

SYNTHESIS OF STRUCTURE-CONTROLLED POLYMERS VIA RUTHENIUM-CATALYZED RING-OPENING METATHESIS POLYMERIZATION

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INTRODUCTION:

Synthetic polymers with controlled microstructures and monomer sequences have desirable macroscopic properties and useful applications.^{1a} Thus, development of synthetic approaches remains an important field for polymer chemists. The biological approaches (such as using DNA templates)^{1b} are efficient in synthesis, but are often limited to small scales and a few functionalities. Chemical approaches, however, enable larger-scale production of polymers with diverse chemical structures. One of the most straightforward methods, iterative synthesis, requires tedious procedures including cycles of coupling and deprotection. Another common approach is radical polymerization,^{1a} but the conditions required for radical propagation are not compatible with a number of functional groups that might be desired. Due to its excellent functional group tolerance, ring-opening metathesis polymerization (ROMP) is becoming a powerful strategy for synthesis of structure-controlled polymers.

RUTHENIUM CATALYST DESIGN FOR STRUCTURAL CONTROL

The key step of ROMP mechanism involves an olefin approaching the metal carbene to form a metallacyclobutane intermediate. Modifying steric constraints imposed by the ligands coordinated to the metal center varies the stability of this intermediate to achieve structural control.

Early ROMP systems for structural control, involving transition metal salts (such as ReCl_5)², rely on *in-situ* generation of active metal carbene species, which are accompanied by side reactions and the formation of metathesis-inactive complexes. Pioneering work by Schrock and coworkers employed discrete molybdenum and tungsten alkylidenes for control over polymer microstructures.³ However these catalysts are sensitive to air, moisture and Lewis-basic functional groups. Grubbs and coworkers developed ruthenium (Ru) alkylidenes with improved stability and functional group tolerance. With introduction of the bulky cyclometalated *N*-adamantyl ligand, *cis*-selectivity of Ru-catalyzed (Figure 1. catalyst **2**) ROMP of norbornene was improved to 95% compared to catalyst **1** which afforded 75%.⁴⁻⁵

Polymers synthesized by less sterically hindered *N*-^tBu-cyclometalated catalyst **3** displayed almost exclusive *cis*-selectivity (99%) and syndiotacticity (99%).⁶ This is postulated to arise from stereogenic metal control, in conjunction with an almost exclusive approach of the

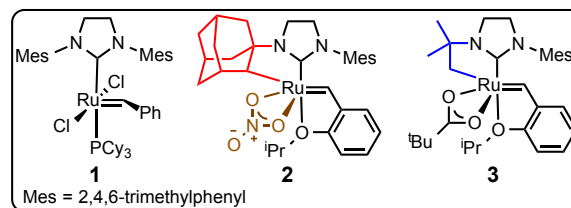


Figure 1. Ru-catalysts for structural control

monomer in an *anti* fashion to the energetically preferred *anti* alkylidene.⁷

SUBSTRATE DESIGN FOR SEQUENCE CONTROL

Ring strain and steric hindrance of monomers are the two key factors that influence the ROMP reactivity. Bulky, strained monomers A (Figure 2) undergo single addition with ruthenium alkylidenes to form ring-opened products. They do not homopolymerize but readily undergo alternating ROMP with a series of unhindered, less strained monomers B.⁸⁻⁹ Introduced steric hindrance on monomer A also suppresses chain-transfer reactions to achieve better control over molecular weight and dispersity.

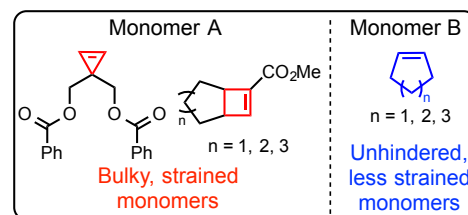


Figure 2. Monomers for alternating ROMP

Alternative strategies utilize relay metathesis to promote the ROMP of unstrained macrocycles by employing an enyne motif as the “polymerization trigger”. (Figure 3) Common functionalities (ester, amide, aliphatic, aromatic, heterocyclic, etc.) are incorporated into polymer backbone in a controlled pattern.¹⁰

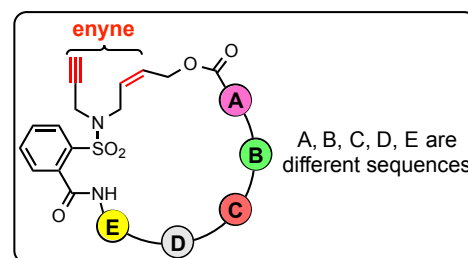


Figure 3. Monomer for macrocyclic ROMP

SUMMARY

Catalyst modification and substrate design have been exploited for the synthesis of controlled polymer microstructures and sequences by ROMP, with improved catalyst stability and functional group tolerance. Future directions are likely to focus on gaining a thorough mechanistic understanding to develop better catalysts and new concepts, such as Ru-based molecular cages, to achieve sequence control of more general substrates.

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