

## The influence of Ni/Nd-based Ziegler–Natta catalyst on microstructure configurations and properties of butadiene rubber

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**ABSTRACT:** Neodymium (Nd)-based Ziegler–Natta catalyst has been well known for preparing polybutadiene rubber (BR) containing high, about 98%, *cis*–1,4 configuration with extremely low gel content providing superior resistance to low-temperature fatigue and abrasion. However, its cost is more expensive than a conventional nickel (Ni)-based catalyst. The Nd-BR has poor processability with high cold flow due to its high linearity and molecular weight. To compare with a traditional process, the BR produced by Ni-based catalyst has higher level of branching resulting in the better processability, but it contains medium amount of gel. To balance the catalyst cost and the BR properties, this article reported the influence of a solution containing Ni- and Nd-based Ziegler–Natta catalyst (Ni/Nd) using diethyl aluminum chloride and triethyl aluminum as co-catalysts on 1,3-butadiene (BD) conversion and physical properties of the elastomeric materials based on obtained rubber (Ni/Nd-BR). In the presence of toluene, the increase in the Ni/Nd molar ratio from 0.0/1.0 to 0.4/0.6 yielded Ni/Nd-BR containing *cis*–1,4 units of 95%–96% with significantly decreasing both levels of *vinyl*–1,2 and *trans*–1,4 configurations from 0.26% to 0.13% and 4.44% to 3.07%, respectively. When cyclohexane was applied as the reaction media, 100% BD conversion was achieved and the Ni/Nd-BR had very low content of *vinyl*–1,2 unit (0.07%). The mechanical properties in terms of tensile properties and abrasion resistance of the elastomer based on Ni/Nd-BR having high *cis*–1,4 and relatively higher *trans*–1,4 configurations were superior to elastomers based on commercial BRs produced by using Ni- and Nd-based catalyst systems. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41834.

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### INTRODUCTION

Many coordination (Ziegler–Natta) type catalysts have been reported for the preparation of polybutadiene rubber (BR) with a high content of *cis*–1,4 configuration. A nickel (Ni)-based catalyst system developed by Bridgestone Tire & Rubber Co., Ltd. and Japan Synthetic Rubber Co., Ltd. has been commercialized to produce BR.<sup>1</sup> This catalyst system produces BR (Ni-BR) containing the high content of *cis*–1,4 configuration (ca. 96%–98%) with high branching, broad molecular weight distribution (MWD) and low cold flow to promote easier processing than a BR having a more linear structure.<sup>1–4</sup> The chemical structure of Ni-BR also consists of a fairly high level of *trans*–1,4 units (ca. 3%) and low level of *vinyl*–1,2 units (ca. 1%).<sup>4,5</sup> Generally, the polymerization of 1,3-butadiene (BD) using Ni-based catalysts comprised of nickel naphthenate, boron trifluoride etherate

( $\text{BF}_3 \cdot \text{Et}_2\text{O}$ ), and trialkylaluminum such as triethylaluminum (TEAL) is carried out in solution such as aliphatic and aromatic solvents.<sup>6</sup> The disadvantage of this polymerization system is more release of butadiene dimer (vinyl cyclohexene), which is harmful to the environment than the polymerization process using lanthanide catalysts.<sup>7</sup> Moreover, the fluorine-containing co-catalyst such as hydrogen fluoride (HF) or  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  required for the Ni-based catalyst system generates strong acid when it contacts water. This can induce equipment corrosion and possible gel-formation in the obtained polymer.<sup>8</sup> The high gel content of Ni-BR also limits the application for the production of high impact polystyrene (HIPS) and acrylonitrile–butadiene–styrene (ABS) resin.<sup>4</sup> Although Ni-BR has a high degree of branching to provide ease of processing, its tensile strength and fatigue resistance are low.<sup>5</sup>

Nowadays, the tire industry is a very large BR consumer, mainly for producing tire treads and side walls.<sup>4,9</sup> According to global trends for the reduction of energy consumption and environmental concerns, tire technology has been developed for better fuel economy by reducing the rolling resistance with better wet skid resistance or safety driving aspects.<sup>10,11</sup> Recently, BR containing 99% *cis*-1,4 microstructure with a very low amount of *vinyl*-1,2 units (<1%) has been produced by using lanthanide catalysts based on neodymium (Nd) coordinating with aluminum halides acting as co-catalysts.<sup>4</sup> The lanthanide catalysts have high solubility in saturated alkanes, which are safer and more environmental friendly than benzene and toluene used as the general solvents in conventional butadiene polymerization.<sup>7</sup> Moreover, the lanthanide catalysts promote high monomer conversion to achieve 100% conversion without gel formation in the resulting product.<sup>7</sup> This catalyst type also produces less content of a butadiene dimer.<sup>7</sup> With respect to the properties of BR produced by the Nd-based catalyst system (Nd-BR), this rubber type with high linearity and very broad molecular mass distribution has the lowest glass transition temperature ( $T_g$ ), about  $-109^\circ\text{C}$ , which is advantage for applications in the very low temperature fatigue.<sup>4</sup>

After crosslinking, the vulcanized Nd-BR also has superior mechanical properties, which are required for the green tire industry such as high abrasion resistance, resilience, and tensile properties including hysteresis (low heat build-up). However, the high linearity of Nd-BR with high molecular weight induces a high cold flow effect resulting in poor extrudability and difficulty in compounding.<sup>2,4</sup>

To combine the desired inherent properties of BR obtained from monocatalyst (Ni- or Nd-based), Jang *et al.*<sup>12</sup> has reported the advantage of using a mixture of Nd salt, Ni salt, organoaluminum compound, and boron trifluoride complexes for producing high *cis*-1,4 BR. They found that this mixed catalyst [neodymium versate ( $\text{NdV}_3$ )/nickel octoate  $\{\text{Ni}(\text{oct})_2\}$ /triisobutylaluminum  $\{\text{Al}(\text{i-Bu})_3\}$ / $\text{BF}_3\text{OEt}_2$  molar ratio = 0.7/0.3/30/1] could provide BR with high BD conversion (99%) and high content of *cis*-1,4 configuration (98.5%). To avoid the use of fluorine-containing co-catalyst as described above, this research work aimed to study the performance of a mixed catalyst containing both Ni and Nd (Ni/Nd) coordinating with general co-catalysts: diethyl aluminum chloride (DEAC) and TEAL used as co-catalysts for BD polymerization. The effects of parameters such as Ni/Nd molar ratios, amounts of co-catalyst and chlorinating agent, reaction temperature and solvent type on BD conversion, microstructure, including molecular weight ( $M_w$ ), and MWD of the obtained Ni/Nd-BR gum were investigated. The vulcanization and mechanical properties of the Ni/Nd-BR vulcanizates were also examined and compared with those of commercial BRs: Ni-BR and Nd-BR obtained from Ni and Nd-based polymerization processes, respectively.

