Tetrahedron 74 (2018) 619–643

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Tetrahedron report 1150

Olefin metathesis polymerization: Some recent developments in the precise polymerizations for synthesis of advanced materials (by ROMP, ADMET)

Yanjun Chen [a, b, 1], Mohamed Mehawed Abdellatif [a, c, 1], Kotohiro Nomura [a, *]

[a] Department of Chemistry, Faculty of Science and Engineering, Tokyo Metropolitan University, Hachioji, Tokyo, 192-0397, Japan
[b] Department of Applied Chemical Engineering, Ningbo Polytechnic, Ningbo, Zhejiang, 315800, China
[c] Chemical Industries Division, Chemistry of Tanning, Materials and Leather Technology, National Research Centre, 33 ElBohout St., BP12622, Dokki-Giza, Egypt

ARTICLE INFO

Article history:
Received 4 November 2017
Received in revised form
18 December 2017
Accepted 20 December 2017
Available online 22 December 2017

Keywords:
Olefin metathesis
ROMP
ADMET polymerization
Endfunctionalization
Ring opening metathesis polymerization

ABSTRACT

Recent results for synthesis of end-functionalized polymers (EFP) by using olefin metathesis polymerization have been introduced including basic characteristics in ring-opening metathesis polymerization (ROMP) of cyclic olefins and acyclic diene metathesis (ADMET) polymerization for synthesis of conjugated polymers. Several approaches were demonstrated for synthesis of EFP by living ROMP using molybdenum (exclusive coupling with aldehyde) and ruthenium catalysts (sacrificial ROMP, chain transfer). *Cis* specific (*Z* selective) ROMPs were achieved by molybdenum, ruthenium, and vanadium catalysts by the ligand modification. The catalytic synthesis of EFP with high *cis* selectivity has been achieved by combined ROMP with chain transfer by $V(CHSiMe_3)(N\text{-}2,6\text{-}Cl_2C_6H_3)[OC(CF_3)_3](PMe_3)_2$. The ADMET polymerization using molybdenum and ruthenium catalysts afforded defect-free, high molecular weight poly(arylene vinylene)s containing all *trans* olefinic double bonds. The methods for precise synthesis of EFPs, exhibiting unique optical properties combined with the end groups, were developed. The catalytic one-pot syntheses for EFPs have also been developed.

Contents

* Corresponding author.
E-mail address: ktnomura@tmu.ac.jp (K. Nomura).
[1] YC and MMA: Equal contribution as the first authors.

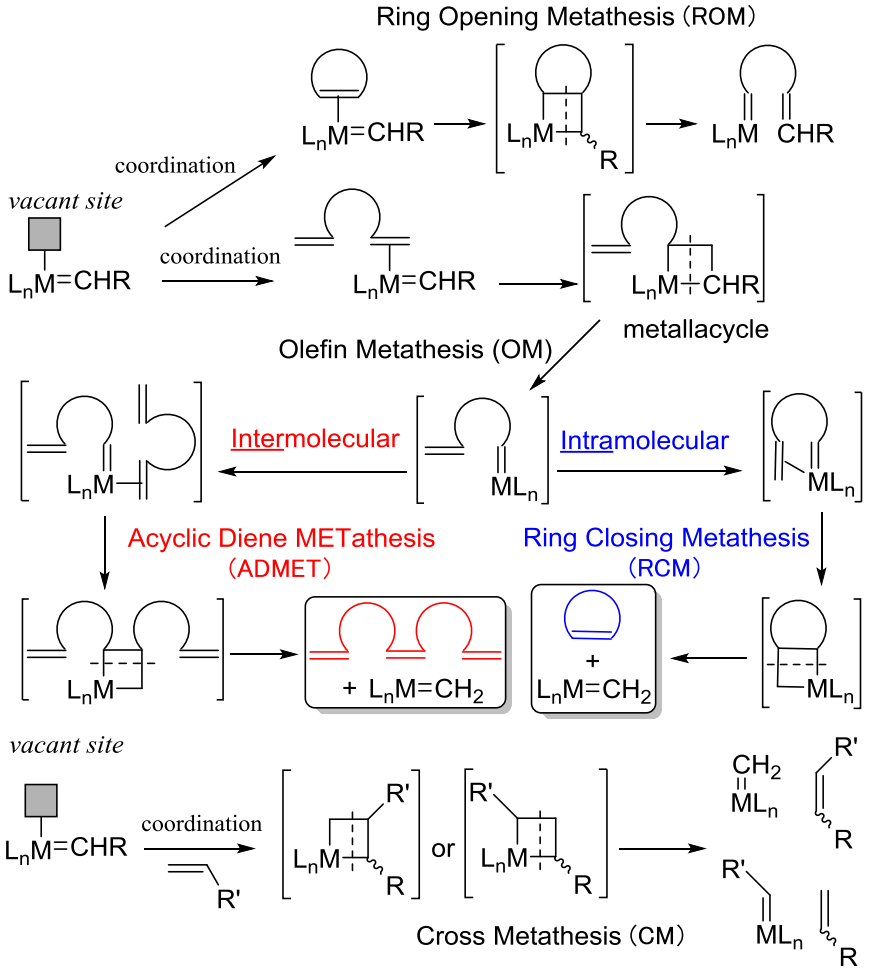
https://doi.org/10.1016/j.tet.2017.12.041
0040-4020/

