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ARTICLE

Styrene-Isoprene and Styrene-1,3-Pentadiene Copolymerisation Catalyzed by Titanium [OSSO]-type Catalysts

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The synthesis of styrene-isoprene and styrene-1,3-pentadiene binary copolymers promoted by the titanium complexes dichloro{1,4-dithiabutanediyl-2,2'-bis(4,6-di-tert-butylphenoxy)}titanium (**1**) and dichloro{1,4-dithiabutanediyl-2,2'-bis[4,6-bis(2-phenyl-2-propyl)phenoxy]}titanium (**2**) activated by methylaluminoxane (MAO) is reported. Both copolymers were obtained in a wide range of composition and the molecular weight distributions obtained from GPC analysis of the copolymers are coherent with material being copolymeric in nature. DSC analysis show an increase of T_g by increasing the amount of styrene in the copolymers, for both binary copolymers. Furthermore, ^{13}C NMR analysis of the copolymer microstructure allowed to assess the monomer block lengths and distribution in the polymer chain revealing a random distribution with the catalyst **1** and **2** for both binary copolymers and a low tendency to form long styrene homosequences. Intriguingly, both in styrene-isoprene and in styrene-1,3-pentadiene copolymers, the catalyst **2** produces polymers with higher vinyl (3,4 for isoprene and 1,2 for 1,3-pentadiene) content respect to catalyst **1** giving interesting insights about the mechanism of stereocontrol for this class of catalysts

Introduction

Copolymerisation of monomers with chemically distinct characteristics is a powerful tool to obtain new polymeric materials possessing unique chemical and physical properties respect to the corresponding homopolymers. Styrene-butadiene (SB) copolymers represent, in this area, by far the most relevant industrial commodity. In particular, styrene-butadiene rubber (SBR) obtained by free radical emulsion processes and the thermoplastic block copolymers (SBS) obtained by solution processes based on living anionic polymerisation catalyzed by alkyl lithium compounds are of fundamental importance in the tyre production.¹ Nevertheless, these commercial SB copolymers possess a low degree of stereoregularity both in styrene sequences and in diene segments because the anionic and radical polymerisation techniques do not allow a precise control over the regiochemistry and stereochemistry during the growth of the polymeric chain.²

In this context, the implementation of a polymerisation process based on transition metal complexes, that promote the polymerisation via coordination-insertion mechanism, is highly desirable because the possibility to control, in this case, both

the regiochemistry and stereochemistry during the polymerisation.³

Indeed, the most covered route to synthesize stereoregular SB copolymers is the use of a titanium catalyst active in the syndiospecific polymerisation of styrene.⁴ In particular, the highly active catalysts based on half-titanocene have been widely used in the copolymerisation of styrene with butadiene. However, the direct polymerisation of styrene with conjugated dienes in the presence of group 4 complexes often face difficulties due to the completely different behaviour of the two classes of monomers for a given catalytic system that leads to a lowering of the catalyst activity and selectivity.

More recently the attention has shifted to rare-earth based catalyst that allows the synthesis of various diblock and multiblock copolymers based on styrene and conjugated dienes such as butadiene and isoprene.⁵

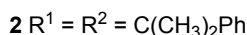
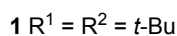
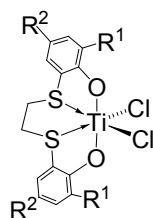
In our hands the [OSSO]-type titanium complex dichloro{1,4-dithiabutanediyl-2,2'-bis(4,6-di-tert-butylphenoxy)}titanium **1** has shown to be versatile catalyst for the copolymerisation of 1,3-alkadienes with styrene and ethylene giving, in some cases, copolymers with unprecedented microstructural features.⁶

In particular we have shown that the catalyst **1** activated by methylaluminoxane is able to efficiently copolymerize

butadiene with styrene^{6d} and *p*-methylstyrene with isoprene and butadiene.⁶ⁱ Furthermore the catalyst **1** also promote the polymerisation of the *E* isomer of 1,3-pentadiene giving a polymer consisting mainly of *trans*-1,2 units with a minor amount of 1,4 units.^{6h}

