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Polymerization of Methyl Methacrylate with the Carbon Tetrachloride/Dichlorotris(triphenylphosphine)ruthenium(II)/Methylaluminum Bis(2,6-di-*tert*-butylphenoxide) Initiating System: Possibility of Living Radical Polymerization[1]

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Introduction. Because of the virtual absence of chain transfer, termination, and other side reactions, living polymerization is among the best methods for the synthesis of polymers with controlled molecular weights and architectures.[4] It is therefore not surprising that, since the discovery of the now classical anionic systems,[5] a number of living polymerizations have been developed by utilizing almost all of the mechanisms of addition and ring-opening polymerizations.[4] Perhaps the only remaining frontier in this aspect would be living radical polymerization, for which attempts have in fact been started quite recently in several research groups.[6-11] In our view, however, well-defined, highly versatile living radical polymerizations are still beyond our reach, and no general principles have been established to achieve living or controlled radical polymerizations. The primary reasons for the difficulty include the high reactivity or low stability of free radicals and their facile coupling and/or disproportionation reactions.

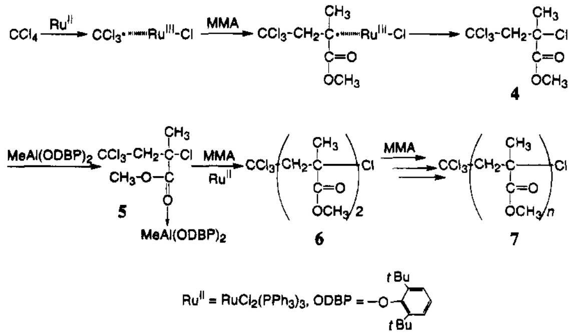
Recently, we have achieved living cationic polymerization of vinyl compounds, where control of the polymerization has long been considered very difficult, due to the instability of the highly reactive carbocationic growing species and their tendency to undergo chain-transfer reactions.[12,13] In these living cationic processes, the unstable growing carbocations are considered to be "stabilized" via the reversible formation of the corresponding covalent or dormant species that rapidly exchange with the ionic counterparts.[14] For example, the living cationic polymerizations of vinyl ethers with the HCl/ZnCl$_2$ initiating system involve the intermediate (**1**) with a carbon–chlorine terminal bond derived from hydrogen chloride (initiator) and the monomer, and the covalent end in **1** is reversibly activated by ZnCl$_2$ into the carbocationic form (**2**) that actually propagates with monomer (eq 1). Our recent NMR analysis of relevant model reactions has indeed shown the Lewis acid-assisted, reversible formation of carbocations from the HCl–vinyl ether adducts and the rapid exchange processes between them.[14]

$$\sim\sim\sim\mathrm{CH_2{-}\underset{OR}{CH}{-}Cl} + \mathrm{ZnCl_2} \rightleftharpoons \sim\sim\sim\mathrm{CH_2{-}\underset{OR}{\overset{\oplus}{C}H}\cdots\overset{\ominus}{Cl}{-}ZnCl_2} \quad (1)$$

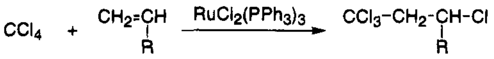
1 **2**

By analogy with the living cationic polymerization, it is expected that well-controlled and perhaps living radical polymerization would also be realized, if the growing radical is reversibly stabilized by a covalent species such as one with the carbon–chlorine bond ($\sim\sim\sim$C–Cl $\rightleftarrows$ $\sim\sim\sim$C$^{\bullet}$). Thus, in this study, we examined the possibility of living radical polymerization via such a mechanism where the dormant intermediate with a carbon–chlorine terminal bond might reversibly be converted into a radical growing species by organometallic compounds.

Scheme 1. Proposed Pathway of the Polymerization of MMA with CCl$_4$/RuCl$_2$(PPh$_3$)$_3$/MeAl(ODBP)$_2$



It has been reported that the reaction of carbon tetrachloride (CCl$_4$) with an alkene (CH$_2$=CHR) catalyzed by dichlorotris(triphenylphosphine)ruthenium(II) [RuCl$_2$(PPh$_3$)$_3$; Ph = C$_6$H$_5$] gives the 1:1 adduct (**3**) in high selectivity and in high yield (eq 2).[15] According to later studies,[16,17] this reaction proceeds by a radical mechanism in which the transient radical intermediate is confined in the coordination sphere of the ruthenium complex and is thereby stabilized to give the high selectivity for the adduct formation.



