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Design of Initiators for Living Radical Polymerization of Methyl Methacrylate Mediated by Ruthenium(II) Complex

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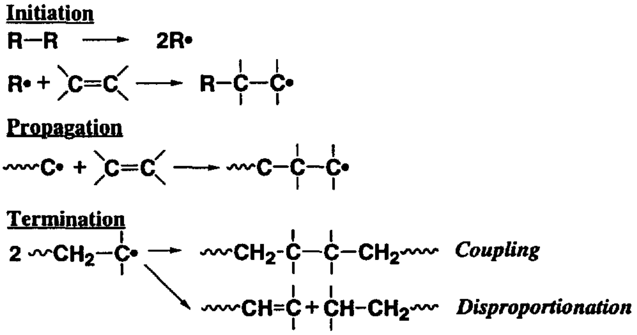
Abstract: A series of initiators have been developed for living radical polymerization of methyl methacrylate (MMA) mediated by ruthenium(II) complexes [e.g., $RuCl_2(PPh_3)_3$; Ph = C_6H_5]. These initiators include chloromethanes, α-chloroesters, α-chloroketones, and α-bromoesters, among which CCl_3COCH_3, $CHCl_2COPh$, and $H(MMA)_2$-Br are the best to give polymers with controlled molecular weights and very narrow MWDs (M_w/M_n = 1.1–1.2). The wide variation of the initiators therefore demonstrates the generality of our transition metal-mediated living radical polymerizations.

INTRODUCTION

Radical Polymerization of Alkene Monomers

Radical polymerization is a chain-growth polymerization mediated by a macromolecular radical intermediate derived from an alkene (vinyl) monomer.[1] As shown in Scheme 1, it consists of a few elementary reactions, including the primary-radical formation via decomposition of an initiator, the addition (initiation) of the primary radical to a monomer to give a monomeric growing radical, and further successive addition (propagation) of the growing radical onto a monomer to grow into a polymeric chain. In addition to these, the radical chain carriers undergo *bimolecular termination* reactions (recombination and disproportionation) that are unique for the electrically neutral radical intermediates, in sharp contrast to the ionic counterparts, for which chain transfer is often more frequent and serious than termination; bimolecular termination between ionic growing ends of like charge is by definition almost impossible.

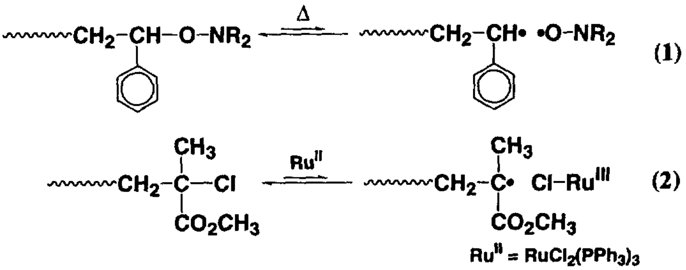


Scheme 1. Elementary reactions in free radical polymerization.

Living Radical Polymerization: Principles

Because of these inherent bimolecular termination reactions, radical polymerization has been considered beyond reach of the precision control that is often achieved in anionic, cationic, and related counterparts where the so-called "living" polymerizations are available; living polymerization is a chain-growth polymerization free from chain transfer, termination, and other chain-breaking side-reactions.[2] The late 1990s, however, has been witnessing a rapid progress all over the world in efforts to achieve living radical polymerizations.[3] These efforts appear to be based on a common strategy (Scheme 2), namely, to suppress the bimolecular termination reactions by converting the growing radicals, reversibly and temporally, into covalent (dormant) species and thereby decreasing the radical concentration. This decrease of radical concentration will in turn decrease the rate of bimolecular termination to a vanishingly small number because of its square dependency.

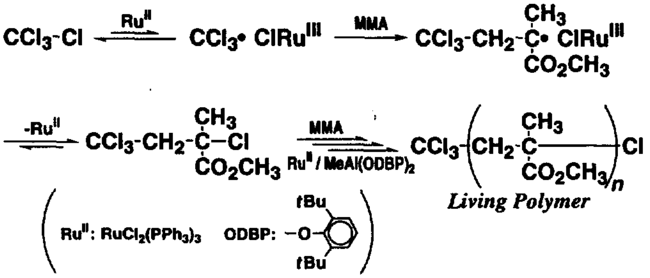
The reversible transformation means that the growing radical and its dormant counterpart are in an exchange equilibrium favored for the covalent side ([dormant species] >> [growing radical]). As already pointed out,[3] the reversibility is also critical in ensuring precise control of polymer molecular weight or the degree of polymerization as defined by [monomer]/[initiator]; the radical–covalent transformation should also be sufficiently faster than propagation to realize narrow molecular weight distributions (MWD) of product polymers. In constructing such living radical polymerization processes, it is therefore required to design, among other reaction conditions, (a) suitable dormant species (—C–X) that carry potentially active sites from which growing radicals can be formed and (b) a mechanism to reversibly generate growing radicals from the dormant species. In short, the key questions are: (a) what is the suitable "capping" moiety (X) for the growing radicals to establish a rapidly interchanging equilibrium between —C–X and —C• (+ •X)? and (b) what is the suitable "activation" mechanism, or "activator" (Y), for such a radical formation from the covalent dormant species (e.g., —C–X + Y→ —C• + •X–Y)?



