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Synthesis of myrcene - isoprene copolymer

Saliha Loughmari,¹ Marc Visseaux,³ Aicha Bouazza,¹ Abderrafia Hafid,² and Abdelaziz El Bouadili^{1*}

¹ Laboratory of Applied Chemistry and Environmental Science, Sultan Moulay Slimane University, FST-BM, P.B 523, 23 000, Beni-Mellal, Morocco

² Laboratory of Organic and Analytical Chemistry, Sultan Moulay Slimane University, FST-BM, P.B 523, 23 000, Beni-Mellal, Morocco

³ Univ. Lille, Centrale Lille, Univ. Artois, UMR 8181, UCCS, Unité de Catalyse et Chimie du Solide, F-59000, Lille, France

Email: aelbouadili@gmail.com

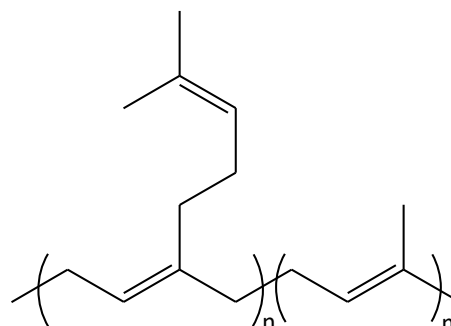
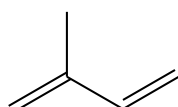
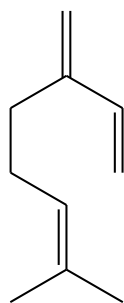
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Abstract

The combination of $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$ and dialkyl magnesium has enabled a notable achievement in the copolymerization process, with potential for new materials with diverse properties. The copolymerization of myrcene and isoprene has been achieved through statistical copolymerization, with yields of up to 84%. This process allows the insertion of isoprene into poly(1,4-trans-myrcene) while maintaining the regio and stereoselectivity of the reaction, even in the presence of high quantities of isoprene. These findings have important implications for the development of new materials with enhanced properties and demonstrate the potential of this copolymerization method for future applications.



Keywords: Coordination polymerization; elastomers; β -myrcene; stereoregular

Introduction

Our societies have become aware of the limitation of non-renewable fossil carbon resources. In this context, there is a real interest in valorizing synthons derived from biomass as alternatives to petrochemical monomers for the synthesis of polymer materials. In this sense, terpenes can represent an interesting alternative to fossil molecules. These products are primarily produced in plants, especially coniferous trees such as pine, and can be found in essential oils of plants. Our particular interest is in myrcene, also known as β -myrcene (7-methyl-3-methylene-1,6-octadiene), an isoprene dimer with a chemical formula $C_{10}H_{16}$, which is present in various essential oils such as lemongrass oil from West India, Formosa, verbena oil, and galbanum oil.¹ Myrcene is a promising alternative to petroleum-based materials, particularly given the increasing concerns surrounding environmental pollution and the gradual depletion of petroleum resources². This conjugated terpene, found in numerous essential oils, can be used to produce 100% bio sourced elastomeric materials, providing an alternative to polybutadiene and other petroleum-based polymers. Most of the polymerization of myrcene is achieved through free radicals or anionic polymerizations. However, polymyrcene, or poly- β -myrcene, has been synthesized via anionic polymerization of myrcene using *sec*-BuLi, resulting in a material containing approximately 85% of 1,4-*cis* enchainments and 15% of 3,4-defects.³ The synthesis of *cis*-polymyrcene has been documented in patent literature using ternary coordination catalysts consisting of triisobutyl aluminum, nickel octanoate, and hydrogen fluoride diethyl ether complex.⁴ Additionally, a patent has described the *trans*-polymerization of myrcene using a catalytic combination of triisobutylaluminum and tetrachlorotitanium.⁵ The first publication describing the polymerization of myrcene using Ziegler-Natta type catalysts was in 1960; however, the 1,4-stereoregularity could not be established.⁶ In 2007, myrcene was homopolymerized via a free radical process in aqueous media in the presence of cyclodextrin, producing mixtures of *cis* and *trans* polymyrcene with low activity.⁷ More recently, Visseaux reported the first 1,4-*trans* regulated polymyrcene using rare-earth metal borohydride complexes^{8,9} and 1,4-*cis* polymyrcene, this last polymer is highly *cis*-stereoregular (up to 98% are obtained) and has limited solubility in common solvents, possibly due to crosslinking.⁸

