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Living Radical Polymerization of *N*,*N*-Dimethylacrylamide with $RuCl_2(PPh_3)_3$-Based Initiating Systems[1]

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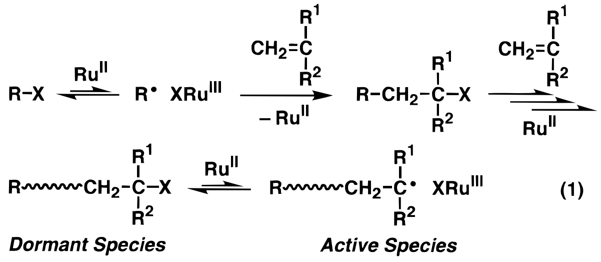
ABSTRACT: *N*,*N*-Dimethylacrylamide (DMAA) was radically polymerized with $RuCl_2(PPh_3)_3$ in conjunction with an alkyl halide (R−X; X = Br, Cl) as an initiator in the presence of Al(O*i*-Pr)$_3$ in toluene at 60−80 °C, where the polymerizations were much faster than that of methacrylates. Specifically with bromides as initiators [CCl_3Br, $CH_3CH(CONMe_2)Br$, $(CH_3)_2C(CONMe_2)Br$, and $(CH_3)_2C(CO_2Et)Br$], the Ru(II) complex induced living radical polymerization of DMAA to give polymers with controlled molecular weights and relatively narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n \sim 1.6$). Similar living polymerizations were also possible for *N*,*N*-diethylacrylamide. ^{1}H NMR analysis of the obtained polymers showed that the polymerization proceeds via activation of the C−Br terminal originating from the bromide initiators by the ruthenium complex.

Introduction

One of the most significant features of radical polymerization is its tolerance to polar functional groups containing oxygen and nitrogen, in contrast to the ionic counterparts where the growing species often undergo side reactions with these groups. Thus, radical polymerization is most widely utilized in addition polymerizations of various vinyl monomers including such polar functional monomers as acryl- and methacrylamides, 2-hydroxyethyl methacrylate, etc.

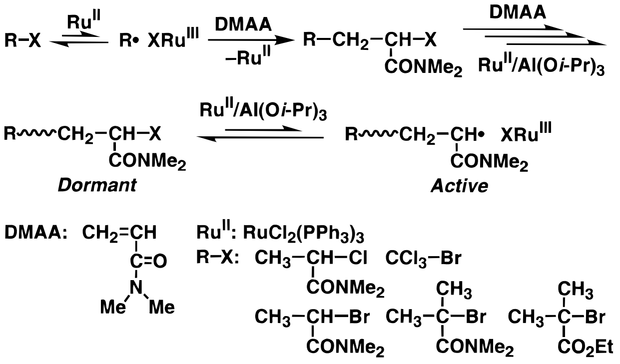
The recent emergence of nitroxide-mediated and metal-catalyzed living radical polymerizations further strengthened their versatility, in which polymer molecular weights and molecular weight distributions (MWDs) can precisely be regulated.[2] Both systems seem to be based on similar concepts where the reactive radical species is in equilibrium with the dormant species with a stable covalent bond. For example, $RuCl_2(PPh_3)_3$-mediated living radical polymerizations involve reversible activation of carbon−halogen bonds via redox reaction of the ruthenium center, such as $\sim\sim$C−X + Ru(II) $\rightleftarrows$ $\sim\sim$C$^\bullet$ X−Ru(III) shown in eq 1. The equilibrium is shifted to the dormant side where the concentration of radical species is most probably kept so low as to diminish bimolecular radical termination and other side reactions.



(1)

The metal-catalyzed systems thus far proved applicable for a variety of radically polymerizable monomers such as methacrylates,[3−12] acrylates,[7,12] styrenes,[12−17] and acrylonitrile,[18] although the complexes and other conditions should be carefully chosen for each monomer.

