Evidence for Living Radical Polymerization of Methyl Methacrylate with Ruthenium Complex: Effects of Protic and Radical Compounds and Reinitiation from the Recovered Polymers[1]

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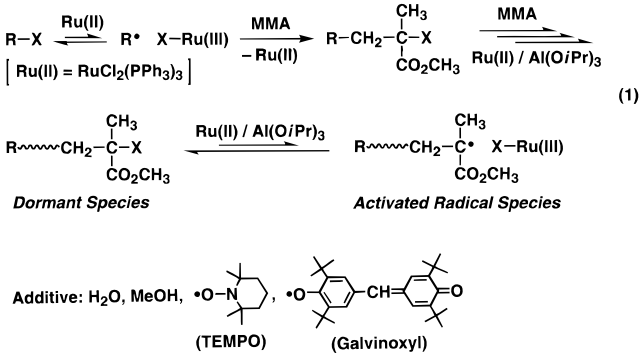
ABSTRACT: The effects of additives such as methanol, water, and radical scavengers (TEMPO and galvinoxyl) were studied in the living polymerization of methyl methacrylate (MMA) with the $PhCOCHCl_2$/$RuCl_2(PPh_3)_3$/$Al(OiPr)_3$ initiating system in toluene at 80 °C. Upon addition of these additives at about 45% conversion, TEMPO and galvinoxyl completely terminated the polymerization, whereas methanol and water did not affect it at all in terms of rate, polymer molecular weight, and its narrow distribution. Living polymerization also occurred even in the presence of relatively high concentrations of methanol (40−1000 mM). The polymers that were recovered after quenching the living polymerization and subsequent purification under atmospheric conditions quantitatively possessed a carbon−chlorine terminal, and they served as a macroinitiator for the living polymerization of MMA in conjunction with $RuCl_2(PPh_3)_3$ and $Al(OiPr)_3$ to induce further molecular weight growth. These results indicate that the living polymerization proceeds via a radical pathway and that the polymer terminal is robust under atmospheric conditions and in the presence of protic compounds, though it readily generates an active end in the presence of the ruthenium and aluminum components.

Introduction

Radical polymerization is the most widely and industrially utilized for usual polymer synthesis because the growing species is tolerant to impurities such as water,[2] in contrast to facile decomposition of the ionic counterparts in the presence of such protic compounds. On the other hand, precision polymer synthesis by radical methods has been considered difficult due to inherent side reactions such as intermolecular radical coupling and disproportionation reactions. Recently, such an image as a less controllable reaction has been changed by the rapid progress in living or controlled radical polymerization systems that permit control of molecular weights and their distributions.[3] There are a few types of initiating systems, but the common key to the control seems to lie in the reversible and rapid formation of dormant species with a covalent bond from the reactive radical species.

In accordance with this context, we have found that a ruthenium(II) complex [$RuCl_2(PPh_3)_3$] led to living polymerization of methyl methacrylate (MMA) in conjunction with alkyl halides (R−X; initiator) and aluminum compounds such as $Al(OiPr)_3$ (eq 1).[4−7] This living polymerization is catalyzed by the one-electron redox reaction of the ruthenium complex and may proceed via a radical species that is generated from reversible and homolytic activation of the carbon−halogen terminal originated from R−X as an initiator. The rapid and reversible interchange equilibrium in turn decreases the instantaneous concentration of the activated form and thereby suppresses termination reactions between the growing radical species. Equally important, the rapid interchange also ensures the virtually equal probability of growth for all dormant species to give uniform molecular weights or narrow molecular weight distributions (MWDs) ($\bar{M}_w/\bar{M}_n \sim 1.1$). Living polymerizations



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based on a similar concept were also possible with CuCl complexed with bipyridine and related ligands.[8−13]

In this study, we have investigated the effects of additives such as water, methanol, and radical scavengers [TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) and galvinoxyl] on the Ru(II)-catalyzed living polymerization of MMA to elucidate the controllability of the reaction, its pathway, and the nature of the intermediate. Although the involvement of radical species in the living polymerization has already been suggested by the preliminary results for the stereoregularity of the polymers and other aspects,[4] supporting evidence has been rather circumstantial, and it has not been clarified how the intermediate is tolerant to ionic or radical compounds. The stability of the dormant polymer terminal was also investigated by the possibility of reinitiation from the recovered polymers after catalysts removal and purification.

