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CONTROLLED SYNTHESIS OF FUNCTIONALIZED POLYMERS BY TRANSITION-METAL-MEDIATED LIVING RADICAL POLYMERIZATION

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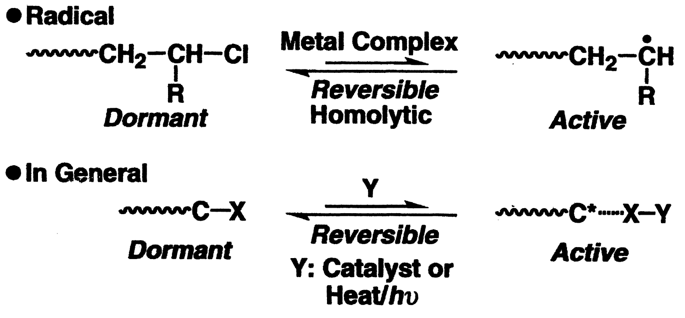
SUMMARY: This paper discusses recent progress in transition-metal-catalyzed living radical polymerizations, partly focusing on the search of metal complex catalysts that play a critical role in controlling polymer molecular weights, their distributions, and architectures. Following a brief overview of the design of initiating systems (initiators and metal catalysts), half-metallocene-type complex catalysts are presented that induce living radical polymerizations of methacrylates, acrylates, and styrene to give markedly narrow molecular weight distributions and controlled molecular weights. Some of these half metallocenes also work in water where suspension living radical polymerization is feasible.

Introduction

Since the first publications in 1994–95[1)], we have been pursuing living radical polymerizations mediated by the initiating systems that consist of an alkyl halide (initiator) and a transition metal complex (catalyst)[2)]. It is now widely recognized that these metal-catalyzed living radical polymerizations, as well as those with stable radicals[3)] and others, involve a dynamic equilibrium between the active growing radical and its dormant counterpart, as schematically shown in a general form and a more specific form for the metal catalysis (Scheme 1)[2c,4)]:



Scheme 1: Dormant–active species equilibria for living polymerizations: a general form (bottom) and for metal-catalyzed systems (top).

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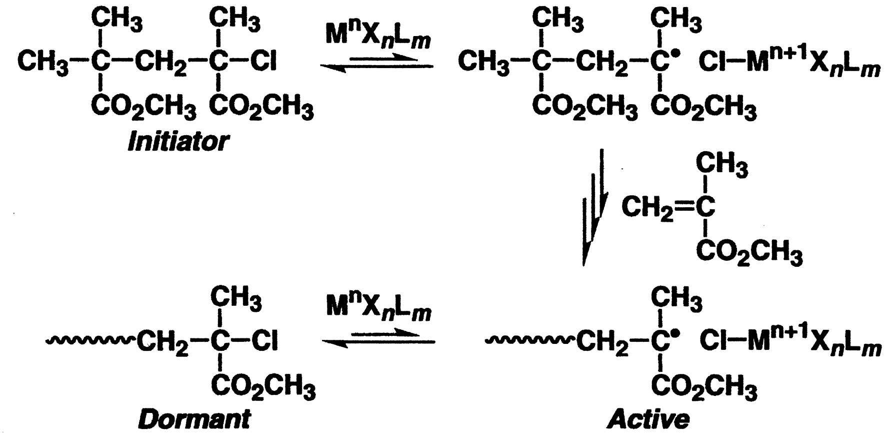
In general, these dormant–active species equilibria are efficiently reversible favoring the dormant side and are thus considered to suppress bimolecular termination reactions, the most serious and inherent chain-breaking step in radical polymerization, by decreasing the instantaneous radical concentration, while still ensuring the fine control of polymer molecular weight and molecular weight distribution (MWD) expected for living polymerizations. To illustrate such reactions, a typical example of our metal-catalyzed living processes is given in Scheme 2, where methyl methacrylate (MMA) can be polymerized into living polymers with the ruthenium(II) chloride - triphenylphosphine complex ($[RuCl_2(PPh_3)_3]$):



Scheme 2: Living radical polymerization of MMA via dormant–active species equilibria mediated by transition metal catalysis ($[M^nX_nL_m]$ = $[RuCl_2(PPh_3)_3]$, $[Ru(Ind)Cl(PPh_3)_2]$, $[FeCl_2(PPh_3)_2]$; Ind = indenyl).