Scheme 1



Acrylamides are among the representative polar monomers in radical polymerization that contains oxygen and nitrogen. Their reactivity is quite different from those of other monomers as expected from their structures and *Q*/*e* values. *N*,*N*-Dimethylacrylamide (DMAA), the simplest among the N,N-disubstitued acrylamides, can be polymerized radically or anionically to afford water-soluble polymers. Recent reports show better control of anionic polymerizations of DMAA and its ethyl version with cesium countercation[19] or metal alkyls[20] as additives. However, no reports, to our knowledge, have been available for metal-catalyzed living radical polymerizations of DMAA and related acrylamides.

In this study, we employed our ruthenium-based systems, R−X/$RuCl_2(PPh_3)_3$, for living radical polymerization of DMAA (Scheme 1).[3,4] Quite recently, nitroxide-based systems have been employed for the polymerization of DMAA to give polymers with relatively narrow MWDs ($\bar{M}_w/\bar{M}_n \sim 1.6$).[21] The same paper reports the failure of DMAA polymerization with the CuBr/2,2′-bipyridine, which might include radical growth. The negative report seems to be not too surprising, because the copper catalysts are often inefficient in inducing radical addition of amide-containing substrates, most probably due to the formation of inactive Cu complexes with the amide.[22] In contrast, $RuCl_2(PPh_3)_3$ is reported to effectively work even in the presence of amide groups. This paper is to report that

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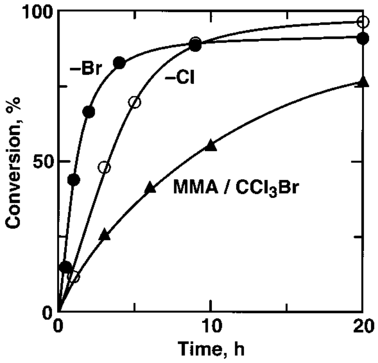

Figure 1. Polymerization of DMAA with $CH_3CH(CONMe_2)X$/$RuCl_2(PPh_3)_3$/$Al(O\textit{i}\text{-}Pr)_3$ in toluene at 80 °C: $[DMAA]_0 = 2.0$ M; $[CH_3CH(CONMe_2)X]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(O\textit{i}\text{-}Pr)_3]_0 = 40$ mM. X = Cl (○); Br (●).

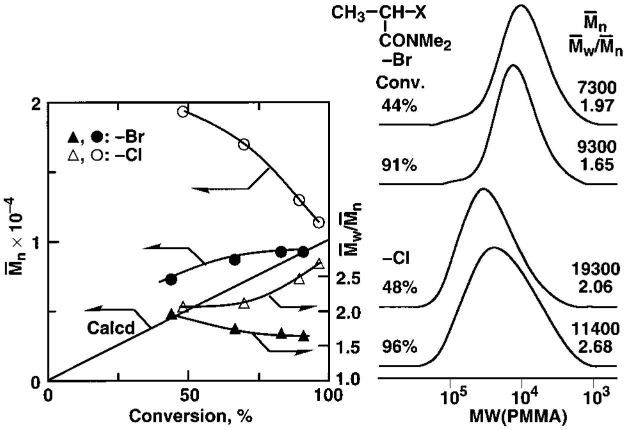

Figure 2. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and SEC curves of poly(DMAA) obtained with $CH_3CH(CONMe_2)X$/$RuCl_2(PPh_3)_3$/$Al(O\textit{i}\text{-}Pr)_3$ in toluene at 80 °C: $[DMAA]_0 = 2.0$ M; $[CH_3CH(CONMe_2)X]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(O\textit{i}\text{-}Pr)_3]_0 = 40$ mM. X = Cl (○, △); Br (●, ▲).

the R−X/$RuCl_2(PPh_3)_3$ initiating system leads to living radical polymerization of DMAA in the presence of $Al(O\textit{i}\text{-}Pr)_3$ to afford polymers with controlled molecular weights and relatively narrow MWDs ($\bar{M}_w/\bar{M}_n \sim 1.6$).[1]

