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## Isoprene chain shuttling polymerisation between *cis* and *trans* regulating catalysts: straightforward access to a new material

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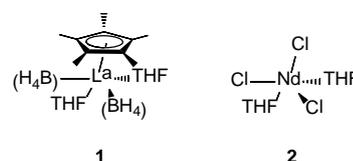
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**Isoprene chain shuttling polymerisation between the 1,4-*trans* regulating Cp\*La(BH<sub>4</sub>)<sub>2</sub>(THF)<sub>2</sub> / Mg<sup>n</sup>BuEt (Cp\* = C<sub>5</sub>Me<sub>5</sub>) and the 1,4-*cis* regulating NdCl<sub>3</sub>(THF)<sub>2</sub> / AlR<sub>3</sub> (R=Et or <sup>t</sup>Bu) systems provides access to stereoblock polyisoprene. In selected experimental conditions, the *trans* segments are semi-crystalline, leading to a thermoplastic elastomer-like material.**

Synthetic polydienes are widely used in our daily life, in pneumatics for instance. They are known for more than 50 years, and yet, there is still a great interest of the scientific community in the field, with notably the design of catalytic systems able to control the microstructure via regio- and/or stereo-selective polymerisations. The control of the macromolecular microstructure at the scale of the blocks, *i.e.* the formation of blocky architectures is also an expanding field.<sup>1</sup> Di and triblock copolymers comprising a stereoregular polydiene block linked to polar blocks were synthesized recently by a combination of coordinative chain transfer polymerisation (CCTP), ring-opening polymerisation and atom-transfer radical polymerisation (ATRP).<sup>2–5</sup> A soft-hard poly(1,4-*cis*-co-1,2 butadiene)-*block*-poly(1,2 butadiene) was synthesized by the sequential addition of triisobutylaluminium in the course of the polymerisation of butadiene mediated by an iron based catalytic system.<sup>6</sup> The sequential introduction of the aluminium alkyl allowed to increase the 1,2-regioselectivity of the reaction. The formation of a poly(1,4-*trans* isoprene)-*block*-poly(1,4-*cis* isoprene) diblock copolymer was reported recently by the sequential introduction of modified methylaluminoxane (MMAO) and Me<sub>2</sub>SiCl<sub>2</sub> in the course of the polymerisation of isoprene mediated by the Nd(BH<sub>4</sub>)<sub>3</sub> / dialkylmagnesium system, affording the drastic switch of the



**Scheme 1.** Structures of the rare earth precatalysts used in this study

stereoselectivity from 1,4-*trans* to 1,4-*cis*.<sup>7</sup> *cis*-*trans* stereomultiblock polyisoprene were, as far as we know, not reported in the literature.

Chain shuttling polymerisation allows the access to multiblock microstructures in a straightforward one-step way.<sup>8</sup> This concept has been developed in the frame of both statistical copolymerisation of two monomers<sup>9–13</sup> and homopolymerisation of a single monomer. Regarding the latter, Busico and coworkers<sup>14</sup> reported the access to isotactic stereoblock polypropylene using a racemic mixture of the chiral isotacticselective (pyridyl-amide)HfMe<sub>2</sub> catalyst for the polymerisation of propylene. The shuttling was allowed by the presence of AlMe<sub>3</sub> in methylaluminoxane (MAO). Ethylene chain shuttling polymerisation was achieved using a  $\alpha$ -diimine Ni(II) bromide and *ansa*-ethylenebis(1- $\eta^5$ -indenyl) Zr chloride complexes.<sup>15</sup> The nickel catalyst produces branched polyethylene blocks through chain walking polymerisation, while the zirconocene leads to linear polyethylene blocks. Regioselective isoprene chain shuttling polymerisation was reported recently by Cui and coworkers using a combination between a 1,4 regulating pyridyl-methylene fluorenyl scandium complex and the 3,4 regulating lutetium analogue.<sup>16</sup>

Our research group previously reported that catalytic systems based on Cp\*La(BH<sub>4</sub>)<sub>2</sub>(THF)<sub>2</sub> (**1**)<sup>15</sup> (Cp\* = C<sub>5</sub>Me<sub>5</sub>) combined to 1 equiv. magnesium dialkyl and several equiv. aluminium trialkyl as chain transfer agent allows a 1,4-*trans* stereospecific CCTP of isoprene.<sup>18</sup> Besides, catalytic systems based on NdCl<sub>3</sub>(THF)<sub>2</sub> (**2**) combined to aluminium alkyls are known since the late eighties to allow the 1,4-*cis* stereospecific CCTP of isoprene<sup>19–20</sup> (although the CCTP terminology was introduced 20 years later<sup>21</sup>). We envisioned thus the formation