## EXPERIMENTAL

### Materials

BD with 95% purity was purchased from Air Liquide (Canada) Co., Ltd. Nickel naphthenate ( $\text{C}_{22}\text{H}_{14}\text{NiO}_4$ ) [2.0% (w/w) in hexane], DEAC (1M in hexane), and TEAL (1M in hexane)

were purchased from Sigma Aldrich. Methanol and toluene (99% purity) were purchased from Sigma Aldrich. Toluene was purified by distillation, with an amount of water being less than 10 ppm by using a molecular sieve and purged with nitrogen gas (99.99% purity) before charging into the polymerization system.  $\text{NdV}_3$  dissolved in cyclohexane [8.8% (w/v)] obtained from Comar Petrochemical (Cape Town, South Africa) was diluted to 1.0% (w/v) in oxygen free-dried toluene before charging into the polymerization system. 2,6-di-*ter*-butyl-4-methylphenol (BMP) and phosphate of polyoxyethylene alkyl phenyl ether (PPA) were purchased from Lanxess Deutschland GbmH (Germany) and Twin Hart International Co., Ltd. (Taiwan), respectively. A solution of the BMP/PPA mixture was prepared by dissolving in toluene at 5.6% (w/v).

Commercial BR obtained by Nd- (Buna CB-24) and Ni-based catalyst with a high content of *cis*-1,4 configuration used for comparison were obtained from Lanxess Co., Ltd (German) and BST Elastomer Co., Ltd. (Thailand), respectively. Chemicals such as zinc oxide (ZnO, Thai-Lysaght Co., Ltd, Thailand), naphthenic oil (P.S.P. Special Ties Co., Ltd, Thailand), carbon black N330 (Thai Carbon Black Public Co., Ltd., Thailand) including sulfur, stearic acid, and *n-tert*-butyl-2-benzothiazone sulfonamide (TBBS) (Kitipiboon Chemical Ltd., Thailand) were used for BR vulcanization.

### Preparation of Ni/Nd-Based Ziegler–Natta Catalyst

The Ni/Nd-based Ziegler–Natta catalyst solution was prepared in a dried-glass ampoule capped with neoprene rubber. About 1.0% (w/v) of the  $\text{NdV}_3$  solution was mixed with Ni, DEAC, and TEAL solutions by varying the Ni/Nd molar ratio from 0.0/1.0 to 1.0/0.0 in the presence of 0.5/1.0 to 3.0/1.0 and 3.0/1.0 to 9.0/1.0 DEAC/Nd and TEAL/Nd molar ratios, respectively. The catalyst solution was then aged in a water bath at  $20^\circ\text{C}$  for 1 h before charging into the polymerization reactor.

### Polymerization of BD

All solution polymerizations were performed in a 0.5 L Parr reactor under a dry nitrogen atmosphere. About 60 g of dry toluene was firstly charged into the reactor followed by the injection of 1.1 mL aged Ni/Nd-based catalyst solution by using a syringe at a desired reaction temperature ( $45^\circ\text{C}$ – $60^\circ\text{C}$ ). Then, 3.01M BD [ca., 15 g BD/batch or toluene/BD = 4/1 (w/w)] was charged into the reaction mixture. The reaction was allowed to proceed for 2 h and the polymerization was terminated by adding 3 mL of BMP/TNP solution. The polymer cement was coagulated in methanol under stirring to obtain the Ni/Nd-BR crumb and then dried in an oven at  $80^\circ\text{C}$  overnight. The monomer conversion was calculated as follows:

$$\% \text{Conversion} = \frac{\text{TSC}}{M} \times 100 \quad (1)$$

where TSC is the total solid BR content (g) and  $M$  is the weight of charged BD monomer (g).

### Characterization of Chemical Structure and Glass Transition Temperature of Ni/Nd-BR

The microstructure of the obtained Ni/Nd-BR gum was analyzed by using attenuated total reflectance Fourier transform infrared spectroscopy (ATR–FTIR, Perkin Elmer FT-IR

spectrometer, Paragon 500). The contents of *cis*-1,4, *trans*-1,4, and *vinyl*-1,2 configurations were determined from the normalization of a peak height at the band absorbance of 738  $\text{cm}^{-1}$  (*cis*-R-CH=CR-H), 910  $\text{cm}^{-1}$  (*vinyl*-R-CH=CR-H), and 964  $\text{cm}^{-1}$  (*trans*-R-CH=CR-H) according to eqs. (2–4), respectively [ISO 12965:200(E)].

$$\%cis = \frac{A_{738}}{A_{738} + A_{910} + A_{964}} \times 100 \quad (2)$$

$$\%vinyl = \frac{A_{910}}{A_{738} + A_{910} + A_{964}} \times 100 \quad (3)$$

$$\%trans = \frac{A_{964}}{A_{738} + A_{910} + A_{964}} \times 100 \quad (4)$$

where  $A_{738}$ ,  $A_{964}$ , and  $A_{910}$  are the peak height of *cis*-1,4, *trans*-1,4, and *vinyl*-1,2, respectively.

To confirm the ATR-FTIR results, the microstructure of Ni/Nd-BR gum dissolved in  $\text{CDCl}_3$  at room temperature was also analyzed by using proton ( $^1\text{H-NMR}$ ) and carbon ( $^{13}\text{C-NMR}$ ) nuclear magnetic resonance spectroscopy (Avance 300, Bruker) with 16 and 10,000 scans, respectively and trimethylsilane (TMS) was used as an internal standard.

$T_g$  of the obtained Ni/Nd-BR samples was evaluated by using a Differential Scanning Calorimetry (DSC-50, Shimadzu). The sample (10 mg) was placed in an aluminum pan and scanned at the testing temperature over the range of  $-130^\circ\text{C}$  to  $50^\circ\text{C}$  at a heating rate of  $5^\circ\text{C}/\text{min}$ . The  $T_g$  value for each sample was calculated from the midpoint of the baseline shift of the DSC thermogram.