Myrcene has also been used as a component in the production of synthetic rubber through copolymerization. These copolymers have been synthesized by a Free radical polymerization of myrcene with 1,3-butadiene, with methyl methacrylate, and with *p*-fluorostyrene.¹⁰ Additionally, myrcene and 1,3-butadiene have been copolymerized using finely divided alkali metal as catalyst and ether as solvent.¹¹ More recently, myrcene has been copolymerized with various comonomers including styrene,¹² conjugated dienes,¹³ ethylene, and propylene¹⁴ using coordinative,^{15, 16} cationic,¹⁷ and anionic^{18,19} polymerization methods. Using a β -diimidosulfonate lutetium catalyst, myrcene and isoprene were polymerized to produce an isotactic-3,4-polymyrcene and isotactic-3,4-polyisoprene sequences.²⁰

Visseaux demonstrated the effectiveness of lanthanide-based catalysts for the polymerization of isoprene^{21,22} and myrcene.^{8,9} This study inspired the authors of the current article to investigate the use of lanthanide borohydrides for statistical copolymerization of 1,4 conjugated dienes.

Results and Discussion

In this study, the statistical copolymerization of myrcene and isoprene was carried out using neodymium borohydride-based coordination catalysts combined with *n*-butylethylmagnesium. Table 1 shows that as the ratio of myrcene to isoprene decreases, the percentage of myrcene incorporated into the copolymer also

decreases. The yield of copolymerization remains relatively constant at around 83-90% for all ratios. The polydispersity index ($PDI = M_w/M_n$; M_w , weight average molecular weight, M_n , number-average molecular weight) also varies slightly between the different ratios.

The copolymerization yielded high amounts of copolymer with minimal variation in yield with respect to the amount of isoprene used, and the microstructure is predicted to be homogenous in terms of the distribution of monomers by the polydispersity. The resulting copolymer has a monomodal molecular weight distribution and a PDI value lower than 2, indicating a single-site character of the copolymerization without the creation of homopolymers. The reaction's regio- and stereo-selectivity in the polymer were maintained even with large amounts of isoprene in the reactive medium, with up to 84% isoprene being incorporated into poly(1,4-trans-myrcene).

Table 1. Myrcene-isoprene statistical copolymerization using $Nd(BH_4)_3(THF)_3$ combined to dialkyl magnesium

Entry ^a	[Myr]/[Isop] ^b	Yield (%)	M_n^c (g/mol)	PDI ^c	Myrcene (%) ^d	Tg ^e (°C)
1	100/0	84	35400	1,47	100	-69.5
2	90/10	84	30000	1,54	72	nd
3	80/20	83	26900	1,48	67	-69
4	70/30	88	27800	1,44	65	nd
5	60/40	86	26300	1,43	59	nd
6	50/50	90	26200	1,87	53	-69
7	40/60	83	27200	1,54	42	nd
8	30/70	85	25700	1,50	38	nd
9	20/80	86	33800	1,39	30	-68
10	10/90	84	30000	1,63	15	nd

^a Experimental conditions : [Myrcene]/[$Nd(BH_4)_3(THF)_3$]= 300, [Isoprene]/[$Nd(BH_4)_3(THF)_3$]= 1000, $V_{toluene} = V_{monomers} = 1\text{mL}$, $T^\circ = 70^\circ\text{C}$, and $t = 2\text{h}$ ^b [Myrcene]/[Isoprene] molar ratio, and [$Nd(BH_4)_3(THF)_3$]/[BEM]=1 molar ratio. ^c Determined by size exclusion chromatography using polystyrene standards. ^d Copolymer composition (myrcene content) Determined by ^{13}C NMR or ^1H NMR. ^e Glass transition temperature determined by differential scanning calorimetry at $10^\circ\text{C}/\text{min}$.

