JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

COMMUNICATION

pubs.acs.org/JACS

Synthesis of *cis,syndiotactic* ROMP Polymers Containing Alternating Enantiomers

Margaret M. Flook, Victor W. L. Ng, and Richard R. Schrock*

Department of Chemistry 6-331, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Supporting Information

ABSTRACT: Ring-opening metathesis polymerization (ROMP) of *rac-endo,exo*-5,6-dicarbomethoxynorbornene (inter alia) yields a *cis,syndio,alt*-polymer, one in which the sequential units in the *cis,syndiotactic* polymer consist of alternating enantiomers. Cis selectivity arises through addition of the monomer to produce an all-*cis*-metallacyclobutane intermediate, while syndioselectivity and alternating enantiomer structures arise as a consequence of inversion of configuration at the metal center with each metathesis step.

A polymer that has a single microstructure often is more desirable since its properties are more sharply defined relative to those of a polymer with a random structure. Ring-opening metathesis polymerized (ROMP)[1] polymers prepared from substituted norbornenes and norbornadienes have rich microstructural possibilities. For several decades the structures of ROMP polymers prepared with classical metathesis catalysts have been studied in detail employing NMR techniques (primarily ^{13}C NMR).[1,2] However, few polymers with primarily a single structure have been found. A possible reason is that a classical catalyst's structure cannot be varied finely and systematically enough in order to produce a "match" between a catalyst and monomer that allows a single polymerization pathway to dominate and produce a polymer with a given single structure. This conundrum seems inescapable with classical catalysts.

The development of alkylidene complexes of Mo and W[3] with known structures and modes of reaction have allowed an increasing number of ROMP polymers to be prepared that have a single microstructure.[4] We recently reported the *Z*-selective and syndioselective polymerization of several ROMP monomers by monoaryloxide monopyrrolide (MAP) imido alkylidene catalysts of Mo to yield *cis,syndiotactic* polymers.[4c,4d] *Z* selectivity is proposed to arise through an addition of the monomer to *syn*-Mo(NAd)(CHCMe$_2$Ph)(Pyr)(OHIPT) (**1a**) to produce an all-*cis*-metallacyclobutane as a consequence of the steric demands of the OHIPT ligand. Syndio selectivity is proposed to arise as a consequence of addition of the monomer selectively trans to the pyrrolide and inversion of configuration at the metal center with each metathesis step.[5] It occurred to us that if syndiotacticity is controlled primarily as a consequence of the inherent chirality at the metal, and the monomer in question is chiral and racemic, then enantiomers of that monomer should be selected in a perfectly alternating fashion. In this paper we demonstrate that this approach can lead to polymers that have a *cis,syndiotactic* structure and an alternating enantiomer sequence in the polymer chain.

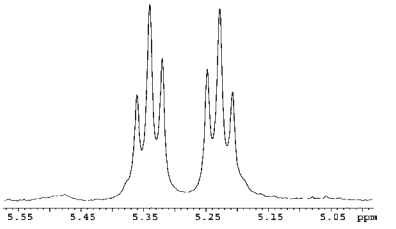
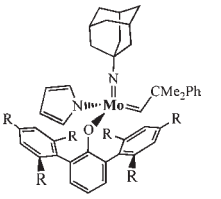


Figure 1. Olefinic region of ^{1}H NMR spectrum of *cis,syndio,alt*-poly-(*rac*-DCMNBE) formed with **1b** ($CDCl_3$, 500 MHz).



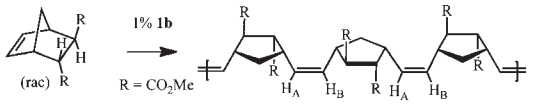
R = i-Pr (**1a**) or Me (**1b**)

