Metal-Catalyzed Living Radical Polymerization and Radical Polyaddition for Precision Polymer Synthesis

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Abstract. The metal-catalyzed radical addition reaction can be evolved into two different polymerization mechanisms, i.e.: chain- and step-growth polymerizations, while both the polymerizations are based on the same metal-catalyzed radical formation reaction. The former is a widely employed metal-catalyzed living radical polymerization or atom transfer radical polymerization of common vinyl monomers, and the latter is a novel metal-catalyzed radical polyaddition of designed monomer with an unconjugated C=C double bond and a reactive C–Cl bond in one molecule. The simultaneous ruthenium-catalyzed living radical polymerization of methyl acrylate and radical polyaddition of 3-butyl 2-chloropropionate was achieved with Ru(Cp*)Cl(PPh3)2 to afford the controlled polymers, in which the homopolymer segments with the controlled chain length were connected by the ester linkage.

1. Introduction
Recent remarkable progress in controlled/living radical polymerizations has enabled the precision polymer synthesis of a wide variety of well-defined polymers, such as end-functionalized, block, graft, and star polymers [1–4]. Among them, the metal-catalyzed living radical polymerization or atom transfer radical polymerization (ATRP) is one of the most efficient systems for various conjugated vinyl monomers, such as methacrylates, acrylates, acrylamides, and styrenes [2, 3]. This polymerization was originally developed from the metal-catalyzed Kharasch or atom-transfer radical addition reaction (ATRA), in which the carbon radical species is generated through the metal-catalyzed cleavage of a carbon–halogen (C–X) bond and adds to an olefin to form the 1:1 adduct of the halide and olefin [5, 6]. The metal-catalyzed living radical chain-growth polymerization proceeds via the metal-catalyzed reversible formation of the growing radical species from the dormant C–X bond and adds to an olefin to form the 1:1 adduct of the halide and olefin [5, 6]. The metal-catalyzed living radical chain-growth polymerization proceeds via the metal-catalyzed reversible formation of the growing radical species from the dormant C–X bond, terminal, and the addition of the growing radical species to the vinyl monomers [7].

In contrast, we quite recently found a novel radical polyaddition reaction of a designed monomer that possesses an active C–X bond and unconjugated C=C double bond via the evolution of the metal-catalyzed ATRA into the step-growth polymerization [8, 9]. In this polymerization, the active or dormant C–X bond in the monomer is activated by the metal catalysts to form a radical species, which adds to the C=C double bond of another monomer molecule to generate a C=C bond as the main chain, along with an inactive C–X bond as the pendant. This radical polyaddition can be catalyzed by the same metal catalyst for the living radical polymerization.

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This short paper will first describe the metal-catalyzed chain-growth living radical polymerization of methyl acrylate (MA) and then the metal-catalyzed step-growth radical polyaddition of a designed monomer (1), in which the unconjugated C=C and reactive C–C bonds are linked via ester linkage. Finally, the simultaneous metal-catalyzed radical living polymerization of MA and radical polyaddition of 1 was examined for novel precision polymer synthesis (scheme 1).

**Metal-Catalyzed Living Radical Polymerization – Chain-Growth Mechanism**

**Metal-Catalyzed Radical Polyaddition – Step-Growth Mechanism**

**Simultaneous Metal-Catalyzed Living Radical Polymerization and Radical Polyaddition**

**Scheme 1.** Metal-catalyzed living radical polymerization and radical polyaddition

2. Experimental

Ru(Cp*)(Cl(PPh)_3)_2 (provided from Wako) and CuCl (Aldrich, 99.99%) were used as received. All metal compounds were handled in a glovebox (VAC Nexus) under a moisture- and oxygen-free atmosphere (O_2, < 1 ppm). Toluene was distilled over sodium benzophenone ketyl and bubbled with dry nitrogen for 15 min just before use. Methyl acrylate (TCI, >99%), methyl 2-chloropropionate (TCI, >95%), N,N,N’,N’’,N’’’-pentamethyldiethylenetriamine (PMDETA) (TCI, >98%), and n-Bu_3N (Wako, >98%) were distilled from calcium hydride under reduced pressure before use. 3-Butenyl 2-chloropropionate (1) was synthesized from 2-chloropropionyl chloride (TCI, >95%) and 3-buten-1-ol (TCI, >98%).

Polymerization was carried out under dry nitrogen in baked glass tubes equipped with a three-way stopcock using syringe techniques.

Monomer conversion was determined from the concentration of residual monomer measured by gas chromatography. Functional group (C=C and C–Cl) conversions were measured by 400 MHz ^1H NMR (Varian Gemini 2000). The number-average molecular weight (M_n), the weight-average molecular weight (M_w), and the molecular weight distribution (MWD) of the polymers were determined by size-exclusion chromatography (SEC) in THF. The columns were calibrated against eight standard poly(methyl methacrylate) samples (Shodex; M_p = 202–1,950,000; M_w/M_n = 1.02–1.09).

