

Copolymerization of 1-hexene and 1-dodecene with 1,3-butadiene by a versatate/diisobutylaluminum hydride/t-butyl chloride catalyst system

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Abstract: The aim of this study was to incorporate an alpha-olefin (1-hexene or 1-dodecene) in a high *cis* polybutadiene chain, using a neodymium versatate/diisobutylaluminum hydride/t-butyl chloride catalyst system. The influence of alpha-olefin on polymerization reaction and polymer characteristics, using different weight ratios of butadiene/ α -olefin, was evaluated. The copolymers were characterized by SEC, FTIR, NMR, TGA and viscosimetric analysis. The thermal stability of the polymer tended to increase with incorporation of alpha-olefins, while its microstructure was not affected. The weight average molecular mass (Mw) tended to increase and the polymerization conversion tended to decrease with increasing alpha-olefins content. The copolymers showed a lower intrinsic viscosity than for the homopolymer. The results indicated that the alpha-olefins were incorporated in the polybutadiene chain.

Keywords: Copolymerization, 1,3-butadiene, alpha-olefin, Ziegler-Natta catalyst, neodymium.

Introduction

Butadiene-1,3 polymerization can yield polymers with different isomeric forms, such as *cis*-1,4, *trans*-1,4, 1,2- vinyl syndiotactic, 1,2-isotactic and 1,2-atactic. Each one has different properties and consequently many applications^[1]. The elastomeric *cis*-1,4-polybutadiene is one of the most important raw materials in the rubber industry. The use of polybutadiene with high content of *cis*-1,4 in tires is advantageous because it improves the mechanical properties of the rubber. These characteristics contribute to the preservation of nature, because the vehicle will consume less fuel and thus emit less pollutant gases into the atmosphere. Catalyst systems based on neodymium are widely used to produce polybutadiene with high content of 1,4-*cis* units (98%)^[2-6]. However, these catalysts also produce a polymer with high linearity and high molecular weight. These characteristics make the polybutadiene hard to process. Thus, there must be a balance between the polymer's physical properties and processability^[5]. Besides the poor processability of high *cis*polybutadiene polymer, the cold-flow characteristic is also problem related to linearity of its chain. In this case, the insertion of branches along the polybutadiene chain also minimizes this effect, since the branches serve as anchors between the polymer chains. Many studies have been carried out but there is still a great need to find new ways to improve the processability of this polymer^[7]. One possible way to improve do this is through the copolymerization of butadiene with alpha-olefins^[5,7].

Copolymerization of butadiene with 1-alkenes has already described in the literature. For example, the copolymerization of butadiene with 1-octene and 1-dodecene using the ternary catalyst system neodymium oxide/triisobutylaluminum/ethylaluminum sesquichloride was studied by Friebe et al.^[8]. These authors showed that only small amounts of 1-alkenes

are incorporated and that no neighboring 1-alkene moieties are present in the copolymer. With increasing amounts of 1-alkene in the monomer feed, the catalyst activity decreased drastically. The *cis*-1,4-content of the butadiene units in the copolymer was around 90%. On the other hand, we did not find any articles that describe the copolymerization of butadiene with 1-hexene and 1-dodecene using a neodymium versatate/diisobutylaluminum hydride/t-butyl chloride catalyst system. However, our group has published a work about polymerization of 1,3-butadiene and octene-1^[9]. The results showed that the polybutadiene microstructure and the degradation temperature (Tmax) were not affected by the octene-1 addition. Moreover, the copolymer molecular mass tended to increase as the octene-1 content increased.

In this study, the aim was incorporate an alpha-olefin (1-hexene or 1-dodecene) in a high *cis* polybutadiene chain, using a neodymium versatate/diisobutylaluminum hydride/t-butyl chloride catalyst system.

Materials and Methods

Materials

The chemicals used in this work were diisobutylaluminum hydride (DIBAH) (Akzo Nobel), neodymium versatate (as hexane solution) (Comar), t-butyl chloride (as hexane solution) (Aldrich Chemical Company, Inc.), hexane (Petroflex Indústria e Comércio S.A., now LANXESS Elastômeros do Brasil S.A., Brazil), 3,5-di-t-butyl-4-hydroxytoluene (BHT) (Shell Brasil Ltda., Brazil), trionylphenyl phosphite (TNPP) (GE Specialty Chemicals), butadiene (as hexane solution) (LANXESS Elastômeros do Brasil S.A.,

Brazil), tetrahydrofuran, PA (THF) (Vetec Química Fina Ltda., Brazil), nitrogen (White Martins S/A, Brazil), 1-hexene, 97% (Aldrich Chemical Company, Inc.) and 1-dodecene 95% (Aldrich Chemical Company, Inc.).

Catalyst synthesis

All materials involved in the catalyst synthesis were dried in an oven at 100 °C for at least 12 hours. The synthesis was carried out in oven-dried nitrogen-purged bottles fitted with rubber septums for 1 hour at 10 °C, under magnetic stirring. The addition order of catalytic components was: DIBAH (Al), neodymium versatate (Nd) and t-butyl chloride (Cl). The molar ratio Cl/Nd/Al was kept constant at 3/1/11. After the reaction time, the catalyst was aged for 24 hours at 10 °C^[2].

