Stereospecific Ring-Opening Metathesis Polymerization of 3-Methyl-3-phenylcylopropene by Molybdenum Alkylidene Initiators

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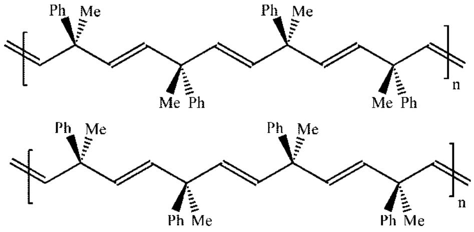
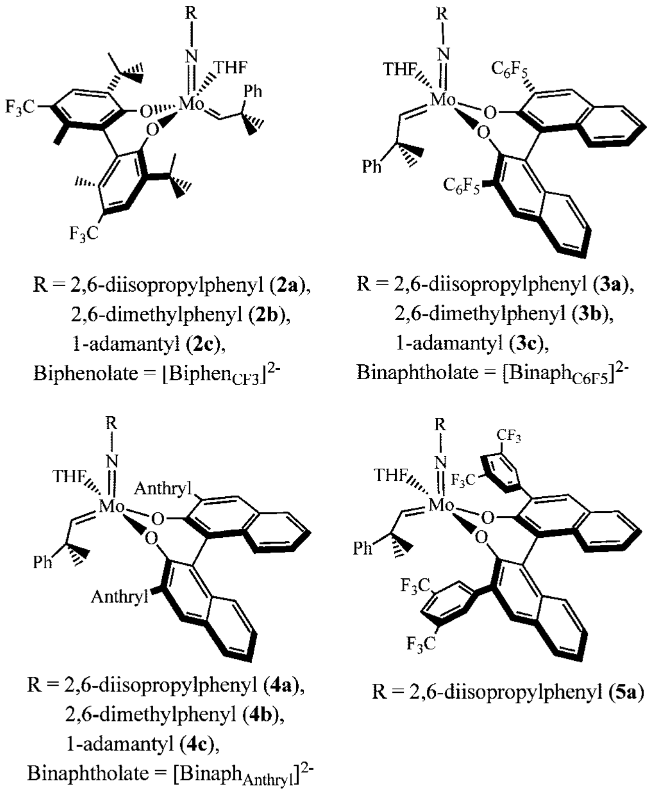
Recently we reported the successful ROMP of 3,3-disubstituted cyclopropenes, e.g., 3-methyl-3-phenylcyclopropene (**1**).[1] To our knowledge this is the only report of ROMP of a cyclopropene.[2] Most of these polymerizations appear to be living, perhaps largely because the alkylidene in the propagating species resembles a neopentylidene or neophylidene species, which are known to be the most stable terminal alkylidenes in the $Mo(NR)(CHR')(OR'')_2$ family toward bimolecular decomposition.[3] It was proposed that *trans* linkages are formed between the repeat units in poly(**1**) as a consequence of steric hindrance in the molybdabicyclopentane intermediate. If the substituents on C(3) of the cyclopropene are different, as is the case for **1**, then tacticity is possible. Below are shown the two regular structures for *trans*-poly(**1**). We report here the preparation of highly tactic *trans*-poly(**1**) through enantiomorphic site control with initiators that are related to those that have been employed for asymmetric metathesis reactions.[4]



trans,isotactic poly(**1**)

trans,syndiotactic poly(**1**)

In Figure 1 are shown several recently reported molybdenum species[5] that contain new biphenolate or binaphtholate ligands. Polymerization of **1**[6] using **2a** yielded a polymer whose ^{13}C NMR spectrum (Figure 2) is characteristic of a relatively long-range order. In particular, a single sharp resonance is observed for the quaternary carbon atom at 46.05 ppm and for the olefinic carbon atom at 137.23 ppm. An IR spectrum of poly(**1**) reveals absorbances at 963 and 982 cm^{-1} of approximately equal intensity that are not present in the spectrum of **1** and that are most consistent with the presence of *trans* C=C bonds in the polymer[7] (see Supporting Information). Therefore, we propose that poly(**1**) prepared with **2a** has a *trans* and highly tactic (>99%) microstructure and that the 46.05 and 137.23 ppm resonances in the ^{13}C NMR spectrum are characteristic of that structure. The ^{1}H NMR spectrum of this polymer is also sharp and well-resolved. DSC studies (Table 1) revealed a glass transition temperature (T_g) of 105 °C, while the GPC displayed a unimodal peak with a PDI of 1.80. Polymerization in THF or with initiators in which the steric bulk of the imido ligand is decreased (as in **2b** or **2c**) also led to tactic *trans*-poly(**1**), but the PDI did not improve (Table 1). The polymer prepared using **2c** revealed a high molecular weight peak (~40% of the total) in addition to that with M_n = 12 000. At this stage it is not clear why the polydispersity indices are relatively high (~2).



