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Catalytic chain transfer (co-)polymerization using borohydridohalflanthanidocene / dialkylmagnesium combinations: polyisoprene CCG and *co-transmetalation* as a new concept to tune the composition of a copolymer

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Abstract

Borohydridohalflanthanidocene / dialkylmagnesium combinations are found to be powerful catalytic systems for the chain transfer polymerization of isoprene and its copolymerization with styrene. A behavior close to a lanthanide catalyzed polyisoprene chain growth on magnesium is reported. Transmetalation is further shown to occur in the course of the statistical copolymerization of isoprene and styrene. For the same monomer feed, the amount of styrene inserted in the copolymer can be increased by a **factor 3 using 10** eq. dialkylmagnesium *vs.* 1 in the range of our experimental conditions. Chain transfer in the course of a metal catalyzed statistical copolymerization may thus be viewed as a new and original way for the control of the composition of a copolymer.

Introduction

Chain transfer polymerization presents various advantages over single component polymerization catalysis, including atom economy, molecular weight control and terminal

functionalization.^[1] Such a process is particularly interesting if the transmetalation between the transition metal and the chain transfer agent shows a rapid and reversible character, and involves all alkyl groups from the main group metal in the absence of other termination reactions. Such a behavior is known as a catalyzed chain growth (CCG), about which our laboratory described more than one decade ago the first example of reversible and living transfer polymerization of ethylene involving lanthanidocene and magnesium dialkyls for the synthesis of long chain dialkylmagnesiums.^[2] We reported recently half-lanthanidocenes / dialkylmagnesium catalytic systems that show good potentialities for styrene transfer polymerization,^[3] and notably the first polystyrene CCG. The same catalytic systems had also shown also good potentialities for the polymerization of isoprene^[4] and its statistical copolymerization with styrene.^[5] Furthermore, the literature devoted to the transmetalation of a growing polydiene chain between a transition metal and aluminum, magnesium or zinc show that so far, the transfer generally occurs with a moderate efficiency,^{[6]-[12]} apart from a tris(aryloxy) lanthanide–dialkylmagnesium mediated butadiene oligomerization from our group.^[11] On the other hand, chain transfer in the course of a statistical copolymerization has been moderately dealt with so far and mainly focused on the chain end functionalization of the resulting copolymers.^{[1];[13]} We report in this contribution preliminary results of our investigations on polymerization reactions using half lanthanidocene–dialkylmagnesium combinations, namely (i) an exceptional dual transfer efficiency in the course of the polymerization of both isoprene and styrene and (ii) the application of this versatile catalytic system as a new and easy route to tune the composition of the resulting styrene-isoprene copolymers.

Experimental

Materials

All operations were performed under dry argon by using Schlenk techniques. Toluene was dried over sodium / benzophenone and distilled over molecular sieves before use. Styrene and isoprene (99% from Aldrich) were dried over calcium hydride, distilled twice over molecular sieves and once just before use. *n*-butylethylmagnesium (20% wt. in heptane from Texas Alkyl) was used as received. The complex $\text{Cp}^*\text{La}(\text{BH}_4)_2(\text{THF})_{2.5}$ (**1**) ($\text{Cp}^*=\text{C}_5\text{Me}_5$) was synthesized by the reaction between 1 eq. $\text{La}(\text{BH}_4)_3(\text{THF})_3$ (synthesized after ^[16]) and 1 eq. KCp^* (synthesized from the reaction between HCp^* and KH) in THF. The reaction mixture was stirred at room temperature for 4 days, filtered and evaporated to dryness. Yield: 91%. ¹H NMR (benzene-*d*₆): 15H, Cp^* at 2.24 and 2.30 ppm, 8H+8H, THF at 1.33 and 3.70 ppm respectively, 8H, BH_4 elapsed in the baseline. After distillation of a slight amount of THF in the NMR tube, the Cp^* signal at 2.30 ppm vanished at the profit of the signal at 2.24 ppm. The signals at 2.30 observed for the crude compound was thus attributed to a bridged THF adduct oligomeric form that dissociates in the presence of THF.^[15] After drying under vacuum 48h at 60 °C, **1** was obtained in the solvent-free form $\text{Cp}^*\text{La}(\text{BH}_4)_2$. Anal. Calcd for $\text{C}_{10}\text{H}_{23}\text{B}_2\text{La}$. C,39.53; H,7.63. Found: C,40.12; H,7.48. The complex $\text{Cp}^*\text{Nd}(\text{BH}_4)_2(\text{THF})_2$ (**2**) was synthesized according to literature procedure.^[14]

