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Copolymerization of Styrene with Butadiene and Isoprene Catalyzed by the Monocyclopentadienyl Titanium Complex $Ti(\eta^5\text{-}C_5H_5)(\eta^2\text{-MBMP})Cl$

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ABSTRACT: Polymerization of butadiene, isoprene, and styrene was investigated using the catalyst $Ti(\eta^5\text{-}C_5H_5)(\eta^2\text{-MBMP})Cl$ (**1**) (MBMP = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxo)) activated with methylaluminoxane (MAO). Syndiotactic polystyrene and *cis*-1,4-polybutadiene were obtained at 50 °C, similarly to other monocyclopentadienyl titanium catalysts previously reported. On the contrary, the **1**/MAO catalyst resulted extremely active in isoprene polymerization, producing polymers with mainly *cis*-1,4 structure and containing head-to-head and tail-to-tail enchainments of the monomer units in a molar concentration of 21.5%. Binary copolymerization of styrene with butadiene yielded block copolymers containing segments of *cis*-1,4-polybutadiene and crystalline syndiotactic polystyrene. The reactivity ratios $r_1 = 70$ and $r_2 = 1.2$ determined by NMR methods confirmed the blocky distribution of the monomers in the copolymer chain. The AFM of copolymers rich in styrene ($x_S = 0.77-0.81$) showed a microphase separation of polybutadiene domains in micrometric scale (average radius 800 nm). Novel copolymers of styrene with isoprene were synthesized using the **1**/MAO catalyst. The ^{13}C NMR chemical shifts of the carbon atoms diagnostic of the different monomer diads and triads were predicted and assigned using properly calculated additive shift factors. The reactivity ratios $r_1 = 18$ and $r_2 = 0.3$ were evaluated by means of NMR methods. Despite the syndiotactic arrangement of the styrene homosequences, the styrene-*co*-isoprene polymers are completely soluble in organic solvents and completely amorphous also at high styrene concentration.

Introduction

High impact polystyrene (HIPS) is a rubber-modified styrenic polymer manufactured in tons scale/year for many practical applications. It consists of a rubber, generally polybutadiene, homogeneously dispersed under the form of discrete particles throughout the hard matrix of atactic polystyrene or styrenic copolymers (e.g., styrene−acrylonitrile (SAN) or acrylonitrile−butadiene−styrene (ABS)).[1] As a consequence of the immiscibility of polystyrene and polybutadiene, the blends of these two polymers as well as the styrene-*b*-butadiene polymers are phase-separated materials in which the morphology and dimension of the rubber particles are determined by the relative volume of the polymers and the synthetic procedure used. The chemical interactions between the polystyrene and rubber domains control the initiation and growth of crazes, eventually formed in the thermoplastic domains, and reinforce the rubber. The morphological control and the size of the rubber nanoparticles are critical for the final properties of the material.[1]

HIPS and copolymers of styrene with conjugated dienes, e.g., SBR, are typically synthesized by means of free radical emulsion processes[2] or solution processes based on living anionic polymerization catalyzed by alkyllithium compounds.[3] The lack of steric control leads to stereoirregular styrene sequences as well as stereo- and regioirregular diene incorporation. In these cases the microstructure of the polymers largely depends on the solvent, monomer concentration, temperature, and the presence of Lewis base additives. Rubber-modified polystyrene can be also obtained polymerizing styrene in a solution containing the rubber or by blending polybutadiene and polystyrene.[1] In the latter the phase inversion is accomplished by hard mixing and curing of the polymer mixture in the reactor. When compared to the blended products, the *in situ* synthesized rubber-in-styrene polymers usually results in a superior product exhibiting higher modulus and equivalent impact strength with less rubber.[1]

Syndiotactic polystyrene is a novel crystalline thermoplastic exhibiting several interesting physical and chemical properties, such as high heat resistance, high crystallization rate, good insulating properties, excellent processing characteristics, outstanding dimensional stability, and low moisture absorption.[4] Similarly to other crystalline polymers, syndiotactic polystyrene suffers the strong limitation to be brittle under normal use conditions. Thus, the synthesis of stereoregular styrene copolymers with conjugated dienes, mainly butadiene and isoprene, is expected to lead to novel high impact polystyrenes that can enlarge the window of practical applications of this polymer.

Syndiotactic polystyrene is typically manufactured by solution processes using monocyclopentadienyltitanium compounds $Cp'TiX_3$ ($Cp' = C_5H_5$, C_5Me_5, or Ind; $C_5H_4(^tBu)$; X = halide, alkoxo, alkyl), activated with methylaluminoxane (MAO).[5] The stereospecific insertion of the monomer on the titanium−alkyl bond is secondary (2,1-insertion),[6] and the polymerization mechanism follows a chain-end or zero-order Markov statistics.[7] The value of the polydispersity index of the average molecular weights ($PDI = M_w/M_n$) for polymers by monocyclopentadienyltitanium catalysts is about 2, suggesting a single site behavior of these catalysts and a reduced chain transfer to the aluminum of MAO. The syndiotactic specific styrene polym-

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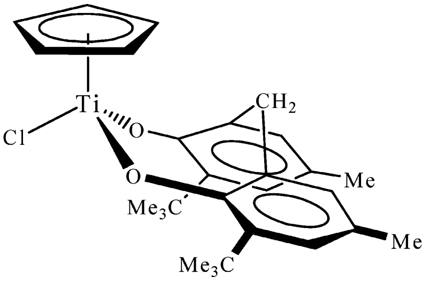


Figure 1. Ti(η^5-C$_5$H$_5$)(η^2-MBMP)Cl (**1**) (MBMP = 2,2′-methylenebis-(6-*tert*-butyl-4-methylphenoxo).

erization catalysts based on cyclopentadienyltitanium compounds are also active in living *cis*-1,4 specific regio- and stereoregular polymerization of butadiene.[8] Copolymerization of styrene with butadiene has been successfully accomplished with the Cp′TiX$_3$/MAO (Cp′ = C$_5$H$_5$, X = Cl, F; Cp′ = C$_5$Me$_5$, X = Me) under different polymerization conditions.[9,10] The resulting copolymers exhibit a blocky nature consisting of crystalline syndiotactic polystyrene segments, with melting points in the range 200−230 °C, and rubber segments of *cis*-1,4-polybutadiene containing 6−12 mol % of isolated 1,2-vinyl units.[10]

To date, there are very few reports on transition-metal-catalyzed polymerization of isoprene and copolymerization of isoprene with styrene because of the low reactivity of this monomer with transition metal organometallics. A limited number of stereoregular isoprene polymers have been described in the literature. Heterogeneous or supported Ziegler−Natta titanium catalysts give *trans*-1,4-polyisoprene (>85 mol %);[11] mixtures of vanadium halides with trialkylaluminum compounds lead to polymers with the same microstructure but in higher yields.[12] Middle-late catalysts based on iron complexes produce 3,4-polyisoprene (up to 99 mol %) with elevated efficiency.[13] Isotactic 3,4-polyisoprene have been obtained with extremely high regio- and stereoselectivity (*mmmm* > 99%) using lanthanide-based catalysts.[14]

CpTiCl$_3$/MAO is scarcely active in styrene-*co*-isoprene polymerization,[15] and a full characterization of the structure of this copolymer was not previously reported. Recently, a novel cyclopentadienyltitanium complex bearing a chelated diphenoxo ligand, namely Ti(η^5-C$_5$H$_5$)(η^2-MBMP)Cl (**1**) (MBMP = 2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxo), Figure 1), has been described as efficient catalyst in *cis*-1,4-isoprene polymerization and syndiospecific styrene polymerization.[16]

This discovery prompted us to investigate the binary copolymerization of styrene with butadiene and isoprene, allowing the synthesis of these copolymers and their full characterization.

