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Living Radical Polymerization of Methyl Methacrylate with Ruthenium Complex: Formation of Polymers with Controlled Molecular Weights and Very Narrow Distributions[1]

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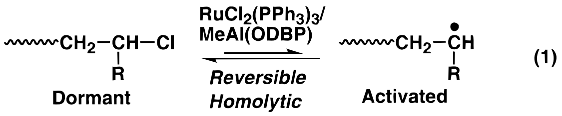
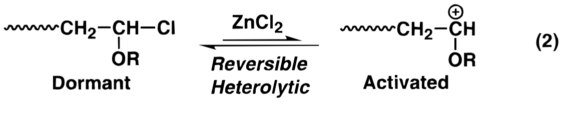
Introduction. Recently, we reported the living polymerization of methyl methacrylate (MMA) with the initiating system of carbon tetrachloride, dichlorotris(triphenylphosphine)ruthenium(II) [$RuCl_2(PPh_3)_3$], and methylaluminum bis(2,6-di-*tert*-butylphenoxide) [MeAl(ODBP)$_2$].[2] This polymerization appears to be a radical process that involves a *reversible* and *homolytic* cleavage of the carbon−halogen terminal assisted by the transition metal complex (eq 1). The ruthenium(II) complex interacts with CCl_4 (as an initiator) to be oxidized from divalent to trivalent followed by the radical addition of $CCl_3^{\bullet}$ to MMA, and then the Ru(III) species is reduced to the original Ru(II) complex to give the CCl_4−MMA adduct with a terminal C−Cl bond.[3] The polymerization proceeds via similar repetitive addition of MMA to the radical species, reversibly generated from the covalent species with the C−Cl terminal. A similar approach to controlled radical polymerizations has been reported independently by Wang and Matyjaszewski.[4]



$$\sim\!\sim CH_2-\underset{R}{CH}-Cl \underset{\text{Reversible Homolytic}}{\overset{RuCl_2(PPh_3)_3/ MeAl(ODBP)}{\rightleftharpoons}} \sim\!\sim CH_2-\underset{R}{\overset{\bullet}{C}H} \quad (1)$$

Dormant Activated

Several other attempts at achieving living/controlled radical polymerizations based on methods different from ours have been made worldwide,[5−16] where stable bonds in the dormant species are cleaved subsequently thermally, photochemically, or by added radical species. In contrast, the Ru(II)-catalyzed polymerization[2] is based on the reversible activation of the covalent carbon−halogen bond by $RuCl_2(PPh_3)_3$ as a redox activator. Our concept of the living radical polymerization is originally derived from living cationic counterparts, where the terminal C−Cl bond is *reversible* and *heterolytically* activated by a Lewis acid (eq 2).[17]



$$\sim\!\sim CH_2-\underset{OR}{CH}-Cl \underset{\text{Reversible Heterolytic}}{\overset{ZnCl_2}{\rightleftharpoons}} \sim\!\sim CH_2-\underset{OR}{\overset{\oplus}{C}H} \quad (2)$$

Dormant Activated

This study is to develop new ruthenium-based living radical polymerizations of MMA with use of alternative initiators and added aluminum compounds in place of CCl_4 and MeAl(ODBP)$_2$, respectively. For this, we employed α-halocarbonyl compounds **1** as potent initiators so that the structures simulate the polymer terminal that may have a halogen atom and a carbonyl group attached to the same carbon atom (cf. eq 1). These include 1,1,1-trichloroacetone (CCl_3COCH_3), α,α-dichloroacetophenone ($CHCl_2COC_6H_5$), and ethyl 2-bromoisobutyrate [$(CH_3)_2CBrCO_2C_2H_5$]. For the added metal compound, aluminum triisopropoxide [Al(O*i*Pr)$_3$] was employed because it gave the best results among metal alkoxides used in preliminary experiments.[18] Herein we report that these new initiating systems give poly(MMA) with very narrow MWDs ($\bar{M}_w/\bar{M}_n < 1.1$) and precisely controlled molecular weights.

