Polymer Bulletin 62, 1–10 (2009)
DOI 10.1007/s00289-008-1006-7

Polymer Bulletin

Effect of alkylaluminum structure on Ziegler-Natta catalyst systems based on neodymium for producing high-cis polybutadiene

Tereza C. J. Rocha[1], **Fernanda M. B. Coutinho**[1, 2] **(✉)**, **Bluma G. Soares**[1]

[1] Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, P.O. Box 68525, 21945-970 Rio de Janeiro, RJ, Brasil
[2] Departamento de Processos Químicos, IQ/UERJ, Rua São Francisco Xavier, 524, Pavilhão Haroldo Lisboa da Cunha, 4° andar, sala 424A, 20550-900, Rio de Janeiro, RJ, Brasil

Received: 19 March 2008 / Revised version: 9 September 2008 / Accepted: 12 September 2008

Summary

In this work, a laboratory scale process for producing polybutadiene with high content of *cis*-1,4 repeating units was studied. A Ziegler-Natta catalyst system constituted of neodymium versatate (catalyst), an alkylaluminum compound (alkylating agent and cocatalyst) and tert-butyl chloride (chlorinating agent) was used. The solvent employed was a mixture of hexane and cyclohexane (80/20 v/v). The objective of this work was to evaluate the effect of alkylaluminum structure and the influence of Al/Nd (5 to 15) molar ratio of long chain alkylaluminium compound (tri(n-hexyl)aluminum) on catalyst activity and polybutadiene characteristics. The alkylaluminum compounds employed in this study were tri(i-butyl)aluminum, tri(n-hexyl)aluminum, tri(n-octyl)aluminum and di(i-butyl)aluminum hydride. The polybutadienes molar masses obtained were strongly influenced by the alkylaluminum structure. Polymers with the highest molar masses were obtained when tri(i-butyl)aluminum, tri(n-hexyl)aluminum and tri(n-octyl)aluminum were employed. However, polymers with the highest contents of *cis*-1,4 units and the lowest molar masses were produced when di(i-butyl)aluminum hydride was employed.

Introduction

Polybutadiene (BR) is the second largest in volume among the synthetic rubbers, next to styrene-butadiene rubber (SBR). The major application of polybutadiene is in tires with over 70% of the polymer produced going into treads and sidewalls. Cured polybutadiene imparts excellent abrasion resistance (good tread wear), and low rolling resistance (good fuel economy) due to its low glass transition temperature (Tg) [1,2].
High cis-polybutadiene is commercially obtained by solution polymerization using Ziegler–Natta catalyst systems based on transition metals and more recently on lanthanides. Among lanthanides, neodymium-based catalysts have merited particular attention because they produce higher *cis*-1,4 units contents than any other system and exhibit pseudo-living character [3,4]. Lately, different types of neodymium systems have been reported in the literature [5,6,7]. The binary systems are derived from AlR_3

and a neodymium complex of the type $NdCl_3.nL$ where the ligand L may be tetrahydrofuran, alcohol, etc [5]. Rao *et al.* employed binary catalyst systems formed by neodymium chloride tripentanolate ($NdCl_3$ x nL, where L= 1-pentanol, 2-pentanol or 3-pentanol) and triethyl aluminum (TEA). The catalyst was prepared by mixing neodymium chloride tripentanolate with TEA and finally ageing it for 30 min. at 25°C. That system produced a polybutadiene with high content of *cis* repeating units (>99%). However, the maximum conversion achieved was 44% [6,7].

Another researchers reported the use of catalyst systems formed by cyclopentadienyl neodymium (CpNd) cocatalyzed by methylaluminoxane (MAO) in 1,3-butadiene polymerization. Although that catalyst system has produced polymers with narrow polydispersion, the *cis*-1,4 repeating units content varied in the range from 30 to 80 %, and the molar masses were very high, making the polymer processing very difficult. Moreover, the solvent used was toluene, what increases the toxicity of the polymerization process relative to the ternary system - $Nd(versatate)_3$/ alkylaluminum/ organic halide - that employs mixtures of cyclohexane and hexane [8,9,10,11,12,13].

