

Precision Control of Radical Polymerization via Transition Metal Catalysis: From Dormant Species to Designed Catalysts for Precision Functional Polymers

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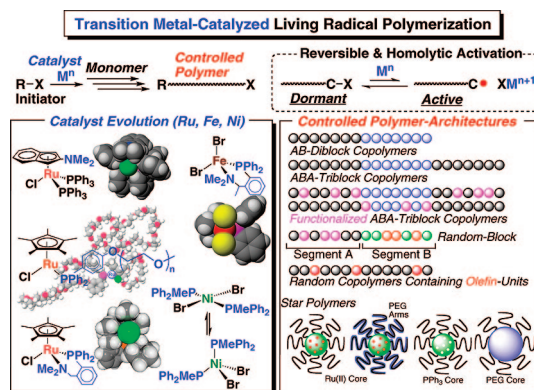
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CON SPECTUS

In the past decade, living radical polymerization has provided one of the most versatile methods to precisely construct designed polymer architectures with complexity and polar functionality. This process takes advantage of carbon-radical intermediates, which tolerate a variety of functional groups in monomers and reaction media. "Transition metal-catalyzed living radical polymerization", one of these living systems, has widely been employed for precision polymer synthesis. Not only can this process produce well-defined functional polymers, but it can also generate hybrids or conjugates with other (often biological) materials. Metal-catalyzed systems retain the advantages of conventional radical polymerization but distinguish themselves through a catalytic reversible halogen exchange equilibrium: the growing radical exists alongside a dormant species—a covalent precursor capped with a terminal halogen from an initiator. The catalyst dictates the selectivity, exchange rate, and control over the polymerization.

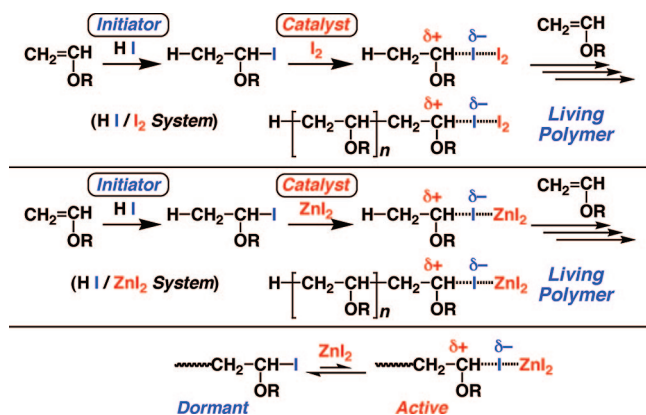
This Account provides an updated overview of our group's efforts in transition metal-catalyzed living radical polymerization with specific emphasis on the design of metal catalysts and the resulting precision polymer syntheses. With increasing use of the living processes as convenient tools for materials synthesis, researchers are currently seeking more active and versatile metal catalysts that are tolerant to functional groups. Such catalysts would enable a wider range of applications and target products, would have low metal content, could be readily removed from products, and would allow recycling. Since we first developed the "transition metal-catalyzed living radical polymerization" with $\text{RuCl}_2(\text{PPh}_3)_3$, $\text{FeCl}_2(\text{PPh}_3)_2$, and $\text{NiBr}_2(\text{PPh}_3)_2$, we have strived to systematically design metal catalysts to meet these new demands. For example, we have enhanced catalytic activity and control through several modifications: electron-donating or resonance-enhancing groups, moderate bulkiness, heterochelation via a ligand, and halogen-donor additives. For some catalysts, the use of amphiphilic and polymeric ligands allow efficient recovery of catalysts and convenient use in aqueous media. We have also used ligand design (phosphines) and other methods to improve the thermal stability of iron- and nickel-based catalysts and their tolerance to functional groups.



1. Introduction

1.1. A Way to Dormant Species for Polymerization Control. The discovery of metal-catalyzed living radical polymerization, the subject of this

Account, may date back to the early 1970s. Interested in cationic vinyl polymerization, the research group of Higashimura in Kyoto found that the molecular weight distribution (MWD) of certain polystyrene and related polymers consisted of two

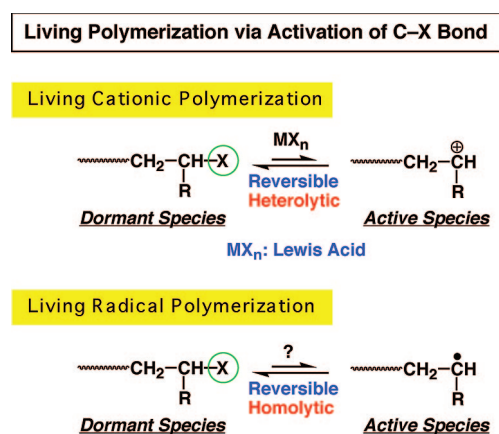
SCHEME 1. Lewis-Acid Catalyzed Living Cationic Polymerization via Dormant Species: Typical Examples for Vinyl Ethers

distinct peaks.¹ The bimodality was later demonstrated to result from an independent and simultaneous propagation of two coexisting intermediates, then coined as “dissociated” and “nondissociated” growing species.

The polymerization of *p*-methoxystyrene with iodine is among the systems in this line, but to our surprise, the lower molecular weight fraction increases as the polymerization proceeds, suggesting a long lifetime of the intermediate therein. At that time, we already knew that the lower fraction originates from the nondissociated species, and the polymer obtained in carbon tetrachloride in fact possesses a fairly narrow and unimodal MWD. Far more important, its number-average molecular weight (M_n) increases nearly linearly with monomer conversion. It was that time, around 1977, when we realized the possibility of living cationic polymerization, despite a long-standing notion that cationic polymerization should be beyond fine control because of the frequent chain transfer from the growing carbocation. In retrospect, the nondissociated species is a herald of the dormant species discussed below.

1.2. Living Cationic Polymerization via Dormant Halogen–Carbon Bond. Extensive efforts were therefore devoted in Kyoto to living cationic polymerization, and in 1983, we eventually reached the first living cationic polymerization, with alkyl vinyl ethers as monomers, initiated with binary initiating systems consisting of a protonic acid (initiator) and a Lewis acid (catalyst) (Scheme 1).² The reactions fulfilled all phenomenological criteria for living polymerization, such as controlled molecular weights and terminal groups, along with impressively narrow MWDs.

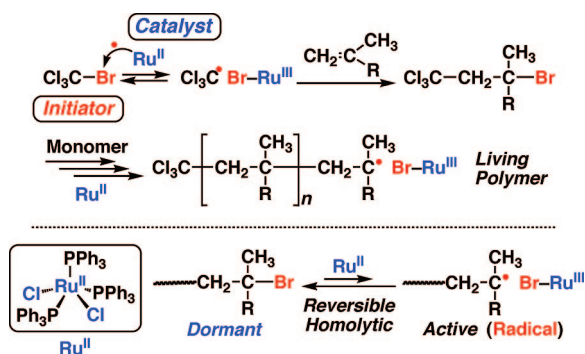
In these living cationic polymerizations,^{3,4} the propagating process involves the electrophilic dissociation of a covalent species (e.g., alkyl halide), derived from an initiator, into a minute concentration of a growing carbocation assisted by a Lewis acidic catalyst (e.g., zinc halides). Most important, this

SCHEME 2. From Living Cationic to Living Radical Polymerizations: A Concept with Dormant Species

process is reversible and dynamic where the covalent species dominates; the dormant end and the growing cation interconvert with each other, fast enough to ensure that all the dormant ends have nearly the same probability to grow and thus to generate narrow MWD. These covalent precursors are now called “dormant” species, a metastable intermediate that is itself incapable of propagating but is responsible for generating a true growing species upon action of a catalyst. Around that time, other living polymerizations mushroomed, most of which are one way or another mediated by dormant species, to establish its general importance in precision control of chain polymerizations hitherto difficult to attain.

