Macromolecules **2007,** *40,* 5638−5643

Articles

Stereoselective Polymerization of Conjugated Dienes and Styrene−Butadiene Copolymerization Promoted by Octahedral Titanium Catalyst

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Received March 5, 2007; Revised Manuscript Received June 4, 2007

ABSTRACT: The ability of the dichloro{1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butylphenoxy)}titanium complex (**1**) to catalyze homopolymerization of conjugated dienes and copolymerization of butadiene with styrene is reported. After proper activation with methylalumoxane, **1** resulted active in the *trans*-1,4 selective polymerization of butadiene and isoprene with good activity. The molecular weight distributions of the polymers are monomodal with the polydispersity indexes, consistent with a single site behavior of the catalyst. Isotactic polystyrene-*co*-*trans*-1,4-polybutadiene with an unprecedented architecture, covering a wide range of compositions ($x_S = 0.15-0.97$), were also obtained. The chemo- and stereoselectivity of butadiene insertion and the isospecific styrene polymerization of the title catalyst are retained when the two monomers are copolymerized. The molecular weight distributions are consistent with the material being copolymeric in nature. The reactivity ratios values and the microstructure analysis (by means of ^{13}C NMR) indicate a random distribution of the two monomers in the polymer chain.

Introduction

The stereoselective polymerization of conjugated dienes promoted by transition metal complexes is an extensively studied topic and a challenging field in both academic and industrial environments for the relevance of these materials as synthetic rubbers.[1] In particular, because of its industrial importance, many studies have been devoted to the *cis*-1,4-butadiene polymerization[2] while the 1,4-*trans* polymerization has received rather limited attention.[3] Pioneering studies on *trans*-1,4-polybutadiene date back to the infancy of Ziegler−Natta catalysis and therefore deal with the use of titanium or vanadium halides activated by aluminum alkyls which produce mixtures of polymers containing variable amounts of *trans*-1,4-polybutadiene.[4] More recently, late transition metal based catalysts have been successfully used for the synthesis of *trans*-1,4-polybutadiene with high selectivity. For an example, Yasuda et al. have obtained *trans*-1,4-polybutadiene with high stereo- and regioselectivity using iron complexes of a tridentate N,N,N-donor ligand activated by modified methylalumoxane (MMAO).[5] Single-component lanthanide tris-allyl complexes and binary systems consisting of neodymium alkoxides or aryl oxides and dialkylmagnesium also allow the synthesis of polybutadiene with high *trans* selectivity (95%) and narrow molecular weight distributions.[6] The discovery of such single-site catalysts has renewed the interest in the synthesis and use of *trans*-selective catalysts also for their unique performances in the copolymerization of conjugated dienes with olefins.[7] In this field styrene−butadiene copolymers represent an interesting target due to the properties of the resulting materials and the large availability and low cost of the starting monomers. A limited number of catalysts have been shown to copolymerize these two monomers,[8] and these examples are confined to lanthanide compounds. In contrast, the efforts to control the stereoselectivity in the group 4 metal complexes catalyzed diene polymerization by judicious choice of the ancillary ligand were unsuccessful. Indeed, soluble titanium compounds activated by methylalumoxane (MAO) produce polybutadiene with prevalently *cis*-1,4 microstructure regardless of ancillary ligands, suggesting that the active species is a Ti(III) complex formed by reduction of the catalyst precursor as observed in syndiospecific styrene polymerization.[9,10]

Recently, a new class of group 4 metal catalyst precursors which incorporate a tetradentate ligand having two phenolate units linked through a 1,*ω*-dithiaalkanediyl bridge S(CH$_2$)$_n$S (n = 2 and 3) was developed.[11] In particular, the dichloro{1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butylphenoxy)}titanium complex (**1**) having a 1,4-dithiabutanediyl bridge (Figure 1)

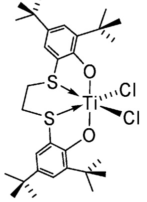

Figure 1. Dichloro{1,4-dithiabutanediyl-2,2′-bis(4,6-di-*tert*-butylphenoxy)}titanium (**1**).

