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Synthesis of Highly Cis, Syndiotactic ROMP Polymers Using Ruthenium Metathesis Catalysts

Lauren E. Rosebrugh, Vanessa M. Marx, Benjamin K. Keitz, Robert H. Grubbs*

Arnold and Mabel Beckman Laboratory of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

Supporting Information Placeholder

ABSTRACT: The first example of ruthenium-mediated ring-opening metathesis polymerization (ROMP) generating highly cis, highly tactic polymers is reported. While the cis content varied from 62 to >95% depending on the monomer structure, many of the polymers synthesized displayed high tacticity (>95%). Polymerization of an enantiomerically pure 2,3-dicarboalkoxynorbornadiene revealed a syndiotactic microstructure.

The precise control of polymer microstructure resulting from the ring-opening metathesis polymerization (ROMP) of substituted norbornenes, norbornadienes, and other strained, cyclic olefins is critical for the development of polymers with well-defined characteristics.[1] These microstructures, which include various tacticities (e.g., syndiotactic, isotactic, or atactic) and double bond configurations (cis vs. trans), have a significant impact on the physical and mechanical properties of the resulted polymer.[2] For example, syndiotactic *cis*-poly(norbornene) is a crystalline polymer with a high melting point, while atactic *trans*-poly(norbornene) is amorphous and low-melting in comparison.[3] Accordingly, the development of olefin metathesis catalysts capable of producing highly stereoregular (>95% a single structure) ROMP polymers is of great interest.

ROMP polymers with high cis content have been synthesized previously using a variety of Re-, Os-, W- and Mo-based metathesis catalysts,[4,5] as well as more recently with a Ru-derived system.[6] However, while many of these catalysts, particularly W- and Mo-based systems, have been shown capable of controlling both the cis/trans ratio and tacticity of ROMP polymers,[4,5] only limited tacticity control has been achieved with ruthenium.[7] In fact, it was highlighted in a recent report by Schrock and coworkers that due to the low barrier of rotation of Ru alkylidenes and consequent inability of the Ru=C bond to enforce the steric pressures necessary to give tacticity, the likelihood of developing a Ru-based metathesis catalyst able to form polymers exhibiting high tacticity appeared increasingly minimal.[5b]

We recently reported on the *Z*-selective ruthenium metathesis catalyst **1** containing a crucial cyclometalated *N*-heterocyclic carbene (NHC) ligand (Figure 1), in which the Ru-C bond is formed via C-H activation induced by the addition of silver pivalate.[8] This catalyst was shown to give on average 80-95% cis content in the ROMP of norbornene and norbornadiene derivatives,[6b] thus demonstrating for the first time the cis-selective ROMP of a wide range of monomers with a single ruthenium-based metathesis catalyst. However, all of the polymers produced by catalyst **1** were atactic.

Herein, we report a new series of cyclometalated catalysts (complexes **2**-**4**) derived from C-H activation of an *N*-*tert*-butyl group. These complexes display ROMP behavior unprecedented for ruthenium-based metathesis catalysts: Not only do these catalysts yield polymers with a generally higher cis content compared to **1** (>95% in many cases), but the polymers produced are also highly syndiotactic, further demonstrating that, similar to their W- and Mo-based counterparts, *Ru-based metathesis catalysts are capable of producing polymers with a wide range of specific microstructure*s without the use of specialized monomers or reaction conditions.

The recent development of a milder method of effecting the salt metathesis and C-H activation of Ru metathesis catalysts using sodium pivalate has enabled the synthesis of complexes with significant alterations to the chelating *N*-alkyl group of the NHC that were previously inaccessible.[9] Using this new approach, we were able to prepare the less sterically encumbered *N*-*tert*-butyl catalysts **2**-**4** (Figure 1).[10] Single-crystal X-ray diffraction of **3** confirmed cyclometallation of the *N*-*tert*-butyl substituent, as well as bidentate coordination of the pivalate ligand. It was also revealed that the *N*-aryl ring is positioned such that the isopropyl substituent resides on the same face as the benzylidene. Structural parameters, including bond lengths and angles, were consistent with those for **1** and its pivalate derivative.[8]

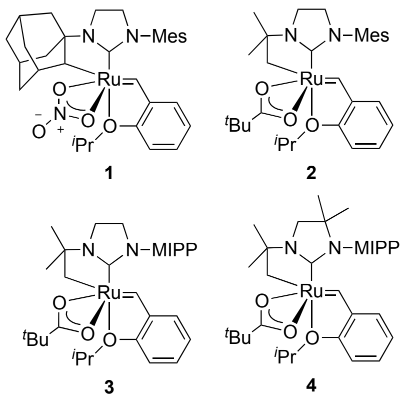


Figure 1. Catalysts **1**-**4**: Mes = 2,4,6-trimethylphenyl; MIPP = 2,6-methylisopropylphenyl.

