Five-Coordinate Rearrangements of Metallacyclobutane Intermediates During Ring-Opening Metathesis Polymerization (ROMP) of 2,3-Dicarboalkoxynorbornenes by Molybdenum and Tungsten Monoalkoxide Pyrrolide (MAP) Initiators

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Five-Coordinate Rearrangements of Metallacyclobutane Intermediates During Ring-Opening Metathesis Polymerization (ROMP) of 2,3-Dicarboalkoxynorbornenes by Molybdenum and Tungsten Monoalkoxide Pyrrolide (MAP) Initiators

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Abstract

Addition of *rac*-DCENBE (2,3-dicarboethoxynorbornene) or *rac*-DCBNBE (2,3-dicarbo-t-butoxynorbornene) to Mo(NAd)(CHCMe$_2$Ph)(Pyr)(OHMT) (**1a**) (Ad = 1-adamantyl, OHMT = 2,6-dimesitylphenoxide, Pyr$^-$ = NC$_4$H$_4^-$) led to the formation of polymers that have a *cis,syndiotactic,alt* structure analogous to the structure observed for the polymer obtained from *rac*-DCMNBE (2,3-dicarbomethoxynorbornene). The PDI of *cis,syndio,alt*-poly(DCBNBE) is low and decreases as the polymer length increases, and there is a linear relationship between the number of equivalents of monomer employed and the molecular weight of the polymers measured in THF versus polystyrene standards. In contrast, polymerization of (+)-DCMNBE by **1a** at 25 °C, 0 °C, -25 °C, and -40 °C, yields a polymer that contains ~25% *trans,isotactic* dyads and 75% *cis,syndiotactic* dyads. A similar polymerization by Mo(NAd)(CHCMe$_2$Ph)(Pyr)(OHIPT) (**1b**) (OHIPT = 2,6-(2,4,6-i-Pr$_3$)$_2$C$_6$H$_3$) gives a polymer that contains *cis,syndiotactic* and *trans,isotactic* dyads in a ratio of ~8:92, respectively. This is the first report of synthesis of a norbornene polymer that has primarily a *trans,isotactic* structure. Addition of 100 equiv of (+)-DCMNBE, (-)-DCENBE, or (-)-DCBNBE to a toluene solution of W(O)(CH-t-Bu)(2,5-Me$_2$NC$_4$H$_2$)(OHMT)(PMe$_2$Ph) (**5**) led to formation is ~99% *cis,syndiotactic* polymer. *Cis,syndiotactic* dyads arise through a mechanism that consists of a *syn* approach of

the monomer to a *syn* alkylidene isomer followed by inversion of configuration at the metal center as a consequence of an exchange of aryloxide and pyrrolide ligands. The mechanism for formation of *trans,isotactic* dyads is one in which the monomer approaches in an *anti* fashion to the *syn* isomer followed by a "turnstile" rotation in the five-coordinate intermediate metallacyclobutane that allows the metallacylic ring to open productively with retention of configuration at the metal center. The metallacyclobutane intermediate that gives rise to *trans,isotactic* dyads in the copolymer could be regarded as a relatively high energy species with a "non-ideal" structure compared to a trigonal bipyramidal or a square pyramidal structure.

INTRODUCTION

Ring-opening metathesis polymerization (ROMP) is a way of making polymers from a variety of strained cyclic olefins, often substituted norbornenes or norbornadienes, employing alkylidene complexes as initiators.[1] Such polymers can contain either *cis* or *trans* C=C double bonds and an *isotactic* or *syndiotactic* relationship between (with norbornenes or norbornadienes, for example) neighboring five-membered rings in dyads contained in the polymer backbone. Since the bulk properties of a given polymer depend to a significant degree on the polymer's primary structure, it is often desirable to prepare a polymer with a single long-range structure.[2] In order to do so one might anticipate that the mechanism should consist of a single type of propagation step at a single type of metal center. The development of "well-defined" alkylidene initiators in the last two decades, the majority of which are based on high-oxidation state imido alkylidene complexes of Mo[3] and W,[3] or Ru(II) complexes,[4] has been of great benefit to ROMP chemistry, since the nature of the initiator can be altered and mechanistic details explored systematically.

The stereochemistry of a ROMP polymer made with a classical (achiral) initiator is usually the result of chain-end control.[1,2] Examples of a high degree of chain-end control of the *cis/trans* content and tacticity of ROMP polymers are rare. Enantiomorphic site control is proposed to be operative in the case of well-defined Mo or W imido alkylidene initiators that contain a chiral biphenolate or binaphtholate. Biphenolate or binaphtholate catalysts often produce polymers that have *cis,isotactic* structures from norbornenes and norbornadienes as a consequence of the monomer approaching the same side of the M=C bond in each propagation step. Recently, a new type of polymerization control has emerged as a consequence of the use of MonoAlkoxidePyrrolide (MAP) initiators of Mo and W with the general formula $Mo(NR)(CHCMe_2Ph)(Pyr)(OR')^3$ that is proposed to result from the fact that the metal itself is a stereogenic center. This new type of control over ROMP polymer structures has been called stereogenic metal control.[2,5] The main feature of stereogenic metal control by MAP initiators in ROMP chemistry is inversion of the metal's configuration with each propagation step and

therefore an approach of monomer to alternate sides of each M=C bond. Stereogenic metal control has allowed the synthesis of ROMP polymers with *cis,syndiotactic* structures,[6] including *cis,syndiotactic,alt* structures prepared from racemic monomers in which enantiomers are incorporated in an alternating fashion into the polymer chain.[7] Examples of racemic monomers that have been polymerized with MAP catalysts to give polymers with *cis,syndiotactic,alt* structures include *endo*,*exo*-2,3-dicarbomethoxynorbornene, *endo*,*exo*-2,3-dicyanonorbornene, and 1-methyl-2,3-dicarbomethoxy-7-oxanorbornene.[7] Since no degenerate metathesis reaction should take place in a ROMP reaction in which a highly strained monomer is employed, the relationship between the chirality at the metal center and any chirality in the last inserted monomer is fixed upon completion of a given insertion.

ROMP of enantiomerically pure monomers is instructive and potentially simpler than ROMP of racemic monomers. If the initiator is a racemic biphenolate or binaphtholate complex of the type Mo(NR)($CHCMe_2Ph$)(diolate), then a polymer with a *cis*,*isotactic* structure can be formed through enantiomorphic site control.[2] Each step in this reaction is identical. However, if the chirality at the metal switches with each insertion of monomer, as has been observed in MAP species, interaction of a (+) monomer with a metal complex with the (*R*) configuration at the metal and interaction of a (+) monomer with a metal complex with the (*S*) configuration at the metal are diastereomeric with respect to one another (ignoring any chirality in the chain itself). Therefore, in order to polymerize an enantiomerically pure monomer by a MAP species it would appear to be necessary to pass through two energetically different intermediates. If one of these two intermediates leads to a result different from the other in terms of *cis vs. trans* C=C bonds, or tacticity, or both, polymers made from enantiomerically pure monomers employing MAP catalysts would be unlikely to have long-range regular structures.[6,7]

Without any restrictions in terms of the propagation steps, four regular polymers in theory can be formed from an enantiomerically pure monomer, namely *cis,syndiotactic*, *trans,isotactic*, *cis,isotactic*, or *trans,syndiotactic*, as shown in Figure 1 for a (+)-2,3-dicarboalkoxynorbornene. *Isotactic* structures are formed when the monomer approaches the

same side of the metal-carbon double bond in each step. In the isotactic structures in Figure 1 the two types of olefinic protons on the same double bond (e.g., H_c and H_d in the *trans,isotactic structure*) are coupled to one another by an amount characteristic of a *cis* or *trans* olefin. Therefore, a regular structure can be assigned through examination of a proton NMR spectrum. In the syndiotactic structures in Figure 1 the two types of olefinic protons on different C=C linkages are not coupled to one another and the *cis* or *trans* nature of the polymer therefore must be assessed on the basis of whether an absorption characteristic of a *trans* olefin (at ~975 cm^{-1}) is present or not.

In this paper we report further studies concerned with the polymerization of 2,3-dicarboalkoxynorbornenes by the catalysts shown in Figure 2. We have been able to observe for the first time the consequences of two competing pseudorotation processes in five-coordinate intermediate metallacyclobutane complexes that either result in inversion of configuration at the metal center and therefore a *cis,syndiotactic* structure or retention of configuration at the metal center and therefore a *trans,isotactic* structure.

RESULTS

Polymerization of t-butyl and ethyl esters analogous to DCMNBE with Mo catalysts

In previous publications we have described polymerization of *rac*-DCMNBE (*rac*-2,3-dicarbomethoxynorbornene) to give *cis,syndiotactic,alt* polymers[7] and polymerization of (+)-DCMNBE with biphenolate and binaphtholate catalysts to give *cis,isotactic*-poly[(+)-DCMNBE].[8] A logical question is how monomers that contain other esters perform in circumstances analogous to those employed for DCMNBE.

Addition of 100 equivalents of either *rac*-DCENBE (2,3-dicarboethoxynorbornene) or *rac*-DCBNBE (2,3-dicarbo-t-butoxynorbornene) to **1a** led to the formation of polymers whose ^{1}H NMR spectra exhibit two pseudo-triplet resonances characteristic of a primarily *cis,syndiotactic,alt* structure (Figures 3b and 3d) that are analogous to those observed for the polymer obtained from *rac*-DCMNBE (Figures 3a and 3c).[7] One or two (in Figure 3d) small

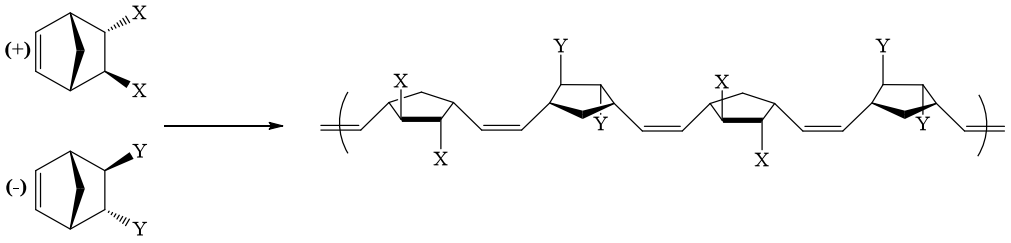
broad resonances are present that we ascribe to ~5% of another type of relationship between dyads in the polymer. On the basis of what is presented later in this paper this relationship is proposed to be *trans,isotactic*.

When fifty equivalents of *rac*-DCBNBE were added to **1a** in toluene-d_8 at 20 °C and a monomer concentration of 29 mM, ^{1}H NMR spectroscopy showed that the monomer was consumed (>99%) within 4 minutes. Under the same conditions, 50 equivalents of enantiomerically pure (-)-DCBNBE required >45 minutes for the monomer to be consumed. These results are consistent with the proposal that polymerization of the racemic monomer is faster because both enantiomers of the monomer can react with a propagating alkylidene through the "favored" diastereomeric monomer/alkylidene combination. In contrast, an enantiomerically pure monomer is forced to react with both enantiomeric forms of the catalyst, and one of these steps should be slower than the other. The disfavored or "mismatched" step then becomes rate-limiting, which is why, we propose, ROMP of (-)-DCBNBE with **1a** is significantly slower than ROMP of *rac*-DCBNBE with **1a**.

Cis,syndio,alt-poly(DCBNBE) was found to be much more soluble in THF than *cis,syndio,alt*-poly(DCMNBE). Therefore, we could perform GPC analysis on polymers made from 50, 100, 200, and 400 equivalents of monomer in THF at room temperature; the polymers prepared employing 700, 1000, and 2000 equivalents of monomer were too insoluble for GPC analysis with the instrument available. All polymers have a structure that is approximately 95% *cis,syndio,alt* (Figure 3d). The PDI of each of the soluble polymers shown in Table 1 is low and decreases as the polymer length increases, both of which suggest that the polymerization is well-behaved. As expected, there is a linear relationship between the number of equivalents of monomer employed and the number average molecular weight of the polymers measured in THF versus polystyrene standards (Figure 4).

An interesting question is whether a *cis,syndiotactic* polymer could be prepared that contains *different enantiomers of two different diesters*, as shown in equation 1. Polymerization of a mixture of (+)-DCMNBE and (-)-DCBNBE yields a polymer whose proton NMR spectrum

is shown in Figure 5. The polymer that was formed employing a 1:1 mixture of (+)-DCMNBE and (-)-DCENBE is similar. Neither polymer shows any significant degree of *cis,syndiotactic* regularity according to proton NMR spectra. This result is not unexpected, since the results of polymerization of *rac*-DCBNBE by **1a** versus (-)-DCBNBE by **1a** described above suggest that the "mismatched" insertion of one enantiomer is about one tenth the rate of the "matched" insertion of the other enantiomer, which apparently is not enough to prevent sequential insertions of one monomer or the other. Results described later also confirm that t-butyl esters react much more slowly than methyl esters. Therefore a controlled formation of the structure shown in equation 1 on the basis only of the chirality of the monomer, but not the identity of X and Y, at this stage seems unlikely.



(1)

Polymerization of (+)-DCMNBE with Mo catalysts

We expected that a polymer with no regular structure would be formed upon attempted polymerization of (+)-DCMNBE with a MAP catalyst.[7] We now find that this prediction is not true for (+)-DCMNBE polymerized with **1a** or **1b**.