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10.1021/ma070543u CCC: $37.00

Table 1. Butadiene Polymerization Results

run[a]	temp (°C)	Al/Ti	conv (%)	*trans*-1,4 (%)	*cis*-1,4 (%)	$M_n \times 10^3$	M_w/M_n
1	−20	500	26	95.6	4.4	2.7	2.0
2	0	500	98	93.2	6.8	3.9	2.2
3	25	500	96	94.6	5.4	4.2	2.3
4	50	500	79	90.7	9.3	5.7	2.5
5	50	1000	87	92.9	7.1	5.7	2.9
6[b]	50	1000	70	87.2	12.8	5.7	4.5

[a] Polymerization conditions: Ti complex (12.5 μmol), MAO, butadiene (0.58 g, 0.0108 mol), toluene (20 mL), polymerization time (4 h). [b] Catalyst aging: the catalyst was treating with MAO at 50 °C for 30 min before the polymerization start.

possesses C_2 symmetry and was shown to be highly active, after proper activation, in isospecific styrene and 4-methyl-1,3-pentadiene polymerization.[12]

Styrene polymerization proceeds through the secondary monomer insertion with an enantiomorphic-site stereocontrol.[13] The active species retains the C_2 symmetry of the precatalyst, mimicking the octahedral sites on the surface of the heterogeneous Ziegler−Natta catalysts. Furthermore, this catalyst was shown to afford propylene−styrene copolymers with unique microstructural features.[14] Here we report on the ability of the title catalyst to promote the stereoselective polymerization of 1,3-alkadiene and efficiently copolymerize styrene with butadiene, giving copolymers with unprecedented microstructural architectures.

Experimental Part

Materials. All manipulations of air- and/or water-sensitive compounds were performed under a nitrogen atmosphere using standard Schlenk techniques or a MBraun drybox. Commercial grade toluene (Carlo Erba) was dried over calcium chloride, refluxed 48 h under a nitrogen atmosphere over sodium, and distilled before use. Polymerization grade 1,3-butadiene, purchased from Società Ossigeno Napoli (S.O.N.), was dried by passing through a column filled with activated molecular sieves (4 Å). Isoprene (Aldrich) was purified by distillation over calcium hydride under nitrogen atmosphere. Styrene (Aldrich) was purified by distillation over calcium hydride under reduced pressure. Methylalumoxane (MAO), purchased from Witco as a 10 wt % solution in toluene, was dried in vacuo at 50 °C to remove toluene and “free” $AlMe_3$ and used as a solid after washing with hexane. The titanium complex **1** was prepared according to the literature procedure.[11a]

Polymerization of 1,3-Butadiene. The polymerization runs were carried out following a standard procedure. A 100 mL flask equipped with a magnetic bar was charged with MAO and butadiene solution (0.58 g, 0.0108 mol) in toluene (15 mL). After equilibration of the solution at the polymerization temperature the reaction was started by injection of a toluene solution (5 mL) of **1** (8 mg, 12.5 μmol). The run was terminated after 4 h by introducing ethanol (15 mL) containing the antioxidant (Wingstay K; 0.5−0.75 phr). The polymer was coagulated in ethanol (200 mL) acidified with aqueous HCl, recovered by filtration, washed with an excess of ethanol, and dried in vacuo at room temperature.

Polymerization of Isoprene. The polymerization runs were carried out following a standard procedure. A 100 mL flask equipped with a magnetic bar was charged with MAO (0.724 g, Al/Ti = 1000), toluene (12 mL), and isoprene (3 mL, 0.03 mol). After equilibration of the solution at the polymerization temperature the reaction was started by injection of a toluene solution (5 mL) of **1** (8 mg, 12.5 μmol). The run was terminated after 6 h by introducing ethanol (15 mL) containing the antioxidant (Wingstay K; 0.5−0.75 phr). The polymer was coagulated in ethanol (200 mL) acidified with aqueous HCl, recovered by filtration, washed with an excess of ethanol, and dried in vacuo at room temperature.

Copolymerization of 1,3-Butadiene and Styrene. The copolymerization runs were carried out following a standard procedure. A 100 mL flask equipped with a magnetic bar was charged with 0.724 g of MAO (0.0125 mol, Al/Ti = 1000), 8 mL of a butadiene solution 1.35 M (0.58 g, 0.0108 mol) in toluene, a variable amount of styrene, and the proper amount of toluene to reach a total volume of 20 mL. After equilibration of the solution at 50 °C the reaction was started by injection of a toluene solution (5 mL) of **1** (8 mg, 12.5 μmol). The run was terminated after 4 h by introducing ethanol (15 mL) and the antioxidant (Wingstay K; 0.5−0.75 phr). The polymer was coagulated in ethanol (200 mL) acidified with aqueous HCl, recovered by filtration, washed with an excess of ethanol, and dried in vacuo at room temperature.