1.3. From Living Cationic to Living Radical Polymerizations. In the early 1990s, we began to explore living radical polymerization by extending the concept of dormant species. Specifically we noted the ambivalence of a carbon–halogen bond in that it can dissociate either heterolytically (ionically) into a carbocation or homolytically (radically) into a carbon radical. Given that the former is catalyzed by a Lewis acid, then it was a logical consequence for us to assume that for the latter, a suitable catalyst should homolytically cleave it and, possibly, initiate controlled radical propagation (Scheme 2).^{5–8} We eventually found the triphenylphosphine complex of ruthenium(II) chloride [RuCl₂(PPh₃)₃; Ph = C₆H₅] to be the very catalyst, to give the first example of what we now call transition metal-catalyzed living radical polymerization.⁵

Scheme 3 illustrates a typical example, the polymerization of methyl methacrylate (MMA) with trichlorobromomethane (initiator) and RuCl₂(PPh₃)₃ (catalyst). The first process is the radical dissociation of the carbon–bromine bond in the initiator, catalyzed by the Ru(II) complex, generating a radical that initiates propagation with MMA; in this step, the catalyst center is oxidized from Ru(II) into Ru(III) while accepting the bromine from the initiator. After some propagation steps, the

SCHEME 3. Metal-Catalyzed Living Radical Polymerization via Dormant Species: A Typical Example with a Ru(II) Catalyst

radical intermediate is sooner or later capped with the bromine from the resulting Ru(III) species, to regenerate a dormant end and the Ru(II) catalyst. The process thus involves a reversible and dynamic equilibrium between the dormant species and the carbon radical, all mediated by a metal complex. The key to the living growth is a very low radical concentration coupled with the reversibility of its generation, thereby suppressing bimolecular radical termination prevailing in conventional radical polymerization.

The finding was first patented in August 1994; the first paper was submitted in September 1994 and appeared in May 1995.^{5,8} Shortly thereafter, similar systems based on copper catalysis were reported by Wang and Matyjaszewski.⁹ Since then, these discoveries triggered explosive and extensive research around the globe, in parallel with other living radical polymerizations based on dormant species, and the development is now history.^{7–9}

In this Account hereafter, we discuss more recent developments in this field, specifically focusing upon our own development of transition metal catalysts and precision synthesis of functional polymers.

2. System Design

2.1. Catalyst Evolution. Metal catalysts are definitely among the most critical components in “metal-catalyzed living radical polymerization”, which has in fact been developed hand-in-hand with their systematic design, or an evolution of catalysts.^{5–9} The required “work” for the catalysis is, as already discussed, the reversible activation of a dormant species or a terminal carbon–halogen bond, where it undergoes a one-electron oxidation/reduction followed by abstraction/release of a halogen. Thus, central metals should afford formation of at least two valence states with one valence difference and should possess a moderate halogen affinity. For these aspects, late transition metals in a lower valence state are generally

1st Generation



Subjects in Metal-Catalyzed Living Radical Polymerization

Controllability

(Narrow MWD, Block Copolymerization)

Activity

(Control with Lower Catalyst-Dose)

Versatility

(Control for Various Monomers:
e.g., Methacrylates, Acrylates, Styrenes)

Tolerance to Functional Group

(Control for Functional Monomers)

Environmental Friendliness

(Removal/Recycle)

FIGURE 1. Catalyst design criteria in metal-catalyzed living radical polymerization.

favorable, although some early transition metals have also been employed. The activation step is apparently triggered by the “one electron transfer” from a catalyst to a dormant terminus, and thus a higher electron density on the metal center would be suitable.

In the early stage of our search, we fortunately discovered the potency of phosphine-based ruthenium [Ru(II)],⁵ iron [Fe(II)],¹⁰ and nickel [Ni(II)]¹¹ complexes, among others, as catalysts for the metal-catalyzed living radical polymerization, and thus we have specifically directed our efforts toward systematically designing metal catalysts via “ligand design”, so as to improve required catalytic aspects: controllability, activity, versatility for monomers (particularly tolerance to functional monomers), and catalyst removal or recycle (Figure 1). The “controllability” implies that a catalyst allows a precisely controlled or living polymerization and well-defined polymer products with controlled molecular weight and narrow MWD.

Herein, primarily confining to our research, we describe the recent “catalyst evolution” in the metal-catalyzed living radical polymerization for three metals: ruthenium, iron, and nickel.

2.2. Ruthenium Catalysts. 2.2.1. General Features.

Ruthenium catalysts are characterized by a wide range of design parameters stemming from their high tolerance to functional groups (or lower oxophilicity) and a variety of ligands including anionic carbon-based conjugating entities. We believe that these advantages would be convincing enough to overcome their potential drawback such as lesser availability, higher cost, and occasional difficulty in removing the metal residues from prod-

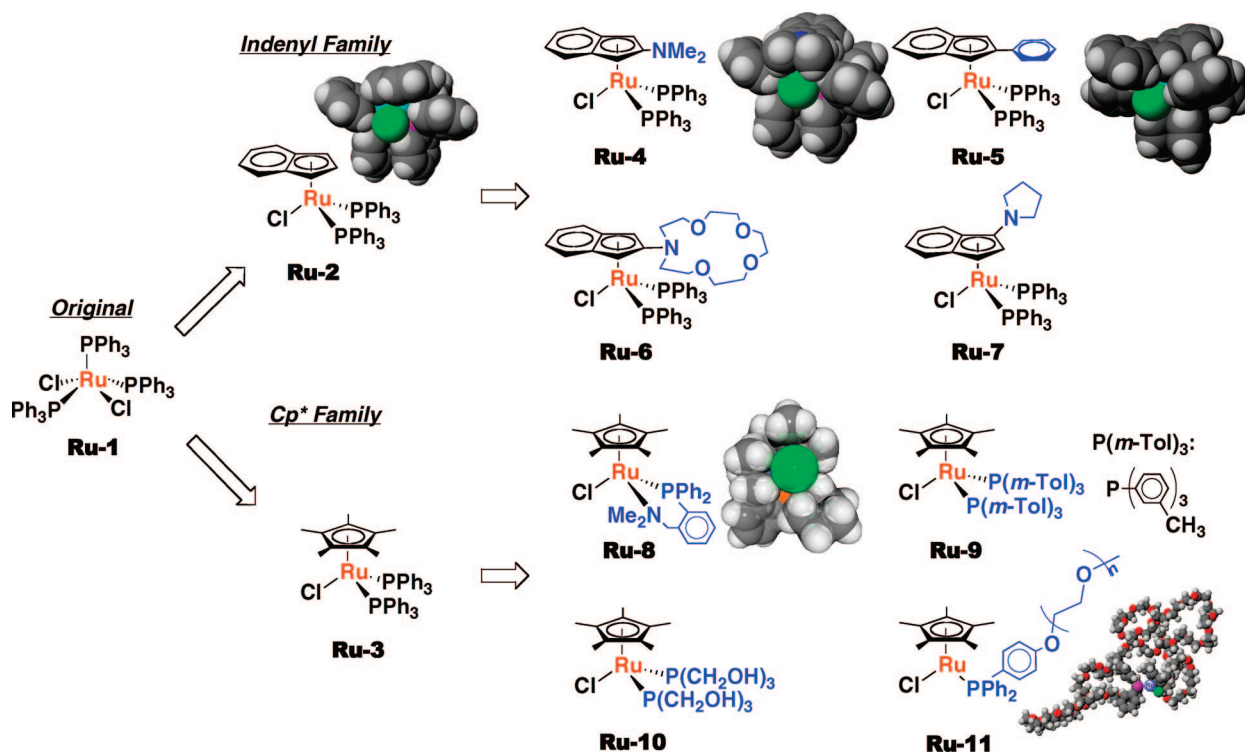


FIGURE 2. Evolution of ruthenium complexes for the catalysts in metal-catalyzed living radical polymerization, synthesized and examined in the authors' group. The space-filling models are based on X-ray crystallographic analysis (**Ru-2**, **Ru-4**, **Ru-5**, and **Ru-8**) or on molecular dynamics optimization (**Ru-11**). Colors are arbitrary in atom labeling: carbon, gray; hydrogen, light gray; chlorine, green; oxygen, red; nitrogen, blue; ruthenium, orange. For the representation of **Ru-8**, the authors thank Kyoko Nozaki (X-ray analysis) and Takuzo Aida (computer graphics), the University of Tokyo.

ucts. Thus, recent design targets of ruthenium catalysts involve a further enhancement in catalytic activity to realize lower catalyst dose and a construction toward a removal/recycle system, without loss of high controllability.

