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Exploring Factors That Determine Cis/Trans Structure and Tacticity in Polymers Prepared by Ring-Opening Metathesis Polymerization with Initiators of the Type *syn*- and *anti*-Mo(NAr)(CHCMe$_2$Ph)(OR)$_2$. Observation of a Temperature-Dependent Cis/Trans Ratio

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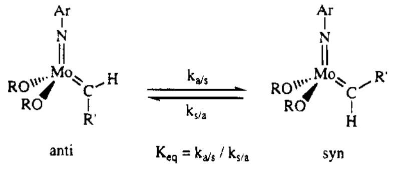
ABSTRACT: The factors that determine the structure (cis/trans and tacticity) of polymers prepared by ring-opening metathesis polymerization (ROMP) from 2,3-bis(trifluoromethyl)norbornadiene (NBDF6) and several bis(carboalkoxy)norbornadienes using well-defined initiators of the type Mo(NAryl)(CHCMe$_2$Ph)(OR)$_2$ (Aryl = a substituted aryl group and OR = a variety of alkoxides) have been explored. The main finding is a dependence of cis/trans structure on temperature; at low temperatures (−35 °C) all-cis polymer is formed and at high temperatures (65 °C) up to 90% trans polymers are formed. These results are consistent with formation of cis polymer from syn alkylidene rotamers and trans polymer from anti alkylidene rotamers in circumstances where syn and anti rotamers can interconvert. Several all-cis polymers prepared from achiral initiators that contain various fluorinated alkoxides were found to be biased toward isotacticity. In one case, however, the polymer was biased toward syndiotacticity.

Introduction

Ring-opening metathesis polymerization (ROMP) is a method of making polymers from a wide variety of cyclic olefins.[1,2] If the olefins are relatively reactive compared to ordinary olefins (e.g., norbornenes and norbornadienes) and "well-defined" initiators are employed, then the polymerization can be living.[3,4] Well-defined initiators for polymerizations of this type that have been used often are complexes of the type Mo(NAryl)(CHCMe$_2$Ph)(OR)$_2$ (Aryl = a substituted aryl group such as 2,6-Me$_2$C$_6$H$_3$).[5] A feature of such species, and perhaps classical metathesis catalysts also,[1] is the presence of syn and anti alkylidene rotamers that may, or may not, interconvert readily compared to the rate of polymerization (eq 1). We recently proposed[6] that syn and anti rotamers of complexes of this type play a major role in determining whether ROMP polymers prepared from several norbornenes or norbornadienes[4,7,8] contain cis or trans double bonds. Syn and anti rotamers whose reactivities could be evaluated (OR = OCMe(CF$_3$)$_2$) were found to have vastly different reactivities and to interconvert at rates that differed by up to 6 orders of magnitude, relatively rapidly ($k_{s/a} = 1$ s^{-1} at 25 °C) when OR = O-*t*-Bu but relatively slowly ($k_{s/a} = 10^{-5}$ s^{-1} at 25 °C) when OR = OCMe(CF$_3$)$_2$. In most cases that were examined K_{eq} was found to be $>10^3$. The rate of rotamer interconversion was found to be faster by approximately three orders of magnitude in ortho-monosubstituted phenylimido complexes such as Mo(N-2-*t*-BuC$_6$H$_4$)(CH-*t*-Bu)[OCMe(CF$_3$)$_2$]$_2$ than in 2,6-disubstituted phenylimido complexes.[6] The single bulky substituent in the ortho position was proposed to promote bending of the imido ligand and therefore a lowering of the barrier to rotamer interconversion by making the orbital that lies in the N−Mo−C plane, the one that is believed to stabilize an alkylidene in the process of rotating 180°, more accessible.



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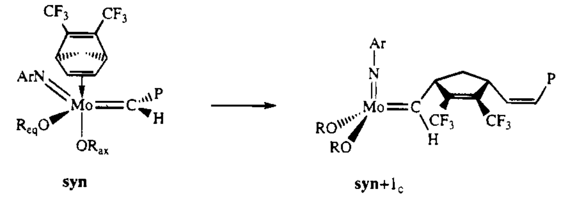
The monomer that has been employed often in investigations of this general type is 2,3-bis(trifluoromethyl)norbornadiene (NBDF6). On the basis of detailed NMR studies,[6] it was proposed that *syn*-Mo(NAr)(CH-*t*-Bu)[OCMe(CF$_3$)$_2$]$_2$ (Ar = 2,6-*i*-Pr$_2$C$_6$H$_3$) reacts with NBDF6 by coordinating to the exo face of the unsubstituted double bond to generate a syn first insertion product having a cis double bond (syn+1$_c$; eq 2), while the anti rotamer reacts (at least 100 times more rapidly) to give a syn first insertion product having a trans double bond (syn+1$_t$; eq 3). *trans*-Poly(NBDF6) prepared from Mo(NAr)(CHCMe$_2$Ph)(O-*t*-Bu)$_2$ was proposed to arise from reactions involving only (unobservable) anti rotamers, since the anti rotamer is kinetically accessible at room temperature ($k_{s/a} \approx 1$ s^{-1}; eq 1) and since studies involving Mo(NAr)(CHCMe$_2$Ph)[OCMe(CF$_3$)$_2$]$_2$ suggest that the anti rotamer is much more



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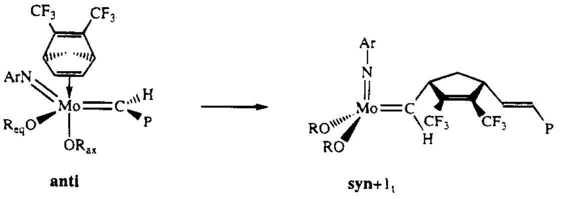

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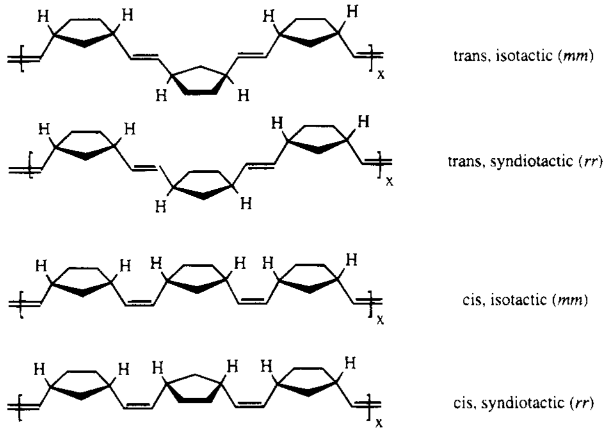
Chart 1. The Four Possible Regular Primary Structures of Polynorbornene



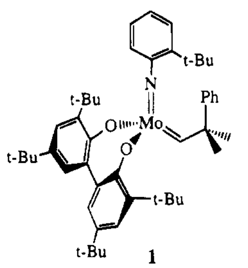
reactive than the syn rotamer. Since $K_{eq} \approx 10^3$, the anti rotamer actually must be at least 10^5 times more reactive than the syn rotamer in order to generate >99% trans double bonds.[6] On the other hand, use of $\mathrm{Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2}$ as the initiator gave *cis*-poly(NBDF6).[9] In this case *syn*-$\mathrm{Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2}$, the predominant species present in solution at 25 °C, *is* reactive enough to react with NBDF6. Since a syn insertion product that contains a cis double bond is formed at each step, the polymer continues to grow from syn rotamers to give *all-cis* poly(NBDF6). Anti rotamers of alkylidene intermediates, even though they are much more reactive, are simply *inaccessible* on the time scale of the polymerization reaction in the $\mathrm{OCMe(CF_3)_2}$ system.

