Living Radical and Cationic Polymerizations in Water and Organic Media

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Summary: This lecture will focus two living polymerizations that can be carried out in water as well as in organic media. The first one is transition metal-catalyzed living radical polymerization, for which Ru(II) and other transition metals play a critical role to control the process; for aqueous systems, Ru(II) and Fe(II) half metallocene complexes are useful. The second is cationic polymerization with water-tolerant Lewis acids as catalysts, including rare earth triflates and boron trifluoride for selected monomers. Discussion will be directed to the design of initiating systems, search of versatile catalysts, and precision synthesis of new polymers.

Introduction

Despite the fact that both radical and cationic polymerizations have been difficult to control, primarily due to, respectively, bimolecular termination of free radical intermediates and chain transfer (β-proton elimination) of carbocationic growing species, we have shown that they can be finely controlled to give *living* radical and cationic polymerizations. Both systems can be initiated with halogen-containing initiators (R–X; X = halogen) coupled with appropriate catalysts (activators): transition metal complexes for radical living polymerization and selected Lewis acids (mostly metal halides) for cationic counterparts. In these living polymerizations, it is now widely accepted that the carbon–halogen terminals, derived from the initiators R–X, form the so-called "dormant" species which can be dissociated into radical or carbocationic growing species by the relevant catalyst. Importantly, the dissociation processes [—C–X + catalyst → —C* X(catalyst); C* = radical $C^{\bullet}$ or carbocation C^{+}] are reversible and in a rapid, dynamic equilibrium, so as to retain a relatively low concentration of the truly active intermediate (—C*) and thus to effectively minimize the side-reactions (termination or chain transfer).

This paper presents a brief overview on these two living polymerizations that we have recently developed, with some emphasis focused on the processes operable in water or similar aqueous media where neither traditional metal-catalyzed nor carbocationic polymerization has been perceived controllable and, above all, possible.

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Transition Metal-Catalyzed Living Radical Polymerization

In 1994–95, we reported the first example of living radical polymerization mediated by a transition metal catalyst[1-3]. Figure 1 illustrates a typical example of such processes where a ruthenium(II) dichloride complex, in conjunction with a halogen-containing initiator, induces a living polymerization of methyl methacrylate (MMA) to give polymers of controlled molecular weights and very narrow molecular weight distributions (MWDs).

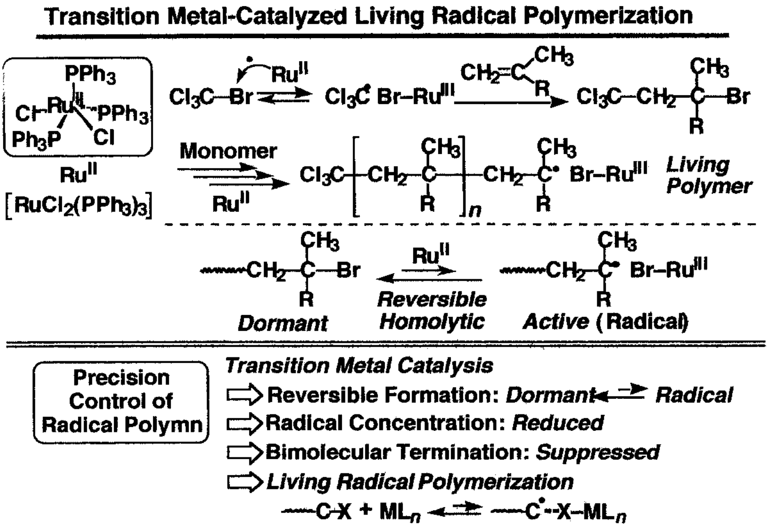
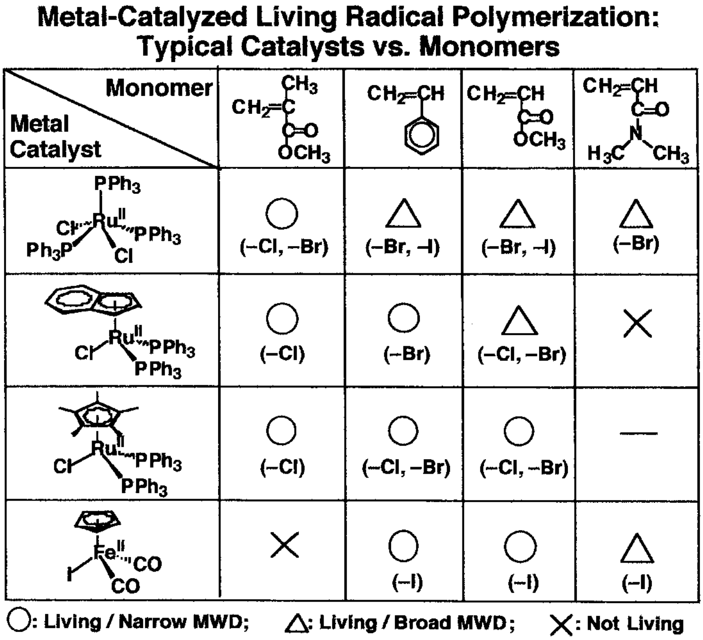


