Living Radical Polymerization in Water and Alcohols: Suspension Polymerization of Methyl Methacrylate with RuCl$_2$(PPh$_3$)$_3$ Complex[1]

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ABSTRACT: Water and alcohols were employed as solvents for the living radical polymerization of methyl methacrylate (MMA) with the R−X/RuCl$_2$(PPh$_3$)$_3$ initiating systems in the presence and absence of Al-(Oi-Pr)$_3$ at 80 °C (initiator R−X: PhCOCHCl$_2$, CCl$_3$Br). These Ru(II)-based systems indeed led to living suspension polymerization even in such protonic solvents to give polymers with controlled molecular weights and narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n = 1.1-1.3$). The living polymerizations in water proceeded faster than those in toluene, and additives such as Al(Oi-Pr)$_3$ were not necessarily required for the polymerization to occur. Especially, the PhCOCHCl$_2$/RuCl$_2$(PPh$_3$)$_3$ initiating system gave high molecular weight poly(MMA) ($\bar{M}_n \sim 10^5$) with narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n \sim 1.1$) in water even without Al(Oi-Pr)$_3$. Similar Ru(II)-mediated living processes were feasible in such alcohols as methanol, isobutyl alcohol, and *tert*-amyl alcohol under similar conditions. The success of these living suspension polymerizations in aqueous and alcoholic media attests their radical mechanism as well as the tolerance of the ruthenium complex and the dormant carbon−halogen bond to water and alcohols, where transition-metal complexes are often deactivated.

Introduction

One of the most distinguishable features of radical polymerization is its tolerance to water, relative to the ionic counterparts, which should be done under stringent conditions without moisture and protonic or basic impurities. Because of the unique feature, suspension, dispersion, and emulsion processes in aqueous or alcoholic media are widely employed in radical polymerizations.[2]
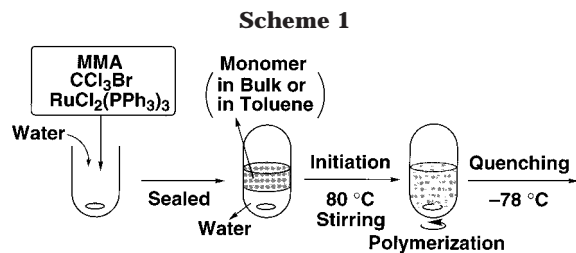
Despite such industrially developed processes, precision polymer synthesis has also become important in radical polymerizations in response to the need for new polymer materials of well-defined, tailor-made architectures.[3] Most of such controlled synthesis has hitherto depended on ionic polymerizations because of the difficulty in controlling radical polymerizations, where neutral radical propagating species almost invariably induce side reactions, particularly bimolecular termination (radical coupling and/or disproportionation). Thus, controlled radical polymerization has been considered difficult for a long time. Quite recently, however, widespread efforts for attaining living or well-controlled radical polymerizations have been made, as witnessed in the current exponential increase in publications, and these new radical processes are now rapidly approaching the controllability that rivals those in ionic polymerizations in terms of molecular weights and their distributions.[4] Most of such controlled radical polymerizations are apparently based upon either the transition-metal catalysis (via reversible activation of carbon−halogen terminal)[4d,5] or nitroxide-mediated processes,[4a,c] among other methods.[4g,h,6]

Recently, we have developed living radical polymerization of methyl methacrylate (MMA) and related acrylic and styrenic monomers mediated by a ruthenium complex [RuCl$_2$(PPh$_3$)$_3$] in toluene and other organic solvents.[6,7] The finely controlled polymerization is considered to proceed via the Ru(II)-assisted reversible and homolytic cleavage of a dormant carbon−halogen ter-

minal originated from an organic halide initiator like dichloroacetophenone (PhCOCHCl$_2$), often in the presence of a metal alkoxide like Al(Oi-Pr)$_3$, as exemplified in eq 1.[8] We have also shown that this polymerization cannot be stopped by addition of methanol and water even in a molar excess over the initiator and the metal catalyst and that the dormant polymer terminal is stable even after the recovery and workup procedures under simple atmospheric and aqueous/acidic conditions.[8] These results prompted us, in this work, to examine the possibility of Ru(II)-mediated living radical polymerization in water and alcohols (suspension process). Another related rationale is that ruthenium complexes are known weakly oxophilic and sometimes water-tolerant, in contrast to most transition-metal complexes that rapidly decompose with moisture. In fact, Grubbs and co-workers reported living suspension ring-opening metathesis polymerization of norbornenes with an air- and moisture-stable ruthenium carbene complex,[9] but similar metal-mediated living processes under radical mechanisms have not been known prior to this work.[1a]

