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Living, Isoselective Polymerization of 4-Methyl-1,3-pentadiene and Styrenic Monomers and Synthesis of Highly Stereoregular Block Copolymers via Sequential Monomer Addition

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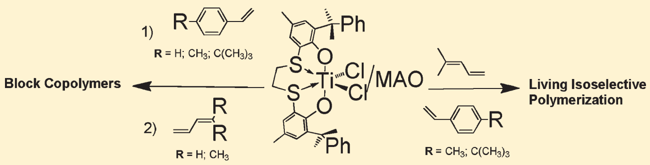
Supporting Information

ABSTRACT: The living, isoselective polymerization of 4-methyl-1,3-pentadiene, 4-methylstyrene, and 4-*tert*-butylstyrene was promoted by using the titanium complex **1** activated by methylaluminoxane (MAO) at room temperature producing highly isotactic polymers. The synthesis of highly isotactic polystyrene-*block*-poly(4-methyl-1,3-pentadiene), poly(4-methylstyrene)-*block*-polystyrene, poly(4-methylstyrene)-*block*-1,4-*trans*-poly(1,3-butadiene), poly(4-methylstyrene)-*block*-polystyrene-*block*-poly(4-methylstyrene), poly(4-methylstyrene)-*block*-polystyrene-*block*-poly(4-methyl-1,3-pentadiene), and poly(4-methylstyrene)-*block*-polystyrene-*block*-poly(4-*tert*-butylstyrene) copolymers was also accomplished for the first time, by sequential monomer addition, in the presence of the system **1** activated by MAO. The thermal features of these polymers clearly show that all copolymer blocks, except the 4-methylstyrene one, are crystalline with melting point values typical of the corresponding homopolymers. The synthesis of a low molecular weight polystyrene sample allowed us to detect the polymer chain ends, giving useful information about the polymerization mechanism.



INTRODUCTION

The precise control over the macromolecular architecture is one of major challenge in synthetic polymer chemistry. In the past years many endeavors have been devoted toward the development of a polymerization technique that allows an accurate regulation of the molecular weight, stereochemistry, and comonomer distribution in the polymer backbone.[1] In this field the keystone has been the achievement of chain-growth polymerization methods that enable consecutive enchainment of monomer units without termination, the well-known living polymerization.[2] In spite of the considerable advances in living or controlled polymerization using anionic,[3] cationic,[4] and radical polymerization,[5] the development of homogeneous Ziegler−Natta catalysts able to promote the living polymerization of olefins and diene has encountered less fortune. The reason for such frustration is due to the existence, in the olefin polymerization, of the β-elimination reactions that result in the initiation of new polymer chains by the catalyst or the chain transfer reactions to the aluminum center of the cocatalyst. In many cases the lifetime of chain formation is on the order of seconds, rendering the formation of block copolymers by sequential monomer addition impossible.

In the past decade, among the large variety of post-metallocene catalysts developed for the olefin polymerization there are various examples of catalysts able to promote the living polymerization of olefins and dienes.[6] It is worth noting that in spite of the interesting features of the stereoregular polymers of styrene there are few example of efficient, living stereoselective polymerization of this monomer.[7]

The living, syndioselective polymerization of styrene and the formation of syndiotactic-polystyrene-*block*-*cis*-1,4-polybutadiene has been reported by Shiono and co-workers which also succeeded in the synthesis of SBS triblock copolymers.[8] In this case, however, the polymerization reactions should be conducted at subambient temperature, producing copolymers with a minor amount (10−20%) of amorphous polymer contaminant that should be extracted in THF.

In the past years the isoselective, living styrene polymerization became also possible by using a titanium complex bearing tetradentate [OSSO] bis(phenolate) ligand activated by $[PhNMe_2H]$-$[B(C_6F_5)_4]$ in the presence of $Al(nOct)_3$ at 25 °C.[9]

We have more recently reported that the titanium complex **1** (see Scheme 1), having in the *ortho* position two cumyl bulky groups, activated by methylaluminoxane, promotes the living stereoregular polymerization of styrene and butadiene and the formation of *isotactic*-polystyrene-*block*-1,4-*trans*-polybutadiene copolymer by sequential monomer addition.[10]

Herein we report the living, isospecific polymerization of 4-methyl-1,3-pentadiene (4-MPD), 4-methylstyrene (PMS), and 4-*tert*-butylstyrene (PTBS) and the formation of new diblock and triblock copolymers by sequential monomer addition in presence of catalytic system **1** activated by MAO. Moreover, the living behavior in styrene polymerization allows the synthesis of an *isotactic*-polystyrene sample with low molecular weight by **1**/MAO.

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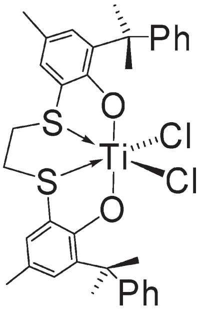
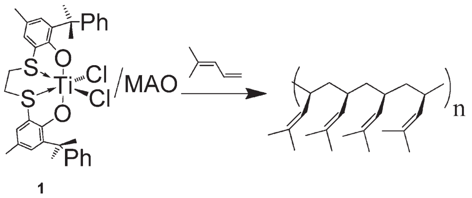
Scheme 1. Dichloro{1,4-dithiabutanediyl-2,2′-bis[4-methyl-6-(2-phenyl-2-propyl)phenoxy}titanium (1)



Scheme 2. Isoselective 4-Methyl-1,3-pentadiene Polymerization



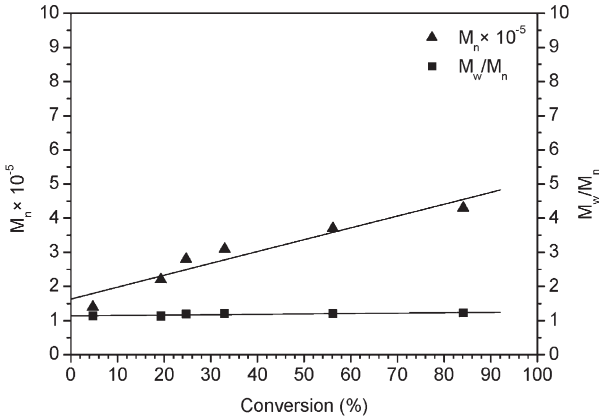


Figure 1. Plot of poly(4-methyl-1,3-pentadiene) M_n (▲) and M_w/M_n (■) versus conversion using 1/MAO at 20 °C, determined by gel permeation chromatography (PS standards).