Besides, the related more steric demanding complex dichloro{1,4-dithiabutanediyl-2,2'-bis[4,6-bis(2-phenyl-2-propyl)phenoxy]}titanium **2** bearing two cumyl groups, when activated by methylaluminumoxane promote the living, isospecific polymerisation of styrene and permits the synthesis of SB diblock copolymers by sequential monomer addition.⁷

Here we report on the ability of the complexes **1** and **2** when activated by methylaluminumoxane to efficiently copolymerise styrene with isoprene (**1**) and 1,3-pentadiene (PD) giving the corresponding copolymers in a wide range of composition and the complete characterization of the resulting products.



Scheme 1 Structure of the complexes **1** and **2**.

Experimental Part

Materials. All air sensitive compounds were manipulated under a nitrogen atmosphere using standard Schlenk techniques or a MBraun drybox. Toluene (Sigma Aldrich) was dried over calcium chloride and refluxed 48 h under nitrogen atmosphere over sodium before using. Styrene was stirred over calcium hydride for one night and then purified by distillation under reduced pressure. Isoprene and *E/Z*-1,3-pentadiene (Sigma Aldrich) were purified by distillation after stirring over calcium hydride for one night. Methylaluminumoxane (MAO) was purchased from Sigma Aldrich as a 10 wt% solution in toluene and used without further purification for the polymerisations involving isoprene and 1,3-pentadiene. The titanium complexes **1** and **2** were prepared according to the literature procedure.⁸

Copolymerisation of styrene and isoprene. The copolymerisation of isoprene and styrene was carried out as follows. A 100 mL glass flask equipped with magnetic stirrer was charged with toluene (40 mL), isoprene (10 mL), a proper amount of styrene and MAO (15 mL; 0.023 mol). After equilibration of the solution at the polymerisation temperature (50°C), a toluene solution (2 mL) of the catalyst (22 μmol) was injected. After 1h, the reaction was stopped with ethanol (15 mL) containing hydroquinone as antioxidant. The polymer was coagulated in ethanol (200 mL) acidified with aqueous HCl, washed with an excess of ethanol, recovered by filtration and dried in vacuo at 40°C.

Copolymerisation of styrene and 1,3-pentadiene. The copolymerisation of 1,3-pentadiene and styrene was carried out as follows. A 100 mL glass flask equipped with magnetic stirrer was charged with toluene (15 mL for **1**, 40 mL for **2**), 1,3-pentadiene (5 mL), a proper amount of styrene and MAO (1.31

g; 0.023 mol). After equilibration of the solution at the polymerisation temperature (50°C), a toluene solution (2 mL) of the catalyst (19 μmol of **1**, 22 μmol of **2**) was injected. After 1h (for catalyst **2**) or 3h (for catalyst **1**), the reaction was stopped with ethanol (15 mL) containing hydroquinone as antioxidant. The polymer was coagulated in ethanol (200 mL) acidified with aqueous HCl, washed with an excess of ethanol, recovered by filtration and dried in vacuo at 40°C.

Characterization of the polymers. The ¹³C NMR spectra of the polymer samples were recorded with a Bruker AVANCE 400 MHz spectrometer, using 5 mm o.d. NMR tubes in which about 30 mg of polymer samples were dissolved in CDCl₃ (0.7 mL) and analyzed at room temperature. Chemical shifts were referred to TMS. The microstructure of the copolymer samples was assessed by comparing the observed resonances with the data from literature. The thermal analysis of the polymers were carried out on TA Instruments DSC Q20 using a heating rate of 10°C/min.

The average molecular weights of the polymer samples were determined at 35°C by a 150 Waters GPC equipped with JASCO 875-UV (254 nm) detector and four PSS columns set consisting of 10⁶, 10⁵, 10⁴ and 10³ Å (pore size) with 10 μm (particle size) column. THF was used as carrier solvent with a flow rate of 1.0 mL/min. The calibration curve was established with polystyrene standards.