Tacticity is believed to be a separate issue, at least in systems that have been explored so far. The four possible regular primary structures of polynorbornene (for purposes of illustration) are shown in Chart 1. It is believed that a molybdacyclobutane complex is formed when the monomer approaches one of the two CNO faces of the pseudotetrahedralcatalyst (eq 2 or 3). The two CNO faces correspond to the two sides of the Mo=C bond. If the monomer approaches the same CNO face in each step, an isotactic polymer is formed; if the monomer approaches alternate CNO faces sequentially, a syndiotactic polymer is formed. If a polymerization process yields all-trans or all-cis polymer, then it is possible in some cases to determine the degree of tacticity in a relatively simple manner by ^{13}C NMR.[1] Recently, it has become possible to prepare highly tactic all-cis polymers with molybdenum initiators that contain a racemic binaphtholate ligand[10] and to prove that related all-cis polymers that contain chiral groups in the ester of a bis(carboalkoxy)norbornadiene are isotactic while all-trans polymers that contain chiral groups in the ester of a bis(carboalkoxy)norbornadiene are syndiotactic.[7] It also has been shown that all-cis polymers prepared from several enantiomerically pure 2,3-disubstituted norbornenes employing molybdenum binaphtholate initiators are isotactic.[7]

Molybdenum alkylidene complexes that contain phenoxide ligands have been relatively little studied. Unlike complexes that contain *tert*-butoxide ligands, both syn and anti rotamers are often observable and they interconvert with activation energies between 15 and 18 kcal mol^{-1}.[11,12] Molybdenum phenoxide complexes that have been briefly investigated as ROMP initiators were found to produce polymers that contain both cis and trans double bonds. On the other hand, "linked" phenoxide ligands such as binaphtholates and biphenolates often give rise to highly cis and highly tactic ROMP polymers.[7,10] In order to explore the origin of cis and trans polymers, we chose to examine phenoxide initiators in this paper. In order to explore how the tacticity of some all-cis polymers varies with the monomer, the imido ligand, and the alkoxide ligand, we chose to examine polymers prepared with $\mathrm{Mo(NAr)(CHCMe_2Ph)(OR)_2}$ initiators where OR = $\mathrm{OCMe(CF_3)_2}$, $\mathrm{OC(CF_3)_3}$, or $\mathrm{OC(CF_3)_2(CF_2CF_2CF_3)}$.

Results

Molybdenum (2-*tert*-Butylphenyl)imido Complexes. We suspected that the rate of rotamer interconversion in molybdenum initiators that contain the (2-*tert*-butylphenyl)imido ligand would be in an "intermediate" range where changes in temperature might dramatically affect the outcome of the polymerization reaction. An initiator that can be purified by recrystallization is most desirable, so $\mathrm{Mo(N\text{-}2\text{-}\mathit{t}\text{-}BuC_6H_4)(CH\text{-}\mathit{t}\text{-}Bu)(OAr)_2}$,[13] an oil, is unsuitable. $\mathrm{Mo(N\text{-}2\text{-}\mathit{t}\text{-}BuC_6H_4)(CHCMe_2Ph)(OR)_2}$ compounds where R = 2-*t*-$\mathrm{BuC_6H_4}$ or 2,4-*t*-$\mathrm{Bu_2C_6H_3}$ were also found to be oils,[14] but $\mathrm{Mo(N\text{-}2\text{-}\mathit{t}\text{-}BuC_6H_4)(CHCMe_2Ph)(BiphenoBu_4)}$ ($\mathrm{BiphenoBu_4}$ = 2,2′-[4,4′,6,6′-*t*-$\mathrm{Bu_4](C_6H_2)_2O_2}$[15,16]) could be prepared as a crystalline THF adduct, **1(THF)**. THF could be removed in vacuo from a sample of **1(THF)** dissolved in a high-boiling, noncoordinating solvent such as toluene, and THF-free **1** thereby obtained. **1**, **1(THF)**, and several related new and known crystalline initiators used in this work are listed in Table 1.



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The ^{1}H NMR spectrum of **1** at 23 °C showed one sharp alkylidene resonance at 10.87 ppm, while the ^{13}C NMR spectrum showed one sharp alkylidene resonance at 279 ppm with a value for $^1J_{CH}$ (120 Hz) characteristic of a syn rotamer.[5,6] No significant change was observed upon cooling the sample to −65 °C. However, the proton NMR spectrum of **1(THF)** in toluene-d_8 at 26 °C showed a broad alkylidene H_α resonance at 11.03 ppm (Figure 1). When the NMR sample of **1(THF)** was cooled, two new alkylidene resonances grew in at 14.08 and 12.85 ppm (Figure 1) and sharpened at the expense of the 11.03 ppm resonance upon further cooling, ultimately to give a spectrum containing two alkylidene resonances in a 1:3 ratio. Addition of THF (~10 equiv) to a sample of **1** in toluene-d_8 at −65 °C generated a sample having the same two alkylidene resonances found in the spectrum of **1(THF)** at low temperature. Therefore we propose that the H_α resonances at 14.08 and 12.85 ppm are due to THF adducts of anti and syn rotamers, respectively, i.e., $\mathbf{1}_{anti}$**(THF)** and $\mathbf{1}_{syn}$**(THF)**. (It is well-documented that H_α resonances in alkylidene complexes in this family move downfield upon adduct formation and that anti H_α resonances are found downfield of syn H_α resonances.[5]) The two tiny resonances at 12.78 and 14.00 ppm observed near the resonances for $\mathbf{1}_{anti}$**(THF)** and $\mathbf{1}_{syn}$**(THF)** could not be identified. They could