The runs for the determination of the reactivity ratios were carried out following the same procedure for the preparation of the copolymer samples using the total volume of 85 mL and a concentration of butadiene of 0.54 M. The experimental conditions for the determination of the reactivity ratios permitted to obtain a low conversion for the monomers (5−7%) and a monomer composition of 34−58 mol % in styrene.

The reactivity ratios $r_1 = k_{SS}/k_{SB}$ and $r_2 = k_{BB}/k_{BS}$ were determined using the Fineman−Ross method and the following linear relationship:

$$[(1 - F)/F]f = r_1 - r_2 f^2/F$$

where F and f are the butadiene/styrene molar ratios in the polymer (by ^1H NMR analysis) and the feed, respectively.

Characterization of the Polymers. The ^{13}C NMR spectra of the polybutadiene samples were recorded with a Bruker AVANCE 400 spectrometer (400 MHz for ^1H and 100 MHz for ^{13}C). Using 5 mm (o.d.) NMR tubes, polymer samples (30 mg) were dissolved in $CDCl_3$ (0.7 mL) and analyzed at room temperature. Chemical shifts were referenced to TMS and calculated by using the residual isotopic impurities of the deuterated solvent. The microstructure of polybutadiene and polyisoprene samples was assessed by comparing the observed resonances with the data reported in the literature.[15] The monomer compositions of the copolymer styrene−butadiene samples were determined by comparing the integrals of the ^1H resonances in the following region (TCDE, 25 °C): 7.30 and 7.00 ppm (5H, m, $CH_2CH(C_6H_5)$); 5.50 and 5.00 ppm (2H, m, $CH_2CH{=}CHCH_2$).

The thermal analysis of the polymers was carried out on a TA Instruments DSC 2920 using a heating rate of 10 °C min^{-1}.

The average molecular weights of the polymer samples were determined at 30 °C with a 150C Waters GPC equipped with JASCO 875-UV (254 nm) and WGE-DR BURES ETA1002 refractive index detectors and three PSS columns set consisting of 10^5, 10^4, and 100 Å (pore size)−5 μm (particle size) column. $CHCl_3$ was used as carrier solvent with a flow rate of 1.0 mL/min. The calibration curve was established with polystyrene standards.

Wide-angle X-ray diffraction (WAXD) patterns in the range $2\theta = 4°−40°$ were obtained with an automatic Philips instrument using the nickel-filtered Cu Kα radiation.

Results and Discussion

Dienes Homopolymerization. The performances of **1**/MAO in butadiene polymerization were explored under different experimental conditions: the main results are summarized in Table 1. The total monomer conversion is generally reached in 4 h at 0 °C. In the range of temperature explored (−20 to 50 °C), the productivity of the catalyst shows values comparable to those of the *cis*-1,4-selective butadiene polymerization

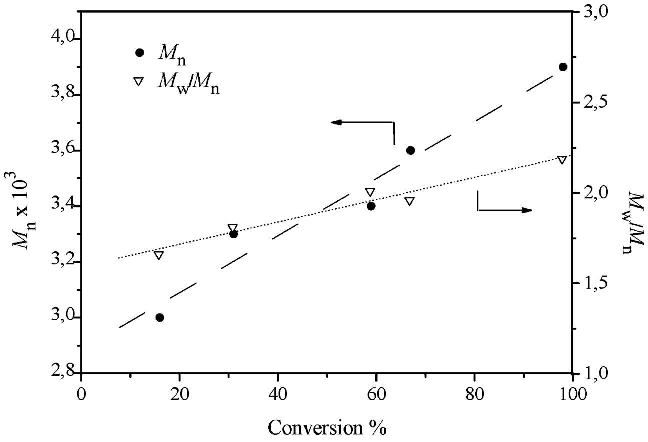


Figure 2. Dependence of molecular weights (M_n) and polydispersity vs monomer conversion in butadiene polymerization promoted by **1**/MAO at 0 °C.

Table 2. Isoprene Polymerization Results

run[a]	temp (°C)	conv (%)	*trans*-1,4 (%)	vinyl-3,4 (%)	$M_n \times 10^3$	M_w/M_n
7	25	1.2	80	20		
8	50	3.1	87	13	4.6	2.3
9	70	13.5	91	9	25.1	1.4

[a] Polymerization conditions: Ti complex (12.5 μmol), MAO (Al/Ti = 1000), isoprene (3 mL, 0.03 mol), toluene (12 mL), polymerization time (6 h).

