

Synthesis of Highly Cis, Syndiotactic Polymers via Ring-Opening Metathesis Polymerization Using Ruthenium Metathesis Catalysts

Lauren E. Rosebrugh, Vanessa M. Marx, Benjamin K. Keitz, and 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

S Supporting Information

ABSTRACT: The first example of ruthenium-mediated ring-opening metathesis polymerization 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 microstructures 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 resulting polymers.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 polymers (comprised of >95% a single structure) via ROMP 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 the W- and Mo-based systems, can provide control over both the cis/trans ratio and the tacticity of the polymers,^{4,5} only limited tacticity control has been achieved with ruthenium.⁷ In fact, a recent report by Schrock and co-workers highlighted the fact that because of the low barrier of rotation of Ru alkylidenes and the 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 that can form polymers exhibiting high tacticity appeared increasingly minimal.^{5b}

We recently reported 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 ROMP of norbornene and norbornadiene derivatives,^{6b} thus demonstrating for the first time cis-selective

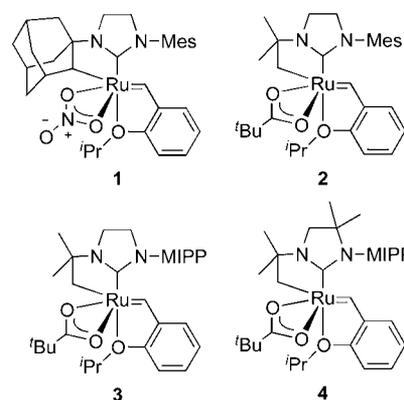


Figure 1. Structures of catalysts **1–4** (Mes = 2,4,6-trimethylphenyl; MIPP = 2-methyl-6-isopropylphenyl).

ROMP of a wide range of monomers with a single Ru-based metathesis catalyst. However, all of the polymers produced by catalyst **1** were atactic.

Herein we report the new series of cyclometalated catalysts **2–4** derived from C–H activation of an *N-tert*-butyl group. These complexes display ROMP behavior that is unprecedented for Ru-based metathesis catalysts, as they yield polymers that not only have generally higher cis contents than those obtained using **1** (>95% in many cases) but also are highly syndiotactic. This provides a further demonstration that like their W- and Mo-based counterparts, Ru-based metathesis catalysts are capable of producing polymers with a wide range of specific microstructures without the use of specialized monomers or reaction conditions.

The recent development of a milder method of effecting 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 the cyclometalation of the *N-tert*-butyl substituent as well as the bidentate coordination of the pivalate ligand and also revealed that the *N*-aryl ring is positioned in such a way that the isopropyl substituent resides on the same face as the benzylidene (Figure 2). The structural parameters, including bond lengths and

Received: June 4, 2013

Published: June 19, 2013

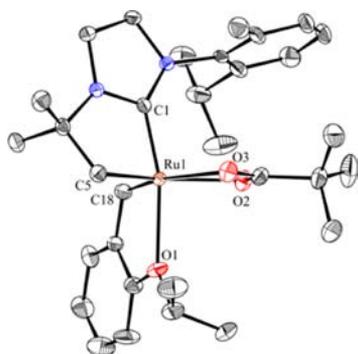


Figure 2. Solid-state structure of **3** with thermal ellipsoids drawn at 50% probability. For clarity, H atoms have been omitted. Selected bond lengths (Å) for **3**: C1–Ru, 1.932; C5–Ru, 2.071; C18–Ru, 1.798; O1–Ru, 2.334; O2–Ru, 2.202; O3–Ru, 2.398.

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	–	–
6	3	>95	54	–	–
6	4	>95	45	–	–
7	2	72	42	–	–
7	3	62	57	–	–
7	4	86	7	–	–

^aConditions: [monomer]/[initiator] = 100:1 in THF (0.25 M in substrate) at room temperature. ^bDetermined by ¹H NMR and ¹³C NMR spectroscopy. ^cIsolated yields. ^dDetermined by gel-permeation chromatography (GPC) with a multiangle light scattering detector. Dashes indicate that the values could not be determined because insolubility of the isolated polymers in THF precluded GPC analysis. ^eThe specific refractive index increment (dn/dc) was determined to be 0.139 ± 0.005 mL/g.

angles, were consistent with those for **1** and its pivalate derivative.⁸

We initiated our ROMP studies by adding **2** to a solution of norbornene (**5**) in tetrahydrofuran (THF) (0.25 M) at room temperature, upon which the solution rapidly became viscous.¹¹ ¹H NMR spectroscopy revealed that the isolated polymer was almost exclusively cis (>95%; Table 1). Furthermore, the ¹³C 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** gave atactic poly-(norbornene) that was only 88% cis.^{6b}

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 ¹³C NMR spectrum: multiple resonances correspond to an atactic polymer, such as the poly(DCMNBD) produced by **1** (Figure 3a), while a singularly tactic polymer

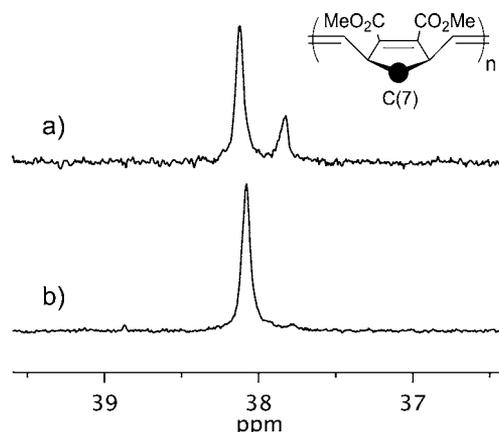


Figure 3. C(7) region of the ¹³C NMR spectra of **poly-6** prepared with (a) **1** (86% cis, atactic) and (b) **2** (>95% cis, >95% tactic).

would be expected to display only one peak in this region because of symmetry.¹³ **Poly-6** produced by catalyst **2** (>95% cis; Table 1) was found to be highly tactic, as the corresponding ¹³C 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 the symmetry of the *N*-aryl group on the tacticity,¹⁴ we evaluated catalysts **3** and **4** containing a cyclometalated *N*-*tert*-butyl group as in **2** but also 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 occur in **3**. Polymerizations of **6** with catalysts **3** and **4** gave **poly-6** that was also >95% tactic in both cases, as determined by ¹³C NMR analysis (Table 1). The **poly-5** produced by these catalysts was also highly cis (>95%) but in both cases slightly less tactic than the **poly-5** generated with **2**.

