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Butadiene polymerization using neodymium versatate-based catalysts: catalyst optimization and effects of water and excess versatic acid

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Abstract

The polymerization of 1,3-butadiene (Bd) in a stirred batch reactor with the ternary catalytic system Nd(versatate)$_3$/$Al_2Et_3Cl_3$/Al(i-Bu)$_2$H in cyclohexane at 70°C has been studied with initial emphasis on the effects of the order of addition of the catalyst components, the concentrations of $Al_2Et_3Cl_3$ and Al(i-Bu)$_2$H. Using in situ catalyst activation, the optimum concentration ratios of Nd(versatate)$_3$/$Al_2Et_3Cl_3$/Al(i-Bu)$_2$H = 1:1:25 at a catalyst concentration of 0.11 mmol Nd/100 g Bd was established and used to determine the influence of water and excess versatic acid ([versatic acid]/[Nd]-3) on polymerization performance. It was found that the optimum catalyst characteristics were obtained when [H_2O][Nd] = 0.11; higher and lower amounts of water decreased conversion, broadened the molecular weight distribution and increased the molecular weight. Increasing the level of excess versatic acid above [excess versatic acid]/Nd] = 0.22 resulted in lower conversions, broader molecular weight distributions and higher molecular weights. Polybutadiene *cis*-1,4 contents were consistently high for all polymerizations (ca. 98%) and were found to be independent of the water content and excess acid level. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Neodymium versatate; Butadiene; Water

1. Introduction

Catalytic systems based on lanthanides (rare earths), and in particular neodymium, have merited a great deal of attention recently for the polymerization of conjugated dienes [1–4]. The main characteristic of these systems is that they yield polymers with high *cis*-1,4 stereospecificity from different types of dienes (e.g. butadiene, isoprene and 1,3-pentadiene) [5]. In addition they yield highly stereospecific diene copolymers [6]. None of the catalytic systems previously identified (e.g. nickel and cobalt catalysts) for the *cis*-1,4 polymerization of dienes show these characteristics [7].

In contrast, η^3-allyl derivatives of lanthanide and neodymium produce polybutadiene with high *trans*-1,4 selectivity [8–10]. In the presence of Lewis acids such as diethylaluminum chloride and methylaluminoxane, high *cis*-1,4-polybutadiene can also be obtained with these η^3-allyl derivatives [9,10].

At present, two types of Neodymium systems are generally used [1]: (a) the ternary system Nd(carboxylate)$_3$/aluminum alkyl halide/ aluminum alkyl where a highly hindered carboxylate group is generally employed [e.g. napthenate [11], versatate [12] or 2-ethyl hexanoate [13]]; and (b) the binary system derived from AlR_3 and a neodymium complex of the type $NdCl_3.nL$ where the ligand L may be tetrahydrofuran, alcohols, etc. [14]. It is noteworthy that catalysts formed from neodymium and didymium (72%, Nd, 20% La, 8% Pr) carboxylates produce high *trans*-1,4-polybutadiene in the presence of magnesium *n*-butyl, isobutyl [15].

The present work discusses results using the ternary system Nd(versatate)$_3$/$Al_2Et_3Cl_3$/Al(i-Bu)$_2$H for the solution polymerization of 1,3-butadiene. In this study, observations relating to catalyst activity, *cis*-1,4-stereospecificity and polymer molecular weight are discussed with respect to catalyst optimization, water content and excess versatic acid level.

2. Experimental

2.1. Materials

Neodymium versatate (NdV_3) catalysts were kindly supplied by Rhône-Poulenc (Rhodia) and were used after

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Table 1
Conversion and SEC data of polybutadienes produced using the in situ activated NdV_3/EASC/DIBAH catalyst system: influence of Nd: EASC mole ratio (conditions: DIBAH:Nd (mole ratio) = 25; [Nd] = 0.11 mmol/100 g Bd; [Bd] = 14 wt.% in cyclohexane; 1 h polymerization temperature = 70°C)