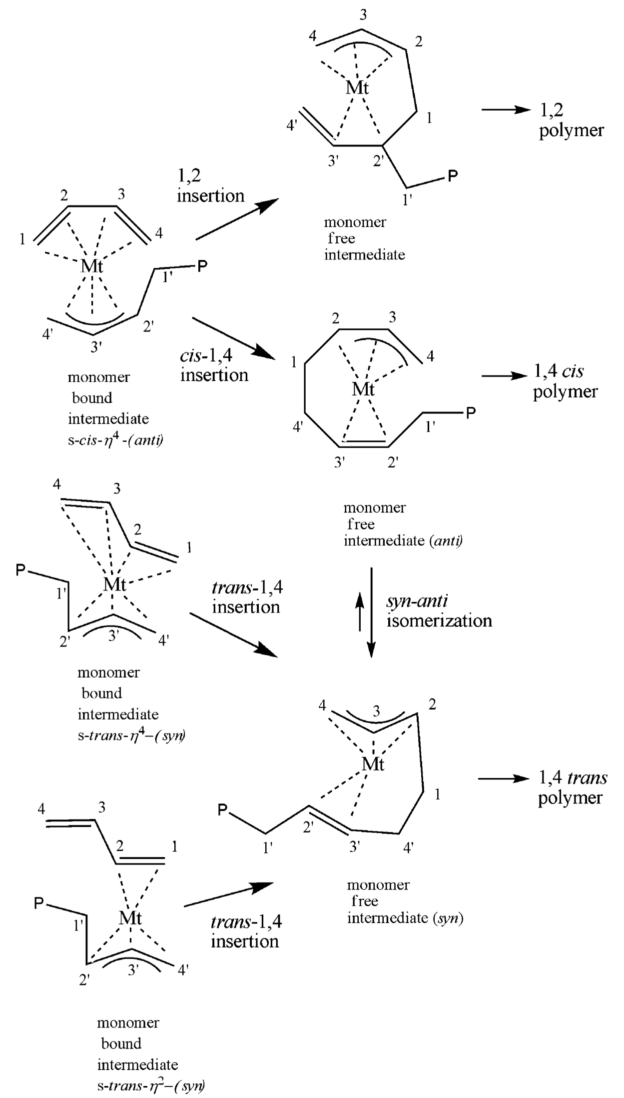
catalysts based on monocyclopentadienyl[9] and bis(phenoxo)-imino titanium compounds at same polymerization temperatures.[10c] The ^{13}C NMR analysis of the polybutadiene samples reveals a prevailingly *trans*-1,4 microstructure of the polymer chain comprising isolated *cis*-1,4 units (4−13 mol %, Table 1) identified by resonances at 129.6 and 130.4 ppm diagnostic of the *cis*−*trans* and *trans*−*cis* butadiene diads, respectively. It is worth noting the absence of 1,2-vinyl enchained butadiene units.

The presence of isolated *cis*-1,4 units in the polymer chain causes an increase of the glass transition temperature (T_g) and a lowering of the melting temperature (T_m) of the *trans*-1,4-polybutadiene segments. In the DSC thermogram of sample 4, T_g and T_m were observed at −70 and 44 °C, respectively.[16] Moreover, a low crystallinity index (10%) was also evidenced by the X-ray powder diffraction pattern in which the reflection at $2\theta = 22.9°$ due to crystalline *trans*-1,4-polybutadiene domains was observed.

The polydispersity indexes (PDI = M_w/M_n) of the *trans*-1,4-polybutadiene obtained at 0 °C are close to 2, consistent with a single-site catalyst, and the plot of the number-averaged molecular weights (M_n) vs monomer conversion is linear at this temperature (see Figure 2). It was previously reported that the benzyl derivatives of the title complex, activated with $B(C_6F_5)_3$ or $[PhNMe_2NH][B(C_6F_5)_4]$, yielded living isospecific polymerization of styrene at 25 °C.[11f] Thus, we propose that the broadening of the molecular weight distribution could be explained considering that the presence of MAO could cause the termination of the growing chain process by chain transfer reaction to aluminum.

The molecular weights increase with the polymerization temperature and monomer conversion, whereas the PDI value increases with polymerization temperature and Al/Ti molar ratio, e.g., from 2.2 (0 °C, Al/Ti = 500) to 2.9 (50 °C, Al/Ti = 500), a partial decomposition of the catalyst under the latter conditions is supposed. As matter of fact, the thermal pretreatment of the catalyst with excess of MAO at 50 °C for 30 min produced a further broadening of PDI value from 2.9 to 4.5 (compare run 5 and 6, Table 1) and a modification of the microstructure: the polybutadiene sample obtained under this condition was contaminated by *cis*-1,4-polybutadiene identified by the ^{13}C NMR signals. This result confirms the decomposition of the catalyst that likely yields Ti(III) species active in *cis*-1,4-specific polymerization of butadiene.[17]