Table 1. Crystalline Mo(VI) Initiators Employed in This Work[a]

complex		δ(H$_\alpha$)[b]	yield (%)	ref
Mo(N-2-*t*-BuC$_6$H$_4$)(CHR)[Bipheno(*t*-Bu)$_4$]	(**1**)	10.87		
Mo(N-2-*t*-BuC$_6$H$_4$)(CHR)[Bipheno(*t*-Bu)$_4$](THF)	[**1**(**THF**)]	11.15	78	
Mo(N-2,6-Me$_2$C$_6$H$_3$)(CHR)[Bipheno(*t*-Bu)$_4$](THF)	[**2**(**THF**)]	11.52[c] 14.10		7
Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHR)[Bipheno(*t*-Bu)$_4$](THF)	[**3**(**THF**)]	11.43[d] 14.30	68	
Mo(N-2-*t*-BuC$_6$H$_4$)(CHR)[OCMe(CF$_3$)$_2$]$_2$	(**4**)	11.79		13
Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHR)(O-2-*t*-BuC$_6$H$_4$)$_2$	(**5**)	11.79[e] 13.37	91	
Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHR)[OCMe$_2$(CF$_3$)]$_2$	(**6**)	11.68		13
Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHR)[OCMe(CF$_3$)$_2$]$_2$	(**7**)	12.12		13
Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHR)[OC(CF$_3$)$_3$]$_2$	(**8**)	12.12		13
Mo(N-2,6-*i*-Pr$_2$C$_6$H$_3$)(CHR)[OC(CF$_3$)$_2$(CF$_2$CF$_2$CF$_3$)]$_2$	(**9**)	12.12		13

[a] R = CMe$_2$Ph. [b] Values are reported in ppm in C$_6$D$_6$ at ~23 °C. [c] 88% syn at ~23 °C in C$_6$D$_6$. [d] 75% syn at ~23 °C in C$_6$D$_6$. [e] 93% syn at ~23 °C in C$_6$D$_6$.

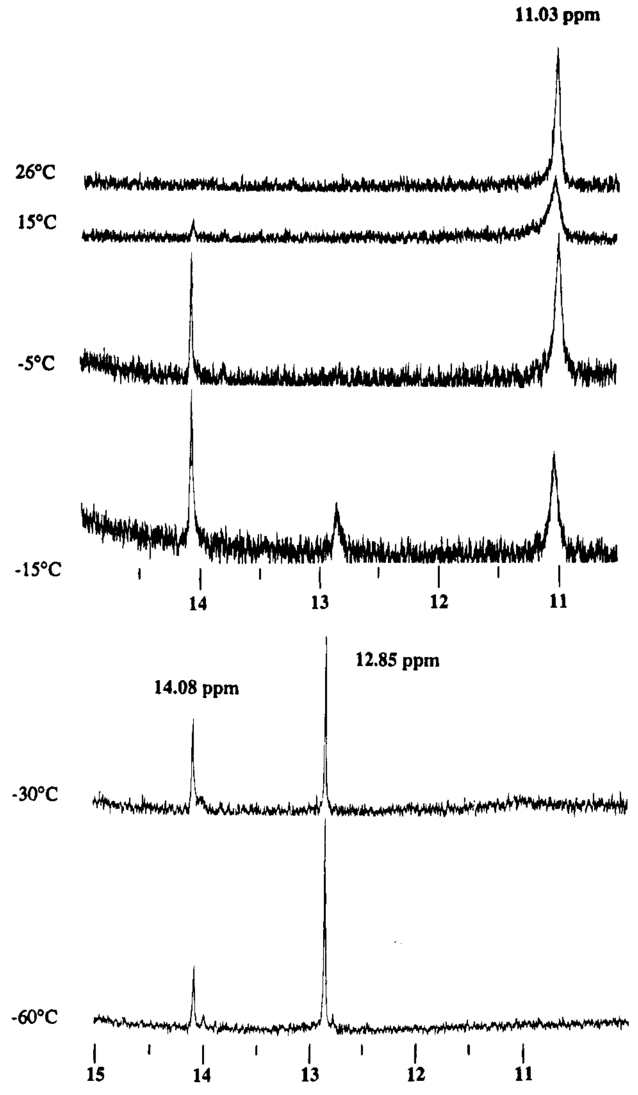

Figure 1. Proton NMR spectra of **1**(**THF**) in the alkylidene H$_\alpha$ region (in toluene-d_8).

possibly be structural isomers in which THF coordinates to the metal in a position other that what is believed to be the favored CNO face.[6] As the temperature of the sample containing **1**$_{anti}$(**THF**) and **1**$_{syn}$(**THF**) is raised, THF appears to come off the syn rotamer more readily than the anti rotamer, as judged by broadening of the 12.85 ppm resonance first at −15 °C (Figure 1) and loss of intensity as the equilibrium shifts toward the THF-free complex. At higher temperatures all resonances coalesce into a single broad alkylidene H$_\alpha$ resonance between 11.0 and 11.1 ppm as the equilibrium shifts virtually entirely toward the base-free form of **1** and THF exchange is rapid on the NMR time scale.

Samples of **1** were photolyzed at −75 °C in toluene in an attempt to produce an observable amount of **1**$_{anti}$. (Photolysis has been found to cause interconversion of syn and anti rotamers of Mo[6] and Re[17] alkylidene rotamers.) However, no **1**$_{anti}$ accumulated after 18 h of photolysis. Either back reaction of **1**$_{anti}$ to **1**$_{syn}$ (photochemical or thermal) is too fast on the chemical time scale at −75 °C or photolysis is not an effective method of effecting anti/syn interconversion in phenoxide complexes. The former seems more likely to be the case, in part since bending of the monosubstituted phenylimido ligand is known to reduce the barrier to alkylidene rotation significantly in OCMe(CF$_3$)$_2$ complexes.[6] Therefore we suspect that **1**$_{syn}$ and **1**$_{anti}$ can equilibrate on the chemical time scale even at −75 °C and that the equilibrium lies well toward the syn rotamer.

It is interesting to note that for the analogous (2,6-diisopropylphenyl)imido complex (**3**(**THF**); Table 1) the anti:syn ratio is 1:3 at room temperature in toluene-d_8. (On the basis of chemical shifts, it is likely that the anti form is the THF adduct and the syn form the THF-free form of **3**.) Perhaps the additional steric hindrance caused by the 2,6-disubstituted phenyl ring decreases the stability of the THF-free syn rotamer relative to the THF adduct of the anti rotamer in addition to significantly slowing the rate of interconversion of anti and syn forms.

Polymerizations Employing 1 as the Initiator. Polymerizations of NBDF6 or DCMNBD (2,3-bis(carbomethoxy)norbornadiene) were carried out with **1** as the initiator in THF, toluene, or dichloromethane (Table 2). In discussing these results, we will assume that **1**$_{anti}$ is in equilibrium with **1**$_{syn}$ on a time scale of the order of the polymerization reaction, that trans double bonds are formed only from anti rotamers and cis double bonds only from syn rotamers, and that only pseudo four-coordinate THF-free complexes are reactive.[6] (We will later discuss whether these assumptions are valid.)