Figure 1. Transition metal-catalyzed living radical polymerization: A typical example and the general principles for precise control of radical polymerization[2,3].

As discussed above in a general form, the key to these living radical polymerizations is the reversible formation of radical species from the dormant carbon–halogen terminal assisted by the Ru(II) catalyst, which undergoes a one-electron oxidation into a Ru(III) species that, after some propagation step, regenerates the dormant end via a one-electron reduction. The intermediate radical concentration is thus kept much lower than in conventional free radical polymerizations, and thereby bimolecular termination is effectively suppressed relative to propagation.

(a) Scope

The following five years or so have witnessed a rapid, systematic, and worldwide development of the transition metal-catalyzed living radical polymerizations in terms of the scope of monomers, catalysts, and initiators, along with the related "precision" synthesis of finely controlled and designed polymers. For example, Figure 2 gives just a small list of catalysts, showing which catalyst is effective or applicable to which monomers of different classes (methacrylates, acrylates, styrenes, etc.). We are currently interested in "half-metallocene" complexes of Ru(II) and Fe(II), because, as shown in the table, they are more active and, equally important, more versatile (applicable to more monomers) than the now classical dichloride/phosphine counterparts[4]. The substituents for these metallocenes are typically indenyl (Ind), cyclopentadienyl (Cp), and pentamethylcyclopentadienyl (Cp*).



Metal-Catalyzed Living Radical Polymerization: Typical Catalysts vs. Monomers

Monomer / Metal Catalyst	$CH_2=C(CH_3)-C(=O)-OCH_3$	$CH_2=CH-C_6H_5$	$CH_2=CH-C(=O)-OCH_3$	$CH_2=CH-C(=O)-N(CH_3)_2$
PPh3, Cl, Ru II, PPh3, Ph3P, Cl	○ (–Cl, –Br)	△ (–Br, –I)	△ (–Br, –I)	△ (–Br)
Ru II, Cl, PPh3, PPh3	○ (–Cl)	○ (–Br)	△ (–Cl, –Br)	×
Ru II, Cl, PPh3, PPh3	○ (–Cl)	○ (–Cl, –Br)	○ (–Cl, –Br)	—
Fe II, I, CO, CO	×	○ (–I)	○ (–I)	△ (–I)

○: Living / Narrow MWD; △: Living / Broad MWD; ×: Not Living

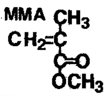
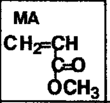
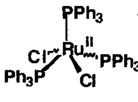
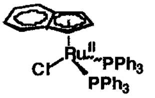
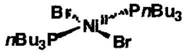
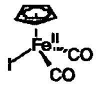
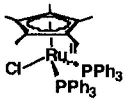
Figure 2. The scope of transition metal-catalyzed living radical polymerization: Typical metal catalysts and monomers.

