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Abstract

The ring-opening metathesis polymerization (ROMP) of enantiomerically pure dicarboalkoxynorbornadienes (2,3-$(CO_2R^*)_2$Norbornadiene where R* = 1R, 2S, 5R-(-)-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** and **2b** 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. Sharp, 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 catalyst.

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-dicarbomethoxy norbornadiene[3] (DCMNBD) can be ring-opened with "well-characterized" catalysts 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 I.) 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]

Recently we have reported that molybdenum catalysts 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. 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 polyDCMNBD relatively simple[8] we realized that it should be possible to determine the tacticity of 2,3-dicarboalkoxy norbornadienes that contain a chiral group in the ester directly and relatively quickly by proton NMR methods. It also should 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-dicarboalkoxy norbornadienes and three enantiomerically pure norbornenes using well-characterized molybdenum ROMP catalysts that are known to yield highly regular polymers. We will show that the all cis polymers are all isotactic and that the 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.

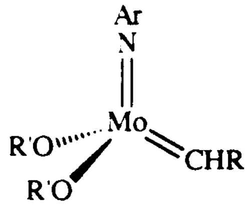
RESULTS

Polymers Prepared from Chiral 2,3-Dicarboalkoxy Norbornadienes.

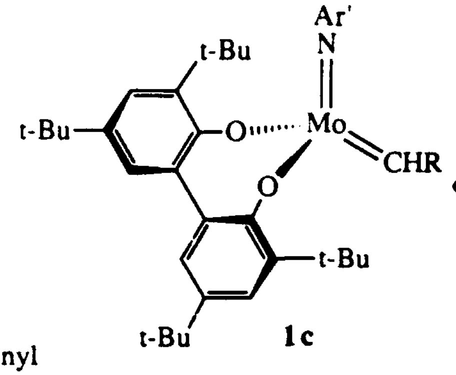
The four possible regular structures of 2,3-disubstituted norbornadienes are shown in Scheme I. In the cis,isotactic polymer (**A**) the olefinic protons are equivalent by virtue of a mirror plane that passes through the midpoint of the c,m (cis,meso) double bond. (Meso refers to the relative chirality of the allylic carbons in the cyclopentene rings on each side of the double bond.) A plane also passes through the methylene group of the cyclopentene ring. 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 plane of the π bond). Therefore cis, highly tactic polymers with either tacticity would be expected to exhibit only one olefinic resonance. (The same arguments apply to trans, isotactic and trans, syndiotactic polymers; Scheme I.) For example, the olefinic resonance is a nearly first-order, relatively sharp doublet in cis,tactic 2,3-dicarbomethoxynorbornadiene prepared employing $Mo(CHCMe_2Ph)(N\text{-}2,6\text{-}Me_2C_6H_3)[(\pm)\text{-}BINO(SiMe_2Ph)_2]$ as the catalyst[8] (Figure 1). The outer weak resonances are believed to be the result of some second order behavior, i.e., a given olefinic proton is coupled primarily via three bonds to one allylic proton, but also via four bonds to the other allylic proton.

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 II) 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 II) a C_2 axis still passes through each double bond, 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 II) would contain inequivalent protons that are not coupled, while a trans,isotactic polymer (**D*** in Scheme II) 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 passes through the olefin bonds 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.

The catalyst initiators employed in this study are **1a-1d** (see below). $Mo(CHCMe_2Ph)(NAr)(O\text{-}t\text{-}Bu)_2$ (**1a**) (Ar = 2,6-i-$Pr_2C_6H_3$) is known to produce high trans, highly tactic poly(NBDF6) and poly(DCMNBD).[6] $Mo(CHCMe_2Ph)(NAr')[(\pm)\text{-}BINO(SiMe_2Ph)_2](THF)$ (**1d**) (Ar' = 2,6-$Me_2C_6H_3$) is the most successful catalyst so far for preparing high cis, tactic poly(NBDF6) and poly(DCMNBD).[8] $Mo(CHCMe_2Ph)(NAr')[BIPH(t\text{-}Bu)_4](THF)$ 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 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** and **1b**. (Anti rotamers normally are observable in Mo phenoxide complexes of this general type.[18])

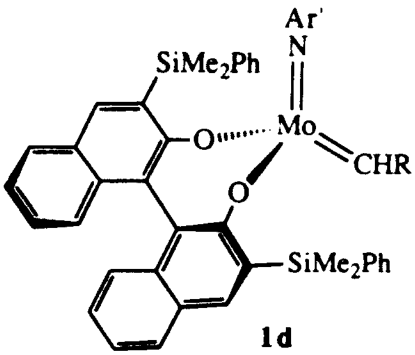


OR' = O-t-Bu (**1a**)
OR' = $OC(CF_3)_3$ (**1b**)
R = CMe_2Ph
Ar = 2,6-diisopropylphenyl
Ar' = 2,6-dimethylphenyl



1c

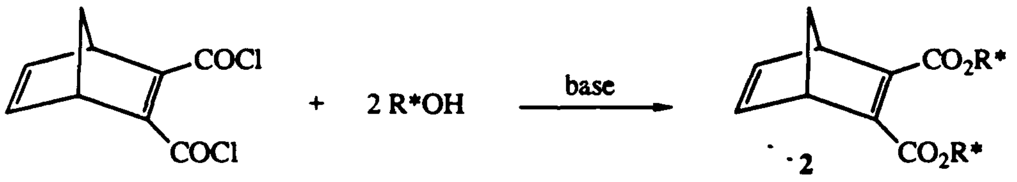
Mo(CHR)(NAr')[BIPH(t-Bu)$_4$]



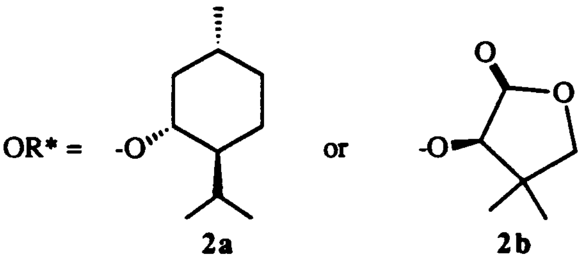
1d

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

Enantiomerically pure dicarboalkoxynorbornadiene derivatives **2a** and **2b** were prepared from the carbonyl chloride derivative[19] in good yield as easily-purified white crystalline solids (equation 1). They are polymerized smoothly by catalysts **1a-1d** in the solvents indicated in



(1)



2a **2b**

Table I. 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 I) were relatively low for all polymers, but not as low as is often true of polymers prepared by living ROMP using well-defined Mo catalysts 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, 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 catalyst is a 1:1 mixture of non-interconvertible 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 yields polymer chains with the narrowest possible molecular weight distribution. The GPC trace for poly(**2a**)/**1d** was not resolved into two peaks. Similar arguments could be used to explain why the polydispersity of polymers prepared using other initiators (**1a**, **1b**, **1c**) is not universally low, and why polydispersities are different using a given initiator in two different solvents.