According to Dong et al. the systems that use MAO as cocatalyst exhibit characteristics of unique site catalyst, i.e., the catalyst sites activity are equivalent in reactivity and are able to induce pseudo-living polymerization of 1,4-cis butadiene. That way is possible to control the polymer molar masses. However, these catalysts request large quantities of MAO, which is an expensive compound [14].

Recently, the first aryldiimine NCN-pincer ligated rare earth metal dichlorides $(2,6\text{-}(2,6\text{-}C_6H_3R_2N{=}CH)_2\text{-}C_6H_3)LnCl_2(THF)_2$ were synthesized via transmetalation between $2,6\text{-}(2,6\text{-}C_6H_3\text{-}R_2N{=}CH)_2\text{-}C_6H_3Li$ and $LnCl_3(THF)_{1\sim3.5}$. These complexes are isostructural monomers with two coordinating THF molecules, where the pincer ligand coordinates to the central metal ion in a tridentate mode, adopting a meridional geometry. Those complexes combined with trialkylaluminum compounds and $[Ph_3C][B(C_6F_5)_4]$ produce homogeneous Ziegler-Natta catalyst systems, which exhibit high activities and produce a polybutadiene with high *cis* content (99,9%) [15].

There are papers in the literature about different types of neodymium systems. Those systems have different components and even though the polymer produced have high *cis* content, generally occurs that the reaction conversion is low, or the polydispersion is large or the molar masses are very high.

The ternary systems have merited a great deal of attention for the polymerization of 1,3-butadiene. They are generally formed by $Nd(versatate)_3$/ alkylaluminum / organic halide and has been currently used in the rubber industry to promote high cis 1,4-polymerization of 1,3-butadiene, because those systems can produce polybutadiene with a *cis* units content up to 99%, low polydispersion, high conversion of monomer to polymer and employ aliphatic solvents. [5,16,17].

In spite of the above mentioned good features of Nd-catalysis only very little is known about the chemical role of the different catalyst components and about the nature of the active catalyst species [18,19]. Recently, a paper reported the impact of the aluminum compound DIBAH in the ternary Ziegler/Natta (Z/N)-catalyst system neodymium versatate (NdV)/diisobutylaluminum hydride (DIBAH)/ethylaluminum sesquichloride (EASC) on the polymerization of 1,3-butadiene. These investigations led to the proposal of a reaction mechanism which accounts for the control of molar masses by the reversible transfer of living polydienyl chains from Nd to the alkylaluminum component DIBAH [20].

In this paper was evaluated the effect of four different alkylaluminum compounds on catalyst activity and on the polybutadienes characteristics. The alkylaluminum compounds employed in this comparative study were tri(i-butyl)aluminum (TIBA), tri(n-hexyl)aluminum (TNHA), tri(n-octyl)aluminum (TNOA) and di(i-butyl)aluminum hydride (DIBAH). Ziegler-Natta catalyst systems constituted of neodymium versatate (catalyst), alkylaluminum compound (alkylating agent and cocatalyst) and t-butyl chloride (chlorinating agent) were used.

Experimental

2.1. Materials

Tri(i-butyl)aluminum (TIBA), tri(n-hexyl)aluminum (TNHA), tri(n-octyl)aluminum (TNOA) and di(i-butyl)aluminum hydride (DIBAH) were purchased from Akzo Nobel. Neodymium versatate was purchased from Rhodia-Rare Earths and Gallium. The hexane solution of butadiene (35% wt/wt) and the mixture of hexane and cyclohexane (80/20 v/v) were obtained from Petroflex S.A, Brazil. t-Butyl chloride was used as received from Aldrich Chemical Company, Inc. 3,5-Di-t-butyl-4-hydroxytoluene (BHT) was purchased from Shell Brasil S/A and trinonylphenyl phosphite (TNPP) was obtained from GE Specialty Chemicals.

2.2. Catalyst synthesis

Catalysts were prepared in oven-dried nitrogen-purged bottles sealed with rubber septa. The hexane solutions of t-butyl chloride and alkylaluminum compounds were used immediately after their preparation. The order of components addition was alkylaluminum, $Nd(versatate)_3$ (Nd) and t-butyl chloride (Cl). The catalyst components molar ratio was Al:Nd:Cl = 11:1:3. The catalysts were aged for 24h before using.