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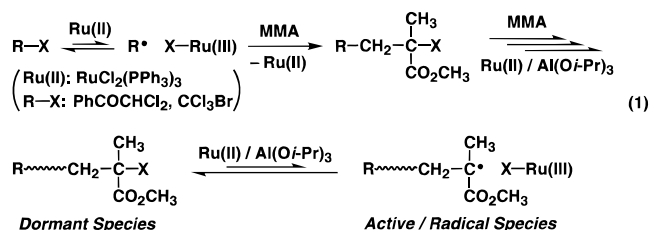
In this study, we examined living radical polymerization of MMA in water and alcohols, especially suspension living radical polymerizations in water by using RuCl$_2$(PPh$_3$)$_3$ in conjunction with an organic halide initiator like PhCOCHCl$_2$ or CCl$_3$Br in the absence of Al(Oi-Pr)$_3$.[1] Quite recently and independently of this work, Teyssié and co-workers briefly reported that

Scheme 1

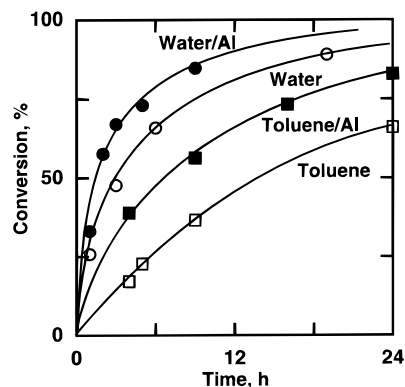

Figure 1. Suspension polymerization of MMA with CCl$_3$Br/RuCl$_2$(PPh$_3$)$_3$/Al(Oi-Pr)$_3$ (●) and CCl$_3$Br/RuCl$_2$(PPh$_3$)$_3$ (○) in water/toluene (MMA/toluene = 1/3.5 v/v, water/organic phase = 1/1 v/v) at 80 °C and polymerization of MMA with CCl$_3$Br/RuCl$_2$(PPh$_3$)$_3$/Al(Oi-Pr)$_3$ (■) and CCl$_3$Br/RuCl$_2$(PPh$_3$)$_3$ (□) in toluene (MMA/toluene = 1/3.5 v/v) at 80 °C. [M]$_0$ = 2.0 M; [CCl$_3$Br]$_0$ = 20 mM; [RuCl$_2$(PPh$_3$)$_3$]$_0$ = 10 mM; [Al(Oi-Pr)$_3$]$_0$ = 40 mM. The concentrations were based on the volume of the organic layer.

transition-metal complexes, such as Ni{C$_6$H$_3$(CH$_2$NMe$_2$)$_2$-o,o'}Br,[5d] Pd(OCOCH$_3$)$_2$/PPh$_3$,[10] and RhCl(PPh$_3$)$_3$,[11] gave poly(MMA) with controlled molecular weights and molecular weight distributions (MWDs) around $\bar{M}_w/\bar{M}_n \sim$ 1.5 under suspension conditions in water; Matyjaszewski and co-workers also employed the CuBr/bipyridines systems for controlled polymerizations of 2-hydroxyethyl acrylate,[12] meth(acrylates),[13] and styrenes[13] in water. The nitroxide-mediated living radical system can also be used in aqueous media as well, e.g., for styrenesulfonic acid sodium salt[13,14] and styrene[15,16] to give polymers of controlled molecular weights. Herein we report that the Ru(II)-based system leads to living radical suspension polymerization of MMA in water to give poly(MMA) of high molecular weights ($\bar{M}_n \sim 10^5$) and narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n \sim$ 1.1) without Al(Oi-Pr)$_3$, clearly faster than those in organic solvents.

