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VALORIZATION OF BIORESOURCES FOR THE PRODUCTIONOF POLYMER USING LANTHANIDE BOROHYDRIDE AS CATALYSTS

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ABSTRACT. The use of natural materials derived from biomass or biodegradable polymer materials can be one of the solutions to be considered in reducing environmental pollution problems. In addition, some polymers have been shown to be biocompatible and thus beneficial in biomedical applications. Therefore, within the framework of this study, we will present the results of the application of lanthanide-borohydride systems ($Nd(BH_4)_3(THF)_3$) combined with n-butylethyl magnesium in the block copolymerization of conjugated dienes (myrcene-styrene) and a conjugated diene with a polar monomer (L-lactide) for the synthesis of bio-sourced elastomers. The analysis of copolymers resulting from the copolymerization between myrcene and styrene shows that it is possible to insert up to 9.9% of styrene. Moreover, the stereoselectivity (1,4-*trans*) of the myrcene motif has not significantly changed, even in the presence of a significant amount of styrene in the reaction medium. The presence of the copolymer wasconfirmed by the observation of a peak at 146 ppm which corresponds to the ipso carbon of styrene.

Keywords: *coordination polymerization, β-myrcene, styrene, L-lactide, biomass, elastomers.*

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INTRODUCTION

Polymeric materials today are derived from monomers obtained from petrochemicals. The current situation with petroleum resources encourages exploring alternative sources of monomers, particularly those derived from agro-resources. On one hand, terpenes and on the other hand, lactide, are among these naturally sourced molecules that should be considered for valorization in this regard Lanthanide borohydrides are advantageous for use as precatalysts in polymerization [1]. One benefit is their ability to produce well-defined compounds that can be analyzed by X-ray, leading to better control over the polymerization process. They are highly soluble and can be accurately monitored using ^{1}H NMR, enabling precise observation of the reaction. Furthermore, these borohydrides are effective pre-catalysts for polymerizing conjugated dienes [2-6], myrcene [7], and olefins [8], and can also initiate the polymerization of polar monomers like cyclic esters [9-12] and acrylates [13-16].

There is growing interest in using polymers derived from biomass as a more sustainable alternative to traditional fossil-based polymers.Biopolymers are being extensively studied as potential replacements for common commodity polymers like polyolefins. Myrcene, a dimer of isoprene, found in many plant oils [17], has shown promise as a starting material for the production of biopolymers. Visseaux and his group achieved the first stereoselective coordination polymerization of myrcene using neodymium and lanthanum borohydride-based catalysts, resulting in highly regulated polymyrcene with 1,4-*cis* and 1,4-*trans* configurations [7]. The same group carried out the copolymerization and terpolymerization of this monomer with styrene and isoprene through coordinative mechanisms [18]. This acyclic monoterpene has been also copolymerized with 1,3-butadiene in a continuous process using finely divided alkali metals as catalysts and ether as a solvent [19]. Recent research has explored copolymerizing myrcene with other comonomers, including conjugated dienes [20], and lactide [21].

Polyolefin chemistry places a lot of attention on the production of block copolymers that contain both olefins and polar monomers since these polar groups can give the hydrocarbon chains useful features like adherence and paintability. Using a single-component lanthanide initiator, the first regulated diblock copolymerization of olefins with methylmethacrylate or caprolactone was accomplished [22].

The main subject of this article concerns the study of the block copolymerization of conjugated 1, 3-dienes, namely myrcene and styrene, as well as the sequential copolymerization of myrcene with lactide. In particular,

we are investigating the use of neodymium trisborohydride ($Nd(BH_4)_3(THF)_3$) combined with n-butylethyl magnesium (BEM) as catalysts in this process.

RESULTS AND DISCUSSION

Copolymerization of myrcene-styrene

The block copolymerisation of myrcene (Myr) and styrene (Styr) using $Nd(BH_4)_3(THF)_3$ combined with (BEM) as the initiator was conducted via a two-step process:

- The first step was the polymerisation of myrcene using [$Nd(BH_4)_3$ $(THF)_3$]/[BEM], [myrcene]/[Nd] = 300, and $V_{toluene}$=1 mL for 2h at 70°C.
- The required amount of styrene was added under the same conditions after 2h with $V_{toluene}$=0,5 mL.

Copolymerization yields and copolymer composition are presented in table 1.