Scheme 1



Attempts to polymerize isoprene were also carried out (Table 2). The conversion is rather low at 20 °C, and the polymer structure is predominantly *trans*-1,4 (80 mol %) containing a minor amount of 3,4 units (20 mol %). Both monomer conversion and catalyst chemoselectivity were found to increase at 70 °C (see run 9, Table 2). The ^{13}C NMR analysis of this sample shows signals for *trans*-1,4-polyisoprene spanned by isolated 3,4 units producing resonances at 44.4, 31.3, and 18.8 ppm due to the methine, methylene, and methyl carbon atoms, respectively. Also in this case the molecular weight distributions of the polymers are monomodal with PDI value lower than 2 at 70 °C.

The observed stereoselectivity can be explained on the basis of the well-established polymerization mechanism proposed for conjugated dienes.[1] *trans*-1,4-Butadiene insertion arises from the s-*trans*-η^4 or η^2 monomer coordination to the metal center, producing the intermediate η^3 coordinated allyl complex in the syn configuration, as depicted in Scheme 1. Alternatively, the

Table 3. Styrene−Butadiene Copolymerization Results

run[a]	[S]/[B]	yield (g)	time (min)	copolymer composition[b]	$M_n \times 10^3$	M_w/M_n
10	1/10	0.43 (61%)	240	$x_S = 0.15$, $x_B = 0.85$	6.5	2.7
11	1/5	0.49 (64%)	240	$x_S = 0.28$, $x_B = 0.72$	7.3	2.7
12	1/2	0.82 (71%)	180	$x_S = 0.46$, $x_B = 0.54$	9.5	2.9
13	1/1	1.66 (97%)	180	$x_S = 0.59$, $x_B = 0.41$	16.7	2.3
14	2/1	2.80 (99%)	120	$x_S = 0.79$, $x_B = 0.21$	27.7	2.4
15	5/1	6.17 (99%)	60	$x_S = 0.89$, $x_B = 0.11$	52.8	2.5
16	10/1	6.30 (99%)	45	$x_S = 0.97$, $x_B = 0.03$	103.2	1.9

[a] Polymerization conditions: 8 mg of complex (12.5 μmol, 6.25×10^{-4} M), 0.58 g of butadiene (0.0108 mol, 0.54 M), 0.72 g of MAO (Al/Ti = 1000), 20 mL of toluene. [b] Determined by ^{1}H NMR analysis.

