# Synthesis of *Cis,syndiotactic* A-*alt*-B Copolymers from Two Enantiomerically Pure *Trans*-2,3-Disubstituted-5,6-Norbornenes

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S *Supporting Information*

ABSTRACT: *Cis,syndiotactic* **A**-*alt*-**B** copolymers, where **A** and **B** are two enantiomerically pure *trans*-2,3-disubstituted-5,6-norbornenes with "opposite" chiralities, can be prepared with stereogenic-at-metal initiators of the type M(NR)-(CHR′)(OR″)(pyrrolide). Formation of a high percentage of alternating **AB** copolymer linkages relies on an inversion of chirality at the metal with each propagating step and a relatively fast formation of an **AB** sequence as a consequence of a preferred diastereomeric relationship between the chirality at the metal and the chirality of the monomer. This approach to formation of an alternating **AB** copolymer contrasts dramatically with the principle of forming **AB** copolymers from achiral monomers and catalysts.

cis,syndiotactic-poly(**A**-*alt*-**B**)

M = Mo or W; R″ = 1-Adamantyl or 2,6-Me$_2$C$_6$H$_3$
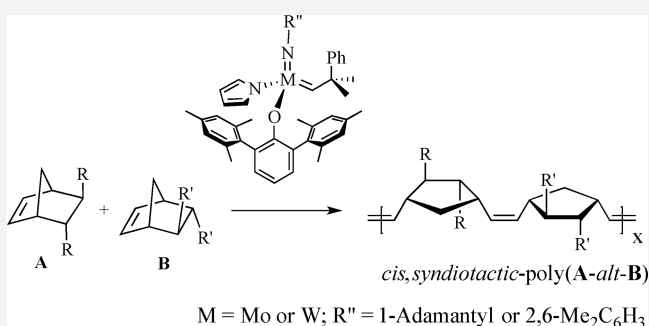
INTRODUCTION

Copolymers in which monomers **A** and **B** are incorporated in an *alternating* manner, poly(**A**-*alt*-**B**), are rare.[1−5] Examples are alternating **AB** copolymers formed from CO and olefins or CO$_2$ and epoxides. In these cases alternation is greatly assisted by the fact that one partner (CO or CO$_2$) does not itself polymerize. A few alternating **AB** copolymers have been formed through ring-opening metathesis polymerization (ROMP) of cyclic olefin monomers,[6−28] but in these circumstances both **A** and **B** usually can be homopolymerized and the stereochemistry of the C=C bond in the polymer is not fixed. One exception is the alternating **AB** copolymer which has all *trans* C=C bonds and <5% **AA** errors formed from a norbornene-like monomer (**B**) that is slow to homopolymerize and cyclooctene or cycloheptene (**A**). The most successful initiators are of the type Mo(NR)(CHCMe$_2$Ph)-[OCMe(CF$_3$)$_2$]$_2$ (R = 2,6-Me$_2$C$_6$H$_3$ or 2,6-*i*-Pr$_2$C$_6$H$_3$), two well-defined alkylidene initiators that contain Mo or W out of many that have proven useful for preparing stereoregular polymers from norbornenes and norbornadienes.[29−35]

Among the well-defined Mo or W initiators are those that contain a stereogenic metal, e.g., **1a–1c**. These initiators can produce a special category of stereoregular **A**-*alt*-**B** copolymers made from a racemic chiral monomer where **A** and **B** are enantiomers. These "**A**-*alt*-**A***" copolymers have a basic *cis, syndiotactic* structure (eq 1), which is readily proven through ^{1}H

cis,syndiotactic-poly(**A**-*alt*-**A***) (1)
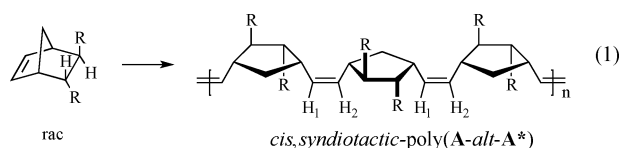
and ^{13}C NMR studies.[36,37] Only one example of a stereoregular **A**-*alt*-**A*** copolymer has been reported in the older literature.[38,39] The *cis* structure is formed when **1a** or **1b** reacts with monomer to yield all *cis* metallacycles in trigonal bipyramidal (TBP) intermediates in which the terphenoxide and the imido ligands are in apical positions, while syndiotacticity results from *an inversion of chirality at the metal center with each step in the polymerization.* Inversion of chirality at the metal forces the olefin to approach first one side of the M=C bond and then the other. Incorporation of enantiomers in an alternating fashion is a consequence of one enantiomer of the racemic monomer reacting more rapidly with one enantiomer (at the metal center) of each propagating species. We have called this mode of control of polymer structure "stereogenic metal control"; although the chirality of the chain end nearest the metal that results from last inserted monomer is not necessarily irrelevant, the determining feature is the lowest energy diastereomeric combination of chirality at the metal and chirality of the monomer. The "errors" in the *cis,syndiotactic*-poly(**A**-*alt*-**A***) structure arise through formation of **AA** and **A*****A*** *cis,syndiotactic* and *trans,isotactic* dyads. *Trans,isotactic* dyads arise through formation of a *trans* metallacyclobutane intermediate (instead of a *cis* metallacyclobutane), which "flips over" before opening, a rearrangement that preserves the configuration at the metal and leads to a *trans* C=C linkage.[37] This mechanistic proposal is based on the fact that polymerization of (+)-DCMNBE (DCMNBE = 2,3-dicarbomethoxynorbornene) by **1a** yields a polymer that contains ∼75% *trans,isotactic* dyads and 25% *cis,syndiotactic* dyads, while **1c** yields a polymer that contains ∼92% *trans,isotactic* dyads and ∼8%

cis,syndiotactic dyads (Figure 1).[37] The olefinic protons in *trans,isotactic* polymer are inequivalent and on the same C=C
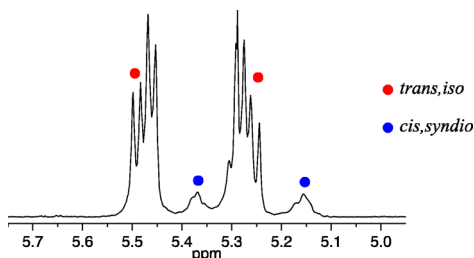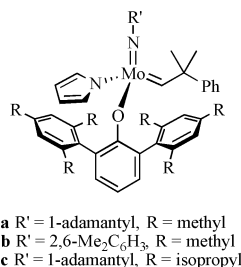