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 indicates that the propagation rate constant (k_p) of **5** exceeds the initiation rate constants (k_i) of **2**–**4**, which would lead to the broad polydispersity indexes (PDIs) observed; this is likely a result of incomplete catalyst initiation, which might be expected on the basis of the relatively low k_i of **2**–**4**.¹⁵

To elucidate the absolute tacticities of the norbornene- and norbornadiene-derived polymers, we employed chiral monomer **7**. Because of the lack of mirror planes relating the monomeric units in the resulting polymers, it was expected that if the polymers produced by **2**–**4** were cis and isotactic, the olefinic protons would be inequivalent (Figure 4a),¹⁶ and a coupling characteristic of olefinic protons would be observed 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 the Supporting Information (SI)]. Furthermore, the cis olefinic protons in

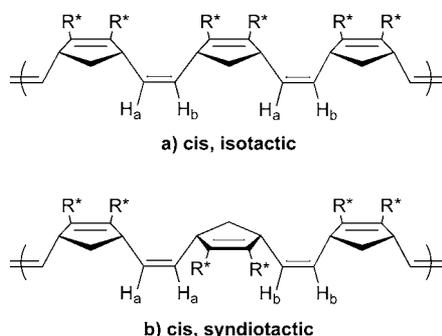


Figure 4. Olefinic protons in the two possible highly cis, regular polymers made from an enantiomerically pure 2,3-disubstituted norbornadiene.

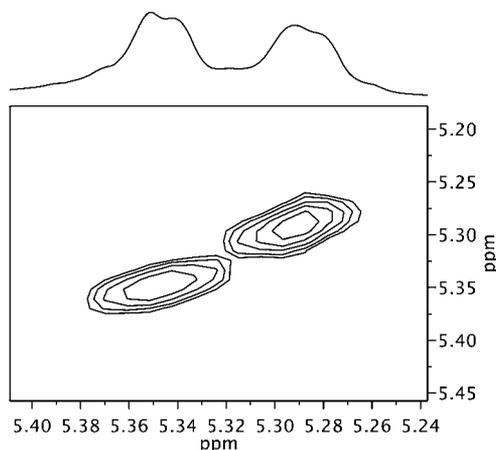


Figure 5. Olefinic proton region of the COSY spectrum of **poly-7** prepared with **2**. The absence of olefinic coupling suggests that the polymer is syndiotactic.

the isolated polymers were uncoupled,¹⁷ strongly suggesting that the obtained **poly-7** was syndiotactic in all cases (Figure 5).

One plausible explanation for the observed tacticity control is that the rate of monomer incorporation is higher than the rate of carbene epimerization.¹⁸ This is presumably in contrast to catalyst **1**, which generates atactic polymers, likely because of the low rate of propagation relative to epimerization. This distinction might be explained by the relative differences in size and symmetry of the carbon chelates 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 or norbornadiene derivative, 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}

Finally, we briefly explored the physical properties of the tactic ROMP polymers in comparison with their atactic counterparts via differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The glass-transition temperature (T_g) of atactic *trans*-poly(norbornene) 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* and syndiotactic, *cis* polymers decomposed at ca. 430 °C (see the SI).

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 were syndiotactic. While it appears that the tacticity of these polymers is derived from the installation of a comparatively small and symmetric *N*-*tert*-butyl group, the exact roles of these factors in the control of the tacticity of the polymers produced by cyclometalated Ru-based systems remain to be determined.

■ ASSOCIATED CONTENT

📄 Supporting Information

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 interest.

■ ACKNOWLEDGMENTS

We thank Mr. Zachary Wickens for helpful discussions. This work was financially supported by the NIH (R01-GM031332), the NSF (CHE-1212767), and the NSERC of Canada (fellowship to V.M.M.). Instrumentation on which this work was carried out was supported by the NIH (NMR spectrometer, RR027690).

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(10) While a nitrate ligand afforded increased activity, stability, and selectivity to **1** compared with other X-type ligands, catalysts **2–4** were significantly more stable in the pivalate form than the analogous nitrate 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 has been well-studied for early, metal-based metallocene polymerization catalysts; the stereoregularity of the resulting polymers is a direct result of the relationship between the stereoselectivities of the two active sites of the metallocene initiator (i.e., homotopic, enantiotopic, or diastereotopic). See: Odian, G. *Principles of Polymerization*; Wiley: Hoboken, NJ, 2004.

(15) The initiation rate constants of catalysts **2–4** at 25 °C are $k_i = 2.8 \times 10^{-3}$, 4.1×10^{-4} , and $1.1 \times 10^{-4} \text{ s}^{-1}$, respectively (see the SI for details). For comparison, $k_i = 8.4 \times 10^{-4} \text{ s}^{-1}$ for **1** and $k_i > 0.2 \text{ s}^{-1}$ for $\text{RuCl}_2(\text{C}_3\text{H}_5\text{N})_2(\text{IMesH}_2)(\text{CHPh})$, 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** were clearly resolved in the ^1H NMR spectrum.

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

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