2.3. Polymerization

The polymerizations were carried out in solution using a 1L stainless steel Parr reactor. The reaction system was inertized through purging with extra dry nitrogen and additionally treated in drying columns packed with activated alumina. A dry hexane solution of butadiene (35% wt/wt) was first charged in the reactor, followed by the addition of dry mixture of hexane and cyclohexane (80/20 v/v). Both components were transferred to the reactor with the aid of nitrogen pressure. The reaction medium was heated up to the stated reaction temperature (70ºC) and then the catalyst was injected with a syringe. Polymerization was terminated by adding a hexane solution of 2,6-di-t-butyl-4-methylphenol (BHT) @ 50% wt/wt and stabilized by adding a hexane solution of TNPP @ 10% wt/wt. The polymer was coagulated in hot water under vigorous agitation and dried in an oven at 65ºC. Reaction conversion was calculated by relating the polymer mass obtained to the monomer mass fed to the reaction medium.

2.4. Polybutadiene characterization

Polymer microstructure was characterized by infrared spectroscopy in a Perkin–Elmer equipment, model Spectrum One, as films formed on KBr cells, prepared from 2% (wt/v) chloroform solutions. The isomers contents were obtained from infrared spectra in the spectral range from 4000 to 400 cm^{-1}, using the absorbances at 725 cm^{-1} (*cis*-1,4), 910 cm^{-1} (1,2-vinyl) and 965 cm^{-1} (*trans*-1,4). In order to make each band integration, individual baselines were traced for each one of them, using the following values as integration limits: from 542 to 895 cm^{-1} (*cis*-1,4), from 898 to 925 cm^{-1} (1,2-vinyl) and from 944 to 976 cm^{-1} (*trans*-1,4). The calculus of infrared absorbance values were carried out by using the Perkin–Elmer ''Spectrum'' software v.3.01. The uncertainty of the results relative to the method of IR analysis is ±1% [21]. 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 30ºC, using THF as solvent at 1 mL/min flow rate. A Universal Calibration Curve, constructed with polystyrene monodisperse standards, was used. Polymer solutions (0.1% wt/wt) were filtered through filters of 0.45 µ*l*m pore diameter before injecting in the chromatograph.

Results and discussion

Alkylaluminum compounds have been employed in Ziegler-Natta catalyst systems for the industrial manufacture of elastomers such as high-*cis* polybutadiene [22,23].

In this work it was evaluated the effect of four different alkylaluminum compounds on catalyst activity and on the high-*cis* polybutadienes characteristics. The alkylaluminum compounds employed in this study were tri(i-butyl)aluminum (TIBA), tri(n-hexyl)aluminum (TNHA), tri(n-octyl)aluminum (TNOA) and di(i-butyl)aluminum hydride (DIBAH). Ziegler-Natta catalyst systems constituted of neodymium versatate (catalyst), alkylaluminum compound (alkylating agent and cocatalyst) and t-butyl chloride (chlorinating agent) were used in this comparative study.

As can be observed in Table 1, polymers with the highest contents of *cis*-1,4 units were obtained when DIBAH and TIBA were employed. The *cis*-1,4 repeating units contents of polybutadienes obtained in this work when DIBAH and TIBA were employed were around 98% and the polymers produced with TNHA and TNOA showed slightly lower *cis*-1,4 units contents (97,5%). Those values show that the type of alkylaluminum compound has a slight influence on the catalyst stereospecificity. The slight variation on the microstructure of polybutadienes as the alkyl group changes indicates that the alkyl aluminum compound practically does not influence the polymerization mechanism.