Scheme 2. Two approaches for living radical polymerization: dormant–growing radical equilibria for precision control.

Transition Metal-Mediated Living Radical Polymerization

Such goals have thus far been achieved by at least two approaches (Scheme 2):[3b,3c] (a) to employ a stable radical to temporarily end-cap the growing radical, as in the system with stable nitroxide radicals (eq 1);[3a,4] and (b) to utilize a transition metal complex to reversibly generate a growing radical from a carbon–halogen covalent terminal as a dormant species (eq 2).[3b,5,6] For example, adopting the second approach, we have recently reported living radical polymerization of methyl methacrylate (MMA) initiated with a combination of an alkyl halide (initiator) and a ruthenium(II) chloride complex, $RuCl_2(PPh_3)_3$ (activator for radical generation; Ph = C_6H_5) (Scheme 3).[5–8]



Scheme 3. Transition metal-mediated living radical polymerization of MMA with CCl_4 (initiator) and $RuCl_2(PPh_3)_3$ (activator) (cf. ref 5).

Thus, in the presence of the Ru(II) complex, carbon tetrachloride (CCl_4)[5] or dichloroacetophenone ($PhCOCHCl_2$)[6] generates a radical that effectively initiates radical polymerization of MMA; weakly Lewis acidic aluminum compounds such as $Al(O\textit{i}Pr)_3$ are sometimes used to accelerate the reaction. Under these conditions the polymerizations conform with the criteria for living polymerization or the virtual absence of chain transfer and termination. Namely, the number-average molecular weights (M_n) of the produced polymers are directly proportional to conversion of MMA monomer and in excellent agreement with the calculated values assuming quantitative initiation and undisturbed propagation (i.e., one living polymer chain per initiator molecule), the polymerization can be resumed by repeatedly adding fresh monomer feeds to the reaction mixtures to continue the linear increase in Mn, and the polymer MWD is very narrow.

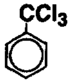
Under these ruthenium(II)-mediated living polymerizations, the complex interacts with the carbon–chloride linkage in the initiator (CCl_4 or others) to generate an initiating radical, as in similar radical-addition reactions of small organic compounds.[9,10] The ruthenium(II) center is thereby one-electron-oxidized into Ru(III) with the chlorine from the initiator, and the resulting carbon radical starts addition to MMA monomer to give polymeric growing radicals. Sooner or later, however, the Ru(III) species undergoes a reverse reaction with a radical growing end via donating its chlorine, and a dormant carbon–chlorine linkage is regenerated. Therefore, such a Ru(II)-assisted transient and reversible formation of the growing radical from the dormant –C–Cl terminal plays a key role in controlling the polymerization and the molecular weights of the products.[3c,3d] Similar living polymerizations may be achieved with not only Ru(II)[5–8] but also Cu(I),[11] Fe(II),[12] and Ni(II)[13,14] complexes; the scope of such transition metal-mediated living radical polymerizations has thus been expanding rapidly.

Objectives of This Work

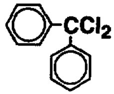
This paper is to discuss the general scope of the initiators for the Ru(II)-mediated living radical polymerization of MMA. Thus far, initiators are confined to carbon tetrachloride[5] and some chloroketones,[6] or sulfonyl chloride derivatives.[15,16] Herein we examined a series of compounds (**1–13**) that carry at least one halogen attached to an alkyl or similar group (see the formulae shown in the next page). These potential initiators include: (a) chlorinated hydrocarbons (**1–4**); (b) α-chloroesters (esters of chlorinated carboxylic acids) (**5–8**); (c) α-chloroketones (**9–10**); and (d) bromoesters (**11–13**). It should be noted that these esters and ketones (**5–13**) bear a halogen on a carbon with a polar carbonyl group and thereby mimic the structure of the dormant poly(MMA) terminal (Scheme 3); in particular, compounds **11** and **13** are authentic models of the monomeric and the dimeric dormant species, respectively from methacrylates.

CCl_4
1

$CHCl_3$
2



3



4

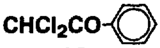
$CCl_3CO_2CH_3$
5

$CHCl_2CO_2CH_3$
6

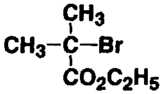
$CH_2ClCO_2CH_3$
7

$CH_3CHClCO_2CH_3$
8

CCl_3COCH_3
9

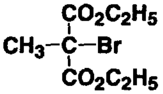


10



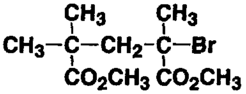
$CH_3-\overset{CH_3}{\underset{CO_2C_2H_5}{C}}-Br$

11



$CH_3-\overset{CO_2C_2H_5}{\underset{CO_2C_2H_5}{C}}-Br$

12



$CH_3-\overset{CH_3}{\underset{CO_2CH_3}{C}}-CH_2-\overset{CH_3}{\underset{CO_2CH_3}{C}}-Br$

13

Herein we report that most of these compounds induce living radical polymerization of MMA in the presence of $RuCl_2(PPh_3)_3$ along with $Al(O\mathit{i}Pr)_3$ to give polymers of controlled molecular weights and very narrow MWDs.

