Formation of Alternating trans-A-alt-B Copolymers through Ring-Opening Metathesis Polymerization Initiated by Molybdenum Imido Alkylidene Complexes

Formation of Alternating *trans*-**A**-*alt*-**B** Copolymers Through Ring-Opening Metathesis Polymerization Initiated by Molybdenum Imido Alkylidene Complexes

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Abstract

Ring-opening metathesis polymerization (ROMP) is used to prepare *trans*-poly(**A**-*alt*-**B**) polymers from a 1:1 mixture of **A** and **B** where **A** is a cyclic olefin such as cyclooctene ($\mathbf{A_1}$) or cycloheptene ($\mathbf{A_2}$) and **B** is a large norbornadiene or norbornene derivative such as 2,3-dicarbomethoxy-7-isopropylidenenorbornadiene ($\mathbf{B_1}$) or dimethylspirobicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate-7,1'-cyclopropane ($\mathbf{B_2}$). The most successful initiators that were examined are of the type $Mo(NR)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ (R = 2,6-$Me_2C_6H_3$ (**1**) or 2,6-*i*-$Pr_2C_6H_3$ (**2**)). The *trans* configuration of the **AB** linkages is proposed to result from the steric demand of **B**. Both *anti*-**MB** and *syn*-**MB** alkylidenes are observed during the copolymerization, where **B** was last inserted into a Mo=C bond, although *anti*-**MB** dominates as the reaction proceeds. *Anti*-**MB** is *lower* in energy than *syn*-**MB**, does not react readily with *either* **A** or **B**, and interconverts slowly with *syn*-**MB** through rotation about the Mo=C bond. *Syn*-**MB** does not readily react with **B**, but it does react slowly with **A** (rate constant ~1 M^{-1} s^{-1}) to give *anti*-**MA** and one *trans*-**AB** linkage. *Anti*-**MA** then reacts with **B** (rate constant ~300 M^{-1} s^{-1} or larger) to give *syn*-**MB** and the second *trans*-**AB** linkage. The reaction has been modeled using experimental data in order to obtain the estimated rate constants above. The reaction between *anti*-**MA** and **A** is proposed to give rise to **AA** linkages, but **AA** dyads can amount to <5%. Several other possible **A** and **B** monomers, initiators, and conditions were explored.

INTRODUCTION

Copolymers in which monomers **A** and **B** are incorporated in a perfectly *alternating* manner (poly(**A**-*alt*-**B**)) are rare.[1] Two examples are alternating **AB** copolymers formed from CO and olefins[1] or CO_2 and epoxides.[1c-f] In each case one monomer (CO or CO_2) itself is not homopolymerized.

In the last fifteen years ring-opening metathesis polymerization (ROMP) has been employed to make alternating **AB** copolymers.[2] The ideal circumstance for preparing an **AB** copolymer is one in which two monomers that are only slowly homopolymerized undergo cross polymerization. An example is the copolymerization of 1-substituted cyclobutenes and cyclohexene with ruthenium alkylidene initiators;[2a] 1-substituted cyclobutenes are not readily homopolymerized for steric reasons and the free energy for polymerization of cyclohexene is positive, so only one cyclohexene (it is proposed) is incorporated between two units of cyclobutene. Cyclooctene is often partnered with a relatively strained olefin such as a norbornene because "back-biting" to give cyclic oligomers can limit the length of poly(cyclooctene) sequences. Formation of an **AB** copolymer with a single structure via ROMP ideally should also include control of the *cis* or *trans* stereochemistry of the new C=C bonds, but this stereochemical control is rare.[2u] Control of tacticity in an AB copolymer has not been reported. In some variations formation of an **AB** copolymer is a consequence of thermodynamic rather than kinetic control.[2v]

To the best of our knowledge all attempts to prepare **AB** copolymers via ROMP employed Ru-based catalysts[3] before the discovery of the **AB** copolymers formed with molybdenum initiators that are the subject of this paper. An exception is the special case of an alternating copolymer where **A** and **B** are enantiomers.[4] In this case a *racemic* norbornene-like monomer is employed along with an initiator whose four-coordinate metal center inverts with each insertion of each enantiomer of the monomer. The preferential reaction of one configuration of the metal with one enantiomer allows enantiomers to be incorporated alternately to give a polymer with a single, so-called, *cis,syndiotactic,alt* structure. Among the well-defined catalysts, so far only molybdenum initiators yield a polymer with a *cis,syndiotactic,alt* structure. The reason why tungsten analogs of successful molybdenum initiators do not yield *cis,syndiotactic,alt* structures is not yet known.

We recently reported the synthesis of four alternating *trans*-**A**-*alt*-**B** copolymers from one of two large norbornadienes ($\mathbf{B_1}$ or $\mathbf{B_2}$, Figure 1) and either cyclooctene ($\mathbf{A_1}$) or cycloheptene ($\mathbf{A_2}$) where $Mo(NR)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ (R = 2,6-$Me_2C_6H_3$ (**1**) or 2,6-*i*-$Pr_2C_6H_3$ (**2**)) is the initiator.[5] Between 92% and 97% **AB** dyads are formed in the *trans*-**A**-*alt*-**B** copolymer from a 1:1 mixture of **A** and **B**, depending on the specific reaction and conditions employed. In a

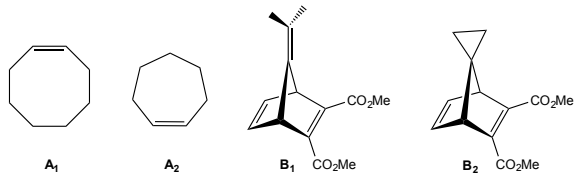


Figure 1. Four monomers used in initial study.

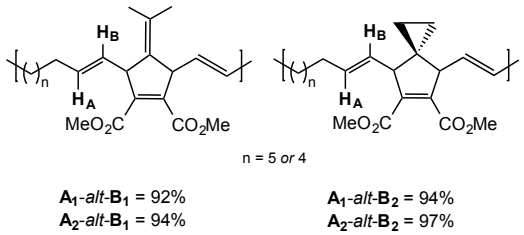


Figure 2. Four copolymers made with initiator **1**.

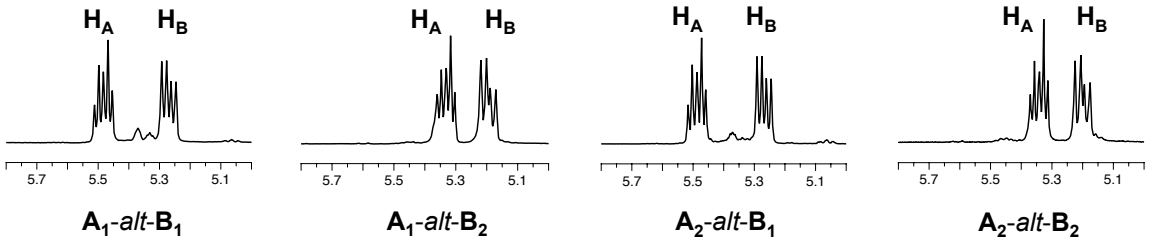


Figure 3. The δ 5.8 to 5.1 ppm region of the ^{1}H NMR spectra for each **A**-*alt*-**B** copolymer made with **1** as the initiator.

typical experiment **A** and **B** (50 equiv of each, 0.4 M in C_6D_6) are consumed to give copolymers after ~2 h. The ^{1}H NMR spectra of these *trans* **A**-*alt*-**B** copolymers contain two olefinic proton resonances; a doublet of triplets for $\mathbf{H_A}$ and a doublet of doublets for $\mathbf{H_B}$ (Figures 2 and 3). The large coupling constant between the olefinic protons ($^3J_{HAHB}$ = ~15.5 Hz) together with a strong IR absorption at ~970 cm^{-1} confirms the presence of *trans* C=C bonds. The resonances that can be ascribed to **AA** olefinic protons (in both *cis* and *trans* dyads) can be observed at 5.33 and 5.38 ppm in the spectra of poly(**A**$_1$-*alt*-**B**$_1$) and poly(**A**$_2$-*alt*-**B**$_1$), but are hidden under the H_A resonance in the spectra of poly(**A**$_1$-*alt*-**B**$_2$) and poly(**A**$_2$-*alt*-**B**$_2$). Integration of the olefinic resonances suggests that the **AA** dyads amount to 92% (**A**$_1$/**B**$_1$), 94% (**A**$_1$/**B**$_2$), 94% (**A**$_2$/**B**$_1$), and 97% (**A**$_2$/**B**$_2$), respectively, in the spectra shown in Figure 3. The precise percentage of **AA** dyads present in a given copolymer varies to some degree with concentration