A $^{13}C\{^{1}H\}$ NMR spectrum of poly(**2a**)/**1a** is shown in Figure 2; a single resonance is observed for each carbon atom in the unsymmetric norbornadiene repeat unit. (See experimental section for details.) 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 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 broad 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 I).

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 single resonances at 5.568 ppm and 5.534 ppm (Figure 3) 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 3) 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 II), we can conclude that trans-poly(**2a**)/**1a** is *syndiotactic*. The tacticity in this case must result from chain end control. (See discussion later.) 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**, **1c**, and **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 each carbon atom in the unsymmetric repeat unit in the polymer (Figure 4) and the cis content was determined by comparing the chemical shift 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 shift 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 ppm and 5.37 ppm (Figure 5). Upon irradiating 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 5) 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 II), cis-poly(**2a**) prepared from catalysts **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.

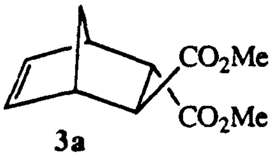
We *assume* (at *this* stage) that the BIPH ligand in **1c** is *not* locked in a given configuration *throughout* the polymerization reaction, and therefore that the isotacticity in poly(**2a**)/**1c** also arises from chain end control.

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

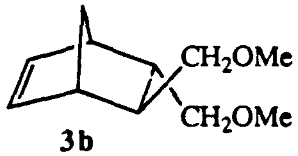
Polymers Prepared from Chiral Disubstituted Norbornenes.

Only four regular structures are possible for a ROMP polymer prepared from an enantiomerically pure disubstituted norbornene. Two of these are shown in Scheme III. In the two possible isotactic polymers (only cis, isotactic is shown) the two different types of olefinic protons should be coupled, while in the two possible syndiotactic polymers (only trans, syndiotactic is shown) the two types of olefinic protons should not be coupled. 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.

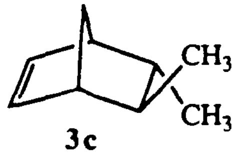
We recently studied the polymerization of enantiomerically pure (> 96% ee) (+)-(5R, 6R)-dimethylnorborn-2-ene (**3c**) with achiral initiators.[9] We found that the polymer obtained employing **1a** was highly trans (~95%), but atactic, while that obtained employing Mo(CH-t-Bu)(NAr)[OCMe(CF_3)$_2$]$_2$ was ~85% cis and had an (arguably) isotactic bias of 78%. Since **3a** and **3b** are intermediates (or close analogs thereof) in the synthesis of **3c**, we included **3a** and **3b** in this study. The object was to determine if high cis, isotactic polymers could be prepared from all three monomers.



3a



3b



3c

Poly(**3a**)/**1a** and poly(**3b**)/**1a** were found to be highly trans and essentially atactic (Table

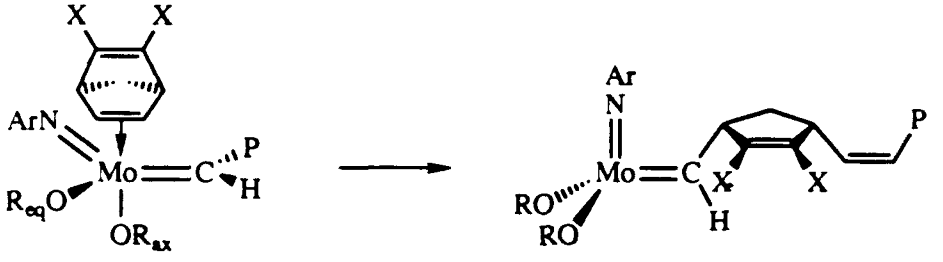
II), as found previously for poly(**3c**)/**1a**.[9] (The assignment of cis and trans double bonds was made by comparing the olefinic and allylic ^{13}C NMR resonances of the two polymers with the previous assignments in poly(**3c**), and the tacticity was determined via integration of ^{13}C NMR resonances 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 eleven resonances for the eleven 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.

It should be noted that bimodal molecular weight distributions were obtained for poly(**3a**)/**1d** and poly(**3b**)/**1d**, with each peak of the bimodal distribution having a low PDI (Figure 2b). (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 II). 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 catalyst sites is significant and the polydispersity is small enough to observe the consequences of that rate difference.

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 crosspeak 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 6. The one-dimensional spectrum shows the olefinic protons to be two doublets of doublets, as expected for coupling to both allylic and olefinic protons (the allylic coupling is also observed as a cross peak in the COSY NMR spectrum).

DISCUSSION

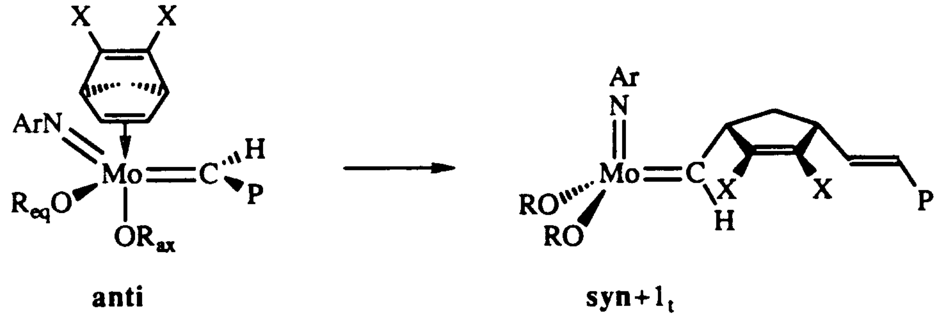
The mechanism of polymerization of norbornenes and norbornadienes by well-characterized catalysts of the type employed in this study has only recently begun to be understood.[4,6,7,20] The most secure proposal at this stage is that poly(NBDF6) or poly(DCMNBD) is formed from a $Mo(CHCMe_2R)(NAr)[OCMe(CF_3)_2]_2$ catalyst via addition of 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,[20] to give an all cis molybdacyclobutane intermediate which breaks up to give another syn rotamer and a cis double bond in the polymer backbone (equation 2). If we can assume that the mechanism of reaction of



syn **syn+1$_c$** (2)

monomers **2a** and **2b** is essentially the same as that of 2,3-dicarbomethoxynorbornadiene, then an all cis isotactic polymer would be the result of adding monomer to the same face of the Mo=C bond in each syn intermediate in the polymerization reaction. This is the essence of enantiomorphic metal site control and was the fundamental reason why the chiral binaphtholate ligand system was chosen. However, complexes that contain the binaphtholate ligand system are not yet as well understood as those that contain unidentate alkoxide ligands (such as $OCMe(CF_3)_2$). Therefore we can only *assume* at this stage that the fundamental reaction steps are the same in the chelating and non-chelating alkoxide systems, i.e., that monomer reacts with 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 syn rotamer is attacked each time. Another surprising aspect of the results presented here is that the biphenolate (BIPH) and $OC(CF_3)_3$ catalyst systems, which must direct the incoming monomer to one Mo=C face through *chain end control*, are relatively successful at doing so. As is true of all polymerizations that rely on chain end control, "mistakes" presumably are propagated. Finally, we should point out that the nature of the imido ligand can be an exceedingly important additional determinant of polymer structure that is only beginning to be appreciated. For example, the $Mo(CHCMe_2Ph)(NAr)[(\pm)\text{-}BINO(SiMe_2Ph)_2]$ catalyst does *not* yield all cis poly(DCMNBD) or poly(NBDF6).[8] 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.