#### Measurement of Gel Content in Ni/Nd-BR

Gel content in the prepared Ni/Nd-BR samples was determined from the content of an insoluble fraction. The sample (0.3 g) was placed on a 80 mesh metal screen and immersed in 100 mL toluene at  $80^\circ\text{C}$  for 24 h. The insoluble fraction trace on the metal screen was dried in a vacuum oven at  $60^\circ\text{C}$  for 2 h. The gel content was calculated as follows:

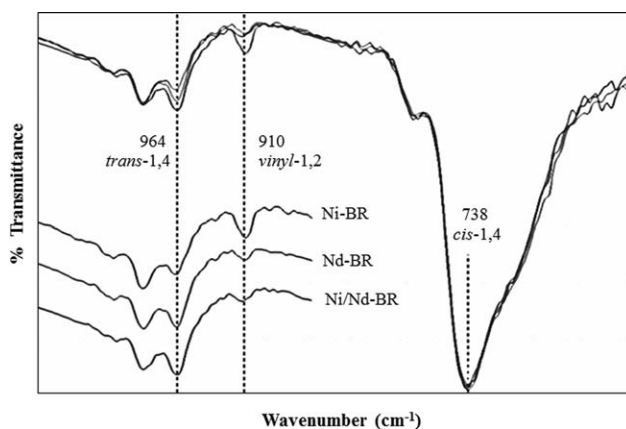
$$\%gel\ content = \frac{\text{Final sample weight}}{\text{Initial sample weight}} \times 100 \quad (5)$$

#### Molecular Weight and MWD of Obtained Ni/Nd-BR

The  $M_w$  and MWD values of the Ni/Nd-BR were evaluated using a gel permeation chromatography (GPC, Water 2690) equipped with a refractive index detector (Water 2410). Tetrahydrofuran (THF) at a flow rate of 1 mL/min at  $25^\circ\text{C}$  was used as the mobile phase. The Ni/Nd-BR dissolved in THF [0.1% (w/v)] was injected into a GPC. A universal calibration curve was prepared by using monodispersed polystyrene standards.

#### Compound Preparation

The Ni/Nd-BR was compounded with 3 parts per hundred of rubber (phr) ZnO, 2 phr stearic acid, 0.9 phr sulfur, 1.5 phr TBBS, 15 phr naphthenic oil, and 60 phr carbon black (N330) by using an internal mixer (Haake, United States) at  $70^\circ\text{C}$  with a rotor speed of 40 rpm followed by sheeting on a two-roll mill at  $50^\circ\text{C}$ . Then, the vulcanization characteristics of the compounded Ni/Nd-BR were evaluated using a moving die rheometer (TECHPRO, Rheotech MD+, United States) at  $160^\circ\text{C}$  with frequency of 1.7 Hz and amplitude of  $0.5^\circ$  to obtain



**Figure 1.** Comparative ATR-FTIR spectra of Ni/Nd-BR and commercial BRs: Ni-BR and Nd-BR.

the minimum ( $M_L$ ) and maximum torques ( $M_H$ ) with a scorch time ( $t_{s1}$ ) and optimum cure time ( $t_{c90}$ ) following ASTM D5289-07.

#### Mechanical Properties of Ni/Nd-BR Vulcanizates

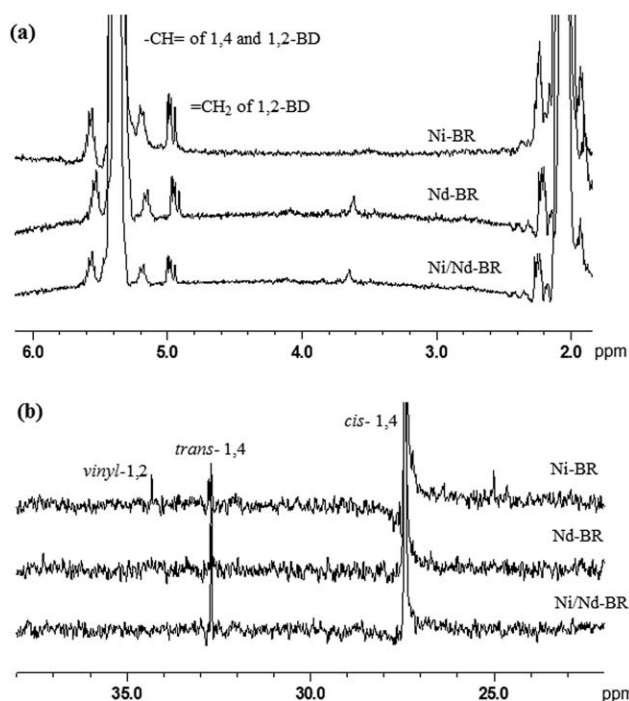
For mechanical properties measurement of Ni/Nd-BR vulcanizates, the tensile properties were also investigated by using a tensile tester (Instron 3366, United States) with a cross-head speed of 500 mm/min according to ASTM D412 (Die C). The abrasion resistance was tested according to DIN 53516 using a DIN abrasion tester (ZWICK, United States). The hardness of all samples was carried out by using a Shore A hardness tester (WALLACE, United States) according to ASTM D2240. Five measurements were recorded for all mechanical properties testing and the obtained average values were reported. All properties of the Ni/Nd-BR vulcanizates were also compared with those of commercial Ni-BR and Nd-BR vulcanizates.

## RESULTS AND DISCUSSION

#### Properties of Ni/Nd-BR

The microstructure in terms of *cis*-1,4, *trans*-1,4, and *vinyl*-1,2 units in the Ni/Nd-BR gum produced from BD polymerization at  $50^\circ\text{C}$  using the Ni/Nd-based catalyst system at a molar ratio of 0.3/0.7 with 1.5/1.0 and 5.0/1.0 DEAC/Nd and TEAL/Nd molar ratios, respectively, was examined by using ATR-FTIR (Figure 1),  $^1\text{H-NMR}$  [Figure 2(a)], and  $^{13}\text{C-NMR}$  [Figure 2(b)] spectroscopy. The results were also compared with that of commercial BRs: Ni-BR and Nd-BR prepared by BD polymerization using Ni and Nd-based Ziegler-Natta catalysts, respectively.