Table 1. Myrcene-styrene copolymerization with $Nd(BH_4)_3(THF)_3$combined to dialkyl magnesium

Entry	Time (h)	[Nd]/ [BEM]	[Styr]/ [Nd]	Yield (%)	Mn [c] (g/mol)	PDI[c]	Myr (%)[d]	Selectivity (%)[e] 1,4-trans/ 3,4
1[a]	2	1	-	84	11000	1.33	100	96.95/3.04
2[b]	2	1	1000	63	10400	1.97	93.27	96.55/ 3.44
3 [b]	2	1.5	1000	81	4400	1.72	91.1	93.86/ 6.13
4 [b]	4	1.5	1000	83	3200	1.78	92.6	87.89/12.1
5 [b]	11	1.5	1000	80	2300	1.55	90.09	84.27/15.72

[a] experimental conditions: $V_{myrcene}$ = $V_{toluene}$ = 1 mL, [Myr]/[Nd]= 300, and the Temperature =70°C.
[b] experimental conditions: $V_{myrcene}$ = $V_{styrene}$ = $V_{toluene}$ = 1 mL, [Myr]/[Nd]= 300, and the Temperature =70°C.
[c] Determined by Steric Exclusion Chromatography.
[d] Copolymer composition (myrcene content) determined by ^{1}H NMR.
[e] The selectivity 1,4-*trans*/3,4-Percentage determined by ^{1}H NMR.

We wanted to study the possibility of creating 1,4-*trans* polymyrcene-block-polystyrene diblock copolymers by adding the styrene at a later stage, after polymerizing myrcene. The block copolymerization of this conjugated dienes using $Nd(BH_4)_3(THF)_3$ and n-buthylethyl magnesium as catalysts in toluene at 70°C displayed 1,4-stereospecificity, which was observed after 2 hours of reaction (polymerization of myrcene).

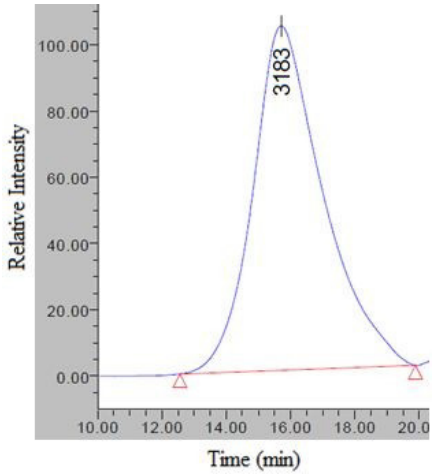

Figure 1: Chromatogram of polymyrcene-block-polystyrene copolymer (Table 1, Entry 4)

All the Steric Exclusion Chromatography (SEC) profiles show the monomodal character (Figure 1), which explains the presence of a copolymer rather than a mixture of two homopolymers, the dispersities (PDI = MW/Mn; Mn is the number-average molecular weight and MW is the weight average molecular weight) are lower than 2. In the presence of 1equiv of BEM in the reactive medium, approximately 6% of styrene can be inserted without affecting the stereoselectivity of the reaction. The microstructure of the copolymer's polymyrcene backbone displayed 84.27% to 96.55% 1,4-*trans* unit. However, when the reaction medium contains 1.5 equiv of BEM, 9% of styrene can be inserted accompanied with a gradual modification of the polymyrcene microstructure from 96.95% 1,4-*trans* to 84.27% 1,4-*trans* with an increase of the 3,4-microstructure in transfer conditions (3.4% 3,4 vs 15,72% 3,4). In addition, by varying the quantity of BEM while keeping a constant myrcene/ styrene ratio, chain transfer reactions to magnesium were observed since the molecular weights decrease as the quantity of BEM in the system increases. This modification in the polymyrcene microstructure and also the variation in the quantity of BEM were previously observed in homopolymerization of myrcene [7a].This increase in the 3,4 ratio within the polydiene is attributed to the steric hindrance induced by the presence of alkyl groups. This hindrance prevents the η^4 coordination mode of myrcene and results in the η^2 coordination mode of the monomer. A decrease in the molar mass of the polymers along with a narrow dispersity is observed, highlighting the presence of reversible transmetallation.

The microstructure of copolymer was determined by the ^{1}H NMR and the ^{13}C NMR. The ^{1}H NMR spectrum in $C_2D_2Cl_4$ (Figure 2) shows the peaks of protons corresponding to 1,4-*trans* polymyrcene in the copolymer and the peaks corresponding to styrene units in the copolymer. The signals between 1 and 1.1 ppm correspond to the methyl proton of the 1,4-double bonds of 1,4-*trans* unit of myrcene and the methylene of the styrene unit in the copolymer. The peak at 1.4 ppm corresponds to the CH_2 hydrogens of myrcene and the CH hydrogens of polystyrene, and the signal at 4.5 ppm corresponds to olefinic resonances assigned to the myrcene motif. The aromatic styrene was detected by presence of protons at 6.5 ppm.