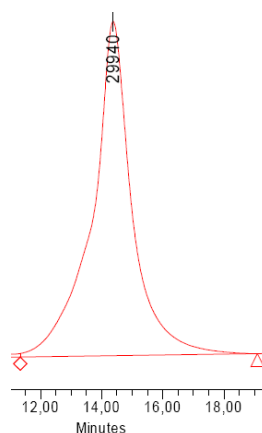


Figure 1. Chromatogram of statistical copolymer Myrcene-Isoprene (Entry5).

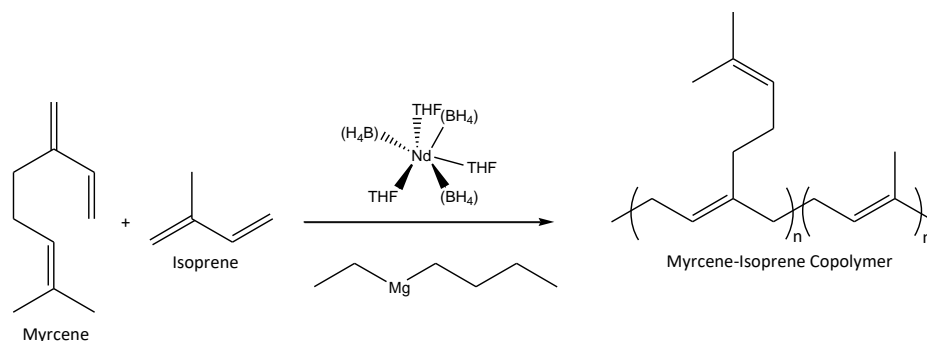


Figure 2. Copolymerization of myrcene and isoprene using neodymium borohydride-based coordination catalysts combined with n-butylethylmagnesium.

The catalytic system composed of a homoleptic neodymium pre-catalyst, namely $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$, and a co-catalyst of dialkylmagnesium type, in the present case n-butylethylmagnesium, was used for the copolymerization of myrcene and isoprene (Figure 2). This catalytic system is already used for the homopolymerization of myrcene⁸ and isoprene.²² Looking at the obtained results, it is observed that the use of a neodymium-based pre-catalyst leads to polydiene polymers with very high 1,4-trans stereoregularity. The in-situ alkylation of $\text{Nd}(\text{BH}_4)_3(\text{THF})_3$ by an alkylating agent (in our case, n-butylethylmagnesium) allows the substitution of a $[\text{Ln}]-(\text{BH}_4)$ bond with a $[\text{Ln}]-\text{R}$ type bond. Subsequently, it is within this bond that the first monomer unit is inserted, giving rise to an allyl-type species. This type of bond is much more reactive than a $[\text{Nd}]-(\text{BH}_4)$ bond.

The structure of the polymers resulting from the synthesis by this catalyst is explained based on how the monomer (myrcene or isoprene) coordinates with the metal center. Furthermore, the coordination of the monomer unit incorporated into the polymer chain in the "trans" position through an η^3 -allyl-type bond to the catalyst leads to the formation of a "syn" conformation.²³ This configuration leads to the formation of 1,4-trans polydiene (Figure 3).

