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Polymerization of Enantiomerically Pure 2,3-Dicarboalkoxynorbornadienes and 5,6-Disubstituted Norbornenes by Well-Characterized Molybdenum Ring-Opening Metathesis Polymerization Initiators. Direct Determination of Tacticity in Cis, Highly Tactic and Trans, Highly Tactic Polymers

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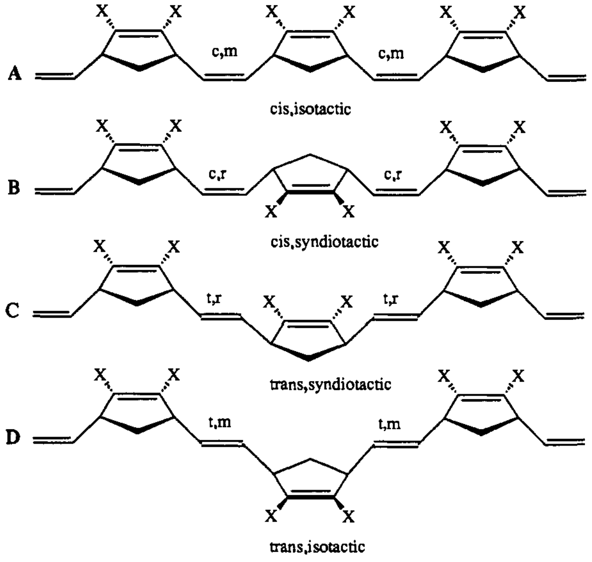
Abstract: The ring-opening metathesis polymerization (ROMP) of enantiomerically pure dicarboalkoxynorbornadienes (2,3-$(CO_2R^*)_2$-norbornadiene where R^* = (1*R*,2*S*,5*R*)-(–)-menthyl (**2a**) or (R)-(–)-pantalactonyl (**2b**)) with Mo$(CHCMe_2Ph)(NAr)(O\text{-}t\text{-}Bu)_2$ (**1a**) (Ar = 2,6-*i*-$Pr_2C_6H_3$) yields high trans, highly tactic polymers. The ROMP of chiral monomers **2a,b** with Mo$(CHCMe_2Ph)(NAr)[OC(CF_3)_3]_2$ (**1b**), Mo$(CHCMe_2Ph)(NAr')[BIPH(t\text{-}Bu)_4]$ (**1c**), and Mo$(CHCMe_2Ph)(NAr')[(\pm)\text{-}BINO(SiMe_2Ph)_2](THF)$ (**1d**) (Ar' = 2,6-$Me_2C_6H_3$) yields high cis, highly tactic polymers. Tacticities can be determined directly by homonuclear (proton/proton) correlation spectroscopy and decoupling experiments. The cis polymers were found to be isotactic, the trans polymers syndiotactic. Related experiments employing enantiomerically pure disubstituted norbornenes (2,3-dicarbomethoxynorborn-5-ene, 2,3-dimethoxymethylnorborn-5-ene, and 5,6-dimethylnorborn-2-ene) showed that high trans polymers prepared with **1a** as the initiator are atactic while high cis polymers prepared with **1d** as the initiator are isotactic. Bimodal molecular weight distributions were observed in some cases when **1d** was employed, consistent with slightly different rates of polymerization of enantiomerically pure substrate by the two different enantiomers of the racemic initiator.

Introduction

Preparing polymers with a regular primary structure is a prerequisite to ultimately controlling the properties of the bulk polymer in a systematic manner. Polymers prepared by ring-opening metathesis polymerization (ROMP) of norbornenes and norbornadienes employing classical metathesis catalysts are rarely regular.[1] In contrast, it has been shown that 2,3-bis(trifluoromethyl)norbornadiene[2] (NBDF6) and 2,3-dicarbomethoxynorbornadiene[3] (DCMNBD) can be ring-opened with "well-characterized" initiators of the type Mo$(CHCMe_2R')(NAr)(OR)_2$ (R' = Me, Ph; Ar = 2,6-*i*-Pr_2-C_6H_3)[4,5] to give highly tactic (>90%) high trans poly(NBDF6) and poly(DCMNBD) when OR = O-*t*-Bu[6] and high cis poly(NBDF6)[7] and poly(DCMNBD)[5] with a tactic bias of ~75% ($(\sigma_m)_c = 0.75$[1]) when OR = $OCMe(CF_3)_2$. (The four possible regular structures of polymers of this type are shown in Scheme 1.) It has been suggested that the high trans poly(NBDF6) and high cis poly(NBDF6) prepared using the initiators mentioned above both have a *syndiotactic* bias (**B** and **C**, respectively) on the basis of the measurement of the value of the relaxed dielectric constant.[7]

Scheme 1. The Four Possible Regular Structures of 2,3-Disubstituted Norbornadienes



Recently we have reported that molybdenum initiators that contain a racemic binaphtholate ligand will polymerize NBDF6 and DCMNBD to polymers that are >99% cis and >99% tactic.[8] The tacticity of these polymers is the same as the bias observed for cis polymers prepared using Mo$(CHCMe_2Ph)(NAr)[OCMe(CF_3)_2]_2$ as the initiator.[7] Therefore both high trans, highly tactic and high cis, highly tactic polymers can now be prepared. It is important to establish exactly what the tacticity is in each case in order to understand the origin of tacticity control and the relationship between primary structure and bulk properties.

[⊗] Abstract published in *Advance ACS Abstracts*, March 15, 1994.

(1) Ivin, K. J. *Olefin Metathesis*; Academic: New York, 1983.

(2) bin Alimuniar, A.; Blackmore, P. M.; Edwards, J. H.; Feast, W. J.; Wilson, B. *Polymer* **1982**, *27*, 1281.

(3) Tabor, D. C.; White, F. H.; Collier, L. W.; Evans, S. A. *J. Org. Chem.* **1983**, *48*, 1638.

(4) Schrock, R. R. *Acc. Chem. Res.* **1990**, *23*, 158.

(5) Fox, H. H.; Lee, J.-K.; Park, L. Y.; Schrock, R. R. *Organometallics* **1993**, *12*, 759.

(6) Bazan, G.; 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.

(7) Feast, W. J.; Gibson, V. C.; Marshal, E. L. *J. Chem. Soc., Chem. Commun.* **1992**, 1157.

(8) McConville, D. H.; Wolf, J. R.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 4413.

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Unfortunately, neither NBDF6 nor DCMNBD is chiral, and therefore ^{13}C NMR methods analogous to those that have been used so extensively to argue for a given tacticity of polymers prepared from enantiomerically pure (or highly enriched) norbor*nenes*[9-14] cannot be employed here. However, since the proton NMR spectrum of cis, tactic poly(DCMNBD) is relatively simple,[8] we realized that it might be possible to determine the tacticity of 2,3-dicarboalkoxynorbornadienes that contain a chiral group in the ester directly and relatively quickly by proton NMR methods. It also might be possible to determine the tacticity of enantiomerically pure 5,6-disubstituted norbornenes, if high trans or high cis, highly tactic polymers can be prepared. In this paper we report the determination of the tacticity of the highly regular polymers prepared from two enantiomerically pure 2,3-dicarboalkoxynorbornadienes and three enantiomerically pure norbornenes using well-characterized molybdenum ROMP initiators that are known to yield highly regular polymers. We will show that these all-cis polymers are all isotactic and that the corresponding all-trans norbornadiene polymers are syndiotactic. (The all-trans norbornene polymers are atactic.) To our knowledge this is the first unambiguous determination of the tacticity of ROMP polymers by direct methods.

Results

Polymers Prepared from Chiral 2,3-Dicarboalkoxynorbornadienes. The four possible regular structures of 2,3-disubstituted norbornadienes are shown in Scheme 1. In the cis, isotactic polymer (A), the olefinic protons are equivalent by virtue of a mirror plane that passes through the midpoint of the c,m (cis,-meso) double bond. (Meso refers to the relative chirality of the allylic carbons in the cyclopentene rings on each side of the double bond.) In the cis, syndiotactic polymer (B), the olefinic protons are related by a C_2 axis that passes through the c,r (cis,racemic) double bond (in the C_2H_2 plane). In both A and B, a plane also passes through the methylene carbon and the midpoint of the C=C bond of each cyclopentene ring. Therefore cis, highly tactic polymers with either tacticity would be expected to exhibit only one olefinic resonance. For example, the olefinic resonance is a nearly first-order, relatively sharp doublet in cis, tactic 2,3-dicarbomethoxynorbornadiene prepared employing Mo(CHCMe$_2$-Ph)(N-2,6-Me$_2$C$_6$H$_3$)[(±)-BINO(SiMe$_2$Ph)$_2$] as the initiator[8] (Figure 1). The outer weak resonances are believed to be the result of some second-order behavior, i.e., the olefinic protons are magnetically inequivalent as a result of different three and four bond couplings to the allylic protons.

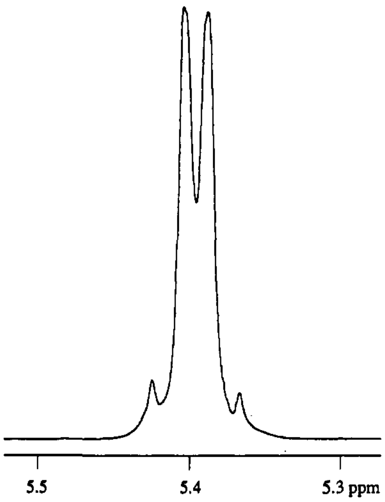
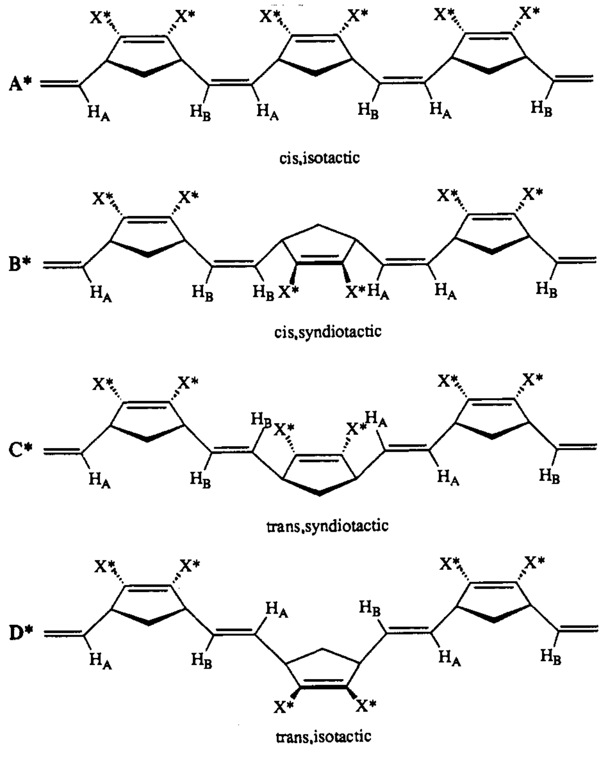


Figure 1. The olefinic resonance in all-cis, highly tactic poly(2,3-dicarbomethoxynorbornadiene).[8]

The same arguments apply to trans, isotactic (D) and trans, syndiotactic (C) polymers (Scheme 1). In C the two olefinic protons are related by a C_2 axis that passes through the midpoint of the double bond perpendicular to the C_2H_2 plane. In D the two olefinic protons are related by an inversion center at the midpoint of the C=C bond. In C and D, a plane of symmetry also passes through the methylene carbon and the midpoint of the C=C bond of each cyclopentene ring.