Results and Discussion

Polymerization of Styrene, Butadiene, and Isoprene. Styrene, butadiene, and isoprene polymerizations catalyzed by the monocyclopentadienyltitanium catalyst **1**/MAO are compared in Table 1. Two parallel sets of polymerization runs were carried out using the commercial solution of MAO in toluene (10 wt % with a trimethylaluminum concentration of 37 mol %) (runs 1−3) as cocatalyst or powder sample of MAO produced by distilling off both the solvent and *not coordinated* trimethylaluminum (*d*-MAO) (runs 4−6).

The head-to-head comparison of the runs 1−3 and 4−6 shows an increment of the polymer yields of about 1 order of magnitude in styrene and isoprene polymerization and a 2-fold increase in butadiene polymerization when the commercial toluene solution of MAO was employed. Moreover, a parallel increase of the PDIs from a value typical of a single site catalyst (runs 5, 6) to that of a multisite catalyst (runs 2, 3) was observed at variance of the used cocatalyst. A possible explanation is that the alkylaluminum compound could increase the molar concentration of Ti(III) species, expected to be the active catalyst species in syndiospecific styrene and conjugated diene polymerization.[17] However, the reaction/coordination of trimethylaluminum with the titanium complex[18] could lead to different catalysts determining the broadening of the average molecular weight distribution.

Despite the cocatalyst employed, the polymerization activities are in the order butadiene > styrene > isoprene. This trend is the same previously observed with CpTiCl$_3$ and other monocyclopentadienyltitanium catalysts.[19] The higher polymerization activity of butadiene was explained in light of the polymerization mechanism proposed for the conjugated alkadienes polymerization.[20] The rate-determining step is the monomer coordination that produces a substantial shift from η^3- to η^1-coordination of the allyl intermediate metal complex followed by monomer insertion (see Scheme 1). The higher coordination energy to the metal of the 2-methylbutenyl chain end vs the butenyl chain ending accounts for the different polymerization activities of isoprene vs butadiene (Scheme 1).

In the case of styrene, the secondary insertion of this monomer onto titanium−polymer bond leads to a benzyl type chain ending that is η^7-coordinated to the metal through the aromatic ring: this coordination has been proposed as the origin of the stereocontrol in syndiospecific styrene polymerization by monocyclopentadienyltitanium catalysts.[17] Indeed, theoretical studies showed that transition states for the insertion of the *cis*-η^4-coordinated monomer is at least 30 kJ lower in energy when the aromatic ring of the last enchained monomer units is coordinated to the metal.[21] The similarity of the transition states and the trend of the coordination energy of the growing polymer chain to the metal explain the observed trend of the polymerization activities.

The chemical structure of the polymers by **1**/MAO is the one expected for addition polymerization catalyzed by monocyclopentadienyltitanium compounds. The syndiotacticity of the polystyrene is very high (*rrrr* > 98%), and the polybutadiene consists of *cis*-1,4 segments spanned by isolated 1,2-vinyl (18 mol %) and *trans*-1,4 (9.3 mol %) units. As a matter of fact, the aliphatic region of the ^{13}C NMR spectrum of this polymer exhibits a main signal at 27.6 ppm, diagnostic of the methylene carbon atoms C$_1$/C$_4$ of the CCC triad (C = *cis*-1,4-butadiene) and additional signals at 25.2, 34.5, and 43.9 ppm, attributed to the methylene carbon atoms C$_4$VC, CV$_1$C, and methine CV$_2$C, respectively (V = 1,2-vinyl).[10] A signal at 33.0 ppm accounts for the methylene carbon atoms T$_1$/T$_4$ of isolated *trans*-1,4-units in CTC sequence (T = *trans*-1,4-butadiene).[22] The ^{13}C resonances diagnostic of the TT and VV diads[23] have not been observed in the spectrum of this sample.

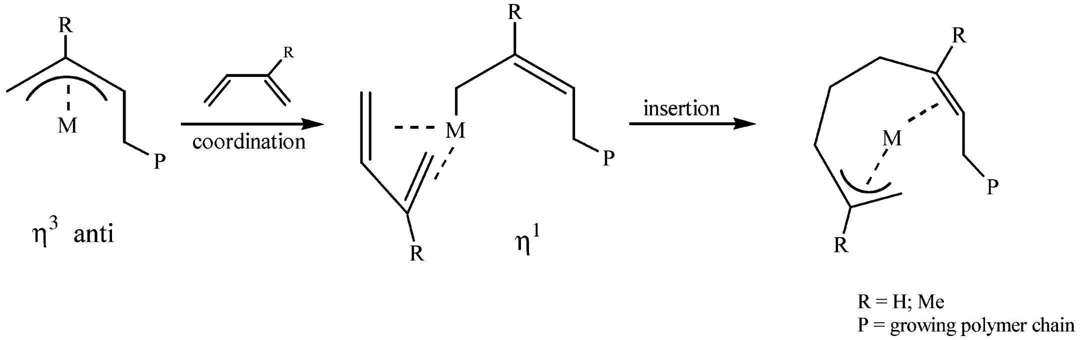
The isoprene polymerization catalyzed by **1**/MAO is mainly *cis*-1,4-specific. The integration of the ^{1}H NMR signals at 5.13 and 4.73 ppm, attributed to the unsaturated methine and methylidene protons of 1,4- and 3,4-units, respectively, indicated a concentration of only 5.4 mol % of 3,4-isoprene (Scheme 2). The ^{13}C NMR signals at 32.4 (C$_1$), 26.6 (C$_4$), and 23.6 (C$_5$) ppm confirmed the *cis*-1,4 enchainment of the monomer units, whereas the signals at 48.1, 30.1, and 18.8 ppm suggested the presence of V$_3$, V$_4$, and V$_5$ carbon atoms of isolated 3,4-units.[24] A thorough inspection of the polymer structure by ^{13}C NMR spectroscopy revealed more interesting structural details. The presence of ^{13}C NMR signals at 30.8 and 28.6 ppm highlighted

Table 1. Polymerization of Styrene, Isoprene, and Butadiene by Ti(η^5-C_5H_5)(η^2-MBMP)Cl (1) (MBMP = 2,2′-Methylenebis(6-*tert*-butyl-4-methylphenoxo) Activated with MAO