Due to the electron deficiency of trialkylaluminum compounds they are capable of forming dimers or trimers. The degree of association of trialkylaluminum compounds is dependent on the steric hindrance of the alkyl groups. As the alkyl size increases the

Table 1. Influence of type of alkylaluminum compound on the microstructure of polybutadienes

Polybutadienes	Microstructure		
	Trans -1,4 (%)	1,2-vinyl (%)	Cis-1,4 (%)
DIBAH	0.86	0.39	98.74
TIBA	1.13	0.65	98.22
TNHA	1.67	0.68	97.65
TNOA	1.61	0.79	97.60

DIBAH = di(i-butyl)aluminum hydride; TIBA= tri(i-butyl)aluminum; TNHA= tri(n-hexyl)aluminum; TNOA = tri(n-octyl)aluminum; *trans*-1,4 = content of *trans*-1,4 units; 1,2 –*vinyl* = content of 1,2 -v*inyl* units; *cis* -1,4 = content of *cis*-1,4 units.

tendency to association decreases. Therefore trimethylaluminum and triethylaluminum are dimers, while TIBA and tri(t-butyl)aluminum are monomeric [24].

The variation of polybutadienes microstructure, when TNHA and TNOA were employed, can be explained. According to some authors [25,26], trialkylaluminum compounds with linear alkyl chains produce polybutadienes with lower contents of *cis* -1,4 units than di(i-alkyl)aluminum hydrides or tri(i-alkyl)aluminum. This difference can be attributed to the alkylaluminum compounds structure in solution. Tri(i-alkyl)aluminum compounds, when in solution, are in the monomeric form, favoring the correct orientation of 1,3-butadiene that results in *cis* units. Di(i-alkyl)aluminum hydrides, even though, trimeric in solution, exhibit a similar structure relative to catalyst complex, observed when tri(i-alkyl)aluminums are used. However, the linear long chain trialkylaluminum compounds, like TNHA and TNOA, produce polybutadienes with slightly lower *cis* contents. That behavior can be attributed to the long chain alkyl group that causes an obstacle to the orientation of the monomer. The bulky alkyl groups in TNHA and TNOA seems to affect the way how butadiene molecules coordinate. The correct orientation of 1,3-butadiene to produce *cis* units depends mainly on the chemical nature of the alkyl ligands attached to the neodymium sites [26,27,28].

The polymer molar masses obtained were strongly influenced by the alkylaluminum structure. Polymers with the highest molar masses and narrowest polydispersion were obtained when trialkylaluminum compounds were employed as cocatalysts (Table 2).

Di(i-alkyl)aluminum hydrides promote more intense chain transfer than trialkylaluminum compounds producing polybutadienes with the lowest molar mass. That difference can be explained by the easier transfer of hydride from DIBAH than an alkyl group from TIBA, TNHA or TNOA. Therefore, the polydispersion was narrower for the polybutadienes produced with catalysts systems containing TIBA, TNHA or TNOA [20,26,27].

Some authors mentioned that polymer molar mass obtained by ternary catalyst systems operating at 50-60ºC, follow the order: Al*i*-Bu_3 > $AlEt_3$ > Al*i*-Bu_2H [29]; Al*i*-Bu_3 > $AlEt_3$ [30]; Al*n*-Hex_3 > Al*n*-Bu_3 > Al*i*-Hex_3 > $AlEt_3$ [25]. In this work, the order verified for polybutadiene molar mass produced by ternary catalyst systems operating at 70ºC, was: Al*n*-$Octyl_3$ > Al*n*-Hex_3 > Al*i*-Bu_3 > Al*i*-Bu_2H. However, there is not a consensus on the literature for long chain alkylaluminum compounds [26].

Table 2. Influence of alkylaluminum compounds on the molar masses of polybutadienes

Polybutadienes	Molar Mass (x 10^{-5})	Polydispersion
	Mw[a]	
DIBAH	4.30	3.54
TIBA	7.34	2.82
TNHA	8.97	2.55
TNOA	10.52	2.54

DIBAH= di(i-butyl)aluminum hydride; TIBA= tri(i-butyl)aluminum ; TNHA= tri(n-hexyl)aluminum; TNOA = tri(n-octyl)aluminum. [a] SEC – THF at 30ºC

The catalyst activity for systems containing linear chain alkylaluminums (TNHA and TNOA) was higher than for those prepared by catalyst systems TIBA or DIBAH. In this paper, the order observed for catalyst activity obtained with the different types of aluminum compounds, was: Al*n*-Octyl$_3$ > Al*n*-Hex$_3$ > Al*i*-Bu$_3$ > Al*i*-Bu$_2$H (Figure 1).