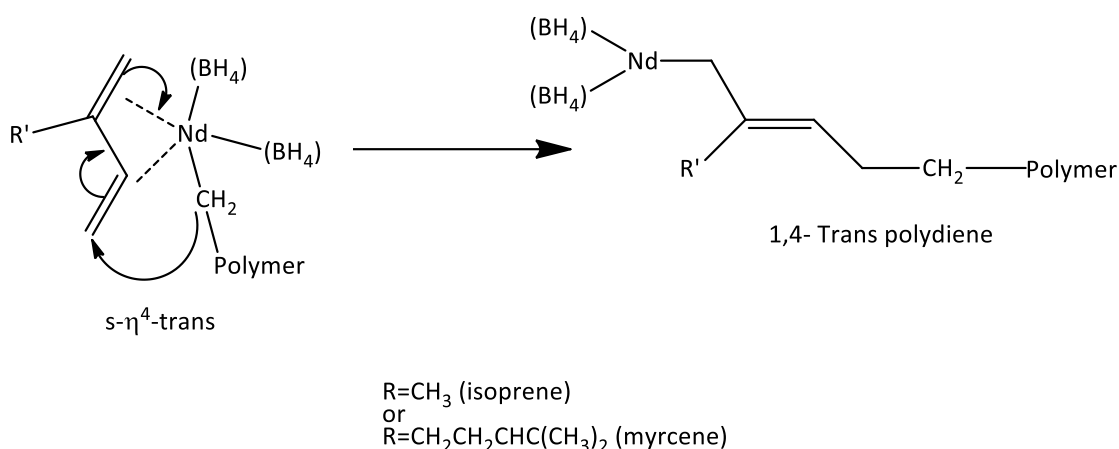


Figure 3. η^4 coordination of monomer (myrcene or isoprene), leading to a 1,4 insertion.

The results obtained from ^1H NMR analysis are not useful due to the identical chemical shifts of the peaks of the two monomers of the copolymer. Therefore, the structure of the copolymer is determined by examining the ^{13}C NMR spectra (as shown in Figure 4). The ^{13}C NMR spectrum of the copolymer revealed the presence of

signals associated to the myrcene unit, the isoprene unit, as well as newly detected signals. In order to determine the nature of the different carbons in the myrcene motif, the signals corresponding to CH₂ groups and quaternary carbons will appear in the lower part of the spectrum, while the signals from CH₃ or CH groups will be reversed. Consequently, in the olefinic region of the spectrum, the presence of two quaternary carbons was highlighted with the highest chemical shifts (C2 at 139.54 ppm and C8 at 131.78 ppm), as well as two CH groups located around 124.84 ppm (C3 and C7). In the aliphatic part of the spectrum, the two most shielded signals correspond to the two CH₃ groups of the myrcene motif (C9 at 18.04 ppm and C10 at 26.10 ppm), while the other four signals correspond to methylene groups (C1 at 37.47 ppm, C4 at 27 ppm, C5 at 27.52 ppm, and C6 at 30.84 ppm). The signals also for poly(1,4-trans-isoprene) are detected at 16.08 ppm, corresponding to the CH₃ carbon (Ce), characterize poly-1,4-trans-isoprene, at 40.17 ppm corresponding to CH₂, at 124.29 ppm corresponding to CH and the quaternary carbon of polyisoprene was detected at 135.01 ppm (Figure 4).