The mechanism of reaction of the t-butoxide Mo catalysts is much less certain. One potentially important feature of t-butoxide catalysts is that alkylidene rotation is relatively fast on the time scale of polymerization.[20] One possibility is that the mechanism is fundamentally the same, except the readily accessible anti rotamer reacts exclusively to yield a syn insertion product (equation 3). The syn insertion product is then converted to an anti rotamer before it can react further with monomer, and all trans polymer thereby is formed (equation 4). Another possibility is



anti **syn+1$_t$** (3)

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

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-dicarboalkoxy norbornadienes prepared here are syndiotactic is consistent with the first scenario, since the required 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.

On the basis of the results presented here (and elsewhere[9]) enantiomerically pure 5,6-disubstituted norbornenes are much more difficult to polymerize stereoselectively than 2,3-dicarboalkoxy norbornadienes. It is intriguing to speculate that the qualitatively higher rate of reaction of the norbornenes relative to the 2,3-dicarboalkoxy norbornadienes 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] In fact only enantiomorphic site control leads to highly regular polymers. 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 a catalyst of the type Mo(CHR)(NAr')[(±)-BINO(SiMe$_2$Ph)$_2$] is basically the same for both types of monomers.

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 is greatly influenced by 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 extremely remote. It is not as secure to extend the results

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

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 norbornadienes and norbornenes are polymerized by the BINO catalyst 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 initiator $Mo(CHCMe_2Ph)(NAr)(O\text{-}t\text{-}Bu)_2$ are also 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 I. All but one 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 7) 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 at least according to the secondary structure of the polymer the opposing dipole moments would lead to a relatively low polarity and presumably a relatively low relaxed dielectric constant for cis,isotactic poly(NBDF6).

Experimental

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/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_2Cl_2 was distilled form CaH_2. Polymerization grade THF was vacuum transferred a second time from sodium benzophenone ketyl. Polymerization grade CH_2Cl_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_2Cl_2 were sparged with argon and stored over activated molecular sieves (4Å).

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, 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_2Cl_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 1206 to 1.03×10^6 MW.

NMR data were obtained at 300 MHz (^1H) and 75.4 MHz (^{13}C) or 500 MHz (^1H) 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 purified by standard methods. 1R, 2S, 5R-(-)-menthol, R-(-)-pantalactone, BBr_3 (1M in CH_2Cl_2), $PhMe_2SiCl$ and t-BuLi were purchased from Aldrich and used as received. $Mo(CHCMe_2Ph)(NAr)(O\text{-}t\text{-}Bu)_2$ was prepared as outlined in the literature.[21] Benzaldehyde was freshly distilled and stored at -40°C. Compounds **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.

$Mo(CHCMe_2Ph)(NAr)[OC(CF_3)_3]_2$ (1b). Compound **1b** was prepared from $KOC(CF_3)_3$[22] and $Mo(NAr)(CHCMe_2Ph)(OTf)_2(DME)$[21] as outlined in the literature[21] (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_6D_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, $^{1}J_{CF}$ = 291, CF$_3$), 84.1 (decet, $^{2}J_{CF}$ = 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 (C_6D_6) δ -73.8 (CF$_3$). Anal. Calcd for $C_{30}H_{29}NF_{18}O_2Mo$: 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'-diol] ([BIPH(t-Bu)$_4$]K$_2$). A THF (5 mL) solution of KCH_2Ph[23] (380 mg, 2.92 mmol) was added to a stirred THF (25 mL) solution of [BIPH(t-Bu)$_4$]H$_2$[24] (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)[25] (913 mg, 1.24 mmol) and [BIPH(t-Bu)$_4$]K$_2$ (510 mg, 1.24 mmol) were combined in diethylether (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 separted into two phases, 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 and 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_6D_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, ArMe, anti), 1.93 (s, CHCMe_2Ph, 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$_2$CH_2), 1.42 (s, CHCMe_2Ph, 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 resonances overlapping; $^{13}C\{^1H\}$ NMR (C_6D_6, 3:1 syn/anti ratio) δ 311.1 (CHCMe$_2$Ph, anti), 288.7 (CHCMe$_2$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 (OCH$_2$CH$_2$), 54.4 (NArMe), 52.3 (NArMe), 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 $C_{50}H_{69}NO_3Mo$: C, 72.53; H, 8.40; N, 1.69. Found: C, 72.77; H, 8.60; N, 1.55.

Preparation of (±)-3,3'-bis(dimethylphenylsilyl)-1,1'-binaphthyl-2,2'-diol [H_2(±)-BINO($SiMe_2Ph$)$_2$]. BBr_3 (80.6 mL, 1M in CH_2Cl_2) was added dropwise to a stirred solution of (±)-3,3'-dibromo-1,1'-binaphthyl-2,2'-dimethyl ether^{26} (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 cooling 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 (±)-3,3'-dibromo-1,1'-binaphthyl-bis(dimethylphenylsilyl) ether ((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, ArH), 7.38 (d, 2, ArH), 7.15-6.79 (m, 18, ArH), 0.20 (s, 6, SiMe), 0.05 (s, 6, SiMe). t-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(dimethylphenyl)-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(dimethylphenyl)-1,1'-binaphthyl-2,2'-diolate] (K_2(±)-BINO($SiMe_2Ph$)$_2$). A THF (5 mL) solution of KCH_2Ph[23] (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.

