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$RuH_2(PPh_3)_4$: An Active Catalyst for Living Radical Polymerization of Methyl Methacrylate at or above Room Temperature[1]

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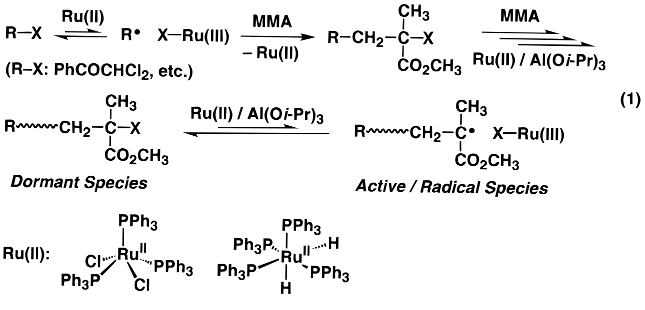
ABSTRACT: Dihydridotetrakis(triphenylphosphine)ruthenium(II) [$RuH_2(PPh_3)_4$] induced a fast living radical polymerization of methyl methacrylate (MMA) in conjunction with an organic chloride initiator [R−Cl: $CHCl_2COPh$] in toluene at 30−80 °C. Added aluminum compounds such as Al(O-*i*-Pr)$_3$ were not needed for the Ru(II)−hydride system unlike the reported $RuCl_2(PPh_3)_3$-based counterpart. The number-average molecular weights of polymers increased in direct proportion to monomer conversion, and the molecular weight distributions were narrow ($\bar{M}_w/\bar{M}_n < 1.2$) even at 30 °C. The polymers possessed one initiator moiety (COPh) at the α-end per one polymer chain. The stereochemistry of the polymers was consistent with that for conventional free radical polymerization in that the fraction of syndiotactic arrangements increases as the reaction temperature is lowered (58% and 67% *rr* triads at 80 and 30 °C, respectively).

Introduction

One of the recent progresses in radical polymerizations is the discovery of transition metal-mediated living processes that precisely control polymer molecular weights and molecular weight distributions (MWDs) for methacrylates, acrylates, styrenes, etc.[2] We first reported that $RuCl_2(PPh_3)_3$ induces living radical polymerization of methyl methacrylate (MMA) in conjunction with organic halides (initiators: CCl_4, $CHCl_2COPh$, etc.) in the presence of aluminum alkoxides such as Al(O-*i*-Pr)$_3$.[3,4] Since then, systems based on other transition metals such as Cu,[5−9] Fe,[10,11] Ni,[12−15] Rh,[16−18] Pd,[19] and Re[20] have been found to be effective in similar living polymerizations where the terminal carbon−halogen bonds originated from the initiators are reversibly and homolytically cleaved by the metal complexes to give radical species (eq 1). In these living processes, the equilibrium between the dormant and the active or radical species, such as $\sim\sim\sim C{-}X + Ru(II) \rightleftarrows \sim\sim\sim C^{\bullet}$ X−Ru(III) shown in eq 1, is shifted to the dormant side, and thereby the concentration of the radical species is most probably kept so low as to diminish bimolecular radical termination and other side reactions. This dynamic equilibrium affects the controllability and the rate of the polymerizations and in turn depends on the nature and activity of metal catalysts and their ligands, which can modify them.



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Ruthenium chemistry has recently progressed to give a great variety of complexes for novel efficient catalytic and stoichiometric reactions.[21] It has also been understood that, particularly for ruthenium complexes, the precise complex design with ligands is especially important for desired reactions to occur. Although our $RuCl_2(PPh_3)_3$-based initiating system is indeed effective in MMA living radical polymerization, it generally requires a long reaction time (sometimes a few days, for completion) and often needs added metal alkoxides such as Al(O-*i*-Pr)$_3$ for acceleration of the reaction.[4,22]

In this work, we employed a halogen-free Ru(II) hydride complex, $RuH_2(PPh_3)_4$, as a catalyst in place of $RuCl_2(PPh_3)_3$ for the living radical polymerization of MMA. The hydride complex has been reported to be more active than $RuCl_2(PPh_3)_3$ in Kharasch addition reactions between CCl_4 and 1-octene,[23] although the finding is still in controversy.[24] Nevertheless, there have thus far been no reports on living radical polymerizations with not only $RuH_2(PPh_3)_4$ but also other metal hydrides. This paper is to show that the ruthenium(II) hydride induces living radical polymerization of MMA with a chloride initiator ($CHCl_2COPh$), much faster than that with $RuCl_2(PPh_3)_3$ and operative even at 30 °C or in the absence of Al(O-*i*-Pr)$_3$ and related aluminum additives.