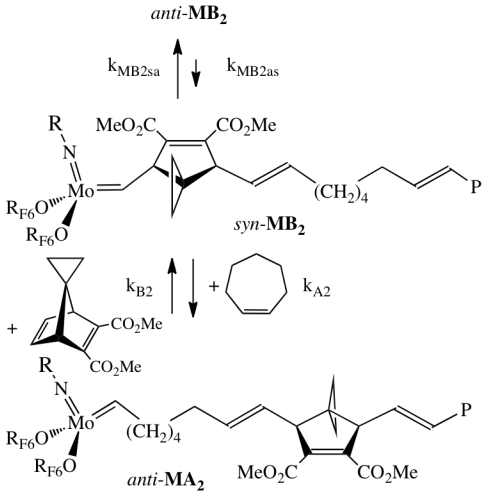


Figure 4. The proposed mechanism to form *trans*-poly(**A**$_2$-*alt*-**B**$_2$).

and temperature. The rate of copolymerization of $\mathbf{A_1}$ and $\mathbf{B_1}$ with **1** is approximately an order of magnitude slower in THF compared to chloroform, benzene, or toluene, as a consequence of competitive binding of THF to *syn* and *anti* propagating species to varying degrees.[5] Polymerizations in THF or other coordinating solvents or in the presence of potential ligands are not discussed in this paper.

Preliminary experiments led us to propose that two propagating species, *syn*-**MB** (in which **B** has inserted last into an M=C bond) and *anti*-**MA** (in which **A** has inserted last into an M=C bond) comprise the core of the mechanism for formation of *trans* **AB** copolymers. The mechanism for copolymerization of $\mathbf{A_2}$ and $\mathbf{B_2}$ is shown in Figure 4. The $\mathbf{A_2}$-*alt*-$\mathbf{B_2}$ copolymer is formed when *syn*-$\mathbf{MB_2}$ reacts with $\mathbf{A_2}$ to give *anti*-$\mathbf{MA_2}$ and one *trans* $\mathbf{A_2B_2}$ linkage, followed by a reaction between *anti*-$\mathbf{MA_2}$ and $\mathbf{B_2}$ to form the other *trans* $\mathbf{A_2B_2}$ linkage and *syn*-$\mathbf{MB_2}$. The *trans* selectivity is proposed to arise as a consequence of the steric demand of $\mathbf{B_2}$. It is proposed that *anti*-$\mathbf{MB_2}$ does not react readily with either $\mathbf{B_2}$ or $\mathbf{A_2}$. *Syn*-$\mathbf{MB_2}$ does not react readily with $\mathbf{B_2}$, but it does react slowly with $\mathbf{A_2}$ to give *anti*-$\mathbf{MA_2}$ and a *trans* $\mathbf{A_2B_2}$ linkage in one of the two reactions in which *trans* $\mathbf{A_2B_2}$ dyads are formed. No $\mathbf{MA_2}$ intermediates are observed.

In this paper we model the reaction to form *trans*-poly($\mathbf{A_2}$-*alt*-$\mathbf{B_2}$) in order to obtain the rate constants k_{B2} and k_{A2} (Figure 4) and explore other **AB** combinations, catalysts, and conditions.

RESULTS AND DISCUSSION

Modeling the formation of poly($\mathbf{A_2}$-*alt*-$\mathbf{B_2}$)

The reaction between $\mathbf{B_2}$ and *syn*-**2** in toluene-d_8 is convenient to study kinetically because *syn*-**2** reacts with around one equivalent of $\mathbf{B_2}$ to yield the *trans* first-insertion product, $\mathbf{MB_{2t}}$, relatively cleanly; homopolymerization of $\mathbf{B_2}$ is very slow. $\mathbf{MB_{2t}}$ can be isolated and characterized;[5] it is primarily (95%) the *anti* isomer at equilibrium. Usually a *syn* alkylidene isomer is more stable than an *anti* isomer in an imido alkylidene complex of Mo or W with K_{eq} ($K_{eq} = k_{as}/k_{sa}$ where k_{as} is the rate constant for conversion of *anti* to *syn*, and k_{sa} the reverse) being over a thousand.[6] We ascribe the lower energy of *anti*-$\mathbf{MB_{2t}}$ relative to *syn*-$\mathbf{MB_{2t}}$ to the steric demand of the alkylidene substituent derived from $\mathbf{B_2}$ in *syn*-$\mathbf{MB_{2t}}$. Since the rate of reaction of $\mathbf{B_2}$ with *syn*-**2** does not depend upon the concentration of $\mathbf{B_2}$ in the range of 5 - 30 times the concentration of *syn*-**2**, it was proposed that only *anti*-**2** reacts with $\mathbf{B_2}$.[5] Monitoring the reaction between *syn*-**2** and 0.4 equiv of $\mathbf{B_2}$ over a period of ~10,000 s by proton NMR revealed that *syn*-$\mathbf{MB_{2t}}$ is formed first and then begins to be converted to *anti*-$\mathbf{MB_{2t}}$ as $\mathbf{B_2}$ is consumed and *syn*-**2** is partially consumed (Figure 5). Therefore, we propose that the mechanism of the reaction between syn-**2** and $\mathbf{B_2}$ is one in which *syn*-**2** must first form *anti*-**2** through rotation of the alkylidene (eq 1), *anti*-**2** reacts with $\mathbf{B_2}$ to yield *syn*-$\mathbf{MB_{2t}}$ (eq 2), and *syn*-$\mathbf{MB_{2t}}$ then is converted

to *anti*-$\mathbf{MB_{2t}}$ through alkylidene rotation (eq 3). The reaction between *anti*-**2** and $\mathbf{B_2}$ (eq 2) is a model for the proposed reaction between *anti*-$\mathbf{MA_2}$ and $\mathbf{B_2}$ in an actual copolymerization. It has been noted in the literature that initiation of *homopolymerization* of 1,7,7-trimethylbicyclo[2.2.1]hept-2-ene (in either *rac* or (-) form) requires a rate-limiting conversion of the *syn* alkylidene isomer of **2** to the *anti* alkylidene isomer.[7]

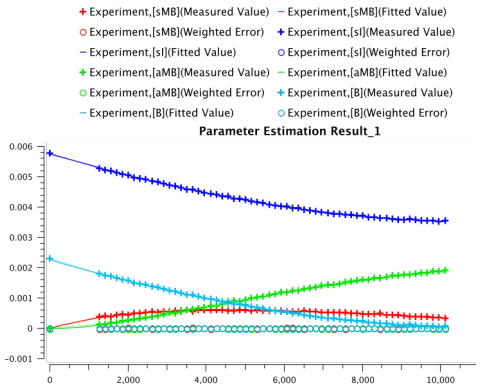
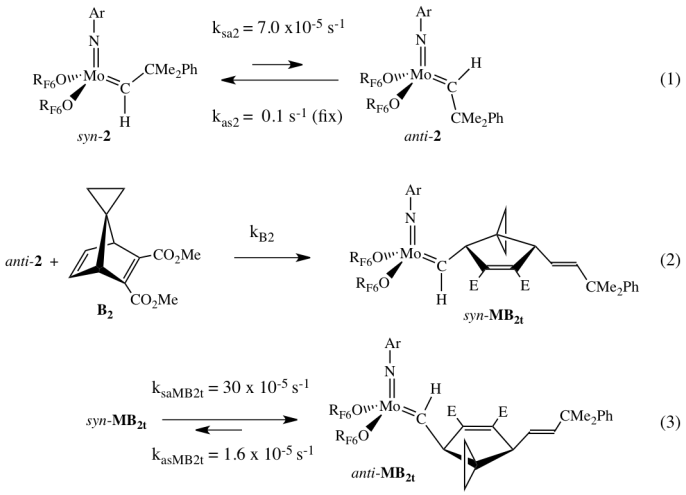


Figure 5. The experimental and modeled reaction of *syn*-**2** with ~0.4 equiv of $\mathbf{B_2}$.