RESULTS AND DISCUSSION

In toluene at 80 °C, methyl methacrylate MMA was polymerized with a series of initiating systems each of which consists of an initiator (R–X), $RuCl_2(PPh_3)_3$, and $Al(O\mathit{i}Pr)_3$. The initiator R–X was selected from the compounds **1**–**13** listed above, and the following conditions were invariably employed to examine the nature of the polymerizations initiated with these ternary initiating systems: $[MMA]_0 = 2.0$ M; $[\text{initiator}]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(O\mathit{i}Pr)_3]_0 = 40$ mM. The primary objective of these experiments is to determine which initiators are best suited for living radical polymerization of MMA and thereby to establish the generality of our approach for the design of the transition metal complex-based initiating systems.

Chlorinated Hydrocarbons (1–4)

The first report for our living radical polymerization employed carbon tetrachloride (**1**) as an initiator to be combined with $RuCl_2(PPh_3)_3$.[5] For comparison's sake, three derivatives of chlorinated methanes **2**–**4** were first examined as initiators. These compounds carry at least two chlorines on a single carbon that also carries either hydrogen or phenyl groups.

All of these multi-halogenated compounds effectively initiated MMA polymerization in the presence of the ruthenium complex (Figure 1). With **1**–**4**, polymerization rate apparently depended on the initiators' structures (time for 90% conversion in hr): CCl_4 (60) ~ $CHCl_3$ (60) > $CPhCl_3$ (>100) > CPh_2Cl_2 (>200). In contrast, di- and monochloromethanes are not able to polymerize MMA under similar conditions. Despite the double chlorine substitution, therefore, CH_2Cl_2 is much less effective in generating radicals than its diphenyl counterpart **4**, suggesting the importance of some conjugating, or radical-stabilizing, substituents, such as phenyl and carbonyl, attached to the α-carbon where a radical is formed.

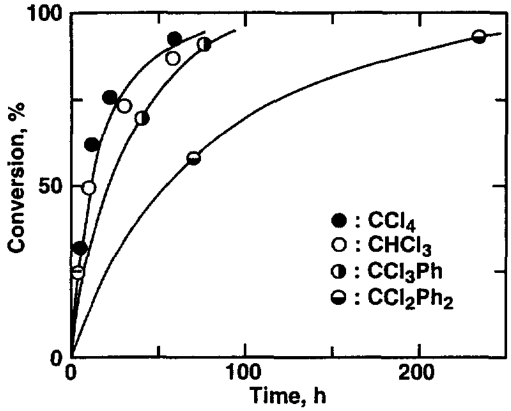


Fig. 1. Chloromethanes (1–4) as initiators for radical polymerization of MMA in conjunction with $RuCl_2(PPh_3)_3$ and $Al(O\mathit{i}Pr)_3$ in toluene at 80 °C: $[MMA]_0 = 2.0$ M; $[\text{initiator}]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(O\mathit{i}Pr)_3]_0 = 40$ mM.

Figure 2 compares the polymer molecular weights and MWDs for the four initiating systems. The polymers with $CHCl_3$ showed MWDs somewhat broader than those with CCl_4, and their molecular weights were larger than the calculated values but increased progressively with increasing conversion. An aromatic version, $CPhCl_3$, led to bimodal MWDs consisting of two narrowly distributed fractions, one of which is of a molecular weights double the other. With CPh_2Cl_2 polymer molecular weights are again proportional to conversion but are higher than the calculated. Interestingly, this compound gave extremely narrow MWDs, but preliminary NMR analysis indicates no trace of an initiator fragment in the product polymers, leaving the real initiating entity ambiguous. Overall, therefore, the three chlorinated hydrocarbons (2–4) are in fact able to initiate MMA polymerization, but the controllability of them could not surpass that with CCl_4.[5]