Scheme 2. Olefinic Protons in the Four Possible Chiral Regular Structures of 2,3-Disubstituted Norbornadienes



In analogous cis or trans, tactic polymers that contain a chiral group in the substituent (X*), mirror planes are no longer present. Therefore, in the cis, isotactic polymer (A* in Scheme 2), the two olefinic protons would be inequivalent and coupled to a degree characteristic of cis olefinic protons in normal olefins. In the cis, syndiotactic polymer containing X* groups (B* in Scheme 2), a C_2 axis still passes through the midpoint of each double bond (in the C_2H_2 plane), but there is no symmetry operation that relates one set of equivalent olefinic protons (H_B) to the other set of equivalent olefinic protons (H_A). One might expect to see two olefinic proton resonances in this circumstance also, but the two olefinic protons would not be coupled. Similar arguments lead to the conclusion that a trans, syndiotactic polymer that contains X* groups (C* in Scheme 2) would contain inequivalent protons that are not coupled, while a trans, isotactic polymer (D* in Scheme 2) would contain inequivalent protons that are coupled. (Olefinic protons H_A (and H_B) in D* are interconverted as a consequence of a C_2 operation about an axis that is coincident with the C=C bond axis in the backbone followed by a translation by one repeat unit.) Therefore an absolute assignment of tacticity would be possible if all-cis and highly tactic or all-trans and highly tactic polymers could be prepared from monomers that contain a chiral group (X*) and if the olefinic proton resonances were sufficiently resolved to determine the magnitude of coupling (if any) between olefinic protons. If inequivalent olefinic protons

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(9) Sunaga, T.; Ivin, K. J.; Oskam, J. H.; Hofmeister, G.; Schrock, R. R. *Macromolecules* **1994**, in press.

(10) Hamilton, J. G.; Ivin, K. J.; Rooney, J. J. *Br. Polym. J.* **1984**, *16*, 21.

(11) Hamilton, J. G.; Ivin, K. J.; McCann, G. M.; Rooney, J. J. *Makromol. Chem.* **1985**, *186*, 1477.

(12) Ho, H. T.; Ivin, K. J.; Rooney, J. J. *Makromol. Chem.* **1982**, *183*, 1629.

(13) Ho, H. T.; Ivin, K. J.; Rooney, J. J. *J. Mol. Catal.* **1982**, *15*, 245.

(14) Ivin, K. J.; Lapienis, G.; Rooney, J. J. *Polymer* **1980**, *21*, 436.

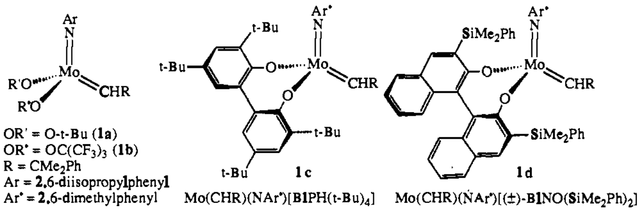
Table 1. Characterization of Poly(**2a**) and Poly(**2b**)

initiator	solvent	monomer	equiv	yield (%)	M_n[a]	M_w/M_n[a]	cis (%)	tacticity
1a	toluene	**2a**	100	97	16 300	1.03	6	syndio
1a	CH_2Cl_2	**2b**	100	78	21 000	1.28	9	syndio
1b	toluene	**2a**	100	97	17 700	1.28	99	iso
1b	CH_2Cl_2	**2b**	50	95	7 400	1.15	99	iso
1c	toluene	**2a**	100	92	22 800	1.09	99	iso
1c	CH_2Cl_2	**2b**	75	93	19 500	1.05	99	iso
1d	THF	**2a**	85	91	21 300	1.19	99	iso
1d	CH_2Cl_2	**2b**	85	91	28 200[b]	1.13[b]	99	iso

[a] Determined by GPC in THF versus polystyrene standards, unless otherwise noted. [b] Determined by GPC in CH_2Cl_2 versus polystyrene standards. Bimodal distribution, see Figure 2.

are coupled, the polymer is isotactic; if they are not coupled, the polymer is syndiotactic.

The initiators employed in this study are **1a-d** (see the following structures). Mo($CHCMe_2Ph$)(NAr)(O-*t*-Bu)$_2$ (**1a**) (Ar = 2,6-*i*-$Pr_2C_6H_3$) is known to produce high trans, highly tactic poly(NBDF6) and poly(DCMNBD).[6] Mo($CHCMe_2Ph$)(NAr′)[(±)-BINO($SiMe_2Ph$)$_2$](THF) (**1d**) (Ar′ = 2,6-$Me_2C_6H_3$) is the most successful initiator so far for preparing high cis, tactic poly(NBDF6) and poly(DCMNBD).[8] Mo($CHCMe_2Ph$)(NAr′)[BIPH(t-Bu)$_4$](THF) has been employed[15] for preparing high cis, highly tactic poly(DCMNBD), and Mo($CHCMe_2Ph$)(NAr)[OC(CF_3)$_3$]$_2$ has been shown to produce high cis poly(NBDF6) and poly(DCMNBD).[16] Initiators of this general type are sometimes obtained in crystalline form as a five-coordinate solvate, but the solvent-free four-coordinate species are believed to be the active species.[4] It should be noted that the BIPH(*t*-Bu)$_4$ ligand is "locked" in one conformation (perhaps *only on the NMR time scale*) in **1c** and that both syn and anti rotamers (3:1 ratio) are observable in NMR spectra run in C_6D_6 at room temperature. The BIPH(*t*-Bu)$_4$ ligand has been found to flip readily on the NMR time scale in a lanthanum complex.[17] Both syn and anti rotamers of **1d** are observed in the absence of coordinating solvents, but only syn rotamers of **1a,b** are observed at 25 °C.[18,19] (Anti rotamers of Mo phenoxide complexes of this general type normally are observable.[20])



OR′ = O-t-Bu (**1a**)
OR′ = OC(CF_3)$_3$ (**1b**)
R = CMe_2Ph
Ar = 2,6-diisopropylphenyl
Ar′ = 2,6-dimethylphenyl

Mo(CHR)(NAr′)[BIPH(t-Bu)$_4$]

Mo(CHR)(NAr′)[(±)-BINO($SiMe_2Ph$)$_2$]

Enantiomerically pure dicarboalkoxynorbornadiene derivatives **2a,b** were prepared from the carbonyl chloride derivative[21] in good yield as easily-purified white crystalline solids (eq 1). They are polymerized smoothly by initiators **1a-d** in the solvents indicated in Table 1. The polymerization reactions were quenched with benzaldehyde, and the polymers were isolated as described in the Experimental Section, usually by precipitation into methanol. The polydispersities (M_w/M_n; Table 1) were relatively low for all polymers, but not as low as is often found for polymers prepared by living ROMP using well-defined Mo initiators of this general type. An interesting finding in the case of poly(**2b**)/**1d** (the notation includes the initiator that was employed, **1d** in this case) is that the GPC shows a distinct (sharp) bimodal distribution of polymer chain lengths (Figure 2), the polydispersity for both peaks taken *together* being 1.13; the polydispersity of each peak is estimated to be ~1.06. The experiment was repeated three times with essentially the same result. We attribute the bimodality to the fact that the initiator is a 1:1 mixture of noninterconvertible enantiomers and that highly regular polymer chains grow from each enantiomeric metal site. Evidently the rates of reaction of the enantiomerically pure monomer at the two enantiomeric metal sites differ, but the nature of the primary structure of the polymer that is formed (see later) is the same in each chain. This result could not be anticipated unless the polymerization is well-behaved and living and polymer chains are obtained that have the narrowest possible molecular weight distribution. The GPC trace for poly(**2a**)/**1d** was not resolved into two peaks. The polydispersity of polymers prepared using other initiators (**1a–c**) is not universally low, and bimodal distributions are not observed, perhaps in part because only **1d** has a fixed chirality at the metal reaction site.

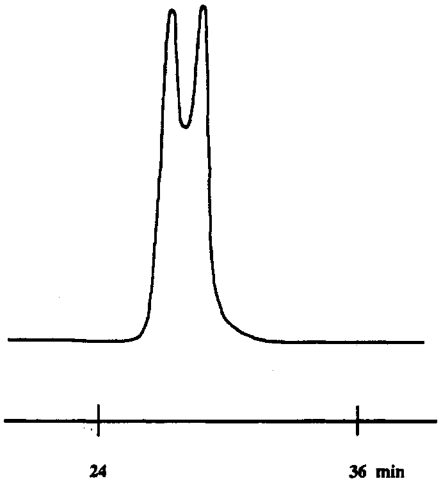
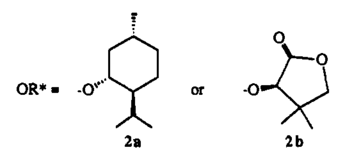


Figure 2. GPC trace of poly(**2b**)/**1d**.



(1)

A $^{13}C\{^1H\}$ NMR spectrum of poly(**2a**)/**1a** is shown in Figure 3; a single resonance is observed for almost all of the 29 inequivalent carbons in the unsymmetric norbornadiene repeat unit. (We believe the coincidence of the resonances for C_5 and C_6 to be accidental; see the Experimental Section for a list of resonance positions.) The cis content can be determined by comparing the chemical shift of the allylic carbon atoms in the polymer (C_1 and C_4 in the monomer) with the chemical shift of

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(15) McConville, D. H.; Schrock, R. R. Unpublished results.

(16) O'Dell, R.; Schrock, R. R. Unpublished results.

(17) Schaverien, C. J.; Meijboom, N.; Orpen, A. G. *J. Chem. Soc., Chem. Commun.* **1992**, 124.

(18) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1993**, *115*, 11831.

(19) Oskam, J. H.; Schrock, R. R. *J. Am. Chem. Soc.* **1992**, *114*, 7588.

(20) Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832.

(21) Maier, G.; Jung, W. A. *Chem. Ber.* **1982**, *115*, 804.