R = 2,6-diisopropylphenyl (**2a**),
2,6-dimethylphenyl (**2b**),
1-adamantyl (**2c**),
Biphenolate = $[Biphen_{CF3}]^{2-}$

R = 2,6-diisopropylphenyl (**3a**),
2,6-dimethylphenyl (**3b**),
1-adamantyl (**3c**),
Binaphtholate = $[Binaph_{C6F5}]^{2-}$

R = 2,6-diisopropylphenyl (**4a**),
2,6-dimethylphenyl (**4b**),
1-adamantyl (**4c**),
Binaphtholate = $[Binaph_{Anthryl}]^{2-}$

R = 2,6-diisopropylphenyl (**5a**)

Figure 1. Initiators that contain relatively electron-withdrawing diolate ligands. Compounds **2a**, **2b**, and **2c** contain racemic biphenolate ligands. All binaphtholate ligands have the *R* configuration, as drawn.

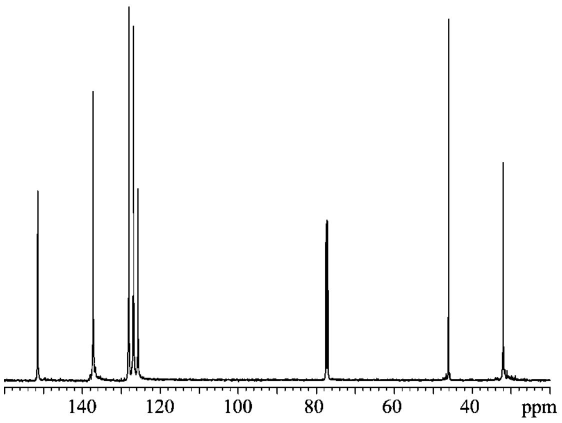


Figure 2. A 125 MHz ^{13}C NMR spectrum (CD_2Cl_2) of tactic *trans*-poly(**1**).

Initiator **3a** also afforded tactic *trans*-poly(**1**) with a relatively low PDI on the basis of ^{13}C NMR and GPC studies. A THF-free version of **3a** (**3a′**) could be prepared by reacting $Mo(NAr)(CHCMe_2Ph)(2,5\text{-}Me_2NC_4H_2)_2$ (Ar = 2,6-diisopropylphenyl; $2,5\text{-}Me_2NC_4H_2$ = 2,5-dimethylpyrrolide) with 1 equiv of $H_2[Binaph_{C6F5}]$ in CH_2Cl_2.[5] The ^{1}H and ^{13}C NMR spectra of poly(**1**) prepared using **3a′** were identical to those prepared using **3a**, although the PDI of the polymer was somewhat higher. So at least in the case of the molybdenum initiator that contains the $[Binaph_{C6F5}]^{2-}$ ligand, the presence of 1 equiv of THF or 2 equiv of 2,5-dimethylpyrrole during polymerization had no

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Table 1. Characterization Data for Poly(1) Prepared in Dichloromethane Using Initiators 2−5

initiator	solvent	PDI[a]	T_g[b]	M_n[a]	yield (%)	tacticity (%)[c]
2a	CH_2Cl_2	1.80	105	12 000	95	99
2a	THF	2.17	105	11 000	96	99
2b	CH_2Cl_2	2.07	105	12 000	98	>99
2b	THF	2.18	105	12 000	95	>99
2c	CH_2Cl_2	1.87	102(100)	12 000	90	>99
2c	THF	2.13	102(100)	9 000	93	>99
3a	CH_2Cl_2	1.18	107(105)	14 000	94	>99
3a′[d]	CH_2Cl_2	1.93	107	10 000	94	>99
3b	CH_2Cl_2	2.12	*f*	22 000	10	atactic
3c	CH_2Cl_2	*f*	*f*	*f*	<10	*f*
4a	CH_2Cl_2	<1.10	102	13 000	90	∼90
4b	CH_2Cl_2	<1.10	102	15 000	95	∼90
4c	CH_2Cl_2	1.90	*f*	25 000	30	atactic
5a[e]	CH_2Cl_2	3.35	87	6 000	60	atactic