2.2.2. Indenyl and Half-Metallocene Complexes. Of particular interest are half-metallocene-type complexes with an indenyl [**Ru-2**, Ru(Ind)Cl(PPh₃)₂, Ind = η^5 -C₉H₇]¹² and a pentamethylcyclopentadiene [**Ru-3**, Ru(Cp*)Cl(PPh₃)₂, Cp* = η^5 -C₅(CH₃)₅]¹³ that turned out to be superior in terms of activity, controllability, and versatility for a variant of monomers. These strongly electron-donating and conjugating cyclic ligands are considered to contribute to an efficient one-electron redox process in the catalysis, as demonstrated by ¹H NMR and cyclic voltammetry.¹⁴ Accordingly, recent developments for ruthenium catalysts are dominated by the two families, as summarized in Figure 2.

Design of the indenyl and Cp* families further improved their catalytic properties. With indenyl-based complexes, we additionally introduced an electron-donating group into the ring to "internally" enhance the catalytic activity. For example, introduction of a dimethyl amino group at the 2-position (**Ru-4**) led to a faster polymerization of methyl methacrylate (MMA) with a cocatalyst [e.g., Al(Oi-Pr)₃ or *n*-Bu_{*n*}NH_{3-*n*} (*n* = 2,

3)] than the nonsubstituted **Ru-2** under same conditions.¹⁵ Despite such acceleration, the MWD of the obtained PMMAs were narrower ($M_w/M_n \approx 1.07$), indicating a faster exchange between dormant and active species with **Ru-4**. Retaining similarly narrow MWD, higher molecular weights are also reached (1000-mer conditions: [MMA]₀ = 8 M; [initiator]₀ = 8 mM) at a low catalyst concentration (0.80 mM) (Figure 3).

Introduction of other electron-donating groups, such as phenyl (**Ru-5**) and azacrown ether (**Ru-6**),¹⁶ also brought about similarly improved catalytic performances. **Ru-6** was designed for an additional feature that its catalytic activity might be tunable via an encapsulation of an alkali cation into the azacrown, in accordance with monomer reactivity. On the other hand, a pyrrolidinyl group at the 1-position (**Ru-7**) resulted in a little broader MWDs ($M_w/M_n > 1.30$), while activity was indeed enhanced.¹⁶ Possibly, the symmetry around the central metal is an important factor determining its electron density and the performance in the halogen exchange.

2.2.3. Chelating Ligand Design. The P–N ligand in **Ru-8**¹⁷ was designed from a background that an externally added amine (e.g., butylamine) as a cocatalyst coordinates to the ruthenium center to enhance catalytic activity.¹⁸ Actually, such a heterochelation enhanced the activity for MMA polym-

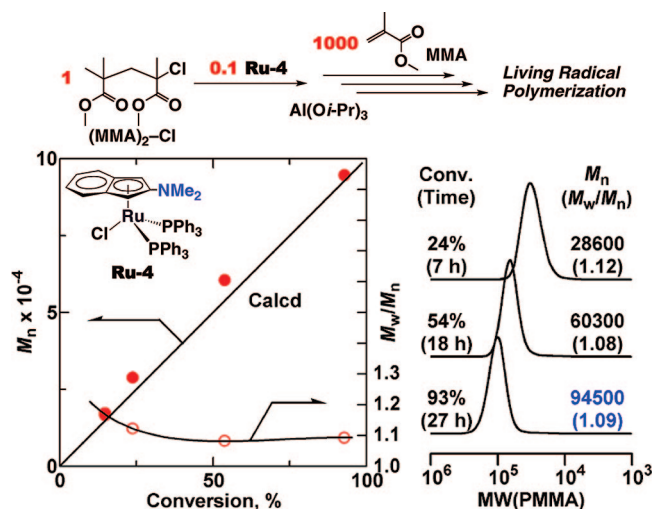
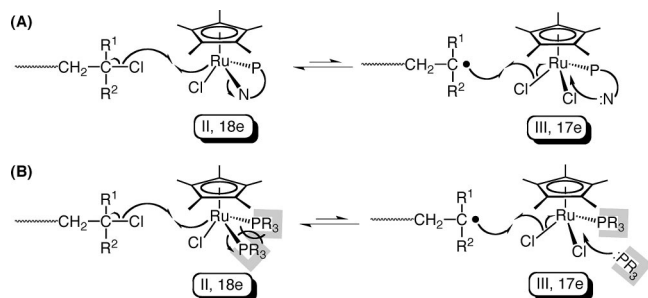


FIGURE 3. MMA polymerization with an aminoindenyl Ru(II) complex (**Ru-4**; Figure 2), an example of highly active and versatile catalysts giving high molecular weight polymers ($DP = 10^3$) with narrow MWD in toluene at 80 °C: $[MMA]_0/[MMA]_2-Cl/[Ru-4]_0/[Al(Oi-Pr)_3]_0 = 8000/8.0/0.8/40$ mM; $(MMA)_2-Cl$, initiator; $Al(Oi-Pr)_3$, cocatalyst. Note that the process is literally catalytic (substrate/catalyst = 10^4 mole ratio).

SCHEME 4. Proposed Mechanism in Reversible Activation with Cp*-Based 18-Electron Ru Complexes

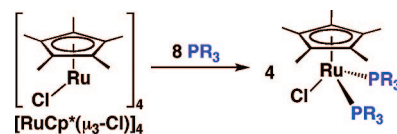


erization, while similar homo P–P or N–N chelating ligands were less effective. These Cp*-based 18-electron complexes must release one ligand to open a vacant site for abstraction of the terminal halogen (radical formation), while the activity enhancement for indenyl derivatives such as **Ru-2** is possibly attributed to indenyl-slipping (from η^5 to η^3). Thus, heterochelation with different coordination power would effectively contribute to a promotion of fast equilibrium via ligand elimination on the activation, as well as via the ligand coordination on the reverse process for halogen-capping of the growing radical (Scheme 4A). From analysis of atom distance for the single-crystal complex with X-ray, the coordination power of the P atom would be stronger than that of N, and thus nitrogen would be more labile, shown in Scheme 4A.

2.2.4. Effects of Phosphines via in Situ Preparation.

The Cp*-based ruthenium complexes are conveniently and cleanly prepared in situ by mixing of a tetramer precursor

SCHEME 5. In Situ Preparation of Cp*-Based Ru Complex from Tetramer Precursor $[RuCp^*(\mu_3-Cl)]_4$



$[RuCp^*(\mu_3-Cl)]_4$ with 2 equiv of phosphine ligands (Scheme 5).¹⁹ We thus employed a series of phosphines for MMA polymerization to examine the effects of ligand basicity and bulkiness (estimated by the cone angle).²⁰ Unexpectedly, the former factor, related to the electron-donating ability, was less effective for catalytic activity, probably because of the full electron donation from the Cp* ligand. In contrast, the latter factor influenced polymer MWD, narrower with a moderately bulky phosphine, most likely by promoting “ligand release” for an activation process or “halogen-back” on deactivation (Scheme 4B). For example, catalyst **Ru-9** with *meta*-tolylphosphine (cone angle = 165°) gave narrower MWDs ($M_w/M_n \approx 1.07$) than the *para*-derivative (cone angle = 145°; $M_w/M_n \approx 1.15$). In addition, **Ru-9** coupled with *n*-BuNH₂ induced a fast polymerization of MMA at 100 °C (~90% conversion in 5 h) still keeping MWD narrow ($M_w/M_n < 1.10$).

