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Communications to the Editor

Half-Metallocene-Type Ruthenium Complexes as Active Catalysts for Living Radical Polymerization of Methyl Methacrylate and Styrene[1]

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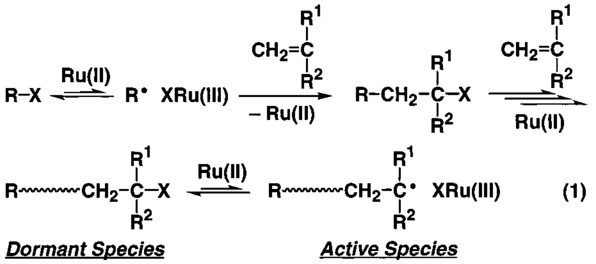
Introduction. Transition-metal catalysis now plays a critical role in precise control of radical polymerization (eq 1).[2] When coupled with suitable initiators, such as alkyl halides (R−X; X = Cl, Br, I) with radical-stabilizing substituents, a variety of group 7−10 transition-metal complexes as catalysts effect living radical polymerization of methacrylates, acrylates, and styrenes to give polymers of well-defined structures, controlled molecular weights, and narrow molecular weight distributions (MWDs). The effective metal catalysts for such living radical polymerization include halides of Ru,[3−6] Cu,[7−12] Fe,[13,14] Ni,[15−17] Rh,[18,19] Pd,[20] and Re[21] with phosphine- or nitrogen-based ligands. Most likely, their primary role is to reversibly generate radicals from the initiator R−X and its polymeric analogues [$\sim$CH$_2$C(R^1)(R^2)−X] via redox reactions or reversible homolytic cleavage of the carbon−halogen linkages through a one-electron oxidation−reduction cycle of the central metals, such as $\sim\text{C–X} + \text{Ru(II)} \rightleftarrows \sim\text{C}^{\bullet}\ \text{X–Ru(III)}$. One of the potential advantages of the metal-mediated living polymerizations is the selectivity and tunable activity of complex catalysts through the design of their ligands in response to the structure of monomers and the growing species therefrom. However, the ligands utilized thus far are confirmed primarily to phosphines, amines, and bipyridines.



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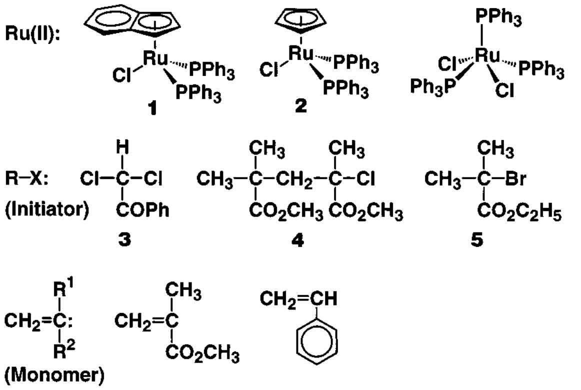

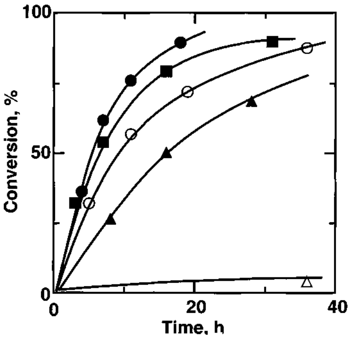

Figure 1. Polymerization of MMA with **3**/ruthenium complex in the presence and absence of Al(O-*i*-Pr)$_3$ in toluene at 100 °C: [MMA]$_0$ = 2.0 M; [**3**]$_0$ = 20 mM; [**1**]$_0$ = 5.0 mM; [**2**]$_0$ = [RuCl$_2$(PPh$_3$)$_3$]$_0$ = 10 mM; and [Al(O-*i*-Pr)$_3$]$_0$ = 40 or 0 mM. **1**/Al(O-*i*-Pr)$_3$ (●); **1** (○); **2**/Al(O-*i*-Pr)$_3$ (▲); **2** (△); and RuCl$_2$(PPh$_3$)$_3$/Al(O-*i*-Pr)$_3$ (■).