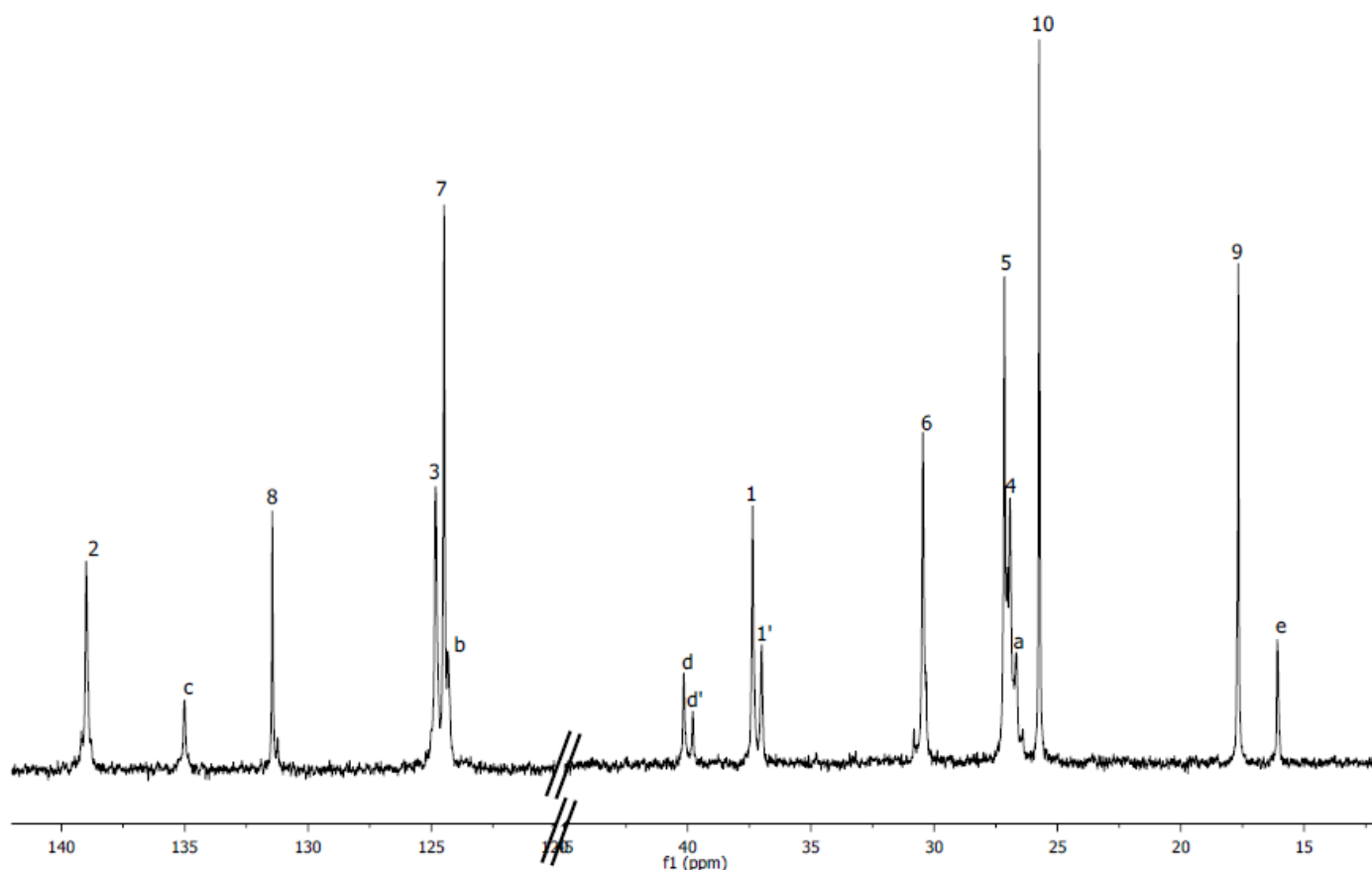


Figure 4. ¹³C NMR spectra of myrcene-Isoprene statistical copolymerization (Entry 3).

Additionally, the ¹³C NMR spectrum of the copolymer also revealed the presence of new signals (see Figure 5). Among these distinctive signals, two were particularly identified at 37 and 39.8 ppm, and they were respectively associated with carbon 1' (poly(1,4-trans myrcene)) and d' (poly(1,4-trans isoprene)). These signals correspond to carbons 1 and d, being part of a sequence involving two different motifs - specifically, a myrcene-isoprene sequence for carbon 1' and an isoprene-isoprene sequence for d' (see Figure 6). As the amount of isoprene increases within the copolymer poly(1,4-trans myrcene-co-1,4-trans isoprene), the significance of the signal 1', indicating the myrcene-isoprene sequences, becomes more pronounced. Conversely, when only 28% of isoprene is incorporated into the copolymer, the signal of poly(1,4-trans isoprene) d' has a low intensity, while

its neighboring signal d' remains distinctly present, indicating the existence of isoprene-myrcene sequences. A similar analysis could be carried out on carbon 4 of poly(1,4-trans myrcene) and a of poly(1,4-trans isoprene). However, these two signals 4 and a, which indicate sequences involving different monomers, are located in a region where their isolation and characterization are complex.

