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Metal Complex-Mediated Living Radical Polymerization: Features, Scope, and Precision Polymer Synthesis

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METAL COMPLEX-MEDIATED LIVING RADICAL POLYMERIZATION: FEATURES, SCOPE, AND PRECISION POLYMER SYNTHESIS

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ABSTRACT

The scope, mechanism, and initiating systems of transition metal-mediated living radical polymerization have been discussed in light of the authors' recent results. For example, a radical propagation is strongly suggested for the polymerization of methyl methacrylate (MMA) with the dichloroacetophenone/$RuCl_2(PPh_3)_3$/$Al(OiPr)_3$ initiating system, because it is immediately terminated by radical quenchers such as galvinoxyl and TEMPO, but is immune to protic polar compounds such as water and methanol. The latter feature also leads to living radical polymerization in methanol and other alcohols and even in water. The product polymers therein are shown to possess a tertiary chloride ω-end that remains intact after work-up with acid and water and can renitiate living polymerization when treated with $RuCl_2(PPh_3)_3$ and $Al(OiPr)_3$. The paper also discusses the precise synthesis of star, telechelic, and end-functionalized polymers by the ruthenium-mediated living radical polymerizations with novel multifunctional and functionalized initiators.

INTRODUCTION

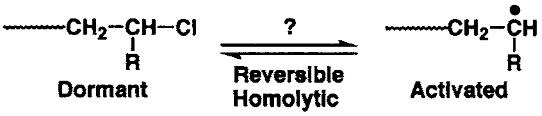
Convincing evidence has recently been accumulated that living or precisely controlled polymerization is now feasible in radical polymerization, which has long been believed difficult to control because of inherently facile radical chain termination reactions. Current literature shows that there are, among others, two major strategies to achieve living radical polymerization: one with stable radical end-cappers [1] and the other with transition metal complexes as a component of initiating systems [2].

This paper discusses some examples of living radical polymerization based on the second approach, their possible mechanism and features, and controlled synthesis of star and end-functionalized polymers.

Strategy for Living Radical Polymerization

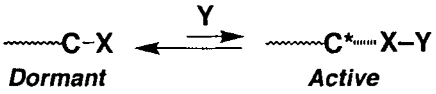
We have proposed that radical chain termination, i.e., recombination and disproportion may be suppressed by generating growing species where a growth active radical species is in a rapidly exchanging equilibrium with a halogen-capped covalent or dormant counterpart (Equation 1). If the dormant carbon-halogen terminal linkage can be homolytically and reversibly cleaved, and if the equilibrium is favored for the dormant side, then the instantaneous concentration of the growing radical end will be extremely low so as to suppress the bimolecular termination reactions, although propagation would be slower, too. Figure 1 summarizes the advantages of such systems in achieving living polymerizations. It has already been demonstrated that this approach indeed leads to a number of living (or controlled) polymerizations by cationic, anionic, group transfer, and other mechanisms [3].

From Figure 1, one can see that the key to achieving such living systems in radical polymerization is to find proper above-discussed "activators" that cleave carbon–halogen and other dormant terminals homolytically and reversibly into active growing radicals. We believe that transition metal complexes are the candidates for such activators.



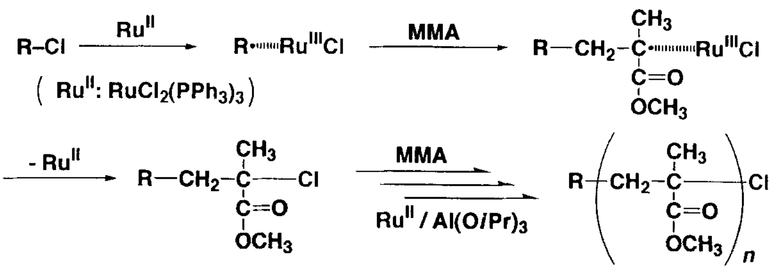
LIVING RADICAL POLYMERIZATION WITH RUTHENIUM COMPLEX: MECHANISM AND FEATURES

On the basis of the strategy above discussed, we have recently developed living radical polymerization of methyl methacrylate (MMA) and related monomers mediated by ruthenium(II) complexes, most typically $RuCl_2(PPh_3)_3$ (Equation 2) [4, 5]. For example, this complex is combined with carbon tetrachloride [4],