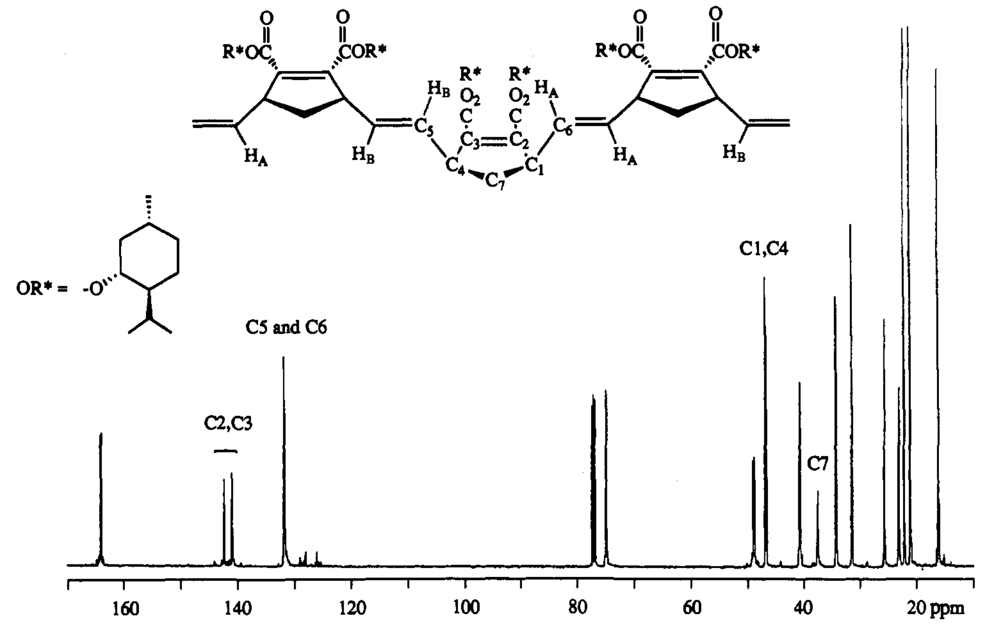


Figure 3. Complete carbon NMR spectrum of *trans*-poly(**2a**)/**1a** in $CDCl_3$.

the allylic carbon atom resonances in poly(2,3-dicarbomethoxynorbornadiene).[6] For poly(**2a**)/**1a** the two relatively sharp allylic carbon atom resonances at 46.7 and 46.8 ppm are observed in the region characteristic of an allylic carbon atom resonance in *trans*-poly(2,3-dicarbomethoxynorbornadiene). Therefore we can conclude that poly(**2a**)/**1a** is highly (~94%) trans. Only one slightly broadened resonance is observed for C_7 in *trans*-poly(**2a**)/**1a** at 37.5 ppm, consistent with poly(**2a**)/**1a** being highly tactic.[7] Similar experiments lead to the conclusion that poly(**2b**)/**1a** is also highly trans and highly tactic (Table 1).

The proton NMR spectrum of poly(**2a**)/**1a** is also consistent with a highly regular primary structure. The olefinic region of the 500-MHz ^{1}H NMR spectrum shows two slightly broad resonances at 5.568 and 5.534 ppm (Figure 4) which sharpen considerably when the allylic protons in the 1 and 4 positions are irradiated. The olefinic region of the 500-MHz ^{1}H,^{1}H homonuclear correlation spectrum (Figure 4) confirms that the two olefinic proton resonances are *not* coupled. On the basis of the arguments presented earlier for the generic trans chiral polymers C* and D* (Scheme 2), we can conclude that *trans*-poly(**2a**)/**1a** is *syndiotactic*. The tacticity in this case must result from chain end control. (See the Discussion.) The proton NMR and ^{1}H,^{1}H COSY spectra of *trans*-poly(**2b**)/**1a** are entirely analogous to those of *trans*-poly(**2a**)/**1a**; therefore *trans*-poly(**2b**)/**1a** is also syndiotactic.

Samples of poly(**2a**) prepared from initiators **1b**–**1d** were virtually identical by ^{1}H and ^{13}C{^{1}H} NMR. A single resonance was observed in the ^{13}C NMR spectrum for most of the carbons in the unsymmetric repeat unit in the polymer (Figure 5). The cis content was determined by comparing the chemical shifts of the allylic carbon atoms in the polymer (C_1 and C_4 in the monomer) at 44.5 and 45.2 ppm with the chemical shifts of the allylic carbon atom resonances in poly(2,3-dicarbomethoxynorbornadiene);[6] the polymer is all-cis. Note that the C_1 and C_4 resonances in the all-cis polymers are upfield of where they are in the all-trans polymers (46.7 and 46.8 ppm; see above). Again only one slightly broadened resonance in the ^{13}C{^{1}H} NMR spectrum associated with C_7 (at 39.3 ppm) can be observed. Therefore *cis*-poly(**2a**) is highly tactic (estimated to be >90%).

The olefinic region of the 300-MHz ^{1}H NMR spectrum of *cis*-poly(**2a**) shows two multiplet patterns at 5.51 and 5.37 ppm (Figure 6). Upon irradiation of the allylic protons in the 1 and 4 positions, the olefinic proton pattern collapses to an AB quartet with an olefinic HH coupling constant whose magnitude is consistent with a cis C=C configuration ($^3J_{HH'}$ = 10 Hz). The olefinic region of the 300-MHz ^{1}H,^{1}H homonuclear correlation spectrum of *cis*-poly(**2a**) (Figure 6) shows strong correlation peaks for the two olefinic proton resonances, confirming that the two olefinic protons are coupled. On the basis of the arguments for the generic all-cis chiral polymers A* and B* presented earlier (Scheme 2), *cis*-poly(**2a**) prepared from initiators **1b**–**1d** must be *isotactic*. It is interesting to note that only the tacticity in poly(**2a**)/**1d** could result from enantiomorphic metal site control. The tacticity in poly(**2a**)/**1b** must result from chain end control. We *assume* (at *this* stage) that the BIPH ligand in **1c** is *not* locked in a given configuration *throughout* the polymerization reaction and, therefore, that the isotacticity in poly(**2a**)/**1c** also arises from a type of chain end control (see the Discussion).

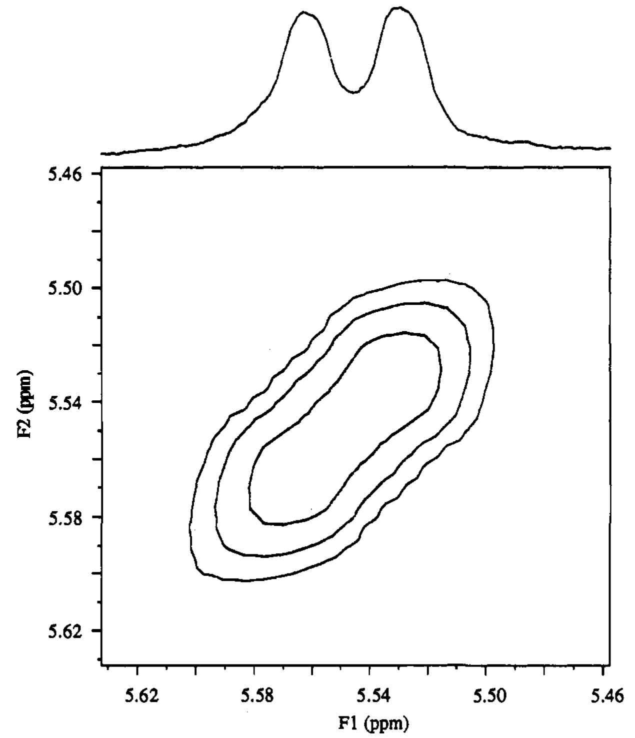


Figure 4. COSY spectrum of *trans*-poly(**2a**)/**1a** in the olefinic proton region.

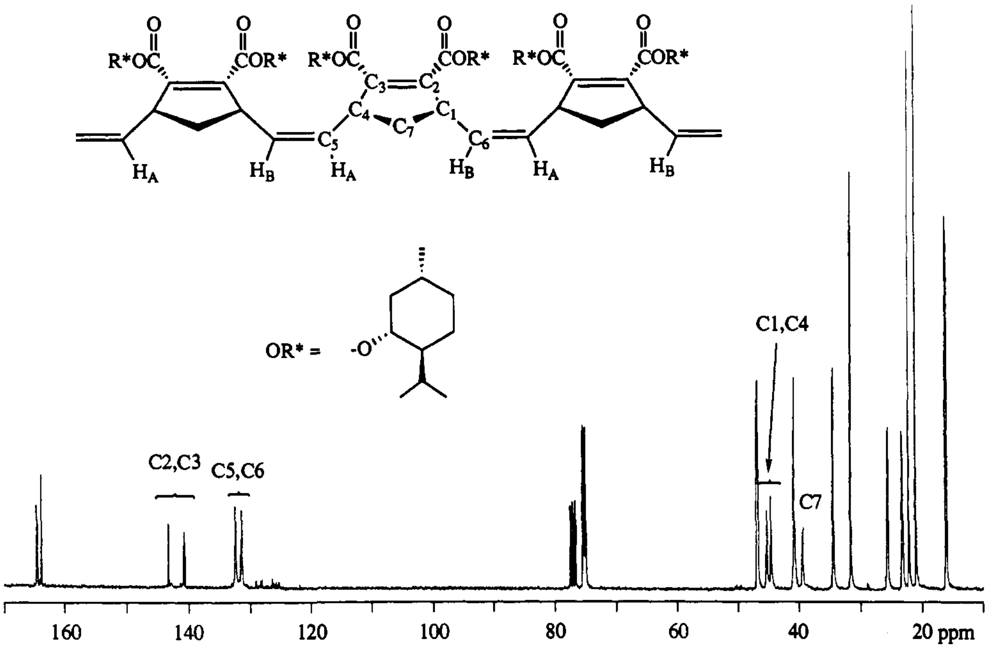


Figure 5. Complete carbon NMR spectrum of *cis*-poly(**2a**) in $CDCl_3$ prepared from initiator **1b**, **1c**, or **1d**.