Results and Discussion

1. Effects of Additives. The effects of additives such as methanol, water, galvinoxyl, and TEMPO were investigated in the living polymerization of MMA with $PhCOCHCl_2/RuCl_2(PPh_3)_3/Al(OiPr)_3$ in toluene at 80 °C. As evident, the first two compounds are protic and

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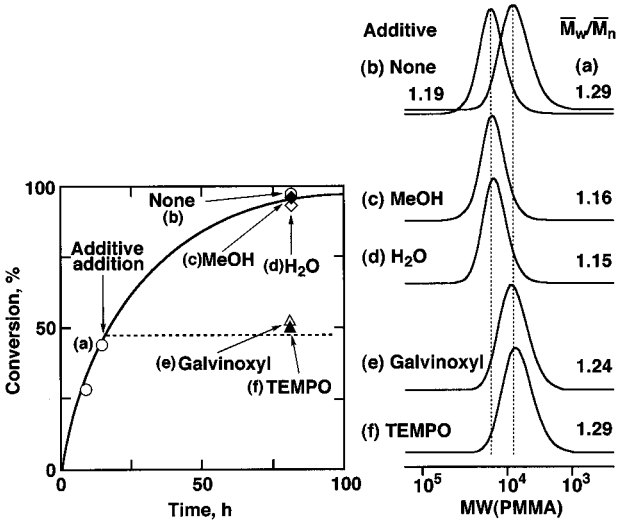


Figure 1. Effects of various additives (△, galvinoxyl; ▲, TEMPO; ◆, MeOH; ◇, H_2O) on the living polymerization of MMA with $PhCOCHCl_2/RuCl_2(PPh_3)_3/Al(OiPr)_3$ in toluene at 80 °C: $[M]_0 = 2.0$ M; $[PhCOCHCl_2]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(OiPr)_3]_0 = 40$ mM. Each additive (200 mM) was added to the polymerization mixture when the conversion reached ca. 45%. The size-exclusion chromatograms are for the product polymers obtained without additive [(a) and (b)] and after the addition of MeOH (c), H_2O (d), galvinoxyl (e), and TEMPO (f). Sample identification (a−f) corresponds to the data points in the time−conversion profile on the left.

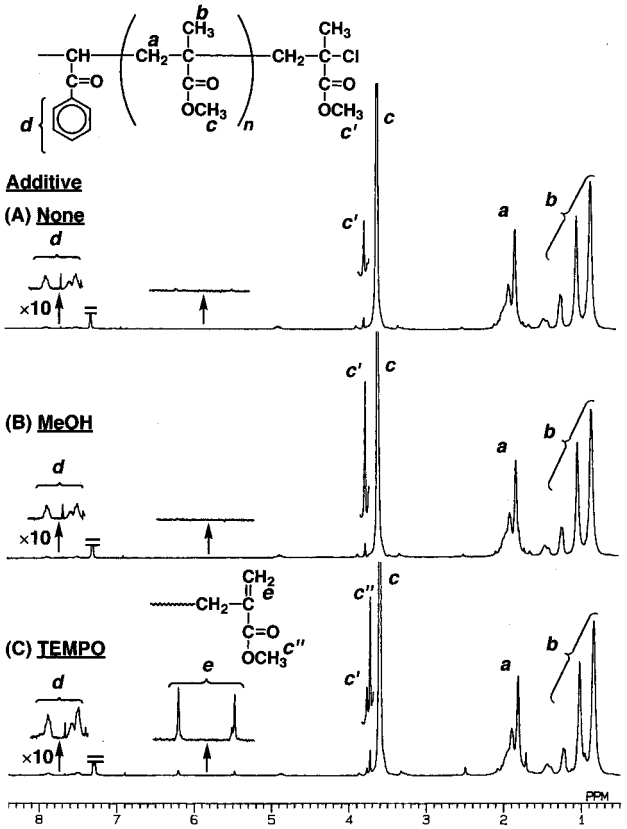


Figure 2. ^1H NMR spectra of poly(MMA) obtained with $PhCOCHCl_2/RuCl_2(PPh_3)_3/Al(OiPr)_3$ in toluene at 80 °C. Additives: (A) none; (B) MeOH; (C) TEMPO. The ^1H NMR spectra denoted as (A), (B), and (C) were for the polymer samples (b), (c), and (f) in Figure 1, respectively.

strong terminators and/or chain transfer agents for anionic polymerizations; the latter two are typical radical scavengers. The polymerization was first run without additives, where conversion reached 44% in 15 h and 97% in 81 h (open circles in Figure 1).[5] Consistent with its living nature as reported already, polymer molecular weights ($\bar{M}_n$) increased with conversion, and the MWDs stayed narrow (chromatograms a and b).

