$_4$, and Sn(O*i*-Pr)$_4$] increased the polymerization rate and afforded polymers of controlled molecular weights, whereas metal chlorides such as SnCl$_4$ and TiCl$_4$ were not effective. The comparison of living and conventional radical polymerizations, along with NMR and CV analysis of model reactions, shows that the added Al(O*i*-Pr)$_3$ interacts with the ruthenium complex and thereby stabilizes the higher oxidation state Ru(III) species to facilitate radical generation from a dormant species.

Experimental Section

Materials. MMA (Tokyo Kasei, >99%) was dried overnight over calcium chloride and distilled twice over calcium hydride under reduced pressure before use. RuCl$_2$(PPh$_3$)$_3$ (Merck, >99%) and Al(O*i*-Pr)$_3$ (Aldrich, >99.99%) were used as received and handled in a glovebox under a moisture- and oxygen-free argon atmosphere (<1 ppm). Ti(O*i*-Pr)$_4$ (Kanto Chemical, 97%), Sn(O*i*-Pr)$_4$ (High Purity Chemicals, 99%), TiCl$_4$ (Aldrich, 99%), and SnCl$_4$ (Aldrich, 99.995%) were used as received. AIBN (Wako Chemicals, >98%) was recrystallized from methanol. CCl$_4$ (Wako Chemicals, HPLC grade), toluene used as solvent, and *n*-octane used as internal standard for gas chromatography were dried overnight over calcium chloride, distilled twice from calcium hydride, and bubbled with dry nitrogen for more than 15 min immediately before use. *n*-Bu$_4$NPF$_6$ (Tokyo Kasei, >99%) was dried under reduced pressure at 100 °C. ClCH$_2$CH$_2$Cl was distilled from P$_2$O$_5$ and bubbled with dry argon for more than 30 min.

Polymerization Procedures. The polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. In a typical example using Al(O*i*-Pr)$_3$, solutions of Al(O*i*-Pr)$_3$ (125 mM in toluene, 3.07 mL, 0.384 mmol) and CCl$_4$ (1.0 M in toluene, 0.192 mL, 0.192 mmol) were added sequentially to a mixture of RuCl$_2$(PPh$_3$)$_3$ (92.0 mg, 0.096 mmol), *n*-octane (0.384 mL), and MMA (2.05 mL, 19.2 mmol) in toluene (3.90 mL) at room temperature under dry nitrogen. The total volume of the reaction mixture was 9.60 mL. Immediately after mixing, six aliquots (1.20 mL each) of the solution were injected into baked glass tubes, which were then sealed and placed in an oil bath 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 using *n*-octane as the internal standard. The quenched reaction solutions were diluted with toluene (ca. 20 mL) and rigorously shaken with an absorbent [KYOWAAD-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); Kyowa Chemical Industry] (ca. 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 yield the products, which were subsequently vacuum-dried overnight.

Polymer Characterization. The $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of the polymers were determined by size-exclusion chromatography in chloroform at 40 °C using 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 Jasco PU-980 precision pump and a Jasco RI-930 refractive index detector. The columns were calibrated against 11 standard poly(MMA) samples (Polymer Laboratories; $\bar{M}_n$ = 630−1 200 000; $\bar{M}_w/\bar{M}_n$ = 1.04−1.22) as well as the monomer.

^{13}C and ^{1}H NMR Spectroscopy and Model Reactions. ^{13}C and ^{1}H NMR spectra were recorded using a JEOL JNM-LA500 spectrometer in C$_6$D$_6$ at 70 °C, operating at 125.78 and 500.16 MHz, respectively. The main parameters were as follows. ^{13}C NMR: spectral width = 33 898.3 Hz (269 ppm), pulse width = 4.75 μs (45 °), acquisition time + pulse delay = 3.0 s, data points = 65 536, number of transients = 1000 (50 min for one spectrum). ^{1}H NMR: spectral width = 12 500 Hz (25.0 ppm), pulse width = 6.20 μs (45 °), acquisition time + pulse delay = 30 s, data points = 32 768, number of transients = 8 (4.0 min for one spectrum). The probe temperature was regulated with a variable temperature apparatus (temperature fluctuation ≤ 0.1 deg). In a typical example of a model reaction with RuCl$_2$(PPh$_3$)$_3$ and Al(O*i*-Pr)$_3$, solutions of RuCl$_2$(PPh$_3$)$_3$ (0.40 mL of 40 mM, 0.016 mmol) and Al(O*i*-Pr)$_3$ (0.40 mL of 160 mM, 0.064 mmol) in C$_6$D$_6$ were mixed in a sample vial under a moisture- and oxygen-free argon atmosphere at room temperature. The mixture was sealed in an NMR tube and placed in the NMR probe at 70 °C. The chemical shifts were determined with reference to residual C$_6$H$_6$ (128 and 7.15 ppm, respectively) in the deuterated solvent.

Electrochemical Experiments. Cyclic voltammograms were recorded using a Hokuto Denko HZ-3000 apparatus. Measurements were carried out under argon at 0.10 V s^{-1} in a ClCH$_2$CH$_2$Cl solution (5.0 mM) containing *n*-Bu$_4$NPF$_6$ (100 mM) as the supporting electrolyte. 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.

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References and Notes

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