Cis, Isotactic Selective ROMP of Norbornenes Fused with N-Arylpyrrolidines. Double Stranded Polynorbornene-Based Ladderphanes with Z-Double Bonds

The MIT Faculty has made this article openly available. Please share how this access benefits you. Your story matters.

| Citation       | Zhu, Lei, Margaret M. Flook, Shern-Long Lee, Li-Wei Chan, Shou-Ling Huang, Ching-Wen Chiu, Chun-Hsien Chen, Richard R. Schrock, and Tien-Yau Luh. “Cis, Isotactic Selective ROMP of Norbornenes Fused with N-Arylpyrrolidines. Double Stranded Polynorbornene-Based Ladderphanes with Z-Double Bonds.” Macromolecules 45, no. 20 (October 23, 2012): 8166-8171. |
|----------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| As Published   | http://dx.doi.org/10.1021/ma301686f                                                                                                                                                               |
| Publisher      | American Chemical Society (ACS)                                                                                                                                                                 |
| Version        | Author’s final manuscript                                                                                                                                                                       |
| Citable link   | http://hdl.handle.net/1721.1/84538                                                                                                                                                              |
| Terms of Use   | Article is made available in accordance with the publisher’s policy and may be subject to US copyright law. Please refer to the publisher’s site for terms of use.                                            |
There is an ever burgeoning interest in the stereoselective formation of double bonds by olefin metathesis. Various catalysts have recently been developed for Z-selectivity in homocoupling, cross metathesis (CM), ring closing metathesis (RCM), and ring opening metathesis polymerization (ROMP). The involvement of a bulky or a chelated ligand is crucial to direct the orientation of the incoming olefin that may lead to the stereoselective formation of a metallacyclobutane intermediate. Alkyne metathesis followed by partial hydrogenation offers an alternative route for the synthesis of Z-olefins. The nature of olefin substrates may also control the stereochemistry of double bonds in olefin metathesis. For example, the presence of a bulky 2-silyl substituent in terminal olefins furnishes exclusively E-silyl-substituted cycloalkenes which are converted to the corresponding Z-alkenes by desilylation. Certain cycloalkenes also undergo ROMP stereoselectively under various conditions. Thus, norbornadiene derivatives give cis, syndiotactic ROMP polymer upon treatment with a Mo-catalyst. Similar reaction with
racemic endo,exo-5,6-dicarbomethoxynorbornene 4 yields predominantly the corresponding polynorbornene with cis,syndio,alt selectivity.\textsuperscript{5c} The key to the success relies on the steric differentiation between small imido and bulky aryloxide ligands resulting all substituents on the metallacyclobutane intermediate to have a \textit{syn} relationship. The inversion of metal configuration in each insertion of the monomeric norbornene derivative during the course of polymerization would be responsible for the syndiotactic selectivity (eq 1). A chelated ruthenium catalyst 7 has recently been disclosed to show cis-selectivity in ROMP of norbornene derivatives.\textsuperscript{5d}

\begin{align*}
\text{ROMPs of norbornenes fused with endo-N-arylpyrrolidine 9 with the first generation Grubbs catalyst 8 yield polynorbornene 10 with isotactic stereochemistry and trans}
\end{align*}
double bonds. This protocol has been employed for the synthesis of a series of double stranded ladderphanes 11. It is noteworthy that the presence of the N-aryl pendant in 9 is indispensable in these transformations. Unlike 1 and 4, the endo site of the norbornene moiety in 9 is highly crowded. It is envisaged that, upon treatment with a Mo catalyst like 3, the mode of interactions between 9 and the molybdenum catalyst could be very different from those shown in eq 1.5a-c In particular, when bulky bidentate substituted biaryl-o,o’-diphenoxide ligand is used,12 the front side of the catalyst 12 would be blocked by the biaryl ligand. Accordingly, the double bond of 9 would interact with molybdenum–carbene moiety from the backside. In order to avoid steric interaction between the endo-pyrrolidine group and the imido ligand as in 14, the orientation of the incoming norbornene moiety 9 would preferentially interact with intermediate 13 via a transition state 15. Polynorbornene 16 thus obtained may adopt a cis, isotactic stereochemistry. Indeed, when enantiomerically pure 4 is treated with 3, that a mixture of the corresponding cis,syndio,alt- and cis,iso,sing-polynorbornenes is obtained can be understood within the framework of the steric interactions between the endo-carbomethoxy substituent and ligands in 3.5c The steric hindrance around the endo site in 9 would be much larger than that in 4. It is therefore felt that a much better cis, isotactic selectivity would be obtained upon treatment with an appropriate molybdenum-carbene catalyst.