[a] Determined by GPC in THF vs polystyrene standards; 100 equiv of monomer was employed. [b] Determined by DSC. Heating and cooling transitions produced identical T_g's, except where noted in parentheses for the cooling transition. [c] Tacticity was determined on the basis of the area of the resonance at 46.05 ppm for the quaternary carbon resonance in the ^{13}C NMR spectrum. For the sake of simplicity, we will assume that all polymers are *trans* and that any polymer with several resonances between 46 and 47 ppm is *trans* and "atactic". [d] Generated *in situ* in CH_2Cl_2 by treating $Mo(NAr)(CHCMe_2Ph)(2,5\text{-}Me_2NC_4H_2)_2$ with $H_2[Binaph_{C6F5}]$. [e] Generated *in situ* in THF by treating $Mo(NAr)(CHCMe_2Ph)(2,5\text{-}Me_2NC_4H_2)_2$ with $H_2[Binaph_{CF3}]$. [f] Not determined.

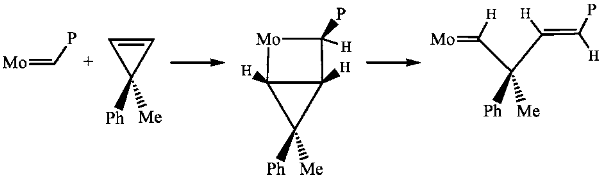
effect on the microstructure of poly(**1**). Polymerization of **1** with **4a** in CH_2Cl_2 yielded ∼90% tactic *trans*-poly(**1**), while poly(**1**) prepared using **5a** that was generated *in situ* by reacting $Mo(NAr)(CHCMe_2Ph)(2,5\text{-}Me_2NC_4H_2)_2$ with 1 equiv of $H_2[Binaph_{CF3}]$[5] in THF yielded a polymer with irregular structure in 60% yield. The high PDI and low molecular weight of poly(**1**) prepared with **5a** suggest that the polymerization is poorly behaved.

In contrast to polymerizations with **2b** or **2c**, initiators **3b**, **3c**, **4b**, and **4c** did not lead to polymers with regular structures. While **4b** afforded a polymer with the 90% bias toward the tactic *trans*-poly(**1**), initiators **3b**, **3c**, and **4c** yielded polymers with little long-range order in relatively low yields.

Initiators **6**−**14** shown in Figure 3 also were explored for polymerization of **1** (Table 2). All compounds shown in Figure 3 are known in the literature[8−12] except **12**, which was prepared through addition of the potassium salt of $H_2[Binaph_{t\text{-}Bu}]$ (3,3′,6,6′-tetra-*tert*-butyl-2-binaphthol)[13] to $Mo(NAr)(CHCMe_2Ph)(OTf)_2(DME)$ in THF. Any tacticity that arises with achiral **6**, **7**, or **8** would have to result from chain end control. The ^1H NMR spectrum of **12** in CD_2Cl_2 showed an alkylidene resonance at 10.71 ppm, which is assigned to the alkylidene proton in the *syn* isomer on the basis of a J_{CH} value of 120 Hz. The relatively broad alkylidene resonance that is observed at 12.70 ppm (5%) we ascribe to an *anti* isomer to which THF is bound in the solid state. Compound **12** is largely THF-free, according to elemental analysis. In contrast, **11**, **13**, and **14** are isolated as THF adducts.[10] Compound **12** is the first binaphtholate derivative that contains *tert*-butyl groups in the 3- and 3′-positions, which we believe to be the reason why even the *anti* isomer of **12** (in contrast to **13** and **14**) does not bind THF strongly. Analogous biphenolate species **9** and **10** are isolated as THF-free species.[9]

The ^1H NMR spectra of all polymers prepared with initiators **6**−**14** contained a broad olefinic proton resonance, while the ^{13}C NMR spectra revealed quaternary carbon resonances in the region between 46 and 47 ppm (as shown for several samples in Figure 4) and olefinic carbon resonances between 135 and 139 ppm. IR spectra of poly(**1**) prepared with **6**, **7**, **9**, **11**, and **14** again reveal IR absorptions at 963 and/or 982 cm^{-1} that are believed to be characteristic of *trans* C=C linkages; in poly(**1**) prepared with **6** or **9** the 982 cm^{-1} absorption dominates (see Supporting Information). Therefore, we tentatively assign these poly(**1**) samples as having the *trans* configuration. Observation of multiple quaternary and olefinic carbon resonances suggests that these poly(**1**) samples do not exhibit long-range order. The polymer prepared employing **14** showed a bias (∼80%) toward tactic *trans*-poly(**1**) (Figure 4, top). DSC analyses revealed a range of glass transition temperatures; a T_g of 42 °C was observed for poly(**1**) prepared using **6**, whereas poly(**1**) prepared using **14** had a T_g of 95 °C. These values should be compared with a T_g of 105 °C for tactic *trans*-poly(**1**) (Table 1).