Figure 1. Olefinic region of the ^{1}H NMR spectrum of the poly[(*R,R*)-DCMNBE] prepared from initiator **1c**. Reprinted with permission from ref 37. Copyright 2012 American Chemical Society.

bond (and therefore coupled to each other with $J_{HH} \sim 16$ Hz[37]) while the olefinic protons in *cis,syndiotactic* polymer are inequivalent and on different C=C bonds (and therefore not coupled to each other). It was also shown that W(O)(CH-*t*-Bu)(OHMT)(Pyr)(PMe$_2$Ph) polymerizes (+)-DCMNBE to give only *cis,syndiotactic*-poly[(+)-DCMNBE].

1a R' = 1-adamantyl, R = methyl
1b R' = 2,6-Me$_2$C$_6$H$_3$, R = methyl
1c R' = 1-adamantyl, R = isopropyl

An interesting question is whether *stereogenic metal control* will direct formation of a copolymer where **A** and **B** are not strictly enantiomers, but have similar structures *and* reactivities toward homopolymerization, are enantiomerically pure, and have "opposite" chirality. If **A** and **B** are significantly different chemically, the resulting polymer could be further manipulated through selective reactions that involve one of the two components within the polymer. We show here that several such *cis,syndiotactic* **A**-*alt*-**B** copolymers can be prepared with Mo (primarily) and W alkylidene initiators.

■ RESULTS AND DISCUSSION

Initial screening experiments employed the four monomers shown in Figure 2, where the **A** monomers have the (2*R*,3*R*)
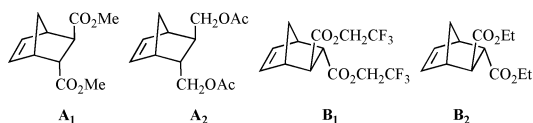

Figure 2. First four monomers employed in this study.

configuration and the **B** monomers have the (2*S*,3*S*) configuration. The ^{13}C NMR spectra of *cis,syndiotactic*-poly(**A**-*alt*-**B**) should reveal four different olefinic carbon resonances, and ^{1}H NMR spectra *could* reveal up to four first order resonances for four different olefinic protons that are coupled pairwise (eq 2). (Overlap of proton resonances could result in non first order ^{1}H NMR spectra.) Racemic **A$_1$** is known to be polymerized by **1a** to give *cis,syndiotactic*-poly[**A$_1$**(*R,R*)-*alt*-

$$\text{(2)}$$

cis,syndiotactic-poly(**A**-*alt*-**B**)
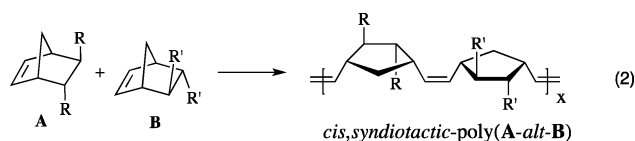
A$_1$(*S,S*)];[37] we find that *cis,syndiotactic,alt* polymers are also formed from racemic **A$_2$**, **B$_1$**, and **B$_2$** (see Supporting Information).

Copolymerization of a mixture of 25 equiv of **A$_1$** and 25 equiv of **B$_2$** with **1a** (0.1 M in toluene-*d$_8$*) as the initiator was complete within seconds to give *cis,syndiotactic*-poly(**A$_1$**-*alt*-**B$_2$**). Its partial ^{13}C NMR spectrum in CDCl$_3$ showed primarily four different olefinic resonances (Figure 3, right), while its ^{1}H NMR spectrum
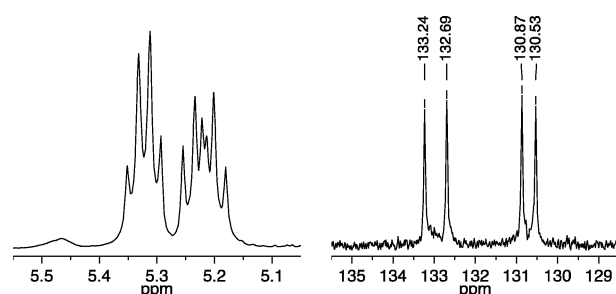

Figure 3. ^{1}H NMR (500 MHz, CDCl$_3$, left) and ^{13}C NMR (125 MHz, CDCl$_3$, right) spectra of *cis,syndiotactic*-poly(**A$_1$**-*alt*-**B$_2$**) (olefinic resonances only).

showed four overlapping first order (pseudo triplet) olefinic proton resonances (Figure 3, left). (See Supporting Information for details.) The broad resonance shown between 5.45 and 5.50 ppm in Figure 3 we propose is half of the pattern that arises from *trans,isotactic* **A$_1$A$_1$** and **B$_2$B$_2$** "errors" (see Figure 1). The other half of the pattern, along with any (minor) pattern that is characteristic of *cis,syndiotactic* **A$_1$A$_1$** and **B$_2$B$_2$** errors (see Figure 1), is buried under the main pattern of four triplets for *cis,syndiotactic*-poly(**A$_1$**-*alt*-**B$_2$**) around 5.30 ppm. If we *assume* that only *trans,isotactic* **A$_1$A$_1$** and **B$_2$B$_2$** dyad resonances are present under the main four triplet resonance, we can estimate that ~94% of the polymer contains *cis,syndiotactic*-poly(**A$_1$**-*alt*-**B$_2$**) dyads. The olefinic carbon resonances for any errors cannot be identified reliably in the partial carbon NMR spectrum shown in Figure 3.

