Macromolecules **2000,** *33,* 5825−5829

Catalytic Activities of Ruthenium(II) Complexes in Transition-Metal-Mediated Living Radical Polymerization: Polymerization, Model Reaction, and Cyclic Voltammetry[1]

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Received December 27, 1999

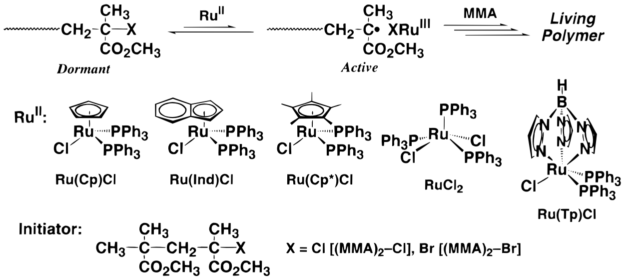
ABSTRACT: Catalytic activities of ruthenium complexes were examined in the metal-catalyzed living radical polymerization of methyl methacrylate (MMA) and in halogen exchange reactions between the dormant species and the ruthenium complex, along with cyclic voltammetry (CV). Among half-metallocene-type ruthenium(II) complexes, the activity increased in the order $Ru(Cp)Cl(PPh_3)_2$ < $Ru(Ind)Cl(PPh_3)_2$ < $Ru(Cp^*)Cl(PPh_3)_2$ ($Cp = \eta^5\text{-}C_5H_5$, $Ind = \eta^5\text{-}C_9H_7$, $Cp^* = \eta^5\text{-}C_5Me_5$); namely, the lower the redox potential of the complex (as measured by cyclic voltammetry), the faster the polymerization and the halogen exchange reaction. There were no apparent correlation, however, among the polymerization, the halogen exchange, and the redox potential for complexes of different structures such as $Ru(Cp)Cl(PPh_3)_2$, $RuCl_2(PPh_3)_3$, and $Ru(Tp)Cl(PPh_3)_2$ [Tp = hydrotris(1-pyrazolyl)borate]. Thus, the catalytic activity of the complexes for the living radical polymerization can be predicted from the halogen exchange reaction or their redox potential in some cases.

Introduction

The reactivities and selectivities in metal-catalyzed reactions can be controlled by selecting suitable metals and ligands of complex catalysts. Among such reactions are radical polymerizations of vinyl monomers, which are now precisely controllable by using various transition-metal complexes of Ru,[2−9] Cu,[10−15] Ni,[16−19] Fe,[20−23] Rh,[24−26] Pd,[27] Re[28] and Mo;[29] a series of reviews are available.[30] A key to controlling radical polymerization with metal complex catalysts lies in the reversible activation of the carbon−halogen bonds at the dormant polymer terminal to produce a growing radical (Scheme 1). During the polymerization, most of the polymer chains exist as the stable dormant species, which makes the radical concentration low enough to suppress the bimolecular termination reactions between the growing radical species.

One of the advantages of metal-catalyzed living radical polymerization is that the catalytic activity of complex catalysts may be tunable by the ligands in response to the structure of monomers and reaction conditions. The ligands reported for the living radical polymerization include halogens, phosphines, amines, pyridines, etc., but it is unclear how to choose the ligands to control their catalytic activity. In this polymerization, as illustrated in Scheme 1, the transition metal complex is likely to undergo one-electron oxidation into a higher oxidation state [e.g., Ru(II) → Ru(III)], via abstraction of the halogen from the dormant species. The metal complexes should thus meet the following criteria: (1) they should be able to receive a halogen from the dormant end; (2) they should be easily oxidized, but the oxidized form should be easily reduced to the original one. The first criterion requires that the complex should be coordinatively unsaturated by itself or should become easily unsaturated by releasing or slipping one of the ligands. The second criterion requires that the redox potential of the complex should be low enough to induce a fast redox reaction via interaction with the halogen at the dormant polymer end. Indeed, a complex of a lower redox potential has a higher catalytic activity in radical addition reactions[31] and related polymerizations.[32] However, the relationship between the activity and the redox potential of transition metal complexes is unclear.