The rate constants for interconversion of *syn*-**2** and *anti*-**2** were determined in 1993.[6] The rate constant for conversion of *anti*-**2** to *syn*-**2** (k_{as2}) was found to be 0.10 s^{-1} at 22 °C through extrapolation of values obtained at lower temperatures in an Eyring plot. From the equilibrium constant at 22 °C in tol-d_8 (k_{as2}/k_{sa2} = 1400) k_{sa2} was then estimated to be $7.0x10^{-5}$ s^{-1}. These two rate constants are probably accurate to ±5% at best. The ratio of *anti*-$\mathbf{MB_{2t}}$ to *syn*-$\mathbf{MB_{2t}}$ at equilibrium can be estimated by proton NMR to be ~95:5. Finally, photolysis of *syn*-**2** at -78 °C yielded a mixture of *anti*-**2** (40%) and *syn*-**2**, which upon treatment with 0.4 equiv of $\mathbf{B_2}$ at low temperature produced a mixture of *syn*-**2** and *syn*-$\mathbf{MB_{2t}}$, the latter of which contains a *trans* C=C bond (see SI). This result proves that *anti*-**2** reacts much more readily with $\mathbf{B_2}$ than *syn*-**2** reacts with $\mathbf{B_2}$, and that exclusively a *trans* C=C bond is formed as a product. Similar results were found in previous studies for 5,6-bistrifluoromethylnorbornadiene.[6] The relatively slow conversion of *syn*-$\mathbf{MB_{2t}}$ to *anti*-$\mathbf{MB_{2t}}$ was then followed at 22 °C in order to obtain k_{saMB2t} = $30x10^{-5}$ s^{-1}. Therefore, k_{asMB2t} can be calculated to be $1.6x10^{-5}$ s^{-1}, assuming that the ratio of *anti*-$\mathbf{MB_{2t}}$ to *syn*-$\mathbf{MB_{2t}}$ is 95:5 at equilibrium. We ascribe the relatively slow rates of interconversion of *syn*-$\mathbf{MB_{2t}}$ and *anti*-$\mathbf{MB_{2t}}$ in each direction to the large substituent in the alkylidene derived from $\mathbf{B_2}$. The only rate constant in equations 1-3 for which no experimental data are available is k_{B2}, which would appear to be relatively large since the reaction shown in equation 2 is "fast." In

fact, to our knowledge no rate constant for a "fast" reaction between an *anti*-alkylidene and a norbornene-like substrate has been measured.

Table 1. The results of modeling the reaction between *syn*-**2** and $\mathbf{B_2}$.

[$\mathbf{B_2}$] (M)	k_{as2} [b]	k_{sa2} [a,b]	k_{asMB2t} [a,b]	k_{saMB2t} [a,b]	k_{B2} [c]
initial values	0.10	7.0	1.6	30	unknown
0.4x[**2**]	0.10	7.50(4)	2.00(10)	43.3(2)	282(8)
0.5x[**2**]	0.10	8.22(13)	2.88(24)	42.9(6)	264(18)

[a] All x 10^{-5} [b]Units are s^{-1}. [c] Units are M^{-1} s^{-1}

The experimental data in Figure 5 were fit using the Levenberg-Marquardt method in COPASI, as described in the Supporting Information. An analogous reaction between *syn*-**2** and $\mathbf{B_2}$ (0.5 equiv) was similarly followed and modeled (see SI). Four of the values in Table 1 were treated as variables while k_{as2} was fixed at 0.10 s^{-1}. Rate constant k_{as2} has to be fixed in order to obtain a value for k_{B2} because k_{as2} and k_{B2} are correlated as a consequence of the fact that *anti*-**2** is either converted to *syn*-**2** (eq 1) or reacts with $\mathbf{B_2}$ (eq 2). The values obtained for k_{sa2}, k_{asMB2t}, and k_{saMB2t} in the modeling study are close to the initial values found through the studies described above; they are shown in Table 1 as "initial values". In the modeling study the *minimum acceptable* value for k_{B2}, the bimolecular rate constant for the reaction between *anti*-**2** and $\mathbf{B_2}$, was found to be ~300 M^{-1} s^{-1}. Use of larger, fixed values for k_{B2} led to no changes in the values for k_{sa2}, k_{asMB2t}, and k_{saMB2t} shown in Table 1. Therefore, we can conclude that k_{B2} is ~300 M^{-1} s^{-1} *or larger*. The minimum error in this k_{B2} could easily be ± 50 M^{-1} s^{-1}.

If we treat k_{sa2} (eq 1) as an unknown in a model in which an irreversible, rate-limiting *syn*-**2** to *anti*-**2** conversion is followed by a rapid and irreversible reaction between *anti*-**2** and $\mathbf{B_2}$, the resulting values that are obtained for k_{sa2} are the same as those shown in Table 1. An irreversible rate-limiting step followed by a rapid formation of product is the source of the large uncertainty in k_{B2}.

The proposed mechanism of copolymerization of $\mathbf{A_2}$ and $\mathbf{B_2}$ by initiator **2** is shown in Figure 4. We know that k_{B2} for the reaction between *anti*-**2** and $\mathbf{B_2}$ ~300^{-1} s^{-1} *or larger* (Table 1). The minimum value for k_{B2} for the reaction between *anti*-$\mathbf{MA_2}$ and $\mathbf{B_2}$ should be significantly greater than 300 M^{-1} s^{-1} in view of what is likely to be a higher reactivity for a relatively small (near the metal) *anti* alkylidene versus an *anti* neophylidene complex (see Figure 4); therefore we employed (arbitrarily) a fixed value of k_{B2} = 700 M^{-1} s^{-1} for modeling the reaction between *anti*-$\mathbf{MA_2}$ and $\mathbf{B_2}$ in an actual copolymerization. In order to account for formation of $\mathbf{A_2A_2}$ linkages, the four ways to form $\mathbf{A_2A_2}$ linkages (*cis* or *trans*) plus the equilibrium between *syn*-$\mathbf{MA_2}$ and *anti*-$\mathbf{MA_2}$ were added to the simulation (see SI). The consumption of $\mathbf{A_2}$ (15 or 35

equiv) and $\mathbf{B_2}$ (15 or 35 equiv) in the presence of $\mathbf{MB_{2t}}$ as the initiator was followed and fit to the model as described in the SI using the Levenberg-Marquardt method in COPASI. The reaction of *anti*-$\mathbf{MA_2}$ with $\mathbf{A_2}$ to give *anti*-$\mathbf{MA_2}$ or *syn*-$\mathbf{MA_2}$ and *cis* or *trans* homopolymer (HP) linkages, respectively, reproduced the experimental results. All rate constants were treated as unknowns except k_{B2}. The second order rate constant (k_{A2}) for the reaction of *syn*-$\mathbf{MB_2}$ with $\mathbf{A_2}$ was found to have a value of ~1 M^{-1} s^{-1} for both runs (see SI for details.) Following only the consumption of $\mathbf{A_2}$ and $\mathbf{B_2}$ is inadequate to determine the number of unknowns in the simulation, in part since the formation of $\mathbf{A_2A_2}$ (HP) linkages is only ~4% in this model (see SI). The time course for consumption of $\mathbf{A_2}$ and $\mathbf{B_2}$ and formation of $\mathbf{A_2B_2}$ (CP) and $\mathbf{A_2A_2}$ (HP) linkages shown in the SI (Figures S5 and S7) is a relatively accurate description of a typical formation of >96% poly(**A**-*alt*-**B**). The main conclusion is that the rate constant (if k_{B2} = 700) for the reaction of *anti*-$\mathbf{MA_2}$ and $\mathbf{B_2}$ is at least ~700 times the value for the rate constant (k_{B2} ~1) for the reaction of *syn*-$\mathbf{MB_2}$ with $\mathbf{A_2}$. The success of formation of *trans*-poly($\mathbf{A_2}$-*alt*-$\mathbf{B_2}$), and the three other alternating copolymers explored initially clearly depends upon the relatively selective reactions between *anti*-$\mathbf{MA_2}$ with $\mathbf{B_2}$ to give *syn*-$\mathbf{MB_2}$ and a *trans* $\mathbf{A_2B_2}$ linkage and that between *syn*-$\mathbf{MB_2}$ and $\mathbf{A_2}$ to give *anti*-$\mathbf{MA_2}$ and a *trans* $\mathbf{B_2A_2}$ (= $\mathbf{A_2B_2}$) linkage. This model is the simplest possible. It does not include any reversibility of the formation of **AA** linkages ("back-biting") or the formation of **AAA** linkages, etc., or ways of forming **AA** linkages other than in the non-stereoselective reaction of *anti*-$\mathbf{MA_2}$ with $\mathbf{A_2}$.

Studies relevant to the formation of poly($\mathbf{A_1}$-*alt*-$\mathbf{B_1}$)

Initiators **1** and **2** behave similarly in copolymerizations, but **1** reacts differently with $\mathbf{B_1}$ than **2** reacts with $\mathbf{B_2}$. The differences between **1** and **2** are subtle. (All details can be found in the SI.)