Addition of 100 equivalents of (+)-DCMNBE to a toluene solution of **1b** led to consumption of the monomer and formation of polymer within 30 minutes. The reaction was quenched through addition of benzaldehyde and the polymer was precipitated in methanol. A ^{1}H NMR spectrum of the resulting polymer showed an unexpected doublet of doublets pattern with a J_{HH} of ~16 Hz that is consistent with the polymer having ~92%% *trans,isotactic* dyads (Figures 1 and 6). IR spectra showed an absorption at 974 cm^{-1} for the polymer prepared from **1b**, as

expected for a primarily *trans* structure. In contrast, polymerization of (+)-DCMNBE by **1a** at 25 °C, 0 °C, -25 °C, and -40 °C, yields a polymer that contains ~25% *trans,isotactic* dyads and 75% *cis,syndiotactic* dyads. It should be noted that the chemical shifts for the *cis,syndio* or *trans,isotactic* dyads are essentially independent of whether the polymer consists of pure *cis,syndio* dyads, *trans,isotactic* dyads, or a random mixture of the two, i.e., olefinic proton chemical shifts are relatively insensitive to structure *beyond* the five-membered rings on each side of a given double bond. This is the first time to our knowledge that a polynorbornene has been prepared that has a relatively high percentage of a *trans,isotactic* structure.[2] It seems unusual that a *trans* polymer should arise from an initiator that has been designed to produce *cis* double bonds.[6] However, it should be noted that while *cis,syndio,alt* polymer is formed from *rac*-DCMNBE with **1a** as the initiator, as described above, with **1b** in toluene a polymer is formed from *rac*-DCMNBE in a yield of only ~50% in 72 hours at room temperature from 100 equivalents of monomer and that polymer has no regular structure.[7]

The percentage of *trans,isotactic* dyads remained at approximately 92% when (+)-DCMNBE was polymerized with initiator **1b** at temperatures between 0 and 40 °C. Polymerization at 0 °C requires 18 h to consume 80% of the (+)-DCMNBE present**.** Polymerization at room temperature was performed with ratios of **1b** to monomer varying from 0.4 to 1 mol%. Concentrations of monomer and **1b** were varied between 100 and 1000 mM and 0.3 to 5.6 mM, respectively. Each of these polymerizations again led to little variation from 92% *trans,isotactic* dyads. We conclude that the ratio of *trans,isotactic* to *cis,syndiotactic* dyads in poly[(+)-DCMNBE] made with initiator **1b** does not vary significantly with concentration and temperature in the ranges that were explored.

Since >98% *cis,isotactic* poly[(+)-DCMNBE] is formed upon polymerization of (+)-DCMNBE with catalyst **2**,[7] we can compare hydrogenated *cis,isotactic*-poly[(+)-DCMNBE] with hydrogenated 92% *trans,isotactic*-poly[(+)-DCMNBE]. Hydrogenations were carried out with tosyl hydrazide.[9] The ^{13}C NMR spectra of the hydrogenated *cis,isotactic* polymer (Figure 7a) and the major resonances in the spectrum of the hydrogenated *trans,isotactic* polymer (Figure

7b) are identical, thus confirming that the saturated polymers are both *isotactic*. Hydrogenation of *cis,syndiotactic*-poly[(+)-DCMNBE] produces what is clearly a different (largely syndiotactic) saturated polymer (Figure 7d), while hydrogenation of the polymer prepared with initiator **3** produces an atactic hydrogenated polymer (Figure 7c). Hydrogenation of *cis,syndio,alt*-poly(*rac*-DCMNBE) (Figure 8) produces a third distinct hydrogenated polymer. Therefore we conclude that the C1-C4 resonances in the three hydrogenated polymers (*isotactic*, *syndiotactic*, *and syndiotactic,alt)* are found at the positions listed in Table 2, and that the C1, C2, and C4 resonances appear to be the most sensitive to structure of the hydrogenated polymers.

When 10 equivalents of (+)-DCMNBE were added to a toluene-d_8 solution of **1b**, the monomer was consumed within 5 minutes, according to an ^{1}H NMR spectrum, but only 37% of the initiator was consumed versus an anthracene internal standard. The ratio of the propagation rate constant versus the initiation rate constant ($r = k_p/k_i$) can be calculated using the equation $M_0/I_0 + r\ln(I/I_0) + (1-r)(I/I_0 - 1) = 0$ for a given initial monomer concentration M_0, initial initiator concentration I_0, and final initiator concentration I.[10] A similar treatment has been used to determine k_p/k_i for several highly living ROMP systems, including the ROMP of substituted norbornadienes with Mo(NAr)(CHCMe$_2$Ph)(O-t-Bu)$_2$.[11] For the ROMP of (+)-DCMNBE, $I/I_0 = 0.63$ and $M_0/I_0 = 10$, so $k_p/k_i = 104$. GPC analysis (in THF) of the polymer obtained using 100 equivalents of (+)-DCMNBE showed a molecular weight (M_n) of 99.9 kilodaltons versus polystyrene standards, which is approximately four times the expected weight based on M_0/I_0, and a PDI of 1.21. The PDI and molecular weight are consistent with a poorly initiating system in which k_p/k_i is ~100.

The observed glass transition temperatures of poly(DCMNBE) samples range from 48.5 °C to 96.8 °C (Table 3). The lowest T_g was observed in the atactic polymer, followed by an increase in T_g in the two isotactic polymers, followed by a further increase in T_g for one syndiotactic polymer. In the case of 95% *cis,syndio,alt*-poly-(*rac*-DCMNBE), no glass transition or melting point was observed below the decomposition temperature of the

polymer (~250 °C). As shown in the last column of Table 3, the variation in the glass transition temperatures of the hydrogenated polymers (temperatures ranged from 40 °C to 58 °C) was considerably less than the variation in the unsaturated polymers, although the same trend is observed, with the T_g for the hydrogenated *cis,syndio,alt* polymer being the highest and for the atactic polymer the lowest.

Polymerizations with W catalysts

Since tungsten imido alkylidene metathesis catalysts can behave quite differently in detail from analogous molybdenum catalysts,[12] we explored several polymerizations of 2,3-dicarboalkoxynorbornenes with tungsten catalysts.

Poly[(+)-DCMNBE] prepared with W(N-3,5-$Me_2C_6H_3$)(CHCMe_2Ph)(Pyr)(OHIPT) (**4**)[13] as the initiator was found to contain 80% *cis,syndiotactic* dyads, judging from the presence of broadened doublet features at 5.38 ppm and 5.17 ppm for the olefinic protons in the polymer in proton NMR spectra. These spectra resemble those obtained for poly[(+)-DCMNBE] prepared with catalyst **1a**. At 40 °C the polymer obtained with **4** as the initiator was 97% *cis,syndiotactic* while polymer obtained at 0 °C was 89% *cis,syndiotactic*. These results are listed in Table 4.

Oxo alkylidene complexes have been shown to be remarkable *Z*-selective catalysts for the homocoupling of terminal olefins.[14] One example is W(O)(CH-t-Bu)(2,5-$Me_2NC_4H_2$)(OHMT)(PMe_2Ph) (**5**; OHMT = 2,6-dimesitylphenoxide). Addition of 100 equiv of (+)-DCMNBE, (-)-DCENBE, or (-)-DCBNBE to a toluene solution of **5** led to full consumption of the monomer within a few minutes. Proton NMR spectra of the resulting poly[(+)-DCMNBE], poly[(-)-DCENBE], and poly[(-)-DCBNBE] in $CDCl_3$ show a highly regular structure with two broadened doublets (coupling ~ 7 Hz to the methine proton) for the olefinic protons. The proton NMR spectrum in the olefinic region for poly[(+)-DCMNBE]$_5$ (polymer prepared with initiator **5**) shown in Figure 9 reveals that the polymer is ~99% *cis,syndiotactic*; a barely visible double doublet resonance at ~5.5 ppm (estimated to be ~1%) can be ascribed to *trans,isotactic* dyads. Since the IR spectra of the polymers do not contain a prominent peak near

975 cm^{-1} typical for *trans* polymers, we conclude that these polymers have a *cis,syndiotactic* structure. The positions of the olefinic resonances in Figure 9 suggest that the minor component of the spectrum in Figure 6 can be ascribed to *cis,syndiotactic* dyads in the largely *trans,isotactic* polymer. In order to confirm this finding, poly[(+)-DCMNBE] and poly[(-)-DCENBE] prepared with **5** as the initiator were hydrogenated using tosyl hydrazide. Hydrogenated poly[(+)-DCMNBE]$_{\mathbf{5}}$ was the pure syndiotactic form with resonances identical to the major resonances for C1, C2, and C4 in Figure 7d at 42.22 (C1), 33.27 (C2), and 38.02 ppm (C4). The carbon NMR spectrum of hydrogenated poly[(-)-DCENBE]$_{\mathbf{5}}$ was compared to spectra of hydrogenated *isotactic*-poly[(+)-DCMNBE] and hydrogenated *syndiotactic*-poly[(+)-DCMNBE]. With chemical shifts of 42.30 for C_1 (iso 42.98; syndio 42.22), 33.32 for C_2 (iso 33.87; syndio 33.27), and 38.14 ppm for C_4 (iso 38.37 ppm; syndio 38.02 ppm), the polymer microstructure of hydrogenated poly[(-)-DCENBE]$_{\mathbf{5}}$ is closest to that for *syndiotactic*-poly[(+)-DCMNBE]. We conclude that poly[(-)-DCMNBE]$_{\mathbf{5}}$, poly[(-)-DCENBE]$_{\mathbf{4}}$, and poly[(-)-DCBNBE]$_{\mathbf{4}}$, all have *cis,syndiotactic* structures. It is not surprising that polymers with 99% *cis,syndiotactic* dyads should be formed by tungsten oxo alkylidene catalysts, since they are more *Z*-selective than analogous tungsten imido alkylidene catalysts.[14]

In order to determine the degree to which ROMP of racemic monomers is favored compared to ROMP of enantiomerically pure monomers, NMR scale polymerization reactions initiated by **5** were monitored by proton NMR. A comparison of the rate of consumption of (+)-DCMNBE and *rac*-DCMNBE (Figure 10) showed that *rac*-DCMNBE and (+)-DCMNBE are polymerized at approximately the same rate. A comparison of the rate of consumption of (-)-DCBNBE and *rac*-DCBNBE (Figure 10) showed that both are polymerized more slowly than (+)-DCMNBE or *rac*-DCMNBE, and *rac*-DCBNBE is polymerized significantly more rapidly than (+)-DCBNBE; both results can be explained in terms of the greater steric demand of a monomer that contains a t-butyl ester. The latter result is similar to what was found for polymerization of (-)-DCBNBE and *rac*-DCBNBE by **1a** described earlier.

In complex **5**, the PMe_2Ph ligand is partially dissociated at room temperature and rapidly exchanging on and off the metal;[14] thus the phosphine might influence the microstructure of the polymer by coordinating and inverting the metal center.[15] In order to investigate the impact of the phosphine ligand on the polymer microstructure, polymerizations were carried out in which complex **5** was stirred with one equivalent of $B(C_6F_5)_3$ in toluene prior to the addition of monomer. In this circumstance the PMe_2Ph ligand is bound to boron, as shown through NMR studies.[14] When (-)-DCENBE or (-)-DCBNBE was polymerized by **5** in the presence of $B(C_6F_5)_3$, the resulting polymers were identical to those obtained with **5** in the absence of $B(C_6F_5)_3$, which suggests that the presence of PMe_2Ph has no impact on the polymer's tacticity under these conditions.

Polymerization of *rac*-DCMNBE, *rac*-DCENBE, and *rac*-DCBNBE with **5** led to the formation of polymers that have no significant absorption near 974 cm^{-1} and therefore are *cis*. When *rac*-DCENBE was polymerized at -35°C, the reaction was complete in two hours, but the tacticity was the same as in the polymer obtained at room temperature, according to proton NMR spectra. An attempted polymerization of *rac*-DCENBE at -78°C yielded no polymer after two hours. Proton NMR spectra of poly(*rac*-DCMNBE)$_{\mathbf{5}}$ (Figure 11a) suggest that the structure is relatively regular, although the carbon NMR spectra of hydrogenated poly(*rac*-DCMNBE) (Figure 11b) reveal that it does not have a regular structure that we recognize, although it is not obvious what other regular structure would be plausible. Therefore at this point we propose that poly(*rac*-DCMNBE)$_{\mathbf{5}}$ is *cis*, but that it has a relatively random structure in terms of tacticity and/or identity of (+) or (-) monomers in the *cis,syndiotactic* chain as a consequence of the approximately equal rate of polymerization of *rac*-DCMNBE and (+)-DCMNBE by initiator **5**.

Studies concerned with the mechanism of formation of *trans,isotactic*-poly[(+)-DCMNBE]

Formation of *trans,isotactic* dyads in poly[(+)-DCMNBE] requires that the monomer approach the same side of the M=C bond in each step and that the metallacyclobutane intermediate be formed either from a *syn* alkylidene through addition of the monomer in an *anti*

fashion or from an *anti* alkylidene through addition of the monomer in a *syn* fashion. (In *syn* or *anti* M=CHR isomers the R group points either toward or away from the imido ligand, respectively. The monomer approach is termed *syn* or *anti* according to whether it points toward or away from the imido ligand, respectively.) Since the OHIPT ligand has been proposed to hinder addition of the monomer in an *anti* fashion in **1b** and similar MAP catalysts,[6] we explored the possibility that the monomer adds in a *syn* fashion to an *anti* alkylidene. In this scenario the *anti* alkylidene would be in rapid equilibrium with the *syn* alkylidene and the *anti* isomer would have to be *significantly* more reactive than the *syn* isomer.