Results and discussion

Copolymerisation of styrene with isoprene

The peculiar behaviour of such catalytic systems in the copolymerisation of dienes and styrene and the scarcity, in the scientific literature, of catalytic systems able to promote the binary copolymerisation of styrene monomers with dienes other than 1,3-butadiene stimulated us to investigate the behaviour of the catalytic systems **1**/MAO and **2**/MAO in the copolymerisation of styrene with isoprene and 1,3-pentadiene. In Table 1 the results relative to the styrene-isoprene copolymers in the presence of both catalysts are presented. Firstly, the catalysts **1** and **2** were employed in the isoprene homopolymerisation (runs 1 and 7). Notably while the catalyst **1** produces polyisoprene with prevalently *trans*-1,4 (91%) and a lower amount of 3,4-units(9%) with a negligible content of *cis*-1,4 units, unexpectedly the more steric demanding catalyst **2** shows a lower degree of stereoselectivity with a higher degree of 3,4 (29%) and *cis*-1,4-insertion (18%) along the polymer chain (run 7). This different behaviour can be ascribed to the increased steric bulk around the metal centre of the complex **2** respect to the complex **1** and the concomitant presence of the methyl group in the 2-position of the isoprene molecule that enforce a 3,4 coordination of the monomer following the classical Cossee mechanism as for the α-olefins, instead of the allylic mechanism, resulting in the formation of the vinylic (3,4) units.¹⁰

The copolymerisation of styrene with isoprene was performed using the **1** and **2** activated by MAO obtaining copolymers in a wide range of compositions (*x*_S = 0.27-0.98; Table 1). Gel permeation chromatography (GPC) analysis of these copolymers showed that the molecular weights distributions are monomodal with a PDI values ranging from 1.3 to 1.7 consistent with their copolymeric nature. The molecular weight, in both cases, increases by increasing the styrene content and for the copolymers with styrene content higher than 86% is sensibly higher for the polymers obtained with the catalyst **2** (run 12 and 13) vis-à-vis catalyst **1** (run 5 and 6).

Table 1. Isoprene-Styrene Copolymerisation by 1/MAO and 2/MAO

entry ^a	catalyst	[S]/[I]	yield g (%)	composition (mol%) ^c			M _w (x10 ³ Da)	M _w /M _n	T _g (°C)	n _s
				S	I _{1,4} (trans/cis)	I _{3,4}				
1	1	-	0.03 (3)	-	91 (91/0)	9	25	1.4	-62.9	-
2	1	0.02	0.1 (2)	33	60 (56/4)	7	21	1.5	-6.2	1.7
3	1	0.03	0.2 (2)	40	53 (48/5)	7	23	1.5	5.9	2.0
4	1	0.05	0.6 (8)	77	22 (21/1)	1	32	1.3	42.7	2.6
5	1	0.1	1.6 (21)	86	14 (13/1)	-	46	1.5	54.2	6.5
6 ^b	1	1.0	1.7 (49)	98	2 (2/0)	-	43	1.7	80.4	35
7	2	-	0.02 (1)	-	71 (53/18)	29	75	1.1	-64.9	-
8	2	0.02	0.1 (1)	27	45 (19/26)	28	6.0	1.2	25.7	1.3
9	2	0.03	0.1 (1)	36	39 (27/12)	25	7.0	1.2	n.d.	1.5
10	2	0.05	0.1 (2)	66	13 (9/4)	21	14	1.5	39.4	2.1
11	2	0.1	0.3 (4)	75	9 (7/2)	16	28	1.4	52.0	3.0
12	2	0.2	1.1 (12)	92	6 (4/2)	2	84	1.3	71.7	6.3
13	2	1.0	10.5 (61)	97	3 (3/0)	-	284	1.6	88.5	34

^a Polymerisation conditions: 22 μmol of complex, 0.1 mol of isoprene, 14.6 mL of MAO (Al/Ti = 1000), 40 mL of toluene, polymerisation time: 1h, temperature: 50 °C. ^b 0.02 mol of isoprene. ^c Determined by ¹H and ¹³C NMR analysis

