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# Stereochemistry of Ring-Opened Metathesis Polymers Prepared in Liquid $CO_2$ at High Pressure Using $Ru(H_2O)_6(Tos)_2$ as Catalyst

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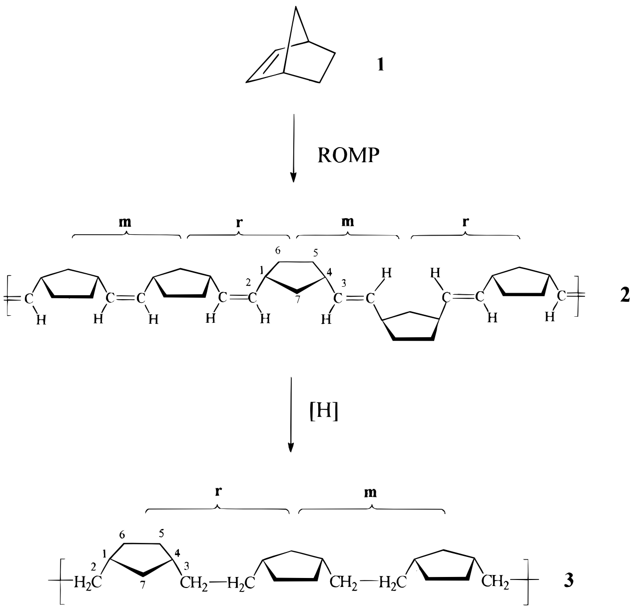
The factors which control the stereochemistry in olefin metathesis processes have excited the interest of various groups of workers over a period of years, and although in general it has been demonstrated that the choice of catalyst system is of primary importance, reaction conditions and the structure of the substrate molecule also play a significant role in the stereochemical outcome of the reaction. In these studies, ring-opening metathesis polymerization (ROMP) of cyclic olefins, such as norbornene, **1**, Scheme 1, and its derivatives has been particularly valuable because the stereochemistry of the product, in terms of both cis/trans ratio and tacticity (*m*/*r* ratio) generally reflect primary events at the catalyst site; this is not the case in the metathesis of acyclic olefins where facile secondary processes lead progressively to the loss of stereospecificity and the necessity for extrapolation of isomer ratios to zero conversion.[1]

In ROMP an important factor which has emerged is that of the role played by the steric requirements of the catalyst site. For example, in the noble metal catalyzed ROMP of dienes such as norbornadiene,[2] 7-methylnorbornadiene,[3] and *endo*-dicyclopentadiene,[4] the monomer can also act as a spectator ligand and a much more sterically demanding catalyst site is generated which results in the production of high cis content polymers. Similar trends have been observed with a variety of well-defined Mo-[5] and W-based[6,7] catalysts where again cis selectivity may increase with increased steric bulk of the ligands and the effect is also observed when using esters and ethers as solvents for the classical $MoCl_5$- or $WCl_6$-based catalysts.[8] The tendency for many medium to high cis content ROMP polymers to have a blocky cis/trans distribution has also been attributed to steric effects. Thus blocks of cis double bonds are believed to be propagated at a site sterically constrained by the last formed cis double bond remaining in the coordination sphere of the metal.[1] In each case stereoselectivity is believed to be due, in effect, to a reduction in the volume available for initial metallacycle formation, which leads to the preferential formation of a less bulky cisoid intermediate and cis products. Here we report what we believe to be the first example of similar effects produced when the ROMP reaction is carried out using a Ru-based catalyst under high pressure,[9] leading to the formation of high cis, syndiotactic poly(norbornene), a structural variation of **2** in Scheme 1 where all the dyad units are cis, *r*.

**Scheme 1. Stereochemical Consequences of Ring-Opening Metathesis Polymerization of Norbornene.**



Reactions were carried out under what we believe to be both heterogeneous and homogeneous conditions, at least with respect to the initial physical state of the catalyst. In the former case, polymer was observed to form at the surface of the solid catalyst, which lies at the bottom of the reactor, thereby encapsulating and deactivating it and so leading to low yields. In the latter case, homogeneous conditions were achieved by initial addition of sufficient degassed methanol to keep the catalyst in solution after the addition of $CO_2$. In these cases polymer was observed to form throughout the reactor.