Copolymerization reaction

The copolymerization was conducted for 2 hours in a stainless steel reactor (Parr) with 1 L capacity, under pressure of 5 kgf/cm² and stirring rate of 300 rpm. The 1,3-butadiene was added to the system in the form of a solution in hexane at 35% w/w. The alpha-olefins were added as received. The components were added to the reactor in the following order: monomers, solvent (hexane), alpha-olefin and catalyst. 1-hexene and 1-dodecene were added in the following butadiene/ α -olefin ratios = 100/0, 99/1, 97/3, 95/5, 90/10, 80/20 and 70/30. The catalytic system was deactivated by the addition of hexane solution of 3,5-di-t-butyl-4-hydroxytoluene (BHT). The copolymer was coagulated in distilled water heated (75 °C) under vigorous stirring (600 rpm) and then dried in an oven with air circulation at 65 °C until constant weight.

Characterization of copolymers

The polymer microstructure was characterized by infrared spectroscopy in a Perkin-Elmer Spectrum One spectroscope, as films formed on KBr cells, prepared from 2% (w/v) chloroform solutions. The isomer repeating units contents were obtained from the absorbances at 725 (*cis*-1,4), 910 (1,2-vinyl), and 965 cm⁻¹ (*trans*-1,4), as described in our previous work^[9]. The polymer molecular weight characteristics were evaluated by size exclusion chromatography (SEC), in a Waters 150-C Plus SEC, fitted with an RI detector at 30 °C, using THF as solvent at 1 mL/min flow rate. We used a universal calibration curve, constructed by using monodisperse polystyrene standards. Polymer solutions (0.1% w/w) were passed through filters of 0.45 μ m pore diameter before being injected in the SEC.

Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of the polymers were obtained by using a TA Q50 instrument in a temperature range of 50-700 °C at constant heating rate of 20 °C/min, under nitrogen atmosphere. During the heating period, the weight loss and temperature difference were recorded as a function of temperature.

The viscosimetric parameters were determined at 30 \pm 0.1 °C, using an Ubbelohde 0B capillary viscometer. Solutions were prepared with the concentration of

0.5% w/v in toluene. By graphic extrapolation to infinite dilution, experimental determination was carried out by counting the efflux time of six dilutions of the sample solutions.

¹H NMR analyses were carried out in a Bruker DRX 300 spectrometer. Spectra were obtained by using 5 mm tubes, CDCl₃ (solvent and lock signal), TMS (reference), at room temperature (20 °C). The samples were diluted in CDCl₃ (0.5% v/v), obtaining solutions of 30% v/v final concentration. The acquisition conditions were pulse duration: 9.2 μ s (90°), with 6 dB attenuation; acquisition time: 2.9 s; interval between pulses: 1.5 s; and number of scans: 64.

Results and Discussion

In this study, all the copolymerization reactions were performed using catalysts composed of diisobutylaluminum hydride (Al), neodymium versatate (Nd) and t-butyl chloride (Cl) (molar ratio Al/Nd/Cl=11/1/3), synthesized under the same conditions (1 hour at 10 °C) and aged for 24 hours at 10 °C.

Moreover, the copolymerization conditions, such as reaction time (2 hours), reaction temperature (70 \pm 3 °C), solvent (hexane), mass of 1,3-butadiene (42 g) and neodymium concentration ([Nd] = 0.23 mmols/100 g of butadiene) were kept constant in all experiments.

The literature^[10-13] shows several possible structures for active sites (Figure 1) formed from the catalytic system used in this work. The existence of these different types of active sites does not mean they all are present at the same time. In each particular catalytic system, different types of active sites can be formed and the proportion of each depends on the preparation conditions employed. Mello et al.^[14] proposed that the predominant catalytic species during the polymerization reaction (under the same conditions applied in this study) are the bimetallic ones. However, the catalytic system used in this work was not active enough to produce homopolymers of alpha-olefins. So, it is impossible to obtain poly(1-hexene) and poly(1-dodecene) with this catalyst system. This assures that the consumption of alpha-olefins occurred only by insertion of these comonomers in the polybutadiene chain.

Influence of alpha-olefin addition on the polymerization conversion

Different contents of alpha-olefins (1, 3, 5, 10, 20 and 30% by weight) were used in the copolymerization reactions. The results showed that, irrespective of the type of alpha-olefin, an increase in the content caused a reduction in the conversion (Figure 2). However, this effect was stronger with longer length of the comonomer used.

In reactions with 1-hexene (Figure 2a), it was not possible to see a significant reduction in conversion rates when this alpha-olefin was added in the reaction. Even with additions up to 20% octene-1, the conversion was high (80%). This result is interesting for possible industrial uses, since it is possible to add up to 20% of 1-octene without causing decrease in conversion.