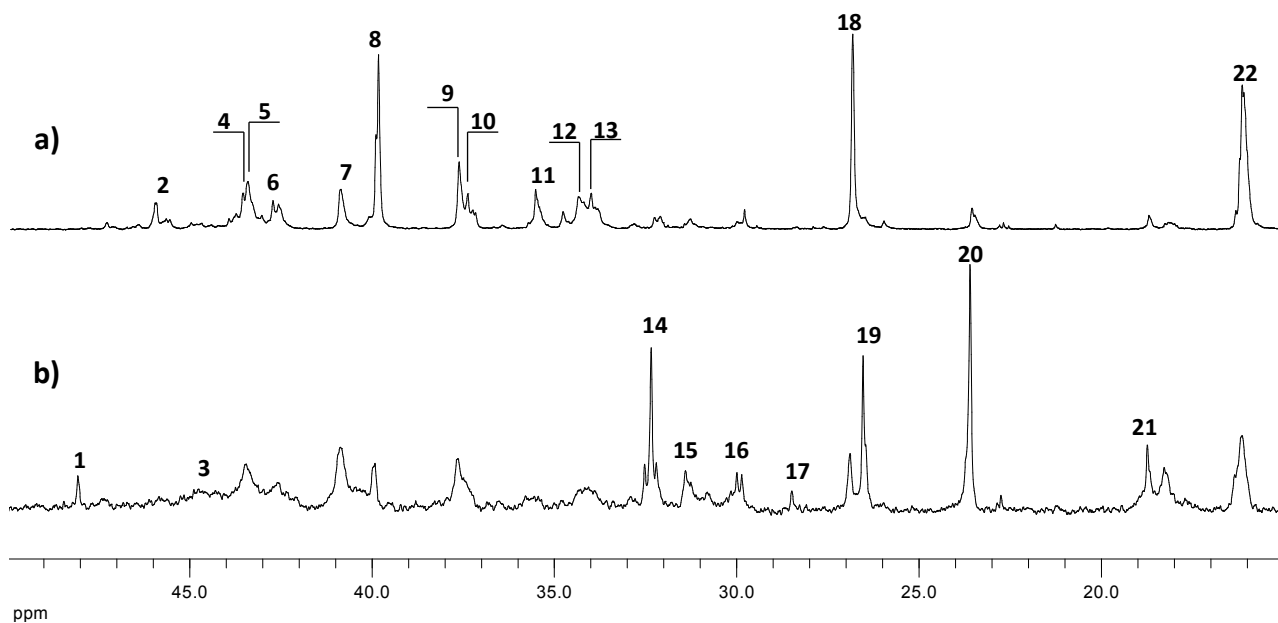


Figure 1. Aliphatic region of the ¹³C NMR spectrum of entry 3 (a, x_S = 0.40) and entry 9 (b, x_S = 0.36) of Table 1

All copolymers are completely soluble in hexane, THF, or chloroform, also when the styrene concentration approaches as high values as x_S = 0.98. As already observed for the *p*-methylstyrene-isoprene copolymers, the T_g values increase by increasing the styrene content ranging from -6.2 °C in the case of the copolymer containing the higher isoprene content (run 2), to a value close to the polystyrene T_g for the polymers containing higher content of styrene (runs 6 and 13). The stereoselectivity properties of the catalyst **1** and **2** displayed in the homopolymerisation of styrene and isoprene are retained in the copolymerisation reactions. Indeed, both the catalysts produce copolymers in which the polystyrene segments are isotactic but, as noted in the isoprene homopolymerisation, the isoprene units are arranged prevalently as *trans*-1,4 in the case of the catalyst **1** while in the case of catalyst **2** a higher content of *cis*-1,4-units and 3,4 units are present. Besides, considering a copolymer with the same monomer feeding (run 2 vs. run 8) it is evident the tendency of catalyst **2** to incorporate a major amount of isoprene. The higher amount of 3,4-units in the polymer chain also causes an increase of the T_g in the copolymers having similar composition (run 4 vs. run 11).