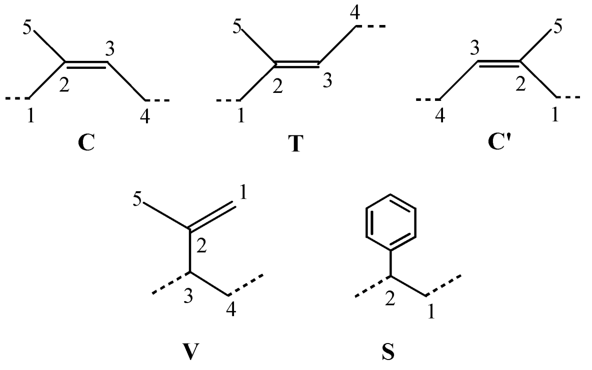
run[a]	monomer	yield (g)	conversion (%)	microstructure (mol %)	$M_w \times 10^3$ (Da)	M_w/M_n
1	styrene	2.25	49.5	*rrrr* > 98.0	33	2.0
2	isoprene	1.19	35.0	$I_{1,4} = 94.6$ $I_{3,4} = 5.4$	566	3.5
3	butadiene	2.61	96.0	$B_{1,4} = 82.0$ $B_{1,2} = 18.0$	1155	3.4
4[b]	styrene	0.296	6.5	*rrrr* > 98.0	46	2.0
5[b]	isoprene	0.165	4.8	$I_{1,4} = 93.4$ $I_{3,4} = 6.6$	755	2.5
6[b]	butadiene	0.763	28.0	$B_{1,4} = 80.4$ $B_{1,2} = 19.6$	3512	2.0

[a] Polymerization conditions: 2.2×10^{-5} mol of catalyst ([Ti] = 5.5×10^{-4} M); MAO (10 wt % toluene solution); Al/Ti = 1000; 5 mL of monomer (5.0×10^{-2} mol); $T = 50$ °C; polymerization time = 20 min. [b] *d*-MAO as cocatalyst.

Scheme 1



Scheme 2



the presence of head-to-head and tail-to-tail enchainment of *cis*-1,4-isoprene units[24] detected in a concentration of 21.5 mol % comparable to that of polyisoprene by $C_5H_4(^tBu)TiCl_3$ and $CpTiCl_3$.[25] Moreover, *cis*-1,4-polyisoprene by $C_5H_4(^tBu)TiCl_3$ exhibited higher concentration of vinyl isoprene units (16.7 mol %) than the polymer by **1** whereas the molar concentrations of the 3,4-vinyl and 1,2-vinyl units in the polymers by $CpTiCl_3$ are 5.9 and 3.5 mol %, respectively.[25] The lack of ^{13}C signals at 16.0, 26.8, and 39.7 ppm attributed to *trans*-1,4-isoprene units suggests an elevated *cis*-1,4-type stereospecificity of the title catalyst in isoprene polymerization. The polybutadiene produced by **1**/MAO exhibits a glass transition temperature (T_g) of −97 °C, a typical value for *cis*-1,4-polybutadiene. On the contrary, the T_g of the polyisoprene by the title catalyst was observed at −54 °C, a temperature value higher than that observed in polyisoprene by anionic polymerization that is typically reported at −73 °C. The increment of the T_g could be tentatively assigned to the high molar concentration of regioirregular isoprene units which could give more stiffness to polymer chains.

Copolymerization of Styrene with Butadiene. The catalytic performances of **1** in the homopolymerization of styrene and butadiene prompted us to copolymerize these monomers in order to highlight differences in the active species of this novel catalyst and $CpTiCl_3$.

Styrene-*co*-butadiene polymerization using the toluene solution of MAO (10 wt % in toluene) were carried out at 50 °C (Table 2). The copolymerization run 14, carried out with the $CpTiCl_3$/MAO catalyst under the same conditions of run 7, was also included for comparison.

Copolymers over the full range of composition were synthesized ($x_S = 0.29-0.81$; runs 7−13 of Table 2). The polymerization yields are comparable to those by the $CpTiCl_3$ catalyst at 25 °C, confirming that the copolymerization rate by monocyclopentadienyltitanium catalysts is roughly independent of temperature.[10] The structural analysis of the copolymers by ^{13}C NMR spectroscopy showed that the styrene homosequences exhibit a syndiotactic arrangement, and the *cis*-1,4-polybutadiene segments include 1,2-vinylbutadiene units in the range 5−9 mol %. Isolated *trans*-1,4-butadiene units are incorporated exclusively in the CTC heterosequence and detected in amount comparable to that observed in the homopolymer (7−10 mol %).

The average monomer block lengths were thus calculated using the ^{13}C NMR assignments and the method previously reported.[10] Styrene block lengths of 8 up to 20 were found in the copolymers with styrene molar fraction in the range $x_S = 0.29-0.81$ (runs 7−13 in Table 2). The reactivity ratios $r_1 = k_{BB}/k_{BS}$ and $r_2 = k_{SS}/k_{SB}$ (k_{ij} is the kinetic constant for the addition of M_i to a growing chain ending with a M_j monomer unit) were evaluated using the following equations:[9]

$$r_1(1/f) = 2[BB]/[BS] \tag{1}$$

$$r_2 f = 2[SS]/[SB] \tag{2}$$

where f is the composition in the feed (f = [S]/[B]) and the mole fraction of the monomer diads SS, BB, and SB (BS) were evaluated by integration of the appropriate ^{13}C NMR signals given in the Experimental Section. The values found for r_1 and

Table 2. Styrene-*co*-butadiene Polymerization by Ti(η^5-C_5H_5)(η^2-MBMP)Cl (1) Activated with MAO

				copolymer composition (mol %)						
run[a]	[S] (mol/L)	S/B	yield (g)	S	$B_{1,4}$	$B_{1,2}$	$M_w \times 10^3$ (Da)	M_w/M_n	n_s	$T_m{}^c$ (°C)
7	1.9	5	1.02	28.7	62.0	9.3			8.5	
8	2.6	7	1.39	33.0	58.0	9.0	57	2.4	9.2	
9	3.0	8	1.35	42.6	50.1	7.3	52	2.0	10.4	235
10	4.0	10	1.96	57.5	36.2	6.3	32	1.9	13.6	241
11	4.4	12	1.80	68.8	28.3	2.9	45	2.0	16.2	247
12	4.8	13	1.75	77.0	21.0	2.0	38	2.1	18.6	250
13	5.2	14	1.57	81.0	14.0	5.0	38	1.9	19.5	254
14[b]	2.6	7	1.12	30.1	59.9	10.0	19	1.6	8.6	

[a] Polymerization conditions: 2.2×10^{-5} mol of catalyst ([Ti] = 5.5×10^{-4} M); MAO (10 wt % toluene solution); Al/Ti = 1000; 1.5×10^{-2} mol of butadiene ([B] = 0.37 M); T = 50 °C; t = 1 h. [b] $CpTiCl_3$/MAO as catalyst. [c] Melting point of the syndiotactic polystyrene segments.

Table 3. Styrene-*co*-isoprene Polymerization by Ti(η^5-C_5H_5)(η^2-MBMP)Cl (1) Activated with MAO

					copolymer composition (mol %)				
run[a]	[S] (mol/L)	[I] (mol/L)	S/I	yield (g)	S	$I_{1,4}$	$I_{3,4}$	$M_w \times 10^3$ (Da)	M_w/M_n
15	1.7	0.57	3	0.89	22.9	71.7	5.4	38	2.4
16	2.3	0.57	4	1.02	43.9	51.9	4.2	28	1.8
17	2.8	0.57	5	1.20	48.1	49.1	2.7	31	1.8
18	3.4	0.57	6	1.12	49.9	47.9	2.2	39	2.3
19	4.0	0.57	7	1.07	58.6	38.1	3.3	37	2.0
20	4.3	0.54	8	1.50	65.3	32.0	2.7	33	1.9
21	5.1	0.57	9	1.37	69.2	27.6	3.1	37	1.9
22	4.8	0.48	10	1.63	69.7	27.5	2.8	35	1.9
23	5.0	0.46	11	1.79	71.3	25.9	2.8	38	2.1
24	5.2	0.43	12	1.60	73.5	22.1	4.4	37	1.9
25[b]	3.4	0.57	6	0.65	33.2	62.3	4.5	n.d.	n.d.