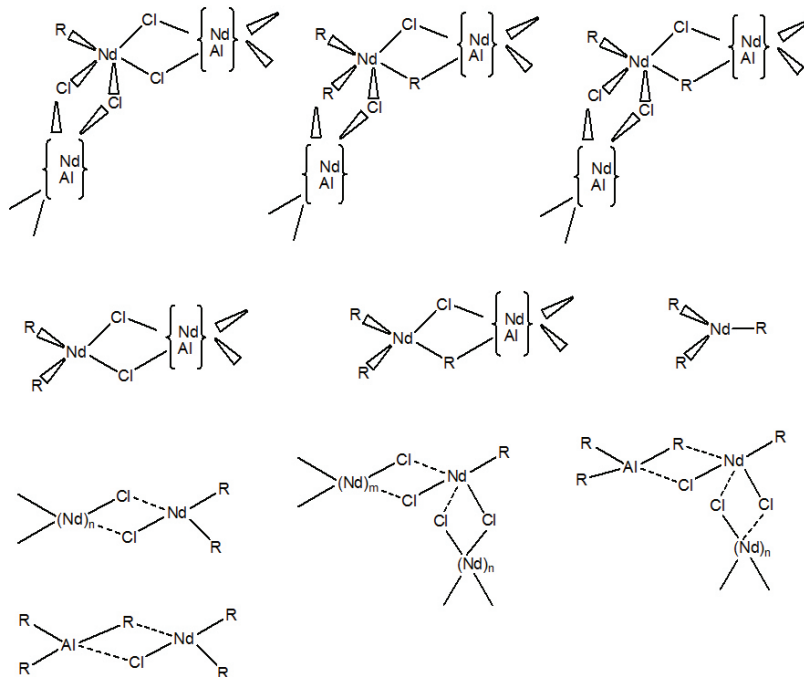


Figure 1. Possible structures of catalytic sites^[10-13].

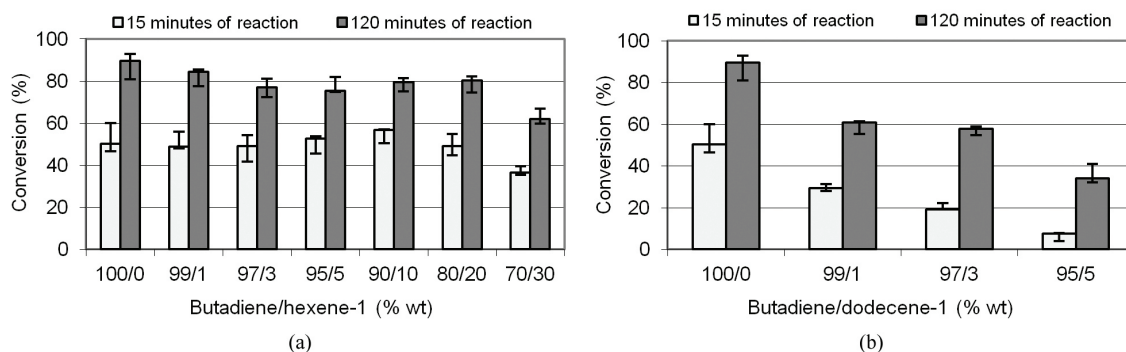


Figure 2. Influence of 1-hexene (a) and 1-dodecene (b) content on the reaction conversion.

Figure 2b shows that adding only 1% 1-dodecene caused a significant reduction in the conversion at the start of the polymerization reaction (15 min). At contents above 5%, no copolymer was obtained at the end of the reaction with 1-dodecene.

An increase in alpha-olefin content (added to the reaction) ensures its greater insertion into the polymer chain. However, the increase in alpha-olefin content can result in a significant inhibition of the reaction kinetics. This fact can be explained by the constant of propagation of the alpha-olefin insertion in the polymer chain. The literature^[15-17] shows that the propagation constant of an alkene in the copolymerization with dienes can be approximately 60 times smaller than the constant that involves the insertion of a diene molecule. Thus, an increase in insertion of comonomer can provoke a decrease in the conversion.

However, even when the propagation constant is higher for the inclusion of molecules of 1,3-butadiene

than for the alpha-olefin, there will be formation of copolymer according to the probabilistic nature of chemical reactions. So, if there are molecules of alpha-olefin in the reaction, molecules of 1,3-butadiene as well as a small fraction of alpha-olefin will be included in the propagating chain, thus generating a random copolymer^[17].

In addition, the higher the level of alpha-olefins added, the more likely is the occurrence of effective shocks to propagating the species and molecules of the comonomers. Thus, with a higher frequency of collisions, the probability of incorporation of branches is higher^[17].

The effect of alpha-olefin length in the conversion, with different contents, is shown in Figure 3. Regardless of the alpha-olefin type added, a trend to reduce the reaction conversion when the alpha-olefin length increased was observed.

When 1-dodecene was used as comonomer, the reduction in the conversion was so significant that no