Polymerization

In a glove box, the borohydrido complex was weighed into a glass vessel. Toluene, the monomer(s) and *n*-butylethylmagnesium were added in this order using syringes. The mixture was magnetically stirred at the reaction temperature for a given time, quenched with methanol, eventually diluted in toluene and poured into methanol, leading to the precipitation of the polymer. Solvents were evaporated under partial vacuum, and the product was dried under vacuum until constant weight.

Measurements

NMR analyses of polyisoprene and copolymer samples were conducted on a AC 300 Brücker at room temperature in $CdCl_3$ and tetrachloroethane-*d*₂, respectively. The chemical shifts were calibrated using the residual resonances of the solvent. Quantitative ¹³C NMR was realized using the zgig sequence (Brücker library). The relaxation time d1 was set to 2,5 and 8s and it was found that a relaxation time of 5s is necessary to allow the relaxation of all carbon nucleus. Size exclusion chromatography (SEC) was performed in THF as eluent at 40°C using a Waters SIS HPLC-pump, a Waters 410 refractometer and Waters styragel column (HR2, HR3, HR4, HR5E) calibrated with polystyrene standards. A correction factor of 0.5 was applied for the determination of the true number-average molecular weight of polyisoprene.^[17] DSC measurements were conducted under nitrogen on a Setaram 141 apparatus at a heating rate of 10°C.min⁻¹ from -120°C to 300°C using around 20 mg samples in aluminum crucibles.

Results

Isoprene transfer polymerization

Representative results of isoprene polymerization using **1** combined to *n*-butylethylmagnesium are presented in Table 1, entries 1-5. The observed molecular weight distributions are monomodal, and the number average molecular weight is close to the calculated one considering two growing chains per magnesium atom. Reasonable polydispersities are obtained, with PDI in the range 1.3-1.6. This highlights a behavior that is close to a lanthanide catalyzed polyisoprene chain growth on magnesium. The transmetalation is accompanied by a modification of the selectivity of the reaction: a 98.5 % 1,4-*trans* polyisoprene is obtained in the presence of 1 eq. *n*-butylethylmagnesium while 39% isoprene units are in a 3,4 enchainment in the macromolecules obtained using 10 eq. chain transfer

agent. Using the neodymium homologue **2** for the transmetalation lead to a broader distribution (PDI 1.9- entry 7), together with a slightly higher amount of 3,4 units.