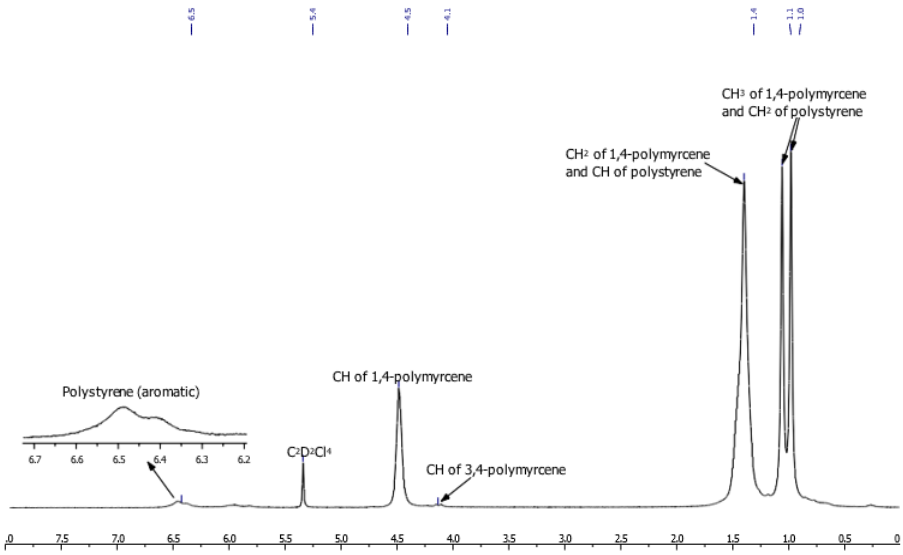

Figure 2: ^{1}H NMR (300 MHz, $C_2D_2Cl_4$) spectrum of myrcene-styrene copolymer (Table 1, Entry 4)

The ^{13}C NMR spectrum (Figure 3) displays the ten signals of poly(1,4-*trans*-myrcene) and the signals correspond to the carbons of the styrene units present in the copolymer. In the olefinic part of the spectrum, a singlet peak is detected at 146 ppm, corresponding to the phenyl ipso carbon (Cc), and chemical shifts are also observed around 140 ppm and 131.4 ppm,

corresponding to the two quaternary carbons of the myrcene unit in the copolymer (C2 and C8), as well as the signals at 128.3 ppm corresponding to aromatic signals. Around 124.8 ppm, we find the chemical shifts of the two CH groups of the myrcene unit (C3 and C7). In the aliphatic part of the spectrum, there are the two most shielded carbons correspond to the CH_3 groups of the myrcene unit (C9 at 17.70 ppm and C10 at 25.8 ppm), we have also detected the four signals corresponding to the methylene groups of the myrcene unit (C1 at 37.4 ppm, C4 at 27 ppm, C5 at 27.2 ppm and C6 at 30.5 ppm). Around 37 ppm, we identify the signal corresponding to the methylene groups of the styrene unit and at 39,9 ppm, we observe the chemical shift of the signal corresponding to the carbon of CH of styrene.

