

Effect of Electron Donors on 1,3-Butadiene Polymerization by a Ziegler–Natta Catalyst Based on Neodymium

Fernanda M. B. Coutinho,^{1,2} Tereza C. J. Rocha,¹ Ivana L. Mello,¹ Denise S. S. Nunes,²
Bluma G. Soares,¹ Marcos A. S. Costa²

¹Instituto de Macromoléculas Professora Eloisa Mano, Universidade Federal do Rio de Janeiro, P.O. Box 68525, CEP 21945-970 Rio de Janeiro, RJ, Brazil

²Instituto de Química, Universidade do Estado do Rio de Janeiro, Rua São Francisco Xavier, 524, CEP 20559-900 Rio de Janeiro, RJ, Brazil

Received 27 October 2004; accepted 1 March 2005

DOI 10.1002/app.22391

Published online in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: High-cis polybutadiene produced by catalyst systems based on a rare earth is an elastomer used to produce green tires. This type of tire presents lower rolling resistance, which allows higher fuel economy, and thus fewer chemical compounds are discharged into the atmosphere. In this work, the influence of electron donors [tetrahydrofuran (THF) and tetramethylethylenediamine (TMEDA)] present in the polymerization solvent on the microstructure and molecular weight characteristics of the polybutadiene produced by neodymium catalysts was studied. The catalyst synthesis was carried out in glass bottles for 1 h at a temperature between 5 and 10°C. The

catalyst components were diisobutylaluminum hydride, neodymium versatate, and *tert*-butyl chloride. The polymerization reaction was carried out for 2 h. The reaction temperature was kept at 70 ± 3°C. The addition of TMEDA or THF above a determined concentration reduced the catalytic activity, molecular weight, and concentration of cis-1,4 units (<96%), whereas the polydispersity increased. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 98: 2539–2543, 2005

Key words: polybutadiene; stereospecific polymers; Ziegler–Natta polymerization

INTRODUCTION

To select a better way to produce high-cis polybutadiene, it is necessary to evaluate the different available technologies. The technology that uses catalysts based on lanthanides is the most recent and was also the most used in the last decade. The systems based on neodymium under adiabatic conditions, using aliphatic solvents, produce high conversions with high solid contents and low residence times in reactors and result in higher productivity. The almost total conversion of the monomer allows the monomer-recovery step to be eliminated, decreasing the investment and operation costs of this process. For these reasons, neodymium technology represents economy of energy and investment, and beyond that, it presents high productivity.^{1–7}

High-cis polybutadiene produced by a neodymium catalyst presents properties such as abrasion resistance, crack resistance, resilience, and low hysteresis

and heat buildup that are superior to those of the polymer produced by other catalysts. Therefore, because of these properties, its main application lies in the pneumatic industry. High-cis polybutadiene is also used in golf balls, hoses, and shoe soles.^{2,8}

In our last article,⁹ we evaluated the possibility of using a solvent recovered from an anionic polymerization process, which could be contaminated with some electron-donor compounds. Now we analyze the influence of these compounds on the polymer characteristics. Thus, the aim of this work is the evaluation of the influence of electron donors [tetrahydrofuran (THF) and tetramethylethylenediamine (TMEDA)], present in the polymerization solvent, on the microstructure and molecular weight characteristics of the polybutadiene produced.

EXPERIMENTAL

Materials

The chemical reagents used in this work were diisobutylaluminum hydride [Al(*i*-butyl)₂H or DIBAH; Akzo Nobel, São Paulo, Brazil], neodymium versatate (Rhodia-Rare Earths and Gallium, São Paulo, Brazil), *tert*-butyl chloride (Aldrich Chemical Co., São Paulo, Brazil), hexane (PA; Vetec Química Fina, Ltd., Rio de Janeiro, Brazil), cyclohexane (PA; Isofar Indústria e Comércio de Produtos Químicos, Ltd., Rio de Janeiro,

Correspondence to: F. M. B. Coutinho (fern@uerj.br or fern@ajato.com.br).