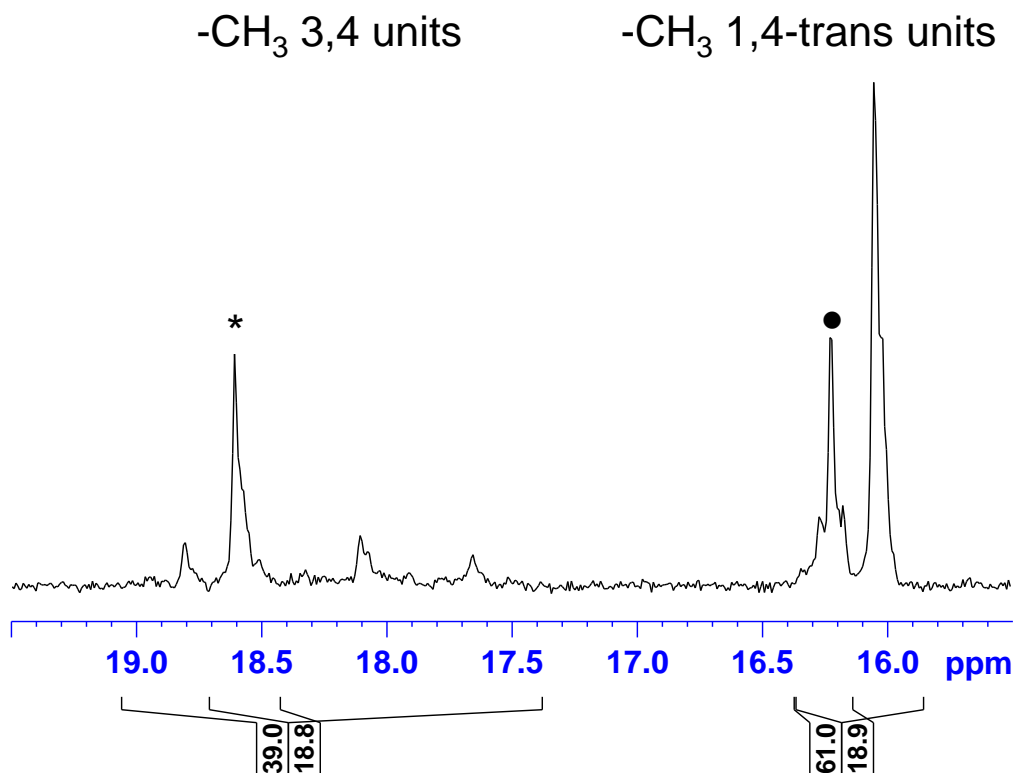


Figure 1. ¹³C NMR spectra of polyisoprene (entry 4) in the methyl zone.

The thermograms of entries 5 and 7 show a unique glass transition temperature, around -47°C vs. -66°C for 1,4-*trans* polyisoprene. Quantitative ¹³C NMR analysis represented Figure 1 shows that among the 61% 1,4-*trans* units, around one third (19%) are located near a 3,4 unit (peak labeled •) while the remaining two thirds (42%) are surrounded by 1,4-*trans* units. The 19% value corresponds well to the integral value of the main peak of the 3,4 zone (labeled *). In other words, among the 39% 3,4 units, around one half (19%) are connected to a 1,4-*trans* unit while the other half (20%) are surrounded by other 3,4 units, as highlighted by a NMR spectra similar to poly(3,4-isoprene). The attribution of these 20% 3,4 units to a pure homopolymer would imply that the copolymer has a microstructure consistent

with the repetition of two 3,4 units between a 1,4-*trans* backbone, which would not lead to a unique signal on the ^{13}C NMR spectra in the $-\text{CH}_3$ zone. These observations, together with the monomodal character of the chromatograms and the presence of a unique glass transition temperature indicates that the 3,4 units are inserted into a 1,4-*trans* backbone, and that the polymer is not a mix between poly(1,4-*trans* isoprene) and poly(3,4-isoprene).

The increase of the proportion of 3,4 units can be due to steric hindrance in the presence of an excess Mg, inducing a higher propensity to insert isoprene in the 3,4 configuration. This latter consideration would be a consequence of a transmetalation occurring in an olefin-like configuration, similar to that reported for styrene. Mechanistic investigations will be dealt with more deeply in a forthcoming study.

Co-transmetalation in the course of a statistical copolymerization

Results obtained on statistical copolymerization of isoprene and styrene starting from a 50/50 molar ratio in the presence of **1** and increasing amount of dialkylmagnesium are reported in Table 1 (entries 8-12). The number-average molecular weight of the copolymer decreases from 45200 to 8100 g/mol as the amount of dialkylmagnesium increases from 1 to 10 equivalents, highlighting the occurrence of a co-transmetalation of the growing macromolecular chain. The resulting molecular weight distributions are monomodal in all cases, and the polydispersity index increases from 1.3 to 1.8, highlighting the probable occurrence of other chain termination pathways and/or a partially irreversible character of the transfer. The amount of styrene inserted in the copolymer increases continuously in the presence of an excess dialkylmagnesium, from 12 to 32% mol, and the content of 3,4 isoprene units increases from 2 to 16% at the expense of the *trans*-selectivity. The glass transition temperature increases from around -57°C to around -31°C with the amount of styrene

inserted. Similar trends are obtained starting from the neodymium half sandwich **2**, with a slightly higher polydispersity however (PDI 2.0-entry 14 vs. 1.8 – entry 12).