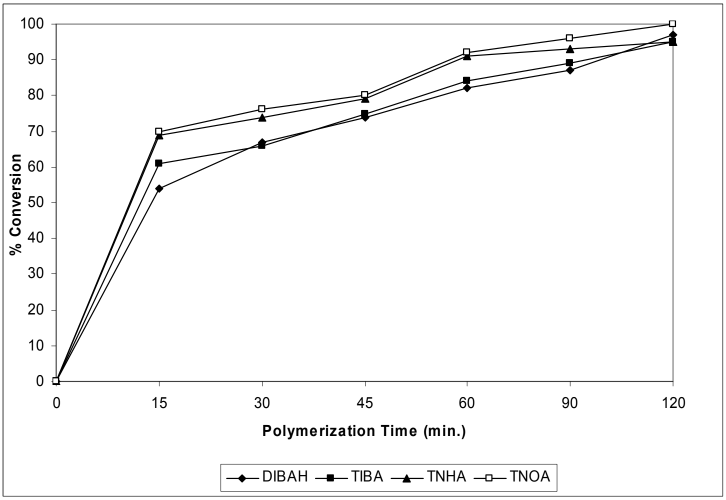

Figure 1 – Influence of the type of alkylaluminum compound on the catalyst activity.

The catalyst activity curves are shown in Figure 1, where conversion is plotted against polymerization time for each alkylaluminum compound employed in the catalyst systems. The decrease of the catalyst activity with increasing alkyl group length seems to be related to the degree of the alkylaluminum association in solution. The association extent in solution, for the trialkylaluminums decrease with the increase of alkyl group size. As Al*n*-Octyl$_3$ (TNOA), Al*n*-Hex$_3$(TNHA) and Al*i*-Bu$_3$ (TIBA) are monomeric, in solution, their alkylating power and consequently catalyst activity increase with the alkyl length. Otherwise, Al*i*-Bu$_2$H (DIBAH) exhibits a trimeric structure, in solution, which reduces its alkylating power and as a consequence the catalyst activity. That behavior is in accordance of Wilson [26]. The author proposed that alkylation of neodymium species happen by the monomeric form of the alkyl-aluminum compounds. In the literature, it seems to exist a consensus about the activity order of the alkylaluminum compounds with short alkyl groups [18,26,31]. However, there are few papers about catalyst systems using higher tri(n-alkyl)aluminum compounds and normally the experimental details are different. Because of that is difficult to make a good comparison about the catalyst activity with catalyst systems using higher tri(n-alkyl)aluminum compounds.

In a second study, was employed only TNHA as alkylaluminum compound and the objective of that study was to evaluate the influence of Al/Nd molar ratio (from 5.0 to 15) on catalyst activity and on the polybutadiene characteristics. The results obtained are shown in Table 3.

The microstructure of polybutadienes produced (Table 3) was not significantly modified when the results of different repeating unit contents are compared in the range from 0 to 100%. However, the Al/Nd molar ratio variation showed an accentuated influence on the microstructure of polybutadienes when theses results are compared in the range from 95 to 100%. Polybutadienes are commercially available in

Table 3. Influence of molar ratio of TNHA on the polybutadienes characteristics

Al/Nd	Microstructure			Molar Mass (x 10^{-5})	Polydispersion
	Trans -1,4 (%)	1,2 - Vinyl (%)	Cis - 1,4 (%)	Mw[a]	
5	0.87	0.65	98.48	6.88	2.93
6	0.88	1.07	98.05	8.90	2.67
7	1.03	0.99	97.98	8.89	2.64
9	1.23	0.94	97.83	8.89	2.63
11	1.67	0.68	97.65	8.97	2.55
15	3.63	0.92	95.60	9.13	2.23