Results and Discussion

1. Living Suspension Polymerization in Aqueous Media. *(a) Polymerization in Water/Toluene Mixtures: Effects of Al(Oi-Pr)$_3$.* The first part of this study was carried out for the suspension polymerization of MMA in water/toluene mixtures with the CCl$_3$Br/RuCl$_2$(PPh$_3$)$_3$ initiating system at 80 °C in the presence and absence of Al(Oi-Pr)$_3$ (see Scheme 1 and also the Experimental Section). Thus, MMA monomer, the initiator (CCl$_3$Br), the catalyst/activator [RuCl$_2$(PPh$_3$)$_3$], and n-octane (an internal standard for gas chromatography) were dissolved in a small amount of toluene, and water was added to the organic solution; in some cases the organic phase additionally contained Al(Oi-Pr)$_3$ as an additive. Unlike conventional suspension or dispersion polymerizations, no dispersants or surfactants (particle stabilizers) were added. Thus, in a strict sense, these polymerizations may not be called "suspension polymerization". In these experiments, the volumes of water and the organic solution were the same, and hereafter in the text and the figure captions, the initial concentrations of the monomer and all the other reagents imply those in the organic phase.

The initially two-layered heterogeneous mixture was then vigorously stirred and kept at 80 °C to initiate the polymerization, while magnetic stirring continued throughout the reaction. Under these conditions, the stirred mixture stayed a brown suspension that consisted of a continuous aqueous phase and finely suspended droplets of the organic phase where MMA polymerized. In predetermined intervals, stirring was stopped, and the mixtures were allowed to cool to room temperature, to regenerate a two-layered mixture, from the upper organic phase of which the resulting polymers were isolated. Visual inspection of batches for different reaction times indicated that the higher the conversion (or polymer content), the more stable the suspension (i.e., slower to phase-separate), perhaps due to an increase in viscosity of the organic phase.

It is also noted that the suspension polymerization is apparently affected by oxygen. All the experiments reported herein have been carried out in closed glasswares under nitrogen to give reproducible results, but when similar reactions were carried out in open systems exposed to air, conversion−time profiles were less reproducible, particularly when stirring was extremely vigorous. We suspect that this is caused by an increased air-to-solution interface area which promotes the radical quenching by oxygen.

Figure 1 shows the time courses of the polymerizations in the water/toluene system with and without Al(Oi-Pr)$_3$, along with those in toluene under the same conditions. Irrespective of the presence and absence of Al(Oi-Pr)$_3$, the polymerization was faster in the aqueous system than in pure toluene. Al(Oi-Pr)$_3$ also made the polymerizations faster in water/toluene than in toluene,[7,18] but note that the reaction in the aqueous system without Al(Oi-Pr)$_3$ is still faster than that in toluene with the additive.

Equally important, the MWDs of the polymers obtained in water/toluene with Al(Oi-Pr)$_3$ were as narrow as those in toluene ($\bar{M}_w/\bar{M}_n \sim$ 1.3) (Figure 2A). The $\bar{M}_n$ increased in direct proportion to monomer conversion and agreed well with the calculated values assuming that one molecule of CCl$_3$Br generates one living polymer chain. This shows that the ruthenium complex led to living radical suspension polymerization of MMA in water. ^{1}H NMR analysis of the obtained polymers also supported that the living suspension polymerization proceeds via the activation of a carbon−halogen terminal, similarly to the polymerization in toluene (see below and Figure 5).