Another important development, in our view, is that some additives can accelerate these Ru(II)- and Fe(II)-catalyzed polymerizations, and these additives include metal alkoxides [$Al(O\textit{i}Pr)_3$, etc.] and amines [Bu_2NH, etc.]. In a typical example, the RuCl(Ind)-($PPh_3)_2$ (Ind = indenyl; Ph = phenyl) catalyst can polymerize MMA in toluene at 80 °C in ca. five hours to nearly quantitative conversion, where polymers have controlled molecular weights and dispersity ratios below 1.15. On the other hand, FeX(Cp*)-$(CO)_2$ (X = halogen) seems effective for styrene, giving similar living polymers from iodide-type initiators.

(b) Living Random Copolymerization

This subject is interesting, because it integrates the advantage of living processes (molecular weight control etc.) with those of radical polymerizations over ionic counterparts that a wide variety of monomer pairs can readily be copolymerized. In fact, the transition metal catalysts discussed above are equally effective in such "living" random copolymerizations, and some examples are compiled in Figure 3, showing typical catalysts for the MMA–methyl acrylate pair. Again, the Cp* catalysts are versatile and effective, and can form living random copolymers of narrow MWDs and molecular weights exceeding 10^5.

Living Random Copolymerization:
Typical Metal Catalysts vs. Monomers

Monomer / Metal Catalyst		*Homopolymerization*		**MMA/MA** *Random copolymer*
		MMA  $CH_2{=}C(CH_3)C(=O)OCH_3$	MA  $CH_2{=}CHC(=O)OCH_3$	
	Al(O*i*-Pr)$_3$	○ (–Cl, –Br)	△ (–Br, –I)	○ (–Cl) ¦ ◎ (–Br)
	Amine	○ (–Cl, –Br)	×	○ (–Cl)
		○ (–Cl)	△ (–Cl, –Br)	○ (–Cl)
		○ (–Br)	△ (–Br)	○ (–Br)
		×	○ (–I)	○ (–I)
		○ (–Cl, –Br)	○ (–Cl, –Br)	◎ (–Cl)

Homopolymn ○: **Living / Narrow MWD (M_w/M_n = 1.1–1.2)**
△: **Living / Broad MWD** ×: **Not Living**

Copolymn ◎: **Living / Narrow MWD (M_w/M_n < 1.5)**
○: **Living / Broad MWD (M_w/M_n > 1.5)**

Figure 3. Living radical copolymerization with transition metal catalysts: Typical catalysts and their applicability for the methyl methacrylate–methyl acrylate comonomer pair.

(c) Core-Functionalized Star Polymers

Along with the development of initiating systems and metal catalysts, we have been pursuing the precision synthesis of new polymers via our living radical polymerizations[3]. A recent example of interest is "core-functionalized" star polymers (Figure 4): Linear living polymers, obtained in a metal-mediated polymerization and kept unquenched, are treated with a small amount of selected divinyl monomers, which are attached to the polymer end as a short segment carrying unreacted vinyl functions in the pendant group. These vinyl moieties then react with the growing radical ends, initiating a "polymer linking" process, to give microgel cores to which a large number of the linear polymers are attached as "arms".

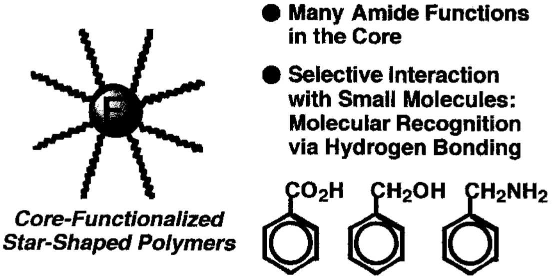


Figure 4. Core-functionalized star polymers by metal-mediated living radical polymerization and polymer linking with a bifunctional acrylamide.

The example shown in Figure 4 is specifically employs a series of bifunctional amide monomers [e.g., $CH_2=CH(CO)NHCH_2NH(CO)CH=CH_2$] as polymer-linking agents, and thus the resulting star polymers carry a large number (sometimes more than a few hundred per core) of amide functions in the microgel core, then coined core-functionalized.