Copolymerization of 25 equiv of (*R,R*)-2,3-(CO$_2$Me)$_2$-norbornene (**A$_1$**) and 25 equiv (*S,S*)-2,3-(CO$_2$CH$_2$CF$_3$)$_2$-norbornene (**B$_1$**) with **1a** (0.1 M in toluene-*d$_8$*) as the initiator was also complete within seconds. The ^{13}C NMR spectrum of the resulting polymer again showed primarily four different olefinic carbon resonances (Figure 4, right), while its ^{1}H NMR spectrum showed four overlapping first order (pseudo triplet) olefinic proton resonances (Figure 4, left), consistent with the formation of *cis,syndiotactic*-poly(**A$_1$**-*alt*-**B$_1$**). A virtually identical *cis,syndiotactic*-poly(**A$_1$**-*alt*-**B$_1$**) polymer was prepared employing **1b** as the initiator (see Supporting Information). It is clear from the spectra in Figure 5 that this *cis,syndiotactic* **A$_1$**-*alt*-**B$_1$** copolymer contains more *trans,isotactic* errors than the *cis,syndiotactic* **A$_1$**-*alt*-**B$_2$** copolymer described above, most likely as a consequence of the more significant differences in reactivity between **A$_1$** and **B$_1$** than between **A$_1$** and **B$_2$**. The 5.50 ppm resonance was integrated, and the % *cis,syndiotactic*-poly(**A$_1$**-*alt*-**B$_1$**) dyads were calculated to be ~90%. Two olefinic carbon resonances for the **A$_1$A$_1$** and **B$_1$B$_1$** "errors" in this case can be seen
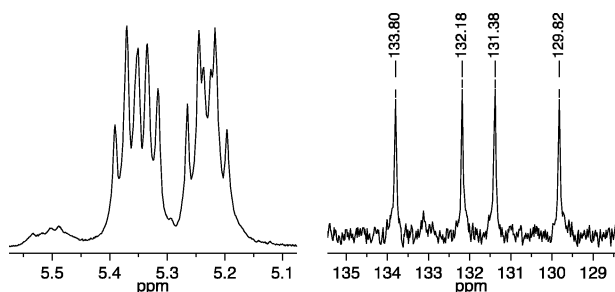
Figure 4. ¹H NMR (500 MHz, CDCl₃, left) and ¹³C NMR (125 MHz, CDCl₃, right) spectra of *cis,syndiotactic*-poly(**A₁**-*alt*-**B₁**) (olefinic resonances only).
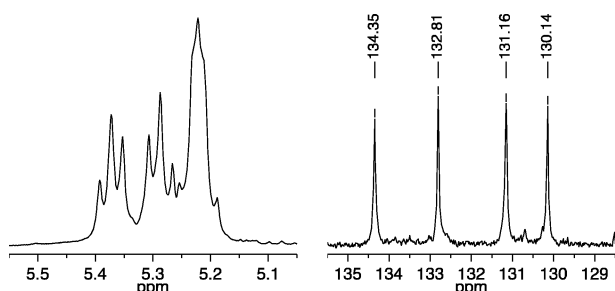
Figure 5. ¹H NMR (500 MHz, CDCl₃, left) and ¹³C NMR (125 MHz, CDCl₃, right) spectra of *cis,syndiotactic*-poly(**A₂**-*alt*-**B₂**) (olefinic resonances only).

at ~133.0 and 128.3 ppm (Figure 4). The ¹⁹F NMR spectrum of *cis,syndiotactic*-poly(**A₁**-*alt*-**B₁**) also reveals two types of overlapping fluorine resonances for **A₁B₁** and **B₁B₁** errors (see Supporting Information), integration of which suggests that the % *cis,syndiotactic*-poly(**A₁**-*alt*-**B₁**) dyads is ~80%.

A third *cis,syndiotactic* polymer was prepared through copolymerization of a mixture of 25 equiv of (*R,R*)-2,3-(CH₂OAc)₂-norbornene (**A₂**) and 25 equiv of (*S,S*)-2,3-(CO₂Et)₂-norbornene (**B₂**) with **1b** as the initiator (Figure 5). The ¹³C NMR spectrum showed primarily four different olefinic carbon resonances, while the ¹H NMR spectrum showed two essentially first order triplet resonances for protons coupled to one another, along with a second order resonance at ~5.23 ppm for two coupled olefinic protons. On the basis of the carbon NMR spectrum we can estimate the number of **A₂A₂** and **B₂B₂** errors to be on the order of 5%.

A fourth example is *cis,syndiotactic*-poly(**A₂**-*alt*-**B₁**). The ¹H NMR spectrum of *cis,syndiotactic*-poly(**A₂**-*alt*-**B₁**) (Figure 6) provides little evidence that the polymer is relatively regular.
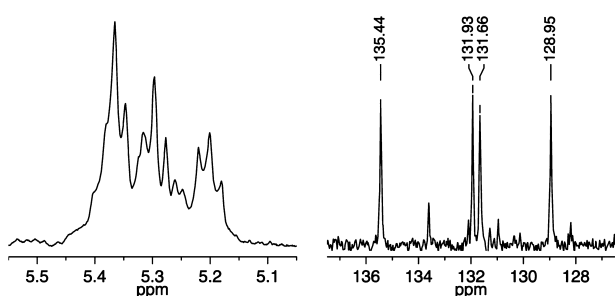
Figure 6. ¹H NMR (500 MHz, CDCl₃, left) and ¹³C NMR (125 MHz, CDCl₃, right) spectra of *cis,syndiotactic*-poly(**A₂**-*alt*-**B₁**) (olefinic resonances only).