1. Background: basics in olefin metathesis catalysts and the mechanism

Olefin metathesis has been recognized as the useful method applied for synthesis of various organic compounds (basic, fine chemicals, pharmaceuticals etc.) and polymeric, advanced materials,[1–5] and it has been known that metal-carbene (alkylidene) complexes play a key role in this catalysis. These reactions such as ring-opening metathesis (ROM, reaction with cyclic olefins), ring closing metathesis (RCM, intramolecular reaction with acyclic diene), and acyclic diene metathesis (ADMET, intermolecular reaction with acyclic diene), cross metathesis (CM, reaction with acyclic olefins) proceed via metallacycle intermediate, as shown in Scheme 1. These carbon-carbon bond formations have been recognized as most effective and important methods in recent organic synthesis as well as polymer synthesis in terms of better atom efficiency and construction of environmentally benign chemical processes, synthetic methods. RCM and ADMET are the metathesis reactions of acyclic dienes and control of the selectivity (among two reactions) would be possible by the substrate concentration employed; ADMET reactions (intermolecular metathesis) are conducted under high substrate concentrations whereas RCM is generally conducted under the low concentration to avoid the intermolecular reactions.

Olefin metathesis catalysts are generally classified as three types shown in Chart 1; (i) transition metal alkylidene (carbene) complexes, metallacycles, (ii) transition metal compounds with metal alkyl cocatalysts (generating active species *in situ*), and (iii) transition metal compounds without metal alkyl cocatalysts or preformed alkylidenes (generating active species *in situ* without alkylating reagent). Both ruthenium-carbene [so called Grubbs type, exemplified as **Ru(1)**-**Ru(4)**] and molybdenum-alkylidene [so called Schrock type, **Mo-F$_0$**, **Mo-F$_6$**] catalysts (Chart 1) are the known successful examples.[1–5] In general, the resultant olefinic double bonds are a mixture of *cis*- and *trans*-forms. Recently, several complex catalysts demonstrate high *cis*-specificity in olefin metathesis reactions including ROMP Scheme 2).[1c,2e,6,7] It has been demonstrated that the ligand modifications play essential roles not only to exhibit the high activity, but also to achieve the stereospecific olefin metathesis reactions.[1,2]

Precise control over macromolecular structure is a central goal in polymer synthesis, and living polymerizations [absence of undesirable side reactions such as chain transfer and termination, accomplished by ring-opening metathesis polymerization (ROMP), group transfer polymerization, controlled radical polymerization, and anionic polymerization] generally provide synthesis of polymers with both controlled molecular weights and narrow molecular weight distributions.[8] Introduction of end functionality has also been one of the most important method that enables grafting of the other polymers with different main chain or introduction of functionalities.[5d,e,l,9,10] Precise control of every detail of the macromolecular structure and chain architecture has enabled the development of numerous advanced polymeric materials that are needed in fields as diverse as coatings and adhesives, electronics,



Scheme 1. Typical olefin metathesis reactions and their basic mechanisms.