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SYNTHESIS AND CHARACTERISATION OF BIO-SOURCED COPOLYMERS CONTAINING MYRCENE AND CONJUGATED DIENE INITIATED BY NEODYMIUM-BASED COORDINATION CATALYSTS

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ABSTRACT

Myrcene is a promising alternative to petroleum-based materials. This conjugated terpene, found in many essential oils, has the potential to be used as a source material for producing elastomers derived entirely from biosourced materials. It could serve as a substitute for polymers like polybutadiene and other types of petroleum-based polymers. At 70°C in toluene, a copolymer poly(1,4-trans-myrcene-co-styrene) and polymyrcene-block-polyisoprene are created using neodymium trisborohydride $Nd(BH_4)_3(THF)_3$ *in combination with n-butylethyl magnesium* ($C_2H_5MgC_4H_9$)*. The use of this catalytic system for the statistical copolymerization of myrcene-styrene is a highly efficient method that leads to the production of a copolymer with excellent stereoregularity and a high yield.* $Nd(BH_4)_3(THF)_3 / C_2H_5MgC_4H_9$ *is also effective in the production of block copolymers (myrcene-isoprene). These resulting copolymers consist of an isoprene content of approximately 41 % and show no significant change in polymyrcene stereoselectivity despite the presence of a significant amount of isoprene. Additionally, the incorporation of myrcene into the copolymers makes it possible to soften the trans-isoprene polymer. Therefore, this catalytic system provides a valuable and promising method for synthesizing copolymers that serve as interesting precursors for biosourced elastomers.*

Keywords: coordination polymerization, β-myrcene, styrene, isoprene, stereoregular.

INTRODUCTION

For the past 60 years, renewable resources have attracted less attention. However, the scarcity of fossil resources, concerns about the greenhouse effect, population growth, and the pursuit of sustainable development have accelerated the shift towards chemically derived products from renewable raw materials. In this context, terpenes form a large family. While they have long been recognized as constituents found in essential oils extracted from various plant parts such as leaves, flowers, and fruits one terpene within this extensive family often overlooked is myrcene [1, 2]. Myrcene (or β-myrcene) is an easily accessible monoterpene. This acyclic terpene possesses a carbon skeleton composed of isoprene units, which are the building blocks of natural rubbe [2, 3]. The use of natural molecular biomass is critical in the development of renewable polymers such as biobased polyurethanes, polyamides, and polyesters, among others.

Currently, organolanthanide catalysts for polymerization are gaining increasing interest because they are non-toxic elements, which is an important factor in the current context of “green chemistry”. Lanthanide-based systems offer high specificity, particularly towards dienes [4]. These precursors have been utilized in organometallic chemistry and produce well-defined compounds characterized by X-ray. Unlike their chloro- homologues, these bohydrido- compounds are highly soluble and can be monitored using ^{1}H NMR. They are highly effective as pre-catalysts in addition polymerization reactions and radical and anionic polymerization of 1,3- conjugated dienes. However, it was the discovery of Ziegler-Natta catalysts in 1950 that introduced coordination polymerizations, which offers immense benefits by controlling the stereo- and regioregularity to produce polymers with specific properties [5 - 8].

In the field of highly active polymerization, catalysts based on lutetium [9] and lanthanides have been employed to polymerize β-myrcene [10,11]. Ring-closing metathesis polymerization [12] and reversible methods of transfer polymerization [13] have also been adopted. Visseaux et al. reported a co- and ter-polymerization of this acyclic monoterpene through chain transfer coordination [14]. Using the living anionic polymerization method, Bolton et al. also synthesized a thermoplastic elastomer based on β-myrcene and α-methyl-p-methylstyrene [15]. Recently, a described system utilized cobalt complexes with (4,6-di-tert-butyl-2-phenol, naphthalene-2-ol)-imine to synthesize poly(methyl methacrylate) and 1,4-*cis* polymyrcene [16]. Anionic copolymerization with isoprene, farnesene, or styrene has also been described to produce block copolymers that serve as interesting precursors for multiblock architectures or bio-sourced thermoplastic elastomers [17]. Myrcene has been copolymerized also through various methods including, cationic polymerization in aqueous emulsion [18], controlled radical polymerizations (RAFT and NMP) [19], phase-separated structure [15], and emulsion using a potassium or ammonium persulfate initiator [20].

The lanthanide trisborohydrides $Ln(BH_4)_3(THF)_3$ are fundamental compounds commonly employed as precursors in organometallic synthesis [21, 22]. They are readily obtained from trichlorides in a single step through metathetic reactions with $NaBH_4$ in THF [23]. When associated with *n*-butylethyl magnesium (BEM), these compounds serve as efficient catalytic systems for the polymerization of ε-caprolactone [24] and methyl methacrylate [25]. They have also been recognized as effective catalysts for the 1,4-*trans*-selective polymerization of conjugated dienes such as styrene [26], isoprene [27, 28], and myrcene [10, 11]. The article focuses on the development of “green” chemistry by focusing on the statistical copolymerization and block copolymerization of an acyclic monoterpene, myrcene, with 1,4-conjugated dienes using lanthanide-based catalysts in combination with *n*-butylethyl magnesium. The catalysts used in the polymerization are based on rare earth metals known for their non-toxic properties. This organometallic coordination polymerization allows control over the stereochemistry of the polymers.

EXPERIMENTAL

Sourcing and preparation of monomers and catalyst

All the procedures were conducted under dry argon using either a glove box or schlenk techniques. Toluene was purified using alumina columns (Mbraun SPS), distilled from trap to trap over sodium / benzophenone ketyl, and then stored on molecular sieves (3A) inside the glove box. β-myrcene, isoprene and styrene from Aldrich were dehydrated using calcium hydride, distilled once over molecular sieves, and once again just before use. n-butylethyl magnesium (the cocatalyst) (20 wt. % in heptane from Texas Alkyls) was used as received. $Nd(BH_4)_3(THF)_3$ (precatalyst) was synthesized following procedures described in the literature [23].

