HAL
archives-ouvertes.fr

A New Family of Styrene/Diene Rubbers

Philippe Zinck, Michael Terrier, André Mortreux, Andreia Valente, Marc
Visseaux

HAL Id: hal-00265327

https://hal.archives-ouvertes.fr/hal-00265327

Submitted on 18 Mar 2008

Unprecedented insertion of styrene single units in polyisoprene using borohydrido rare earths / dialkylmagnesium catalysts : a new family of SBR rubbers.

Philippe Zinck[*], Michaël Terrier, André Mortreux, Andreia Valente and Marc Visseaux[*]

Unité de Catalyse et Chimie du Solide, UMR CNRS 8181,

ENSCL, Cité Scientifique, 59652 Villeneuve d'Ascq, France

marc.visseaux@ensc-lille.fr

Keywords: Catalysis, copolymerization, stereospecific polymers, rubber.

Introduction

The introduction of functional groups such as styrene in the backbone of polydienes is of interest for many fields of applications. Styrene-dienes copolymers commonly referred to as SBR rubbers were initially synthesized by radical and anionic processes, yielding poorly stereoregular materials. Higher selectivities[1] were achieved with the development of transition metal catalysis. Poly(1,4-*cis* butadiene–*co*-styrene) was by far the most widely studied SBR,[2] probably due to low price of butadiene vs. other conjugated dienes. Besides petroleum derivatives, isoprene was also used as a monomer for random copolymerization with styrene. This field was pioneered by radical polymerization in emulsion in water using potassium persulfate as initiator.[3] The anionic random copolymerization of isoprene and styrene was reported a decade later using lithium and sodium metals as well as alkyllithium as initiators.[4] As far as we know, the coordinative random polymerization of isoprene and styrene was only achieved in the 90's. Simple metal complexes were combined to various magnesium and aluminium based cocatalysts: rare earths trichloride[5] and halocarboxylate,[6] nickel[7] and neodymium acetylacetonate[8] and half-titanocenes[9] originally developed for the

1

syndiotactic polymerization of styrene. The resulting polyisoprene backbones were mostly *cis*-stereoregular.[5,7] It must be here noticed that vulcanized poly(1,4-*trans* isoprene) exhibits better applicative properties such as hardness or abrasion resistance by a factor 1.5 to 2 as compared to vulcanized poly(1,4-*cis* isoprene)[10] or vulcanized polybutadiene.[11] Catalysts affording the insertion of styrene in poly(1,4-*trans* isoprene) are thus of interest not only from an academic point of view, but also regarding the applicative potentialities of the resulting material.

The insertion of single styrene units has been achieved in polyethylene using notably constrained geometry catalysts[12], and single repeat unit insertions (SRUI) where notably reported for olefins and non-conjugated dienes in polyisoprene,[13] for butadiene[14] and norbornene[15] in polyethylene and in the frame of acyclic diene metathesis polymerization.[16] SRUI derives from a particular feature of the catalyst/comonomers combination, and its understanding may pave the way to catalysts enabling a fine control of the microstructure.

We developed recently borohydrido organolanthanides catalytic systems that afford the polymerization of isoprene and styrene,[17] the metal-carbon active bond being generated *in-situ* from the alkylation of the metal complex by a dialkylmagnesium compound.[18] We report herein the unprecedented insertion of single styrene units in poly(1,4-*trans* isoprene) using $Nd(BH_4)_3(THF)_3$ (**1**), $La(BH_4)_3(THF)_3$ (**2**) and $Cp*Nd(BH_4)_2(THF)_2$ (**3**) combined to *n*-butylethylmagnesium with styrene content up to 30%.

Results and discussion

Typical experiments conducted at 50°C in toluene and stopped after 2 hours are reported Table 1. The true nature of the copolymer is assessed Figure 1 by the presence of new signals on the ^{13}C NMR spectra corresponding to isoprene – styrene diads. The polyisoprene backbone shows a 96-98% 1,4-*trans* microstructure similar to that of the

2

homopolymer. Up to 30% styrene can be inserted in the range of our experimental conditions, yielding polymers with narrow molecular weight distributions. The presence of pentamethylcyclopentadienyl-Cp* in the coordination sphere of the neodymium atom allows a slightly higher quantity of styrene to be inserted, together with narrower molecular weight distributions (entries 8-10). The activity of the neodymium based systems is among the highest reported for isoprene / styrene random copolymerizations: 15-55 vs. 0.1-10 kg/mol/h for rare earths based systems,[5-6,8] 40 and 200 for Ni[7] and Ti[9] based catalytic systems, respectively. Replacing the neodymium atom by lanthanum results in a significant decrease of the activity, together with slight decreases of the amount of styrene insertion and the selectivity of the reaction (entries 3-4).