Considering that the methyl group in *para*-position does not significantly affect the ¹³C NMR chemical shifts of the carbon atoms in the main chain the attributions of the ¹³C signals were performed using the previously reported data for the *p*-methylstyrene-isoprene copolymers.⁶¹

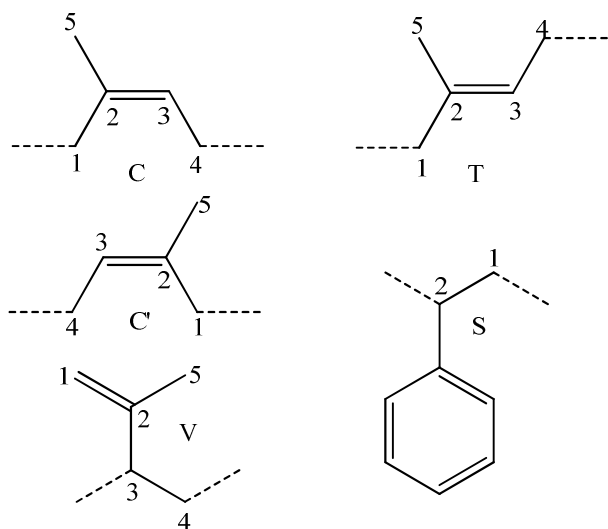
In Figure 1 the spectra of the copolymers obtained in presence of the catalyst **1** (a, run 3) and catalyst **2** (b, run 9) having similar composition are shown. On one hand, the ¹³C NMR spectrum (a) of the S-I copolymers by catalyst **1** exhibit signals attributed to isotactic styrene triad SSS and TT (T = *trans*-1,4-isoprene) (see Scheme 2) corresponding to *trans*-1,4-isoprene dyad respectively. In detail the ¹³C NMR spectrum of the S-I copolymers by catalyst **1** showed S homosequences in isotactic arrangement with diagnostic signals for SS₁S and SS₂S at 43.4 and 40.9 ppm, respectively, and for the isoprene units the main signals are due to the TT₁ and T₄T dyads at 39.9 and 26.9 ppm. In addition, the presence of 3,4 and *cis*-1,4 isoprene units is only detectable from the signals relative to the methyl of the isoprene unit respectively at 18.7 ppm and 23.6 ppm denoting that these units are isolated along the polymer backbone.

On the other hand the spectrum of the copolymer obtained in the presence of the catalyst **2** clearly shows a higher amount of *cis*-1,4 and 3,4 isoprene units. As a matter of fact the signal relative to the methyl C₅ and V₅ are sensibly higher than that relative to the trans-1,4-units T₅. Consequently the signals relative to the VS₁V, CS₂C and VS₁C' are also present. A complete assignment was made by comparison with the literature data^{4f,6i} and the results are reported in Table 2. Finally the average styrene block lengths for copolymers obtained in the presence of catalyst **1** and **2** are ranging between 1.7-35 in the first case and between 1.3-34 in the second case revealing for both systems a relative low tendency to form long styrene homosequences.

Table 2. ¹³C NMR assignment in the styrene-isoprene copolymers produced in the presence of **1** and **2**/MAO.

Peak number	Sequence	Chemical shift (observed)	Chemical shift (from literature) ^{4f,6i}
1	VS ₁ V	48.1	48.4
2	TS ₂ T/CS ₂ C	45.7	45.8
3	VS ₁ C'	44.9	44.8
4	TS ₂ S	43.6	43.5
5	SS ₁ S	43.4	43.2
6	SS ₂ T	42.6	42.5
7	SS ₂ S	40.9	40.9
8	TT ₁	39.9	40.0
9	TST ₁	37.7	38.2
10	SST ₁	37.4	38.2
11	TS ₁ T	35.6	35.4
12	SS ₁ T	34.8	35.0
13	ST ₄ S/T ₄ SS	34.1	34.1
14	CC ₁ C	32.5	32.4
15	C'C ₁	31.4	30.8
16	SC ₁ C/SC ₁ S/VC ₁	30.0	30.1
17	C ₄ C'	28.4	28.6
18	T ₄ T	26.9	26.9
19	CC ₄ C	26.5	26.6
20	C ₅	23.6	23.7
21	V ₅	18.7	18.8
22	T ₅	16.2	16.2

^aThe numbering and symbols are those indicated in Scheme 2.



Scheme 2. Structures of styrene (S) and *cis* (C, C'), *trans* (T) and *vinyl* (V) isoprene.

