Synthesis and characterization of high *cis*-polymyrcene using neodymium based catalysts

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Summary

The renewable resource monomer β-myrcene was polymerized employing two different catalyst systems based on neodymium isopropoxide and neodymium versatate as catalysts, three different alkylaluminum compounds as co-catalysts and two different organoboron compounds as activators, using cyclohexane as solvent and evaluating different [B]/[Nd], [Al]/[Nd] and [Cl]/[Nd] molar ratios. The two studied catalyst systems in conjunction with the different reaction conditions were compared to establish their effects on monomer conversion, catalytic activity and final properties of resulting products. All elastomeric products were analyzed by size exclusion chromatography, nuclear magnetic resonance and differential scanning calorimetry in order to determine their molecular weights, microstructures and thermal behaviors.

Keywords: β-myrcene, coordination polymerization, neodymium catalyst

1. Introduction

In the last years, there has been an increasing interest for finding alternative petroleum-based polymers, such as materials produced from biological and renewable resources [1-4]. Sugars, vegetable oils and terpenes are among the most common monomers sources to produce bio-based polymers [5-8]. Terpenes are natural unsaturated hydrocarbons produced mainly by plants -particularly conifers- that share most of them the 2-methyl-1,4-butadiene group in their chemical structures [9]. Some of these types of compounds have been studied as monomers in polymerization processes to generate entirely bio-based polymers [10], principally those monoterpenes that can be obtained in huge masses from the turpentine distillation where the *β*-myrcene [$CH_2=CH-C(CH_2-CH_2-CH=C(CH_3)_2)=CH_2$] can be mentioned among these products.

The microstructure in the elastomers derived from dienes can be controlled via a selective or stereospecific polymerization and this option is important because the isomers identity influences the final properties in the resulting polydienes. The *β*-myrcene has been mostly studied as monomer or co-monomer by anionic [11-14] and radical polymerizations [15-16] since time ago, but those coordinative processes that comprise the syntheses of polydienes with controlled isomeric structures have been just recently reported. Thus, there are in the literature some reports related to the syntheses of polymyrcenes rich in the *cis*-, *trans*- or 3,4-structure, all of them producing elastomers with different properties. For example, polymyrcenes with a high content of the *trans*-structure were obtained by Georges et al. in 2014 by using a catalytic system based on lanthanum, and *n*-butylethyl magnesium plus triisobutylaluminum as co-catalysts. The molar ratio Mg/[La] was fixed in 1 and the Al was studied in 9, 19 and 39 ratios, establishing long reaction times (48 hours) and mild yields

(65- 85%); elastomers produced in all cases presented a glass transition temperature (T_g) around -68 °C and a *trans*-isomer content close to 98% [17]. On the other hand, Liu et al. reported in 2015 the syntheses of polymyrcenes rich in the 3,4-isomer (80 to 99%) by using a *β*-diimidosulfonate lutetium dialkyl complex as catalyst, whereas trityltetra(pentafluorophenyl)borate and triisobutylaluminum were employed as co-catalysts at a ratio [Lu]/B/Al=1/1/5. Quantitative yields and elastomeric products with a T_g around -40 °C were obtained as a result of low temperatures (25°C) and short reaction times (0.1 to 3 hours) [18]. Earlier, in 2012, Loughmari et al. had reported the syntheses of polymyercenes rich in the 3,4-isomer, but also samples with a high content of the *cis*-structure depending on the molar ratios of reactants utilized. They reported neodymium borohydride/tetrahydrofuran and *n*-butylethyl magnesium as catalyst and co-catalyst respectively, at a molar ratio Mg/Nd=1. This selective coordination polymerization of *β*-myrcene resulted in products with approximately 90% of the *cis*-structure but once the ratio Mg/Nd was increased to 5 or more, the resulting products were rich in the 3,4-structure [19]. The *β*-myrcene, as well as other renewable resource monomers are taking importance to be investigated in the manufacture of bio-based polymeric products with the main purpose of gradually replacing the petroleum-based polymers. In this subject, the selective polymerization of *β*-myrcene to generate bio-based elastomers of controlled microstructure has been scarce studied. As it was previously mentioned, different kinds of catalyst systems based on neodymium, lutetium or lanthanum have been reported for this purpose. Here, it is reported the selective coordination polymerization of *β*-myrcene employing two different ternary catalyst systems based on neodymium (which are highly effectives in 1,3-diene polymerizations [20,21]) constituted by: i) Nd(O*i*-Pr)$_3$/TIBA (or DIBAH)/B1(or B2) and, ii) NdV /TIBA/DEAC (see

Experimental Part for abbreviations); where cyclohexane was used as solvent. Results are discussed -in a comparison mode- in terms of catalysts and co-catalysts types, as well as their molar ratios; evaluating polymer yields, molecular weight distributions, *cis*-1,4 microstructure content and thermal properties.

2. Experimental Part

2.1. Materials

All manipulations were carried out in a glove box or under inert atmosphere using a dual vacuum-argon line and standard Schlenk techniques. The monomer β-myrcene (from Aldrich) was distilled before use. The catalysts neodymium isopropoxide ($Nd(O\textit{i}\text{-}Pr)_3$) and neodymium versatate (NdV_3) were obtained from Strem Chemicals and Rodhia respectively. The co-catalysts triisobutylaluminum ($Al(\textit{i}\text{-}Bu)_3$ or TIBA), diisobutylaluminum hydride ($Al(\textit{i}\text{-}Bu)_2H$ or DIBAH) and diethylaluminum chloride ($AlEt_2Cl$ or DEAC) were acquired from Aldrich, 1.0 M in hexane for all of them. The activators N,N-dimethylanilinium tetra(pentafluorophenyl)borate ($[HNMe_2Ph][B(C_6F_5)_4]$ or B1) and trityltetra(pentafluorophenyl)borate ($[CPh_3][B(C_6F_5)_4]$ or B2) were purchased from Strem Chemicals. All catalyst, co-catalyst and activators were used as received. The solvents cyclohexane and toluene (Aldrich) were twice distilled from sodium under argon atmosphere before use and they were handled under inert atmosphere.