Microstructure analysis from the ^{13}C NMR spectra in the polystyrene zone (40-45 ppm) is rendered difficult by the simultaneous presence of signals from isoprene-isoprene and styrene-isoprene sequences. A detailed analysis of the ^{1}H NMR spectra in the ethylenic proton zone (Figure 2) shows in turn that styrene is inserted in the form of a single molecule. A new signal can be observed at lower field as styrene is inserted, whose intensity increases with the amount of styrene. The deconvolution of the spectra in this zone reveals that the intensity of the new signal corresponds to twice the molar ratio of styrene in the copolymer (Table 2). This means that the signal corresponds to the =CH proton of isoprene units that are neighbouring a styrene unit, and that each unit of styrene is surrounded by two isoprene units. A slight deviation from this calculation is observed for high content of styrene (32%) when a halfneodymocene is used as the precatalyst (entry 10). This can be due to (i) St-St sequences or to (ii) a partially alternating structure, where the ratio of neighbouring isoprene vs. styrene equals 1, that can result from the batch process. The values of the reactivity ratio ($r_1 = 0.09$ and $r_2 = 7.5$ for **1**; $r_1 = 0$ and $r_2 = 6$ for **3** – see SI) act for hypothesis (ii): r_1 equals / close to 0 means that the catalytic system does not allow / favour the insertion of styrene in a Ln-St

bond. This is probably due to steric and/or electronic requirements, since the halfneodymocene **3** leads to a smaller r_1 reactivity ratio than the precursor **1.** The presence of two coordinated bulky and electron-rich groups around the neodymium, i.e the penultimate styrene unit and the pentamethylcyclopentadienyl ligand leads to an increase of both the electronic density and the steric hindrance. This may render the coordination of a second styrene molecule difficult / impossible, and favour that of a smaller and more coordinating isoprene molecule. As a consequence, k_{11} and r_1 equals / are close to 0, and one can observe SRUI.

The single insertion is confirmed by the NMR spectra in the phenyl *ipso* carbon region represented Figure 3d. The sharp singlet observed around 145.8 ppm is characteristic of a styrenic unit in a single and unique environment, in a similar way to poly(ethylene-*alt*-styrene)[19] or isotactic (mm triads) and syndiotactic (rr triads – Figure 3c) polystyrene.[20] The presence of mr triads where the constitutional repeating unit is surrounded by units in a different configuration leads indeed to a broadening of the phenyl *ipso* signal, as represented Figure 3a,b. ^{13}C NMR data are moreover consistent with two styrene insertion modes, the major mode being attributed to a 2,1 insertion into a 1,4-trans PI backbone.[21]

The presence of large amounts of styrene in the medium does not alter the selectivity of the reaction, in contrast to *cis* stereospecific pathways. In this latter case, increasing the styrene / isoprene molar ratio in the medium leads generally to important decreases of the amount of 1,4-*cis*[6b;7-8] units at the expense of 1,4-*trans*[7] and 3,4 sequences[8]. This is usually explained by a back-biting coordination mechanism involving the coordination of the double bond of the penultimate monomer on the catalyst.[22] This coordination is believed to play a significant role in the stereocontrol of the reaction, and the presence of electron-donor substances in the medium may not be inactive toward it. This back-biting based mechanism can not be advanced for our trans-specific system, the trends observed here leading to SBR

materials characterized by 30% styrene content together with a 96-98% 1,4-*trans* microstructure (entry 5 and 10).

The insertion of styrene single units leads further to the disappearance of the crystalline fraction of the poly(1,4-*trans* isoprene) backbone, yielding a gummy elastomer in most cases. Only one semi-crystalline material is obtained with precatalyst **1** for low amount of styrene insertion, highlighting polyisoprene fractions of high cristallinity. The introduction of the Cp[*] ligand in the coordination sphere of the neodymium atom affords in turn narrower chemical composition distributions that lead to amorphous polymeric materials. The glass transition of the copolymer lies as expected between that of the homopolymers, i.e -70 and 100°C for polyisoprene and polystyrene respectively. The absence of second order transition around -70 and 100°C together with the monomodal character of the molecular weight distribution (see SI) indicates that homopolymers are not formed in the course of the reaction, in accordance with a single active species, most probably an allyl. The stereoselective polymerization of dienes is indeed believed to proceed via a π-allyl mediated mechanism involving a η_3-η_1 rearrangement[1,20-21] and lanthanide-allyl complexes are able to initiate the polymerization of styrene.[24] Mechanistic investigations in relation with deeper NMR investigations of the microstructure are currently under course.

