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Articles

Titanium Monoamidinate−MAO Catalysts: Some Information about Active Species and Stereochemical Polymerization Mechanisms

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ABSTRACT: This paper reports stereospecific polymerization of propene, 1,3-butadiene, and styrene, in the presence of titanium trichloroamidinate/MAO catalysts, under different reaction conditions. Comparison of the structures of the polymers obtained at different temperatures provides some information about the active species involved in promoting the stereospecific polymerizations of the different monomers.

1. Introduction

According to the literature, group 4 metal amidinates (precatalysts), in the presence of methylaluminoxane (MAO, cocatalyst), provide homogeneous catalytic systems promoting polymerization of a variety of hydrocarbon monomers including ethylene, propene, 1,3-butadiene, and styrene.[1,2]

For example, pseudoctahedral zirconium and titanium bisamidinate dihalide A_2MX_2−MAO systems (A = amidinate) efficiently promote ethylene polymerization, as well as polymerization of propene with site-controlled isotactic stereospecificity increasing while increasing the concentration of the monomer.[1c,e−g,i]

Titanium monoamidinate trihalides ($ATiX_3$) and MAO provide versatile catalytic systems, that, depending on the reaction conditions, promote polymerization of propene to either prevailingly syndiotactic or prevailingly isotactic polymer, 1,3-butadiene to either prevailingly *trans*-1,4 or prevailingly *cis*-1,4 polymer as well as polymerization of styrene to highly syndiotactic polymer.[1a−c,h,i]

In this paper, we will try to provide a frame that hopefully should help understanding the behavior of the $ATiX_3$−MAO catalysts, by comparing the results of a number of polymerizations of propene, 1,3-butadiene, and styrene performed (in different conditions) in the presence of the precatalysts reported in Chart 1.

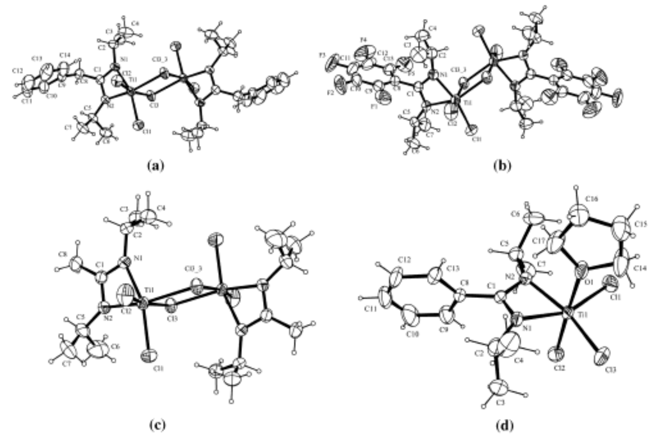
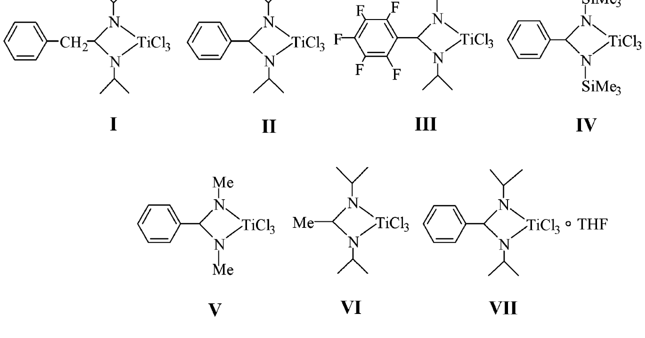


Figure 1. Ortep views of centrosymmetric dimers of **I** (a), **III** (b), and **VI** (c), respectively. Thermal ellipsoids are drawn at the 50% probability level. (d) Ortep view of **VII**. Thermal ellipsoids are drawn at the 30% probability level.

Chart 1. Schematic Representation of the Synthesized Precatalysts



2. Results and Discussion

2.1. Precatalysts. The precatalysts reported in Chart 1 (synthesized as reported in the Experimental Part) have been identified by ^{1}H NMR analysis [**I** (CD_2Cl_2), δ 1.39 (d, 12H), δ 3.89 (m, 2H), δ 3.99 (s, 2H), δ 7.20−7.40 (m, 5H, Ph); **II** (CD_2Cl_2), δ 1.40 (d, 12H), δ 3.58 (m, 2H), δ 7.37 (2H, Ph), δ 7.57 (3H, Ph); **III** (C_6D_6), δ 1.40 (d, 12H), δ 3.14 (m, 2H); **IV** (C_6D_6), δ 0.15 (s, 18H), δ 6.6−7.20 (5H, Ph); **V** (C_6D_6), δ 1.90 (s, 3H), δ 2.67 (s,

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Table 1. Selected Bond Lengths (Å) and Bond Angles (deg) with Esd's in Parentheses[a]

	I	**III**	**VI**	**VII**
Ti−Cl1	2.255(1)	2.238(3)	2.255(2)	2.270(1)
Ti−Cl2	2.285(2)	2.225(4)	2.258(1)	2.288(1)
Ti−Cl3	2.485(2)	2.384(4)	2.533(1)	2.305(1)
Ti−Cl3_3	2.463(1)	2.576(5)	2.453(2)	
Ti−N1	2.094(2)	2.069(3)	2.071(2)	2.057(3)
Ti−N2	1.953(2)	2.004(3)	1.967(2)	2.054(3)
Ti−O1				2.154(2)
C1−N1	1.309(3)	1.312(4)	1.315(3)	1.321(3)
C1−N2	1.359(3)	1.338(4)	1.347(3)	1.330(3)
C1−C8	1.510(4)	1.494(4)	1.493(3)	1.488(3)
N1−Ti−N2	65.21(9)	64.7(1)	65.07(8)	63.91(9)
Cl3−Ti−Cl3_3	78.28(4)	78.7(1)	77.01(2)	
Ti−Cl3−Ti_3	101.72(4)	101.3(1)	102.99(2)	
Cl1−Ti−Cl2	94.41(5)	97.2(2)	95.95(3)	94.31(5)

[a] Label _3 refers to the (−*x*, -*y* + 1, −*z* + 1) symmetry operation for complexes **I** and **VI**, and to (-*x* + 1, -*y* + 1, −*z*) for **III**.