2.2. Polymerization Procedure

Polymerizations were carried out under argon atmosphere in a 1 liter stainless steel Parr reactor equipped with a turbine-type mechanical stirrer. Heating was realized by an electrical resistance and cooling by the flow of cold water through an internal tubing coil; both cooling and heating were operated by a PDI controller. A typical polymerization procedure using the Nd(O*i*-Pr)$_3$ as catalyst is described as follows: the β-myrcene monomer and cyclohexane as solvent were added into the reactor and it was heated until it reached the established temperature under 100 rpm of stirring. The catalyst system was injected to the reactor by means of a syringe following the next order: (i) a solution of B1 in toluene and, (ii) a solution comprising Nd(O*i*-Pr)$_3$ (in a mixture 50% toluene/50% cyclohexane, volume ratio) + TIBA; this solution was aged at room temperature for 1 hour before to be injected into the reactor. Several samples were taken in order to evaluate gravimetrically the polymer yield evolution. The polymerization reaction was deactivated by adding acidified methanol. The polymyrcene obtained was stabilized with Irganox 1076, precipitated in methanol and dried under vacuum. Different TIBA/Nd(O*i*-Pr)$_3$ and B1/Nd(O*i*-Pr)$_3$ molar ratios were studied with this catalyst system. Nd(O*i*-Pr)$_3$/DIBAH/B1 and Nd(O*i*-Pr)$_3$/TIBA/B2 were the other catalyst systems studied employing Nd(O*i*-Pr)$_3$ as catalyst.

In the case of NdV$_3$ as catalyst the procedure was as follows: cyclohexane as solvent was added into the reactor and it was heated until 50 °C, then TIBA, NdV$_3$ and DEAC were injected sequentially and the catalyst system was aged for 10 minutes into the reactor. The polymerization started by adding the β-myrcene into the reactor. Deactivation and purification steps were identical those previously described. Different TIBA/NdV$_3$ and DEAC/NdV$_3$ molar ratios were studied with this catalyst system.

2.3. Characterization

Molecular weights of samples were determined by size exclusion chromatography (SEC) using a PLGel mixed column in a Hewlett-Packard instrument (HPLC series 1100) equipped with a refractive index detector. Calibration was carried out with polystyrene standards and tetrahydrofuran (HPLC grade from Aldrich) was used as eluent at a flow rate of 1 ml/min.

Microstructure of polymyrcene samples was calculated by ^{1}H and ^{13}C nuclear magnetic resonance (NMR) using a JEOL Eclipse-300 MHz spectrometer. $CDCl_3$ was used as solvent and the analyses were performed at room temperature. The isomer 3,4, in relation with the isomer 1,4 (*cis* + *trans*) was determined by the ^{1}H NMR spectrum by integrating signals in the region of olefinic groups located in the range from 4.7 to 5.3 ppm and the ratio *cis*/*trans* was calculated by the ^{13}C NMR spectrum (proton gated decoupling no-NOE experiments) by integrating also signals of olefinic groups. The Figures 1 and 2 show the ^{1}H and ^{13}C NMR spectra respectively corresponding to Run , in order to illustrate the assignment of signals.

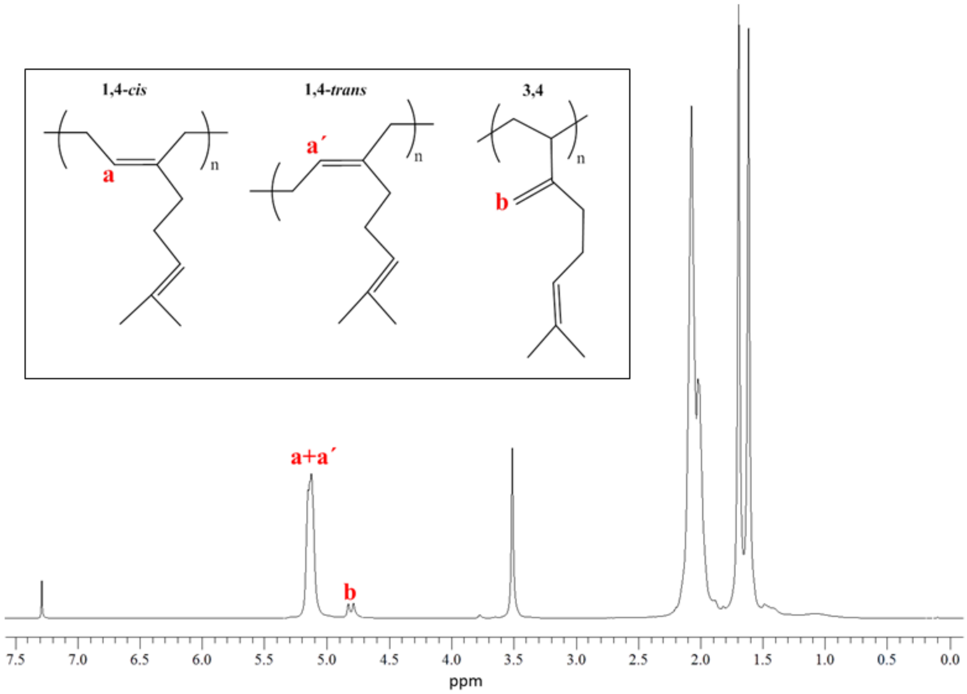


Figure 1. ${}^{1}H$ NMR spectrum of polymyrcene from Run 3 ($CDCl_3$ as solvent).

