Iron Catalyzed Ring-Opening Metathesis Polymerization (ROMP)

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Overview

The olefin metathesis reaction is among the most important catalytic carbon-carbon double bond formation reactions. The most widely used catalysts for this reaction are Mo- and Ru- carbene complexes which are expensive and toxic 1. Here we provide a new process for olefin metathesis reaction using iron-catalyzed ring opening metathesis polymerization (ROMP) of olefins that forms polynorbornene with unprecedented stereoregularity and high molecular weight using economical and non-toxic metals.

The Need

Mo- and Ru-carbene catalysts are the most common choice for the olefin metathesis reaction but they have economical and toxicological drawbacks. Although it has been anticipated that an iron-based catalyst would be an economical and biocompatible substitute of the Ru-catalysts, there is no report of a well-defined iron-based olefin metathesis catalyst. Being the most abundant and biocompatible transition metal, a catalyst based on iron would be ideal for the olefin metathesis reaction. However, this is challenging2, due to the tendency of iron alkylidene complexes, which are envisioned as intermediates in this reaction, to catalyze alkene cyclopropanation.

The Solution

Prof. David Milstein and his team developed a novel iron-catalyzed ROMP of olefins which leads to several new catalytic reactions.

Technology Essence

The team synthesized new iron complexes and their derivatives using new bulky pyridine-phosphine (PN) ligands. The catalytic activity of the paramagnetic complexes was examined, including ROMP of norbornene and its derivatives. The initiation mechanism of the different catalysts and the effect of the PN ligand structure were studied, including screening of several FeCl2(PN) complexes, discovering that fine tuning of steric and electronic factors of the ligand is essential for the catalytic activity.

Applications

- New polymeric materials.
- New engineering materials.
- A polynorbornene product using iron-based catalyst.

Advantages

- Non-toxic metal solution.
- Economical and biocompatible substitute of the Ru-catalysts.
- Forms high stereoregular and molecular weight (>10^7 g/mol) polynorbornene.

Development Status

Prof. Milstein and his team discovered iron-catalyzed ROMP of norbornene and its derivatives utilizing dearomatization of pyridine-based ligands. They showed, for the first time, that by proper ligand design, iron-complexes can be efficient, economical and biocompatible catalysts for olefin metathesis reactions. Moreover, the iron-catalyst enables production of isotactic trans-polynorbornene that has not been accessible using other catalysts. In addition, a record high molecular weight polymer was obtained. The team went on to propose a mechanism for the ROMP on norbornene catalyzed based on the experimental observations.

Market Opportunity

ROMP is one of the largest scale applications of the olefin metathesis reaction in the chemical industry. The development of the iron catalyzed ROMP will accelerate further development of iron metathesis catalysts. ROMP with well-defined organometallic catalysts is a versatile method for the preparation of well-defined polyolefines. Therefore, it could be implemented in a range of industrial processes for the synthesis of polymers, and bulk and fine chemicals[3].

References

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Patent Status

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