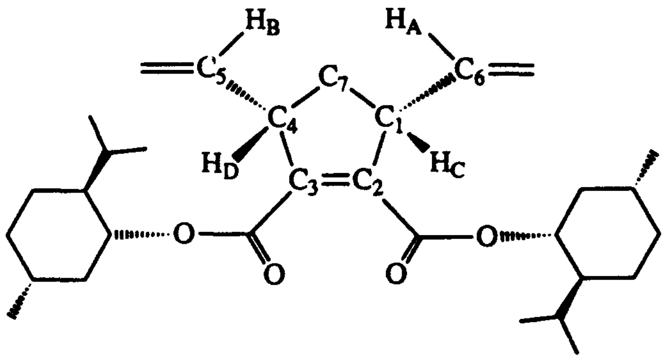
Mo($CHCMe_2Ph$)(NAr')[(±)-BINO($SiMe_2Ph$)$_2$](THF) (1d). A THF (1 mL) solution of K_2[(±)-BINO($SiMe_2Ph$)$_2$] (179 mg, 0.284 mmol) was added dropwise to a stirred THF (5 mL) solution of Mo($CHCMe_2Ph$)(NAr')(OTf)$_2$(DME)[25] (209 mg, 0.284 mmol) at -40°C. The solution was stirred for 1 h and the 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 (OCH_2CH_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-dicarboxymenthylnorbornadiene (2a). A solution of 2,3-$(COCl)_2$norbornadiene[19] (9.05 g, 41.7 mmol) in THF (50 mL) was added dropwise to a stirred THF (200 mL) solution of 1R, 2S, 5R-(-)-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 washed with dilute HCl, $NaHCO_3$ and NaCl solutions. The organic layers were dried over Na_2SO_4 and the ether 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_2CH), 3.86 (m, 2, =CHC*H*), 2.25-2.12 (m, 4), 2.06 (dt, 1, =CHCHH_2), 1.76 (dt, 1, =CHCHH_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_2CH), 72.8 (CO_2CH), 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 overlapping. $[\alpha]^{26} = -76.8$ (c = 3.80, CH_2Cl_2).

Synthesis of 2,3-dicarboxypantalactonylnorbornadiene (2b). A solution of 2,3-$(COCl)_2$norbornadiene[19] (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

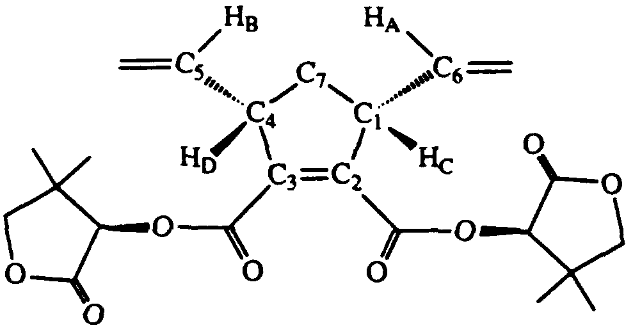
NaCl solutions. The organic layers were dried over $MgSO_4$ and treated with charcoal. The solvent was removed under vacuum to give a pink solid. The residue was recrystallized twice from a mixture of ethyl acetate and hexane to yield 4.32 g (73%) of a white crystalline product. A CH_2Cl_2 solution of 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_2CH), 5.38 (s, 1, CO_2CH), 4.02 (m, 2, =CHC*H*), 2.34 (d, 1, =CHCHCH_2), 2.13 (d, 1, =CHCHCH_2), 1.21 (Me), 1.17 (Me), 1.12 (Me), 1.08 (Me); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 171.6 (CO_2CH_2), 171.5 (CO_2CH_2), 163.1 (=CCO_2), 162.3 (=CCO_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 overlapping. $[\alpha]^{26}$ = 14.7 (c = 3.25, CH_2Cl_2).

Trans-poly(2,3-dicarboxymenthylnorbornadiene) (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 centrifuge (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_2CH), 74.7 (CO_2CH), 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 overlapping.



Trans-poly(2,3-dicarboxypantalactonylnorbornadiene) (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 centrifuge (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 (CMe_2), 39.8 (C_7), 22.9 (Me), 20.0 (Me), 19.8 (Me), other resonances overlapping.



Cis-poly(2,3-dicarboxymenthylnorbornadiene) (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 catalyst **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 stirring volume of methanol (50 mL) which caused the polymer to precipitate. The polymer was isolated by centrifuge (96 mg, 91%) and dried. See trans-poly(2a) for numbering scheme: ^1H 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_2CH), 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); $^{13}C\{^1H\}$ 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_2CH), 74.9 (CO_2CH), 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 overlapping.

Cis-poly(2,3-dicarboxypantalactonylnorbornadiene) (cis-poly(2b)/1d). A CH_2Cl_2 (1 mL) solution of monomer **2b** (113 mg, 0.279 mmol) was added in one portion to a rapidly stirred solution of catalyst **1d** (3.2 mg, 0.0033 mmol) in CH_2Cl_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_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 (103 mg, 91%) and dried. See trans-poly(2) for numbering scheme. ^1H NMR ($^{13}C\{^1H\}$ NMR (CD_2Cl_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 (+)-(2S,3S)-dicarbomethoxynorborn-5-ene (3a). (+)-(2S,3S)-Dicarbo-l-methyloxynorborn-5-ene dicarboxylic acid (11 mmole) was dissolved in methanol (60 mL) and treated with concentrated sulfuric acid (2 mL) at room temperature for 12 h. Following standard work-up 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: ^1H 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 (+)-(2S,3S)-dimethoxymethylnorborn-5-ene (3b). (+)-(2S,3S)-dihydroxymethylnorborn-5-ene (10 mmole) was treated with methyl iodide (30 mmole) in the presence of sodium hydride (30 mmole) in THF (80 mL) at 50 °C under argon for 1.5 h. Following standard work-up 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: ^1H 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 containing 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 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** and **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)/1d. ^{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); $^{13}C\{^1H\}$ 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); $^{13}C\{^1H\}$ 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

Acknowledgments. RRS thanks the Navy for supporting research on ring opening metathesis polymerization. DHM thanks the Natural Sciences and Engineering Research Council of Canada for a postdoctoral fellowship. GEH thanks the National Institutes of Health for a postdoctoral fellowship (F32 GM14263).