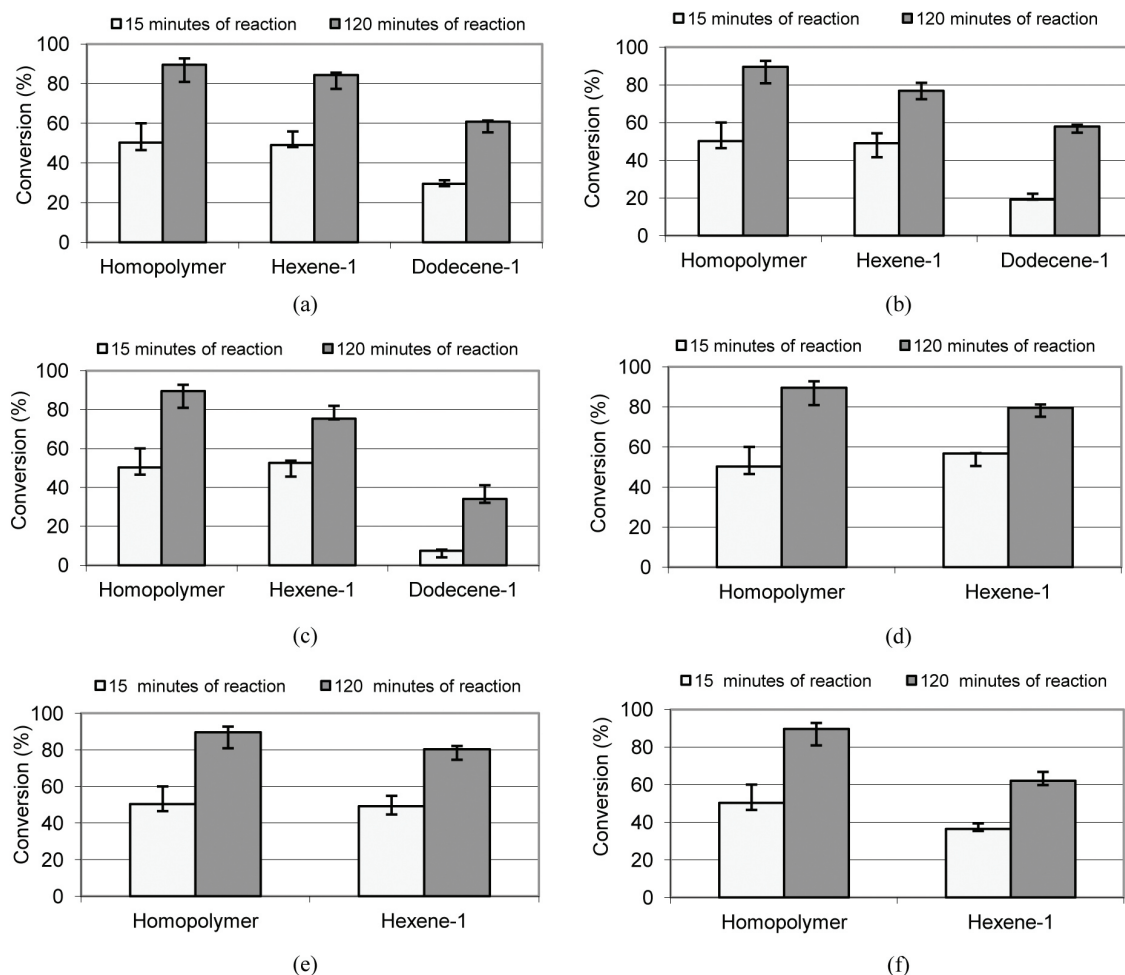


Figure 3. Influence of alpha-olefin incorporation on the reaction conversion: butadiene/ α -olefin = 99/1 (a), 97/3 (b), 95/5 (c), 90/10 (d), 80/20 (e) and 70/30 (f) (Homopolymer = Butadiene/ α -olefin = 100/0).

polymer was formed when about 10% wt of 1-dodecene was added. This occurred because when an alpha-olefin is used as comonomer in the copolymerization reaction with 1,3-butadiene, the two carbon atoms that form the double bond (in the alkene structure) are inserted in the polymeric chain, leaving the other atoms as a branch. Thus, the branches formed when 1-dodecene is added in the reaction medium must contain ten carbon atoms, which are sufficiently long to cause a stereo hindrance, which impairs the access of monomer molecules to the active sites, slowing the chain growth. Figure 4 shows a mechanism of alpha-olefin insertion proposed by us.

Figure 5 shows ^1H NMR spectra of butadiene homopolymer (Figure 5b) and butadiene/dodecene=99/1 (Figure 5a). Although the spectra have similar appearance, Table 1 shows that the areas relative to chemical shifts of hydrogen atoms from $(\text{CH}_3)\text{R}$ terminals (0.8-1.0 ppm) and hydrogen from CH_2 units (1.0-2.7 ppm) increased when the butadiene copolymerization with 1-dodecene occurred. This indicates that the addition of 1-dodecene probably formed branches in the polybutadiene chain, as proposed in Figure 4b.

Influence of alpha-olefin addition on microstructure

Stereospecific catalyst systems, like Ziegler-Natta catalysts based on neodymium, are able to produce *cis*-1,4 polybutadiene (homopolymer) with greater control of microstructure, higher molecular mass and narrower molecular mass distribution^[8,19-22]. Table 2 shows that the addition of alpha-olefins does not change the polymer microstructure. This proves that the active site was not modified by addition of alpha-olefin. Probably the reaction mechanism to produce high content of *cis*-1,4 units was not modified (Figure 4a)^[9,18,23,24]. This characteristic is industrially important, because polybutadiene with high content of *cis*-1,4 units has useful properties, such as abrasion resistance, crack resistance, resilience, hysteresis and heat buildup. Thus, it is possible to affirm that the catalyst system used in this study is appropriate to synthesize high *cis* polybutadiene branched with the alpha-olefins studied (1-hexene and 1-dodecene).