Over these five years we have been exploiting new initiating systems (initiator/metal catalyst pairs) to be applicable in a variety of radically polymerizable monomers. This paper first presents a concise overview of the current status of such system design and then illustrates some of the recent examples with half-metallocene-type Ru(II) and Fe(II) complexes which have proved highly effective for methacrylates, acrylates, and styrene to form polymers of controlled molecular weights and markedly narrow MWDs.

System Design: Initiating Systems and Monomers

Figures 1–3 compile representative examples of initiators, metal catalysts, and monomers, respectively, which have been used in living radical polymerizations.

Initiators. Among other possibilities, alkyl halides (R–X; X = Cl, Br, I) have been shown to be most effective for metal-catalyzed living radical polymerization (Fig. 1)[2c]. The alkyl groups (R) are such that carry an α-substituent to stabilize, or promote the formation of radicals therefrom, including carbonyls and multiple halogens. As often happens in other living polymerizations, the alkyl groups mimicking the growing ends (monomer radicals) are suitable. The halogens (X) apparently depend on the monomers to be used; namely, chlorine and bromine are suited for methacrylates, whereas iodine is better for styrene derivatives.

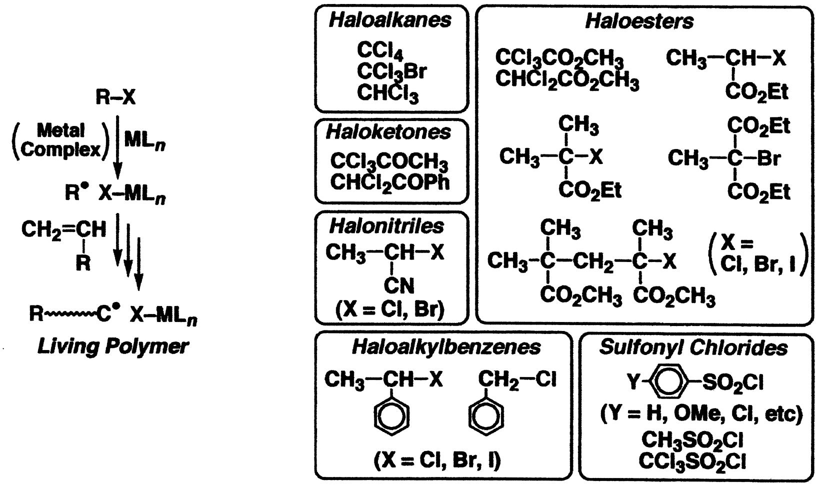


Fig. 1: Initiators for transition-metal-catalyzed living radical polymerizations.

Metal Complex Catalysts. Obviously, these components are specifically important in the living radical polymerizations via metal catalysis. For the recent few years, we in Kyoto have been focusing our research efforts to expand and, hopefully, generalize, the scope of these metal catalysts (Fig. 2). The current list includes group 7–11 transition metal elements as catalyst centers, such as Ru(II), Ni(II), Ni(0), Fe(II), and Re(V), among others.

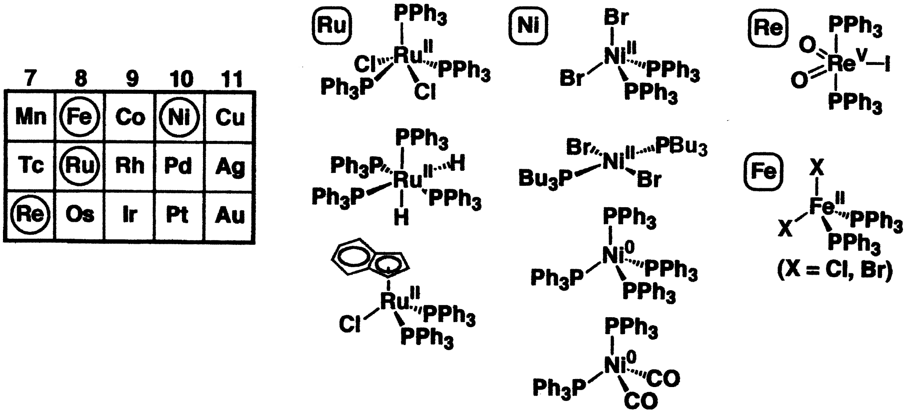


Fig. 2: Transition-metal-complex catalysts for living radical polymerizations.