TNHA= tri(n-hexyl)aluminum; Al/Nd = molar ratio; *Trans* -1,4 = contents of *trans*-1,4 units; 1,2 - *Vinyl* = contents of 1,2 - *Vinyl* units; *Cis* -1,4 = contents of *cis*-1,4 units.
[a] SEC – THF at 30ºC

three main forms: one containing 1,4-*cis* repenting unit levels around 40%, which is called *low-cis* polybutadiene, the second one with levels in the range from 92 to 97%, called *medium-cis* and the last one with levels above 98%, called *high-cis*. The demand for theses three products, each with its own distinct properties, comes from major consumption segments, tires and retreads, with *high-cis* polybutadiene being the most appropriate for those applications. Thus, the slight variation on the microstructure of the polybutadiene is important for the application at hand. The contents of *cis*-1,4 repeating units varied, in the range from 98 to 95 %, with the increase of Al/Nd molar ratio. On the other hand, the contents of *trans* -1,4 repeating units increased with the increase of Al/Nd molar ratio. The polymerization of 1,3-butadiene by transition metal catalysts envolves an insertion of allylic type resulting in η_3–butenyl group formation. The butadiene produces only one type of butenyl group in its insertion between the growing chain and the transition metal, that can exist in two isomeric forms, *anti* and *syn*, which are in equilibrium. The form *syn* results in *trans*-1,4 polymerization, and the *anti* form produces *cis*-1,4 polymerization. The formation of *cis* and *trans* units in butadiene polymerization is related to the anti-*syn* isomerism of the η_3–butenyl group. There is an agreement in the literature that the butenyl group structure depends on the coordination mode of the monomer. An *anti* butenyl group is formed when the incoming monomer is *cis*-η^4 coordinated. A *syn* butenyl group can derive, in principle, from a *trans*-η^2 or *trans*-η^4 coordination of the monomer, but also from *anti-syn* isomerization of allylic group. Consequentely, 1,3-butadiene can coordinate with the transition metal through only one double bond (monodentade coordination) resulting in *trans*-η^2 form or with the two double bonds (bidentade coordination) resulting in *trans*-η^2 or *trans*-η^4 forms. It was mentioned in several papers that *anti* and *syn* forms are in equilibrium, and that when no bulky group is present at C_2 of butenyl group the equilibrium is completely shifted toward the *syn* form, which is thermodynamically more stable. The formation of a *trans* vs. a *cis* unit seems to be controlled by the relative rate of the two process: the insertion of a new monomer molecule into the allylic group and the isomerization of *anti* allylic group to the more stable *syn* form. If the insertion process is more rapid than the isomerization process a *cis* unit could be formed, otherwise isomerization occurs, with the consequent formation of a *trans* unit. According with the literature, the variation on the microstructure can be attributed to the presence of electron donors in the reaction medium. Electron donors are able to occupy one coordination site, forcing the new incoming monomer molecule to coordinate with only one double bond (monodentade coordination). This behavior can result in a decrease of *cis*-1,4 repeating units content and, consequently, an increase on *trans*-1,4 units [32,33]. Alkylaluminum compounds can act like electron donors (donating alkyl groups) competing with the monomer for one of coordination sites [31]. Thus, the increase of *trans*-1,4 units with the increase of Al/Nd molar ratio may be attributed to a more intense competition between the monomer and alkylaluminum compound to occupy one of coordination sites [26,27].

The effect of Al/Nd molar ratio on the molar masses of polymers was studied. In the range from 5 to 15, the polybutadiene molar masses were only slightly influenced by the variation of Al/Nd. However, polymers with the lowest molar masses were obtained when the Al/Nd = 5/1 (MW = 7.0 x 10^5) was employed (Table 2). That behavior may be attributed to the low quantity of alkyl aluminum to act as a scavenger of moisture and impurities that may be present in the reaction medium provoking an increase on the chain transfer reactions [18]. According with the literature, the increase of Al/Nd, in the range from 10 to 30, result on a decrease of the polymer molar masses provoked by chain transfer reactions increase with alkylaluminum [20,26,27]. However, works using catalyst systems for producing polybutadiene at Al/Nd molar ratios lower than 10/1 practically is not found in the literature.

