Communication

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

Eun Sil Jang, Jeremy M. John, and Richard R. Schrock

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

Eun Sil Jang, Jeremy M. John, and Richard R. Schrock*

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

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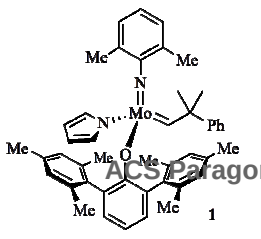
Supporting Information Placeholder

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-$Me_2C_6H_3$)(CHCMe_2Ph)(OHMT)(pyrrolide) (**1**) as the initiator (OHMT = O-2,6-$Mesityl_2C_6H_3$). 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 stereochemistries (*cis vs. trans,* and tacticity) are not fixed. In 2011 we reported[3a] that polymerization of a *rac*-2,3-disubstituted-5,6-norbornene yields a polymer with a *cis,syndiotactic* basic structure[3,4] 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 metal[6] 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.



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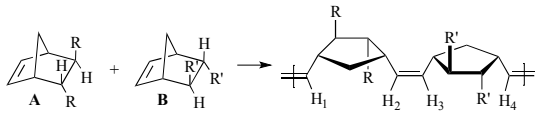
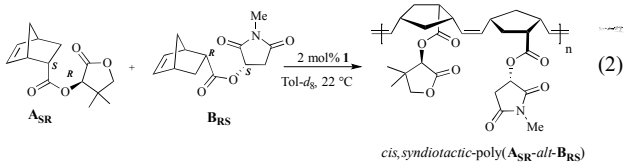
We have shown recently that two monomers that have the same 2,3-disubstituted-5,6-norbornene "chiral motif," but slightly different R and R' substituents in each monomer (eq 1) can be polymerized through ROMP initiated by **1** to give a poly(**A**-*alt*-**B**) copolymer in which **A** and **B** are not strictly enantiomers.[8] This structure is readily confirmed through ^{13}C 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 proposed[8] to be both **AA** and **BB** *trans,isotactic* dyads[3b] 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.[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.



(1)

Copolymerization of a mixture of 25 equiv of $\mathbf{A_{SR}}$ and 25 equiv of $\mathbf{B_{RS}}$ (eq 2) with **1** as initiator (0.1 M in tol-d_8) was complete in less than one minute to give a



(2)

polymer that precipitated out of toluene. The partial ^{13}C NMR spectrum of this polymer in $CDCl_3$ (Fig 1 left) showed four olefinic carbon resonances consistent with it having the *cis*,*syndiotactic*,*alt* structure. Although the partial ^{1}H NMR spectrum of this polymer showed two pseudo-triplet olefinic proton resonances at 5.21 and 5.28 ppm having $^3J_{HH}$ = 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* $\mathbf{A_{SR}A_{SR}}$ and/or $\mathbf{B_{RS}B_{RS}}$ dyads near 5.46 ppm (estimated[8]) suggests that *cis*,*syndiotactic*-poly($\mathbf{A_{SR}}$-*alt*-$\mathbf{B_{RS}}$) contain few, if any, *trans,isotactic* errors.

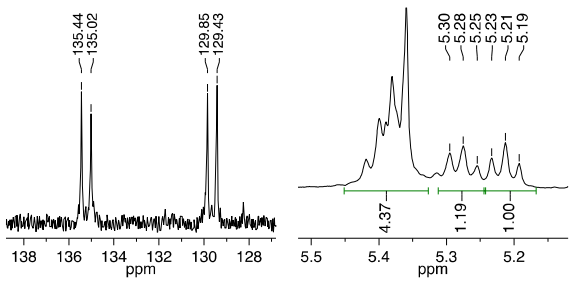


Figure 1. The partial ^{13}C NMR ($CDCl_3$, 20 °C, 126 MHz) spectrum (left) and ^{1}H NMR ($CDCl_3$, 20 °C, 500 MHz) spectrum (right) of *cis*,*syndiotactic*-poly($\mathbf{A_{SR}}$-*alt*-$\mathbf{B_{RS}}$).