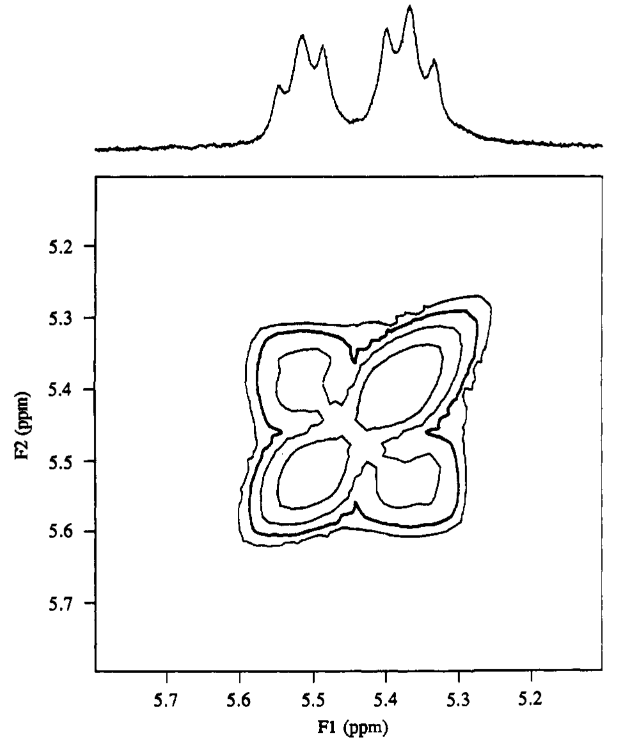
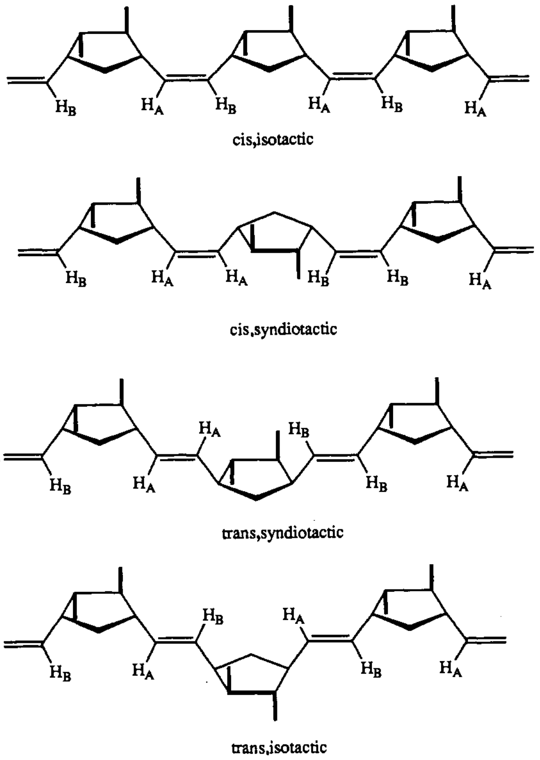


Figure 6. COSY spectrum of *cis*-poly(**2a**) in the olefinic proton region.

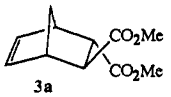
Scheme 3. The Four Possible Regular Polymers Made from an Enantiomerically Pure 5,6-Disubstituted Norbornene



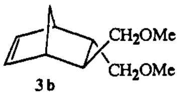
The results obtained for *cis*-poly(**2b**) prepared with initiators **1b**–**1d** were entirely analogous to those obtained for *cis*-poly(**2a**), consistent with these samples of *cis*-poly(**2b**) also being isotactic.

Polymers Prepared from Chiral Disubstituted Norbornenes. Only four regular structures are possible for a ROMP polymer prepared from an enantiomerically pure disubstituted norbornene (Scheme 3). In the syndiotactic polymers the two different types of olefinic protons should not be coupled. In cis, syndiotactic polymers, the protons on a given double bond are related by a C_2 axis that lies in the C_2H_2 plane and passes through the midpoint of the C=C bond, while in trans, syndiotactic polymers, the protons on a given double bond are related by a C_2 axis that passes through the midpoint of the C=C bond perpendicular to the C_2H_2 plane. In the cis, isotactic or trans, isotactic polymers, the protons found in a given double bond are inequivalent. If highly regular polymers can be prepared, and if the olefinic proton resonances can be resolved, then it also should be possible to determine the tacticity of these polymers directly by proton NMR methods; inequivalent olefinic protons that are coupled imply isotacticity, while inequivalent olefinic protons that are not coupled imply syndiotacticity.

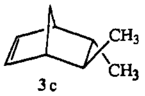
We recently studied the polymerization of enantiomerically pure (> 96% ee) (+)-(5*R*,6*R*)-dimethylnorborn-2-ene (**3c**) with achiral initiators.[9] We found that the polymer obtained employing **1a** was highly trans (~95%) but atactic, while that obtained employing $Mo(CH\text{-}t\text{-}Bu)(NAr)[OCMe(CF_3)_2]_2$ was ~85% cis



3a



3b



3c

and had an (arguably) isotactic bias of 78%. Since **3a**,**b** are intermediates in the synthesis of **3c** (or close analogs of **3c**), we included **3a**,**b** in this study. The object was to determine if high cis, isotactic polymers could be prepared from all three monomers.

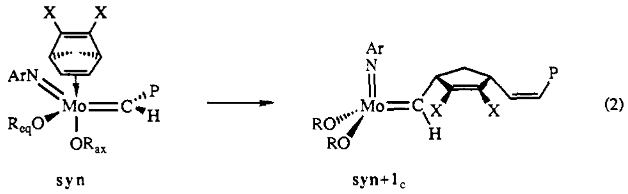
Poly(**3a**)/**1a** and poly(**3b**)/**1a** were found to be highly trans and essentially atactic (Table 2), as found previously for poly(**3c**)/**1a**.[9] (The assignment of cis and trans double bonds was made by comparing the olefinic and allylic ^{13}C NMR resonances of the two polymers with the previous assignments in poly(**3c**), and the tacticity was determined via integration of ^{13}C NMR resonances in the same manner as described for poly(**3c**).) Poly(**3a**)/**1c** was found to be highly cis but not highly tactic. Only polymers prepared employing initiator **1d** were found to be highly cis and highly tactic. This is readily confirmed for poly(**3a**)/**1d** and poly(**3b**)/**1d** by ^{13}C NMR spectra of the polymers, which show only 11 resonances for the 11 distinct carbon atoms in the repeating unit. Poly(**3c**)/**1d** had such limited solubility in all standard solvents that a high-quality ^{13}C NMR spectrum could not be obtained. However, a ^{1}H NMR spectrum of poly(**3c**)/**1d** could be obtained in 1,2-dichlorobenzene-d_4 at 85 °C and compared with the ^{1}H NMR spectra of poly(**3a**)/**1d** and poly(**3b**)/**1d**. On this basis we conclude that poly(**3c**)/**1d** is also highly cis and tactic. It should be noted that M_n values by viscometry for poly(**3a**)/**1d** and poly(**3b**)/**1d** are far greater than the values found for the less regular or atactic polymers, which suggests that the poly(**3a**)/**1d** and poly(**3b**)/**1d** do not behave as random coils in solution.

Bimodal molecular weight distributions (analogous to the GPC shown in Figure 2) were found by GPC for poly(**3a**)/**1d** and poly(**3b**)/**1d**, with each peak of the bimodal distribution having a low PDI. (Poly(**3c**)/**1d** was too insoluble for GPC studies at room temperature.) In the case of poly(**3a**)/**1d**, the ratio of the two molecular weights was 1.55, and in the case of poly(**3b**)/**1d**, the ratio of the two molecular weights was 2.21 (Table 2). The reason for bimodal distributions is the same as that proposed for polynorbornadienes prepared employing initiator **1d**. Two chains are observed because the difference in the rate of chain growth at the two enantiomorphic initiator sites is significant and the polydispersity is small enough to observe the consequences of that rate difference. The rate difference is approximately equal to the ratio of the two molecular weights.

The proton NMR spectra of poly(**3a**)/**1d**, poly(**3b**)/**1d**, and poly(**3c**)/**1d** (in 1,2-dichlorobenzene-d_4 at 85 °C) all show two olefinic resonances. COSY ^{1}H NMR spectra all show a cross peak for the two olefinic protons, indicating that the two olefinic protons are coupled and therefore that poly(**3a**)/**1d**, poly(**3b**)/**1d**, and poly(**3c**)/**1d** are all isotactic. The COSY spectrum of cis-poly(**3c**)/**1d** is shown in Figure 7. The one-dimensional spectrum shows the olefinic protons to be two doublets of doublets, as expected for coupling of a given olefinic proton to both the allylic and the other olefinic proton. The allylic coupling is also observed as a cross peak in the COSY NMR spectrum.

Discussion

The mechanism of polymerization of norbornenes and norbornadienes by well-characterized initiators of the type employed in this study has only recently begun to be understood.[4,6,7,18,19] Although fundamental questions remain, such as whether the substrate can attack on either the CNO or COO face of the pseudotetrahedral catalyst, a proposal has been made that explains the origin of formation of cis or trans double bonds in the polymer backbone.[18] The proposal is that poly(NBDF6) or poly(DCMNBD) is formed from a Mo(CHCMe$_2$R)(NAr)[OCMe(CF$_3$)$_2$]$_2$ initiator via addition of the monomer to one of the two CNO faces (essentially the two Mo=C faces) of a syn rotamer, the only accessible rotamer on the time scale of the polymerization reaction,[18] to give an all-cis molybdacyclobutane intermediate. This all cis molybdacyclobutane complex then rearranges to give a syn rotamer and form a cis double bond in the polymer backbone (eq 2). Although the two CNO catalyst faces, or, alternatively, the two faces of the Mo=C bond, are equivalent in the initiator, they are not equivalent in any propagating species by virtue of the chirality of C_β in the alkylidene ligand. If (for reasons that are not obvious) the incoming monomer is directed to the *same* face of the Mo=C bond in each syn intermediate in the polymerization reaction (chain end control), then an all-cis isotactic polymer would be the result. We assume that the mechanism of reaction of monomers **2a**,**b** is essentially the same as that of 2,3-dicarbomethoxynorbornadiene and that cis isotactic polymers are formed by chain end control from initiator **1b**.



(2)

Complexes that contain the binaphtholate ligand system are not yet as well understood as those that contain unidentate alkoxide ligands.[18] Preliminary studies suggest that syn and anti rotamers interconvert much more rapidly than they do for hexafluoro-*tert*-butoxide catalysts. Therefore we can only *assume* at this stage that the fundamental reaction steps are the same in the chelating and nonchelating alkoxide systems, i.e., that the monomer attacks the CNO face of a *syn* rotamer selectively in the binaphtholate system to give a syn insertion product and a cis C=C bond, and that one face of the Mo=C bond in the syn rotamer is attacked each time, primarily if not exclusively by virtue of the fixed chirality at the metal center. This is the essence of "enantiomorphic site control"; the structure of the polymer chain is controlled by the fixed chirality (either enantiomer) at the metal center. If the chirality at the metal center overwhelms any directing influence by chain end control, then "mistakes" will be corrected, perhaps in the next insertion step. This stands in contrast to polymerizations that rely on chain end control where "mistakes" are propagated. We should point out that the Mo(CHCMe$_2$Ph)(NAr)[(±)-BINO(SiMe$_2$Ph)$_2$] initiator does *not* yield all-cis poly(DCMNBD) or poly(NBDF6).[8,18] It was proposed that the isopropyl substituents in the NAr ligand are sterically too encumbering in that particular circumstance to allow the syn rotamer to react exclusively (to give cis polymer); some trans polymer is formed via anti rotamers. If this proposal is correct then it becomes clear that the nature of the imido ligand can be an exceedingly important additional determinant of polymer structure. We stress that this interpretation is only a working hypothesis. In any given circumstance the incoming monomer might add to the Mo=C bond in the syn rotamer the "wrong way" and lead to a trans C=C bond. In sterically crowded circumstances we might expect the rates of reactions in which the monomer approaches the "right" way and the "wrong" way to differ to a significantly greater degree than in sterically less crowded circumstances.