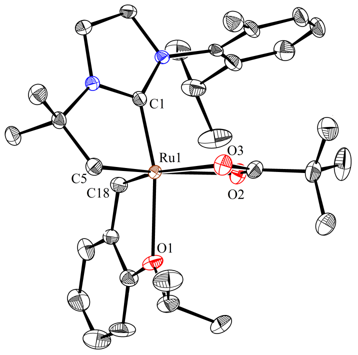


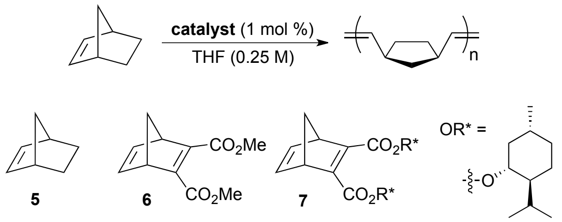
Figure 2. Solid-state structure of **3**, with thermal ellipsoids drawn at 50% probability. For clarity, hydrogen atoms have been omitted. Selected bond lengths (Å) for **3**: C1-Ru 1.932, C5-Ru 2.071, C18-Ru 1.798, O1-Ru 2.334, O2-Ru 2.202, O3-Ru 2.398.

We initiated our ROMP studies by adding **2** to a solution of norbornene (**5**) in THF (0.25 M) at room temperature, upon which the solution rapidly became viscous.[11] The isolated polymer was found to be almost exclusively cis (>95%) by ^{1}H NMR spectroscopy (Table 1). Furthermore, the ^{13}C NMR spectrum of **poly-5** prepared with **2** was found to be consistent with literature reports for highly tactic poly(norbornene).[12] In comparison, performing the same reaction at room temperature with catalyst **1** gives atactic poly(norbornene) that is only 88% cis.[6b]

In order to test whether the observed tacticity control was specific to norbornene, we turned to the more complex monomer 2,3-dicarbomethoxynorbornadiene (DCMNBD, **6**). The tacticity of poly(DCMNBD) is readily determined by analyzing the C(7) region of the ^{13}C NMR: multiple resonances correspond to an atactic polymer, such as the poly(DCMNBD) produced by **1** (Figure 3a), while a singularly tactic polymer would be expected to display only one peak in this region due to symmetry.[13] **Poly-6** produced by catalyst **2** (>95% cis; Table 1) was found to be highly tactic, in that the corresponding ^{13}C NMR spectrum contained primarily one carbon resonance in the C(7) region, consistent with a tacticity of >95% for the all-cis triads (Figure 3b).

To probe the effect of symmetry of the *N*-aryl group on tacticity,[14] we evaluated two catalysts (**3**, **4**) containing a cyclometalated *N*-*tert*-butyl group similar to **2** but with an asymmetric *N*-aryl group (Figure 1). The geminal dimethyl backbone of **4** was installed to prevent any rotation of the *N*-aryl group that might be occurring in **3**. Polymerization of **6** with catalysts **3** and **4** gave **poly-6** that was also >95% tactic in both cases as determined by ^{13}C NMR (Table 1). **Poly-5** produced by these catalysts, was also highly cis (>95%), albeit slightly less tactic in both cases than **poly-5** generated with **2**.

Table 1. Polymerization of Monomers 5-7 with Catalysts 2-4.[a]



monomer	catalyst	cis, %[b]	yield, %[c]	M_n, kDa[d]	PDI[d]
5	**2**	>95	79	605[e]	1.41
5	**3**	>95	88	521[e]	1.49
5	**4**	>95	84	424[e]	1.45
6	**2**	>95	78	--[f]	--[f]
6	**3**	>95	54	--	--
6	**4**	>95	45	--	--
7	**2**	72	42	--	--
7	**3**	62	57	--	--
7	**4**	86	7	--	--

[a]Conditions were [monomer]/[initiator] = 100:1 in THF (0.25M in substrate) at RT. [b]Determined by ^{1}H NMR and ^{13}C NMR spectroscopy. [c]Isolated yields. [d]Determined by gel-permeation chromatography (GPC) with a multiangle light scattering (MALS) detector. [e]The specific re-

fractive index increment (dn/dc) was determined to be 0.139 ± 0.005 mL/g. [ef]Here and below: Not determined because insolubility of the isolated polymer in THF precluded GPC analysis.