Scheme 1. Living Radical Polymerizations with Ru(II) Complexes



This work is the first attempt to examine the activity of various ruthenium(II) complexes in living radical polymerization by electrochemical analysis as well as in metal-catalyzed halogen exchange reactions. The complexes include half-metallocene-type ruthenium complexes such as $Ru(Cp)Cl(PPh_3)_2$ ($Cp = \eta^5\text{-}C_5H_5$), $Ru(Ind)Cl(PPh_3)_2$ ($Ind = \eta^5\text{-}C_9H_7$), $Ru(Cp^*)Cl(PPh_3)_2$ ($Cp^* = \eta^5\text{-}C_5Me_5$), $RuCl_2(PPh_3)_3$, and $Ru(Tp)Cl(PPh_3)_2$ [Tp = hydrotris(1-pyrazolyl)borate]. $Ru(Ind)Cl(PPh_3)_2$ has already shown high activity in living radical polymerization;[7] the Cp* and Tp complexes may have high activities because of the electron-donating nature of the ligands. Tp is isoelectronic to Cp and forms a stable complex with transition metals.[33,34] We investigated the polymerization of MMA with these complexes (Scheme 1) and the halogen exchange reaction between the halogen-capped dormant polymer terminal and the ruthenium complexes (Scheme 2), which should occur via the radical species that is similar to or the same as the propagating radical species. The catalytic activities of the Ru(II) complexes in these reactions are discussed

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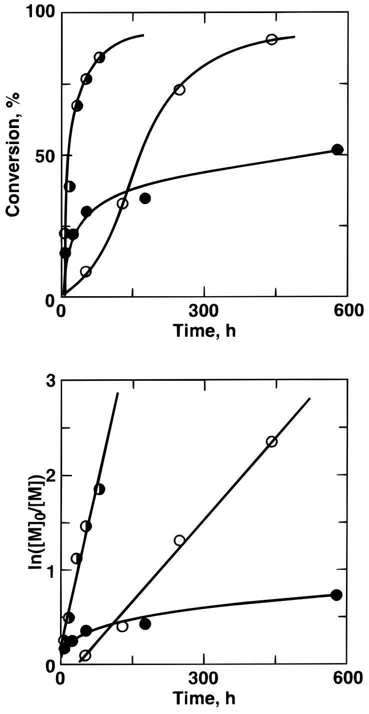
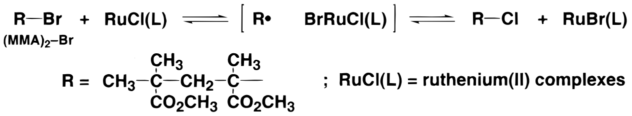


Figure 1. Polymerization of MMA with (MMA)$_2$−Cl/Ru complex in toluene at 80 °C: [MMA]$_0$ = 4.0 M; [(MMA)$_2$−Cl]$_0$ = 40 mM; [Ru complex]$_0$ = 5.0 mM. Ru complex: Ru(Cp)Cl (○); Ru(Ind)Cl (◑); Ru(Cp*)Cl (●).

Scheme 2. Halogen Exchange Reactions between Dormant-End Model [(MMA)$_2$−Br] and Ru(II) Complexes



in relation to their oxidation/reduction potential measured by cyclic voltammetry (CV). In the following text, the phosphines ligands are omitted for simplicity; e.g., Ru(Cp)Cl means Ru(Cp)Cl(PPh$_3$)$_2$.

Results and Discussion

1. Ruthenium(II) Complexes Based on Cp Ligand. (a) Polymerization. MMA was polymerized with the Cp-based ruthenium complexes in conjunction with (MMA)$_2$−Cl as an initiator in toluene at 80 °C; (MMA)$_2$−Cl refers to the chlorine-capped MMA dimer, (CH$_3$)$_2$C(CO$_2$CH$_3$)CH$_2$C(CH$_3$)(CO$_2$CH$_3$)Cl, separately synthesized and purified.[4,35] The polymerization with Ru(Cp)Cl proceeded slowly but quantitatively with some induction period (Figure 1). Note that throughout this work additives such as Al(O*i*-Pr)$_3$ were not employed.[2−4] The complex with the more electron-donating indenyl ligand, Ru(Ind)Cl, induced a faster polymerization without an induction period. With Ru(Cp*)Cl, which has the most electron-donating Cp* ligand among the three Cp-based catalysts, the polymerization proceeded rapidly in the early stage but leveled off around MMA conversion 50%. This is probably due to the fact that Ru(Cp*)Cl actively generates a high concentration of the growing radicals in the very early stage of the polymerization, resulting in termination and/or an inactive ruthenium(III) species (see below).