Photolysis of **1b** in toluene-d_8 in Pyrex NMR tubes with 350 nm light at -78 °C led to formation of a mixture that contains ~40% of a new alkylidene resonance at 13.51 ppm with J_{CH} of 148 Hz characteristic of an *anti* alkylidene (Figure 12). Decay of the *anti* species to the *syn* species was followed at -40 °C, -30 °C, and -20 °C in order to obtain first order rate constants ($k_{a/s}$) for conversion of *anti* to *syn* alkylidene of 2.1 x 10^{-4} s^{-1} (-40°), 7.8 x 10^{-4} s^{-1} (-30°), and 46.2 x 10^{-4} s^{-1} (-20°). From an Eyring plot (Figure 13) $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ can be calculated to be 17.51 kcal/mol and 0.36 eu, respectively and the value of $k_{a/s}$ at 298K can be calculated to be 0.96 s^{-1} employing the equation derived from the Eyring plot shown in Figure 13.

In order to determine $k_{s/a}$ (the rate constant for conversion of the *syn* to the *anti* alkylidene) it is necessary to determine a value for K_{eq} ($k_{a/s}/k_{s/a}$). Proton NMR spectra of samples of **1b** that had been recrystallized multiple times from pentane showed traces of several resonances after 10,000 scans besides that due to *syn*-**1b**, but none corresponded to an *anti*-**1b** resonance according to the chemical shifts of all alkylidene resonances in addition to those for *syn*-**1b**. We estimate that an alkylidene resonance with an intensity of ~5% or more that of the downfield ^{13}C satellite resonance on the alkylidene resonance for *syn*-**1b** could have been observed. Therefore, the equilibrium constant is on the order of 4000 or more and the value for $k_{s/a}$ is on the order of 2.5 x 10^{-4} s^{-1} or less. If only the *anti* isomer were to react with monomer a $k_{s/a}$ of 2.5 x 10^{-4} s^{-1} would give rise to a half-life for initiation of several hours and to an extremely slow polymerization overall. This circumstance has been proposed in the case of the

slow polymerization of 1,7,7-trimethylnorbornene by Mo(NAr)($CHCMe_2Ph$)[$OCMe(CF_3)_2$]$_2$ to a *trans* polymer ($k_{s/a} = 7x10^{-5}$ s^{-1}).[16] Therefore, we conclude that neither initiation via solely *anti*-**1b** at room temperature nor propagation via solely *anti* insertion products seems likely.

After photolysis of **1b** at -78 °C the concentration of the *anti* alkylidene was determined by NMR analysis in a pre-cooled probe at -60 °C. One equivalent of (+)-DCMNBE (relative to the *anti* alkylidene) was then added via syringe from a stock solution at -78 °C. A new alkylidene resonance was observed at 11.52 ppm that amounted to 16% of the total alkylidene resonances, which includes the *anti* alkylidene resonance of the initiator (19%) and the *syn* resonance of the initiator (65%). Two new broad olefinic resonances were observed at 5.73 and 5.41 ppm in addition to olefinic resonances for the unreacted monomer. The olefinic resonance for the polymer is observed essentially at 5.41 ppm. When one equivalent of monomer was added to a solution of **1b** at -78 °C that had not been subjected to photolysis, no new alkylidene resonance was observed. Therefore we propose that the new alkylidene resonance at 11.52 ppm in the photolyzed sample is for a *syn* first insertion product formed upon addition of the monomer in a *syn* fashion to the *anti* alkylidene at -78 °C. These experiments prove that the *anti* initiator is more reactive than the *syn* initiator. However, some *anti* initiator is observed at -60 °C in the presence of unreacted monomer in the photolyzed sample after 35 minutes. Either the *anti* form is not *orders of magnitude* more reactive than the *syn* initiator or the *anti* form initiates slowly relative to the rate of propagation, or both.

When the above photolyzed sample in the presence of (+)-DCMNBE was warmed slowly to room temperature only olefinic resonances for poly-[(+)-DCMNBE], the *syn* initiator, and a new alkylidene doublet ($J_{HH} = 7.5$ Hz) at 11.76 ppm characteristic of the polymer are observed. The alkylidene resonance at 11.52 ppm and the olefinic resonance at 5.73 ppm, which are assigned to the first insertion product of *anti*-**1b**, are not present.

When solutions of **1b** (unphotolyzed) and (+)-DCMNBE at -78 °C were warmed, the monomer began to be consumed at about -40 °C. NMR analysis in toluene-d_8 shows a doublet at 5.56 ppm and a doublet of doublets 5.36 ppm in addition to two double doublets at 5.47 and 5.39

ppm ascribed to the *trans* olefinic protons in the polymer backbone. gCOSY analysis shows that the proton giving rise to the doublet at 5.56 ppm and the proton giving rise to the double doublet at 5.36 ppm are coupled to one another with J_{HH} = 15 Hz characteristic of a *trans* double bond in a CH=CHCMe$_2$Ph end group (Figure 14). Olefinic proton resonances of the CH=CHCMe$_2$Ph end group are present in samples that had or had not been photolyzed at -78 °C. Also, the polymer structure is the same (~92% *trans,isotactic*) for poly[(+)-DCMNBE]$_{\mathbf{1b}}$ regardless of whether the solution was subjected to photolysis or not before adding monomer and warming the sample slowly to room temperature.

Attempted polymerization of (+)-DCMNBE at -78 °C does not yield polymer in 4 h. If *anti* alkylidenes are the initiating and propagating species then *anti* alkylidenes are simply not thermally accessible at low temperature. Therefore, we conclude that although *anti*-**1b** is more reactive than *syn*-**1b** at low temperature, *anti*-**1b** and *anti* forms of propagating species do not appear to be relevant to the polymerization of (+)-DCMNBE as a consequence of their extremely low concentrations and relatively slow rate of formation from *syn* isomers. Therefore, *syn* isomers appear much more likely to be the initiating and propagating alkylidene isomers.

DISCUSSION

Formation of *cis,syndiotactic* dyads is consistent with *syn* addition of the monomer to a *syn* alkylidene and inversion of configuration of the metal with each insertion. If the monomer is enantiomerically pure, then reaction of the monomer with the metal having one configuration should be slower than reaction of the monomer with the metal having the other configuration. The "mismatched" (less favorable) step is ~10% the rate of the favorable step in the case of polymerization of *rac*-DCBNBE by **1a**, but the overall result is still a *cis,syndiotactic* polymer (Scheme 1a). When the initiator is **5**, the differences in the rates of polymerization of *rac*-DCMNBE and (+)-DCMNBE are small (Figure 10). However, the differences in the rates of polymerization of (-)-DCBNBE and *rac*-DCBNBE with **5** are again large (Figure 10). It is clear that steric factors play a significant role in the overall rate of polymerization and therefore

that stereogenic metal control is not the sole determinant of the polymer's structure.

The crucial step in formation of *cis,syndiotactic*-poly[(+)-DCMNBE] (Scheme 1a) consists of *syn* approach of the monomer to a *syn* alkylidene. However, the mechanism of formation of *trans,isotactic*-poly[(+)-DCMNBE] is not obvious. We initially proposed that the mechanism of formation of *trans,isotactic*-poly[(+)-DCMNBE] consists of two distinct propagation steps that produce the same stereochemical result. In one step the monomer approaches a *syn*-S_{Mo} species in an *anti* fashion to yield an *anti*-R_{Mo} insertion product (Scheme 1b), even though approach of the monomer in an *anti* fashion *should* be discouraged by the large aryloxide ligand, at least according to the principles of *Z*-selective reactions with MAP species.[6] Addition of the monomer in a *syn* manner to the *anti*-R_{Mo} isomer (Scheme 1b) must be followed by a reaction between the *anti* isomer and the monomer, *before* the *anti* isomer can convert to a *syn* isomer. The reason is that rotation about the alkylidene does not change the configuration at the metal, so a different tacticity will result than is observed if the *syn* isomer that forms from the *anti* isomer is the one that reacts with monomer. A key assumption is that in each step the metal inverts its configuration.[17] Inversion at the metal can be viewed as a turnstile exchange of the aryloxide and pyrrolide ligands. We have concluded that the mechanism proposed in Scheme 1b is not sensible because of the stringent requirements, i.e., *two* different steps are required and the *anti* alkylidene must react with the monomer in a *syn* manner before the *anti* alkylidene can convert to a reactive *syn* alkylidene. The lack of either a significant dependence of the amount of *trans,isotactic* polymer on the temperature or the monomer concentration would argue against what we propose is the unnecessarily convoluted mechanism shown in Scheme 1b.

Our realization that metallacyclobutane rings that give rise to *trans* C=C bonds may *themselves* be prone to a turnstile rotation led to the mechanism shown in Scheme 1c. The key feature of this mechanism is that the metallacyclobutane intermediate is formed through an *anti* approach of the monomer to the *syn* alkylidene. The metallacyclobutane then "flips over" in order to allow opening of the MC_3 ring to yield another *syn* alkylidene at a rate that is competitive with the rate of exchange of pyrrolide and aryloxide ligands. Since the new

alkylidene is *syn* the process can be repeated, *and* the configuration at the metal never changes. The possibility that the monomer could approach the *anti* alkylidene in a *syn* fashion to give a metallacyclobutane that undergoes a pseudorotation, again without changing the configuration at the metal, can be dismissed on the basis of observations earlier that suggest that the *anti* alkylidene is inaccessible in a polymerization reaction. It should be noted in Scheme 1c that only one intermolecular step is required and that retention of the configuration of the metal eliminates any possibility of a "mismatch" propagation step in a reaction involving a pure enantiomer. Therefore, we are left with the proposal that a *syn* addition of monomer to a *syn* alkylidene gives rise to inversion at the metal and formation of a *cis,syndiotactic* dyads, while an *anti* addition of monomer to a *syn* alkylidene gives rise to retention of the configuration at the metal and formation of a *trans,isotactic* dyads. Competition between these two mechanisms easily could be relatively insensitive to temperature and monomer concentration, as we have observed.

Why does the metallacycle in which the α and α' substituents are *trans* to one another undergo a turnstile rearrangement in competition with exchange of pyrrolide and aryloxide ligands? We propose that turnstile rearrangements of metallacycles having *trans* α and α' substituents are simply especially facile compared to turnstile rearrangements of the all *cis* metallacycles that are intermediates that lead to *cis,syndiotactic*-poly[(+)-DCMNBE] (Scheme 1a). The metallacycles that give rise to *trans* olefins, whatever overall geometry they may be, are already likely to be twisted as a consequence of the *trans* α and α' substitution pattern. The product of a turnstile rearrangement of a metallacyclobutane that has a *trans* α and α' substitution pattern also would have a *trans* α and α' substitution pattern, so this type of rearrangement could be relatively facile.

Interconversions of trigonal bipyramidal and square pyramidal molybdenum bisalkoxide metallacyclobutane complexes through some pseudorotation process have been known for more than twenty years.[18] Interconversion of SP and TBP metallacyclobutanes have also been observed in complexes that contain a sterically demanding C_2-symmetric biphenolate or

binaphtholate ligand.[19] Evidence suggests that TBP/SP interconversions take place intramolecularly at room temperature in unsubstituted metallacyclobutanes (on the NMR time scale) or on a slower (chemical) time scale for β-substituted metallacyclobutanes. Interconversions of TBP and SP metallacyclobutanes have been proposed to take place via rearrangement of the metallacyclobutanes themselves rather than through reformation of olefin/alkylidene intermediates; the latter seems unlikely when an olefin as strained as a norbornene is involved. No turnstile rotation process in a metallacyclobutane complex has been quantified.

A fluxional process has been documented recently for a structurally characterized metallacyclo*pentane* complex, $Mo(NAr)(C_4H_8)(OSiPh_3)_2$, which is formed upon treating $Mo(NAr)(CH_2CH_2)(OSiPh_3)_2$ with ethylene.[20] The fluxional process was proposed to consist of either a five-coordinate rearrangement of an intact metallacyclopentane or of a Mo(VI) alkenyl hydride species formed through a reversible β hydride elimination. The activation parameters ($\Delta H^{\ddagger}$ = 18.0(0.3) kcal/mol and $\Delta S^{\ddagger}$ = 15.6(1.2) eu) at 298 K suggested that the rate is $>10^3$ s^{-1}.

The studies described here suggest that rearrangements of five-coordinate metallacyclobutane intermediates in a $M(D)(C_3H_zR_{3-z})(X)(Y)$ (M = Mo or W, D = imido or oxo) intermediate (where the R substituents are not necessarily the same) are *required* in order for the olefin product to leave the metallacyclobutane via a (lowest energy) pathway that is analogous to that through which the metallacycle was formed. In some metallacyclobutanes interconversion of X and Y (with resulting inversion at M) is faster than interconversion of C_α and $C_{\alpha'}$ in the metallacycle (with no inversion at M). Turnstile rotations are required when X and Y are significantly different electronically (e.g., pyrrolide and aryloxide ligands), but could take place rapidly on the chemical time scale in a variety of $M(D)(C_3H_zR_{3-z})(X)(Y)$ species in which X and Y are the same, e.g., when both are alkoxides. Therefore, rearrangements of five-coordinate metallacyclobutanes may be an inherent feature of metathesis catalysts of the type discussed here in a wide variety of circumstances, and such rearrangements may allow facile access to the lowest energy, often selective, pathway to products.