$$\mathrm{CCl_4} + \mathrm{CH_2{=}\underset{R}{CH}} \xrightarrow{\mathrm{RuCl_2(PPh_3)_3}} \mathrm{CCl_3{-}CH_2{-}\underset{R}{CH}{-}Cl} \quad (2)$$

3

It then occurred to us that, if the carbon–chlorine bond of the adduct **3** or its polymeric analogs is further converted ("activated") into a radical by RuCl$_2$(PPh$_3$)$_3$, the resulting radical species could successively react (propagate) with alkene monomers without undesirable side reactions to induce *living radical* polymerization. Herein we report possible living radical polymerization of methyl methacrylate (MMA) with an initiating system that consists of CCl$_4$ and RuCl$_2$(PPh$_3$)$_3$.[1]

Results and Discussion. (a) Polymerization of MMA. Polymerization of MMA with the CCl$_4$/RuCl$_2$(PPh$_3$)$_3$ system was first attempted in toluene at 60 °C ([MMA]$_0$ = 2.0 M, [CCl$_4$]$_0$ = 20 mM, [RuCl$_2$(PPh$_3$)$_3$]$_0$ = 10 mM). Under these conditions, however, no polymer was obtained even after 40 h.

Thus we additionally employed methylaluminum bis(2,6-di-*tert*-butylphenoxide) [MeAl(ODBP)$_2$] (40 mM) in an attempt to activate the carbon–chlorine bond of the CCl$_4$–MMA adduct (**4**), which was expected to form (cf. eq 2 and Scheme 1). With the ternary initiating system, CCl$_4$/RuCl$_2$(PPh$_3$)$_3$/MeAl(ODBP)$_2$, the polymerization of MMA indeed occurred without an induction period, and monomer conversion reached 90% in 4 h (Figure 1).[18] Figure 1 also shows the logarithmic conversion data (filled circles), i.e., ln([M]$_0$/[M]) vs t, where [M]$_0$ and [M] denote the monomer concentrations at time 0 and t, respectively. The first-order rate plots are linear, indicating that the polymerization is internally of first order with respect to monomer and that the concentration of the growing species remains constant. In sharp contrast, no polymerizations occurred in the absence of RuCl$_2$(PPh$_3$)$_3$ or MeAl(ODBP)$_2$. These control experiments show that the three components, CCl$_4$, RuCl$_2$-

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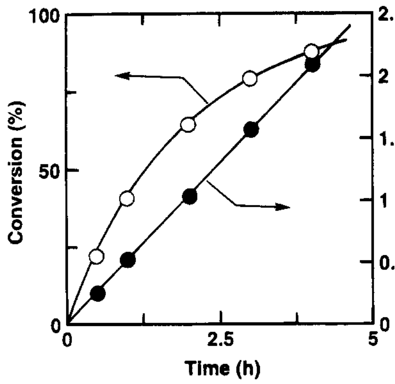

Figure 1. Polymerization of MMA with $CCl_4/RuCl_2(PPh_3)_3/MeAl(ODBP)_2$ in toluene at 60 °C: $[MMA]_0 = 2.0$ M; $[CCl_4]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[MeAl(ODBP)_2]_0 = 40$ mM.

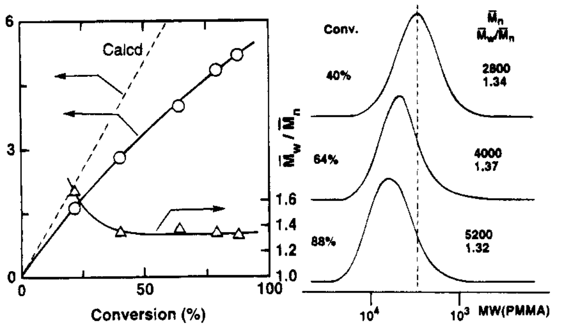

Figure 2. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(MMA) obtained with $CCl_4/RuCl_2(PPh_3)_3/MeAl(ODBP)_2$ in toluene at 60 °C: $[MMA]_0 = 2.0$ M; $[CCl_4]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[MeAl(ODBP)_2]_0 = 40$ mM.

