Amine Additives for Fast Living Radical Polymerization of Methyl Methacrylate with $RuCl_2(PPh_3)_3$[1]

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ABSTRACT: A series of amines were effective as additives for the control and rate enhancement of the living radical polymerization of methyl methacrylate (MMA) with $RuCl_2(PPh_3)_3$. On addition of *n*-Bu_3N and *n*-Bu_2NH, the polymerization with R−Cl/$RuCl_2(PPh_3)_3$ in toluene at 80 °C reached 90% conversion in 50 h and 94% in 20 h, respectively, while only 46% in 120 h without additives. The polymers obtained with *n*-Bu_3N and *n*-Bu_2NH had controlled molecular weights that increased in direct proportion to monomer conversion and narrow MWDs ($M_w/M_n = 1.1-1.2$). This is in sharp contrast to the uncontrolled molecular weights and broad MWDs ($M_w/M_n = 1.7-2.0$) obtained in the additive-free systems. Primary amines like *n*-$BuNH_2$ and cyclic secondary amines like piperidine induced much faster polymerizations to result in broad MWDs ($M_w/M_n = 1.7-1.8$). Other additives such as pyridines, amides, alcohols, phenols, esters, and dimanies were not effective as additives for the ruthenium-catalyzed polymerizations. Interactions between the added amines and $RuCl_2(PPh_3)_3$ were observed by ^1H NMR analysis of the mixtures, where the amines coordinate to the ruthenium center and form highly active mononuclear ruthenium complexes.

Introduction

Metal-catalyzed living radical polymerization has now been developed and utilized for a wide variety of monomers.[2] The initiating systems therein generally consist of a transition metal complex and an organic halide; via reversible redox reaction the former activates the carbon−halogen bond originated from the latter to generate the initiating or the growing radical species. The metal complexes or catalysts can be derived from transition metals such as Ru, Cu, Fe, Ni, Re, etc., and carry appropriate ligands such as phosphines, amines, and others.[2] The systems have thus been designed by employing various metal centers as well as ligands according to monomers so that the polymerizations are controlled.

Along with controlling polymerizations, an important goal is to increase the catalytic activity because of the inherently low rate of living radical polymerizations, for which the current general rationale is to introduce the dormant species that is in fast equilibrium with the growing radical species and predominates over the latter. A way to enhance the catalytic activity is, once again, to design catalysts in terms of central metals and ligands. For example, electron-donating ligands seem favorable because they can increase the electron density of the metal center and thus lower its redox potential or facilitate the redox reaction.[3,4] Thus, $Ru(Ind)Cl(PPh_3)_2$ (Ind = indenyl) is more active than its dichloride counterpart, $RuCl_2(PPh_3)_3$, for acrylic and styrenic monomers.

Besides catalyst design, the use of additives not only alters an uncontrolled radical polymerization into a controlled one but also accelerates them. For instance, the $RuCl_2(PPh_3)_3$/alkyl chloride systems need an additive such as $MeAl(ODBP)_2$ (ODBP = 2,6-di-*tert*-butylphenoxy)[5] and $Al(Oi\text{-}Pr)_3$[6,7] for faster and better controlled polymerizations to occur. The polymerization in the absence of additives is slow and results in less controlled molecular weights with broad molecular weight distributions (MWDs) ($M_w/M_n \sim 1.5$), whereas addition of $Al(Oi\text{-}Pr)_3$ narrows the MWDs ($M_w/M_n = 1.1-1.3$) and increases the rate by 3−4 times.[7] A similar effect of the aluminum compound is also observed for the other transition metal catalysts such as Cu,[8−10] Fe,[11] Ni,[12] and Re.[13] Though the working mechanism of these additives is not established yet, they presumably interact with the metal catalysts to enhance their activity and thereby the redox reaction for radical generation.[7] Alternative additives in the copper-based systems include phenols,[14−16] benzoic acids,[17] and carboxylate salts,[18] which increase the rate of the copper-catalyzed controlled radical polymerizations without affecting their narrow MWDs. These additives most probably substitute the bidentate nitrogen-based ligands such as bipyridines and pyridinimines on the copper center to convert the dimeric species into a highly active monomeric species. A zerovalent metal such as Cu(0) and Fe(0) can be employed as an effective additive, which reduces an inactive metal species [Cu(II) and Fe(III)], accumulated by side reactions, into an active form [Cu(I) and Fe(II)].[19,20] In this case, the additive itself can be changed into an active catalyst by oxidation.

This study is to develop new additives other than metal alkoxides for control and rate enhancement of the $RuCl_2(PPh_3)_3$-catalyzed living radical polymerization of methyl methacrylate (MMA). The additives include nitrogen- and oxygen-based organic compounds such as amines, pyridines, amides, alcohols, phenols, and esters (Scheme 1), which may interact with the ruthenium complex to affect its catalytic activity. We have found that amines induce fairly fast polymerization and that secondary and tertiary amines such as *n*-Bu_2NH and *n*-Bu_3N give polymers with controlled molecular weights and narrow MWDs ($M_w/M_n = 1.1-1.2$).