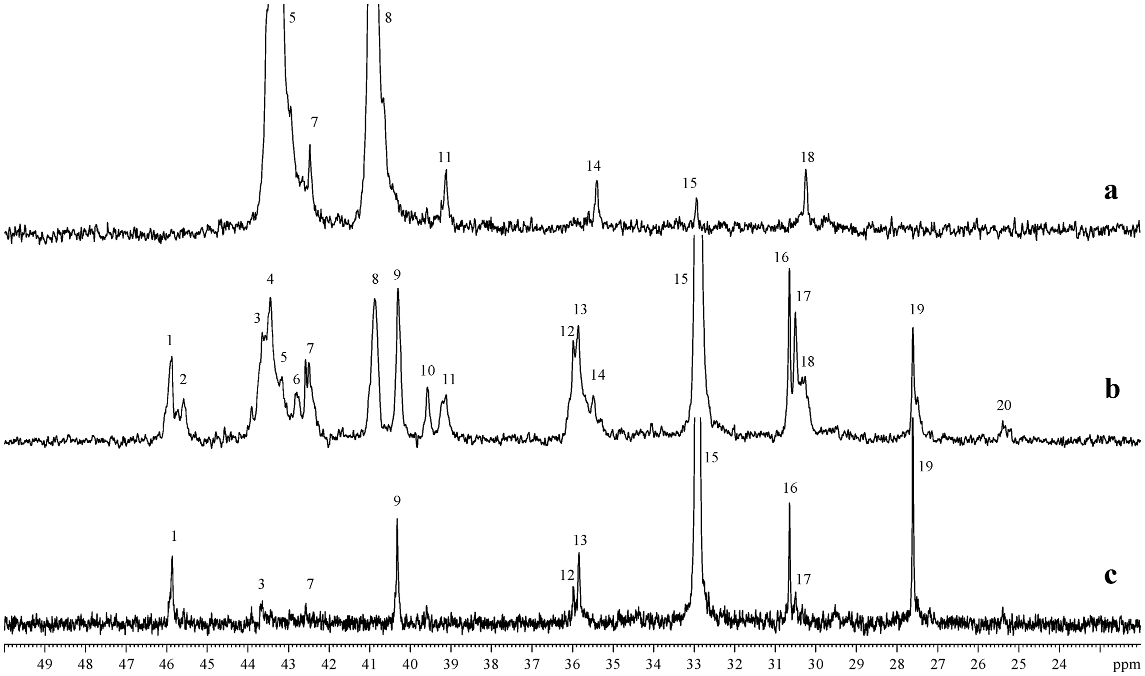


Figure 3. Aliphatic region of the ^{13}C NMR spectra of samples with $x_S = 0.97$ (a), 0.46 (b), and 0.15 (c). The numbering of the spectral lines is reported in Table 4 (300 MHz, $CDCl_3$, δ in ppm).

Table 4. Selected ^{13}C NMR Assignments for the Monomer Triads in the iPS−B Copolymer Produced with 1/MAO

line	triad[a]	calcd chemical shifts (ppm)[b]	exptl chemical shifts (ppm)	$\Delta\delta$
1	TS_2T	45.59	45.87	0.28
2	CS_2T	45.88	45.59	0.29
3	SS_1T	43.48	43.65	0.17
4	SS_2T	43.82	43.45	0.37
5	SS_1S		43.21	
6	SS_1C	43.77	42.80	0.97
7	TS_2S	43.36	42.48	0.88
8	SS_2S		40.88	
9	TST_1	39.80	40.33	0.53
10	CST_1	39.80	39.58	0.22
11	SST_1	39.80	39.12	0.68
12	STS_1	36.85	36.00	0.85
13	TS_1T	36.44	35.85	0.59
14	TS_1S	36.85	35.40	1.45
15	T_4T/TT_1		32.95	
16	T_4ST	30.53	30.66	0.13
17	ST_4S	30.53	30.51	0.02
18	T_4SS	30.53	30.26	0.27
19	C_4T/CT_1	27.32	27.62	0.30
20	C_4S	25.09	25.40	0.31

[a] The numbering and the symbol are those indicated in Scheme 2. [b] Chemical shifts calculated by the incremental shift factors by Sato et al. (see ref 18).

η^4-*cis* coordination of the monomer produces both 1,2-butadiene insertion and the η^3-intermediate π-allyl complex in the anti configuration: the latter leads to the *cis*-1,4 insertion of the butadiene or *trans*-1,4 through syn−anti isomerization of the π-allyl complex.

The complete absence in the polymer chain of 1,2-vinyl units and the elevated *trans*-1,4 selectivity of the title catalyst suggest that the s-*cis*-η^4 coordination of the monomer is unlike. In conclusion, the bulky tetradentate 1,4-dithiabutanediyl-2,2′-bis-(4,6-di-*tert*-butylphenoxy) ligand seems to hamper the s-*cis*-η^4 coordination of butadiene, producing the s-*trans*-η^4 or η^2 intermediate in syn configuration that evolves exclusively toward *trans*-1,4 polymerization. Of course, the presence of isolated *cis*-1,4 units in the polybutadiene sample accounts for the occasional syn−anti isomerization of the π-allyl intermediate of the growing polybutadiene chain.

Styrene−Butadiene Copolymerization. Styrene−butadiene copolymers with styrene molar fractions (x_S) covering a full range of composition ($x_S = 0.15-0.97$) were obtained at 50 °C in the same experimental conditions used for butadiene homopolymerization (see Table 3). Gel permeation chromatography analysis of these copolymers showed that the molecular weights distributions are monomodal with a PDI values close to 2, consistent with the material being copolymeric in nature. Exhaustive hexane extraction of the copolymers rich in styrene ($x_S = 0.79-0.97$) confirmed the absence of *trans*-1,4-polybutadiene contaminant. The increment of the M_n values with the increase of x_S in the copolymers can be ascribed to the increased amount of styrene in the feed.