Copolymerisation of styrene with 1,3-pentadiene

As in the case of isoprene also in the case of 1,3-pentadiene the catalyst **1** and **2** were firstly tested in the homopolymerisation reactions. As already observed only the *E*-1,3-pentadiene is polymerised while the *Z*-PD is completely unreactive.^{6h} Because of the large availability and low cost of the mixture of isomers we then used such mixture in which the *E*-isomer is the major component (2/1 ratio). The *E*-isomer is polymerized. Notably, also in this case the behaviour of the two catalysts shows some difference regarding the stereoselectivity. Indeed, the more bulky complex **2** gives a polymer containing a major amount of 1,2-units 77% vs. 65% (runs 21 and 14) confirming the tendency, observed in the case of isoprene, of more steric demanding metal complex to produce a polymer with higher vinyl content (3,4 in the case of isoprene and 1,2 in the case of 1,3-pentadiene). It is worth remarking that the difference in the stereoselectivity between the catalysts **1** and **2** is less pronounced for 1,3-pentadiene with slightly preference of the more bulky catalyst **2** to give a higher content of 1,2-units. Actually, considering that there is no difference in the stereoselectivity in the case of butadiene polymerisation producing in both cases a polymer with high *trans*-1,4 content ($\geq 95\%$),^{6d,7a} the results obtained in the case of isoprene and 1,3-pentadiene show that both increasing the steric bulk on the metal centre and increasing the size of the monomer result in a progressive increment of the vinyl (1,2 or 3,4) content in the resulting polymer. In particular, for isoprene, that can be considered a 2-methyl substituted butadiene the 1,4-*trans* stereochemistry is still the preferred for the catalyst **1** (91% run 1) while for the more sterically congested catalyst **2** become important the content in the final polyisoprene of 3,4-units (29% run 7). In the case of 1,3-pentadiene the 1,2 regiochemistry is favoured over 1,4 for both catalysts (runs 14 and 21 Table 3) and become almost exclusive in the case of 4-methyl-1,3-pentadiene^{7b,9} clearly showing the synergic effect of the catalyst-monomer structure in determining the stereochemistry of the resulting polymers for 1,3-alkadienes for this family of catalysts. A series of styrene-1,3-pentadiene copolymers with a wide range of composition ($x_s = 0.10-0.85$) were obtained by using the catalysts **1** and **2** activated by MAO. GPC analysis of these copolymers showed that the molecular weights distributions are monomodal with PDI values ranging from 1.2 to 1.9 confirming the copolymeric nature of the material. The molecular weight, in both cases, increases by increasing the styrene content and there is not an appreciable difference between the two catalytic systems. As already observed for the styrene-isoprene copolymers, also in this case the T_g values increase by increasing the styrene content ranging from -15.2 °C in the case of the copolymer containing the higher 1,3-pentadiene content (run 22) to a value of 56.8 °C for the polymer containing higher styrene content (run 20). Remarkably, by using the same molar ratio between the two comonomers the styrene-1,3-pentadiene copolymers contain a higher amount of the diene monomer compared to the styrene-isoprene copolymers produced with same catalytic system (run 11 table 1 vs. run 24 table 3) denoting a higher reactivity for this monomer respect to the isoprene

Table 3. 1,3-pentadiene-Styrene Copolymerisation by 1/MAO and 2/MAO

entry ^a	catalyst	[S]/[PD]	yield g (%)	composition (mol%) ^c			M _w (x10 ³ Da)	M _w /M _n	T _g (°C)	n _s
				S	PD _V	PD _T				
14	1		0.4(12)	-	65	35	94	1.3	-9.7	-
15 ^b	1	0.02	0.4(11)	10	62	28	90	1.5	-8.6	2.1
16	1	0.03	0.9(42)	39	41	20	118	1.5	-0.3	3.0
17	1	0.1	0.3 (13)	52	37	11	107	1.5	6.2	5.7
18 ^b	1	0.5	5.0 (80)	60	34	6	314	1.4	34.4	7.5
19	1	1.0	4.3 (95)	71	22	7	364	1.2	50.6	9.6
20	1	2.0	6.8 (82)	80	13	7	620	1.9	56.8	10.1
21	2		0.8 (13)	-	77	23	131	1.1	-7.1	-
22 ^c	2	0.02	1.7 (41)	8	65	27	170	1.2	-15.2	2.8
23 ^c	2	0.03	2.2 (52)	14	58	28	180	1.2	-12.4	2.9
24 ^c	2	0.1	3.8(80)	27	52	21	210	1.3	-1.4	3.6
25 ^d	2	0.5	1.8 (75)	63	25	12	290	1.3	30.3	5.2
26 ^d	2	1.0	3.2 (93)	74	18	8	305	1.4	47.3	7.9
27 ^d	2	2.0	3 (100)	85	10	5	274	1.4	49.4	9.8