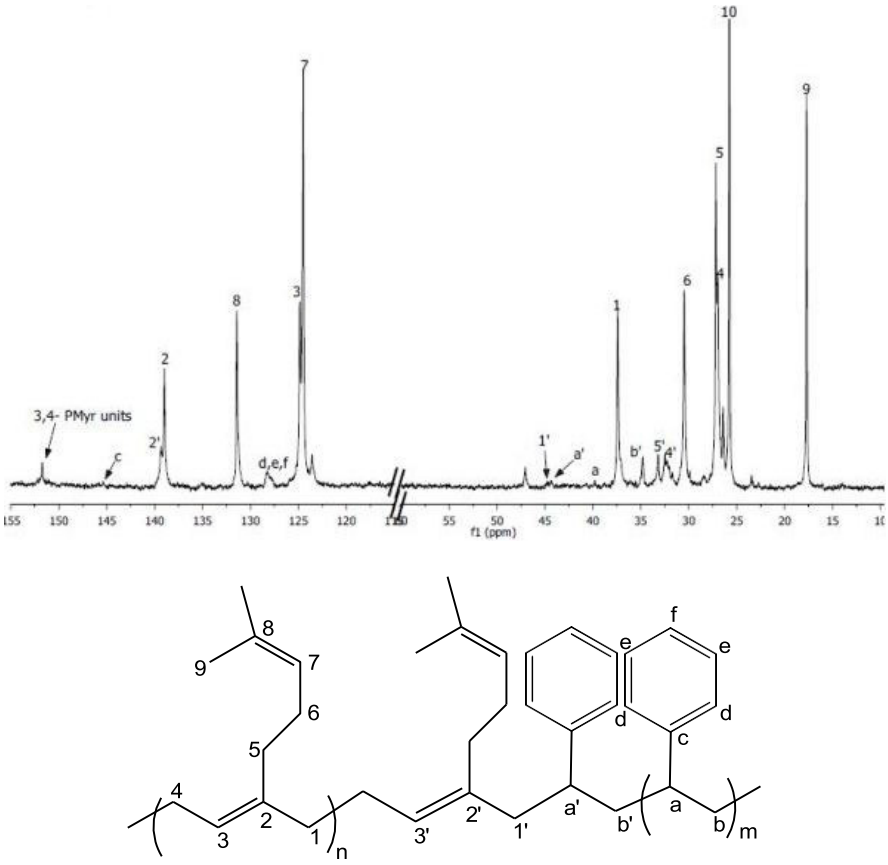

Figure 3: ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of myrcene-styrene copolymer (Table 1, Entry 4) and assignments.

The ^{13}C NMR data shows the *presence of new peaks 1' and a' corresponds to the association of a* myrcene unit with a styrene. The carbon in the polymyrcene backbone show two signals each. The main signal corresponds to polymyrcene (C1) (i.e., when the unit is adjacent to two other myrcene units). The signal referred to as (carbon') (C1') is attributed to the myrcene-styrene enchainments (Figure 3).

Copolymerization of myrcene-lactide

The Table 2 provides a summary of our attempts to synthesize a block copolymer from myrcene and lactide. A diblock copolymer of polymyrcene/ polylactid was obtained by adding the two monomers sequentially. Myrcene was polymerized in toluene for 2 hours at 70°C using neodymium trisborohydride ($Nd(BH_4)_3(THF)_3$) associated with n- butylethyl magnesium (BEM) as catalysts. Once the first polymyrcene block had formed, as indicated by a rise in viscosity, a solution of L- lactide was added, and the solution was stirred for an additional 4 hours at 50°C, resulting in a visible increase in viscosity.

Table 2: Myrcene-lactide copolymerization
with lanthanide borohydrides systems

Entry[a]	[myrcene]/[Nd][f]	[lactide]/[Nd][f]	[Nd][f]/BEM	Yield (%)
1[b]	300	50	1	70
2[c]	300	100	1	88
3[d]	300	50	1	72
4[e]	300	50	1,5	78

[a] Experimental conditions for myrcene: $V_{toluene}$=1mL, T°=70°C, t=2h.
[b] After the polymerization of myrcene, we add soluble lactide in 0,5 mL of toluene.
[c] After the polymerization of myrcene, we add soluble lactide in 1 mL of toluene.
[d] After the polymerization of myrcene, we add soluble lactide in 0,5 mL of THF.
[e] After the polymerization of myrcene, we add soluble lactide in 1 mL of THF.
[f] [Nd]= $[Nd(BH_4)_3(THF)_3]$.

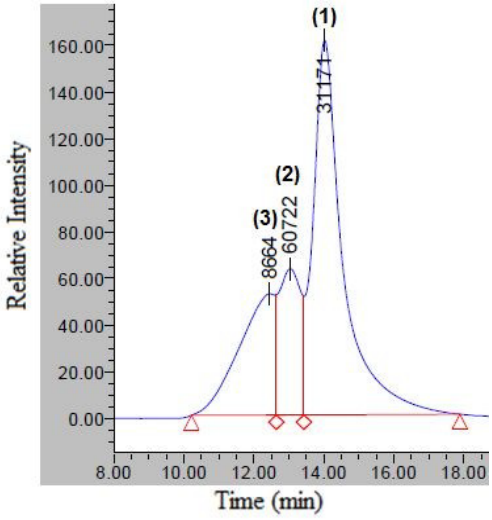

Figure 4: Chromatogram of the myrcene-lactide copolymer obtained using toluene as solvent (Table 2, Entry 1)