The polymers obtained in the suspension polymerization without Al(Oi-Pr)$_3$ had also narrow MWDs ($\bar{M}_w/\bar{M}_n \sim$ 1.3) that are comparable to those obtained in the presence of Al(Oi-Pr)$_3$ (Figure 2B). The $\bar{M}_n$ was directly proportional to monomer conversion and in agreement with the calculated values. Thus, Al(Oi-Pr)$_3$ is unnecessary for the RuCl$_2$(PPh$_3$)$_3$-mediated living radical suspension polymerization in water. These results are in contrast to that the polymerization in toluene without Al(Oi-Pr)$_3$ results in slower reactions, broader MWDs, and less controlled molecular weights (e.g., $\bar{M}_n$ = 9800 and $\bar{M}_w/\bar{M}_n$ = 1.65 at 68% conversion).
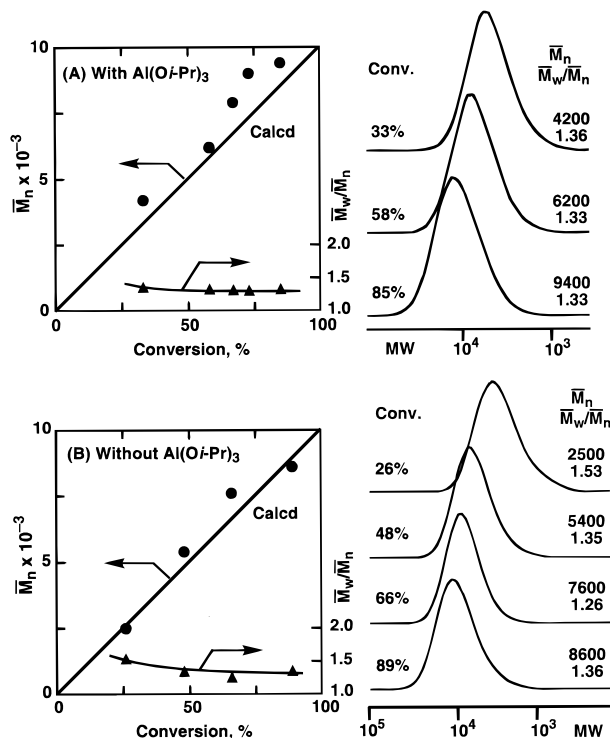
Figure 2. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(MMA) obtained with CCl$_3$Br/RuCl$_2$(PPh$_3$)$_3$/Al(Oi-Pr)$_3$ (A) and CCl$_3$-Br/RuCl$_2$(PPh$_3$)$_3$ (B) in toluene/water (MMA/toluene = 1/3.5 v/v, water/organic phase = 1/1 v/v) at 80 °C. [M]$_0$ = 2.0 M; [CCl$_3$Br]$_0$ = 20 mM; [RuCl$_2$(PPh$_3$)$_3$]$_0$ = 10 mM; [Al(Oi-Pr)$_3$]$_0$ = 40 mM. The diagonal solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per CCl$_3$Br molecule.
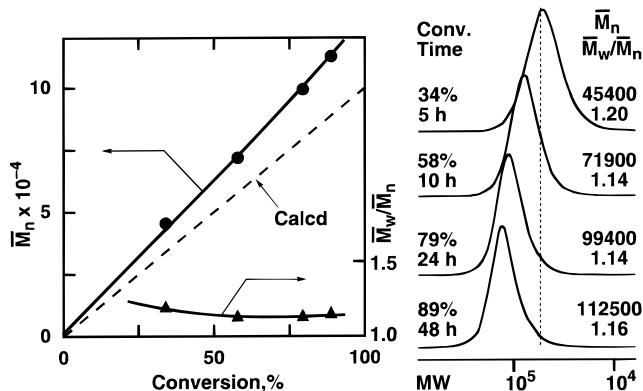
**Figure 3.** Synthesis of higher molecular weight PMMA with PhCOCHCl$_2$/RuCl$_2$(PPh$_3$)$_3$ in toluene/water (MMA/toluene = 1.4/1 v/v, water/organic phase = 2/1 v/v) at 80 °C. [M]$_0$ = 5.0 M; [PhCOCHCl$_2$]$_0$ = 5.0 mM; [RuCl$_2$(PPh$_3$)$_3$]$_0$ = 10 mM. The diagonal dashed line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per PhCOCHCl$_2$ molecule.

The first-phase experiments thus demonstrated not only that the Ru(II)-mediated living radical polymerization is in fact feasible in water but also that its notable features include the greater reaction rate and the simpler initiating system without Al(Oi-Pr)$_3$.