Results and Discussion

(a) $RuH_2(PPh_3)_4$ vs $RuCl_2(PPh_3)_3$. The ruthenium hydride was employed for the polymerization of MMA with $CHCl_2COPh$ as an initiator in toluene at 60 °C. As shown in Figure 1, the Ru(II)−hydride system induced a smooth polymerization without an induction phase even in the absence of additives, and conversion reached 48% in 4 h and 90% in 54 h. The polymerization was thus much faster than that with $RuCl_2(PPh_3)_3$ where conversion reached 77% in 461 h.[4] Similar to the Ru(II)−chloride system, the addition of Al(O-*i*-Pr)$_3$ accelerated the polymerization, whereas the effect was not so outstanding in the early stage.

The MWDs of the polymers obtained with $RuH_2(PPh_3)_4$ were narrow, with or without the aluminum additive ($\bar{M}_w/\bar{M}_n < 1.2$) (Figure 2). On the other hand, with $RuCl_2(PPh_3)_3$, the effects of Al(O-*i*-Pr)$_3$ were obvi-

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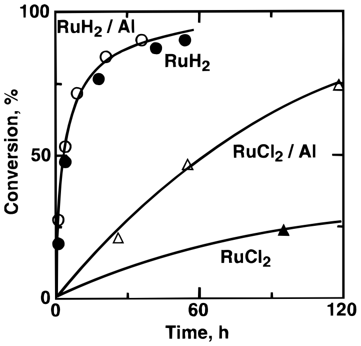

Figure 1. Polymerization of MMA with $CHCl_2COPh/Ru-X_2(PPh_3)_n$ in the presence or absence of $Al(O\text{-}i\text{-}Pr)_3$ in toluene at 60 °C: $[M]_0 = 2.0$ M; $[CHCl_2COPh]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = [RuH_2(PPh_3)_4]_0 = 10$ mM; $[Al(O\text{-}i\text{-}Pr)_3]_0 = 40$ mM. Catalyst systems: (●) $RuH_2(PPh_3)_4$; (○) $RuH_2(PPh_3)_4/Al(O\text{-}i\text{-}Pr)_3$; (▲) $RuCl_2(PPh_3)_3$; (△) $RuCl_2(PPh_3)_3/Al(O\text{-}i\text{-}Pr)_3$.

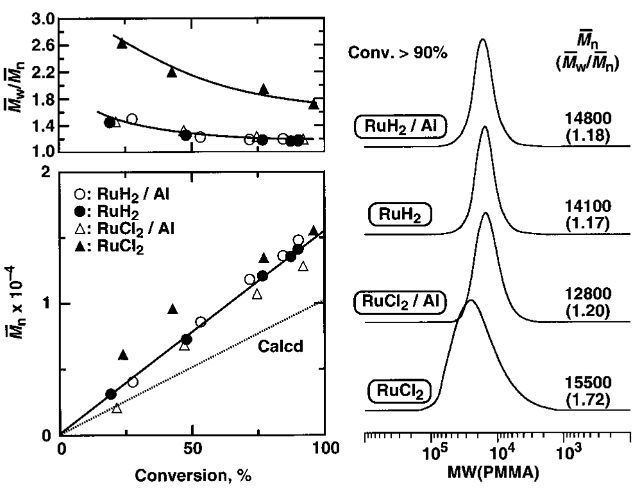

Figure 2. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(MMA) obtained with $CHCl_2COPh/RuX_2(PPh_3)_n$ in the absence or presence of $Al(O\text{-}i\text{-}Pr)_3$ in toluene at 60 °C: $[M]_0 = 2.0$ M; $[CHCl_2COPh]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = [RuH_2(PPh_3)_4]_0 = 10$ mM; $[Al(O\text{-}i\text{-}Pr)_3]_0 = 40$ mM. Catalyst systems: (●) $RuH_2(PPh_3)_4$; (○) $RuH_2(PPh_3)_4/Al(O\text{-}i\text{-}Pr)_3$; (▲) $RuCl_2(PPh_3)_3$; (△) $RuCl_2(PPh_3)_3/Al(O\text{-}i\text{-}Pr)_3$.