However, inspection of the ¹³C NMR spectrum shows primarily four olefinic resonances, consistent with a relatively high percentage (estimated ~90%) of the proposed structure. The complexity seen in the ¹H NMR spectrum can be traced to the overlap and second order nature of the proton resonances. At least four carbon resonances for **A₂A₂** and **B₁B₁** errors can be seen in the ¹³C NMR spectrum.

Twelve other Mo and W initiators were explored for making *cis,syndiotactic*-poly(**A₁**-*alt*-**B₁**), but none was as efficient as **1a** or **1b**, at least according to proton NMR spectroscopy (see Supporting Information for details). The failure of more than two initiators (so far) to produce *cis,syndiotactic* **A**-*alt*-**B** copolymers of the type described here is not surprising if one considers the complexity of the stereoregular ROMP reaction[29] and the need to control formation of **A₁A₁** and **B₁B₁** errors. The requirements that the metal has a stereogenic center, that its configuration must switch with each insertion of **A** or **B**, and that the polymerization be controlled primarily by the chirality of the stereogenic metal are demanding.

Four additional enantiomerically pure monomers (Figure 7) were prepared, and five **AₓBᵧ** combinations were found to give
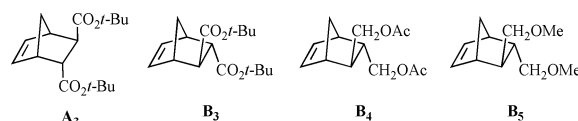
Figure 7. Four additional monomers.

copolymers with >90% alternating **AB** dyads using **1b** as the initiator, according to their ¹H and ¹³C NMR spectra (see Supporting Information for a complete list of reactions employing **Aₓ** and **Bᵧ**). The percentage of *trans,isotactic* and/or *cis,syndiotactic* errors was estimated to be in the range of 5−10%.

Copolymerization of **A₂** and **B₃** ((*S,S*)-(CO₂-*t*-Bu)₂-norbornene) using **1b** yielded a CDCl₃-soluble polymer whose ¹H NMR spectrum showed primarily two resonances, a triplet at 5.34 ppm and a second order resonance at 5.23 ppm that integrated to three times its relative intensity (Figure 8). Weak
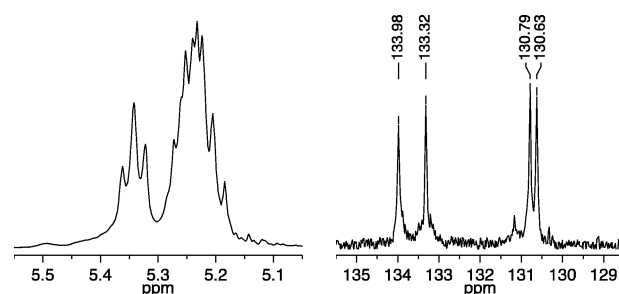
Figure 8. ¹H NMR (500 MHz, CDCl₃, left) and ¹³C NMR (125 MHz, CDCl₃, right) spectra of *cis,syndiotactic*-poly(**A₂**-*alt*-**B₃**) (olefinic resonances only).

and broad resonances near 5.50 and 5.45 can be attributed to *trans,isotactic* errors. The presence of primarily four olefinic resonances in the ¹³C NMR spectrum at 134.0, 133.3, 130.8, and 130.6 ppm suggests that the *cis,syndiotactic*-poly(**A₂**-*alt*-**B₃**) structure is of the order of 90%.

Copolymerization of **A₁** and (*S,S*)-(CH₂OAc)₂-norbornene (**B₄**) proceeded smoothly to give another CDCl₃ soluble polymer. The ¹H NMR spectrum of the isolated polymer showed two pairs of overlapping olefinic proton resonances and

weak resonances at 5.45−5.50 for *trans,isotactic* errors (Figure 9). However, the ^{13}C NMR spectrum showed primarily four olefinic

Figure 9. ^{1}H NMR (500 MHz, CDCl$_3$, left) and ^{13}C NMR (125 MHz, CDCl$_3$, right) spectra of *cis,syndiotactic*-poly(**A$_1$**-*alt*-**B$_4$**) (olefinic resonances only).
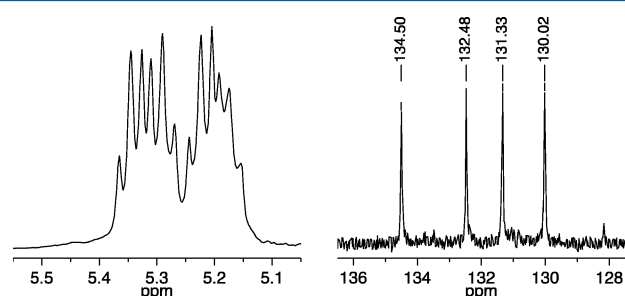
resonances, which confirm that the polymer has largely the *cis,syndiotactic,alt* structure. Given the successful copolymerization of (R,R)-(CH$_2$OAc)$_2$-norbornene (**A$_2$**) with (S,S)-(CO$_2$Et)$_2$-norbornene (**B$_2$**; Figure 5), the formation of *cis,syndiotactic*-poly(**A$_1$**-*alt*-**B$_4$**) is not surprising. The resonance attributed to *trans,isotactic* errors is much more pronounced when **1a** is used as the initiator (see Supporting Information).