[a] Polymerization conditions: 2.2×10^{-5} mol of catalyst ([Ti] = 6.3×10^{-4} M); MAO (10 wt % toluene solution); Al/Ti = 1000; 2.0×10^{-2} mol of isoprene; T = 50 °C; t = 1 h. [b] The catalyst $CpTiCl_3$/MAO was treated for 10 min at 25 °C and then injected into the polymerization solution at 50 °C.

r_2 are in the ranges 62−78 and 0.9−1.6, respectively, and the reactivity ratio products in the range 56−125. The latter value, found higher than unity, suggests a blocky distribution of the monomers in substantial agreement with the previous results reported for styrene-*co*-butadiene polymerization catalyzed by $CpTiCl_3$.[9] The styrene-*co*-butadiene polymers by **1** exhibit melting points of the crystalline segments in the range 235−254 °C (see Table 2) in correspondence of styrene molar fractions in the range $x_S = 0.43-0.81$. The M_w values are in the range of 38−57 kDa, and the average molecular weights distributions are narrow, with PDIs close to 2, in agreement with the value expected for polymers by single site catalysts. In conclusion, the title catalyst exhibited performances in styrene-*co*-butadiene polymerization very similar to that of $CpTiCl_3$.

Copolymerization of Styrene with Isoprene. Copolymerization of styrene with isoprene was thus attempted under conditions comparable to those used in styrene-*co*-butadiene for a better understanding of the polymerization behavior of **1** and to characterize this novel copolymer by syndiospecific styrene polymerization catalyst. The monomer composition in the feed was calibrated in order to get copolymers with a styrene molar fraction in the range $x_S = 0.23-0.73$ (runs 15−24 of Table 3). It is worth noting that despite the different activities observed in the homopolymerization of butadiene and isoprene (see Table 1), the yields in styrene-*co*-butadiene polymerization are similar to those observed in styrene-*co*-butadiene polymerization.

The average molecular weights are in the range 28−39 kDa, and the PDI values are typical of copolymers by single site catalysts. The copolymers are solid at high concentration of styrene (runs 22−24) and waxy when the isoprene concentration is increased up to 77.0 mol % (runs 15−20). All copolymers are completely soluble in hexane, THF, or chloroform, also when styrene concentration approaches as high values as x_S = 0.70.

The DSC profiles exhibit T_g values increasing in the range from −33.6 to 54.9 °C as the styrene content in the copolymer sample is increased in the range $x_S = 0.23-0.73$. Endo peaks corresponding to the melting of syndiotactic polystyrene, expected in the temperature range 200−273 °C, were not observed also in the samples containing elevated concentration of styrene.

In Table 3 a styrene-*co*-isoprene polymerization run catalyzed by $CpTiCl_3$/MAO (run 25) was included for comparison. The microstructure of the copolymer obtained in this run is very similar to that produced by **1**/MAO, only showing a slightly higher content of regioirregular isoprene units (31.0 mol %) and lower amount of *trans*-1,4-units (1.3 mol %). In contrast, the productivity of these two catalysts is quite different. When the copolymerization was carried out in the same experimental conditions used for **1**/MAO, the productivity of $CpTiCl_3$ is rather low (0.030 g of copolymer in 1 h) and increases if the catalyst is aged for 10 min at 25 °C and then injected in monomers solution at 50 °C, according to the procedure proposed by Miyazawa et al.[25] However, also in this case this still remain lower than that observed with the title catalyst.

This result indicates that the replacement of 2,2′-methylenebis(6-*tert*-butyl-4-methylphenoxo) for two chlorine atoms produces an increase of the polymerization activity of monocyclopentadienyltitanium complexes in the styrene-*co*-isoprene polymerization. The same effect was found by Miyazawa et al. in the *cis*-1,4-specific polymerization of isoprene using the $C_5H_4(^tBu)TiCl_3$ catalyst at ambient or lower temperature.[25] They found that the alkyl substitution at the cyclopentadienyl ring increased the polymerization activity in styrene, butadiene, and isoprene polymerization. Moreover, living properties were found in butadiene polymerization carried out at −25 °C, in agreement with the pioneering studies of Soga et al. on butadiene polymerization catalyzed by $CpTiCl_3$.[8]

Table 4. Chemical Shift Additive Factors

unit	carbon position	factor (ppm)
styrene	α(Φ)	16.4
	β(Φ)	7.2
	γ(Φ)	−1.8
cis-1,4-isoprene	C_1(α)[a]	−2.44
	C (*β*)[a]	0.17
	C (*γ*)[a]	−0.12
	β_C(Me)	5.06
	γ_C(Me)	−1.61
	γ'_C(Me)	1.2
trans-1,4-isoprene	T_1(α)[a]	3.00
	T(*β*)[a]	0.05
	T(*γ*)[a]	−0.41
	β_T(Me)	7.32
	γ_T(Me)	−2.06
	γ′T(Me)	−4.44
3,4-isoprene	V_3(α)[a]	14.55
	V(*β*)[a]	5.46
	V(*γ*)[a]	−2.40
	β_V(Me)	3.91
	γ_V(Me)	−1.61

[a] Additive shift factors reported by Sato et al.[28]

Nomura et al. extensively studied the effect of 2,6-substituted aryloxo ligands on the performances of monocyclopentadienyltitanium complexes in styrene polymerization.[34] These authors proposed that this class of ligands could enhance both stereospecificity and activity of the titanium catalysts in styrene polymerization. Our results confirm the increased activity in isoprene and styrene-*co*-isoprene polymerization by titanium compounds carrying substituted aryloxo ligand. A possible explanation of this phenomenon is that this ligand, as well as the alkyl substitution at the cyclopentadienyl ligand, increases the reaction rate leading to Ti(III) active species determining an increased molar concentration of the active catalyst in the polymerization conditions. Further studies on this subject are in progress and will be reported elsewhere.

NMR Characterization of Styrene-*co*-isoprene Polymers. Structural characterization was carried out in order to establish monomer insertion and distribution in the copolymer chain. The chemioselectivity of isoprene insertion was evaluated by integration of the ^{1}H NMR resonances diagnostic of 1,4- and 3,4-insertion which produce signals at 5.15 and 4.78 ppm, respectively. The compositions of styrene (S), 1,4-isoprene ($I_{1,4}$), and 3,4-isoprene ($I_{3,4}$) are given in Table 3. The 3,4-vinyl isoprene content is roughly constant and changes from 2.2 mol % (run 18, $x_S = 0.50$) to 5.4 mol % (run 15, $x_S = 0.23$). The concentration of regioirregular (head-to-head or tail-to-tail) isoprene units in the copolymer chain is slightly higher (26.0 mol %) than that observed in the homopolymer. Although the polyisoprene by **1** catalyst did not exhibit *trans*-1,4-units, isolated units with this stereochemistry are found in the copolymers in concentrations of 2.1−3.5 mol %.