For the reversible formation of radicals from the initiators, which is an oxidation–reduction cycle with regard to the catalyst, these metal centers should be able to assume at least two oxidation states such as Ru(II) and Ru(III). Most of these catalysts are therefore derived from the so-called late transition metals. Detailed mechanistic and physicochemical analyses such as cyclic voltammetry would be needed to enhance design of the catalysts.

Monomers. So far, nearly all classes of the so-called conjugated monomers have been available for the metal-mediated living radical polymerizations, including methacrylates, acrylates, and styrenes (Fig. 3). Some polar monomers, such as 2-hydroxyethyl methacrylate and acrylamides, may also be employed, as selected initiating systems are tolerant to unprotected functional groups (hydroxy, in particular). A current problem is that none of metal-based initiating systems are applicable to ethene, butadiene, vinyl chloride, vinyl acetate, and other non-conjugated monomers.

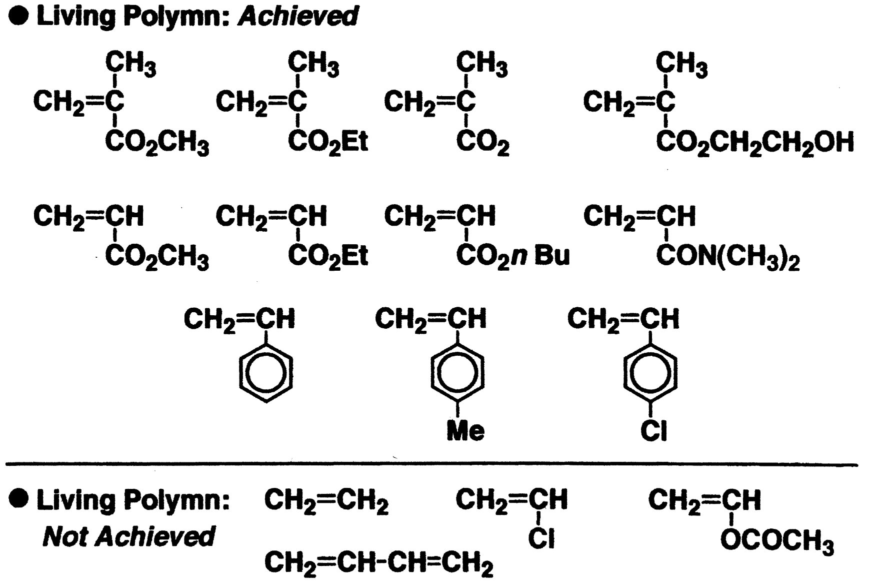
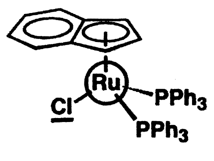


Fig. 3: Monomers for transition-metal-catalyzed living radical polymerizations of methacrylates, acrylates, styrenes, and related polar functional vinyl compounds.

Half-Metallocene-Type Catalysts for Living Radical Polymerizations

We have recently found that half-metallocenes of Ru(II) and Fe(II) are highly active and efficient catalysts for living radical polymerizations. Their cyclopentadienyl (Cp) and indenyl (Ind) ligands supposedly enhance the catalytic activity via their electron-donating and conjugated structures which facilitate the one-electron oxidation–reduction process in the dormant–active species equilibrium (Schemes 1 and 2). Representative examples follow.

Ru(II)-Indenyl Complexes. When coupled with alkyl chlorides as initiators, a ruthenium-indenyl complex, $[RuCl(Ind)(PPh_3)_2]$, induces living radical polymerizations of methacrylates and styrene (Fig. 4)5).



