

Z-Selective and Syndioselective Ring-Opening Metathesis Polymerization (ROMP) Initiated by Monoaryloxidepyrrolide (MAP) Catalysts

(Richard R. Schrock et al. *Macromolecules*, 2010, 43, 7515–7522)

Abstract (from paper):

We report the Z-selective and syndioselective polymerization of 2,3-bis(trifluoromethyl)-bicyclo[2.2.1]hepta-2,5-diene (NBDF6) and 3-methyl-3-phenylcyclopropene (MPCP) by monoaryloxide monopyrrolide imido alkylidene (MAP) catalysts of Mo. The mechanism of polymerization with *syn*-Mo(NAd)(CHCMe₂Ph)(Pyr)(OHIPT) (**1**; Ad=1-adamantyl, OHIPT=O-2,6-(2,4,6-i-Pr₃C₆H₂)₂C₆H₃) as the initiator is proposed to consist of addition of monomer to the *syn* initiator to yield a *syn* first insertion product and propagation via *syn* insertion products. In contrast, the mechanism of polymerization with *syn*-Mo(NAr)(CHCMe₂Ph)(Pyr)(OTPP) (**4**; Ar = 2,6-i-Pr₂C₆H₃, OTPP = 2,3,5,6-Ph₄C₆H) as the initiator at -78 °C consists of addition of monomer to the *syn* initiator to yield an *anti* first insertion product and propagation via *anti* insertion products. Polymerizations of NBDF₆ and MPCP at room temperature initiated by **4** led to polymers without a regular structure. We propose that the syndiotacticity of *cis* polymers is the consequence of the required inversion at the metal center with each insertion of monomer, i.e., *stereogenic metal control* of the polymer structure. We also propose that the two mechanisms for forming *cis*, *syndiotactic* polymers arise as a consequence of the relative steric bulk of the imido and phenoxide ligands.

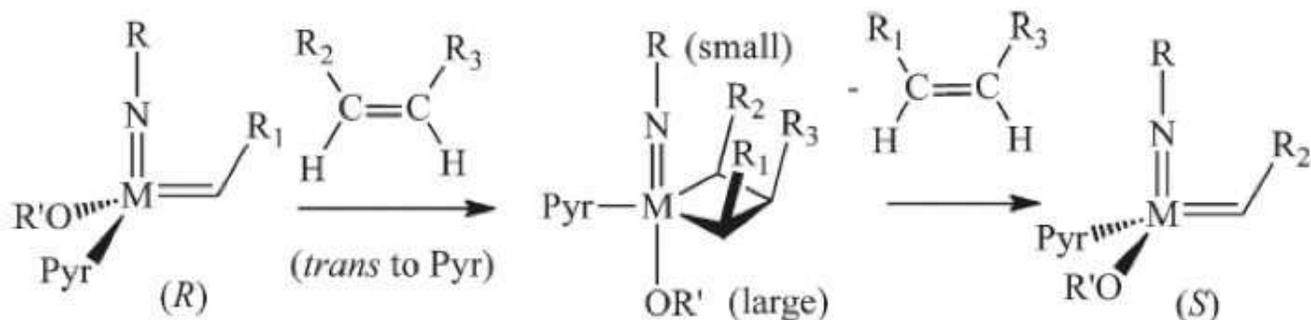
Background:

The use of M(NR)(CHR')(OR'')₂ (M = Mo or W) olefin metathesis catalysts for ring-opening metathesis polymerization (ROMP) has led to an increase in our understanding of how polymers that have a regular and long-range structure (in terms of *cis/trans* linkages and tacticities) can be formed from norbornenes or substituted norbornadienes. Monoaryloxidepyrrolide (MAP) catalysts of the type M(NR)(CHR')(OR'')(Pyr) (M = Mo or W) where Pyr is pyrrolide itself (NC₄H₄⁻) or a substituted pyrrolide (e.g., 2,5-dimethylpyrrolide) have a key feature is the presence of a *stereogenic metal center*. MAP catalysts are particularly useful for Z-selective metathesis reactions. Z-selectivity is possible when the olefin attacks the metal *trans* to the pyrrolide in a *syn* alkylidene isomer (one whose substituent points toward the imido group) to yield metallacyclobutane intermediates in which all substituents point toward the axial imido ligand and away from the axial OR' group.

(continued)

Background (continued):

It is proposed that tungsten or molybdenum MAP species have (i) intermediate trigonal- bipyramidal metallacyclobutanes containing axial imido and alkoxide ligands and (ii) the stereochemistry at the metal inverts as a consequence of each forward metathesis step ($R_1, R_2, R_3 = \text{alkyl groups}$).