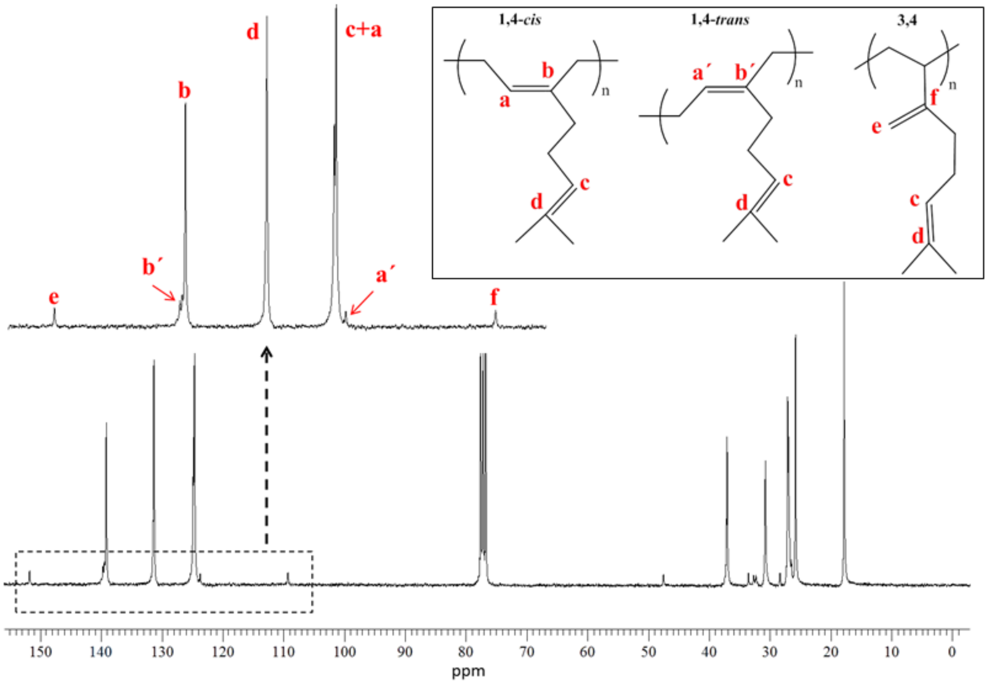


Figure 2. ${}^{13}C$ NMR spectrum of polymyrcene from Run 3 ($CDCl_3$ as solvent).

Differential scanning calorimetry (DSC) thermograms were obtained using a TA Instruments, DSC 2920. The analyses were carried out under inert atmosphere using a heating rate of 5 °C/min; each sample was analyzed twice in order to eliminate the thermal history.

Dynamic-mechanical analysis (DMA) were carried out using a DMA Q800, TA Instruments. The test was performed in a tensile mode, using thin films (0.12 mm), with 1 Hz of frequency, deformation amplitude of 3 μm, temperature ramp of 3 °C/min and temperature analysis range of -110 °C to 0 °C.

Film samples were prepared using a Carver hydraulic press applying 1 Ton of pressure at 50 °C during 1 minute. These films were stored at low temperature (-30 °C) in order to avoid deformation of the samples.

3. Results and Discussions

3.1. β-Myrcene polymerization with $Nd(Oi\text{-}Pr)_3$ and NdV_3 catalysts

The $Nd(O\textit{i}\text{-}Pr)_3$ and NdV_3 precursors were examined in β-myrcene coordination polymerization in cyclohexane; in the first case, changing [Al]/[Nd] and [B]/[Nd] ratios and aluminum and borate sources; in the second case with the variation of [Al]/[Nd] and [Cl]/[Nd] ratios. The results are summarized in Tables 1, 2, 3 and 4.

Table 1. β-Myrcene polymerization catalyzed by $Nd(O\textit{i}\text{-}Pr)_3$.

Run	Al source	B Source	[Al]/[Nd]	[B]/[Nd]	Yield (%)	k_a[a] (L mol^{-1} min^{-1})	M_n[b] (g mol^{-1})	M_w/M_n
1	TIBA	B1	25	1.2	87.66	36.02	318000	5.35
2	TIBA	B1	35	1.2	94.32	52.74	209000	5.82
3	TIBA	B1	45	1.2	96.25	63.08	71100	3.28
4	TIBA	B1	35	0.9	97.31	64.90	155300	8.79

5	TIBA	B1	35	1.5	87.66	32.68	305000	5.96
6	TIBA	B2	35	1.2	99.84	108.83	240000	6.66
7	DIBAH	B1	35	1.2	92.08	40.58	8500	2.42

Note: isothermal polymerizations were performed in cyclohexane at 60 °C for 90 min; B1 is $[HNMe_2Ph][B(C_6F_5)_4]$ and B2 is $[CPh_3][B(C_6F_5)_4]$; [cyclohexane] = 7.45 M, [β-myrcene] = 0.5112 M, [Nd] = 0.6578mM.

[a] The apparent first order rate constant k_a was calculated taking into account the kinetic law – d[M]/ *dt* = k_a[Nd][M] and from plots ln(1-x) = *f* (*t*), where x is the polymer yield.

[b] Determined by gel permeation chromatography (GPC) with polystyrene standards.

Table 2. Microstructures and glass transition for polymyrcenes obtained with Nd(O*i*-Pr)$_3$ catalyst.

Run	*cis*-1,4[a] (%)	*trans*-1,4 [a] (%)	3,4 [a] (%)	T_g[b] (°C)
1	92.4	3.8	3.8	-66.64
2	92.7	3.4	3.9	-67.91
3	92.4	3.5	4.0	-67.49
4	93.0	2.6	4.4	-68.25
5	91.9	3.8	4.3	-66.67
6	-	-	4.1	-66.27
7	90.2	3.9	5.9	-68.83

[a] The microstructures were determinate by 1H and 13C NMR spectroscopy

[b] Determined by differential scanning calorimetry (DSC)

Table 3. β-Myrcene polymerization catalyzed by NdV$_3$.

Run	Al source	Cl Source	[Al]/[Nd]	[Cl]/[Nd]	Yield (%)	k_a[a] (L mol^{-1} min^{-1})	M_n[b] (g mol^{-1})	M_w/M_n
8	TIBA	DEAC	10	3	92.89	17.06	154000	4.09
9	TIBA	DEAC	20	3	95.53	19.91	77000	3.46
10	TIBA	DEAC	30	3	98.99	21.61	30000	3.52
11	TIBA	DEAC	20	0.5	19.20	1.44	100000	4.34
12	TIBA	DEAC	20	1	90.05	16.04	48000	6.65
13	TIBA	DEAC	20	5	98.00	23.10	45000	4.92

Note: isothermal polymerizations were performed in cyclohexane at 50 °C for 90 min; [cyclohexane] = 8.30 M, [β-myrcene] = 0.5828 M, [Nd] = 0.00235M.

[a] The apparent first order rate constant k_a was calculated taking into account the kinetic law – d[M]/ *dt* = k_a[Nd][M] and from plots ln(1-x) = *f* (*t*), where x is the polymer yield.

[b] Determined by gel permeation chromatography (GPC) with polystyrene standards.

Table 4. Microstructure and glass transition for polymyrcenes obtained with NdV_3 catalyst.