Contract grant sponsors: Conselho Nacional de Desenvolvimento Científico e Tecnológico; Fundação Carlos Chagas Filho de Amparo à Pesquisa do Estado do Rio de Janeiro; Petroflex Indústria & Comércio.

TABLE I
Electron-Donor Contents Added to the
Polymerization Solvent

Electron donor	Content (ppm)
THF	0
	20
	40
	100
	150
	200
TMEDA	0
	1
	5
	15

Brazil), 3,5-di-*tert*-butyl-4-hydroxytoluene (BHT; Shell Brasil S/A, São Paulo, Brazil), trinonylphenyl phosphite (TNPP; GE Specialty Chemicals, São Paulo, Brazil), a hexane solution of butadiene (Petroflex S.A, Rio de Janeiro, Brazil), and THF (PA; Vetec Química Fina).

Catalyst synthesis

The catalysts were prepared in an oven-dried, nitrogen-purged bottle sealed with a rubber septum. The hexane solutions of *tert*-butyl chloride and DIBAH were used immediately after their preparation. The order of component addition was DIBAH (Al), Nd(versatate)₃ (Nd), and *tert*-butyl chloride (Cl). The catalyst component molar ratio was Al/Nd/Cl = 11:1:3.

Polymerization

All polymerizations were carried out in a 1-L stainless steel Parr reactor. To the Parr reactor were added a solvent (freshly dried with sodium and distilled or industrially recovered), electron donors (Table I), 1,3-butadiene, and a catalyst solution. The polymerizations were terminated after 2 h by the addition of a BHT hexane solution and stabilized by the addition of a TNPP/Irganox hexane solution. The polymer was coagulated under stirring in distilled water at 80°C for

1 h. Finally, it was dried at 65°C until a constant weight was obtained.

Polymer characterization

The polymer microstructure was characterized by infrared spectroscopy with a PerkinElmer Spectrum One instrument as films formed on KBr cells, prepared from 2% (wt/v) chloroform solutions. The concentrations of the isomeric repeating units were obtained from the absorbances at 725 (cis-1,4), 910 (1,2-vinyl), and 965 cm⁻¹ (trans-1,4).¹⁰

The polymer molecular weight characteristics were evaluated by size exclusion chromatography (SEC) with a Waters 150-C Plus SEC instrument fitted with a refractive-index detector at 30°C, with THF as the solvent at a 1 mL/min flow rate. A universal calibration curve was used, constructed with monodisperse polystyrene standards. Polymer solutions (0.1% w/w) were filtered with filters of a 0.45- μ m pore diameter before injection into the chromatograph.

RESULTS AND DISCUSSION

The addition of TMEDA and THF above a determined concentration produced a decrease in the concentration of cis-1,4 units and an increase in the concentration of trans-1,4 units, whereas the 1,2-vinyl concentration remained constant at 0.6% (Fig. 1).

As can be observed in Figure 1, the concentration of cis-1,4 units sloped from 99.2 to 96.9% and that of trans-1,4 units increased from 0.3 to 3.1% as the TMEDA concentration increased. The same behavior was verified when THF was used. In this case, the concentration of cis-1,4 units decreased from 99.2 to 95.3%, and that of trans-1,4 units increased from 0.3 to 4.0%.