A solution of **1** in toluene-d_8 was photolyzed at 350 nm for 3 h at –78 °C. A new resonance at 13.02 ppm ($^1J_{CH}$ = 156 Hz; 45%) that was observed in the ^{1}H NMR spectrum at –50 °C was assigned to *anti*-**1** on the basis of the large value for $^1J_{CH}$ compared to $^1J_{CH}$ for the *syn* isomer (at 12.02 ppm, $^1J_{CH}$ = 122 Hz). The conversion of *anti*-**1** to *syn*-**1** above –50 °C was followed versus an internal standard at four temperatures over a 15 °C range to obtain four values for k_{as1} at those temperatures. An Eyring plot led to values for $\Delta H^{\ddagger}$ (17.1 kcal/mol) and $\Delta S^{\ddagger}$ (-7.4 eu) and a calculated value for $\Delta G^{\ddagger}_{298}$ at 22 °C (19.3 kcal/mol) and a k_{as1} at room temperature of 0.045 s^{-1}. K_{eq1} (= k_{as1}/k_{sa1}) was determined to be 1400 through integration of the resonances for *syn* and *anti* at room temperature. These values should be compared with those for **2** ($\Delta H^{\ddagger}$ = 18.3 kcal/mol, $\Delta S^{\ddagger}$ = -2 eu, $\Delta G^{\ddagger}_{298}$ = 18.3 kcal/mol), and K_{eq2} = 1400, respectively).[6] The value for k_{sa2} at room temperature was calculated to be 3.2 x 10^{-5} s^{-1} employing the value for K_{eq2}. The values for k_{as1} (0.045 s^{-1}) and k_{sa2} (3.2 x 10^{-5} s^{-1}) compared to k_{as1} (0.10 s^{-1}) and k_{sa1} (7 x 10^{-5} s^{-1}) suggest that *anti*-

1 and *syn*-**1** interconvert at about half the rate that *anti*-**2** and *syn*-**2** interconvert, but K_{eq1} and K_{eq2} are the same (1400).

When 0.7 – 0.8 equivalents of $\mathbf{B_1}$ were added to a toluene solution of **1** at room temperature, $\mathbf{B_1}$ was fully consumed within 20 minutes. Two doublets ($^3J_{HH}$ of 3.3 Hz and 7.6 Hz) were observed in the alkylidene region of the proton NMR spectrum. Two olefinic proton resonances were observed for two isomers having *cis* C=C stereochemistry, *not trans*, according to the value for $^3J_{HH}$ (12 Hz). With the aid of ^{1}H-^{1}H COSY and ^{1}H-^{13}C HSQC, individual olefinic resonances were found to arise from *syn* and *anti* isomers of the first insertion product. The major isomer ($^3J_{HH}$ of 3.3 Hz) was found to have $^1J_{CH}$ = 157 Hz and therefore was assigned to be *anti*-$\mathbf{MB_{1}}_{cis}$, while the minor isomer ($^3J_{HH}$ of 7.6 Hz) was assigned to be *syn*-$\mathbf{MB_{1}}_{cis}$. At room temperature, *anti*-$\mathbf{MB_{1}}_{cis}$ and *syn*-$\mathbf{MB_{1}}_{cis}$ slowly reached equilibrium and K_{eqMB1} (=[*syn*-$\mathbf{MB_{1}}_{cis}$]/[*anti*-$\mathbf{MB_{1}}_{cis}$]) was found to be 5/95, the same as K_{eqMB2} (*vide supra*). We propose that *syn*-$\mathbf{MB_{1}}_{cis}$ results from the reaction between *syn*-**1** and $\mathbf{B_1}$, while *anti*-$\mathbf{MB_{1}}_{cis}$, the minor product, results from isomerization of *syn*-$\mathbf{MB_{1}}_{cis}$ to *trans*-$\mathbf{MB_{1}}_{cis}$. We propose that the smaller imido group in *syn*-**1** is why the major first-insertion product is *syn*-$\mathbf{MB_{1}}_{cis}$.

When $\mathbf{B_1}$ (0.45 equiv) in a toluene-d_8 solution was added to a mixture of *syn*-**1** and *anti*-**1** at −50 °C, complete consumption of *anti*-**1** was observed after 10 minutes according to ^{1}H NMR spectra. Approximately 30% of *anti*-**1** was converted back to *syn*-**1** after 10 minutes at −15 °C, so consumption of *anti*-**1** at −50 °C results mainly from the reaction of *anti*-**1** with $\mathbf{B_1}$. In the alkylidene region, the *syn*-$\mathbf{MB_{1}}_{trans}$ isomer of the first insertion product was formed, as confirmed by the coupling constants of the alkylidene and the olefinic protons. When the temperature was raised to −40 °C, *syn*-**1** started to react with $\mathbf{B_1}$ to form *syn*-$\mathbf{MB_{1}}_{cis}$. At −10 °C, the two overlapping alkylidene peaks of *syn*-$\mathbf{MB_{1}}_{cis}$ and *syn*-$\mathbf{MB_{1}}_{trans}$ could be observed in the proton NMR spectrum. All assignments were determined through ^{1}H-^{1}H COSY experiments. All details can be found in the SI.

From the above experiments we conclude that *anti*-**1** reacts with $\mathbf{B_1}$ at low temperatures to give *syn*-$\mathbf{MB_{1}}_{trans}$ much more rapidly than *syn*-**1** reacts with $\mathbf{B_1}$ to give *syn*-$\mathbf{MB_{1}}_{cis}$, consistent with approach of $\mathbf{B_1}$ to both *syn*-**1** and *anti*-**1** with the cage pointing toward the imido ligand. However, *at 22 °C* the opposite is found; *syn*-**1** reacts with $\mathbf{B_1}$ to give *syn*-$\mathbf{MB_{1}}_{cis}$. Therefore the reaction of *syn*-**1** with $\mathbf{B_1}$ at 22 °C is *not* a good model for a copolymerization reaction of $\mathbf{A_1}$ and $\mathbf{B_1}$ by initiator **1**. It should be noted that the crystallographically characterized first-insertion product of the reaction of $\mathbf{B_1}$ with *syn*-Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$ has a *syn*,*trans* geometry,[8] which *suggests* (but does not prove) that the *syn* first-insertion product arises through a reaction between $\mathbf{B_1}$ and *anti*-Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$.[9] The *syn* first-insertion product derived from Mo(NAr)(CH-*t*-Bu)(O-*t*-Bu)$_2$ and $\mathbf{B_1}$ does *not* react further with $\mathbf{B_1}$, even at 50 °C. Initiator **1** *does* polymerize 50 equivalents of $\mathbf{B_1}$ (>96% conversion after 24 h) at 22 °C, but the isolated

polymer is not stereoregular. Polymerization of $\mathbf{B_1}$ is slow compared to the timescale of a copolymerization of $\mathbf{A_1}$ and $\mathbf{B_1}$ by *syn*-**1**, which is why the resulting *trans*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_1}$) has few, if any, $\mathbf{B_1B_1}$ errors. It is important to note that even though *syn*-**1** reacts with $\mathbf{B_1}$ to give *syn*-$\mathbf{MB_{1}}_{cis}$ at 22 °C (*vide infra*), only *anti*-$\mathbf{MA_1}$ is present as an intermediate under catalytic conditions and it is proposed to react with $\mathbf{B_1}$ to give *syn*-$\mathbf{MB_1}$ that contains a *trans* C=C linkage before any *syn*-$\mathbf{MA_1}$ can form.