Run	*cis*-1,4[a] (%)	*trans*-1,4[a] (%)	3,4[a] (%)	T_g[b] (°C)
8	96.6	2.3	1.2	-62.38
9	97.3	1.4	1.3	-62.71
10	96.7	2.0	1.3	-64.71
11	96.4	2.0	1.6	
12	96.4	2.4	1.2	-62.49
13	97.7	1.3	1.1	-63.29

[a] The microstructures were determinate by 1H and 13C NMR spectroscopy
[b]Determined by differential scanning calorimetry (DSC)

3.1.1. *Effect of [Al]/[Nd]and [B]/[Nd]ratios with* $Nd(Oi\text{-}Pr)_3/[HNMe_2Ph][B(C_6F_5)_4]/Al(i\text{-}Bu)_3$ *ternary catalytic system*

Variations in the concentrations both aluminum and boron had a significant effect on the β-myrcene polymerization. In this sense, the Figures 3 and 4 show the polymer yield as a function of polymerization time varying both [Al]/[Nd] and [B]/[Nd] ratios. It was observed that the polymer yield increase with increasing [Al]/[Nd] ratio from 25 to 45 (Run 1, 2 and 3 in Table 1) while the molecular weight (M_n) tended to decrease. This behavior is attributed to the triple role of the aluminum-based activators in Neodymium-based catalytic systems: a) activation of the Nd precursor in order to form the active species [22, 23], b) control of molecular weight through chain transfer reactions [24] and c) as scavenger for impurities such moisture or excess carboxylic acid, and has been reported for both binary and ternary catalytic systems in the polymerization of dienes. In several of these reports the highest polymerization yield was obtained at ratios [Al]/[Nd] in the range of 40 to 60 [21, 25, 26] with an invariable decrease in molecular weight of the obtained polymer. This same trend was observed in our experimental results, in which the highest polymerization yield was obtained with the ratio [Al]/[Nd] = 45, this results suggest that an increase in [Al]/[Nd] ratio produce a higher concentration of active species, reducing molecular weight and increasing the monomer conversion. Chain transfer effect caused by the increment in [Al]/[Nd] ratio is observed by a reduction in Mw/Mn. A different behavior was observed by increasing the [B]/[Nd] ratio from 0.9 to 1.5 (Run 4, 2 and 5 in Table 1), the highest polymer yield was obtained at close equimolarity ratios and decrease at higher [B]/[Nd] ratios, meanwhile the molecular weight (M_n) tended to increase when the amount of borane compound increases.

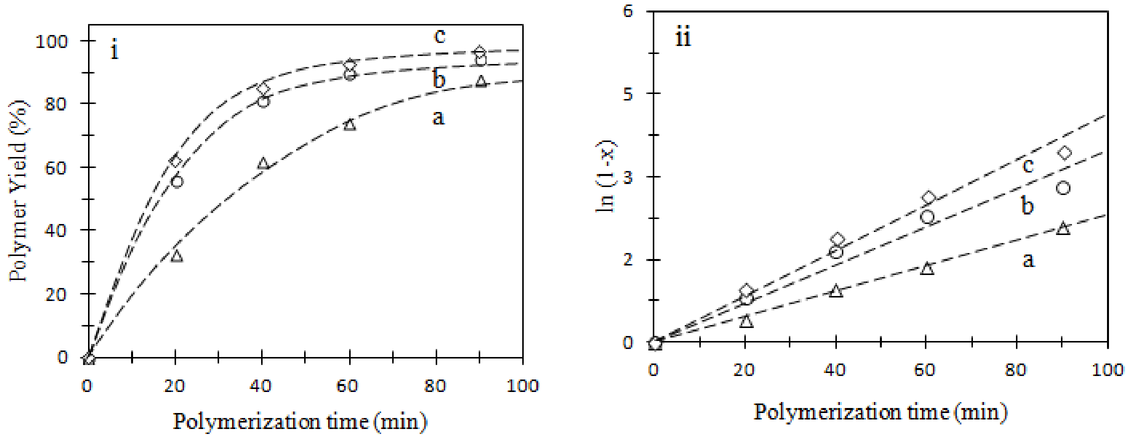


Figure 3. i)Polymer yield as a function of polymerization time and ii) Dependence of ln (1-x) on polymerization time for different ratios [Al]/[Nd] = a) 25, b) 35 and c) 45 by using Nd(O*i*-Pr)$_3$ catalyst in cyclohexane at 60 °C, [cyclohexane] = 7.45 M, [β-myrcene] = 0.5112 M, [Nd] = 0.6578mM, [B/Nd] = 1.2.

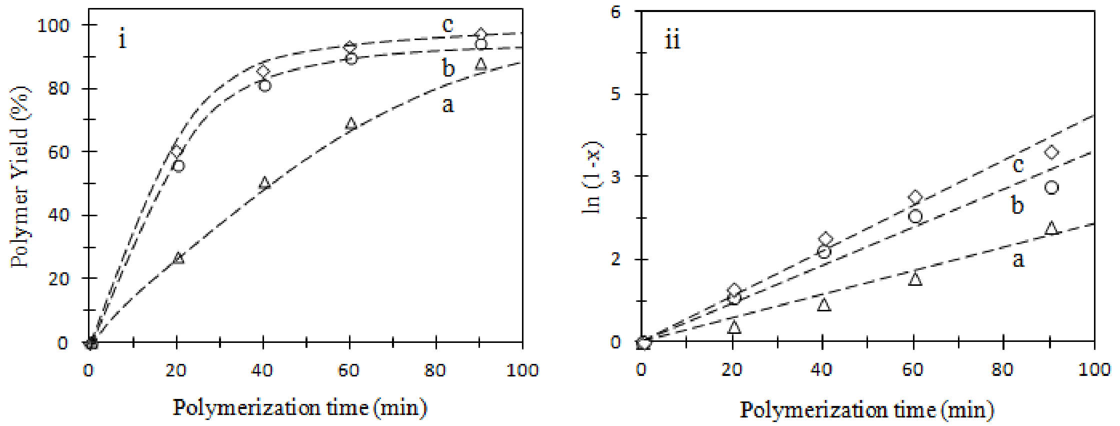


Figure 4. i)Polymer yield as a function of polymerization time and ii) Dependence of ln (1-x) on polymerization time for different ratios [B]/[Nd] = a) 0.9, b) 1.2 and c) 1.5 by using Nd(O*i*-Pr)$_3$ catalyst in cyclohexane at 60 °C, [cyclohexane] = 7.45 M, [β-myrcene] = 0.5112 M, [Nd] = 0.6578mM, [Al/Nd] = 35.