Table 1. Homopolymerization of 4-Methyl-1,3-pentadiene with 1/MAO

run[a]	t (min)	M_w/M_n	$M_n \times 10^{-5}$	$M_n^{theo} \times 10^{-5}$	yield (g)	conv (%)
1	5	1.14	1.4	0.3	0.03	4.7
2	10	1.13	2.2	1.4	0.14	19.3
3	15	1.19	2.8	1.8	0.18	24.7
4	20	1.20	3.1	2.4	0.24	33.0
5	25	1.22	3.7	4.0	0.40	56.2
6	30	1.23	4.3	6.0	0.60	84.1

[a] Polymerization conditions: 4-methyl-1,3-pentadiene (8.7 mmol), Ti complex (1.0 μmol), Al/Ti = 12 000, toluene (10 mL). Polymerization temperature = 20 °C.

The ^{1}H and ^{13}C NMR analysis of this sample gives us new insights into the active species involved in styrene homopolymerization as well as on the initiation and termination reactions.

■ RESULTS AND DISCUSSION

Homopolymers. In Table 1, the data concerning the homopolymerization, promoted by the complex **1**/MAO (see Scheme 2), under optimized conditions, of 4-MPD, are reported. It is worth reminding that the related titanium complex bearing *tert*-butyl groups instead of two cumyl groups in the *ortho* positions promotes the isoselective 1,2 polymerization of the 4-MPD monomer but not in living fashion.[11]

In order to extend to 4-MPD the possibility to obtain a living polymerization process, we evaluated the performance of the catalyst **1** activated by MAO in the polymerization of such monomer, by plotting the number-average molecular weight, M_n, and the molar weight distribution, M_w/M_n, of the isotactic poly-1,2-(4-MPD) samples obtained in each run as a function of their monomer conversion values (see Figure 1 and Table 1).

It is apparent from Figure 1 that the M_n value increases linearly with 4-MPD conversion, while the M_w/M_n values keep almost constant (1.13−1.23). These results and the good agreement between the experimental and theoretical molecular weight clearly indicate a living behavior of the 4-MPD polymerization at room temperature. Furthermore, a living behavior is also observed for the homopolymerizations of PMS and PTBS giving, also in these cases, highly isotactic polymers with narrow molecular weight distribution (see Supporting Information). The DSC analysis shows that, according to the literature,[12] the as-formed *i*-poly(4-methyl-1,3-pentadiene) and *i*-poly(4-*tert*-butylstyrene) samples are crystalline, while the *i*-poly(4-methylstyrene) ones are amorphous.

Block Copolymers. Owing to the living behavior and the high stereoselectivity of **1**/MAO in the homopolymerizations of a wide range of monomers such as 4-methyl-1,3-pentadiene, 4-methylstyrene, and 4-*tert*-butylstyrene as well as styrene and butadiene ones,[10] we decided to test this catalyst in several diblock and triblock copolymerizations in order to prove its efficiency in the synthesis of materials with unique microstructural features. As a matter of fact, it seems interesting to produce well-defined block copolymers, creating new polymeric architectures with promising physical, mechanical, and chemical properties.

We have succeeded in obtaining the following diblock and triblock copolymers: *i*-polystyrene-*block*-*i*-poly(4-methyl-1,3-pentadiene), *i*-poly(4-methylstyrene)-*block*-*i*-polystyrene, *i*-poly(4-methylstyrene)-*block*-1,4-*trans*-poly(1,3-butadiene), *i*-poly(4-methylstyrene)-*block*-*i*-polystyrene-*block*-*i*-poly(4-methylstyrene), *i*-poly(4-methylstyrene)-*block*-*i*-polystyrene-*block*-*i*-poly(4-methyl-1,3-pentadiene), and *i*-poly(4-methylstyrene)-*block*-*i*-polystyrene-*block*-*i*-poly(4-*tert*-butylstyrene). All block copolymerizations were performed by sequential monomer addition, in the presence of the system **1** activated by MAO, at 25 °C, leaving each monomer reacting the necessary time for its complete consumption before the addition of the following monomer. As reported in Tables 2−5, it is possible to obtain copolymers with high molecular weight and narrow molecular weight distribution, within a wide range of compositions, the yield is close, in any case, to the total conversion, and no broadening of the molecular weight distribution with polymerization time is observed. Moreover, the ^{13}C NMR

Table 2. Diblock Copolymers of Styrene and 4-Methyl-1,3-pentadiene by Sequential Monomer Addition with 1/MAO

run[a]	X_S (feed)[b]	X_S (copolymer)[c]	X_S (copolymer)[d]	M_n[e] (g/mol × 10^{-3})	M_w/M_n[e]	M_n[f] (g/mol × 10^{-3})	M_w/M_n[f]	$T_{m,P4MPD}$[g] (°C)	$T_{m,PS}$[h] (°C)	$T_{g,P4MPD}$[i] (°C)	$T_{g,PS}$[k] (°C)
7	0.10	0.22	0.10	24.9	1.05	114.2	1.34	85.9/123.3	219.6	15.9	n.d.[j]
8	0.20	0.28	0.28	41.7	1.05	127.3	1.20	87.4/124.1	221.3	19.4	94.3
9	0.30	0.33	0.35	60.6	1.06	148.0	1.32	89.0/123.8	221.6	16.8	95.4
10	0.40	0.45	0.44	79.4	1.07	159.4	1.19	89.5/123.1	222.4	15.6	92.7
11	0.50	0.59	0.52	123.2	1.08	209.1	1.16	88.5/124.8	222.9	12.3	97.2
12	0.60	0.62	0.53	161.0	1.09	237.8	1.19	88.4/125.4	222.3	13.1	98.7
13	0.70	0.72	0.60	209.1	1.09	317.6	1.16	85.3/132.6	223.2	n.d.[j]	98.8
14	0.80	0.81	0.84	340.8	1.27	390.6	1.28	88.7/126.8	223.9	n.d.[j]	99.8