Polymerization of **1** with chiral initiators of the type employed here is potentially complex. If *trans* linkages are produced, the monomer must add to the Mo=CHP (P = growing polymer) bond to yield a molybdabicyclopentane intermediate in which P and the cyclopropane ring are *trans* to one another, as shown in eq 1. However, the two faces of the C=C bond in the cyclopropene are inequivalent; the Mo=CHP species may be either a *syn* or *anti* isomer, and there are two different CNO faces in a four-coordinate chiral alkylidene species where an olefin is believed to add to the metal. Therefore, for an all *trans* polymer, eight distinct (diastereomeric) propagating pathways appear to be possible from a single metal center, which can be narrowed down to four pathways if the addition through one face of the cyclopropene is more selective for steric reasons (for example as shown in eq 1). It should be noted that an initiator that contains a racemic or enantiomerically pure diolate ligand will yield a polymer with the same microstructure as long as no chain transfer occurs between metal centers.



(1)

If the five-coordinate molybdabicyclopentane species does not rearrange before the intermediate opens to yield the new alkylidene, the Mo=CHP isomer that forms when a cyclopropene inserts will be the opposite to that of the initial isomer; i.e., a *syn* isomer would yield an *anti* isomer, or vice versa. The alkylidene then would have to rotate about the Mo=C bond in order to form the preferred (i.e., most reactive) *syn* or *anti* isomer for the next insertion. If this pathway is operative, then an isotactic polymer would result. The rate of rotation about the Mo=C bond has been shown to vary by several orders of magnitude among a collection of bisalkoxide imido alkylidene complexes,[14] but quantitative data are difficult or impossible to obtain in general. It has also been found that *syn* and *anti* isomers can have dramatically different reactivities, but again quantitative data are difficult or impossible to obtain.

Under the aforementioned circumstances we were somewhat surprised that highly regular poly(**1**) was possible. We were also intrigued to find such a subtle dependence of tacticity with what appear to be small changes in the initiators. For example, use of **9** (Figure 3) as an initiator led to an *all-trans* polymer (it is proposed) with little order (Table 2, Figure 4), while use of **2a** (Figure 1), in which the methyl groups in the 5- and 5′-positions of the biphenolate are fluorinated, led to highly tactic *trans*-poly(**1**) (Figure 2, Table 1). Direct attachment of fluorinated groups to the binaphtholate backbone (as in **3a**) is also required for forming tactic *trans*-poly(**1**). Finally, the nature of the imido group can make a difference (as in the **3** series of initiators) or