From Figure 1, the ATR-FTIR spectra of all BR samples showed high intensity of the absorption peak at  $738.5\text{ cm}^{-1}$  reflecting a high level of *cis*-1,4 configuration in the range of 96%–98% (Table I). The content of *cis*-1,4 unit in the Ni/Nd-BR at 96.6% was in the same range as that of commercial Nd-BR (97.6%) and Ni-BR (96.3%). Regarding the absorption peak at  $965\text{ cm}^{-1}$  attributed to the *vinyl*-1,2 structure, the intensity of this structure for Ni/Nd-BR (0.14%) was lower than that of the commercial Ni-BR (1.80%). It indicated that the Ni/Nd mixed catalyst could promote a high content of *cis*-1,4 units with a very low amount of *vinyl*-1,2 configuration. This could be



**Figure 2.** Chemical structure of BRs comparatively analyzed by (a)  $^1\text{H}$ -NMR and (b)  $^{13}\text{C}$ -NMR spectroscopy.

explained in that the high performance of Nd in the Ni/Nd mixed catalyst induced the high polymerization rate to form the external  $\sigma$ -allyl species rather than the internal one resulting in a decrease in the opportunity to form *vinyl*-1,2 structure in BR.<sup>13</sup> However, the intensity of the absorption peak at  $910\text{ cm}^{-1}$  attributed to the *trans*-1,4 configuration of Ni/Nd-BR was highest. It can be seen that the amount of *trans*-1,4 units in the Ni/Nd-BR was 3.26%, which was higher than that of the commercial BRs (1.90% for Ni-BR and 2.12% for Nd-BR). Similar results were earlier reported for BR produced by a Ni-based Ziegler-Natta catalyst, usually having a high amount of *trans*-1,4 configuration.<sup>5,14</sup>

The microstructure of Ni/Nd-BR was also determined by using  $^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectroscopy and compared with those of commercial BRs as shown in Figure 2(a,b), respectively. The  $^1\text{H}$ -NMR spectra of all BR samples [Figure 2(a)] showed signals in the range of 4.8–5.2 ppm and 5.2–5.8 ppm, which are assigned to  $=\text{CH}_2$  of *vinyl*-1,2 configuration and  $-\text{CH}=\text{}$  of 1,4-butadiene and 1,2-butadiene units, respectively.<sup>15</sup> The results also showed that the signals for  $=\text{CH}_2$  of *vinyl*-1,2 configuration of Nd-BR and Ni/Nd-BR were lower than those of the Ni-BR sample. From the  $^{13}\text{C}$ -NMR spectra of all BR samples [Figure 2(b)], the microstructure of these samples showed peaks at 27.4, 32.7, and 34.0 ppm attributed to the *cis*-1,4, *trans*-1,4 and *vinyl*-1,2 configurations, respectively.<sup>16</sup> This was consistent to the results observed from ATR-FTIR and  $^1\text{H}$ -NMR spectroscopy showing a very low intensity of the *vinyl*-1,2 structure signal for the Nd-BR and Ni/Nd-BR samples.

To evaluate the  $T_g$  value of BR samples, Table I shows that the all BR sample had  $T_g$  in the range of  $-110^\circ\text{C}$  to  $-111^\circ\text{C}$ . Generally, the  $T_g$  of these materials is dependent on the structural arrangement.

It has been reported that the BR containing high contents of *cis*-1,4 and *trans*-1,4 configurations had a low  $T_g$  value (ca.,  $-106^\circ\text{C}$  to  $-107^\circ\text{C}$ ), whereas BR with a high amount of the *vinyl*-1,2 unit in the structure of 1,2-atactic or 1,2-syndiotactic had higher  $T_g$  values such as  $-4^\circ\text{C}$  or  $-28^\circ\text{C}$ , respectively.<sup>3</sup> Moreover, the results in Table I showed that the gel content of Ni/Nd-BR (0.55%) was much lower than that of the commercial Ni-BR (1.47%). This implied that the existing *vinyl*-1,2 configuration could induce the gel formation via re-incorporation of internal unsaturation units for Ni-BR system.<sup>14,17</sup>

### BD Polymerization Using Ni/Nd-Based Ziegler–Natta Catalyst

The effect of reaction parameters on the BD polymerization using Ni/Nd-based Ziegler–Natta catalyst in terms of BD conversion and physical properties of the obtained Ni/Nd-BR gum was investigated. The univariate experiments of BD polymerization with the central condition (BD concentration = 3.01M, Ni/Nd molar ratio = 0.3/0.7, TEAL/Nd molar ratio = 5.0/1.0 and DEAC/Nd molar ratio = 1.5/1.0) were performed in the presence of toluene at  $50^\circ\text{C}$  for 2 h.

**Effect of Catalyst Components.** The effect of catalyst components such as the molar ratios of Ni/Nd, TEAL/Nd, and DEAC/Nd on the BD polymerization in terms of BD conversion, microstructure,  $M_n$ , and MWD of the obtained Ni/Nd-BR gum are shown in Figure 3 and Table II.

For the effect of the Ni/Nd molar ratio on BD conversion [Figure 3(a)], it was found that 76.3% BD conversion was achieved when BD polymerization was activated without the use of Ni (Ni/Nd molar ratio = 0.0/1.0). The obtained BR gum had only 95.3% *cis*-1,4 and 0.26% *vinyl*-1,2 configurations with a fairly high level of *trans*-1,4 units (4.44%) (Table II). Generally, the Nd catalyst coordinated with triethylaluminum chloride ( $\text{Et}_3\text{AlCl}_3$ ) and diisobutylaluminum hydride ( $\text{Al}^i\text{Bu}_2\text{H}$ ) [ $[\text{Nd}(\text{OCOR})_3/\text{Et}_3\text{AlCl}_3/\text{Al}^i\text{Bu}_2\text{H}] = 1/1/8$ ] could provide a BR with 98% *cis*-1,4 unit and 1% *trans*-1,4 configuration.<sup>4</sup> In our work, it was possible that the co-catalysts (DEAC and TEAL) applied in this system were not appropriate for the Nd-based catalyst to produce BR with a high content of the *cis*-1,4 structure and a low level of *trans*-1,4 units. Moreover, this system lacked the addition of water, which is normally required to react with aluminum alkyl to generate a reactive aluminoxane, which is an electron donor for a typical BD polymerization using Nd-based catalyst.<sup>16,18</sup> When the amount of Ni species was