Polymers were characterized, Table 1, by GPC and the cis/trans double bond ratio was determined by $^1H$ and $^{13}C$ NMR spectroscopy. The tacticity of the various high cis polymer samples may be estimated by inspection of the $^{13}C$ NMR spectra, Figure 1, of their hydrogenated derivatives, **3**.[10] Here, unlike the spectra of the unsaturated precursors, the $C^{5,6}$ and the $C^7$ resonances are sensitive to the tacticity of the various ring dyads and triads, and in the case of atactic polymers, these signals appear as partially resolved doublets and triplets, respectively. The analysis shows that the high cis polymers are highly syndiotactic[11] whereas the mainly trans polymers are atactic. This indicates that the high-cis propagating metallacarbene maintains a very specific geometry without relaxation between propagation steps.[1]

The results, which are presented in Table 1, show several interesting features; for example, reactions carried out with bulk monomer or in pure $CO_2$ are more cis stereospecific than those in methanol or $CO_2$/methanol, and the former polymers have a blocky distribution[1] of cis and trans double bonds as judged from their $^{13}C$ NMR spectra, an effect also observed for high cis content polymers when using Os-based catalysts in polymerizations at atmospheric pressure.[12] The stereoselectivity of the ROMP reaction can depend

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**Table 1. Polymerization of 1 Using $Ru(H_2O)_6(Tos)_2$ under Different Reaction Conditions**

| polym medium | % yield[a] | % cis | $M_n \times 10^{-3}$ | MWD | tacticity[b] |
|---|---|---|---|---|---|
| bulk | 20 | 77 | 272 | 2.7 | syndio. |
| $CO_2$, 2500 psi | 19 | 76 | 269 | 2.5 | syndio. |
| $CO_2$, 4000 psi | 34 | 87 | 77 | 1.9 | syndio. |
| $CO_2$, 5000 psi | 32 | 90 | 187 | 2.5 | syndio. |
| MeOH | 92 | 26 | nc | nc | atactic[c] |
| $CO_2$/MeOH, 5000 psi | 29 | 32 | 58 | 3.7 | atactic[c] |
| $CO_2$/MeOH, 5000 psi | 26 | 37 | 55 | 3.4 | atactic[c] |

[a] Yield of polymer after 5 h of reaction. [b] Estimated from the hydrogenated derivative. [c] Polymers have a syndiotactic bias.

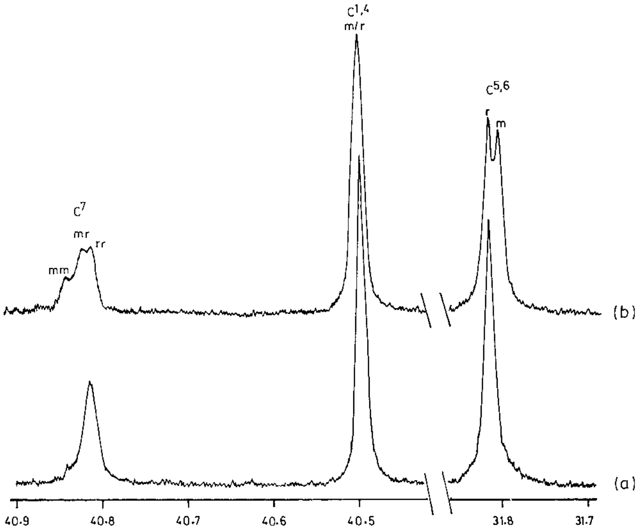


**Figure 1.** $^{13}C$ NMR spectra of hydrogenated polymers: (a) syndiotactic polymer, originating from 90% cis poly(norbornene) prepared in liquid $CO_2$ at 5000 psi and (b) atactic polymer with a small syndiotactic bias originating from 32% cis poly(norbronene) prepared in liquid $CO_2$/MeOH at 5000 psi.