^a Polymerisation conditions: 19 μmol of complex, 3.0 x 10⁻² mol of 1,3-PD, 1.31 g of MAO (Al/Ti = 1200), 15 mL of toluene, polymerisation time: 3h, temperature: 50 °C. ^b 5.0 x 10⁻² mol of 1,3-PD. ^c Polymerisation conditions: 22 μmol of complex, 46.0 x 10⁻² mol of 1,3-PD, 15 mL of MAO (Al/Ti = 1000), 40 mL of toluene, polymerisation time: 1h, temperature: 50 °C. ^d Same conditions of c, but with 2.0 x 10⁻² mol of 1,3-PD. ^e Determined by ¹H and ¹³C NMR analysis; PD_V = vinyl (e.g. 1,2)1,3-PD units; PD_T = *trans*-1,4-PD units.

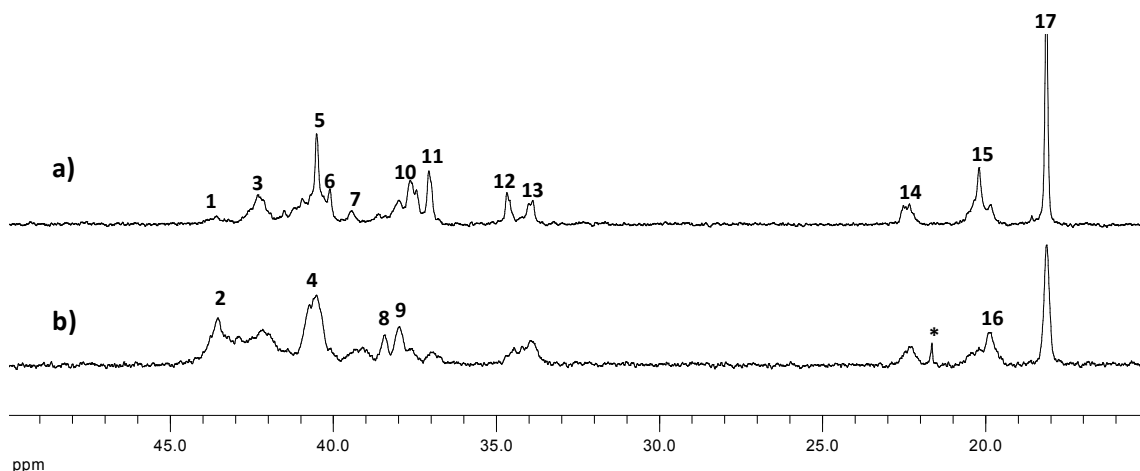
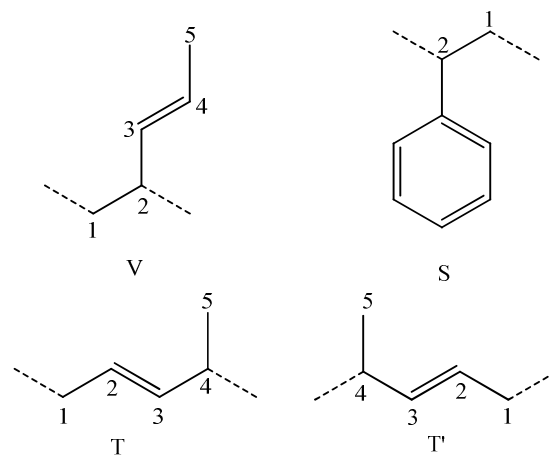


Figure 2. Aliphatic region of the ¹³C NMR spectra of entry 23 (a, x_s = 0.14) and entry 25 (b, x_s = 0.63) of Table 3. Peak marked with * is due to toluene.