All of the discussion above presumes that metallacyclic intermediates have structures that are similar to the low energy TBP or SP metallacycles that have been observed, and in many cases, structurally characterized. However, there is no proof that TBP or SP metallacycles are required intermediates. "Non-ideal" metallacycles may form that are higher in energy, more fluxional, and more prone to open to yield product than metallacycles that are close to TBP or SP structures. Distorted, relatively high energy metallacycles also might be more likely to be found in the sterically demanding circumstances that prevail in the MAP catalysts that we have been exploring.

CONCLUSION

We have shown that 2,3-dicarboalkoxynorbornenes can be polymerized in a well-behaved manner to yield *cis,syndiotactic,alt* polymers when the monomer is *racemic*, and usually *cis,syndiotactic* structures when the monomer is enantiomerically pure. Formation of *cis,syndiotactic* dyads requires that the aryloxide and pyrrolide ligands exchange to give a metallacyclobutane complex in which the metallacyclobutane can open to yield product; this process leads to inversion of configuration at the metal with each insertion step. Formation of *trans,isotactic* dyads from an enantiomerically pure monomer is possible if the metallacyclobutane ring undergoes a exchange of C_{α} and $C_{\alpha'}$ before it opens to give the new alkylidene; the metal does not invert in this case. Pseudorotation processes seem likely in other systems that involve metathesis of acyclic olefins by high oxidation state Mo and W catalysts, especially if the product olefin cannot leave the metallacyclobutane in the same manner as the substrate added to form the metallacyclobutane. The metallacyclobutane intermediate that gives rise to *trans,isotactic* dyads could be regarded as a relatively high energy species with a "non-ideal" structure. All of our findings suggest that the lowest energy pathway and the resulting polymer structure can be a sensitive function of the structure of the monomer itself.

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Supporting Information Available. All experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

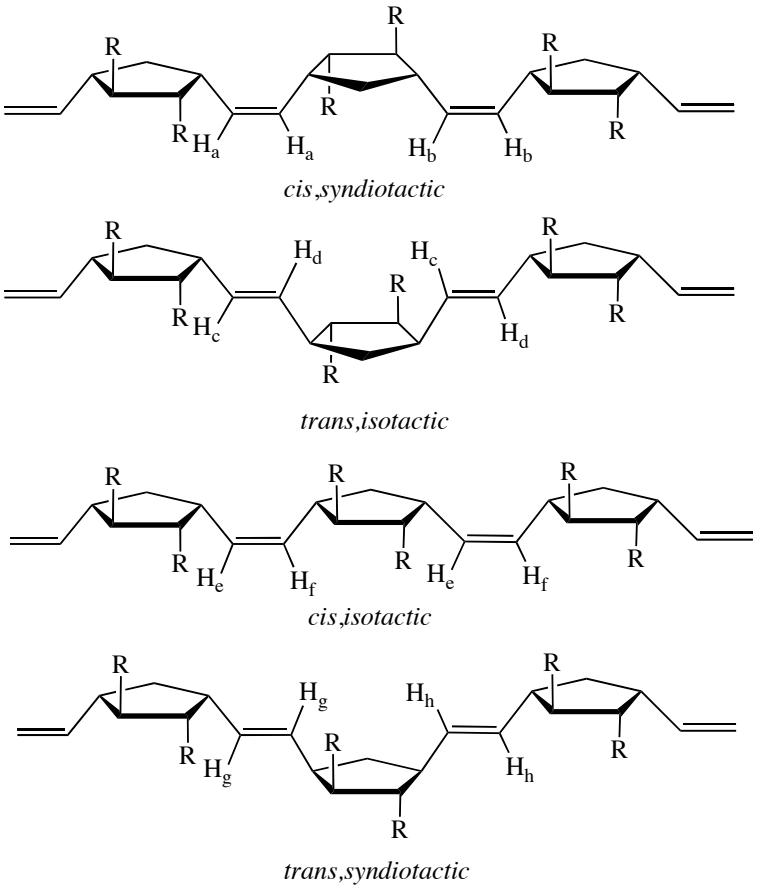
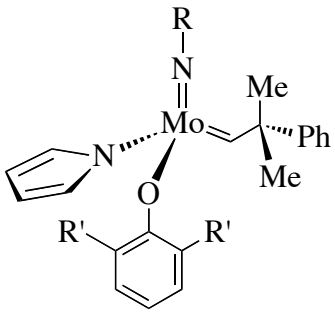
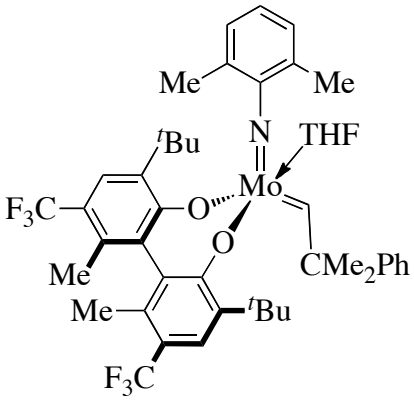


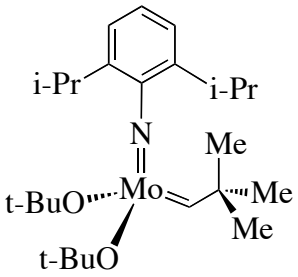
Figure 1. The four possible structures (at the triad level) formed from a (+)-2,3-dicarboalkoxynorbornene.



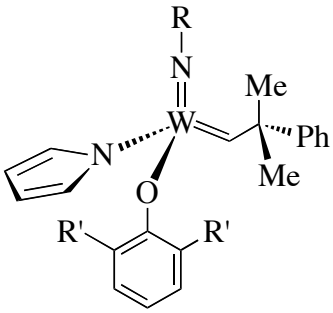
1a; R = Ad, R' = Mesityl
1b; R = Ad, R' = 2,4,6-i-$Pr_3C_6H_2$
1c; R = 2,6-$Me_2C_6H_3$, R' = Mesityl



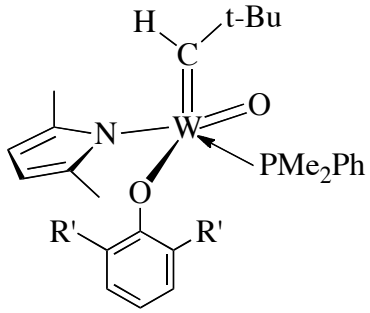
2



3



4; R = 2,6-$Me_2C_6H_3$, R' = 2,4,6-i-$Pr_3C_6H_2$



5; R' = 2,4,6-$Me_3C_6H_2$

Figure 2. Catalysts employed for polymerization of 2,3-dicarboalkoxynorbornenes.

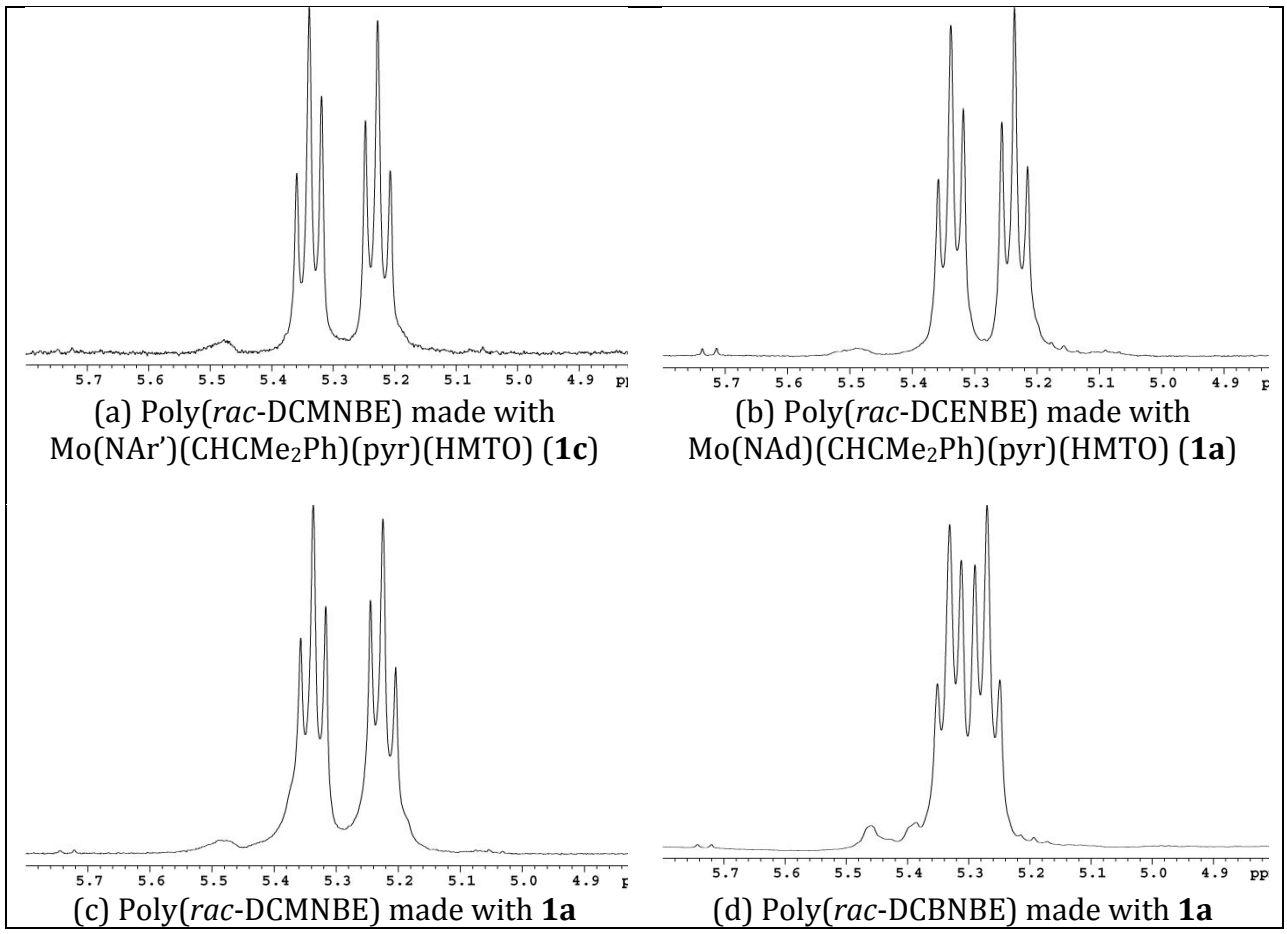


Figure 3. Proton NMR spectra (olefinic region, recorded in $CDCl_3$) of polymers prepared from the initiators shown.

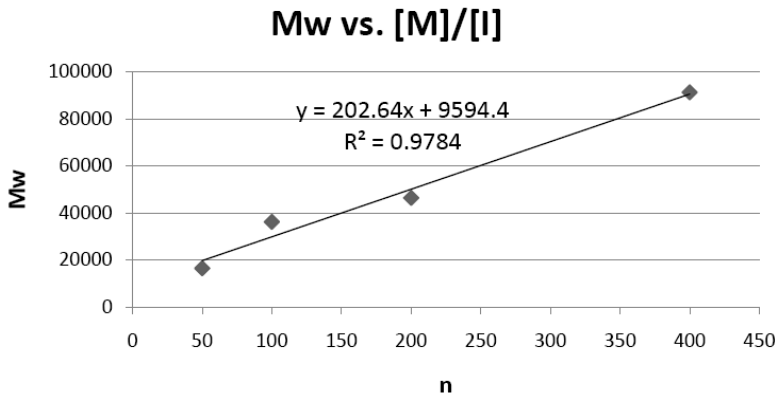


Figure 4. The molecular weight (M_n) of poly(*rac*-DCBNBE)

(in THF versus polystyrene) versus equivalents of monomer added.