Formation of $\mathbf{A_1}$-*alt*-$\mathbf{B_1/B_2}$, $\mathbf{A_2}$-*alt*-$\mathbf{B_1/B_2}$, $\mathbf{A_1/A_2}$-*alt*-$\mathbf{B_1}$, $\mathbf{A_1/A_2}$-*alt*-$\mathbf{B_2}$ and $\mathbf{A_1/A_2}$-*alt*-$\mathbf{B_1/B_2}$ copolymers

The initial studies suggest that $\mathbf{B_1}$ and $\mathbf{B_2}$ behave similarly and $\mathbf{A_1}$ and $\mathbf{A_2}$ behave similarly in forming the four possible stereoregular alternating **AB** copolymers. Therefore three, or even all four monomers, can be employed to make copolymers in which $\mathbf{A_1}$, $\mathbf{A_2}$, $\mathbf{B_1}$, and $\mathbf{B_2}$ are (it is proposed) randomly distributed within the polymer microstructures, but *trans*-$\mathbf{A_x}$-*alt*-$\mathbf{B_y}$ dyad relationships are maintained (Figure 6). For example, polymerization of 50 equivalents of $\mathbf{A_1}$ using initiator **1** (0.2 M in $CDCl_3$), 25 equivalents of $\mathbf{B_1}$, and 25 equivalents of $\mathbf{B_2}$ produced a $CDCl_3$-soluble copolymer within 2h at 22 °C in which both *trans* copolymer dyads could be observed (Figure 6). The remaining three combinations ($\mathbf{A_2}$-*alt*-$\mathbf{B_1/B_2}$, $\mathbf{A_1/A_2}$-*alt*-$\mathbf{B_1}$, and $\mathbf{A_1/A_2}$-*alt*-$\mathbf{B_2}$) produced similar copolymers (Figure 6). The patterns for $\mathbf{H_{A1}}$ and $\mathbf{H_{A2}}$ overlap essentially completely in the spectra for $\mathbf{A_1/A_2}$-*alt*-$\mathbf{B_1}$ and $\mathbf{A_1/A_2}$-*alt*-$\mathbf{B_2}$ in Figure 6, but those for $\mathbf{H_{B1}}$ and $\mathbf{H_{B2}}$ are separated. Overlap of $\mathbf{H_{A1}}$ and $\mathbf{H_{A2}}$ patterns accounts for the slightly lower fidelity in the $\mathbf{H_{A1}}$ and $\mathbf{H_{A2}}$ patterns when both $\mathbf{A_1}$ and $\mathbf{A_2}$ are present. An equimolar mixture of $\mathbf{A_1}$:$\mathbf{A_2}$:$\mathbf{B_1}$:$\mathbf{B_2}$ (0.2 M in $CDCl_3$) can be polymerized to yield a polymer whose ^{1}H NMR spectrum is a combination of those obtained for the $\mathbf{A_1}$-*alt*-$\mathbf{B_1/B_2}$ and $\mathbf{A_2}$-*alt*-$\mathbf{B_1/B_2}$ copolymers (top of Figure 6).

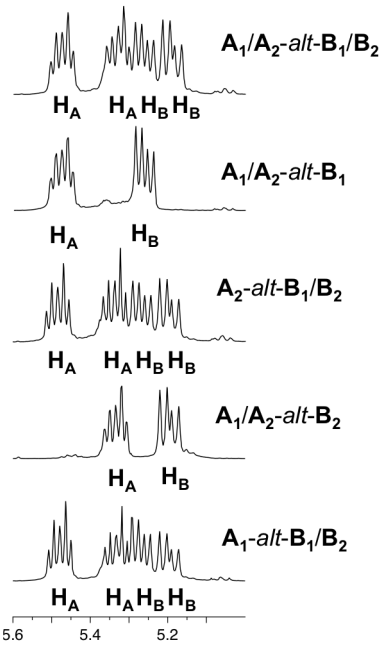


Figure 6. The ^{1}H NMR spectra between 5.2 and 5.5 ppm of $\mathbf{A_1}$-*alt*-$\mathbf{B_1/B_2}$, $\mathbf{A_2}$-*alt*-$\mathbf{B_1/B_2}$, $\mathbf{A_1/A_2}$-*alt*-$\mathbf{B_1}$, and $\mathbf{A_1/A_2}$-*alt*-$\mathbf{B_2}$ prepared using **1**.

"Sequence editing" in copolymerizations to give alternating **AB** copolymers has been reported in the literature for some ruthenium-initiated copolymerizations, *i.e.*, cyclooctene is largely polymerized first and then "edited" down to some relatively short sequence before the

norbornene-like monomer irreversibly reacts with the **MA** alkylidene to form an **AB** linkage.[10,11] $\mathbf{A_1}$ (25 equiv) was added **1** to give poly$\mathbf{A_1}$, followed by addition of $\mathbf{B_1}$ (25 equiv). Five days later, virtually no high quality (>90%) *trans*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_1}$) was observed. Therefore, sequence editing is not a competitive pathway on the time scale of an $\mathbf{A_1}$/$\mathbf{B_1}$/**1** copolymerization in this system in toluene-d_8.

Synthesis of other *trans* $\mathbf{A_1B_y}$ copolymers

Other $\mathbf{A_1B_y}$ combinations were found to yield copolymers with ≥ 80% alternating $\mathbf{A_1B_y}$ linkages, as shown in Figure 7. The most successful were $\mathbf{B_3}$, $\mathbf{B_4}$, and $\mathbf{B_5}$, which are close relatives of $\mathbf{B_2}$. Formation of copolymer from $\mathbf{A_1}$ and $\mathbf{B_6}$ was relatively slow, with three days being required to form ~90% *trans* $\mathbf{A_1B_6}$ linkages. Repeating the copolymerization of $\mathbf{A_1}$ and $\mathbf{B_6}$ at 50 °C for 8 h resulted in the total consumption of $\mathbf{A_1}$ with little copolymer formation. Heating this sample (24 h at 50 °C) resulted in polymerization of the remaining $\mathbf{B_6}$, but still little copolymer was formed. These observations also rule out "editing" of poly(cyclooctene) sequences as the major mechanism of forming $\mathbf{A_1B_6}$ linkages. We ascribe the relatively high percentage of $\mathbf{A_1A_1}$ dyads in *trans*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_9}$) to the slower reaction of $\mathbf{B_9}$ with *anti*-$\mathbf{MA_1}$ than $\mathbf{B_1}$ with *anti*-$\mathbf{MA_1}$ for electronic reasons.

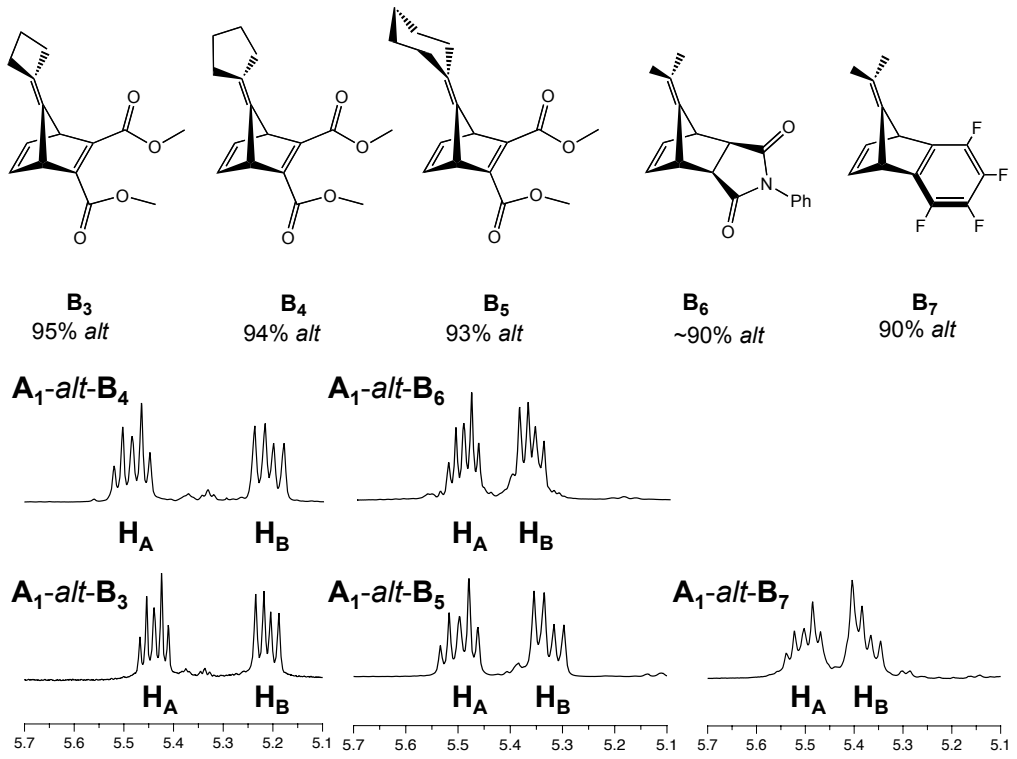


Figure 7. Proton ^{1}H NMR spectra between 5.60 and 5.15 ppm of $\mathbf{A_1}$-*alt*-$\mathbf{B_x}$ prepared using **1** as an initiator.