We do not know whether complexes that contain the biphenolate (BIPH(t-Bu)$_4$) ligand are configurationally stable over the time required to form an entire given polymer chain, even though this seems unlikely. Therefore we cannot say at this stage whether cis isotactic polymers formed from initiator **1c** result from chain end control or enantiomorphic site control. Actually, the two become blurred if the BIPH(t-Bu)$_4$) ligand is not configurationally stable over the time required to form an entire polymer chain.

Table 2. Characterization of Poly(**3a**), Poly(**3b**), and Poly(**3c**)

initiator	monomer	equiv	yield (%)	M_n[a]	M_w/M_n	cis (%)	tacticity
1a	**3a**	100	88	18 000[b]	1.05	10	(atactic)
1a	**3b**	100	98	18 000[c]	1.10	8	60
1a[d]	**3c**	115	94	12 000[e]	1.08	5	(atactic)
1c	**3a**	100	98	38 000[b]	1.04	96	60–78
1d	**3a**	100	86	[f]	1.17[f]	>99	93 (iso)
1d	**3b**	100	88	[g]	1.32[g]	>99	91 (iso)
1d	**3c**	50	88			~95[h]	~95[h] (iso)

[a] Measured by viscometry; calibrated versus polystyrene standards. [b] M_n(calcd) = 21 000. [c] M_n(calcd) = 18 200. [d] These data have been published elsewhere.[9] [e] M_n(calcd) = 14 000. [f] Bimodal distribution; M_p = 105 000 and 163 000. [g] Bimodal distribution; M_p = 95 000 and 43 000. [h] Estimated on the basis of the ^{1}H NMR spectrum in 1,2-dichlorobenzene-d_4 at 85 °C.

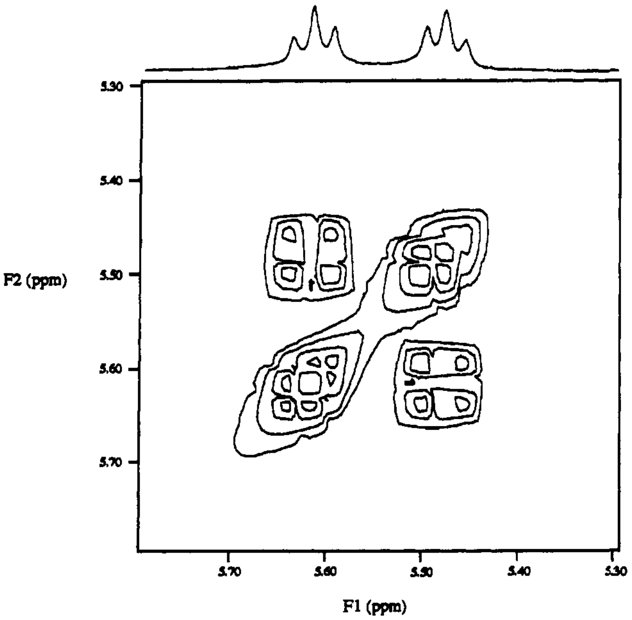
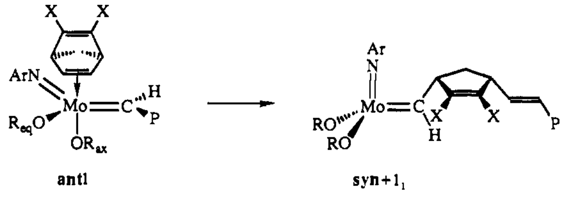


Figure 7. COSY spectrum of *cis*-poly(**3c**)/**1d** in the olefinic proton region.

If enantiomers of the BIPH(*t*-Bu)$_4$ ligand were to interconvert rapidly with respect to chain propagation, then two diastereomers would be formed for a fixed chirality at C_β of the alkylidene ligand in some propagating species. Selective reaction of one diastereomer could still lead to a cis isotactic polymer. This might be called a type of "enhanced chain end control," if the control of the polymer structure is thereby more efficient than if only achiral alkoxides are present.

The mechanism of reaction of the *tert*-butoxide Mo catalysts is much less certain. One complicating and potentially important feature of *tert*-butoxide catalysts is that alkylidene rotation is relatively fast on the time scale of polymerization of the monomers employed here, i.e., both syn and anti rotamers are accessible on the time scale of polymerization.[18] Therefore, if the reactivity of the anti rotamer is very much greater than the reactivity of the syn rotamer, but still slow with respect to the rate of rotamer interconversion, the polymer chain could propagate solely via anti rotamers.[18] Therefore, one possibility is that the mechanism of chain propagation is fundamentally the same, except the readily accessible anti rotamer reacts exclusively to yield a syn insertion product (eq 3). The syn insertion product is then converted to an anti rotamer before it can react further with the monomer, and the all-trans polymer thereby is formed (eq 4). Another possibility is that the monomer attacks the COO face of the catalyst when the alkylidene is partially rotated. The alkylidene would preferentially rotate away from the monomer (in order to give a trans metallacycle) and in one direction or the other in response to the chirality of the chain end. The fact that the 2,3-dicarboalkoxynorbornadienes prepared here are syndiotactic is consistent with the first scenario. Syn to anti alkylidene ligand rotation amounts to monomer attack *alternatively* at one CNO face and then the other, a requirement for syndiotactic polymer formation. Other explanations are possible but less consistent with experimental findings available at this stage. We have noted that if alkylidene rotation is fast on the time scale of the insertion step a partially or wholly rotated alkylidene might allow rapid attack by the monomer at the COO face of the catalyst.[18] If such scenarios prove to be true in some circumstances, then understanding tacticity and cis/trans selectivity will be significantly more difficult.



(3)

$$\text{anti} \xrightarrow{\text{NBDF}_6} \text{syn}+1_t \overset{\text{fast}}{\rightleftharpoons} \text{anti}+1_t \xrightarrow{\text{NBDF}_6} \text{syn}+2_{t,t} \xrightarrow{\text{etc.}} \text{all trans} \qquad (4)$$

On the basis of the results presented here (and elsewhere[9]), enantiomerically pure 5,6-disubstituted norbornenes are more difficult to polymerize stereoselectively than 2,3-dicarboalkoxynorbornadienes. It is intriguing to speculate that the qualitatively higher rate of reaction of the norbornenes relative to the 2,3-dicarboalkoxynorbornadienes would lead to less selective reactions in general (lower cis/trans selectivity and lower tacticity). The formation of relatively high trans but atactic polymers employing **1a** as the initiator further confirms that chain end control is negligible in these circumstances and that stereoselectivity (and perhaps even fundamental mechanistic steps) is monomer dependent.[9] Highly regular polymers are obtained in circumstances consistent only with enantiomorphic site control. The fact that polymers prepared from **1d** are all cis and isotactic is consistent with the proposed propagation via syn rotamers, CNO face attack, and enantiomorphic site control. Formation of cis, isotactic polynorbornenes as well as norbornadienes suggests that to a first approximation the mechanism of polymerization by an initiator of the type Mo(CHR)(NAr')[(±)-BINO(SiMe$_2$Ph)$_2$] is basically the same for substituted norbornenes and norbornadienes.

It remains to be determined whether high cis, tactic poly(NBDF6) and poly(DCMNBD) prepared with initiator **1d** are isotactic. We have not been able yet to convert poly(DCMNBD) into one of the ester derivatives described here (or vice versa) and therefore cannot say with certainty at this stage. However, we have seen no evidence that the principles that determine the cis/trans ratio and tacticity change significantly as a consequence of the chirality or lack thereof in the alkyl group of the ester, i.e., the probability that cis polymers formed from the chiral esters are isotactic, yet *cis*-poly(DCMNBD) is syndiotactic, seems remote. It is not as secure to extend the results found here to *cis*-poly(NBDF6), i.e., we cannot be as certain that *cis*-poly(NBDF6)[8] is also isotactic. However, since the nature of the substituent in a given type of monomer does not seem to result in a dramatic change in the structure of the resulting polymer (e.g, poly(**3a**)/**1d** = poly(**3b**)/**1d** = poly(**3c**)/**1d**), since both

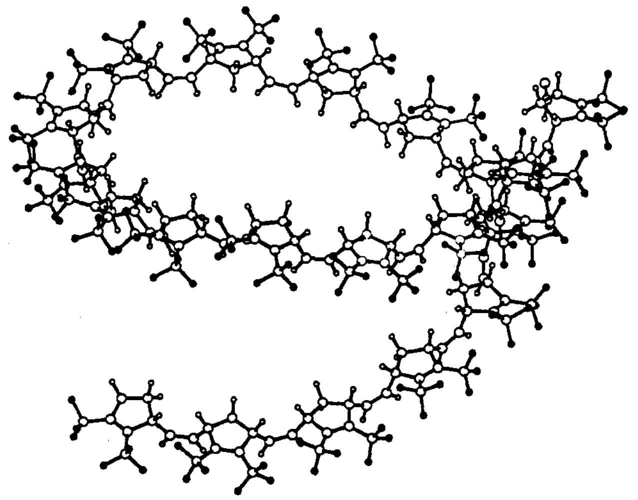


Figure 8. Calculated structure (MM2, CAChe system) of the 25 mer of poly(NBDF6).

norbornadienes and norbornenes are polymerized by the BINO initiator to give cis, isotactic polymers, and since analogous poly(NBDF6) and poly(DCMNBD) samples are very similar to one another by ^{13}C NMR, *cis*-poly(NBDF6) is likely also to be isotactic. Similar reasoning would lead us to believe that high trans, tactic poly(NBDF6) and poly(DCMNBD) prepared with the Mo(CHCMe$_2$Ph)(NAr)(O-*t*-Bu)$_2$ initiator are also likely to be syndiotactic.

If *cis*-poly(NBDF6) is isotactic, then it would seem on the basis of the primary structure that the polarity and therefore the relaxed dielectric constant should be larger than it is.[7] Molecular mechanics calculations were carried out on a CAChe system on 25 mers of poly(NBDF6) that have the four regular structures shown in Scheme 1. Three were found to have an extended linear chain structure. The 25 mer of cis, isotactic poly(NBDF6) was found to have a helical structure (Figure 8) with about 13 monomer units per helical turn. We speculate that the helical structure is a consequence of steric interaction between the CF$_3$ groups in neighboring monomer units. *If* this "gas phase" calculation is some indication of the bulk structure of cis, isotactic poly(NBDF6), then the opposing dipole moments might lead to a relatively low polarity and a relatively low relaxed dielectric constant for cis, isotactic poly(NBDF6).

