Transition Metal-Mediated Living Radical Polymerization toward Precision Functional Polymers via Catalyst Design

Mitsuo Sawamoto, Makoto Ouchi

Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, Katsura, Nishikyo-ku, Kyoto 615-8510, Japan
sawamoto@star.polym.kyoto-u.ac.jp

Introduction

Radical polymerization is no doubt among the most important chain-growth (addition) polymerizations by which millions of tons of polymer materials are produced. Recent development of a variety of *living radical* polymerization further enhanced its importance, and already about a decade ago we developed transition metal-mediated living radical polymerization (Figure 1) [1,2], which is now under extensive and fast development in both academia and industry.

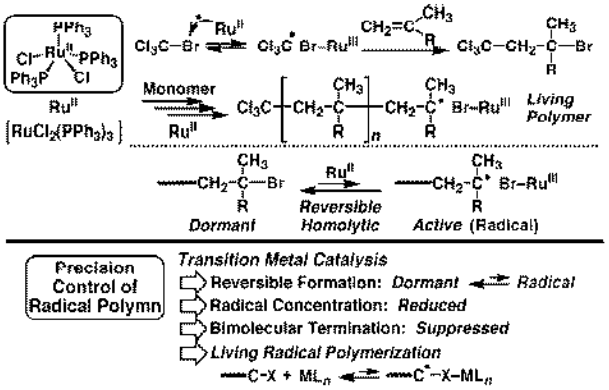

Figure 1. Metal-catalyzed living radical polymerization: An example, mechanism, and characteristics.

This lecture will present an overview of recent advances in this unique process, particularly focusing the following topics (Figure 2):
(A) Design of Transition Metal Complexes: Evolution of Catalysts
(B) New Ruthenum and Iron Catalysts: Active and Versatile
(C) Functional Methacrylates for Advanced Functional Polymers
(D) Functional Star Polymers: Microgel Cores for Metal Catalysts

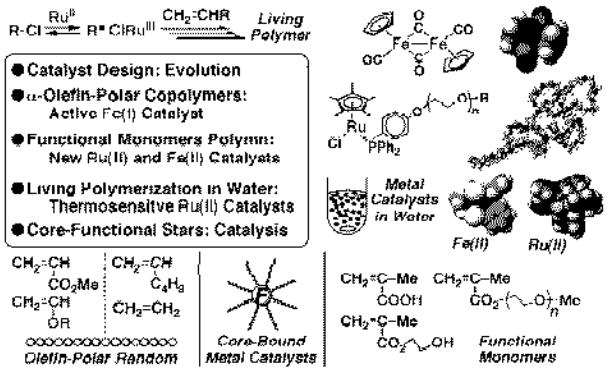

Figure 2. Metal-catalyzed living radical polymerization: Recent advances focused on catalysts and functional polymers.

Design of Transition Metal Complexes

Evolution of Catalysts. The reaction pathway illustrated in Figure 1 shows the importance of transition metal catalysts in our living radical polymerization, in which the dormant carbon–halogen terminal should be dissociated reversibly and homolytically. Extensive search and development of late transition metal complexes in our and other laboratories thus led to a variety of efficient catalysts to realize finely controlled (living) radical polymerizations.

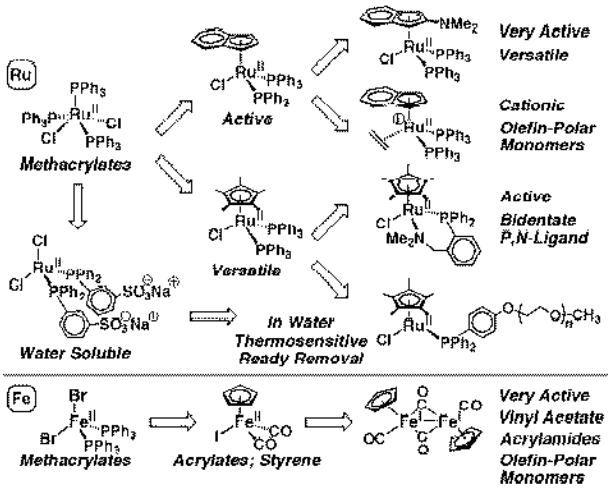

Figure 3. Transition metal catalysts for living radical polymerization: Evolution tree via systematic ligand modification.