Experiments

The precatalyst was weighed in an aluminium weighing boat in a glovebox and then poured into a flask. Toluene, the monomer(s) and the cocatalyst were introduced in this order by means of syringes. The flask was removed out of the glovebox, and the solution magnetically stirred at 70°C for a given time. The polymerization was then quenched with acidified methanol once the flask was opened to the air. The resulting solution was added into a large volume of methanol containing a stabilizing agent. The off-white polymer was filtered off and under vacuum until constant weight.

Product characterization

The ^{1}H and ^{13}C NMR spectra of polymyrcene homopolymer and poly(myrcene-co-styrene) copolymer were obtained on a Bruker Avance 300 spectrometer at 300K. ^1H NMR experiments for homopolymyrcene and myrcene-isoprene copolymers were conducted in $CDCl_3$, while poly(myrcene-co-styrene) copolymers were obtained in $C_2D_2Cl_4$.

Size exclusion chromatography (SEC) was conducted in THF at 40°C with a flow rate of 1 mL min^{-1}, using a Waters SIS HPLC-pump, a Waters 410 refractometer, and a Waters Styragel column (HR2, HR3, HR4, HR5E). Polystyrene standards were used for calibration.

DSC measurements were conducted under a nitrogen atmosphere using a Setaram 141 instrument, with a heating rate of 10°C per min, ranging from -120 to 100°C. Approximately 30 mg samples were utilized and placed in aluminum crucibles.

RESULTS AND DISCUSSION

Statistical (myrcene-styrene) copolymers

The neodymium borohydride-based coordination catalysts associated with 1 equivalent of *n*-butylethyl magnesium are effective for the stereospecific polymerization of myrcene (myr) [10] and styrene (styr) [26], this system has also demonstrated high efficiency for the statistical copolymerization of myrcene-styrene (Fig. 1). The experimental conditions and yields of this copolymerization are presented in Table 1.

The representative copolymerization experiments of myrcene-styrene, catalyzed by $Nd(BH_4)_3(THF)_3$ associated with n-buthylethyl magnesium at 70°C in toluene, stopped

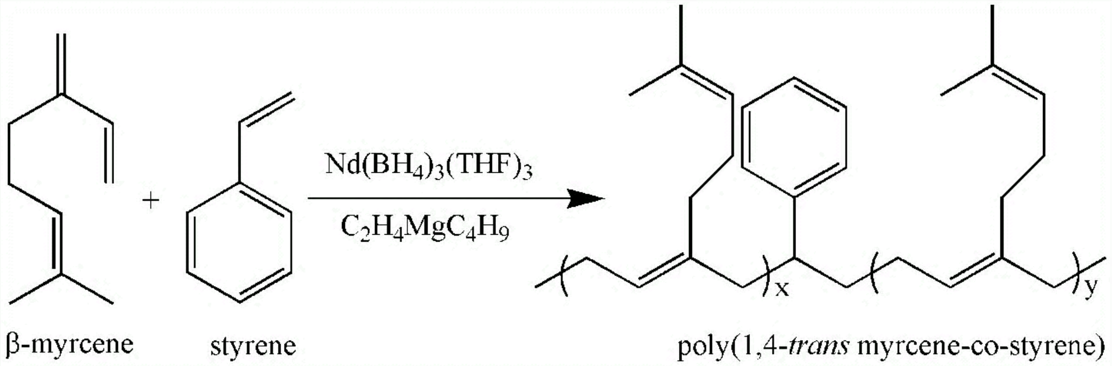

Fig. 1. Copolymerization of myrcene and styrene using $Nd(BH_4)_3(THF)_3$ associated with n-buthylethyl magnesium as catalysts.

Table 1. Myrcene-styrene statistical copolymerization with $Nd(BH_4)_3(THF)_3$ combined to n-buthylethyl magnesium (BEM).

Enty[a]	[Myr] / [Styr][b]	yield, %	M_n^c g mol^{-1}	PDI[c]	Myrcene, %[e]	Microstructure, 1,4- / 3,4-, %[f]	$K_{PMyr'} \times 10^{-4}$, dL g^{-1d}	α[d]	Tg[g], °C
1	100 / 0	84	40900	1.7	100	99.03 / 0.97	0.746	0.772	-69.5
2	90 / 10	75	38600	1.61	96.89	99 / 1	0.746	0.772	nd
3	80 / 20	68	30700	1.77	95.23	98.9 / 1.1	0.746	0.772	-65.5
4	70 / 30	65	22400	1.61	94.51	98.91 / 1.09	0.746	0.772	nd
5	60 / 40	63	17900	1.77	93.27	98.87 / 1.13	0.746	0.772	nd
6	50 / 50	61	14700	1.46	89.28	98.88 / 1.12	0.746	0.772	-57
7	40 / 60	50	10900	1.59	88.60	98.91 / 1.09	0.746	0.772	nd
8	30 / 70	43	8500	1.86	84.31	98.8 / 1.2	0.746	0.772	nd
9	20 / 80	37	5100	1.6	83.70	98.99 / 1.01	0.746	0.772	-45
10	10 / 90	30	4100	1.4	83.10	98.86 / 1.14	0.746	0.772	nd