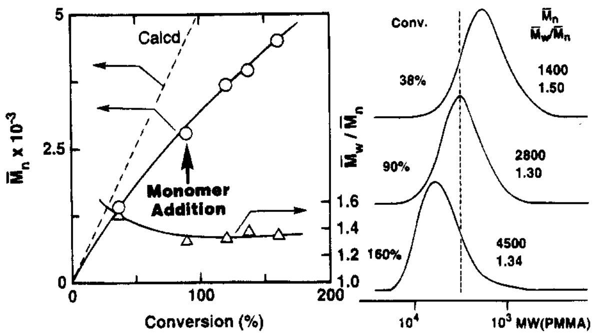

Figure 3. $\bar{M}_n$, $\bar{M}_w/\bar{M}_n$, and MWD curves of poly(MMA) obtained in a monomer-addition experiment with $CCl_4/RuCl_2(PPh_3)_3/MeAl(ODBP)_2$ in toluene at 60 °C: $[MMA]_0 = [MMA]_{add} = 2.0$ M; $[CCl_4]_0 = 40$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[MeAl(ODBP)_2]_0 = 40$ mM.

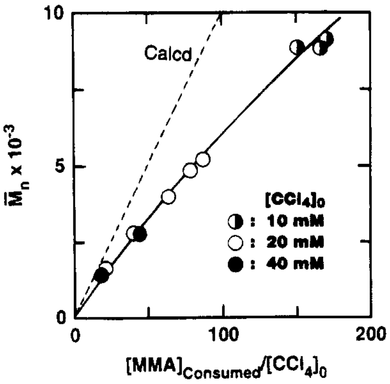

Figure 4. $\bar{M}_n$ as a function of $[CCl_4]_0$ in the polymerization of MMA with $CCl_4/RuCl_2(PPh_3)_3/MeAl(ODBP)_2$ in toluene at 60 °C: $[MMA]_0 = 2.0$ M; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[MeAl(ODBP)_2]_0 = 40$ mM; MMA conversion = 20–90%. $[CCl_4]_0$ (mM): (◑) 10; (○) 20; (●) 40.

$(PPh_3)_3$, and $MeAl(ODBP)_2$, are necessary in polymerizing MMA under these conditions.

Figure 2 shows the number-average molecular weights ($\bar{M}_n$), the polydispersities ($\bar{M}_w/\bar{M}_n$), and the molecular weight distributions (MWDs) of the polymers obtained with the three-component initiating system.[19] The $\bar{M}_n$ increased with monomer conversion, though less than the calculated values assuming that one polymer chain is formed per molecule of CCl_4. The $\bar{M}_w/\bar{M}_n$ of the polymer was fairly narrow ($\bar{M}_w/\bar{M}_n = 1.3$–$1.4$) and became narrower as conversion increased. These results suggest the generation of long-lived growing species.

To confirm the living nature of the system furthermore, monomer-addition experiments were carried out. Namely, when a fresh feed of MMA was added into the system where the monomer was almost consumed, the added MMA was smoothly polymerized, and the molecular weights of the polymers further increased (Figure 3). These facts indicate that the polymerization proceeds in a living fashion. The MWD remained as narrow as before the monomer addition.

To clarify the role of CCl_4 in the system, another series of experiments was carried out, where the initial concentration of CCl_4 was varied (10–40 mM), while those of $RuCl_2(PPh_3)_3$ (10 mM), $MeAl(ODBP)_2$ (40 mM), and MMA (2.0 M) were kept constant. In either case, polymerizations occurred without induction periods, and the CCl_4 was completely consumed at the initial stage of the polymerizations, as confirmed by gas chromatography. Figure 4 plots the $\bar{M}_n$ of the polymers against the ratio of the consumed concentration of MMA to the initial concentration of CCl_4. Because $\bar{M}_n$ is almost inversely proportional to the initial concentration of CCl_4, it is considered to act as an initiator. This result and the linear first-order plot in Figure 1 support the occurrence of a living-type polymerization.