The initial experiments (table 2, entries 1 and 2) were conducted in toluene. After allowing the first block of myrcene to grow, lactide was added. The reaction mixture immediately solidifies. The SEC curve of the resulting polymer clearly shows the presence of three peaks with equal average molar masses of 31100, 60700, and 8700 g/mol, respectively, which may correspond to the two homopolymers and the block copolymer (see Figure 4). A sample taken before the addition of lactide showed that the mass of the first block of myrcene is approximately 31000 g/mol. Therefore, peak (1) corresponds to polymyrcene alone, likely due to the deactivation of the system at the time of adding the second monomer. Polymerization of lactide under the same conditions showed that the mass of the polylactide is significantly lower than 31100 g/mol, thus, peak (3) could be assigned to polylactide, while peak (2) could be assigned to a diblock polymyrcene-polylactide.

Additional experiments (table 2, entries 3 and 4) were performed in the presence of THF to reduce the reactivity of the system and thus achieve better reaction control. At best, bimodal SEC curves with PDI=1.75 and Mn=13500 g/mol, was obtained (Figure 5) when the reaction medium contains 1.5 equiv of BEM (table 2, entry 4).

The ^{1}H NMR spectrum of the copolymer in $CDCl_3$ (shown in Figure 6, spectrum 2) displayed signals corresponding to 1,4-*trans* polymyrcene (5 ppm (2H); 2 ppm (8H); 1.5 and 1.6 ppm (6H)) and polylactide signals (5 ppm (2H); 1.5 ppm (6H).

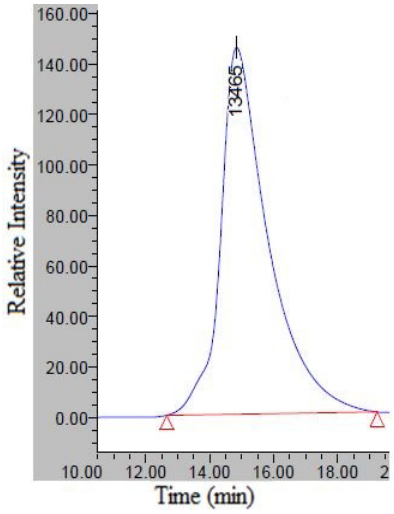

Figure 5: Chromatogram of the myrcene-lactide copolymer obtained usingTHF as solvent (Table 2, Entry 4).

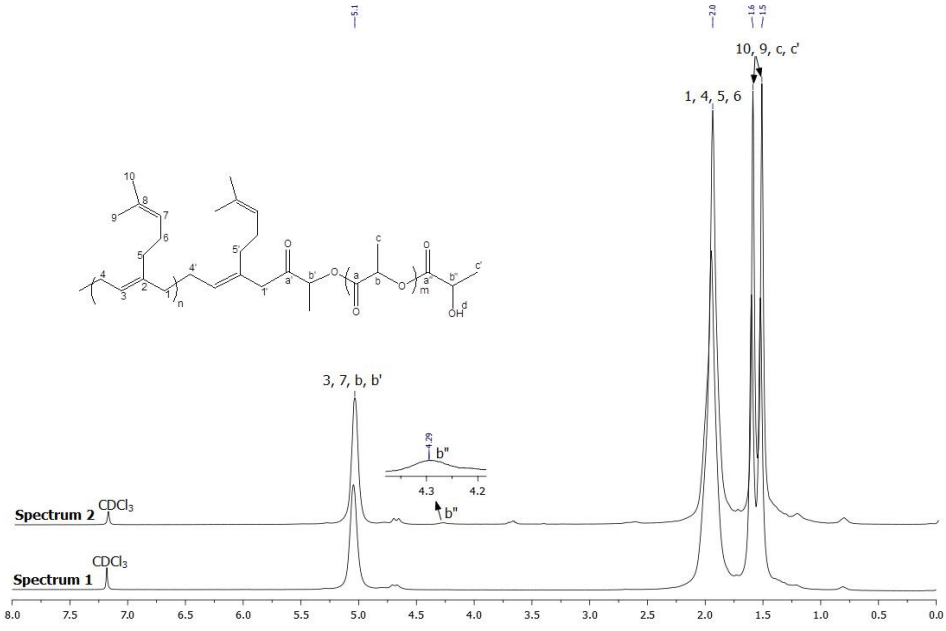

Figure 6: Spectrum 1:^{1}H NMR (300 MHz, $CDCl_3$) spectrum of homopolymyrcene; Spectrum 2: ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of myrcene-lactide copolymer (Table 2, Entry 4)

The new appearing resonance signal at 4,3 ppm of copolymer was assigned to the proton of the methine linked to hydroxyl group.