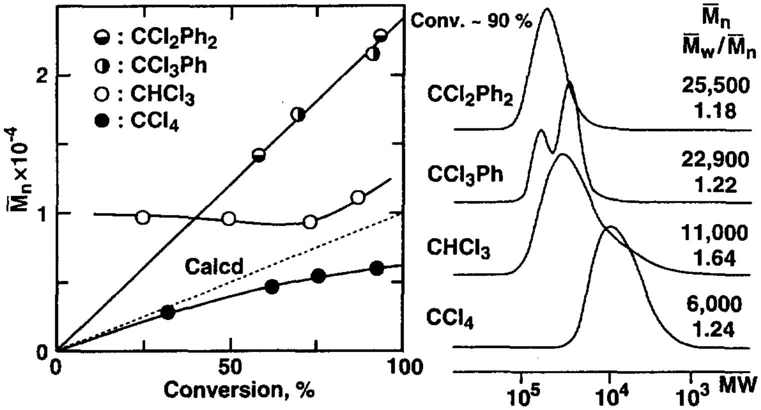


Fig. 2. Living radical polymerization with chloromethanes (1–4): molecular weights and MWDs of polymers obtained with chloromethane/$RuCl_2(PPh_3)_3$/$Al(O\mathit{i}Pr)_3$ initiating systems in toluene at 80 °C: $[MMA]_0 = 2.0$ M; $[\text{initiator}]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(O\mathit{i}Pr)_3]_0 = 40$ mM; conversion for MWD samples ≥ 90 % (see Fig. 1).

α-Chloroesters (5–8)

These compounds are methyl esters derived from chloroacetic acids (**5**–**7**) and chloropropionic acid (**8**). The monochloroesters, **7** and **8**, are not effective initiators for MMA; the acetate **7** could not initiate polymerization at all, whereas the propionate **8** gave high molecular weights that were independent of conversion. These trends indicate that multiple halogens on a single carbon is needed for effective initiation from α-chloroesters.

Accordingly, the trichloro- and dichloroacetates (**5** and **6**, respectively) smoothly polymerized MMA at nearly the same rates as with CCl_4 (Figure 3).[17] The produced polymers showed fairly narrow MWDs (M_w/M_n < 1.2); the M_n increased in direct proportion to conversion and were very close to the calculated values for living polymers (Figure 4). Thus living radical polymerizations of MMA are feasible with these polyhalogenated esters.

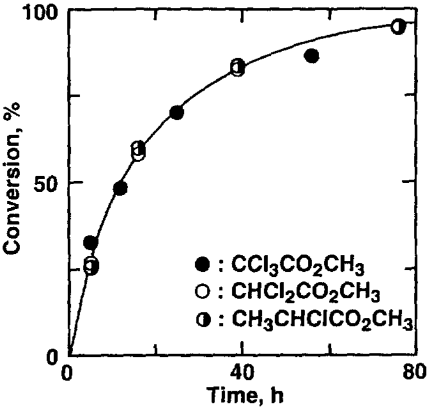


Fig. 3. α-Chloroesters (**5**–**7**) as initiators for radical polymerization of MMA in conjunction with $RuCl_2(PPh_3)_3$ and $Al(OiPr)_3$ in toluene at 80 °C: $[MMA]_0$ = 2.0 M; $[initiator]_0$ = 20 mM; $[RuCl_2(PPh_3)_3]_0$ = 10 mM; $[Al(OiPr)_3]_0$ = 40 mM.

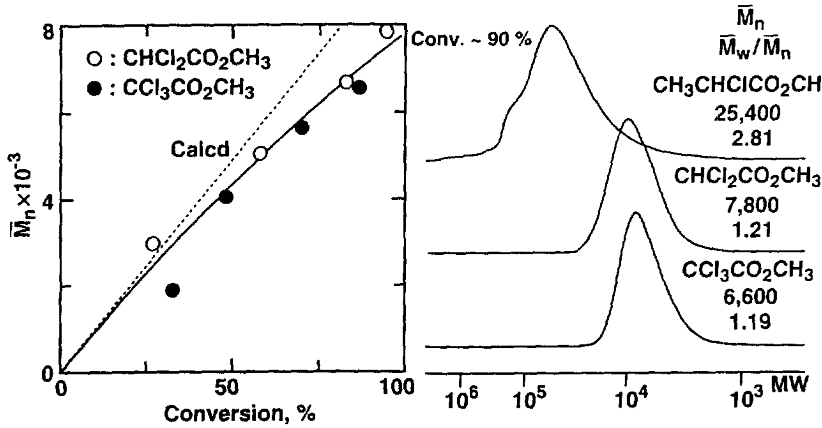


Fig. 4. Living radical polymerization with α-chloroesters (**5**–**7**): molecular weights and MWDs of polymers obtained with α-chloroester/$RuCl_2(PPh_3)_3$/$Al(OiPr)_3$ initiating systems in toluene at 80 °C: $[MMA]_0$ = 2.0 M; $[initiator]_0$ = 20 mM; $[RuCl_2(PPh_3)_3]_0$ = 10 mM; $[Al(OiPr)_3]_0$ = 40 mM; conversion for MWD samples ≥ 90 % (see Fig. 3).