The polydispersion of polymers was only slightly influenced by the variation of Al/Nd molar ratio. As was mentioned previously, the polydispersion is, generally, lower for polybutadienes obtained by catalysts based on trialkylaluminum compounds.

Moreover, the Al/Nd molar ratio had an accentuated influence on the catalyst activity of butadiene polymerization (Figure 2).

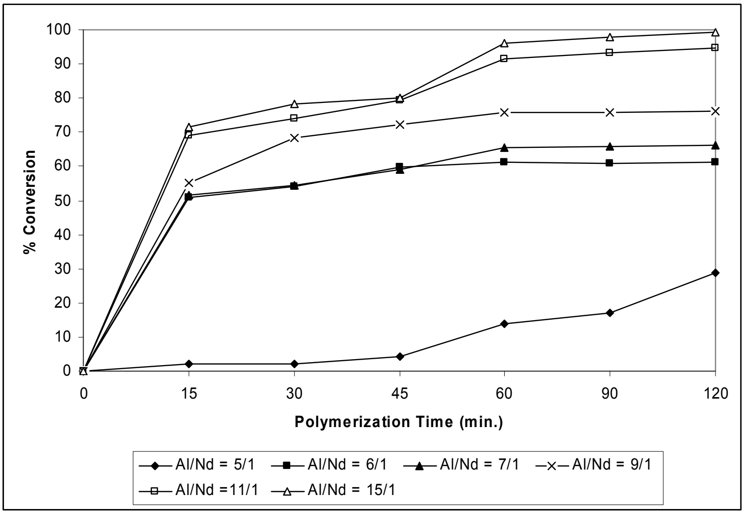

Figure 2 – Influence of the ration molar Al/Nd of TNHA on the catalyst activity

The catalyst activity was the highest at Al/Nd = 15/1, where the complete conversion was obtained in short time of polymerization. The catalyst activity seems to depend on the quantity of alkylaluminum compound present in solution. In this study, for Al/Nd lower than 11/1 it was verified a decrease in the catalyst activity. That result can be attributed to the insufficient quantity of alkylaluminum to act as a scavenger of moisture and in the process of the catalyst formation.

Conclusion

The *cis*-1,4 repeating units contents obtained for polybutadienes when DIBAH and TIBA were employed were around 98%. The polymers produced with TNHA and TNOA showed slightly lower *cis*-1,4 units contents, around 97%. Those values show that the type of alkylaluminum compound influences on the catalyst stereospecificity.

Polymers with the highest molar masses and narrowest polydispersion were obtained when TIBA, TNHA and TNOA were employed. DIBAH promoted more intense chain transfer reactions than TIBA, TNHA and TNOA. That difference can be explained by the easier chain transfer of hydride from DIBAH than the alkyl group from TIBA, TNHA or TNOA. As a consequence, the polydispersion was narrower for the polybutadienes obtained using catalysts based on TIBA, TNHA or TNOA.

In this work, the order for catalyst activity obtained for the different types of alkylaluminum compounds was: $\mathrm{Al}n\text{-Octyl}_3$ > $\mathrm{Al}n\text{-Hex}_3$ > $\mathrm{Al}i\text{-Bu}_3$ > $\mathrm{Al}i\text{-Bu}_2\mathrm{H}$. That result indicates that catalyst activity is related with alkyl group length of the alkylaluminum compounds. TNOA, TNHA and TIBA are monomeric, in solution, presenting higher alkylating power and catalyst activity.

Al/Nd molar ratio variation for TNHA had an accentuated influence on the catalyst activity and on polybutadiene characteristics (microstructure, molar masses and polydispersion). Those results show that the amount of alkylaluminum compound exerts an important role in the catalytic system for producing polybutadiene with high content of *cis*-1,4 repeating units.

Acknowledgements. The authors thank Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro (FAPERJ) and Petroflex Ind. & Com. for financial support.