Experimental Section

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques unless otherwise specified. Pentane was washed with sulfuric acid/nitric acid (95/5 v/v), sodium bicarbonate, and water, stored over calcium chloride, and distilled from sodium benzophenone ketyl under nitrogen. Reagent grade diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen. Toluene was distilled from sodium, and CH$_2$Cl$_2$ was distilled form CaH$_2$. Polymerization grade THF was vacuum transferred a second time from sodium benzophenone ketyl. Polymerization grade CH$_2$Cl$_2$ was vacuum transferred from CaH$_2$. Polymerization grade toluene was stored over sodium/potassium alloy and passed through alumina prior to use. Benzene-*d*$_6$, CDCl$_3$, toluene-*d*$_8$, and CD$_2$Cl$_2$ were sparged with argon and stored over activated molecular sieves (4 Å).

HPLC grade solvents were used in GPC runs and were degassed prior to use. Gel permeation chromatography (GPC) was carried out using a Waters Ultrastyragel 10573, Shodex KF-802.5, 803, 804, 805, and 800P columns, a Viscotek Differential Refractometer/Viscometer H-500, and a Spectroflow 757 absorbance detector on samples 0.1–0.3% (w/v) in THF or CH$_2$Cl$_2$ which were filtered through a Millex-SR 0.5-μm filter in order to remove particulates. GPC columns were calibrated versus polystyrene standards (Polymer Laboratories Ltd.) which ranged from MW = 1206–1.03 × 10^6.

NMR data were obtained at 300 (^{1}H) and 75.4 MHz (^{13}C) or 500 (^{1}H) and 125.7 MHz (^{13}C) and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are listed in hertz. Spectra were obtained at 25 °C unless otherwise noted. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN analyzer. Optical rotations were measured at 20 °C in chloroform with a Perkin-Elmer 243B polarimeter using a sodium lamp set at 589 nm (cell length = 1.0 dm). Chiral gas chromatography (GC) was performed using CHROMPACK CP-Cyclodextrin-β-2,3,6-M-19 as the chiral support.

All chemicals used were reagent grade and were purified by standard methods. (1*R*,2*S*,5*R*-(−)-menthol, (*R*)-(−)-pantalactone, BBr$_3$ (1 M in CH$_2$Cl$_2$), PhMe$_2$SiCl, and *t*-BuLi were purchased from Aldrich and used as received. Mo(CHCMe$_2$Ph)(NAr)(O-*t*-Bu)$_2$ was prepared as outlined in the literature.[22] Benzaldehyde was freshly distilled and stored at −40 °C. Compound **3c** and the corresponding diacid and dihydroxymethyl species were prepared as described previously.[9] Stock solutions of the initiators in toluene were employed in order that the quantity of initiator is known as accurately as possible.

Mo(CHCMe$_2$Ph)(NAr)[OC(CF$_3$)$_3$]$_2$ (1b). Compound **1b** was prepared from KOC(CF$_3$)$_3$[23] and Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME)[22] as outlined in the literature[22] (78% yield): ^{1}H NMR δ (toluene-*d*$_8$) 12.87 (s, 1, C*H*CMe$_2$Ph), 7.12 (d, 2, H$_o$ Ph), 7.05 (dd, 2, H$_m$ Ph), 6.96 (t, 1, H$_p$ NAr), 6.94 (t, 1, H$_p$ Ph), 6.89 (d, 2, H$_m$ NAr), 3.46 (sept, 2, C*H*Me$_2$), 1.52 (s, 6, CHC*Me*$_2$Ph), 1.12 (d, 12, CH*Me*$_2$); ^{13}C NMR (C$_6$D$_6$) δ 298.6 (d, J_{CH} = 122, *C*HCMe$_2$Ph), 154.9 (C$_{ipso}$ NAr), 148.9 (C$_o$ NAr), 147.2 (C$_{ipso}$ Ph), 130.5 (C$_p$ NAr), 128.6 (C$_o$ Ph), 126.9 (C$_p$ Ph), 125.9 (C$_m$ Ph), 123.8 (C$_m$ NAr), 121.4 (q, $^1J_{CF}$ = 291, CF$_3$), 84.1 (decet, $^2J_{CF}$ = 31, O*C*(CF$_3$)$_3$), 57.4 (CH*C*Me$_2$Ph), 30.6 (CHC*Me*$_2$Ph), 29.0 (*C*HMe$_2$), 23.8 (CH*Me*$_2$); ^{19}F NMR (C$_6$D$_6$) δ −73.8 (CF$_3$). Anal. Calcd for C$_{30}$H$_{29}$NF$_{18}$O$_2$Mo: C, 41.25; H, 3.35; N, 1.60. Found: C, 41.18; H, 3.45; N, 1.60.

Preparation of Dipotassium [3,3′,5,5′-Tetra-*tert*-butylbiphenyl-2,2′-diolate] ([BIPH(*t*-Bu)$_4$]K$_2$). A THF (5 mL) solution of KCH$_2$Ph[24] (380 mg, 2.92 mmol) was added to a stirred THF (25 mL) solution of [BIPH-(t-Bu)$_4$]H$_2$[25] (600 mg, 1.46 mmol) at room temperature. The mixture was stirred for 2 h, and the THF was removed in vacuo to yield 661 mg (93%) of a white solid. The dipotassium salt is sufficiently pure for subsequent reactions.

Mo(CHCMe$_2$Ph)(NAr′)[BIPH(*t*-Bu)$_4$] (1c). Mo(NAr′)(CHCMe$_2$Ph)(OTf)$_2$(DME)[26] (913 mg, 1.24 mmol) and [BIPH(*t*-Bu)$_4$]K$_2$ (510 mg, 1.24 mmol) were combined in diethyl ether (15 mL). Excess triethylamine (800 mL) was added, and the yellow colored solution turned deep red-orange. The solution was allowed to stir for 12 h, after which time the solution had separated into two phases, with a small amount (~0.5 mL) of pale yellow liquid below a red-orange solution. The red-orange solution was decanted away from the pale yellow liquid. The red-orange ether solution was passed through a pad of Celite and then taken to dryness in vacuo. The residue was redissolved in ether, again the solution filtered through a pad of Celite, and the resulting solution taken to dryness in vacuo. The resulting residue was extracted with pentane to afford a red-orange pentane solution. Concentration of this solution followed by cooling overnight to −40 °C gave a yellow-orange solid, yield 85%: ^{1}H NMR (C$_6$D$_6$, 3:1 syn/anti ratio) δ 14.12 (s, C*H*CMe$_2$Ph, anti), 11.67 (s, C*H*CMe$_2$Ph, syn), 7.80 (d, Ar*H*, syn), 7.62 (d, Ar*H*, anti), 7.59 (d, Ar*H*, syn), 7.52 (d, Ar*H*, syn), 7.42 (d, Ar*H*, anti), 7.39 (d, Ar*H*, syn), 7.30 (d, Ar*H*, anti), 7.25–6.68 (m, Ar*H*), 3.53 (m, OC*H*$_2$CH$_2$), 2.42 (s, Ar*Me*, anti), 2.29 (s, Ar*Me*, anti), 1.93 (s, CHC*Me*$_2$Ph, anti), 1.65 (s, *t*-Bu, anti), 1.64 (s, *t*-Bu, anti), 1.57 (s, *t*-Bu, syn), 1.56 (s, *t*-Bu, syn), 1.55 (m, OCH$_2$C*H*$_2$), 1.42 (s, CHC*Me*$_2$Ph, syn), 1.36 (s, *t*-Bu, anti), 1.35 (s, *t*-Bu, anti), 1.31 (s, *t*-Bu, syn), 1.24 (s, *t*-Bu, syn), other overlapping resonances; ^{13}C{^{1}H} NMR (C$_6$D$_6$, 3:1 syn/anti ratio) δ 311.1 (*C*HCMe$_2$Ph, anti), 288.7 (*C*HCMe$_2$Ph, syn), 160.6, 157.4, 156.7, 156.0, 151.4, 149.9, 143.7, 143.2, 142.1, 141.3, 140.0, 138.9, 137.1, 136.3, 135.3, 134.7, 133.7, 132.1, 129.0, 128.5, 126.6, 126.5, 126.10, 126.15, 125.4, 124.9, 123.4, 72.0 (O*C*H$_2$CH$_2$), 54.4 (NAr*Me*), 52.3 (NAr*Me*), 36.2, 36.0, 34.65, 34.60, 34.5, 34.4, 32.3, 32.0, 31.8, 31.6, 31.2, 30.9, 29.1, 25.3, 22.7, 19.9, 19.4, 14.2 (other resonances were obscured). Anal. Calcd for C$_{50}$H$_{69}$NO$_3$Mo: C, 72.53; H, 8.40; N, 1.69. Found: C, 72.77; H, 8.60; N, 1.55.

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(22) Schrock, R. R.; Murdzek, J. S.; Bazan, G.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.

(23) Kotun, S. P.; Anderson, J. D. O.; DesMarteau, D. D. *J. Org. Chem.* **1992**, *57*, 1124.

(24) Schlosser, R. R.; Hartmann, J. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 508.

(25) Hay, A. S.; Becker, H.-D. U.S. Patent 3,549,712, 1970.

(26) Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organomet. Chem.* **1993**, *459*, 185.

Preparation of (±)-3,3′-Bis(dimethylphenylsilyl)-1,1′-binaphthyl-2,2′-diol [H_2-(±)-BINO($SiMe_2Ph$)$_2$]. BBr_3 (80.6 mL, 1 M in CH_2Cl_2) was added dropwise to a stirred solution of (±)-3,3′-dibromo-2,2′-dimethoxy-1,1′-binaphthyl[27] (6.80 g, 14.4 mmol) in CH_2Cl_2 (300 mL) at 0 °C. The mixture was stirred at room temperature for 6 h. The excess BBr_3 was decomposed by adding H_2O (200 mL) at 0 °C. The mixture was extracted with CH_2Cl_2 (8 × 100 mL), dried over Na_2SO_4, and evaporated to give a quantitative yield of (±)-3,3′-dibromo-1,1′-binaphthy-2,2′-diol (H_2-(±)-BINOBr$_2$). Solid imidazole (958 mg, 14.1 mmol) and a THF (10 mL) solution of $PhMe_2SiCl$ (2.40 g, 14.1 mmol) were added to a stirred THF (30 mL) solution of crude H_2-(±)-BINOBr$_2$ (2.50 g, 5.63 mmol). The mixture was stirred for 12 h at 60 °C. After it was cooled to room temperature, the mixture was poured into saturated aqueous $NaHCO_3$ (200 mL) and extracted with CH_2Cl_2 (3 × 100 mL). The solvent was removed in vacuo to yield 3.85 g (96%) of crude (±)-2,2′-bis(dimethylphenylsiloxy)-3,3′-dibromo-1,1′-binaphthyl ((Me_2PhSi)$_2$(±)-BINOBr$_2$). No attempt was made to chromatograph this material, as it hydrolyzes readily: ^1H NMR (C_6D_6) δ 7.80 (s, 2, Ar*H*), 7.38 (d, 2, Ar*H*), 7.15–6.79 (m, 18, Ar*H*), 0.20 (s, 6, Si*Me*), 0.05 (s, 6, Si*Me*). *tert*-Butyllithium (5.2 mL, 1.7 M in pentane) was added over 3 min to a stirred THF (25 mL) solution of (Me_2PhSi)$_2$-(±)-BINOBr$_2$ (1.80 g, 2.53 mmol) at −20 °C. The solution was warmed to room temperature and stirred for 30 min. The solution was poured into saturated NH_4Cl (200 mL) and extracted with CH_2Cl_2 (5 × 100 mL). The organic layer was dried over Na_2SO_4 and concentrated to 3 mL. The crude product was chromatographed on silica gel and eluted with hexane (500 mL) to yield 1.20 g (86%) of (±)-3,3′-bis(dimethylphenylsilyl)-1,1′-binaphthyl-2,2′-diol (H_2-(±)-BINO($SiMe_2Ph$)$_2$) as a white solid: ^1H NMR (C_6D_6) δ 8.08 (s, 2, Ar*H*), 7.70 (d, 2, Ar*H*), 7.69 (d, 2, Ar*H*), 7.63 (d, 2, Ar*H*), 7.28–6.95 (m, 12, Ar*H*), 4.77 (s, 2, O*H*), 0.703 (s, 6, Si*Me*), 0.698 (s, 6, Si*Me*).