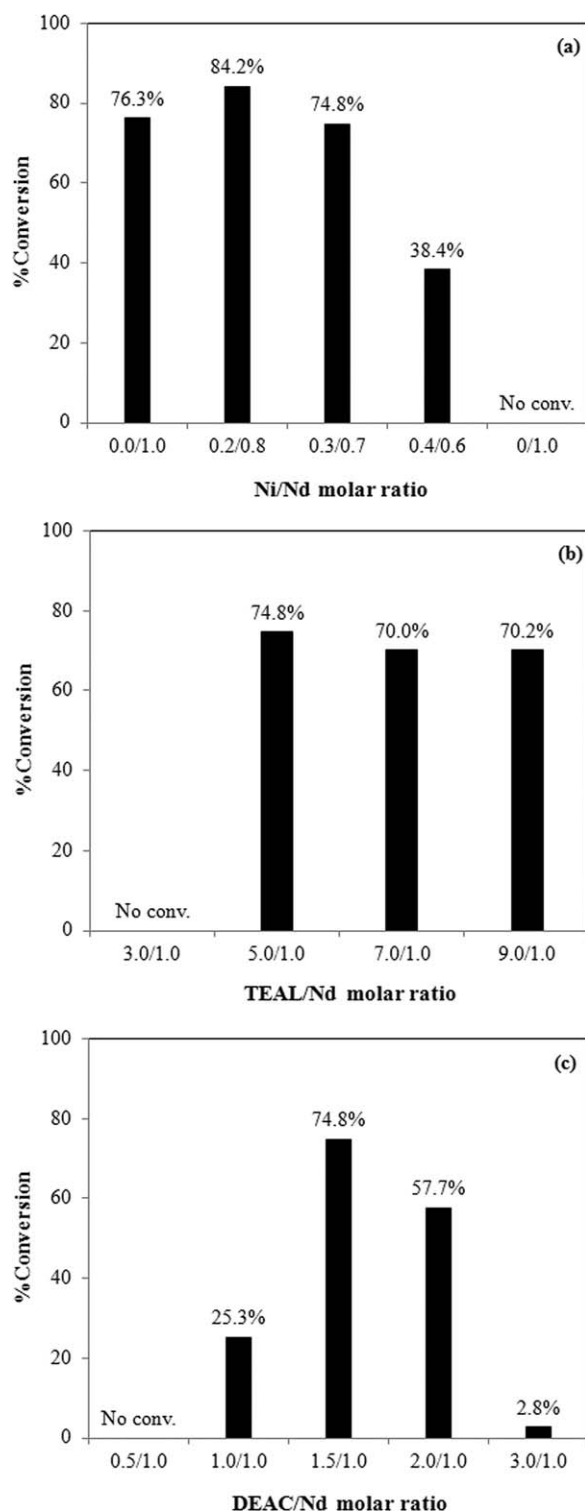
**Table I.** Microstructure,  $T_g$ , and Gel Content of BRs

BR	Microstructure (%)			$T_g$ ( $^\circ\text{C}$ )	Gel content (%)
	<i>Cis</i> -1,4	<i>Trans</i> -1,4	<i>Vinyl</i> -1,2		
Ni-BR <sup>a</sup>	96.3	1.90	1.80	-110.4	1.47
Nd-BR <sup>b</sup>	97.6	2.12	0.28	-111.0	0
(Ni/Nd)-BR <sup>c</sup>	96.6	3.26	0.14	-110.8	0.55

<sup>a</sup> Commercial BR obtained from BST Elastomer Co., Ltd.

<sup>b</sup> Commercial BR obtained from Lanxess Co., Ltd.

<sup>c</sup> BR prepared from Ni/Nd-based catalyst (Condition: [BD] = 3.01M, Ni/Nd molar ratio = 0.3/0.7, TEAL/Nd molar ratio = 5.0/1.0, and DEAC/Nd molar ratio = 1.5/1.0 at  $50^\circ\text{C}$  for 2 h in toluene).



**Figure 3.** Effect of the catalyst components on BD conversion: (a) molar Ni/Nd ratio, (b) TEAL/Nd molar ratio, and (c) DEAC/Nd molar ratio (Condition: [BD] = 3.01 M at 50 °C for 2 h in toluene).

increased in the mixed Ni/Nd-based catalyst, the BD conversion increased approaching a maximum value of 84% at the Ni/Nd molar ratio of 0.2/0.8. Above this point, the conversion tended to decrease and no polymeric product formed when only the Ni

species was applied (Ni/Nd molar ratio = 1.0/0.0). The previous literature reported that the use of a chlorinating agent such as DEAC might be inappropriate for Ni in BD polymerization since the fluorine-containing substances such as  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  was the best Lewis acid used as the co-catalyst for the Ni-based catalyst system.<sup>6,19</sup>

For the microstructure and physical properties of the obtained Ni/Nd-BR (Table II), when the Ni/Nd molar ratio increased from 0.2/0.8 to 0.4/0.6, the content of *cis*-1,4 configuration in the Ni/Nd-BR slightly increased from about 95% to 97%. Whereas, the amount of *trans*-1,4 and *vinyl*-1,2 units decreased from about 5% to 3% and 0.3% to 0.1%, respectively. This was due to the synergistic effect from both Nd and Ni species to form BR with a higher content of *cis*-1,4 configuration and lower amount of *vinyl*-1,2 units.<sup>1,3,4</sup> Thus, it could be noticed that this Ni/Nd-based catalyst system exhibited the specific properties to produce BR containing a high content of *cis*-1,4 configuration with a low amount of *vinyl*-1,2 units (<0.3%). It was also found that the BD polymerization using the higher Ni/Nd molar ratios (0.3/0.7 to 0.4/0.6) provided Ni/Nd-BR with a lower  $M_w$  ( $5.22 \times 10^5$ – $5.89 \times 10^5$ ) with a broader MWD (2.4–3.6) than the BR produced by using only the Nd-based catalyst ( $6.89 \times 10^5$ ). This was due to the effect of Ni catalyst generally producing BR with lower linearity and  $M_w$  than BR obtained from the Nd-based catalyst system.<sup>1,4</sup> In addition, the higher Ni/Nd molar ratio produced Ni/Nd-BR with higher MWD reflecting the higher degree of branching resulting from the influence of Ni-based catalyst.