3. Results and discussion

3.1. Metal-catalyzed radical living polymerization of MA

First, we investigated the ruthenium-catalyzed living radical polymerization of MA using Ru(Cp*)(Cl(PPh)_3)_2 and methyl 2-chloropropionate (2), which has a similar secondary C–Cl bond to 1, in the presence of n-Bu_3N in toluene at 80 °C. The polymerization occurred smoothly (figure 1A) to give the polymers with relatively narrow MWDs (figure 1C). However, the MWDs were slightly broader than those obtained with the methyl methacrylate dimer-type initiator [H–(MMA)_2–Cl], which has a more reactive C–Cl bond [10], indicating a slower initiation from 2. The M_n of the polymers increased in direct proportion to monomer conversion and agreed well with the calculated values, assuming that one molecule of 2 generates one living polymer chain (figure 1B).
These results indicate that living radical polymerization of MA proceeds via reversible activation of C–Cl bond originating from the chloride initiator 2.

3.2. Metal-catalyzed radical polyaddition of 1

The metal-catalyzed radical polyaddition of 1 was conducted with CuCl/PMDETA in toluene at 60 °C [11]. The monomers were consumed smoothly and almost completely irrespective of the slow reaction (figure 2A). The consumption of the two functional groups in 1, C=C and C–Cl, occurred at the same rate and was slower than that of 1, indicating the 1:1 intermolecular addition reaction. The SEC curves of the obtained polymers shifted to high molecular weights as the polymerization proceeded (figure 2C). The $M_n$ of the products progressively increased and was close to the calculated line for the step-growth polymerization, assuming that $M_n$ increases in inverse proportion to $1-p$, where $p$ and MW(1) mean the consumption of the functional group and the molecular weight of the monomer (1) (figure 2B) [9]. The MWD increased with conversion and was also close to the calculated value of 2 for step-growth polymerization.

Thus, the polymerization of 1 proceeds via the expected intermolecular radical polyaddition, which is based on the metal-catalyzed C–Cl activation similar to the metal-catalyzed living radical polymerization.
3.3. **Simultaneous metal-catalyzed radial living polymerization of MA and polyaddition of 1**

The simultaneous metal-catalyzed living radical polymerization of MA and radical polyaddition of 1 ([MA]₀/[1]₀ = 4000/40 mM) was then investigated by the ruthenium catalyst in toluene at 80 °C. As shown in figure 3A, both the monomers were consumed simultaneously, where the consumption of 1 was faster than that of MA. During the early stage of the polymerization, the $M_n$ of the obtained polymers increased in direct proportion to the conversion of MA and agreed well with the calculated value, assuming that one molecule of 1 generates one polymer chain (figure 3B). Furthermore, the SEC curves were relatively narrow and shifted to high molecular weights along with the consumption of MA (figure 3C). These results indicate that living radical polymerization of MA first proceeds via reversible activation of the C–Cl terminal derived from the C–Cl bond of 1 via the metal-catalyzed initiation. However, in the later stage, the molecular weight of the polymers drastically increased along with change of the unimodal SEC curves into multimodal, indicating that the polyaddition reaction occurred between the living polymer chains possessing C=C and C–Cl groups at the α- and ω-chain ends, respectively, both of which originated from 1. Due to the lower reactivity of the unconjugated double bond of 1, the polyaddition reaction was slower than the addition polymerization of MA and resulted in a progressive increase of the molecular weight in the later stage of the reaction.

![Figure 3](image)

**Figure 3.** Simultaneous metal-catalyzed living radical polymerization of MA and radical polyaddition of 1 with Ru(Cp*)Cl(PPh₃)₂/n-Bu₃N in toluene at 80 °C: [MA]₀/[1]₀/[Ru(Cp*)Cl(PPh₃)₂]₀/[n-Bu₃N]₀ = 4000/40/4/40 mM.

In conclusion, the simultaneous radical living polymerization and radical polyaddition occur via the same metal-catalyzed radical formation reaction to afford the controlled polymers, in which the homopolymer segments with the controlled chain length were connected by the ester linkage.

**References**

[1] Hawker C J, Bosman A W and Harth E 2001 *Chem. Rev.* **101** 3661
[2] Kamigaito M, Ando T and Sawamoto M 2001 *Chem. Rev.* **101** 3689
[3] Matyjaszewski K and Xia J 2001 *Chem. Rev.* **101** 2921
[4] Moad G, Rizzardo E and Thang S H 2005 *Aust. J. Chem.* **58** 379
[5] Kharasch M S, Jensen E V and Urry W H 1945 *Science* **102** 128
[6] Iqbal J, Bhatia B and Nayyar N K 1994 *Chem. Rev.* **94** 519
[7] Kato M, Kamigaito M, Sawamoto M and Higashimura T 1995 *Macromolecules* **28** 1721
[8] Satoh K, Mizutani M and Kamigaito M 2007 *Chem. Commun.* 1260
[9] Mizutani M, Satoh, K and Kamigaito M 2009 *Macromolecules* **42** 472
[10] Watanabe Y, Ando T, Kamigaito M and Sawamoto M 2001 *Macromolecules* **34** 4370
[11] Xia J and Matyjaszewski K 1997 *Macromolecules* **30** 7697