Thanks to these concentrated and localized amide functions, these star polymers can interact with some polar organic compounds, such as benzoic acid, through hydrogen bonding with the amide group.

(d) Living Radical Polymerization in Water

In general, transition metal complexes are not stable in water and similar polar media, often loose their catalytic activity, but some class of Ru(II) compounds are known to be less oxophilic and thereby active as catalysts even under aqueous conditions. This is indeed the case for the Ru(II)-catalyzed living radical polymerization (Figure 5).

For example, the three catalysts shown in Figure 5 can be employed for MMA and other monomers that are polymerized efficiently into living polymers of controlled and sometimes fairly high molecular weights beyond 10^5. Typically, the monomer, an initiator, and a Ru(II) catalyst are mixed either in bulk monomer or in a small amount of toluene, and the solution is vigorously mixed into an excess of water to form a suspension. On elevating temperature, living polymerization has been found to proceed in the fine droplets, as in those in organic media.

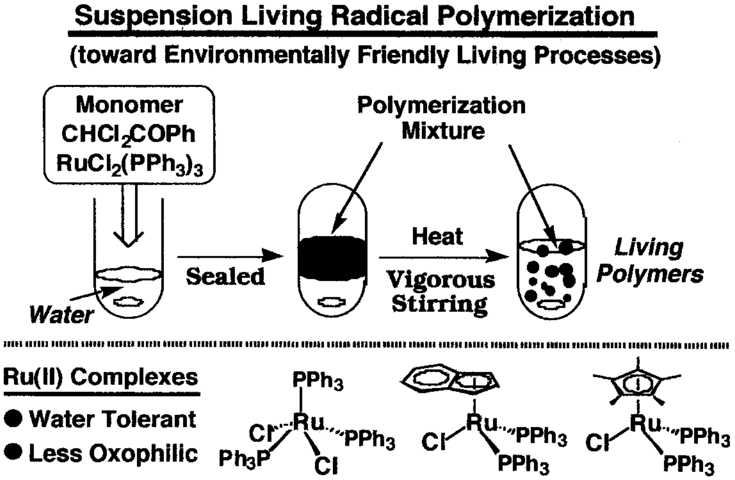


Figure 5. Suspension living radical polymerization in water: A schematic illustration.

Recent results in our laboratories also show that FeXCp*(CO)2 is similarly tolerant to water and catalyzes living radical polymerizations of acrylates and styrene.

As readily expected, these living processes feasible in water would be of interest as future production of polymers under environmentally benign conditions. No doubt, the critical factor is to develop metal catalysts that withstand an excess of water, and another aspect would be water-soluble metal catalysts that can medicate similar precision polymerizations in homogeneous aqueous systems for water-soluble monomers such as acrylic acid and acrylamide.

Cationic Polymerization in Water or in Aqueous Solution

In contrast to the notion that cationic polymerization must be carried out under stringently anhydrous conditions, we have recently found that sometimes it is not the case. As summarized in Figure 6, the use of water-tolerant Lewis acids as catalysts permits us to carry out cationic polymerizations either in water (suspension or emulsion systems) or in polar solvents containing excess water.

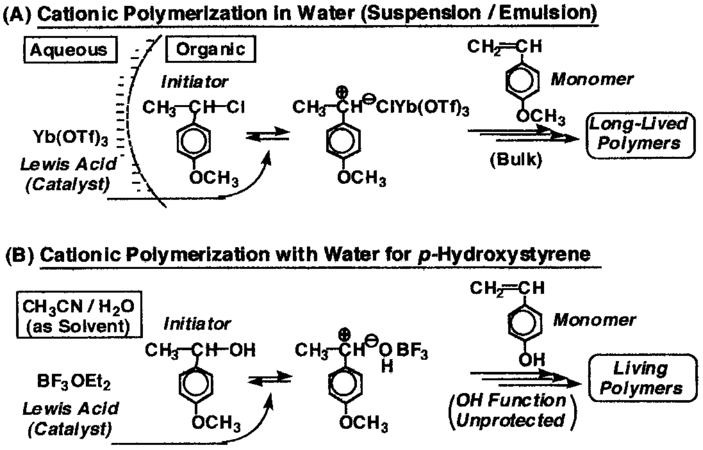


Figure 6. Cationic polymerizations in water or in aqueous solution with water-tolerant Lewis acid catalysts[5,6].