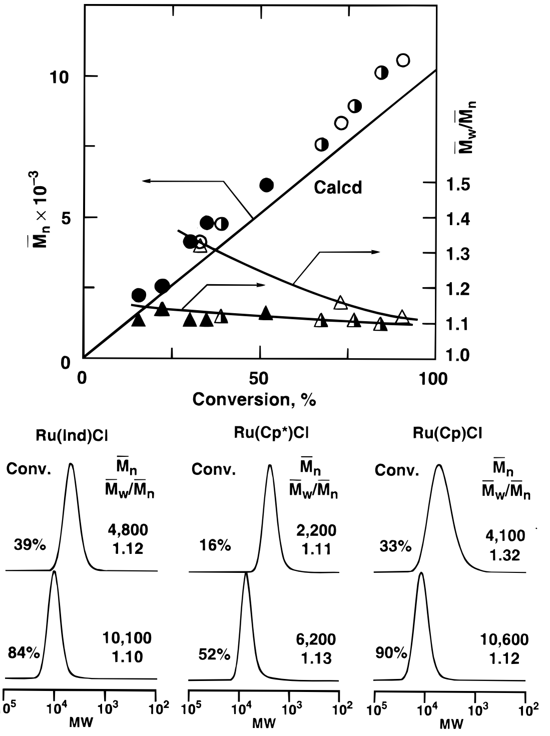


Figure 2. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(MMA) obtained with (MMA)$_2$−Cl/Ru complex in toluene at 80 °C: [MMA]$_0$ = 4.0 M; [(MMA)$_2$−Cl]$_0$ = 40 mM; [Ru complex]$_0$ = 5.0 mM. Ru complex: Ru(Cp)Cl (○, △); Ru(Ind)Cl (◑, ▲); Ru(Cp*)Cl (●, ▲).

Figure 2 shows the number-average molecular weights ($\bar{M}_n$) and molecular weight distributions (MWDs) of the polymers obtained with these complexes. The $\bar{M}_n$ was directly proportional to monomer conversion and agreed well with the calculated values assuming that one initiator produces one polymer chain. The MWD with Ru(Cp)Cl was relatively broad at low conversions ($\bar{M}_w/\bar{M}_n$ ∼ 1.3) and became narrower ($\bar{M}_w/\bar{M}_n$ ∼ 1.1) as the reaction proceeded. The more active complexes Ru(Ind)Cl and Ru(Cp*)Cl gave narrower MWDs ($\bar{M}_w/\bar{M}_n$ ∼ 1.1) even at low conversions. These results suggest that the latter two complexes, with electron-donating groups, not only generate a higher concentration of radicals (fast polymerizations) but also mediate faster interconversion between dormant and active species to lead to better controlled $\bar{M}_n$ and narrow MWDs.

(b) Halogen Exchange. The catalytic activities of the ruthenium complexes were then compared in the halogen exchange reactions illustrated in Scheme 2. Thus, model reactions were carried out with (MMA)$_2$−Br, which is a model compound of the Br-capped dormant species, and an equimolar amount of the ruthenium complexes in toluene-d_8 at 60 °C. The reactions were monitored by ^{1}H NMR,[4] as shown in Figure 3, where their extent is expressed as the ratio of the (MMA)$_2$−Cl produced to the sum of the halide-terminated species [(MMA)$_2$−Br + (MMA)$_2$−Cl].

The halogen exchange proceeded much faster than the corresponding polymerization with the same catalyst, despite the fact that the former was carried out at a lower temperature (60 vs 80 °C). The rate increased in the order Ru(Cp)Cl < Ru(Ind)Cl < Ru(Cp*)Cl. The faster halogen exchange suggests a faster interconversion between dormant and active species. This is consistent with the observations that Ru(Ind)Cl gives narrower MWDs than Ru(Cp)Cl does (Figure 2). The halogen exchange with Ru(Cp*)Cl was the fastest, where the bromine-terminated (MMA)$_2$−Br was com-