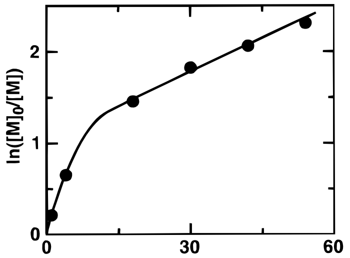

Figure 3. Logarithmic conversion data for polymerization of MMA with $CHCl_2COPh/RuH_2(PPh_3)_4$ in toluene at 60 °C: $[M]_0 = 2.0$ M; $[CHCl_2COPh]_0 = 20$ mM; $[RuH_2(PPh_3)_4]_0 = 10$ mM.

ous; the MWDs in its absence were broad ($\bar{M}_w/\bar{M}_n \geq 1.7$).[22] The number-average molecular weights ($\bar{M}_n$) increased in direct proportion to monomer conversion, though higher than the calculated values assuming that one molecule of $CHCl_2COPh$ generates one living polymer chain. Thus, the $RuH_2(PPh_3)_4$-based system led to a fast and living polymerization of MMA without added aluminum compounds.

Figure 3 shows the logarithmic conversion data, $\ln([M]_0/[M])$ ([M] is the monomer concentration at time

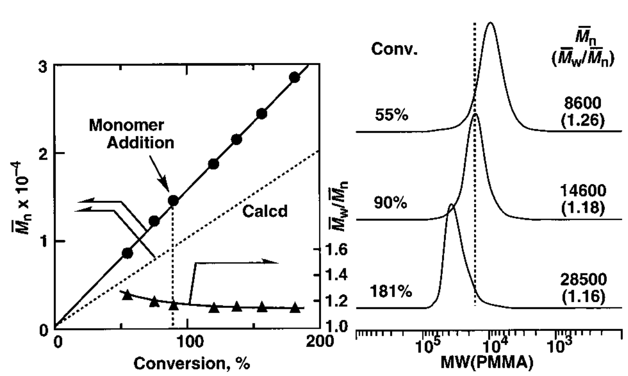

Figure 4. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(MMA) obtained in monomer-addition experiments with $CHCl_2COPh/RuH_2(PPh_3)_4$ in toluene at 60 °C: $[M]_0 = [M]_{add} = 2.0$ M; $[CHCl_2COPh]_0 = 20$ mM; $[RuH_2(PPh_3)_4]_0 = 10$ mM.

t), plotted against *t* in the polymerization with $RuH_2(PPh_3)_4$ in the absence of $Al(O\text{-}i\text{-}Pr)_3$. The straight line changes its slope around 15 h (conversion ~ 70%), beyond which point the reaction decelerates. This suggests a decrease in catalytic activity of the complex or a partial loss of living ends. The latter possibility can be excluded, as will be confirmed herein, by the living nature of the polymerization in monomer-addition experiments. The former possibility is supported by the color change of the reaction mixtures, which suggests some change in the complex with time. For example, the $RuH_2(PPh_3)_4$ solution in toluene was dark greenish yellow, which turned reddish purple on mixing with a solution containing MMA and $CHCl_2COPh$. Furthermore, the reaction mixture gradually turned dark orange with time or conversion. These color changes indicate that $RuH_2(PPh_3)_4$ reacts with the monomer or the initiator to form another complex that further changes with time. The reaction between MMA and $RuH_2(PPh_3)_4$ has already been reported where the mixture affords $Ru^{II}H[CH{=}C(CH_3)CO_2CH_3](PPh_3)_3$.[25] The complex can also react with $CHCl_2COPh$,[26] similarly to the reaction with Ph_2CO, to give an orthometalated arenyl Ru(II) hydride complex. Alternatively, $RuH_2(PPh_3)_4$ can be reduced into an Ru(0) complex.[21] The higher activity of $RuH_2(PPh_3)_4$ is anticipated from that hydrogen is less electron withdrawing than chlorine, but the real catalyst of the polymerization is unknown yet.

(b) Living Polymerization of MMA. To investigate the living nature of the polymerization with $CHCl_2COPh/RuH_2(PPh_3)_4$ without $Al(O\text{-}i\text{-}Pr)_3$, a fresh feed of MMA was added to the reaction mixture in toluene at 60 °C when most of the initial charge of MMA was consumed (>90% in 48 h). Although the second-phase polymerization was not as fast (cf. Figure 3), it also induced a quantitative polymerization where 91% of the additional feed was consumed in an additional 460 h. As shown in Figure 4, the $\bar{M}_n$ of the resulting polymers further increased in direct proportion to conversion, and the MWDs were narrow even after the monomer addition. Thus, the Ru(II)−hydride initiating system induces living polymerization of MMA without any additives, similarly to $Ru(Ind)Cl(PPh_3)_2$[27] and $RuCl_2(p\text{-cymene})(PCy_3)$,[28] as reported quite recently.

