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Synthesis of Cis,syndiotactic-A-alt-B Copolymers from Enantiomerically Pure Endo-2-Substituted-5,6-Norbornenes

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ABSTRACT: Cis,syndiotactic A-alt-B copolymers, where A and B are two enantiomerically pure endo-2-substituted-5,6-norbornenes with "opposite" chiralities of the endo-2-substituted-5,6-norbornene skeleton, can be prepared using Mo(N=2,6-Me2C6H3)(CHCMe2Ph)(OHMT)(pyrrolide) (I) as the initiator (OHMT = O-2,6-MesitylC6H3). Formation of a high percentage of A-alt-B dyads is proposed to rely on an inversion of chirality at the metal with each propagating step and a kinetically preferred diastereomeric relationship between a given chirality at the metal in propagating species and the chirality of the endo-2-substituted-5,6-norbornene skeleton. We also demonstrate that A-alt-B copolymers can be modified to give new variations which may not be accessible through direct copolymerization.

Copolymers in which monomers A and B are incorporated in an alternating manner, poly(A-alt-B), are rare.1 A significant number of AB copolymers have been formed through ring-opening metathesis polymerization (ROMP),2 although in the vast majority of cases the polymers do not have pure A-alt-B structures, and the stereochimistries (cis vs. trans, and tacticity) are not fixed. In 2011 we reported3a that polymerization of a rac-2,3-disubstituted-5,6-norbornene yields a polymer with a cis,syndiotactic basic structure3,4 in which the two enantiomers of the monomer are incorporated alternately to give poly(A-alt-A*), a special type of copolymer in which A and A* are enantiomers. The most successful of the initiators we tried was rac-1, a member of the MAP (MonoAryloxidePyrrolide) family in which the metal is a stereogenic center.5 A polymerization that gives cis linkages is attributed to restricted formation of any trans metallacyclobutane intermediate as a consequence of the presence of the large terphenoxide ligand. Important requirements for forming poly(A-alt-A*) are (i) an inversion of the chirality at the metal6 with each insertion and (ii) a preference for formation of one diastereomeric intermediate in each step of the "cross-polymerization" (A/A*) step. To our knowledge the only other ROMP that gives a stereoregular cis,syndiotactic-A-alt-A* copolymer was reported by Hamilton and coworkers,7 who deduced that inversion of configuration of the metal site in a heterogeneous catalyst was required for formation of cis,syndiotactic-poly(A-alt-A*) from rac-1-methylbicyclo[2.2.1]hept-2-ene.

We have shown recently that two monomers that have the same 2,3-disubstituted-5,6-norborne "chiral motif," but slightly different R and R' substituents in each monomer (eq 1) can be polymerized through ROMP initiated by 1 to give a poly(A-alt-B) copolymer in which A and B are not strictly enantiomers.8 This structure is readily confirmed through 13C NMR analysis of the polymers, which reveals resonances for four different olefinic carbons. Proton NMR spectra can be definitive, but are often compromised by overlap of proton resonances and non-first order olefinic proton resonances. The non-propagating "errors" in the polymer shown in eq 1 were proposed8 to be both AA and BB trans, isotactic dyads3b formed from trans metallacyclobutane intermediates that "flip over" before they open to
give a syn propagating species, a process that leads to retention of configuration at the metal for that step and consequently an isotactic structure.\textsuperscript{3a} We turned to an exploration of enantiomerically pure endo-2-substituted-5,6-norbornenes in order to determine whether only disubstitute monomers can form an A-alt-B copolymer.

\begin{equation}
\text{cis} + \text{A} \rightarrow \text{cis} - \text{B} \quad \text{(1)}
\end{equation}

Copolymerization of a mixture of 25 equiv of A<sub>SR</sub> and 25 equiv of B<sub>RS</sub> (eq 2) with I as initiator (0.1 M in tol-<i>d</i><sub>6</sub>) was complete in less than one minute to give a polymer that precipitated out of toluene. The partial \textsuperscript{13}C NMR spectrum of this polymer in CDCl<sub>3</sub> (Fig 1 left) showed four olefinic carbon resonances consistent with it having the cis,syndiotactic,alt structure. Although the partial \textsuperscript{1}H NMR spectrum of this polymer showed two pseudo-triplet olefinic proton resonances at 5.21 and 5.28 ppm having \textit{J}<sub>HH</sub> = 10 Hz (Fig 1 right), the remaining two olefinic proton resonances overlap with each other and with methine proton resonances belonging to the pantolactone (at 5.36 ppm) and the methylsuccinimide (at 5.37 ppm). The absence of proton resonances corresponding to trans, isotactic A<sub>SR</sub>A<sub>SR</sub> and/or B<sub>RS</sub>B<sub>RS</sub> dyads near 5.46 ppm (estimated\textsuperscript{3b}) suggests that cis,syndiotactic-poly(A<sub>SR</sub>-alt-B<sub>RS</sub>) contain few, if any, trans, isotactic errors.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{The partial \textsuperscript{13}C NMR (CDCl<sub>3</sub>, 20 °C, 126 MHz) spectrum (left) and \textsuperscript{1}H NMR (CDCl<sub>3</sub>, 20 °C, 500 MHz) spectrum (right) of cis,syndiotactic-poly(A<sub>SR</sub>-alt-B<sub>RS</sub>).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{Six additional monomers explored here.}
\end{figure}