The MMA polymerization with the ternary initiating system apparently proceeds by a radical mechanism, as indicated by the following results. For example, the polymerization was perfectly inhibited by the addition of 1,1-diphenyl-2-picrylhydrazyl (DPPH) or galvinoxyl, which are well-known inhibitors for radical reactions. When DPPH, 5 equiv to CCl_4, was added into the system prior to the addition of $RuCl_2(PPh_3)_3$ and $MeAl(ODBP)_2$, no polymer was obtained after 8 h. Also, upon addition of DPPH or galvinoxyl, 5 equiv to CCl_4, to another polymerizing system where conversion reached about 60%, the polymerization was immediately and completely stopped at that stage. Furthermore, ^{13}C NMR analysis (67.8 MHz) showed that the polymers thus obtained were predominantly syndiotactic (*rr*:*rm*:*mm* = 64:33:3), very similar in steric structure to poly(MMA) (e.g., *rr*:*rm*:*mm* = 62:35:3) radically prepared with AIBN in toluene at 60 °C.[20]

(b) Proposed Polymerization Pathway. From the results summarized as above, we propose that the MMA polymerization with the $CCl_4/RuCl_2(PPh_3)_2/MeAl(ODBP)_2$ initiating system proceeds by a radical mechanism as shown in Scheme 1. The first process may be the $RuCl_2(PPh_3)_3$-catalyzed formation of the trichloromethyl radical from CCl_4, where the ruthenium is oxidized by one electron from divalent to trivalent. The resulting radical subsequently adds to MMA to form the 1:1 adduct (**4**) with a carbon–chlorine bond.[15–17] During the addition, the ruthenium is in turn reduced from trivalent to divalent. As experimentally demonstrated in this study (see above), the CCl_4−MMA adduct per se is unable to react further with excess MMA even in the presence of the ruthenium complex.

In the presence of $MeAl(ODBP)_2$, in contrast, this bulky Lewis acid may coordinate the ester carbonyl of the adduct (**4**) (schematically as in **5**) to activate the carbon−chlorine bond, and now the ruthenium complex may generate a radical therefrom, as it does with CCl_4. To this transient radical species from **4**, MMA may now add to form a dimer (**6**) that again carries a carbon−chlorine terminal. Similarly, the dimeric species (**6**) may propagate further with the dual aid of $RuCl_2(PPh_3)_3$ and $MeAl(ODBP)_2$ into its chlorine-capped polymeric homologs (**7**).

Therefore, the polymerization would be via a radical mechanism that consists of repetitive additions of MMA to **6** and **7** across their carbon−chlorine linkages at the growing end. In this regard, CCl_4 acts as an initiator from which each polymer chain is derived (see Figure 4 and the relevant text). Another feature is that both $RuCl_2(PPh_3)_3$ and $MeAl(ODBP)_2$ are indispensable in inducing the propagation reaction in a living fashion. In particular, the use of the aluminum Lewis acid differentiates the polymerization from the corresponding ruthenium-catalyzed additions of CCl_4 to olefins (eq 2), which proceed without it.[15−17] In addition, a key to the controlled polymerization of MMA reported herein probably lies in the reversible activation of the growing carbon−chlorine terminal (**7**) by $RuCl_2(PPh_3)_3$ and $MeAl(ODBP)_2$ and/or in the possible stabilization of the resulting radical species by the coordination of the ruthenium complex.

In conclusion, a well-controlled or living polymerization of MMA has been achieved with the ternary initiating system consisting of CCl_4, $RuCl_2(PPh_3)_3$, and $MeAl(ODBP)_2$. Evidence suggests the polymerization to proceed by a radical mechanism. Further study is now in progress in our laboratories to establish the scope and mechanism of the polymerization, as well as to clarify the roles of $RuCl_2(PPh_3)_3$ and $MeAl(ODBP)_2$ therein.

References and Notes

(1) This work was presented in part at the 43rd Symposium on Macromolecules, Society of Polymer Science, Fukuoka, Japan, Oct 1994; Paper 12P2c31.

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(18) 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 is given below. The polymerization was initiated by adding, via dry syringes, solutions of $MeAl(ODBP)_2$ (0.20 mL) and $RuCl_2(PPh_3)_3$ (1.0 mL) in toluene sequentially in this order, into a mixture (1.3 mL) of MMA (0.54 mL), *n*-heptane (0.16 mL), and CCl_4 (0.0048 mL) in toluene at 25 °C; thus the total volume of the reaction mixture was 2.5 mL. Immediately after mixing, the solution was placed in a water bath kept at 60 °C. In predetermined intervals, the polymerization was terminated by cooling the reaction mixtures to −78 °C and adding methanol (0.50 mL). Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography with *n*-heptane as an internal standard. The quenched reaction solutions were diluted with toluene (ca. 20 mL), washed successively with dilute hydrochloric acid and water, and evaporated to dryness to give the products, which were subsequently vacuum dried overnight.

(19) 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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