We chose first to examine *endo,exo*-5,6-dicarbomethoxynorbornene (DCMNBE), a ROMP monomer that is prepared and resolved readily.[4b] Addition of 100 equiv of *rac*-DCMNBE to *syn*-Mo(NAd)(CHCMe$_2$Ph)(Pyr)(OHMT) (**1b**) proceeded at an acceptable rate (100 equiv over a period of 1 h in toluene). Only two pseudotriplet olefinic proton resonances are present in the proton NMR spectrum of the resulting highly regular polymer (Figure 1), consistent with a structure in which two inequivalent protons (H_A and H_B, eq 1) are on one double bond and coupled to one another with a J_{HH} value typical of *cis* J_{HH} couplings (~11 Hz), as confirmed through a proton/proton COSY spectrum (Figure S3 in Supporting Information). The ^{13}C NMR spectrum (at 125 mHz) is also sharp and free of any significant fine structure associated with structural irregularities (see Figure S2 in Supporting Information). These results are consistent with a basic *cis,syndiotactic* structure in which the repeat units in the polymer chain are enantiomers of one another (eq 1). We will call this a *cis,syndio,alt* structure (*alt* for alternating). We ascribe the weak resonance at 5.47 ppm in the ^{1}H NMR spectrum of the polymer displayed in Figure 1 to the presence of a small fraction of *trans* double bonds. If the 5.47 ppm

Received: December 6, 2010
Published: January 25, 2011

dx.doi.org/10.1021/ja110949f | *J. Am. Chem. Soc.* 2011, 133, 1784–1786

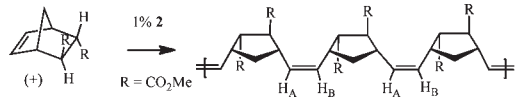
resonance is ascribed to one proton, then this microstructural error comprises <5% of the *cis,syndio,alt* structure.



(1)

A *cis,syndiotactic* structure made from a single enantiomer (*cis, syndio,sing*) could be formed from *rac*-DCMNBE either through perfect kinetic resolution (with a maximum yield of 50% of the polymer) or through formation of a perfect diblock copolymer that contains *cis,syndio,sing* blocks constructed from the two enantiomers. In either case, any extended *cis,syndio,sing* structure would contain uncoupled protons on different C=C bonds as a consequence of a local C_2 axis that passes through each C=C bond. Therefore, these possibilities can be discarded. An attempt to prepare *cis,syndio,sing*-polyDCMNBE through polymerization of enantiomerically pure (+)-DCMNBE with **1b** led only to a polymer with no long-range structure. This result could have been anticipated since two different types of propagation steps would be required to polymerize (+)-DCMNBE with **1b**, and it is unlikely that both types of propagation steps would yield the same result that is found in a single type of propagation step in the reaction between **1b** and *rac*-DCMNBE.

Formation of *cis,isotactic* ROMP structures are possible through enantiomeric site control.[4a,4b,6] Addition of enantiomerically pure (+)-DCMNBE to Mo(NAr)(CHCMe$_2$Ph)(*rac*-3,3′-di-*tert*-butyl-5,5′-bis-trifluoromethyl-6,6′-dimethyl-1,1′-biphenyl-2,2′-diolate)[6a] (**2**; Ar = 2,6-Me$_2$C$_6$H$_3$) produces an all-*cis* polymer with a single structure that contains two inequivalent coupled olefinic protons, but both proton and carbon NMR spectra of this polymer (eq 2) are distinct from those of *cis,iso, alt*-polyDCMNBE prepared employing **1b** (see Figure S4 in Supporting Information). All data are consistent with this polymer being *cis,iso,sing*-polyDCMNBE (eq 2). As expected, polymerization of *rac*-DCMNBE with **2** yields a polymer with no long-range order since two different types of propagation steps again would have to give the same structural result.



(2)

We then turned to polymerization of *endo,exo*-5,6-dicyanonorbornene (DCNNBE). When 100 equiv of *rac*-DCNNBE was added to **1b** in dichloromethane, the reaction mixture immediately became thick and cloudy. A ^{1}H NMR spectrum showed that the monomer was completely consumed within one hour. The resulting white solid polymer is essentially insoluble in $CDCl_3$, CD_2Cl_2, or toluene-d_8 and has limited solubility in acetone-d_6. However, a ^{1}H spectrum of sufficient quality could be obtained in acetone-d_6 at 50 °C. The olefinic region of the ^{1}H NMR spectrum of polyDCNNBE (Figure 2) displays two pseudotriplet resonances, suggesting that this polymer exhibits a highly regular *cis,syndio,alt* structure. The limited solubility of this polymer precluded obtaining its ^{13}C NMR spectrum. However, on the basis of the ^{1}H NMR data alone, it is apparent that the *cis,syndio,alt* selectivity also is realized for DCNNBE polymerized by **1b**.