Results and Discussion

1. Polymerization of *N*,*N*-Dimethylacrylamide with R−X (X = Cl, Br)/$RuCl_2(PPh_3)_3$.

Polymerizations of DMAA were carried out with $CH_3CH(CONMe_2)X$ (X = Cl, Br) as initiators coupled with $RuCl_2(PPh_3)_3$ and $Al(O\textit{i}\text{-}Pr)_3$ in toluene at 80 °C (Figure 1). These initiators are also considered as unimer models of poly(DMAA) with chloride or bromide terminal. Both initiators induced smooth polymerizations that reached 90% conversion within 10 h. The polymerization proceeded faster with the bromide than with the chloride, although the conversion with the former leveled off beyond 90%, and invariably DMAA polymerized much faster than MMA under similar conditions. This indicates that the reactivity of acrylamide monomers is also high with the $RuCl_2(PPh_3)_3$-based system as in conventional radical polymerization.

Figure 2 shows the number-average molecular weights ($\bar{M}_n$), $\bar{M}_w/\bar{M}_n$, and size-exclusion chromatograms (SEC) of the poly(DMAA) thus obtained. The $\bar{M}_n$ with the bromide initiator increased with monomer conversion and was close to the calculated value, one polymer chain per the bromide molecule, although they were based on a calibration against poly(MMA) standard samples. The MWDs became narrower with conversion, and the peak shifted to high molecular weight as the polymerization proceeded. This shows that the bromide initiator leads to controlled polymerization of DMAA with the Ru(II) complex. On the other hand, the $\bar{M}_n$ with the chloride were higher than the calculated values and decreased with conversion along with broadening of the MWDs. This is probably due to the low reactivity of the C−Cl bonds relative to the bromide, which results in slow initiation and slow interconversion between the dormant and the radical species. Thus, the bromide initiator is more suited for controlling of DMAA polymerizations. Similar results were also obtained in the $RuCl_2(PPh_3)_3$-catalyzed living radical polymerization of styrene.[16]

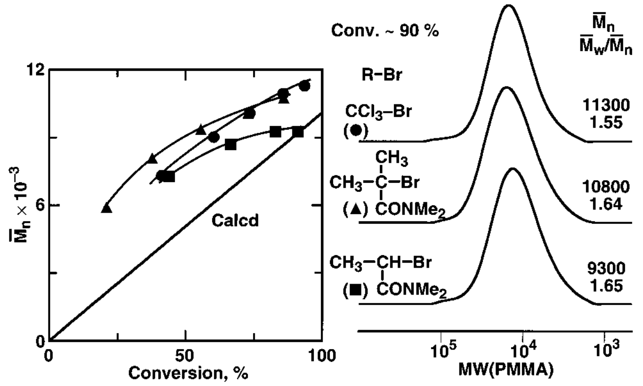

Figure 3. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and SEC curves of poly(DMAA) obtained with R−Br/$RuCl_2(PPh_3)_3$/$Al(O\textit{i}\text{-}Pr)_3$ in toluene at 80 °C: $[DMAA]_0 = 2.0$ M; $[R\text{−}Br]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(O\textit{i}\text{-}Pr)_3]_0 = 40$ mM. (●) CCl_3Br; (▲) $(CH_3)_2C(CONMe_2)Br$; (■) $CH_3CH(CONMe_2)Br$.

To search for more effective initiators, several bromides were also employed in toluene at 80 °C. These include $CH_3CH(CONMe_2)Br$, $(CH_3)_2C(CONMe_2)Br$, and CCl_3Br. The second is a unimer model of poly(*N*,*N*-dimethylmethacrylamide) with a C−Br terminal. All the bromides induced smooth polymerizations at nearly the same rates (cf. Figure 1). As shown in Figure 3, the $\bar{M}_n$ increased with conversion and were close to the calculated values. The MWDs were unimodal and relatively narrow ($\bar{M}_w/\bar{M}_n = 1.5$−$1.6$). Thus, all the bromides can act as effective initiators for DMAA. It is noteworthy that the methacrylamide-type initiator can be effective for the acrylamide; *N*,*N*-dimethylmethacrylamide cannot be polymerized with the Ru(II) complex[23] similarly to conventional radical systems due to the steric hindrance of the monomer.[24]

