Control of stereochemistry in atom transfer radical addition and step-growth radical polymerization by chiral transition metal catalysts

Takamasa Soejima [a], Kotaro Satoh [a,b,*], Masami Kamigaito [a,*]

[a] Department of Applied Chemistry, Graduate School of Engineering, Nagoya University, Nagoya 464-8603, Japan
[b] Precursory Research for Embryonic Science and Technology, Japan Science and Technology Agency, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

ABSTRACT

A series of chiral transition metal catalysts of ruthenium(II), iron(II), copper(I), and rhodium(I) were used to control the stereochemistry in the step-growth radical polymerization of 3-butenyl 2-chloropropionate (BCP) with both unconjugated C=C and reactive C–Cl bonds in a single molecule and atom transfer radical addition (ATRA) as a model reaction for the polymerization. Among the various metal catalysts with chiral ligands, $Ru_2Cl_4[(-)\text{-DIOP}]_3$ [DIOP=2,3-(isopropylidenedioxy)-2,3-dihydroxy-1,4-bis(diphenylphosphanyl)butane] induced asymmetric ATRA with 10% *ee* between CCl_4 and 3-butenyl acetate (BAc), which has an unconjugated C=C bond as a model olefin of the monomer. However, this ruthenium catalyst was not sufficiently active to induce ATRA between the C–Cl bond in methyl 2-chloropropionate (MCP), which is a model chloride for the monomer, and the C=C bond in BAc, as well as the step-growth radical polymerization of BCP. Whereas chiral iron and copper catalysts, such as $FeCl_2/(-)\text{-DIOP}$ and $CuCl/(-)\text{-sparteine}$, efficiently allowed the ATRAs and the step-growth radical polymerization to result in the desired 1:1 adducts and oligomers, respectively, almost no optical activity was observed for the products. However, the diastereoselectivity was changed in both the ATRA and the polymerization by the metal catalysts with chiral or achiral ligands.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Recent progress in radical chemistry has enabled controlled synthesis of various small organic molecules with high yield and high selectivity as well as a variety of macromolecules with complex architectures.[1,2] In many of these recently developed radical reactions, transition metal catalysts play important roles in inducing and mediating selective reactions in high yield.

In Kharasch addition or atom transfer radical addition (ATRA),[3] various efficient transition metal catalysts have been developed by using appropriate metals, oxidation states, and ligands and have improved the yield of the products.[4–7] In the typical metal-catalyzed ATRA, a low-valent transition metal catalyst, such as copper(I), ruthenium(II), iron(II), and nickel(II), abstracts the halogen atom from a starting halogen compound via one-electron oxidation of the metal center, thus resulting in the radical species,

which adds to the carbon–carbon double bond of a starting olefin and then generates a new carbon-centered radical species. The halogen on the oxidized metal catalyst then transfers to the resulting radical species via one-electron reduction of the metal center, thus generating the product of the 1:1 adduct between the halide and olefin and regenerating the low-valent metal catalyst. This reaction has been widely used for the synthesis of simple organic halides and complicated molecules via cyclization and/or cascade or domino-type reactions.[7–9]

This chemistry has been further developed to control chain-growth radical polymerizations of mostly conjugated vinyl monomers, such as acrylics and styrenes, and has led to the discovery of metal-catalyzed living radical polymerization or atom transfer radical polymerization (ATRP), in which the propagating radical species is reversibly generated from the carbon–halogen bond of the initiator halide and the resulting dormant polymer chain-end halide via reversible one-electron redox reaction of the metal catalyst (Scheme 1A).[10–14] The metal-catalyzed controlled radical formation via reversible activation of the carbon–halogen bond enables controlled propagation of the polymer chain to regulate the

* Corresponding authors. Tel.: +81 52 789 5400; fax: +81 52 789 5112; e-mail addresses: satoh@apchem.nagoya-u.ac.jp (K. Satoh), kamigait@apchem.nagoya-u.ac.jp (M. Kamigaito).

(A) Metal-Catalyzed Living Radical Polymerization or ATRP

$(Mt^n: Ru^{II}, Cu^I, Fe^{II}, Ni^{II}, etc)$
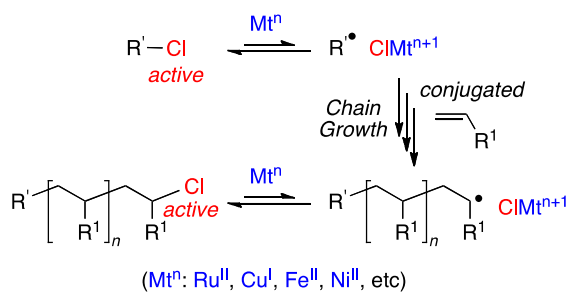
(B) Metal-Catalyzed Step-Growth Polymerization
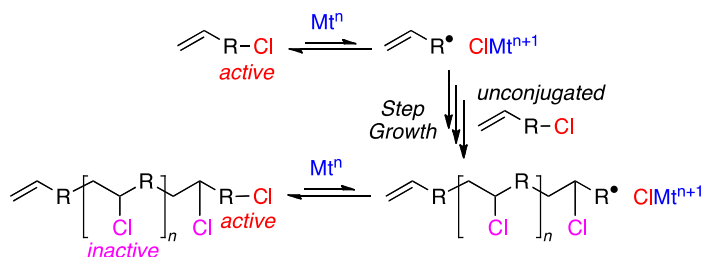
Scheme 1. (A) Metal-catalyzed living radical polymerization or ATRP of conjugated vinyl monomers and (B) metal-catalyzed step-growth radical polymerization of designed monomers that have unconjugated C=C and reactive C–Cl bonds.