The literature¹¹ shows that the presence of electron-donor compounds in a polymerization solvent provokes a decrease in cis-1,4 units and an increase in trans-1,4 units. This occurs because electron donors such as amines and ethers are able to occupy a coor-

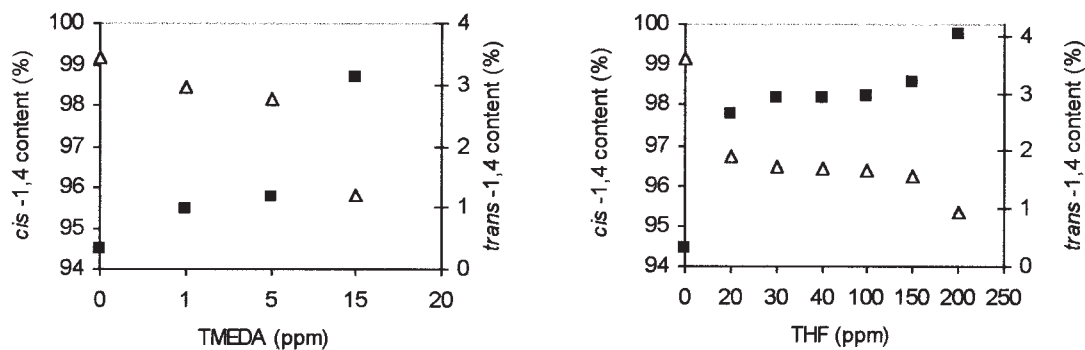


Figure 1 Influence of TMEDA and THF on the concentration of (Δ) cis-1,4 and (\blacksquare) trans-1,4 units of polybutadiene.

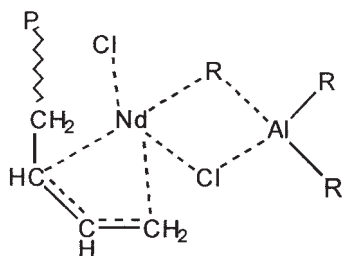


Figure 2 η^3 -Butenyl group structure.

dination site, forcing the new incoming monomer molecule to coordinate with only one double bond.

The first insertion of a monomer molecule (initiation) results in the formation of an η^3 -butenyl group (Fig. 2), and the propagation of the polymeric chain occurs with the insertion of new monomer molecules into the η^3 -butenyl bond, between the transition metal and the last monomer unit, a new η^3 -butenyl bond being formed after each new monomer insertion.¹²

The η^3 -butenyl bond between the growing chain and the transition metal can exist in two isomeric forms, anti and syn (Fig. 3). These forms are in equilibrium, and when no bulky group is present at C₂ of the butenyl group, the equilibrium at room temperature is shifted toward the syn form, which is thermodynamically more stable.^{13,14}

The chemoselectivity of polymerization, that is, the formation of a 1,2 unit versus a 1,4-unit, depends on whether the new incoming monomer molecule reacts at C₁ or C₃ of the butenyl group. If the insertion occurs at C₁, cis-1,4 or trans-1,4 units will result (this depends on whether the butenyl group is anti or syn, respectively), whereas the insertion at C₃ will result in 1,2-vinyl units (Fig. 4).¹⁴⁻¹⁶

Nowadays, there is a general agreement that the butenyl group structure depends on the mode of monomer coordination (Fig. 5). An *anti*-butenyl group is formed when the incoming monomer is cis- η^4 coordinated, whereas a *syn*-butenyl group can result, in principle, from trans- η^2 or trans- η^4 monomer coordi-

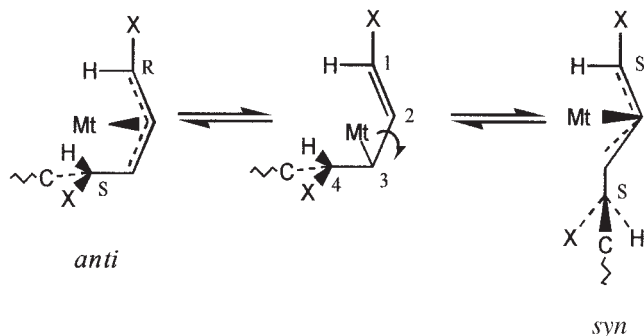


Figure 3 Equilibrium of anti and syn isomeric forms of the η^3 -butenyl group.