Results and Discussion

1. Control and Rate Enhancement with *n*-Butylamines.

(a) MMA Polymerization. First, a series of

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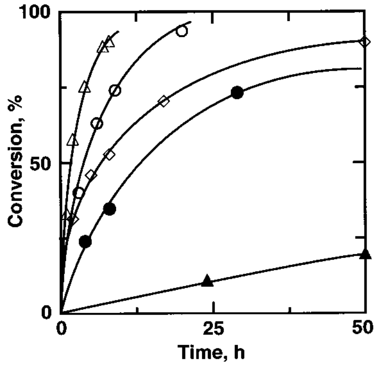
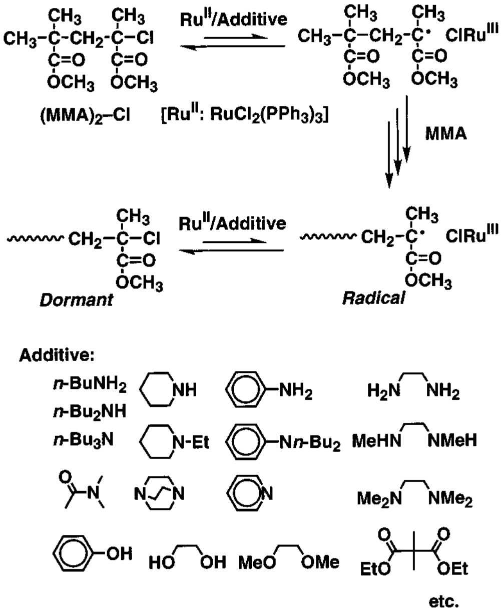


Figure 1. Polymerization of MMA with $(MMA)_2-Cl/RuCl_2(PPh_3)_3$/additive in toluene at 80 °C: $[MMA]_0 = 2.0$ M; $[(MMA)_2-Cl]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[additive]_0 = 40$ mM. Additive: n-$BuNH_2$ (△), n-Bu_2NH (○), n-Bu_3N (◇), $Al(O$*i*$-Pr)_3$ (●), none (▲).

Scheme 1



n-butylamines (n-$BuNH_2$, n-Bu_2NH, and n-Bu_3N) were examined as additives for the polymerization of MMA with the $(MMA)_2-Cl/RuCl_2(PPh_3)_3$ initiating system in toluene at 80 °C. The additive-free polymerization proceeded so slowly as to reach 95% conversion in 556 h and gave polymers with uncontrolled molecular weights and broad MWDs ($M_n = 22\,900$, $M_w/M_n = 2.02$; $M_n(\text{calcd}) = 9700$). Addition of three amines, 4 times molar excess over the ruthenium complex, led to a dramatic rate enhancement, in the order of n-Bu_3N < n-Bu_2NH < n-$BuNH_2$; i.e., the conversion reached 90% or beyond in 50 h with n-Bu_3N, in 20 h with n-Bu_2NH, and in 8 h with n-$BuNH_2$, as shown in Figure 1. These polymerizations proceeded invariably faster than that with $Al(O$*i*$-Pr)_3$ (93% in 124 h) under the same conditions. A similar rate enhancement has been reported in a $RuCl_2(PPh_3)_3$-based system with silica gel supported amine ligands.[21]

The M_n of the polymers obtained with n-Bu_3N and n-Bu_2NH increased in direct proportion to monomer conversion and agreed well with the calculated values assuming that one molecule of initiator generates one living polymer chain (Figure 2), although they were slightly higher than the calculated values. The MWDs were narrower than that with $Al(O$*i*$-Pr)_3$ ($M_w/M_n = 1.15$ and 1.19 vs 1.31). In contrast, the polymers obtained with n-$BuNH_2$ additive, which induced the fastest polymerization, had uncontrolled molecular weights and broader MWDs ($M_n = 14\,300$, $M_w/M_n = 1.75$). Thus, n-Bu_3N and n-Bu_2NH proved efficient not only in enhancing the polymerization but also in controlling molecular weights for the radical polymerization of MMA with $RuCl_2(PPh_3)_3$. They most probably interact with the ruthenium complex to increase the catalytic activity, which results in a higher concentration of the radical species and a faster exchange reaction.