The search for A-alt-B copolymers was expanded to include the monomers shown in Fig 2. Copolymerization of 25 equiv of A<sub>SR</sub> and 25 equiv of C<sub>RS</sub> (0.1 M in toluene-<i>d</i><sub>6</sub>) was complete in less than one minute to give a tolulene-d<sub>s</sub>-soluble polymer whose \textsuperscript{13}C NMR spectrum in CDCl<sub>3</sub> showed four different olefinic carbon resonances, consistent with the polymer having a cis,syndiotactic-A<sub>SR</sub>-alt-C<sub>RS</sub> structure (Fig 3, left). The partial proton NMR spectrum (Fig 3, right) is not convincing that the degree of order is high, in part because the pantolactone methine resonance (at 5.36 ppm) overlaps with the four olefinic proton resonances.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3.png}
\caption{The partial \textsuperscript{13}C NMR (CDCl<sub>3</sub>, 25 °C, 125 MHz) spectrum (left) and \textsuperscript{1}H NMR (CDCl<sub>3</sub>, 25 °C, 500 MHz) spectrum (right) of cis,syndiotactic-poly(A<sub>SR</sub>-alt-C<sub>RS</sub>).}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{The partial \textsuperscript{13}C NMR (CDCl<sub>3</sub>, 20 °C, 126 MHz) spectrum (left) and \textsuperscript{1}H NMR (CDCl<sub>3</sub>, 20 °C, 500 MHz) spectrum (right) of cis,syndiotactic-poly(C<sub>SR</sub>-alt-B<sub>RS</sub>). *Residual catalyst decomposition peaks.}
\end{figure}

GPC analysis was performed on four cis,syndiotactic-poly(A<sub>SR</sub>-alt-C<sub>RS</sub>) samples made from 25, 50, 75, and 100 equivalents of A<sub>SR</sub> and C<sub>RS</sub> (each). The olefinic proton patterns in proton NMR spectra were all the same as that shown in Fig 3 (right). The GPC peaks were monomodal, the molecular weights increased steadily, and the <i>D</i> values were between 1.35 and 1.55. (See SI for details.)

A third cis,syndiotactic polymer was prepared from 25 equiv of C<sub>SR</sub> and 25 equiv of B<sub>RS</sub>. The olefinic region of the \textsuperscript{13}C NMR spectrum of the resulting polymer (Fig 4 left) clearly shows four distinct olefinic carbon resonances. The resonances at 128.1 and 126.3 ppm are believed to result from catalyst decomposition products, while the small resonance at 131.4 ppm we propose arises from an insertion error (exact type unknown). The olefinic region of the \textsuperscript{1}H NMR spectrum of cis,syndiotactic-poly(C<sub>SR</sub>-alt-B<sub>RS</sub>) (Fig 4 right) is com-
The ability to modify a toluene-\(d_8\)-soluble copolymer. The partial \(^{13}C\) NMR spectrum (Fig 5 left) showed primarily four olefinic resonances consistent with the formation of cis, syndiotactic-poly(AsR-alt-CRR). However, a significant number of minor olefinic resonances between 133 and 134 ppm and between 131 and 132 ppm suggest that the structure is not as regular as that for cis,syndiotactic-poly(AsR-alt-CRR) (Fig 3 left). The partial \(^1H\) NMR spectrum of cis,syndiotactic-poly(AsR-alt-CRR) (Fig 5 right) is even less informative than that for cis,syndiotactic-poly(AsR-alt-CRR) (Fig 3). We conclude that the "second" chirality in the monomer (here CRR or CRRs) is not a major determinant of the overall polymer structure, at least in this case.