Influence of alpha-olefin addition on molecular mass

Figure 6 shows that for any content of alpha-olefin added, the number average molecular mass (M_n)

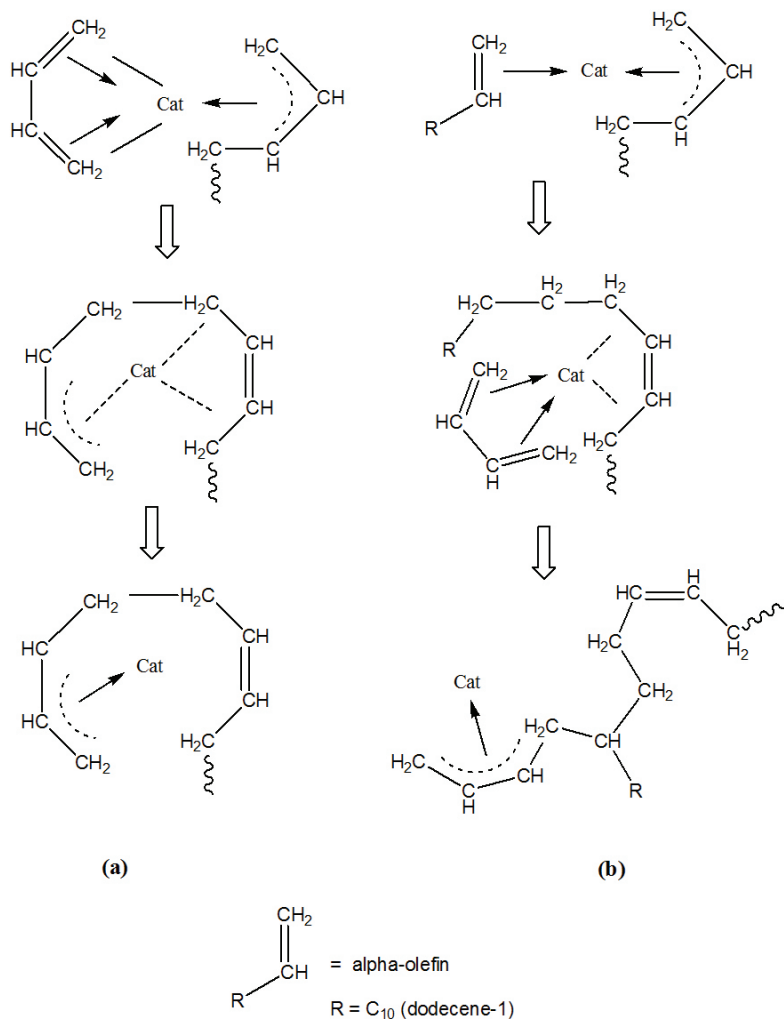


Figure 4. Cis-polybutadiene formation, according to Porri^[18] (a) and a scheme of alpha-olefin insertion in the polybutadiene chain proposed by us (b).

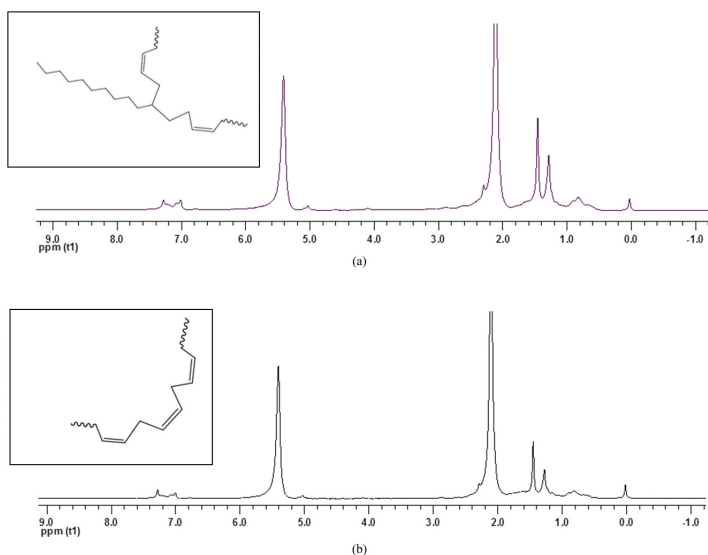


Figure 5. ¹H NMR spectrum of butadiene/dodecene =99/1 copolymer (a) and 1,3-butadiene homopolymer (b).

Table 1. ¹H NMR signal characteristics.

Type of hydrogen	Chemical shift range (δ ppm)	Signal area (%)	
		Homopolymer ^(a)	Copolymer ^(b)
(CH ₃)R terminals	0.8-1.0	4.96	5.33
(CH ₂) _n	1.0-2.7	64.60	68.06
Hs - vinyl group	4.6-5.2	0.80	0.70
R ₂ C = CHR vinyl	5.3-5.7	24.30	22.50
Hs - group 1,4 (<i>cis</i> and <i>trans</i>)	6.9-7.4	3.10	4.360

^(a)Homopolymer = Butadiene/α-olefin = 100/0. ^(b)Copolymer = Butadiene/dodecene = 99/1.

Table 2. Influence of alpha-olefin addition on polymer characteristics.