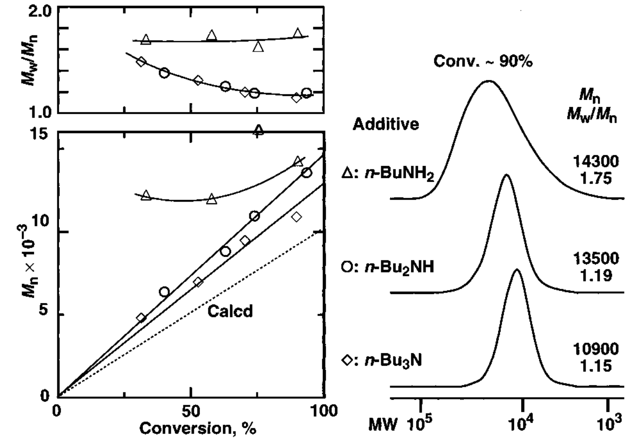


Figure 2. M_n, M_w/M_n, and SEC curves of poly(MMA) obtained with $(MMA)_2-Cl/RuCl_2(PPh_3)_3$/butylamines in toluene at 80 °C: $[MMA]_0 = 2.0$ M; $[(MMA)_2-Cl]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[additive]_0 = 40$ mM. Additive: n-$BuNH_2$ (△), n-Bu_2NH (○), n-Bu_3N (◇).

A smaller amount of amines, equimolar to the ruthenium complex (10 mM), was also employed under otherwise the same conditions and resulted in a slightly slower polymerization, which was still faster than the additive-free system. Conversion reached 93% in 77 h with n-Bu_3N, in 49 h with n-Bu_2NH, and in 57 h with n-$BuNH_2$. The polymers obtained with n-Bu_3N and n-Bu_2NH had controlled molecular weights and narrow MWDs ($M_w/M_n = 1.18$ and 1.15, respectively), while n-$BuNH_2$ resulted in broad MWDs ($M_w/M_n = 1.79$).

To investigate the living nature of the polymerization with n-Bu_2NH, a fresh feed of monomer was added to the reaction mixture when the initial charge of the monomer has nearly been consumed (Figure 3). The added monomer feed was smoothly polymerized, and about 90% of the added monomer was consumed within an additional 24 h. The M_n of the polymers further increased in direct proportion to monomer conversion to reach 2.5×10^4. The MWDs stayed narrow even after the monomer addition ($M_w/M_n = 1.24$). However, the size exclusion chromatogram (SEC) of the polymers obtained at 190% conversion showed some shoulder, around the position where the polymers in the first phase eluted.

This is attributed to a partial loss of the living or the dormant end during the polymerizations. ^1H NMR analysis of the polymers obtained with these amines showed a small amount of olefin terminal groups [$\sim\sim\sim CH_2C(CO_2CH_3){=}CH_2$],[22] probably caused by disproportionation of the growing radical species or via β-H elimination from the radical species;[23] the large majority of the terminal groups were the chlorine group [$\sim\sim\sim CH_2C(CO_2CH_3)(CH_3)-Cl$].[24] The fast reaction may result from a higher concentration of the radical species,

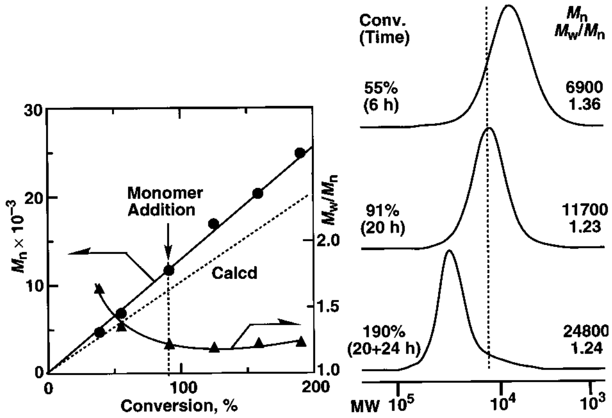


Figure 3. M_n (●), M_w/M_n (▲), and SEC curves of poly(MMA) obtained in a monomer-addition experiment with $(MMA)_2{-}Cl/RuCl_2(PPh_3)_3/n\text{-}Bu_2NH$ in toluene at 80 °C: $[MMA]_0 = [MMA]_{add} = 2.0$ M; $[(MMA)_2{-}Cl]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[n\text{-}Bu_2NH]_0 = 40$ mM.