The first six entries in Table 2 show data for samples of poly(NBDF6)$_{100}$. Homogeneous polymerizations were observed when THF was employed as a solvent, but in toluene another phase formed as polymerization progressed. Yields were high at room temperature or above but low at low temperatures, even with a polymerization time of 48 h. At temperatures below −10 °C we propose that polymerization is slowed down to a significant degree simply by coordination of THF (competitive inhibition), most strongly to the anti rotamer. (The anti rotamer is known to have a greater affinity for σ-donor

Table 2. NBDF6 and DCMNBD 100-Mers Prepared Employing 1 as the Initiator[a]

monomer	T (°C)	solvent	time (h)	cis/trans[b]	PDI[c]	yield (%)
NBDF6	−35	THF	48	100/0		~5
NBDF6	−10	THF	48	100/0		~5
NBDF6	15	THF	24	83/17	1.38	43
NBDF6	23	THF	5	58/42	1.17	90
NBDF6	23	toluene[d]	5	32/68	1.34	98
NBDF6	65	THF	5	24/76	1.10	99
DCMNBD	−35	CH_2Cl_2	12	100/0		36
DCMNBD	23	toluene	1	54/46		93
DCMNBD	50	toluene	1	35/65		96
DCMNBD	80	toluene	1	19/81		93

[a] NBDF6 = 2,3-bis(trifluoromethyl)norbornadiene; DCMNBD = 2,3-bis(carbomethoxy)norbornadiene. [b] Measured by ^1H and ^{13}C NMR as described elsewhere.[9,10] [c] In THF versus polystyrene standards. [d] Immiscible phase formed during polymerization. One equivalent of THF present.

bases such as phosphines.[5]) THF therefore selectively "poisons" the anti rotamer by competing more effectively with the monomer for the coordination site in the anti rotamer than in the syn rotamer. Consequently, only cis bonds are produced via syn rotamers at −35 °C since effectively only the THF-free syn alkylidene is accessible. However, the reaction is extremely slow since so little THF-free alkylidene is available. Conversely, at 65 °C THF is dissociating readily to give both anti and syn four-coordinate alkylidene intermediates. Since syn/anti interconversion is believed to be rapid, the majority of the polymer arises via anti intermediates, and 76% trans polymer is formed. Poly(NBDF6) prepared at 23 °C in THF has approximately a 1:1 ratio of trans and cis double bonds. In toluene at 23 °C reaction of the monomer with the anti form is no longer as inhibited by THF as it is at low temperature, and the trans content therefore increases from what it is in pure THF, from 42 to 68% (Table 2).

Polymerization of 2,3-bis(carbomethoxy)norbornadiene with **1** in toluene yielded analogous results (Table 2). Polymerization at −35 °C was carried out in dichloromethane in order to enhance solubility of the polymer at that temperature. At −35 °C a 36% yield of 100% cis polymer was realized in 12 h. At higher temperatures in toluene the trans content steadily increased to 81% at 80 °C. A control experiment ruled out the possibility that trans polymer results from isomerization of cis double bonds in the polymer (secondary metathesis). *all-cis*-Poly(DCMNBD) (100-mer) that had been prepared using **2(THF)** as the initiator[10] was added to the living alkylidene generated by adding 10 equiv of DCMNBD to **1**, and the mixture was heated for 2 h at 80 °C. The trans content did not increase to any significant degree, consistent with slow secondary metathesis, even at 80 °C.

In order to confirm that syn and anti rotamer accessibility is the origin of the dependence of polymer structure on temperature, it would be desirable to show that the cis/trans structure of polymers prepared with $OCMe(CF_3)_2$ initiators, where a syn rotamer is known to generate syn+1_{cis} (eq 2) while an anti rotamer generates syn+1_{trans} (eq 3),[6] is also temperature dependent. It is already known that both syn and anti rotamers of $OCMe(CF_3)_2$ complexes are qualitatively much more reactive in toluene than they are in THF and that the reactivity of an anti rotamer decreases more significantly in THF than the reactivity of a syn rotamer in THF, relative to their reactivities in toluene.

The best known $OCMe(CF_3)_2$ initiator is $Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ (**7**), which generates *high-cis*-poly(NBDF6) in toluene or THF at 25 °C (Table 3).[9] At 65 °C the cis content drops to 88% for poly(NBDF6) prepared in toluene and to 83% for poly(NBDF6) prepared in THF (Table 3), consistent with greater participation of the anti rotamer (to give trans polymer) in reactions at the higher temperatures. Polymerizations employing $Mo(N\text{-}2\text{-}t\text{-}BuC_6H_4)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ (**4**) must be carried out at −35 °C in order to achieve a similarly high cis content because rotamer interconversion in $Mo(N\text{-}2\text{-}t\text{-}BuC_6H_4)$ complexes is about 3 orders of magnitude faster than in NAr complexes.[6] When the temperature is raised to 65 °C, the cis content drops to 29%. These results are consistent with the proposal that a higher rate of rotamer interconversion leads to higher trans polymer as a consequence of a greater accessibility of anti rotamers and that THF reduces the reactivity of an anti rotamer more strongly than a syn rotamer to produce a polymer with a higher cis content compared to a polymer prepared in toluene. Predictably, polymer yields are lower in THF or at low temperatures as a consequence of slow and incomplete polymerization.

Table 3. Poly(NBDF6) 100mers prepared with various initiators at various temperatures.

T (°C)	solvent	time (h)	cis/trans[a]	PDI[b]	yield (%)
$Mo(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ (**7**)					
25	toluene	5	97/3	1.28[c]	100
65	toluene	5	88/12	1.29[c]	94
23	THF	5	96/4	1.29	27[d]
65	THF	5	83/17	1.98	45[d]
$Mo(N\text{-}2\text{-}t\text{-}BuC_6H_4)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ (**4**)					
−35	toluene	24	97/3	1.56[c]	83
23	toluene	5	78/22	1.18	100
	THF	5	87/13		21[d]
65	toluene	5	29/71	1.32[c]	97
$Mo(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(CHCMe_2Ph)[Bipheno(t\text{-}Bu)_4]$ (**3**)					
−35	THF	48			0
23	THF	5	99/1	1.33	98
65	THF	5	90/10	1.19	96
$Mo(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(CHCMe_2Ph)(O\text{-}2\text{-}t\text{-}BuC_6H_4)_2$ (**5**)					
−35	THF	50	78/22		23
23	THF	5	69/31	1.28	90
	toluene	5	65/35	1.82	92
65	THF	5	39/61	1.14	100
$Mo(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(CHCMe_2Ph)[OCMe_2(CF_3)]_2$ (**6**)					
−35	toluene	48	56/44	1.99	63[d]
23	toluene	5	36/64	1.24	100
65	toluene	5	9/91	1.61[c]	95
23	THF	5	50/50	1.32	50[d]
65	THF	5	13/87	1.34[c]	99

[a] Measured as described elsewhere.[9,10] [b] In THF versus polystyrene standards. [c] Significant amount of double molecular weight peak was detected. The PDI value includes the double molecular weight peak. [d] Incomplete polymerization.

Two other new (2,6-diisopropylphenyl)imido phenoxide initiators (**3** and **5**) were used to make poly$(NBDF6)_{100}$ at various temperatures and the results compared with those obtained employing **6** as the initiator (Table 3). The trend of the effect of temperature on cis/trans structure using all three initiators is toward higher trans content of the polymer at higher temperature and in toluene. The formation of predominantly cis polymer employing **3** was expected since the analogous neopentylidene initiator also yields virtually all-cis polymer.[6] At 65 °C some decrease in the cis content is observed, analogous to the results employing **7** (Table 3).