α-Chloroketones (9–10)

As reported briefly,[6] these two chloroketones are among the best initiators thus far known for living radical polymerization of MMA with the ruthenium complex (Figure 5). As summarized in Figure 5, they give polymers with controlled molecular weights and very narrow MWDs that are narrower than those with corresponding chloroesters [e.g., M_w/M_n: 1.15 (**10**; $CHCl_2COPh$) versus 1.21 (**5**; $CHCl_2CO_2CH_3$)].[17] Thus, initiation is faster with the ketones than with the ester counterparts, due to the stronger electron-withdrawing power of the ketone's carbonyl that induces further polarization of the carbon–chlorine linkage in the initiator and thereby facilitates radical generation therefrom with the Ru(II) complex. If the stronger electron-withdrawing power of the ketone carbonyl is important, this suggests that chloronitriles should be equally good (not examined yet), except when the cyano group therein forms a strong complex with the ruthenium center to deactivate it in radical generation.

The polymers thus obtained with **9** and **10** possessed one initiator fragment per molecule, as analyzed by NMR (see below for structural analysis). Overall, therefore, these chloroketone are among the best initiators thus far known for the transition metal-mediated living radical polymerization of MMA and related monomers.

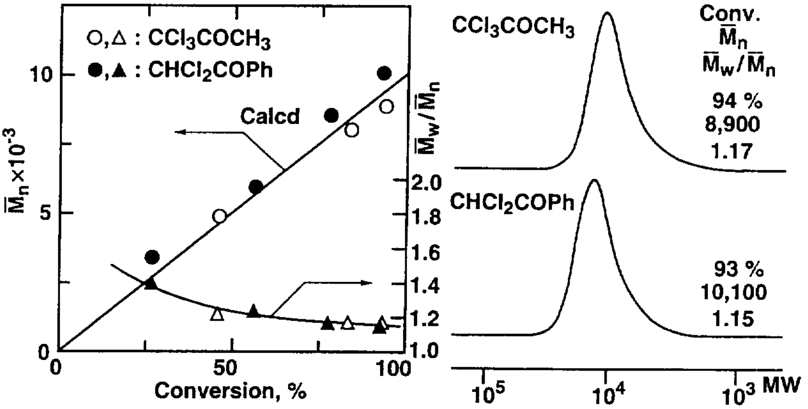


Fig. 5. Living radical polymerization with α-chloroketones (**9** and **10**): molecular weights and MWDs of polymers obtained with α-chloroketone/$RuCl_2(PPh_3)_3$/$Al(OiPr)_3$ initiating systems in toluene at 80 °C: $[MMA]_0 = 2.0$ M; $[initiator]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(OiPr)_3]_0 = 40$ mM; conversion for MWD samples ≥ 90 % (cf. ref 6).

α-Bromoesters (11–13)

In addition to the ten chlorides (**1**–**10**) thus far discussed, these three bromides **11**–**13** were also examined for living radical polymerization with the ruthenium complex. Structurally, the ester **11** can be regarded a "monomeric" model of the dormant end (cf. Scheme 3) where the bromine is attached to a tertiary carbon bearing an ester substituent. Relative to **11**, malonate **12** carries two geminal esters on the carbon where the bromine is located. On the other hand, another ester **13** is an authentic "dimeric" model of the dormant end with two MMA units and a terminal bromide on the tertiary carbon. Under the standard conditions, all these bromides induced MMA polymerization at nearly the same rates as with CCl_4 and other chlorides (Figure 6), indicating that, when coupled with ruthenium chloride, the bromide initiators can initiate MMA radical polymerization (see below also).

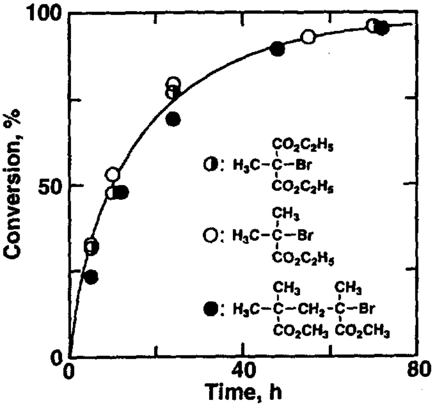


Fig. 6. α-Bromoesters (11–13) as initiators for radical polymerization of MMA in conjunction with $RuCl_2(PPh_3)_3$ and $Al(O\textit{i}Pr)_3$ in toluene at 80 °C: $[MMA]_0 = 2.0$ M; $[\text{initiator}]_0 = 20$ mM; $[RuCl_2(PPh_3)_3]_0 = 10$ mM; $[Al(O\textit{i}Pr)_3]_0 = 40$ mM.

Also invariably they gave polymers whose M_n were directly proportional to conversion and close to the calculated values, although the M_n with the monomer-type ester **11** is higher than the calculated during the early stage of the polymerization. The MWDs with **11–13** are also very narrow (Figure 7), but close inspection shows that they progressively narrow in the order: **11** (monomeric) > **12** (malonate) > **13** (dimeric). Both M_n and MWD for **11** in comparison to the other two show that the initiation from the monomeric bromide is appreciably slower. Introducing an additional ester into **11** leads to the malonate **12**, which gave faster initiation and thus narrower MWDs.