Figure 3 just presents typical examples, as showing how the original ruthenium dichloride has been improved in terms of activity and versatility (applicability to a wide range of monomers).

New Ruthenium and Iron Catalysts. Among complexes of late transition metals, those of Ru(II), Fe(II), Fe(I), Ni(II), and Cu(I) are particularly useful. Figure 4 gives a small list of new ruthenium and iron catalysts developed in our group. Ruthenium analogs are of importance, because of their high tolerance to polar functional groups that often poison sensitive organometallyic compounds, whereas iron counterparts are potentially more active and, in particular, safe, inexpensive, and easy to remove, while their tolerance to functional groups is thus far limited.

More specifically, the three Ru(II) indenyl complexes (Figure 4, top row) with electron-donating ligands are all active and applicable to acrylic and styrenic monomers including those of pendent functionality; another version with a poly(ethylene glycol) (PEG) ligand is thermosensitive (hydrophilic at lower temperature but lipophilic at elevated temperature) and is able to mediate dispersion living polymerization n water and is easy to remove via phase-transfer catalysis coupled with its thermosensitivity. The two iron counterparts are also active, and the binuclear version is especially useful in copolymerization of polar monomers (acrylates, etc.) with α-olefins (ethylene, 1-hexene, etc.) (Figure 5).

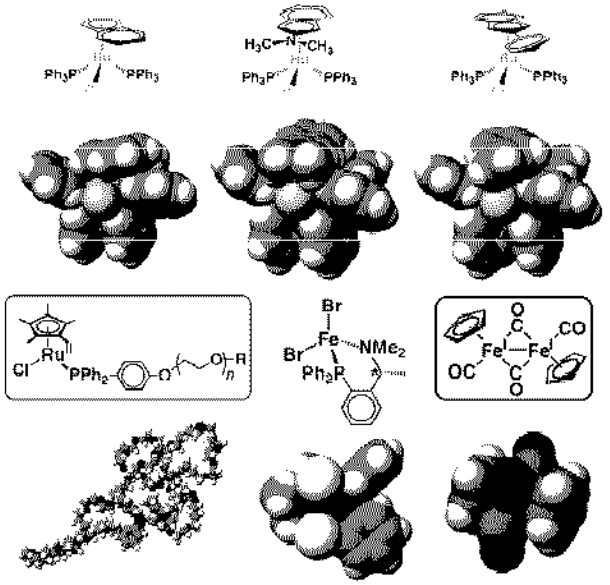

Figure 4. New ruthenium and iron complexes: Active and versatile catalysts for living radical polymerization.

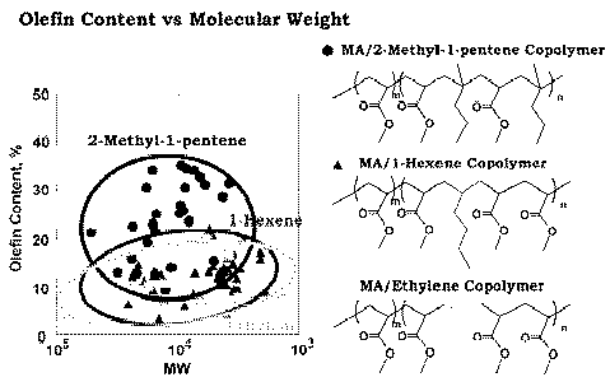

Figure 5. Random copolymerization of methyl acrylate (a polar monomer) and three α-olefins: Scope of polymer molecular weight and olefin content.