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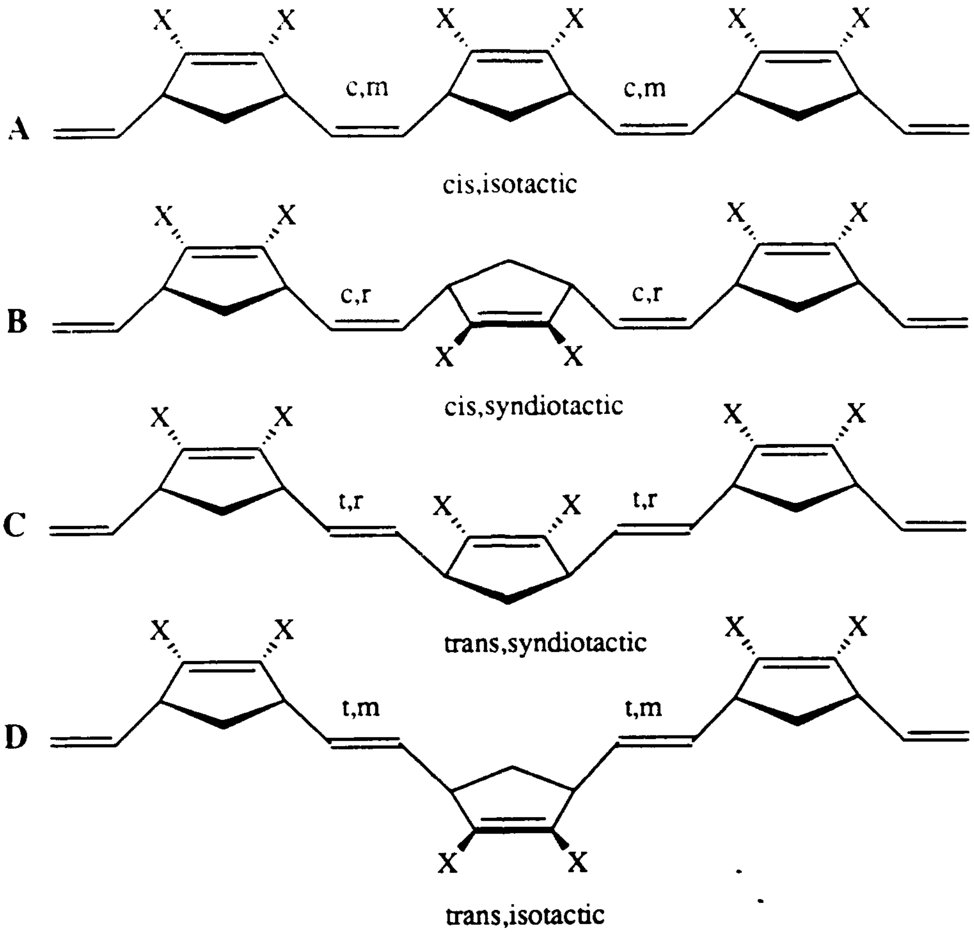
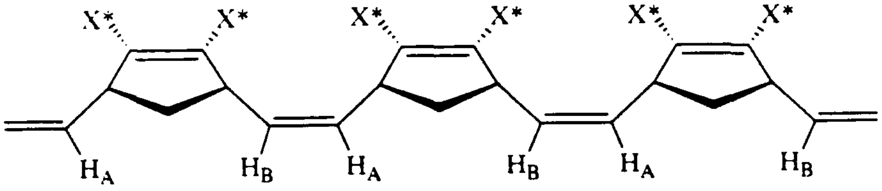
Scheme I. The Four Possible Regular Structures of 2,3-Disubstituted Norbornadienes.



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

A*



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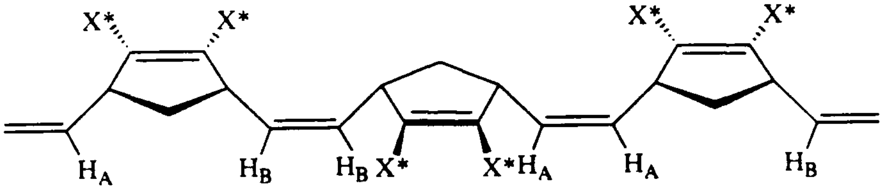
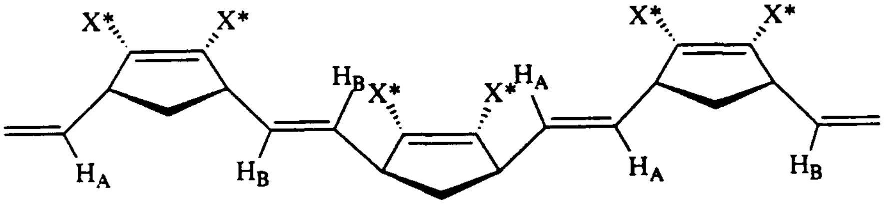


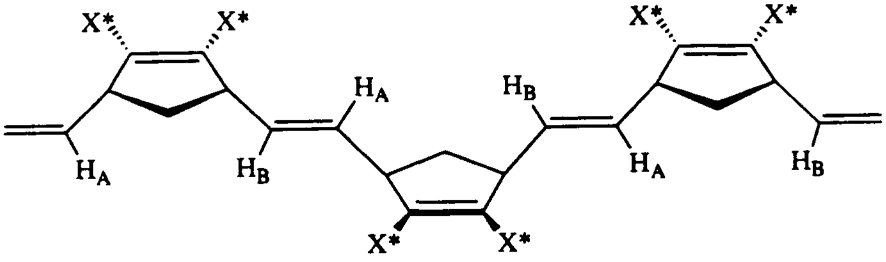
cis,syndiotactic

C*



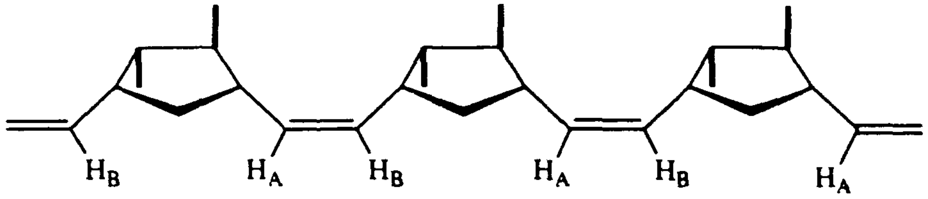
trans,syndiotactic

D*

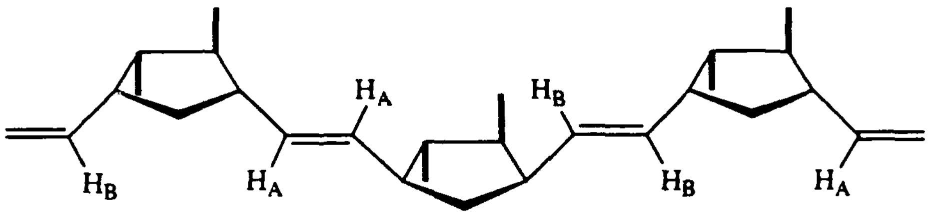


trans,isotactic

Scheme III. Two of the Four Possible Regular Polymers made from an Enantiomerically Pure 5,6-Disubstituted Norbornene.



cis,isotactic



trans,syndiotactic

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

Initiator	Solv	Monomer	Equiv	Yield (%)	M_n[a]	M_w/M_n[a]	Cis (%)	Tacticity
1a	Toluene	**2a**	100	97	16300	1.03	6	syndio
1a	CH_2Cl_2	**2b**	100	78	21000	1.28	9	syndio
1b	Toluene	**2a**	100	97	17700	1.28	99	iso
1b	CH_2Cl_2	**2b**	50	95	7400	1.15	99	iso
1c	Toluene	**2a**	100	92	22800	1.09	99	iso
1c	CH_2Cl_2	**2b**	75	93	19500	1.05	99	iso
1d	THF	**2a**	85	91	21300	1.19	99	iso
1d	CH_2Cl_2	**2b**	85	91	28200[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.