References

1. Pires NMT, Ferreira AA, Lira CH, Coutinho PLA, Nicoline LF, Soares BG, Coutinho FMB. J. Apll. Polym. Sci. 2006; 99: 88.
2. Kwag G, Kim P, Han S, Lee S, Choi H, Kim S. J. Apll. Polym. Sci. 2007; 105: 477.
3. Rocha TCJ, Soares BG, Coutinho FMB, Costa MAS. Polím.: Ciênc. e Tecnol. 2005;15: 39.
4. Mello, IL, Delpech MC, Coutinho FMB, Albino FFM. J. Braz. Chem. Soc. 2006; 17:194.
5. Quirk RP, Kells AM, Yunlu K, Cuif J P. Polymer. 2000; 41: 5903.
6. Rao GSS, Upadhyay VK, Jain RC. J. Apll. Polym. Sci. 1999; 71: 595.
7. Rao GSS, Upadhyay VK, Jain RC. Die Angew. Makromol. Chem. 1997; 251: 193.
8. Ricci G, Italia S, Giarrusso A, Porri L. J. Organometal. Chem. 1993;451: 67.
9. Cui L, Ba X, Teng H, Ying L, Li K, Jin Y. Polym. Bull. 1998; 40: 729.
10. Kaita S, Hou Z, Wakatsuki Y. Macromolecules. 1999; 32: 9078.
11. Kaita S, Yamanaka M, Horiuchi AC, Wakatsuki Y. Macromolecules. 2006; 39: 1359.
12. Miyazawa A, Kase T, Soga K. Macromolecules. 2000; 33: 2796.
13. Bonnet F, Visseaux M, Baudry DB. J. Organometal. Chem. 2004; 689: 264.
14. Dong W, Endo K, Toshio M. Macromol. Chem. Phys. 2003; 204: 104.
15. Gao W, Cui D. J. Am. Chem. Soc. 2008; 130 (14): 4984.
16. Wilson DJA, Jenkins DK. Polym. Bull. 1992; 27: 407.

17. Wilson DJA, Jenkins DK. Polym. Bull. 1995; 34: 257.
18. Friebe L, Nuyken O, Windisch H, Obrecht W. Macromol. Chem. 2002; 203: 1055.
19. Kwag, G. Macromolecules. 2002; 35: 4875.
20. Friebe L, Windisch H, Nuyken O, Obrecht W. J. Macromol. Sci. Part A. 2004; A41: 245.
21. Mendham J, Denney RC, Barnes JD, Thomas MJK. Vogel's Textbook of Quantitative Chemical Analysis, Cap. 18, 386-399. Prentice-Hall, New York, 2000.
22 Allinger NL, Cava MP, Jongh DC, Johnson CR, Lebel NA, Stevens CL. Organic Chemistry. Worth Publishers, Inc. New York, 1976.
23. Klimpel MG, Anwander R, Tafipolsky M, Scherer W. Organometallics.2001; 20: 3983.
24. Cotton FA, Wilkinson G, Murilo CA, Bochmann M. Advanced Inorganic Chemistry, Cap. 19, 1108-1129. John Wiley & Sons, Inc, New York, 1999.
25. Throckmorton MC. Kaut. U. Gummi Kunstst. 1969; 22: 293.
26. Wilson DJ. J. Macromol. Polym. Sci. Part A: Polym. Chem. 1995; 33: 2505.
27. Friebe L, Nuyken O, Obrecht W. Adv. Polym. Sci. 2006; 204: 1.
28. Mazzei A. Makromol. Chem.1981; 4: 61.
29. Kozlov VG, Sigaieva NN, Nefediev KV, Savel'eva IG, Marina NG, Monakov YB. J. Polym. Sci.: Part A: Polym. Chem.1994; 32: 1237.
30. Witte, J. Die Angew. Makromol. Chem. 1981; 94: 119.
31. Porri L, Ricci G, Italia S, Cabassi F. Polym. Commun. 1987; 28: 223.
32. Rocha TCJ, Coutinho FMB, Nunes DSS, Soares BG, Costa MAS, Mello IL. J. Applied Apll. Polym. Sci. 2005; 98: 2539.
33. Mello, IL, Coutinho FMB, Nunes DSS, Soares BG, Costa MAS, Maria LCS. Eur. Polym. J. 2004; 40: 635.