$Ru(Ind)Cl(PPh_3)_2$

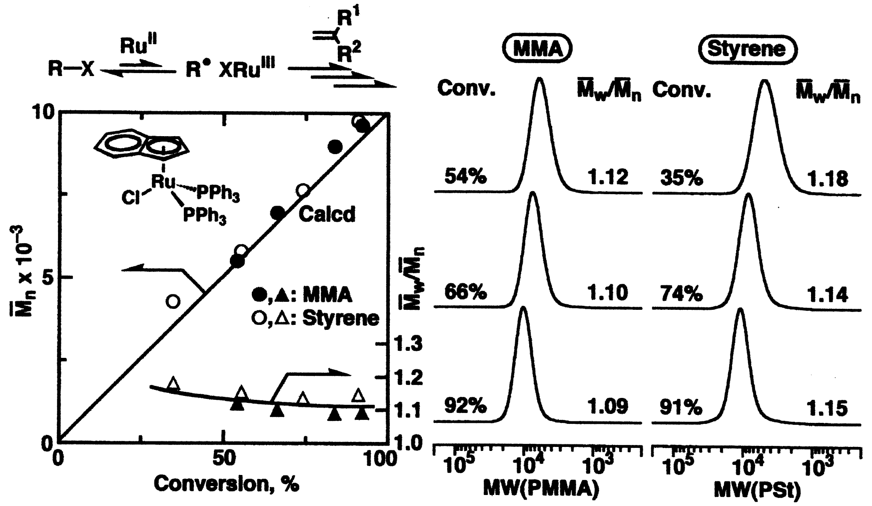
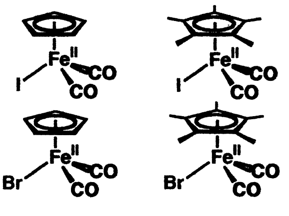


Fig. 4: Living radical polymerizations of MMA and styrene with $[RuCl(Ind)(PPh_3)_2]$ (concentrations in mM: MMA 4000, $H\text{-}(MMA)_2\text{-}Cl$ 40, Ru(II) 4.0, $Al(Oi\text{-}Pr)_3$ 40, styrene 4000, $H\text{-}(EMA)_2\text{-}Br$ 40, Ru(II) 2.0, $Al(Oi\text{-}Pr)_3$ 80, toluene, 100 °C).

For MMA, for example, the polymerization is clearly faster than those with $[RuCl_2(PPh_3)_3]$, a conventional Ru(II) catalyst for our purpose; the indenyl catalyst does not necessarily require activating additives such as $Al(O\textit{i}Pr)_3$ often needed for the dichloride and other catalysts. In particular, the $[RuCl(Ind)(PPh_3)_2]$-based systems routinely give living polymers with very narrow MWDs ($M_w/M_n < 1.1$) and molecular weights in excellent agreement with the calculated values expected from the monomer/initiator ratio. The high catalyst activity permits to reduce the metal complex concentration and to lower polymerization temperature (100–30 °C).

As shown in Fig. 5, it is also possible to synthesize living poly(MMA) with high molecular weights in the range of 10^5 (DP > 1000).

Fe(II)-Cyclopentadienyl Complexes. As shown below, a series of Fe(II)-Cp halide carbonyl complexes ($[FeXCp(CO)_2]$ and $[FeXCp^*(CO)_2]$, X = Br or I; Cp = cyclopentadienyl, Cp* = pentamethyl-cyclopentadienyl) can readily be obtained commercially or prepared from the



corresponding bimetallic precursors. The complexes are crystalline, air-stable, moisture-tolerant and phosphine-free half-metallocenes, which can be conveniently employed for living radical polymerization[6].

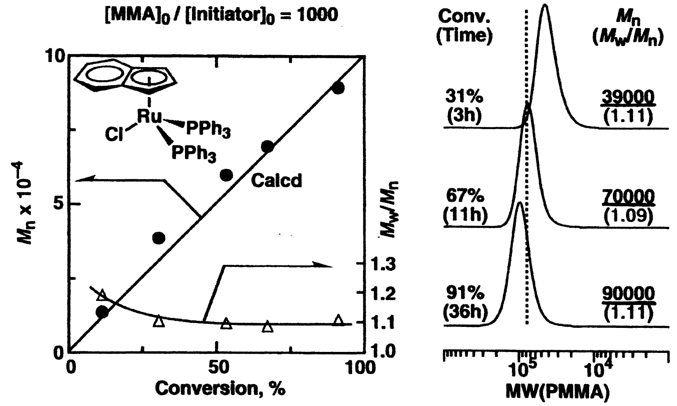


Fig. 5: High-molecular-weight poly(MMA) via a living radical polymerization with $[RuCl(Ind)(PPh_3)_2]$ ($[MMA]_0 = 8.0$ M, $[PhCOCHCl_2] = 8$ mM, $[Ru(Ind)Cl(PPh_3)_2] = 2$ mM, toluene, 100 °C).