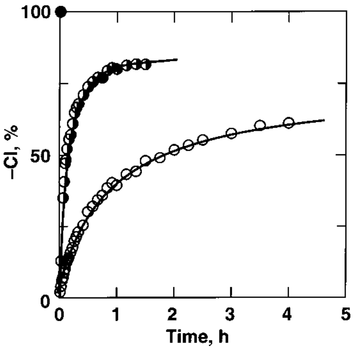


Figure 3. Halogen exchange reaction between $(MMA)_2{-}Br$ and Ru complexes in toluene-d_8 at 60 °C: $[(MMA)_2{-}Br]_0 = 5.0$ mM; $[\text{Ru complex}]_0 = 5.0$ mM. Ru complex: Ru(Cp)Cl (○); Ru(Ind)Cl (◑); Ru(Cp*)Cl (●). Cl− = $[(MMA)_2{-}Cl]/\{[(MMA)_2{-}Cl] + [(MMA)_2{-}Br]\}$ (by NMR).

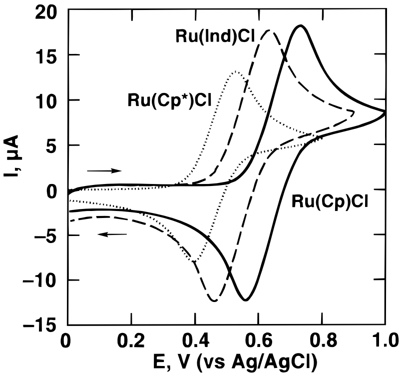


Figure 4. Cyclic voltammograms of Ru complexes in $ClCH_2CH_2Cl$ at 30 °C: $[\text{Ru complex}]_0 = 5.0$ mM; $[n\text{-}Bu_4NPF_6]_0 = 100$ mM (supporting electrolyte). Scan rate = 0.10 V s^{-1}. Ru complex: (—) Ru(Cp)Cl; (- - -) Ru(Ind)Cl; (• • •) Ru(Cp*)Cl.

pletely converted into the chlorine counterpart $(MMA)_2{-}Cl$ within 1 min. In these fast reactions, the $(MMA)_2{-}Cl$ decomposed into olefins via disproportionation. These facts are also consistent with the high rate and the termination in the polymerization with the same catalyst (see Figure 1). On the other hand, olefinic byproducts were absent in the halogen exchange with Ru(Cp)Cl or Ru(Ind)Cl, which means that the radical concentration is very low.

(c) Cyclic Voltammetry. The ruthenium complex probably undergoes one-electron redox reaction between Ru(II) and Ru(III) in the activation/deactivation process illustrated in Scheme 1. The lower redox potential of the complex should increase the interconversion. We thus measured the redox potentials of the complexes by CV. The measurement was carried out in 1,2-dichloroethane at 30 °C with $n\text{-}Bu_4NPF_6$ as a supporting electrolyte. All complexes showed waves corresponding to the Ru(II) $\rightleftarrows$ Ru(III) interconversion, which were highly reproducible as quasi-reversible in each of several scans (Figure 4). The redox potential decreased in the order Ru(Cp)Cl > Ru(Ind)Cl > Ru(Cp*)Cl [Ru(Cp)Cl: $E_{pa} = 0.73$ V, $E_{pc} = 0.56$ V, $E_{1/2} = 0.65$ V. Ru(Ind)Cl: $E_{pa} = 0.63$ V, $E_{pc} = 0.46$ V, $E_{1/2} = 0.55$ V. Ru(Cp*)Cl: $E_{pa} = 0.53$ V, $E_{pc} = 0.40$ V, $E_{1/2} = 0.46$ V]. The order agrees with the rate of halogen exchange. Therefore, the complex with a lower redox potential induces a faster polymerization and a faster interconversion between dormant and active radical species, at least for the series of the three Cp-based half-metallocene Ru(II) complexes.

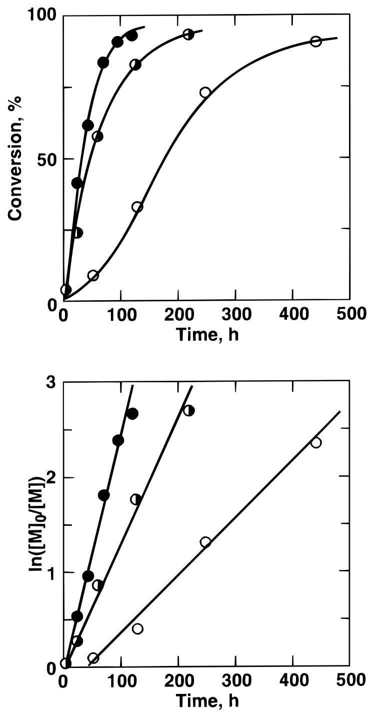


Figure 5. Polymerization of MMA with $(MMA)_2{-}Cl$/Ru complex in toluene at 80 °C: $[MMA]_0 = 4.0$ M; $[(MMA)_2{-}Cl]_0 = 40$ mM; $[\text{Ru complex}]_0 = 5.0$ mM. Ru complex: Ru(Cp)Cl (○); $RuCl_2$ (◑); Ru(Tp)Cl (●).