Interestingly, a hydrophilic ligand $[P(CH_2OH)_3]$; **Ru-10** not only induced a living polymerization of MMA in conjunction with an amine additive in THF ($M_w/M_n \approx 1.3$) but allowed facile and near-quantitative catalyst removal by precipitation into methanol to give colorless powdery polymers. A “polymeric” ligand bearing an amphiphilic and thermally responsible poly(ethylene glycol) chain $[PPh_2-PEG]$; **Ru-11** also afforded a removable and possibly recyclable catalyst that undergoes a thermally controlled phase-transfer catalysis, too.²¹ With a suitable PEG chain length, the complex is totally soluble in water at room temperature and turns hydrophobic above its transition threshold (~80 °C). Thus, after the MMA polymerization in a hydrophobic solvent (toluene) at high temperature, the catalyst can be transferred, upon cooling, into an aqueous phase of degassed water. From the organic phase, controlled PMMAs ($M_w/M_n \approx 1.1$) were obtained with ca. 97% of the catalyst residue [28 ppm (ICP analysis) removed], and the recovered catalyst from the aqueous phase can be reused for polymerization of MMA.

2.3. Iron Catalysts. 2.3.1. General Features.

Iron complexes, with a group 8 metal as with the ruthenium counterparts, have also been employed for metal-catalyzed living radical polymerization (Figure 4). Development of iron-based catalysts would become more significant in that they may offer readily and abundantly available, cheaper, safer, and more environmentally friendly systems. We first found that

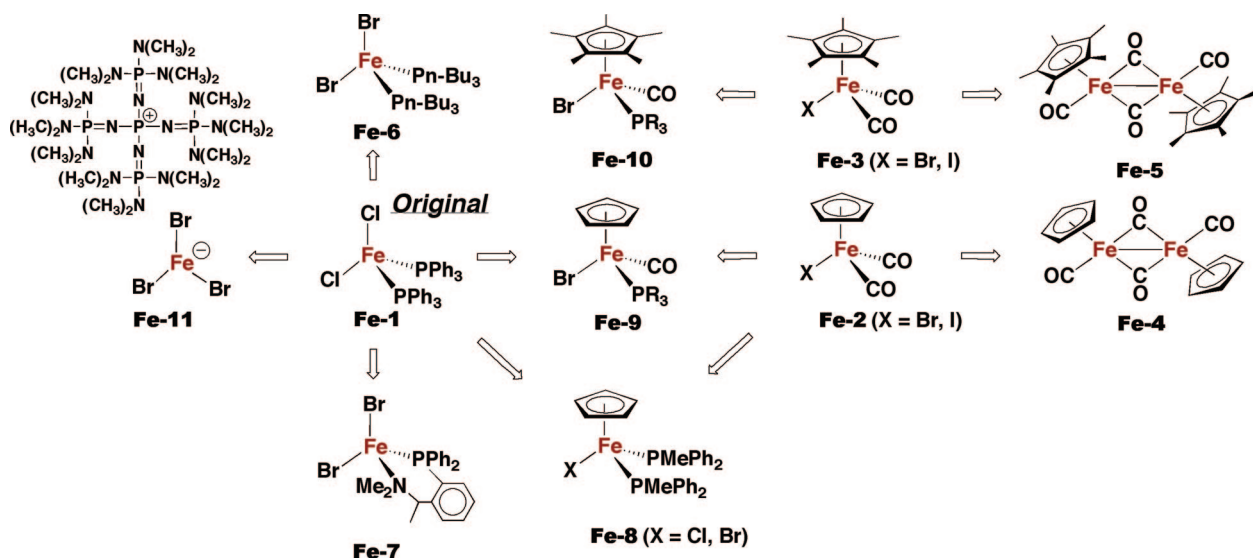


FIGURE 4. Evolution of iron complexes for the catalysts in metal-catalyzed living radical polymerization synthesized and examined in the authors' group.

$\text{FeCl}_2(\text{PPh}_3)_2$ (**Fe-1**) catalyzed living radical polymerization of MMA¹⁰ and later that a series of half-metallocene complexes with carbonyl ligands (**Fe-2–Fe-5**) were useful for polymerizations of styrenes and acrylates.^{22–24} More recently we have developed iron catalysts (**Fe-6–Fe-11**) for functionalized methacrylates that have been unsuited for conventional and functionality-sensitive iron complexes.

2.3.2. Phosphine Ligand Design. As with the Ru(II) family, increasing electron density tended to accelerate polymerization with iron complexes. With FeBr_2 , for example, a basic alkyl phosphine ligand (Pn-Bu_3 ; **Fe-6**) induced a faster polymerization of MMA than a phenylphosphine derivative (PPh_3 ; **Fe-1**).²⁵ However, simultaneous improvement on activity (rate) and controllability (M_w/M_n) for **Fe-6** was difficult, strongly depending on catalyst concentration (at 10 mM, 5 h for conv = 90%, $M_w/M_n = 1.42$; at 4 mM, 47 h for conv = 89%, $M_w/M_n = 1.27$). In contrast, with a P–N ligand (**Fe-7**), both factors were simultaneously improved, particularly when combined with $\text{Al}(\text{O}i\text{-Pr})_3$ or an additive mimicking the P–N ligand (9 h for 90% conv, $M_w/M_n \approx 1.16$).²⁶

Though half-metallocene iron complexes with multiple carbonyl (CO) ligands (**Fe-2–Fe-5**) were not useful for controlling MMA polymerization, a CO-free cyclopentadiene (Cp) complex with methyldiphenylphosphine [**Fe-8**; $\text{CpFe}(\text{PMePh}_2)_2$] works for MMA in conjunction with $\text{Al}(\text{O}i\text{-Pr})_3$ ($M_w/M_n = 1.3–1.4$). In this regard, Cp complexes bearing one carbonyl and one phosphine ligands (**Fe-9** and **Fe-10**) would be interesting.

2.3.3. Phosphazanium Halide Ligands. We also employed phosphazanium halide salts (PZN^+X^- ; X = Cl, Br, I) to ligate FeX_2 for polymerization of MMA.²⁷ With the

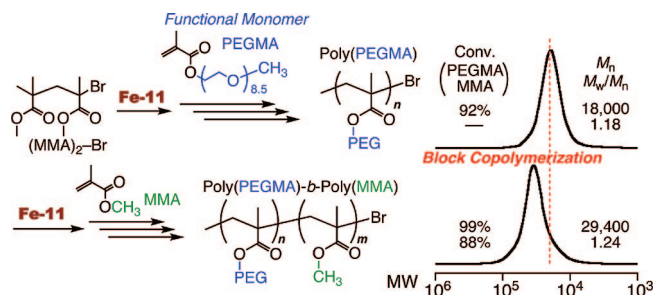


FIGURE 5. High controllability and tolerance to functional monomers of $\text{FeBr}_2/\text{PZN-Br}$ catalyst (**Fe-11**) in sequential block copolymerization of PEGMA and MMA in THF at 60 °C. First feed, $[\text{PEGMA}]_0/[(\text{MMA})_2\text{-Br}]_0/[\text{FeBr}_2]_0/[\text{PZN-Br}]_0 = 1000/20/10/10$ mM; second feed, $[\text{MMA}]_0/[\text{FeBr}_2]_0/[\text{PZN-Br}]_0 = 2000/5.0/5.0$ mM.

extremely bulky and charge-delocalized cation, these salts modify the iron halide by providing an additional halide onto the metal. The in situ forming complex (**Fe-11**) from an equimolar mixture of FeBr_2 and PZN^+Br^- efficiently induced a living radical polymerization of MMA in THF at 60 °C. The molecular weight and MWD were controlled up to $M_n \approx 10^5$ ($M_w/M_n \approx 1.1–1.2$). The catalytic activity clearly surpasses that with alkylammonium or alkylphosphonium bromide, and the ionic catalyst is readily removed from polymer solution with water to <5 ppm. The PZN iron catalyst was also effective for PEG-functionalized methacrylates (PEGMA) to give controlled polymers including PEGMA–MMA block copolymers (Figure 5). This result is significant because phosphine-based iron catalysts (**Fe-1**, **Fe-6**, and **Fe-7**) were not able to catalyze the polymerization of such functional monomers.