3H), δ 6.72−7.10 (m, 5H, Ph); **VI** (CD_2Cl_2), δ 1,44 (d, 12H), 2,25 (s, 3H), 3,88 (m, 2H); **VII** (C_6D_6), δ 1.32 (m, 4H, THF), δ 1.51 (d, 12H), δ 3.51 (m, 2H), δ 3.88 (m, 4 H, THF), δ 6.76−7.18 (m, 5H, Ph)] and, in some cases, by X-ray analysis (**I**, **III**, **VI**, **VII**).

Molecular drawings of monoamidinate titanium trichlorides **I**, **III**, and **VI**, are reported in Figure 1, parts a−c, respectively. The complexes form centrosymmetric dimers through μ-Cl bridge atoms as already reported in the literature for $\{[(C_6H_5)C(N{-}SiMe_3)_2]TiCl_3\}_2$.[3] Selected bond lengths and angles are reported in Table 1.

The bond lengths, reported in Table 1, are not significantly different for **I**, **III**, and **VI**. As expected, the Ti−Cl distances are not equivalent (those involving μ-chloro atoms are ∼0.2 Å longer).

Coordination around Ti of **I**, **III**, and **IV** may be considered as distorted octahedral. The main distortion is due to the valence angles N1−Ti−N2 and Cl3−Ti−Cl3_3 quite far from 90° (see Table 1). The two μ-chlorine atoms occupy one axial and one equatorial position, while the three remaining equatorial positions are occupied by two N atoms and by one non bridging Cl. Also Ti−N and C1−N distances are not equivalent; in particular, the Ti−N1 and C1−N2 distances are longer than Ti−N2 and C1−N1, respectively. This effect, that has been found in several chlorocomplexes of Ti(IV) with bidentate ligands having N or O as donors,[3,4] is systematic and apparently not due to steric effects but is probably related to the different efficiency of dπ−pπ interactions between Ti and the two N atoms, due to the presence of a Cl bridge atom. In fact, only for the N atom lying in the plane of chloro bridge (that is N2) should the dπ−pπ contributions with Ti be less affected by the p orbitals of the Cl bridge atom.

Obviously, the structure of the tetrahydrofuranate **VII** (Figure 1d) shows significant differences. The compound is monomeric, and the three Ti−Cl bond lengths are equivalent among them as well as the two Ti−N distances. The octahedral coordination around Ti is more regular, the distortion being only due to the bond angle N1−Ti−N2. The conformation of the molecule is almost C_s symmetric, since the phenyl ring and the tetrahydrofuran molecule, which has planar conformation, are almost coplanar and perpendicular to the equatorial coordination plane of Ti. The slight deviation from the truly C_s symmetry is probably due to packing interactions.

2.2. Propene Polymerization. Table 2 reports the results of propene polymerizations performed at low temperature (−60 °C) in the presence of the precatalysts of Chart 1 and MAO.

The structures of (prevailingly syndiotactic) samples 1−4 and 7 (here and in the following the polymer samples are numbered according to the run numbering) look very similar within each other, with almost the same stereochemical triad composition[5] (e.g., for sample 1 *rr* = 53%, *mr* = 42%, *mm* = 5%), and not too different percentages of vicinal methyls (related to the regiospecificity of the polyinsertion).[6]

As already pointed out in a previous paper,[1h] the amounts of *mm*, *mr*, and *rr* stereochemical triads of samples 1−4 and 7 alike are compatible with either (1) a syndiotactic-specific polyinsertion controlled by the chain or (2) a site controlled syndiotactic-specific polyinsertion with the occurrence of frequent *backskips*.

It is possible to choose between these two statistical models of the steric control by comparing the results of polymerizations performed with different concentrations of the monomer. In fact, the *mm*, *mr*, and *rr* triad compositions of samples 1, 9, 10, and 11 of Tables 2 and 3, obtained at different monomer concentrations and under otherwise identical conditions, are the same (within the limits of the experimental accuracy), and this shows that the stereochemistry of the syndiospecific polyinsertion is ultimately controlled by the chain (1,3−unlike asymmetric induction by the last unit of the growing chain end).

It is worth noting that the low M_w/M_n ratios (M_w = weight-average molecular weight; M_n = number-average molecular weight) reported in Table 2, e.g., for samples 1 and 3, show that the corresponding catalytic systems are "single site". In addition, the ratios between the yields and the M_n's of runs 1−3 are close to the amounts

Table 2. Propene Polymerizations at Low Temperature (−60 °C) in the Presence of the Precatalysts of Scheme 1, Activated with MAO

run[a]	precatalyst	time (h)	yield (g)	[*rr*] (%)	[*mr*] (%)	[*mm*] (%)	vicinal methyl fraction (%)	M_w ($\times 10^4$)	M_n ($\times 10^3$)	M_w/M_n
1	**I**	16	0.40	53	42	5	2.5	1.2[c]	7.0[c]	1.76[c]
2	**II**	17	0.63	55	41	4	2.3		7.3[d]	
3	**III**	17	1.10	52	43	5	3.2	1.5[c]	9.0[c]	1.71[c]
4	**IV**	16	0.32	53	40	7	4.8			
5	**V**	16	0.05	29	32	39	1.8			
6	**VI**	16	0.05	20	39	41	1.7			
7	**VII**	16	0.30	51	40	9	2.5			
8[b]	**I**	16	0.07	32	28	40	5.0			

[a] All the polymerization runs, but 8, have been performed (at −60 °C) in 30 mL of toluene, using 5×10^{-5} mol of precatalyst, 1×10^{-2} mol of MAO, and 15 g of propene (5.9 mol·L^{-1}). [b] Same polymerization condition as run 1, but the catalyst is preformed at 20 °C, aged for 30 min, and precooled at −60 °C before supplying the monomer. [c] From GPC analysis. [d] Calculated from ^{13}C NMR spectra, as reported in the Experimental Part.