Tacticity of High-Cis Polymers Prepared from $Mo(NAryl)(CHCMe_2Ph)(OR)_2$ Initiators (OR = OC-

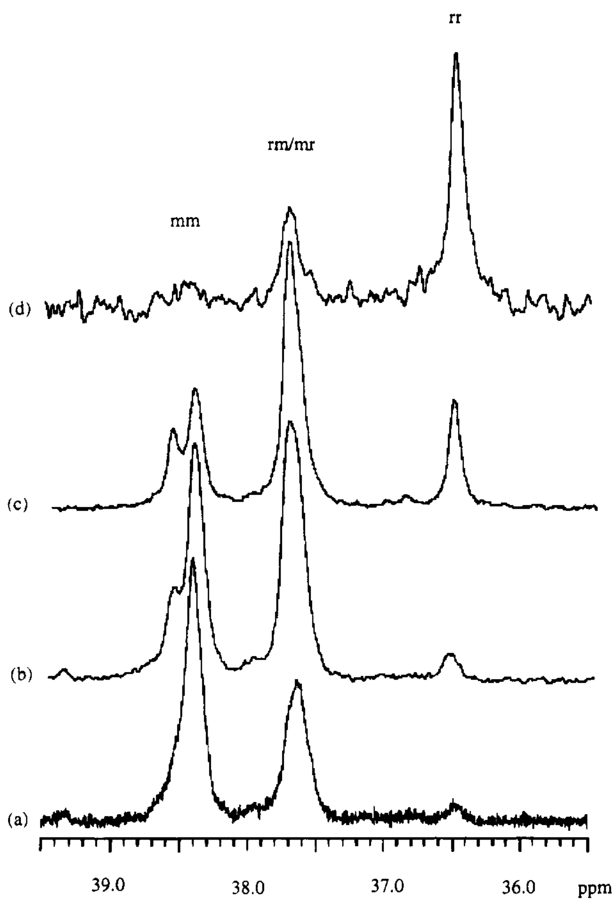

Figure 2. 125 MHz ^{13}C NMR spectra of the methylene region (C7) region of *high-cis*-poly(NBDF6) prepared in (a) run 1, (b) run 2, (c) run 5, and (d) run 10 in Table 4.

$Me(CF_3)_2$, $OC(CF_3)_3$, or $OC(CF_3)_2(CF_2CF_2CF_3)$). The tacticity of all-cis or all-trans polymers prepared from norbornenes and norbornadienes in many cases can be determined by ^{13}C NMR methods.[1] For example, the resonance for what was C(7) in a norbornadiene monomer is often sensitive to the orientation of the five-membered rings on each side of a given ring in the polymer; therefore for an all-cis polymer three resonances for C(7) (in an isotactic, a syndiotactic, or an atactic triad (Chart 1)) are often observed, usually in a nonstatistical fashion. Additional structure is usually attributed to sensitivity of C(7) to structural variations beyond the triad level. In this section we examine how tacticity varies with the alkoxide and monomer for initiators which lead to high-cis polymers. In some cases polymers begin to precipitate during the course of the polymerization reaction, but so far we have found that a heterogeneous polymerization reaction (e.g., in toluene) does not yield results (in terms of PDI, cis content, or tacticity) that are significantly different from those found for a homogeneous reaction (e.g., in THF). We will assume that all polymerizations described here that give rise to a polymer with a high cis content and low PDI are living, although that has not been proven in every case. In several cases the reaction time has been doubled or trebled without consequence in terms of cis content or PDI, consistent with slow secondary metathesis reactions. The yields of all polymerization reactions are high.

In Figure 2a are shown the C(7) resonances in the ^{13}C spectrum of *high-cis*-poly(NBDF6)$_{200}$ (98%) (PDI = 1.10; Table 4) prepared using **7** as the initiator in THF.[9] On the basis of analogous polymers prepared from bis(carboalkoxy)norbornadiene monomers that contain chiral groups in the ester,[7] it has been suggested that the most downfield C(7) resonance is in a ring in a m,m or isotactic triad. The bias toward isotacticity is a consequence of some chain end control. Virtually the same result is obtained for poly(NBDF6) prepared in toluene (run 2, Table 4; Figure 2b). (The additional structure on the isotactic resonance for C(7) at ~38.5 ppm is most likely ascribable to a sensitivity to structure beyond the triad level.) Polymers prepared in solvent mixtures (runs 3 and 4, Table 4) are analogous to those prepared in runs 1 and 2. The % mm triads drops slightly (from 62% in run 2 to 52% in run 11) when $Mo(N\text{-}2,6\text{-}Me_2C_6H_3)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ is employed as the initiator.

Polymerization of NBDF6 by the $Mo(NAr)(CHCMe_2Ph)[OC(CF_3)_3]_2$ initiator in toluene (run 5, Table 4) produces a virtually all-cis polymer that contains only ~40% isotactic triads (Figure 2c), while polymer produced by the $Mo(NAr)(CHCMe_2Ph)[OC(CF_3)_2(CF_2CF_2CF_3)]_2$ initiator (run 10) produces a high-cis polymer that contains 77% *syndiotactic* triads (Table 4, Figure 2d). There is no way to rationalize such results on the basis of our present knowledge of these catalyst systems. The effect of several solvents on the resulting polymer prepared from the $Mo(NAr)(CHCMe_2Ph)[OC(CF_3)_3]_2$ initiator was minimal (runs 6–9). Polymers prepared from $N\text{-}2,6\text{-}Me_2C_6H_3$ or N-2-*t*-BuC_6H_4 initiators (runs 11–14) again were between 52 and 88% *iso*tactic. The contrast between the syndiotacticity of the polymer prepared in run 10 and the isotacticity of the polymer prepared in run 13 is dramatic. The fact that polymer prepared in run 14 is still virtually all cis, and therefore most likely arises from syn rotamers, is interesting in view of the fact that the rate of syn to anti conversion is probably approximately 3 orders of magnitude higher than the rate of syn to anti conversion in a complex that contains a NAr or a $N\text{-}2,6\text{-}Me_2C_6H_3$ ligand.[6]

Polymerization of bis(carbomethoxy)norbornadiene by $Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ gives essentially an all-cis polymer whose ^{13}C NMR spectrum in the C(7) region (Figure 3a) is similar to the spectrum of poly(NBDF6) shown in Figure 2a, except the three C(7) resonances in poly[bis(carbomethoxy)norbornadiene] are closer together than they are in poly(NBDF6). It has been argued that both polymers are biased toward isotacticity (mm).[7] The poly[bis(carbomethoxy)norbornadiene] prepared with the F9 and F13 initiators (runs 16 and 17) is essentially the same as that in run 15. Similar polymers are prepared with an initiator that contains the $N\text{-}2,6\text{-}Me_2C_6H_3$ ligand (runs 18–20). The dramatic change in tacticity observed in the sequence of runs 2, 5, and 10, but not runs 15, 16, and 17, suggests that tacticity can sensitively depend upon the nature of the monomer and at the same time, of course, the intermediate alkylidenes formed from it in the polymerization reaction.