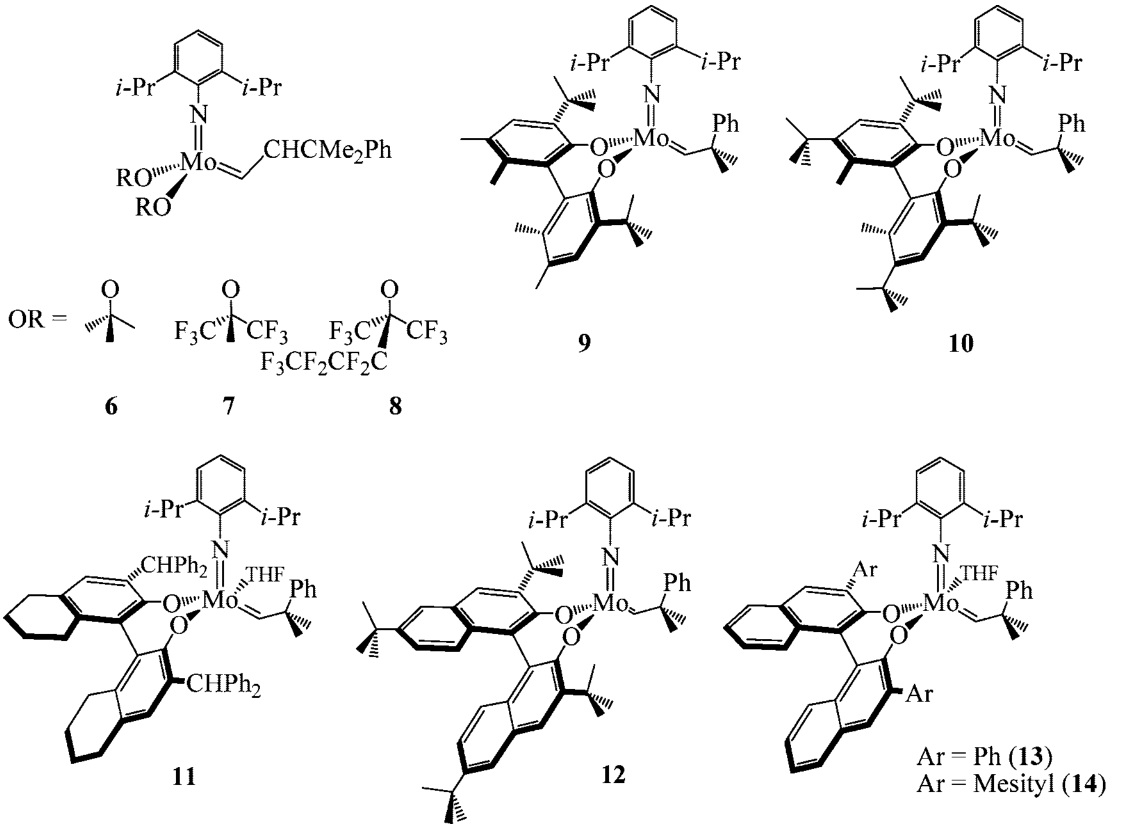


Figure 3. Some of the initiators screened for the preparation of poly(**1**). All biphenolate or binaphtholate ligands are racemic.

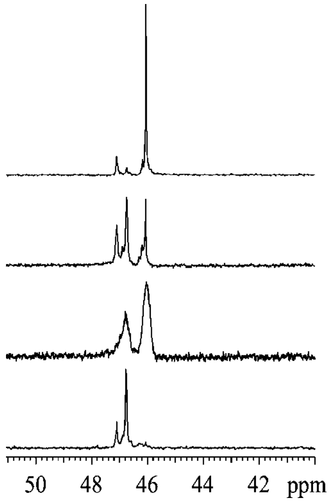


Figure 4. Quaternary carbon region in ^{13}C NMR spectra of poly(**1**) in CD_2Cl_2 prepared employing initiators **6** (bottom), **7**, **9**, and **14** (top).

Table 2. Characterization Data for Poly(1) Prepared in Dichloromethane Using Initiators 6−14[a]

initiator	PDI[b]	T_g (°C)[c]	M_n[b]	yield (%)	tacticity[d]
6	1.50	42	13 000	97	atactic
7	<1.10	85	12 000	95	atactic
8	1.12	60	18 000	90	atactic
9	<1.10	85	12 000	95	atactic
10	<1.10	80	13 000	96	atactic
11	1.18	85	11 000	80	atactic
12	<1.10	80	16 000	98	atactic
13	<1.10	85	15 000	99	atactic
14	<1.10	95	14 000	98	∼80%

[a] Ratio of monomer to initiator is 100. [b] Determined by GPC in THF vs polystyrene standards. [c] Determined by DSC. The T_g was idential in heating and cooling transitions. [d] Determined on the basis of the quaternary carbon resonance at 46.05 ppm in the ^{13}C NMR spectrum.

not (as in the **2** series of initiators). It is not intuitively obvious as to what details of initiator behavior (including interconversion of *syn* and *anti* isomers and their likely different reactivities) led to formation of tactic *trans*-poly(**1**) in high yield. All that can be said at this stage is that more electron-poor and highly crowded metal centers seem to favor the formation of poly(**1**) with a long-range order.

Finally, none of the results presented here reveal which tacticity is responsible for the 46.05 ppm quaternary carbon resonance and the 137.23 olefinic carbon resonance in the ^{13}C NMR spectrum of tactic *trans*-poly(**1**). We hope to be able to determine the tacticity through methods related to those employed to determine tacticities in certain *cis* and *trans* polynorbornene derivatives[15] or through isolation and structural characterization of oligomers. We also hope to be able to determine to what extent other 3,3-disubstituted cyclopropenes can be polymerized stereoselectively.

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

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(6) Polymerizations of **1** were carried out in dichloromethane through addition of 100 equiv of **1** to each initiator. Polymerizations were allowed to run for 2 h and were then quenched with a large excess of benzaldehyde. The resulting polymers were precipitated in methanol and analyzed by gel permeation chromatography (GPC), differential scanning calorimetry (DSC), and proton and ^{13}C NMR spectroscopy.

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