2. Living Polymerization with CCl_3Br/$RuCl_2(PPh_3)_3$.

In the polymerization with CCl_3Br/$RuCl_2(PPh_3)_3$/$Al(O\textit{i}\text{-}Pr)_3$ in toluene at 80 °C, a fresh feed of DMAA was added to the reaction mixture when the initial charge of the monomer was almost consumed (91% conversion in 6 h). As shown in Figure 4, the ensuing polymerization was slower and needed an additional 50 h to reach 186% (open circles in Figure 4A). Similar experiments at 60 °C showed, in contrast, that the first-phase polymerization was slower than at 80 °C (92% conversion in 17 h) but that the second phase gave an 86% conversion of the added monomer in an additional 37 h without significant retardation (filled circles in Figure 4A).

The $\bar{M}_n$ of the polymers obtained at 80 °C increased with monomer conversion even after the monomer addition but leveled off beyond 150% (open circles in

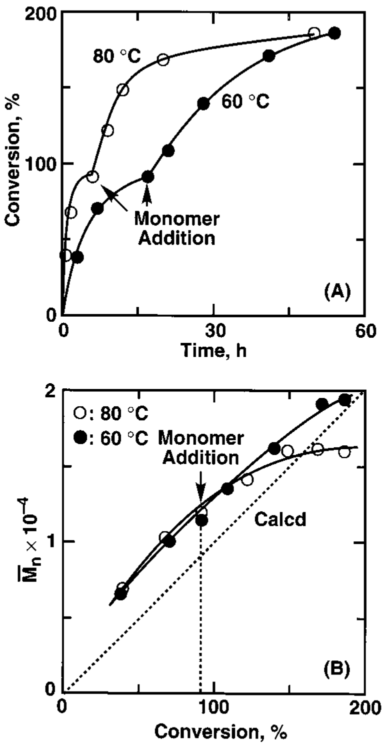

Figure 4. Monomer-addition experiments with $CCl_3Br/RuCl_2(PPh_3)_3/Al(Oi\text{-}Pr)_3$ in toluene at 80 and 60 °C: $[DMAA]_0 = [DMAA]_{add} = 2.0$ M; $[CCl_3Br]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM. (○) 80 °C; (●) 60 °C.

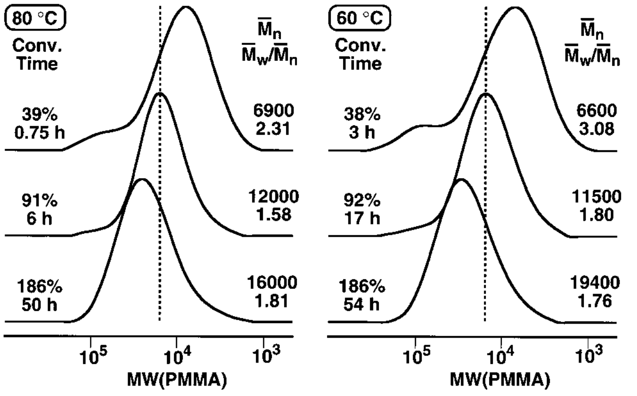

Figure 5. SEC curves of poly(DMAA) obtained with monomer-addition experiments with $CCl_3Br/RuCl_2(PPh_3)_3/Al(Oi\text{-}Pr)_3$ in toluene at 80 and 60 °C: $[DMAA]_0 = [DMAA]_{add} = 2.0$ M; $[CCl_3Br]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM.

Figure 4B). The MWDs became broader after the addition despite the shift of SEC curves to high molecular weight (Figure 5). Evidently, a partial loss of the living end occurs at 80 °C via some side reactions.