These behaviors are clearly associated to the formation as a less amount of active species. According to Masuda et al. [27] excess amounts of borane compound, might be cause of excessive cleavage of the bridging part in the active species formed by the reaction of Nd and Al compounds, according to the mechanism of active species formation proposed by Boisson et al. [28], hence the new species formed lose catalytic activity. This decrease in the number of active species also explain the narrowing of the molecular weight distribution with the increase in the [B]/[Nd] ratio. On the other hand, the polymyrcenes obtained present multimodal molecular weight distribution (see Figure 5) which can be attributed to the creation of several types of active species with different reactive capacity and stability.

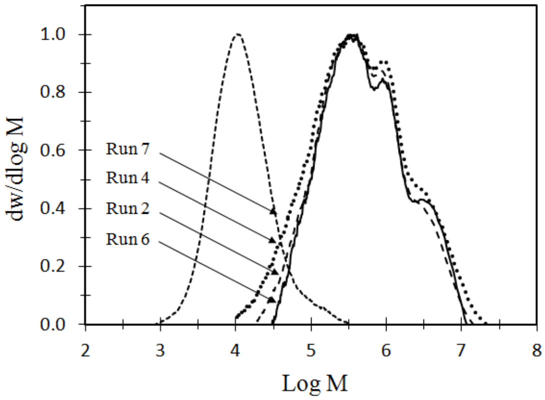


Figure 5. GPC curves of polymyrcenes obtained in cyclohexane at 60 °C using Nd(O*i*-Pr)$_3$ catalyst (Table 1, Runs 2, 4, 6 and 7).

According to Masuda et al. and Boisson et al. the reaction mechanism for 1,3-diene polymerization with Nd-based catalyst combined with aluminum alkyl such as Al(*i*-Bu)$_3$ and boron compounds ([X][B $(C_6F_5)_4$] (X= CPh_3 or $HNMe_2Ph$), consider firstly the formation of a heterometallic species with bridges of isobutyl and/or ligand of Nd nucleus, which can be reduced in active heterometallic cationic complex trough the abstraction of $O(CHMe_2)$ or $N(SiMe_3)_2$ ligands containing in Nd-based catalyst [27, 28] by $[HNMe_2Ph]$ cation containing in the boron compound. Taking into account that the ligand environment of the Nd nucleus of the active complex determines their catalytic activity, the variation in the alkylated (substitution of $O(CHMe_2)$ ligand by alkyl R) heterometallic cationic complex could generate more than one type of active species. According the Figure 5, the three different molecular weight populations corresponding to Run 2 and Run 4 are formed by at least three distinct active species, which is consistent with the number of possible alkylated and unalkylated heterometallic cationic complex.

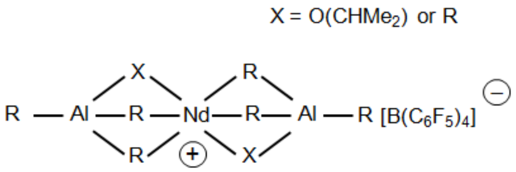


Figure 6. Heterometallic cationic complex formed by the $Nd(OiPr)_3/[HNMe_2Ph][B(C_6F_5)_4]/Al(i\text{-}Bu)_3$ ternary catalyst system.

The high *cis*-1,4 microstructure of polymyrcenes of around 97 % were obtained, which showed are independent on the [Al]/[Nd] ratio in agreement to reported by others works related with Nd-catalyzed polymerization of 1,3-diene monomers **[**27, 29**]**. By the other hand, when the [B]/[Nd] ratio increases from 0.9 to 1.5 the *cis*-1,4 content decreased slightly from 93 to 91.9. This reduction could be explained considering that an excess of boron compound produces in addition a less amount of active species, also a reduction in the number of available coordination sites, therefore it is expected that the η^4-coordination of β-myrcene tends to reduced. Under this scenario, the η^2-coordination increases and causes an increase in the *trans*-1,4 microstructure as observed in Table 2.

3.1.2. Effect of aluminum and borate sources with Nd$(Oi\text{-}Pr)_3$ *catalyst*

In order to evaluated the effect of different alkyl aluminum and boron compounds in β-myrcene polymerization, $Al(i\text{-}Bu)_2H$ and $[CPh_3][B(C_6F_5)_4]$ were used. In Table 1 it can see that the polymer yield reached in Run 7 was 92.08 % and the molecular weight (M_n) obtained was considerably lower (8500 g/mol) than that obtained using $Al(i\text{-}Bu)_3$ (Table 1, Run 2, 209000 g/mol) at the same [Al]/[Nd] ratio = 35. These results can be explained in terms of a more facile chain transfer reaction of a hydride moiety from $Al(i\text{-}Bu)_2H$ than isobutyl group from either $Al(i\text{-}Bu)_2H$ or $Al(i\text{-}Bu)_3$ by a living polymyrcene-chain. It is also clear that the PDI = 2.42 was the lowest obtained and surprisingly with unimodal MWD (see Figure 5, Run 7). Using $Al(i\text{-}Bu)_3$ as alkyl aluminum, the β-myrcene polymerization seem to be performed with chain transfer reaction fast compared to chain propagation and reversible, where the chain termination do not take place and the MWD not present a broadening. Meanwhile the *cis*-1,4 content of 90.2 % is due to the fact that species derived from $Al(i\text{-}Bu)_2H$ have the ability to reduce the η^4-coordination [24]. When the $[CPh_3][B(C_6F_5)_4]$ was used in the catalyst system, was obtained the highest polymer yield of 99.84 % (Run 6) and the molecular weight (M_n) attained (24000 g /mol) was slightly higher than that obtained using $[HNMe_2Ph][B(C_6F_5)_4]$ (Run 2, 209000 g/mol) at the same [Al]/[Nd] ratio = 35 and [B]/[Nd] ratio = 1.2. The reason for these changes in polymer yield and M_n varying the nature of boron compound could be associated with the ability to reduce the metal nucleus of Nd and produce active cationic complex and produce active cationic complex more stables. According to Giardello et al. [30] the use of $[CPh_3][B(C_6F_5)_4]$ in generating cationic complex has the advantage of introducing weakly coordinating $B(C_6F_5)_4^-$ without coproduction of a potentially coordinating-inhibiting Lewis base (NR_3) when the $[HNR_3][B(C_6F_5)_4]$ is used. The presence of an exogeneous amine base depresses the molecular weight [30] and in our case also the polymer yield. Meanwhile, the *cis*-1,4 contents of around 92.5 % is not affected significantly by the kind of boron compound.