The ^{13}C NMR spectrum (illustrated in Figure 7, spectrum 2) displays ten signals corresponding to the units of poly(1,4-*trans*-myrcene) as well as signals attributable to polylactide. In the aliphatic part of the spectrum, the presence of two peaks corresponding to the CH_3 groups of the myrcene motif within the copolymer are observed (C9 at 17.7 ppm and C10 at 25.8 ppm), along with a peak of the CH_3 carbon of a lactic acid unit at 16.7 ppm.

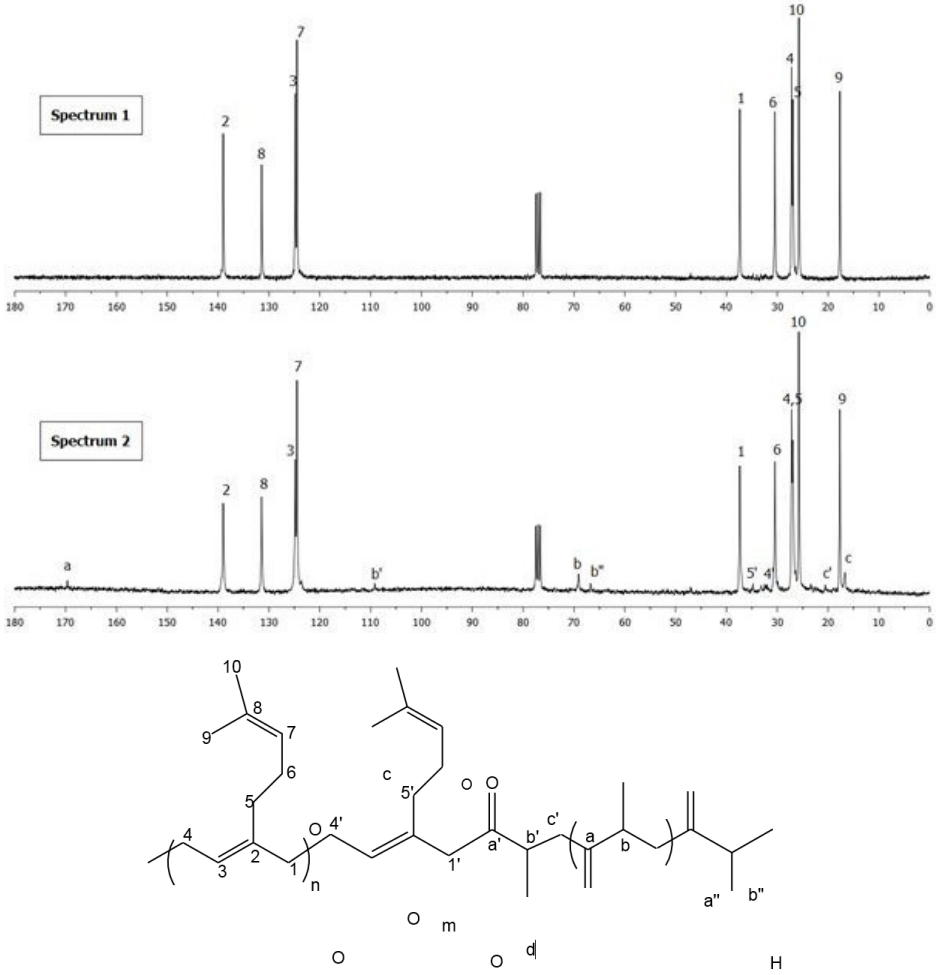

Figure 7: Spectrum 1:^{13}C NMR (75 MHz, $CDCl_3$) spectrum of homopolymyrcene; Spectrum 2: ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of myrcene-lactide copolymer (Table 2, Entry 4) and assignements

Furthermore, four signals corresponding to methylene groups of the myrcene motif (C1 at 37.4 ppm, C4 at 27 ppm, C5 at 27.2 ppm, and C6 at 30.5 ppm) are detected, as well as those of the lactic acid motif around 69.2 ppm. In the olefinic part of the spectrum, the highest chemical shifts correspond to the C=O carbon of polylactide at 169.7 ppm, as well as the two quaternary carbons of the myrcene motif (C2 at 139 ppm and C8 at 131.4 ppm). Additionally, around 124.8 ppm, the signals corresponding to two CH groups of the myrcene motif (C3 and C7) are observed. The ^{13}C NMR data shows additional peaks representing the combination of a myrcene unit with a lactic acid unit. The carbon in the polymyrcene backbone shows two distinct signals. The main signal corresponds to the polymyrcene, where the unit is located next to two other myrcene units, while another signal called (carbon') is assigned to the myrcene-lactic acid linkages in the copolymer (Figure 7). In addition, the ^{13}C NMR indicates that approximately 10% of L-lactide can be incorporated into the polymer without affecting the stereo-selectivity of the reaction. The ^{1}H and ^{13}C NMR signals were assigned on the basis of thepolymyrcene-polylactide diblock [23].