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**Table 1.** Isoprene polymerisation mediated by **1** and/or **2** combined to magnesium and aluminium alkyls <sup>a</sup>

Entry	Cat 1/2	AlR <sub>3</sub>	Tol (ml)	Time (h)	Yield (%)	% <i>Trans</i> <sup>b</sup>	% <i>Cis</i> <sup>b</sup>	% 3,4 <sup>b</sup>	<i>M<sub>n</sub></i> g/mol <sup>c</sup>	<i>D<sub>m</sub></i> <sup>c</sup>	DPn block <sup>d</sup>		N block <sup>e</sup>	<i>T<sub>g</sub></i> <sup>f</sup> (°C)	<i>T<sub>m</sub></i> <sup>f</sup> (°C)	$\Delta H_m^f$ (J/g)
											<i>trans</i>	<i>cis</i>				
1	100/0	-	1	2	82	98	0	2	23300	1.20	-	-	-	-64.7	58.0	65.3
2	0/100	Et	1	0.5	61	0	97	3	12400	2.63	-	-	-	-63.2	-	-
3	0/100	iBu	1	0.33	68	0	99	1	22600	2.31	-	-	-	-63.0	-	-
4	50/50	Et	2	18	76	68	30	2	21000	2.39	4.2	1.7	51.9	-67.4	-	-
5	50/50	iBu	2	18	87	75	24	1	6400	2.58	7.1	1.7	10.8	-66.8	38.6	7.5

<sup>a</sup> Experimental conditions : **1** = Cp\*La(BH<sub>4</sub>)<sub>2</sub>(THF)<sub>2</sub>, **2** = NdCl<sub>3</sub>(THF)<sub>2</sub>, n(La) = n(Nd) = 1.10<sup>-5</sup> mol, [IP]/[La + Nd] = 1000, [La]/[Mg] = 1, [Mg] = Mg<sup>n</sup>BuEt, [Nd]/[Al] = 20, [Al] = AlEt<sub>3</sub> or Al<sup>i</sup>Bu<sub>3</sub>, 50°C in toluene. <sup>b</sup> Microstructure determined by <sup>1</sup>H (entries 1-3) or <sup>13</sup>C quantitative NMR (entries 4-5) in CDCl<sub>3</sub>. <sup>c</sup> Number-average molecular weight determined by size exclusion chromatography (SEC) in THF using polystyrene standards and corrected by a factor 0.5<sup>22-23</sup> and dispersity. <sup>d</sup> Number-average degree of polymerisation of the blocks determined by quantitative <sup>13</sup>C NMR spectroscopy. DPn<sub>trans</sub> = C4(39.83 ppm) / C4' (40.07 ppm) + 1; DPn<sub>cis</sub> = C6 (32.31 ppm) / C6' (32.02 ppm) + 1. <sup>e</sup> Total number of blocks determined by Mn/68/(DPn<sub>trans</sub> + DPn<sub>cis</sub>); <sup>f</sup> Glass transition temperature, melting temperature and melting enthalpy determined by differential scanning calorimetry.

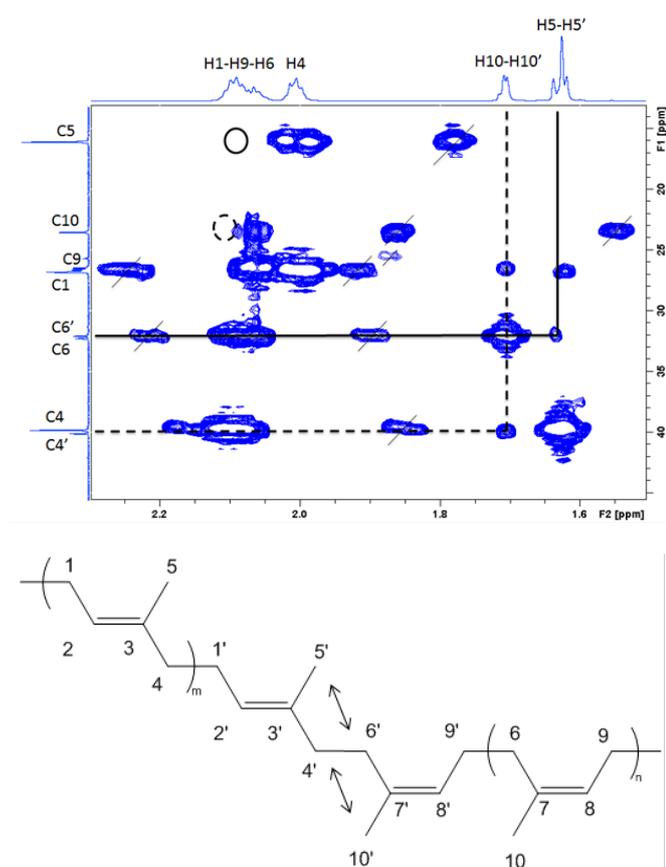
of *cis-trans* stereomultiblock polyisoprene by chain shuttling polymerisation using a combination of these two catalytic systems. As poly(1,4-*trans* isoprene) is semi-crystalline at room temperature, the formation of thermoplastic elastomers-like materials was further expected. We report herein the unprecedented chain shuttling polymerisation of isoprene between a *trans* and a *cis* regulating catalyst.