Rac-$\mathbf{B_8}$ (Figure 8) has been copolymerized with cyclooctene by ruthenium initiators to give a copolymer that contains a mixture of *cis* and *trans* double bonds.[2] The copolymer prepared using Grubbs 1st generation initiator (82% yield, 73% $\mathbf{A_1}$-*alt*-$\mathbf{B_8}$) could be improved to ~90% $\mathbf{A_1}$-*alt*-$\mathbf{B_8}$ employing a modified Grubbs 2nd generation initiator. The polymerization of 100 equivalents of $\mathbf{A_1}$ and $\mathbf{B_8}$ (0.1 M in $CDCl_3$) by **1** was complete within 2 h at 22 °C to yield a $CDCl_3$-soluble, yellow polymer. The ^{1}H NMR spectrum of isolated of $\mathbf{A_1}$-*alt*-$\mathbf{B_8}$ showed four resonances in the olefinic region; a doublet for $\mathbf{H_{A'}}$ at 5.72 ppm, a double doublet for $\mathbf{H_A}$ at 5.64 ppm, and a pair of overlapping multiplets for $\mathbf{H_B}$ and $\mathbf{H_{B'}}$ at 5.80 and 5.87 ppm, respectively (Figure 9). The coupling between $\mathbf{H_{A'}}$ and $\mathbf{H_{B'}}$ was found to be ~15 Hz characteristic of *trans* C=C bonds. The methine proton resonance in the polymer was located at 4.74 ppm. All assignments were corroborated through ^{1}H COSY and HSQC NMR experiments. The relatively simple and sharp ^{1}H and ^{13}C NMR resonances for poly($\mathbf{A_1}$-*alt*-$\mathbf{B_8}$) are consistent with a *trans* head-to-tail polymer having $\mathbf{A_1B_8}$ linkages in excess of 85% and essentially only *trans* C=C

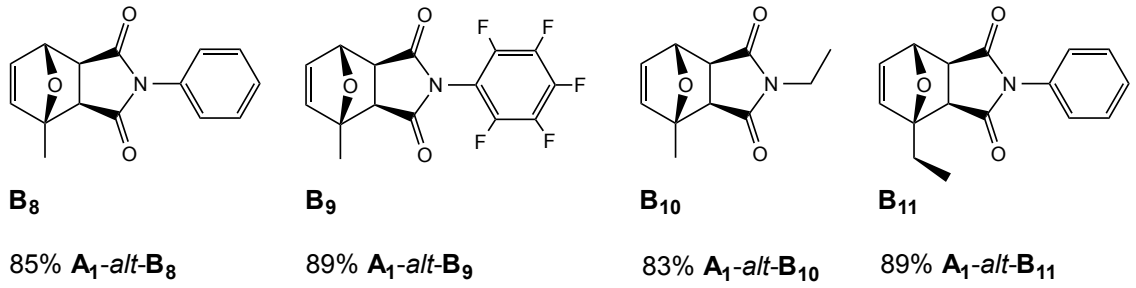


Figure 8. ^{1}H NMR spectra from 6.0 to 5.4 ppm of $\mathbf{A_1}$-*alt*-$\mathbf{B_x}$ prepared using **1** as an initiator.

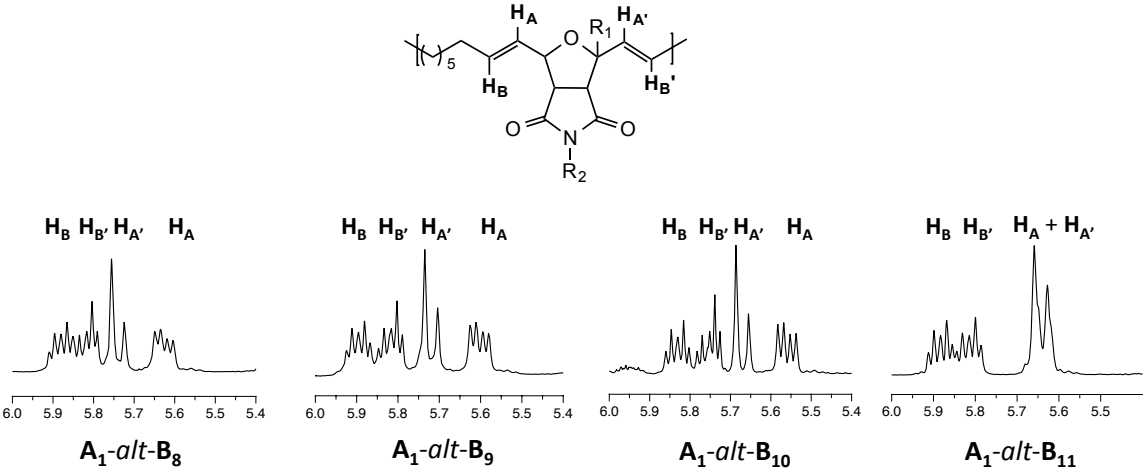


Figure 9. ^{1}H NMR spectra from 6.0 to 5.4 ppm of $\mathbf{A_1}$-*alt*-$\mathbf{B_x}$ prepared using **1** as an initiator.

bonds. Copolymerization of *rac*-$\mathbf{B_8}$ with cyclooctene was impractically slow under conditions where *rac*-$\mathbf{B_8}$ was copolymerized. We assume that the enantiomers of $\mathbf{B_8}$ are incorporated randomly in poly($\mathbf{A_1}$-*alt*-$\mathbf{B_8}$) and related copolymers.

Monomer $\mathbf{B_9}$ was only slightly more selective towards the formation of **AB** linkages than $\mathbf{B_8}$ and $\mathbf{B_{10}}$ (89%, 85% and 83% **A**-*alt*-**B**, respectively). A copolymer with 89% $\mathbf{A_1B_{11}}$ linkages was formed when $\mathbf{B_{11}}$ was employed as a monomer. The ^{1}H NMR spectrum of poly($\mathbf{A_1}$-*alt*-$\mathbf{B_{11}}$) contained resonances for the two $\mathbf{H_A}$ protons ($\mathbf{H_A}$ and $\mathbf{H_{A'}}$) at 5.63 ppm and a pair of multiplets for $\mathbf{H_B}$ and $\mathbf{H_{B'}}$ at 5.80 and 5.87 ppm, respectively, a proposal that is supported by *g*COSY experiments.

Catalyst screening and other experiments

Copolymerizations involving equal amounts of $\mathbf{A_2}$ and $\mathbf{B_2}$ were chosen in order to ascertain the efficienty of initiators **3-13** (Figure 10).

Compound **4**,[12] a tungsten analog of **1**, led to no appreciable consumption of $\mathbf{A_2}$ and $\mathbf{B_2}$ after 24 h. The polymer that could be observed after several days appeared to be an intractable mixture of copolymer and homopolymer dyads of $\mathbf{A_2}$ and $\mathbf{B_2}$.

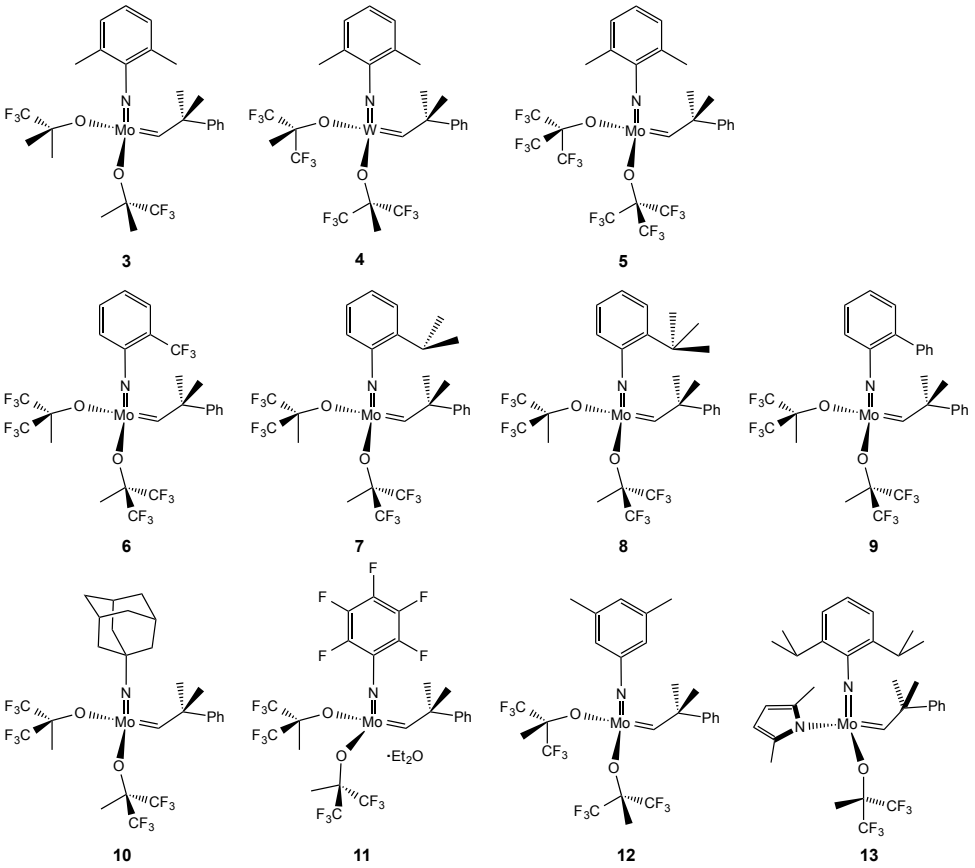


Figure 10. Initiators **3** - **13** explored for *alt*-ROMP using $\mathbf{A_2}$ and $\mathbf{B_2}$ as monomers.