Entry [a]	Precatalyst	Styrene in feed (mol %)	Yield (%)	Activity (kg.mol^{-1}.h^{-1})	Styrene in polymer (mol %) [b]	1,4-*trans* polyisoprene units (%) [b]	1,4-*cis* polyisoprene units (%) [b]	3,4 polyisoprene units (%) [b]	$\overline{M_n}$ [c] (g/mol)	PDI [d]	T_g (°C) [f]	T (°C) [f]
1	**1**	0	85	60	-	96	2	2	72 000	2.0	- 66	
2	**1**	20	88 [e]	54	5	98	< 0.5 [g]	2	65 000	1.6	- 61	
3	**1**	50	90 [e]	38	15	97	1	2	43 000	1.8	- 54	
4	**2**	50	24 [e]	13	11	94	4	2	15 000	1.5	- 63	
5	**1**	80	79 [e]	17	27	98	2	< 0.5 [g]	23 000	1.8	- 40	
6	**1**	100	17	18	-	-	-	-	10 000	1.6	n.d	
7	**3**	0	66	47	-	98	0	2	67 000	1.8	- 66	
8	**3**	20	70 [e]	42	5	97	0	3	66 000	1.6	- 66	
9	**3**	50	74 [e]	32	16	98	0	2	47 000	1.4	- 51	
10	**3**	80	69 [e]	15	32	96	< 0.5 [g]	4	27 000	1.4	- 30	
11	**3**	100	8	8	-	-	-	-	8 000	1.5	n.d	

(a)   2h reaction at 50°C in 0.5 ml toluene; molar ratio Monomer/Nd/Mg 2000/1/1

(b)   Determined by ^1H NMR spectroscopy

(c)   Number-average molecular weight measured by size exclusion chromatography

(d)   Polydispersity index measured by size exclusion chromatography –PDI=M_w/M_n

(e)   Isoprene yield (weight percentage)

(f)   Determined by differential scanning calorimetry (10°C/min)

(g)   Signal of the corresponding defect too small to be integrated (< 0.5%)

Table 1. Copolymerization results.

Entry [a]	Precatalyst	Styrene in feed (mol %)	Styrene units in copolymer (mol %) [b]	Regular isoprene units in copolymer (%) [c]	1,4-*trans* isoprene neighbouring units in copolymer (%) [c]
2	1	20	5	84	11 (10) [d]
3	1	50	15	57	28 (30) [d]
5	1	80	27	21	52 (53) [d]
4	2	50	11	66	23 (22) [d]
8	3	20	5	86	9 (9) [d]
9	3	50	16	50	34 (32) [d]
10	3	80	32	12	56 (64) [d]