(a) Suspension and Emulsion Cationic Polymerization in Water into Long-Lived Polymers

One approach is to utilize rare-earth metal triflates (trifluromethanesulfonates) as catalysts; because the large ionic radii and the high coordination number of these metals, along with the strong electron-withdrawing nature of the triflate substituent, these salts are highly soluble in water and exhibit strong Lewis acidity therein (Figure 6A)[5]. A typical example is ytterbium triflate, $Yb(OTf)_3$ ($OTf = OSO_2CF_3$), which turned out to induce cationic polymerization of vinyl ethers and *p*-alkoxystyrenes when couple with a suitable halogen-containing initiator such as the hydrogen chloride adducts of the latter monomers; for these monomers, also, the resultant polymers are of a long lifetime and their molecular weights increase with conversion.

These polymerizations can be performed either in suspension (similar to the corresponding living radical systems) or in emulsion (with tetraalkylammonium salts as surfactants), and separate analysis shows that they in fact involve carbocationic species surviving in the organic phase exposed to bulk water. Copper and zinc triflates may also be used in place of the rare-earth salts, though less active.

(b) Cationic Polymerization with Water for (Unprotected) *p*-Hydroxystyrene

The second approach is for homogeneous polymerization of unprotected *p*-hydroxystyrene (*p*-vinylphenol) in acetonitrile solvent containing an excess of water[6]. The Lewis acid of choice herein is, rather surprisingly, boron trifluoride etherate (BF_3OEt_2), one of the most conventional and oft-employed Lewis acids for cationic polymerization, and it is also important to combine it with initiators where the hydroxyl group is the anionic leaving group for carbocation formation (Figure 6B). The boron compound apparently has a strong oxophilicity so as to specifically interact with the hydroxyl group in the initiator for selective initiation.

This initiating system is applicable to the unprotected *p*-hydroxystyrene whose phenolic group is of course often disturbs ionic polymerization, not mention to the insolubility of the monomer and the polymer in common (less polar) organic solvents and thus further complicate its direct polymerization. Nevertheless, the BF_3OEt_2-catalyzed process withstands the phenolic groups in the monomer and cleanly induces its cationic polymerization. The reaction is carried out in the polar solvent in which addition of water is also required to keep the controllability. Under these conditions, the products, similar to living polymers, have a long lifetime, where the molecular weight can be controlled. The same initiating system can be applied to styrene polymerization.

[1] T. Higashimura, M. Sawamoto, M. Kamigaito, Jpn. Patent Appl. 179850 (Aug. 1994); Kokai, 41117 (Feb. 13, 1996).

[2] (a) M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules* **1995**, *28*, 1721. (b) T. Ando, M. Kato, M. Kamigaito, M. Sawamoto, T. Higashimura, *Macromolecules* **1996**, *29*, 1070.

[3] For a recent review: M. Sawamoto, M. Kamigaito, *CHEMTECH* **1999**, *29*(6), 30.

[4] (a) H. Takahashi, M. Kamigaito, M. Sawamoto, *Macromolecules* **1999**, *32*, 3820. (b) Y. Kotani, M. Kamigaito, M. Sawamoto, *Macromolecules* **2000**, *33*, 3543.

[5] K. Satoh, M. Kamigaito, M. Sawamoto, *Macromolecules* **1999**, *32*, 3827; *Macromolecules* **2000**, *33*, 4660; *Macromolecules* **2000**, *33*, 5836; *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 2728.

[6] K. Satoh, M. Kamigaito, M. Sawamoto, *Macromolecules* **2000**, *33*, 5405; *Macromolecules* **2000**, *33*, 5830; *Macromolecules* **2001**, *34*, in press.