Alpha-olefin	1,3-butadiene/ alpha-olefin	Microstructure			[η] _H (dL/g)	T _{max} (°C)
		<i>cis</i> -1,4	<i>trans</i> -1,4	vinyl-1,2		
1-hexene	100/0	95	4	1	3.348	480
	99/1	96	3	1	2.545	482
	97/3	96	3	1	1.891	479
	95/5	95	4	1	3.067	481
	90/10	96	3	1	2.947	479
	80/20	96	3	1	3.557	476
	70/30	97	2	1	3.421	477
1-dodecene	100/0	95	4	1	3.348	480
	99/1	94	5	1	2.922	479
	97/3	94	5	1	3.145	477
	95/5	94	5	1	nd ^(c)	480
	90/10	nd ^(c)	nd ^(c)	nd ^(c)	nd ^(c)	nd ^(c)
	80/20	nd ^(c)	nd ^(c)	nd ^(c)	nd ^(c)	nd ^(c)
	70/30	nd ^(c)	nd ^(c)	nd ^(c)	nd ^(c)	nd ^(c)

^(a)[η]_H = Intrinsic viscosity by Huggins' equation. ^(b)T_{max} = Temperature at maximum weight loss rate. ^(c)nd = no determined.

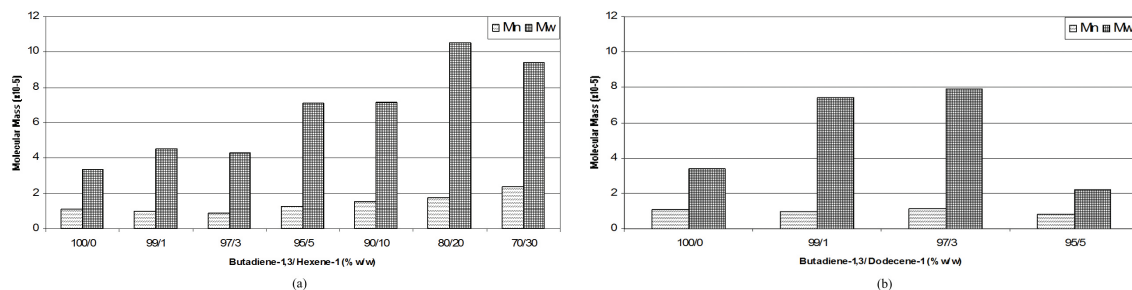


Figure 6. Influence of 1-hexene (a) and 1-dodecene (b) content on molecular mass.

and weight average molecular mass (Mw) underwent significant variations with the comonomer addition. There is a trend to increase the molar mass by increasing the content of comonomer added. This result was expected, since raising the comonomer content in the reaction (keeping the concentration of 1,3-butadiene constant in all reactions) increases the probability of insertion of alpha-olefin in the polymer chain, thus resulting in a copolymer with higher molecular mass.

However, the effect on the weight average molecular mass (Mw) is more significant than on the number molecular mass (Mn), because the number of polymeric chains formed during the reaction was practically the same in all reactions.

To understand the behavior between the weight average molecular mass (Mw) and the number molecular mass (Mn), it is important to analyze their mathematical definitions. Mn is more strongly influenced by the number

of chains present in a sample, while Mw is more related to the length of the polymeric chains. Therefore, the molecular mass results presented in this work confirmed that the different alpha-olefins used were incorporated in the polymeric chain.

The effect of alpha-olefin length on the molecular mass of the copolymers, with different contents, is shown in Figure 7. It can be seen that the greater the alpha-olefin length, the greater are the increases in the number molecular mass and weight average molecular mass.

When 1-dodecene was used as comonomer, even in the weight ratio of 99/1 (1,3-butadiene/alpha-olefin), a significant decrease in the reaction conversion (60%) (Figure 3a) was observed with an accentuated increase in the molecular mass (Mw = 7.2 × 10⁵) (Figure 7a) in relation to homopolymer (1,3-butadiene/alpha-olefin = 100/0). When 3% wt of 1-dodecene was added, the conversion decreased substantially (20%) (Figure 3b)