A full characterization of these copolymers was thus attempted by ^{13}C NMR spectroscopy. It is worth noting that few data are currently available in the literature for experimental and theoretical ^{13}C NMR chemical shifts of styrene-*co*-isoprene polymers. The Grant and Paul rules modified for branching and unsaturated carbon−carbon bond position and additive shift factors properly calculated in stereoirregular styrene-*co*-isoprene polymers by anionic processes[26] failed in attributing the ^{13}C NMR signals observed in the spectra of the copolymers by **1**/MAO catalyst.

To definitively assign at triad level the ^{13}C NMR resonances in styrene-*co*-isoprene polymers by syndiospecific styrene polymerization catalyst, we preliminary determined additive shift factors for the substituents of the main chain, namely the phenyl group and the methyl of the isoprene unit.

Table 5. Selected ^{13}C NMR (CDCl$_3$, 400 MHz, 25 °C) Chemical Shifts Determined for the Monomer Triads in the Styrene-*co*-isoprene Polymers by 1/MAO

		chemical shift (ppm)			
line	sequence[a]	obsd	calcd[b]	lit.[c]	Δ*δ*
1	T_5	16.2		15.8	0.4
2	V_5	18.8		18.7	0.1
3	C_5	23.7		23.2	0.4
4	SC'_4	26.0	26.2		−0.2
5	T_4C	26.4		26.4	0.0
6	CC_4C	26.6		26.7	−0.1
7	SC_4C	26.8	27.0		−0.2
8	C_4C'[d]	28.6		28.5	0.1
9	SC_1S	29.9	30.1		−0.2
	SC_1C				
10	CSC_1	30.1	30.2		−0.1
	SSC_1				
	VC_1			29.9	0.2
11	$C'C_1$[e]	30.8		30.7	0.1
12	C_4V	31.5		31.3	0.2
13	CC_1C	32.4		32.1	0.3
	CC_1S		32.4		0.0
14	CC_4S	34.2	33.6		0.6
	C_4SS				
	SC_4S				
15	CS_1C	34.4	34.1		0.3
16	C_4SC	35.6−35.8	35.3		0.3
	T_4SC		35.7		0.1
17	SS_1C	36.1	35.8		0.3
18	ST_1	38.0	37.8		0.2
19	C'_1S	39.3	39.2		0.1
20	CT_1	40.2		39.9	0.3
21	SS_2S	40.8		40.6[f]	0.2
22	SS_2C	40.9	42.8		−1.9
23	$C'S_2S$	41.1	41.7		−0.6
24	S_1VS	42.1	43.1		−1.0
25	CS_2S	43.7	43.3		0.4
26	CS_1S, $C'S_1S$	43.9	43.5		0.4
27	SS_1S	44.1		43.9[f]	0.2
28	SVS_1	44.4	44.6		−0.2
29	VS_1C'	44.8	44.8		0.0
30	CS_2C	46.6	45.7		0.9
31	TV_3C	46.8		47.1	−0.3
32	CV_3C	48.2		47.8	0.4
33	VS_1V	48.4	48.5		−0.1

[a] The numbering and symbols are those indicated in Scheme 2. [b] Chemical shift values calculated in this work using the procedure explained in the text. [c] Chemical shift values reported in ref 24. [d] Cis−cis tail-to-tail junction ($-CH_2-C(CH_3)=CH-\mathit{CH_2}-\mathit{CH_2}CH=C(CH_3)-CH_2-$). [e] Cis−cis head-to-head junction ($-CH_2-CH=C(CH_3)\mathit{CH_2}-\mathit{CH_2}C(CH_3)=CH-CH_2-$). [f] Chemical shift reported in ref 10.

The additive shift factor for the methine carbon [α(Φ)], carrying the aromatic ring, was calculated by subtracting the reference value of 29.6 ppm, corresponding to the methylene carbon $S_{\delta\delta}$ of a polymethylene chain, to the experimental value of the methine carbon atom EES_2E, observed at 46.00 ppm in styrene-*co*-ethylene polymers.[27] The same approach permitted the chemical shift additive factors for *β*(Φ) and *γ*(Φ), corresponding to the additive factor for the aromatic ring in *β* and *γ* position to an assigned methylene carbon, to be calculated using the reference values of the methylene carbon atoms EES_1EE (36.83 ppm) and EE_2SEE (27.85 ppm). These shift factors are in good agreement with the values determined by Sato et al. in low-molecular-weight model compounds.[28]

The contribution of the methyl group C_5 in the *β*-position to the methylene carbon C_1 of the *cis*-1,4-isoprene unit [β_C(Me)] was calculated by subtracting the experimental values of the methylene carbon CC_1C in *cis*-1,4-polybutadiene from the shift value of the same carbon atom in *cis*-1,4-polyisoprene. Analo-

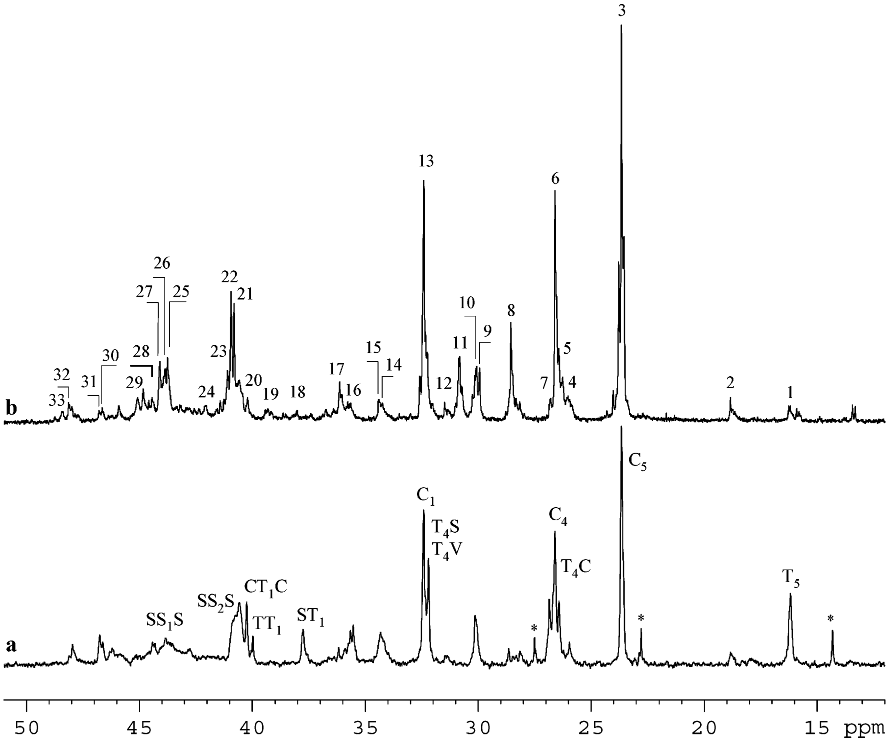
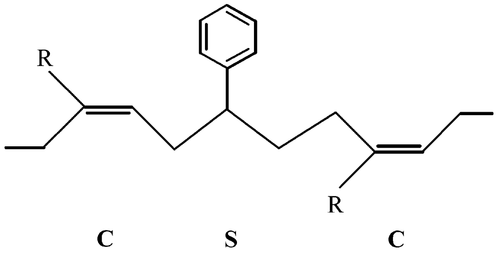