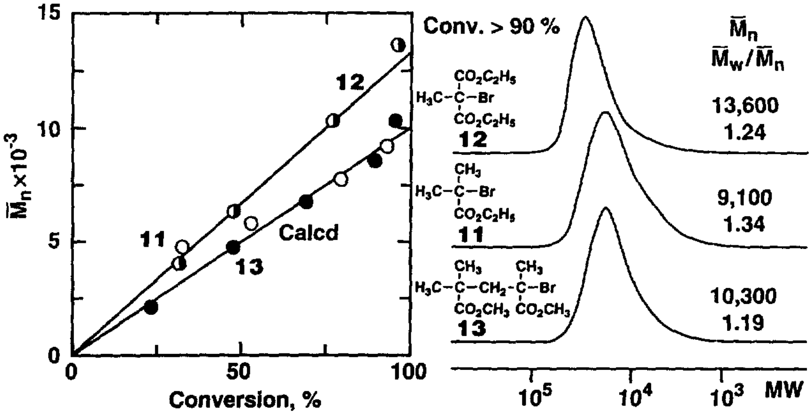


Fig. 7. Living radical polymerization with α-bromoesters (11–13): molecular weights and MWDs of polymers obtained with α-bromoester/$RuCl_2(PPh_3)_3$/$Al(O\textit{i}Pr)_3$ initiating systems in toluene at 80 °C: $[MMA]_0 = 2.0$ M; $[\text{initiator}]_0 = 10$ mM; $[RuCl_2(PPh_3)_3]_0 = 40$ mM; $[Al(O\textit{i}Pr)_3]_0 = 20$ mM; conversion for MWD samples > 90 % (see Fig. 6).

Equally interesting, the dimeric form **13** apparently initiates polymerization faster than the monomeric counterpart **11**, despite that the terminal bromides therein are nearly the same in structure. The clear difference between **11** and **13** suggests some different (steric and/or electric) environments around the bromides. Thus, overall, the dimeric ester **13** appears among the best initiators, rivaling the chloroketones **9** and **10**, for living radical polymerization of MMA.

End-Group Analysis

Three poly(MMA) samples of narrow MWDs, obtained with the dichloroester **6**, the dichloroketone **10**, and the bromomalonate **12**, were analyzed by ^{1}H NMR spectroscopy (Figure 8). As expected from the proposed reaction pathway (Scheme 3), these polymers showed signals that indicate the attachment of terminal halogens to the poly(MMA) backbone, and particularly useful are the resonances of the terminal MMA unit with a chloride or bromide end group: $\sim\sim CH_2-CX(CH_3)(COOCH_3)$ (X = Cl, Br). For example, a small signal (*c*1), adjacent to the large methoxy peak (*c*) of the main chain substituent, is due to the terminal ester methoxy protons. The terminal methylene unit also gives distinct but small signals (*b*1 and *b*2) at 2.5 and 2.8 ppm.

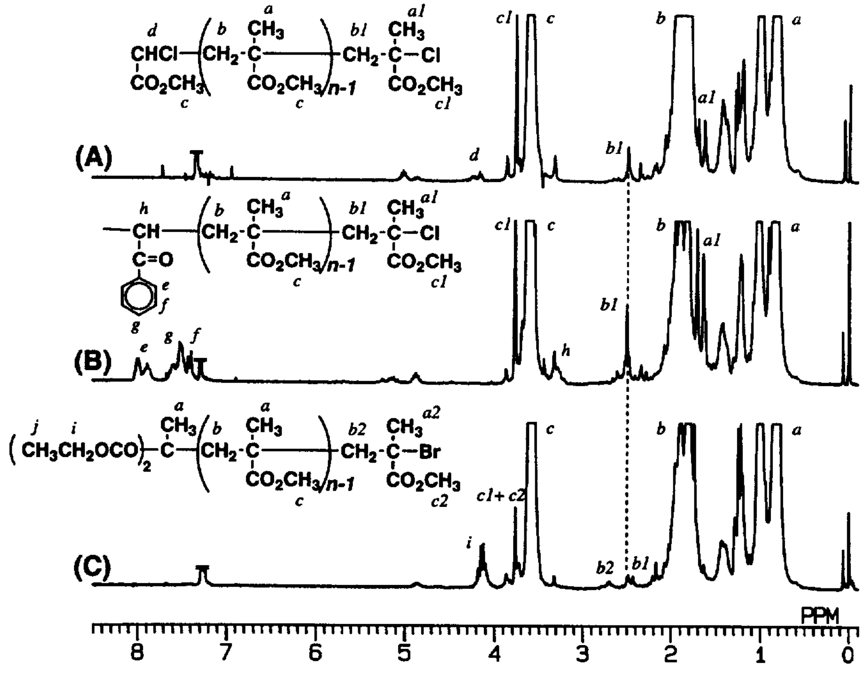


Fig. 8. ^{1}H NMR spectra of poly(MMA) obtained in living radical polymerization with $RuCl_2(PPh_3)_3$ and $Al(O\textit{i}Pr)_3$ in toluene at 80 °C. Initiator: (A) dichloroester **6**; (B) dichloroketone **10**; (C) bromomalonate **12**. See Table 1 for other details.