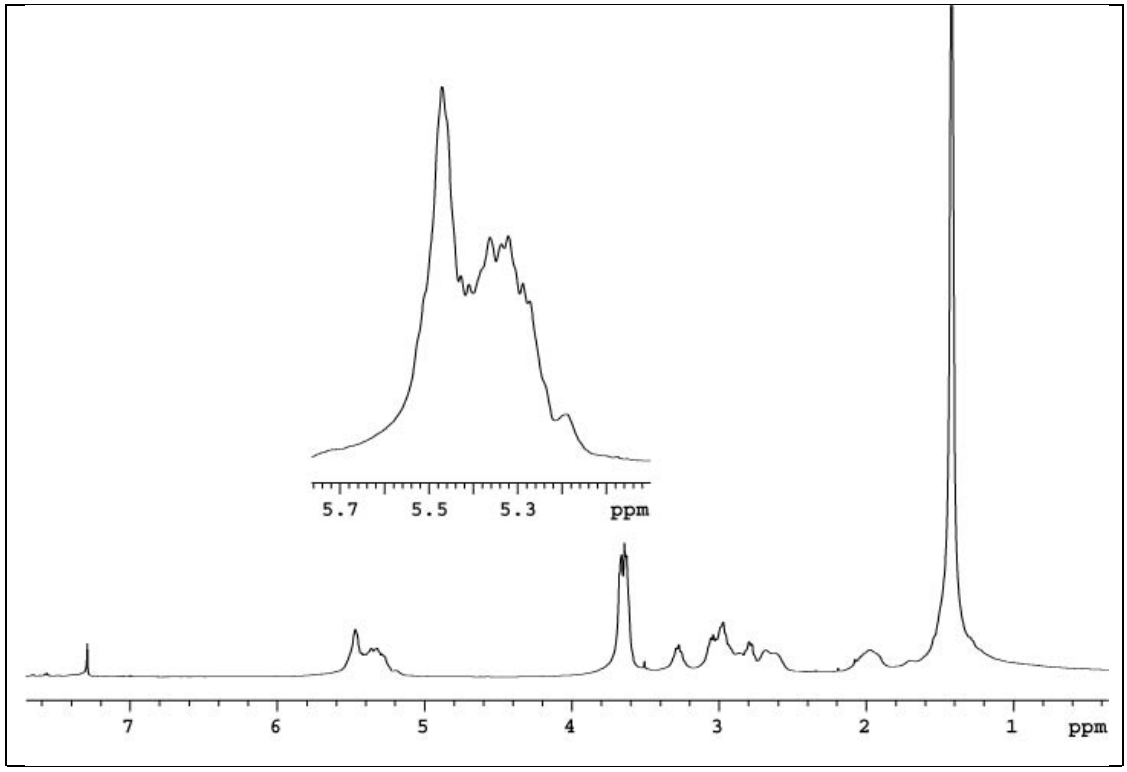


Figure 5. ^{1}H NMR spectrum (in $CDCl_3$) of polymer obtained from a mixture of 50 equivalents of (+)-DCMNBE and 50 equivalents of (-)-DCBNBE employing **1a** as an initiator at room temperature in toluene.

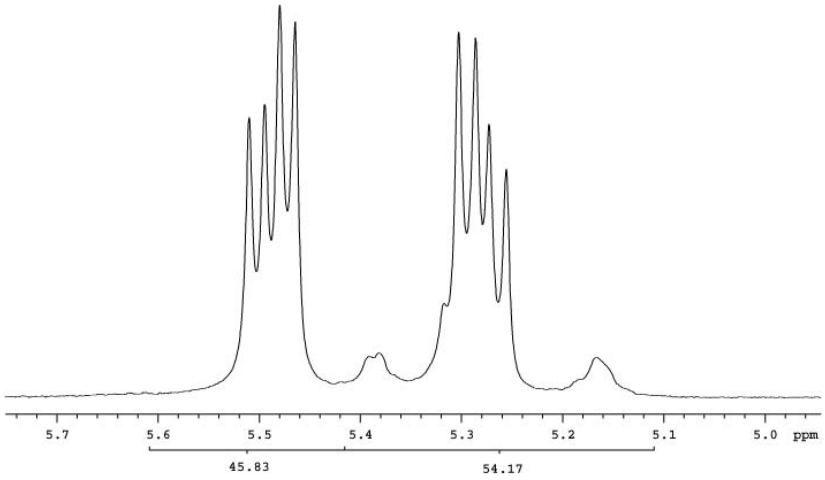


Figure 6. The olefinic region of the ^{1}H NMR spectrum (in $CDCl_3$) of highly *trans*,*isotactic*-poly-[(+)-DCMNBE] prepared with initiator **1b**.

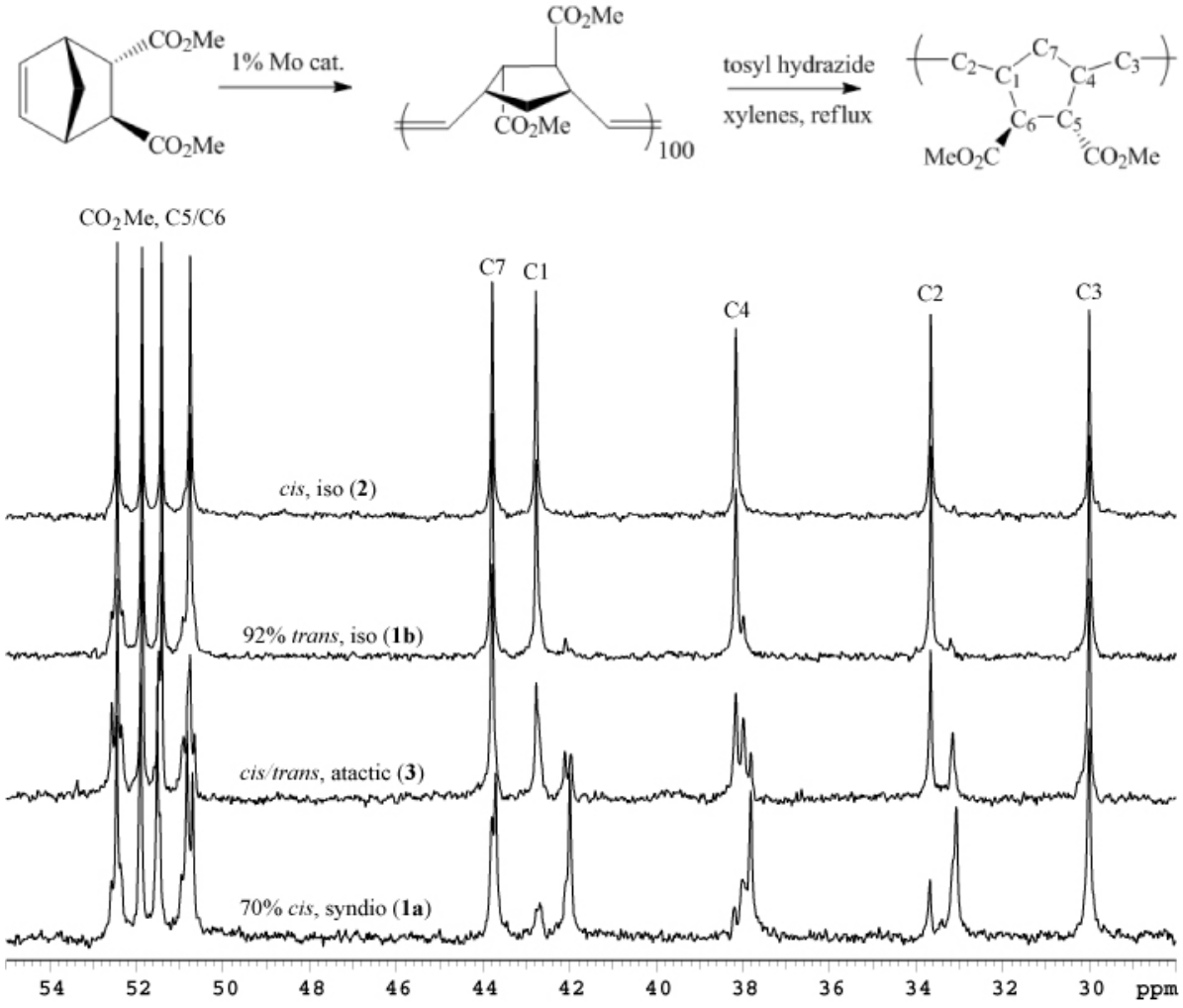


Figure 7. Partial ^{13}C NMR spectra of hydrogenated poly[(+)-DCMNBE] (in $CDCl_3$) prepared with four Mo catalysts (Figure 7a at the top to Figure 7d at the bottom).

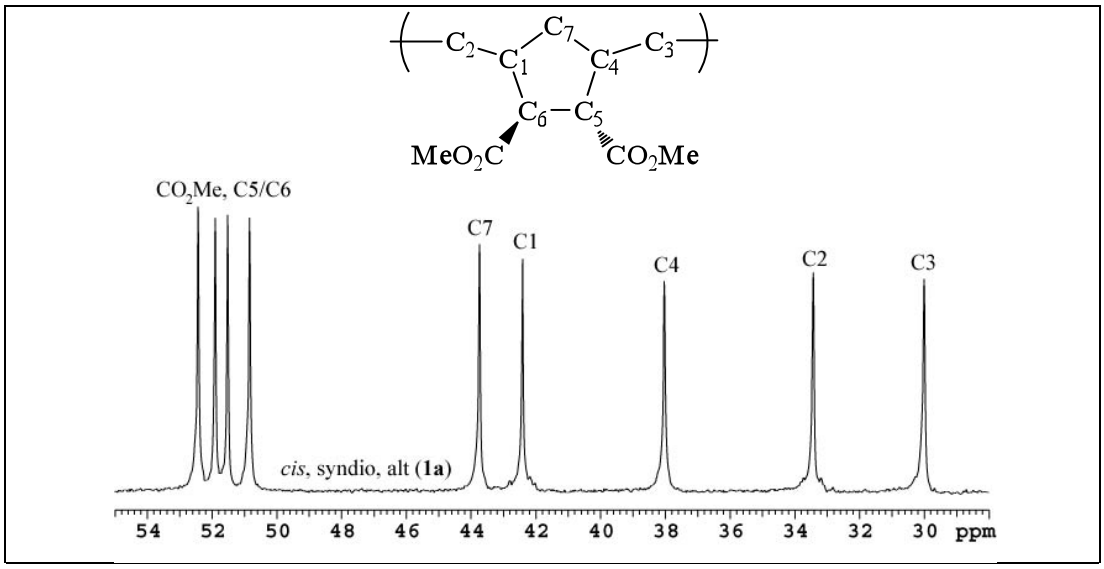


Figure 8. Partial ^{13}C NMR spectrum of hydrogenated *cis,syndio,alt*-poly[*rac*-DCMNBE] (in $CDCl_3$) prepared with initiator **1a**.

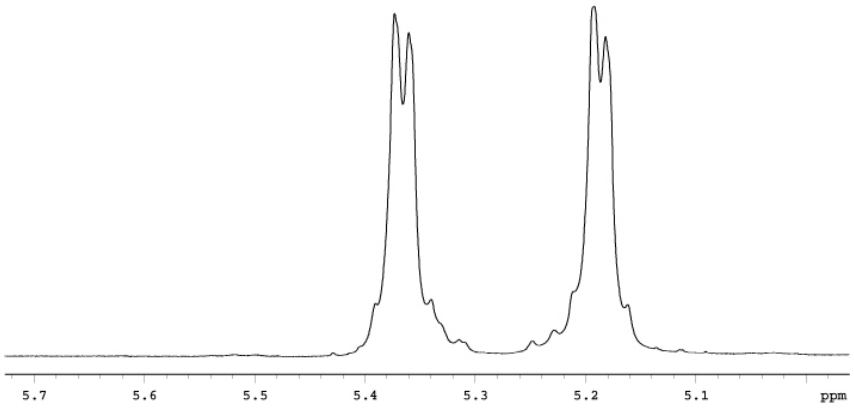


Figure 9. Proton NMR spectrum of *cis,syndiotactic*-poly[(+)-DCMNBE] (in $CDCl_3$) prepared with **5** as the initiator.

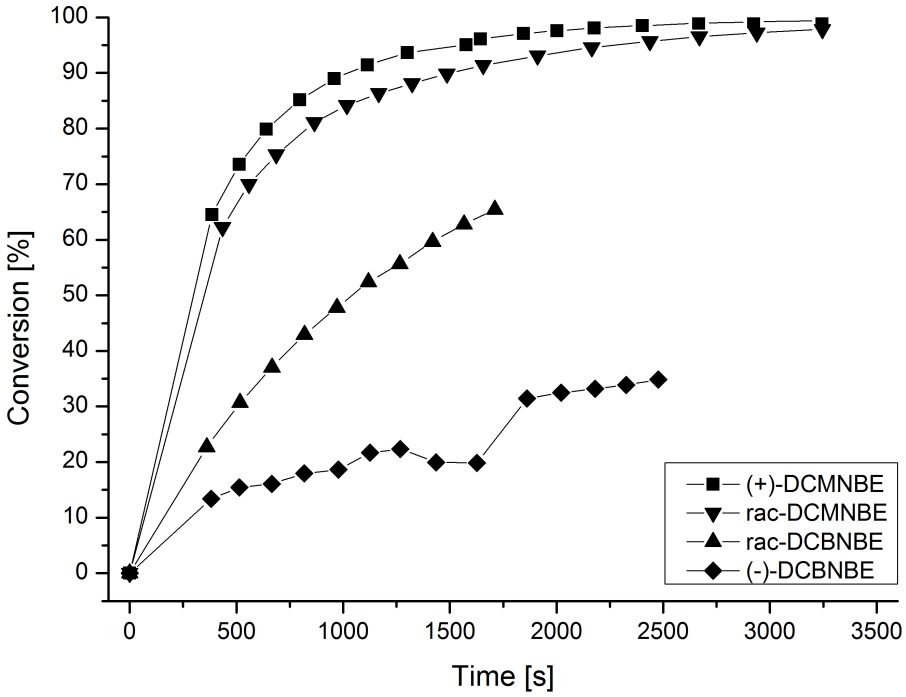


Figure 10. The consumption of *rac*-DCMNBE vs. (+)-DCMNBE and *rac*-DCBNBE vs. (-)-DCBNBE (all 0.116 M) in CD_2Cl_2 by 0.1% **5**.