At about 45% conversion, the additives, 10 equiv to the initiator, $PhCOCHCl_2$, were added to the polymerization mixtures. In the systems with galvinoxyl and TEMPO, conversion did not increase further within experimental error (open and filled triangles in Figure 1, respectively), and the polymerization clearly ceased even when it was kept unquenched beyond 80 h, where the system without the additives reached nearly quantitative conversion. The molecular weights did not increase, either, and stayed unchanged after the addition (chromatograms e and f). These indicate that the polymerization was immediately and completely terminated by galvinoxyl and TEMPO.

In sharp contrast, the addition of methanol and water did not affect the living polymerization (filled and open diamonds, respectively); the polymerization proceeded at almost the same rate as in the absence of the protic additives, and the molecular weights of the polymers further increased thereafter, while maintaining narrow MWDs (chromatograms c and d). The produced polymers had almost the same molecular weights and distributions as that obtained without these protic compounds (chromatogram b). Overall, therefore, the R−X/ruthenium-mediated living polymerization proceeds via not an ionic but a radical pathway, and the growing species as well as the catalysts (initiating systems) are tolerant to the protic compounds.

The terminal structures of the polymers obtained with and without the four additives were analyzed by ^1H NMR spectroscopy. As shown in Figure 2A, the polymers from the additive-free system show the small signals of the phenyl groups (d) originating from the initiator's aromatic ketone moiety and the methyl ester protons (c′) adjacent to the chlorine atom at the ω-end, in addition to the large absorptions (a, b, and c) of the main-chain repeat units.[4] There were no remarkable differences between the spectrum of the polymers obtained with and without added methanol (Figure 2, B and A, respectively); the carbon−chlorine bond at the ω-end remains intact even after the addition of methanol.

In contrast, the polymers obtained after the addition of TEMPO exhibited signals at 5.5 and 6.2 ppm, which were characteristic of olefinic methylene protons (e). Another additional signal (c″), ascribed to the methyl ester protons adjacent to the double bond, appeared between the main-chain methyl ester protons (c) and chlorinated terminal protons (c′). The observed peak intensity ratio of c″ to the alkene protons (e) was 1.2, which is close to the calculated value of 1.5, taking account the error due to the overlapping of the small peak (c″) on the large absorption (c). No signals were observed indicative of the attachment of TEMPO to the polymer terminal, which may be due to the unstable PMMA−TEMPO terminal as observed in the TEMPO-mediated radical polymerization of MMA.[14] These spectral data indicate that a hydrogen radical was abstracted from the C−Cl terminal, most probably by added TEMPO, to form the inactive chain end with the exo-methylenic double bond (eq 2). The percentage of the hydrogen abstraction was about 70%, as estimated from the peak intensity ratio of c″ to c′. Similar abstraction was also observed in the polymers obtained in the presence of galvinoxyl. The TEMPO-assisted

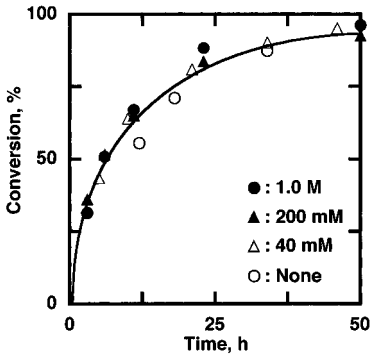
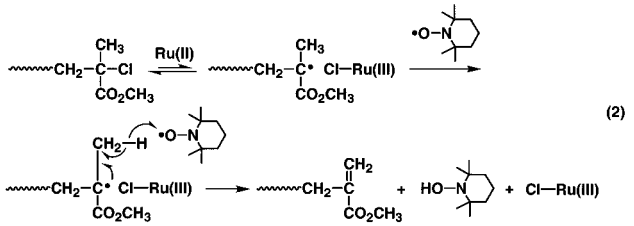


Figure 3. Polymerization of MMA with $PhCOCHCl_2/RuCl_2(PPh_3)_3/Al(OiPr)_3$ in the presence of methanol in toluene at 80 °C. $[M]_0 = 2.0$ M; $[PhCOCHCl_2]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(OiPr)_3]_0 = 40$ mM; $[MeOH]_0 = 0$ (○), 40 (△), 200 (▲), 1000 (●) mM.

formation of the unsaturated terminal therefore suggests the involvement of a radical growing end.



