A Handful of Sustainable Routes for Catalytic Ring-Opening Metathesis Polymerization

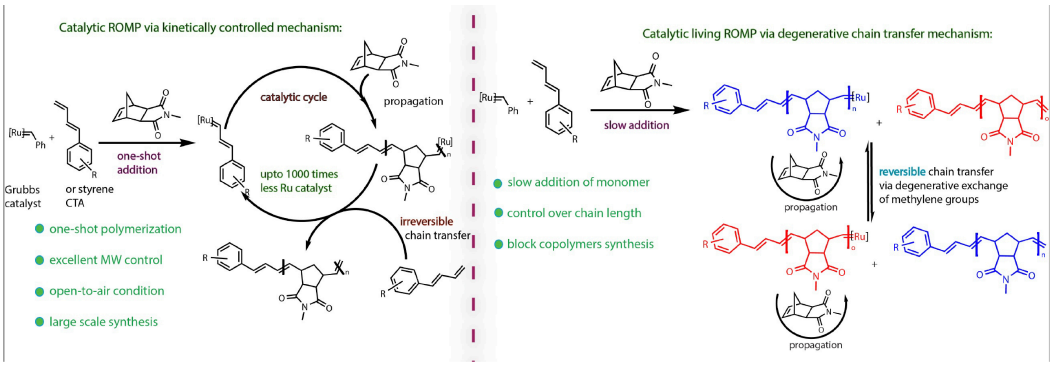
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For many decades, the ring-opening metathesis polymerization (ROMP) using Grubbs complexes has been a well-known technique. However, stoichiometric amounts of toxic and expensive Ru complexes are required with respect to the number of polymer chains formed for typical ROMP. In 2022, our group discovered that conjugated 1,3 dienes[1] and styrenes[2] can act as effective chain transfer agents (CTAs) that catalytically allow for polymerization, reducing the required amount of Ru complex by up to 1000 times compared to classical syntheses. Our detailed mechanistic analysis uncovered a new kinetically controlled chain transfer mechanism. Furthermore, our catalytic method allows access to structurally new block copolymer combinations that were previously unachievable[3].

Moreover, we have recently revealed that using the same CTAs under slow monomer addition conditions can achieve a degenerative exchange mechanism[4]. This mechanism involves the reversible exchange of vinyl groups (derived from CTAs such as styrene), giving the macroscopic impression that all polymer chain ends can propagate quasi-simultaneously. It turns out that virtually all ROMP polymers prepared over the last 50 years have carried the correct end-group for degenerative exchange, meaning they could be activated again and turned into block copolymers with only sub-stoichiometric quantities of Grubbs catalysts.

This discovery has exciting implications for the field of ROMP and may pave the way for more sustainable and cost-effective polymer synthesis.



(1) Indradip Mandal, Ankita Mandal, Md. Atiur Rahman, Andreas F. M. Kilbinger, *Chem. Sci.* **2022**, *13*, 12469–12478.
(2) Indradip Mandal, Andreas F. M. Kilbinger, *JACS Au* **2022**, *2*, 2800–2808.
(3) Indradip Mandal, Ankita Mandal, Andreas F. M. Kilbinger, *ACS Macro Lett.* **2022**, *11*, 1384–1389.
(4) Indradip Mandal, Andreas F. M. Kilbinger, *Under revision (Angew. Chem.,* **2023***).*