(c) Quenching Study. For mechanistic understanding, a radical scavenger (galvinoxyl or TEMPO) or an anion scavenger (methanol or water) (10 equiv to $CHCl_2COPh$) was added to the polymerization mixtures at ca. 50% conversion (Figure 5). Upon addition of galvinoxyl

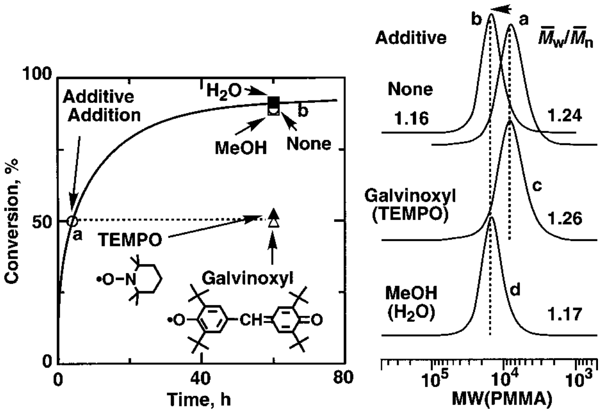

Figure 5. Effects of various additives (△, galvinoxyl; ▲, TEMPO; □, MeOH; ■, H_2O) on the living polymerization of MMA with $CHCl_2COPh/RuH_2(PPh_3)_4$ in toluene at 60 °C: $[M]_0 = 2.0$ M; $[CHCl_2COPh]_0 = 20$ mM; $[RuH_2(PPh_3)_4]_0 = 10$ mM; $[\text{additive}]_{add} = 200$ mM. The size-exclusion chromatograms are for the product polymers obtained without additive (a and b) and after the addition of galvinoxyl (TEMPO) (c) and MeOH (H_2O) (d). Sample identification (a–d) corresponds to the data points in the time–conversion profile on the left.

or TEMPO, the polymerizations clearly ceased (no MMA consumption over 50 h), while the system with added methanol or water reached nearly quantitative conversion. Polymer molecular weight was unchanged after the addition of radical scavengers, whereas those with anion quenchers increased in direct proportion to monomer conversion while keeping narrow MWDs, similarly to those without quenching.

Thus, the $RuH_2(PPh_3)_4$-mediated living polymerization can be completely terminated by radical scavengers but not by protonic scavengers, and therefore proceeds via not an ionic but a radical mechanism, as do those with $RuCl_2(PPh_3)_3$.[29] More than 20 years ago, Komiya et al. proposed a coordination mechanism for a polymerization of MMA with $RuH_2(PPh_3)_4$ but without halide initiators.[30] In contrast, our polymerization with the hydride most probably proceeds via a radical mechanism where the terminal C–Cl bond is homolytically cleaved by the Ru(II) complex, as supported by the ^1H NMR analysis of the products (see below).

(d) Effects of Temperature. The fast living polymerization with $RuH_2(PPh_3)_4$ prompted us to use the complex at varying temperatures, especially at an ambient temperature in the absence of $Al(O\text{-}i\text{-}Pr)_3$. Polymerizations indeed occurred even at 30 °C to consume 95% of MMA in 300 h (Figure 6). Such highly active catalysts based on Cu(I) complexes have already been reported,[31,32] but none with ruthenium counterparts. The polymerization at 80 °C seemed to stop around 80% probably due to the thermal instability of the complex. In all cases, the resulting polymers had unimodal and narrow MWDs ($\bar{M}_w/\bar{M}_n \sim 1.2$), where the molecular weights increased with conversion.