(a)   *2h reaction at 50°C in 0.5 ml toluene; molar ratio Monomer/Nd/Mg 2000/1/1*
(b)   *Determined by ^{1}H NMR spectroscopy*
(c)   *Determined by ^{1}H NMR spectroscopy after deconvolution - "Regular" units are isoprene units that are only involved in Ip-Ip sequences, and not in St-Ip sequences*
(d)   *In brackets, calculated number considering two neighbouring units per styrene*
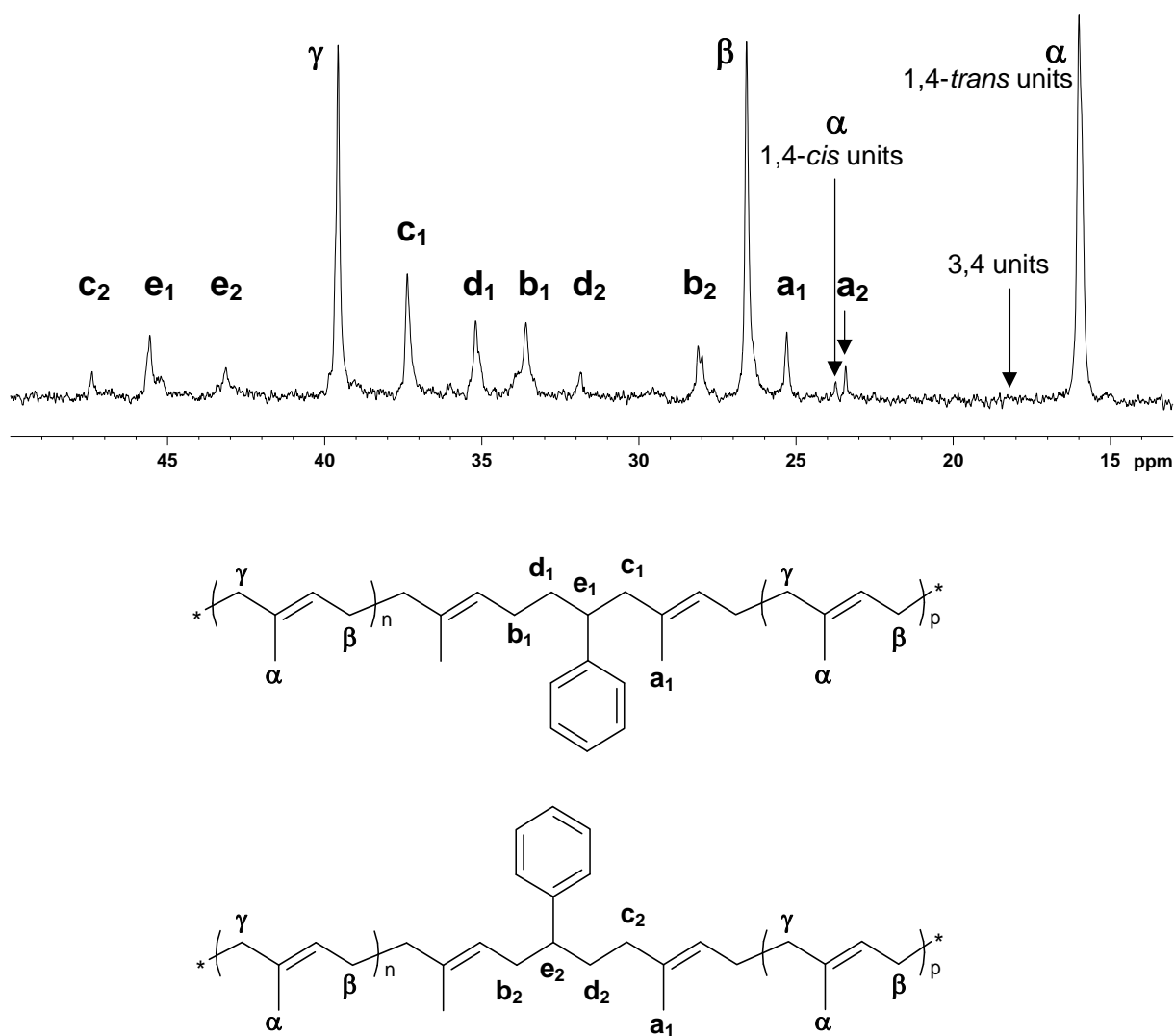
Table 2. Environment of styrene units.

