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Novel Olefin Metathesis Polymerization Methods

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Olefin metathesis involves the shuffling of olefin fragments by scission and regeneration of carbon-carbon double bonds. It has three types i.e. cross-metathesis, ring-closing metathesis and ring-opening metathesis polymerization (ROMP). It is most commonly catalyzed by ruthenium complexes due to their high tolerance towards various functional groups, oxygen and moisture. ROMP is defined as the ring-opening of strained cyclic olefins to yield linear polymers. ROMP has emerged as one of the most popular polymerization methods due to its ability to produce polymers with narrow dispersities and controlled molecular weight, and block copolymers from functional monomers. Thus, this method of polymerization fulfils all the criteria of a living polymerization.

In a conventional living ROMP, one molecule of ruthenium complexes can initiate one polymer chain. This leads to high loadings of expensive ruthenium complexes if the short polymer chains are targeted. This challenge has been addressed by the development of a reversible chain-transfer agent (CTA). This reversible CTA has allowed the synthesis of polymers from functional monomers using catalytic amounts of ruthenium complexes. The molecular weight of the polymers is controlled by monomer to CTA ratio. This procedure has also allowed the synthesis of block copolymer.

Generally, the synthesis of block copolymers by ROMP is achieved by sequential monomer addition which can easily lead to contamination and hence unwanted termination of chain growth. In order to address this challenge, a one-step protocol for the synthesis of block copolymers from the mixture of monomers with different reactivities by ROMP has been developed.

The strain free monomer such as cyclohexene cannot be polymerized by ROMP. A mechanistically interesting cascade ring-opening/ring-closing metathesis (RO/RCM) polymerization has been developed to polymerize cyclohexene in combination with norbornene present within a molecule. The synthesized polymers have narrow dispersities and good molecular weight control.

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