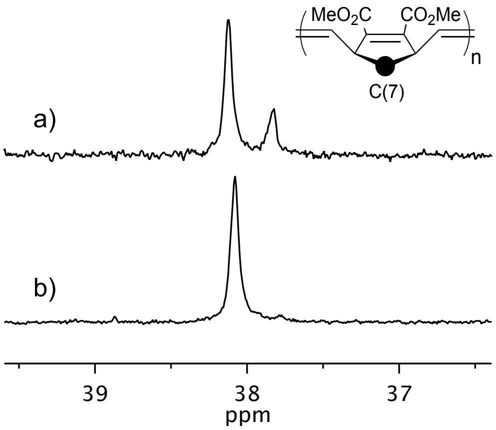
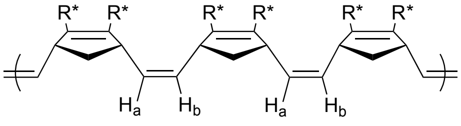


Figure 3. The C(7) ^{13}C NMR region of poly(DCMNBD) (**poly-6**) prepared with a) **1** (86% cis, atactic) and b) **2** (>95% cis, >95% tactic).

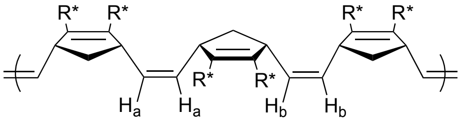
As had previously been observed with **1**, the experimental number-average molecular weights (M_n) for **poly-5** prepared using catalysts **2-4** were significantly higher than the theoretical values (Table 1). This is indicative that k_p of **5** exceeds k_i of **2-4**, which would lead to the broad PDIs observed; this is likely a result of incomplete catalyst initiation and might be expected based on the relatively low initiation rate constants of **2-4**.[15]

To elucidate the absolute tacticities of the norbornene- and norbornadiene-derived polymers, we employed chiral monomer **7**. Due to the lack of mirror planes relating the monomeric units in the resulting polymers, it is expected that if the polymers produced by **2-4** were cis, isotactic, the olefinic protons would be inequivalent (Figure 4a).[16] As such, we should observe a coupling characteristic of olefinic protons by NMR spectroscopy. Conversely, in a cis, syndiotactic polymer, the cis olefinic protons would be related by a C_2 axis passing through the midpoint of the double bond and would therefore be equivalent and not coupled (Figure 4b). While **poly-7** produced by catalysts **2-4** was only 62-86% cis (Table 1), the tacticity of the all-cis triads remained very high for all three catalysts (see Figures S14 and S15 in Supporting Information). Furthermore, the cis olefinic protons in the isolated polymers were uncoupled,[17] strongly suggesting that **poly-7** is syndiotactic in all cases (Figure 5).

One plausible explanation for the observed tacticity control is that the rate of monomer incorporation is faster than the rate of carbene epimerization.[18] This is presumably in contrast to catalyst **1**, which, likely due to the slow rate of propagation relative to epimerization, generates atactic polymers. This distinction might be explained by the relative differences in size and symmetry of the carbon chelate in catalysts **1** and **2**. The reduced bulk of the cyclometalated *N-tert*-butyl group of **2** (vs. the *N*-adamantyl chelate in **1**) likely results in fewer unfavorable steric interactions between the catalyst and the approaching bulky norbornene and norbornadiene derivatives, thus increasing the overall rate at which the monomers are incorporated.[19] The local symmetry about the Ru-C bond in **2-4** is postulated to account for the syndioselectivity.[14,18]



a) cis, isotactic



b) cis, syndiotactic

Figure 4. Olefinic protons in the two possible highly-cis, regular polymers made from an enantiomerically pure 2,3-disubstituted norbornadiene.