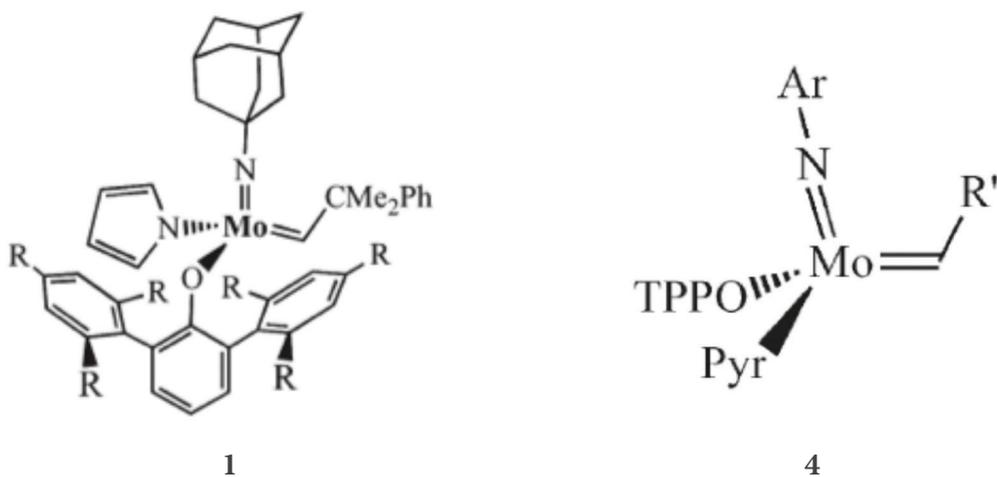


Objectives of the study:

In previous studies with bisalkoxide (or biphenolate or binaphtholate) catalysts and some monomers (DCMNBD = 2,3-dicarbomethoxynorbornadiene or NBDF6 = 2,3-bis(trifluoromethyl)-bicyclo[2.2.1]hepta-2,5-diene), it has been proposed that the monomer approaches the metal pointed toward the imido group (ene_{syn}), even when the imido group is relatively sterically demanding like the diisopropylphenylimido group. For each step of this type, a cis double bond is formed from a syn isomer (and the insertion product is syn) and a $trans$ double bond is formed from an $anti$ isomer (and the insertion product is syn). The key questions are here whether syn and $anti$ isomers of the growing polymer chain can interconvert readily under the conditions of the polymerization and which isomer is more reactive toward a given monomer. To clarify these issues the effect of the catalyst ratio, temperature of the polymerization and irradiation were studied extensively by ^{13}C NMR, and IR spectroscopy to determine the architecture of the polymers including tacticity. Furthermore, the steric outcome of the propagation step was also investigated. If only one $C=C$ face adds to the $M=C$ bond, then four propagation steps are possible and where cis polymers are formed the only two possible pathways are $syn+ene_{syn}$ and $anti+ene_{anti}$. The $syn+ene_{syn}$ situation would most likely arise when the imido ligand is “small” and the $anti+ene_{anti}$ situation when the imido ligand is “large” with respect to the aryloxy. In order to determine the effect of the relative size of the ligands two MAP catalysts were investigated in ROMP (**1** and **4**) (see next page).

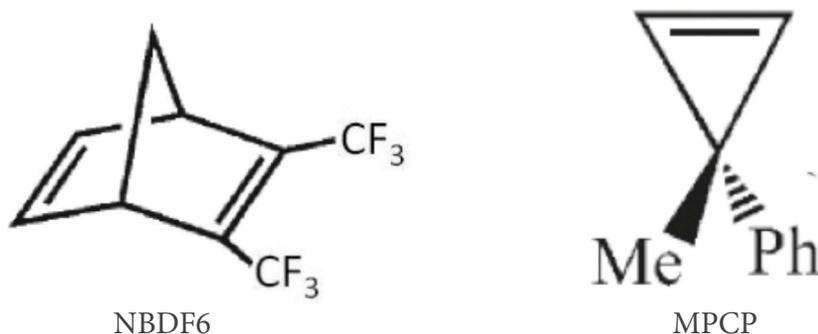
Catalysts studied:

Monoaryloxo monopyrrolide imido alkylidene (MAP) catalysts



R = *i*-Pr, Ar = 2,6-diisopropylphenyl, Pyr=pyrrolide, OTTP=2,3,5,6-tetraphenylphenoxide In 4 the imido ligand is larger than adamantylimido and the phenoxide ligand is smaller than OHIPT= O-2,6-(2,4,6-*i*-Pr₃C₆H₂)₂C₆H₃) in 1.