Figure 2. Aliphatic region of the ^{13}C NMR solution spectra (400 MHz, $CDCl_3$, 25 °C, TMS, δ in ppm) of the styrene-*co*-isoprene polymers obtained with (a) anionic polymerization promoted by $^{n}BuLi$ in hexane (% S = 48.0) and (b) **1**/MAO catalyst (run 18, % S = 49.9). The signals are labeled according to the numbering and the symbols used in Table 5. The signals labeled with an asterisk correspond to the *n*-butyl group carbons.

gously, the β_T(Me) was calculated on the basis of the chemical shift value of the methylene carbon of the TT_1T triad in *trans*-1,4-polyisoprene and *trans*-1,4-polybutadiene.[29] The γ_C(Me) additive factor was calculated by subtracting both the chemical shift values of the C_4C (*cis*-1,4-*cis*-1,4-butadiene diad) and the β_C(Me) value from the shift value of C'_1 of the head-to-head regioirregular isoprene diad $-CH_2-CH{=}C(CH_3)CH_2-CH_2C(CH_3){=}CH-CH_2-$.[24] The γ'_C(Me) shift factor, corresponding to the deshielding of the C_5 methyl group at the C_4 of the same isoprene unit, was calculated by subtracting the chemical shift of C_4C to the value of the same carbon in a regiorregular tail-to-tail isoprene diad.[24] Thus, the γ_T(Me) of the *trans*-1,4-isoprene was calculated by comparison of the experimental values of C_4C (26.60 ppm) and T_4C (26.4 ppm) resonances; the γ'_T(Me) effect by comparison of the T_4T signal in *trans*-1,4-polybutadiene (32.90 ppm) and *trans*-1,4-polyisoprene (26.9 ppm).[29] Finally, the β_V(Me) shift factor was obtained by evaluating the chemical shift difference of the methine carbon CV_3C (48.14 ppm)[24] in polybutadiene and polyisoprene assuming that the δ_C(Me) values of the adjacent isoprene units are negligible. The additive shift factors above calculated are listed in Table 4; in this table the additive shift factors $F(n)$ [F = C, T, V; $n = \alpha, \beta, \gamma$) proposed by Sato[28] for the effect of a double bond with *cis, trans,* or 1,2-vinyl configuration on the chemical shift of a carbon atom of the main chain are also reported and used in our calculations (see above).

Thus, we defined a method for predicting the ^{13}C NMR chemical shift values in styrene-*co*-isoprene polymers based on the chemical shifts previously determined in styrene-*co*-butadiene polymers by titanium catalysts implemented with the additive shift factors determined by Sato and in this work. This method would account for (i) the syndiospecificity and secondary insertion of styrene, (ii) the elevated *cis*-1,4 chemioselectivity of the titanium catalyst, and (iii) the conformational effect of the copolymer chain comprising phenyl substituents and unsaturated group in the main chain. The calculated and experimental chemical shifts as well as the corresponding attributions of the ^{13}C NMR chemical shifts of the saturated carbon atoms are listed in Table 5 and displayed in Figure 2 (the numbering and symbols are those indicated in Scheme 2).

Scheme 3



R = H, CH_3

Herein we report two examples that show how the chemical shift of the carbon atoms in styrene-*co*-isoprene polymers can be calculated, namely those of the methylene carbons CS_1C (line 15) and CSC_1 (line 10) of the CSC triad (Scheme 3).

For the former, the methylene ^{13}C signal CS_1C, detected at 35.7 ppm in styrene-*co*-butadiene polymers, is used as starting value.[10] The chemical shift of the same carbon atom in styrene-*co*-isoprene polymer is obtained by adding the γ_C(Me) shift factor (−1.61 ppm) to give an expected chemical shift of 34.1 ppm. With regard to the chemical shift of the methylene carbon CSC_1 the starting value is that of the C_4SC signal at 25.11 ppm in styrene-*co*-butadiene polymer; there the β_C(Me) shift factor (5.06 ppm) has been added to lead to an expected value of 30.2 ppm.

It is noteworthy that the monomer sequences are oriented because of the secondary insertion of styrene and 3,4-vinyl and *cis*-1,4 of the isoprene (see, e.g., the CSC sequence in Scheme 3).

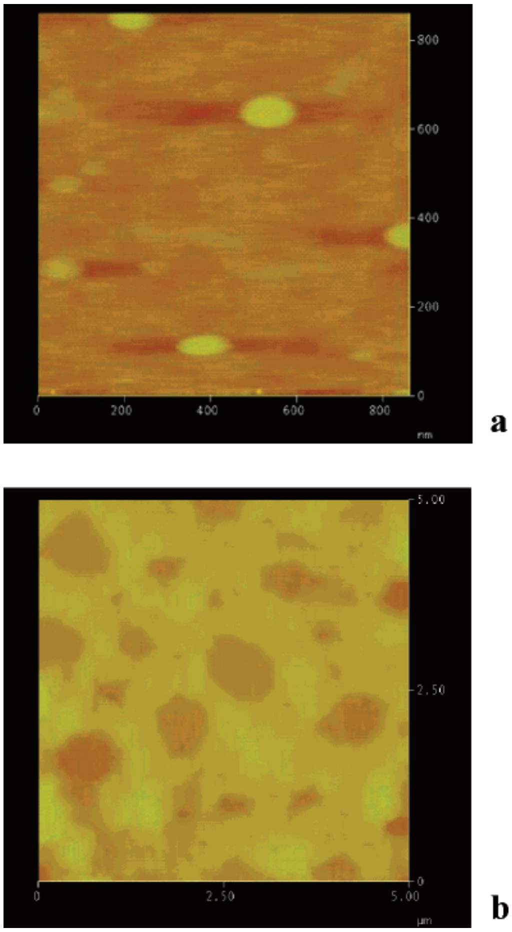


Figure 3. AFM micrograph (height image) of thin, spin-coated film of (a) styrene-*co*-isoprene polymer sample **20**, $x_S = 0.65$ (scan size: 863 nm), and (b) styrene-*co*-butadiene polymer sample **13**, $x_S = 0.81$ (scan size: 5 μm), stained with OsO_4.

The ^{13}C chemical shifts diagnostic of the monomer triads containing isolated styrene units, namely CSC_1 (line 10), CS_1C (line 15), and C_4SC (line 16), were calculated using the method above-described. The agreement ($\Delta\delta$) between the calculated and experimental values for these signals is very good (see Table 5). With regard to the monomer triads including the syndiotactic SS diad, the two pairs of methylene carbons, namely SSC_1 (line 10) and SS_1C (line 17) as well as C_4SS (line 14) and CS_1S (line 26), produce signals with equal intensity, and the agreement between the calculated and experimental chemical shift values is satisfactory. The methylene CS_1S signal is partly overlapped with the methine CS_2S signal, but the two ^{13}C NMR signals can be distinguished by DEPT NMR experiments. The spectral lines 4 and 23 account for regioirregular *cis*-4,1-enchained isoprene units (C′):[30] the agreement between the calculated and experimental chemical shifts of the SC'_4 and $C'S_2S$ monomer sequences is also good. Unfortunately, the $C'S_1S$ signal (line 26) overlaps other methylene signals in the spectral region 43.5−44.0 ppm and thus cannot be unequivocally assigned.