Inspection of ^{13}C NMR spectra of the copolymers revealed that the chemo- and stereoselectivity of butadiene insertion and the isospecificity of styrene polymerization by the title catalyst is retained when the two monomers are copolymerized. As

Table 5. Triad Content and Glass Transition Temperature of Samples 10−16

		triad[a]										
sample	copolymer composition	SSS	SST	TSS	STS	TST	CST	SSC	TT	TC	n_S[b]	T_g[c] (°C)
10	$x_S = 0.15$	0.00	0.01	0.01	0.03	0.08	0.00	0.00	0.79	0.08	1.1	−56
11	$x_S = 0.28$	0.04	0.04	0.04	0.05	0.10	0.02	0.00	0.66	0.05	1.7	−36
12	$x_S = 0.46$	0.15	0.09	0.09	0.07	0.07	0.03	0.05	0.42	0.03	2.2	−16
13	$x_S = 0.59$	0.29	0.08	0.13	0.06	0.05	0.02	0.08	0.27	0.02	3.2	9
14	$x_S = 0.79$	0.51	0.07	0.10	0.05	0.02	0.02	0.09	0.13	0.01	4.8	47
15	$x_S = 0.89$	0.75	0.06	0.09	0.05	0.00	0.00	0.00	0.05	0.00	12.0	50
16	$x_S = 0.97$	0.93	0.01	0.01	0.00	0.00	0.00	0.00	0.05	0.00	95.0	78

[a] Styrene (S), *trans*-1,4-butadiene (T), *cis*-1,4-butadiene (C). [b] Average styrene block lengths. [c] Glass transition temperatures by DSC analysis.

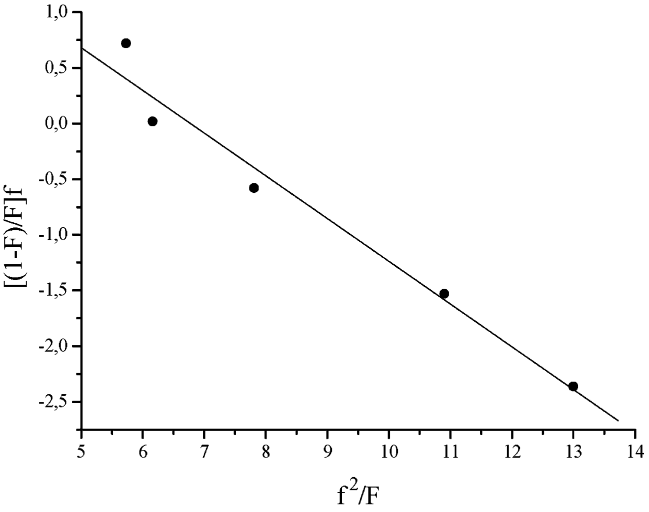


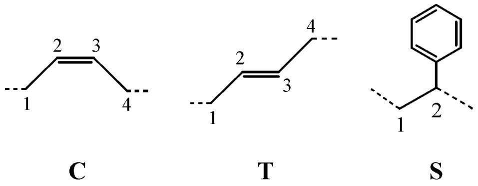
Figure 4. Finemann−Ross plot for styrene−butadiene copolymerization by **1**/MAO and least-squares best-fit line (f = [butadiene]/[styrene] in feed and F = [butadiene]/[styrene] mole ratio in polymer).

matter of fact, the ^{13}C NMR spectrum of the copolymer with highest styrene content (Figure 3a, $x_S = 0.97$, Table 3, run 16) exhibits two intense resonances corresponding to the methylene and methine carbon atoms of the isotactic polystyrene triad SSS (lines 5 and 8, Table 4), and the ^{13}C NMR spectrum of the copolymer with highest butadiene content (Figure 3c, $x_S = 0.15$, Table 3, run 10) exhibits one intense resonance corresponding to the methylene carbon atom of the TT diad (line 15, Table 4).

Interpretation of the ^{13}C NMR spectra at triad level of the monomer heterosequences was performed using the previously attributions achieved in low molecular weight copolymers and properly deuterated model compounds. In particular, Sato et al. reported incremental shift factors for the methine or methylene carbon atoms in α-, β-, and γ-position from the 1,2-vinyl (V), styrenyl (S), and *cis* (C) or *trans* (T) 1,4-butenyl units. The stereochemical effects of the SS, SV, and VV diads were also considered by these authors.[18]

Thus, chemical shifts of the ^{13}C NMR signals diagnostic of different monomer triads are listed in Table 4 for the aliphatic region, and the assignments are displayed in Figure 3. The numbering and the symbols are indicated in Scheme 2. The ^{13}C NMR spectrum of the copolymer with highest styrene content (Figure 3a, $x_S = 0.97$, Table 3, run 16) shows less intense resonances at 42.48, 39.12, 35.40, and 30.26 ppm, attributed to TS (lines 7, 14, 18) and ST (line 11) diads. The attribution at triad level is not straightforward. Keeping in mind that the chemical shifts of the TS and ST diad are not influenced by the preceding or following monomeric unit[18] and considering that (i) the composition of sample 16 is rich in styrene and (ii) the ^{13}C NMR signals of the TS and ST diads are downfield shifted with respect to the same signals in the ^{13}C NMR spectrum of butadiene-rich sample 10 (Figure 3c), we tentatively assign the above cited resonances to the TSS and SST triads.