[a] Polymerization conditions: Ti = 10.0 μmol; [Al]/[Ti] 1200; T_{run} = 25 °C; V_{tot} = 20 mL; 4-methyl-1,3-pentadiene (8.7 mmol) and the proper amount of styrene; polymerization time: 1 h (styrene) + 2 h (4-methyl-1,3-pentadiene). [b] Styrene molar fraction in the feed. [c] Styrene molar fraction in copolymer determined from ^{13}C NMR spectra. [d] Styrene molar fraction in copolymer determined from GPC. [e] Relative to the isotactic polystyrene block. [f] Relative to the *isotactic*-polystyrene-*block*-poly(4-methyl-1,3-pentadiene) copolymer. [g] Melting temperature relative to the poly(4-methyl-1,3-pentadiene) block in the resulting *isotactic*-polystyrene-*block*-poly(4-methyl-1,3-pentadiene) copolymer, determined by 10 °C/min heating rate DSC scans. [h] Melting temperature relative to the isotactic polystyrene block in the resulting *isotactic*-polystyrene-*block*-poly(4-methyl-1,3-pentadiene) copolymer, determined by 10 °C/min heating rate DSC scans. [i] Glass transition temperature relative to the *isotactic* poly(4-methyl-1,3-pentadiene) block in the resulting *isotactic*-polystyrene-*block*-poly(4-methyl-1,3-pentadiene) copolymer, determined by 10 °C/min heating rate DSC scans. [j] Not determined. [k] Glass transition temperature relative to the isotactic polystyrene block in the resulting *isotactic*-polystyrene-*block*-poly(4-methyl-1,3-pentadiene) copolymer, determined by 10 °C/min heating rate DSC scans.

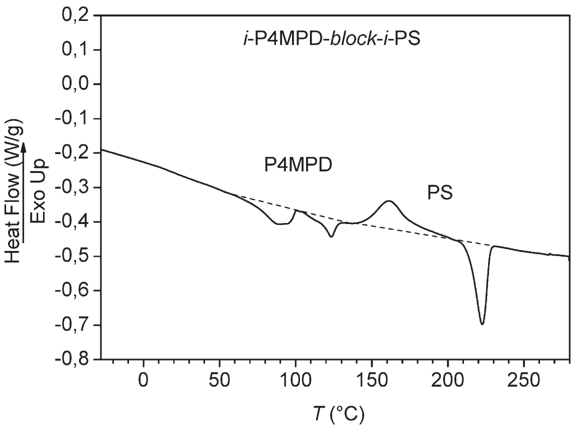


Figure 2. DSC curve of the first heating scan of *i*-poly(styrene)-*block*-*i*-poly(4-methyl-1,3-pentadiene) copolymer sample obtained in run 11.

analysis of copolymers shows that they possess an high degree of stereoregularity.

Diblock Copolymers. *i-Poly(styrene)-block-i-poly(4-methyl-1,3-pentadiene).* In Table 2, the results relative to the synthesis of *isotactic*-poly(styrene)-*block*-*isotactic*-poly(4-methyl-1,3-pentadiene) samples are reported. As shown in Table 2, it is possible to obtain copolymers within a wide range of compositions (styrene molar fraction, X_S, value ranging between 0.10 and 0.84), the yield is close, in any case, to the total conversion, and no broadening of the molecular weight distribution with polymerization time is observed. It is worth noting that X_S values in obtained copolymer samples, determined by GPC and ^{13}C NMR techniques, are in good agreement (see Table 2).

In the DSC thermograms of the resulting copolymers endothermic peaks characteristic of the *isotactic* polystyrene and of the *isotactic* poly-1,2-(4MPD) appear. Particularly, the heating thermograms of the *i*-poly(styrene)-*block*-*i*-poly(4-methyl-1,3-pentadiene) samples exhibit three endothermic phenomena. In Figure 2, the DSC thermogram relative to the first heating scan of copolymer sample obtained in run 11 is reported, as an example. The endotherm at highest temperature is clearly due to the melting of crystalline *i*-polystyrene block (see Figure 2). The broad exotherm who precedes this endotherm is due to the crystallization of *i*-polystyrene block.

The melting peak temperature, T_m, of *i*-polystyrene block slightly increases from 219.6 to 223.9 °C, as the M_n values of the block increases from 24.9 to 340.8 × 10^{-3} g/mol (see Table 2). Two broad endotherms, at lowest temperature, are both due to *i*-poly(4-methyl-1,3-pentadiene) block (see Figure 2). The endothermic peak in the range between 85.9 and 89.5 °C (see Table 2) corresponds to transition from the crystalline modification I to the crystalline modification II of the *i*-poly(4-methyl-1,3-pentadiene), while the endotherm ranging from 123.1 to 132.6 °C probably corresponds to the melting of the more stable form II.[11] It is worth noting that the T_m values of both blocks are in agreement with that those of the corresponding homopolymers. The glass transitions of both blocks are not evident during first heating scan. The analysis of the second heating scans shows two distinct T_g values for the two polymer blocks. The T_g values of *i*-poly(4-methyl-1,3-pentadiene) and of *i*-poly(styrene) blocks are clearly apparent at ≈12.3–19.4 and ≈93.0–100.0 °C, respectively.

i-Poly(4-methylstyrene)-block-i-poly(styrene). The data concerning the synthesis of *i*-poly(4-methylstyrene)-*block*-*i*-poly(styrene) are reported in Table 3.