(b) Synthesis of High Molecular Weight Polymers. The living radical suspension polymerization was then applied to the synthesis of higher molecular weight poly-(MMA) [$\bar{M}_n$(calcd) $\sim$ 10^5; DP$_n$ = 1000]. The polymerization was carried out with PhCOCHCl$_2$/RuCl$_2$(PPh$_3$)$_3$ but without Al(Oi-Pr)$_3$ in a water/toluene media (water/organic phase = 2/1 v/v), which proceeded smoothly without an induction phase and reached 90% in 48 h.
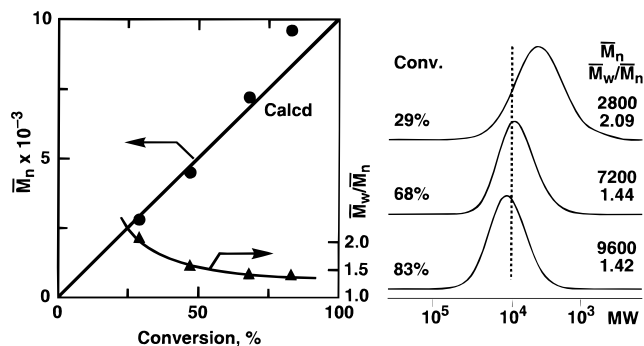
Figure 4. Suspension polymerization of MMA with CCl$_3$Br/RuCl$_2$(PPh$_3$)$_3$ in water (water/organic phase = 1/1 v/v) at 80 °C. [M]$_0$ = 9.0 M; [CCl$_3$Br]$_0$ = 90 mM; [RuCl$_2$(PPh$_3$)$_3$]$_0$ = 10 mM. The diagonal solid line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per CCl$_3$Br molecule.
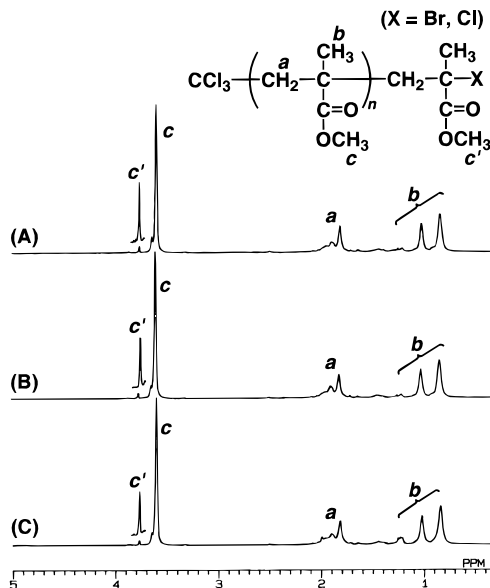
Figure 5. ^{1}H NMR spectra of poly(MMA) obtained in water/toluene and in toluene with CCl$_3$Br/RuCl$_2$(PPh$_3$)$_3$ at 80 °C: (A) suspension, in water/toluene without Al(Oi-Pr)$_3$ (cf. Figure 2B); (B) suspension, in water/toluene with Al(Oi-Pr)$_3$ (cf. Figure 2A); (C) homogeneous in toluene with Al(Oi-Pr)$_3$ (cf. Figure 1).

The obtained polymer had narrow molecular weight distributions throughout the reaction ($\bar{M}_w/\bar{M}_n$ = 1.1–1.2) (Figure 3). The $\bar{M}_n$ increased in direct proportion to monomer conversion up to 1.1 × 10^5 (or DP$_n$ ~ 1100) and were close to the calculated values assuming that one molecule of PhCOCHCl$_2$ generates one living polymer chain. Thus, the suspension polymerization is also suited for the synthesis of high molecular weights PMMA with controlled molecular weights and narrow MWDs. Despite such high molecular weights, the products stayed in finely dispersed droplets of the organic phase without forming larger flocculates or precipitates during the reaction.

(c) Bulk Polymerization in Water without Toluene. Finally, we examined polymerization of MMA without toluene in water; namely, all the components of the CCl$_3$Br/RuCl$_2$(PPh$_3$)$_3$ initiating system and n-octane standard were dissolved in bulk MMA monomer to form an organic phase. Water was then added (the same volume as the organic mixture), and under vigorous and continuous stirring, the polymerization was initiated by immediate heating to 80 °C. Because of the use of bulk MMA instead of toluene for solution, the initial mono-

mer concentration (9.0 M) was 4.5 times higher than in the water/toluene system (2.0 M) already discussed, and the initiator concentration was thus raised from 20 mM (Figures 1 and 2) to 90 mM, so as to keep polymer molecular weights similar.