Scheme 2



In Figure 3c the less intense resonances (lines 1, 9, 13, 16) are attributed to isolated styrene unit (TST). The calculated chemical shifts for the methine TS_2T and the methylene TST_1, TS_1T, T_4ST carbon atoms are found in good agreement with the experimental values. Moreover, the comparison with the spectrum of Figure 3a corroborates these attributions. The resonances at 36.00 and 30.51 ppm (lines 12 and 17) were thus tentatively attributed to the STS_1 and ST_4S of the alternate styrene−butadiene sequence.

In the ^{13}C NMR spectrum of the copolymers with an intermediate composition (Figure 3b, $x_S = 0.46$, Table 3, run 12) most of the resonances have been attributed by comparing the ^{13}C NMR spectra of the samples 10 and 16. The resonances corresponding to the lines 2, 10, and 20 were respectively attributed to CS_2T, CST_1, and C_4S carbon atoms of the CST triad, whose calculated chemical shifts better match the experimental values. The resonance corresponding to the line 6 was attributed to the SS_1C carbon atom of the SSC triad. The signals 3, 4, and 5 appear as a unique broad resonance; the DEPT experiment (see Supporting Information) performed on this sample permitted to distinguish the resonance of the methine SS_2T carbon atom (line 4) from that of the methylene SS_1T and SS_1S carbon atoms (lines 3 and 5). In Table 5 the triad content of samples 10−16 together with average styrene block lengths[19] were reported. The reactivity ratios $r_1 = k_{SS}/k_{SB}$ and $r_2 = k_{BB}/k_{BS}$ for butadiene−styrene copolymerization catalyzed by **1**/MAO were evaluated. As the butadiene insertion is mainly *trans*-1,4 specific, a binary copolymerization scheme and the terminal model in which only the last inserted monomer units at the active catalyst site influence the propagation reaction were assumed.

To minimize the composition drift, the copolymerization reactions were stopped after 10 min, corresponding to a monomer conversion of 5−7%. The reactivity ratios obtained from the Fineman−Ross[20] plot in Figure 4 are $r_1 = 2.60$ and $r_2 = 0.98$. These values indicate a preference for insertion of styrene vs butadiene when the last inserted monomer unit in the growing polymer chain is styrene. On the other hand, both monomers have comparable reactivity after a butadiene insertion. This behavior could be ascribed to the higher stability of the η^3 allyl intermediate formed between the growing polymeric chain and the metal center when the last inserted monomer is a butadiene compared to that formed with styrene. The product of the reactivity ratios ($r_1r_2 = 2.5$) indicates a tendency of the monomers to form random copolymers with short styrene homosequences, in agreement with the microstructure determined by ^{13}C NMR analysis.

Despite the stereoregularity of styrene blocks, copolymers are amorphous also when rich in styrene. The styrene-*co*-*trans*-1,4-butadiene polymers by **1**/MAO (samples 10−16) exhibit T_g values in the range determined by the T_g values of PB and iPS: in particular, the T_g increases from −56 to 78 °C as the styrene content in the copolymer sample is increased in the range $x_S = 0.15-0.97$.

Conclusions

To the best of our knowledge, **1**/MAO is the first homogeneous titanium catalyst mimicking the octahedral active species of the heterogeneous titanium catalysts active in *trans* selective polymerization of butadiene and isoprene with good activity. Furthermore, the synthesis of styrene-*co*-*trans*-1,4-butadiene polymers containing isotactic styrene segments was also possible for the first time. The reactivity ratios values and the microstructure analysis by ^{13}C NMR indicate a random distribution of the two monomer in the polymer chain. These results not only confirm that the C_2 symmetric octahedral structure of the precatalyst is retained in *trans*-1,4 selective conjugated dienes polymerization but that this catalyst is a powerful tool for the synthesis of new materials with unprecedented molecular architectures.

Acknowledgment. Financial support for this research from Regione Campania (Italy) (LR 28/5/2002 “Nuovi complessi pseudo-ottaedrici per la polimerizzazione delle 1-olefine”) and Ministero dell’Università e della Ricerca Scientifica (MURST, Roma, Italy; PRIN-2004: “Organometallic catalysis of polymerisation for the achievement of elastomers and nanostructured materials”) is gratefully acknowledged.

Supporting Information Available: ^{13}C NMR spectra of homo- and copolymers by **1**/MAO. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA070543U