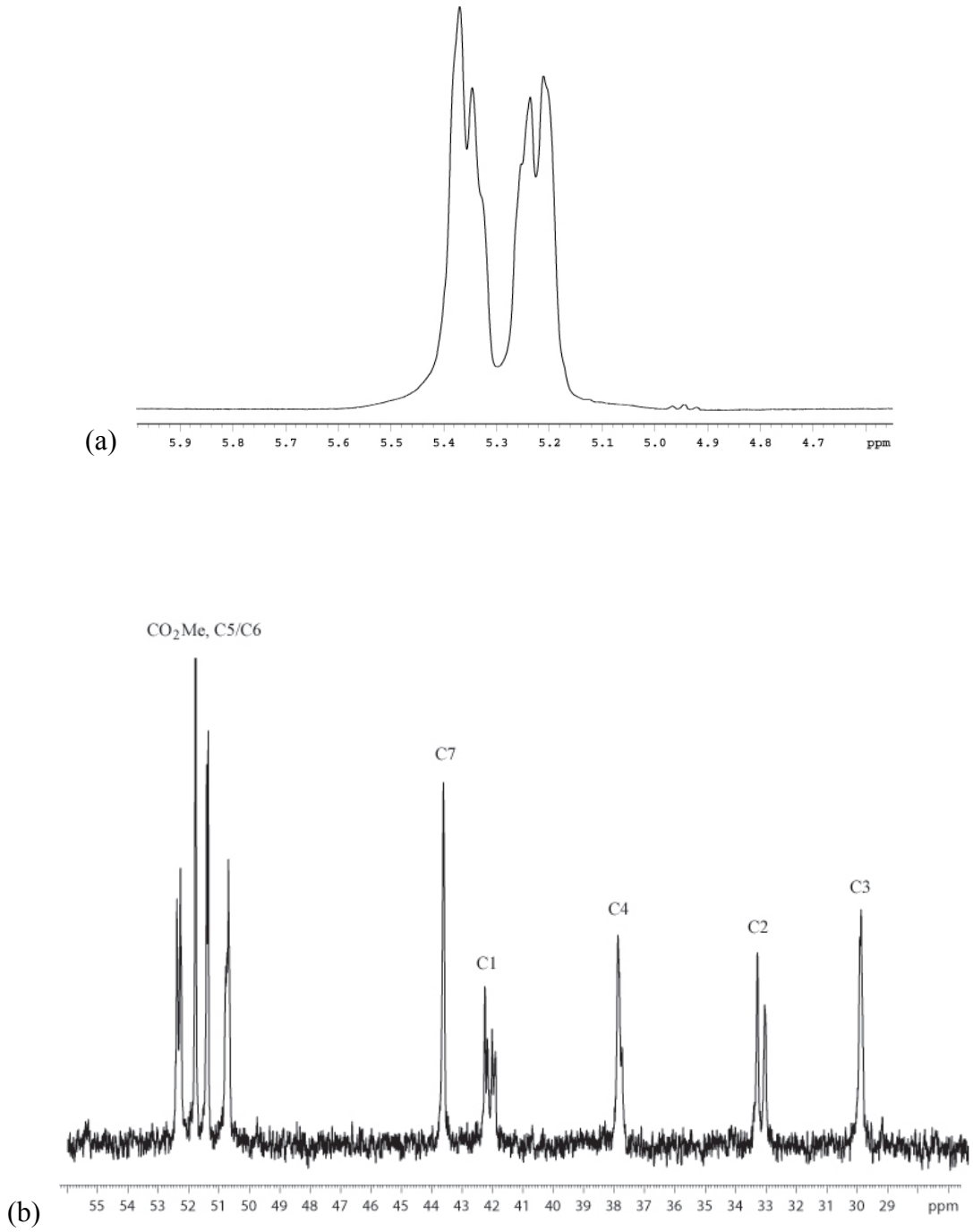


Figure 11. (a) Proton NMR spectrum (500 MHz in $CDCl_3$) in the olefinic region of poly(*rac*-DCMNBE)$_{\mathbf{5}}$ and (b) ^{13}C NMR spectrum (100 MHz in $CDCl_3$) of hydrogenated poly(*rac*-DCMNBE)$_{\mathbf{5}}$.

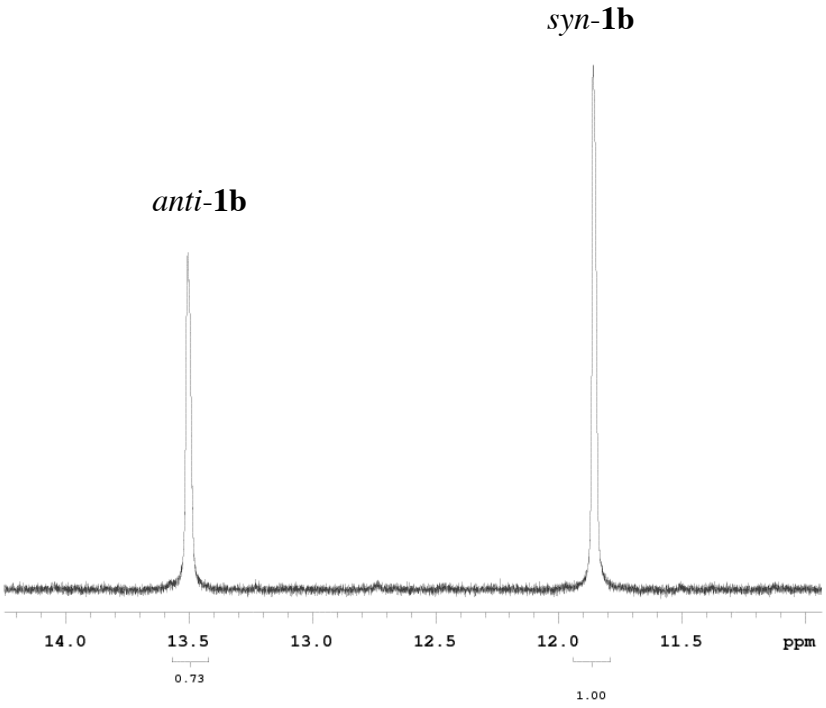


Figure 12. Alkylidene region of the ^{1}H NMR spectrum of *syn*-**1b** at -60 °C after photolysis at 366 nm at -78 °C.

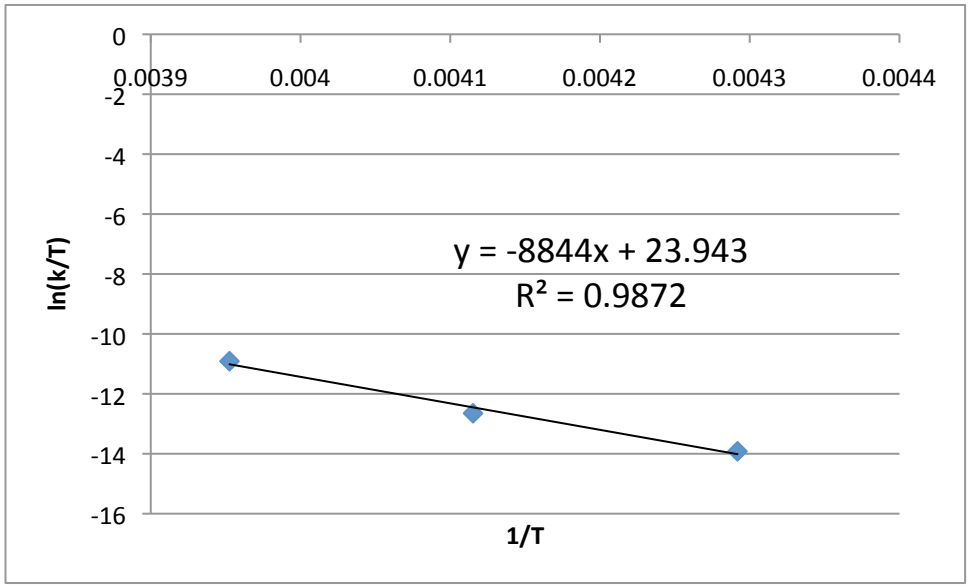


Figure 13. An Eyring plot for conversion of *anti*-**1b** to *syn*-**1b**.

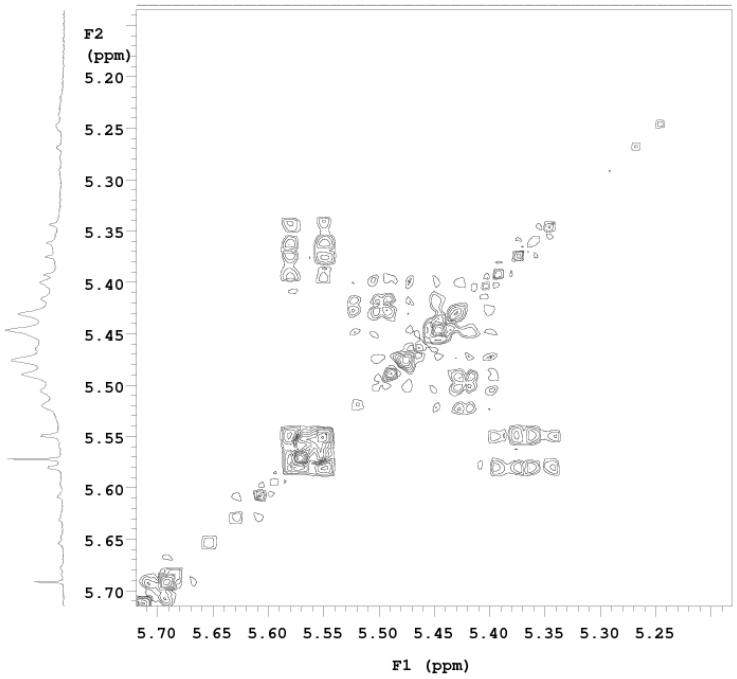
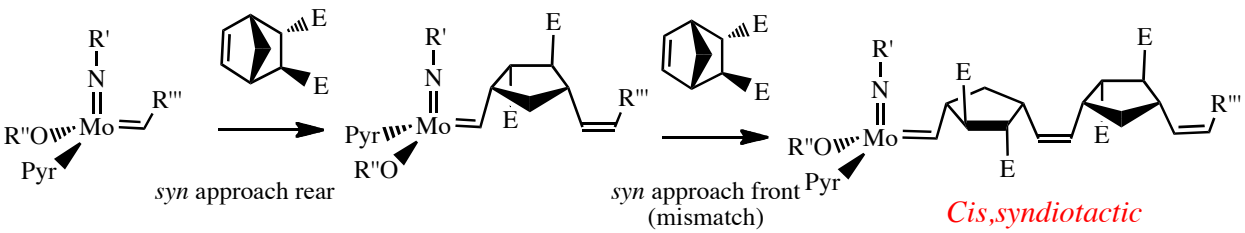
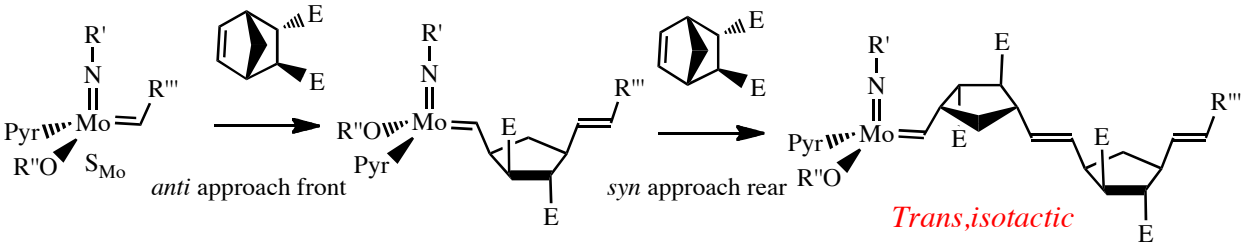


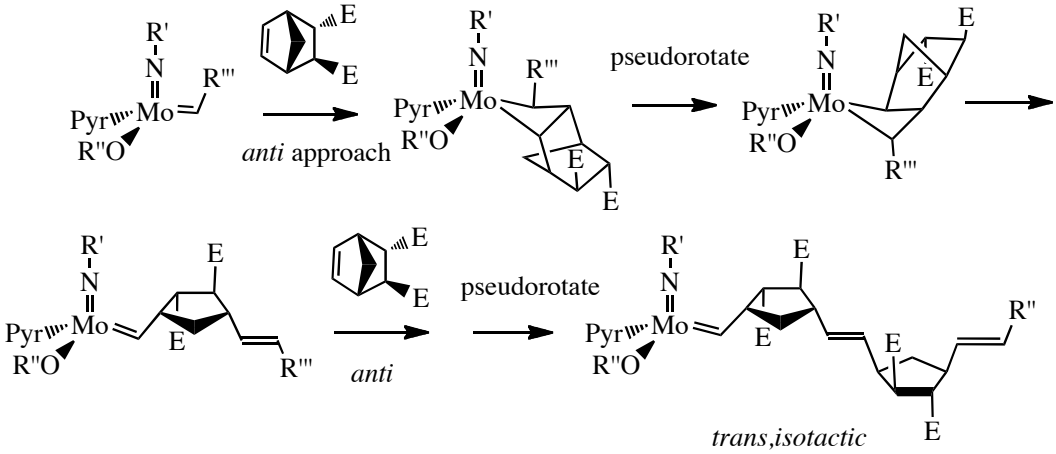
Figure 14. The gCOSY NMR spectrum of the olefinic region of a solution of (+)-DCMNBE and **1b** in toluene-d_8.