The comparison of the ^{13}C NMR spectra of two styrene-*co*-isoprene polymers (Figure 2), produced with the same styrene molar fraction by means of different synthetic procedures, namely anionic polymerization promoted by ^{n}BuLi in hexane at 50 °C ($x_S = 0.48$; Figure 2a) and addition polymerization catalyzed by **1**/MAO (run 18; $x_S = 0.50$; Figure 2b), further confirmed our attributions. On inspection of these spectra it can be soon envisaged some differences. In the spectrum of the copolymer by anionic process the methylene and methine signals of the SSS triads are spread in the ranges 40.26−40.95 ppm (SS_2S) and 43.80−44.40 ppm (SS_1S) because of the stereoirregular placement of styrene units. Moreover, the content of *trans*-1,4-units in this copolymer is notably higher ($T = 13.8$ mol %), and the resonances due to this monomer unit at 16.2 (T_5, line 1, Table 5), 26.4 (T_4C, line 5), 37.8 (ST_1, VT_1, line18), 40.2 (CT_1, line 20), and 46.8 ppm (TV_3C, line 31) and that at 39.9 ppm corresponding to the methylene carbon of the TT_1 diad[24] appear with increased intensity. In the copolymer by **1**/MAO only signals attributed to isolated T units are detected because of the elevated chemioselectivity of the catalyst. Moreover, the ^{13}C signals corresponding to the monomer triads comprising the syndiotactic styrene diad are sharper and well-defined whereas those diagnostic of regioirregular insertion of isoprene units are only observable in the spectrum of Figure 2b (lines 8 and 11).

Table 6. Composition in Diads, Reactivity Ratios, and Average Styrene Block Length for the Styrene-*co*-isoprene Polymers (Samples 15, 18, and 24)

		copolymer composition in diads (mole fraction)[b]							
run	f^a	[SS]	[II]	[SI]	[IS]	r_1	r_2	r_1r_2	n_S
15	3	0.10	0.66	0.11	0.12	17	0.3	5.1	1.9
18	6	0.25	0.46	0.16	0.13	19	0.3	5.7	2.3
24	12	0.45	0.23	0.16	0.16	17	0.2	3.4	4.1

[a] S/I molar ratio in the monomer feed (reaction solutions). [b] Evaluated according to the procedure described in the Experimental Section.

Attempts to evaluate the reactivity ratios by means of the Finemann and Ross method failed because the concentration of the head-to-head and tail-to-tail regioirregular isoprene units is elevated, and the kinetics of the styrene-*co*-isoprene polymerization catalyzed by **1**/MAO cannot be described through a simple scheme of a binary copolymerization. Thus, we evaluated the reactivity ratios for three samples, namely 15, 18, and 24, representative of the composition range of the copolymer synthesized ($x_S = 0.23, 0.50, 0.73$), using the method above-reported. In Table 6 the diad concentration, the reactivity ratios $r_1 = k_{II}/k_{IS}$ and $r_2 = k_{SS}/k_{SI}$, and the reactivity ratio product r_1r_2, calculated on the basis of the composition of these copolymers, are reported.[9]

The r_1 and r_2 values are about 18 and 0.3, respectively, with an average reactivity ratio product of 4.7. Although the absolute value is higher than unity and suggests a tendency toward blockiness of the monomer distribution in the polymer chain, it is significantly lower than that found in styrene-*co*-butadiene polymerization and supports a closer reactivity of styrene and isoprene. In particular, the r_1r_2 value found in styrene-*co*-butadiene polymerization is higher of at least 1 order of magnitude than that found in styrene-*co*-isoprene polymerization. To gain a closer insight into the monomer distribution, we evaluated the average styrene block lengths using the method based on the copolymer composition defined at triad level (see Table 6).[10,31] The highest average value of n_S is about four ($x_S = 0.73$), thus too short to produce segments of crystalline syndiotactic polystyrene. As a matter of fact, the styrene-*co*-isoprene polymers by **1**/MAO catalyst are completely amorphous under the range of compositions explored.

Copolymers Morphology. To spread further light on the morphology and confirm the monomer distribution in the polymer chain of these copolymers, two representative samples were analyzed by atomic force microscopy (AFM). The AFM micrograph of Figure 3a corresponding to a film of the copolymer **20** ($x_S = 0.65$, Table 3) produced by spin-coating of a chloroform solution (2.5 wt %) showed a remarkable homogeneity as expected for a pseudo-random distribution of the two monomers.

On the contrary, the styrene-*co*-butadiene polymer with the same composition (sample 12, $x_S = 0.77$, Table 2) exhibits a phase-separated morphology of the hard and soft domains consisting of syndiotactic polystyrene and *cis*-1,4-polybutadiene, respectively. The film by spin-coating of the chloroform solution of this sample, stained with OsO_4, exhibits domains of *cis*-1,4-polybutadiene with average dimension of nearly 862 nm (Figure 3b) detected as dark spots in the AFM micrograph. Multiblock copolymers consisting of atactic polystyrene and segments of *cis*- and *trans*-1,4-polybutadiene, produced by reactive extrusion, showed similar morphology: the presence of spheres of polybutadiene of a few tenths of a nanometer was observed after heating of the sample at 100 °C.[32] Few examples of block styrene-*co*-diene polymers including stereoregular styrene homosequences have been reported and studied in detail. Diblock copolymers of isotactic polystyrene and polybutadiene (M_n(PS) = 41 kDa; M_n(PB) = 11 kDa) showed the formation of polybutadiene particles of hundred nanometers after molding at 260 °C followed by quenching at ambient temperature.[33]

The study of microphase separation in block copolymers of styrene and diene is of technological and scientific interest; the detailed characterization of the morphology in styrene-*co*-butadiene polymers by this titanium catalyst is in progress and will be reported elsewhere.

Conclusions

Syndiospecific styrene polymerization and *cis*-1,4-specific polymerization of butadiene and isoprene have been reported with the monocyclopentadienyltitanium catalyst **1**/MAO. A significant effect of trimethylaluminum on the catalyst performances has been observed: the alkylaluminum compound increases the polymer yields but produces a broadening of the PDIs of the polymer products likely as a consequence of a reaction with the active species. Syndiotactic polystyrene-*co*-*cis*-1,4-polybutadiene multiblock polymers were synthesized with the **1**/MAO catalyst, and the microstructure assessed by ^{13}C NMR spectroscopy was found similar to that produced by classical monocyclopentadienyltitanium catalysts. A phase-separated morphology showing domains of *cis*-1,4-polybutadiene with an average diameter of 800 nm included in a matrix of syndiotactic polystyrene was shown for the first time. This result confirmed the multiblock structure of the copolymer chain anticipated by DSC analysis and kinetic investigation of the copolymerization reaction. Indeed, melting points of the syndiotactic polystyrene domains were found in the range 235−254 °C, and the product of the reactivity ratios determined by NMR methods is much larger than unity.

The performances of **1** in styrene-*co*-isoprene polymerization were also investigated. A full characterization of the copolymer microstructure was defined by ^{13}C NMR analysis using properly calculated additive shift factors and chemical shift attributions carried out on styrene-*co*-butadiene polymer by monocyclopentadienyltitanium catalysts. The estimated reactivity ratio r_1 and r_2 and the styrene average block lengths n_S suggested a pseudo-random distribution of the two monomers, corroborated by the DSC and AFM analysis of the copolymers.

These findings evidenced the peculiar role of the aryloxo ligand in conjugated diene polymerization catalyzed by monocyclopentadienyltitanium compounds.