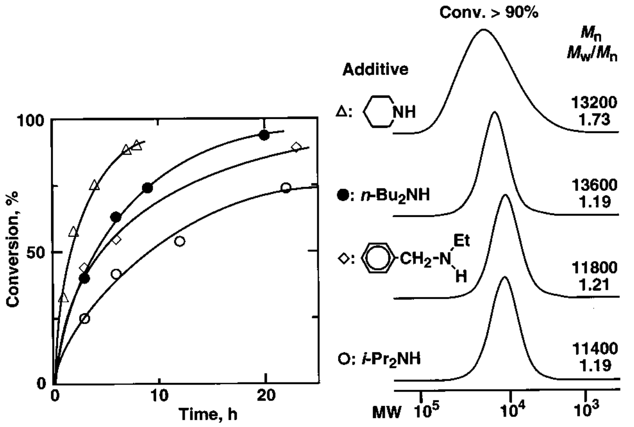


Figure 4. Polymerization of MMA with $(MMA)_2{-}Cl/RuCl_2(PPh_3)_3$/secondary amine in toluene at 80 °C: $[MMA]_0 = 2.0$ M; $[(MMA)_2{-}Cl]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; [secondary amine]$_0$ = 40 mM. Secondary amine: piperidine (△), n-BuNH$_2$ (●), N-ethylbenzylamine (◇), diisopropylamine (○).

which also results in such side reactions. The content of olefin terminal groups increases with an increase of the polymerization rate [3.6% (n-Bu$_3$N), 11.4% (n-Bu$_2$NH), and 22.5% (n-BuNH$_2$), with 40 mM amines at ~90% conversion (the same samples for the SEC curves in Figure 2)]. The olefin content can be decreased by using a lower concentration of amines [with 10 mM of amines; 1.3% (n-Bu$_3$N) and 4.0% (n-Bu$_2$NH)].

Another possible cause of the olefin end is chain transfer to the amines, as suggested by the chain-transfer constant of n-Bu$_3$N about 50 times larger than that of toluene [C_s(n-Bu$_3$N) = 25.7, C_s(toluene) = 0.567; in free radical polymerization of MMA at 70 °C[25]]. However, it is considered less serious because the amine content in the polymerization mixture was 170−680 times less than that of the solvent.

(b) Structure and Basicity of Butylamines. These fast polymerizations are most probably due to the formation of highly active catalysts via interaction between the amine additives and the ruthenium complex, as suggested by the color changes of the reaction mixture. The dark brown solution of the monomer containing $RuCl_2(PPh_3)_3$ changed into pale green on addition of n-BuNH$_2$ even at room temperature, and the color persisted during the polymerization at 80 °C. n-Bu$_2$NH resulted in a similar color change while the reaction mixture became dark red on heating to 80 °C. No color change occurred with n-Bu$_3$N at room temperature, whereas the solution turned to dark red during the polymerization, as it did with the secondary amine. These results show that all of these amines interact with the ruthenium complex and most likely form new complexes,[26] but they cannot explain which amines are effective in controlling and accelerating the polymerizations.

The coordinating ability of amines depends on the electron density of the nitrogen atom as well as the steric hindrance. The former can be estimated from the basicity or pK_a, which increases in the order n-Bu$_3$N (9.93) < n-BuNH$_2$ (10.61) < n-Bu$_2$NH (11.25) in water at 25 °C.[27] Obviously, the basicity order has no close correlation between the polymerization rate and the controllability. The steric hindrance apparently decreases in the order n-Bu$_3$N > n-Bu$_2$NH > n-BuNH$_2$, and this may reflect the order of the polymerization rates, because less bulky amines can more easily coordinate to the ruthenium center. The interaction between $RuCl_2(PPh_3)_3$ and these amines was studied by ^{1}H NMR (see below).

2. Various Amines. (a) Secondary Amines. Among a series of n-butylamines, a secondary amine, n-Bu$_2$NH, was most effective in both control and enhancement of the $RuCl_2(PPh_3)_3$-mediated radical polymerization. Secondary amines with varying basicity and structure were thus examined as possible additives.

As shown in Figure 4, piperidine, similar in basicity to n-Bu$_2$NH [pK_a(water, 25 °C) = 11.12],[27] induced the fastest polymerization in this study, reaching 91% conversion in 8 h. However, the obtained polymers had uncontrolled molecular weights and broad MWDs ($M_w/M_n = 1.73$), as observed with n-BuNH$_2$ (see above). This is most probably due to the lower steric hindrance of the cyclic amine, as with a primary amine, both of which can strongly interact with the ruthenium complex to generate too high a concentration of growing radicals. Bulky *sec*-amines such as N-ethylbenzylamine [pK_a(water, 25 °C) = 9.64][27] and diisopropylamine [pK_a(water, 25 °C) = 10.91][27] led to slower polymerizations than n-Bu$_2$NH, where the conversion reached 91% in 24 h and 95% in 50 h, respectively. These two bulky amines gave controlled molecular weights and narrow MWDs, similarly to n-Bu$_2$NH.