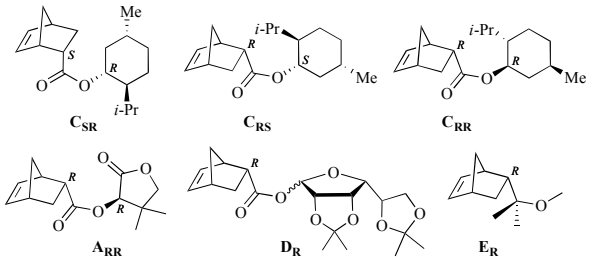


Figure 2. Six additional monomers explored here.

The search for **A**-*alt*-**B** copolymers was expanded to include the monomers shown in Fig 2. Copolymerization of 25 equiv of $\mathbf{A_{SR}}$ and 25 equiv of $\mathbf{C_{RS}}$ (0.1 M in toluene-d_8) was complete in less than one minute to give a toluene-d_8-soluble polymer whose ^{13}C NMR spectrum in $CDCl_3$ showed four different olefinic carbon resonances, consistent with the polymer having a *cis*,*syndiotactic*-$\mathbf{A_{SR}}$-*alt*-$\mathbf{C_{RS}}$ 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.

GPC analysis was performed on four *cis,syndiotactic*-poly($\mathbf{A_{SR}}$-*alt*-$\mathbf{C_{RS}}$) samples made from

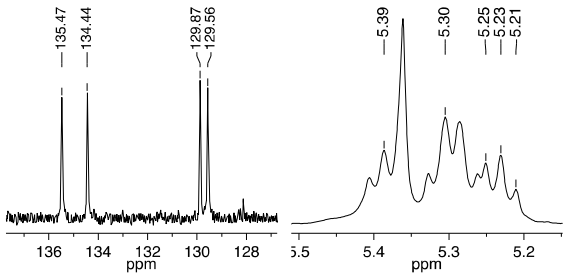


Figure 3. The partial ^{13}C NMR ($CDCl_3$, 25 °C, 125 MHz) spectrum (left) and ^{1}H NMR ($CDCl_3$, 25 °C, 500 MHz) spectrum (right) of *cis*,*syndiotactic*-poly($\mathbf{A_{SR}}$-*alt*-$\mathbf{C_{RS}}$).

25, 50, 75, and 100 equivalents of $\mathbf{A_{SR}}$ and $\mathbf{C_{RS}}$ (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 $Đ$ values were between 1.35 and 1.55. (See SI for details.)

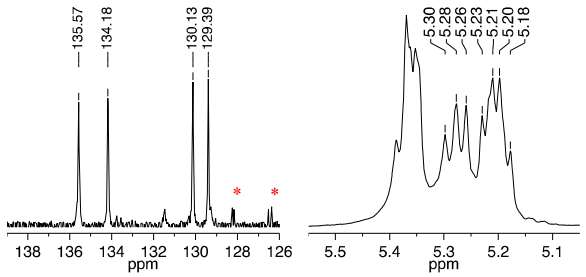


Figure 4. The partial ^{13}C NMR ($CDCl_3$, 20 °C, 126 MHz) spectrum (left) and ^{1}H NMR ($CDCl_3$, 20 °C, 500 MHz) spectrum (right) of *cis*,*syndiotactic*-poly(**C$_{SR}$**-*alt*-**B$_{RS}$**). *Residual catalyst decomposition peaks.

A third *cis*,*syndiotactic* polymer was prepared from 25 equiv of **C$_{SR}$** and 25 equiv of **B$_{RS}$**. The olefinic region of the ^{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 ^{1}H NMR spectrum of *cis*,*syndiotactic*-poly(**C$_{SR}$**-*alt*-**B$_{RS}$**) (Fig 4 right) is complicated by overlap and is not itself convincing that the polymer structure is highly regular.

Copolymerization of **A$_{SR}$** and **C$_{RR}$** (25 equiv of each) proceeded smoothly to give 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(**A$_{SR}$**-*alt*-**C$_{RR}$**). 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(**A$_{SR}$**-*alt*-**C$_{RS}$**) (Fig 3 left). The partial ^{1}H NMR spectrum of *cis*,*syndiotactic*-poly(**A$_{SR}$**-*alt*-**C$_{RR}$**) (Fig 5 right) is even less informative than that for *cis*,*syndiotactic*-poly(**A$_{SR}$**-*alt*-**C$_{RS}$**) (Fig 3). We conclude that the "second" chirality in the monomer (here **C$_{RR}$** or **C$_{RS}$**) is not a major determinant of the overall polymer structure, at least in this case.