The copolymer derived from **A$_3$** ((R,R)-(CO$_2$-*t*-Bu)$_2$-norbornene) and **B$_5$** ((S,S)-(CH$_2$OMe)$_2$-norbornene) showed two higher ordered olefinic proton resonances of equal intensity in CDCl$_3$, (Figure 10) along with resonances for **A$_3$A$_3$** and **B$_5$B$_5$**
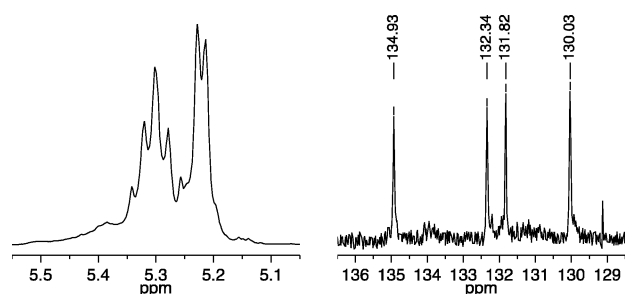

Figure 10. ^{1}H NMR (500 MHz, CDCl$_3$, left) and ^{13}C NMR (125 MHz, CDCl$_3$, right) spectra of *cis,syndiotactic*-poly(**A$_3$**-*alt*-**B$_5$**) (olefinic resonances only).

errors. The two overlapping proton resonances were not well-resolved, making assessment of the errors in the polymer structure difficult. However, the ^{13}C NMR spectrum showed primarily four olefinic resonances, consistent with formation of largely *cis,syndiotactic*-poly(**A$_3$**-*alt*-**B$_5$**). Copolymerization of **A$_1$** and **B$_5$** gives *cis,syndiotactic*-poly(**A$_1$**-*alt*-**B$_5$**) (Figure 11), the proton NMR spectrum of which resembles that of *cis,syndiotactic*-poly(**A$_2$**-*alt*-**B$_2$**) (Figure 5). The second order olefinic proton resonance at 5.33 ppm was shifted to higher frequency with respect to two coupled triplet proton resonances, revealing the resonances for *trans,isotactic* errors. Copolymerization of **A$_3$** with **B$_2$** gave *cis,syndiotactic*-poly(**A$_3$**-*alt*-**B$_2$**) (Figure 12), which contains <10% errors.

It is important to establish whether the tungsten analogue of **1b** (**1b$_w$**) is an equally efficient catalyst. Addition of 50 equiv of *rac*-DCBNBE (DCBNBE = 2,3-dicarbo-*t*-butoxynorbornene) to a toluene solution of **1b$_w$** led to full consumption of the monomer within 10 min. Only two pseudo triplet olefinic proton resonances ($^3J_{HH}$ = 10 Hz) are present in the ^{1}H NMR spectrum

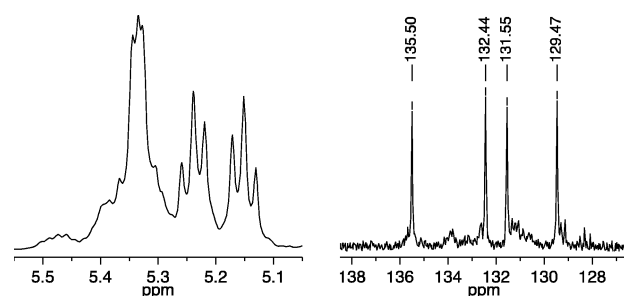**Figure 11.** ^{1}H NMR (500 MHz, CDCl$_3$, left) and ^{13}C NMR (125 MHz, CDCl$_3$, right) spectra of *cis,syndiotactic*-poly(**A$_1$**-*alt*-**B$_5$**) (olefinic resonances only).
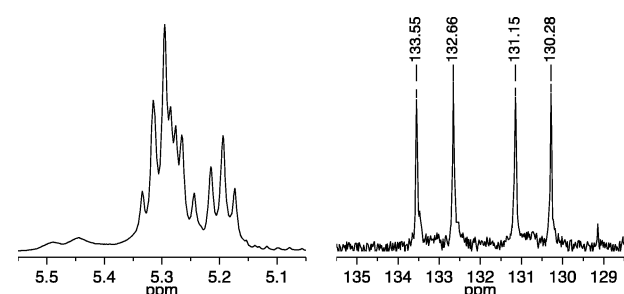

Figure 12. ^{1}H NMR (500 MHz, CDCl$_3$, left) and ^{13}C NMR (125 MHz, CDCl$_3$, right) spectra of *cis,syndiotactic*-poly(**A$_3$**-*alt*-**B$_2$**) (olefinic resonances only).

of the resulting polymer (Figure 13a). The ^{13}C NMR spectrum is also sharp and free of any significant fine structure associated with structural irregularities (see Supporting Information). These results are consistent with a *cis,syndiotactic,alt* structure for the polymer. The two small broad resonances assigned to
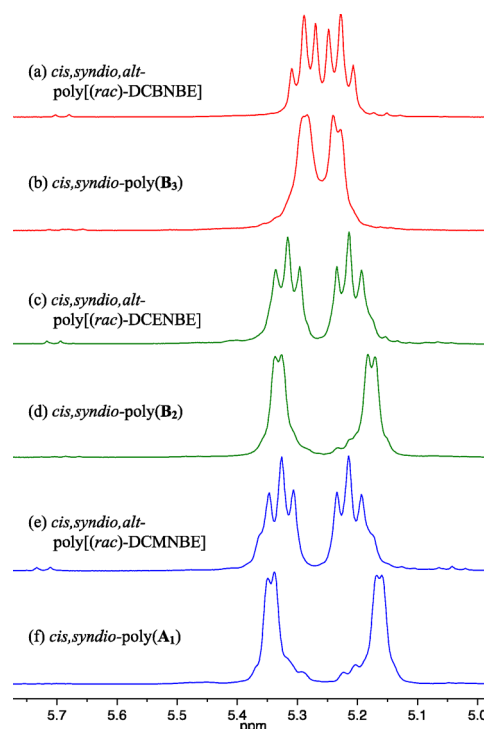

Figure 13. ^{1}H NMR (500 MHz, CDCl$_3$) spectra for *cis,syndiotactic* polymers synthesized using **1b$_w$** (olefinic resonances only).