(b) Tertiary Amines. Several tertiary amines were also added to the ruthenium-catalyzed polymerizations under the same conditions (Figure 5). Cyclic tertiary amines such as 1-ethylpiperidine and 1,4-diazabicyclo[2.2.2]octane induced faster polymerizations than n-Bu$_3$N. In contrast to the secondary cyclic amine, they afforded polymers with controlled molecular weights and narrow MWDs. A less basic and more bulky aniline derivative, N,N-dibutylaniline [pK_a(water, 19 °C) = 6.30],[27] resulted in a much slower polymerization at almost the same rate as that in the absence of additives. The polymerization reached 89% conversion in 481 h to give broad MWDs ($M_w/M_n = 2.02$). However, the molecular weights became closer to the calculated values than that without additives, which suggests some minor effects.

(c) Bidentate Amines. Another candidate of amine-based additives is a bidentate or multidentate amine, which can interact with the ruthenium complex more strongly than the monoamines. In the copper-catalyzed radical polymerizations, multidentate amines work effectively as ligands for CuBr and CuCl while monoamines are totally ineffective.[28] Figure 6 shows the

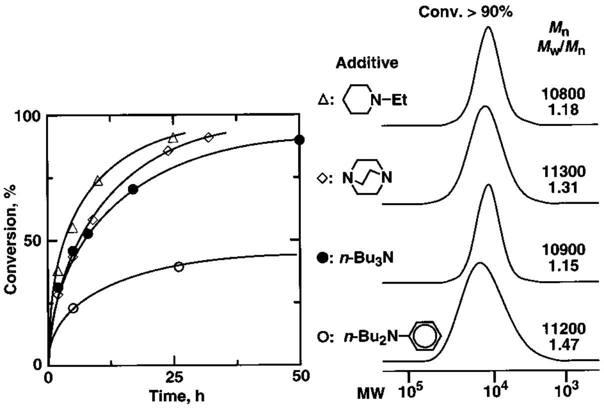


Figure 5. Polymerization of MMA with $(MMA)_2-Cl/RuCl_2(PPh_3)_3$/tertiary amine in toluene at 80 °C: $[MMA]_0 = 2.0$ M; $[(MMA)_2-Cl]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; [tertiary amine]$_0 = 40$ mM. Tertiary amine: 1-ethylpiperidine (△), 1,4-diazabicyclo[2.2.2]octane (◇), *n*-Bu_3N (●); *N,N*-dibutylaniline (○).

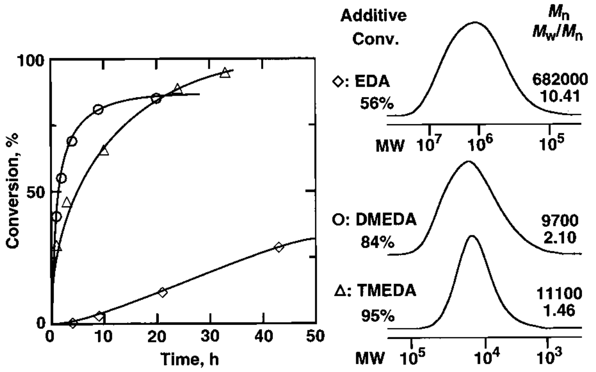


Figure 6. Polymerization of MMA with $(MMA)_2-Cl/RuCl_2(PPh_3)_3$/bidentate amine in toluene at 80 °C: $[MMA]_0 = 2.0$ M; $[(MMA)_2-Cl]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; [bidentate amine]$_0 = 40$ mM. Bidentate amine: ethylenediamine (◇), *N,N′*-dimethylethylenediamine (○), *N,N,N′,N′*-tetramethylethylenediamine (△).

polymerizations with $RuCl_2(PPh_3)_3$ in the presence of a series of ethylenediamines.

Unsubstituted ethylenediamine (EDA) resulted in a slow and incomplete polymerization to give poly(MMA)s of extremely high molecular weights and very broad MWDs ($M_w/M_n \geq 10$). The monomer/catalyst solution turned from dark brown to green on its addition. This indicates that the bidentate amine strongly interacts with the ruthenium complex to form a coordinatedly saturated inactive or less active catalyst and that thermal polymerizations occur concurrently. At a lower concentration (10 mM), a slow polymerization occurred (92% conversion in 116 h) with an induction period to give uncontrolled and high molecular weights.

With a secondary diamine, *N,N′*-dimethylethylenediamine (DMEDA), conversion reached 69% in 4 h but leveled off around 85%. The molecular weights of the polymers were almost unchanged with conversion (10 000−14 000), and the MWDs were broad (M_w/M_n 1.8−2.1). This indicates that a highly active catalyst forms whereas side reactions frequently occur during the early stages of the polymerizations. On decreasing the amine concentration, the reaction became nearly quantitative (90% conversion in 20 h) but still resulted in still broad MWDs ($M_w/M_n = 1.64$).