Figure 1. ^{13}C NMR spectra of a poly(1,4-*trans* isoprene-*co*-styrene) containing 15% mol. styrene obtained using precatalyst **1**. The proposed assignment of the signals is based on DEPT experiments. Styrene insertion mode is represented by under script numbers (primary-1 and secondary-2) and was assigned arbitrarily.
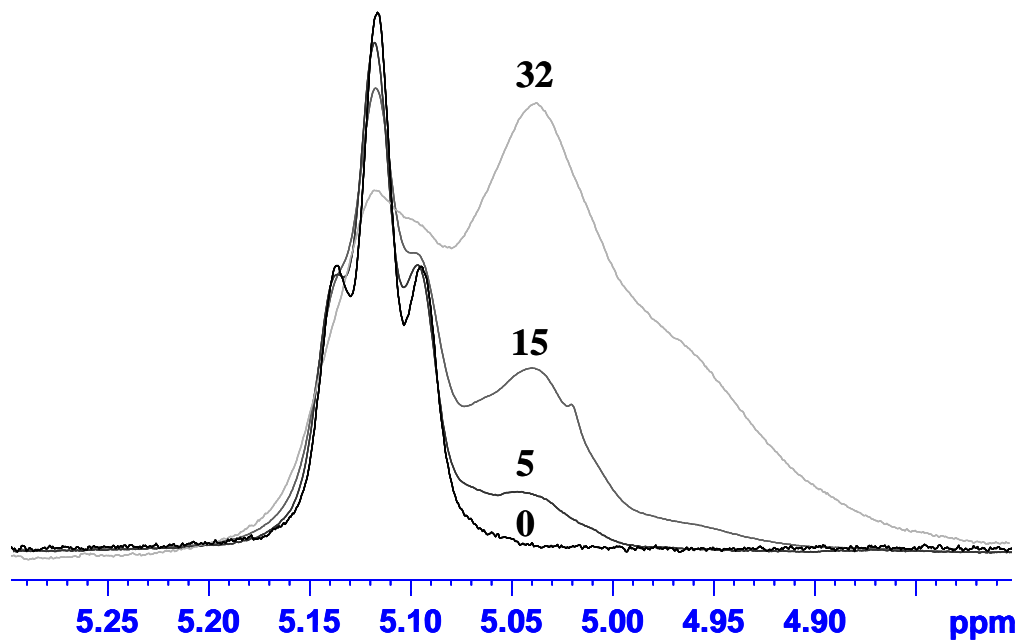
Figure 2. ^{1}H NMR spectra of polyisoprene and poly(1,4-*trans* isoprene-*co*-styrene) in the ethylenic proton zone corresponding to entry 1 (0% styrene inserted, polyisoprene), 8 (5% styrene inserted), 3 (15% styrene inserted) and 10 (32% styrene inserted).
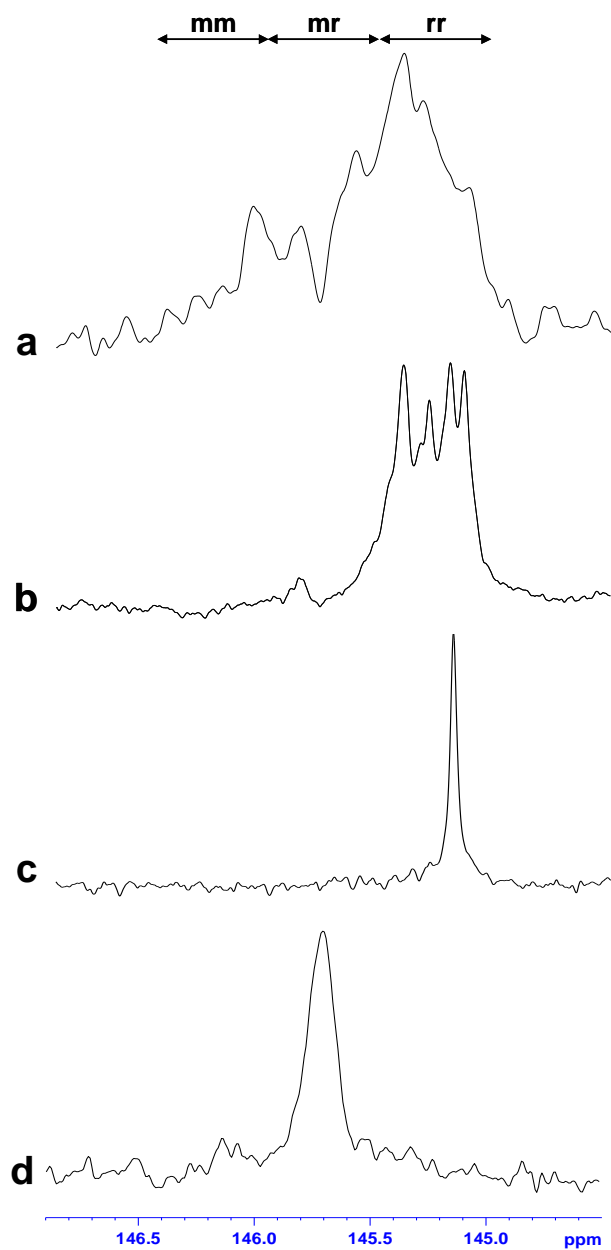
Figure 3. ^{13}C NMR spectra in the phenyl *ipso* carbon region for atactic polystyrene resulting from an AIBN initiated radical polymerization (a), for syndiotactic rich (85%) and fully syndiotactic polystyrene resulting from a coordinative polymerization using **3** / *n*-butylethylmagnesium (b) and CpTiCl$_3$/MAO (c) respectively and for poly(1,4-*trans* isoprene-*co*-styrene) obtained using precatalyst **1** (entry 5).