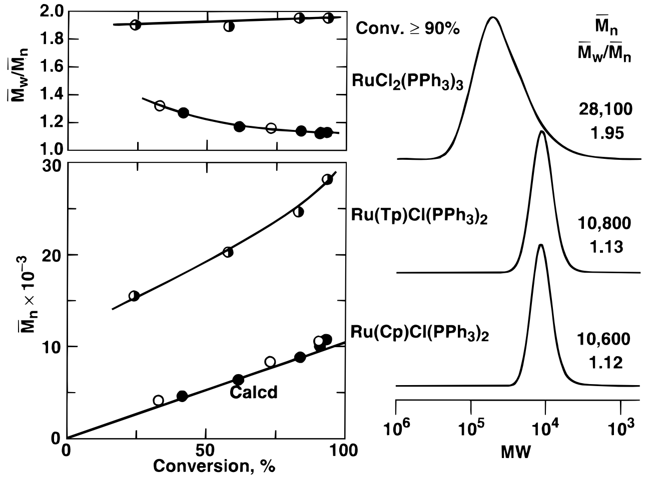


Figure 6. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(MMA) obtained with $(MMA)_2{-}Cl$/Ru complex in toluene at 80 °C: $[MMA]_0 = 4.0$ M; $[(MMA)_2{-}Cl]_0 = 40$ mM; $[\text{Ru complex}]_0 = 5.0$ mM. Ru complex: Ru(Cp)Cl (○, △); $RuCl_2$ (◑, ▲); Ru(Tp)Cl (●, ▲).

2. Other Ruthenium(II) Complexes. We then examined the polymerization, the halogen exchange reaction, and the redox potential of other ruthenium complexes [$RuCl_2$ and Ru(Tp)Cl] relative to Ru(Cp)Cl.

(a) Polymerization. Polymerizations were carried out with $(MMA)_2{-}Cl$ as an initiator. Both $RuCl_2$ and Ru(Tp)Cl led to faster polymerizations than Ru(Cp)Cl did (Figure 5). The polymerization rate increased in the order Ru(Cp)Cl < $RuCl_2$ < Ru(Tp)Cl.

$\bar{M}_n$ and MWD curves of the polymers obtained with $RuCl_2$ and Ru(Tp)Cl are shown in Figure 6. In all cases, $\bar{M}_n$ increased with monomer conversion. Especially, Ru(Tp)Cl gave polymers whose $\bar{M}_n$ agreed well with the calculated values. The MWDs became narrower with conversion, as observed for Ru(Cp)Cl. Thus, the Tp complex also induced living radical polymerization of MMA, where the reaction was faster than that with the

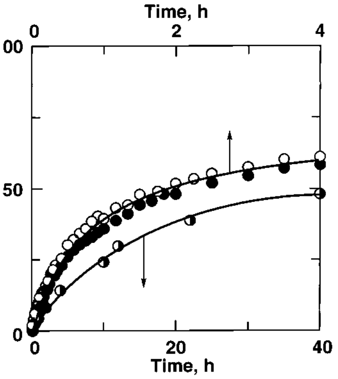


Figure 7. Contents of $(MMA)_2{-}Cl$ in the halogen exchange reaction between $(MMA)_2{-}Br$ and Ru complexes in toluene-d_8 at 60 °C: $[(MMA)_2{-}Br]_0 = 5.0$ mM; $[\text{Ru complex}]_0 = 5.0$ mM. Ru complex: Ru(Cp)Cl (○), $RuCl_2$ (◑), Ru(Tp)Cl (●). $Cl- = [(MMA)_2{-}Cl]/\{[(MMA)_2{-}Cl] + [(MMA)_2{-}Br]\}$ (by NMR).