Copolymerization of AsR and ARR in toluene-\(d_8\) yielded cis, syndiotactic-poly(AsR-alt-ARR). The partial \(^{13}C\) NMR spectrum contained four sharp olefinic carbon resonances (Fig 6 left) with just a hint of resonances (at \(-131.5, -133.5\)) that we again ascribe to structural errors (cf. Fig 5 left). The partial \(^1H\) NMR spectrum of this copolymer (Fig 6 right) showed two complex patterns that result from overlap of the methine resonances in the two pantolactone groups with two sets of olefinic proton resonances. Formation of cis,syndiotactic-poly(AsR-alt-ARR) also suggests that it is largely the "primary" chirality in the monomer, what we call the "chiral motif," that regulates formation of the highly structured copolymer.

Copolymerization of AsR and Dr (25 equiv of each) produced cis, syndiotactic-poly(AsR-alt-Dr), whose carbon and proton NMR spectra are similar to those in Fig 5 (see SI).

In order to test whether an ester functionality that contains a second chiral entity is necessary, we prepared E\(R\) from B\(RS\) and paired it with AsR (25 equiv each). The \(^{13}C\) NMR spectrum (Fig 7 left) of the resulting cis, syndiotactic-poly(AsR-alt-ERS) is without significant errors. The \(^1H\) NMR spectrum is one of the more convincing that the structure is highly regular and the olefinic proton NMR resonances are first order. The synthesis of cis,syndiotactic-poly(CSR-alt-ERS) is nearly as successful (see SI), while the synthesis of one A-alt-B copolymer in which one of the monomers is the TMS derivative of E\(R\) was relatively unsuccessful (see SI).

Cis,syndiotactic poly(AsR-alt-BRS) was hydrolyzed over the course of 4 days in a mixture of CHCl\(_3\), THF, and water that contained a large excess of LiOH. The result is formation of cis, syndiotactic poly(AsS-alt-ARS) (eq 3) whose \(^{13}C\) and \(^1H\) NMR spectra in DMSO-\(d_6\) are shown in Fig 8. We also have shown that cis,syndiotactic-poly(AsR-alt-ERS) can be transesterified as shown in eq 4 to yield cis,syndiotactic-poly(AsS-alt-ERS) (Fig 9). The ability to modify A-alt-B copolymers to yield others that may not be prepared directly from the respective monomers adds a significant degree of flexibility to the method.
monomers that have a single endo substituent on the chiral C2 position (eqs 2 and 3) may be more successful in the long run for preparing alternating copolymers in large variety than one based on 2,3-disubstituted-5,6-norbornenes (eq 1). It remains to be seen what other chiral motifs will allow A-alt-B polymers to be synthesized with high fidelity, what substituents are optimum, what functionalities can be changed through post polymerization modification to yield A-alt-B polymers that cannot be prepared directly from the corresponding monomers, and what are the errors and how they can be avoided.