We now wish to report the first cis, isotactic- polynorbornenes from the reactions of 9 and related bisnorbornenes 18 and 20 with 12.
Treatment of 9 with 12a in DCM at rt for 2 h followed by quenching with PhCHO afforded 16a in 68% yield and the results are summarized in Table 1. Similar result was obtained from the reaction of 9 with 12b. The $^{13}$C NMR spectrum of 16a shows four single peaks at δ 39.2, 40.4, 47.5, and 49.4 attributed to the ring carbons of the
azabicyclooctane skeletons for each of the monomeric unit. These results suggest that there is a symmetry plane between adjacent monomeric units in 16a and the double bonds should therefore be in cis configuration. This pattern is completely different from those of 10a having trans double bonds and isotactic structure, which exhibits essentially two sets of $^{13}$C signals in the high field region because of the lack of the symmetric plane between adjacent monomeric units. The same hydrogenated product 17 obtained from the diimide reductions of 16a and of 10a indicates that both 16 and 10 should have same isotactic stereochemistry.

Polynorbornene-based double-stranded and triple stranded ladderphanes have recently been disclosed by 8-catalyzed ROMP of the corresponding bis- and tris-norbornene monomers. One of the most important criteria for the successful synthesis of these ladderphanes relies on the stereoselective formation of single stranded polynorbornenes. It is therefore believed that the molybdenum-catalyzed stereoselective synthesis of cis, isotactic-16 mentioned above has paved the way for the access of ladderphanes with Z-double bonds. Thus, reaction of 18 with a catalytic amount of 12a in DCM afforded ladderphane 19 in 50% yield. The $^{13}$C
Table 1. Gel permeation chromatography results of polymers.

| Polymer | $M_n$   | $M_w$   | PDI | $n^a$ |
|---------|---------|---------|-----|-------|
| 16a     | 55,300  | 69,600  | 1.3 | 195   |
| 17      | 55,600  | 69,000  | 1.2 | 195   |
| 19      | 11,500  | 14,600  | 1.3 | 16    |
| 16b     | 4,500   | 5,500   | 1.2 | 16    |
| 21      | 14,900  | 17,200  | 1.2 | 24    |
| 16c     | 7,100   | 8,400   | 1.2 | 25    |
| 22      | 12,800  | 16,900  | 1.3 | 18    |
| 10b     | 5,700   | 7,000   | 1.2 | 20    |
| 23      | 9,600   | 11,200  | 1.2 | 16    |
| 10c     | 4,700   | 5,800   | 1.2 | 17    |

$^a$Degree of polymerization.

NMR spectrum of 19 shows characteristic signals at $\delta$ 38.8, 40.6, 40.9, and 46.5 attributed to the carbons of the azabicyclooctane moieties with two double bond substituents in cis configuration. Ethanolysis of 19 with NaOEt gave 86% yield of 16b. In a similar manner, ladderphane 21 was obtained in 56% yield from the 12a-catalyzed ROMP of 20. Again, 21 was transformed into 16c by ethanolysis with NaOEt. Similar degree of polymerization for 19 and 16b and for 21 and 16c further support the double stranded nature of 19 and 21. The corresponding ladderphanes 22 and 23 with all trans double bonds were prepared from 18 and 20 by 8-catalyzed ROMPs for comparison. Ethanolysis of 22 and 23 gave 10b and 10c, respectively having trans, isotactic stereochemistry.
It is known that polynorbornene-based double stranded ladderphanes 11 with trans double bonds can form a two-dimensional well-oriented array on highly ordered pyrolytic graphite surface (HOPG) as revealed by scanning tunneling microscopy (STM).\textsuperscript{11,13} Stacking interaction between styrene and vinyl end groups along the longitudinal axis of the polymer and van der Waals interaction between polymeric backbones in the second dimension may be responsible for such ordered pattern.\textsuperscript{13} Polymers 19 and 21 have similar end groups (styrene and substituted vinyl). It is therefore envisaged that a similar aggregate may also be formed from these ladderphanes with all cis double bonds. Indeed, the STM image of 19 shown in Figure 1 exhibits a nice two-dimensional array. The relatively bright and dark features of the lamellae are ascribed, respectively, to the aromatics and norbornyl moieties based on their tunneling efficiency. High resolution images (Figure 1b) show the nominal width of $\sim 2.5$ nm and the spacing of 0.5–0.6 nm between linkers, consistent with the corresponding dimensions of 19. The stability of the assembly
for 19 appears inferior to that of its trans analogue 22. After being subjected to STM scanning, the former becomes disordered after a couple of imaging frames while the latter is unaffected. The observation suggests weaker interactions of the cis polymer 19 with the substrate and between the terminal groups.