Monomers studied:



Results:

1. ROMP of 2,3-Bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene (NBDF6) with 1.

Polymerization of NBDF6 was investigated at various catalyst/monomer ratio. Addition of 100 equiv of NBDF6 to 1 in toluene led to the formation of a white solid within minutes. The obtained polyNBDF₁ has predominantly a *cis* structure since it lacks a strong absorption around 970 cm⁻¹ characteristic of *trans* olefins. Systematic reduction of the NBDF6 equivalency revealed that polyNBDF₁ begins to be insoluble when 10 equiv has been incorporated, thus, it cannot be the consequence of a runaway polymerization.

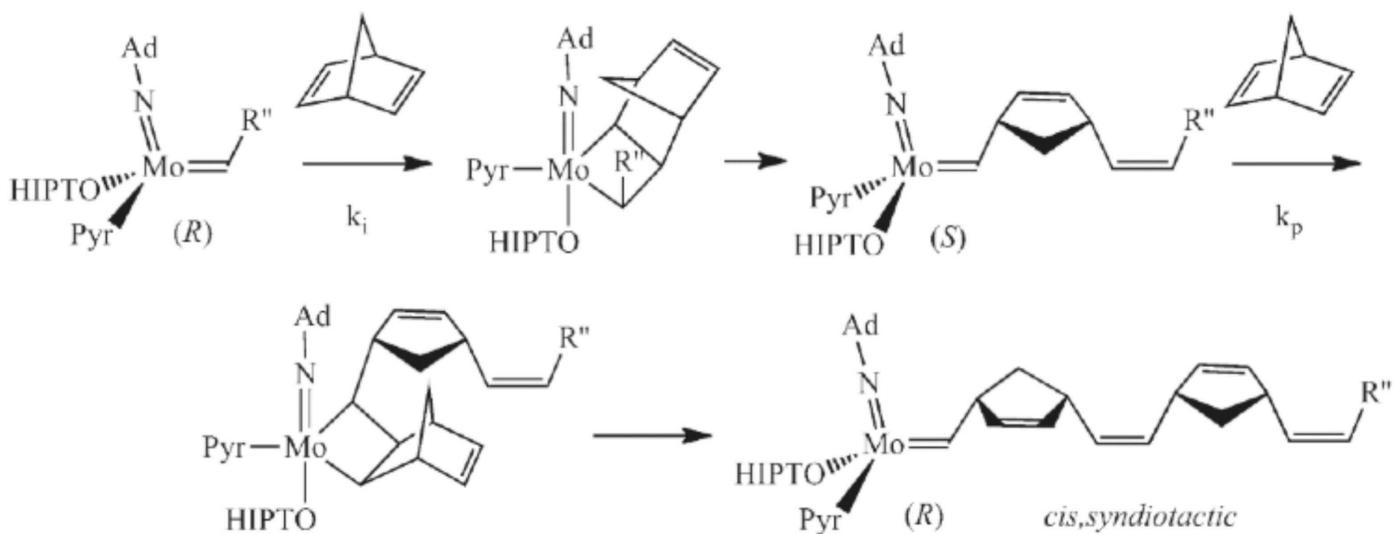
(continued)

Results (continued):

A large body of further evidence including analysis of chemical shifts and coupling constants of ^{13}C NMR spectra indicated that ROMP with **1** leads to *cis,syndiotactic* structure. For example, comparison of the ^{13}C NMR spectra of previous results obtained with bisalkoxide catalysts revealed that the structure is neither *trans,syndiotactic* nor *cis,isolactic*, while the data were consistent with similar previous findings where *cis,syndiotactic* structure was elucidated.

In summary, polymerization with **1** as the initiator takes place with norbornadienes as shown below.

Cis,syndiotactic structures are generated via *syn* initiation and propagation with the monomer approaching the metal *trans* to the pyrrolide and pointing toward the adamantylimido group (*ene_{syn}*). Syndiotacticity arises solely as a consequence of the monomers adding to alternating faces of the $\text{M}=\text{C}$ bonds in a chiral, racemic catalyst.