In addition to these ω-end resonances, the initiator fragments lead to characteristic α-end signals: the methine signal *d* (Figure 8A) for the –CHCl– unit derived from the dichloroacetate **6**; the aromatic protons peaks *e*–*g* (Figure 8B) for the benzene ring from the ketone **10**; and the ester ethyl quartet *i* (Figure 8C) for the malonate moiety from **12**. Integrated intensity of these end-group signals relative to the main-chain resonances (*c*/3*d* for **6**, *2c/3e* for **10**, and *4c/3i* for **12**) give the degree of polymerizations of the respective samples (Table 1). All the observed DPn data are in excellent agreement with the calculated values for quantitative attachment of the initiator fragments. In conjunction with the attachment of the ω-end halogens, these observations further support the proposed reaction pathway and also the absence of chain transfer and termination, which would lead to different and uncontrolled end groups.

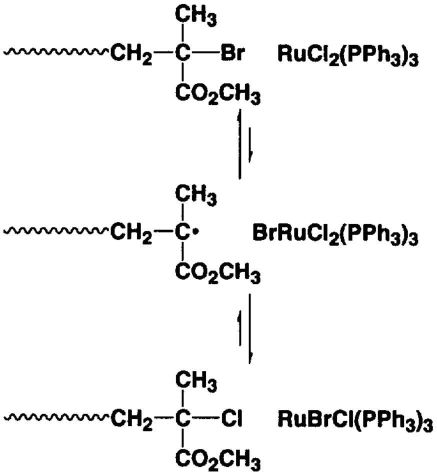
Table 1. $\overline{\mathrm{DP}}_n$ **and** $\overline{F}_n$ **of Poly(MMA) Obtained with R–X/RuCl$_2$(PPh$_3$)$_3$/Al(O*i*Pr)$_3$**[a]

	$\overline{\mathrm{DP}}_n$		
initiator (R–X)	SEC[b]	NMR[c]	$\overline{F}_n$[d]
$CHCl_2CO_2CH_3$[e]	64.6	60.6	1.07
$CHCl_2COPh$[f]	23.4	22.9	1.02
$CH_3CBr(CO_2C_2H_5)_2$[e]	43.0	36.0	1.19

[a] $[MMA]_0$ = 2.0 M, $[RuCl_2(PPh_3)_3]_0$ = 10 mM, $[Al(O\mathit{i}Pr)_3]_0$ = 40 mM; in toluene, at 80 °C. [b] [$\overline{M}_n$(SEC) - MW(initiator moiety)]/MW(MMA). [c] From ^{1}H NMR peak intensity ratio; (c+c1)/3d [$CHCl_2CO_2CH_3$], 2(c+c1)/3e [$CHCl_2COPh$], 4(c+c1+c2)/3i [$CH_3CBr(CO_2C_2H_5)_2$]. See Figure 7 and text. [d] $\overline{\mathrm{DP}}_n$(SEC)/$\overline{\mathrm{DP}}_n$(NMR). [e] $[\text{initiator}]_0$ = 20 mM. [f] $[\text{initiator}]_0$ = 40 mM.

The NMR spectra further give some insight into the initiation and propagation steps, which have remained rather obscure before. For example, the sample with the dichloroacetate **6** showed the methine signal *d* for the structure –CHCl(CO_2CH_3), which indicates that only one of the two chlorines in the acetate has been involved in the initiation step. In contrast, such a chlorinated methine signal is absent in the sample from the dichloroketone **10**, suggesting that in this case *both* chlorines have been utilized in the initiation step; namely, this ketone is a bifunctional initiator.[17] In fact, while the DPn (22.9) based on the NMR signal of the initiator fragment (the aromatic protons *e–g*; Table 1) agreed well with the SEC value, the signal intensity ratio (*2c/3b1*) for the ω-end methylene gave a DPn (11.7) that was reduced into about one half. Thus, the sample is most likely capped with two halogens at both chain ends.

With the bromomalonate initiator **12** in conjunction with Ru(II) chloride complex, the ω-end signals are twofold, *b1* and *b2* (Figure 8C). The dual terminal signals are in contrast to the single methylene signals (*b1*) for the chloride-type initiators **6** and **10** (Figures 8A and 8B), and one of the two signals for **12** appears at the same position as the chloride terminal. Therefore, the polymers from the **12**/$RuCl_2(PPh_3)_3$ system consist of two ω-end groups, one with a chlorine (peak *b1*) and the other with a bromine (peak *b2*), and the former most likely comes from the chlorines in the $RuCl_2$ complex. These spectral results thus demonstrate the occurrence of halogen exchange between the original bromide terminal from the bromoester initiator and the chlorine from the ruthenium complex (Scheme 4). Such an exchange should occur only when the ruthenium complex interacts with the terminal halogen by which it is one-electron oxidized and generates a transient radical species (cf. Scheme 3).