2. Living Polymerization in the Presence of Methanol. The virtual absence of the effects of methanol addition urged us to investigate the possibility of the living polymerization of MMA in the presence of the alcohol. A series of polymerizations were carried out with $PhCOCHCl_2/RuCl_2(PPh_3)_3/Al(OiPr)_3$ at varying concentrations (0−1.0 M) of methanol in toluene at 80 °C; in these runs the alcohol was added to the monomer solution before the addition of the initiator and the activators (Ru and Al compounds). As shown in Figure 3, polymerizations occurred irrespective of the methanol concentration, and the overall rates did not depend on it, even in the presence of as much as 1.0 M methanol (filled circles), 50 equiv to initiator or half the amount of monomer (open circles).

The MWDs of the polymers thus obtained were as narrow as that in the absence of methanol ($\bar{M}_w/\bar{M}_n \leq 1.2$; Figure 4). The number-average molecular weights ($\bar{M}_n$) increased in direct proportion to monomer conversion at all alcohol concentrations. The $\bar{M}_n$ became slightly larger than the calculated values with increasing alcohol concentration. This may be due to a slight loss of living ends in the presence of a large amount of methanol. However, living polymerization occurs even under these highly protic conditions, and apparently it does not serve as a terminator (as in anionic polymerization) or a chain-transfer agent (as in immortal polymerization).[15] These further confirm the radical mechanism of the Ru(II)-catalyzed living polymerization.

To our knowledge, there are only a few systems that induce living polymerizations with narrow MWDs in the presence of protic compounds. For example, living radical systems based on nitroxyl radicals led to living polymerization of styrenesulfonic acid in aqueous ethylene glycol to give polymers with narrow MWDs.[16] The other examples are Ru-catalyzed ring-opening metathesis polymerizations of norbornane derivatives in aqueous emulsion systems[17] and immortal polymerizations

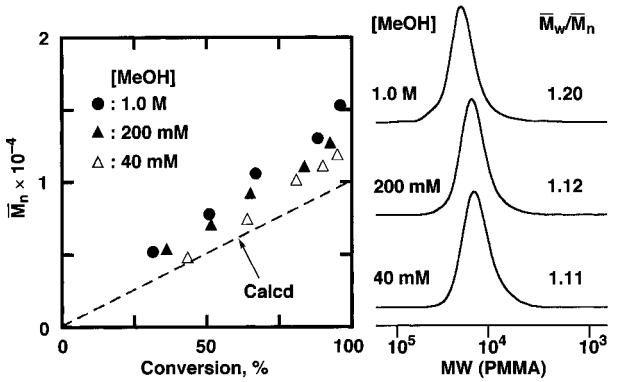


Figure 4. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(MMA) obtained with $PhCOCHCl_2/RuCl_2(PPh_3)_3/Al(OiPr)_3$ in the presence of methanol in toluene at 80 °C. $[M]_0 = 2.0$ M; $[PhCOCHCl_2]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(OiPr)_3]_0 = 40$ mM; $[MeOH]_0 = 40$ (△), 200 (▲), 1000 (●) mM. The diagonal dashed line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per $PhCOCHCl_2$ molecule. Conversion for MWD curves > 90%.

of epoxides and lactones with aluminum porphyrin in the presence of methanol.[15] Therefore, the success of our ruthenium-based living radical polymerization is not only due to the radical intermediate in the polymerization (and perhaps its very low concentration) but also due to the stability of the ruthenium complex against methanol, which is in fact synthesized in methanol from $RuCl_3$ and PPh_3,[18] and to the low oxophilicity of ruthenium unlike other transition metals. $Al(OiPr)_3$ may react with methanol to give aluminum methoxides, which, however, are as effective as the isopropoxy analog in the Ru(II)-catalyzed living polymerizations.[19] The tolerance to methanol further suggests that the Ru-mediated living radical polymerization may proceed in bulk methanol and related alcohols, which is now under investigation in our group.

3. Reinitiation from the Recovered Polymers. As mentioned above (eq 1), this living polymerization is considered to proceed via activation of the ω-end dormant C−Cl bond by $RuCl_2(PPh_3)_3$. We thus examined the stability of the dormant terminal by isolation of the polymer under atmospheric conditions and subsequent polymerization from the recovered polymers.

