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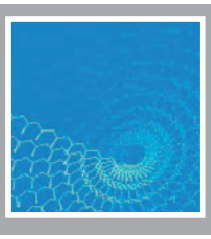

Polymer and Colloid Highlights

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Chemo- and Stereoselective ROMP

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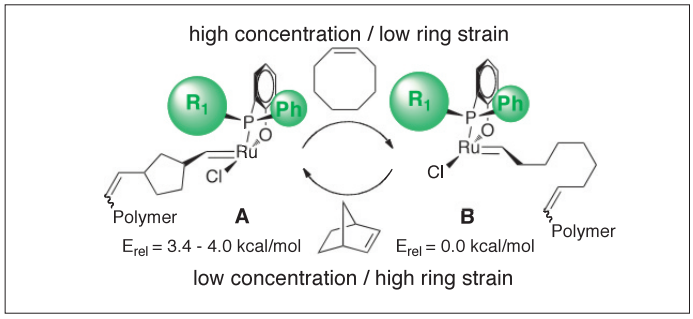
Ring Opening Metathesis Polymerization (ROMP) has been applied as a powerful tool in the synthesis of a variety of complex materials.[1] Besides the functional groups the properties of a polymer are to a great extent determined by its backbone microstructure, which is still a challenging task to control with ROMP. It is for example well known that the *cis* forms of polycyclopentene or polybutadiene exhibit a lower melting point over their *trans* counterparts.[2] The solution to selective synthesis is catalyst design as exemplified in stereoselective Ziegler-Natta polymerization of propylene by C_2 and C_s symmetric metallocenes: catalyst symmetry and polymer tacticity are directly related.[3] In order to gain control over (a) the sequence and (b) the double bond geometry in a norbornene-cyclooctene ROMP copolymer we developed a new class of ruthenium carbene complexes with bidentate phosphine ligands.

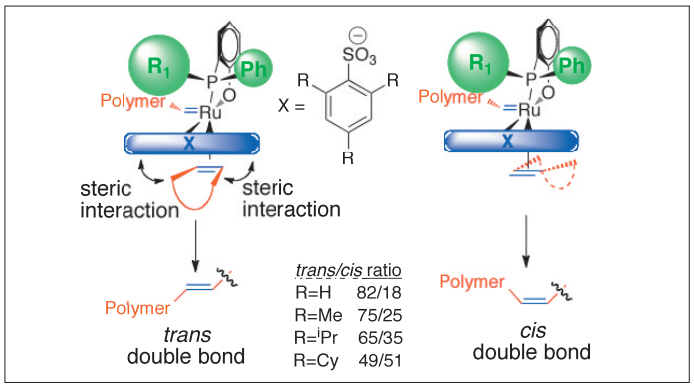
Chemoselectivity by Diastereomeric Site Control

Preceding mechanistic work in our group has identified alternating inversion at a stereogenic ruthenium center during the course of polymerization.[4] The two participating carbene states (A and B in Scheme 1) become diastereomeric (different in energy) for our complexes that are chiral at Ru and chiral at P.

This allows for selective distinction of two monomers (norbornene and cyclooctene) by their ring strain to yield a totally alternating copolymer. The correlation of the chemoselectivity with the bulkiness of substituent R_1 strongly suggests that ring strain, and hence site-control is the only directing factor.[5] This is different from a chain-end control mechanism, where steric bulk



Scheme 1. Mechanism of chemoselectivity by diastereomeric site control.



Scheme 2. Mechanism of stereocontrol by bulky sulfonate ligands.

or the stereochemistry of the immediately preceding insertion determines the preference.[6]

Orthogonal Control of Stereoselectivity

The orientation of the cyclic substrate with respect to the growing polymer chain on the other hand should be responsible for whether *cis* or *trans* moieties are formed (Scheme 2). With our catalyst system we were able to demonstrate that a bulky anionic substituent X (a 2,4,6-trialkylbenzenesulfonate) *cis* to the supporting phosphine ligand is able to force the formation of *cis* double bonds *via* a *syn*-metallacyclobutane intermediate.[7] By increasing the size of X the *cis*-selectivity could be progressively improved up to 51%. Most importantly the degree of alternation remains unchanged throughout this series demonstrating the independent control of the two types of selectivity.

Recent success by Hoveyda and Schrock applying stereogenic-at-metal molybdenum complexes has demonstrated that completely Z-selective metathesis transformations are possible.[8] However, the greater functional group tolerance of ruthenium systems renders this approach particularly interesting for subsequent further developments.

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