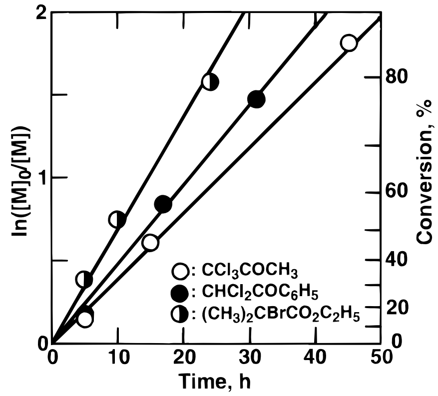


Figure 1. First-order plots for the polymerization of MMA with **1**/$RuCl_2(PPh_3)_3$/Al(O*i*Pr)$_3$ in toluene at 80 °C: $[MMA]_0 = 2.0$ M; $[\mathbf{1}]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(OiPr)_3]_0 = 40$ mM. **1**: CCl_3COCH_3; $CHCl_2COC_6H_5$; $(CH_3)_2CBrCO_2C_2H_5$.

Results and Discussion. (a) Living Polymerization of MMA. MMA was polymerized with the three α-halocarbonyl compounds in conjunction with $RuCl_2(PPh_3)_3$ and Al(O*i*Pr)$_3$ in toluene at 80 °C.[19] All three systems induced relatively slow but quantitative polymerizations, and the conversion reached over 90% in 60−80 h; time for 50% conversion: CCl_3COCH_3, 16 h; $CHCl_2COC_6H_5$, 14 h; $(CH_3)_2CBrCO_2C_2H_5$, 9 h. As shown in Figure 1, the logarithmic conversion data, ln([M]$_0$/[M]) ([M] is the monomer concentration at time *t*), plotted against time *t*, gave straight lines passing through the origin, which shows constant concentrations of the growing species during the polymerizations.

The MWDs obtained with the two ketone initiators were narrow ($\bar{M}_w/\bar{M}_n < 1.2$), and the polydispersity ratios were smaller than those obtained with CCl_4 under the same conditions (Figure 2).[20] The number-average molecular weights ($\bar{M}_n$) increased in direct proportion to monomer conversion and agreed well with the calculated values based on the assumption that one molecule of the initiators generates one living polymer chain.

To examine the living nature of the polymerizations with the two chloroketones, a fresh feed of monomer was added to the reaction mixtures when the initial charge of the monomer had been consumed. The added monomer feed was smoothly polymerized, and the $\bar{M}_n$ of the polymer further increased in direct proportion to monomer conversion and agreed well with the calculated values (Figure 3). The MWD stayed very narrow even after monomer addition, and especially $CHCl_2COC_6H_5$ gave the narrowest MWD ($\bar{M}_w/\bar{M}_n < 1.1$). Furthermore, the polymers obtained with the aromatic ketone showed ultraviolet absorption unlike the polymers from the other two initiators that lack aromatic moieties. The ultraviolet and the refractive index traces in size exclusion chromatography (SEC) were almost identical over the entire molecular weight range. The ultraviolet absorption thus demonstrates the attachment of the phenyl group at the polymer α-terminal (see below), which shows that $CHCl_2COC_6H_5$ functions as the initiator. Thus, living polymerizations of MMA can be achieved with the α-halocarbonyl compounds/$RuCl_2(PPh_3)_3$/Al(O*i*Pr)$_3$ to form polymers with controlled molecular weights and very narrow MWDs.

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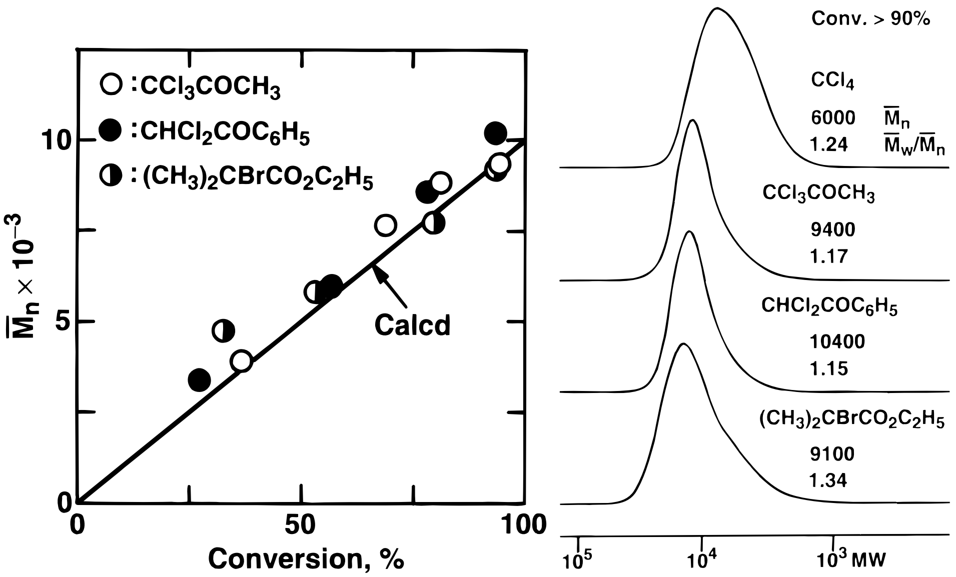