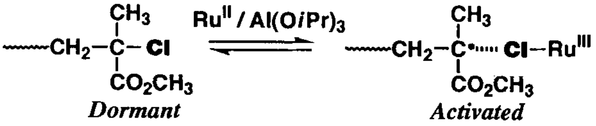
Features	⇒	Advantages
[Dormant] >> [~~C*]	⇒	Better Control (No Side Reactions)
Reversible	⇒	Mol. Wt. Control ($DP_n = [M] / [Initiator]_0$)
Fast Exchange	⇒	Narrow MWD (Equal Probability of Propagation)

Figure 1. Living polymerization via a dormant–active species equilibrium: features and advantages.



$$R{-}Cl \xrightarrow{Ru^{II}} R\cdots Ru^{III}Cl \xrightarrow{MMA} R{-}CH_2{-}\underset{\underset{OCH_3}{C=O}}{\overset{CH_3}{C}}\cdots Ru^{III}Cl$$
$$(\ Ru^{II}: RuCl_2(PPh_3)_3\ )$$
$$\xrightarrow{-Ru^{II}} R{-}CH_2{-}\underset{\underset{OCH_3}{C=O}}{\overset{CH_3}{C}}{-}Cl \xrightarrow[Ru^{II}/Al(OiPr)_3]{MMA} R\left(CH_2{-}\underset{\underset{OCH_3}{C=O}}{\overset{CH_3}{C}}\right)_n Cl$$

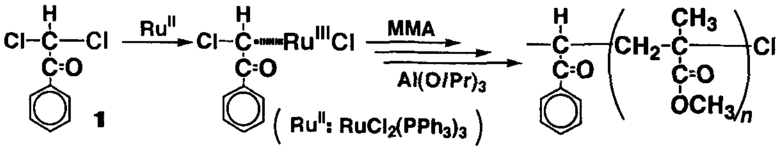
dichloroacetophenone (**1**) [5], and similar halogen-containing compounds [5] (R–X; initiator) to induce living MMA polymerization. The reaction sequence shown in Equation 2 involves repetitive cleavage of the terminal carbon–chlorine bonds derived from the initiator, assisted by the ruthenium complex, and thereby a reversible equilibrium between dormant and active radical species is achieved (Equation 3).



$$\underset{\textit{Dormant}}{\sim\!CH_2{-}\underset{CO_2CH_3}{\overset{CH_3}{C}}{-}Cl} \overset{Ru^{II}/Al(OiPr)_3}{\rightleftharpoons} \underset{\textit{Activated}}{\sim\!CH_2{-}\underset{CO_2CH_3}{\overset{CH_3}{C}}\cdots Cl{-}Ru^{III}}$$

Typical Examples

The dihaloketone **1**, coupled with $RuCl_2(PPh_3)_3$, efficiently polymerizes MMA in the presence of an aluminum alkoxide (probably as co-catalyst) such as



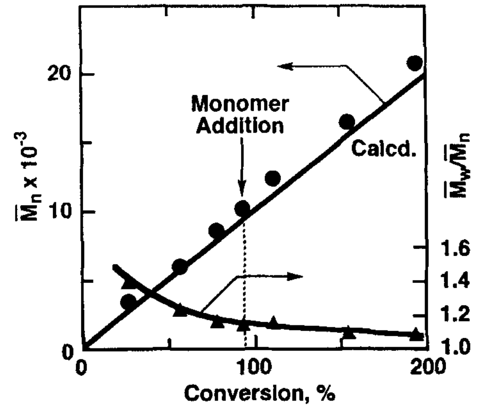


Figure 2. Living radical polymerization of MMA (2.0 M) with 1/$RuCl_2(PPh_3)_3/Al(OiPr)_3$ (20/10/40 mM) in toluene at 80°C [5].

$Al(OiPr)_3$ in toluene at temperatures from 60–100°C (Equation 4) [5]. The reaction shows characteristics consistent with living polymerization (Figure 2): polymer molecular weight (M_n) increases in direct proportion to MMA conversion, further increases upon addition of a fresh monomer feed to a completely polymerized reaction mixture, and is in close agreement with the calculated value assuming the formation of one polymer chain per initiator **1**; the product polymers exhibit very narrow molecular weight distribution (MWDs; $M_w/M_n \leq 1.1$).