2. ROMP of 3-methyl-3-phenylcyclopropene (MPCP) with **4**.

Polymerization of MPCP at 20 °C with **4** led to a polymer with no regular structure. However, at -78 °C employing **4** as the initiator, the polyMPCP₄ thus formed has a regular structure that is identical with the *cis,syndiotactic*-polyMPCP₁ as described above. As the temperature of polymerization is increased from -78 to 46 °C in separate experiments, the regularity of the polymer decreases steadily.

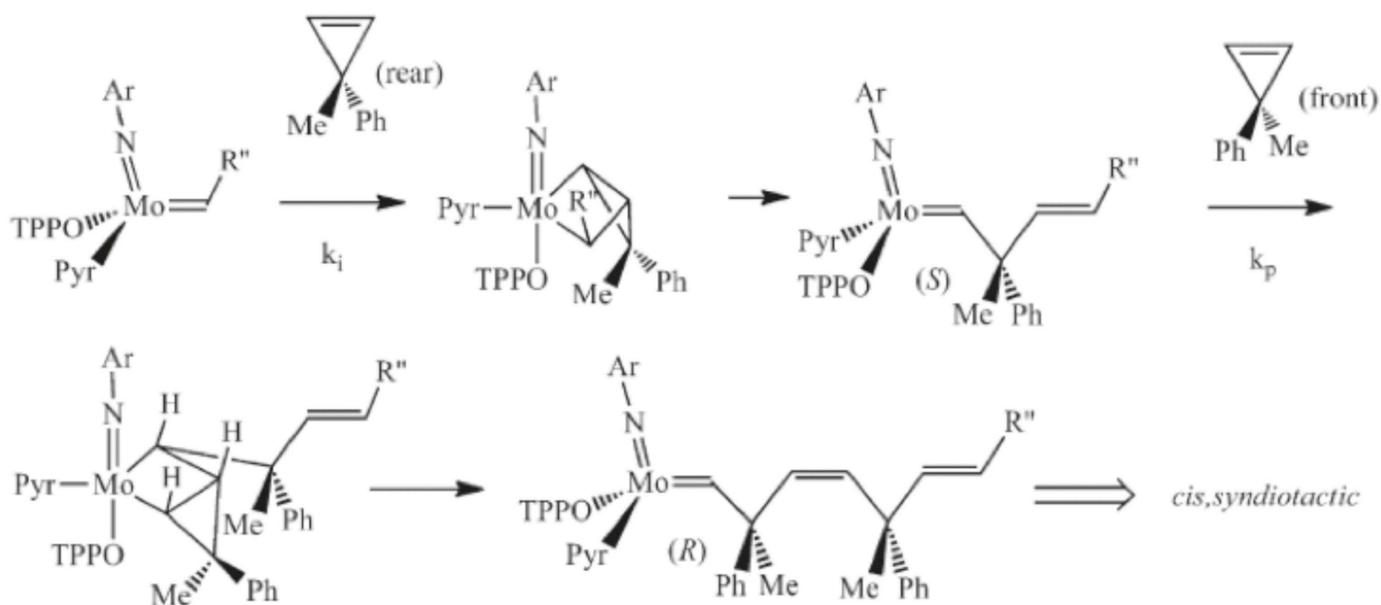
Reducing the monomer ratio (while increasing the initiators') resulted in various results that provided rational of the following mechanism. In addition, photolysis of the initiator led to *anti-4* and its ROMP reaction was also studied compared with *syn-4* initiation.

(continued)

Results (continued):

In summary, it appeared that *anti* species form in the reaction between MPCP, and the *syn* initiator at low temperatures and the *anti* alkylidene insertion products do not readily convert to *syn* species at low temperature. Therefore, *cis,syndiotactic*-polyMPCP (except for the first C=C bond) is formed as shown below.

Cis,syndiotactic-PolyMPCP is obtained at low temperatures since only *anti* species are available on the time scale of the polymerization at low temperature. It is assumed that the methyl face of the C=C bond adds to the metal in the propagation step. Again *cis,syndiotacticity* was confirmed by ^{13}C NMR, IR and through comparison with previous attempts with bisalkoxides and other MAPs.



Conclusion:

It has been shown that *Z*-selective reactions in ROMP have some generality and that *syndiotacticity* (for *cis* polymers) is predictable as a consequence of the mechanism through which MAP catalysts operate, i.e., inversion of configuration at the metal center with each forward metathesis step (*stereogenic metal control*). Two mechanisms of forming the same *cis,syndiotactic* ROMP polymer have resulted from inverting the relative sterics of the imido and phenoxide ligands. MAP species that contain an *anti* alkylidene can be observed, either as intermediates in a ROMP reaction or upon photolysis of *syn* alkylidenes.