Table 3. Propene Polymerizations at Different Monomer Concentrations

run[a]	precatalyst	time (h)	yield (g)	propene (mol·L^{-1})	[*rr*] (%)	[*mr*] (%)	[*mm*] (%)
9	**I**	16	0.58	7.1	52	38	9
10	**I**	17	0.42	4.8	53	40	7
11	**I**	16	0.33	2.4	53	37	10

[a] The polymerizations have been performed in toluene at −60 °C, using 5×10^{-5} mol of precatalyst I, 1×10^{-2} mol of MAO, and variable amounts of propene, in a total volume of 50 mL.

Table 4. Propene Polymerizations at Higher Temperature (+20 °C) with Some Precatalysts of Scheme 1

run[a]	pre-catalyst	time (h)	yield (g)	[propene] (mol·L^{-1})	[*rr*] (%)	[*mr*] (%)	[*mm*] (%)	vicinal methyl fraction (%)
12	**I**	2	1.20	6.5	25	33	42	7
13	**II**	2	1.19	6.5	22	34	44	9
14	**III**	2	1.25	6.5	24	32	44	4
15	**VI**	0.5	0.06	6.5	14	39	47	8

[a] Polymerizations have been performed at 20 °C in a 250 mL glass autoclave by introducing, sequentially, toluene (120 mL), MAO (4×10^{-3} mol) and precatalyst (2×10^{-5} mol), with a propene concentration of 6.5 mol·L^{-1}.

by mole of Ti amidinate used in these runs, suggesting that the conversion of the precatalyst to active species is complete and that polymerization involves scanty chain transfer or termination processes, if any.

The larger yield of run 3 (and the higher M_n), in comparison with runs 1, 2, 4, and 7 of Table 2, strongly suggests that the perfluorophenyl substituent of the amidinate ligand increases the electrophilicity of the active species.

Surprisingly, the stereochemical triad compositions and the amounts of vicinal methyls of samples 5 and 6 (Table 2) show that these samples are prevailingly isotactic and somewhat more regioregular than samples 1−4 and 7. In addition, the percent of *mr* triads, in comparison with the *mm* and the *rr*, is enough lower than expected for a Bernoullian sequence of *m* and *r* diads, as to suggest that these samples consist of a mixture of prevailingly isotactic and prevailingly syndiotactic chains and (or), possibly, iso and syndio stereoblock chains.

When polymerizations are performed with any precursor of Chart 1 at higher temperatures (e.g., in Table 4 are reported some runs at +20 °C), or even at −60 °C but after preaging the catalyst at +20 °C (run 8 of Table 2), the percent of *mm* triads in the resulting polymers always overcomes that of the *rr*'s, and the fraction of vicinal methyls is larger (compare, e.g., the results of runs 12−15 reported in Table 4 and run 8 of Table 2 with the other runs of Table 2). In addition, the corresponding polymers include fractions of dramatically different stereochemical structure and molecular weights.

Table 5. Molecular Weights of Fractions of Sample 14

sample 14	mp (°C)	M_w ($\times 10^5$)	M_n ($\times 10^5$)	M_w/M_n	vicinal methyl fraction (%)
whole polymer		8.7	0.6	14.5	4
fraction 1	145	10.2	3.9	2.6	≪1
fraction 2	135	11.1	4.3	2.6	<1
fraction 3		1.4	0.17	8.2	7

For example, sample 14 was roughly fractionated by stirring the polymer in boiling heptane during 5 h and recovering the insoluble material (fraction 1, 12%). A further fraction (40%) was obtained by cooling the solution from 98 to 20 °C and recovering the crystallized material (fraction 2). Fraction 3 (48%) was obtained by precipitating the polymer still dissolved in heptane at 20 °C, with methanol. Fraction 1, insoluble in boiling heptane, melts at 145 °C, and the ^{13}C NMR spectrum (see Figure 2a) shows that it is quite regioregular and highly isotactic with a stereochemical methyl pentad composition approximately as follows: *mmmm* = 80%, *mmmr* = 8%, *mmrr* = 8%, *mrrm* = 4%,[5] diagnostic of isotactic polypropylene arising from a polyinsertion controlled by the chiral metal of the active species.[7] Fraction 2 melts at 135 °C, and the ^{13}C NMR spectrum (see Figure 2b) shows that the structure is still very regioregular and largely isotactic with 55.5% of *mmmm* pentads. Both fractions have high average molecular weights, with narrow distributions (see Table 5). Fraction 3, on the contrary, does not crystallize; the structure is stereoirregular and quite regioirregular (Figure 2c). The average molecular weight is comparatively much lower, with a very broad distribution (see Table 5). It is also worth noting that the intensities of the resonances of the methyl stereochemical pentads (see the expansion of the region 17−21 ppm of the ^{13}C NMR spectrum of fraction 3, in Figure 2c), are not as expected for polypropylene chains consisting of a Bernoullian sequence of *m* and *r* stereochemical diads. Even for the whole sample 14, the ratio between the polymer yield and the M_n is not much different from the mole amount of the precatalyst (2×10^{-5} mol). Taking into consideration the amount and the M_n's (much higher for fractions 1 and 2 in comparison with fraction 3) of the different fractions, one could guess that the species promoting the formation of the stereoirregular fraction outnumber the species promoting isotactic specific polymerization, but are less active.