polymer chain length, which is determined by the feed ratio of the vinyl monomer to the halide. This technique has permitted the synthesis of a wide variety of polymer architectures, including end-functionalized, block, gradient, star, and graft copolymers and more complicated structural polymers.[15–19]

Recently, we have evolved ATRA into another type of polymerization mechanism, i.e., step-growth polymerization, in which a designed monomer that has an unconjugated carbon–carbon double bond and a reactive carbon–chlorine bond is polymerized between the monomers and then the resulting oligomers, finally producing polymers via the formation of an inactive carbon-–chlorine bond attached to the main chains on each step-growth addition reaction (Scheme 1B).[20,21] To produce linear high molecular weight polymers in the metal-catalyzed step-growth polymerization, judiciously designed monomers and appropriate metal catalysts are required: the monomer must possess the complementary pair of the unconjugated C=C and reactive C–Cl bonds, which are linked via appropriate groups and lengths so that the intramolecular cyclization of the monomer is diminished. The oxidized metal catalyst should return the halogen to the resulting radical species from the unconjugated olefin to construct the linear polymer chain. This polymerization can be further utilized for the synthesis of sequence-regulated vinyl copolymers via the step-growth polymerization of the sequence-regulated monomers that have built-in vinyl monomer sequences between the unconjugated C=C and reactive C–Cl bonds.[22]

Another challenging topic in Kharasch addition or ATRA is the control of stereochemistry during the radical addition reaction.[23–41] Among several strategies for this challenge, chiral metal catalysts of ruthenium(II) and rhodium(I) with (+) or (−)-DIOP ligands [DIOP=2,3-(isopropylidenedioxy)-2,3-dihydroxy-1,4-bis(diphenylphosphanyl)butane] have been used for ATRA between CCl₃Br or arenesulfonyl chloride (ArSO₂Cl) and olefins, such as styrene, methyl methacrylate, and methyl acrylate, to produce optically active adducts with moderately high enantioselectivity (*ee*=10–40%) for radical reactions.[27–30,41] In this reaction, the chiral induction is achieved during the formation of a carbon–halogen bond via halogen transfer from the oxidized metal complex with

the chiral ligand to the resulting carbon radical species of the olefin. Therefore, it is difficult to control the tacticity, that is, the stereochemistry between the adjacent monomer units in the main chains, during the metal-catalyzed living radical polymerization or ATRP of common vinyl monomers by chiral metal catalysts.[42–47] However, the control of stereochemistry during metal-catalyzed step-growth radical polymerization is possible by using an efficient chiral metal complex, because the stereochemistry during each propagation is determined by the halogen-transfer process from the chiral metal complex in the higher oxidation state.[20,21]

This study focused on the control of the stereochemistry during the metal-catalyzed step-growth radical polymerization of 3-butenyl 2-chloropropionate (BCP) using chiral ligands on the metal catalysts (Scheme 2). To complete this study, we first investigated the metal-catalyzed ATRA between the model compounds of the halide and the olefin for the monomer using several Ru(II), Rh(I), Cu(I), and Fe(II) catalysts possessing chiral ligands, such as (−)-DIOP and (−)-sparteine (Sp), and investigated the enantioselectivity and diastereoselectivity by NMR and chiral HPLC analyses of the product adducts obtained by ATRA. Then, the metal-catalyzed step-growth radical polymerization of BCP was investigated using the chiral metal catalysts for possible control of the stereochemistry during radical polymerization.

2. Results and discussion

2.1. Atom transfer radical addition between CCl₄ and 3-butenyl acetate with chiral transition metal catalysts

ATRA between CCl₄ and 3-butenyl acetate (BAc), in which CCl₄ is a typical reactive halide in ATRA and BAc has the same unconjugated olefin as that of BCP, was examined with various chiral transition metal catalysts, including Ru₂Cl₄[(−)-DIOP]₃, RhCl with (−)-DIOP (1.1 equiv), FeCl₂ with (−)-DIOP (1.0 equiv), and CuCl with (−)-Sp (2.0 equiv). Table 1 summarizes the ATRAs with a series of the chiral catalysts at varying temperatures in CCl₄.

The radical addition reactions proceeded almost quantitatively in most cases, except for that of FeCl₂/(−)-DIOP, producing the 1:1