Figure 4 shows the MWDs and $\bar{M}_n$ of the obtained polymers. The $\bar{M}_n$ increased with conversion and agreed with the calculated values. The MWDs were slightly broader than those obtained in the presence of toluene ($\bar{M}_w/\bar{M}_n \sim 1.4$). This is probably due to the low solubility of $RuCl_2(PPh_3)_3$ into MMA and increased viscosity in organic particles due to the formation of poly(MMA). Similar living polymers were also obtained at a lower concentration of the initiator ($[CCl_3Br]_0 = 30$ mM) or higher DP_n. These results indicate that $RuCl_2(PPh_3)_3$-mediated living radical suspension polymerization is also possible with bulk monomer suspended in water. Further experiments are in progress to improve the molecular weight and MWD control in these bulk systems.

(d) Polymer Structures. Figure 5 compares the ^1H NMR spectra of poly(MMA) obtained in a water/toluene mixture (water/organic phase = 1/1 v/v) without and with $Al(Oi\text{-}Pr)_3$ and in toluene with $Al(Oi\text{-}Pr)_3$; in common the $CCl_3Br/RuCl_2(PPh_3)_3$ initiating system was employed at 80 °C, and the molecular weights of the polymers are similar in the range of 2000 in $\bar{M}_n$. Comparison immediately shows that, whether formed in the aqueous media (Figure 5A,B) or in the organic solution (Figure 5C), the three poly(MMA) samples possess virtually the same primary structures with the tertiary halogen attached to the ω-end, along with nearly the same stereoregularity. Namely, the halogen-capped terminal structure is indicated by the characteristic signals of the ester methyl (3.8 ppm) and the methylene (2.5 ppm) protons in the MMA unit adjacent to the halogen,[8,19] and the splitting pattern of the pendant α-methyl groups (0.7–1.3 ppm) shows $\sim$65% triad syndiotacticity for all the three samples.

The structural similarity, along with the susceptibility to oxygen/air (see above), supports that even in the suspension processes in the aqueous media, the Ru(II)-assisted radical propagation proceeds which is probably the same as in the organic homogeneous system in toluene. The radical mechanism in the aqueous or suspension systems seems, however, not too surprising, if one considers that the net reaction takes place in organic droplets that would serve as "microreactors" mimicking those in bulk organic solution.

2. Living Polymerization in Alcohols and CH_2Cl_2. Following the living polymerizations in water, alcohols such as methanol, isobutyl alcohol, and *tert*-amyl alcohol were employed as solvents for $RuCl_2(PPh_3)_3$-mediated MMA polymerizations coupled with $PhCOCHCl_2$ in the presence of $Al(Oi\text{-}Pr)_3$ at 80 °C. The polymerizations in alcohols proceeded faster than in toluene (Figure 6A). The initially homogeneous, transparent, and brown reaction mixtures became turbid (but without apparent precipitates) as the polymerizations reached high MMA conversion, due to the low solubility of the formed poly-(MMA) in the alcohols.