Copolymers with molar styrene fraction, X_S, values ranging from 0.32 to 0.90 have been prepared. The DSC analysis of the as formed *i*-poly(4-methylstyrene)-*block*-*i*-poly(styrene) samples show that the *i*-PS block is crystalline with melting temperature, T_m values ranging from 231 to 235 °C. The glass transition temperatures of the two blocks, T_g, are not clearly evident, in the first DSC heating run, while in the thermograms relative to the second heating scan, two different T_g values are observed, for diblock samples with X_s ranging between 32.0 and 77.0 mol % (see Table 3). The presence of two T_g values suggests the presence of two separate amorphous polymer block domains.

i-Poly(4-methylstyrene)-block-1,4-trans-polybutadiene. In Table 4, the results relative to the synthesis of *i*-poly(4-methylstyrene)-*block*-1,4-*trans*-polybutadiene samples are reported.

Table 3. Diblock Copolymers of 4-Methylstyrene and Styrene by Sequential Monomer Addition with 1/MAO

			PP MS-block		(PP MS-*b*-PS)			
run[a]	X_{PMS} (feed)[b]	X_{PMS} (copolymer)[c]	M_n[d] (g/mol × 10^{-3})	M_w/M_n[d]	M_n[e] (g/mol × 10^{-3})	M_w/M_n[e]	$T_{\mathrm{m,PS}}$[f] (°C)	T_g[g] (°C)
15	0.10	0.10	23.8	1.05	202.0	1.13	230.6	98.8
16	0.20	0.23	47.4	1.06	185.1	1.16	233.4	90.4/99.5
17	0.30	0.29	62.2	1.07	193.9	1.13	234.8	99.9/114.6
18	0.40	0.37	73.5	1.07	182.4	1.17	234.3	100.1/125.0
19	0.80	0.68	105.9	1.08	148.7	1.14	233.7	101.3/125.5

[a] Polymerization conditions: Ti = 10.0 μmol; [Al]/[Ti] 1200; T_{run} = 25 °C; V_{tot} = 30 mL; polymerization time: 1 h (4-methylstyrene) + 1 h (styrene). [b] 4-Methylstyrene molar fraction in the feed (the molar amounts of monomer are reported in the Experimental Part). [c] 4-Methylstyrene molar fraction, determined from GPC. [d] Relative to the *isotactic* poly(4-methylstyrene) block. [e] Relative to the *isotactic*- poly(4-methylstyrene)-*block*-poly(styrene). [f] Melting temperature relative to the *isotactic* polystyrene block in the resulting *isotactic*-poly(4-methylstyrene)-*block*-poly(styrene)copolymer, determined by 10 °C/min heating rate DSC scans. [g] Glass transition temperature relative to the *isotactic*-poly(4-methylstyrene)-*block*-poly(styrene) copolymer, determined by 10 °C/min heating rate DSC scans.

Table 4. Diblock Copolymers of 4-Methylstyrene and 1,3-Butadiene by Sequential Monomer Addition with 1/MAO

			PP MS-block		(PP MS-*b*-PB)[e]		
run[a]	X_{PMS} (feed)[b]	X_{PMS} (copolymer)[c]	M_n[d] (g/mol × 10^{-3})	M_w/M_n[d]	M_n[e] (g/mol × 10^{-3})	M_w/M_n[e]	$T_{\mathrm{m,PB}}$[f] (°C)
20	0.20	0.33	54.8	1.06	94.5	1.36	46.3/85.3
21	0.40	0.53	80.6	1.07	118.4	1.24	47.6/86.8
22	0.50	0.62	98.3	1.07	137.1	1.20	49.8/90.1
23	0.60	0.74	123.7	1.08	163.7	1.18	46.6/94.1
24	0.80	0.85	146.0	1.09	177.7	1.13	93.4

[a] Polymerization conditions: Ti = 10.0 μmol; [Al]/[Ti] 1200; T_{run} = 25 °C; V_{tot} = 30 mL; polymerization time: 1 h (4-methylstyrene) + 3 h (butadiene). [b] 4-Methylstyrene molar fraction in the feed (the molar amounts of monomer are reported in the Experimental Part). [c] 4-Methylstyrene molar fraction, determined from ^{1}H NMR spectra. [d] Relative to the *isotactic*-poly(4-methylstyrene) block. [e] Relative to the *isotactic*-poly(4-methylstyrene)-*block*-1,4-*trans*-poly(butadiene). [f] Melting temperature relative to the 1,4-*trans*-polybutadiene block in the resulting *isotactic*-poly(4-methylstyrene)-*block*-1,4-*trans*-poly(butadiene), determined by 10 °C/min heating rate DSC scans.

As shown in Table 4, copolymers within a wide range of compositions (4-methylstyrene molar fraction, $X_{\mathrm{p,MS}}$, value ranging between 0.33 and 0.85) are obtained, the yield is close, in any case, to the total conversion, and no broadening of the molecular weight distribution with polymerization time is observed. The DSC heating scans of the as-formed *i*-poly(4-methylstyrene)-*block*-1,4-*trans*-polybutadiene samples show two endothermic phenomena relative to the 1,4-*trans*-PB block: the first one, ranging from 46.0 to 50.0 °C, is probably due to the transition from the crystal to the meso-phase of the 1,4-*trans*-PB, while the second one, which ranges between 85.3 and 94.1 °C, is due to the melting of the mesophase.[13] The glass transition temperatures, T_g, of the two blocks are not clearly distinguished.