[a] experimental conditions: [a] $[Nd(BH_4)_3(THF)_3]$ / [BEM] = 1, [Myrcene] / $[Nd(BH_4)_3(THF)_3]$ = 300, [Styrene] / $[Nd(BH_4)_3(THF)_3]$ = 1000, $V_{(toluene)} = V_{(monomers)}$ = 1 mL, and T = 70°C for 2h. [b] [Myrcene] / [Styrene] molar ratio. [c] Determined by size exclusion chromatography using polystyrene standards. [d] K and α, the Mark-Houwink-Sakurada constants. [e] Copolymer composition (myrcene content) determined by NMR ^1H. [f] 1,4- / 3,4- Percentage determined by ^1H NMR . [g] Glass transition temperature determined by differential scanning calorimetry at 10°C min^{-1}.

after 2 h, demonstrated 1,4-stereospecificity. The Steric Exclusion Chromatography (SEC) analyses of the copolymers (Fig. 2) reveal a monomodal curve, which is a first argument to affirm that there is no formation of either of the homopolymers under our experimental conditions. we also observe (Table 1) a narrow distribution of molar masses with PDI < 2 (PDI = M_W / M_n; M_n is the number-average molecular weight and M_W is the weight average molecular weight), confirming the monosite nature of catalysis already observed in the homopolymerizations of myrcene [10], styrene [26], and isoprene [28]. The molar masses gradually decrease with the increase in the quantity of styrene in the reaction medium. Since the copolymerization yield is essentially that of myrcene, it is normal to see the molar masses decrease when less myrcene is introduced into the polymerization medium. In addition, the presence of large amounts of styrene in the reactive medium did not affect the stereoselectivity of the reaction, with up to 16 % styrene being inserted under the experimental conditions, and the copolymer's polymyrcene backbone showed a 90.8 % 1,4-*trans* microstructure, this found selectivity allowed us to deduce the Mark-Houwink-Sakurada constants, K and α, of the polymyrcene in the copolymer [29].

Regardless of the initial monomer ratios, styrene has been incorporated into the resulting copolymer, as evidenced by the appearance of new signals in ^{1}H and ^{13}C NMR spectroscopy characteristic of the styrene motif. Spectrum assignment was performed based on the literature references for 1,4-poly(β-myrcene) [10, 14]. The copolymer ^{1}H NMR spectrum (Fig. 3) indicates the presence of signals corresponding to 1,4-*trans* polymyrcene in the copolymer and the protons of the styrene aromatic units in the copolymer along with other

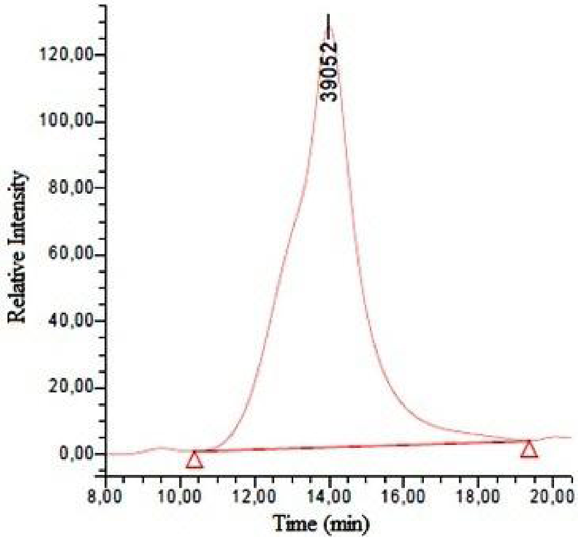

Fig. 2. Chromatogram of myrcene-styrene copolymer (Table 1, Entry 3).

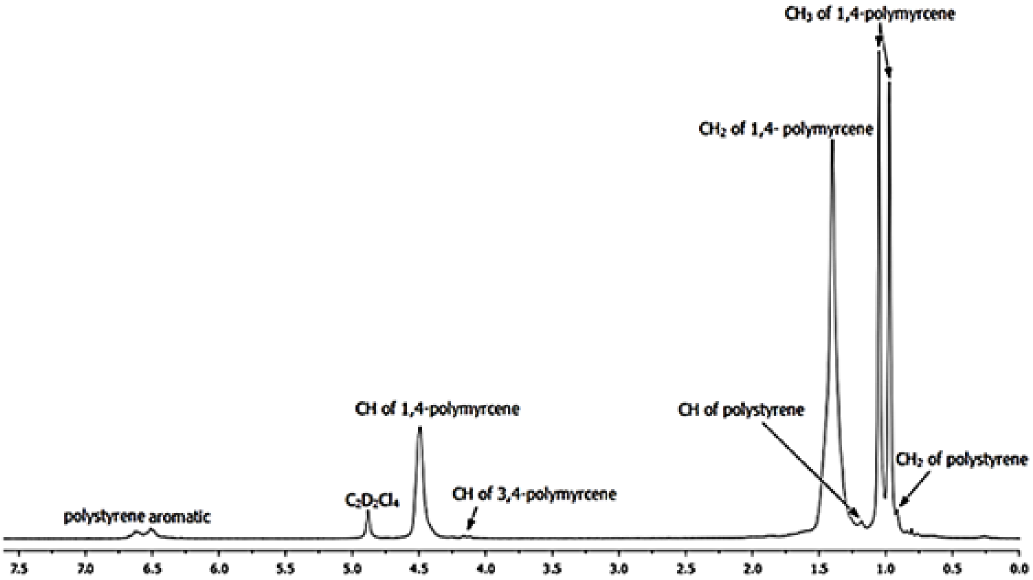

Fig. 3. ^{1}H NMR (300 MHz, $C_2D_2Cl_4$) spectrum of poly(1,4-*trans*-myrcene-co-styrene) (Table 1, Entry 3).

additional signals. Myrcene units in the copolymers are determined by the presence of signal at 1 - 1.7 ppm, corresponds to the methyl proton of the 1,4-*trans* unit, and by the peak at 2 ppm attributed to the CH_2 hydrogens, while the signal at 5.1 ppm indicative of olefinic resonances assigned to the double bonds of the 1,4-*trans* unit of myrcene. The presence of the styrene units in the copolymers was detected by the presence of aromatic protons at 7.2 ppm correspond to styrene aromatic, by existence of peaks around 1 - 1.7 ppm which depict the methylene group of styrene units, and by presence the signal 2 ppm corresponding to hydrogens of the CH group of styrene units.