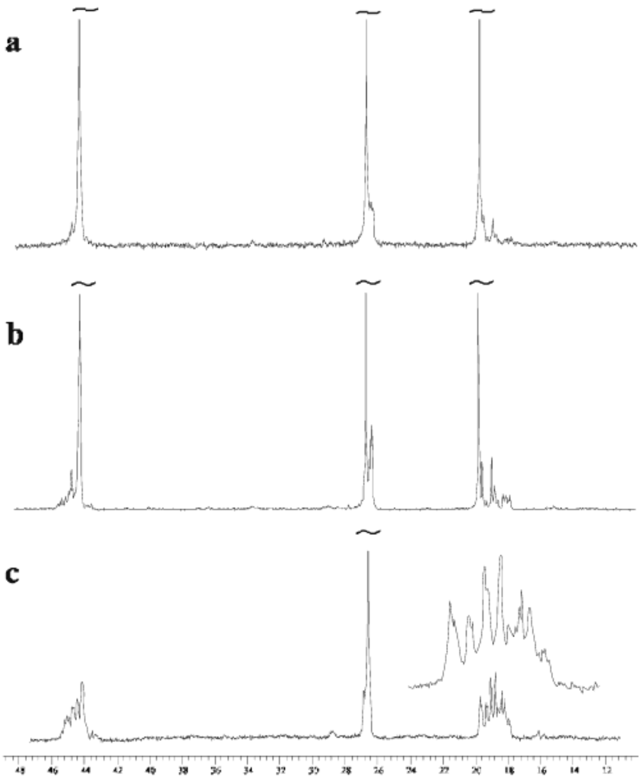


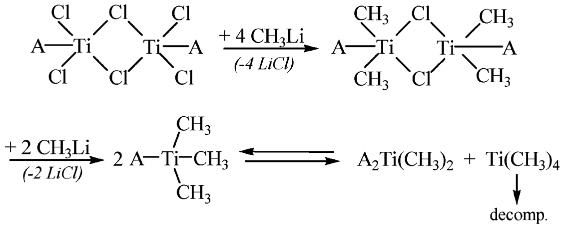
Figure 2. 75.47 MHz ^{13}C NMR spectra of polypropylene sample 12: (a) fraction 1; (b) fraction 2; (c) fraction 3. Spectra are recorded in $C_2D_2Cl_4$ at 110 °C; HMDS scale.

Table 6. Polymerizations of Styrene and 1,3-Butadiene with Some Precatalysts Reported in Chart 1

run[a]	precatalyst	monomer	temp (°C)	time (h)	yield (g)	NMR microstructure
16	**I**	styrene	25	1	0.08	syndiotactic
17	**I**	styrene	50	1	0.10	syndiotactic
18	**I**	styrene	−60	16	0.04	atactic
19[b]	**I**[b]	styrene	−60	16	0.04	syndiotactic
20	**I**	1,3-butadiene	0	3	0.25	1,4-cis (84%)/1,4-trans (16%)
21	**III**	1,3-butadiene	−20	3	0.20	1,4-cis (86%)/1,4-trans (16%)
22	**III**	1,3-butadiene	−60	16	0.10	1,4-trans (80%)/1,4-cis (20%)
23[b]	**III**[b]	1,3-butadiene	−60	3	0.05	1,4-cis (83%)/1,4-trans (17%)
24	**VI**	1,3-butadiene	−60	3	0.11	1,4-cis (85%)/1,4-trans (15%)

[a] All the polymerizations have been performed in 30 mL of toluene, using 5×10^{-5} mol of precatalyst and 1×10^{-2} mol of MAO and either 9.1 g of styrene or 18 g of 1,3 butadiene. Details are reported in the Experimental Part. [b] Polymerizations with preaged catalyst as reported in the Experimental Part.

Scheme 1. Alkylation and Disproportionation of Dimeric $ATiX_3$



The melting temperatures and the stereochemical pentad compositions of fractions 1 and 2 of sample 14 are not too different from that of polypropylene obtained by Eisen et al.[1e,i] (*mmmm* = 57%, mp 120 °C), in the presence of bisamidinate $[p\text{-}MeC_6H_4C(N{-}SiMe_3)_2]_2TiCl_2$/MAO under similar polymerization conditions. The M_w/M_n ratios of these fractions also suggest that they arise from a single active species, while the broad M_w distribution of fraction 3 and of the whole polymer shows that, of course, the whole catalytic system, at 20 °C, is multisite.

According to Flores and co-workers,[1a] reaction of $\{[(C_6H_5)C(NSiMe_3)_2]TiCl_3\}_2$ with 2 equiv of CH_3Li affords dimethyl amidinate chloride, retaining chlorine bridge. A larger amount of CH_3Li produces monomeric trimethyl amidinate, that subsequently disproportionates to dimethyl bisamidinate and unstable $Ti(CH_3)_4$, that decomposes with Ti reduction[8] (see Scheme 1).

In view of these results, Occam's razor[9] suggests that, at low temperature, in the presence of a large amount of MAO, complete alkylation and cationization[10] of the amidinate precatalysts of Chart 1 (including tetrahydrofuranate **VII)**:

$$ATi(CH_3)_3 + MAO \rightleftarrows [ATi(CH_3)_2]^+ + [(MAO){-}CH_3]^-$$

produces a single site catalyst, that at low temperature (when enough stable) promotes, via primary insertion, chain-controlled prevailingly syndiotactic specific polyinsertion of propene.[1h]

Disproportionation of these $(TiAR_2)^+$ cations (with $R = CH_3$ or growing polymer chain), occurring at a higher temperature (or, partially, even at −60 °C for complexes **V** and **VI**) should produce, inter alia, (chiral) A_2TiR^+ cations that, according to Eisen and co-workers, promote site-controlled isotactic specific polymerization of propene, via primary insertion.[1e,f,i]

Probably, the results of runs 5 and 6 deviate, in comparison with runs 1, 2, 3, 4, and 7 (Table 2), simply suggesting that disproportionation, in the presence of the precatalysts **V** and **VI**, is not negligible even at −60 °C. At present, it is not apparent where the structure of polypropylene-like fraction 3 of Table 5 might come from.