Polymerization of ethyl, isopropyl, and *tert*-butyl bis(carboalkoxy)norbornadiene derivatives (runs 21–25) yields high-cis polymers whose ^{13}C NMR spectra (Figure 3b–d) in the region of the resonance for C(7) appear to be analogous to that for the bis(carbomethoxy) derivative (Figure 3a). However, we cannot be certain that the spectrum shown in Figure 3d can be ascribed to highly isotactic polymer, i.e., that the rm/mr C(7) resonance does not simply overlap with the mm C(7)

Table 4. Polynorbornadienes Prepared Using Mo(NAryl)(CHCMe$_2$Ph)(OR)$_2$ Initiators

run	monomer	aryl	OR	solv	equiv	time (h)	M_n(found)[a]	PDI[a]	cis (%)	tacticity (%)
1	$(CF_3)_2$[b]	(*i*-Pr)$_2$	F6	thf	200	5	45700	1.10	98	75 (mm)
2			F6	tol	100		19500	1.05	98	62 (mm)
3			F6	tol (10 thf)	100		18600	1.12	98	60 (mm)
4			F6	tol (10 MeCN)	100		15800	1.06	98	57 (mm)
5			F9	tol	100	2	21100	1.04	99	40 (mm)
6			F9	pentane	100		17300	1.07	98	56 (mm)
7			F9	$CF_3C_6H_5$	100		16200	1.04	99	53 (mm)
8			F9	CH_2Cl_2	100		13200	1.04	99	59 (mm)
9			F9	DME	100		16700	1.03	99	44 (mm)
10			F13	tol	40	4	6300	1.08	95	77 (rr)
11		Me$_2$	F6	tol	100		23200	1.09	99	52 (mm)
12			F9	tol	100		11200	1.07	99	85 (mm)
13			F13	tol	39	1	5400	1.11	99	88 (mm)
14		*t*-Bu	F9	tol	100	0.4	18300	1.10	99	67 (mm)
15	$(CO_2Me)_2$[c]	(*i*-Pr)$_2$	F6	tol	100		16400	1.04	98	60 (mm)
16			F9	tol	100		15400	1.19	97	61 (mm)[d]
17			F13	tol	100		14900	1.20	99	54 (mm)
18		Me$_2$	F6	tol	100		20100	1.16	96	52 (mm)
19			F9	tol	100		18900	1.17	99	71 (mm)
20			F13	tol	50		9900	1.12	99	69 (mm)
21	$(CO_2Et)_2$[e]	(*i*-Pr)$_2$	F9	tol	100		20200	1.26	97	71 (mm)
22	$(CO_2i\text{-}Pr)_2$[f]		F9	tol	100		11800	1.27	97	65 (mm)
23	$(CO_2\text{-}t\text{-}Bu)_2$[g]		F6	tol	100		21300	1.15	99	88 (mm)
24			F9	tol	100		21700	1.16	99	95 (mm)
25			F13	tol	100		18700	1.42	99	90 (mm)

[a] By GPC viscometry employing refractometer data. [b] 100-mer MW = 23032, including end groups. [c] 100-mer MW = 21042, including end groups. [d] At 213 K, PDI = 1.09, 99% cis, 73% (mm). [e] 100-mer MW = 23822, including end groups. [f] 100-mer MW = 26652, including end groups. [g] 100-mer MW = 239462, including end groups.

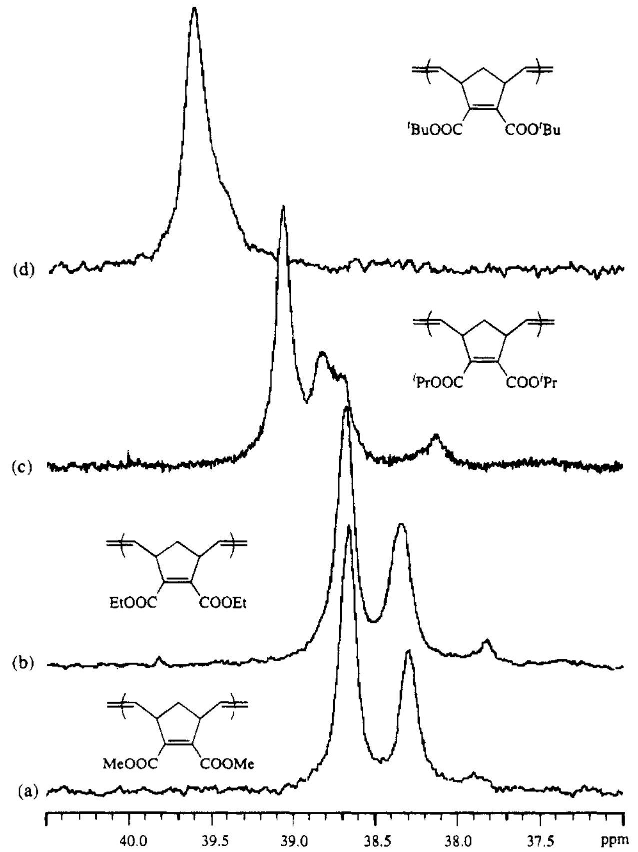

Figure 3. Four polymers prepared in (a) run 16, (b) run 21, (c) run 22, and (d) run 24 in Table 4.

resonance to give what only appears to be highly isotactic polymer. The results shown in Table 4 (runs 23–25) make the assumption that no C(7) resonances overlap. If this is true, then there would appear to be some tendency toward isotacticity as the size of the alkyl group in the bis(carboalkoxy)norbornadiene derivative increases.

Discussion

The most important result reported here is that the cis/trans structure of ROMP polymers is temperature dependent in a manner that is consistent with the proposed equilibrium between a less active syn form (that gives cis polymer) and a more reactive anti form (that gives trans polymer), as shown in eq 4. Confirmation would require detailed knowledge of the temperature dependencies of the rates of the first-order reactions, $k_{a/s}$[anti] and $k_{s/a}$[syn], as well as the second-order propagation reactions, k_a[anti][monomer] and k_s[syn][monomer]. Unfortunately, none actually is known. Nevertheless, circumstances that would give rise to the observed result can be imagined, in part because the temperature dependencies of the first-order reactions (rotamer interconversion) and second-order reactions (reactions with monomer) are likely to be significantly different; $\Delta S^\ddagger$ for the second-order propagation reactions should be relatively large and negative, which should lead to a less dramatic dependence of the rate on temperature, as shown in Figure 4. Therefore at low temperatures the polymer chain can grow more rapidly than syn and anti rotamers can interconvert. Since the predominant rotamer (in the absence of THF) is syn and the reaction between a syn rotamer and monomer is proposed to produce a syn rotamer, polymerization at low temperature in toluene or dichloromethane would give rise to cis polymer, as observed. In THF at low temperature the anti form can be observed, but it binds THF more strongly. The syn rotamer, which dissociates THF more readily than the anti rotamer, therefore becomes the more reactive. Above the "crossover" point (the temperature where the rates of rotamer interconversion and chain growth are equal, at some monomer concentration), equilibration of syn and anti rotamers

$$\text{trans,syn} \xleftarrow[\text{monomer}]{k_a} \text{anti} \underset{k_{s/a}}{\overset{k_{a/s}}{\rightleftharpoons}} \text{syn} \xrightarrow[\text{monomer}]{k_s} \text{cis,syn} \qquad (4)$$