This communication is to report that a "half-metallocene-" type ruthenium(II) chloride, Ru(Ind)Cl(PPh$_3$)$_2$ (**1**; Ind = indenyl; Ph = C$_6$H$_5$), is an efficient and markedly active catalyst for living radical polymerizations of methyl methacrylate (MMA) and styrene. Obviously, this complex is characterized by its highly electron-donating, conjugated indenyl ligand that, in conjunction with the single chlorine of the Ru(II) center, would affect the nature and the catalytic activity of the complex in the metal-mediated living radical polymerizations. For both monomers, the Ru(II)−indenyl complex proved more active than the dichloride counterpart RuCl$_2$(PPh$_3$)$_3$ previously reported[3,4] to give polymers with precisely controlled molecular weights and markedly narrow MWDs, perhaps the narrowest among those obtained in the Ru(II)-mediated living radical polymerizations. For comparison, another analogue with a cyclopentadienyl (Cp) ligand, Ru(Cp)Cl(PPh$_3$)$_2$ (**2**), was also examined.

Ruthenium complexes with Cp-type ligands and their derivatives have recently been employed in organic reactions in which carbene and related intermediates are involved, and the effects of these ligands are studied in some examples.[22,23] Ruthenium halides with phosphine ligands such as RuCl$_2$(PPh$_3$)$_3$ also catalyze radical addition reactions[24] and radical polymerizations[3−6] via redox reaction of the ruthenium center between Ru(II) and Ru(III). A key to the control of these radical reactions lies in the redox potential of the complexes that should be suited for efficient but reversible homolytic cleavage of carbon−halogen bonds. The redox

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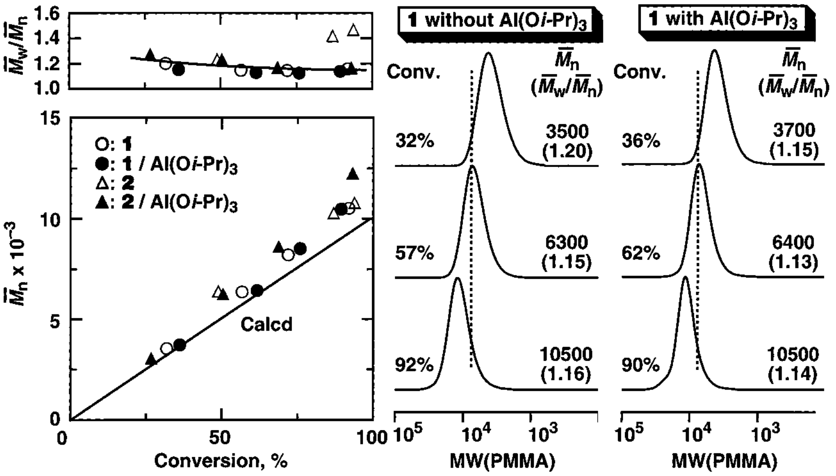

Figure 2. $\overline{M}_n$, $\overline{M}_w/\overline{M}_n$, and MWD curves of poly(MMA) obtained with **3**/**1** or **2** in the presence and absence of Al(O-*i*-Pr)$_3$ in toluene at 100 °C: [MMA]$_0$ = 2.0 M; [**3**]$_0$ = 20 mM; [**1**]$_0$ = 5.0 mM; [**2**]$_0$ = 10 mM; and [Al(O-*i*-Pr)$_3$]$_0$ = 40 or 0 mM. **1**/Al(O-*i*-Pr)$_3$ (●); **1** (○); and **2**/Al(O-*i*-Pr)$_3$ (▲); **2** (△). The diagonal solid line indicates the calculated $\overline{M}_n$, assuming the formation of one living polymer per **3** molecule.

potential of the Cp-based ruthenium complexes can be tuned by their ligands (e.g., Cp vs Ind), but there have been no reports on the use of these ruthenium complexes as catalysts for the radical addition reactions.

In this paper, we report that the indenyl derivative **1** is a markedly active and excellent catalyst which induces living radical polymerizations of both MMA and styrene in conjunction with organic halides to give polymers of narrow MWDs ($\overline{M}_w/\overline{M}_n \sim 1.1$). The MMA living polymerization with **1** proceeds smoothly even at a low concentration of **1** (~1.0 mM), without aluminum additives, and over a wide range of temperatures (60−100 °C). The first two features, along with the very narrow MWD, demonstrate that Ru(Ind)Cl(PPh$_3$)$_2$, a half-metallocene Ru(II) chloride, clearly differs from, and most probably excels, the dichloride counterpart.

