Highly Cis-1,4 Selective Polymerization of Conjugated Dienes Catalyzed by N-heterocyclic Carbene-ligated Neodymium Complexes

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Abstract  Neodymium complexes containing N-heterocyclic carbene (NHC) ligands, NdCl3(x-1,3-RJ[NCH=]2C), THF, (Nd1: R = 2,6-x-Et2C6H4, x = 0; Nd2: R = 2,6-x-Et2C6H4, x = 1; Nd3: R = 2,4,6-x-Me3C6H2, x = 1) were synthesized and employed as precatalysts for the coordination polymerization of conjugated dienes (butadiene and isoprene). In combination with triisobutylaluminum (TIBA), Nd1 promoted butadiene polymerization to produce extremely high cis-1,4 (up to 99.0%) polybutadienes with high molecular weight (Mw = 250–780 kg mol⁻¹). The Nd1/TIBA catalytic system also exhibited both high catalytic activity and cis-1,4 selectivity (up to 97.8%) for isoprene polymerization. The catalytic activity, molecular weight and molecular weight distribution of resulting polydienes were directly influenced by Al/Nd molar ratio, aging method, and polymerization temperature. Very interestingly, the high cis-1,4 selectivity of the catalyst towards butadiene and isoprene kept almost unchanged under different reaction conditions. The cis-1,4 polyisoprenes with high molecular weight (Mw = 210–530 kg mol⁻¹) and narrow molecular weight distribution (Mw/Mn = 1.9–2.7) as well as high cis-1,4 selectivity (~97%) could be synthesized by using the aged Nd1/TIBA catalytic system in the presence of isoprene (100 equivalent to Nd) at low Al/Nd molar ratios of 6–10. Polyisoprenes with low molecular weights (Mw = 12–76 kg mol⁻¹) and narrow molecular weight distributions (Mw/Mn = 1.7–2.6) were obtained by using Nd2 and Nd3 as precatalysts, indicating that the molecular weight of resulting polyisoprenes can be adjusted by changing the substitutes of ligand in Nd complex.

Keywords  Neodymium complex; N-heterocyclic carbene ligand; Coordination polymerization; Cis-1,4 selectivity; Aging method

INTRODUCTION

Cis-1,4 selective polymerization of conjugated dienes, e.g., butadiene and isoprene, is of great importance in synthetic rubber industry to produce the high cis-1,4 polydienes with excellent properties such as excellent elasticity, high fatigue and crack resistance.[1] Catalyst, which mainly decides the catalytic activity and the microstructure of resulting polymers, plays an important role in the industrial production of polydienes.[2–3]

Therefore, much effort has been devoted to developing various catalysts for producing polydienes with high cis-1,4-regularity and controlled molecular weight.[2–5] Rare earth based catalysts stand out as being highly active and selective for butadiene and isoprene polymerizations.[2–5] In general, these rare earth based catalysts are divided into two types: Ziegler-Natta catalytic system and cationic catalytic system.[3–5] The Ziegler-Natta rare earth metal catalysts, mainly the binary systems (LnCl3/R3Al) and ternary systems (LnL2/R2Al-X, Ln = lanthanide; L = carboxylate, phosphate, alkyl, or aryl oxide; X = compounds containing halogen atom), have been used in the synthetic rubber industry because of their advantages in easy preparation, thermal stability, and low moisture and air sensitivity.[3–5] The addition of oxygen-containing ligands, e.g., alcohols[6–8] and tetrahydrofuran,[9] enhanced the catalytic activity of the binary systems. Bidentate aminate,[10–12] β-diketimines,[13,14] iminopyrrole,[15] indolide-imine,[15] aminopyridinato,[16] aminomethacrylic,[17] or alkoxy N-heterocyclic carbene[18] ligands, and tridentate pincer ligands, such as N,N,N′,N′′,N′′′-pentamethylimidazolium,[19] N,N,N′,N′′,N′′′-pentamethylpyrazol,[20] and N,N′,N′′-octarene,[24] showed high catalytic activity and cis-1,4 selectivity toward conjugated diene polymerization.[10–20] The chemical structures of ancillary ligands could steer the behavior of the coordination polymerization and characteristics of the resulting polymers. The concept that the ligand plays regulatory role in the catalytic behavior of the catalyst was used to design Ziegler-Natta rare-earth metal catalysts. In the presence of triisobutylaluminum (AlBu3), neodymium complexes containing heterocyclic Schiff base[21] as precatalysts, 8-hydroxyquinolines,[21] quinolinylcarboxylates,[21] or NCN-pincer ligand[23] show high catalytic activity for isoprene polymerization with high cis-1,4 stereospecificity (95%–98%).