In contrast, the $\bar{M}_n$ for 60 °C increased nearly in proportion to conversion throughout the two-stage polymerization and was close to the calculated values (filled circles in Figure 4B). The relatively narrow MWDs shifted to high molecular weight after the monomer addition (Figure 5). Thus, living polymerization of DMAA is possible with the use of a bromide initiator such as CCl_3Br in conjunction with $RuCl_2(PPh_3)_3$ and $Al(Oi\text{-}Pr)_3$ in toluene at 60 °C.

3. Polymer Terminal Structure. For polymer end group analysis, DMAA was polymerized with another bromide, $(CH_3)_2C(CO_2Et)Br$, a unimer model of poly(ethyl methacrylate) with a C−Br bond and ethyl groups suitable for NMR detection.[25] In toluene at 80 °C, the polymerization proceeded at the same rate as with the other bromides. As shown in Figure 6, the $\bar{M}_n$ of the polymers increased with monomer conversion (open circles), similarly to those obtained with the other bromide initiators (cf. Figure 3) The MWDs were narrow similarly ($\bar{M}_w/\bar{M}_n \sim 1.6$). Thus, the methacrylate-type initiator with the C−Br bond also induced living polymerization of DMAA.

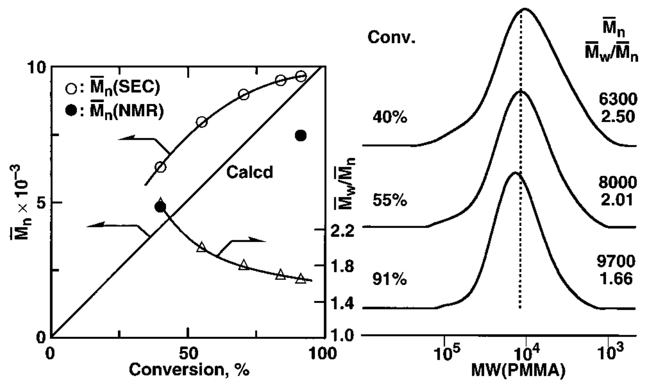

Figure 6. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and SEC curves of poly(DMAA) obtained with $(CH_3)_2C(CO_2Et)Br/RuCl_2(PPh_3)_3/Al(Oi\text{-}Pr)_3$ in toluene at 80 °C: $[DMAA]_0 = 2.0$ M; $[(CH_3)_2C(CO_2Et)Br]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(Oi\text{-}Pr)_3]_0 = 40$ mM.

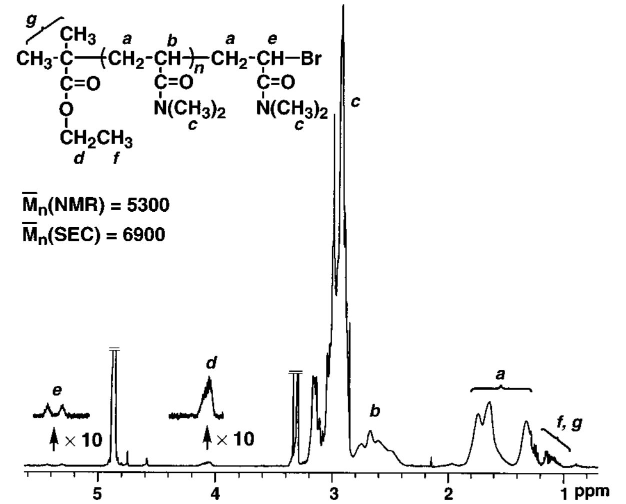

Figure 7. ^1H NMR spectrum (500 MHz, in CD_3OD at 25 °C) of poly(DMAA) obtained with $(CH_3)_2C(CO_2Et)Br/RuCl_2(PPh_3)_3/Al(Oi\text{-}Pr)_3$ in toluene at 80 °C.