The prepolymers were synthesized as usual with $PhCOCHCl_2/RuCl_2(PPh_3)_3/Al(OiPr)_3$ in toluene at 80 °C, and the reaction was quenched by lowering the temperature after 8 h at 35% conversion. After the reaction mixture was poured into *n*-hexane dropwise, the precipitate was dissolved in toluene. The solution was treated with a solid absorbent to remove the metal residues, washed with water, and evaporated to dryness, to give the product polymers, which were further purified by preparative SEC to be completely free from the contamination of the catalyst residues. All these recovery procedures were carried out under not inert gas but simple atmospheric conditions. The $\bar{M}_n$ and $\bar{M}_w/\bar{M}_n$ of the obtained sample were 3700 and 1.33, respectively (Figure 6, top chromatogram).[20] ^1H NMR analysis revealed that it possessed the initiator moiety originating from $PhCOCHCl_2$ at the α-end and the C−Cl bond at the ω-end as with the sample shown in Figure 2A. The number-average functionality calculated from the phenyl groups and the main-chain methyl ester protons is 1.12; namely, one molecule of $PhCOCHCl_2$ generates one living PMMA chain.[4] The well-defined prepolymers thus obtained were freeze-dried, dissolved in purified toluene, and then used as a possible macro-

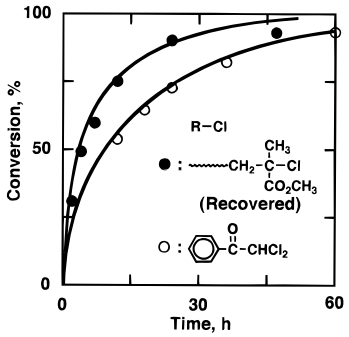


Figure 5. Polymerizations of MMA with recovered polymers ($\bar{M}_n$ = 3700, $\bar{M}_w/\bar{M}_n$ = 1.33, and $\bar{F}_n$ = 1.12) and $PhCOCHCl_2$ in conjunction with $RuCl_2(PPh_3)_3$ and $Al(OiPr)_3$ in toluene at 80 °C. Initiator: recovered polymers (●); $PhCOCHCl_2$ (○). $[M]_0$ = 2.0 M; $[\text{recovered polymers}]_0 = [PhCOCHCl_2]_0$ = 20 mM; $[RuCl_2(PPh_3)_3]_0$ = 10 mM; $[Al(OiPr)_3]_0$ = 40 mM.

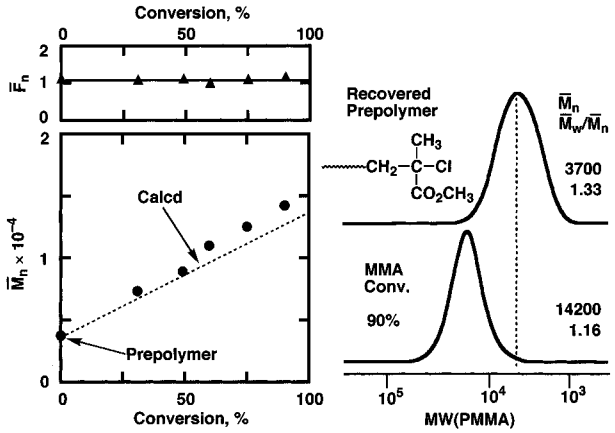


Figure 6. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, $\bar{F}_n$, and MWD curves of poly(MMA) obtained with recovered polymers/$RuCl_2(PPh_3)_3/Al(OiPr)_3$ in toluene at 80 °C. $[M]_0$ = 2.0 M; $[\text{recovered polymers}]_0$ = 20 mM; $[RuCl_2(PPh_3)_3]_0$ = 10 mM; $[Al(OiPr)_3]_0$ = 40 mM. The diagonal dotted line indicates the calculated M_n assuming the formation of one living polymer per molecule of the recovered polymers. $\bar{F}_n$ indicates the average number of the initiator's aromatic moiety (α-end) per polymer chain as determined by ^{1}H NMR (see text).

initiator for further living polymerization of MMA in conjunction with $RuCl_2(PPh_3)_3$ and $Al(OiPr)_3$.