Triblock Copolymers. As above-reported, we also obtained highly stereoregular triblock copolymers: *i*-poly(4-methylstyrene)-*block*-*i*-poly(styrene)-*block*-*i*-poly(4-methylstyrene), *i*-poly(4-methylstyrene)-*block*-*i*-poly(styrene)-*block*-*i*-poly(4-methyl-1,3-pentadiene), and *i*-poly(4-methylstyrene)-*block*-*i*-poly(styrene)-*block*-*i*-poly(4-*tert*-butylstyrene). For all triblock copolymer samples, the polymer yield is close, in any case, to the total conversion. In Table 5, the results of these syntheses are summarized.

As shown in Table 5, the as-formed triblock copolymers have high molecular weight, and no broadening of the molecular weight distribution with polymerization time is observed. In Figure 3, as an example, the GPC profile of the triblock *i*-poly(4-methylstyrene)-*block*-*i*-poly(styrene)-*block*-*i*-poly(4-methylstyrene) sample (run 25) is shown and compared with those of aliquots of *i*-poly(4-methylstyrene) (A-block) and *i*-poly(4-methylstyrene)-*block*-*i*-poly(styrene) (AB-diblock) taken from the polymerization mixture after the formation of each block (see Table 5).

The shift of GPC traces toward higher molecular weight regions, after each step in the synthesis, via sequential monomer addition, of the ABA triblock copolymer confirms that this process proceeds in a living fashion (see Figure 3). Analogous results were obtained in GPC analysis of the ABX triblock copolymer samples (see Table 5, runs 26 and 27).[14]

The thermal features of the triblock copolymers was investigated by means of DSC analysis. The *isotactic* polystyrene segment (B-block) of *i*-poly(4-methylstyrene)-*block*-*i*-poly(styrene)-*block*-*i*-poly(4-methylstyrene) sample (run 25, ABA) is crystalline (T_m = 232 °C), while the two *isotactic* poly(4-methylstyrene) segments (A-blocks) are amorphous. As reported in Table 5, in *i*-poly(4-methylstyrene)-*block*-*i*-poly(styrene)-*block*-*i*-poly(4-methyl-1,3-pentadiene) and *i*-poly(4-methylstyrene)-*block*-*i*-poly(styrene)-*block*-*i*-poly(4-*tert*-butylstyrene) samples (ABC- and ABD-triblock copolymers of Table 5, respectively), the *i*-poly(styrene), *i*-poly(4-methyl-1,3-pentadiene) and *i*-poly(4-*tert*-butylstyrene) blocks are crystalline (B-, C-, and D-blocks of Table 5, respectively) while the *isotactic* poly(4-methylstyrene) segment (A-block) is amorphous.

End-Groups Analysis of Low Molecular Weight Isotactic Polystyrene. The regiochemistry of insertion of styrene with this family of catalysts was already investigated by performing the polymerization in presence of ^{13}C-enriched Al(CH$_3$)$_3$.[16b] Under these conditions we found that the polymerization is highly regioselective in the initation step, giving exclusively the chain end due to the secondary insertion (e.g., a methine−Ti bond is formed) of styrene into the Ti−CH$_3$ bond. The living behavior of catalytic system **1**/MAO in the polymerization of styrene allow us also to synthesize an isotactic polystyrene sample with low molecular weight in which it is possible to detect the end groups in natural abundance by using ^{1}H and ^{13}C NMR techniques. The styrene concentration and the polymerization time were properly chosen (see Experimental Part) in order to obtain a sample of *isotactic* polystyrene having a low molecular weight value (M_n, of 3.2 × 10^3 Da) and a narrow molecular weight distribution, (M_w/M_n = 1.12). The average molecular weight, M_n, determined by GPC and NMR techniques are in good agreement. The full attribution of ^{1}H and ^{13}C NMR chain end signals was performed giving new insights into polymerization mechanism involved in styrene polymerization with **1**/MAO. Figure 4 shows the ^{13}C NMR spectrum of the aliphatic and aromatic regions of this sample. One can observe, in addition to the main peaks due to the isotatctic polystyrene chain, the presence in the aliphatic region of the resonances (12.2, 28.7, and 44.7 ppm) expected for the secondary insertion of the styrene unit into the Ti-CH$_3$ bond (**A** in Scheme 3) and the presence of the resonances (33.6, 37.4, and 43.9 ppm) relative to the protonolysis of the growing chain with the same regiochemistry (**B** in Scheme 3).[17−19]

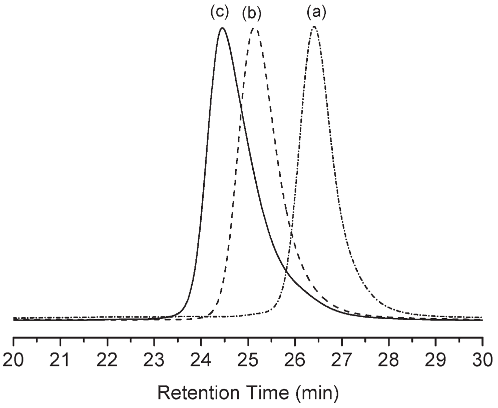


Figure 3. GPC traces of the ABA-triblock copolymer (run 25) after each step in the polymerization: (a) *isotactic*-poly(4-methylstyrene) (A-block), (b) *isotactic*-poly(4-methylstyrene)-*block*-*isotactic*-polystyrene (AB-diblock), and (c) *isotactic* poly(4-methylstyrene)-*block*-*isotactic*-polystyrene-*block*- *isotactic*-poly(4-methylstyrene) (ABA-triblock) (see Table 5).

