NMR Characterization of High cis Polybutadiene

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Abstract: *In this work a laboratory scale process was studied for the production of polybutadiene with high content of cis-1,4 repeating units. A Ziegler-Natta catalytic system constituted of neodymium versatate (Nd), tert-butyl chloride (Cl) and an organoaluminium compound (Al) was used. The influence of the organoaluminium (cocatalyst) type, Al/Nd and Cl/Nd molar ratios on the polymer microstructure was verified. The polymers microstructures were characterized by ^{13}C nuclear magnetic resonance (NMR). The maximum content of cis-1,4 repeating units determined by ^{13}C-NMR was 97.37%.*

Resumo: *Neste trabalho foi estudado um processo de polimerização de butadieno, em escala de laboratório, para obtenção de polibutadieno com alto teor de unidades repetitivas 1,4-cis. Foi utilizado um sistema catalítico do tipo Ziegler-Natta constituído por versatato de neodímio (Nd), cloreto de tert-butila (Cl) e um composto organo-alumínio (Al). Foi estudada a influência do tipo de organo-alumínio (cocatalisador) da razão molar Al/Nd e Cl/Nd sobre a microestrutura do polibutadieno obtido. Os polímeros foram caracterizados por espectroscopia de ressonância magnética nuclear de carbono-13 em solução. A quantidade máxima de unidades repetitivas 1,4 - cis determinada por RMN de ^{13}C em solução foi 97,37%.*

Introduction

The importance of the stereoregular polybutadiene synthesis is demonstrated by the strong dependence of physical properties on the microstructure of repeating units formed during the specific polymerization conditions and process.[1] Synthesis of highly stereoregular polybutadiene became possible after introducing Ziegler-Natta catalysts. Nowadays the catalyst development is concentrated in 4f orbital electrons of rare-earth elements instead of 3d-electrons of transition metals.[2] Among the rare-earth metals, neodymium shows the highest catalytic activity, keeping high *cis*-stereoespecificity. Accordingly, the microstructure characterization is required, and carbon-13 (^{13}C) solution nuclear magnetic resonance spectroscopy (NMR) is one of the best techniques to be employed for this purpose. NMR allows us to obtain detailed information on the sequence of monomer linking and distribution along macromolecular chains.[3-9] Thus, the main purpose of this work was to establish a relationship between the catalyst synthesis conditions and the resultant polybutadiene microstructure evaluated by ^{13}C solution NMR.

Experimental

1,3-Butadiene obtained from Petroflex was purified passing through columns packed with KOH and molecular sieves (3Å). The catalysts were ternary systems constituted by Nd(versatate)$_3$, alkylaluminium and t-butyl chloride. Three different alkylamluminium were used: triethylaluminium / (TEA), triisobtylaluminium / (TIBA) and diisobtylaluminium hydride (DIBAH). The

catalysts were synthesized and left to age for 24h at 5°C. Polymerizations were carried out in hexane solution at 0°C in glass bottles.

Microstructure determination was carried out by employing ^{13}C solution NMR[10-13], by integrating the area of the olefinic carbons located in the range from 142 to 145 ppm. All analyses were performed on a VARIAN MERCURY 300, at 75.4 MHz frequency for ^{13}C. It was used a single pulse sequence, 90° pulse with a recycle delay 1s, in a probe ambient temperature in deuterated chloroform with proton gated decoupling.

Results and Discussion

The experimental results showed that the type and length of aluminum alkyl radical affected the cis-1,4 repeating units content of the polybutadienes produced.[11] Table 1 shows that the length of organoaluminium alkyl radical has a slight influence on the catalyst stereoselectivity, decreasing the cis-1,4 content as the alkyl length increases:

TEA > DIBAH > TIBA

These results may be attributed to the stereohindrance of the alkyl group. When this group is smaller, a more controlled cis-1,4 insertion is allowed (Figure 1).

Table 1. Effect of the type of organoaluminium and Al/Nd molar ratio on the polybutadiene cis-1,4 repeating units content

Organoaluminium	Molar Ratio Al:Nd	cis-1,4 (%)	trans-1,4 (%)	vinyl-1,2 (%)
DIBAH	20:1	96.3	3.4	0.3
	30:1	95.2	4.5	0.3
	40:1	93.6	6.0	0.4
TIBA	20:1	90.0	9,2	0.8
	30:1	85.6	13.6	0.8
	40:1	84.4	14.8	0.8
TEA	20:1	97.4	2.3	0.3
	30:1	96.5	3.2	0.3
	40:1	94.3	5.2	0.5

(Polymerization conditions: time:30 min, temp.: 10°C, pressure: 1,13atm, [Cl]/[Nd]= 3, [Nd]= 2 mmol/l, solvent: hexane, PB = polibutadiene)

We found that 1,2-vinyl contents were practically not affected by the experimental conditions employed in this work. As expected, trans-1,4 contents vary in the opposite direction relative to cis-1,4 contents.