Table II. 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	18000[b]	1.05	10	(atactic)
1a	**3b**	100	98	18000[c]	1.10	8	60
1a[d]	**3c**	115	94	12000[e]	1.08	5	(atactic)
1c	**3a**	100	98	38000[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) = 21000.

[c] M_n(calcd) = 18200. [d] These data have been published elsewhere.[9] [e] M_n(calcd) = 14000.

[f] Bimodal distribution; M_p = 105000 and 163000. [g] Bimodal distribution; M_p = 95000 and 43000.

[h] Estimated on the basis of the ^1H NMR spectrum in 1,2-dichlorobenzene-d_4 at 85 °C.

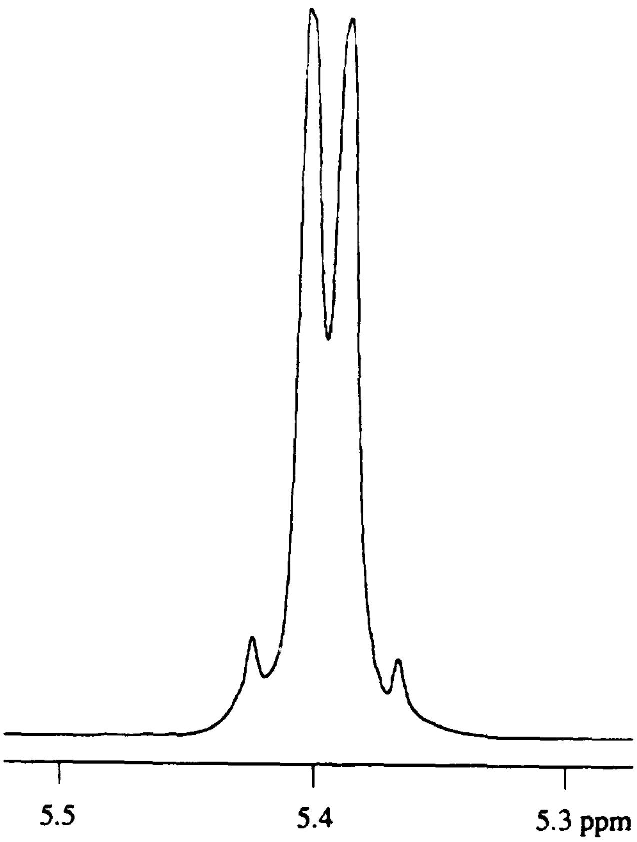
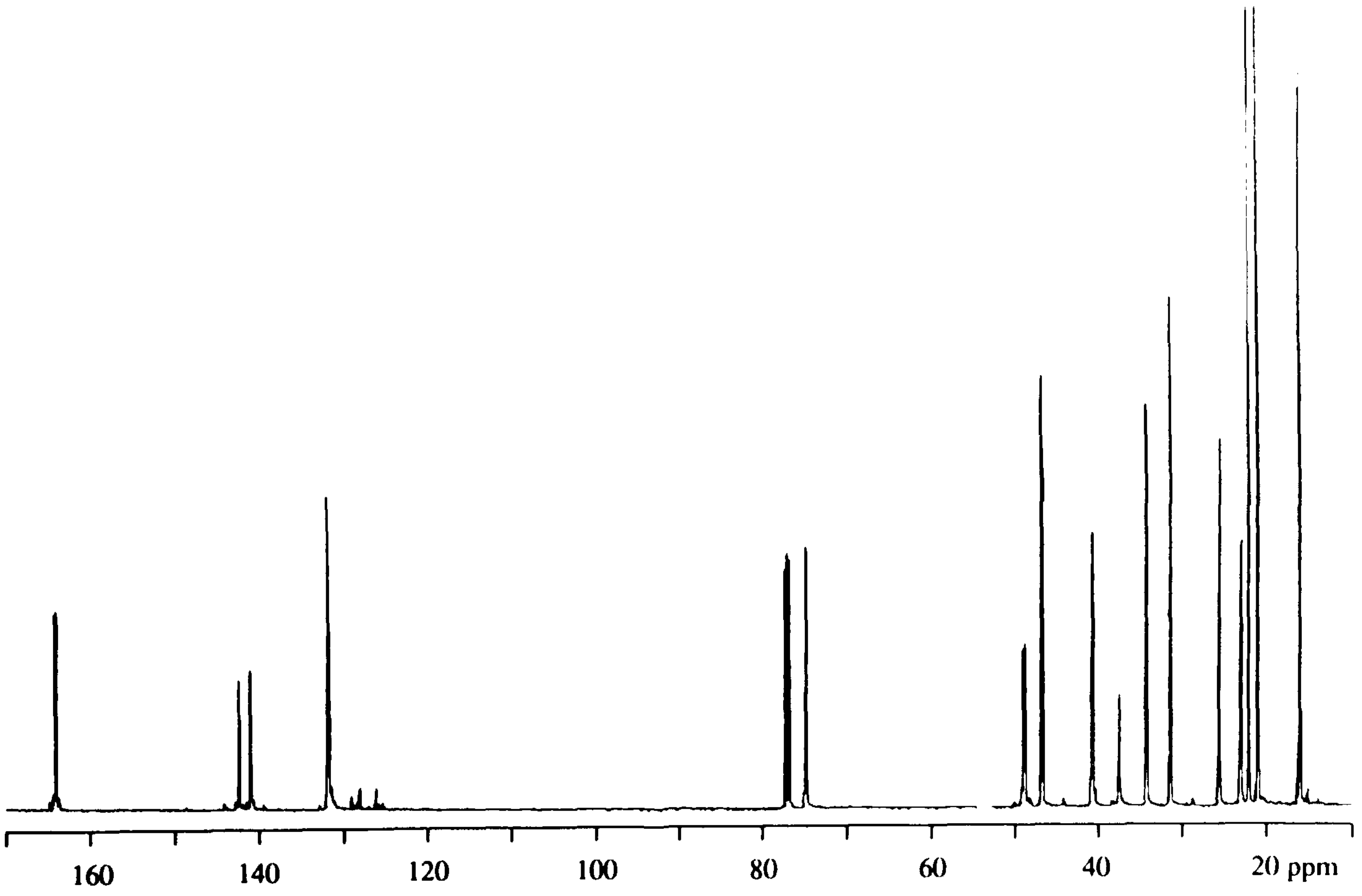