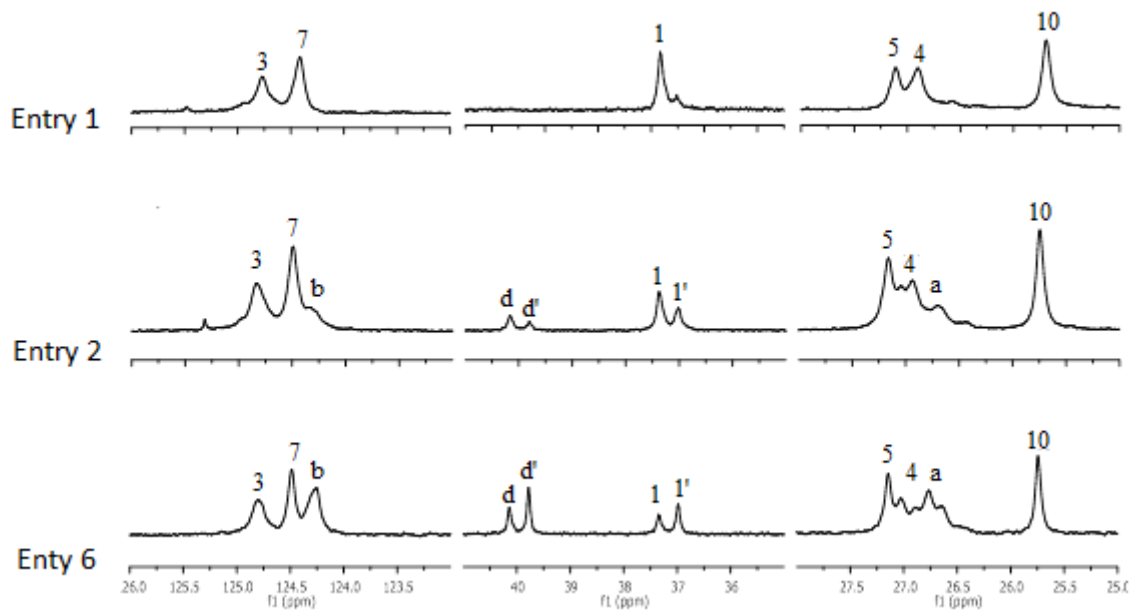


Figure 5. ^{13}C NMR spectra of poly(1,4-trans-myrcene) (entry1) and poly(myrcene-co-isoprene) (entries 2,6). (25-28 ppm), (35-41 ppm) and (123-126 ppm) zones.

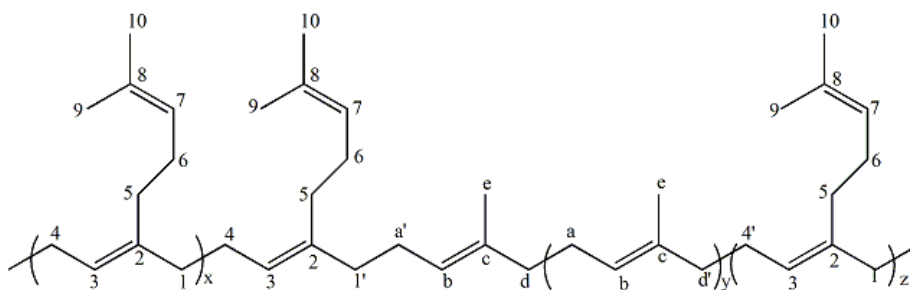


Figure 6. Microstructure of myrcene-isoprene copolymer.

The polymyrcene backbone of the copolymer showed a 90.8% 1,4-trans microstructure (C1 carbon at 37.47 ppm show a 1,4-trans-stereo-specificity of polymyrcene), which is similar to that of the homopolymer. Moreover, myrcene is preferentially incorporated into the copolymer, which is an outcome that was not anticipated. It might have been expected that isoprene would be favored for insertion due to the lower steric hindrance of its CH_3 group compared to the side chain of myrcene. However, given this result, it is possible to consider a stabilizing effect of the unsaturation present in this chain, thereby promoting the unsaturation of myrcene motifs.

In order to confirm what had been observed previously, namely the high reactivity of myrcene compared to isoprene towards the catalytic system, the reactivity ratios of each of the comonomers were determined. The

Fineman and Ross²⁴ method was used to calculate the reactivity ratios for the $\text{Nd}(\text{BH}_4)_3(\text{THF})_3/\text{BEM}$ system. The values obtained are r_1 (myrcene) = 1.69 and r_2 (isoprene) = 0.98. These ratios reflect the ease with which the catalytic system chains one myrcene molecule behind another (r_1) or one isoprene molecule behind another (r_2). The reactivity ratio value of myrcene (r_1) indicates the higher reactivity of this monomer in the copolymerization. In our experimental conditions we used, it was possible to add 28% to 85% isoprene to the copolymer. Initially, we observed that increasing the amount of isoprene led to a higher rate of insertion in the copolymer, which varied between 28% and 85%, with a value of 47% observed for the 50/50 myrcene/isoprene ratio.