2.3.4. Vinyl Acetate Polymerization. Vinyl acetate (VAc) is among the monomers whose radical polymerization has been quite difficult to control because of the instability of the

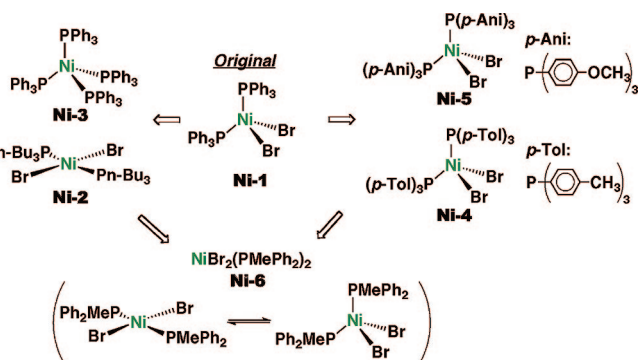


FIGURE 6. Evolution of nickel complexes for catalysts in metal-catalyzed living radical polymerization synthesized and examined in the authors' group.

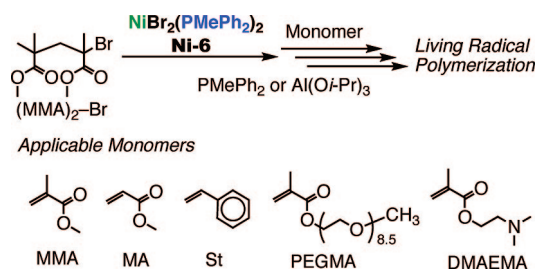
nonconjugating and highly reactive VAc growing radical and frequent chain transfer. However, we developed a controlled polymerization of VAc with a dimeric Fe(I) carbonyl-Cp complex (**Fe-4**) coupled with an iodo initiator and an additive such as $\text{Al}(\text{O}i\text{-Pr})_3$ or $\text{Ti}(\text{O}i\text{-Pr})_4$.²⁸ Although the MWDs of the product were not very narrow, M_n control is possible up to 50 000; the SEC curve shifted to higher molecular weight keeping the unimodal shape, indicating generation of long-lived propagating species. The dimer complexes (**Fe-4** and **Fe-5**) seem to be potentially active to activate the stronger carbon–halogen bond derived from VAc.

2.4. Nickel Catalysts. 2.4.1. General Features.

Nickel catalysts for living radical polymerization are thus far limited in number (Figure 6). Representative are $\text{NiBr}_2(\text{PPh}_3)_2$ (**Ni-1**),¹¹ $\text{NiBr}_2(\text{P}n\text{-Bu}_3)_2$ (**Ni-2**),²⁹ $\text{Ni}(\text{PPh}_3)_4$ (**Ni-3**),³⁰ and bis(ortho-chelated) arylnickel $[\text{Ni}\{o,o'(\text{CH}_2\text{NMe}_2)_2\text{C}_6\text{H}_3\}\text{Br}]$, the last reported by Teyssie et al.³¹ In general, Ni(II) rather than Ni(0) and Ni(I) seems to be suitable, and the characteristics of these catalysts in living radical polymerization are similar to the Fe(II) family, potentially active, readily available, easy to remove from organic solvents and polymers, but in turn sensitive to polar functional groups. Additionally, geometrical structures are more important in Ni(II) complexes in determining their catalytic activity and stability.

2.4.2. Ligand Design. Recently, we embarked on developing nickel catalysts and thus examined various phosphines (PR_3) as ligands for nickel dibromide (NiBr_2) in MMA polymerization with a bromide initiator. Highly basic ligands such as *para*-tolyl- and *para*-methoxyphosphines (**Ni-4** and **Ni-5**) induced faster polymerizations than does triphenylphosphine (**Ni-1**).³² **Ni-4** and **Ni-5** apparently give controlled polymers, judged from their fairly narrow and unimodal MWDs ($M_w/M_n \approx 1.2\text{--}1.4$). However, closer inspection of MWD indicated a portion of shorter dead chains, probably caused by the lower

SCHEME 6. $\text{NiBr}_2(\text{PMePh}_2)_2$ for Living Radical Polymerization of Various Monomers



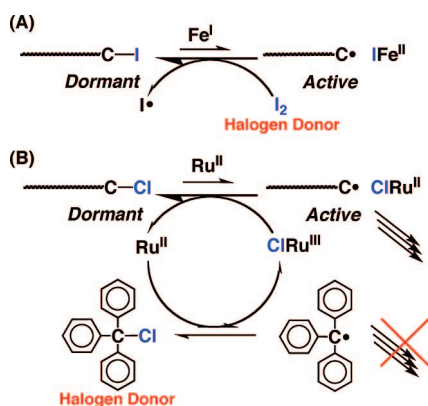
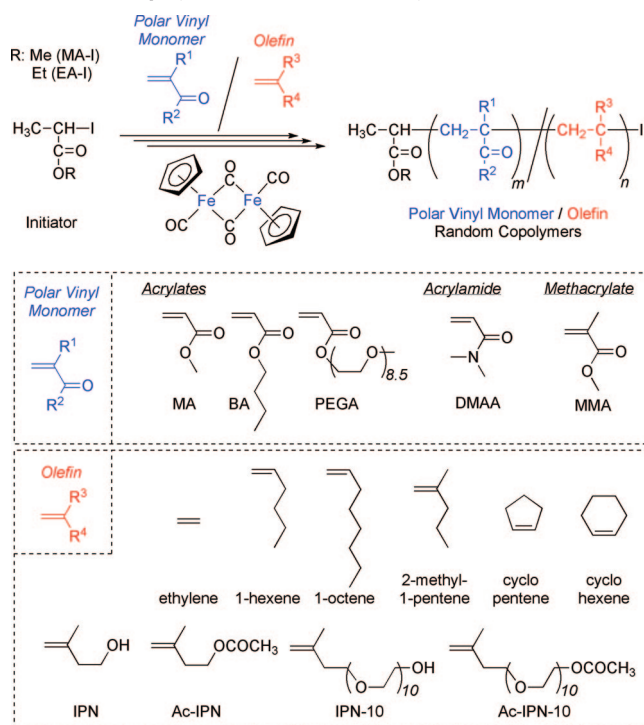
thermal stability of the complexes or their Ni(III) oxidized states that are known to assume “pseudotetrahedral” structures.

In contrast, an alkylphosphine complex (**Ni-2**), with a “square planar” structure, is thermally more stable and in fact survives during the polymerization, allowing the resulting polymer to continue to grow upon addition of a fresh monomer feed.³² Nevertheless, with its axial positions vacant, the planar form of **Ni-2** is in turn more vulnerable to polar functionality and unsuitable for PEGMA and (dimethylamino)ethyl methacrylate (DMAEMA).

2.4.3. Functionality-Tolerant Catalysts. From these backgrounds, we focused on Ni(II) complexes with methylphenylphosphines ($\text{PMe}_n\text{Ph}_{3-n}$, $n = 1, 2$), because they are in an equilibrium between “square planar” and “pseudotetrahedral” forms³³ and besides the Ni(III) complexes are stable enough to be isolated. As a result, $\text{NiBr}_2(\text{PMePh}_2)_2$ (**Ni-6**) catalyzes a well-controlled polymerization of MMA ($M_w/M_n \approx 1.2\text{--}1.3$) in the presence of excess ligand as an additive.³² The catalyst shows a sustainable controllability to allow a monomer addition experiment and is widely applicable for monomers including functionalized methacrylates: methyl acrylate (MA), styrene (St), MMA, PEGMA, and DMAEMA (Scheme 6). Despite such tolerance, the complex reacts with water to form hydrate and is easily removable from hydrophobic polymers (<30 ppm).