As will be discussed later in this paper, the scope of this type of living polymerizations has rapidly been expanded to include a variety of initiators [R–X; (Equation 2)], transition metal complexes, and applicable monomers. The following sections discuss some features of the ruthenium-mediated living radical polymerization.

Effects of Radical and Protic Terminating Agents

A persistent question for our ruthenium-based systems is "Are they in fact radical processes?" With regards to this point, we have recently studied the effects

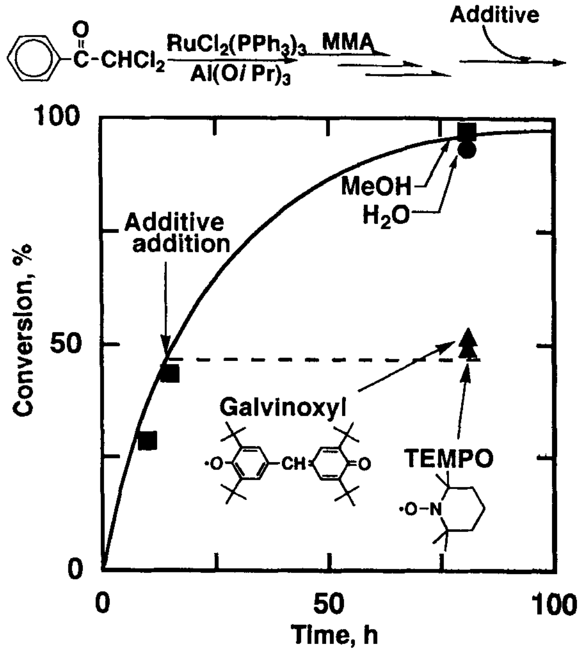


Figure 3. Effects of potential terminating agents (200 mM) on the living polymerization of MMA (2.0 mM) with 1/$RuCl_2$-$(PPh_3)_3$/Al(O*i*Pr)$_3$ (20/10/40 mM) in toluene at 80°C [6]. Each additive was added to a reaction mixture at ca. 45% conversion.

of possible terminating agents on the living polymerization with the **1**/$RuCl_2(PPh_3)_3$/Al(O*i*Pr)$_3$ initiating system (20/10/40 mM) in toluene at 80°C [6, 7]. The terminating agents included galvinoxyl and TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) as radical quenchers and methanol and water as carbanion quenchers. The living polymerization was allowed to proceed to ca. 50% conversion, at which point these compounds (200 mM) were added (Figure 3).

The radical additives immediately terminated the reaction, as evidenced by the virtual absence of conversion increase for a prolonged time. In sharp contrast, the protic agents, though present 10-fold molar excess over the initiator, did not affect the progress of monomer consumption, and the polymers obtained in their presence had nearly the same molecular weight and MWDs as narrow as those of the products without the additives. These findings strongly support the occurrence of radical propagation.

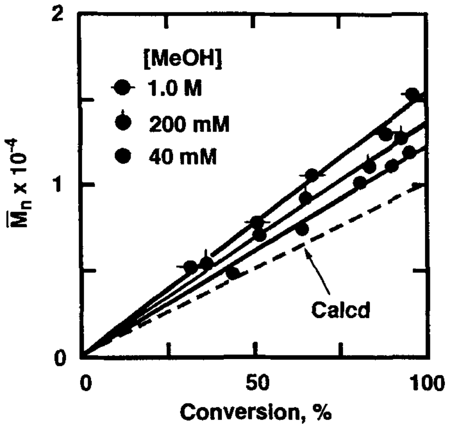


Figure 4. Living polymerization of MMA (2.0 M) with 1/$RuCl_2$-$PPh_3)_3$/ Al(O*i*Pr)$_3$(20/10/40 mM) in toluene at 80°C in the presence of methanol (40 mM – 1.0 M, as indicated) [6].