This catalytic system allowed to achieve a stereoselective copolymerization reaction, resulting in the production of poly(1,4-trans myrcene-co-1,4-trans isoprene) with a trans content of 90.8%. The glass transition temperatures (T_g) observed for these copolymers (Table 1) are consistent and fall between those of the two homopolymers (-69.5°C for poly(1,4-trans myrcene) and -67°C for poly(1,4-trans isoprene)) indicating that the two connected polymers are miscible. Furthermore, the addition of myrcene to the copolymer allows for the modulation of T_g and the softening of the trans-isoprene polymer, in the sense that polymyrcene remains amorphous⁸ (transparent appearance), even when it is in the trans configuration. In contrast, trans-polyisoprene is semi-crystalline²² and remains in a harder material form.

Conclusions

In this study, neodymium borohydride-based coordination catalysts was combined with n-butylethylmagnesium to carry out a statistical copolymerization of myrcene and isoprene. The resulting poly(1,4-trans-myrcene-co-1,4-trans-isoprene) showed high stereoregularity and good yields. The high selectivity observed in this process is attributed to the coordination of unsaturation to the metal during copolymerization. This catalytic system allows the synthesis of random copolymers which serve as interesting precursors for biosourced thermoplastic elastomers. This approach provides a promising method for the synthesis of new amorphous copolymers. The successful realization of this method may have important implications in the fields of materials science and polymer chemistry. Further research could explore the potential of this technique for other monomer combinations.

Experimental Section

General. It is a widespread practice to carry out reactions under inert conditions to prevent any unwanted reactions with atmospheric oxygen or moisture. The use of a glove box or Schlenk techniques under dry argon is a common method to achieve these conditions. Purification of solvents such as toluene is also necessary to remove any impurities that could interfere with the reaction. Molecular sieves are often used for this purpose as they can selectively adsorb water molecules, it was purified using an alumina column (Mbraun SPS), and stored on molecular sieves (3A) in a glove box after being distilled over sodium/benzophenone ketyl. Similarly, the use of dried (over calcium hydride) and distilled (over molecular sieves, and then distilled a second time right before use) reactants (β -Myrcene and isoprene) is important to ensure the purity of the starting materials. n-butylethyl magnesium (BEM) (20 wt % in heptane from Texas Alkyls), was utilized as received. Finally, the synthesis of the catalyst ($\text{Nd}(\text{BH}_4)_3(\text{THF})_3$) is carried out using previously reported procedures from the literature.²⁵

It's important to note that the use of a glovebox and dry argon is necessary to avoid any moisture or air contact that could interfere with the reaction. Toluene, β -Myrcene, isoprene and n-butylethyl magnesium were added to the flask in this order using syringes. The mixture was taken out of the glovebox, and magnetically stirred at 70 °C for 2 h. The polymerization was then quenched with acidified methanol once the flask was opened to the air. The resulting solution mixture was added to a sizable amount of methanol containing 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT) as stabilizing agent. Finally, the white polymer is filtered and vacuum-dried to ensure a consistent weight.

The copolymers were analyzed using NMR techniques. ^1H experiments were performed on polymyrcene homopolymer and poly(myrcene-co-isoprene) copolymers prepared in CDCl_3 . Quantitative ^{13}C NMR was performed using the zgig sequence in CDCl_3 . The NMR analyses were performed on an AC 300 Bruker at room temperature.

Size exclusion chromatography (SEC) was performed at 40 °C using THF as eluent (1 mL/min) and a Waters Styragel column (HR2, HR3, HR4, HR5E) calibrated with polystyrene standards.

Differential Scanning Calorimetry (DSC) measurements were performed in a nitrogen environment using a Setaram 141 apparatus at a heating rate of 10 °C /min from -120 to 100 °C using around 30 mg samples in aluminum crucibles.

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