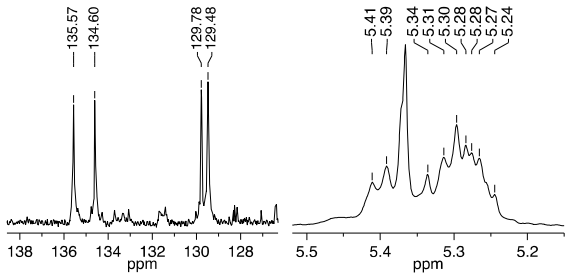


Figure 5. The partial ^{13}C NMR ($CDCl_3$, 20 °C, 126 MHz) spectrum (left) and ^{1}H NMR ($CDCl_3$, 20 °C, 500 MHz) spectrum (right) of *cis*,*syndiotactic*-poly(**A$_{SR}$**-*alt*-**C$_{RR}$**).

Copolymerization of **A$_{SR}$** and **A$_{RR}$** in toluene-d_8 yielded *cis*,*syndiotactic*-poly(**A$_{SR}$**-*alt*-**A$_{RR}$**). The partial ^{13}C NMR spectrum contained four sharp olefinic carbon resonances (Fig 6 left) with just a hint of resonances (at ~131.5 and ~133.5) that we again ascribe to structural errors (*cf.* Fig 5 left). The partial ^{1}H 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(**A$_{SR}$**-*alt*-**A$_{RR}$**) 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.

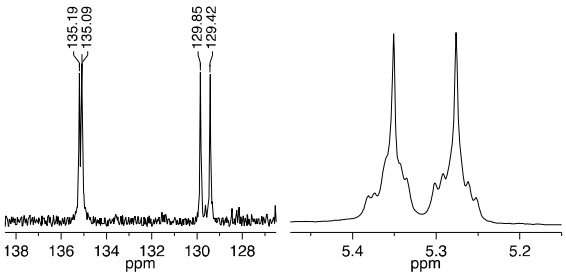


Figure 6. The partial ^{13}C NMR ($CDCl_3$, 20 °C, 126 MHz) spectrum (left) and ^{1}H NMR ($CDCl_3$, 20 °C, 500 MHz) spectrum (right) of *cis*,*syndiotactic*-poly(**A$_{SR}$**-*alt*-**A$_{RR}$**).

Copolymerization of **A$_{SR}$** and **D$_{R}$** (25 equiv of each) produced *cis*,*syndiotactic*-poly(**A$_{SR}$**-*alt*-**D$_{R}$**), 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 **A$_{SR}$** (25 equiv of each). The ^{13}C NMR spectrum (Fig 7 left) of the resulting *cis*,*syndiotactic*-poly(**A$_{SR}$**-*alt*-**E$_{R}$**) is without significant errors. The ^{1}H 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(**C$_{SR}$**-*alt*-**E$_{R}$**) 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).

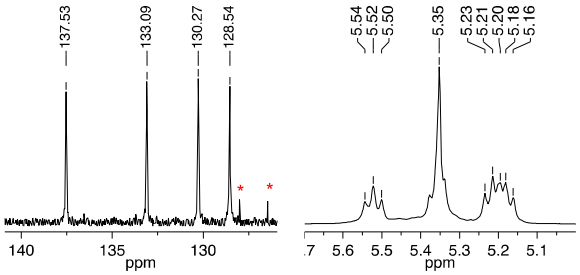
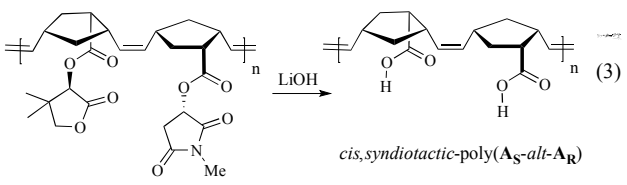


Figure 7. The partial ^{13}C NMR ($CDCl_3$, 20 °C, 126 MHz) spectrum (left) and ^{1}H NMR ($CDCl_3$, 20 °C, 500 MHz) spectrum (right) of *cis*,*syndiotactic*-poly(**A$_{SR}$**-*alt*-**E$_{R}$**). *Residual catalyst decomposition peaks.