Table 4. ¹³C NMR assignment in the styrene-1,3-pentadiene copolymers produced in the presence of 2/MAO.

Peak number	Sequence	Chemical shift (observed)	Chemical shift (from literature) ^{61,12}
1	SS ₂ T	43.7	43.5
2	SS ₁ T	43.5	43.4
3	SS ₁ S/TV ₁ V	42.9-42.3	43.2-42.6
4	SS ₂ S	40.9	40.9
5	VV ₁ V	40.5	40.9
6	T ₄ T	40.1	40.3
7	VT ₁	39.5	38.6
8	T ₄ S	38.6	37.9
9	VV ₂ S	38.0	37.7
10	VV ₂ V	37.6	37.7
11	TT ₁	37.1	36.8
12	T ₄ V	34.7	34.5
13	T ₄ T	33.9	33.9
14	T ₅ V ₅	22.6	22.0
15	T ₅ T	20.2	20.0
16	T ₅ T'	19.8	20.0-20.2
17	V ₅ V	18.1	17.9

^aThe numbering and symbols are those indicated in Scheme 3.



Scheme 3. Structures of styrene (S) and *trans* (T, T') and vinyl (V) 1,3-pentadiene.

A deeper insight into the microstructural features of the copolymers comes from the inspection of the ^{13}C NMR spectra of the copolymers at different compositions. In Figure 2 the spectra of the copolymer containing 14% of 1,3-pentadiene (run 23) and 63% (run 25) of 1,3-pentadiene are shown. As evident from the signals in the methyl region, the 1,3-pentadiene is mainly present as 1,2-*trans* and in lower amount as 1,4 showing that the copolymerisation with styrene does not affect the stereochemistry of insertion of the diene monomer respect to the homopolymerisation. Moreover the aliphatic region of the spectra clearly shows the signals due to the styrene and 1,3-pentadiene homosequences and the signals attributable to the styrene-1,3-pentadiene heterodyads. The complete attribution is reported in the table 4 following the nomenclature in the Scheme 3. It is worth noting that in this case the copolymers obtained in the presence of the catalyst **1** and **2**, having similar composition, do not show appreciable microstructural differences. Furthermore these new copolymer presents even shorter styrene homosequences due the higher relative reactivity of the 1,3-pentadiene respect to isoprene.

Conclusions

In this work we have reported the binary copolymerisation of styrene with isoprene and 1,3-pentadiene promoted by two catalytic systems based on [OSSO]-type titanium complexes activated by methylaluminumoxane. Notably both catalysts are able to promote the copolymerisation of styrene with isoprene and 1,3-pentadiene giving the resulting copolymers with a wide range of compositions and in good yield. The complete characterization by GPC, DSC and ^{13}C NMR of the resulting copolymers showed that is possible to obtain copolymers having different microstructural features by changing the catalytic system. As a matter of fact, on one hand the styrene-isoprene copolymers obtained by using the catalyst **1** show a high stereoselectivity for styrene and isoprene giving polymer chain in which the styrenic monomer homosequences are isotactic and the isoprene monomers are inserted preferentially with 1,4-*trans*-selectivity. On the other hand the catalyst **2** gives copolymers with isotactic styrene homosequences but the isoprene segments contain a high degree of 3,4 and 1,4-*cis* units. In the case of the styrene-1,3-pentadiene both catalysts give copolymers with similar microstructure. These results show not only the versatility of these catalysts in the copolymerisation reactions with styrenic and diene monomers but shed more light on the catalyst structure-reactivity relationship for the stereoselective polymerisation of diene with this class of catalysts.

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† Electronic Supplementary Information (ESI) available: ^{13}C NMR and DEPT 135 of the copolymers of listed in Table 1 and 3. Equations for the evaluation of the average styrene block length. DSC curves of the copolymers in Table 1 and 3.

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