In contrast to these results, *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) induced a smooth polymerization, which reached 95% conversion in 33 h. The molecular weights increased with conversion and became closer to the calculated values based on monomer/initiator mole ratio. The MWDs became narrower with increasing conversion ($M_w/M_n = 2.03$ at 30%, 1.81 at 46%, 1.59 at 66%, and 1.46 at 95%). These results indicate that the tertiary diamine can be effective for the controlled polymerization with $RuCl_2(PPh_3)_3$, though inferior to *n*-Bu_2NH in terms of rate and controllability.

3. Other Additives. Table 1 summarizes the effects of amines and other additives upon the $R-X/RuCl_2(PPh_3)_3$-mediated radical polymerizations of MMA. Living radical polymerization can be achieved with unsubstituted aniline (entry 5), but the rate is almost the same as that in the absence of additives. The slow reaction is primarily due to the low basicity [pK_a(water, 25 °C) = 4.60][27] along with the bulky structure around nitrogen. On addition of 40 mM of pyridine, another weak base [pK_a(water, 25 °C) = 5.21],[27] no polymerizations proceeded, most probably due to its strong coordination with the metal center (entry 6). Though the polymerization occurred with a lower concentration (10 mM), the reaction was still slow and gave uncontrolled polymers (entry 7). There were no significant effects of *N,N*-dimethylacetamide on the rate as well as on the molecular weights (entry 8).

Oxygen-based compounds such as alcohol (entries 12 and 13), ether (entry 14), and ester (entry 15) are not effective additives except for phenol. Addition of 40 mM phenol slightly accelerated the polymerization (entry 9), but there were no effects on the rate with a smaller amount (entry 10). The polymers obtained under both conditions had uncontrolled molecular weights and broad MWDs irrespective of the concentrations.

These results indicate that amine additives are most effective in increasing the rates of the $R-X/RuCl_2(PPh_3)_3$-mediated radical polymerization of MMA among the employed nitrogen- and oxygen-based organic compounds. Controlled polymerizations can be achieved with the use of aliphatic, linear, and less bulky secondary or tertiary monoamines, with *n*-Bu_2NH being the best in terms of fast and controlled polymerizations. There was no direct correlation between the basicity of amines and the polymerization rate. They most probably interact with the ruthenium complex and change the structure into a more active form.

4. NMR Analysis of Interaction between Amines and $RuCl_2(PPh_3)_3$. Mixtures of $RuCl_2(PPh_3)_3$ and a series of *n*-butylamines were then analyzed by ^1H NMR to clarify these interactions. Figure 7 shows a series of ^1H NMR spectra of the mixtures in toluene at 0 °C, where the samples were obtained by mixing in toluene-d_8 followed by heating at 80 °C for 1 h.

All of these amines caused spectral changes in the aromatic protons of the triphenylphosphines of $RuCl_2(PPh_3)_3$. The spectrum of $RuCl_2(PPh_3)_3$ alone (Figure 7A) shows the signals of free PPh_3 [*a* (meta) and *b* (ortho and para protons)] in addition to the PPh_3 coordinated to the ruthenium center.[29] The free PPh_3 was 38% or about one-third of all PPh_3 on the basis of the peak area ratios (see the Experimental Section). This is most probably due to the release of one triphenylphosphine group followed by the formation of a dinuclear ruthenium complex in toluene, as already reported (Scheme 2).[30,31]

The relative amount of free PPh_3 was almost unchanged on addition of *n*-Bu_3N (30%) and *n*-Bu_2NH

Table 1. Polymerization of MMA with R−X/$RuCl_2(PPh_3)_3$ in the Presence of Various Additives[a]

entry	additive	$[additive]_0$, mM	initiator	time, h	conv, %	M_n	M_w/M_n
1	none	0	$(MMA)_2$−Cl	120	46	32 100	1.76
2	none	0	$(MMA)_2$−Cl	269	75	32 500	1.79
3	none	0	$(MMA)_2$−Cl	556	95	22 900	2.02
4	none	0	EMA-Br	146	93	11 400	2.01
5	aniline	40	$(MMA)_2$−Cl	481	85	8 800	1.34
6	pyridine	40	$(MMA)_2$−Cl	150	0		
7	pyridine	10	$(MMA)_2$−Cl	150	62	28 500	1.88
8	$CH_3C(O)N(CH_3)_2$	40	$(MMA)_2$−Cl	372	75	20 100	1.95
9	phenol	40	$(MMA)_2$−Cl	172	80	16 900	1.82
10	phenol	10	$(MMA)_2$−Cl	172	57	18 700	1.81
11	$HOCH_2CH_2OH$	40	EMA−Br	167	92	11 800	1.72
12	$(CH_3)_2C(OH)CH_2C(OH)(CH_3)_2$	40	$(MMA)_2$−Cl	166	72	30 400	1.73
13	$(CH_3)_2C(OH)C(OH)(CH_3)_2$	40	$(MMA)_2$−Cl	502	91	27 500	1.99
14	$CH_3OCH_2CH_2OCH_3$	40	EMA−Br	162	93	12 700	1.90
15	$C_2H_5OC(O)C(CH_3)_2CO_2C_2H_5$	40	EMA−Br	148	89	15 700	1.94

[a] $[MMA]_0 = 2.0$ M; $[R-X]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[additive]_0 = 0-40$ mM; toluene; 80 °C.