Results and Discussion. 1. Living Polymerization of MMA. MMA was polymerized with the Cp-based complexes, **1** and **2**, in conjunction with dichloroacetophenone (CHCl$_2$COPh, **3**) as an initiator in the presence and absence of Al(O-*i*-Pr)$_3$ in toluene at 100 °C (Figure 1).[25] The Cp complex **2** indeed induced polymerization of MMA in the presence of Al(O-*i*-Pr)$_3$ without an induction phase (filled triangles), whereas the polymerization without the isopropoxide was very slow (open triangles; 87% conversion for 320 h).

In contrast, the Ind complex **1** led to a smooth MMA polymerization even in the absence of Al(O-*i*-Pr)$_3$ (open circles). Equally important, the polymerization with Al(O-*i*-Pr)$_3$ (filled circles) was faster than that with RuCl$_2$(PPh$_3$)$_3$ (filled squares) although the concentration of **1** was lower (5.0 vs 10 mM). Thus, **1** is a more active catalyst than RuCl$_2$(PPh$_3$)$_3$, and the activity decreases in the order: **1** > RuCl$_2$(PPh$_3$)$_3$ > **2**.

Figure 2 shows the number-average molecular weights ($\overline{M}_n$) and the MWDs of the polymers obtained with **1** and **2** in the absence and presence of Al(O-*i*-Pr)$_3$.[26] The polymers with **1** had very narrow MWDs ($\overline{M}_w/\overline{M}_n$ = 1.1−1.2) throughout the reactions either with or without Al(O-*i*-Pr)$_3$, where the MWDs were slightly narrower in the presence of the additive. The $\overline{M}_n$ increased in direct proportion to monomer conversion and agreed well with the calculated values, assuming that one molecule of the initiator (**3**) generates one living polymer chain. These results are in contrast to those with RuCl$_2$(PPh$_3$)$_3$, which induces a sluggish polymerization and gives broader MWDs ($\overline{M}_w/\overline{M}_n$ = 1.5−2.0) in the absence of Al(O-*i*-Pr)$_3$ under otherwise the same conditions.

In the presence of Al(O-*i*-Pr)$_3$, the Cp complex **2** also gave narrow MWDs ($\overline{M}_w/\overline{M}_n < 1.2$) and $\overline{M}_n$ that increased in direct proportion to monomer conversion and agreed well with the calculated values. The MWDs obtained without Al(O-*i*-Pr)$_3$ were narrow in the initial stage of the polymerization ($\overline{M}_w/\overline{M}_n \approx 1.2$) but became broader over 80% conversion ($\overline{M}_w/\overline{M}_n$ = 1.4−1.5) probably due to the slow reaction.

These results show that **1** and **2** induce living radical polymerization of MMA in conjunction with **3** in toluene at 100 °C and, in particular, that Al(O-*i*-Pr)$_3$ is not necessary for **1** to effect the living process. Similar living polymerizations of MMA with the use of **1** were also achieved even at a lower concentration of **1** (1.0 mM) and at lower temperatures, 80 and 60 °C. Such a high activity of the indenyl complex is probably ascribed to the electron-donating indenyl ligand or to the ring slippage of the indenyl ring from η^5 to η^3.[27] The former effect results in lowering the oxidation potential of the Ru(II) species, which favors the formation of radical species from organic halides (initiators).[28] The latter "indenyl" effect was often observed in the reactions with Cp-based complexes; for example, the acceleration of CO substitution of metal carbonyls by introduction of an Ind ligand[29] and the higher activity of **1** in isomerization of allyl alcohols than that of **2**.[22] In our polymerizations, the ring slippage may change the 18-electron state of **1** into the 16-electron counterpart, which favors the interaction of the Ru(II) species with the terminal C−Cl bond via the transient formation of a 17-electron species.[30] The high activity of **1** is now under investigation by NMR and cyclic voltammetry analysis.[31]

We also employed a monofunctional initiator, dimethyl-2-chloro-2,4,4-trimethylglutarate (**4**), in conjunction with **1** in toluene at 80 °C. The initiator **4** is the authentic dimer of MMA capped with a chlorine and thus is regarded as a model compound of the dormant poly(MMA).[32] As shown in Figure 3, this initiating system also gave very narrow MWDs in the presence of Al(O-*i*-Pr)$_3$ ($\overline{M}_w/\overline{M}_n \approx 1.1$).