3.1.3. Effect of [Al]/[Nd]and[B]/[Nd]ratios in the $NdV_3/Al(i\text{-}Bu)_3/AlEt_2Cl$ ternary catalyst system.

The influence of the variation in the [Al]/[Nd] and [Cl]/[Nd] ratios on the polymer yield, molecular weight, MWD and microstructure of the different polymyrcenes obtained are shown in Figures 7, 8 and 9 and Tables 3 and 4. It can be seen that as [Al]/[Nd] ratio increased from 10 to 30 the polymer yield gradually increases from 92.89 % (Run 8) to 98.99 % (Run10) and the molecular weight (M_n) of the polymyrcenes decreases from 150000 g/mol (Run 8) to 30000 g /mol (Run 10). According to Jang et al. during the 1,3-diene polymerization catalyzed by a Nd-based ternary system, the aluminum alkyl such as $Al(i\text{-}Bu)_3$ play two essential roles; the first of them involves the alkylation process causing the formation of active species. This fact increases the concentration of active Nd from which Nd-C σ bonds are formed whereby the polymer yield tends to increase. The second role, is the function as a chain transfer agent which can react with growing polymer chains resulting in the formation of dead polymer chains and new Nd-C σ bonds from which new centers are formed and produce new polymer chains with molecular weight less than the theoretical. The MWD decreases very slightly from 4.09 to 3.52, however the different MWD obtained exhibit bimodality (see Figure 9, Runs 9, 10 and 13). It is know that two different active species having different reactive capacity and stability are formed in 1,3-diene polymerization catalyzed by Nd-based ternary system (Figure 10) [31], high activity but short life active species and slow growing but stable active species. In this sense the obtained polymyrcene with different molecular weight as consequence of distinct active species can cause the bimodality in the MWD. Whereas high *cis*-1,4 contents remains around 97 % (see Table 4) which are independent on the [Al]/[Nd] ratio.

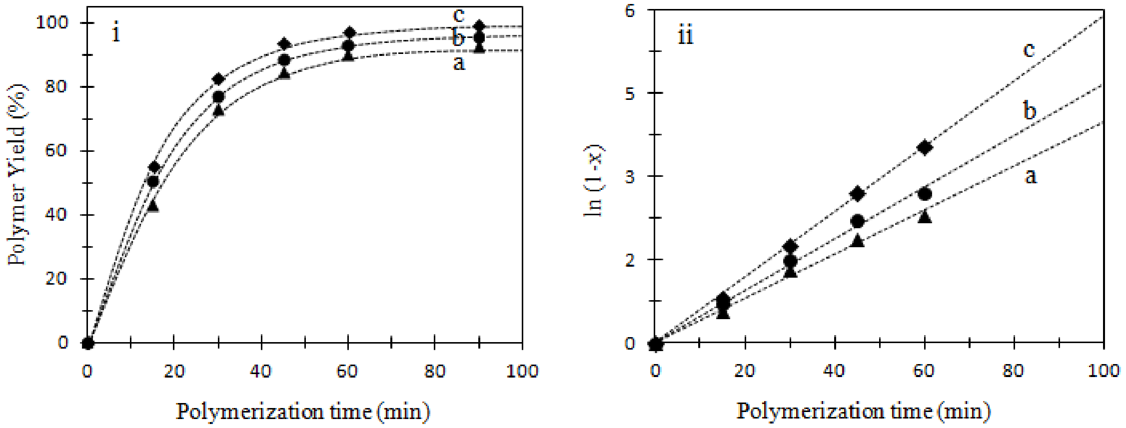


Figure 7. i)Polymer yield as a function of polymerization time and ii) Dependence of ln (1-x) on polymerization time for different ratios Al/Nd = a) 10, b) 20 and c) 30 by using NdV_3 catalyst in cyclohexane at 50 °C, [cyclohexane] = 8, [β-myrcene] = 0.5828 M, [Nd] = 0.00235M, [Cl/Nd] = 3.

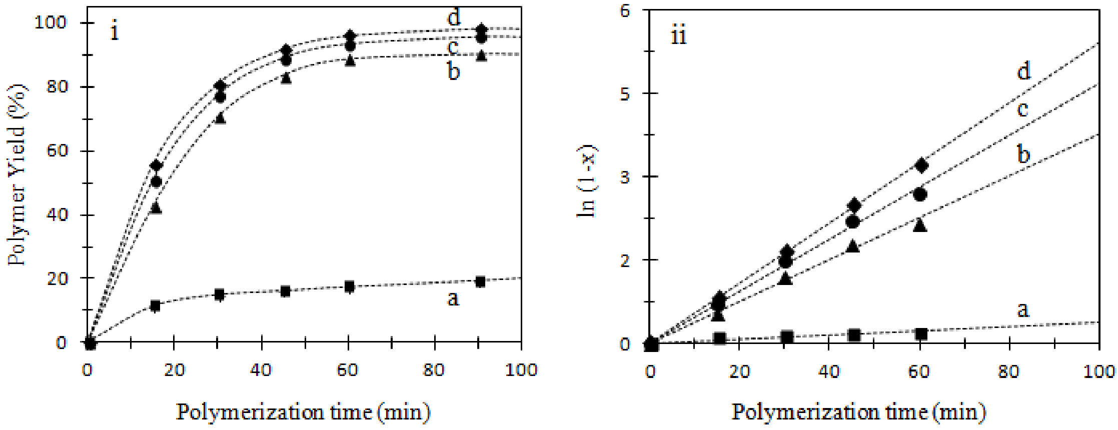


Figure 8. i)Polymer yield as a function of polymerization time and ii) Dependence of ln (1-x) on polymerization time for different ratios Cl/Nd = a) 0.5, b) 1, c) 3 and d) 5 by using NdV_3 catalyst in cyclohexane at 50 °C, [ciclohexane] = 8.30 M, [*β*-myrcene] = 0.5828 M, [Nd] = 0.00235M, [Al/Nd] = 20.