trans,isotactic dyads, in the olefin region of poly(*rac*-DCBNBE) prepared from **1a**, are absent from the spectrum of poly(*rac*-DCBNBE) prepared from **1b**$_w$. The reason is that polymerization of (*S,S*)-DCBNBE with **1b**$_w$ gives *cis,syndiotactic*-poly[(*S,S*)-DCBNBE] with the ^{1}H NMR spectrum shown in Figure 13b; there is no evidence for a *trans,isotactic* structure. The olefinic proton resonances of *cis,syndiotactic*-poly[(*S,S*)-DCBNBE] are located in the middle of the olefinic proton resonances for poly(*rac*-DCBNBE) (Figure 13a), which makes it difficult to assess the percentage of microstructural errors formed in this copolymer using ^{1}H NMR spectroscopy. However, when racemic DCENBE (DCENBE = 2,3-dicarboethoxynorbornene) and *rac*-DCMNBE are polymerized by **1b**$_w$ under similar conditions, the olefinic proton triplet resonances are broadened, Figures 13c and 13e. The positions of the minor component within the olefinic proton resonances of poly(*rac*-DCENBE) and poly(*rac*-DCMNBE) are visible and can be unambiguously ascribed to *cis,syndiotactic* dyads in the largely *cis,syndiotactic,alt* structure (compare Figures 13c−13e).

As reported previously,[37] (+)-DCMNBE and *rac*-DCMNBE are polymerized at approximately the same rate using W(O)-(CHCMe$_3$)(OHMT)(Pyr)(PMe$_2$Ph). In contrast, (−)-DCBNBE and *rac*-DCBNBE are polymerized at different rates. The sharp olefinic resonances in the ^{1}H and ^{13}C spectra of poly(*rac*-DCBNBE) prepared from **1a** as the initiator are consistent with a lower percentage of *cis,syndiotactic* errors. A similar trend is seen when one inspects the ^{1}H and ^{13}C NMR spectra of poly(*rac*-DCBNBE) using **1b**$_w$ (Figure 13a).

The proton and carbon NMR spectra of the **A**$_3$-*alt*-**B**$_2$ copolymers derived from **1a**, **1b**, and **1b**$_w$ are compared in Figures 14 and 15. Initiators **1b** and **1b**$_w$ appear to yield the

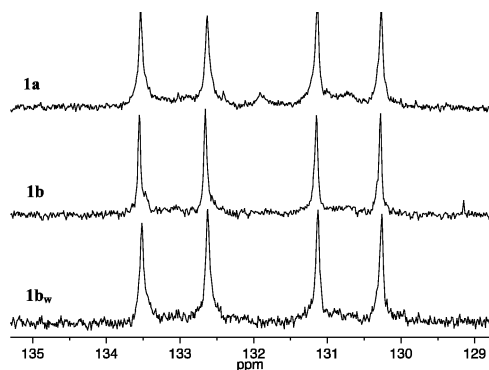**Figure 14.** ^{13}C NMR spectra (125 MHz, CDCl$_3$) of *cis,syndiotactic*-poly(**A**$_3$-*alt*-**B**$_2$) (olefinic resonances only) formed with initiators **1a**, **1b**, and **1b**$_w$.

highest percentages of *cis,syndiotactic* **A**$_3$-*alt*-**B**$_2$ structures with *trans,isotactic* errors being formed when **1b** is employed and *cis,syndiotactic* errors being formed when **1b**$_w$ is employed.

CONCLUSIONS

Cis,syndiotactic **A**-*alt*-**B** copolymers, where **A** and **B** are two enantiomerically pure *trans*-2,3-disubstituted-5,6-norbornenes with "opposite" chiralities, can be prepared with stereogenic-at-metal initiators of the type M(NR)(CHR′)(OHMT)(pyrrolide) (R = 1-adamantyl or 2,6-Me$_2$C$_6$H$_3$; R′ = CMe$_2$Ph; M = Mo or W). The errors when Mo initiators are employed are primarily *trans,isotactic* **AA** and **BB** dyads, while the errors when a W initiator is employed are *cis,syndiotactic* **AA** and **BB** dyads. Formation of a high percentage of alternating **AB** copolymer
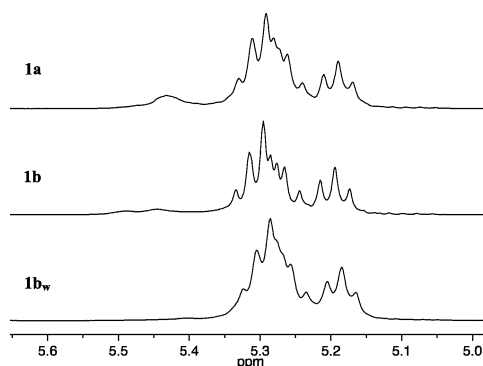
Figure 15. ^{1}H NMR spectra (500 MHz, CDCl$_3$) of *cis,syndiotactic*-poly(**A**$_3$-*alt*-**B**$_2$) (olefinic resonances only) formed with initiators **1a**, **1b**, and **1b**$_w$.

linkages relies on an inversion of chirality at the metal center with each propagating step and faster formation of an **AB** sequence than an **AA** or **BB** sequence as a consequence of a preferred diastereomeric relationship between the chirality at the metal and the chirality of the monomer.

EXPERIMENTAL SECTION

Representative Polymerization. A mixture of 21.0 mg (0.1 mmol, 25 equiv) of **A**$_1$ and 34.6 mg (0.1 mmol, 25 equiv) of **B**$_1$ in 0.5 mL of toluene-d_8 was added to a solution of 3.0 mg (0.004 mmol) of **1b** in 0.5 mL of toluene-d_8. The reaction mixture thickened within seconds. ^{1}H NMR spectroscopy was used to monitor the course of the reaction. Once complete, the reaction mixture was exposed to air and poured into 35 mL of MeOH. The precipitated *cis,syndiotactic*-poly(**A**$_1$**B**$_1$) was allowed to settle. The solvent was decanted, and the polymer was dried *in vacuo*.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acscentsci.6b00200.