For the effect of TEAL concentration on the conversion of BD polymerization [Figure 3(b)], the use of TEAL/Nd molar ratio at 3.0/1.0 was not sufficient to activate the BD polymerization. When the TEAL/Nd molar ratio increased from 5.0/1.0 to 9.0/1.0, the BD conversion slightly increased to about 70%–75% since TEAL could act as the oxygen and moisture scavenger in the system.<sup>20</sup> However, TEAL gave lower activity than other organoaluminum compounds for lanthanide catalysts such as triisobutylaluminum or diisobutylaluminum hydride.<sup>21</sup> It was also found that the increase in the TEAL/Nd molar ratio slightly affected the content of *cis*-1,4 microstructure of the obtained Ni/Nd-BR (%*cis*-1,4 = 96%–97%). Moreover, it was observed that the higher TEAL/Nd molar ratio from 5.0/1.0 to 9.0/1.0 decreased the amount of *trans*-1,4 configuration in the obtained Ni/Nd-BR from 3.26% to 2.52%. Normally, the increase in the amount of alkylaluminum compounds acting as the electron donors to compete with the new coming BD monomer for occupying one coordination site of catalyst promotes the formation of *trans*-1,4 unit.<sup>20</sup> However, TEAL could be used as the co-catalyst for both Ni and Nd in the catalyst mixture.<sup>13,19</sup> Thus, it was possible that the combination of Ni and Nd for catalyzing the BD polymerization could decrease the steric hindrance obtained from high TEAL concentration resulting in the reduction of monodentate coordination to form *trans*-1,4 structure. For the *vinyl*-1,2 unit in the Ni/Nd-BR, Table II indicated that the increase in the TEAL/Nd molar ratio from 5.0/1.0 to 9.0/1.0 provided the amount of *vinyl*-1,2 structure in the range of 0.14%–0.28%, which was still < 1%. This

**Table II.** Effect of the Catalyst Components on Microstructure,  $M_w$ , and MWD of Ni/Nd-BR Gum

Ni/Nd	TEAL/Nd	DEAC/Nd	Microstructure (%)			$M_w$ ( $\times 10^5$ )	MWD
			<i>Cis</i> -1,4	<i>Trans</i> -1,4	<i>Vinyl</i> -1,2		
0.0/1.0	5.0/1.0	1.5/1.0	95.3	4.44	0.26	6.89	2.5
0.2/0.8	5.0/1.0	1.5/1.0	94.8	4.93	0.27	5.89	2.2
0.3/0.7	5.0/1.0	1.5/1.0	96.6	3.26	0.14	5.22	2.4
0.4/0.6	5.0/1.0	1.5/1.0	96.8	3.07	0.13	5.82	3.6
0.3/0.7	7.0/1.0	1.5/1.0	96.0	3.80	0.20	6.06	2.6
0.3/0.7	9.0/1.0	1.5/1.0	97.2	2.52	0.28	7.10	2.8
0.3/0.7	5.0/1.0	1.0/1.0	96.6	3.16	0.24	6.15	2.8
0.3/0.7	5.0/1.0	2.0/1.0	96.4	3.45	0.15	5.10	2.4
0.3/0.7	5.0/1.0	3.0/1.0	97.0	2.32	0.68	13.1	13.4

Condition: [BD] = 3.01M at 50°C for 2 h in toluene.

phenomena has been observed for the BD polymerization catalyzed by using  $\text{NdCl}_3$ -TEAL.<sup>13</sup>

To consider the  $M_w$  and MWD of the Ni-Nd-NR, Table II exhibited that the  $M_w$  and MWD of the resulting BR increased from  $5.22 \times 10^5$  to  $7.10 \times 10^5$  and from 2.4 to 2.8, respectively when the TEAL/Nd molar ratio increased from 5.0/1.0 to 9.0/1.0. In this range of TEAL concentration, it could act as the scavenger of moisture and impurities possibly presented in the reaction medium at low concentration. However, some previous literatures reported that the use of high concentration of alkyl aluminum compounds (alkyl aluminum/Nd = 10–30) could induce the chain transfer reaction to decrease the  $M_w$  of the resulting BR.<sup>13,20</sup>

The effect of DEAC concentration on the BD conversion and the physical properties of the Ni/Nd-BR is shown in Figure 3(c) and Table II. From Figure 3(c), it was suggested that the BD polymerization did not occur when a DEAC/Nd molar ratio of 0.5/1.0 was used. A maximum BD conversion of 74.8% was obtained when the DEAC/Nd molar ratio increased to 1.5/1.0. This can be explained in that the DEAC acted as a chlorinating agent to transfer chloride onto Nd providing the active sites for the insertion of the BD monomer to form *cis*-1,4 configuration.<sup>22</sup> However, an overdose of DEAC/Nd molar ratio at 2.0/1.0 and 3.0/1.0 drastically decreased the conversion to 57.7% and 2.8%, respectively, possibly due to catalyst precipitation to form insoluble  $\text{NdCl}_3$  particles, which decreased the catalytic activity.<sup>22,23</sup> To consider the effect of the DEAC concentration on the microstructure of the Ni/Nd-BR (Table II), an increase in the DEAC concentration did not significantly affect the content of *cis*-1,4 configuration (96%–97%) in the obtained Ni/Nd-BR. However, an increase in the DEAC concentration decreased the amount of *trans*-1,4 units, while the amount of the 1,2-*vinyl* configuration was still lower than 1.0%. This behavior was similar to the BD polymerization catalyzed by Nd/diisobutyl aluminium hydride (DIBAH)/ethylaluminium sesquichloride (EASC) in that the existence of the halide species promoted the production of BR with a low *trans*-1,4 content.<sup>22</sup> This could be explained in that the chloro ligands in the presence of alkylaluminum compounds are reversibly removed

from Nd to provide active sites, which were preferable for the insertion of BD monomer in the *cis*-1,4 mode.<sup>22</sup>

Considering the  $M_w$  and MWD, when the DEAC/Nd molar ratio increased (1.0/1.0 to 2.0/1.0), the  $M_w$  and MWD of the obtained Ni/Nd-BR decreased. Here the DEAC acted as a chain transferring agent in the polymerization.<sup>23</sup> However, with an overdose of DEAC concentration at a DEAC/Nd molar ratio of 3.0/1.0, the produced Ni/Nd-BR had a very high  $M_w$  ( $13.1 \times 10^5$ ) with a broad MWD (13.4). This phenomenon has also been reported from the BD polymerization using  $\text{NdV}_3$ /*tert*-butyl chloride (t-BuCl)/DIBAH system.<sup>23</sup>

**Effect of Reaction Parameters.** The influence of reaction parameters such as BD concentration, reaction temperature, and toluene/cyclohexane wt ratio on BD conversion, microstructure,  $M_w$ , and MWD of the Ni/Nd-BR gum is summarized in Table III.