References

[1] B.A. Dolgoplosk, S.I. Beilin, Y.V. Korshak, K.L. Makovetsky, E.I. Tinyakova, *J. Polym. Sci.* **1973**, *11*, 2569

[2] S.K.H. Thiele, D.R. Wilson, *J. Macromol. Sci.* **2003**, *C43 (4)*, 581

[3] E. Dyer, D.L. Munroe, *J. Am. Chem. Soc.* **1946**, *68*, 2726.

[4] D.J. Kelley, A.V. Tobolsky, *J. Am. Chem. Soc.* **1959**, *81*, 1597.

[5] X. Xu, X. Ni, Z. Shen, *Chin. J. Chem.* **2004**, *22*, 764.

[6] [6a] Y. Jin, P. Wang, F. Pei, G. Cheng, L. Cui, C. Song, *Polym. Commun.* **1996**, *37*, 349 ;

[6b] E. Kobayashi, S. Kaita, S. Aoshima, J. Furukawa, *J. Polym. Sci., Polym. Chem.* **1998**, *36*, 2283.

[7] K. Endo, K. Masaki, *Macromol. Rapid Commun.* **1995**, *16*, 779.

[8] Q. Zhang, X. Ni, Y. Zhang, Z. Shen, *Macromol. Rapid Commun.* **2001**, *22*, 1493.

[9] [9a] C. Pellechia, A. Proto, A. Zambelli, *Macromolecules* **1992**, *25*, 4450; [9b] N. Naga, Y. Imanishi, *J. Polym. Sci., Polym. Chem.* **2003**, *41*, 939.

[10] P. Boochathum, S. Chiewnawin, *Eur. Polym. J.* **2001**, *37*, 429.

[11] J. Song, B. Huang, D. Yu, *J. Appl. Polym. Sci.* **2001**, *82*, 81.

[12] J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nickias, R.K. Rosen, G.W. Knight, S. Lai, Eur. Pat. Appl. 416815, 1990 (to Dow Chemical Co.); *Chem. Abstr.* **1991**, *115*, 93163.

[13] F. Bonnet, M. Visseaux, D. Baudry, A. Dormont, *Macromolecules* **2002**, *35*, 1143.

[14] J. Thuilliez, V. Monteil, R. Spitz, C. Boisson, *Angew. Chem.* **2005**, *117*, 2649.

[15] M. Arndt, I. Beulich, *Macromol. Chem. Phys.* **1998**, *199*, 1221.

[16] D.W. Smith, Jr, K.B. Wagener, *Macromolecules* **1993**, *26*, 3533.

[17] [17a] F. Bonnet, M. Visseaux, A. Pereira, D. Barbier-Baudry, *Macromolecules* **2005**, *38*, 3162; [17b] P. Zinck, D. Barbier-Baudry, A. Loupy, *Macromol. Rapid Commun.* **2005**, *26*, 46; [17c] P. Zinck, M. Visseaux, A. Mortreux, *Z. Anorg. All. Chem.* **2006**, *632*, 1943.

[18] J.F. Pelletier, A. Mortreux, X. Olonde, K. Bujadoux, *Angew. Chem.* **1996**, *35*, 1854.

[19] G. Xu, *Macromolecules* **1998**, *31*, 2395.

[20] N. Ishihara, T. Seimiya, M. Kuramoto, M. Hoi, *Macromolecules* **1986**, *19*, 2464.

[21] D. Barbier-Baudry, A. Dormond, P. Desmurs, *C.R. Acad. Sci. Paris t.2* **1999**, *IIc*, 375.

[22] Furukawa, *Pure Appl. Chem.* **1975**, *42*, 495.

[23] S. Tobish, R. Taube, *Organometallics* **1999**, *18*, 5204.

[24] [24a] D. Barbier-Baudry, E. Camus, A. Dormond, M. Visseaux, *Appl. Organometal. Chem.* **1999**, *13*, 813; [24b] E. Kirillov, C.W. Lehmann, A. Razavi, J.F. Carpentier, *J. Am. Chem. Soc.* **2004**, *126*, 12240.

Table of content

The insertion of styrene single units in polyisoprene has been accessed for the first time using borohydrido rare earths / dialkylmagnesium systems, yielding a new family of SBR rubbers. The resulting poly(1,4-*trans* isoprene − *co* − styrene) exhibits quite narrow molecular weight distributions, with up to 30% styrene inserted. The presence of a bulky and electron-rich ligand in the coordination sphere of the metal leads to a slight increase of the amount of styrene inserted, together with narrower chemical composition and molecular weight distributions. The presence of important quantities of styrene in the medium does not alter the selectivity of the reaction, as observed for *cis* stereoselective polymerization mechanisms.