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.

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Category
Materials/Other
Selection of Available Technologies

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What is the Problem?

Cyclic polymers are promising building blocks for novel organic materials. Their unique thermal and physical properties have broad applications in biomaterials, energy and sustainability, providing the impetus to develop new methods for their preparation. For acyclic polymers, advances in W, Mo, and Ru initiators design have allowed for widespread adoption of valuable methodologies for this synthesis. 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. For cyclic polymers, W and Mo metathesis initiators can work for both alkene and alkyne monomers, but examples are largely limited to hydrocarbon feedstocks. Despite the overwhelming success of Ru initiators, the Ru ring-expansion metathesis polymerization (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 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. The technology demonstrates 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, the technology is an adaptable platform for the study and application of cyclic macromolecules via REMP.

What is the Competitive Advantage?

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:

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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