The polymers thus obtained with $(CH_3)_2C(CO_2Et)Br$ (44% DMAA conversion) were analyzed by ^1H NMR spectroscopy after purification by preparative SEC (see Experimental Section). As shown in Figure 7, there appeared characteristic signals of the initiator moiety; e.g., peak *d* was attributed to the methylene protons of the ethyl ester group at the α-end, in addition to the large absorptions of the main-chain repeat units (*a*, *b*, and *c*). The $\bar{M}_n$ [$\bar{M}_n$(NMR)] of the sample, obtained from the peak intensity ratio of ($b + c$) to *d* on assumption that one initiator moiety is attached to one poly(DMAA) chain, was 5300. The $\bar{M}_n$(SEC) of the purified sample was 6900,[26] higher than the $\bar{M}_n$(NMR), because the former was determined on the basis of a PMMA calibration. A similar analysis of the poly(DMAA) obtained at 90% conversion gave $\bar{M}_n$(NMR) = 8900 and $\bar{M}_n$(SEC) = 11 500. The ratio of $\bar{M}_n$(NMR) to $\bar{M}_n$(SEC) is 0.77 for both samples. When we also apply this ratio to $\bar{M}_n$(SEC)

Table 1. Polymerization of DEAA and NIPAA with R−Br/RuCl$_2$(PPh$_3$)$_3$/Al(O*i*-Pr)$_3$[a]

entry	monomer	R−Br	time, h	conv, %	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
1	DEAA	CCl$_3$Br	0.5	25	3000	3.07
2			2	53	4600	1.97
3			8	93	5500	1.59
4	NIPAA	(CH$_3$)$_2$C(CO$_2$Et)Br	2	43	6100	2.12
5			4.5	54	6800	2.24
6			551	89	8100	2.60

[a] In toluene at 80 °C (for DEAA) and 100 °C (for NIPAA); [M]$_0$/[R−Br]$_0$/[RuCl$_2$(PPh$_3$)$_3$]$_0$/[Al(O*i*-Pr)$_3$]$_0$ = 2000/20/10/40 mM.

of as-obtained polymers to estimate $\bar{M}_n$(NMR) (open circles in Figure 6), the $\bar{M}_n$(NMR) almost agreed with the calculated values.

The small absorption around 5.4 ppm (peak *e*) was attributed to the methine proton adjacent to the ω-end bromine, showing that the polymerization is indeed initiated from the bromide initiator. The ratio of the ω- to α-end obtained by their peak intensity ratio was 0.59, which suggests partial loss of the bromide ω-terminal during the polymerization or the workup processes.

4. Polymerization of Other Acrylamides. We investigated briefly polymerizations of other acrylamides, *N*,*N*-diethylacrylamide (DEAA) and *N*-isopropylacrylamide (NIPAA), with the use of the R−Br/RuCl$_2$(PPh$_3$)$_3$/Al(O*i*-Pr)$_3$ initiating system in toluene (Table 1). Similar controlled polymerizations of DEAA were achieved to afford polymers with controlled molecular weights and relatively narrow MWDs. The Ru(II)-based system induced the polymerization of NIPAA, but the polymerizations were not quantitative and uncontrolled in contrast to the N,N-disubstitued acrylamides such as DMAA and DEAA.

In conclusion, a ruthenium(II) complex, RuCl$_2$(PPh$_3$)$_3$, has been shown to be tolerant to amide functions and induces living radical polymerization of DMAA. The suitable initiators include bromides such as CCl$_3$Br. The polymerization proceeds via activation of the C−Br bond originated from the initiator by the ruthenium complex.