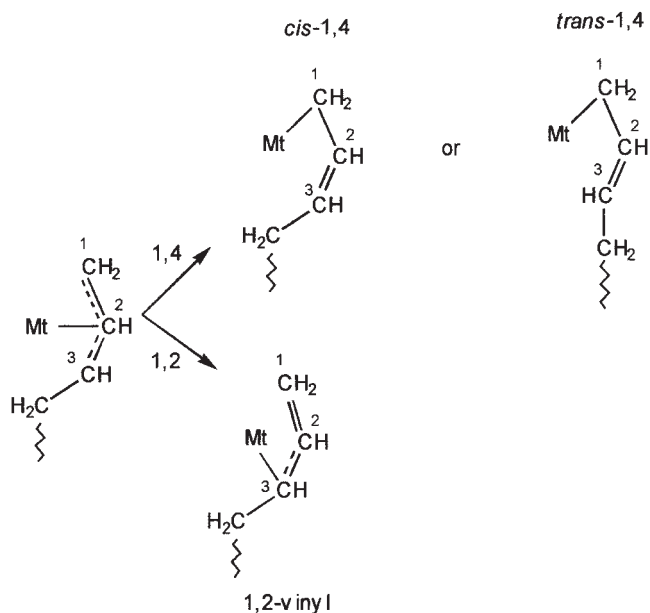


Figure 4 Butadiene polymerization chemoselectivity.

nation and also from an anti-syn isomerization of the allylic group. Thus, the 1,3-dienes can coordinate with the transition metal through only one double bond, forming a trans- η^2 ligand, or with both double bonds, forming a cis- η^4 or trans- η^4 ligand.^{17,18}

The formation of trans units versus cis units is controlled by the relative rate of the insertion process of the new incoming monomer into the allylic link and by the anti-syn isomerization rate.¹³

Thus, as shown in Figure 5, the trans-1,4 units can be formed via route a₁ or a₂ → a' → a'' or via b → b' → b'', and the cis-1,4 units are formed via route b → b' → b''. However, when electron donors are added to the catalyst system, which is highly stereospecific to the cis polymerization of butadiene, one of the vacancies of the transition metal available to coordinate with the monomer is occupied by the electron donor, and this forces the monomer to η^2 -trans coordination. As a result, a trans-1,4 repeating unit will be obtained with the route a₂ → a' → a''.

The reaction yield (Fig. 6) and the average molecular weights [number-average molecular weight (M_n) and weight-average molecular weight (M_w)] decreased and the polydispersity (Fig. 7) increased with the addition of electron donors (THF and TMEDA).

The decrease in the reaction yield when TMEDA was added to the reaction medium can be attributed to the poisoning of the catalyst sites. However, the decrease in the molecular weight in the presence of electron donors (THF and TMEDA) and the increase in the polydispersity are connected to the enhancement of chain-transfer reactions, favored by the medium polarity increasing.