The effect of Al/Nd molar ratio on polybutadiene microstructure was also studied. It was possible to verify a clear relationship between Al/Nd molar ratio and the

polybutadiene cis-1,4 content.[12] Table 1 shows that the cis-1,4 content decreased when Al/Nd molar ratio increased. Probably the high concentration of organoaluminium employed produced excessive alkylation or reduction of the active center (Nd), decreasing stereoselectivity to form cis-1,4 units.
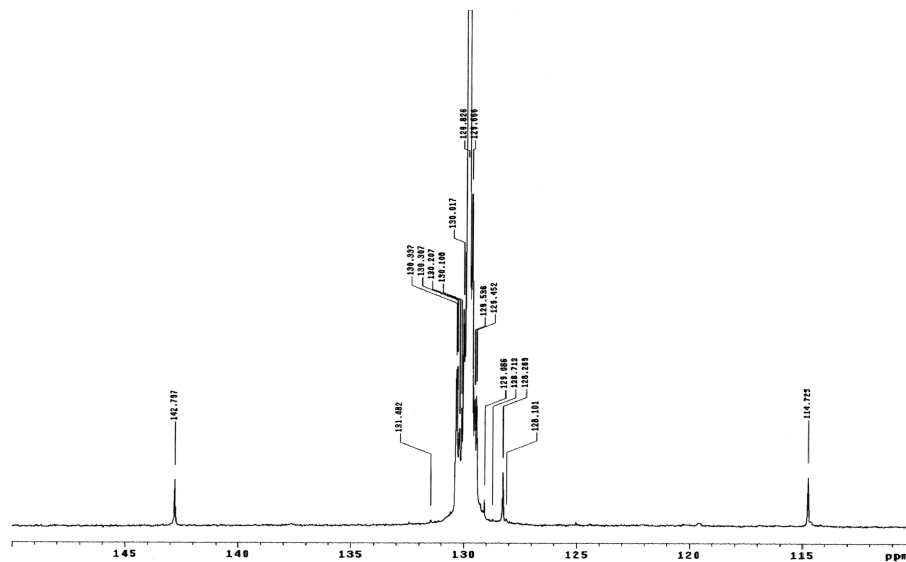
Figure 1. ^{13}C solution NMR spectrum of cis-1,4 polybutadiene

Table 2 also shows that cis-1,4 content is less influenced by the Al/Nd molar ratio when DIBAH was used. This fact may be attributed to the lower alkylation power of this organoaluminium.

Table 2. Effect of Cl/Nd molar ratio on polybutadiene stereoregularity

Alkylamluminium	Molar ratio Cl/Nd	Cis-1,4 %	Trans-1,4 %	Vinyl-1,2 %
DIBAH	0.5:1	96.7	2.9	0.4
	1:1	93.5	6.2	0.3
	3:1	96.2	3.5	0.3
	5:1	96.5	2.2	0.8
TIBA	0.5:1	92.3	7.0	0.7
	1:1	95.4	4.3	0.3
	3:1	90.0	9.3	0.8
	5:1	90.3	9.3	0.4
TEA	0.5:1	-	-	-
	1:1	96.6	3.0	0.4
	3:1	97.4	2.4	0.3
	5:1	95.5	4.4	0.1

(Polymerization conditions: time:30 min, temp.: 10°C, pressure: 1,13 atm, [Al]/[Nd]= 20, [Nd]= 2 mmol/l, solvent: hexane)

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The effect of Cl/Nd molar ratio on the cis-1,4 repeating units content is not clear cut (Table 2). It would be necessary to carry out a more extended study on that parameter to draw a more complete conclusion. The highest cis-1,4 content (97.4%) was obtained[6] when TEA was used as cocatalyst and when Cl/Nd molar ratio was 3, as can be seen in Figure 2.
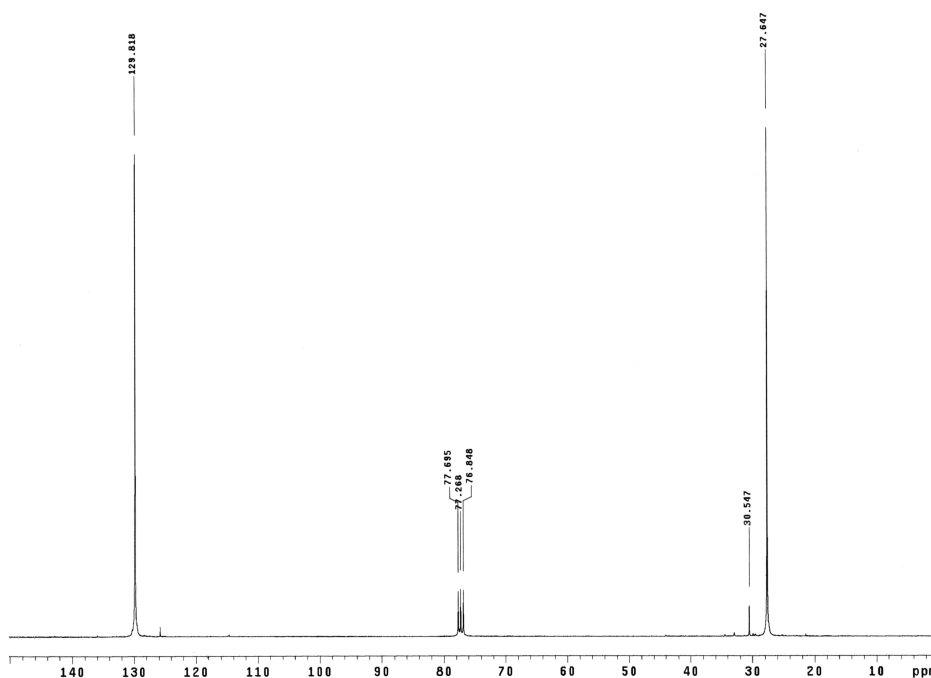

Figure 2. ^{13}C solution NMR spectrum of highest cis-1,4 content

Conclusion

The length of the cocatalyst alkyl radical influences stereoselectivity, decreasing the cis-1,4 content as that length increases. Therefore, the lowest cis-1,4 content (90.0%) was produced when TIBA was employed whereas the highest (97.4%) was obtained using TEA. It was observed a decrease in the cis-1,4 repeating units content when Al/Nd molar ratio was increased. The t-butyl chloride did not show any influence on the catalyst stereoselectivity in the range studied.

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