The results obtained show that lanthanide borohydrides are efficient initiators for the block copolymerization of 1,4 conjugated dienes with lactide, resulting in copolymers with well-defined structures. Additionally, the presence of functionalizable terminal groups, such as the vinyl group inthe polydiene block and the hydroxy group in the polylactide block, allows for further modification of the copolymer structure. These terminal groups can be used to attach other functional groups or polymers, leading to the formation of more sophisticated structures with tailored properties.

CONCLUSION

Neodymium trisborohydride ($Nd(BH_4)_3(THF)_3$) precatalysts combined with n-butylethyl magnesium are effective catalysts for the copolymerization of myrcene with styrene. Indeed, the addition of one equivalent of n-butylethyl magnesium in the reaction medium allows the incorporation of approximately 6.7% of styrene into the copolymer, while the structure of the polymyrcene backbone in this copolymer presents about 96.55% of 1,4-*trans* units. However, by increasing the amount of n-butylethyl magnesium increases in the reaction medium up to 1.5 equivalents, it is possible to incorporate 9.9% of styrene, resulting in a modificationof the polymyrcene microstructure with an increase of the 3,4 microstructure under transfer conditions (from 3.44% to 15.72% of 3,4).

The $Nd(BH_4)_3(THF)_3$/BEM system also allows the synthesis of block copolymer of 1,4-*trans* polymyrcene/polylactide, by reducing the reactivity of the polymerization medium through the addition of a solvent such as THF. These studies provide a valuable and promising method for the synthesis of copolymers that serve as interesting precursors for bio-sourced products, thus opening new possibilities for the development of advanced materials with suitable properties.

EXPERIMENTAL SECTION

Materials

All operations were performed under dry argon using a glove box or schlenk techniques. Toluene was purified through alumina column (Mbraun SPS), stored, trap-to-trap distilled over sodium/benzophenone ketyl, then stored on molecular sieves (3A) in a glove box. β-myrcene and styrene (from Aldrich) were dried over calcium hydride, distilled once over molecular sieves, and once again just before use. Lactide was purified by recrystallization in toluene and stored under argon. n-butylethyl magnesium (BEM) (20 wt % in heptane from Texas Alkyls), was used as received. $Nd(BH_4)_3(THF)_3$ was prepared using a method described in the literature [24].

Polymerisation procedure

It is important to note that the use of a glovebox and dry argon is necessary to ensure that moisture and oxygen do not interfere with the reaction. The precatalyst, which is the initial form of the catalyst before activation, was weighted in an aluminum weighting boat inside the glove box to avoid contact with air. Then, the toluene solvent, monomers and cocatalyst were added sequentially using syringes to prevent contamination. The solution was then stirred at 70°C for a specific time to allow the polymerization reaction to occur. After completion of the reaction, the flask was opened to air, and the reaction was quenched with acidified methanol. This step stops the polymerization reaction and stabilizes the resulting polymer. The polymer was then isolated and dried under vacuum until a constant weight was achieved. The use of BHT as a stabilizing agent helps prevent degradation of the polymer during the drying process.

Polymer characterization

The ^{1}H and ^{13}C NMR spectra of polymers were recorded at 300 K, on a Bruker Avance 300 spectrometer.^{1}H experiments of polymyrcene homopolymer and myrcene-lactide copolymers were made in $CDCl_3$ while poly(myrcene-

co-styrene) copolymers were analyzed in $C_2D_2Cl_4$.The quantitative ^{13}C NMR of homopolymers and copolymers were performed in $CDCl_3$ using the zgig sequence from the Bruker library.

Size exclusion chromatography (SEC) was performed in THF as the eluent at 40 °C with a flow rate of 1 mL/min. The chromatography system used a Waters SIS HPLC-pump, a Waters 410 refractometer, and a Waters Styragel column (HR2, HR3, HR4, HR5E), which was calibrated with polystyrene standards.