ASSOCIATED CONTENT

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

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REFERENCES

(1) (a) Odian, G. Principles of Polymerization, Fourth Edition; John Wiley & Sons, Inc.: Hoboken, New Jersey, 2004. (b) Coates, G. W. Chem. Rev. 2000, 100, 1223-1252. (c) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. J. Am. Chem. Soc. 1998, 120, 11018-11019. (d) Platel, R. H.; Hodgson, L. M.; Williams, C. K. Polymer Reviews 2008, 48, 11-63. (e) Super, M.; Berluche, E.; Costello, C.; Beckman, E. Macromolecules 1997, 30, 368-372. (f) Darenbourg, D. J.; Holtcamp, M. W. Macromolecules 1995, 28, 7577-7579. (g) Coates, G. W.; Moore, E. R. Angew. Chem. Int. Ed. 2004, 43, 6618-6639. (h) Kramer, J. W.; Tretiak, D. S.; Dunn, E. W.; Castro, P. M.; Roisnel, T.; Thomas, C. M.; Coates, G. W. J. Am. Chem. Soc. 2009, 131, 16042-16044. (2) (a) Jeong, H.; John, J. M.; Schrock, R. R. Organometallics 2015, 34, 5136-5145. (b) Ding, L.; Zheng, X.-Q.; Lu, R.; An, J.; Qiu, J. Polym. Int. 2014, 63, 997-1002. (c) Tan, L.; Parker, K. A.; Sampson, N. S. Macromolecules 2014, 47, 6572-6579. (d) Lee, H.-K.; Bang, K.-T.; Hess, A.; Grubbs, R. H.; Choi, T.-L. J. Am. Chem. Soc. 2015, 137, 9262-9265. (e) Elling, B. R.; Xia, Y. J. Am. Chem. Soc. 2015, 137, 9922-9926. (f) Tan, L.; Li, G.; Parker, K. A.; Sampson, N. S. Macromolecules 2015, 48, 4793-4800. (g) Buchmeiser, M. R.; Ahmad, I.; Gurram, V.; Kumar, P. S. Macromolecules 2011, 44, 4098-4106. (h) Abbas, M.; Wappel, J.; Slugovc, C. Macromol. Symp. 2012, 311, 122-125. (i) Song, A.; Parker, K. A.; Sampson, N. S. Org. Lett. 2010, 12, 3729-3731. (j) Song, A.; Parker, K. A.; Sampson, N. S. J. Am. Chem. Soc. 2009, 131, 3444-3445. (k) Vehlov, K.; Wang, D.; Buchmeiser, M. R.; Blechert, S. Angew. Chem., Int. Ed. 2008, 47, 2615-2618. (l) Suthasup, S.; Shiotsuki, M.; Masuda, T.; Sanda, F. J. Am. Chem. Soc. 2009, 131, 10546-10551. (m) Nakade, H.; Ilker, M. F.; Jordan, B. J.; Uzun, O.; LaPointe, N. L.; Coughlin, E. B.; Rotello, V. M. Chem. Commun. 2005, 3271-3273.
Wang, D.; Vehlow, K.; Reinhardt, I.; Kühnel, C.; Decker, U.; Blechert, S.; Buchmeiser, M. R. *Chem. Eur. J.* 2009, 15, 9451-9457. (o) Vehlow, K.; Lichtenheldt, M.; Wang, D.; Blechert, S.; Buchmeiser, M. R. *Macromol. Symp.* 2010, 296, 44-48. (p) Ilker, M. F.; Coughlin, E. B. *Macromolecules* 2002, 35, 54-58. (q) Bornand, M.; Torker, S.; Chen, P. *Organometallics* 2007, 26, 3585-3596. (r) Romulus, J.; Tan, L.; Weck, M.; Sampson, N. S. *ACS Macro Lett.* 2013, 2, 749-752. (s) Daeffler, C. S.; Grubbs, R. H. *Macromolecules* 2013, 46, 3288-3292. (t) Demel, S.; Slugovec, C.; Stelzer, F.; Fodor-Csorba, K.; Galli, G. *Macromol. Rapid Commun.* 2003, 24, 636-641. (u) Choi, T.-L.; Rutenberg, I. M.; Grubbs, R. H. *Angew. Chem. Int. Ed.* 2002, 41, 3839-3841. (v) Al Samak, B.; Amir-Ebrahimi, V.; Corry, D. G.; Hamilton, J. G.; Rigby, S.; Rooney, J. J.; Thompson, J. M. *J. Mol. Catal. A: Chem.* 2000, 169, 13-21. (3) (a) Flook, M. M.; Ng, V. W. L.; Schrock, R. R. *J. Am. Chem. Soc.* 2011, 133, 1784-1786. (b) Flook, M. M.; Börner, J.; Kilyanek, S.; Gerber, L. C. H.; Schrock, R. R. *Organometallics* 2012, 31, 6231-6243. (c) Jeong, H.; Ng, V. W. L.; Börner, J.; Schrock, R. R. *Macromolecules* 2015, 48, 2006-2012. (4) (a) Schrock, R. R. *Acc. Chem. Res.* 2014, 47, 2457-2466. (b) Forrest, W. P.; Weis, J. G.; John, J. M.; Axtell, J. C.; Simpson, J. H.; Swager, T. M.; Schrock, R. R. *J. Am. Chem. Soc.* 2014, 136, 10910-10913. (c) Jeong, H.; John, J. M.; Schrock, R. R.; Hoveyda, A. H. *J. Amer. Chem. Soc.* 2015, 136, 2239-2242. (d) Autenrieth, B.; Jeong, H.; Forrest, W. P.; Axtell, J. C.; Ota, A.; Lehr, T.; Buchmeiser, M. R.; Schrock, R. R. *Macromolecules* 2015, 48, 2480-2492. (e) Autenrieth, B.; Schrock, R. R. *Macromolecules* 2015, 48, 2493-2503. (f) Hyvl, J.; Autenrieth, B.; Schrock, R. R. *Macromolecules* 2015, 48, 3148-3152. (5) Schrock, R. R. *Chem. Rev.* 2009, 109, 3211–3226. (6) Marinescu, S. C.; Schrock, R. R.; Li, B.; Hoveyda, A. H. *J. Am. Chem. Soc.* 2009, 131, 58-59. (7) Hamilton, J. G.; Ivin, K. J.; Rooney, J. J. *Brit. Polym. J.* 1984, 16, 21. (b) Hamilton, J. G.; Ivin, K. J.; Rooney, J. J.; Waring, L. C. *J. Chem. Soc., Chem. Comm.* 1983, 159. (8) Jang, E. S.; John, J. M.; Schrock, R. R. *ACS Cent. Sci.* 2016, 2, 631-636.
TOC Graphic

cis,syndiotactic-poly(\text{ASR-alt-ER})