2.5. Control with Halogen Donors. A pivotal point in living radical polymerization is the fast and dynamic equilibrium between dormant and active species (Scheme 3). Namely, one should promote not only the forward step (radical formation) but the reverse step (regeneration of a dormant end) as well.

Noting this process is a halogen-capping, we examined the use of a halogen source for its promotion on the basis of “equilibrium-principle” or “mass-law” effect (Scheme 7). For this strategy, the additive should not serve as an initiator or a chain transfer agent. The first example is the addition of iodine into the Fe-catalyzed polymerization of MA or *N,N*-dimethylacrylamide (DMAA) with an iodide initiator (Scheme 7A).²⁴

SCHEME 7. Halogen Donors for Transition Metal-Catalyzed Living Radical Polymerization**SCHEME 8.** Copolymerization of Polar Vinyl Monomers and Olefins

More recently we have found that triphenylmethyl halides ($\text{Ph}_3\text{C-X}$; $\text{X} = \text{halides}$) are effective for the same purpose (Scheme 7B).³⁴ Addition of $\text{Ph}_3\text{C-Cl}$ enables the living MA polymerization with the $(\text{MMA})_2\text{-Cl/Ru-2}$ [$\text{Ru}^{\text{II}}(\text{Ind})\text{Cl}$] system, while the original additive-free system was ill-controlled. **Ru-2** reversibly activates the added halide into the triphenylmethyl radical ($\text{Ph}_3\text{C}^\bullet$), too stable and bulky to initiate or to terminate MA polymerization. The dissociation is faster than with the bromine-capped poly(MA), and hence the “common” oxidized complex [$\text{Ru}^{\text{III}}(\text{Ind})\text{Cl}_2$] “shifts” the equilibrium toward dormant species. The halogen-donor approach is particularly useful when one intends to tame a process where the exchange equilibrium is favorably shifted to the radical side or the method³⁵ with corresponding

deactivator (higher valence complex) is difficult, caused by its solubility or stability.

3. Precision Polymer Synthesis

The development of metal-catalyzed living radical polymerization has opened new vistas to conveniently synthesize a wide variety of well-defined polymers, particularly functionalized polymers, under relatively mild conditions. In this section, we discuss recent advances in such “precision” polymer synthesis, specifically random copolymerization, terminal transformation, block copolymers, and core-functionalized star polymers. A detailed review covering the status in this area before 2000 is available.⁷ The key is to select suitable catalytic systems for desired polymers.

3.1. Random Copolymerization. 3.1.1. General Features. A notable advantage of radical polymerization is that a wide variety of monomers can be randomly copolymerized, in sharp contrast to ionic and coordination polymerizations, where even a minor structural variation in monomers imposes a considerable difference in reactivity and thereby often hampers formation of truly random (statistical) copolymers. It is therefore important to introduce a living process into radical random copolymerization, with its unique advantage of ready copolymerizability. Additionally, if bimolecular termination is effectively suppressed, this implies the products, which are an accumulation of polymers formed from the onset to the end of a reaction, to have basically a uniform composition on the molecular level; note that, in a conventional radical copolymerization, the products may be an ill-defined mixture of copolymers with differing compositions because of termination.

3.1.2. Polar Vinyl Monomers and Olefins. In particular, for example, a controlled copolymer of α -olefins (1-alkenes) and polar vinyl monomers has attracted attention for modification of the corresponding homopolymer. However, the two monomers are by definition antithetical in terms of their polymerizability; the former suited for coordination polymerization and the latter for radical polymerization.

We examined the possibility of employing our metal-catalyzed living radical polymerization for such a process, with use of an exceptionally active iron catalyst ($[\text{FeCp}(\text{CO})_2]_2$; **Fe-4**) (Scheme 8).³⁶ Typically, an equimolar mixture of MA and 1-hexene is copolymerized with the **Fe-4/MA-I/Al(Oi-Pr)₃** system. Rather surprisingly, though hydrocarbon olefins have long been believed nearly inert under usual radical reaction conditions at 60 °C, 1-hexene does polymerize with the iron catalyst, though much less reactive than MA, to give well-controlled random copolymers ($M_n = 15\,500$, $M_w/M_n = 1.63$, 1-hexene content: 13 mol

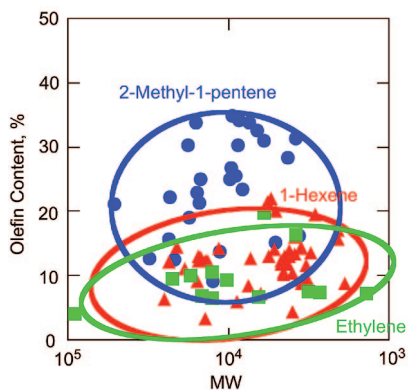


FIGURE 7. Olefin content in random copolymers of MA and olefins in iron-catalyzed living radical polymerization.

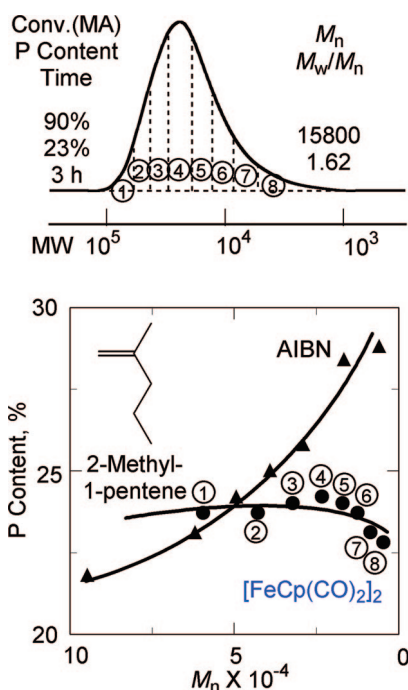


FIGURE 8. Compositional distribution in MA–2-methyl-1-pentene copolymers against molecular weight.

%). Particularly important is that the product involves main-chain olefin units, while long homosequences of the hexene are virtually absent. The olefin content can be increased up to 20% without serious loss of the controllability.

Other olefins, such as 1-octene, 2-methyl-1-pentene, and ethylene, are also efficiently copolymerized with MA via the iron-catalyzed system to yield copolymers ($M_w/M_n = 1.5–1.8$). Figure 7 summarizes the ranges of olefin content and overall molecular weight for three olefins. 2-Methyl-1-pentene, an α,α -disubstituted alkene, was more efficiently incorporated into copolymers, obviously due to the higher stability of the growing radical. These copolymers are characterized by a compositional uniformity (Figure 8); that is, the composition little depends on molecular weight, while the olefin content in the corresponding products

from conventional radical copolymerization sharply decreased with increasing molecular weight.

Additional functionalization of these olefin copolymers was also achieved by use of dimethylacrylamide (DMAA), poly(ethylene glycol methyl ether acrylate) (PEGA), and 1-hydroxybutyl-5-hexene.³⁷ In addition to the iron catalysts, some Ru(II) complexes are effective in the copolymerization, such as **Ru-2** and **Ru-3**, and they also catalyzed controlled copolymerizations of MMA with olefins (olefin content < 10 mol %).