As shown in Figure 5, the polymerization occurred smoothly without an induction phase (filled circles). The overall rate was slightly larger than that with $PhCOCHCl_2/RuCl_2(PPh_3)_3/Al(OiPr)_3$ (open circles) otherwise under the same conditions. This may be due to the faster initiation from the polymer terminal than from the C−Cl bond in $PhCOCHCl_2$.[19]

As conversion of the added MMA increases, the SEC chromatograms for the polymers shifts to higher molecular weights without any contamination of the residual (unreacted) prepolymers. Importantly, the MWDs for the second-phase polymerization were considerably narrower than that of the prepolymer (e.g., $\bar{M}_w/\bar{M}_n$ = 1.16 vs 1.33 in Figure 6). The M_n (increment from that of the prepolymer) increased in direct proportion to monomer conversion and agreed well with the calculated values assuming that one living polymer chain forms from one prepolymer molecule. This shows that the recovered prepolymer works as a macroinitiator to further induce living polymerization of MMA with the aid of $RuCl_2(PPh_3)_3$ and $Al(OiPr)_3$.

The polymers obtained from the macroinitiator also had the carbon−chlorine terminal and the acetophenone unit originating from the prepolymer's α-end. The number-average functionality of the initiator unit (by ^{1}H NMR) was plotted against conversion (filled triangles in Figure 6). The $\bar{F}_n$ was close to unity throughout the reaction, which again shows that one molecule of the recovered polymers generates one living polymer chain via activation of the dormant C−Cl terminal.

Higher molecular weight polymers ($\bar{M}_n$ = 26 200; $\bar{M}_w/\bar{M}_n$ = 1.15), obtained by quenching the living polymerization ($[MMA]_0/[PhCOCHCl_2]_0/[RuCl_2(PPh_3)_3]_0/[Al(OiPr)_3]_0$ = 3000/10/10/40 mM) at 73% conversion, were also employed as macroinitiators for the living polymerization of MMA.[21] As shown below, the polymerization induced a further molecular weight increase in direct proportion to conversion, while keeping narrow MWDs throughout the reaction.

time (h)	(Prepolymer)	3	7	22
MMA conv (%)		40	68	93
$\bar{M}_n \times 10^{-4}$	2.62	4.04	4.93	5.93
$\bar{M}_w/\bar{M}_n$	1.15	1.16	1.12	1.12

Thus, the dormant polymer terminal exclusively consists of the C−Cl bond, which is so stable even under atmospheric conditions that it can reinitiate living radical polymerization quantitatively even after its recovery and purification. This equally holds for polymers of relatively high molecular weights.

In conclusion, the Ru(II)-catalyzed living polymerization most probably proceeds via a radical mechanism as suggested by the facts that the reaction was completely inhibited by radical scavengers but not affected at all by water and methanol. The living polymerization is tolerant to such protic compounds, and the dormant polymer terminal is robust even throughout recovery under atmospheric conditions. These indicate the possibility of living polymerization not only in alcoholic or aqueous media but also of functional monomers with pendent protic groups. These points are now under investigation in our group.

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. $PhCOCHCl_2$ (Wako Chemicals; purity >99%) was dried overnight over calcium chloride and doubly distilled over calcium hydride under reduced pressure before use. $RuCl_2(PPh_3)_3$ (Merck; purity >99%), $Al(OiPr)_3$ (Aldrich; purity >99.99%), methanol (Wako Chemicals; infinity pure grade, purity >99.8%), water (Wako Chemicals; distilled), galvinoxyl (Aldrich), and TEMPO (Aldrich; purity >98%) were used as received. 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 tubes. A typical example is given below.[5] The polymerization was initiated by adding solutions of $Al(OiPr)_3$ (0.10 mmol in 0.80 mL) and $RuCl_2(PPh_3)_3$ (0.025 mmol in 1.0 mL) in toluene, sequentially in this order, to a mixture (0.70 mL) of MMA (0.54 mL, 5.0 mmol), *n*-octane (0.16 mL), and $PhCOCHCl_2$ (0.0071 mL, 0.05 mmol) in toluene at room temperature. The total volume of the reaction mixture was thus 2.5 mL. Immediately after mixing, the solution was placed in a water bath kept at 80 °C. The additives were added via dry syringes as a toluene solution (0.50 mL) when the conversion reached ca. 45% (15 h). For the polymerization in the presence of methanol, it was added to a monomer solution before mixing other ingredients, the reaction mixture was sealed in glass tubes under nitrogen, and the reaction was