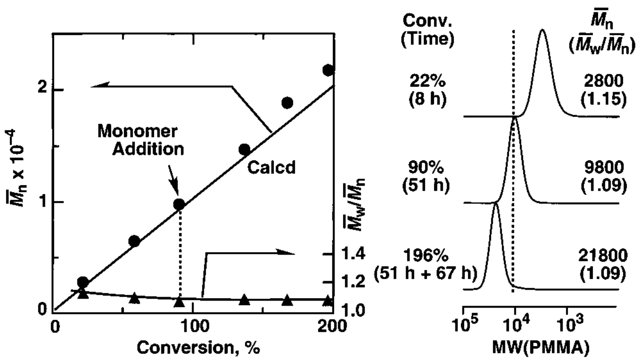

Figure 3. $\overline{M}_n$, $\overline{M}_w/\overline{M}_n$, and MWD curves of poly(MMA) obtained in a monomer-addition experiment with **4**/**1**/Al(O-*i*-Pr)$_3$ in toluene at 80 °C: $[MMA]_0 = [MMA]_{add} = 4.0$ M; $[\mathbf{4}]_0 = 40$ mM; $[\mathbf{1}]_0 = 4.0$ mM; and $[Al(O\text{-}i\text{-}Pr)_3]_0 = 40$ mM. The diagonal solid line indicates the calculated $\overline{M}_n$, assuming the formation of one living polymer per **4** molecule.

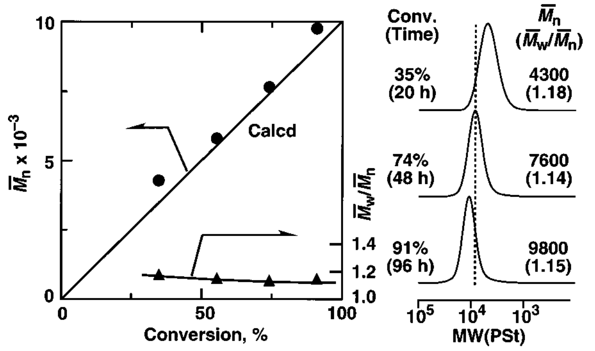

Figure 4. $\overline{M}_n$, $\overline{M}_w/\overline{M}_n$, and MWD curves of polystyrene obtained with **5**/**1**/Al(O-*i*-Pr)$_3$ in toluene at 100 °C: $[\text{styrene}]_0 = 4.0$ M; $[\mathbf{5}]_0 = 40$ mM; $[\mathbf{1}]_0 = 2.0$ mM; and $[Al(O\text{-}i\text{-}Pr)_3]_0 = 80$ mM. The diagonal solid line indicates the calculated $\overline{M}_n$, assuming the formation of one living polymer per **5** molecule.

To further examine the living nature of the polymerization with **1**, a fresh feed of monomer was added to the reaction mixtures from initiator **4** when the initial charge of the monomer has been almost consumed. The added monomer feed was smoothly polymerized, and the $\overline{M}_n$ of the polymer further increased in direct proportion to monomer conversion and agreed well with the calculated values. The MWDs stayed very narrow even after the monomer addition ($\overline{M}_w/\overline{M}_n < 1.1$). The poly(MMA) has probably the narrowest MWDs among those obtained thus far in the transition-metal-catalyzed radical polymerizations initiated with a monofunctional initiator.[33,34] These show that the indenyl complex **1** isan active and efficient catalyst in living radical polymerization of MMA.