Similar living polymerizations were also possible in the presence of $Al(O\text{-}i\text{-}Pr)_3$ at 30–80 °C. These results show that $RuH_2(PPh_3)_4$ induced living polymerization of MMA even around room temperature irrespective of the existence of $Al(O\text{-}i\text{-}Pr)_3$, and the ruthenium hydride is thus the most active among the reported ruthenium catalysts for living radical polymerizations.[2–4,27,28]

(e) End Group and Steric Structures. The living polymers of narrow MWDs obtained with the $CHCl_2COPh/RuH_2(PPh_3)_4$ system were then analyzed by ^1H NMR spectroscopy (Figure 7). In addition to the large absorptions of the main-chain poly(MMA) units (d, e, and f), there appeared the characteristic signals of the initiator moiety; e.g., peaks a–c attributed to the aromatic protons of the phenyl ketone group at the α-end. In addition, the small signals e′ (near e) and f′ (near f) were attributed to the methylene and the ester methyl protons, respectively, adjacent to the chlorine atom at the ω-end. The number-average degrees of polymerization (DP_n) obtained from the peak intensity ratios, (f + f′)/a and (f + f′)/e′, were 123 [DP_n(NMR, α-end)] and 135 [DP_n(NMR, ω-end)], respectively, on the assumption that $CHCl_2COPh$ acts as a bifunctional initiator.[33] These were in close agreement with that by size exclusion chromatography [DP_n(SEC) = 144] calibrated against standard poly(MMA) samples (see Experimental Section). The number-average end functionality ($\bar{F}_n$) of the α-end and ω-end, obtained as DP_n(SEC)/DP_n(NMR), were 1.17 and 1.07, respectively. Thus, the living polymerization proceeded via the activation of the C–Cl bond originated from $CHCl_2COPh$ by $RuH_2(PPh_3)_4$ and not via insertion into a possibly formed C–Ru bond. A set of small peaks g appeared around 5–6 ppm, which were attributed to the exo-methylene protons of the ω-terminal generated via disproportionation between polymer terminals. The content of the olefinic terminal, however, was only 5%, and most of the ω-end proved to be the chloride. The unsaturated terminal most probably forms during the very early stage of the polymerization, as suggested by the fast reaction in the early stage and the absence of dead polymers after the monomer addition (see above). The MALDI–TOF–MS analysis also shows that such unsaturated polymer

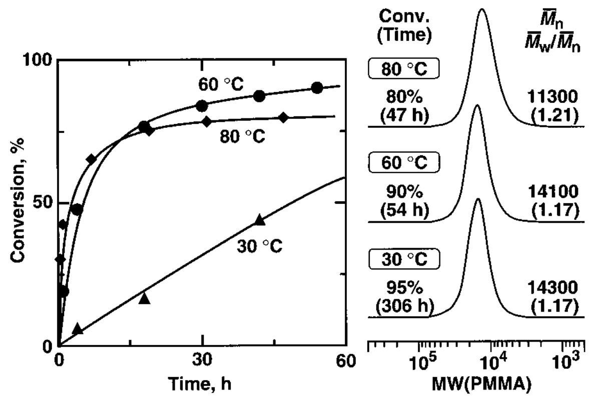

Figure 6. Effects of temperature on polymerization of MMA with $CHCl_2COPh/RuH_2(PPh_3)_4$ in toluene: $[M]_0 = 2.0$ M; $[CHCl_2COPh]_0 = 20$ mM; $[RuH_2(PPh_3)_4]_0 = 10$ mM. Key: (◆) 80 °C; (●) 60 °C; (▲) 30 °C.

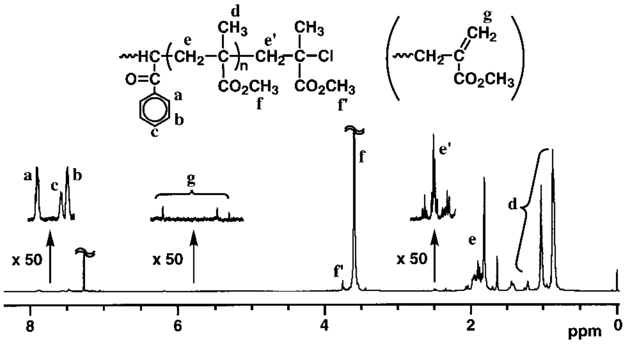

Figure 7. ^1H NMR spectrum of poly(MMA) obtained with $CHCl_2COPh/RuH_2(PPh_3)_4$ in toluene at 60 °C. DP_n(NMR, α-end) = 123; DP_n(NMR, ω-end) = 135; DP_n(SEC) = 144; $\bar{M}_w/\bar{M}_n$ (SEC) = 1.16.