Figure 1. STM images of 19 exhibiting submicron, long-range order array. Image size: (a) 80x80 nm (b) 8x8 nm. Imaging conditions of $E_{\text{bias}}$ and $I_{\text{tunneling}}$: (a) 0.90 V, 50 pA, (b) 0.90 V, 90 pA. Sample preparation: dropcasting 10-•L 19-containing phenyloctane on HOPG and subsequently being shear-aligned by removal excess solvent with a piece of tissue.

In summary, we have described the first synthesis of cis, isotactic polynorbornenes stereoselectively using a molybdenum-carbene catalyst. The presence of endo-fused N-arylpyrrolidine moiety in monomeric norbornenes may play a pivotal role to direct the stereoselectivity of the ROMP of these norbornenes catalyzed by 12. The present results using molybdenum catalyst 12 complement the previous works employing ruthenium catalyst 8 on the ROMP of polynorbornenes fused with endo-N-arylpyrrolidine monomers. It is worth noting that morphology of ladderphanes with Z double bonds (e.g. 19 and 21) on HOPG behave similarly to those with E double bonds.

1. For reviews, see: (a) Cordova, A.; Rios, R. Angew. Chem. Int. Ed. 2009, 48, 8827-8831. (b) Schrock, R. R. Dalton Trans 2011, 40, 7484-7495. (c)
Gottumukkala, A. L.; Madduri, A. V. R.; Minnaard, A. J. ChemCatChem 2012, 4, 462-467.

2. (a) Jiang, A. J.; Zhao, Y.; Schrock, R. R.; Hoveyda, A. H. J. Am. Chem. Soc. 2009, 131, 16630-16631. (b) Peryshkov, D. V.; Schrock, R. R.; Takase, M. K.; Müller, P.; Hoveyda, A. H. J. Am. Chem. Soc. 2011, 133, 20754-20757. (c) Marinescu, S. C.; Schrock, R. R.; Müller, P.; Takase, M. K.; Hoveyda, A. H. Organometallics 2011, 30, 1780-1782. (d) Keitz, B. K.; Endo, K.; Herbert, M. B.; Grubbs, R. H. J. Am. Chem. Soc. 2011, 133, 9686-9688.

3. (a) Ibrahem, I; Yu, M.; Schrock, R. R.; Hoveyda, A. H. J. Am. Chem. Soc. 2009, 131, 3844-3845. (b) Endo K.; Grubbs, R. H. J. Am. Chem. Soc. 2011, 133, 8325-8327. (c) Banchet-Cadeddu, A.; Henon, E.; Dauchez, M.; Renault, J.-H.; Monneaux, F.; Haudrechy, A. Org. Biomol. Chem. 2011, 9, 3080-3104.

4. (a) Malcolmson, S. J.; Meek, S. J.; Sattely, E. S.; Schrock, R. R.; Hoveyda, A. H. Nature 2008, 456, 933-937. (b) Sattely, E. S.; Meek, S. J.; Malcolmson, S. J.; Schrock, R. R.; Hoveyda, A. H. J. Am. Chem. Soc. 2009, 131, 943-953. (c) Yu, M.; Wang, C.; Kyle, A. F.; Jakubec, P.; Dixon, D. J.; Schrock, R. R.; Hoveyda, A. H. Nature 2011, 479, 88-93.

5. (a) Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Muller, P.; Hoveyda, A. H. J. Am. Chem. Soc. 2009, 131, 7962-7963 (b) Flook, M. M.; Gerber, L. C. H.; Debelouchina, G. T.; Schrock, R. R. Macromolecules 2010, 43, 7515-7522. (c) Flook, M. M.; Ng, V. W. L.; Schrock, R. R. J. Am. Chem. Soc. 2012, 134, 1784-1786. (d) Keitz, B. K.; Fedorov, A.; Grubbs, R. H. J. Am. Chem. Soc. 2012, 134, 2040-2043.