EASC:Nd (mole ratio)	Conversion (%)	M_w (g/mol)	M_w/M_n
0.5	64	410,000	5.8
1.0	86	230,000	3.6
1.5	84	220,000	3.9
2.0	73	300,000	4.7
4.0	58	560,000	8.2

dilution with dried cyclohexane. Al(*i*-Bu)$_2$H (DIBAH) (1.0 M solution in cyclohexane, Aldrich Chemicals) and $Al_2Et_3Cl_3$ (EASC) (97%, Aldrich Chemicals) were diluted prior to use with dried cyclohexane. 1,3-Butadiene gas (99.5%, Matheson Gas Products) was passed, prior to use, through a purification column consisting of a 60/40 mixture of molecular sieves (types 4A & 13X, Union Carbide) and activated alumina (type A201, La Roche Industries). Nitrogen gas (99%, Linde gas) was passed, prior to use, through a purification column consisting of a 60/40 mixture of molecular sieves and activated alumina. Cyclohexane, (99%, Fisher Scientific) was initially stored over activated alumina for 48 h, nitrogen sparged and then passed through a purification column consisting of a 60/40 mixture of molecular sieves and activated alumina. Water contents of solutions and solvents were determined by potentiometric Karl Fischer titration. The cyclohexane water content was found to be 5 ppm.

2.2. Catalyst

All catalysts were activated in situ. Catalyst components were added sequentially to the Bd/cyclohexane mixture with a 5 min period between additions. All manipulations were carried out under an inert nitrogen atmosphere using standard Schlenk line techniques [16].

2.3. Polymerization

The 200 ml cylindrical glass reactor used for polymerization was initially 'baked out' by heating under vacuum at 70°C for 60 min. The reactor was cooled to ca. 15°C and then charged with cyclohexane and butadiene in that order to give 14 wt.% monomer in solution. The catalyst components were added to the reactor using Hamilton gas tight® syringes. The reactor was maintained at 70°C and was continuously stirred during polymerization in order to prevent monomer diffusion limitations [2]. Catalyst levels were 0.11 mmol Nd/100 g Bd. Polymerization was terminated by venting off any residual monomer and coagulating the polymer in a 2 wt.% 2,6-di-*t*-butyl-4-methylphenol (BHT)/methanol mixture. Polymers were dried at 60°C in vacuo. Conversions were calculated from the % wt. of isolated polymer compared to the initial charge of monomer and were reproducible to within 4%. The control experiment was performed in the presence of 5.2 ppm of water and 6 ppm of excess versatic acid.

2.4. Characterization

The percentage of stereoisomeric units of the polymers was measured using infrared spectroscopy (IR) and nuclear magnetic resonance (NMR). IR analysis was performed using a Beckman 2100 FTIR spectrophotometer according to the method of Haslam et al. [17]. Films were cast from cyclohexane solution onto KBr plates. The isomer absorbances occur at 740 cm^{-1} (*cis*-1,4), 970 cm^{-1} (*trans*-1,4) and 910 cm^{-1} (vinyl). ^{13}C NMR analysis was performed using a 200 MHz Varian Gemini-200 spectrometer according to the method of Katritzky and Weiss [18]. The spectra were obtained in deuterated chloroform at room temperature (TMS as internal standard). The concentration of polymer solutions was 9% (w/v). The isomer absorbances for methylene groups in high *cis*-1,4-polybutadienes occur at 27.4 ppm (*cis*-1,4 in a *cis*-*cis* diad), 32.7 ppm (*trans*-1,4; in a *trans*–*cis* diad) and 34.0 ppm (vinyl; in a vinyl-*cis* diad) [19]. The samples were scanned over a period of approximately 14 h for a total of 22896 scans with a 33 s pulse delay. Size exclusion chromatography (SEC) data were obtained from a Waters 150-C plus SEC fitted with a Viscotek 150R viscometer and an RI detector. A three styragel-HR column set (10^2, 10^2–10^4 and 10^3–10^6 Å) maintained at 35°C was employed. Tetrahydrofuran was used as eluant at a flow rate of 1.0 ml/min. Polystyrene standards (Polymer Laboratories) were used to calibrate the system and molecular weights for high *cis*-1,4 polybutadienes were determined using the Universal Calibration method [20]. Sample solutions of concentration 0.025% (w/v) were filtered through a 0.45 μm screen prior to injection.

3. Results and discussion

3.1. Catalyst optimization

3.1.1. The effect of $Al_2Et_3Cl_3$ concentration

Similar catalyst systems of the type used in this work ($NdV_3/Al_2Et_3Cl_3$/Al(*i*-Bu)$_2$H) have merited attention in the literature particularly with respect to the influence of the type and concentration of aluminum alkyl and aluminum alkyl halide [4,5,12,21–24]. While the emphasis of this study was to elucidate the effects of water and excess versatic acid on polymerization performance, it was considered that first this specific catalyst system should be subjected to an optimization study using the control polymerization conditions described in Section 2.