Initiators **3**[4] and **5** were less selective than **1** towards *alt*-ROMP. The $\mathbf{F_9}$ initiator (**5**) yielded more *cis* linkages, while the $\mathbf{F_3}$ initiator (**3**) was more *trans* selective and more active towards the homopolymerization of $\mathbf{B_2}$ (Figure 11 and Table 2). Transferring the steric bulk from the *ortho* to the *meta* positions of the *N*-phenyl imido ligand (in the form of a 3,5-dimethylphenylimido ligand in **12**) increased the % *cis* dyads (Table 2).[13] A similar effect was observed using mono-*o*-substituted *N*-phenyl imido ligands. The % *trans* dyads increased as the size of the 2-substituent increased from trifluoromethyl to *t*-butyl. These screening results

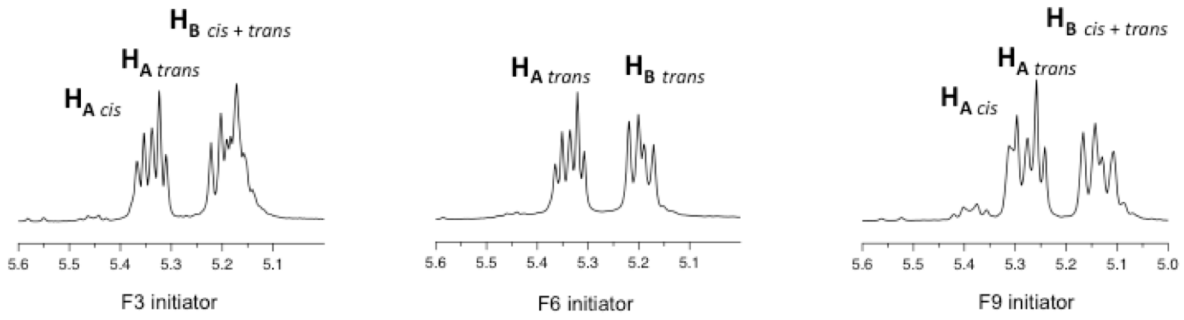


Figure 11. ^{1}H NMR spectra from 5.6 to 5.0 ppm of $\mathbf{A_2}$-*alt*-$\mathbf{B_2}$ copolymers prepared using $\mathbf{F_3}$, $\mathbf{F_6}$ and $\mathbf{F_9}$ as initiators.

Table 2. The consequence of changing the alkoxide and imido ligands.[a]

Entry	Catalyst	Time (h)	Conversion (%)	AB linkages (%)	*cis* : *trans* AB linkages (%)
1	Mo(N-2,6-$Me_2C_6H_3$)(CHCMe$_2$Ph)[OC(CF_3)$_3$]$_2$	8.5	80	85	15 : 85
2	Mo(N-2,6-$Me_2C_6H_3$)(CHCMe$_2$Ph)[OCMe(CF_3)$_2$]$_2$	2	>99	97	01 : 99
3	Mo(N-2,6-$Me_2C_6H_3$)(CHCMe$_2$Ph)[OCMe$_2$$CF_3$]$_2$	6	>99	78	03 : 97
4	Mo(N-3,5-$Me_2C_6H_3$)(CHCMe$_2$Ph)[OCMe(CF_3)$_2$]$_2$	1	>99	99	40 : 60
5	Mo(N-2-$CF_3C_6H_4$)(CHCMe$_2$Ph)[OCMe(CF_3)$_2$]$_2$	1	>99	93	26 : 74
6	Mo(N-2-*i*-PrC_6H_4)(CHCMe$_2$Ph)[OCMe(CF_3)$_2$]$_2$	1	>99	93	28 : 72
7	Mo(N-2-PhC_6H_4)(CHCMe$_2$Ph)[OCMe(CF_3)$_2$]$_2$	1	>99	85	34 : 66
8	Mo(N-2-*t*-BuC_6H_4)(CHCMe$_2$Ph)[OCMe(CF_3)$_2$]$_2$	24	>99	99	20 : 80

[a] Conditions: 50 equiv $\mathbf{A_2}$ and $\mathbf{B_2}$ (0.1 M in $CDCl_3$) at 22 °C. % Conversion, % AB linkages, *cis*:*trans* ratio determined from ^{1}H NMR spectra of isolated polymers.

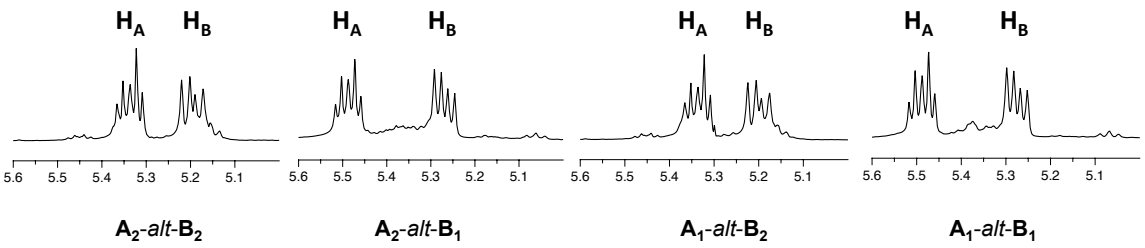


Figure 12. ^{1}H NMR spectra from 5.6 to 5.0 ppm of **A**-*alt*-**B** prepared using **13** as the initiator.

comprise a cause and effect that can be traced to the size of the imido ligand, with "smaller" imido ligands allowing more *cis* dyads to form. Replacing the phenylimido ligand with the adamantylimido (in **10**) or NAr^{F} ligands (in **11**) led to mixtures of copolymer and homopolymer dyads.

Because monoalkoxide pyrrolide (MAP) initiators generally give high % *cis* polymers, we did not expect Mo(NAr)(CHCMe$_2$Ph)(Me$_2$Pyr)[OCMe(CF$_3$)$_2$] (**13**)[14] to be a successful initiator for *alt*-ROMP to give a *trans* alternating copolymer. Table S6 in the SI summarizes the results of the copolymerizations obtained with $\mathbf{B_1}$ or $\mathbf{B_2}$ plus either cyclooctene or cycloheptene using **13** as initiator. The only copolymers that were formed with >85% AB linkages were $\mathbf{A_1}$-*alt*-$\mathbf{B_2}$ and $\mathbf{A_2}$-*alt*-$\mathbf{B_2}$ (Figure 12; Table S6, entries 1 and 3). Copolymers made from $\mathbf{B_1}$ had 82% and 72% **AB** linkages with $\mathbf{A_1}$ and $\mathbf{A_2}$, respectively (Table S6, entries 2 and 4). Initiator **13** was less active towards monomers with lower ring strain ($\mathbf{A_2}$). The fact that **13** does not yield high *cis* copolymers can be ascribed to the preferred formation of *trans* dyads when employing $\mathbf{B_1}$ and $\mathbf{B_2}$, i.e., monomer control of *cis*/*trans* content.

We briefly explored a temperature effect on *cis*/*trans* selectivity of a reaction involving Mo(N-2-*i*-PrC$_6$H$_4$)(CHMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ (**7**) as the initiator. We found that decreasing the temperature from 22 °C to –30 °C slightly increased the percentage of *cis* linkages, but also increased the tendency for the formation of $\mathbf{A_2A_2}$ linkages (Table S7). When the polymerization of $\mathbf{A_1}$ and $\mathbf{B_1}$ by **1** at room temperature, which gives 92% *trans*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_1}$), was carried out at 65 °C, little change was observed (~90% $\mathbf{A_1A_1}$ dyads).

Two polymers were subjected to GPC studies in THF relative to polystyrene. *Trans*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_1}$) (50/50 equiv) prepared with initiator **1** showed a unimodal peak in the GPC with M_n = 30.3 kDa ($Đ_M$ = 2.04), while *trans*-poly($\mathbf{A_1}$-*alt*-$\mathbf{B_2}$) showed a unimodal peak in the GPC with M_n = 36.8 kDa ($Đ_M$ = 1.74). (See the SI for the GPC traces.) The lowest possible average molecular weight for each is ~18,000, so the observed M_n, if it is relatively accurate, is approximately double the lowest possible.