The acceleration of the polymerization was also observed in a mixed solvent of methanol and toluene (methanol/toluene = 1.3/1 v/v, 42 vol % methanol to the whole reaction mixture) as shown in Figure 6B. The enhanced rate is probably due to the formation of a more active ruthenium catalyst by interaction with alcohols
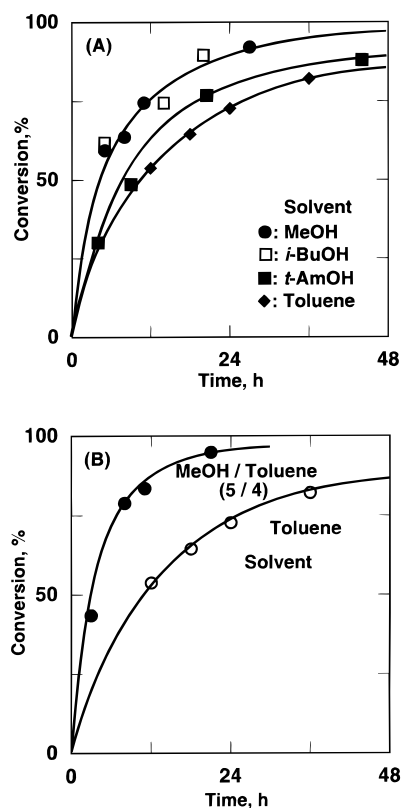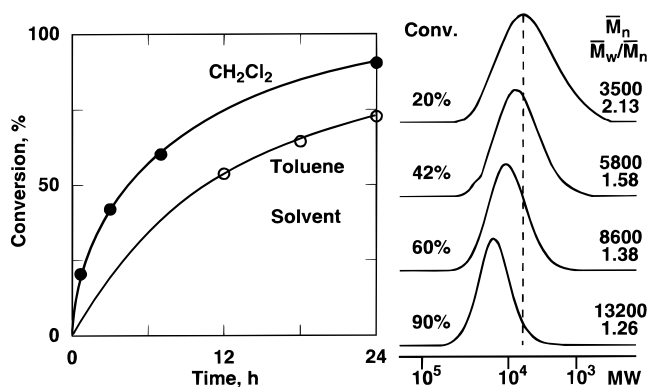

Figure 6. Polymerization of MMA with $PhCOCHCl_2/RuCl_2$-$(PPh_3)_3/Al(Oi\text{-}Pr)_3$ in various alcohols (A) and methanol/toluene (1.3/1 v/v) (B) at 80 °C. $[M]_0 = 2.0$ M; $[PhCOCHCl_2]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM. Solvents in (A): methanol (●), isobutyl alcohol (□), *tert*-amyl alcohol (■), toluene (◆).
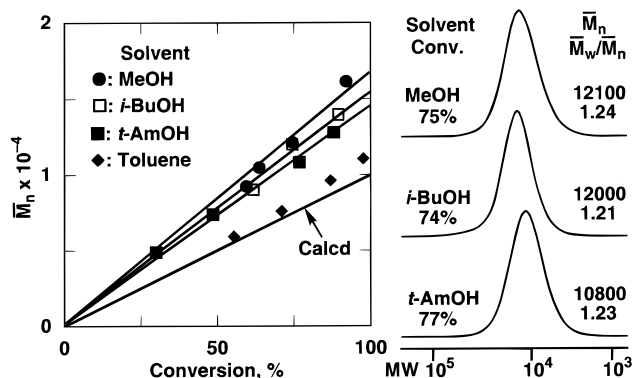
Figure 7. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(MMA) obtained with $PhCOCHCl_2/RuCl_2(PPh_3)_3/Al(Oi\text{-}Pr)_3$ in alcohols at 80 °C. $[M]_0 = 2.0$ M; $[PhCOCHCl_2]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM. The "Calcd" line indicates the calculated $\bar{M}_n$ assuming the formation of one living polymer per $PhCOCHCl_2$ molecule. Conversion for MWD curves $\sim$ 75%. Solvents: methanol (●), isobutyl alcohol (□), *tert*-amyl alcohol (■), and toluene (◆).

and/or faster propagation in polar solvents, although addition of a smaller amount of methanol (4.2 vol %, 1.0 M) to the toluene system had almost no significant effects on polymerization rate as already described in our previous paper.[8]

The polymers obtained in these alcoholic solvents had narrow MWDs ($\bar{M}_w/\bar{M}_n \sim 1.2$, Figure 7), similar to those obtained in toluene or in water. The number-average molecular weights ($\bar{M}_n$) increased in direct proportion to monomer conversion. They were slightly larger than the calculated values, assuming that one molecule of

Figure 8. Polymerization of MMA with PhCOCHCl$_2$/RuCl$_2$-(PPh$_3$)$_3$/Al(Oi-Pr)$_3$ in CH$_2$Cl$_2$ at 80 °C. [M]$_0$ = 2.0 M; [PhCO-CHCl$_2$]$_0$ = 20 mM; [RuCl$_2$(PPh$_3$)$_3$]$_0$ = 10 mM; [Al(Oi-Pr)$_3$]$_0$ = 40 mM.