The variation of the concentrations of $Al_2Et_3Cl_3$ (EASC) and Al(*i*-Bu)$_2$H (DIBAH) may exert a decisive influence on conversion, stereospecificity and molecular weight of the polymerization. The effect of the EASC concentration was studied and the findings are presented in Table 1. The

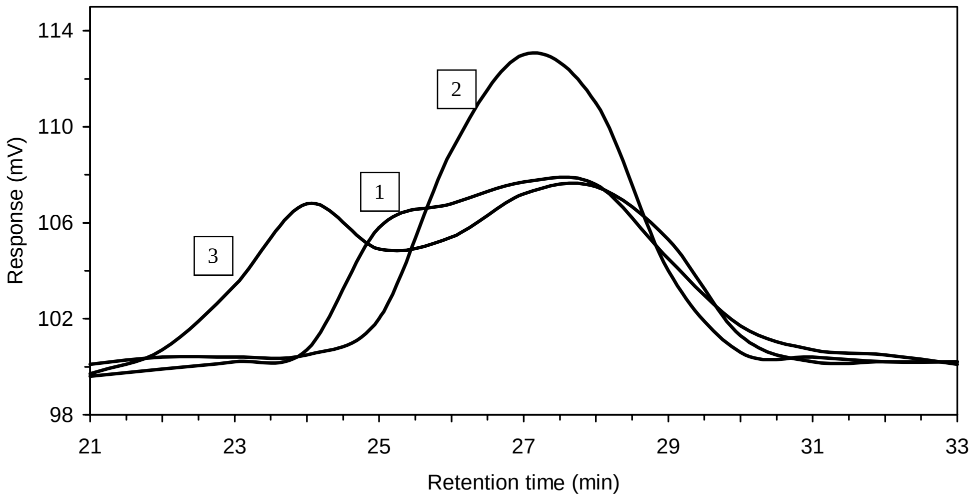


Fig. 1. SEC traces of polybutadienes prepared at different EASC:Nd mole ratios. EASC:Nd mole ratio = 0.5 [1]; EASC:Nd mole ratio = 1.0 [2]; EASC:Nd mole ratio = 4.0 [3].

concentration of EASC should clearly be optimized since the results suggest that the EASC:Nd mole ratio affects the number and nature of the catalytic sites created during polymerization. It has been proposed that two different sites are generated in Nd-catalyzed polymerization, fast but short lived centers created on insoluble particles and slow growing but stable soluble sites [25,26]. Evidence for more than one type of active catalytic center comes from the many studies that have identified bimodal SEC traces with Nd-based catalytic systems particularly at low conversion [3,12,21]. Porri and coworkers [13,27] have proposed that changes in catalyst activity can be explained in terms of different stabilities of σ-type Nd-C bonds, which are formed during initiation and also by chain transfer reactions with aluminum alkyls [3]. The second (slow) type of chain growth has been described as proceeding in a quasi-living manner [24].

It can be seen that increasing the concentration of EASC increases conversion to a maximum corresponding to an $Al_2Et_3Cl_3$:Nd mole ratio of 1.0 for this system under the described conditions. Increasing the $Al_2Et_3Cl_3$:Nd mole ratio further, however, decreases the activity of the catalyst system as reported by Reichert and coworkers [12] using EASC/NdV_3 and triisobutylaluminum. Such observations are also consistent with the work of Oehme et al. [23], Wilson and Jenkins [24] and Gehrke et al. [26]. It is felt that at the low halide level studied (EASC:Nd mole ratio = 0.5) a lower concentration of active sites will be created because of insufficient chlorine; hence the lower conversion and higher polymer molecular weight observed. At high EASC:Nd mole ratios (e.g. 4) the observed behavior (low conversion, broad MWD) may result from the agglomeration of insoluble $NdCl_3$ particles resulting from “over-chlorination” [24]. Furthermore at an EASC:Nd mole ratio of 4.0 the polymer is bimodal (Fig. 1) which may be explained by the earlier argument given that these types of systems have two types of active species present during polymerization. Hence high EASC concentrations appear to form both the sites which lead to high molecular weight and those which lead to lower molecular weight resulting in a very broad molecular weight distribution.