REFERENCES

1. J. Jenter; N. Meyer; P. W. Roesky; S. K. H. Thiele; G. Eickerling; W. Scherer; *Chem. Eur J.,* **2010**, *16*, 5472 - 5480.
2. M. Visseaux; M. Mainil; M. Terrier; A. Mortreux; P. Roussel; T. Mathivet; M. Destarac; *Dalton Trans*., **2008**, *34*, 4558 - 4561.
3. M. Terrier; M. Visseaux; T. Chenal; A. Mortreux*, J. Polym. Sci., Part A: Polym. Chem.,* **2007**, *45*, 2400 - 2409.
4. F. Bonnet; C. D. C. Violante; P. Roussel; A. Mortreux; M. Visseaux; *Chem. Commun.,* **2009**, 3380 - 3382.
5. A. Ventura; T. Chenal; M. Bria; F. Bonnet; P. Zinck; Y. Ngono-Ravache; E. Balanzat; M. Visseaux; *European Polymer Journal*., **2013**, *49*, 4130 - 4140.
6. P. Zinck; D. Baudry; A. Loupy; *Macromol Rapid Commu.,* **2005**, *26*, 46 – 51.
7. a) S. Loughmari; A. Hafid; A. Bouazza; A. EL Bouadili; P. Zinck; M. Visseaux; *J. Polym. Sci. Part A: Polym. Chem.*, **2012**, *50*, 2898 - 2905. b) S. Georges; M. Bria; P. Zinck; M. Visseaux; *Polymer.*, **2014**, *55*, 3869 - 3878.
8. M. Visseaux; T. Chenal; P. Roussel; A. Mortreux; *J. Organomet. Chem.*, **2006**, *691*, 86 – 92.
9. S. M. Guillaume; M. Schappacher; A. Soum; *Macromolecules*, **2003**, *36*, 54 - 60.
10. I. Palard; A. Soum; S. M. Guillaume, *Macromolecules*, **2005**, *38*, 6888 - 6894.
11. N. Barros; P. Mountford; S. M. Guillaume; L. Maron; *Chem. Eur. J.*, **2008**, *14*, 5507- 5518.
12. A. C. Albertsson; I. K. Varma; *Biomacromolecules*, **2003**, *4*, 1466 - 1486.
13. F. Bonnet; A. C. Hillier; A. Collins; S. R. Duberley; P. Mountford; *Dalton Trans.*, **2005**, 421- 423.
14. D. Barbier Baudry; F. Bouyer; A. S. M. Bruno; M. *Visseaux; Appl. Organomet. Chem.,* **2006**, *20*, 24 - 31.
15. N. Barros; M. Schappacher; P. Dessuge; L. Maron; S. M. Guillaume; *Chem. Eur. J.,* **2008**, *14*, 1881-1890.
16. M. Schappacher; N. Fur; S. M. Guillaume; *Macromolecules*, **2007**, *40*, 8887–8896.
17. W. J. Runckel; L. A. Goldblatt; *Ind. Eng. Chem.*, **1946**, *38*, 749.

18. S. Georges; A. O. Touré; M. Visseaux.; P. Zinck; *Macromolecules*, **2014**, *47*, 14, 4538-4547.
19. A. H. Gleason; J. F. Nelson; US Patent 2829065; **1958**.
20. a) D. H. Lamparelli; V. Paradiso; F. D. Monica; A. Proto; S. Guerra; L. Giannini; C. Capacchione; *Macromolecules*., **2020**, *53*, 1665 -1673. b) S. Loughmari; M. Visseaux; A. Bouazza; A. Hafid; A. El Bouadili; Arkivoc., **2023,** *8*, 202312045.
21. C. Zhou; Z. Wei; X. Lei; Y. Li; *RSC. Adv.*, **2016**, *6*, 63508 – 63514.
22. G. Desurmont; T. Tokimitsu; H. Yasuda; *Macromolecules*, **2000**, *33*, 7679 – 7681.
23. a) C. Zhou; Z. Wei; C. Jin; Y. Wang; Y. Yu; X. Leng; Y. Li; Polymer., **2018**, *138*, 57- 64. b) I. Adoumaz; Valorization of bioresources for the production of polymer films using waterborne latex or nanostructuring block copolymers; University of Pauand Adour country, **2020**, Chapter 5, pp. 208 - 210.
24. Mirsaidov, U.; Shaimuradov, I. B.; Khikmatov, M.; *Russ. J. Inorg. Chem.*, **1986**, *31*, 1321-1323.