Figure 1. The olefinic resonance in all cis, highly tactic poly(2,3-dicarbomethoxy norbornadiene).[8]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120
100
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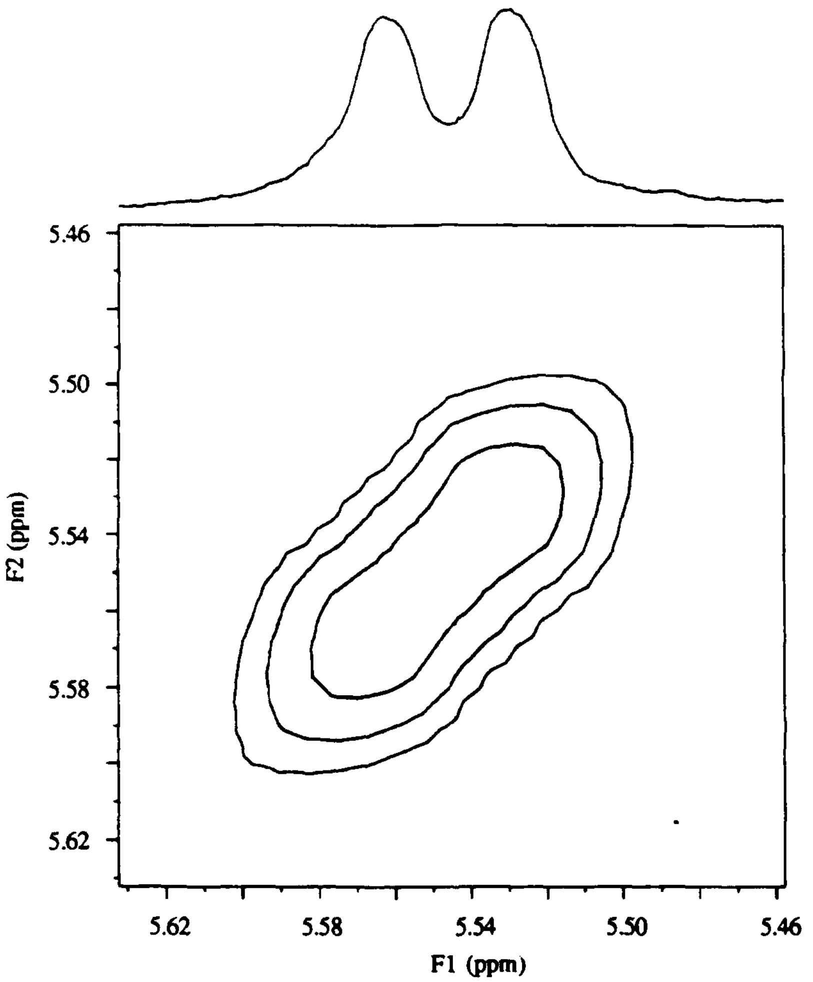
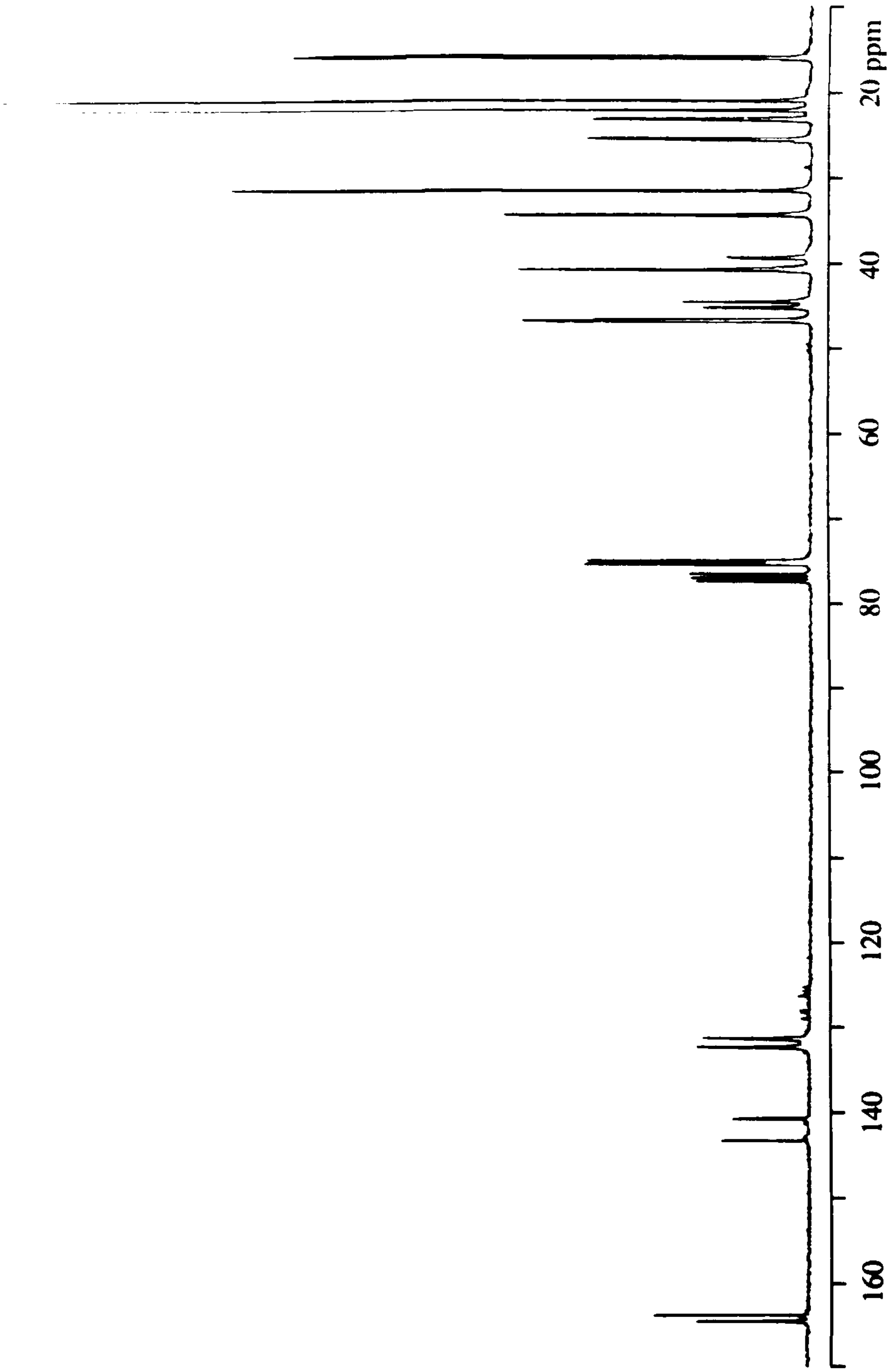