The observed chain ends **A** and **B** are those expected for a living polymerization in which the polymerization starts into the Ti−CH$_3$ bond and the termination only occurs by quenching the polymerization in acidified ethanol (protonolysis). Unexpectedly, the resonances (46.4, 130.4, and 133.7 ppm) relative to the chain end **C** due to the β-hydride elimination reaction with *cis* configuration[18] are clearly visible in the spectrum.[19]

The presence of the unsaturated end group **C** seems incompatible with a living chain growth mechanism and with the narrow molecular weight distribution of the polystyrene. However, the absence of the resonances relative to the chain end due to initiation into the Ti−H bond suggests that the β-hydrogen reaction does not represent an irreversible termination reaction but the unsaturated polymer chain is a resting state in equilibrium with chain growth state (see Scheme 4).

This scenario is very similar to that hypothesized for the controlled, syndiospecific polymerization of styrene promoted by Cp*Ti(CH$_2$Ph)$_3$/B(C$_6$F$_5$)$_3$[18] and supports the observation that, even in the "living" stereospecific styrene polymerization promoted by titanium catalysts, the β-hydrogen reaction is not completely suppressed but represents rather a dormant state.

■ CONCLUSIONS

The catalyst **1** activated by MAO is able to promote living polymerization of 4-methyl-1,3-pentadiene, 4-methyl-styrene, and 4-*tert*-butylstyrene to give highly isotactic poly-1,2-(4-methyl-1,3-pentadiene), poly(4-methylstyrene), and poly(4-*tert*-butylstyrene), respectively. Furthermore, the sequential monomer addition, at room temperature, in the presence of **1**/MAO allowed the facile synthesis of several highly stereospecific, diblock, and triblock copolymer samples with high molecular weight and within a wide range of monomer compositions. All the polymer blocks in obtained copolymers, except the poly (4-methylstyrene) one, are crystalline as the corresponding homopolymers. We are currently investigating the properties of these new copolymeric materials and looking for possible applications.

Table 5. Triblock Copolymers of 4-Methylstyrene (A), Styrene (B), 4-Methyl-1,3-pentadiene (C), and 4-*tert*-Butylstyrene (D) via Sequential Monomer Addition

	A	B	X	A	B	X	A-block		AB-diblock		ABX-triblock				
run[a]	X_A[b]	X_B[b]	X_X[b]	X_A[c] (copolymer)	X_B[c] (copolymer)	X_X[c] (copolymer)	M_n (g/mol × 10^{-3})[d]	M_w/M_n[d]	M_n (g/mol × 10^{-3})[e]	M_w/M_n[e]	M_n (g/mol × 10^{-3})[f]	M_w/M_n[f]	$T_{m,B}$[g] (°C)	$T_{m,X}$[h] (°C)	T_g[i] (°C)
25[j]	31.8	36.4	31.8	36.0	39.5	24.5	102.8	1.07	202.1	1.12	271.9	1.20	232.3		102.1
26[k]	30.4	34.8	34.8	39.4	38.4	22.2	129.9	1.07	241.5	1.16	314.7	1.27	227.4	83.2	15.2/100.6/108.0
27[l]	34.9	39.9	25.2	40.0	42.0	18.0	136.1	1.08	261.3	1.14	339.9	1.23	227.4	292.1	98.5/108.5

[a] Polymerization conditions: Ti =10.0 μmol; [Al]/[Ti] = 1200; T_{run} = 25 °C; V_{tot} = 40 mL; polymerization time: 1.5 h (A-monomer) + 1.5 h (B-monomer) +1.5 h (X-monomer). [b] Monomer molar fractions in the feed. [c] Monomer molar fractions in the resulting triblock copolymer, determined from GPC. [d] M_n and M_w/M_n values, determined from GPC, relatives to the first isotactic poly(4-methylstyrene) (A) block. [e] M_n and M_w/M_n values, determined from GPC, relatives to the isotactic-poly(4-methylstyrene)-*block*-poly(styrene) (AB-diblock). [f] M_n and M_w/M_n values, determined from GPC, relatives to the ABX-triblock copolymer. [g] Melting temperature relative to the isotactic poly(styrene), (B-), block in the resulting ABX-triblock copolymer, determined by the first DSC heating scan. [h] Melting temperature relative to the X-block in the resulting ABX-triblock copolymer, determined by the first DSC heating scan. [i] T_g value determined by the second DSC heating scan. [j] ABA-triblock copolymer. [k] ABC-triblock copolymer. [l] ABD-triblock copolymer.