started as described above. The recovered polymers for reinitiation were freeze-dried from benzene for 12 h after purification by preparative SEC. 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 a solid, porous absorbent [Kyowaad-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); Kyowa Chemical] (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 room temperature on three polystyrene gel columns (Shodex K-802 + K-803 + K-804) 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; $\bar{M}_n$ = 630−220000; $\bar{M}_w/\bar{M}_n$ = 1.06−1.22) as well as the monomer. ^{1}H NMR spectra were recorded in $CDCl_3$ at 25 °C on a JEOL JNM-GSX270 spectrometer, operating at 270.7 MHz. Polymers for ^{1}H NMR analysis and reinitiation 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 45th Annual Meeting of the Society of Polymer Science, Nagoya, Japan, May 1996; paper IIC05: Nishikawa, T.; Ando, T.; Kamigaito, M.; Sawamoto, M. *Polym. Prepr. Jpn.* **1996**, *45* (2), 131.

(2) For a recent review on radical polymerization, see: Moad, G.; Solomon, D. H. *The Chemistry of Free Radical Polymerization*; Elsevier Science: Oxford, 1995.

(3) For recent reviews on living/controlled radical polymerizations, see: (a) Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. *Trends Polym. Sci.* **1994**, *2*, 66. (b) Davis, T. P.; Kukulj, D.; Haddleton, D. M.; Maloney, D. R. *Trends Polym. Sci.* **1995**, *3*, 365. (c) Hawker, C. J. *Trends Polym. Sci.* **1996**, *4*, 183. (d) Sawamoto, M.; Kamigaito, M. *Trends Polym. Sci.* **1996**, *4*, 371. (e) Sawamoto, M.; Kamigaito, M. *Polymer Synthesis (Materials Science and Technology Series)*; Schlüter, A.-D., Ed.; Wiley: New York, in press.

(4) Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. *Macromolecules* **1995**, *28*, 1721.

(5) Ando, T.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 1070.

(6) Kotani, Y.; Kato, M.; Kamigaito, M.; Sawamoto, M. *Macromolecules* **1996**, *29*, 6979.

(7) Matsuyama, M.; Kamigaito, M.; Sawamoto, M. *J. Polym. Sci., Part A: Polym. Chem.* **1996**, *34*, 3585.

(8) Wang, J.-S.; Matyjaszewski, K. *J. Am. Chem. Soc.* **1995**, *117*, 5614.

(9) Wang, J.-S.; Matyjaszewski, K. *Macromolecules* **1995**, *28*, 7901.

(10) Gaynor, S. G.; Edelman, S.; Matyjaszewski, K. *Macromolecules* **1996**, *29*, 1079.

(11) Patten, T. E.; Xia, J.; Abernathy, T.; Matyjaszewski, K. *Science* **1996**, *272*, 866.

(12) Percec, V.; Barboiu, B. *Macromolecules* **1995**, *28*, 7970.

(13) Percec, V.; Barboiu, B.; Neumann, A.; Ronda, J. C.; Zhao, M. *Macromolecules* **1996**, *29*, 3665.

(14) Solomon, D. H.; Rizzardo, E.; Cacioli, P. U.S. Patent 4581429, 1986.

(15) (a) Asano, S.; Aida, T.; Inoue, S. *J. Chem. Soc., Chem. Commun.* **1985**, 1148. (b) Aida, T.; Maekawa, Y.; Asano, S.; Inoue, S. *Macromolecules* **1988**, *21*, 1195.

(16) Keoshkerian, B.; Georges, M. K.; Boils-Boissier, D. *Macromolecules* **1995**, *28*, 6381.

(17) Lynn, D. M.; Kanaoka, S.; Grubbs, R. H. *J. Am. Chem. Soc.* **1996**, *118*, 784.

(18) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12*, 237.

(19) Ando, T.; Kamigaito, M.; Sawamoto, M. *Macromolecules*, in press.

(20) The relatively broad MWD of this sample is just due to the low conversion at which it was obtained, and not due to side reactions during the polymerization. As already reported,[5] the MWD progressively narrows as conversion increases to reach narrow distributions with $\bar{M}_w/\bar{M}_n \leq 1.1$.

(21) Polymerization conditions: $[MMA]_0/[prepolymer]_0/[RuCl_2(PPh_3)_3]_0/[Al(OiPr)_3]_0$ = 3000/10/10/40 mM, in toluene at 80 °C.

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