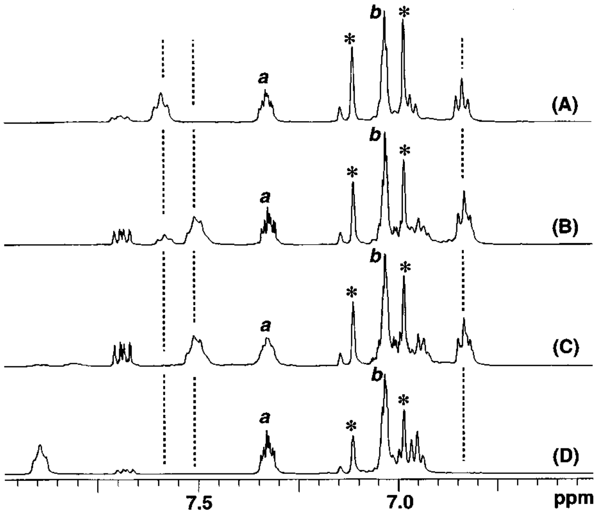
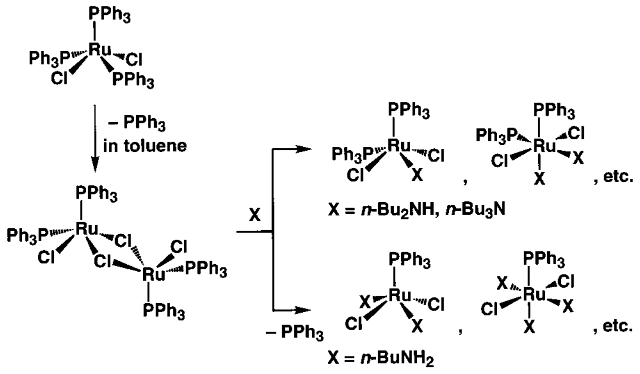


Figure 7. ^1H NMR spectra of $RuCl_2(PPh_3)_3$ (A), $RuCl_2(PPh_3)_3$/*n*-Bu_3N (B), $RuCl_2(PPh_3)_3$/*n*-Bu_2NH (C), and $RuCl_2(PPh_3)_3$/*n*-$BuNH_2$ (D) in toluene-d_8 at 0 °C. $[RuCl_2(PPh_3)_3] = 20$ mM; $[amine]_0 = 80$ mM. The peaks marked by *a* and *b* are of free PPh_3. The asterisked signals are due to the undeuterated aromatic hydrogens of toluene-d_8.

Scheme 2



(33%) (Figure 7, B and C, respectively). This means no additional phosphine release occurs by its addition. However, new peaks appeared at 7.5 ppm along with decrease or disappearance of the peaks at 7.6 ppm. (The latter can be seen in the spectrum of the Ru complex alone; no assignment was yet made.) This indicates that the added amines collapse the dinuclear complex into the mononuclear form via coordination to the ruthenium center without additional loss of PPh_3. The high activity of the ruthenium catalyst in the presence of these amines is due to the formation of a mononuclear complex as well as the increase of electron density of the ruthenium center via coordination of an electron-donating nitrogen compound. Isolation of the new complexes has been attempted and is still under way.

In contrast, *n*-$BuNH_2$ increases the ratio of free PPh_3 to 51% and leads to complete disappearance of the original peaks at 7.6 and 6.85 ppm (Figure 7D). Along with these changes, a new peak appears at 7.9 ppm, which was not observed with *n*-Bu_3N and *n*-Bu_2NH. This shows that *n*-$BuNH_2$ results in another type of complex, different from those with *n*-Bu_3N and *n*-Bu_2NH.[32] Alternatively, there is a possibility of coordination of MMA to the ruthenium center in the polymerization mixture.

In conclusion, appropriate secondary and tertiary amines (*n*-Bu_2NH, etc.) are effective at enhancing the rate and controlling the $RuCl_2(PPh_3)_3$-mediated living radical polymerization of MMA. This was caused by in-situ formation of a highly active amine-coordinated mononuclear ruthenium complex.