The halide concentration ([EASC]/[Nd]) does not influence the stereospecificity of the polymerization. The observed *cis*-1,4 contents were 98% throughout the studied range of EASC concentrations investigated, as observed by Wilson and Jenkins [24]. To ensure the validity of such values, agreement was sought between determinations using IR [17] and ^{13}C NMR techniques [18,19]. There was excellent agreement between the respective methods; therefore, subsequent analyses in this work were performed

Table 2
Conversion, microstructure and SEC data of polybutadienes produced using the in situ activated NdV_3/EASC/DIBAH catalyst system: influence of Nd: DIBAH mole ratio (conditions: EASC:Nd (mole ratio) = 1; [Nd] = 0.11 mmol/100 g Bd; [Bd] = 14 wt.% in cyclohexane; 1 h polymerization; temperature = 70°C)

DIBAH:Nd (mole ratio)	Conversion (%)	M_w (g/mol)	M_w/M_n	*Cis*-1,4 (%)
10	64	390,000	3.0	99
25	88	210,000	3.5	98
30	90	180,000	4.1	98
40	98	150,000	5.3	99
60	98	110,000	7.8	96

Table 3
Conversion, microstructure and SEC data of polybutadienes produced using the in situ activated NdV_3/EASC/DIBAH catalyst system: influence of the order of addition (conditions: Nd: EASC: DIBAH (mole ratio) = 1:1:25, [Nd] = 0.11 mmol/100 g Bd; [Bd] = 14 wt.% in cyclohexane; 1 h polymerization; temperature = 70°C)

Order of addition	Conversion (%)	M_w (g/mol)	M_w/M_n	*Cis*-1,4 (%)
EASC, Nd, DIBAH	57	430,000	7.5	98
DIBAH, EASC, Nd	76	390,000	5.7	97
DIBAH, Nd, EASC	84	210,000	3.4	98

using IR. It is worth mentioning that with the in situ activated NdV_3/EASC/DIBAH catalyst system described herein, the vinyl content of the polymer was always in the range of only 0.5–0.6%.

3.1.2. The effect of $Al(i\text{-}Bu)_2H$ concentration

The conversion increases initially with increasing concentration of DIBAH and reaches a plateau at 98% when [DIBAH]/[Nd] = 40 (Table 2). The increase in conversion may be due to an increase in the concentration of alkylated species and hence an increase in the concentration of active species. Clearly the effective molar ratio can vary from 25 to 40. The preferred ratio was chosen to be 25 since this stoichiometry provided an acceptable conversion, molecular weight and a narrow molecular weight distribution of 3.5 for this catalyst used at high temperature (70°C).

Stereospecificity was somewhat influenced by the concentration of DIBAH. At a mole ratio of 60/1 ([DIBAH]/[Nd]), the *cis*-1,4 content falls to 96% whereas at lower ratios values of 98–99% were observed. Polymers with molecular weights ranging from 390,000 to 110,000 g/mol may be obtained. The observed decrease in molecular weight and the accompanying increase in molecular weight distribution (from ca. 3 to 8) indicates a strong transfer reaction to DIBAH, as reported by other research groups for the alkylaluminum components of these catalysts [6,12,22].

3.1.3. Order of addition of catalyst components

Different orders of catalyst component addition using in situ and preformed catalysts are commonly reported in the literature. The following orders of addition have been reported: Burford et al. [22] Nd + $AlEt_2Cl$ + $Al(i\text{-}Bu)_3$; Knauf et al. [4] $Al(i\text{-}Bu)_2H$ + $Al_2Et_3Cl_3$ + Nd; Oehme et al. [23] Nd + $Al_2Et_3Cl_3$ + $Al(i\text{-}Bu)_3$; Wilson and Jenkins [25] Nd + $Al(i\text{-}Bu)_2H$ + t-BuCl. As Table 3 shows the addition order with the studied $NdV_3/Al_2Et_3Cl_3/Al(i\text{-}Bu)_2H$ catalyst affected conversion, molecular weight and molecular weight distribution.

These results offer some insight into the nature of the catalyst. Catalysts prepared with addition order EASC + Nd + DIBAH are known to be heterogeneous [13] and in this study this addition order formed a catalyst which exhibited the lowest conversion, highest molecular weight and broadest molecular weight distribution. It is concluded from these results that the % conversion observed after 60 min of polymerization in this study follows the following order of apparent catalyst activity: DIBAH + Nd + EASC > DIBAH + EASC + Nd > EASC + Nd + DIBAH. Furthermore, SEC analyses illustrated that the addition order EASC + Nd + DIBAH leads to polymer with some bimodal character (Fig. 2) whereas the other addition sequences studies led to more monomodal-like distributions. These observations once again suggest that with this in situ activated Nd-based catalytic system two types of active site are generated during polymerization and their relative concentrations may be governed by the addition sequence. Clearly, the formation of insoluble sites is promoted when using EASC + Nd + DIBAH. Conversely using DIBAH + Nd + EASC seems to promote formation of a different type of active center, perhaps a