Upon analysing the ^{13}C NMR (Fig. 4), the carbon signals of the myrcene backbone separated based on their neighbouring motifs. The most significant signal is attributed to the polymyrcene. Due to the predominant presence of this acyclic monoterpene within the copolymer, myrcene-myrcene sequences will be the most abundant, determining the microstructure of the copolymer. The ten signals of poly(1,4-*trans*-myrcene) were identified: In the olefinic portion of the spectrum, we can note four signals associated to the quaternary carbons (C_2 at 139 ppm and C_8 at 131.4 ppm) and to the two ethylenic carbons (C_3 at 124.9 ppm and C_7 at 124.5 ppm). Then, there are six signals in the aliphatic region: four signals for the methylene groups (C_1 at 37.4 ppm, C_4 at 27 ppm, C_5 at 27.2 ppm, and C_6 at 30.5 ppm), and two signals for the methyl groups (C_9 at 17.7 ppm and C_{10} at 25.8 ppm). The signal indicating the existence of styrene units appeared in the range of 127 ppm to 128 ppm. A peak around 145.7 ppm corresponding to the ipso carbon of styrene, which is characteristic of a styrenic unit in a unique and single environment (Fig. 4), similar to poly(isoprene-co-styrene) [29]. The styrene-myrcene enchainments (carbon' and carbon'') were represented in Fig. 4. The split of two signals could indicate the occurrence of both 1,4- and 4,1- polymerization modes of the conjugated diene, resulting in primary and secondary insertion of styrene. This theory was also supported in the production of poly(isoprene-co-styrene) copolymers using similar catalytic systems [29].

The results in Table 1 show that up to 16 % of styrene was incorporated under the experimental conditions, this is confirmed by the reactivity ratios of styrene (r_2 = 0.01) (Fig. 5) calculated using the Fineman and Ross method [30]. This value also indicates that the catalytic system does not promote the insertion of styrene into a Ln-styrene bond. This was attributed to steric and/or electronic requirements. The reactivity ratio of myrcene (r_1 = 5.01) reflect to the higher reactivity of this monomer and the ease with which the catalytic system chains one myrcene molecule behind another. The DSC analysis was utilized to ascertain the glass transition temperatures (Tg) of poly(β-myrcene-co-styrene) with varying compositions (Table 1). All the produced poly(β-myrcene-co-styrene) copolymers exhibit a singular Tg value, which increases as the quantity of styrene in the copolymer grows (Fig. 6), and the Tg in each of the cases falls between those of the two homopolymers (-69.5°C for polymyrcene and 100°C for polystyrene). This observation reaffirms the creation of statistical copolymers.

Block copolymers (myrcene-isoprene)

The catalytic system $Nd(BH_4)_3(THF)_3$ / (BEM) is a highly efficient initiator for the homopolymerization of isoprene, leading to the formation of a *trans*-stereospecific polymer with a high conversion (up to 97.7 %) [28]. This neodymium-based catalytic system is also effective for the homopolymerization of myrcene, producing a *trans*-stereospecific polymer (up to 90.8 %) [10]. Based on these results, we applied this catalytic system to the block copolymerization of β-myrcene and isoprene. The coordination copolymerization of these two conjugated dienes was carried out through a two-step procedure.

- In the first stage, myrcene polymerization was carried out using $[Nd(BH_4)_{3(}THF)_3]$ / [BEM] with a ratio of [myrcene] / $[Nd(BH_4)_3(THF)_3]$ = 300, and $V_{toluene}$ = 1 mL, at 70°C for 2 h.
- After 2 h, the required amount of isoprene was introduced under the same conditions, with $V_{toluene}$ = 0.5 mL.

Our objective was to explore the production potential of diblock copolymers consisting of 1,4-*trans* polymyrcene and 1,4-*trans* polyisoprene (Table 2). This was achieved by introducing isoprene at a later stage in the polymerization process of these two conjugated dienes. Furthermore, adding myrcene to the copolymer softens the *trans*-isoprene polymer, in the sense that polymyrcene remains amorphous [10], even when adopting a *trans* configuration. In contrast, *trans*-polyisoprene is semi-crystalline and remains a harder material [28].