Racemic 1-methyl-5,6-dicarbomethoxy-7-oxanorbornadiene is polymerized by **1b** (1%) to give a polymer (eq 3) whose

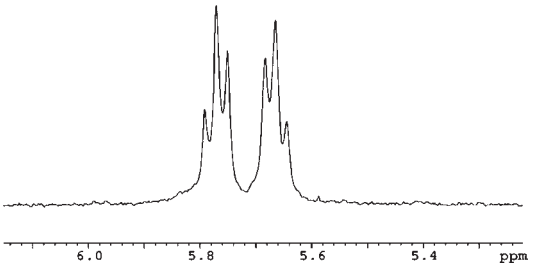
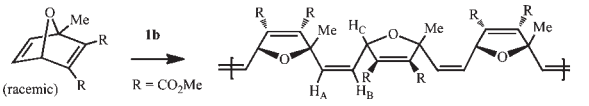


Figure 2. ^{1}H NMR spectrum of *cis,syndio,alt*-polyDCNNBE formed with **1b** (acetone-d_6, 500 MHz, 50 °C).

proton and carbon NMR spectra are consistent with a *cis,syndio, alt* structure. In the proton NMR spectrum the resonances for H_A (d), H_B (~t), and H_C (d) are all clearly visible with J_{AB} = 11.5 Hz and J_{BC} = 9.5 Hz. We estimate that the polymer has >95% of the *cis,syndio,alt* structure. The assignments have been proven through proton/carbon HSQC 2D-NMR (Figure S7 in Supporting Information). Polymerization of 1-methyl-5,6-dicarbomethoxy-7-oxanorbornadiene with **1b** confirms that *cis,syndio,alt*-polymers can be formed from monomers that are dramatically different from *endo,exo*-5,6-disubstituted monomers described above.



(3)

Polymerization of DCMNBE with **1a** in toluene is exceedingly slow; only ~50% of the expected poly-DCMNBE was formed in 72 h at room temperature. NMR studies show that this poly-DCMNBE has no long-range regular structure. We propose that the rate and selectivity of this polymerization suffer from steric overcrowding. Similarly, attempted polymerization of 1-methyl-5,6-dicarbomethoxy-7-oxanorbornadiene by **1a** also led to a polymer with no regular structure. At the same time, attempted polymerization of *rac-endo,exo*-5,6-dimethylnorbornene, *rac*-1-methylnorbornene, and *rac-endo,exo*-5,6-dimethoxymethylnorbornene with **1b** did not yield polymers with a highly regular structure. It is proposed that these three catalyst/monomer combinations do not provide *enough* steric crowding to result in formation of a polymer with a single structure. Clearly a suitable "match" between the catalyst and the monomer is required. The ability to adjust the sterics of the catalyst (and/or monomer) finely gives us hope that suitable catalysts can be found among the many molybdenum and tungsten MAP possibilities that are now available for polymerization of a variety of monomers.

We conclude that *cis,syndio,alt* structures are formed through a combination of *Z*-selective and stereogenic metal control when the metal's configuration inverts with each insertion of monomer. To the best of our knowledge there is only one example of a polymer containing alternating enantiomers in the literature; it is a polymer prepared through ROMP of *rac*-1-methylnorbornene with $ReCl_5$;[2a,2e] precisely how the structure arises is not known. However, in a prescient statement the authors proposed that "the inherent chirality of the metal centre seems to be of paramount importance in controlling tacticity [...] with little or no influence by chirality in the permanent ligands or in the polymer chain ends."[2c]

It should be noted that virtually no polymers with any single microstructure have been prepared with Ru catalysts.[7,8] One

dx.doi.org/10.1021/ja110949f |*J. Am. Chem. Soc.* 2011, 133, 1784–1786

possibility is that not enough variations have been explored. However, the problem may be of a more fundamental nature; the carbene simply rotates too readily about the Ru=C bond when the steric hindrance that is required in order to form a specific structure is significant. This problem was noted by Rooney and co-workers in studies involving classical Ru and Os catalysts; "The intrinsic activity of the [Ru]=CHP moiety seems to be too low to withstand in general the adverse factor of steric compression, unlike the analogous [Os]=CHP propagating species."[2c] The barrier to rotation of the carbene in a generic NHC dichloride Ru catalyst has now been calculated to be only a few kcal/mol at best.[9] The presence of *syn*- and *anti*-isomers of Mo or W catalysts, and their high reactivity in general, make possible the results reported here. It seems increasingly unlikely that an equivalent circumstance will be found in Ru catalyst systems.