Entries representative of the polymerisation of isoprene mediated by Cp\*La(BH<sub>4</sub>)<sub>2</sub>(THF)<sub>2</sub> (**1**) combined to 1 equiv. *n*-butylethylmagnesium and NdCl<sub>3</sub>(THF)<sub>2</sub> (**2**) combined to 20 equiv. trialkylaluminium (AlEt<sub>3</sub> or Al<sup>i</sup>Bu<sub>3</sub>) are presented in Table 1, entries 1-3. The polymerisations are stereospecific, yielding poly(1,4-*trans* isoprene) (entry 1) and poly(1,4-*cis* isoprene) (entries 2 and 3), respectively, in 30 min to 2 h. The molecular weight distribution is narrow considering **1** (figure SI1), and broad with **2**, (figure SI2) as reported in the early study.<sup>20</sup> Polymerisations conducted using a 50/50 mixture of **1** and **2** combined to 1 equiv. *n*-butylethylmagnesium and 20 equiv. trialkylaluminium are further reported in Table 1 (entries 4-5). For these experiments conducted in the presence of the two complexes, each catalyst solution *i.e.* **1**/Mg<sup>n</sup>BuEt and **2**/AlR<sub>3</sub> (R = Et or *i*Bu) were prepared separately before being mixed. In these experimental conditions, AlR<sub>3</sub> plays the role of both the alkylating agent for **2** and the chain transfer/shuttling agent of the system. The polymerisation in the presence of the two catalysts remains 1,4 regiospecific, the *trans* stereoisomer being majority. From the chromatograms (see figure SI3 in the SI section), the molecular weight distribution is broad, as observed using the **2**/AlR<sub>3</sub> system alone. Although one can not

distinguish the two populations that should be observed in the absence of shuttling between the two catalysts, it is not possible to prove unambiguously the occurrence of chain shuttling by SEC. NMR proved in turn to be a convenient tool for this prospect.

<sup>1</sup>H NMR and <sup>13</sup>C NMR spectra of entries 1-5 together with those of a physical mixture between poly(1,4-*trans* isoprene) and poly(1,4-*cis* isoprene) (entries 1+2) are presented in the SI section. Signals representative of poly(1,4-*trans* isoprene) and poly(1,4-*cis* isoprene) can be distinguished on the <sup>13</sup>C spectra of the samples made in the presence of the two catalysts precursors (see also Fig. 1 on the 2D spectrum). The C4 and C6 carbons signals relative to *trans* and *cis* units respectively are split in 2 signals, which is not the case in the <sup>13</sup>C NMR spectra of the physical mixture. The HMBC analysis (Fig. 1 and figure SI14) shows further two correlations that are not observed on the spectrum resulting from a physical mixture of poly(1,4-*trans* isoprene) with poly(1,4-*cis* isoprene) (Figure SI15), between the carbon C4' and the proton H10' (dashed line in Fig. 1) and between the carbon C6' and the proton H5' (solid line in Fig. 1) respectively. These correlations shows that a substantial amount of covalent bonds exists between *cis* and *trans* stereoisomers, a clear evidence of the occurrence of chain shuttling polymerisation between the *cis* regulating Nd center and the *trans* regulating half-lanthanocene catalyst.<sup>24</sup> In addition, no correlation signals between C5 and H9 (black solid circle) are observed indicating that there are no occurrences of head-to-tail *trans-cis* linkages. The situation is probably similar between C10 and H1 (dashed circle),