2.3. Styrene and 1,3-Butadiene Polymerization.

Table 6 reports polymerizations of styrene and 1,3-butadiene performed in the presence of some precatalysts of Scheme 1, activated with MAO.

Runs 18, 22, and 24 have been performed at −60 °C, by adding the precatalysts to precooled toluene solutions of the monomers and MAO. Runs 19 and 23 have been performed by allowing to react MAO and the precatalysts in toluene at 25 °C for 30 min (preaging) and cooling, at −60 °C; the monomers also precooled at −60 °C were subsequently added to the catalyst solutions. Finally runs 16, 17, 20, and 21 have been performed at the temperatures reported in Table 6, by adding the precursor to the thermostated solutions already containing MAO and the monomer.

The polymerizations performed at relatively high temperature (−20, 0, 25, 50 °C) or even at −60 °C, but with preaged catalyst (runs 19 and 23), produce high molecular weight (e.g., for sample 17, $M_w = 1{,}9 \times 10^5$, $M_n = 3{,}9 \times 10^4$) syndiotactic polystyrene and prevailingly 1,4-*cis*-polybutadiene (^{13}C NMR spectra are reported in Figure 3); the assignments are according to refs 11 and 12.

From the ratio between the yield and the M_n of sample 17, one can observe that the mol amount of syndiotactic polystirene macromolecules produced (2.5×10^{-6}) is 5% of the mol amount of the precatalyst (5×10^{-5} mol).

Run 22, performed at − 60 °C by adding the precatalysts to the precooled reaction medium already containing MAO and the monomer, produces prevailingly 1,4-*trans*-polybutadiene[13] (^{13}C NMR spectrum[12] is reported in Figure 4a). Run 18 (also performed at −60 °C), as well as a "blank" polymerization run performed under the same conditions, but without any amidinate precatalyst, only produces traces of stereoirregular polystyrene.

Finally, polymerization of 1,3-butadiene by using precatalyst **VI** produces prevailingly 1,4-*cis*-polybutadiene even at −60 °C and without preaging the catalyst (see run 24 and Figure 4b).

The results of Tables 6 in comparison with the ones of Tables 2−4 concerning polymerization of propene show that (1) the reaction conditions promoting syndiospecific polymerization of propene also promote 1,4-trans polymerization of 1,3-butadiene, and (2) the reaction conditions promoting isospecific polymerization of propene also promote syndiotactic specific polymerization of styrene and 1,4-cis polymerization of 1,3-butadiene.

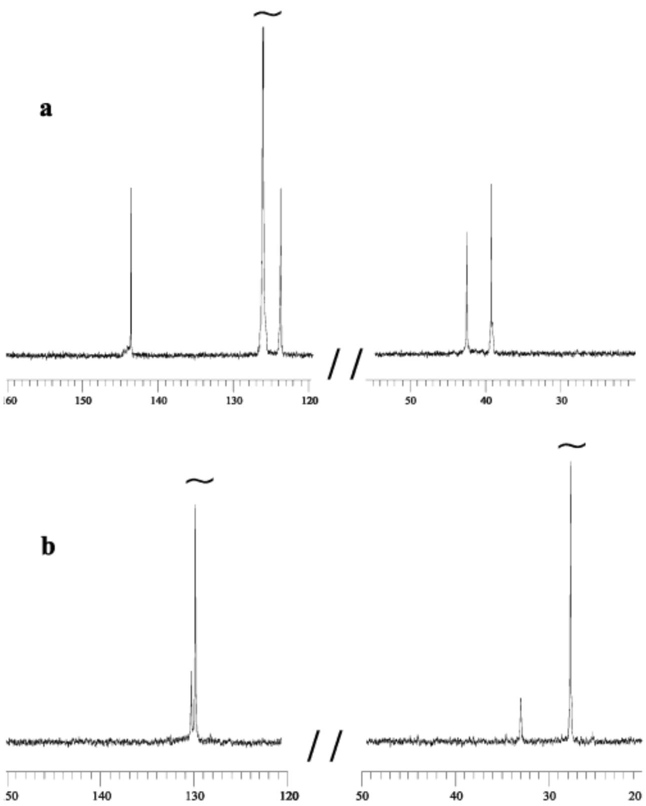


Figure 3. (a) 62.89 MHz ^{13}C NMR spectrum of sample 13 (s-PS), recorded in $C_2D_2Cl_4$ at 110 °C, HMDS scale; (b) 75.47 MHz ^{13}C NMR spectrum of sample 21 (prevailingly 1,4-*cis*-polybutadiene), recorded in $CDCl_3$ at 25 °C, TMS scale (see refs 11 and 12).

A possible explanation of these results, in agreement with previous papers concerning the active species promoting syndiospecific polymerization of styrene[14] and 1,4-cis polymerization of 1,3-butadiene,[15] and with the observation by Flores[1a] about disproportionation, requires at least three different cationic active species:

(1) The first active species arising, at low temperature, from alkylation of the monoamidinate by MAO and cationization as shown in section 2.2 (Scheme 2) would promote syndiotactic polymerization of propene and 1,4-trans polymerization of 1,3-butadiene. This species does not promote either syndiospecific polymerization of styrene or 1,4-cis polymerization of 1,3-butadiene.