PhCOCHCl$_2$ generates one living polymer chain. We suspect some side reactions that deplete a small part of the initiator in the alcohol.

These results showed that the Ru(II)-catalyzed living polymerization can be achieved in protic solvents such as alcohols that should be carefully removed from the reaction mixture in usual precision polymer synthesis via ionic polymerizations.

To confirm solvent-polarity effects on the polymerization, we examined methylene chloride (CH$_2$Cl$_2$) as a polar solvent. The polymerization in CH$_2$Cl$_2$ was faster than in toluene (90% vs 73% MMA conversion in 24 h, Figure 8) under otherwise the same reaction conditions. The obtained polymers had narrow MWDs and the $\bar{M}_n$ that increased in direct proportion to monomer conversion. A slightly broader MWD in CH$_2$Cl$_2$ is due to the propagation faster than the exchange reaction between the dormant and activated species.

In conclusion, the Ru(II)-based initiating system induced living radical suspension polymerization of MMA in water or in alcohols to give polymers with controlled molecular weights and distributions. The success not only conforms with the radical mechanism of the polymerization but also demonstrates the high stability of the dormant carbon−halogen terminal and of the ruthenium catalyst in water and alcohols. This process would be feasible with other metal complexes or monomers and also applicable for precision synthesis of block copolymer, random copolymers. Studies in these lines are now in progress in our group.

Experimental Section

Materials. MMA (Tokyo Kasei, purity >99%) was dried overnight over calcium chloride and distilled twice under calcium hydride under reduced pressure before use. PhCO-CHCl$_2$ and CCl$_3$Br (both Wako Chemicals, purity >99%) were doubly distilled over calcium hydride under atmospheric and reduced pressure, respectively, before use. RuCl$_2$(PPh$_3$)$_3$ (Merck, purity >99%) and Al(Oi-Pr)$_3$ (Aldrich, purity >99.99%) were used as received. Toluene and n-octane (internal standard for gas chromatography) were dried overnight over calcium chloride, distilled twice over calcium hydride. Isobutyl alcohol and $tert$-amyl alcohol (both Wako Chemicals, purity >99%) were dried over activated molecular sieves 4 Å overnight. Methanol (Wako Chemicals, infinity pure grade, purity >99.8%) and water (Wako Chemicals; distilled) were used as received. All the solvents were used after being 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 glass tubes equipped with a three-way stopcock or in sealed glass vials. A

typical example is given below. The reaction mixture was prepared by adding solutions of CCl$_3$Br (0.040 mmol in 0.04 mL), Al(Oi-Pr)$_3$ (0.080 mmol in 0.64 mL), RuCl$_2$(PPh$_3$)$_3$ (0.020 mmol in 0.80 mL) in toluene, sequentially in this order, into a mixture (0.52 mL) of MMA (0.428 mL, 5.0 mmol) and n-octane (0.092 mL) at room temperature, and to this homogeneous organic solution was added distilled water (2.0 mL). The volume of the organic layer was 2.0 mL (i.e., MMA/toluene = 1/3.5 v/v), and the total volume of the reaction mixture was thus 4.0 mL (i.e., water/organic phase = 1/1 v/v). The reaction vials were sealed under nitrogen and placed in a water bath kept at 80 °C under vigorous stirring. The polymerization was terminated by cooling the reaction mixtures to 0 °C without addition of any quenchers. Upon stopping magnetic stirring, the cooled reaction mixture underwent phase separation to form a two-layered mixture. Monomer conversion was determined from the concentration of residual monomer in the organic phase measured by gas chromatography with n-octane as an internal standard. The upper organic layer was then isolated, diluted with toluene (∼ 20 mL), and rigorously shaken with a solid porous absorbent [Kyowaad-2000G-7 (Mg$_{0.7}$-Al$_{0.3}$O$_{1.15}$); Kyowa Chemical] (∼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-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 °C on a JEOL JNM-GSX270 spectrometer, operating at 270.7 MHz. Polymers for ^{1}H NMR analysis were fractionated by preparative SEC (column: Shodex K-2002) to be freed from low molecular impurities originating from the catalysts.

References and Notes

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