In particular, the Fe(II)-Cp iodides are suitable for living styrene polymerization to give very narrow MWDs, much narrower than those from $[RuCl_2(PPh_3)_3]$ previously reported by us (Fig. 6).

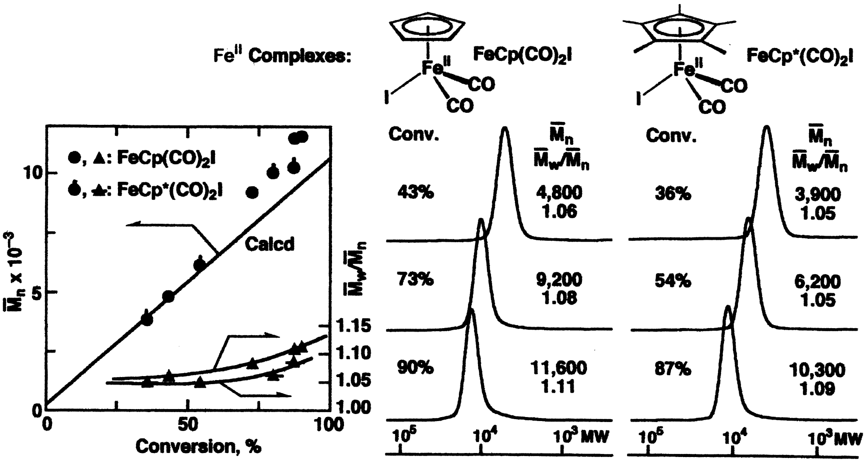
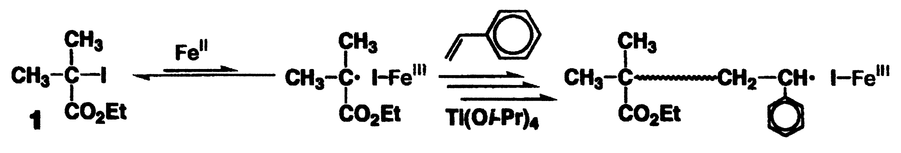


Fig. 6: Living radical polymerizations of styrene with $[FeICp(CO)_2]$ and $[FeICp^*(CO)_2]$ (Cp^* = pentamethylcyclopentadienyl; $[styrene]_0 = 6.0$ M, $[1]_0 = 60$ mM, $[Fe(II)]_0 = 10$mM, $[Ti(Oi\text{-}Pr)_4] = 100$mM, toluene, 80 °C).

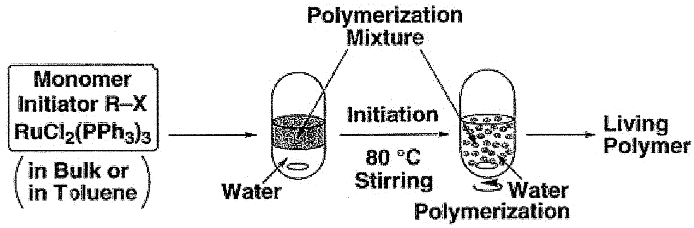
For styrene, it seems important to use an iodide initiator for fine control of polymerization, and thus the Fe(II)-Cp iodide would be most suited to avoid halogen exchange between the catalyst and the dormant end.



Synthetic Aspects

As expected, the metal-catalyzed living radical polymerizations can be applied to the precision synthesis of block, amphiphilic, end-functionalized, star-shaped, and other functionalized polymers of designed architectures; living and random copolymerizations are also possible for a variety of monomer pairs, inheriting a merit of free radical polymerizations.

Suspension Living Radical Polymerization. Another unique aspect is that, as illustrated in Scheme 3, some of these polymerizations are feasible in aqueous and alcoholic media, while retaining their living characters7). The basis of this aspect is the tolerance of the Ru(II)-catalyzed polymerization towards protonic compounds, whereas they are readily terminated by nitroxide and related stable radicals8). Thus, for example, in the presence of a large amount of water, the polymerization proceeds as in organic media to give living polymers from MMA, styrene, and other monomers. The catalysts for such "suspension living polymerization" include $[RuCl_2(PPh_3)_3]$ and $[RuCl(Ind)(PPh_3)_2]$.



Scheme 3: Suspension living radical polymerization in water with a Ru(II) catalyst.

Acknowledgments

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