An increase in the BD concentration from 2.53M to 3.31M enhanced its conversion from 47.4% to 80.5%. When BD concentration increased from 2.53M to 3.01M, the  $M_w$  of Ni/Nd-BR increased from  $4.22 \times 10^5$  to  $5.22 \times 10^5$  and a content of *cis*-1,4 configuration in the Ni/Nd-BR increased from 94.9% to 96.6% with the lower amounts of *trans*-1,4 (from 4.91% to 3.26%) and *vinyl*-1,2 structures (from 0.19% to 0.14%). However, the increase in the BD concentration to 3.31M decreased  $M_w$  of Ni/Nd-BR to  $3.95 \times 10^5$  and the content of *cis*-1,4 units to 93.6% with higher amounts of *trans*-1,4 (5.77%) and *vinyl*-1,2 configurations (0.63%). This could be explained in that the higher BD concentration induced higher reaction medium viscosity to provide lower BD mobility favoring monodentate coordination with the catalyst sites to form a *trans*-1,4 configuration.<sup>24</sup> This phenomenon was also reported for BD polymerization using Ziegler-Natta type catalyst systems containing Ni-dithiophosphate or Ni-dithiocarbamate and DEAC, which provided BR having lower molecular mass and higher content of *trans*-1,4 units when BD concentration increased.<sup>25</sup>

The effect of reaction temperature (40°C–60°C) on the conversion and the physical properties of Ni/Nd-BR was presented in Table III. The results indicated that the BD conversion increased from 66.1% to 80.0% on increasing the reaction temperature from 45°C

**Table III.** Effect of the Reaction Parameters on Microstructure,  $M_w$ , and MWD of Ni/Nd-BR Gum

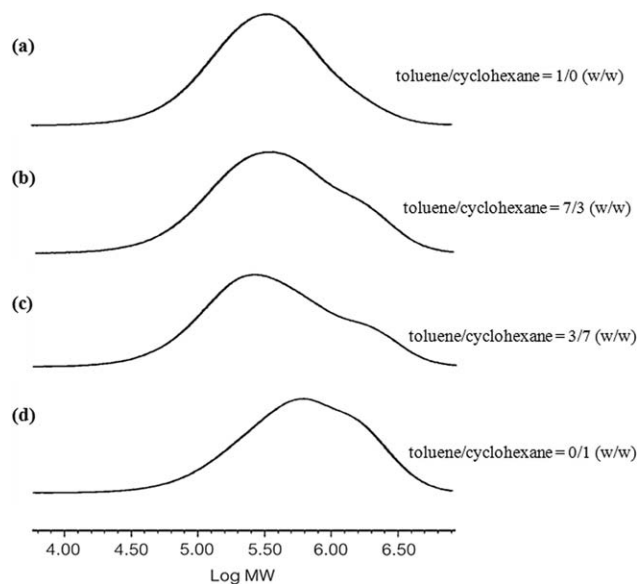
[BD] (M)	Temp (°C)	Toluene/ cyclohexane (w/w)	Conversion (%)	Microstructure (%)			$M_w$ ( $\times 10^5$ )	MWD
				<i>Cis</i> -1,4	<i>Trans</i> -1,4	<i>Vinyl</i> -1,2		
2.53	50	1.0/0.0	47.4	94.9	4.91	0.19	4.22	2.4
3.01	50	1.0/0.0	74.8	96.6	3.26	0.14	5.22	2.4
3.31	50	1.0/0.0	80.5	93.6	5.77	0.63	3.95	2.4
3.01	45	1.0/0.0	66.1	95.5	4.23	0.27	5.12	2.6
3.01	60	1.0/0.0	80.0	94.0	5.44	0.56	4.19	3.0
3.01	50	0.7/0.3	82.2	96.4	3.41	0.19	5.97	3.1
3.01	50	0.3/0.7	98.9	96.4	3.49	0.11	8.55	3.1
3.01	50	0.0/1.0	100	95.6	4.33	0.07	10.8	2.8

Condition: Ni/Nd molar ratio = 0.3/0.7, TEAL/Nd molar ratio = 5.0/1.0, DEAC/Nd molar ratio = 1.5/1.0, and reaction time = 2 h.

to 60°C. On comparing with our previous work,<sup>26</sup> the Co/Nd-based Ziegler–Natta catalyst could activate BD polymerization at 55°C to achieve the same conversion (ca., 80%) as with the Ni/Nd catalyst system, but the BD conversion decreased to about 57% when the reaction temperature was increased to 60°C. This implied that the Ni/Nd mixed catalyst in corporation with DEAC and TEAL had higher resistance to thermal decomposition than the Co/Nd mixed catalyst system. From the microstructure evaluation, the content of *cis*-1,4 units slightly decreased with increasing temperature possibly due to the enhancement of the *cis*-*trans* isomerization rate promoting the formation of *trans*-1,4 and *vinyl*-1,2 configurations.<sup>24</sup> It was also observed that when the reaction temperature increased, the  $M_w$  of Ni/Nd-BR decreased while the MWD increased. This could be explained in that the higher temperature promoted the effect of a chain transfer reaction resulting in a decrease in the  $M_w$  of polymer with a higher degree of chain branching and an increasing MWD of the obtained polymeric product.<sup>24</sup>