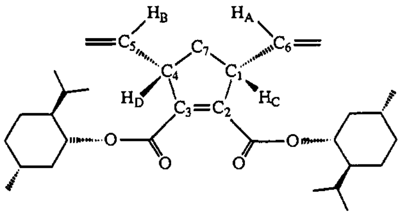
Preparation of Dipotassium [(±)-3,3′-Bis(dimethylphenylsilyl)-1,1′-binaphthyl-2,2′-diolate] (K_2-(±)-BINO($SiMe_2Ph$)$_2$). A THF (5 mL) solution of KCH_2Ph[24] (432 mg, 3.31 mmol) was added to a stirred THF (25 mL) solution of H_2-(±)-BINO($SiMe_2Ph$)$_2$ (920 mg, 1.65 mmol) at room temperature. The colorless solution turned canary yellow. The stirring was continued for 2 h, and the THF was removed under vacuum to yield 999 mg (96%) of a yellow solid. The dipotassium salt is sufficiently pure for subsequent reactions.

Mo($CHCMe_2Ph$)(NAr′)[(±)-BINO($SiMe_2Ph$)$_2$](THF) (1d). A THF (1 mL) solution of K_2[(±)-BINO($SiMe_2Ph$)$_2$] (179 mg, 0.284 mmol) was added dropwise to a stirred THF (5 mL) solution of Mo($CHCMe_2Ph$)(NAr′)(OTf)$_2$(DME)[26] (209 mg, 0.284 mmol) at −40 °C. The solution was stirred for 1 h and the THF removed under vacuum. The product was extracted with pentane and the solution filtered through a pad of Celite. Concentrating and cooling this solution to −40° gave a canary yellow crystalline solid, yield 65%: ^1H NMR (C_6D_6, 1:1 syn/anti ratio) δ 14.10 (s, C*H*CMe$_2$Ph, anti), 10.95 (s, C*H*CMe$_2$Ph, syn), 8.27 (s, Ar*H*, anti), 8.22 (s, Ar*H*, syn), 8.10 (s, Ar*H*, syn), 7.95 (s, Ar*H*, anti), 7.80–6.60 (m, Ar*H*), 3.43 (br, THF), 2.17 (s, Ar*Me*, syn and anti), 1.80 (s, CHC*Me*$_2$Ph, anti), 1.72 (s, CHC*Me*$_2$Ph, anti), 1.53 (s, CHC*Me*$_2$Ph, syn), 1.27 (s, CHC*Me*$_2$Ph, syn), 1.17 (br, THF), 0.89, 0.87, 0.84, 0.83, 0.82, 0.77, 0.71, 0.66 (Si*Me*, syn and anti); $^{13}C\{^1H\}$ NMR (C_6D_6, 1:1 syn/anti ratio) δ 296.7 (*C*HCMe$_2$Ph, $^1J_{CH}$ = 147 Hz, anti), 281.4 (*C*HCMe$_2$Ph, $^1J_{CH}$ = 119 Hz, syn), 167.5, 166.3, 162.0, 160.6, 156.7, 155.8, 150.7, 149.9, 143.3, 141.9, 140.5, 140.1, 139.2, 138.8, 137.9, 137.0, 136.95, 136.90, 136.85, 136.80, 134.85, 134.80, 134.7, 134.4, 134.1, 131.3, 130.9, 130.7, 130.2, 129.8, 129.6, 129.4, 129.10, 129.05, 128.9, 128.7, 127.2, 126.9, 126.55, 126.50, 126.45, 126.35, 126.30, 126.25, 126.20, 125.2, 124.5, 123.9, 121.2, 121.0, 118.0, 118.0, 71.9 (O*C*H$_2$CH$_2$), 54.3 (NAr*Me*), 53.3 (NAr*Me*), 34.3, 32.3, 30.6, 28.7, 27.6, 25.2, 22.7, 19.4, 18.6, 14.2, 0.7 (Si*Me*), 0.2 (Si*Me*), −0.2 (Si*Me*), −0.2 (Si*Me*), −0.6 (Si*Me*), −0.9 (Si*Me*), −1.0 (Si*Me*), −1.3 (Si*Me*). Anal. Calcd for $C_{58}H_{61}NO_3Si_2Mo$: C, 71.65; H, 6.32; N, 1.44. Found: C, 71.28; H, 6.77; N, 1.51.

Synthesis of 2,3-Bis((menthyloxy)carbonyl)norbornadiene (2a). A solution of 2,3-(COCl)$_2$-norbornadiene[21] (9.05 g, 41.7 mmol) in THF (50 mL) was added dropwise to a stirred THF (200 mL) solution of (1*R*,2*S*,5*R*)-(−)-menthol (14.33 g, 91.72 mmol) and pyridine (7.26 g, 91.8 mmol) under nitrogen. Stirring was continued for 16 h as a white precipitate formed. The THF was removed under vacuum and the mixture partitioned between ether (150 mL) and water (100 mL). The aqueous phase was extracted with ether (3 × 100 mL), and the combined extracts were washed with dilute HCl, $NaHCO_3$, and NaCl solutions. The organic layers were dried over Na_2SO_4, and the ether was removed to yield a white residue. The residue was recrystallized twice from MeOH to yield 9.21 g (48%) of a white crystalline product. A THF solution of the monomer was passed through alumina prior to polymerization: ^1H NMR (C_6D_6) δ 6.70 (m, 2, C=C*H*), 5.04 (m, 2, CO$_2$C*H*), 3.86 (m, 2, =CHC*H*), 2.25–2.12 (m, 4), 2.06 (dt, 1, =CHCHC*H*$_2$), 1.76 (dt, 1, =CHCHC*H*$_2$), 1.47 (m, 6), 1.15 (m, 6), 0.93–0.79 (d, 18, C*H*); $^{13}C\{^1H\}$ NMR (C_6D_6) δ 164.7 (CO), 164.6 (CO), 152.3 (=CCO$_2$), 151.9 (=CCO$_2$), 142.8 (=CH), 142.4 (=CH), 74.7 (CO$_2$*C*H), 72.8 (CO$_2$*C*H), 54.0, 53.8, 47.4, 41.3, 34.6, 31.5, 31.4, 26.6, 23.9, 22.2, 20.9, 16.7 (other resonances are overlapping). $[\alpha]^{26} = -76.8$ (c = 3.80, CH_2Cl_2).

Synthesis of 2,3-Bis((pantalactonyloxy)carbonyl)norbornadiene (2b). A solution of 2,3-(COCl)$_2$-norbornadiene[21] (3.14 g, 14.5 mmol) in THF (10 mL) was added dropwise to a stirred THF (80 mL) solution of (*R*)-(−)-pantalactone (4.51 g, 34.6 mmol) and pyridine (2.74 g, 34.6 mmol) under nitrogen at 0 °C. Stirring was continued for 1 h, at which time the product precipitated from THF. The mixture was refluxed for 45 min, then cooled to room temperature. The remaining solid was added to a large volume of water (500 mL) and the solid collected by filtration. The solid was dissolved in EtOAc (250 mL) and washed with dilute HCl, Na_2CO_3, and NaCl solutions. The organic layers were dried over $MgSO_4$ and treated with charcoal. The solvent was removed under vacuum to give a pink solid. The residue was recrystallized twice from a mixture of ethyl acetate and hexane to yield 4.32 g (73%) of a white crystalline product. A CH_2Cl_2 solution of the monomer was passed through alumina prior to polymerization: ^1H NMR ($CDCl_3$) δ 6.91 (m, 2, =C*H*), 5.39 (s, 1, CO$_2$C*H*), 5.38 (s, 1, CO$_2$C*H*), 4.02 (m, 2, =CHC*H*), 2.34 (d, 1, =CHCHC*H*$_2$), 2.13 (d, 1, =CHCHC*H*$_2$), 1.21 (Me), 1.17 (Me), 1.12 (Me), 1.08 (Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 171.6 (*C*O$_2$CH$_2$), 171.5 (*C*O$_2$CH$_2$), 163.1 (=C*C*O$_2$), 162.3 (=C*C*O$_2$), 153.8 (=CCO$_2$), 152.5 (=CCO$_2$), 142.4 (=CH), 141.9 (=CH), 76.1, 75.4, 75.3, 72.8, 53.8, 53.6, 40.1, 40.0, 30.93, 22.7 (Me), 19.6 (Me) (other resonances are overlapping). $[\alpha]^{26} = 14.7$ (c = 3.25, CH_2Cl_2).

***trans*-Poly(2,3-bis((menthyloxy)carbonyl)norbornadiene) (*trans*-Poly(2a)/1a).** A toluene (1 mL) solution of **1a** (10 mg, 0.018 mmol) was added in one portion to a rapidly stirred solution of monomer **2a** (830 mg, 1.82 mmol) in toluene (10 mL). Stirring was continued for 12 h. Benzaldehyde (100 μL), was added and the reaction was stirred for an additional 12 h. The toluene solution was added dropwise to a rapidly stirring volume of methanol (50 mL) which caused the polymer to precipitate. The polymer was isolated by centrifugation (810 mg, 97%) and dried: $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 164.2 (CO), 164.1 (CO), 142.3 (C_2 or C_3), 140.9 (C_2 or C_3), 131.7 (C_5 and C_6), 74.9 (CO$_2$*C*H), 74.7 (CO$_2$*C*H), 49.0, 48.8, 46.8 (C_1 or C_4), 46.7 (C_1 or C_4), 40.7, 40.6, 37.5 (C_7), 34.3, 31.5, 31.4, 25.62, 25.60, 23.2, 23.0, 22.2 (Me), 22.1 (Me), 21.1 (Me), 21.0 (Me), 16.15 (Me), 16.12 (Me) (other resonances are overlapping).