Experimental Section

Materials. All of the additives were purchased from Aldrich, used without further purification, and handled in a glovebox (M.Braun Labmaster 130) under a moisture- and oxygen-free argon atmosphere (H_2O <1 ppm; O_2 <1 ppm): butylamine (99.5%), dibutylamine (>99.5%), tributylamine (>98.5%), piperidine (>99.5%), diisopropylamine (>99.5%), *N*-ethylbenzylamine (97%), 1-ethylpiperidine (99%), 1,4-diazabicyclo[2.2.2]-octane (98%), *N,N*-dibutylaniline (97%), ethylenediamine (>99.5%), *N,N'*-dimethylethylenediamine (99%), *N,N,N',N'*-tetramethylethylenediamine (>99.5%), aniline (>99.5%), pyridine (99.8%), *N,N*-dimethylacetamide (99.8%), phenol (>99%), ethylene glycol (99.8%), ethylene glycol dimethyl ether (99.5%), 2,4-dimethyl-2,4-pentanediol (99%), pinacol (98%), and diethyl dimethylmalonate (98%). MMA (Tokyo Kasei; >99%) was dried overnight over calcium chloride and distilled twice from calcium hydride under reduced pressure before use. $RuCl_2(PPh_3)_3$ (Merck; >99%) and Al(O*i*-Pr)$_3$ (Aldrich; >99.99%) were used as received and handled in the glovebox. Dimethyl 2-chloro-2,4,4-trimethylglutarate [$(MMA)_2$−Cl, initiator] was prepared and recrystallized from hexane.[33] Toluene (Wako; >99%) was dried overnight over calcium chloride and distilled over sodium benzophenone. The internal standard for gas chromatography, *n*-octane (Wako; >99%), was 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. A typical example for MMA polymerization with the $(MMA)_2-Cl/RuCl_2(PPh_3)_3/n\text{-}Bu_2NH$ is given below. In a 50 mL round-bottomed flask was placed $RuCl_2(PPh_3)_3$ (101 mg, 0.105 mmol), and toluene (7.5 mL), *n*-octane (0.45 mL), MMA (2.25 mL, 0.0210 mol), and solutions of $(MMA)_2-Cl$ (0.244 mL of 859 mM in toluene, 0.21 mmol) and $n\text{-}Bu_2NH$ (0.072 mL, 0.43 mmol) were added sequentially in this order at room temperature under dry nitrogen. The total volume of the reaction mixture was thus 10.5 mL. Immediately after mixing, aliquots (1.5 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 or tetralin as internal standards.

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. For example, the yield of the products obtained at 20 h was 0.2427 g; i.e., 81%, which was slightly lower than that by gas chromatography (94%) due to the partial loss of polymers during the workup.

^{1}H NMR Analysis of Mixtures of $RuCl_2(PPh_3)_3$ and Amines. The sample preparation was carried out by the syringe technique under dry nitrogen in a baked glass tube equipped with a three-way stopcock. In the glass tube was placed $RuCl_2(PPh_3)_3$ (19.2 mg, 0.020 mmol), and toluene-d_8 (0.80 mL) and a solution of amine (0.20 mL of 400 mM in toluene-d_8, 0.080 mmol) were added sequentially in this order at room temperature under dry nitrogen. Immediately after mixing, an aliquot (0.60 mL) of the solution was injected into an NMR tube (5 mm diameter), which were then sealed and placed in an oil bath kept at 80 °C for 1 h. After the mixture was cooled to 0 °C, ^{1}H NMR spectra were recorded at 0 °C on a JEOL JNM-LA500 spectrometer, operating at 500.16 MHz.

The ratio (r) of free PPh_3 was calculated by the following equation: $r = (5/2)[a/(A - B)]$, where a, A, and B are the peak areas of signal a, all the protons in aromatic regions, and the undeuterated aromatic hydrogens of toluene-d_8, respectively. The peak area of B was obtained from the peak intensity (C) of the undeuterated methyl hydrogens of toluene-d_8, which can be observed at 2.1 ppm without any overlapping of other peaks. The B/C ratio, obtained from the ^{1}H NMR spectrum of the same toluene-d_8 under the same conditions and with the same measurement parameters, was 0.8413 and then was employed for the calculation.

Other Measurements. The MWD, M_n, and M_w/M_n values of polymers were measured in chloroform at 40 °C on three polystyrene gel columns [Shodex K-805L (pore size: 20−1000 Å; 8.0 mm i.d. × 30 cm) × 3; flow rate 1.0 mL/min] connected to a Jasco PU-980 precision pump and a Jasco 930-RI refractive index and 970-UV ultraviolet detectors. The columns were calibrated against 11 standard poly(MMA) samples (Polymer Laboratories; $M_n = 630-220\,000$; $M_w/M_n = 1.06-1.22$) as well as the monomer. ^{1}H NMR spectra of the obtained polymers were recorded in $CDCl_3$ at 25 °C on a JEOL JNM-LA500 spectrometer, operating at 500.16 MHz. Polymers for ^{1}H NMR analysis were fractionated by preparative SEC (column: Shodex K-2002).

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References and Notes

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