Concluding remarks

The influence of an excess organometallic compound on the polymerization of dienes has been studied in the literature. The sole high efficiency reported for diene as far as we know concerns a neodymium catalyzed oligobutadiene chain growth on magnesium (1100 g/mol).^[11] To the best of our knowledge, if the changes in selectivity observed here have already been reported in the literature ^{[4a];[10a,c];[18]}, the polyisoprene transfer efficiency close to 100% obtained with our systems is noteworthy and unprecedented for molecular weight as high as 6000 - 30 000 g/mol. Furthermore, the influence of reversible transmetalation of the growing macromolecular chain on the composition of a copolymer has never been studied systematically as far as we know (although some experimental results were reported,^[13] the changes in copolymer composition remained unnoticed by the authors). In this study, we found that due to the dual CGC character of the half lanthanidocene catalyst, the composition of the copolymer can be easily changed by modifying the ratio of chain transfer agent in the reactive mixture. The comonomer content in a copolymer is usually tailored by reactor feed, catalyst modification or process considerations.^[19] The co-transmetalation can thus be viewed as a new and original route for the control of the composition of a copolymer. The influence of experimental parameters including feed is currently under studies, together with a deeper structural analysis of the polymers as well as mechanistic insights.

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Table 1. Isoprene and isoprene / styrene chain transfer (co-)polymerization

Entry ^{a)}	Metal	Ip/St	Mg Eq.	Time (h)	Yield (%)	\overline{M}_n ^{b)} (g/mol)	PDI	\overline{M}_n calc. ^{c)} (g/mol)	St ^{d)} (%)	Isoprene microstructure ^{e)}		Tg ^{f)} (°C)
										1,4- <i>trans</i> (%)	3,4 (%)	
1	La	1/0	1	2	73	64400	1.4	50500	-	98.5	1.5	-66
2	La	1/0	2	5	95	30800	1.3	32700	-	97	3	<i>n.d</i>
3	La	1/0	3	8	84	18500	1.5	19200	-	91	9	<i>n.d</i>
4	La	1/0	5	20	78	8800	1.6	10800	-	85	15	<i>n.d</i>
5	La	1/0	10	40	86	6200	1.6	5800	-	61	39	-48
6	Nd	1/0	1	2	76	43400	1.3	51700	-	98	2	-66
7	Nd	1/0	10	40	54	4300	1.9	3700	-	54	46	-47
8	La	1/1	1	2	48	45200	1.3	-	12	98	2	-57
9	La	1/1	2	5	54	41600	1.5	-	14	97	3	-53
10	La	1/1	3	8	56	25500	1.7	-	16	95	5	-53
11	La	1/1	5	20	79	18900	1.8	-	27	90	10	-36
12	La	1/1	10	40	58	8100	1.8	-	32	84	16	-31
13	Nd	1/1	1	2	30	54600	1.4	-	11	98	2	-59
14	Nd	1/1	10	40	39	7100	2.0	-	29	84.5	15.5	-35

^{a)} Reactions conducted at 50°C in 1.5 ml toluene using 1.5 ml isoprene ($1.5 \cdot 10^{-2}$ mol) for entries 1-7 and 1.1 ml styrene (10^{-2} mol) / 1 ml isoprene (10^{-2} mol) for entries 8-14. Monomer / Ln = 2000

^{b)} Number-average molecular weight determined by size exclusion chromatography corrected for polyisoprene (entries 1-4), in equivalent PS for entries 5-8 5,6 et 7 sont des manip faites avec uniquement l'isoprène: pourquoi en eq PS?

^{c)} Calculated polyisoprene number average molecular weight considering the yield and two growing chains per magnesium atom

^{d)} Styrene content of the copolymer from ¹H NMR measurements [^{3c}]

^{e)} From NMR measurements. The 1,4-cis content was found to be <1% in all cases

^{f)} from DSC measurements at 10°C/m