Cis,*syndiotactic* poly(**A$_{RS}$**-*alt*-**B$_{RS}$**) 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(**A$_{S}$**-*alt*-**A$_{R}$**) (eq 3) whose ^{13}C and ^{1}H NMR spectra in DMSO-d_6 are

shown in Fig 8. We also have shown that *cis,syndiotactic*-poly(**A**$_{SR}$-*alt*-**E**$_{R}$) can be transesterified as shown in eq 4 to yield *cis,syndiotactic*-poly(**A**$_{S}$'-*alt*-**E**$_{R}$) (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.



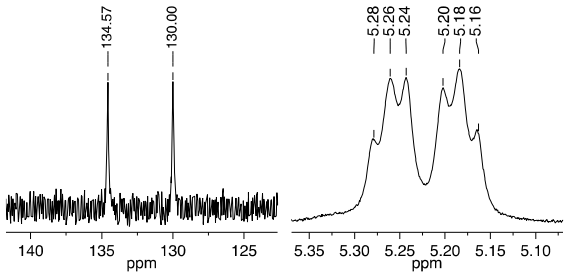
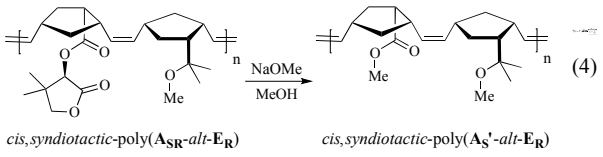


Figure 8. The partial ^{13}C NMR (DMSO-d_6, 20 °C, 126 MHz) spectrum (left) and ^{1}H NMR (DMSO-d_6, 20 °C, 500 MHz) spectrum (right) of *cis,syndiotactic*-poly(**A**$_{S}$-*alt*-**A**$_{R}$).



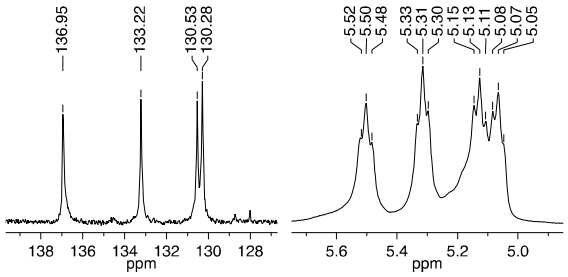


Figure 9. The partial ^{13}C NMR ($CDCl_3$, 20 °C, 126 MHz) spectrum (left) and ^{1}H NMR ($CDCl_3$, 20 °C, 500 MHz) spectrum (right) of *cis,syndiotactic*-poly(**A**$_{S}$'-*alt*-**E**$_{R}$).

We have found significant differences between molybdenum and tungsten as initiators in many of the stereoselective polymerizations that we have explored in the past several years. In fact, the attempted synthesis of *cis,syndiotactic*-poly(**A**$_{SR}$-*alt*-**E**$_{R}$) with **1**$_{W}$ (the tungsten analog of **1**) yielded a polymer with significantly more errors than that formed when **1** is the initiator (see SI). However, it is too early to speculate about the origin of the efficiency of Mo catalysts versus W analogs.

We conclude that *cis,syndiotactic*-**A**-*alt*-**B** copolymers can be formed from enantiomerically pure *endo*-2-substituted-5,6-norbornenes with a substituent at C2 of the appropriate size that allows the configuration of each chiral metal in propagating intermediates derived from **1** to distinguish the primary chiral motif of each chiral norbornene in the mixture. We propose that only two propagation steps out of a possible 2^5 (*syn* or *anti* alkylidenes, *cis* or *trans* metallacycles, two chain ends, two monomers, and two M=C bond faces) dominate to give the results we have observed here; these two are M=**A**P (where monomer **A** is last inserted and P is polymer) reacting with **B** and M*=**B**P reacting with **A** (where M and M* are the two configurations at M), all in a *cis,syndiotactic* manner *via syn* alkylidene intermediates and with inversion of the metal configuration (M and M*) in each step. **A**-*alt*-**B** copolymers prepared from 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.

AUTHOR INFORMATION

Corresponding Author rrs@mit.edu

Author Contributions ESJ and JMJ contributed equally to this work.

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