6. Liu, P.; Xu, X.; Dong, X.; Keitz, B. K.; Herbert, M. B.; Grubbs, R. H.; Houk, K. N. J. Am. Chem. Soc. 2012, 134, 1464-1467.

7. For reviews, see: (a) Fürstner, A.; Davies, P. W. Chem. Commun. 2005, 18, 2307-2320. (b) Davies, P. W. In Metathesis in Natural Product Synthesis; Cossy, J.; Arseniyadis, S.; Meyer, C. Eds., 2010, Wiley-VCH; pp. 205-223. (c) Davies, P. W. In Handbook of Cyclization Reactions; Ma, S. Ed., 2010, Wiley-VCH; Vol 1, 599-623.
8. (a) Wang, Y.; Jimenez, M.; Hansen, A. S.; Raiber, E.-A.; Schreiber, S. L.; Young, D. W. *J. Am. Chem. Soc.* **2011**, *133*, 9196-9199.  
(b) Gallenkamp, D.; Fürstner, *A. J. Am. Chem. Soc.* **2011**, *133*, 9232-9235.

9. (a) Lin, W.-Y.; Murugesh, M. G.; Sudhakar, S.; Yang, H.-C.; Tai, H.-C.; Chang, C.-S.; Liu, Y.-H.; Wang, Y.; Chen, I-W. P.; Chen, C.-h.; Luh, T.-Y. *Chem. Eur. J.* **2006**, *12*, 726-730.  
(b) Lin, W.-Y.; Wang, H.-W.; Liu, Z.-C.; Xu, J.; Chen, C.-W.; Yang, Y.-C.; Huang, S.-L.; Yang, H.-C.; Luh, T.-Y. *Chem. Asian J.* **2007**, *2*, 764-774.

10. Lee, J. C.; Parker, K. A.; Sampson, N. S. *J. Am. Chem. Soc.* **2006**, *128*, 4578-4579.

11. (a) 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*, 726-730.  
(b) Lin, N.-T.; Lin, S.-Y.; Lee, S.-L.; Chen, C.-h.; Hsu, C.-H.; Hwang, L.-P.; Xie, Z.-Y.; Chen, C.-H.; Huang, S.-L.; Luh, T.-Y. *Angew. Chem. Int. Ed.* **2007**, *46*, 4481-4485.  
(c) Yang, H.-C.; Lee, S.-L.; Chen, C.-h. Lin, N.-T.; Yang, H.-C.; Jin, B.-Y.; Luh, T.-Y. *Chem. Commun.* **2008**, 6158-6160.  
(d) Chou, C.-M.; Lee, S.-L.; Chen, C.-H.; Biju, A. T.; Wang, H.-W.; Wu, Y.-L.; Zhang, G.-F.; Yang, 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*, 12579-12585.  
(e) Yang, K.-W.; Xu, J.; Chen, C.-H.; Huang, H.-H.; Yu, T. J.-Y.; Lim, T.-S.; Chen, C.-h.; Luh, T.-Y. *Macromolecules* **2010**, *43*, 5188-5194.  
(f) Chen, C.-W.; Chang, H.-Y.; Lee, S. L.; Hsu, I-J.; Lee, J.-J.; Chen, C.-h.; Luh, T.-Y. *Macromolecules* **2010**, *43*, 8741-8746.  
(g) Wang, H.-W.; Chen, C.-H.; Lim T.-S.; Huang S.-L.; Luh, T.-Y. *Chem. Asian J.* **2011**, *6*, 524-533.  
(h) Huang, H.-H.; Chao, C.-G.; Lee, S.-L.; Wu, H.-J.; Chen, C.-h.; Luh, T.-Y. *Org. Biomol. Chem.* **2012**, 0000.

12. Singh, R.; Czekelius, C.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *Organometallics* **2007**, *26*, 2528-2539.

13. Lee, S.-L.; Lin, N.-T.; Liao, W.-C.; Chen, C.-h.; Yang, H.-C.; Luh, T.-Y. *Chem. Eur. J.* **2009**, *15*, 11594-11600.

14. Lee, S.-L.; Chi, C.-Y. J.; Huang, M.-J.; Chen, C.-h.; Li, C.-W.; Pati, K.; Liu, R.-S. *J. Am. Chem. Soc.* **2008**, *130*, 10454-10455.