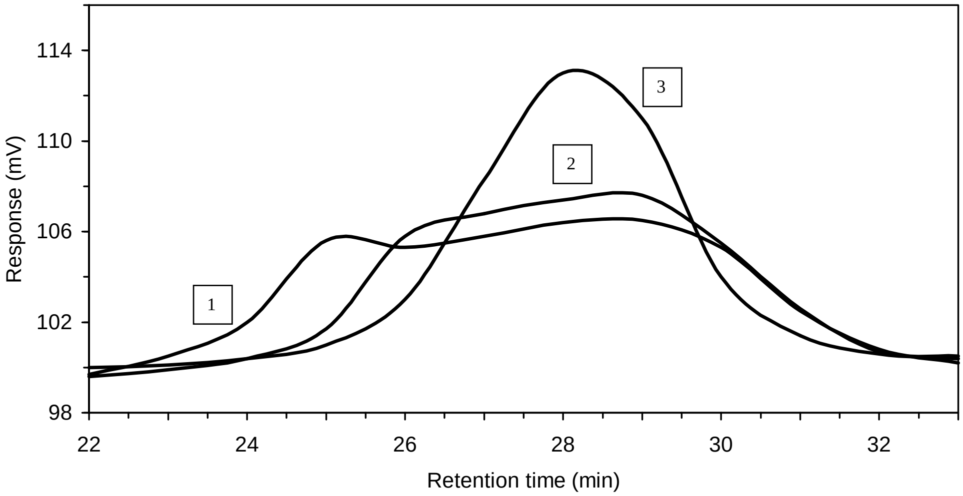


Fig. 2. SEC traces of polybutadienes prepared using different orders of catalyst component addition. EASC + Nd + DIBAH [1]; DIBAH + EASC + Nd [2]; DIBAH + Nd + EASC [3].

Table 4
Conversion, microstructure and SEC data of polybutadienes produced using the in situ activated NdV_3/EASC/DIBAH catalyst system: influence of water content (water content of solvent and neodymium solution determined by Karl Fischer titration. Total water corresponds to the total water from the solvent and the small amount of catalyst solution added. Conditions: Nd:EASC:DIBAH (mole ratio) = 1:1:25, [Nd] = 0.11 mmol/100 g Bd; [Bd] = 14 wt.% in cyclohexane; 1 h polymerization; temperature = 70°C)

H_2O:Nd (mole ratio)	Conversion (%)	M_w (g/mol)	M_w/M_n	*Cis*-1,4 (%)
0.008	55	560,000	6.7	99
0.030	69	470,000	5.5	98
0.051	84	210,000	3.8	98
0.11	86	230,000	3.5	99
0.76	77	250,000	4.7	98
1.51	68	300,000	4.2	98

soluble site formation, leading to a narrower molecular weight distribution of 3.4.

The optimum composition of the catalyst system was considered to be $NdV_3/Al_2Et_3Cl_3/Al(i\text{-Bu})_2H = 1:1:25$ with a DIBAH + Nd + EASC addition sequence and this protocol was used for the following investigations. It is important to note that similar ratios of components have been reported by other researchers for analogous catalyst systems [3–5,12,13,27]

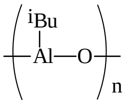
3.2. Water content

It is well established that water is an important component for the stereospecific polymerization of 1,3-butadiene using Co-based Ziegler–Natta catalyst systems [28]. However, the influence of water on Neodymium-catalyzed polymerization has received little attention. In proposing a mathematical model to describe the kinetics of butadiene polymerizations using a NdV_3/ $Al_2Et_3Cl_3/Al(i\text{-Bu})_3$ catalyst, Pross et al. [12] mentioned that they could obtain reproducible polymerization results only if water was excluded from the solvent (<5 ppm). However, they reported that the amount of water in the catalyst solution (25–700 ppm) did not make a difference, presumably because of the small amount of catalyst solution utilized. Carbonaro et al. [29] indicated that addition of limited amounts of water was beneficial to catalytic activity at $[Al]/[H_2O]$ molar ratios of 2/1.

Our results suggest that with this in situ activated NdV_3/ EASC/DIBAH (molar ratios = 1:1:25) catalyst system, the total water content does in fact affect catalytic behavior. The conversion is seen to increase to a maximum as the molar ratio of water (solvent plus catalyst solution) to neodymium ($[H_2O]/[Nd]$) increased from 0.008 to 0.11 (Table 4).