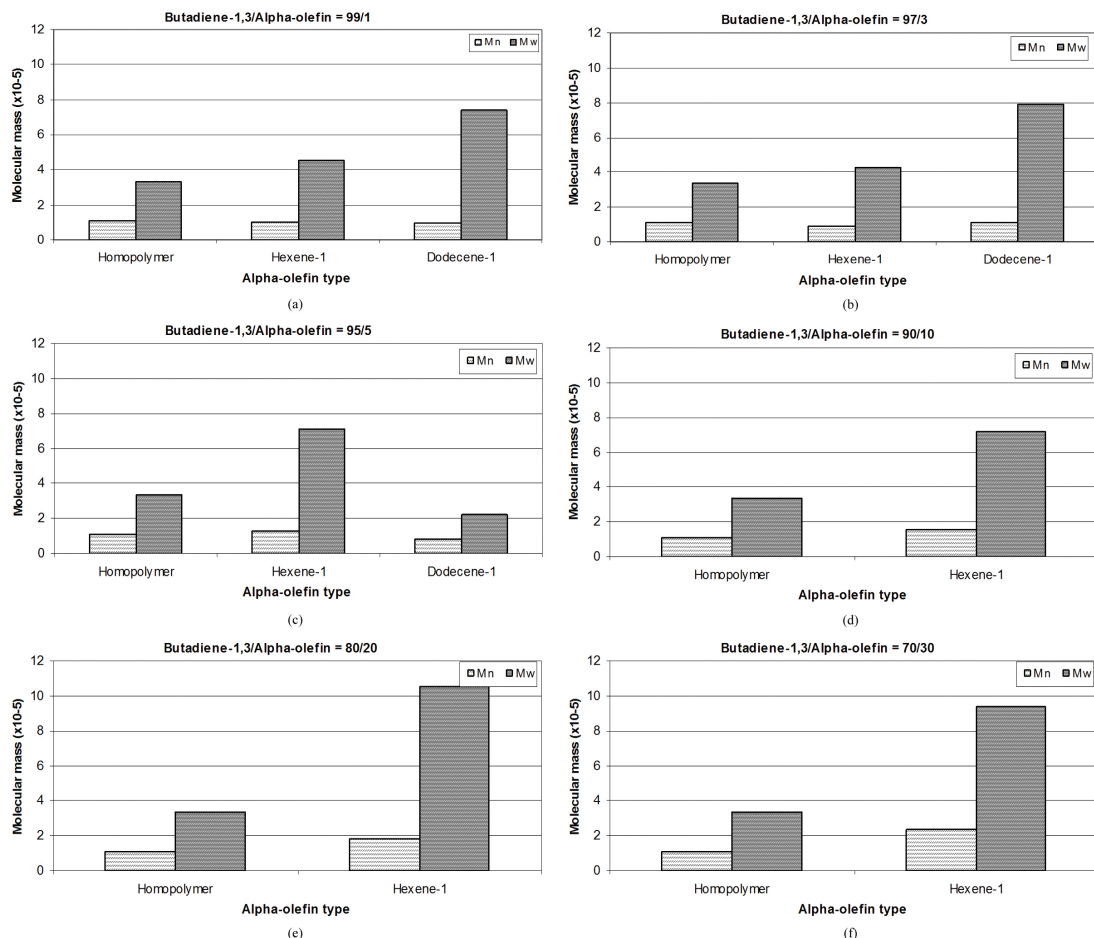


Figure 7. Influence of each alpha-olefin, with different contents, on the molecular mass (Homopolymer = Butadiene/alpha-olefin = 100/0).

and the molecular mass increased more ($M_w = 8.0 \times 10^5$) (Figure 7b) in relation to homopolymer (1,3-butadiene/alpha-olefin = 100/0). This behavior confirmed that the alpha-olefin molecule was inserted, in branched form, in the polybutadiene chain. The same result is observed when 1-hexene is the comonomer.

The way active sites are available for coordination with the monomer is a factor that should be taken into consideration. The presence of long branches makes the insertion of new monomer molecules more difficult, as a consequence producing shorter polymer chains (lower molecular mass). This explains the result shown in Figure 6c for 1-dodecene.

Influence of alpha-olefin addition on intrinsic viscosity

Viscosimetric analysis is important, since the inclusion of branching in the polymer chain changes its behavior in solution, giving different viscosity values.

The effect observed when a polymer is added in a solvent depends on the concentration, molecular mass and the chain conformation. Thus, viscosity measurement is an appropriate method to obtain information about the length and shape of a macromolecule in solution.

It is important to guarantee that the solution concentration is small enough that each polymer chain

can has the ability to move alone, i.e., in this case the solutions are in a diluted or Newtonian system. The analysis of viscosity of a dilute polymer solution allows obtaining parameters related to the isolated chain, such as intrinsic viscosity.

The critical concentration can be defined by the deviation in the relation $\log \eta_{sp} \times \log c[\eta]$. The parameter $c[\eta]$ (dimensionless coil overlap parameter, where c is the concentration) reveal the total volume occupied by the polymeric chain. To affirm that the fluid is in a Newtonian system, the relation between $\log \eta_{sp}$ and $\log c[\eta]$ must be linear. Figure 8 presents the graph of $\log \eta_{sp} \times \log c[\eta]$ from the copolymers obtained in this work. A linear relation was observed for all the samples, independent of the alpha-olefin type and content, thus proving that all determinations were carried out in a Newtonian system.

Several mathematical equations are available in the literature^[25] to determine the intrinsic viscosity $[\eta]$ of a polymer solution by graphical extrapolation. In this study we used the Huggins equation (Equation 1):

$$\eta_{sp}/c = [\eta]_H + k_H [\eta]_H^2 c \quad (1)$$

where: η_{sp} = specific viscosity; c = concentration of the solution; $[\eta]_H = \lim_{c \rightarrow 0} [\eta]$; η_{red} = intrinsic viscosity and k_H = Huggins constant.

The viscosity of a solution is a function of the polymer's molecular mass and its structure. Polymer samples can have the same molecular mass but different structures (linear or branched), thus having different lengths and shapes.

Table 2 shows the influence of different contents of alpha-olefin on the polymers' intrinsic viscosity. There is no tendency in the intrinsic viscosity values because the copolymer samples have different molecular mass, and a higher content of alpha-olefin increases the influence on the molecular mass.

