

RECENT ADVANCES IN CASCADE METATHESIS POLYMERIZATION

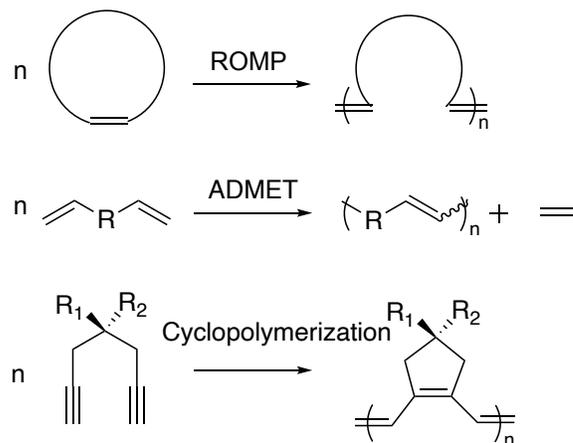
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INTRODUCTION

Over the past two decades, olefin metathesis reactions have become one of the most powerful methods for the synthesis of both small and large molecules. A variety of different olefin metathesis polymerization methods such as ring opening metathesis polymerization (ROMP),¹ acyclic diene metathesis (ADMET) polymerization,² and cyclopolymerization,³ have been widely employed to prepare well-defined macromolecules (Scheme 1). Although high functional group tolerance and precise control over the entire polymerization process can be achieved, most metathesis polymerization techniques rely on simple organic reactions such as ring opening and condensation, limiting the monomer scope and polymer complexity. Therefore, an interest in cascade metathesis polymerization has emerged recently, especially inspired by the success of cascade olefin metathesis reactions in complex, small molecule synthesis.⁴

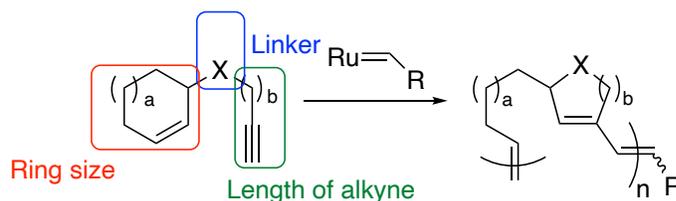
Scheme 1. Typical Metathesis Polymerization.



RING CLOSING/RING OPENING CASCADE

Choi and coworkers reported the first cascade metathesis polymerization combining cyclohexene and terminal alkyne units into the monomer.⁵ Although both cyclohexenes and terminal alkynes are typically poor monomers, extremely fast and highly regioselective ring closing/ring opening, living cascade metathesis polymerization is observed with enyne monomers (Scheme 2). Detailed mechanistic studies reveal that the terminal alkyne acts as a directing group to first react with the ruthenium catalyst, enabling the subsequent, efficient and selective intramolecular metathesis. The ring size of the cycloalkene, the length of alkyne, and linker units are then investigated systematically, showing a dramatic impact on monomer reactivity.⁶

Scheme 2. Ring Closing/Ring Opening Cascade Polymerization.

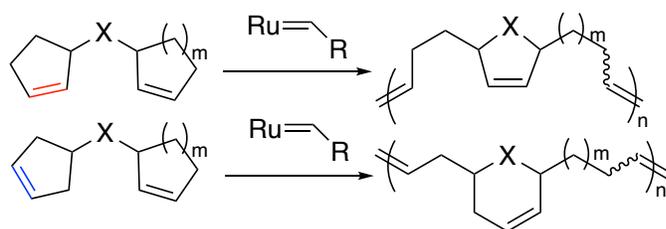


RING OPENING/RING CLOSING CASCADE

Choi and coworkers reported another cascade metathesis polymerization system with monomers containing two cyclopentene units in 2015.⁷ In this case, the ruthenium catalyst tends to first open one

cyclopentene ring, followed by a subsequent ring closing metathesis to form a five-membered polymer backbone (Scheme 3). More challenging monomers containing ring strain free cyclohexene units were also investigated. Only polymers with relatively low molecular weight and broad dispersity were obtained due to the insufficient driving force for polymerization. By shifting the position of the olefin from the 3-position to the 4-position on the cyclopentene unit, much higher polymerization efficiency was achieved enabled by the formation of a thermodynamically more favored six-membered ring backbone.⁸

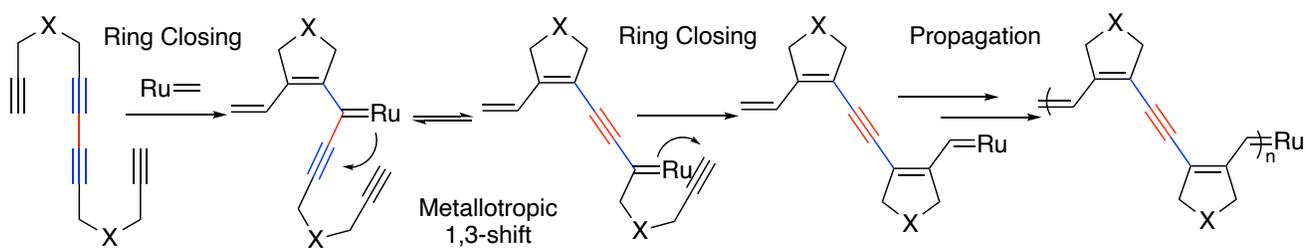
Scheme 3. Ring Opening/Ring Closing Cascade Polymerization.



RING CLOSING/METALLOTROPY CASCADE

The first example that combines olefin metathesis and a metallotropic 1,3-shift reaction was reported by Choi and coworkers in 2017 using tetrayne monomers (Scheme 4).⁹ Conjugated polyenynes containing specific sequences of three double bonds (Z-E-Z) and one triple bond were prepared by a controlled, living cascade metathesis polymerization. More challenging hexayne monomers can also be polymerized by five independent intramolecular transformations.¹⁰ A kinetic study reveals that polymerizations follow first-order kinetics to the monomer, indicating the metallotropic 1,3-shift is fast and not the rate-determining step in propagation.

Scheme 4. Ring Closing/Metallotropy Cascade Polymerization.



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