Scheme 1a. A mechanism that produces *cis,syndiotactic*-poly[(+)-DCMNBE].

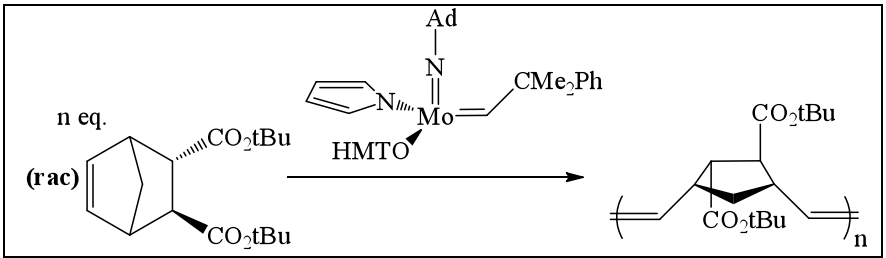


Scheme 1b. A mechanism that produces *trans,isotactic*-poly[(+)-DCMNBE].



Scheme 1c. The favored mechanism for forming *trans,isotactic* poly-[(+)-DCMNBE].

Table 1. GPC studies of poly(*rac*-DCBNBE) samples (M_n in THF vs. polystyrene).



n	Conversion	M_n	PDI
50	>99%	16400	1.05
100	>99%	36200	1.03
200	>99%	46400	1.03
400	>99%	91300	1.02

Table 2. Chemical shifts of C1-C4 in *isotactic, syndiotactic, and syndiotactic,alt* hydrogenated poly(DCMNBE) polymers (ppm in $CDCl_3$).

Tacticity	C1	C4	C2	C3
Iso	42.98	38.37	33.87	30.22
Syndio	42.13,[a] 42.22[b]	37.96,[a] 38.02[b]	33.21,[a] 33.27[b]	30.13[a,b]
Syndio,alt	42.50	38.12	33.52	30.09

[a] From the sample shown in Figure 7d. [b]From the sample of hydrogenated pure *cis,syndiotactic*-poly[(+)-DCMNBE]$_5$.

Table 3. DSC studies of poly[DCMNBE] samples and hydrogenated versions.

Initiator	% Cis	Tacticity	Unsat T_g	Hydrog T_g
3	40%	atactic	48.5 °C	39.9 °C
2	>98%	iso	80.4	52.5
1b	8%	iso	78.7	52.1
1a (-20°C)	75%	syndio	96.8	51.0
1a	95%	syndio/alt	>250	57.6

Table 4. Polymerization of enantiomerically pure 2,3-dicarboalkoxynorbornenes with tungsten catalysts.

W Cat	Monomer	T (°C)	Polymer structure
5	(+)-DCMNBE	22	>99 % *cis,syndio*
5	(-)-DCENBE	22	>99 % *cis,syndio*
5	(-)-DCBNBE	22	>99 % *cis,syndio*
4	(+)-DCMNBE	0	89% *cis,syndio*
4	(+)-DCMNBE	40	97% *cis,syndio*
4	(+)-DCMNBE	22	80% *cis,syndio*

References

[1] (a) Ivin, K. J.; Mol, J. C. *Olefin Metathesis and Metathesis Polymerization*; Academic Press: San Diego, 1997. (b) *Handbook of Metathesis*. *Applications in Polymer Synthesis*, Grubbs, R. H., Ed.; Wiley-VCH: Weinheim, 2003; Vol. 3. (c) Buchmeiser, M. R. *Chem*. *Rev*. **2000**, *100*, 1565.

[2] Schrock, R. R. *Dalton Trans*. **2011**, *40*, 7484.

[3] (a) Schrock, R. R. *Chem*. *Rev*. **2002**, *102*, 145. (b) Schrock, R. R.; Hoveyda, A. H. *Angew*. *Chem*. *Int*. *Ed*. **2003**, *42*, 4592. (c) Schrock, R. R. *Chem*. *Rev*. **2009**, *109*, *109*, 3211. (d) Schrock, R. R. *J*. *Chem*. *Soc*., *Dalton Trans*. **2001**, 2541.

[4] (a) Grubbs, R. H., Ed. *Handbook of Metathesis*; Wiley-VCH: Weinheim, 2003; Vol. 1 and 2. (b) Vougioukalakis, G. C.; Grubbs, R. H. *Chem*. *Rev*. **2010**, *110*, 1746.

[5] Brunner, H. *Angew*. *Chem*. *Int*. *Ed*. **1999**, *38*, 1194.

[6] (a) Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J*. *Am*. *Chem*. *Soc*. **2009**, *131*, 7962. (b) Flook, M. M.; Gerber, L. C. H.; Debelouchina, G. T.; Schrock, R. R. *Macromolecules* **2010**, *43*, 7515.

[7] Flook, M. M.; Ng, V. W. L.; Schrock, R. R. *J*. *Am*. *Chem*. *Soc*. **2011**, *133*, 1784.

[8] O'Dell, R.; McConville, D. H.; Hofmeister, G. E.; Schrock, R. R. *J*. *Am*. *Chem*. *Soc*. **1994**, *116*, 3414.

[9] Harwood, H. J.; Russell, D. B.; Verthe, J. J. A.; Zymonas, J. *Die Makromolekulare Chemie* **1973**, *163,* 1.

[10] Gold, L. *J. Chem. Phys.* **1958**, *28*, 91.

[11] Bazan, G. C.; Khosravi, E.; Schrock, R. R.; Feast, W. J.; Gibson, V. C.; O'Regan, M. B.; Thomas, J. K.; Davis, W. M. *J. Am. Chem. Soc.* **1990**, *112*, 8378.

[12] Yu, M.; Wang, C.; Kyle, A. F.; Jakubec, P.; Dixon, D. J.; Schrock, R. R.; Hoveyda, A. H. *Nature* **2011**, *479*, 88.

[13] Marinescu, S. C.; Schrock, R. R.; Müller, P.; Takase, M. K.; Hoveyda, A. H. *Organometallics* **2011**, *30*, 1780.

[14] Peryshkov, D. V.; Schrock, R. R.; Takase, M. K.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2011**, *133*, 20754.

[15] Marinescu, S. C.; Schrock, R. R.; Li, B.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 58.

[16] (a) Feast, W. J.; Gibson, V. C.; Ivin, K. J.; Kenwright, A. M.; Khosravi, E. *J. Molec. Catal.* **1994**, *90*, 87. (b) Feast, W. J.; Gibson, V. C.; Ivin, K. J.; Kenwright, A. M.; Khosravi, E. *J. Chem. Soc., Chem. Commun.* **1994**, 1399.

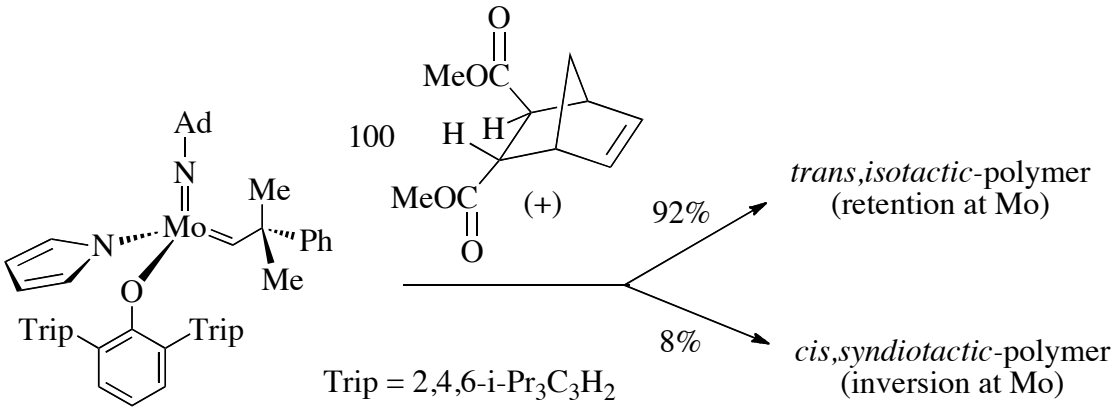
[17] (a) Ramirez, F. *Acc. Chem. Res.* **1968**, *1*, 168. (b) Mislow, K. *Acc. Chem. Res.* **1970**, *3*, 321. (c) Muetterties, E. L. *J. Am. Chem. Soc.* **1969**, *91*, 1636. (d) Muetterties, E. L. *J. Am. Chem. Soc.* **1969**, *91*, 4115. (e) Muetterties, E. L. *Acc. Chem. Res.* **1970**, *3*, 266. (f) Moberg, C. *Angew. Chem. Int. Ed.* **2011**, *50*, 10290.

[18] (a) Feldman, J.; DePue, R. T.; Schaverien, C. J.; Davis, W. M.; Schrock, R. R. in *Advances in Metal Carbene Chemistry*, Schubert, U.; Ed.; Kluwer Academic Publishers: Boston, 1989, p. 323. (b) Feldman, J.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 2266. (c) Schrock, R. R.; DePue, R. T.; Feldman, J.; Yap, K. B.; Yang, D. C.; Davis, W. M.;Park, L. Y.; DiMare, M.; Schofield, M.; Anhaus, J.; Walborsky, E.; Evitt, E.; Krüger, C.; Betz, P. *Organometallics* **1990**, *9*, 2262. (d) Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R. *Organometallics* **1990**, *9*, 2535. (e) Robbins, J.; Bazan, G. C.; Murdzek, J. S.; O'Regan, M. B.; Schrock, R. R. *Organometallics* **1991**, *10*, 2902. (f) Feldman J.; Schrock, R. R. *Prog. Inorg. Chem.* **1991**, *39*, 1.

[19] (a) Tsang, W. C. P.; Hultzsch, K. C.; Alexander, J. B.; Bonitatebus, P. J., Jr.; Schrock, R. R.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2003**, *125*, 2652. (b) Tsang, W. C. P.; Jamieson, J. Y.; Aeilts, S. A.; Hultzsch, K. C.; Schrock, R. R.; Hoveyda, A. H. *Organometallics* **2004**, *23*, 1997.

[20] Marinescu, S. C.; King, A. J.; Schrock, R. R.; Singh, R.; Müller, P.; Takase, M. K. *Organometallics* **2010**, *29*, 6816.

TOC


Ad
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MeOC
(+)
O
92%
8%
trans,isotactic-polymer
(retention at Mo)
cis,syndiotactic-polymer
(inversion at Mo)
Trip = 2,4,6-i-Pr3C3H2

Five-Coordinate Rearrangements of Metallacyclobutane Intermediates During Ring-Opening Metathesis Polymerization (ROMP) of 2,3-Dicarboalkoxynorbornenes by Molybdenum and Tungsten Monoalkoxide Pyrrolide (MAP) Initiators.

Margaret M. Flook, Janna Börner, Stefan M. Kilyanek, Laura C. H. Gerber, and Richard R. Schrock*

Experimental details.

Experimental Section

General Details. All air-sensitive manipulations were performed under nitrogen in a drybox or using Schlenk techniques. All glassware was oven-dried and allowed to cool under vacuum or nitrogen before use. NMR spectra were obtained on Bruker 400 MHz and Varian 500 MHz spectrometers, 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, methylene chloride 5.32, toluene 2.09; ^{13}C (δ) benzene 128.39, chloroform 77.16, methylene chloride 54.00, toluene 20.40). GPC analyses were obtained on a Waters GPC instrument and the molecular weights in THF were compared to polystyrene standards. IR spectra were recorded on a Nicolet S10 FT-IR spectrometer. All reagents were used without further purification unless noted otherwise. Pentane was washed with H_2SO_4, then water and saturated aqueous $NaHCO_3$, and dried over $CaCl_2$ pellets over a period of 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. 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.

(+)-DCMNBE and endo,exo-2,3-dimethoxymethylnorbornene, were synthesized according to published procedures.[i] (-)-Bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid was synthesized according to the published procedure for (+)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid[ii] but using (+)-menthol as the chiral starting material instead of the reported (-)-menthol. Liquid monomers were dried with calcium hydride, freeze-pump-thaw degassed, and distilled before use. Solid monomers were dried under vacuum, passed as a toluene solution through activated alumina, and dried over molecular sieves before use.

Compounds **1a**[iii] and **1b**[iv] have been isolated and fully characterized and shown to behave in ROMP reactions the same way as the complexes prepared *in situ*. Complex **1c** was shown to

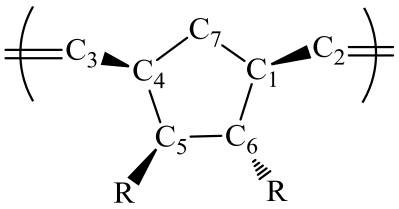
be formed fully *in situ* upon addition of HMTOH to Mo(NAr')($CHCMe_2Ph$)$(Pyr)_2$, but it could not be isolated in crystalline form.[v] It has been isolated via a new synthetic method to be reported elsewhere.[vi] Complexes **1a - 1c** were prepared *in situ* in a reaction between the corresponding bispyrrolide complexes, Mo(NR)($CHCMe_2Ph$)$(Pyr)_2$ (R = Ad or Ar') and one equivalent of HMTOH or HIPTOH. Complexes **2**,[vii] **3**,[viii] **4**,[ix] and **5**[x] were prepared according to literature procedures.

Dimethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (rac-DCMNBE). This compound has been reported previously[xi] and was prepared by an adapted procedure. Freshly distilled cyclopentadiene (14.7 g, 0.222 mol) was added to a 50 mL toluene suspension of dimethyl fumarate (28.9 g, 0.200 mol, 0.9 eq). The mixture was allowed to stir overnight, after which all volatiles were removed at 30 °C under reduced pressure: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.27 (mult., 1H, olefinic); 6.07 (mult., 1H, olefinic); 3.71 (s, 3H, CO_2*Me*); 3.64 (s, 3H, CO_2*Me*); 3.37 (t, 1H); 3.25 (s, 1H); 3.12 (s, 1H); 2.68 (d, 1H); 1.60 (d, 1H); 1.45 (d, 1H).

Diethyl bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate (rac-DCENBE and (-)-DCENBE). These known compounds have been prepared by an adapted procedure.[v] Racemic bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid (1.09 g, 6.0 mmol) was dissolved in 30 mL ethanol and concentrated sulfuric acid (4 mL of 95% aq soln, 71 mmol, 11.9 eq) was added. After stirring for 48 hours at room temperature, the mixture was extracted with hexanes. The organic layer was washed with aqueous sodium bicarbonate solution, followed by water and brine, and then dried with magnesium sulfate. The hexane solution was filtered and all volatiles were removed under reduced pressure, leaving a colorless oil. The ^{1}H NMR spectrum of the oil matched that of the reported compound. The enantiomerically pure version, (-)-DCENBE, was prepared in the same manner, starting from enantiomerically pure (-)-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.27 (mult, 1H, olefinic); 6.06 (mult., 1H, olefinic); 4.16 (mult., 2H, $CO_2CH_2CH_3$); 4.10 (mult., 2H, $CO_2CH_2CH_3$); 3.37 (t, 1H); 3.26 (s, 1H); 3.11 (s, 1H); 2.67 (d, 1H); 1.61 (d, 1H); 1.44 (d, 1H); 1.27 (t, 3H, $CO_2CH_2CH_3$); 1.23 (t, 3H, $CO_2CH_2CH_3$).

Representative polymerization procedure. Monomer (0.449 mmol, 100 equiv) was dissolved in 1 mL toluene, and added to a 1 mL toluene solution of initiator (4.49 μmol) under stirring. The progress of the reaction was monitored by diluting aliquots of the reaction mixture with C_6D_6 or $CDCl_3$ and recording the ^1H NMR spectra. After consumption of the monomer was observed, excess benzaldehyde (~200 μL) was added and the mixture was stirred for at least one hour. The polymer was precipitated by adding the mixture dropwise to 100 mL of vigorously stirred methanol, affording a fine white to off-white solid. The solid was isolated by filtration over a fine glass frit or centrifugation, washed with methanol and dried *in vacuo*. Polymer yields were above 90% in all cases unless otherwise noted in the text.

Numbering system for polynorbornenes:



***Cis*,syndio,alt-poly[*rac*-DCMNBE].** ^1H NMR ($CDCl_3$, 500 MHz) δ 5.34 (dd, 1H, olefinic, J_{HH} = 10.4 Hz, 11.8 Hz), 5.23 (dd, 1H, olefinic, J_{HH} = 10.4 Hz, 11.8 Hz), 3.66 (s, 3H, CO_2*Me*), 3.61 (s, 3H, CO_2*Me*), 3.31 (m, 2H, C_4H, C_1H), 3.08 (m, 1H, C_5H), 2.98 (m, 1H, C_6H), 2.09 (m, 1H, C_7H), 1.36 (m, 1H, C_7H); ^{13}C NMR (C_6D_6, 125 MHz) δ 174.22, 172.94 (*C*O_2Me), 133.23, 130.84 (C_2, C_3), 52.99, 52.50 (CO_2*Me*), 52.00, 51.73 (C_1, C_4), 42.24, 40.86 (C_5, C_6), 39.41 (C_7).

***Cis*,syndio,alt-poly[*rac*-DCBNBE].** ^1H NMR ($CDCl_3$, 500 MHz) δ 5.30 (dd, 1H, olefinic, J_{HH} = 12.0 Hz, 10.1 Hz); 5.24 (dd, 1H, olefinic, J_{HH} = 12.0 Hz, 10.3 Hz); 3.29 (t, 1H); 3.01 (mult., 2H); 2.80 (mult., 1H); 2.11 (t, 1H); 1.41 (s, 9H, CO_2*tBu*); 1.37 (s, 9H, CO_2*tBu*); ^{13}C NMR (C_6D_6, 125 MHz) δ 172.81, 171.98 (*C*O_2Me), 133.18, 130.63 (C_2, C_3), 80.51, 80.31 (CO_2*C*Me_3), 54.24, 53.12 (C_1, C_4), 41.60, 40.81 (C_5, C_6), 39.15 (C_7), 28.25, 28.16 (CO_2C*Me*$_3$).

***Cis*,syndio,alt-poly[*rac*-DCENBE].** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.33 (dd, 1H, olefinic, J_{HH} = 11.7 Hz, 9.9 Hz); 5.23 (dd, 1H, olefinic, J_{HH} = 11.7 Hz, 10.4 Hz); 4.00-4.17 (mult., 4H, $CO_2CH_2CH_3$); 3.34 (mult.; 1H); 3.23 (t, 1H); 3.07 (mult., 1H); 2.95 (t, 1H); 2.10 (mult.; 1H); 1.36 (mult., 1H); 1.22 (t, 3H, $CO_2CH_2CH_3$); 1.19 (t, 3H, $CO_2CH_2CH_3$).

***Trans*,isotactic-poly[(+)-DCMNBE].** ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.49 (dd, 1H, olefinic, J_{HH} = 15.7 Hz, 7.7 Hz), 5.28 (dd, 1H, olefinic, J_{HH} = 15.7 Hz, 8.4 Hz), 3.66 (s, 3H, CO_2Me), 3.62 (s, 3H, CO_2Me), 3.25 (m, 1H, C_5H), 2.96 (m, 2H, C_4H, C_1H), 2.66 (m, 1H, C_6H), 1.97 (m, 1H, C_7H), 1.47 (m, 1H, C_7H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 174.37; 173.33 (CO_2Me); 133.22; 130.28 (C_2, C_3); 52.29; 52.03 (CO_2Me); 51.86; 51.71 (C_1, C_4); 46.82; 44.39 (C_5, C_6); 39.29 (C_7).

Cis,syndiotactic-poly[(+)-DCMNBE]. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.37 (d, 1H, olefinic C*H*, ^{3}J = 6 Hz); 5.19 (d, 1H, olefinic C*H*, ^{3}J = 5 Hz); 3.66 (s, 3H, OCH_3); 3.60 (s, 3H, OCH_3); 3.32 (m, 2H); 3.07 (m, 1H); 2.98 (m, 1H); 2.06 (m, 1H); 1.36 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 174.17; 172.92; 132.66; 131.19; 52.67; 52.16; 52.02; 51.83; 42.25; 40.65; 38.95.

Cis,syndiotactic-poly[(-)-DCENBE]. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.35 (d, 1H, olefinic C*H*, ^{3}J = 7 Hz); 5.19 (d, 1H, olefinic C*H*, ^{3}J = 7 Hz); 3.99-4.16 (m, 4H, OCH_2); 3.31 (m, 1H); 3.23 (t, 1H, ^{3}J = 9 Hz); 3.07 (m, 1H); 2.93 (t, 1H, ^{3}J = 9 Hz); 2.07 (q, 1H, ^{3}J = 7 Hz); 1.36 (m, 1H); 1.20 (m, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 125 MHz) δ 173.71; 172.55; 132.68; 131.08; 60.74; 60.64; 52.96; 52.17; 42.07; 40.74; 39.00.

Cis,syndiotactic-poly[(-)-DC^{t}BuNBE]. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 5.29 (d, 1H, olefinic C*H*, ^{3}J = 7 Hz); 5.24 (d, 1H, olefinic C*H*, ^{3}J = 7 Hz); 3.25 (m, 1H); 3.06 (m, 1H); 3.01 (t, 1H, ^{3}J = 9 Hz); 2.77 (t, 1H, ^{3}J = 9 Hz); 2.10 (m, 1H); 1.41 (s, 9H, CH_3); 1.37 (s, 9H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 172.98; 172.03; 132.79; 131.14; 80.60; 80.34; 54.23; 53.22; 41.70; 40.94; 39.02; 28.33.

Representative Hydrogenation Procedure. Poly-(+)-DCMNBE (72 mg, 0.343 mmol of olefinic groups) prepared using **1b** as catalyst was suspended in 2 mL xylenes under a nitrogen atmosphere. Tosyl hydrazide (446 mg, 2.4 mmol, 7 eq per olefin) was added to the mixture. The mixture was heated to 100 °C, at which point the cloudy mixture became clear. After further heating to 115 °C, gas evolution was observed, and the mixture was heated to 130 °C for a further 90 minutes until gas evolution ceased. The solution was cooled to 50 °C and xylenes were removed under reduced pressure. Methanol was added to the resulting solid and the milky white methanol suspension was decanted off of the gooey solid polymer. The polymer was redissolved in minimum chloroform, and reprecipitated from methanol to give a stringy white solid which was isolated and rinsed with methanol. The entire hydrogenation procedure was repeated until ^{1}H NMR spectroscopy showed complete disappearance of the olefin resonances.

Hydrogenated isotactic-poly[(+)-DCMNBE]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.67 (s, 6H, CO_2*Me*); 3.16 (mult, 1H); 2.79 (mult, 1H); 2.19 (br s, 1H); 1.99 (mult, 2H); 1.65 (br s, 1H); 1.36 (mult, 2H); 1.10 (mult, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 175.59; 174.74 (*C*O_2Me); 52.66; 52.08; 51.63; 50.97; 44.00; 42.98; 38.37; 33.87; 30.22.

Hydrogenated syndiotactic-poly[(+)-DCMNBE]: (only major resonances reported) ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.67 (s, 6H, CO_2*Me*); 3.17 (mult, 1H); 2.80 (mult, 1H); 2.19 (br s, 1H); 2.01 (mult, 2H); 1.63 (br s, 1H); 1.38 (mult, 2H); 1.10 (mult, 2H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 175.54; 174.60 (*C*O_2Me); 52.60; 52.03; 51.66; 50.97; 43.84; 42.13; 37.96; 33.21; 30.13.

Hydrogenated syndiotactic-poly[-(-)-DCENBE]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.08 (m, 1H); 1.16 (m, 1H); 1.26 (m, 6H, C*H*$_3$); 1.40 (m, 2H); 1.65 (m, 1H); 1.99 (m, 1H); 2.05 (br s, 1H); 2.18 (br s, 1H); 2.78 (dd, 1H, C*H*, ^{3}J = 9 Hz, ^{3}J = 6 Hz); 3.13 (dd, 1H, C*H*, ^{3}J = 9 Hz, ^{3}J = 6 Hz); 4.13 (m, 4H, OC*H*$_2$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 175.16; 174.17; 60.69; 60.54; 52.80; 51.14; 43.78; 42.30; 38.14; 33.32; 30.18; 14.39.

Hydrogenated syndio,alt-poly[*rac*-DCMNBE]: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 3.67 (s, 6H, CO_2*Me*); 3.17 (mult, 1H); 2.80 (mult, 1H); 2.23 (br s, 1H); 1.99 (mult, 2H); 1.64 (br s, 1H);

1.35 (mult, 2H); 1.17 (mult, 1H); 1.08 (mult, 1H); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 175.52; 174.66 (*C*O_2Me); 52.52; 51.99; 51.61; 50.93; 43.83; 42.50; 38.12; 33.52; 30.09.

References

[i] O'Dell, R.; McConville, D. H.; Hofmeister, G. E.; Schrock, R. R. *J. Am. Chem. Soc.* **1994**, *116*, 3414.

[ii] Sunaga, T.; Ivin, K. J.; Hofmeister, G. E.; Oskam, J. H.; Schrock, R. R. *Macromolecules* **1994**, *27*, 4043.

[iii] Flook, M. M.; Ng, V. W. L.; Schrock, R. R. *J. Am. Chem. Soc.* **2011**, *133*, 1784.

[iv] Flook, M. M.; Jiang, A. J.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2009**, *131*, 7962.

[v] Margaret M. Flook, Ph.D. Thesis, Massachusetts Institute of Technology, 2011.

[vi] A. G. Lichtscheidl, unpublished results.

[vii] Singh, R.; Czekelius, C.; Schrock, R. R.; Müller, P.; Hoveyda, A. H. *Organometallics* **2007**, *26*, 2528.

[viii] Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

[ix] Marinescu, S. C.; Schrock, R. R.; Mueller, P.; Takase, M. K.; Hoveyda, A. H. *Organometallics* **2011**, *30*, 1780.

[x] Peryshkov, D. V.; Schrock, R. R.; Takase, M. K.; Müller, P.; Hoveyda, A. H. *J. Am. Chem. Soc.* **2011**, *133*, 20754.

[xi] H. Koch. *Monatsh. Chem.* **1962**, *93*, 1343.