Figure 2. $\bar{M}_n$ and MWD curves of poly(MMA) obtained with **1**/RuCl$_2$(PPh$_3$)$_3$/Al(O*i*Pr)$_3$ in toluene at 80 °C: [MMA]$_0$ = 2.0 M; [**1**]$_0$ = 20 mM; [RuCl$_2$(PPh$_3$)$_3$]$_0$ = 10 mM; [Al(O*i*Pr)$_3$]$_0$ = 40 mM.

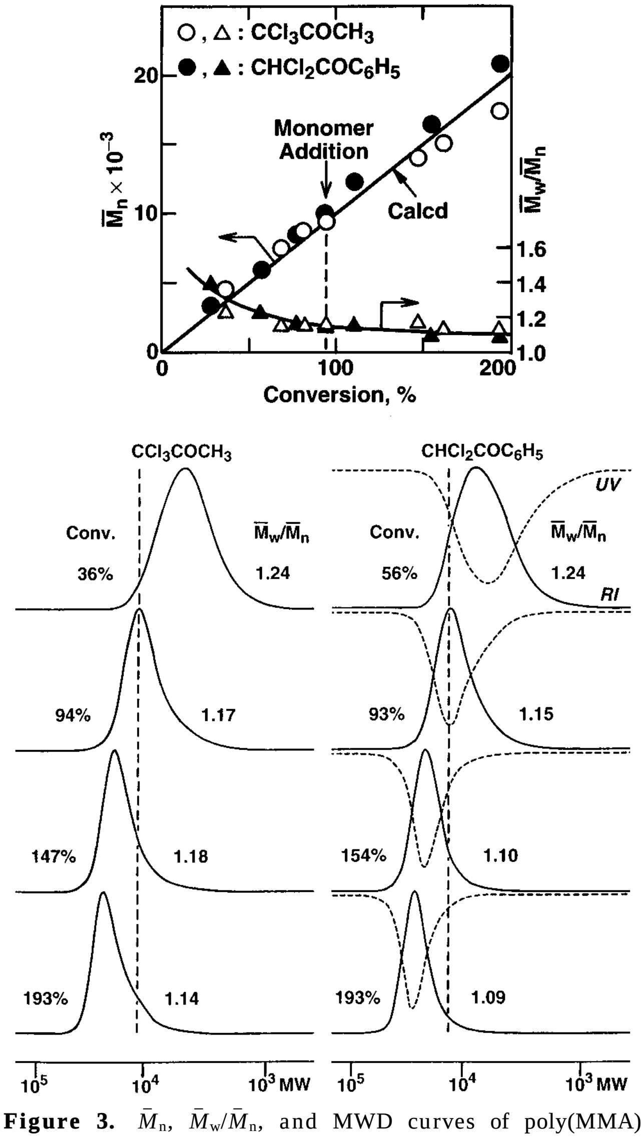


Figure 3. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(MMA) obtained in a monomer addition experiment with **1**/RuCl$_2$(PPh$_3$)$_3$/Al(O*i*Pr)$_3$ in toluene at 80 °C: [MMA]$_0$ = [MMA]$_{add}$ = 2.0 M; [**1**]$_0$ = 40 mM; [RuCl$_2$(PPh$_3$)$_3$]$_0$ = 10 mM; [Al(O*i*Pr)$_3$]$_0$ = 40 mM. (—) RI detection; (- - -) UV detection at 256 nm.