The literature describes that the hydrodynamic volume of a branched polymer is lower than the value presented by a linear one. The reason for this is that the covalent links that exist in a branched polymer limit the expansion coefficient and consequently reduce the intrinsic viscosity $[\eta]$. When polymer samples have branches with the same length but with different quantities, no significant differences in the hydrodynamic volume will be seen, so the viscosity will be practically the same. However, when materials with different molecular masses are analyzed, an increase of viscosity will result in a proportional increase in the molecular mass.

When dodecene-1 was used as comonomer, some differences in the intrinsic viscosity values could be observed. This was expected, since according to the literature^[26] the influence on material properties becomes more significant only with comonomers having at least 10 carbon atoms. Nevertheless, the reduction in the propagation constant because of the stereo hindrance provoked by dodecene-1 was so strong that with the reaction time used in this work (2 hours), no polymer was obtained from the addition of 5% wt of dodecene-1.

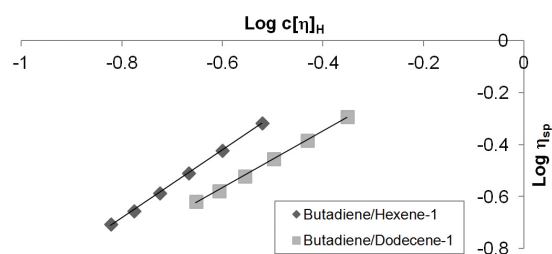
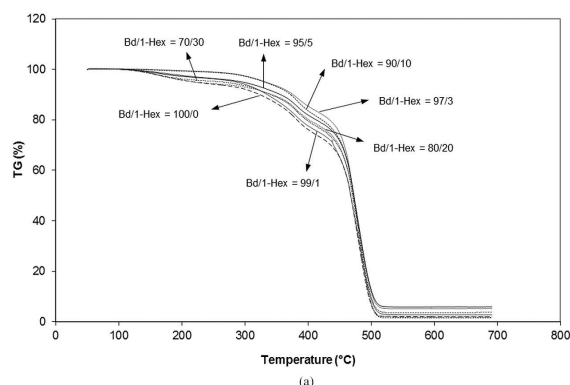


Figure 8. $\text{Log } \eta_{sp}$ versus $\text{log } c[\eta]_H$ (butadiene/ α -olefin = 95/5).



Influence of alpha-olefin addition on thermal stability

Table 2 shows the temperature obtained by thermogravimetric analysis (TG) at which the degradation rate was highest (T_{max}). The results showed there was no change in T_{max} by adding any of the alpha-olefins evaluated under the conditions used in this study.

According to^[27], there should not be significant variations in T_{max} when there is no change in the polymer matrix (here *cis*-1,4 polybutadiene) even with the insertion of different types and contents of alpha-olefins.

Anatawaraskul et al.^[28] verified that the incorporation of comonomer in polymeric chain can promote a variation in the onset temperature. This fact can be observed in Figure 9. There was a trend to higher thermal stability for the copolymers with higher content of alpha-olefin (higher branch content). An exception to this behavior occurred with when the 1,3-butadiene/1-dodecene ratio was 95/5. However, in this case, the lower thermal stability can be explained by the lower molecular mass.

Some factors can modify the thermal properties of a polymer: molecular symmetry, comonomer content, branch content, molecular mass and molecular crystallinity. As discussed before, there were no significant differences in the microstructure of the samples analyzed. Therefore, the changes in the thermal stability of these materials can be explained by the comonomer content, and consequently the branched content, in the polymeric chain. As can be seen in the TG results, the increase in the alpha-olefin incorporation in the polymeric chain resulted in an increase in the materials' thermal stability.

The literature contains findings that indicate the insertion of alpha-olefins in the polymeric matrix influences the crystallinity of samples, modifying the thermal properties^[29-31]. In this way, it is possible to suggest that the presence of alpha-olefin in the polybutadiene chain creates crystalline segments, generated by the packing of the branches, resulting in the increase of the materials' thermal stability.

Conclusions

1-hexene and 1-dodecene were incorporated in the polybutadiene chain using a Ziegler-Natta ternary catalyst system based on neodymium without changing its microstructure. The addition of alpha-olefin decreased

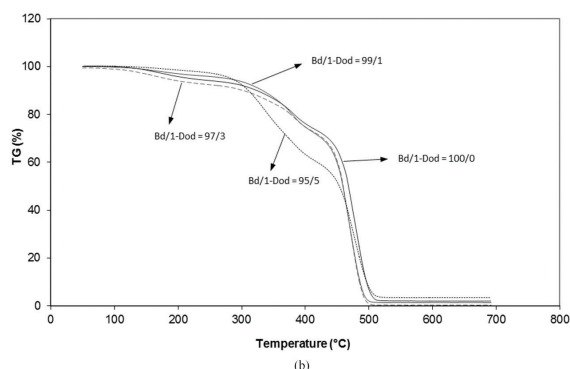


Figure 9. Influence of alpha-olefin addition on the thermal stability of the copolymers: 1-hexene (a) and 1-dodecene (b).

the reaction conversion. The number average molecular mass (Mn) was not significantly changed; while the weight average molecular mass (Mw) tended to increase with higher content and alpha-olefin size. The copolymers showed a lower intrinsic viscosity value when compared with the homopolymer. The temperature of maximum thermal degradation did not change significantly between the samples synthesized in this work.

Acknowledgments

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