Living Polymerization in Alcohols and Water

Based on the observed tolerance towards toward protic and polar compounds, the ruthenium-mediated MMA polymerization was then carried out in the presence of varying amounts of methanol (Figure 4) [6]. Regardless of the alcohol concentration in the range of 20 mM–1.0 M, living polymerization proceeded smoothly without serious adverse effects, even when it was in a large excess, and the polymers showed narrow MWDs whose molecular weights are invariably proportional to conversion.

Separate experiments further demonstrated that similar living radical polymerizations are feasible with methanol, 1-butanol, 2-methyl-2-butanol, and even water as solvents [7]. This suggests the possibility of emulsion polymerization in a living fashion, and research in this line is now in progress in our laboratories.

Living Polymerization from Recovered Polymers

The reaction pathway shown in Equation 4 indicates that the polymers from the 1/$RuCl_2(PPh_3)_3$/Al(O*i*Pr)$_3$ initiating system should carry a chloride group at the ω-end derived from the initiator. ^1H NMR structural analysis in fact con-firmed this structure and nearly quantitative end functionality [6].

Equally important, the recovered polymers turned out to reinitiate living MMA polymerization upon treatment with a mixture of $RuCl_2(PPh_3)_3$ and

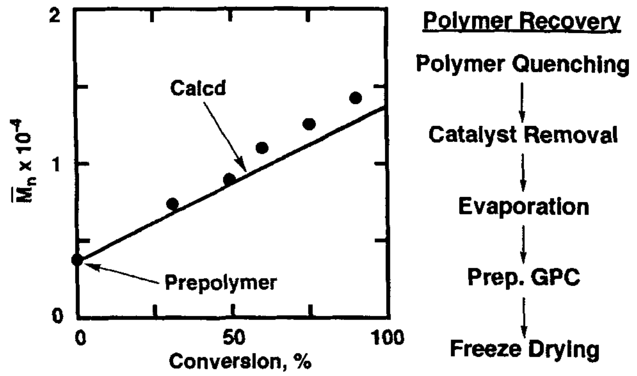


Figure 5. Living polymerization of MMA (2.0 M) with poly(MMA) (20 mM) in conjunction with an additional feed of $RuCl2(PPh_3)_3/Al(O\mathit{i}Pr)_3$ (10/40 mM) in toluene at 80°C [6]. Prepolymer: M_n = 3700; M_w/M_n = 1.33; from **1**/$RuCl_2(PPh_3)_3/Al(O\mathit{i}Pr)_3$ (cf. Figure 2).

$Al(O\mathit{i}Pr)_3$, i.e., the other two components of the original initiating system (Figure 5) [6]. Thus, a polymer sample obtained from initiator **1** was separated from the ruthenium- and aluminum-containing residues, washed with water, isolated by evaporation and preparative size-exclusion chromatography, freeze-dried, and finally mixed with MMA monomer and subsequently a $RuCl_2(PPh_3)_3/Al(O\mathit{i}Pr)_3$ mixture in toluene at 80°C. Polymerization ensued that was faster than that with **1** otherwise under the same conditions. Polymer molecular weight increased linearly from the value of the prepolymer sample and was in close agreement with the calculated values based on the quantitative and living propagation from the chlorine-capped prepolymer; the MWD of the product was even narrower than the starting material. The successful re-initiation shows the quantitative attachment and high stability of the ω-end chloride.

SCOPE OF TRANSITION METAL-MEDIATED LIVING RADICAL POLYMERIZATION

Since the development of the ruthenium-mediated living radical polymerization, we have also made efforts to generalize our strategy and to expand the scope of initiating systems and application to precisely controlled polymer synthesis. Figure 6 summarizes some of the current status of such aspects.