The steric exclusion chromatography chromato-

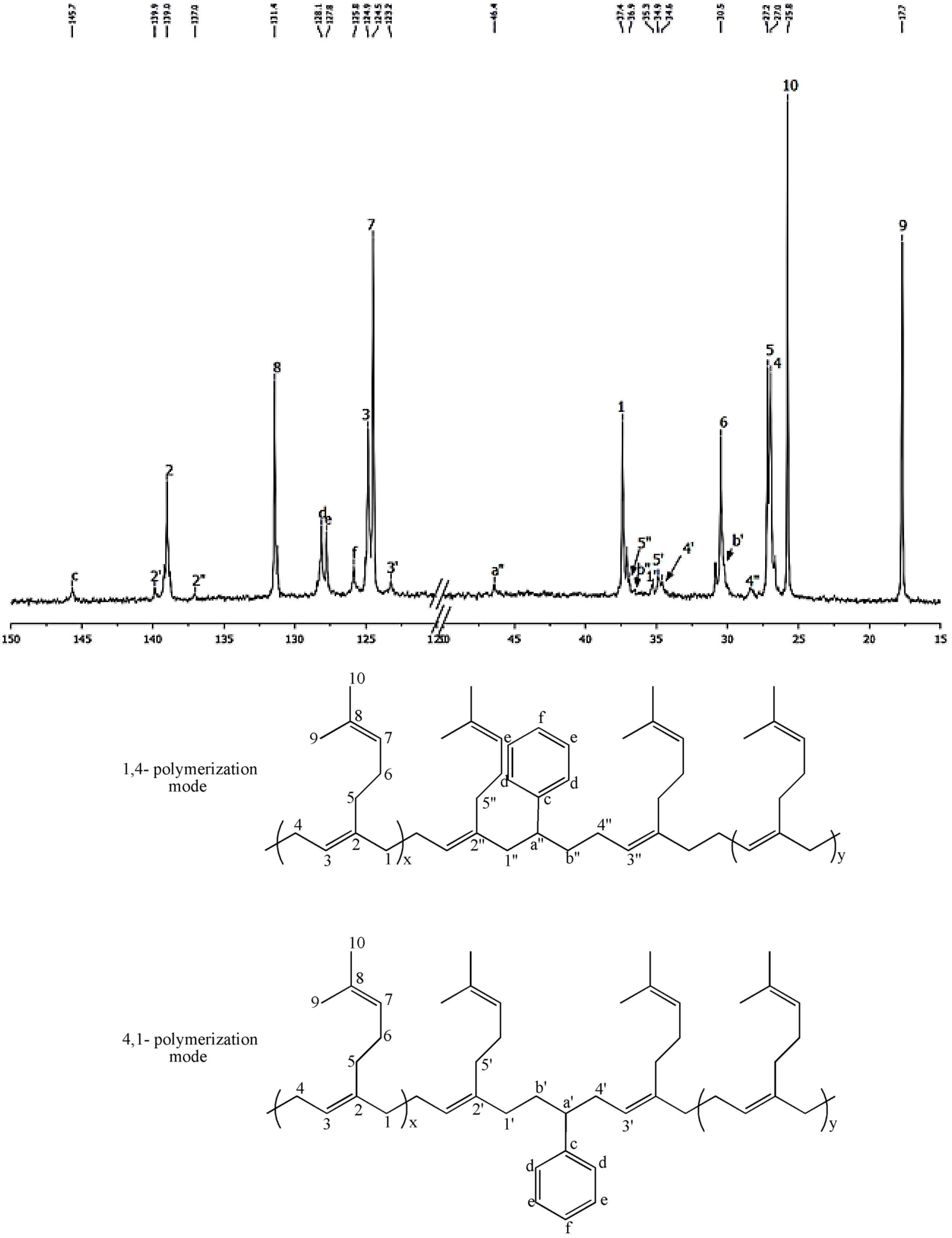

Fig. 4. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of poly(1,4-*trans*-myrcene-co-styrene) (Table 1, Entry 3), and assignments.

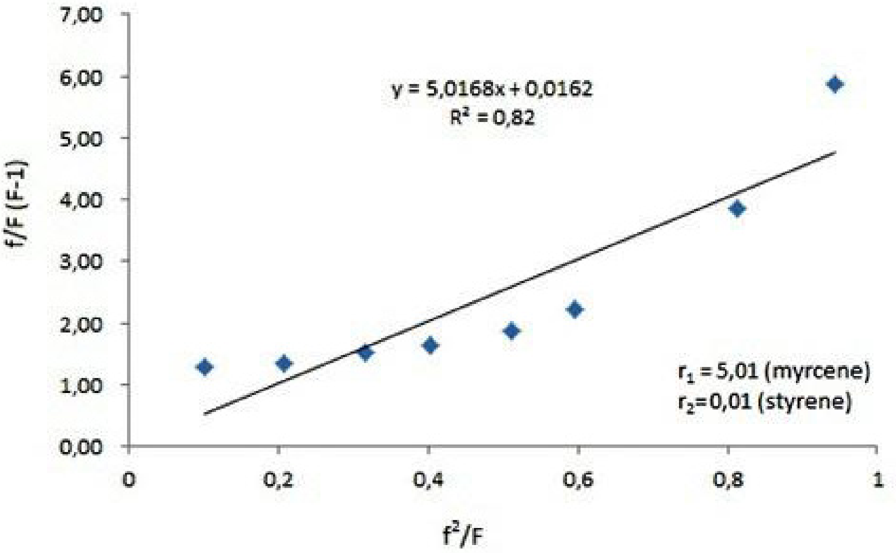

Fig. 5. Calculation of reactivity ratios according to the Fineman and Ross method.

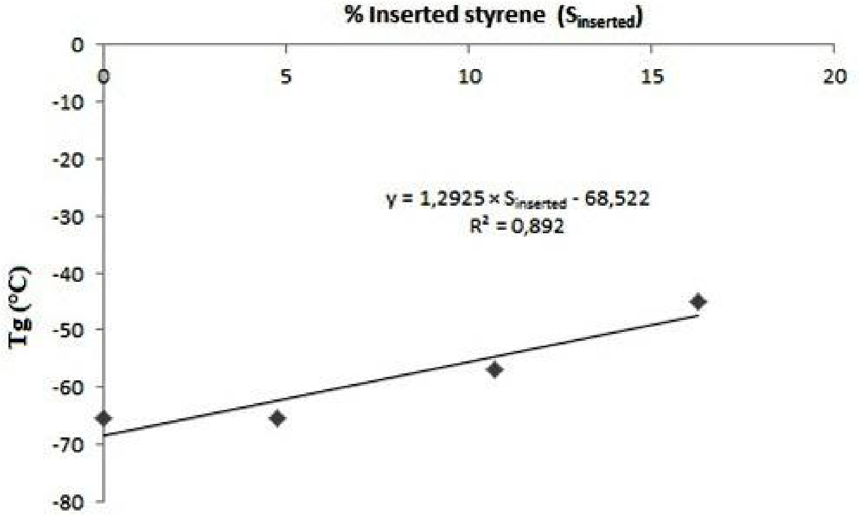

Fig. 6. Plot of Tg as a function of the rate of inserted styrene (Linear regression).