(2) Disproportionation of this species should provide bisamidinate alkyl titanium cations. According to the literature, these cations promote isospecific polymerization of propene[1e,h,g,i] (see section 2.1) but, at least under mild conditions, are unable to promote syndiotactic specific polymerization of styrene.[1a]

(3) The literature reports a variety of catalytic systems promoting syndiotactic-specific polymerization of styrene, based either on half-sandwich titanocenes or on homoleptic titanium compounds.[16] Among them, $Ti(CH_2-C_6H_5)_4$/MAO[16c,d] particularly corroborates the idea that, in the title catalyst, the styrene syndiotactic specific active species arise from reaction of $Ti(CH_3)_4$ (from disproportionation) with MAO. The literature consistently shows that the catalytic systems promoting styrene syndiotactic specific polymerization also promote 1,4-cis polymerization of 1,3-butadiene.[15b,c]

The possible structure of these active species is discussed in previous papers.[14,17]

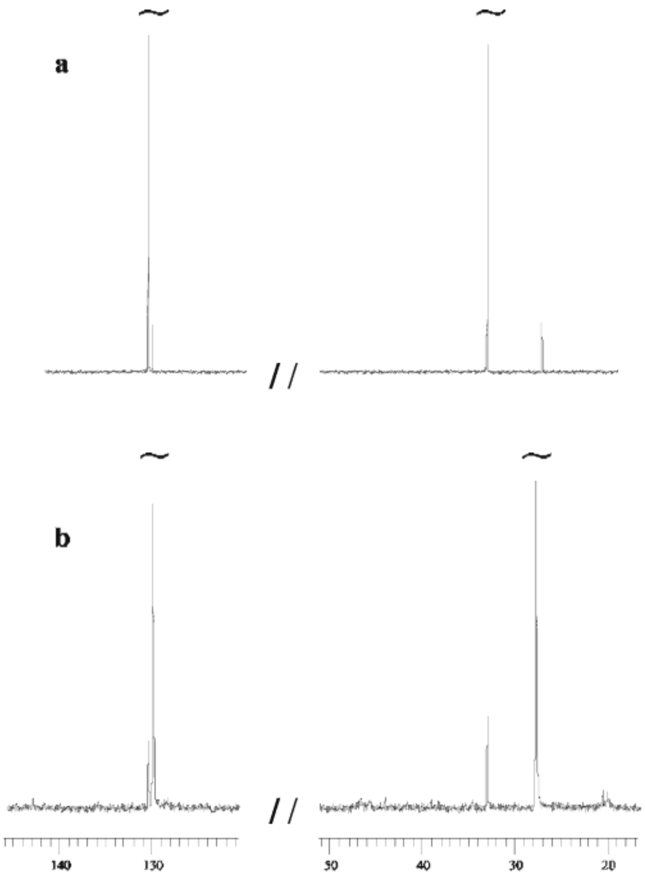


Figure 4. 75.47 MHz ^{13}C NMR spectra of (a) sample 22 (prevailingly 1,4-*trans*-polybutadiene) and (b) sample 24 (prevailingly 1,4-*cis*-polybutadiene). Spectra are recorded in $CDCl_3$ at 25 °C, TMS scale.

3. Conclusion

The consistent changes observed for propene, styrene, and 1,3-butadiene polymerization, in the presence of Ti monoamidinate/MAO, when changing the reaction conditions, together with other results already reported in the literature,[1a−c,h] can be tentatively rationalized (certainly oversimplifying) by assuming that low temperature reaction, between the precatalyst and the cocatalyst, almost quantitatively affords termolabile cationic active species with Ti^{IV} carrying two alkyls and one amidinate ligand.

Primary polyinsertion of propene on the titanium alkyl bonds of these cations would produce, at low temperature, prevailingly syndiotactic polypropylene, with the stereochemistry of the insertion controlled by the chain (1,3 *unlike* asymmetric induction), as reported in ref 1h. This species does not promote either syndiospecific polymerization of styrene[1a] or 1,4-cis polymerization of 1,3-butadiene, but only affords prevailingly 1,4-*trans*-polybutadiene.

As mentioned in the Discussion, according to the literature, trimethyl titanium amidinates are unstable and, more or less quickly, depending on the temperature and the particular amidinate ligand, disproportionate, affording C_2 symmetric dimethyl bisamidinate and TiR_4.[1a] The monoamidinate dialkyl cations could similarly disproportionate (possibly more slowly) affording, in the presence of MAO, bisamidinate alkyl cations that, according to the literature, promote isotactic polymerization of propene via primary insertion and stereochemistry controlled by the (chiral) titanium.[1e,f,h,i]

Table 7. Crystal, Collection, and Refinement Data for I, III, VI, and VII

	I	III	VI	VII
chem formula	$C_{14}H_{21}N_2TiCl_3$	$C_{13}H_{14}F_5N_2TiCl_3$	$C_8H_{17}N_2TiCl_3$	$C_{17}H_{27}N_2O_1TiCl_3$
fw	371.58	447.51	295.44	429.66
T (K)	293	293	293	293
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/a$	$P2_1/c$	$P2_1/n$	$P2_1/c$
a (Å)	12.679(9)	8.901(4)	10.616(9)	9.809(5)
b (Å)	10.317(6)	13.70(2)	10.874(4)	14.264(3)
c (Å)	14.49(1)	15.42(5)	11.685(5)	15.265(7)
β (deg)	110.65(4)	98.9(1)	96.28(8)	101.43(7)
V (Å^3)	1774(2)	1857(7)	1341(1)	2143(2)
Z, D_x (g/cm^3)	4, 1.392	4, 1.601	4, 1.464	4,1.332
μ (mm^{-1})	0.93	0.94	1.20	0.78
θ_{max} (deg)	27.9	28.0	27.97	27.66
data/params	4239/185	4493/221	3221/179	4963/217
R1, wR2[a]	0.0391, 0.084	0.0459, 0.124	0.0308, 0.0821	0.0465, 0.1249
R1, wR2[b]	0.0775, 0.0966	0.0612, 0.1355	0.0383, 0.0860	0.0864, 0.1418

[a] On F ($I > 2\sigma(I)$). [b] All data on F^2.