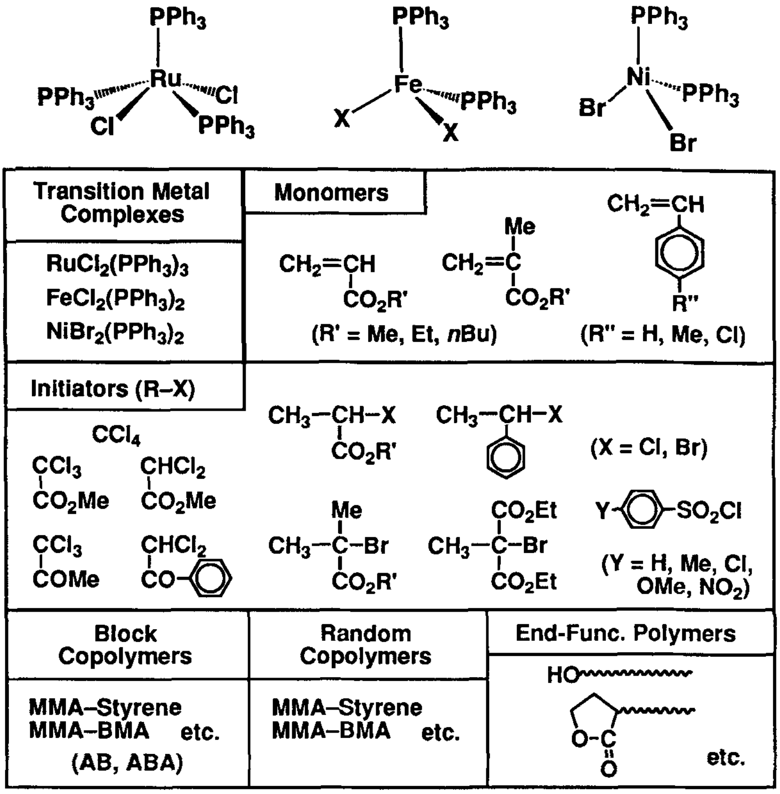
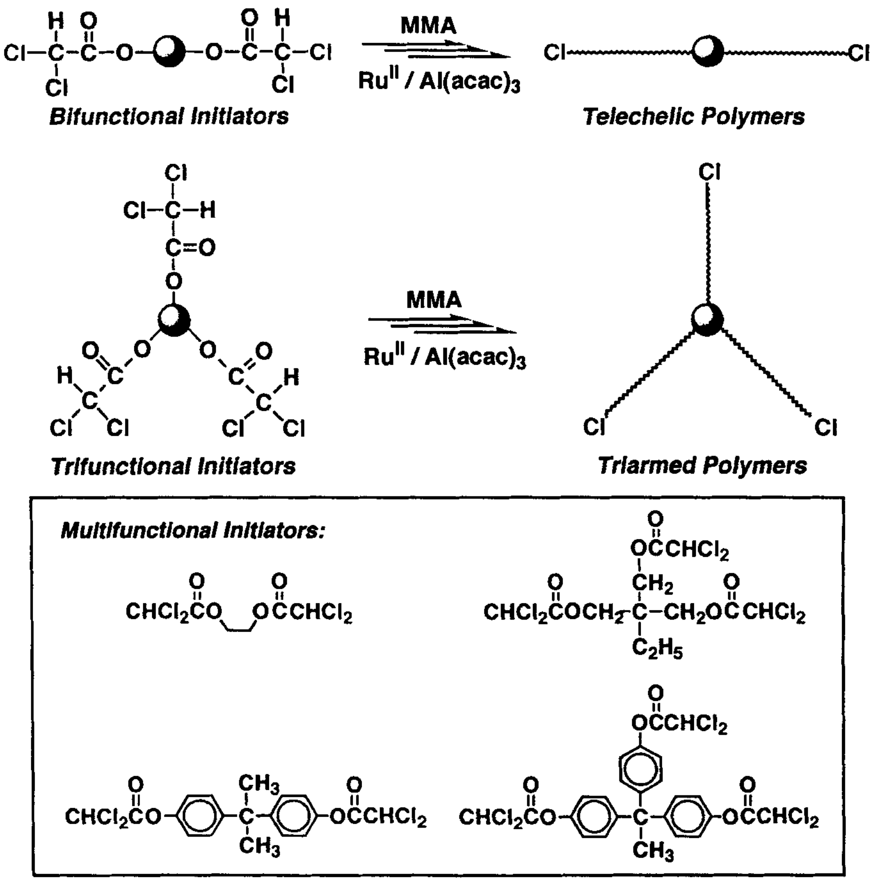


Figure 6. Scope of transition metal-mediated living radical polymerization: Monomers, initiators (R–X), metal complexes, and precision polymer synthesis.