Table 2. Copolymerization yields and copolymer composition.

Entry	Time, h	[Nd] / [BEM][c]	[Isop] / [Nd][d]	Yield, %	Mn, g mol^{-1}[e]	PDI[e]	Myr, %[f]	Selectivity 1,4- / 3,4-, % [g]
1[a]	2	1	-	84	40900	1.7	100	99.03 / 0.97
2[b]	3	1	1000	76	13400	1.75	69.50	96.87 / 3.13
3[b]	4	1.5	1000	80	9900	1.35	58.70	94.03 / 5.97
4[b]	5	3	1000	79	7900	1.92	67.6	92.16 / 7.84

[a] Experimental conditions: [a] $N_{Nd} = 2.10^{-5}$ mol; $V_{myrcene} = V_{toluene} = 1$ mL; [Myr] / [Nd] = 300; and the T = 70°C. [b] Experimental conditions: $V_{myrcene} = V_{isoprene} = V_{toluene} = 1$ mL, [myrcene] / [$Nd(BH_4)_3(THF)_3$] = 300, and the T = 70°C. [c] [$Nd(BH_4)_3(THF)_3$] / [BEM] molar ratio. [d] [myrcene] / [isoprene] molar ratio. [e] Determined by Steric Exclusion Chromatography. [f] Copolymer composition (myrcene content) determined by ^{13}C NMR. [g] The selectivity1,4-trans / 3,4- Percentage determined by ^{1}H NMR.

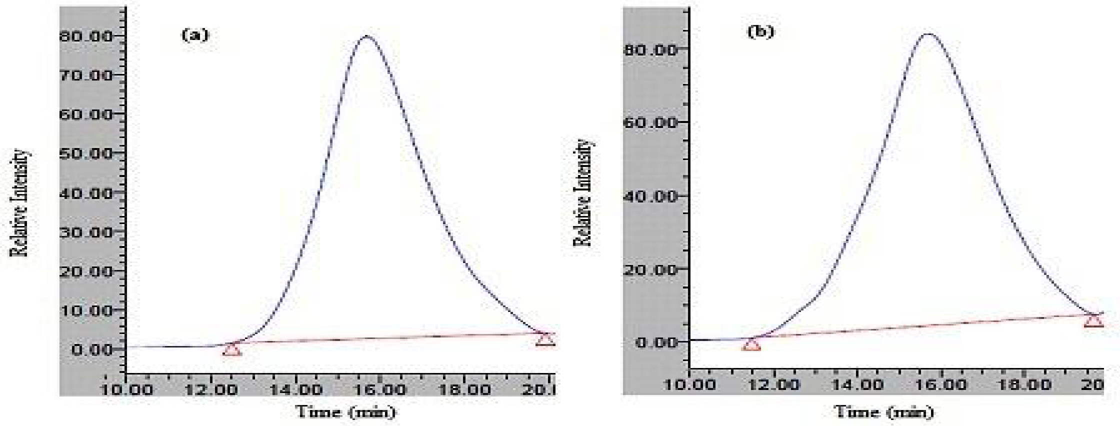

Fig. 7. Chromatogram of (a) homopolymyrcene (Table 2, Entry 1); (b) myrcene-isoprene copolymer (Table 2, Entry 2).

grams for all samples consistently exhibit a monomodal character (Fig. 7), which explains the presence of a copolymer rather than a mixture of two homopolymers. Furthermore, the dispersities remain below 2, underscoring the relatively narrow molecular weight distribution. Remarkably, the introduction of 1 eq. of BEM into the reactive medium allows for the incorporation of approximately 35.5 % of isoprene. The structural arrangement of the copolymer's polymyrcene backbone exhibited a range of 96.87 % for the 1,4-*trans* unit. However, if the quantity of BEM increases in the reaction medium to Eq. 3, it becomes possible to incorporate 41.3 % of isoprene, leading to a change in the microstructure of polymyrcene accompanied by a rise in the 3,4-microstructure under transfer conditions (from 3.13 % 3,4 to 7.84 % 3,4). Moreover, when varying the quantity of BEM in the in the reaction medium, we observed that a transfer of the polymer chains from the metal to the magnesium took place since the molecular weights decrease as the quantity of BEM in the system increases. This transformation in the microstructure of polymyrcene, along with the modification in the quantity of BEM, had been previously obtained in the homopolymerization of myrcene [10]. This rise in the 3,4-proportion within the polydiene is linked to the steric hindrance caused by the existence of alkyl groups. In addition, the coordination of myrcene to form a 1,4-motif within the polymer chain would not be favoured, and instead, a coordination of one of the double bonds would occur. This would lead to the formation of a 3,4- motif.