This frame can justify both syndiotactic and highly isotactic polypropylene as well as partially syndiotactic–isotactic stereoblock polypropylene (depending on whether disproportionation occurs at the beginning of the polymerization, when R is methyl or even during the propagation when R is already a prevailingly syndiotactic growing polymer chain). The active species promoting syndiospecific polymerization of styrene and 1,4-cis polymerization of 1,3-butadiene should arise, directly or indirectly, from $Ti(CH_3)_4$ (coming from disproportionation)/MAO and reduction of Ti to a lower oxidation state.[14]

Accordingly, the literature reports $Ti(C_6H_5CH_2)_4$/MAO,[16b−d] among a number of catalytic systems consisting of homoleptic Ti compounds and MAO, promoting syndiotactic-specific polymerization of styrene and also suggests a possible structure for the cationic active species involved,[14] as well as, some features of the stereochemical polymerization mechanism (cis addition,[18] secondary insertion[19] of the monomer, and chain control of the stereochemistry of the polyinsertion[20]).

4. Experimental Section

General Procedures and Materials. Reactions and manipulations were performed either in an inert-atmosphere (N_2) glovebox or by using standard Schlenk and high-vacuum-line techniques. Unless otherwise reported, the reagents were purchased from Aldrich and used without further purification. MAO (Witco) was used as a solid after distillation of the solvent. Toluene, heptane, tetrahydrofuran (THF), and diethyl ether (Carlo Erba) were distilled from sodium/benzophenone ketyl, whereas CH_2Cl_2 (Carlo Erba) was distilled from CaH_2.

Polymerization grade propene and butadiene (SON) were used without further purification. Styrene was distilled from CaH_2 under reduced pressure and stored at −20 °C under nitrogen.

CD_2Cl_2 and C_6D_6 purchased from Cambridge Isotope Laboratories, Inc., were purified by vacuum transfer from the appropriate drying agent (Na/Ph_2CO or CaH_2) and stored over 4 Å molecular sieves.

Precatalysts I—V. $[(C_6H_5)CH_2C(N-i\text{-}Pr)_2]TiCl_3$ **(I)**, $[(C_6H_5)C(N-i\text{-}Pr)_2]TiCl_3$ **(II)**, and $[(C_6F_5)C(N-i\text{-}Pr)_2]TiCl_3$ **(III)** were synthesized as reported in a previous paper.[1h]

Precatalyst $[(C_6H_5)C(N-SiMe_3)_2]TiCl_3$ **(IV)** was synthesized according to the literature.[3] Precatalyst $[(C_6H_5)C(N-Me)_2]TiCl_3$ **(V)** was synthesized according to the procedure reported for the complex $[(p\text{-}MeC_6H_5)C(N-Me)_2]TiCl_3$.[1b]

Precatalyst VI. CH_3Li (17 mL, 0.032 mol, 1.9 M solution Et_2O) was slowly added to a solution of 1,3-diisopropylcarbodiimmide (4.0 g, 0.032 mol) in 30 mL of light petroleum at 0 °C while stirring. Stirring was continued for 6 h at 25 °C. Removal of the solvent in vacuo led to $CH_3-C(N-i\text{-}Pr)_2Li$ tetrahydrofuranate as a white powder.

Subsequent reaction of a portion of this salt (4.4 g, 0.02 mol) with chlorotrimethylsilane (2.5 mL, 0.02 mol) in toluene (35 mL) and workup of the reaction mixture afforded $CH_3-C[N(SiMe_3)(i\text{-}Pr)]N(i\text{-}Pr)$ as a brown oil. The pure product (3.9 g, 0.018 mol) was isolated by high vacuum distillation (70 °C, 2×10^{-3} mbar) as a colorless oil. According to the procedure described by Fenske et al.,[3] slow addition of a solution of $CH_3-C[N(SiMe_3)(i\text{-}Pr)]N(i\text{-}Pr)$ (6.9×10^{-3} mol in 9 mL of CH_2Cl_2) to a solution of $TiCl_4$ (0.75 mL, 6.9×10^{-3} mol) in CH_2Cl_2 (7 mL) afforded compound **VI** as a moisture sensitive red-wine microcrystalline solid (1.8 g, 90%)

Precatalyst VII. $C_6H_5C(N-i\text{-}Pr)_2MgBr$ tetrahydrofuranate (5.5 g, 0.018 mol), prepared as reported in ref 1h, was slowly added to a solution of $TiCl_4{\cdot}2THF$ (6.01 g, 0.018 mol) in CH_2Cl_2 (15 mL) affording compound **VII** as a moisture-sensitive dark-red microcrystalline solid (90%).

X-ray Characterization of Titanium Monoamidinate Complexes. Suitable crystals for structure determination were obtained, for complexes **I**, **III**, **VI** and **VII**, by slow crystallization from a CH_2Cl_2 solution at −20 °C and sealed in Lindemann capillaries in inert atmosphere (N_2).

Data collection was performed on an Enraf-Nonius MACH 3 automated single-crystal diffractometer, in the ω/θ scan mode, using graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Semiempirical absorption correction (ψ scans) was applied in all cases. The structures were solved by direct methods (SHELXS program of SHELX 97 package[21]) and refined by the full matrix least-squares method (SHELXL program of the same package). Refinement was on F^2 against all independent measured reflections. C, N, Cl, and Ti were anisotropic, with H atoms in calculated positions and riding on carrier atoms. Largest peak and hole in the last Fourier difference were (e·Å^{-3}): 0.28 and −0.28 for **I**, 0.56 and −0.51 for **III**, 0.48 and −0.47 for **VI,** and 0.43 and −0.40 for **VII**. Some crystal, collection, and refinement data are reported in Table 7.

Polymerizations of Propene. Polymerizations (runs 1−7 and 9−11) at low temperature (−60 °C) were carried out according to the following procedure. First, 100 mL glass reactors with magnetic stirrers were charged under nitrogen with 30 mL of toluene and 1×10^{-2} mol of MAO. The solutions were cooled with liquid nitrogen, the inert gas was evacuated, and the proper amount of propene (see Tables 2−4) was condensed into the reactors. The reactors were thermostated at −60 °C, and polymerizations were initiated by injecting 5×10^{-5} mol of Ti precatalyst dissolved in 1 mL of CH_2Cl_2. Polymerizations were quenched by pouring the reaction mixture into acidified ethanol, and the precipitated polymers were recovered by filtration, washed with fresh ethanol, and dried in vacuo at 70 °C.