sensitively on reaction conditions and catalyst ligation, and there are many instances where a change in these factors can radically alter the cis/trans ratio in the resulting polymer.[1] In the present case the dramatic fall in cis content, on the introduction of methanol to the reaction medium, may be due to propagation by a species in which one or more of the $H_2O$ ligands is displaced by methanol, although it is not obvious why such a species would be less stereoselective. It is, however, significant that the addition of methanol has the effect of solubilizing the catalyst, and an alternative explanation may be that the change in cis content is due to the change in the physical state of the propagating species. The key observation, however, is that increasing the pressure at which both homogeneous *and* heterogeneous reactions are conducted results in enhanced cis stereoselectivity.

We believe that the increased cis stereoselectivity observed in the present work and that observed when bulky ligands are present at the catalyst site (vide supra) are mechanistically related. In both cases the volume available for metallacycle formation is reduced and a less bulky cis metallacycle then becomes the preferred intermediate. The approximate volume difference involved may be calculated from the cis/trans ratio by the following kinetic analysis. Equations 1 and 2 represent the formation of cis and trans units, respectively, where $k_c$ and $k_t$ are the rate constants for the formation of cis and trans metallacycles respectively and the $k_c/k_t$ ratio may be taken as equivalent to the cis/trans ratio as measured from the spectra of the polymers which are assumed to be primary products.

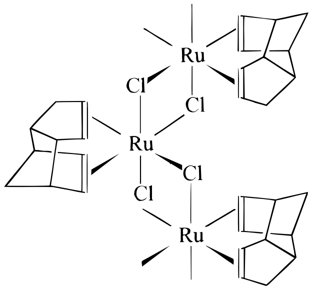
$$M + P_n \xrightarrow{k_c} [MP_n]_c \rightarrow P_{n+1} \tag{1}$$

$$M + P_n \xrightarrow{k_t} [MP_n]_t \rightarrow P_{n+1} \tag{2}$$

Applying standard thermodynamic equations[13] (eq 3) where $P$ is pressure and $C$ is a constant of integration, which may be zero, a rough estimate of this molar

$$\ln\left(\frac{\%\ \text{cis}}{\%\ \text{trans}}\right) = \ln\left(\frac{k_c}{k_t}\right) = \left(-\frac{\Delta V_c}{RT} + \frac{\Delta V_t}{RT}\right)P + C \tag{3}$$

volume difference can be made from the limited data. This volume, ~160 cm$^3$, is the extra molar volume required to make $[MP_n]_t$ ocompared with $[MP_n]_c$. It is interesting that it is about the same as the molar volume of *endo*-dicyclopentadiene, which, when present as a spectator ligand on the Ru-based catalyst, **4**, during the polymerization of **1** at atmospheric pressure, induces a normally high trans directing initiator to become very high cis directing.[14] While bulky permanent or spectator ligands can provide this volume constraint in the propagating step, we also believe that the last formed unit, when cis, while remaining in the coordination sphere of the metal as the next propagation cycle commences,[1] can occasion the same effect.



**4**

Finally, we believe that the high pressure reaction conditions, rather than being inherently responsible for the induction of syndiotacticity, Table 1, merely allows the Ru catalyst to realize its potential to produce syndiotactic polymer, by increasing the cis content. This is based on the observation that in polymers formed from 5,5-dimethylnorbornene[15] and anti-7-methylnorbornene,[16] using other Ru-based initiators, where tacticity associated with both cis and trans double bonds is readily determined, cis double bond ring dyads were highly syndiotactic while the trans were atactic. It follows then that the $^{13}C$ NMR spectra of the hydrogenated polymers derived from even low cis content poly(norbornene)s, e.g., Figure 1b, show an overall syndiotactic bias. This is also a feature of the related Os-based catalysts where the high cis poly(norbornene)s are syndiotactic.[10]

This demonstration of the use of high pressure to control stereochemistry in metathesis polymerization has important implications for coordination polymerization reactions in general.

**Supporting Information Available:** Text giving details of polymer synthesis and experimental procedures (2 pages).

Ordering and access information is given on any current masthead page.

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