Fig 1. 2D HMBC spectrum of entry 4. Artefacts are crossed†



indicating no tail-to-head *cis-trans* linkages, although the proximity of H6, with which a correlation is expected, may prompt caution. This NMR analysis suggests thus that *cis-trans* links between the blocks are of the head-to-head type. This can be understood under the hypothesis of a 4,1 polymerization of isoprene mediated by **2** / AlR<sub>3</sub> (see scheme S11). Fractionation experiments enabling to separate poly(1,4-*cis* isoprene) and poly(1,4-*trans* isoprene) from a physical mixture of the two polymers<sup>25-26</sup> were conducted and did not allow to extract any polymer. The integration of the C4' and C6' signals vs. C4 and C6 respectively on the quantitative <sup>13</sup>C NMR spectrum enables to determine a number-average degree of polymerisation (DP<sub>n</sub>) for the *trans* and *cis* blocks respectively, given in Table 1. The poly(1,4-*trans* isoprene) blocks have a higher DP<sub>n</sub> than the poly(1,4-*cis* isoprene) blocks, the latter having a DP<sub>n</sub> around 1.7 in the reported experimental conditions whatever the aluminium based cocatalyst. Al<sup>i</sup>Bu<sub>3</sub> as chain shuttling agent leads to a higher DP<sub>n</sub> for the *trans* blocks than AlEt<sub>3</sub> (7.1 vs. 4.2). This leads to a total number-average number of blocks per macromolecule of more than 50 for entry 4, and of ca. 12 for entry 5. The overall transfer efficiency in the course of the chain shuttling polymerization is higher for Al<sup>i</sup>Bu<sub>3</sub> vs. AlEt<sub>3</sub>, while it is the opposite for the NdCl<sub>3</sub> / AlR<sub>3</sub> systems. The former follows actually the same trend as that observed for the 1/Mg<sup>n</sup>BuEt/AlR<sub>3</sub> system<sup>18</sup> which can be understood on the

basis of a higher activity of the active species derived from **1** in chain shuttling conditions.

In agreement with the literature, differential scanning calorimetry analyses indicate that while poly(1,4-*trans* isoprene) is semi-crystalline at room temperature (entry 1), poly(1,4-*cis* isoprene) is fully amorphous (entries 2-3). The glass transition temperatures of the two elastomer precursors are around -65°C and -63°C respectively. The thermal properties measured for entries 4 and 5 shows that the stereoblock polyisoprene synthesized using AlEt<sub>3</sub> (entry 4) is fully amorphous, while the material obtained using Al<sup>i</sup>Bu<sub>3</sub> as chain shuttling agent (entry 5) is semi-crystalline. This difference can be related to the length of the *trans* blocks, the higher DP<sub>n</sub> obtained for entry 5 vs. entry 4 favouring crystallisation. The decrease of the melting enthalpy between the first and the second heating (Table S11) indicates further that the material as a slow crystallization kinetics. Wide angle X-Ray Scattering (WAXS) analyses (figure S116) reveal that the crystalline form involved in the new material is the same as that observed for pure poly(1,4-*trans* isoprene), confirming that pure *trans* polyisoprene segments have been formed during the synthesis. The mechanical properties of the new material were finally characterized. Entry 4 was found to lead to films that were too soft and too sticky to be characterized, in a similar way to poly(1,4-*cis* isoprene). Poly(1,4-*trans* isoprene) could not be characterized either as fragmentation of the films occurred during their formation. Entry 5 led in contrast to films strong enough to be characterized. The new stereoblock material is ductile with a strain at break near 100% and an elastic modulus around 2 MPa (Fig S117). A polyisoprene with a 70/30 *trans-cis* microstructure synthesized using a single catalyst<sup>27</sup> did also lead to a melting temperature (see Table S11), but its sticky character did not allow the formation of films suitable for mechanical testing. It should be noted that *cis-trans* stereomultiblock polybutadiene were characterized in the past, but crosslinking had to be realized before affording a material with mechanical properties.<sup>28</sup> The synthesis of these elastomer precursors is unfortunately poorly described.<sup>29</sup>

In conclusion, we report for the first time the chain shuttling polymerisation of isoprene between a *trans* and a *cis* regulating catalysts and the structural characterization of the resulting stereomultiblock polyisoprene. We are now exploring the windows of microstructures that this type of chain shuttling catalytic system can offer in order to develop a class of thermoplastic elastomers available from a one-step reaction and a single monomer.

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## Notes and references

‡ Artefact: a common artefact is the appearance of one-bond correlations. HMBC is "tuned" to detect the small couplings arising from long-range interactions, but this is not perfect. These one-bond artefacts appear as doublets in  $f_2$ , with  $J = 1$  J CH this splitting is itself useful information. However, most of the time, one should be wary of these artefacts. They are usually easy to identify as they will appear as pairs of peaks (proton split by  $\sim 60 - 160$  Hz one bond J-coupling).

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