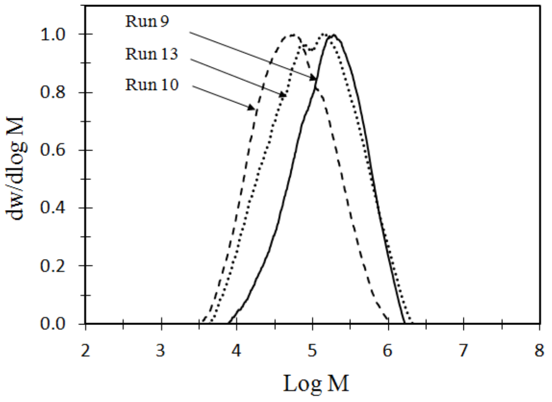
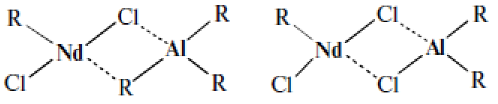


Figure 9. GPC curves of polymyrcenes obtained in cyclohexane at 50 °C using NdV_3 catalyst (Table 3, Runs 9, 10 and 13).



i) ii)

Figure 10. Possible species that has high reactive capacity formed during the polymerization process from Nd-based catalyst system.

Meanwhile from Figure 8 and Table 3 it can be seen that the increase on the [Cl]/[Nd] ratio result in an increase in the polymer yield as a result of the formation of a greater number and type of active species during polymerization curse. According to Kwag et al. in the butadiene (BD) polymerization, the Nd precursor is first alkylated and subsequently chlorinated, the first and subsquent insertions of BD occur into a Nd – C bond, this process is easier by the presence of Nd – Cl bonds (ionic character) [23]. By the other hand, a significant decrease in molecular weight from 100000 g/mol to 45000 g/mol (in Table 3 Run 11 and 13) was observed. This result is attributed by the two roles of $AlEt_2Cl$ as a chain transfer agent and halide donor [32]. The MWD obtained with the highest [Cl]/[Nd] ratio= 5 exhibits a remarkable bimodality. Again the MWD it is created by active species that produces polymyrcene with high molecular weight and others active species that produce polymyrcene with low molecular weight, resulting in a broad molecular weight distribution.

The *cis*-1,4 contents slightly increase as the [Cl]/[Nd] ratio increase; this tendency is in good agreement with the reported in the literature. Although a specific explanation for this effect is not reported, according to Pires et al. [33] a lower reaction medium viscosity (in our case because a lower molecular weight) provides higher monomer molecules mobility, thus favoring their complexation to the catalyst sites in the appropriate configuration which can increase the *cis*-1,4 microstructure. Additionally, Kwag et al. suggest that by coordination of chloride to Nd, 4f orbitals are induced and the *cis* coordination of dienes is enhanced. In addition, the coordination back-biting of the penultimate double bond of the poly(butadiene)yl chain is favored. As a consequence anti-*syn* isomerization is blocked and *cis*-1,4 contents are increased [34]. It is important to mention that is mandatory that the above process must be accompanied by a η^4-coordination of β-myrcene induced by higher chlorination.

In the technology of catalytic systems based on neodymium, the rate of polymerization or the decrease of the monomer concentration during the course of the polymerization can be described by first-order kinetics [21, 24, 35]. In order to corroborate the validity of the first-order kinetics, this relation was examined by means of plots ln (1-x) versus polymerization time (see Figures 3ii, 4ii, 7ii and 8ii). The linear relations were obtained which indicated that the first-order kinetics with respect to the monomer concentration is applicable in the β-myrcene polymerization both Nd(O*i*-Pr)$_3$ and NdV$_3$ catalyst. From plots in Figures 3ii, 4ii, 7ii and 8ii, it is to possible to evaluate the apparent first-order rate constant (k_a) and the values are summarized in Tables 2 and 4. The k_a were found to be in the range of 32.68-108.83 L mol^{-1} min^{-1} using Nd(O*i*-Pr)$_3$ catalyst and 1.44-23.10 L mol^{-1} min^{-1} employing NdV$_3$ catalyst.

According to Tables 2 and 4, the glass transition obtained using Nd(OiPr)$_3$ was in the range of -66.27 to -68.83 °C and -62.38 to -64.71 °C with NdV$_3$. In the Figure 11 is shown the T_g as a function of *cis*-1,4 content for all different polymyrcenes obtained using both Nd(O*i*-Pr)$_3$ and NdV$_3$. It is clearly seen a tendency where the T_g shifts to higher temperatures with higher values of *cis*-1,4. At the moment we do not have an explanation for this results, however this behavior is contrary to the reported for polybutadiene, where higher values of *cis*-1,4 lead to lower values of glass transition [36].

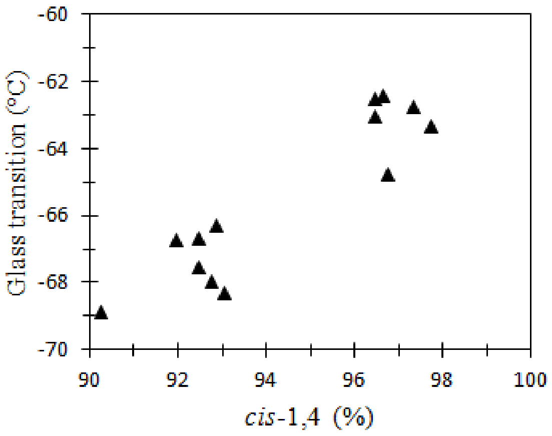


Figure 11. Glass transition as a function of *cis*-1,4 content for different polymyrcenes obtained using both $Nd(Oi\text{-}Pr)_3$ and NdV_3.

3.2 Dynamic-mechanical analysis

It could be expected that the structure and behavior of synthetic polymyrcene present some similarities with natural rubber properties, as both polymers are derived from natural terpenes. Natural rubber is a viscoelastic material that is characterized by a contribution of elastic and damping behavior. Dynamic mechanical analysis is an important technique that allows to evaluate this kind of materials that show both elastic and viscous behavior and particularly is very useful to identify the performance of elastomers, both cured and uncured compounds. Typically, dynamic mechanical analysis has been used to evaluate the effect of different charges in rubber viscoelastic performance, as is reported in several papers of the literature [37, 38, 39, 40, 41]. In general, the objective of adding a charge to the rubber compound is to modify the rubbery plateau observed in the storage modulus curve and to change the damping behavior of the material, since this properties are very important for final applications of the elastomer. In order to identify the viscoelastic behavior of the polymyrcene synthesized in this work, dynamic mechanical analysis was carried out to some samples with the higher molecular weight and were compared to natural rubber (NR) and to a 1,4-cis-polybutadiene (cisPB).