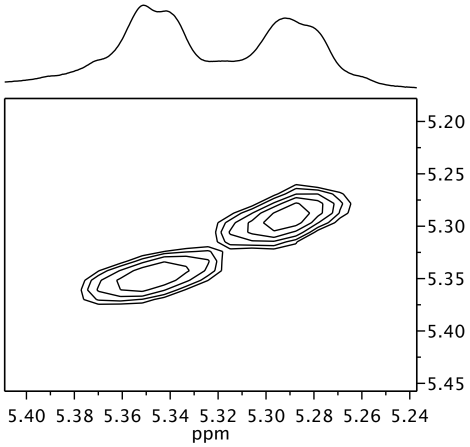


Figure 5. COSY spectrum of **poly-7** prepared with **2** in the olefinic proton region. The absence of olefinic coupling suggests that the polymer is syndiotactic.

Finally, we sought to briefly explore the physical properties of tactic ROMP polymers in comparison to their atactic counterparts via differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The T_g of atactic *trans*-polynorbornene is 37 °C.[3a] As expected, the T_g of **poly-5** was significantly higher at *ca.* 70 °C, consistent with a higher packing order due to the increased stereoregularity of the polymer. Both the atactic, trans polymer and the syndiotactic, cis **poly-5** decomposed at *ca.* 430 °C (see Supporting Information).

In spite of expectations to the contrary, we have demonstrated the ability of Ru-based metathesis catalysts to yield highly cis, highly tactic polymers. ROMP of a chiral norbornadiene monomer suggested that these polymers are syndiotactic. While it appears that the tacticity of these polymers is derived from the installation of a comparatively small, symmetric *N*-*tert*-butyl group, the exact role of these factors in the control of the tacticity of polymers produced by cyclometalated Ru-based systems remains to be determined.

ASSOCIATED CONTENT

Experimental details and characterization data for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

rhg@caltech.edu

Notes

The authors declare no competing financial interests.

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(10) While a nitrato ligand afforded increased activity, stability and selectivity to **1** compared to other X-type ligands, catalysts **2**-**4** were significantly more stable in the pivalate form than the analogous nitrato species. It is also important to note that complex **2** quickly decomposed upon exposure to terminal olefins and therefore was ineffective at mediating cross metathesis.

(11) For convenience, catalyst solutions were prepared in a glovebox. However, **2** was determined to be relatively air-stable in the solid state (minimal decomposition after exposure to air for 3 h).

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(14) The relationship between symmetry and tacticity is well-studied for early, metal-based metallocene polymerization catalysts; the stereoregularity of the resulting polymers is a direct result of the relationship of the stereoselectivities of the two active sides of a metallocene initiator (i.e., homotopic, enantiotopic, or diastereotopic). See: Odian, G. Principles of Polymerization; John Wiley & Sons, Inc., Hoboken, New Jersey, 2004.

(15) The initiation rate constants (25 °C) of catalysts **2**-**4** are 2.8×10^{-3} s^{-1} (**2**), 4.1×10^{-4} s^{-1} (**3**), and 1.1×10^{-4} s^{-1} (**4**) (see ESI for details). For comparison, the initiation rate constant of **1** is 8.4×10^{-4} s^{-1}, and >0.2 s^{-1} for RuCl$_2$(C$_5$H$_5$N)$_2$(IMesH$_2$)(CHPh), which is the preferred catalyst for ROMP. For a discussion of initiation in ruthenium metathesis catalysts, see: (a) Sanford, M. S.; Love, J. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 6543. (b) Love, J. A.; Morgan, J. P.; Trnka, T. M.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 4035.

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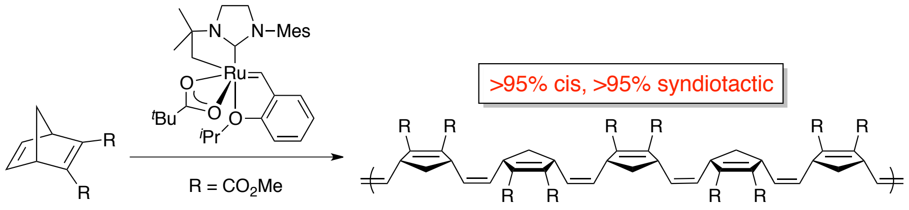
(17) The cis and trans olefinic protons of **poly-7** are clearly resolved in the ^{1}H NMR.

(18) Detailed mechanistic studies are ongoing and will be reported in due course.

(19) Indeed, catalysts **2**-**4** are generally less stable than **1**, which might also be a result of decreased steric protection (see ref. 10).


N−Mes
Ru
O
O
O
tBu
iPr
R
R
R = CO2Me
>95% cis, >95% syndiotactic