The solvent media used for the BD polymerization is also an important factor for the product yield and stereospecificity of the obtained BR product.<sup>27,28</sup> Many solvents are applied in the BD polymerization such as aliphatic, cycloaliphatic, and aromatic hydrocarbons. Although the aromatic hydrocarbons have lower reactivity than aliphatic and cycloaliphatic solvents due to a higher efficiency to competitively coordinate with catalytic active sites than the monomers, aromatic solvents such as toluene have higher boiling points (ca. 110°C–111°C), which are safer than the aliphatic ones having lower boiling point such as hexane (ca., 69°C). Thus, our work aimed to increase the efficiency of toluene by mixing it with a chain closed aliphatic solvent such cyclohexane (boiling point = ca. 80°C–81°C). From Table III, the conversion increased from 74.8% to 100% when the amount of cyclohexane in the reaction media was increased from 1.0/0.0 to 0.0/1.0 (w/w) toluene/cyclohexane. This implied that cyclohexane was more appropriate for BD polymerization than toluene since the benzyl-H atom of toluene could be transferred to the allyl-end of the BD chain resulting in the termination of the polymer chain propagation.<sup>29</sup>

For the effect of solvents on the microstructure, the use of toluene, cyclohexane and their mixture at various weight ratios had no significant effect on *cis*-1,4 unit (95%–96%). However, when the amount of cyclohexane in the toluene/cyclohexane mixture increased from 1.0/0.0 to 0.0/1.0 (w/w), the amount of *trans*-1,4 unit slightly increased from 3.41% to 4.33% with significantly decreasing the amount of *vinyl*-1,2 structure from 0.19% to 0.07%. This implied that the use of cyclohexane as the media for BD polymerization could promote the influence of Ni in the Ni/Nd-based catalyst to produce BR with a higher amount of *trans*-1,4 configuration. Moreover, cyclohexane might facilitate both Ni and Nd species performance to suppress the formation of *vinyl*-1,2 units in the obtained Ni/Nd-BR product. From the GPC chromatograms as shown in Figure 4, the  $M_w$  of the Ni/Nd-BR increased from  $5.97 \times 10^5$  to  $10.8 \times 10^5$  with a slight change of MWD when the cyclohexane amount was increased. Previous work has reported that the



**Figure 4.** GPC chromatograms of the Ni/Nd-BR produced in the presence of toluene/cyclohexane at various weight ratios.

**Table IV.** Cure Characteristics and Mechanical Properties of BR Vulcanizates

Properties	Ni-BR <sup>a</sup>	Nd-BR <sup>b</sup>	Ni/Nd-BR <sup>c</sup>
Curing characteristics at 160°C			
$M_L$ (dN m)	2.84 ± 0.35 <sup>d</sup>	2.97 ± 0.01	2.95 ± 0.34
$M_H$ (dN m)	16.8 ± 2.4	17.5 ± 0.03	16.9 ± 2.59
$ts_1$ (min)	2.37 ± 0.34	2.32 ± 0.01	2.37 ± 0.30
$tc_{90}$ (min)	6.40 ± 0.42	6.44 ± 0.04	6.39 ± 0.42
Mechanical properties			
Tensile strength (MPa)	13.9 ± 0.9	13.8 ± 0.3	15.4 ± 0.5
Elongation at break (%)	434 ± 27	379 ± 11	444 ± 10
Hardness (Shore A)	59.3 ± 0.5	61.0 ± 0.6	62.5 ± 0.8
Abrasion resistance (volume loss, mm <sup>3</sup> )	25.3 ± 2.7	20.9 ± 0.6	21.3 ± 1.1

<sup>a</sup>Commercial BR obtained from BST Elastomer Co., Ltd.

<sup>b</sup>Commercial BR obtained from Lanxess Co., Ltd.

<sup>c</sup>BR prepared from Ni/Nd-based catalyst (Condition: [BD] = 3.01M, Ni/Nd molar ratio = 0.3/0.7, TEAL/Nd molar ratio = 5.0/1.0, and DEAC/Nd molar ratio = 1.5/1.0 at 50°C for 2 h in toluene).

<sup>d</sup>Standard deviation.

cyclohexane in the NdV<sub>3</sub>/t-BuCl/DIBAH system could promote the chain transfer effect resulting in a reduction in the  $M_w$  of BR with a higher MWD value.<sup>28</sup> On comparing with this work, it can be postulated that the use of the Ni/Nd-based catalyst possibly decreased the chain transfer effect of the cyclohexane and also reduces the formation of chain branching resulting in the MWD reduction observed for the Ni/Nd-BR.

#### Vulcanization of Ni/Nd-BR: Cure Characteristics and Mechanical Properties

The cure characteristics and mechanical properties of Ni/Nd-BR compared with the commercial Ni-BR and Nd-BR are presented in Table IV. It was found that the cure characteristics in terms of minimum ( $M_L$ ) and maximum torques ( $M_H$ ), scorch time ( $ts_1$ ), and optimum cure time ( $tc_{90}$ ) of the compounded Ni/Nd-BR were similar to those of the commercial BRs.

From the mechanical properties of vulcanized BR samples, the crosslinked materials based on Ni/Nd-BR had the highest tensile strength (15.4 MPa), elongation at break (444%), and hardness (62.5) with the lowest volume loss during testing of abrasion resistance (21.3 mm<sup>3</sup>). These excellent properties were attributed to both of high contents of *cis*-1,4, which could induce the strain-induce crystallization process,<sup>1</sup> and higher amount of *trans*-1,4 configurations in the Ni/Nd-BR. Moreover, it was possible that the slightly higher amount of *trans*-1,4 units in the obtained Ni/Nd-BR promoted a higher crystallinity in the polymer backbone to induce slightly higher hardness and abrasion resistance of Ni/Nd-BR than other commercial high *cis*-1,4 BRs.<sup>14,30,31</sup>

#### CONCLUSIONS

The Ni/Nd-based Ziegler-Natta catalyst cooperated with DEAC and TEAL used as the co-catalysts was successful to prepare high *cis*-1,4 BR (94%–97%) with relatively higher *trans*-1,4 configuration (2%–5%) and a low amount of 1,2-*vinyl* unit (<1%). The level of *trans*-1,4 unit could be decreased by increasing the amount of co-catalysts: TEAL and DEAC. In the

presence of cyclohexane, the BD polymerization catalyzed by the Ni/Nd-based catalyst achieved to 100% BD conversion and the obtained Ni/Nd-BR had a very low amount of *vinyl*-1,2 units (0.07%). The mechanical properties such as tensile strength, elongation at break, and hardness including the abrasion resistance of the elastomeric materials based on obtained Ni/Nd-BR was superior to that of the commercial BRs. These were attributed to the high contents of *cis*-1,4 and relatively higher *trans*-1,4 configurations in the Ni/Nd-BR resulting from the influence of both Nd and Ni species applied to the BD polymerization.

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