***trans*-Poly(2,3-bis((pantalactonyloxy)carbonyl)norbornadiene) (*trans*-Poly(2b)/1a).** A CH_2Cl_2 (1 mL) solution of **1a** (5 mg, 0.009 mmol) was added in one portion to a rapidly stirred solution of monomer **2b** (367 mg, 0.907 mmol) in CH_2Cl_2 (5 mL). Stirring was continued for 8 h. Benzaldehyde (100 μL) was added, and the reaction was stirred for an additional 12 h. The CH_2Cl_2 solution was added dropwise to a rapidly stirring volume of hexane (50 mL) which caused the polymer to precipitate. The polymer was isolated by centrifugation (286 mg, 78%) and dried: $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ 171.6 (CO), 171.5 (CO), 163.4 (CO), 163.1 (CO), 142.6 (C_2 or C_3), 142.4 (C_2 or C_3), 131.9 (C_5 or C_6), 131.7 (C_5 or C_6), 76.1, 75.8, 75.6, 48.7 (C_1 or C_4), 48.6 (C_1 or C_4), 40.3 (*C*Me$_2$), 39.8 (C_7), 22.9 (Me), 20.0 (Me), 19.8 (Me) (other resonances are overlapping).

***cis*-Poly(2,3-bis((menthyloxy)carbonyl)norbornadiene) (*cis*-Poly(2a)/1d).** A solution of monomer **2a** (106 mg, 0.232 mmol) in THF (1 mL) was added in one portion to a rapidly stirred solution of initiator **1d** (3 mg, 0.003 mmol) in THF (5 mL). Stirring was continued for 8 h. Benzaldehyde (50 μL) was added, and the reaction was stirred for an additional 12 h. The THF solution was added dropwise to a rapidly

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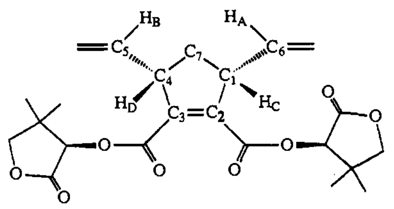
(27) Lingenfelter, D. S.; Helgeson, R. C.; Cram, D. J. *J. Org. Chem.* **1981**, *46*, 393.



stirred volume of methanol (50 mL) which caused the polymer to precipitate. The polymer was isolated by centrifugation (96 mg, 91%) and dried. See *trans*-poly(**2a**) for numbering scheme: ^{1}H NMR (CDCl$_3$) (all resonances are broad) δ 5.52 (m, 1, H$_A$ or H$_B$), 5.37 (m, 1, H$_A$ or H$_B$), 4.68 (m, 2, CO$_2$C*H*), 3.96 (m, 1, H$_C$ or H$_D$), 3.81 (m, 1, H$_C$ or H$_D$), 2.52 (s, 1), 2.10 (m, 2), 1.94 (m, 2), 1.64 (d, 4), 1.41 (m, 5), 0.89 (d, 6), 0.85 (d, 6), 0.71 (d, 6), 0.68 (d, 6); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 164.5 (CO), 163.8 (CO), 143.2 (C$_2$ or C$_3$), 140.6 (C$_2$ or C$_3$), 132.2 (C$_5$ or C$_6$), 131.2 (C$_5$ or C$_6$), 75.3 (CO$_2$*C*H), 74.9 (CO$_2$*C*H), 46.8, 46.7, 45.2 (C$_1$ or C$_4$), 44.5 (C$_1$ or C$_4$), 40.76, 40.73, 39.3 (C$_7$), 34.3, 31.5, 25.6, 25.5, 23.2, 23.1, 22.16 (Me), 22.13 (Me), 21.13 (Me), 21.00 (Me), 16.3 (Me), 16.0 (Me) (other resonances are overlapping).

***cis*-Poly(2,3-bis((pantalactonyloxy)carbonyl)norbornadiene) (*cis*-Poly(2b)/1d).** A CH$_2$Cl$_2$ (1 mL) solution of monomer **2b** (113 mg, 0.279 mmol) was added in one portion to a rapidly stirred solution of initiator **1d** (3.2 mg, 0.0033 mmol) in CH$_2$Cl$_2$ (5 mL). Stirring was continued for 8 h. Benzaldehyde (50 μL) was added, and the reaction was stirred for an additional 12 h. The CH$_2$Cl$_2$ solution was added dropwise to a rapidly stirred volume of hexane (50 mL) which caused the polymer to precipitate. The polymer was isolated by centrifugation (103 mg, 91%) and dried. See *trans*-poly(**2**) for numbering scheme: ^{13}C{^{1}H} NMR (CD$_2$Cl$_2$) δ 172.2 (CO), 172.1 (CO), 164.5 (CO), 163.3 (CO), 147.1 (C$_2$ or C$_3$), 139.4 (C$_2$ or C$_3$), 133.9 (C$_5$ or C$_6$), 130.9 (C$_5$ or C$_6$), 76.9, 76.6, 76.5, 76.3, 45.9 (C$_1$ or C$_4$), 44.0 (C$_1$ or C$_4$), 40.9 (*C*Me$_2$), 40.6 (*C*Me$_2$), 39.8 (C$_7$), 23.5 (Me), 23.1 (Me), 20.5 (Me), 20.1 (Me).

Preparation of (+)-(2*S*,3*S*)-2,3-Dicarbomethoxynorborn-5-ene (3a). (+)-(2*S*,3*S*)-l-(Methyloxy)norborn-5-ene-2,3-dicarboxylic acid (11 mmol) was dissolved in methanol (60 mL) and treated with concentrated sulfuric acid (2 mL) at room temperature for 12 h. Following standard workup procedures, the crude product was distilled from calcium hydride under vacuum (65 °C, 0.1 mm; 70%; $[\alpha]_D = +130.8°$, $c = 1.9$ g/dL in CHCl$_3$) and passed through activated alumina prior to use: ^{1}H NMR (CDCl$_3$) δ 6.25 (dd, $J = 5.5, 3.1, 1$), 6.04 (dd, $J = 5.6, 2.8, 1$), 3.69 (s, 3H), 3.62 (s, 3H), 3.35 (dd, $J = J' = 4.1, 1$), 3.23 (broad, 1), 3.12 (broad, 1), 2.66 (dd, $J = 4.5, 1.7, 1$), 1.59 (broad doublet, $J = 8.8, 1$), 1.43 (m, 1).

Preparation of (+)-(2*S*,3S)-2,3-(Dimethoxymethyl)norborn-5-ene (3b). (+)-(2*S*,3*S*)-2,3-(Dihydroxymethyl)norborn-5-ene (10 mmol) was treated with methyl iodide (30 mmol) in the presence of sodium hydride (30 mmol) in THF (80 mL) at 50 °C under argon for 1.5 h. Following standard workup procedures, the crude product was distilled from sodium under vacuum (43–44 °C, 0.4 mm; 89%; $[\alpha]_D = +84.2°$, $c = 2.8$ g/dL in CHCl$_3$). The optical purity of **3b** was established to be 96% ee by chiral gas chromatography: ^{1}H NMR (CDCl$_3$) d 6.18 (dd, $J = 5.6, 3.3, 1$), 5.99 (dd, $J = 5.8, 3.1, 1$), 3.47 (dd, $J = 9.4, 5.7, 1$), 3.33 (s, 3), 3.28 (s, 3), 3.25 (dd, $J = J' = 9.4, 1$), 3.14 (dd, $J = 9.1, 6.5, 1$), 3.00 (dd, $J = J' = 9.1, 1$), 2.83 (broad, 1), 2.68 (broad, 1), 1.79 (m, 1), 1.41 (s, 1), 1.40 (s, 1), 1.14 (m, 1).

Polymerization Reactions. The following is a typical polymerization procedure. **1a** (5.5 μmol) and toluene (6 mL) were added to a 20-mL vial equipped with a stir bar. A solution of **3b** (0.55 mmol) dissolved in toluene (1 mL) was then added all at once. The reaction solution was stirred for 5 h and quenched with benzaldehyde (two drops, 12 h). The resultant solution was concentrated to give a tan residue. The residue was dissolved in THF (2 mL), and the polymer was precipitated in methanol (200 mL). The polymer was isolated by centrifugation and dried *in vacuo*. Polymerizations using initiators **1c**,**1d** were performed in THF; ^{5} equiv of the monomer was added first, followed by the remaining monomer after 1 h.[5] Polymerization times ranged from 1 to 6 h and quenching times from 5 to 12 h. The precipitated polymers were isolated by either centrifugation or filtration.

Poly(3a)/1: ^{1}H NMR (CDCl$_3$) δ 5.34 (dd, $J = J' = 10.2, 1$), 5.14 (dd, $J = J' = 10.4, 1$), 3.65 (s, 3), 3.57 (s, 3), 3.25 (m, 1), 3.12 (dd, $J = 9.3, 7.5, 1$), 2.93 (dd, $J = 8.9, 7.7, 1$), 1.98 (m, 1), 1.41 (m, 1); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 174.2, 173.2, 133.4, 129.7, 53.2, 52.3, 51.9, 51.5, 41.7, 40.5, 40.1.

Poly(3c)/1d: ^{1}H NMR (1,2-dichlorobenzene-*d*$_4$ at 85 °C) δ 5.52 (dd, $J = J' = 11.0, 1$), 5.39 (dd, $J = J' = 10.0, 1$), 3.19 (m, 1), 2.54 (m, 1), 2.24 (m, 1), 1.79 (m, 1), 1.36 (m, 2), 1.17 (d, $J = 6.0, 3$), 1.14 (d, $J = 7.0, 3$).

Poly(3b)/1d: ^{1}H NMR (CDCl$_3$) δ 5.25 (dd, $J = 12.0, 6.3, 1$), 5.21 (dd, $J = 12.3, 6.3, 1$), 3.32 (m, 2), 3.28 (m, 2), 3.26 (s, 3), 3.25 (s, 3), 2.91 (m, 1), 2.58 (m, 1), 2.08 (m, 1), 1.85 (m, 1), 1.73 (m, 1), 1.25 (m, 1); ^{13}C{^{1}H} NMR (CDCl$_3$) δ 134.6, 130.4, 75.0, 74.1, 58.7, 58.5, 49.4, 45.3, 41.1, 40.4, 39.7.

COSY NMR Spectra. These spectra were obtained on a Varian Unity-300 or VXR-500 spectrometer, using the standard COSY experiment contained in the software package. Following are some important acquisition parameters for poly(**3a**), poly(**3c**), and poly(**3d**)

polymer	sfrq (MHz)	sw (Hz)	tof	np	temp (°C)
poly(**3a**)/**1d**	300	2376.1	31.0	1024	21
poly(**3c**)/**1d**	500	3651.6	−374.8	2048	85
poly(**3b**)/**1d**	500	4033.1	−670.0	2048	21

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