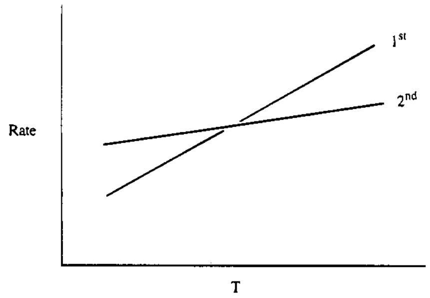

Figure 4. Possible relative temperature dependencies of the rate of second-order chain growth versus first-order rotamer interconversion.

becomes fast relative to chain growth, so ultimately chain growth is rate limiting, k_a[anti][monomer] is roughly of the same magnitude as k_s[syn][monomer], and both cis and trans polymers form.

The circumstance shown in eq 4 is analogous to the situation encountered in catalytic asymmetric hydrogenation of amino acid precursors by cationic rhodium catalysts.[18] In that case the enantiomeric product that is observed near room temperature arises via reaction of molecular hydrogen with the unobservable minor rhodium diastereomer. A significant difference between the Rh system and the system discussed here (in the *absence* of a coordinating solvent) is that the two diastereomeric rhodium complexes equilibrate via loss and recoordination of substrate, not a simple first-order interconversion as proposed here. Nevertheless, at low temperatures (or high dihydrogen pressures) interconversion of rhodium diastereomeric complexes cannot compete with reaction of the "wrong" (major) rhodium complex with dihydrogen, and the observed ee consequently decreases. (It is assumed that the chirality of the product that results from the major diastereomer is opposite that arising from the minor diastereomer.)

A good example of a "crossover" of the rate of first- and second-order reactions with temperature is the "trapping" of an alkyl hydride intermediate in a rhodium hydrogenation catalyst system.[19]

Some confirmation of the proposed behavior of syn and anti rotamers of $Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$ for forming cis and trans polymers, respectively, is the polymerization of 1,7,7-trimethylnorbornene.[20,21] The (extremely slow) rate of polymerization is independent of monomer concentration, the observed rate constant corresponds to the value for $k_{s/a}$, and the polymer that is formed contains trans double bonds, all consistent with chain growth via anti rotamers. Apparently 1,7,7-trimethylnorbornene is so bulky that it does not react with *syn*-$Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$, but it does react rapidly with *anti*-$Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$. Since a syn form is the result of the reaction between an anti form and monomer, the slow conversion of a syn form to an anti form becomes the rate-limiting step in this particular polymerization reaction. This result emphasizes the extent to which the nature of the monomer can change the mechanism of polymerization. It also illustrates that selective formation of a syn rotamer from *either* a syn or anti rotamer is a key feature that leads to the observed phenomena.

Unfortunately, none of what we propose in eq 4 can be confirmed independently for phenoxide-containing initiators, since we cannot measure rotamer interconversion or test relative reactivities of syn and anti rotamers. Therefore, we cannot discount the possibility that both cis and trans polymers can form from only the syn rotamer, or even both syn and anti rotamers, and that cis selectivity simply breaks down at higher temperatures. It should be noted that even if the source of cis and trans double bonds in these ROMP polymers is what we propose, there is some indication that the arylimido functionality plays a major role in directing the approach of the monomer to the CNO face of the propagating alkylidene and therefore that selectivity will not be independent of the imido group.[6]

We have found all-cis polymers prepared by a variety of achiral initiators to be biased toward giving isotactic polymers by chain end control. However, it is not possible at this stage to rationalize the degree of isotacticity, or why it reverses in one case (run 10). Ideally we would have to know (via molecular mechanics calculations) the relative ease of a given monomer approaching the two faces of the syn Mo=C bond in the living alkylidene formed from a given monomer. That possibility does not seem likely in the near future.

Experimental Procedures

All experiments were performed under a nitrogen atmosphere in a Vacuum Atmospheres drybox or by standard Schlenk techniques unless otherwise specified. Reagent grade diethyl ether and tetrahydrofuran were distilled from sodium benzophenone ketyl under nitrogen. Polymerization grade THF was vacuum transferred twice from sodium benzophenone ketyl. Polymerization grade toluene was stored over NaK alloy and passed through alumina prior to use.

HPLC grade solvents were used in gel permeation chromatography (GPC) runs and were degassed prior to use. GPC was carried out using Waters Ultrastyragel 10573, Shodex KF-802.5, -803, -804, -805, and -800P columns, an H-500 Viscotek differential refractometer/viscometer, and a Spectroflow 757 absorbance detector on 0.1–0.3% (w/v) samples in THF 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 = 1260 to MW 2.75 × 10^6. NMR data were obtained at 300 MHz and are listed in parts per million downfield from tetramethylsilane. Chemical shifts vary somewhat from sample to sample in the case of THF adducts, perhaps as a consequence of some chemical shift dependence on concentration and temperature. Spectra were obtained at 25 °C unless otherwise noted. Elemental analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN analyzer.

All the chemicals used were reagent grade and purified by standard methods. Benzaldehyde was purchased from Aldrich and was distilled over Na and passed over alumina before use. $Mo(N\text{-}2\text{-}t\text{-}BuC_6H_4)(CHCMe_2Ph)(OTf)_2(DME)$,[13] $Mo(N\text{-}2\text{-}t\text{-}BuC_6H_4)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$[13] (**4**), $Mo(N\text{-}2,6\text{-}Me_2C_6H_3)(CHCMe_2Ph)[Bipheno(t\text{-}Bu)_4]$[10] (**2**), $Mo(NAr)(CHCMe_2Ph)(O\text{-}2\text{-}t\text{-}BuC_6H_4)_2$[12] (**5**), $Mo(NAr)(CHCMe_2Ph)[OCMe_2(CF_3)]_2$[13] (**6**), $Mo(NAr)(CHCMe_2Ph)[OCMe(CF_3)_2]_2$[22] (**7**), $Mo(NAr)(CHCMe_2Ph)[OC(CF_3)_3]_2$,[13] and $Mo(NAr)(CHCMe_2Ph)[OC(CF_3)_2(CF_2CF_2CF_3)]_2$[13] were prepared as described in the literature.