Experimental details for all reactions and all supporting NMR characterization of polymers (PDF)

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) Odian, G. *Principles of Polymerization*, 4th ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2004.

(2) Coates, G. W. Precise Control of Polyolefin Stereochemistry Using Single-Site Metal Catalysts. *Chem. Rev.* **2000**, *100*, 1223−1252.

(3) Cheng, M.; Lobkovsky, E. B.; Coates, G. W. Catalytic Reactions Involving C1 Feedstocks: New High-Activity Zn(II)-Based Catalysts for

the Alternating Copolymerization of Carbon Dioxide and Epoxides. *J. Am. Chem. Soc.* **1998**, *120*, 11018−11019.

(4) Super, M.; Berluche, E.; Costello, C.; Beckman, E. Copolymerization of 1,2-Epoxycyclohexane and Carbon Dioxide Using Carbon Diioxide as Both Reactant and Solvent. *Macromolecules* **1997**, *30*, 368−372.

(5) Darensbourg, D. J.; Holtcamp, M. W. Catalytic Activity of Zinc(II) Phenoxides Which Possess Readily Accessible Coordination Sites. Copolymerization and Terpolymerization of Epoxides and Carbon Dioxide. *Macromolecules* **1995**, *28*, 7577−7579.

(6) Vehlow, K.; Wang, D.; Buchmeiser, M. R.; Blechert, S. Alternating Copolymerizations Using a Grubbs-Type Initiator with an Unsymmetrical, Chiral N-Heterocyclic Carbene Ligand. *Angew. Chem., Int. Ed.* **2008**, *47*, 2615−2618.

(7) Song, A.; Parker, K. A.; Sampson, N. S. Synthesis of Copolymers by Alternating ROMP (AROMP). *J. Am. Chem. Soc.* **2009**, *131*, 3444−3445.

(8) Song, A.; Parker, K. A.; Sampson, N. S. Cyclic Alternating Ring-Opening Metathesis Polymerization (CAROMP). Rapid Access to Functionalized Cyclic Polymers. *Org. Lett.* **2010**, *12*, 3729−3731.

(9) Sutthasupa, S.; Shiotsuki, M.; Masuda, T.; Sanda, F. Alternating Ring-Opening Metathesis Copolymerization of Amino Acid Derived Norbornene Monomers Carrying Nonprotected Carboxy and Amino Groups Based on Acid-Base Interaction. *J. Am. Chem. Soc.* **2009**, *131*, 10546−10551.

(10) Nakade, H.; Ilker, M. F.; Jordan, B. J.; Uzun, O.; LaPointe, N. L.; Coughlin, E. B.; Rotello, V. M. Duplex strand formation using alternating copolymers. *Chem. Commun.* **2005**, 3271−3273.

(11) Lichtenheldt, M.; Wang, D.; Vehlow, K.; Reinhardt, I.; Kühnel, C.; Decker, U.; Blechert, S.; Buchmeiser, M. R. Alternating Ring-Opening Metathesis Copolymerization by Grubbs-Type Initiators with Unsymmetrical N-Heterocyclic Carbenes. *Chem. - Eur. J.* **2009**, *15*, 9451−9457.

(12) Vehlow, K.; Lichtenheldt, M.; Wang, D.; Blechert, S.; Buchmeiser, M. R. Alternating Ring-Opening Metathesis Copolymerization of Norborn-2-ene with cis-Cyclooctene and Cyclopentene. *Macromol. Symp.* **2010**, *296*, 44−48.

(13) Ilker, M. F.; Coughlin, E. B. Alternating Copolymerizations of Polar and Nonpolar Cyclic Olefins by Ring-Opening Metathesis Polymerization. *Macromolecules* **2002**, *35*, 54−58.

(14) Bornand, M.; Torker, S.; Chen, P. Mechanistically Designed Dual-Site Catalysts for the Alternating ROMP of Norbornene and Cyclooctene. *Organometallics* **2007**, *26*, 3585−3596.

(15) Romulus, J.; Tan, L.; Weck, M.; Sampson, N. S. Alternating Ring-Opening Metathesis Polymerization Copolymers Containing Charge-Transfer Units. *ACS Macro Lett.* **2013**, *2*, 749−752.

(16) Daeffler, C. S.; Grubbs, R. H. Catalyst-Dependent Routes to Ring-Opening Metathesis Alternating Copolymers of Substituted Oxanorbornenes and Cyclooctene. *Macromolecules* **2013**, *46*, 3288−3292.

(17) Abbas, M.; Wappel, J.; Slugovc, C. Alternating Diene Metathesis Polycondensation (ALTMET) − Opitimizing Catalyst Loading. *Macromol. Symp.* **2012**, *311*, 122−125.

(18) Buchmeiser, M. R.; Ahmad, I.; Gurram, V.; Kumar, P. S. Pseudo-Halide and Nitrate Derivatives of Grubbs andGrubbs-Hoveyda Initiators: Some Structural Features Related to the Alternating Ring-Opening Metathesis Copolymerization of Norborn-2-ene with Cyclic Olefins. *Macromolecules* **2011**, *44*, 4098−4106.

(19) Demel, S.; Slugovc, C.; Stelzer, F.; Fodor-Csorba, K.; Galli, G. Alternating Diene Metathesis Polycondensation (ALTMET) − AVersatile Tool for the Preparation of Perfectly Alternating AB Copolymers. *Macromol. Rapid Commun.* **2003**, *24*, 636−641.

(20) Choi, T.-L.; Rutenberg, I. M.; Grubbs, R. H. Synthesis of A,B-Alternating Copolymers by Ring-Opening-Insertion-Metathesis Polymerization. *Angew. Chem., Int. Ed.* **2002**, *41*, 3839−3841.