The copolymer's microstructure was analysed using both ^{1}H NMR and ^{13}C NMR techniques. In the ^{1}H NMR spectrum (Fig. 8), distinct proton peaks were identified, indicating the presence of 1,4-*trans* polymyrcene units within the copolymer. Specifically, signals in the range of 1.6 to 1.7 ppm were attributed to the methyl protons of the 1,4-*trans* unit. The peak at 2 ppm corresponded to the CH_2 hydrogens, while the signal at 5.2 ppm was linked to olefinic resonances attributed to the double bonds of the 1,4-*trans* unit. The ^{1}H NMR spectrum indicating also the proton peaks of 1,4-*trans* polyisoprene units within the copolymer, the peak at 1.6 ppm corresponded to CH_3 protons of the 1,4-*trans* unit. The signal at 2 ppm attributed to the CH_2 hydrogens and the signal at 5.2 ppm was attributed to the double bonds of the 1,4-*trans* unit. The findings from the ^{1}H NMR analysis are limited usefulness due to the identical chemical shifts of the peaks originating from the two monomers present in the copolymer. Consequently, the structure of the copolymer is established by evaluating the ^{13}C NMR spectrum (Fig. 9). The ^{13}C NMR spectrum of the copolymer shown the existence of signals linked to both the myrcene unit and the isoprene unit, along with the identification of novel signals. To elucidate the nature of distinct carbons within the myrcene motif in the copolymer, two types of signals are distinguished. Specific signals related to CH_2 groups and quaternary carbons appear in the unshielded part of the spectrum, while signals from CH_3 or CH groups have signals in the shielded part of the spectrum. Consequently, in the olefinic region of the spectrum, two quaternary carbons exhibit the highest chemical shifts (C_2 at 138.9 ppm and C_8 at 131.4 ppm). There are also two CH groups around 124.5 ppm (C_3 and C_7). In the aliphatic region of the

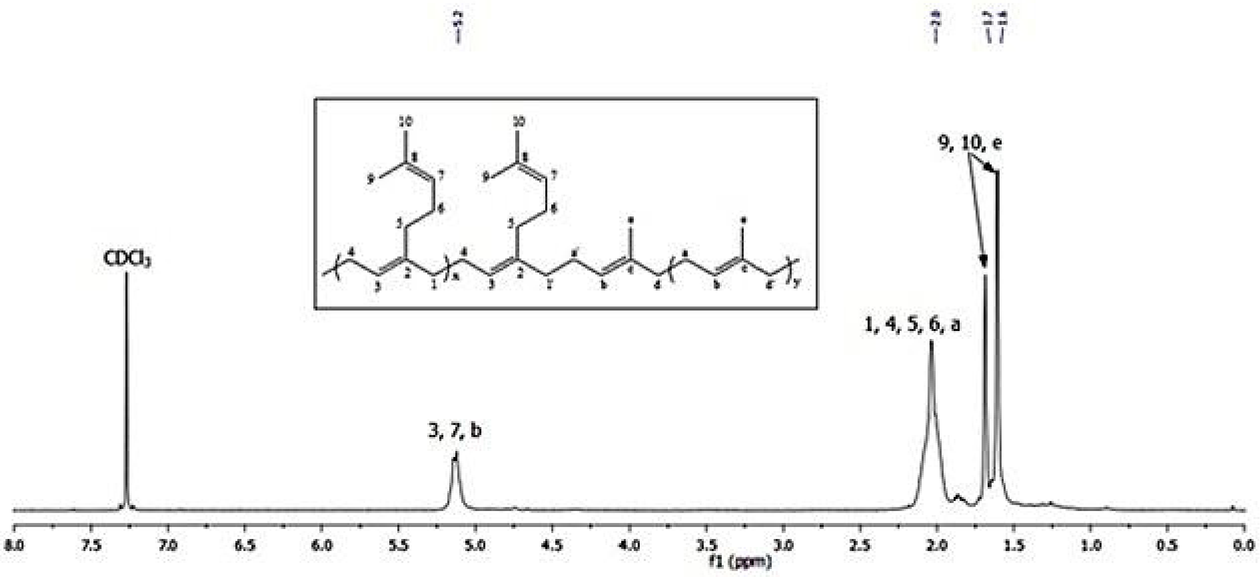

Fig. 8. ^{1}H NMR (300 MHz, $CDCl_3$) spectrum of Myrcene-Isoprene copolymerization (Table 2, Entry 2).

spectrum, the two most shielded signals correspond to CH_3 groups in the myrcene motif (C_9 at 17.7 ppm and C_{10} at 25.8 ppm), while the remaining four signals correspond to methylene groups in the same motif (C_1 at 37.4 ppm, C_4 at 26.7 ppm, C_5 at 27.2 ppm, and C_6 at 30.5 ppm). The ^{13}C NMR spectrum also reveal signals attributed to the different types of carbon within poly(1,4-*trans*-isoprene). These signals apparent at 16 ppm, indicating the presence of CH_3 carbon (C_e) specific to 1,4-*trans* polyisoprene. Another signal is observed at 25.8 ppm, which corresponds to CH_2 groups (C_a and C_d). Additionally, a signal detected at 124.3 ppm, indicating the presence of CH groups (C_b) of isoprene motif. Notably, the NMR spectrum identifies a signal at 134.9 ppm, indicative of the quaternary carbon (C_c) within polyisoprene. Furthermore, the ^{13}C NMR spectrum of the copolymer also unveiled the existence of novel signals (see in Fig. 8). Among these distinctive signals, one was particularly identified and 37.1 ppm, and it was associated with carbon 1' (1,4-*trans* polymyrcene). This signal corresponds to carbon 1 forming part of a sequence involving the myrcene-isoprene unit (Fig. 9).

Mechanism of the Selectivity

In polymerization of conjugated dienes using a dual Ln / Mg catalyst, all reported outcomes result in a polymer that is predominantly 1,4-*trans*-regular [10, 28]. This selectivity is linked to the active species involved: the consensus is that *cis*-polymerization is more favourable kinetically, while *trans*-polymerization is thermodynamically favoured. During the process, the active species undergoes isomerization from anti to syn, leading to the formation of *trans*-polymer [32, 33]. Theoretical studies have provided support for this proposition [34]. Hsieh suggested that the rate of anti - syn isomerization is greatly influenced by the structural composition of the diene monomer [32]. When using lanthanide catalysts, polymerizing a 1,4-disubstituted diene exclusively produces 1,4-*trans* polymer. Another proposal suggests that steric hindrance around the metal's active site could lead to *trans*-polymerization by preventing the bidentate coordination mode of the incoming monomer [33]. This steric hindrance and resulting *trans*-orientation might also be connected to the creation of bimetallic Ln - Mg species [36, 37].