Synthesis of A_xB_1 Copolymers that Contain A_3, A_4, and A_5

Three other **A** monomers were explored for forming alternating copolymers with $\mathbf{B_1}$ using **1** as initiator (Figure 13). All three monomers gave >75% $\mathbf{A_xB_1}$ linkages (x = 3-5). The results of copolymerizations involving $\mathbf{A_3}$, $\mathbf{A_4}$, and $\mathbf{A_5}$ are summarized in Table S8 and in Figure 13. $\mathbf{A_4}$-*alt*-$\mathbf{B_1}$ is > 85% *trans* with a proton NMR spectrum much like that for $\mathbf{A_1}$-*alt*-$\mathbf{B_1}$ (Figure 3), but shifted slightly downfield. The pattern of H_A resonances in the spectrum for $\mathbf{A_3}$-*alt*-$\mathbf{B_1}$ is relatively complex as a consequence of two olefin faces being present, and therefore two possible relationships between $\mathbf{A_3}$ and $\mathbf{B_1}$ in a dyad. The pattern for H_B in $\mathbf{A_3}$-*alt*-$\mathbf{B_1}$ is a relatively simple double doublet. Copolymer $\mathbf{A_5}$-*alt*-$\mathbf{B_1}$ shows a relatively high percentage of $\mathbf{A_5A_5}$ dyads with a resonance at 5.35 ppm. The reaction between *anti*-$\mathbf{MA_5}$ and $\mathbf{A_5}$ must simply be more competitive relative to the reaction between *anti*-$\mathbf{MA_5}$ and $\mathbf{B_1}$.

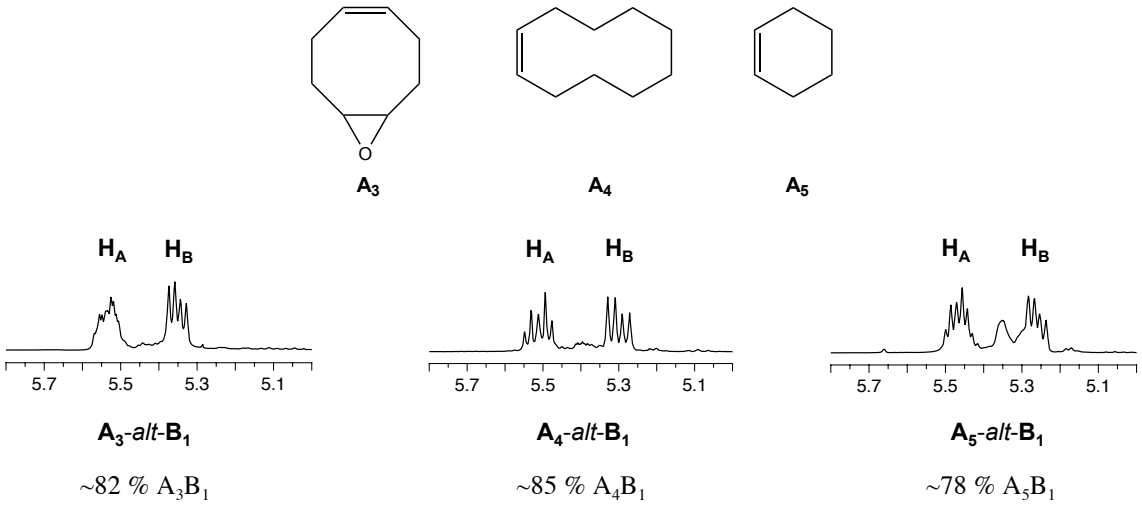


Figure 13. Partial ^{1}H NMR spectra of poly($\mathbf{A_x}$-*alt*-$\mathbf{B_1}$) prepared using initiator **1**.

CONCLUSIONS

The work described here suggests that *trans*-poly(**A**-*alt*-**B**) polymers are formed through a finely balanced set of two reactions analogous to those shown for *trans*-poly($\mathbf{A_2}$-*alt*-$\mathbf{B_2}$) in Figure 4 and partially elucidated for *trans*-poly($\mathbf{A_2}$-*alt*-$\mathbf{B_2}$) through modeling studies. The large size of **B** creates a situation where *anti*-**MB** is *lower* in energy than *syn*-**MB** *and* does not react with *either* **A** or **B** relative to the rate of conversion of *anti*-**MB** to *syn*-**MB**. *Syn*-**MB** then reacts with **A** faster than it reacts with **B** to give *anti*-**MA** and a *trans* **AB** dyad. *Anti*-**MA** reacts with both **A** and **B** competitively before (we propose) any *anti*-**MA** can isomerize to *syn*-**MA.** The

rate of the reaction between *anti*-**MA** and **B** to give a *trans* **AB** dyad and *syn*-**MB** versus the rate of the reaction between *anti*-**MA** and **A** to give both *cis* and *trans* **AA** dyads we propose is essentially equal to the percentage of **AB** dyads formed. Formation of an all *trans* **AB** copolymer is "monomer controlled" in that the *anti* alkylidene derived from one monomer (**MA**) is naturally converted to the *syn* isomer formed from the other monomer (**MB**) and *vice versa* during formation of the **AB** copolymer.

EXPERIMENTAL

General considerations. All air-sensitive manipulations were performed under nitrogen in a glovebox or using Schlenk techniques. All glassware was oven-dried and allowed to cool under vacuum or nitrogen before use. ^{1}H and ^{13}C NMR spectra were obtained on 500 MHz or 400 MHz spectrometers. ^{19}F NMR spectra were obtained on 400 MHz spectrometers. All chemical shifts are reported in δ (parts per million) and referenced to residual ^{1}H/^{13}C signals of the deuterated solvent (^{1}H(δ) benzene 7.16, chloroform 7.26, tetrahydrofuran 3.58, toluene 2.08; ^{13}C(δ) benzene 128.06, chloroform 77.16, toluene 20.43; ^{19}F(δ) external PhF standard -113.15). Low temperature ^{1}H NMR experiments were conducted on a variable temperature 500 MHz spectrometer capable of a temperature range of -100 °C to +150 °C. ^{1}H-^{1}H gCOSY, HSQC, DEPT NMR experiments were conducted on a 500 MHz spectrometer. Pentane was washed with H_2SO_4, followed by water and saturated aqueous $NaHCO_3$, and dried over $CaCl_2$ pellets over at least two weeks prior to use in the solvent purification system. HPLC grade diethyl ether, toluene, tetrahydrofuran, pentane, and methylene chloride were sparged with nitrogen and passed through activated alumina. In addition, benzene was passed through a copper catalyst. Organic solvents were then stored over activated 4 Å Linde-type molecular sieves. Deuterated solvents were degassed and stored over activated 4 Å Linde-type molecular sieves. Benzaldehyde was distilled and stored under nitrogen. Monomers **B$_1$**,[15] **B$_2$**,[16] **B$_6$**,[17] **B$_7$**,[18] **B$_8$**,[10] **B$_{10}$**,[19] and **B$_{11}$**[20] were prepared according to published literature procedures. Monomers **A$_1$** (95%, Alfa Aesar), **A$_2$** (>96%, TCI America), **A$_3$** (>98.5%, Aldrich) and **A$_5$** (>99%, Aldrich) were distilled before use. Monomer **A$_4$** was prepared according to a published literature procedure.[21] Complexes **1**,[13] **2**,[22] **3**,[12] **5**,[12] **6**,[12] **7**,[12] **8**,[12] **9**,[12] **10**,[12] **12**,[12] and **13**[13] were prepared according to literature procedures. Syntheses of **4** and **11** are reported here. Unless otherwise noted, all other reagents were obtained from commercial sources and used as received. ATR-FT-IR spectra were acquired using a Nicolet 6700 FT-IR with a Ge crystal for ATR and peak locations are reported in cm^{-1}.

Supporting Information. Experimental details for all syntheses and experiments summarized in the text (33 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

Notes. The authors declare no competing financial interests.

Acknowledgements. R.R.S. thanks the Department of Energy (DE-FG02-86ER13564) for financial support. We thank Dr. Julia Kalow in the group of Professor Timothy M. Swager for measuring the molecular weight of two copolymers. We also thank Dr. Peter E. Sues for useful discussions and Dr. Jonathan C. Axtell for the gift of monomer $\mathbf{B_7}$.

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TOC Graphic for

Formation of Alternating *trans*-**A**-*alt*-**B** Copolymers Through Ring-Opening Metathesis Polymerization Initiated by Molybdenum Imido Alkylidene Complexes

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