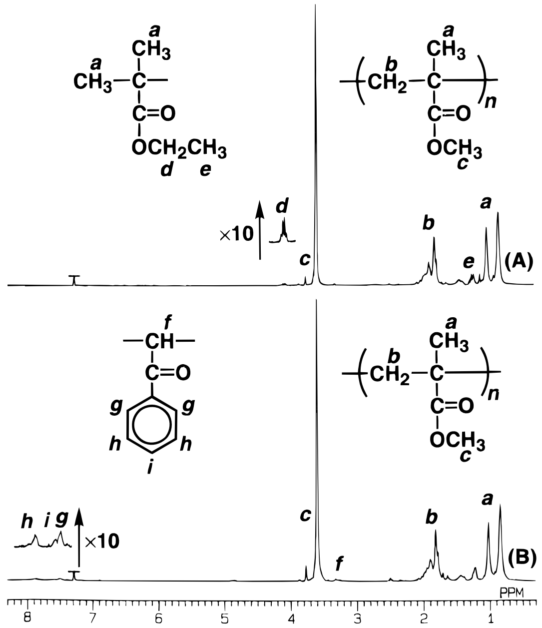


Figure 4. ^{1}H NMR spectra of poly(MMA) obtained with **1**/RuCl$_2$(PPh$_3$)$_3$/Al(O*i*Pr)$_3$ in toluene at 80 °C. **1**: (CH$_3$)$_2$CBrCO$_2$C$_2$H$_5$ (A); CHCl$_2$COC$_6$H$_5$ (B).

(b) End-Group Analysis. The terminal structures of the obtained polymers were then analyzed by ^{1}H NMR spectroscopy (Figure 4). Besides the large absorptions of the repeat units of MMA, there are characteristic signals originating from the α-halocarbonyl compounds as initiators. The methylene protons of the ethyl ester group derived from (CH$_3$)$_2$CBrCO$_2$C$_2$H$_5$ and the *meta* protons of the phenyl group from CHCl$_2$COC$_6$H$_5$ were seen at 4.1 ppm in Figure 4A and 7.9 ppm in Figure 4B, respectively. The small peak at 3.8 ppm next to a large peak c is that of the methyl ester group adjacent to the terminal chlorine at the *ω*-end. The $\overline{DP}_n$ for these poly(MMA) was determined from the peak intensity ratio of the methylene d or the *m*-phenyl protons h to the methyl ester protons c of the main chain (2c/3d or 2c/3h, respectively). As shown in Table 1, $\overline{DP}_n$'s are in excellent agreement with the values from size exclusion chromatography calibrated

Table 1. $\overline{\mathrm{DP}}_n$ and $\bar{F}_n$ of Poly(MMA) Obtained with 1/RuCl$_2$(PPh$_3$)$_3$/Al(O*i*Pr)$_3$[a]

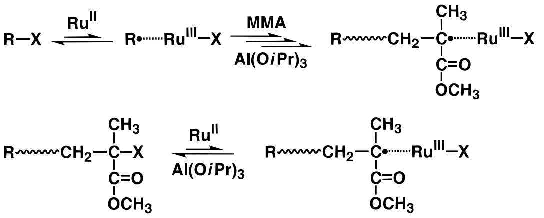
initiator (**1**)	$\overline{\mathrm{DP}}_n$ SEC[b]	$\overline{\mathrm{DP}}_n$ NMR[c]	$\bar{F}_n$[d]
$(CH_3)_2CBrCO_2C_2H_5$	48.9	46.1	1.06
$CHCl_2COC_6H_5$	58.4	58.0	1.01

[a] $[M]_0/[\mathbf{1}]_0/[RuCl_2(PPh_3)_3]_0/[Al(OiPr)_3]_0 = 2000/20/10/40$ mM; in toluene, at 80 °C. [b] $[\bar{M}_n(\mathrm{SEC}) - \mathrm{MW(initiator\ moiety)}]/\mathrm{MW(MMA)}$. [c] From ^{1}H NMR peak intensity ratio; 2c/3d [$(CH_3)_2CBrCO_2C_2H_5$], 2c/3h [$CHCl_2COC_6H_5$]. See Figure 4. [d] $\overline{\mathrm{DP}}_n(\mathrm{SEC})/\overline{\mathrm{DP}}_n(\mathrm{NMR})$.

against standard poly(MMA) samples.[20] The number-average end functionality ($\bar{F}_n$) of the initiator moiety was determined from $\overline{\mathrm{DP}}_n$(SEC)/$\overline{\mathrm{DP}}_n$(NMR). The values are very close to unity, indicating that these α-halocarbonyl compounds in fact serve as the initiator that forms one living poly(MMA) chain per molecule.