Scheme 4. Halogen exchange reaction at the growing site in living radical polymerization with Ru(II) complex.

CONCLUDING REMARKS

This work has shown that, in addition to CCl_4[5] and α-haloketones,[6] a series of organic halides (R–X; see formulae **1–13** above) are effective initiators for living radical polymerization of MMA where $RuCl_2(PPh_3)_3$ is employed as an "activator" (or catalyst) that effectively generates initiating radicals in the presence of Al(O*i*Pr)$_3$. When structurally appropriate, these halides R–X initiate living polymerization of MMA to form polymers with controlled molecular weights and narrow MWDs. The structural features of the suitable R–X initiators appear to include: (a) the attachment of more than one halogen on the carbon where the initiating radical is formed; (b) the attachment of a carbonyl, ester, or phenyl group(s) that will facilitate the homolytic dissociation of the halogen or will stabilize the carbon radical to be formed therefrom by polar and/or resonance effects; and probably (c) some steric congestion around the α-carbon (radical center). The initiators that fall in this category include α-haloalkanes (*e.g.*, CCl_4 and CCl_3Br), α-haloketones (*e.g.*, $CHCl_2COR$; R = Ph, CH_3), α-haloesters [*e.g.*, $CHCl_2CO_2CH_3$ and $(CH_3)_2CBr(CO_2CH_3)$], and the ω-brominated MMA dimer **13**.

To achieve living radical polymerization based on R–X and transition metal complexes, it will be important to design initiating systems that effectively establish the dormant-active radical equilibrium [Scheme 2 (eq 2) and Scheme 3] that considerably decreases the radical concentration but reversibly generates a certain amount of the growing radical for controlled propagation to occur.[3b–3d] To this end the use of Ru(II) and other transition metal complexes is crucial, and the initiators thus far known are almost exclusively organic halides. As shown in this paper, furthermore, the judicious choice of initiators R–X is equally crucial for precise control of polymer molecular weight distributions, so that the radical generation (or initiation) from R–X can sufficiently be faster than propagation.

Because of these aspects, initiating systems with combinations of organic halides and transition metal complexes will be versatile and flexibile; namely, one can finely design structures and activities of both components to be suited for a large variety of radically polymerizable monomers and for reaction conditions including those in aqueous media (emulsion, dispersion, and suspension polymerizations). Further progress in this area is anticipated.

EXPERIMENTAL SECTION

Materials

Reagents. MMA, toluene (solvent), and initiators **1-12** were of commercial source and purified by double distillation over calcium hydride before use.[6,8]

Synthesis of Dimeric Initiator 13. Dimethyl 2-bromo-2,4,4-trimethylglutarate (**13**) was synthesized as follows:[18,19] In a 500-mL, three-neck, round-bottomed dry flask equipped with two pressure-equalizing dropping funnels and a magnetic stirring bar, a commercial 2.0 M solution of lithium diisopropylamide (20 mL; 40 mmol; in a heptane/THF/ethylbenzene mixed solvent; Aldrich) was diluted under dry nitrogen with 110 mL THF, and the solution was cooled to –78 °C. To this was added dropwise under dry nitrogen a solution of dimethyl 2,4-dimethylglutarate (**14**) (5.0 mL; 25.6 mmol; Aldrich) in THF (10 mL) over a period of 10 min. The mixture was further stirred at the same temperature for 1 hr, methyl iodide (3.1 mL; 50 mmol; Nakarai Tesque) was added dropwise over 5 min, and stirring was continued for an additional 2 hr. The resultant solution was allowed to warm to room temperature, diluted with ether (100 mL), and treated with water (100 mL). The aqueous layer was extracted with ether (50 mL). The combined organic phase was washed three times with 1*N* hydrochloric acid (50 mL each) and then three times with deionized water (100 mL each), dried over anhydrous sodium sulfate overnight, and evaporated under reduced pressure to give dimethyl 2,2,4-trimethylglutarate as a brown oil.[18]

In a round-bottomed flask equipped with a magnetic stirring bar was placed a heterogeneous mixture of the entire crude trimethylglutarate, *N*-bromosuccinimide (5.0 g), benzoyl peroxide (0.25 g), and carbon tetrachloride (40 mL), and it was irradiated with ultraviolet light at around 30 °C for 4 hr.[19] The mixture was filtered and evaporated to dryness under reduced pressure to give the bromoester **13**, which as purified by recrystallization from ethanol (six times) and stored in brown ampoules under dry nitrogen: overall isolated yield from the dimethylglutarate **14**, 11 wt%; purity > 95 %; ^{1}H NMR (270 MHz, $CDCl_3$) δ 1.10 (s, 3H, CH_3), 1.25 (s, 3H, CH_3), 1.90 (s, 3H, CH_3), 2.80 (s, 2H, CH_2), 3.70 (s, 3H, CO_2CH_3), 3.80 (s, 3H, CO_2CH_3).

Procedures

The procedures for polymerization and polymer characterization (size exclusion chromatography and NMR) have already been reported.[6,8]

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