(21) Al Samak, B.; Amir-Ebrahimi, V.; Corry, D. G.; Hamilton, J. G.; Rigby, S.; Rooney, J. J.; Thompson, J. M. Dramatic solvent effects on ring-opening metathesis polymerization of cycloalkenes. *J. Mol. Catal. A: Chem.* **2000**, *160*, 13−21.

(22) Konzelman, J.; Wagener, K. B. Acyclic Diene Metathesis (ADMET) Polymerization. Synthesis of Perfectly Alternating Copolymers from a Single Monomer. *Macromolecules* **1996**, *29*, 7657−7660.

(23) Wu, Z.; Grubbs, R. H. Preparation of Alternating Copolymers from the Ring-Opening Metathesis Polymerization of 3-Methylcyclobutene and 3,3-Dimethylcyclobutene. *Macromolecules* **1995**, *28*, 3502−3508.

(24) Ding, L.; Zheng, X.-Q.; Lu, R.; An, J.; Qiu, J. Perfectly AB-alternating copolymers via alternating diene metathesis polymerization: one-step synthesis, characterization and properties. *Polym. Int.* **2014**, *63*, 997−1002.

(25) Tan, L.; Parker, K. A.; Sampson, N. S. A Bicyclo[4.2.0]octene-Derived Monomer Provides Completely Linear Alternating Copolymers via Alternating Ring-Opening Metathesis Polymerization (AROMP). *Macromolecules* **2014**, *47*, 6572−6579.

(26) Lee, H.-K.; Bang, K.-T.; Hess, A.; Grubbs, R. H.; Choi, T.-L. Multiple Olefin Metathesis Polymerization That Combines All Three Olefin Metathesis Transformations: Ring-Opening, Ring-Closing, and Cross Metathesis. *J. Am. Chem. Soc.* **2015**, *137*, 9262−9265.

(27) Elling, B. R.; Xia, Y. Living Alternating Ring-Opening Metathesis Polymerization Based on Single Monomer Additions. *J. Am. Chem. Soc.* **2015**, *137*, 9922−9926.

(28) Tan, L.; Li, G.; Parker, K. A.; Sampson, N. S. Ru-Catalyzed Isomerization Provides Access to Alternating Copolymers via Ring-Opening Metathesis Polymerization. *Macromolecules* **2015**, *48*, 4793−4800.

(29) Schrock, R. R. Synthesis of Stereoregular Polymers through Ring-Opening Metathesis Polymerization. *Acc. Chem. Res.* **2014**, *47*, 2457−2466.

(30) Forrest, W. P.; Weis, J. G.; John, J. M.; Axtell, J. C.; Simpson, J. H.; Swager, T. M.; Schrock, R. R. Stereospecific Ring-Opening Metathesis Polymerization of Norbornadienes Employing Tungsten Oxo Alkylidene Initiators. *J. Am. Chem. Soc.* **2014**, *136*, 10910−10913.

(31) Jeong, H.; John, J. M.; Schrock, R. R.; Hoveyda, A. H. Synthesis of Alternating *trans*-AB Copolymers Employing Ring-Opening Metathesis Polymerization Initiated by Molybdenum Alkylidenes. *J. Am. Chem. Soc.* **2015**, *137*, 2239−2242.

(32) Jeong, H.; Ng, V. W. L.; Börner, J.; Schrock, R. R. Stereoselective Ring-Opening Metathesis Polymerization (ROMP) of Methyl-N-(1-phenylethyl)-2-azabicyclo[2.2.1]hept-5-ene-3-carboxylate by Molybdenum and Tungsten Initiators. *Macromolecules* **2015**, *48*, 2006−2012.

(33) Autenrieth, B.; Jeong, H.; Forrest, W. P.; Axtell, J. C.; Ota, A.; Lehr, T.; Buchmeiser, M. R.; Schrock, R. R. Stereospecific Ring-Opening Metathesis Polymerization (ROMP) of *Endo*-Dicyclopentadiene by Molybdenum and Tungsten Catalysts. *Macromolecules* **2015**, *48*, 2480−2492.

(34) Autenrieth, B.; Schrock, R. R. Stereospecific Ring-Opening Metathesis Polymerization (ROMP) of Norbornene and Tetracyclododecene by Mo and W Initiators. *Macromolecules* **2015**, *48*, 2493−2503.

(35) Hyvl, J.; Autenrieth, B.; Schrock, R. R. Proof of Tacticity of ROMP Polymers Through Post Polymerization Modification. *Macromolecules* **2015**, *48*, 3148−3152.

(36) Flook, M. M.; Ng, V. W. L.; Schrock, R. R. Synthesis of *cis,syndiotactic* ROMP Polymers Containing Alternating Enantiomers. *J. Am. Chem. Soc.* **2011**, *133*, 1784−1786.

(37) Flook, M. M.; Börner, J.; Kilyanek, S.; Gerber, L. C. H.; Schrock, R. R. Five-Coordinate Rearrangements of Metallacyclobutane Intermediates During Ring-Opening Metathesis Polymerization (ROMP) of 2,3-Dicarboalkoxynorbornenes by Molybdenum and Tungsten Monoalkoxide Pyrrolide (MAP) Initiators. *Organometallics* **2012**, *31*, 6231−6243.

(38) Hamilton, J. G.; Ivin, K. J.; Rooney, J. J. ¹³C N.m.r. Spectra of Ring-opened Polymers of 1-Methylbicyclo[2.2.1]hept-2-ene and their Hydrogenated Products *Brit. Br. Polym. J.* **1984**, *16*, 21−33.

(39) Hamilton, J. G.; Ivin, K. J.; Rooney, J. J.; Waring, L. C. Alternating Copolymerization of Enantiomers of 1-Methylbicyclo[2.2.1]hept-2-ene by a Metathesis Catalyst. *J. Chem. Soc., Chem. Commun.* **1983**, 159−161.