Possibly, $CHCl_2COC_6H_5$ acts as a bifunctional initiator, because this compound has two chlorine atoms at the α-carbon adjacent to the carbonyl group. In fact, a methine group [$C_6H_5C(O)CHCl-CH_2$], which would be generated if it acts as a monofunctional initiator, cannot be seen in 5.2 ppm, but a methine group f [$CH_2-(C_6H_5C(O))CH-CH_2$] was observed at 3.2 ppm which would be generated if it acts as a bifunctional initiator. This point is now under investigation. At any rate, the α-halocarbonyl compounds are efficient initiators which quantitatively generate living poly(MMA) chains.

These results indicate that the living polymerization proceeds via the activation of carbon−halogen bonds derived from the α-halocarbonyl compounds by the Ru(II) complex in the presence of the aluminum compound (eq 3). These systems have thus generalized our notion that the living radical polymerizations proceed via the reversible and homolytic cleavage of carbon−halogen bonds by transition metal complexes. In conclusion, the α-halocarbonyl compounds/RuCl$_2$(PPh$_3$)$_3$/Al(O*i*Pr)$_3$ system induced living polymerization of MMA in toluene even at 80 °C to give well-controlled polymers with very narrow MWDs. Extensive studies are now underway in our laboratories to determine the scope and mechanism of the ruthenium-based living radical polymerization.



$$R{-}X \underset{}{\overset{Ru^{II}}{\rightleftharpoons}} R\bullet\cdots Ru^{III}{-}X \underset{Al(OiPr)_3}{\xrightarrow{MMA}} R{\sim\sim}CH_2{-}C(CH_3)(C{=}O)(OCH_3)\bullet\cdots Ru^{III}{-}X$$

$$R{\sim\sim}CH_2{-}C(CH_3)(C{=}O)(OCH_3){-}X \underset{Al(OiPr)_3}{\overset{Ru^{II}}{\rightleftharpoons}} R{\sim\sim}CH_2{-}C(CH_3)(C{=}O)(OCH_3)\bullet\cdots Ru^{III}{-}X \quad (3)$$

References and Notes

(1) This work was presented in part at the following meetings. (a) The 209th National Meeting on the American Chemical Society, Anaheim, CA, April 1995; POLY-180. Sawamoto, M.; Kato, M.; Kamigaito, M.; Higashimura, T. *Polym. Prepr.* (*Am. Chem. Soc., Div. Polym. Chem.*) **1995**, *36* (1), 539. (b) The 44th Annual Meeting of the Society of Polymer Science, Yokohama, Japan, May 1995; paper IPd024: Ando, T.; Kato, M.; Kamigaito, M. Sawamoto, M. *Polym. Prepr. Jpn.* **1995**, *44* (2), 110.

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(18) Ando, T.; Kato, M.; Kamigaito, M. Sawamoto, M. *Polym. Prepr. Jpn.* **1995**, *44* (2), 111. The role of the added aluminum alkoxide has not been clarified yet and is now under investigation. It may interact with the carbonyl group at the polymer terminal or of the monomer to facilitate the polymerization or induce ligand exchange with the ruthenium complex to produce more active complex.

(19) The polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock. All reagents were used after ordinary purifications, and the toluene solvent was bubbled with dry nitrogen for more than 15 min immediately before use. A typical example with $CHCl_2COC_6H_5$ is given below. The polymerization was initiated by adding, via dry syringes, solutions of Al(O*i*Pr)$_3$ (0.80 mL) and RuCl$_2$(PPh$_3$)$_3$ (1.0 mL) in toluene sequentially, in this order, into a mixture (0.70 mL) of MMA (0.54 mL), *n*-octane (0.16 mL), and $CHCl_2COC_6H_5$ (0.0071 mL) in toluene at 25 °C. The total volume of the reaction mixture was 2.5 mL. Immediately after mixing, the solution was placed in a water bath kept at 80 °C. In predetermined intervals, the polymerization was terminated by cooling the reaction mixtures to −78 °C and adding methanol (~1.0 mL). 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 (~20 mL) and rigorously shaken with an absorbent [Kyowaad-2000G-7 ($Mg_{0.7}Al_{0.3}O_{1.15}$); Kyowa Chemical Industry Co., Ltd.] (~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 vacuum dried overnight.

(20) The $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD of the polymers were determined by size exclusion chromatography in chloroform with a calibration based on 11 poly(MMA) standard samples (Polymer Laboratories; $\bar{M}_n$ = 630−220 000; $\bar{M}_w/\bar{M}_n$ = 1.06−1.22).

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