Polymerizations of propene at higher temperature (+20 °C, runs 12−15) have been performed in a 250 mL glass autoclave by introducing 120 mL of toluene, MAO (4×10^{-3} mol), and 2×10^{-5} mol of the proper Ti precatalyst. The catalyst solution was fed with C_3H_6 at a pressure of 6 atm for 2 h while stirring. The autoclave was vented and the polymer recovered as previously described. Run 8 was performed by adding the precooled monomer to the reactor already containing the solvent, MAO, and **I**, aged and precooled as reported in Table 2.

Polymerizations of Styrene. Polymerizations (runs 16−18) were carried out in 100 mL glass reactors equipped with magnetic stirrers, by sequentially introducing 30 mL of toluene, 5×10^{-5} mol of Ti precatalyst (dissolved in 5 mL of toluene), and 1×10^{-2} mol of MAO. After thermostating at the reaction temperature (see Table 6), polymerizations were initiated by addition of 10 mL (9.1 g) of prethermostated styrene. Polymerizations were stopped by introducing a few milliliters of ethanol and the polymers were worked out according to the usual procedure. For run 19, the amount of reagents and the polymerization procedure were the same as for runs 16−18, but the catalyst was preformed by mixing **I** with MAO at 25 °C in toluene solution and aging at 25 °C for 30 min. The solution of the catalyst was subsequently thermostated at −60 °C and the polymerization initiated by addition of precooled styrene.

Polymerizations of 1,3-Butadiene. Polymerizations (runs 20, 21, 22, and 24) were performed by introducing 30 mL of toluene and 1×10^{-2} mol of MAO into 100 mL glass reactors equipped with magnetic stirrers. Solutions were cooled with liquid nitrogen, the inert gas was evacuated, and 1,3-butadiene (18 g) was condensed into the reactors. The reactors were thermostated at the polymerization temperature (see Table 6), and the polymerizations were initiated by addition of 5×10^{-5} mol of Ti precatalyst dissolved in 1 mL of CH_2Cl_2.

Polymerizations were quenched by introducing a few milliliters of ethanol. The polymers were worked out and recovered as usual, and they were dried in vacuo at room temperature.

The amount of reagents and the polymerization procedure for run 23 were the same as for runs 20, 21, 22, 24, but the catalyst was preformed by mixing the monoamidinate complex of titanium with MAO, in toluene solution at −20 °C, and aging the catalyst at −20 °C for 30 min. The solution was subsequently thermostated at −60 °C and the polymerization initiated by addition of a precooled (−60 °C) solution of 1,3-butadiene in toluene.

NMR Analysis. ^1H NMR spectra of the titanium precatalysts were recorded on a Bruker AM 400 spectrometer at room temperature. The samples were prepared by dissolving 5 mg of compound into 0.5 mL of CD_2Cl_2 or C_6D_6. Chemical shifts are reported relative to tetramethylsilane (TMS). The ^{13}C NMR spectra of the polymers were recorded either on a Bruker AM 250 spectrometer operating at 62.89 MHz in the FT mode or on a Bruker AV 300 spectrometer operating at 75.47 MHz in the FT mode. The samples were prepared by dissolving 40 mg of polymer into 0.5 mL of 1,1,2,2-tetrachlorodideuterioethane (for spectra at high temperature, 110 °C) or in $CDCl_3$ (for spectra at room temperature). The chemical shifts are reported relative to hexamethyldisiloxane (HMDS) for polypropylene and polystyrene spectra recorded at 110 °C or to tetramethylsilane (TMS) for spectra recorded at 25 °C (polybutadiene and stereoirregular polypropylene). The spectra were recorded using the following parameters: 5 mm dual $^{13}C/^{1}H$ probe; acquisition time, 2.044 s; spectral width, 80 ppm; time domain, 32K; size, 32K; relaxation delay, 2 s; 90° pulse angle. Composite pulse proton decoupling was achieved with the WALTZ 16 sequence for the spectra recorded with AV 300 while BB decoupling mode was used with AM 250. Fourier transformation was performed without further correction. The stereochemical structure and the amount of regioirregular arrangement of polypropylene have been evaluated from the areas of the methyl ^{13}C resonances, according to the assignments reported in refs 6 and 22 and taking into consideration the necessary relationship between the amount of stereochemical sequences. (e.g., $m = mm + {}^1/_2\, mr$; $r = rr + {}^1/_2\, mr$).

The relevant resonances for polystyrene and polybutadiene are according to refs 10 and 11, respectively.

GPC and Polymers Molecular Weight. Molecular weights (M_w, M_n, and polydispersity) of polypropylene samples 1, 3, and 14 (including the fractions of sample 14) and of polystyrene sample 17 have been determined by GPC analysis by Dr. C. Zannoni of "Polimeri Europa", Novara, Italy.

Analysis were performed on a Waters 150C instrument, using 1,2,4-trichlorobenzene as solvent at 135 °C and a set of Waters Styragel GPC columns (HT3, HT4, HT5, HT6) for high temperature. For the calibration curve we used commercial polystyrenes standards (Polymer Laboratories).

The values of M_n for the syndiotactic polypropylene samples 2 and 4 have been evaluated from the ratios between four times the summation of the areas of ^{13}C NMR resonances of the methyls of the chain (10−21 ppm) and that of the methyls of the isobutyl end group[23] (21.8−24 ppm) taking into consideration that every chain has two isobutyl end groups.[1h]

Melting Temperatures. Differential scanning calorimetry (DSC) measurements of the melting temperatures of polymer sample were carried out with a DSC 2920 TA instrument in flowing nitrogen atmosphere. Each analysis involved a heating−cooling−heating cycle from 30 to 200 °C at heating rate of 10 °C/min. The peak temperature of the melting endotherms has been reported as melting temperature.

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Supporting Information Available: Detailed crystallographic data, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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