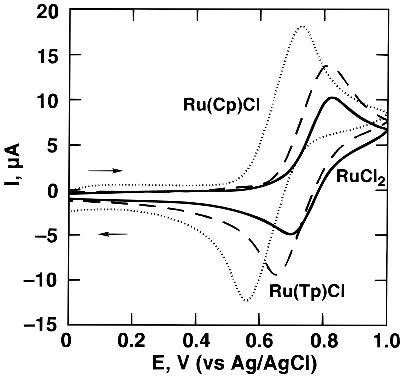


Figure 8. Cyclic voltammograms of Ru complexes in $ClCH_2CH_2Cl$ at 30 °C: $[\text{Ru complex}]_0 = 5.0$ mM; $[n\text{-}Bu_4NPF_6]_0 = 100$ mM (supporting electrolyte). Scan rate = 0.10 V s^{-1}. Ru complex: (—) Ru(Cp)Cl; (- - -) $RuCl_2$; (· · ·) Ru(Tp)Cl.

Cp complex. The $\bar{M}_n$ of the polymers obtained with $RuCl_2$ were higher than the calculated values, and the MWDs were broader. This is due to the absence of additives, as already reported.[3,4,34]

(b) Halogen Exchange. The rate of halogen exchange with Ru(Tp)Cl was almost the same as that with Ru(Cp)Cl (Figure 7). However, the exchange reaction with $RuCl_2$ was more than 10 times slower than that with the Cp and Tp complexes, although it has twice as much chlorine. The slow exchange suggests the slow interconversion between the dormant and the active species in the polymerization with $RuCl_2$, which results in broader MWDs.

(c) Cyclic Voltammetry. CV analyses of $RuCl_2$ and Ru(Tp)Cl were also carried out for comparison of the redox potentials and the catalytic activities. The quasi-reversible voltammograms are shown in Figure 8. The redox potential decreased in the order $RuCl_2 \sim$ Ru(Tp)-Cl > Ru(Cp)Cl [$RuCl_2$: $E_{pa} = 0.83$ V, $E_{pc} = 0.71$ V, $E_{1/2} = 0.77$ V. Ru(Tp)Cl: $E_{pa} = 0.81$ V, $E_{pc} = 0.65$ V, $E_{1/2} = 0.73$ V], which does not agree with the order of the halogen exchange reaction [Ru(Cp)Cl $\sim$ Ru(Tp)Cl $\gg$ $RuCl_2$]. This suggests that the activity of the complexes cannot be simply predicted from the CV when the complexes are not analogous in structure. Even between electronically equivalent Tp and Cp, there is no correlation in activity and redox potential. This may be due to the difference in the number of coordinating atoms (three nitrogens for the former and five carbons for the latter).

In conclusion, the catalytic activity correlated to the halogen exchange rate and the redox potential among the half-metallocene-type ruthenium(II) complexes: the lower the redox potential of the complex, the higher the catalytic activity. However, the activity of the complex cannot be simply correlated to the redox potential among complexes whose structures are somewhat dissimilar.

Experimental Section

Materials. MMA (Tokyo Kasei, >99%) was dried overnight over calcium chloride and distilled twice over calcium hydride under reduced pressure before use. $Ru(Cp)Cl(PPh_3)_2$ (STREM, 99%), $Ru(Ind)Cl(PPh_3)_2$ (STREM, >98%), and $RuCl_2(PPh_3)_3$ (Merck, >99%) were used as received and handled in a glovebox under a moisture- and oxygen-free argon atmosphere (H_2O, <1 ppm; O_2, <1 ppm). Toluene (solvent, Wako; guaranteed reagents) and *n*-octane (internal standard for gas chromatography, Nacalai Tesque; 98%) were dried overnight over calcium chloride, distilled twice over calcium hydride, and bubbled with dry nitrogen for more than 15 min immediately before use. $n\text{-}Bu_4NPF_6$ (Tokyo Kasei, >99%) was dried under reduced pressure at 100 °C. 1,2-Dichloroethane (Wako, >99%) was distilled over P_2O_5 and bubbled with dry argon for more than 30 min. Initiators $(MMA)_2{-}Cl$ and $(MMA)_2{-}Br$ were prepared according to the literature.[4,35]