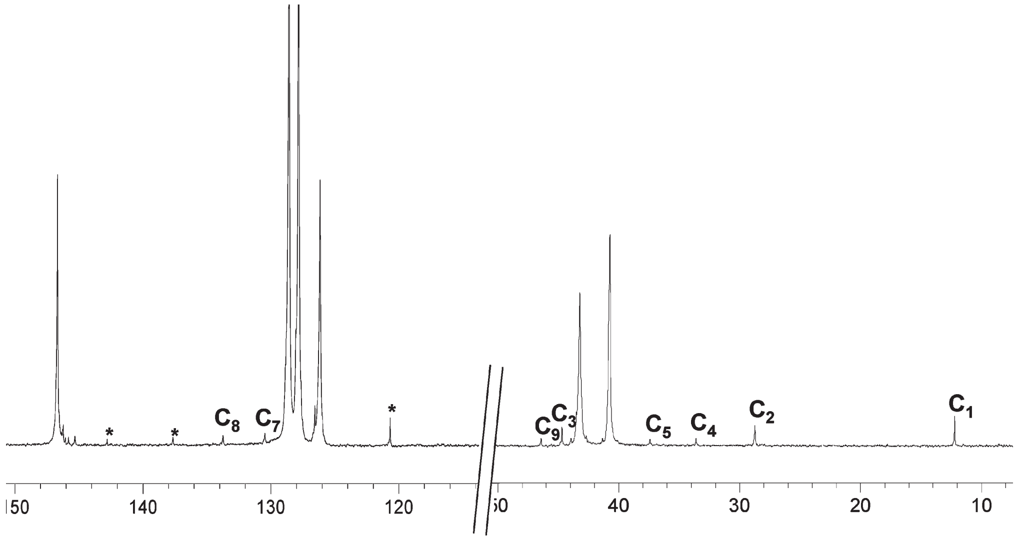
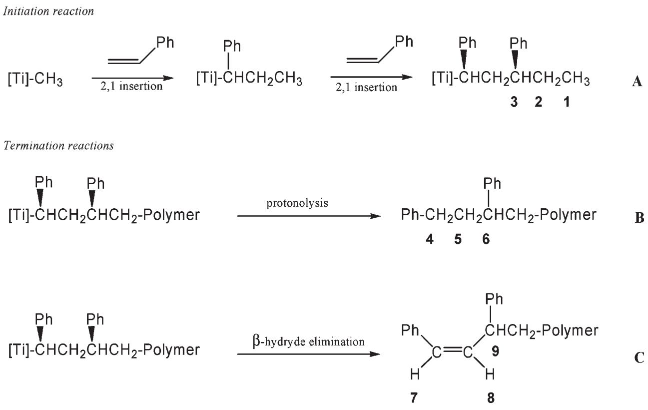
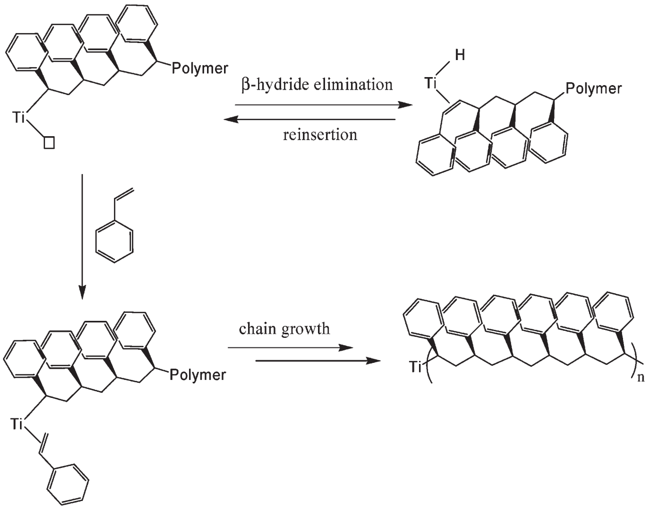


Figure 4. $^{13}C\{^1H\}$ NMR spectrum of a low molecular weight (3.2×10^3 Da) *isotactic* polystyrene sample prepared in the presence of catalyst **1**/MAO. The numbering of the resonances follows Scheme 2. The peaks marked with an asterisk are probably due e to the aromatic carbons of the chain ends.

Scheme 3. Isotactic Polystyrene Chain Ends



Scheme 4. Proposed Mechanism for the Formation of Unsaturated Chain Ends



Finally, the end-group analysis of a polystyrene sample with low molecular weight gave new insights into polymerization mechanism involved in styrene polymerization with **1**/MAO.

■ 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). Styrene and para-substituted styrenes (Aldrich) were purified by distillation under reduced pressure after stirring over calcium hydride for 10 h. 4-Methyl-1,3-pentadiene, synthesized in our laboratory, according to a literature procedure,[15] was used, as prepared, without further purification procedure. Methylalumoxane (MAO), purchased from Aldrich 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. Catalyst precursor **1** was prepared as previously reported.[16a]

Polymerization of Styrene at Low Molecular Weight. The polymerization run was carried out as follows. A 100 mL flask equipped with a magnetic bar was charged with toluene (6 mL), MAO (0.700 g, Al/Ti = 120), and 0.1 mL (1.0 mmol) of styrene. After equilibration of the solution at the polymerization temperature (25 °C) the reaction was started by injection of a toluene solution (4 mL) of the catalyst (10.0 μmol). The run was terminated after 15 min, and the polymer was coagulated by introducing ethanol (100 mL) acidified with aqueous HCl. The polymer was recovered by filtration, washed with an excess of ethanol, and dried in vacuo at room temperature.

Homopolymerization of Substituted Styrenes (Runs 1−6MS and 1TBS−5TBS). For 4-methylstyrene and 4-*tert*-butylstyrene monomers, the polymerization runs were carried out following a standard procedure. A 100 mL flask equipped with a magnetic bar was charged with toluene (20 mL), MAO (0.700 g, Al/Ti = 12000), and substituted styrene (8.3 mmol). After equilibration of the solution at the polymerization temperature (20 °C) the reaction was started by injection of a toluene solution (1 mL) of the catalyst (1.0 μmol). The run was terminated after the desired time 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.

Homopolymerization of 4-Methyl-1,3-pentadiene (Runs 1−6). The polymerization runs were carried out following a standard procedure. was charged with toluene (10 mL), MAO (0.700 g, Al/Ti = 12000), and 4-methyl-1,3-pentadiene (8.7 mmol). After equilibration of the solution at the polymerization temperature (20 °C) the reaction was started by injection of a toluene solution (1 mL) of the catalyst (1.0 μmol). The run was terminated after the desired time 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.

Sequential Diblock Copolymerization of Styrene and 4-Methyl-1,3-pentadiene (Runs 7−14). The sequential block copolymerization runs of styrene with 4-methyl-1,3-pentadiene were carried out as follows. A 100 mL flask equipped with a magnetic bar was charged with toluene, MAO (0.700 g, Al/Ti = 1200), and styrene. After equilibration of the solution at the polymerization temperature (25 °C) the reaction was started by injection of a toluene solution (1 mL) of the catalyst (10.0 μmol). After 1 h of polymerization a small amount of the polymer solution was taken out for the evaluation of the conversion of styrene monomer and the molecular weights of the corresponding styrene polymer blocks. The 4-methyl-1,3-pentadiene monomer was then rapidly added to this flask. The copolymerization continuously proceeded for an additional time of 2 h and then was terminated 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.