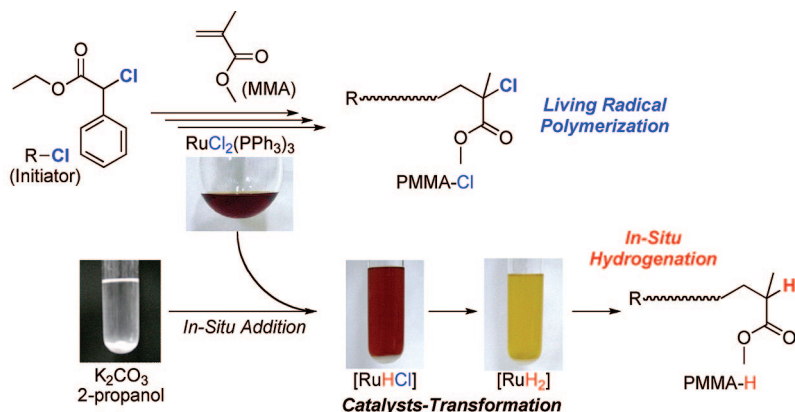
3.1.3. Vinyl Ether Copolymers. Vinyl ethers (VEs) are usually not expected to polymerize in a radical mechanism, but they do copolymerize with MA in the ruthenium-mediated system $[\text{RuCp}^*\text{Cl}(\text{PPh}_3)_2 (\mathbf{Ru-3})/n\text{-Bu}_3\text{N}]$.³⁸ Herein suppression of cationic polymerization of VE and decomposition of VE terminus are imperative; the electron-rich monomer may polymerize with a potentially Lewis acidic metal catalyst, and the halogen-capped VE terminus is susceptible to acid-assisted ionization and elimination. Thus, the ruthenium catalysts were more suitable than the more Lewis acidic iron counterparts. For the leaving halogen (X), bromine seems to be better suited than chlorine and iodine in terms of activity and suppression of the HX elimination. The typical results obtained from MA and ethyl vinyl ether are the followings: $M_n = 15\,000$, $M_w/M_n = 1.40$, VE content 5.0 mol %.

3.2. Terminal Transformation: Hydrogenation. In accordance with the proposed pathway (Scheme 3), the polymer terminus (dormant end) in metal-catalyzed living radical polymerization invariably and quantitatively carries the halogen originating from the initiator. This unique feature is advantageous as a reservoir of active radical intermediates for block polymerization and end functionalization, but it in turn imposes a potential drawback of product instability.

Recently we have developed an efficient and convenient method for the hydrogenation of the terminal halogen, where a Ru(II) polymerization catalyst is further utilized for another catalysis after in situ “catalyst transformation” (Scheme 9).³⁹ For example, after living radical polymerization of MMA, the catalyst $\text{RuCl}_2(\text{PPh}_3)_3 (\mathbf{Ru-1})$ is in situ transformed into the corresponding hydrides by addition of K_2CO_3 (base) and 2-propanol (hydrogen source). Upon treatment, the reaction mixture immediately changes color from the original red-brown (RuCl_2) through red-purple (RuClH) to yellow (RuH_2), while the terminal chlorine is quantitatively hydrogenated, as analyzed by ^1H NMR, MALDI-TOF MS, and SEC.

3.3. Block Copolymers. Thanks to the high activity, controllability (perfect end functionality), and tolerance to functional groups, metal-catalyzed living radical polymerization offers a series of (functionalized) block polymers of varying

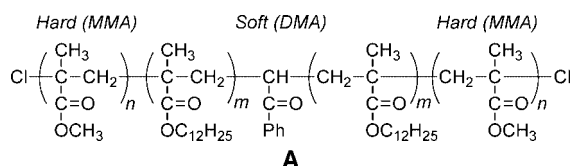
SCHEME 9. Tandem Hydrogenation of Terminal Halogen via Ruthenium Catalysts



structures and segment sequence for a variety of monomers. Figure 9 illustrates some examples.

3.3.1. Triblock Copolymers: Thermoplastic Elastomers.

We have synthesized all methacrylate ABA triblock copolymers (structure **A**), where dodecyl methacrylate (DMA) and



methyl methacrylate (MMA) are employed for, respectively, the rubbery low T_g center block and the coagulating high T_g

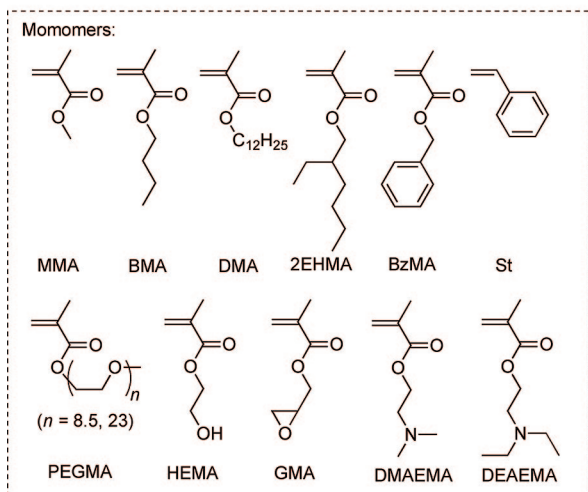
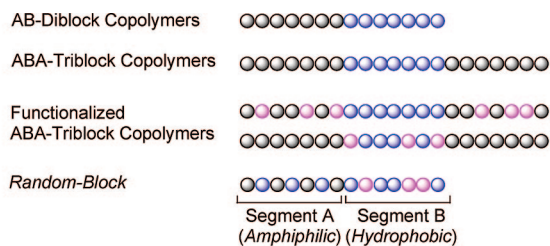
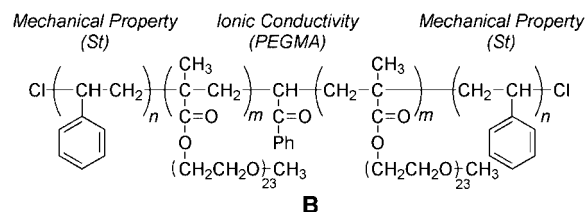


FIGURE 9. Block copolymers obtained from ruthenium-catalyzed living radical polymerization.

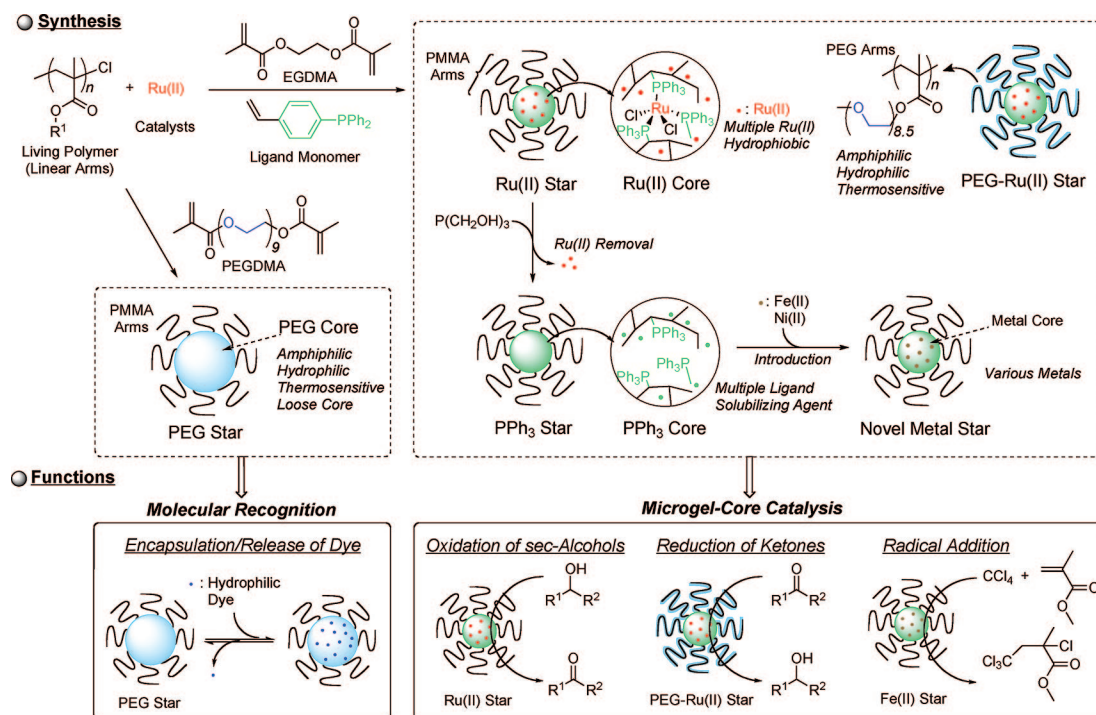
outer block for reversible physical cross-linking.⁴⁰ Typically, a series of MMA–DMA–MMA triblock copolymers can be obtained with dichloroacetophenone as bifunctional initiator coupled with the $Ru(Ind)Cl(PPh_3)_2$ (**Ru-2**)/ n -Bu₃N catalyst system, all with very narrow MWD ($M_w/M_n < 1.2$), high blocking efficiency (>97%), overall $M_n = 20\,000$ – $500\,000$, and MMA content 10–40%. The products indeed behave like elastomers.