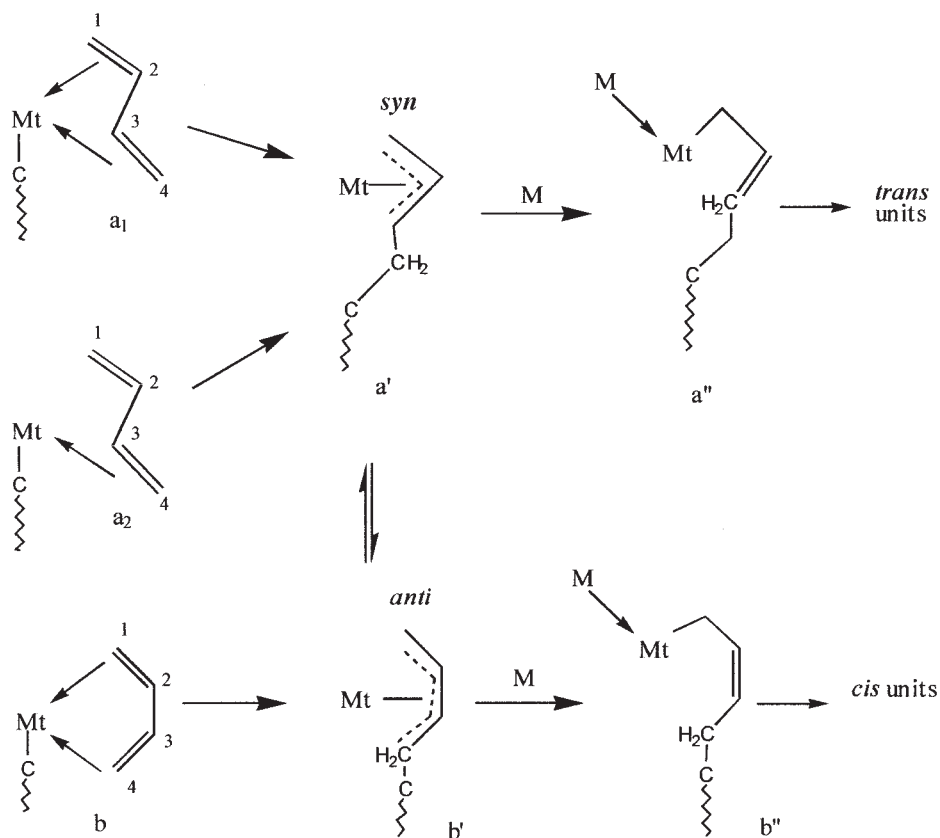


Figure 5 Scheme of the formation of cis-1,4 and trans-1,4 units in 1,3-butadiene polymerization.

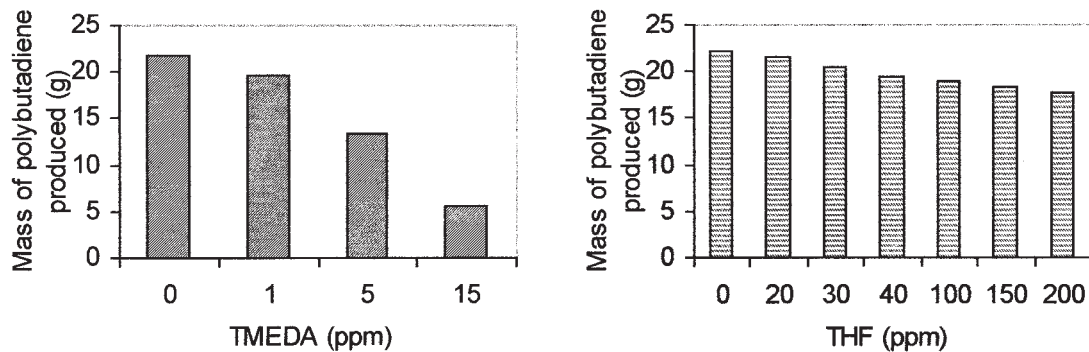


Figure 6 Influence of the electron-donor concentration on the polymerization reaction yield.

