Reinvigorated Cyclic Ruthenium Initiators for Enhanced Ring-Expansion Metathesis Polymerization

This technology offers a tethered ruthenium-based initiator for common linear polymerizations. This system improves polymerization kinetics for initiator stability and enables more versatility.

Technology ID

BDP 8400

Category

Materials/Other
Selection of Available Technologies

Authors

Matthew Golder

Learn more

What is the Problem?

Cyclic polymers are promising building blocks for novel organic materials; their "endless" hoop-like architectures display drastically different behaviors in solution and the solid-state compared to their linear counterparts. Their smaller hydrodynamic radii and lack of chain ends contribute to unique thermal and physical properties; applications spanning biomaterials, energy and sustainability provide the impetus to develop new methodologies for their preparation. Most synthetic examples involve acyclic ring-closures or ring-expansion polymerizations (REP) account for most synthetic examples. With advanced synthetic applications in mind, the latter is arguably more convenient as the cyclic initiator facilitates both monomer insertion and templated ring-closure. Despite myriad REP reaction classes, ring-expansion metathesis polymerization (REMP) remains one of the most versatile ways to access cyclic macromolecules. For acyclic polymers, advances in W, Mo, and Ru ring opening metathesis polymerization (ROMP) initiator design have allowed for widespread adoption of this valuable methodology. W and Mo initiators are quite active and desirable for certain applications, but often initiators are derived from more air and functional group tolerant ruthenium N -heterocyclic carbene (NHC) complexes, such as Grubbs 2nd (G2) and 3rd (G3) generation scaffolds. A sterically demanding NHC imparts stability, while a bulky benzylidene ensures facile ligand dissociation. For cyclic polymers, W and Mo metathesis initiators can facilitate REMP of both alkene and alkyne monomers, but examples are largely limited to hydrocarbon feedstocks. Despite the overwhelming success of Ru ROMP initiators, the Ru REMP initiators developed by Grubbs have never been optimized to the same extent as G2 and G3. Therefore, a need exists for a tunable cyclic Ru-NHC platform for REMP that improves upon the current poor molecular weight control, limited stability, and slow polymerizations. The present invention seeks to fulfill this need and provides further advantages.

What is the Solution?

The solution is a reinvigorated tethered ruthenium-based initiator that utilizes key design features of common acyclic Grubbs-type initiators for linear polymerizations. We demonstrate the controlled synthesis of functionalized cyclic polynorbornenes through gel permeation chromatography coupled with multi-angle light scattering and viscometry. Judicious ligand modifications to current cyclic ruthenium-based initiators not only drastically improves polymerization kinetics, but also leads to improved initiator stability. Overall, our technology is an adaptable platform for the study and application of cyclic macromolecules via REMP.

What Differentiates it from Solutions Available Today?

Current synthetic strategies that utilize cyclic olefin monomer feedstocks suffer from poor functional group tolerance, low initiator stability, and/or slow reaction kinetics. This technology addresses these issues, enabling more versatile and user-friendly technologies.

Patent Information:

WO2022216628

References

1. Teng-Wei Wang, Pin-Ruei Huang, Jayme L. Chow, Werner Kaminsky, and Matthew R. Golder(44317) , https://pubs.acs.org/doi/10.1021/jacs.1c03491, American Chemical Society