3.3.2. Triblock Copolymers: Ion-Conducting Solid Electrolytes. St–PEGMA–St triblock copolymers (structure **B**) are also prepared by the bifunctional Ru(II) initiating system



system $[RuCl_2(PPh_3)_3]$ (**Ru-1**) or $RuCp^*Cl(PPh_3)_2$ (**Ru-3**). The products are designed as potential lithium ion-conducting, film-forming solid polymer electrolytes for secondary lithium batteries.⁴¹ PEGMA here carries a relatively long PEG pendent chain ($n = 23$) for ensuring good ion conductivity; the outer styrene segments are to form mechanically strong film. The optimized products undergo clear phase separation, and this seems critical in attaining high ion conductivity and excellent charge–discharge characteristics.

3.3.3. Functionalized Random Block Copolymers. An interesting combination of random and block copolymerization of functional methacrylates leads to functionalized “random-block” copolymers in which each segment is a random copolymer of methacrylates (Figure 9). Segment A (amphiphilic or hydrophilic) is composed of MMA and PEGMA, and segment B (hydrophobic and bulky) involves BMA, 2EHMA, and BzMA. Despite the use of as many as four to five monomers,

SCHEME 10. Synthesis and Functions of Core-Functionalized Star Polymers via Ruthenium-Catalyzed Living Radical Polymerization

each step proceeds cleanly, and the block architecture separates differing functions, while the random segmental structure ensures balanced distribution of different functions intended as, for example, advanced amphiphilic pigment dispersants.

3.4. Core-Functionalized Star Polymers. Microgel-core star polymers are generally prepared by a linking reaction of linear living polymers (arms) in the presence of a small amount of a bifunctional monomer (linking agent).^{42,43} We have already demonstrated the feasibility of this strategy in our metal-catalyzed living radical polymerization. The inner core (microgel core) is a locally cross-linked network that may be considered as a “solubilized” gel and may prove a unique network system and a nanoscale reaction space, provided that suitable functionality is incorporated. Thus, we have examined the direct functionalization of the microgel core in star polymers by ruthenium-catalyzed living radical polymerization (Scheme 10); these are herein called “core-functionalized” star polymers.

3.4.1. Metal-Bearing Microgel-Core Star Polymers. Rather accidentally in part, we found that Ru(II) catalysts, originally employed for living radical polymerization, are effectively entrapped into the microgel core. This is particularly true when the linking (core-forming) reaction is carried out via a random copolymerization of a bifunctional methacrylate and

a phosphine-functionalized styrene; the latter is evidently to place a number of phosphine ligands on the core (Scheme 10, upper left).

Ruthenium-bearing microgel star polymers [Ru(II) Star] are thus synthesized by the linking reaction of living poly(MMA) with ethylene glycol dimethacrylate (EGDMA) and a phosphine-carrying styrene (CH₂=CH-C₆H₄-PPh₂) in >90% yield.⁴⁴ Ruthenium complex RuCl₂(PPh₃)₃ (**Ru-1**) was in situ encapsulated into the microgel core because of a highly localized ligating space in the core originating from the phosphine monomer; note that typically as many as a few hundred phosphine moieties are incorporated into a nanometer-sized microgel core. Namely, this is direct transformation of “polymerization catalysts” into “star polymer catalysts”. In most cases, the complex capture is nearly quantitative; 100 ruthenium per core. The employment of PEGMA for arm parts leads to amphiphilic solubility (soluble in alcohols and water) and unique thermosensitivity (UCST = 31 °C in 2-propanol).⁴⁵

The core-bound metals can easily be interchanged via the following two steps: (1) removal of core-bound ruthenium with a hydrophilic phosphine [P(CH₂OH)₃] to obtain an “empty” star with the in-core phosphine ligands free and (2) reloading of metal salts and complexes such as FeCl₂ and NiBr₂(PPh₃)₂ into the core via ligand exchange.

3.4.2. Microgel-Core Catalysis. The metal-bearing microgel star polymers were regarded as homogeneous/heteroge-

neous hybrid polymer-supported catalysts with a microgel reaction space; metal-encapsulating dendrimer catalysts have also been reported.⁴⁶ For example, Ru(II)Star efficiently catalyzed the homogeneous oxidation of *sec*-alcohols into ketones with a unique substrate selectivity, even at a quite low catalyst feed (Ru/substrate = 1/1000). These star catalysts could be reused three times without any loss of catalytic activity even with the recovery under air.

PEG–Ru(II)Star allowed homogeneous reduction of various ketones into alcohols in 2-propanol with higher activity (turnover frequency approximately 1000 h⁻¹) than the conventional counterpart [RuCl₂(PPh₃)₃]. The star catalysts also realized thermoregulated phase-transfer hydrogenation of a hydrophobic ketone (2-octanone) in 2-propanol/H₂O biphasic media (1/1, v/v) with high activity and recycling efficiency.

3.4.3. PEG-Functionalized Microgel Star Polymers. In sharp contrast to conventional star polymers with small, hard, and hydrophobic microgel cores, novel star polymers with large, soft, amphiphilic, and thermosensitive microgel cores are prepared with a dimethacrylate carrying a long polyether (PEG) spacer [PEGDMA; (CH₂CH₂O)_n, n = 9; M_n = 550].⁴⁷ As expected, the star had larger radius of gyration in DMF (SEC-MALLS analysis) and higher mobility in the core (¹H NMR) than those with EGDMA. The PEG core can also reversibly encapsulate and release the hydrophilic dye (orange G, insoluble in CHCl₃).

BIOGRAPHICAL INFORMATION

Makoto Ouchi, born in Osaka, Japan (1973), received his B.S. (1996), M.S. (1998), and Ph.D. degrees (2001) from Kyoto University. His doctoral study was on stereo- and regiospecific cationic polymerizations via designed Lewis acids and counteranions under the direction of Professor Mitsuo Sawamoto, where he received a Research Fellowship for Young Scientist of the Japan Society for the Promotion of Scientists (1998–2001). During 2001–2004, he worked in Toyota Central R&D Laboratories, Inc., as a researcher to develop poly(lactic acid)-based materials for automobile parts. In 2004, he moved to the Graduate School of Engineering of Kyoto University as an Assistant Professor of the Department of Polymer Chemistry. Now, he is a visiting associate at California Institute of Technology working with Professor David A. Tirrell (2007–2008). His research interests include development of novel precision polymerization systems with designed catalysts/polymerization fields.

Takaya Terashima, born in Shiga, Japan (1978), received his B.S. (2002), M.S. (2004), and Ph.D. degrees (2007) from Kyoto University. His doctoral study was on development of multifunctional designer catalysts via living radical polymerization, especially focused on star polymer catalysis and tandem catalysis, under the direction of Professor Mitsuo Sawamoto, where he

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Mitsuo Sawamoto, born in Kyoto, Japan (1951), received his B.S. (1974), M.S. (1976), and Ph.D. degrees (1979) in polymer chemistry from Kyoto University. After postdoctoral research at the Institute of Polymer Science, The University of Akron, Akron, OH (1980–1981), he joined the faculty of the Department of Polymer Chemistry, Kyoto University, in 1981 as a research instructor and is currently Professor of the Department of Polymer Chemistry, Graduate School of Engineering, Kyoto University, since 1994. He serves as an executive member of the Science Council of Japan, a titular member of IUPAC Polymer Division, President (2008–2010) of the Society of Polymer Science, Japan, and one of the Editors of the *Journal of Polymer Science, Part A, Polymer Chemistry*. He received, among others, Award of the Society of Polymer Science, Japan (1992), Divisional Research Award of the Chemical Society of Japan (1999), and Arthur K. Doolittle Award of PMSE Division, the American Chemical Society (2002).

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