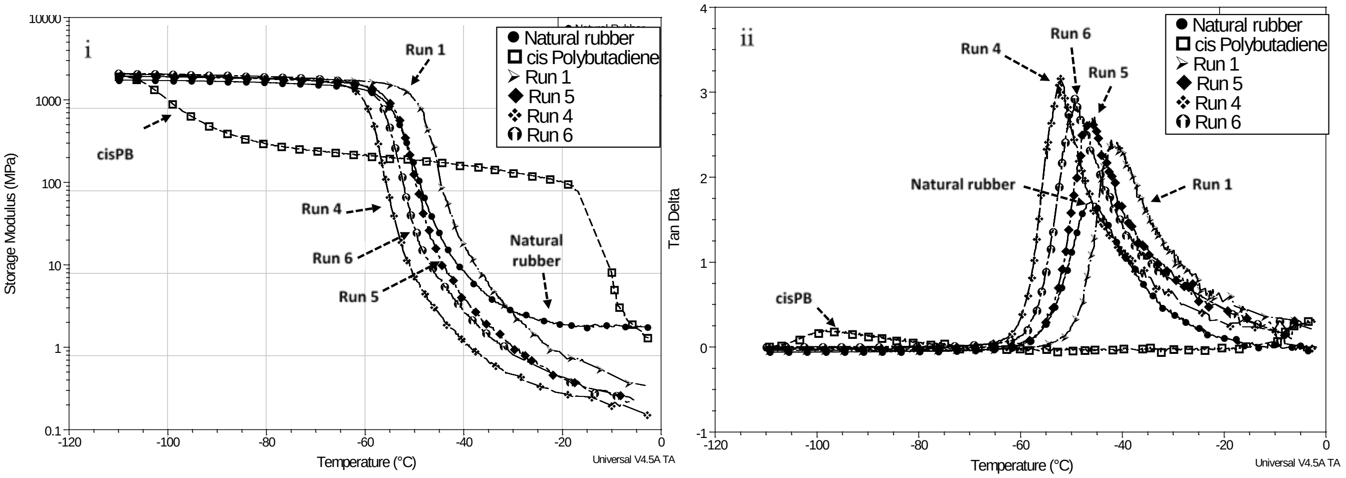


Figure 12. Dynamic-mechanical analysis of polymyrcene samples compared with natural rubber and synthetic high-cis polybutadiene. i) Storage modulus dependence with temperature; ii) tan δ dependence with temperature.

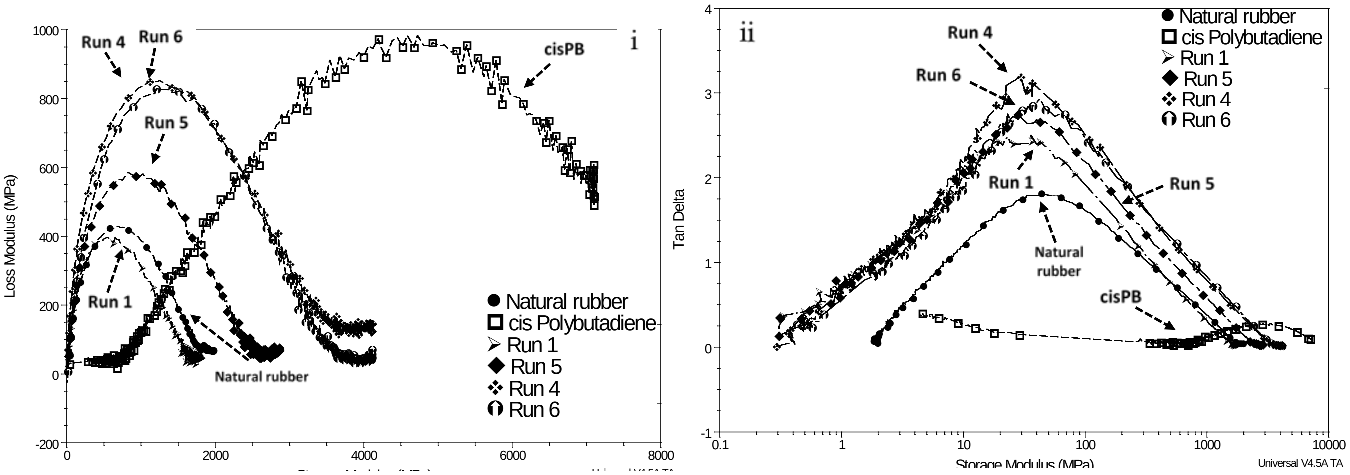


Figure 13. Dynamic-mechanical analysis of polymyrcene samples compared with natural rubber and synthetic high-cis polybutadiene. i) Cole-Cole plot; ii) tan δ dependence with storage modulus.

Sample	Tg [°C] Tan δ	Onset G' [°C]	Damping factor Tan δ_{max}
Natural Rubber	-46.57	-55.11	1.779
cisPB	-98.75	-104.9	0.242
Run 1	-42.63	-48.88	2.401
Run 4	-52.39	-60.02	3.186
Run 5	-46.24	-54.48	2.717
Run 6	-49.5	-56.99	2.873

4. Conclusion

$Nd(Oi\text{-}Pr)_3$ in combination with $[HNMe_2Ph][B(C_6F_5)_4]$ (or $[CPh_3][B(C_6F_5)_4]$) and $Al(i\text{-}Bu)_3$ or $Al(i\text{-}Bu)_2H$), and the NdV_3 activated with $Al(i\text{-}Bu)_3/AlEt_2Cl$, has high catalytic activity for β-myrcene polymerization in cyclohexane. It produced polymyrcenes with high molecular masses and broad molecular mass distribution, where the β-myrcene polymerization exhibited first-order kinetics of monomer consumption. Additionally, they proved to be stereospecific catalyst system, both generating polymyrcenes with high cis-1,4 microstructure content. The polymer yield, cis-1,4 microstructure, molecular mass, and molecular mass distribution of products can be regulated by varying the nature of borane and alkylaluminum compounds, as well as their molar ratios ([B]/[Nd] and [Al]/[Nd]) using $Nd(Oi\text{-}Pr)_3$ and [Cl]/[Nd] with NdV_3. Under the established reaction conditions, it was possible to obtain polymyrcene with 92-96% of cis-1,4 content, Mn from 30000-300000 g/mol, and with a glass transition temperature of -66 to -62 °C.

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