■ ASSOCIATED CONTENT

Supporting Information. Experimental details for all reactions and supporting NMR data for polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
rrs@mit.edu

■ ACKNOWLEDGMENT

We are grateful to the Department of Energy (DE-FG02-86ER13564) and the U.S. Army (Institute for Soldier Nanotechnology, under Contract DAAD-19-02-D-0002 with the U.S. Army Research Office) for research support. V.W.L.N. also thanks the Agency for Science, Technology and Research (Singapore) for an A*STAR International Fellowship and J. Simpson for assistance with 2D NMR experiments.

■ REFERENCES

(1) Ivin, K.J.; Mol, J.C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, 1997.

(2) (a) Hamilton, J. G.; Ivin, K. J.; Rooney, J. J. *Br. Polym. J.* **1984**, *16*, 21. (b) Hamilton, J. G. *Polymer* **1998**, *39*, 1669. (c) Amir-Ebrahimi, V.; Hamilton, J. G.; Rooney, J. J. *NATO Sci. Ser., II* **2002**, *56*, 45. (d) Amir-Ebrahimi, V.; Corry, D. A. K.; Hamilton, J. G.; Rooney, J. J. *J. Mol. Catal. A: Chem.* **1998**, *133*, 115. (e) Hamilton, J. G.; Ivin, K. J.; Rooney, J. J.; Waring, L. C. *J. Chem. Soc., Chem. Commun.* **1983**, 159.

(3) (a) Schrock, R. R. *Chem. Rev.* **2002**, *102*, 145. (b) Schrock, R. R. *Chem. Rev.* **2009**, *109*, 3211–3226.

(4) (a) McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413. (b) O'Dell, R.; McConville, D. H.; Hofmeister, G. E.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 3414. (c) Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7962. (d) Flook, M. M.; Gerber, L. C. H.; Debelouchina, G. T.; Schrock, R. R. *Macromolecules* **2010**, *43*, 7515.

(5) (a) Sattely, E. S.; Meek, S. J.; Malcolmson, S. J.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 943. (b) Schrock, R. R.; King, A. J.; Marinescu, S. C.; Simpson, J. H.; Müller, P. *Organometallics* **2010**, *29*, 5241.

(6) (a) Singh, R.; Czekelius, C.; Schrock, R. R.; Müller, P. *Organometallics* **2007**, *26*, 2528. (b) Singh, R.; Schrock, R. R. *Macromolecules* **2008**, *41*, 2990.

(7) (a) Grubbs, R. H., Ed. *Handbook of Metathesis*; Wiley-VCH: Weinheim, 2003; Vols. 1−3.(b) Vougioukalakis, G. C.; Grubbs, R. H. *Chem. Rev.* **2010**, *110*, 1746. (c) Buchmeiser, M. R. *Chem. Rev.* **2000**, *100*, 1565. (b) Bielawski, C. W.; Grubbs, R. H. *Prog. Polym. Sci.* **2007**, *32*, 1. (c) Smith, D.; Pentzer, E. B.; Nguyen, S. T. *Polym. Rev.* **2007**, *47*, 419.

(8) (a) Lee, J. C.; Parker, K. A.; Sampson, N. S. *J. Am. Chem. Soc.* **2006**, *128*, 4578. (b) Yang, H.-C.; Lin, S.-Y.; Yang, H.-C.; Lin, C.-L.; Tsai, L.; Huang, S.-L.; Chen, I. W.-P.; Chen, C.-H.; Jin, B.-Y.; Luh, T.-Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 726. (c) Chou, C.-M.; Lee, S.-L.; Chen, C.-H.; Biju, A. T.; Wang, H.-W.; Wu, Y.-L.; Zhang, K.-W.; Lim, T.-S.; Huang, M.-J.; Tsai, P.-Y.; Lin, K.-C.; Huang, S.-L.; Chen, C.-H.; Luh, T.-Y. *J. Am. Chem. Soc.* **2009**, *131*, 12579.

(9) Straub, B. F. *Adv. Synth. Catal.* **2007**, *349*, 204.