2. Living Polymerization of Styrene. The success in living radical polymerization of MMA with **1** prompted us to employ this catalyst to styrene. Thus, styrene was polymerized with **1** coupled with a monofunctional unimer-type initiator with a bromide end [$(CH_3)_2C(CO_2C_2H_5)Br$; **5**] in the presence of Al(O-*i*-Pr)$_3$ in toluene at 100 °C. This initiator is employed in preference to the chloride analogue, because, for styrene, bromides are more suited for fine polymerization control.[35,36]

A smooth polymerization occurred without an induction phase, and the conversion reached 91% in 96 h. As shown in Figure 4, the MWDs of the obtained polystyrene was very narrow throughout the reactions ($\overline{M}_w/\overline{M}_n \sim 1.1$). The $\overline{M}_n$ increased in direct proportion to monomer conversion and agreed well with the calculated values assuming that one molecule of **5** generates one living polymer chain.[37] The system with **1** is superior to the reported $RuCl_2(PPh_3)_3$-based system that gives broader MWDs in styrene polymerization ($\overline{M}_w/\overline{M}_n \sim 1.8$).[35] To our knowledge, there have been only a few metal complex catalysts that lead to such narrow MWDs for both MMA and styrene.[33]

In conclusion, the indenyl complex $Ru(Ind)Cl(PPh_3)_2$ (**1**) led to living radical polymerization of MMA and styrene in conjunction with organic halide initiators to give very narrow MWDs ($\overline{M}_w/\overline{M}_n \approx 1.1$) and controlled molecular weights. Our current investigations for this promising catalyst are being directed to block and random copolymerizations between MMA and styrene and the possibility of stereoregulation in living radical polymerizations by manipulating Cp derivatives.[38]

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(25) The polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock or in baked and sealed glass tubes. All reagents were used after ordinary purifications, and the toluene solvent was bubbled with dry nitrogen for more than 15 min immediately before use. A typical example with **1** in conjunction with **3** is given below. Toluene (1.43 mL), *n*-octane (1.15 mL), MMA (5.48 mL), and solutions of **3** (800 mM in toluene; 0.64 mL) and Al(O-*i*-Pr)$_3$ (125 mM in toluene; 4.10 mL) were added into **1** (39.7 mg) sequentially in this order at room temperature under dry nitrogen; the total volume of the reaction mixture was thus 12.8 mL. Immediately after mixing, aliquots (1.6 mL each) of the solution were injected into baked glass tubes (1.6 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 *n*-octane as an internal standard. The quenched reaction solutions were diluted with toluene (ca. 10 mL) and rigorously shaken with an absorbent [KYOWAAD-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); Kyowa Chemical Industry Co., Ltd.] (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 give the products, which were subsequently vacuum-dried overnight.

(26) The $\overline{M}_n$, $\overline{M}_w/\overline{M}_n$, and MWD of polymers were determined by size-exclusion chromatography in chloroform with a calibration based on twelve standard samples: for poly(MMA), Polymer Laboratories, $\overline{M}_n = 630-1\,200\,000$, $\overline{M}_w/\overline{M}_n = 1.04-1.22$; for polystyrene, Pressure Chemical Co., $\overline{M}_n = 580-1\,547\,000$, $\overline{M}_w/\overline{M}_n < 1.1$. ^1H NMR spectra were recorded in $CDCl_3$ at 25 °C on a JEOL JNM-LA500 spectrometer, operating at 500.16 MHz. Polymers for ^1H NMR analysis were fractionated by preparative SEC (column: Shodex K-2002).

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(33) The sulfonyl chlorides/CuCl or CuBr/4,4′-bis(nonyl)-2,2′-bipyridine systems are reported to give narrow MWDs ($\overline{M}_w/\overline{M}_n \approx 1.1$) in both MMA and styrene polymerizations though diphenyl ether should be sometimes employed for more precise control of MWDs;[11] see also: Grimaud, T.; Matyjaszewski, K. *Macromolecules* **1997**, *30*, 2216.

(34) The $RuCl_2(PPh_3)_3$-based system gave poly(MMA) with narrow MWDs ($\overline{M}_w/\overline{M}_n = 1.09$) when coupled with an apparently bifunctional initiator, $CHCl_2COPh$.[4]

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(37) ^1H NMR analysis of the polymers showed that the ω end of the polystyrene obtained with **5**/**1** is $\sim CH_2CH(Ph)-X$ (X = Cl, Br), a mixture of the bromide originating from **5** and the chloride via halogen exchange reaction with **1** during the polymerization.[5]

(38) The poly(MMA)s obtained with **1** in toluene at 80 °C were predominantly syndiotactic (*rr*:*rm*:*mm* = 57:38:4) and thus very similar in steric structure to poly(MMA) (e.g., *rr*:*rm*:*mm* = 58:38:4) radically prepared with AIBN in toluene at 80 °C.

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