Figure 3. The olefinic region of the 500 MHz homonuclear correlation spectrum of poly(**2a**)/**1a** in $CDCl_3$ at 25°C.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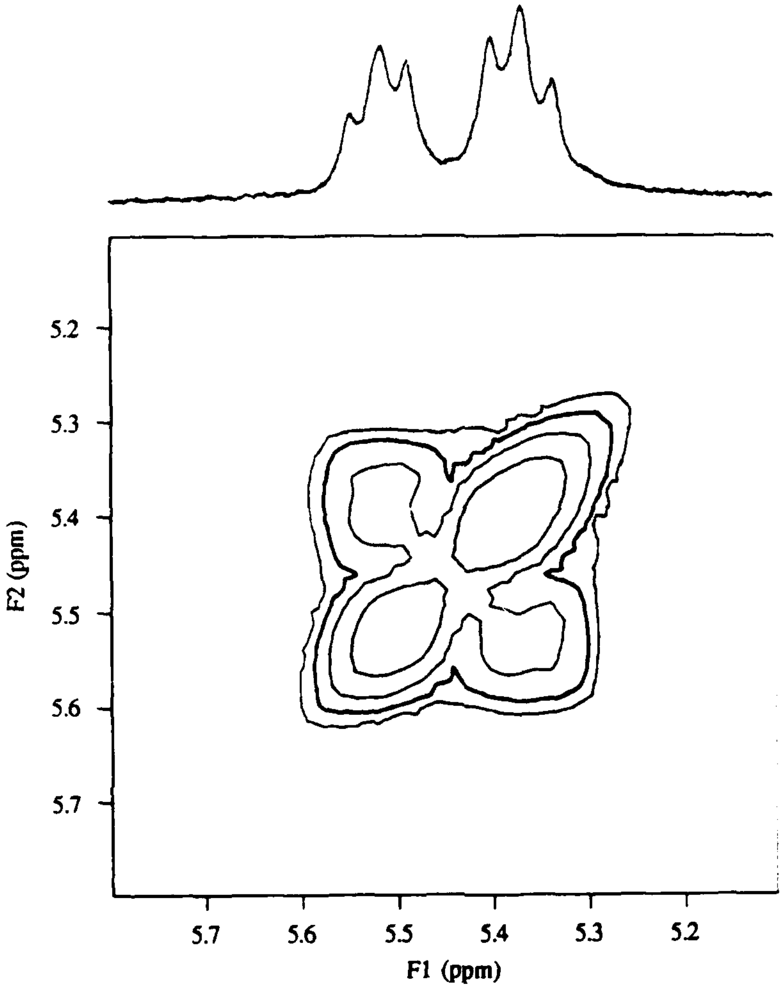

Figure 5. The olefinic region of the 300 MHz homonuclear correlation spectrum of cis-poly(**2a**) in $CDCl_3$ at 25°C.

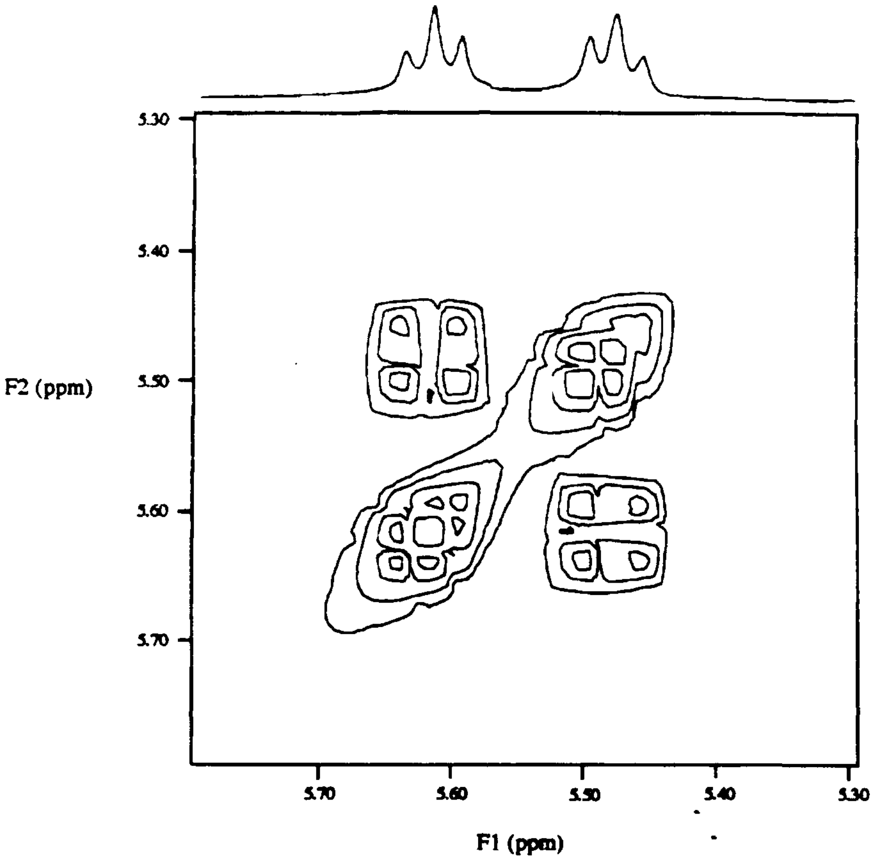

Figure 6. The olefinic region of the 500 MHz homonuclear correlation spectrum of cis-poly(3c)/**1d** (50 mer) in 1,2-dichlorobenzene-d_4 at 85 °C.

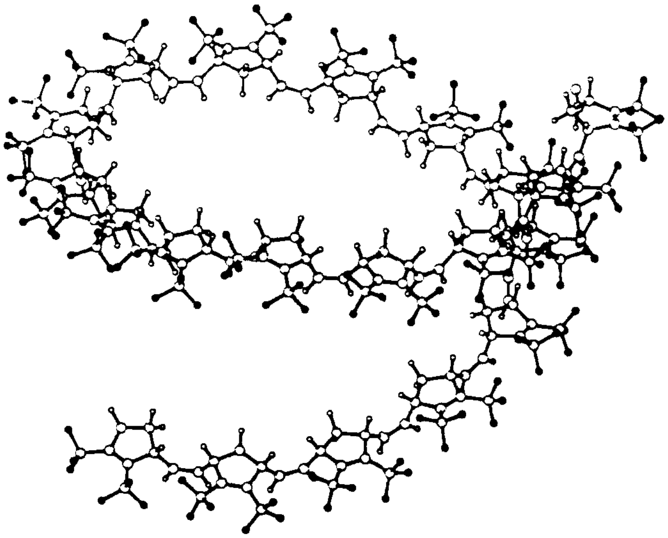

Figure 7. Calculated structure (MM II, CaCHE system) of the 25 mer of poly(NBDF6).