Precision Functional Polymers

Multifunctional *Random–Block* Copolymers of Functional Methacrylates. Thanks to the tolerance toward polar functions, the ruthenium complexes shown in Figure 4 can polymerize a variety of methacrylates that carry pendent functional groups. Recent findings include the so-called random–block copolymerization (Figure 6) in which different sets of alkyl and functionalized methacrylates are sequentially polymerized; each step is a living and random copolymerization, and thus two segments are different random copolymers with different and multiple functionalities such as PEG for good solubility and amphiphilicity, benzyl for π-π interaction with a aromatic pigment, and a branched alkyl for steric protection agains particle coagulation.

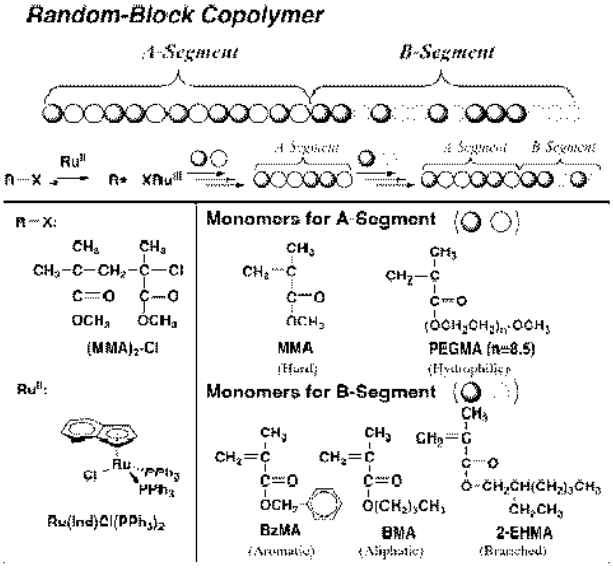

Figure 6. Multifunctional *random–Block* copolymers by Ru(II)-catalyzed living polymerization.

Functional Star Polymers. Linear living polymers can be linked together by treatment with a bifunctional monomer, and when the latter linking agent is at a low concentration, the products are entirely soluble star polymers where a microgel core from the bifunctional monomer carries a large number of linear arms derived from the starting living polymers.

We have extended this methodology by additionally including ligan-type linking agent and thereby placed a large number of phosphines in the core network (Figure 7) [3]. Thus, the functionalized core is now able to encapsulate ruthenium and iron complexes to form interesting star polymer catalysts. In particular, the core-bound complexes elude poisoning with water and air and catalyze organic reactions sometimes more efficient than their isolated counterparts

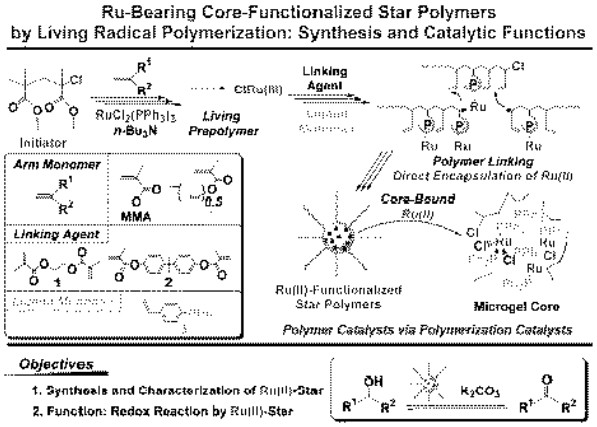

Figure 7. Core-functionalized star polymers by metal-mediated living radical polymerization: From a polymerization catalyst to a core-bound polymer catalyst.

References

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

[2] (a) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.* **2001**, *101*, 3689. (b) Sawamoto, M.; Ouchi, M. *Acc. Chem. Res.* In press.

[3] Terashima, K.; Kamigaito, M.; Baek, K.-Y.; Ando, T.; Sawamoto, M. *J. Am. Chem. Soc.* **2003**, *125*, 5288.