Table 1. Tacticity[a] of PMMA by Ru(II) Catalysts[b]

initiating system	temp (°C)	*rr*	*mr*	*mm*
AIBN	80	58	38	4
$RuCl_2(PPh_3)_3/Al(O\text{-}i\text{-}Pr)_3$	80	56	39	5
$RuH_2(PPh_3)_4/Al(O\text{-}i\text{-}Pr)_3$	80	58	37	5
$RuCl_2(PPh_3)_4$	80	59	37	4
$RuCl_2(PPh_3)_4/Al(O\text{-}i\text{-}Pr)_3$	60	64	35	1
$RuCl_2(PPh_3)_4$	60	62	35	3
$RuCl_2(PPh_3)_4/Al(O\text{-}i\text{-}Pr)_3$	30	67	31	2

[a] Determined by ^{13}C NMR from the C═O absorptions. [b] Polymerizations were carried out in toluene. $CHCl_2COPh$ was employed as the initiator except for the run with AIBN; $[MMA]_0/[CHCl_2COPh]_0/[Ru(II)]_0/[Al(O\text{-}i\text{-}Pr)_3]_0 = 2000/20/10/40$ mM.

terminal is attributed to small amounts of the low molecular weight polymers that still remain in the later stage of the polymerization.[34]

^{13}C NMR analyses showed that the obtained polymers were more or less syndiotactic, similar to samples prepared with AIBN and with $RuCl_2(PPh_3)_3$ (Table 1). There were almost no effects of $Al(O\text{-}i\text{-}Pr)_3$ on their tacticity. Lowering the temperature increased the racemic (*rr*) content, which would be expected for a free-radical polymerization. These also support the radical propagation mechanism with the hydride.

In conclusion, $RuH_2(PPh_3)_4$ coupled with $CHCl_2COPh$ induced fast living radical polymerization of MMA without any other additives. The living polymerization is also feasible at a temperature as low as 30 °C. Similar to that with $RuCl_2(PPh_3)_3$, the polymerization seems to proceed via the homolytic and reversible activation of carbon−halogen bonds at the polymer terminal by the redox reaction of the ruthenium center. This study has thus widened the scope of the transition metal-catalyzed living radical polymerizations in terms of active catalysts usable even around room temperature.

Experimental Section

Materials. MMA (Tokyo Kasei; purity >99%) was dried overnight over calcium chloride and distilled twice over calcium hydride under reduced pressure before use. $RuH_2(PPh_3)_4$ (Aldrich; purity >95%), $RuCl_2(PPh_3)_3$ (Merck; purity >99%), and $Al(O\text{-}i\text{-}Pr)_3$ (Aldrich; purity >99.99%) 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). $CHCl_2COPh$ (Wako Chemicals; purity >99%) was doubly distilled over calcium hydride under reduced pressure before use. Toluene (solvent) and *n*-octane (internal standard for gas chromatography) were dried overnight over calcium chloride, distilled twice over calcium hydride, and bubbled with dry nitrogen for more than 15 min immediately before use.

Polymerization Procedures. Polymerization was carried out by the syringe technique under dry nitrogen in baked glass tubes equipped with a three-way stopcock or in baked and sealed glass vials. In a 50 mL round-bottomed flask was placed $RuH_2(PPh_3)_4$ (184 mg), and toluene (11.54 mL), *n*-octane (0.72 mL), MMA (3.42 mL), and solutions of $CHCl_2COPh$ (1.0 M in toluene; 0.32 mL) were added sequentially in this order at room temperature under dry nitrogen. The total volume of the reaction mixture was thus 16.0 mL. Immediately after mixing, aliquots (2.0 mL each) of the solution were injected into baked glass tubes, which were then sealed (except when a stopcock was used) 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 dried overnight under vacuum at room temperature.

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 40 °C on three polystyrene gel columns (Shodex K-805L × 3) 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; $\bar{M}_n = 630-220\,000$; $\bar{M}_w/\bar{M}_n = 1.06-1.22$) as well as the monomer. ^{1}H NMR spectra were recorded in $CDCl_3$ at 25 or 55 °C on a JEOL JNM-LA500 spectrometer, operating at 500.16 MHz for ^{1}H or at 125.78 MHz for ^{13}C, respectively. Polymers for NMR analysis were carefully fractionated by preparative SEC (column: Shodex K-2002) to be free from catalyst residues without loss of MMA oligomers if present.

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(1) This work was presented in part at the following meetings: (a) The 46th Symposium on Macromolecules, the Society of Polymer Science, Nagoya, Japan, October 1997; paper 1B18: Takahashi, H.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1997**, *46* (8), 1504. (b) The 47th Annual Meeting of the Society of Polymer Science, Kyoto, Japan, May 1998; paper II-3−12: Takahashi, H.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1998**, *47* (2), 149. (c) 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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