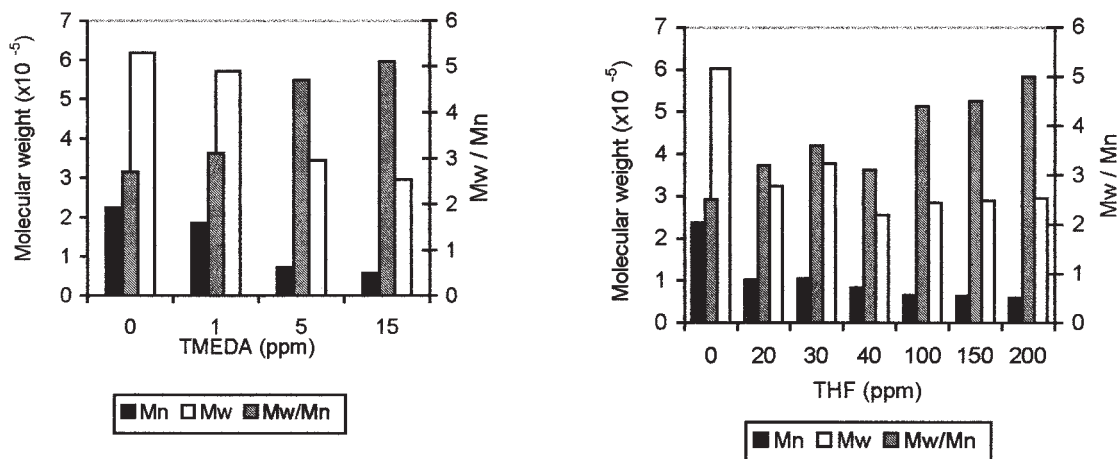


Figure 7 Influence of the electron-donor concentration on the molecular weight characteristics of polybutadiene.

CONCLUSIONS

The addition of TMEDA or THF to the polymerization solvent provoked a decrease in the reaction yield, molecular weight, and concentration of cis-1,4 units (<96%), whereas the polydispersity became wider.

References

1. Jenkins, D. K.; Ansell, P. J. U.S. Pat. 5,017,539 (1991).
2. Pires, N. M. T.; Coutinho, F. M. B.; Costa, M. A. S.; Maria, L. C. S.; Mello, I. L.; Nunes, D. S. S. *Rev Quím Ind* 2002, 719, 15.
3. Jang, Y. C.; Kwag, G. H.; Kim, A. J.; Lee, S. H. *Eur. Pat. EP 1 031 583 A1* (1999).
4. Nicolini, L. F.; Campos, C. R. A.; Lira, C. H.; Coutinho, P. L. A. *Eur. Pat. EP 1 055 659 A1* (2000).
5. Porri, L.; Ricci, G.; Shubin, N. *Macromol Symp* 1998, 128, 53.
6. Ansell, P. J.; Williams, H. D. U.S. Pat. 5,686,371 (1997).
7. Steinhäuser, N.; Obrecht, W. U.S. Pat. Appl. 20020035226 (2002).
8. Mello, I. L.; Coutinho, F. M. B.; Nunes, D. S. S.; Soares, B. G.; Costa, M. A. S.; Maria, L. C. S. *Quím Nova* 2004, 27, 277.
9. Mello, I. L.; Coutinho, F. M. B.; Nunes, D. S. S.; Soares, B. G.; Costa, M. A. S.; Maria, L. C. S. *Eur Polym J* 2004, 40, 635.
10. Schröder, E.; Müller, G.; Arndt, K. *Polymer Characterization*; Hanser: Munich, 1989; p 215.
11. Porri, L.; Giannini, U.; Pino, P. In *Encyclopedia of Polymer Science and Engineering*; Mark, H. F.; Bikales, N. M.; Overberger, C. G.; Menges, G., Eds.; Wiley: New York, 1987; Vol. 8, p 200.
12. Porri, L.; Giarrusso, A.; Ricci, G. *Macromol Symp* 1991, 48, 293.
13. Porri, L.; Giarrusso, A.; Ricci, G. *Polym Sci Ser A* 1994, 36, 1421.
14. Porri, L.; Giarrusso, A.; Ricci, G. *Prog Polym Sci* 1991, 16, 405.
15. Destri, S.; Gallazzi, M. C.; Giarrusso, A.; Porri, L. *Makromol Chem Rapid Commun* 1980, 1, 293.
16. Gallazzi, M. C.; Giarrusso, A.; Porri, L. *Makromol Chem Rapid Commun* 1981, 2, 59.
17. Porri, L.; Gallazzi, M. C. *Makromol Chem Rapid Commun* 1983, 4, 485.
18. Dolgoplosk, B. A.; Tinyakova, Y. I. *Polym Sci USSR* 1998, 19, 2805.