The polymer's architecture formed through the catalytic synthesis is elucidated by the interaction between the monomer (myrcene or isoprene) and the metal center. Additionally, when the monomer unit is integrated into the polymer chain in the "*trans*" orientation, facilitated by an η^3 - allyl - type bond with the catalyst, it prompts the creation of a "syn" conformation [38]. This arrangement results in the development of a 1,4-*trans* polydiene structure (Fig. 9).

CONCLUSIONS

A neodymium borohydride-based coordination catalyst, associated with dialkyl magnesium, has been employed for copolymerizing myrcene-styrene and myrcene-isoprene. This combination leads to the production of poly(1,4-*trans*-co-styrene) containing between 3.11 and 16.9 % of inserted styrene. Also leads to polymers consisting of an isoprene content of approximately 41 %. Analysis of the ^{13}C spectra of myrcene-styrene copolymers suggests that each styrene motif is singly inserted between several myrcene units.

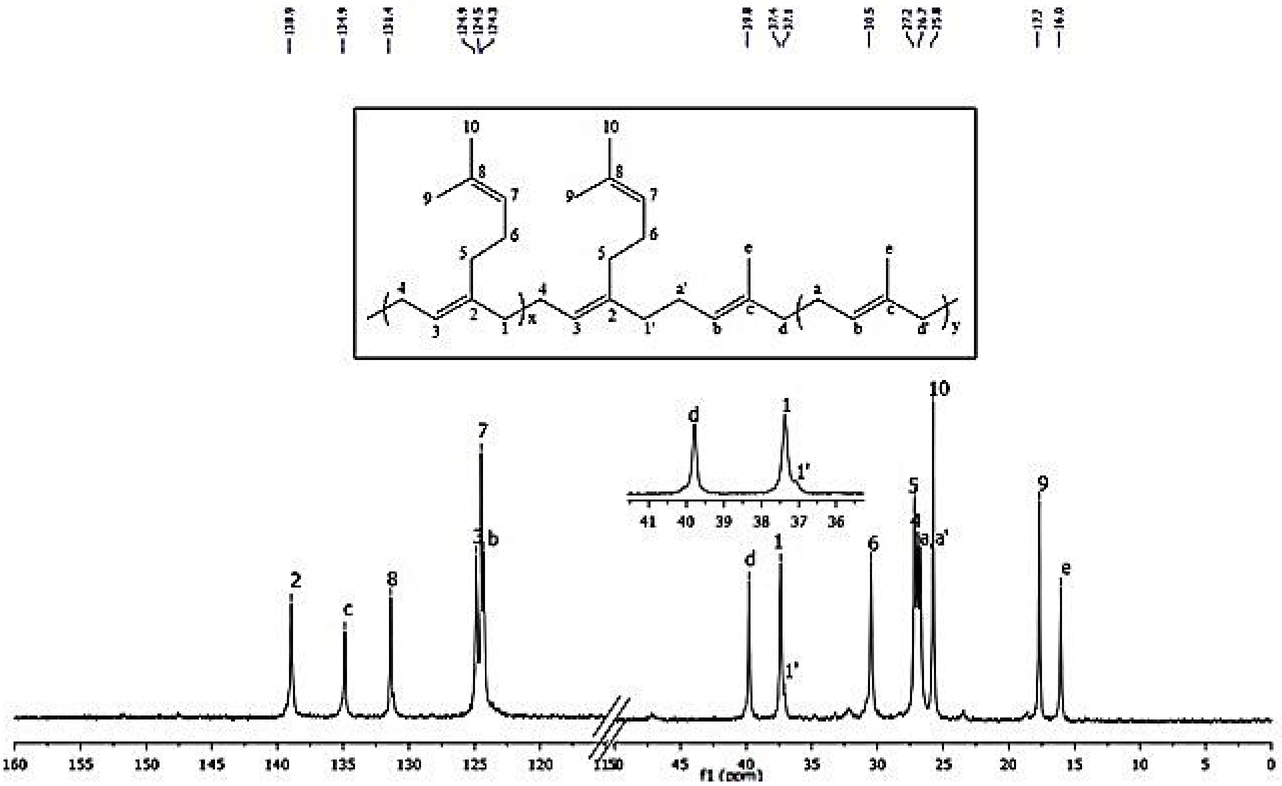

Fig. 9. ^{13}C NMR (75 MHz, $CDCl_3$) spectrum of myrcene-isoprene copolymerization (Table 2, Entry 2).

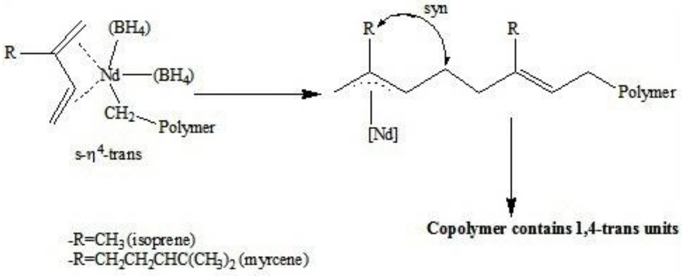

Fig. 10. η^4 coordination of monomer (myrcene or isoprene), leading to 1,4-*trans* units.

This observation is further confirmed by the determination of reactivity ratios, highlight the significantly greater reactivity of myrcene compared to styrene. Interestingly, the presence of significant quantities of styrene in the reaction medium does not appear to affect the selectivity of the reaction. This study presents a valuable and promising approach for creating copolymers that serve as intriguing precursors for bio-based elastomers.

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