Sequential Diblock Copolymerization of 4-Methylstyrene and Styrene (Runs 15−19). The sequential block copolymerization runs of 4-methylstyrene with styrene were carried out as follows. A 100 mL flask equipped with a magnetic bar was charged with toluene, MAO (0.700 g, Al/Ti = 1200) and 4-methylstyrene (run 15: 1.8 mmol; run 16: 3.5 mmol; run 17: 5.2 mmol; run 18: 7.0 mmol; run 19: 8.3 mmol). After equilibration of the solution at the polymerization temperature (25 °C) the reaction was started by injection of a toluene solution (1 mL) of the catalyst (10.0 μmol). After 1 h of polymerization a small amount of the polymer solution was taken out for the evaluation of the conversion of the 4-methylstyrene monomer and the molecular weights of the corresponding 4-methylstyrene polymer blocks. The styrene monomer was then rapidly added to this flask. The copolymerization continuously proceeded for an additional time of 1 h and then was terminated 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.

Sequential Diblock Copolymerizations of 4-Methylstyrene and 1,3-Butadiene (Runs 20−24). The sequential block copolymerization runs of 4-methylstyrene with 1,3-butadiene were carried out as follows. A 100 mL flask equipped with a magnetic bar was charged with toluene, MAO (0.700 g, Al/Ti = 1200), and 4-methylstyrene (run 20: 3.8 mmol; run 21: 6.8 mmol; run 22: 8.3 mmol; run 23: 10.6 mmol; run 24: 13.7 mmol). After equilibration of the solution at the polymerization temperature the reaction was started by injection of a toluene solution (1 mL) of the catalyst (10.0 μmol). After 1 h of polymerization a small amount of the polymer solution was taken out for the evaluation of the conversion of the 4-methylstyrene monomer and the molecular weights of the corresponding 4-methylstyrene polymer blocks. A toluene solution of 1,3-butadiene (2.3 M) was then rapidly added to this flask. The copolymerization continuously proceeded for an additional time of 3 h and then was terminated 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.

Sequential Triblock Copolymerizations (Runs 25−27). The syntheses of *i*-poly(4-methylstyrene)-*block*-*i*-poly(styrene)-*block*-*i*-poly(4-methylstyrene) (ABA-triblock), *i*-poly(4-methylstyrene)-*block*-*i*-poly(styrene)-*block*-*i*-poly(4-methyl-1,3-pentadiene) (ABC-triblock), and *i*-poly(4-methylstyrene)-*block*-*i*-poly(styrene)-*block*-*i*-poly(4-*tert*-butylstyrene) (ABD-triblock) were carried out as follows. A 100 mL flask equipped with a magnetic bar was charged with toluene (36 mL), MAO (0.700 g, Al/Ti = 1200), and 4-methylstyrene (1 mL, 7.6 mmol). After equilibration of the solution at the polymerization temperature (25 °C) the reaction was started by injection of a toluene solution (1 mL) of the catalyst (10.0 μmol). After 1.5 h of polymerization a small amount of the polymer solution was taken out for the evaluation of the conversion of the 4-methylstyrene monomer and the molecular weight of the corresponding first 4-methylstyrene polymer block (A-block). The styrene monomer (1 mL, 8.7 mmol) was then rapidly added to this flask. The copolymerization continuously proceeded for an additional time of 1.5 h. A small amount of the copolymer solution was taken out for the evaluation of the conversion of the styrene monomer, the molecular weight of the corresponding 4-methylstyrene-*block*-styrene copolymer (AB-diblock) and of the second styrene polymer block. The monomer (1 mL) required to form the third polymer block of copolymer was then rapidly added to the flask. The copolymerization continuously proceeded for an additional time of 1.5 h and then was terminated by introducing ethanol (15 mL) containing the antioxidant (Wingstay K; 0.5−0.75 phr). The ABA-, ABC-, and ABD-triblock copolymers were 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.

Characterization of the Polymers. The ^{1}H and ^{13}C NMR spectra of the styrene homopolymer sample at low molecular weight and of diblock and triblock copolymers samples were recorded on a Bruker AVANCE DRX 300 or 400FT-NMR spectrometers (300 MHz for ^{1}H and 75 MHz for ^{13}C or 400 MHz for ^{1}H and 100 MHz for ^{13}C, respectively). Using 5 mm (o.d.) NMR tubes, polymer samples (30 mg) were dissolved in 1,1,2,2-tetrachlorodideuterioethane-d_2 ($C_2D_2Cl_4$) (0.7 mL) or $CDCl_3$ and analyzed at 298 K. Chemical shifts were referenced to TMS and calculated by using the residual isotopic impurities of the deuterated solvent. The thermal analysis of the polymers was carried out on TA Instruments DSC-2920 calibrated against an indium standard (T_m = 156.6 °C), with scans at 10 °C/min heating rate under a flowing nitrogen atmosphere. Specimens were sealed in aluminum pans.

The average molecular weights of the polymer and copolymer samples were determined at 35 °C by 150 Waters instrument GPCV 2000 equipped with JASCO 875-UV(254 nm) and WGE-DR BURES ETA1002 refractive index detectors, using four PSS columns set consisting of, 10^6, 10^5, 10^4, and 10^3 Å (pore size) with 10 μm (particle size). Tetrahydrofuran was the carrier solvent used with a flow rate of 1.0 mL/min. The calibration curve was established with polystyrene standards.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Plots of M_n and M_w/M_n versus conversion for PMS and PTBS polymerization using **1**/MAO and ^{1}H and ^{1}H/^{13}C HMQC and DEPT135 for the low molecular weight polystyrene sample and the DCS thermograms and GPC traces of the triblock copolymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) See Supporting Information for the ^{1}H NMR, DEPT 135, and HMQC experiments that allow us to unambiguously assign the resonances relative to the chain ends.