It may be speculated that the water interacts with DIBAH (the order of addition to the reactor was DIBAH, Nd, EASC) and generates an alumoxane-type species. If this is the case, such species clearly promote polymerization at $[H_2O]/[Nd]$ molar ratios up to 0.11. Coupled with the activity increase at these water levels was a decrease in M_w values and a narrowing of the molecular weight distribution. These effects which may be due to an increase in active center concentration or to an increase in chain transfer reactions.

Alumoxanes of the type illustrated in Eq. (1) may be formed via the interaction of DIBAH with the water present in the polymerization. The work of Wilson [2] shows that high levels of alumoxanes are necessary to achieve significant catalytic activity with these types of systems.



$$\left(\overset{^{i}Bu}{\overset{|}{Al}}-O\right)_n \quad (1)$$

However, rather than focusing on their ability as an alkylating agent, alumoxanes may also be considered as electron donors because of the oxygen bridge between the two Al atoms. Hence, they can possibly coordinate to the metal center during polymerization and this feature could be responsible for the particular behavior observed herein. It is widely reported that with rare earth catalyst systems the addition of a Lewis base is capable of affecting the characteristics of the polymerization [6,26].

Polymerizations, however, conducted with molar ratios of water ($[H_2O]/[Nd]$) as high as 0.76 and 1.51 are noteworthy for their lower levels of conversion, higher molecular weights and broader molecular weight distributions compared to the runs with $[H_2O]/[Nd] = 0.11$. Such behavior may be attributed to a lower DIBAH concentration being insufficient to fully alkylate all the Nd species capable of forming active centers, formation of different types of active centers or to an overall decrease in chain transfer reactions.

In spite of these effects of water on conversion, molecular weight and molecular weight distribution, there was very little effect of changing water levels on the stereochemistry of the polymerization ($\geqslant 98\%$ *cis*-1,4). The proposed formation of alumoxanes appears not to influence the mode of orientation of the incoming butadiene monomer and the *anti*/*syn* equilibrium proposed to rationalize *cis*/*trans* enchainment [2].

3.3. Excess versatic acid level

The effect of the excess versatic acid (versatic acid in excess of the stoichiometric 3 mol of versatic acid/1 mol of neodymium) {excess = ([versatic acid]/[Nd] − 3)} on the polymerization of butadiene was studied under the

Table 5
Conversion, microstructure and SEC data of polybutadienes produced using the in situ activated NdV_3/EASC/DIBAH catalyst system: influence of excess versatic acid (excess versatic acid corresponds to the amount of versatic acid present in excess of the stoichiometric amount ([versatic acid]/[Nd] − 3). Conditions: Nd: EASC: DIBAH (mole ratio) = 1:1:25; [Nd] = 0.11 mmol/100 g Bd; [Bd] = 14 wt.% in cyclohexane; 1 h polymerization; temperature = 70°C)

Excess versatic acid: Nd (mole ratio)	Conversion (%)	M_w (g/mol)	M_w/M_n	*Cis*-1,4 (%)
0.22	88	220,000	3.4	97
0.54	63	330,000	4.7	97
0.91	59	310,000	5.4	98
1.43	53	380,000	5.8	97
1.66	55	370,000	5.2	97

optimum conditions identified earlier. An increase in the excess versatic acid above [excess acid]/[Nd] = 0.22 was found to be detrimental to the polymerization even at relatively low levels (Table 5). These results suggest that excess versatic acid destroys active centers since a fall in conversion, an increase in M_w values and a broadening of the molecular weight distribution are observed.

4. Conclusions

This study has demonstrated that the initiating catalyst system $NdV_3/Al_2Et_3Cl_3/Al(i\text{-}Bu)_2H$ in cyclohexane is effective for the polymerization of 1,3-butadiene following in situ activation. The % conversion, polymer molecular weight and molecular weight distribution are dependent on the molar ratios of EASC, DIBAH and NdV_3, the order of addition of the catalyst components, the water content ($[H_2O]/[Nd]$) and the amount of excess versatic acid {excess = ([versatic acid]/[Nd] − 3)}. However, our results suggest that the studied Nd-based catalytic system is relatively tolerant to changes in the reaction stoichiometry. In the view of the authors, this is an extremely important characteristic of the Nd-based system, which should not be overlooked and is particularly relevant from an industrial perspective.

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