Experimental Section

General Procedure and Materials. All manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques and a MBraun drybox. Commercial grade toluene (Carlo Erba) was dried over calcium chloride, refluxed 48 h under 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 (3 Å). Isoprene (Aldrich) and styrene (Aldrich) were purified by distillation over calcium hydride and stored under nitrogen at −20 °C. Methylaluminoxane (MAO) was purchased from Witco as a 10 wt % solution in toluene. Powder sample of MAO (*d*-MAO) was prepared by distilling off the toluene and not coordinated trimethylaluminum followed by washing with hexane and drying in a vacuum. $CpTiCl_3$ (Aldrich) and OsO_4 (4 wt % water solution, Aldrich) were used as received. The titanium complex **1** was prepared according to the literature procedure.[16]

Polymerization of Styrene, Butadiene, and Isoprene. Styrene, butadiene, and isoprene polymerizations (Tables 1) were carried out using the following typical procedure. A 100 mL flask equipped with a magnetic stir bar was charged with toluene, monomer (1.5×10^{-2} mol), and MAO (Al/Ti molar ratio = 1000) solution (runs 1−3) or *d*-MAO (runs 4−6) to reach the total volume of 40 mL. After equilibration of the solution at 50 °C, the reaction was started by injection of a toluene solution of **1** (11 mg, 2.2×10^{-5} mol, 2 mL of toluene) and stopped by addition of ethanol acidified with aqueous HCl after 20 min. The polymer was coagulated in acidic (HCl) ethanol, containing the antioxidant Wingstay K (0.5−0.75 phr). The polymer is finally recovered by filtration, washed with fresh ethanol, and dried in a vacuum at room temperature.

Styrene-*co*-butadiene Polymerization. A typical polymerization procedure is reported. A 100 mL flask equipped with a magnetic stir bar was charged with MAO (10 wt % toluene solution, Al/Ti = 1000), a toluene solution of butadiene (9 mL, 1.66 M), styrene (15 mL; styrene/butadiene molar ratio = 10), and toluene to reach a total volume of 40 mL. After equilibration of the solution at 50 °C the reaction was started by injection of a toluene solution (2 mL) of **1** (11 mg, 2.2×10^{-5} mol). The run was terminated by addition of ethanol (15 mL) after 1 h. The polymer was coagulated in acidic (HCl) ethanol containing the antioxidant Wingstay K (0.5−0.75 phr) and finally, recovered by filtration, washed with an excess of fresh ethanol and dried in a vacuum at room temperature.

Styrene-*co*-isoprene Polymerization. A typical polymerization procedure is reported. A 100 mL flask equipped with a magnetic stir bar was charged with MAO (10 wt % toluene solution, Al/Ti = 1000), 17.2 mL of styrene), 2.3 mL of isoprene (styrene/isoprene molar ratio = 7), and toluene to reach a total volume of 35 mL. After equilibration of the solution at 50 °C the reaction was started by injection of a toluene solution (2 mL) of **1** (11 mg, 2.2×10^{-5} mol). The run was terminated by addition of ethanol (15 mL) after 1 h. The polymer was coagulated in acidic (HCl) ethanol containing the antioxidant Wingstay K (0.5−0.75 phr) and, finally, recovered by filtration, washed with an excess of fresh ethanol, and dried in a vacuum at room temperature.

Anionic Styrene-*co*-isoprene Polymerization. A 100 mL flask equipped with a magnetic stir bar was charged with hexane (20 mL), styrene (5 mL), isoprene (4.4 mL), and ^{n}BuLi (1.2 mL, 2.5 M, in hexane). The polymerization was terminated after 4 h by introducing ethanol (15 mL) containing the antioxidant (Wingstay K, 0.5−0.75 phr). The copolymer was isolated according to the conventional procedure.

Characterization. ^{1}H and ^{13}C NMR spectra were recorded using a Bruker AVANCE 400 spectrometer (400 MHz for ^{1}H and 100 MHz for ^{13}C). The polymer samples were dissolved in $CDCl_3$ (0.5 m L, 20 wt %) and analyzed at room temperature in a 5 mm o.d. NMR tube. The chemical shifts were referred to tetramethylsilane (TMS) using the residual isotopic impurities of the deuterated solvent. The microstructure of polybutadiene and polyisoprene was assessed by comparison with literature.[22−24] The monomer composition of the styrene-*co*-butadiene polymers were determined by integration of the ^{1}H resonances in the following region (δ in ppm, TCDE, 25 °C): 7.07 and 6.56 (5*H*, m, $CH_2CH(C_6H_5)$); 5.58 (1*H*, m, $CH_2CH_2(CH{=}CH_2)$), and 5.38 (2*H*, m, $CH_2CH{=}CHCH_2$). The monomer compositions of the styrene-*co*-isoprene polymers were determined by integration of the ^{1}H resonances in the following region (in ppm, TCDE, 25 °C): 7.25 and 6.50 (5*H*, m, $CH_2CH(C_6H_5)$); 5.13 (1*H*, m, $CH_2(CH_3)C{=}CHCH_2$), and 4.80 (2*H*, m, $CH_2CH(CH_3)C{=}CH_2$).

Thermal analysis was carried out on TA Instruments DSC 2920 calorimeter (heating rate = 10 °C/min). Molecular weight and molar mass distribution of polymers were determined by gel permeation chromatography (GPC) analysis carried out at 30 °C, using THF as solvent and narrow MWD polystyrene standards as reference. The measurements were performed on a Waters 1525 binary system equipped with a Waters 2414 RI detector using four columns (range 1000−1 000 000 Å).

Atomic Force Microscopy. AFM analysis of thin, spin-coated polymer films were carried out with a Dimension 3100 AFM (Digital Instruments, Santa Barbara, CA) operating in tapping mode. Commercial probe tips with nominal spring constants from 20 to 100 N m^{-1}, resonance frequencies in the range 200−400 kHz, and tip radius from 5 to 10 nm were used. Topographic and phase contrast AFM images (image size: 20 μm × 20 μm) of sample were acquired in air at room temperature using a data scale of 1 μm for the height and 60° for the phase.

Sample preparation: two or three drops (150 μL) of a 2.5 wt % solution in chloroform of the copolymer were spin-coated on a glass surface for 15−20 s under ambient conditions at a speed of 1600 rpm. The samples were analyzed by AFM soon after their preparation. The styrene-*co*-butadiene polymer sample was exposed to OsO_4 vapors (1 wt % water solution) for 25 min and then scanned to identify the rubber domain.

Evaluation of Reactivity Ratios. The r_1 and r_2 reactivity ratios in styrene-*co*-butadiene polymerization were calculated using eqs 1 and 2 and copolymer composition defined at the diad level.[9] The molar fractions of the diads SS, BS, and BB were determined by integration of the following ^{13}C NMR signals:

$$[SS] = SS_2S$$

$$[BB] = {}^1/_2C_1C$$

$$[BS] = SS_1C + CS_2S + CS_2C$$

Analogously, the r_1 and r_2 in styrene-*co*-isoprene polymerization were evaluated by using the following relationships:

$$[SS] = 2SS_2S + SS_2C + CS_2S + C'S_2S$$

$$[II] = 2CC_4C + C_4C' + CT + CV + SC_4C$$

$$[SI] = SS_2C + CS_1C + SV + SC_4C + SC'_4$$

$$[IS] = CS_2S + C'S_2S + CS_1C + CC_4S + C'_1S$$

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