$Mo(N\text{-}2\text{-}t\text{-}BuC_6H_4)(CHCMe_2Ph)[Bipheno(t\text{-}Bu)_4](THF)$ [1(THF)]. $K_2[Bipheno(t\text{-}Bu)_4]\cdot THF$ (390 mg, 0.70 mmol), prepared from 4,4′,6,6′-tetra-*tert*-butyl-2,2′-biphenol and KO-*t*-Bu, was added as a solid to a precooled (−30 °C) solution of $Mo(N\text{-}2\text{-}t\text{-}BuC_6H_4)(CHCMe_2Ph)(OTf)_2(DME)$ (500 mg, 0.65 mmol) in 50 mL of THF. The mixture was stirred for 6 h and the solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 and the insoluble potassium salts were removed by filtration. The filtrate was concentrated and layered with pentane in order to crystallize the product: yield 0.38 g (68%); ^1H NMR (toluene-d_8) δ 11.03 (br s, 1, H_α), 7.80–6.70 (m, 13, H_{aryl}), 3.55 (m, 4, OCH_2CH_2), 1.86 (s, 3, CH_3), 1.61 (s, 9, CMe_3), 1.47 (s, 9, CMe_3), 1.44 (m, 4, OCH_2CH_2), 1.31 (s, 9, $\mathrm{C}\mathit{Me}_3$), 1.28 (s, 9, $\mathrm{C}\mathit{Me}_3$), 1.24 (s, 3, $\mathrm{C}\mathit{H}_3$), 1.17 (s, 9, $\mathrm{C}\mathit{Me}_3$); ^{1}H NMR (toluene-d_8, −60 °C) δ 14.08 (s, anti H_α), 12.85 (s, syn H_α); partial ^{13}C NMR (toluene-d_8, −60 °C) δ 311.2 ($\mathit{C}\mathrm{HCMe_2Ph}$, anti), 299.5 ($\mathit{C}\mathrm{HCMe_2Ph}$, syn).

Mo(N-2-*t*-BuC$_6$H$_4$)(CHCMe$_2$Ph)[Bipheno(t-Bu)$_4$] (1). The THF-free complex was obtained quantitatively as a dark-red powder by dissolving **1(THF)** in toluene and removing all solvent in vacuo: ^{1}H NMR (toluene-d_8) δ 10.87 (s, 1, H_α), 7.80−6.75 (m, 13, $\mathrm{H}_{\mathrm{aryl}}$), 1.87 (s, 3, $\mathrm{C}\mathit{H}_3$), 1.61 (s, 9, $\mathrm{C}\mathit{Me}_3$), 1.47 (s, 9, $\mathrm{C}\mathit{Me}_3$), 1.30 (s, 9, $\mathrm{C}\mathit{Me}_3$), 1.28 (s, 9, $\mathrm{C}\mathit{Me}_3$), 1.17 (s, 9, $\mathrm{C}\mathit{Me}_3$), 1.14 (s, 3, $\mathrm{C}\mathit{H}_3$); ^{13}C NMR (toluene-d_8) δ 279.9 (d, $^1J_{\mathrm{CH}} = 120$, $\mathrm{CHCMe_2Ph}$), 156.7, 155.9, 153.0, 151.9, 144.8, 144.7, 141.7, 141.6, 132.9, 132.3, 129.7, 128.9, 128.8, 127.3, 126.7, 126.6, 126.5, 126.3, 126.0 ($\mathrm{C}_{\mathrm{aryl}}$), 55.2 ($\mathit{C}\mathrm{Me_2Ph}$), 37.0 ($\mathit{C}\mathrm{Me_3}$), 36.6 ($\mathrm{C}\mathit{Me}\mathrm{MePh}$), 35.8 ($\mathrm{CMe}\mathit{Me}\mathrm{Ph}$), 35.2 ($\mathit{C}\mathrm{Me_3}$), 35.1 ($\mathit{C}\mathrm{Me_3}$), 33.3 ($\mathit{C}\mathrm{Me_3}$), 32.1 ($\mathrm{C}\mathit{Me}_3$), 32.0 ($\mathit{C}\mathrm{Me_3}$), 31.9 ($\mathrm{C}\mathit{Me}_3$), 31.0 ($\mathrm{C}\mathit{Me}_3$), 30.4 ($\mathrm{C}\mathit{Me}_3$). Anal. Calcd for $\mathrm{C_{48}H_{65}NO_2Mo}$: C, 73.54; H, 8.36; N, 1.79. Found: C, 73.87; H, 8.18; N, 1.51.

Mo(NAr)(CHCMe$_2$Ph)[Bipheno(*t*-Bu)$_4$](THF) [3(THF)]. The synthesis was similar to that of **1(THF)** employing Mo(NAr)(CHCMe$_2$Ph)(OTf)$_2$(DME) in place of Mo(N-2-*t*-BuC$_6$H$_4$)(CHCMe$_2$Ph)(OTf)$_2$(DME): ^{1}H NMR ($\mathrm{C_6D_6}$) δ 14.06 (s, anti H_α), 11.46 (s, 1, syn H_α), 7.80−6.90 (m, 12, $\mathrm{H}_{\mathrm{aryl}}$), 3.81 (sept, 2, $\mathrm{C}\mathit{H}\mathrm{Me_2}$), 3.52 (br s, 2, $\mathrm{OC}\mathit{H}_2\mathrm{CH_2}$), 1.90 (s, 3, $\mathrm{C}\mathit{H}_3$), 1.60 (d, 6, $\mathrm{CH}\mathit{Me}_2$), 1.55 (s, 18, $\mathrm{C}\mathit{Me}_3$), 1.42 (s, 3, $\mathrm{C}\mathit{H}_3$), 1.29 (br s, 13, $\mathrm{C}\mathit{Me}_3$ and $\mathrm{OCH_2C}\mathit{H}_2$), 1.20 (s, 9, $\mathrm{C}\mathit{Me}_3$), 0.96 (d, 6, $\mathrm{CH}\mathit{Me}_2$). Anal. Calcd for $\mathrm{C_{54}H_{77}NO_3Mo}$: C, 73.36; H, 8.78; N, 1.58. Found: C, 73.23; H, 9.49; N, 1.43.

Polymerization Reactions. The following is a typical procedure. A solution of NBDF6 (310 mg, 1.36 mmol) in 4 mL of toluene was added to a solution of **4** (10.0 mg, 13.6 μmol) in 1 mL of toluene, and the mixture was heated to 65 °C in an oil bath. After 5 h at 65 °C benzaldehyde (14.0 μL, 134 μmol, 10 equiv) was added to react with any alkylidene present. The mixture was stirred for 1 h and the polymer was precipitated in methanol and dried in vacuo to give 300 mg of polymer (97%). For polymerizations at low temperature, a precooled (−35 °C) solution containing the monomer was added to the cold solution of the initiator and the mixture was kept at approximately −35 °C in the drybox freezer. The mixture was stirred several times during the polymerization reaction.

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