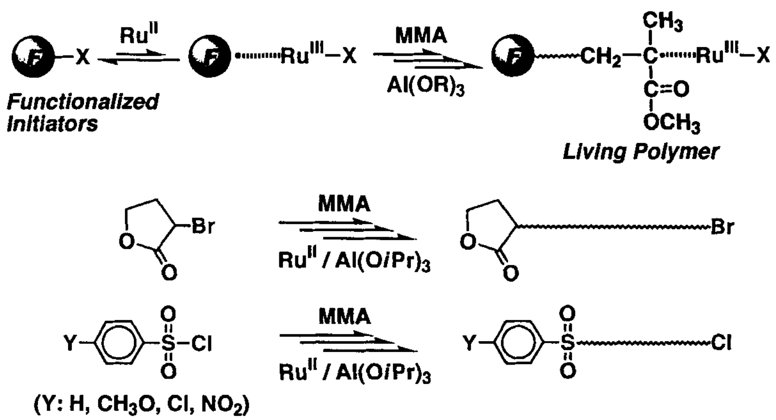
Initiators (R–X) and Metal Complexes

In addition to carbon tetrachloride [4] and dichloroacetophenone [5], a series of halogen-containing compounds are now available for living radical polymerization. These are almost invariably polyhalo-compounds; typical examples include di- and trichloroacetates, adducts of methacrylates with hydrogen chloride or bromide, and trichlorobromomethane [8]. Multifunctional initiators are also developed (see below).

It is of particular importance to establish the scope of metal complexes that are effective for our living radical polymerization, because this knowledge will certainly help us understand the exact mechanism of the metal-mediated living radical polymerization. Although the scope has apparently not been established yet, several transition metal complexes other than $RuCl_2(PPh_3)_3$ are found effective,



Scheme 1. Multifunctional initiators for the synthesis of star polymers and telechelic polymers by living radical polymerization.



Scheme 2. Synthesis of end-functionalized polymers by living radical polymerization with functionalized initiators.

including phosphine complexes of Fe(II) [9] and Ni(II) [10], along with other complexes of Cu(I) [11].

Precision Polymer Synthesis

Block Copolymers and Living Random Copolymers

As with MMA, living radical polymerization is possible for other methacrylates, acrylates, and styrene derivatives. Sequential living polymerization with the $CCl_4/RuCl_2(PPh_3)_3/Al(OiPr)_3$ and related initiating systems then leads to a series of block copolymers [12]. Examples involve the following monomers to be coupled with MMA: butyl methacrylate; methyl and ethyl acrylates; and styrene.

Interestingly, mixtures of MMA and methyl acrylate can also be polymerized with the same initiating system to give living and random (statistical) copolymers [13]. NMR analysis indicates efficient cross propagation; the molecular weights of the copolymers increases proportionally to total polymer yield.

Star Polymers: Multifunctional Initiators

Alkyl dichloroacetates are good initiators for the ruthenium-based living radical polymerization of MMA; one of the two chlorines attached to the ester group serves as an effective initiation site. Extension of this finding led to a series of di- and trifunctional initiators where dichloroacetates are attached to a aliphatic or aromatc core moiety derived from the corresponding alcohol or phenol (Scheme 1) [14]. The multiple initiation sites quantitatively induce living propagation to give narrowly distributed poly(MMA); each arm chain is capped with a tertiary chloride. Thus, these products are triarmed star polymers and telechelic polymers.

End-Functionalized Polymers

As summarized in Scheme 2, initiators to be coupled with $RuCl_2(PPh_3)_3$/-$Al(OiPr)_3$ may also bear some functionality, and living polymerization therefrom thus gives end-functionalized polymers. For example, 2-bromolactones initiates such living polymerization to give lactone-capped poly(MMA) that would be of interest as new macromonomer to combine polyester and poly(MMA) chains in graft copolymers [15].

Another class of functionalized initiators is arylsulfonyl chloride [16, 17]. The treatment with $RuCl_2(PPh_3)_3$ [16] or other complexes [17] most likely generates sulfur-centered radicals that polymerize MMA and styrene. The ring-substituents in the arylsulfonyl groups are in turn attached to the α-end of the polymers and serve as end functionality. These systems are also interesting in that not only carbon radicals but also sulfur radicals are effective in living radical polymerization.

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