Preparation of Ru Complexes. $Ru(Cp^*)Cl(PPh_3)_2$ (**3**) was synthesized from $[Ru(Cp^*)Cl_2]_n$[36] and PPh_3 according to the literature.[37] Yield = 1.80 g (83%). ^1H NMR (CD_2Cl_2): δ 7.7−6.6 (br, 30 H, Ph), 0.99 (s, 15 H, CH_3). Anal. Calcd for $C_{46}H_{45}ClP_2Ru$: C, 69.38; H, 5.70; Cl, 4.45. Found: C, 69.31; H, 5.77; Cl, 4.39. $Ru(Tp)Cl(PPh_3)_2$ (**5**) was also prepared according to the literature.[38] Anal. Calcd for $C_{45}H_{40}BClN_6P_2Ru$: C, 61.83; H, 4.61; Cl, 4.06. Found: C, 61.53; H, 4.86; Cl, 4.17.

Polymerization Procedures. The polymerization was carried out under dry nitrogen in baked and sealed glass tubes.[7] A typical example with $Ru(Cp)Cl(PPh_3)_2$ is given below. In a 50 mL round-bottomed flask was placed $Ru(Cp)Cl(PPh_3)_2$ (34.9 mg, 0.0480 mmol), and toluene (4.64 mL), *n*-octane (0.386 mL), MMA (4.11 mL, 38.4 mmol), and solutions of $(MMA)_2{-}Cl$ (0.463 mL of 830 mM in toluene, 0.384 mmol) were added sequentially in this order at room temperature under dry nitrogen. The total volume of the reaction mixture was thus 9.60 mL. Immediately after mixing, aliquots (1.20 mL each) of the solution were injected into baked glass tubes, 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. 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 give the products, which were subsequently vacuum-dried overnight. Polymer yield was lower than that expected from conversion because of partial loss of poly(MMA) during the workup.

Polymer Characterization. The $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD of the polymers were determined by size-exclusion chromatography in chloroform at 40 °C on the three polystyrene gel columns [Shodex K-805L (pore size: $10-10^5$ μm; 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 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.

^1H NMR Spectroscopy in Model Reactions. A typical example of halogen exchange reaction with Ru(Cp)Cl is given below. Solutions of Ru(Cp)Cl (0.75 mL of 6.67 mM, 0.0050 mmol) and $(MMA)_2{-}Cl$ (0.25 mL of 20 mM, 0.0050 mmol) in toluene-d_8 were mixed in a sample vial under moisture- and oxygen-free argon atmosphere at room temperature. The mixture was sealed in an NMR tube and then heated to 60 °C in the NMR prove. ^{1}H NMR spectra were recorded on a JEOL JNM-LA500 spectrometer in toluene-d_8 at 60 °C, operating at 500.16 MHz. The main parameters were as follows: spectral width = 10 000 Hz (19.99 ppm), pulse width = 6.20 μs (45°), acquisition time + pulse delay = 12.0 s, data points = 32 768, number of transients = 4 (1.0 min for one spectrum). The probe temperature was regulated with a variable temperature apparatus (temperature fluctuation $\leq$0.1 deg). The spectra were obtained in predetermined intervals, and the halogen-exchange ratios were determined from the peak intensity ratios of the signal of the bromine compound and that of the produced chlorine compounds.

Electrochemical Experiments. Cyclic voltammograms were recorded on a Hokuto Denko HZ-3000 apparatus. Measurements were carried out under argon at 0.10 V s^{-1} in a $ClCH_2CH_2Cl$ solution (5.0 mM) containing n-Bu_4NPF_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.

Acknowledgment. With appreciation M.S. and M.K. acknowledge the support from the New Energy and Industrial Technology Development Organization (NEDO) under the Ministry of International Trade and Industry (MITI), Japan, through the grant for “Precision Catalytic Polymerization” in the Project “Technology for Novel High-Functional Material” (1996−2000). T.A. is grateful to the Japan Society for the Promotion of Sciences for the Young Scientists Fellowship and the partial support of this work by the Grant-in-Aid for Scientific Research (No. 9552) from the Ministry of Education, Science, Culture, and Sports, Japan.

References and Notes

(1) This work was presented in part at the following meetings: (a) The 48th Annual Meeting of the Society of Polymer Science, Kyoto, Japan, May 1999; paper IPd034: Ando, T.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1999**, *48* (2), 137. (b) The 48th Symposium on Macromolecules, the Society of Polymer Science, Niigata, Japan, Oct 1999; paper IIIB07: Ando, T.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1999**, *48* (8), 1726.

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MA9921596