Experimental Section

Materials. DMAA (Wako Chemicals, purity >98%) and DEAA (Kohjin, purity >99%) were dried overnight over calcium chloride and distilled over calcium hydride under reduced pressure before use. NIPAA (Wako Chemicals, purity >98%) was recrystallized from *n*-hexane. DMMA was synthesized from methacryloyl chloride and dimethylamine in THF at 0 °C and distilled over calcium hydride under reduced pressure. RuCl$_2$(PPh$_3$)$_3$ (Merck, purity >99%) and Al(O*i*-Pr)$_3$ (Aldrich, purity >99.99%) were used as received and handled in a glovebox under a moisture- and oxygen-free argon atmosphere (H$_2$O <1 ppm; O$_2$ <1 ppm). CCl$_3$Br and (CH$_3$)$_2$C(CO$_2$Et)Br (both Wako Chemicals, purity >99%) were double distilled over calcium hydride under atmospheric and reduced pressure, respectively, before use. Toluene (solvent) and tetralin (internal standards for gas chromatographic analysis of the monomers) were dried overnight over calcium chloride, distilled twice over calcium hydride, and bubbled with dry nitrogen for more than 15 min immediately before use.

Synthesis of Initiators. *N*,*N*-Dimethyl-2-chloropropanamide [CH$_3$CH(CONMe$_2$)Cl] was prepared by the reaction between 2-chloropropionyl chloride (Tokyo Kasei) and dimethylamine (Aldrich Chemical, 2.0 M solution in THF). In a round-bottomed flask filled with dry nitrogen, 2-chloropropionyl chloride (20.0 mL, 0.206 mol) was added dropwise to dimethylamine solution (206 mL, 0.412 mol). The reaction mixture was stirred at room temperature for 24 h and filtered. The filtrate was evaporated to remove THF. The crude products were distilled under reduced pressure to give the product (purity >99% by ^{1}H NMR). CH$_3$CH(CONMe$_2$)Br and (CH$_3$)$_2$C(CONMe$_2$)Br were prepared by similar methods.

Polymerization Procedures. Polymerization was carried out by the syringe technique under dry nitrogen in sealed glass tubes. A typical example for polymerization of DMAA with CCl$_3$Br/RuCl$_2$(PPh$_3$)$_3$/Al(O*i*-Pr)$_3$ is given below: RuCl$_2$(PPh$_3$)$_3$ (0.0959 g) was dissolved with toluene (4.12 mL) and tetralin (0.42 mL). Then DMAA (2.06 mL), a toluene solution of Al(O*i*-Pr)$_3$ (3.20 mL), and a toluene solution of CCl$_3$Br (0.20 mL) were added into the RuCl$_2$(PPh$_3$)$_3$ solution, sequentially in this order. Immediately after mixing, the solution was placed in an oil bath at 80 °C. 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 tetralin as internal standard for DMAA. The quenched reaction solutions were evaporated to dryness to give the products, which were subsequently dried overnight.

Measurements. The MWD, $\bar{M}_n$, and $\bar{M}_w/\bar{M}_n$ ratios of the polymers were measured by size-exclusion chromatography in DMF containing 10 mM LiBr at 40 °C on three polystyrene gel columns (Shodex KF-805L × 3) that were connected to a Jasco PU-980 precision pump and a Jasco 930-RI refractive index detector. The columns were calibrated against nine standard poly(MMA) samples (Polymer Laboratories; $\bar{M}_n$ = 3100−1 200 000, $\bar{M}_w/\bar{M}_n$ = 1.06−1.22) as well as MMA monomer. ^{1}H NMR spectra were recorded in CD$_3$OD 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 as DMF eluent (column: Tosoh TSK-gel α-3000).

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(23) No polymerization of *N*,*N*-dimethylmethacrylamide occurred with H−(MMA)$_2$−Cl/RuCl$_2$(PPh$_3$)$_3$/Al(O*i*-Pr)$_3$ (20/10/40 mM) in toluene at 80 °C as long as 50 days.
(24) N,N-Disubstituted methacrylamides cannot be homopolymerized by conventional radical polymerization, whereas they can be compolymerized with radically polymerizable monomers such as methyl acrylate. See: Yokota, K.; Oda, J. *Kogyo Kagaku Zasshi (J. Ind. Chem.)* **1970**, *73*, 224.
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(26) The $\bar{M}_n$(SEC) (6900) of a sample after the purification was slightly higher than that before the purification (6300) (see Figure 6) due to some loss of low molecular weight fractions along with separation of low molecular weight catalyst residues in purification.

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