Neodymium carbene (NHC) has become an organo-catalyst and ubiquitous ligand in organometallic chemistry because of its extraordinary electron richness and facile access to structurally diverse analogues.[22] Scandium trialkyl complexes containing...
N-heterocyclic carbene ligand have been reported as precatalysts for α-olefin polymerization with excellent catalytic activity.\cite{36,37} We also reported that the copolymerization of ethylene with propylene was realized by vanadium complexes containing NHC ligands and both the catalytic activity and microstructure of the resulting copolymers were influenced by the chemical structure of the NHC ligands.\cite{38,39} Therefore, introduction of NHC ligand to NdCl\(_2\) facilitates the coordination polymerization of the conjugated dienes. Herein, the synthesis with both high activity and regioselectivity for the coordination is of great interest for the introduction of NHC ligand to NdCl\(_2\). Ethylene with propylene was realized by vanadium complexes.\cite{40,41} The Nd complex of NdCl\(_2\) was measured by titration according to the reported methods.\cite{40}

**EXPERIMENTAL**

**General Considerations**

All manipulations of air- and moisture-sensitive compounds were performed in a nitrogen atmosphere using standard Schlenk techniques or under a nitrogen atmosphere in a drybox. Tetrahydrofuran (THF, Beijing Chemical Works) was distilled under nitrogen atmosphere and refluxed over sodium benzophenone for dehydration, and then stored in the drybox in the presence of molecular sieves (4Å). NdCl\(_2\)·THF\cite{41} and NHC ligand\cite{42} were prepared according to the reported methods. Chlorobenzene (C\(_6\)H\(_5\)Cl, Tianjin Fuchen Chemical Co.) was freshly distilled from phosphoric anhydride. Hexanes and cyclohexane (Beijing Yanshan Petrochemical Co.) were dried over calcium hydride (Ca\(_2\)) and distilled before use. Isoprene (purity: 99.9%, Beijing Yanshan Petrochemical Co.) was freshly distilled from Ca\(_2\) before use. Butadiene (Beijing Yanshan Petrochemical Co.) and triisobutylaluminium solution in hexanes (0.74 mol·L\(^{-1}\)) were used as received.

**Synthesis and Characterization of Nd Complexes**

The NHC ligands with different substitutes at the N-phenyl rings were prepared according to the reported method.\cite{40} The THF solution of 1,3-(2,6-iPr\(_2\)C\(_6\)H\(_4\))\(_2\)N(CH=)\(_2\)C\(_6\)H\(_5\) (C\(_{12}\)H\(_{11}\)) was added to a flask with NdCl\(_2\)·THF (1.15 g, 2.7 mmol) and THF (15 mL). Then the mixture was stirred for 5 h at 25 °C. The resultant solution was filtered through a Celite pad, and the filter cake was washed by THF. The solvent was further removed in vacuo.

Ndc\(_{12}\)(1,3-(2,6-iPr\(_2\)C\(_6\)H\(_4\))\(_2\)N(CH=)\(_2\)C\(_6\)H\(_5\))·THF (Nd\(_{1}\)) was obtained as white solid. Anal. Calcd. for C\(_{23}\)H\(_{35}\)Cl\(_2\)NdO: C 49.50, H 5.54, N 4.28, Nd 22.02%. Found: C 49.00, H 5.33, N 4.55, Nd 21.87%. Nd\(_3\) was obtained as white solid in a yield of 91%. Anal. Calcd. for C\(_{39}\)H\(_{47}\)Cl\(_3\)Nd\(_2\): C 47.88, H 5.14, N 4.28, Nd 23.00%. Found: C 47.29, H 4.88, N 4.87, Nd 22.66%.

**Procedure of Conjugated Diene Polymerization**

All the operations were conducted under an atmosphere of dry nitrogen. For the polymerization using the in situ prepared catalyst, the conjugated diene monomers (butadiene or isoprene) and solvent were introduced into a vessel and Al\(_2\)Bu\(_3\) was added. Then, the solution of Nd complex was introduced into the vessel to start the coordination polymerization of conjugated diene at a defined temperature. For the polymerization using the aged catalyst, the mixture of Nd complex and Al\(_2\)Bu\(_3\) in the presence of different amounts of monomer was aged at the fixed temperature for the designated time in advance. The conjugated diene monomers (butadiene or isoprene) and solvent were introduced into a vessel and then the aged catalyst solution was added to start the coordination polymerization of conjugated diene at a defined temperature. The vessel with stirring was placed in a bath with constant temperature during the polymerization. After a definite time, the polymerization was terminated by addition of ethanol containing 1% of 2,6-di-tert-butyl-4-methylphenol. Then the mixture was poured into ethanol containing a small amount of hydrochloric acid. The precipitated polymer was further washed by ethanol and then was dried under vacuum at 45 °C until a constant weight.

**Characterization of Resulting Polymers**

Molecular weights of resulting polybutadienes and polyisoprenes, i.e. number-average molecular weight (M\(_n\)), weight-average molecular weight (M\(_w\)), and polydispersity index (PDI, M\(_w\)/M\(_n\)), were determined by gel permeation chromatography (GPC) using a Waters 1515-2410 system equipped with Waters RI 2410 and UV 2489 detectors and four Waters styragel HT3-4.5-6 columns (Milford, MA). The polymer sample was dissolved in THF with concentration of 2 g·L\(^{-1}\). The THF was used as eluent and the flow rate of the mobile phase was 1.0 mL·min\(^{-1}\) at 30 °C. The calibration curve was obtained by polystyrene standard. The contents of cis-1,4, trans-1,4, and 1,2 structures of resulting polydiene were determined using FTIR analysis according to the reported method.\cite{43} The film of the copolymer was prepared by spreading a small amount of dichloromethane (CH\(_2\)_Cl\(_2\)) solution of the copolymer on the slice of KBr after the evaporation of CH\(_2\)_Cl\(_2\). The copolymer was characterized on a Nexus 670 FTIR spectrophotometer (Nicolet, Madison, WI).

**RESULTS AND DISCUSSION**

**Synthesis of Nd Complexes with NHC Ligands**

The reaction of equimolar quantities of NHC ligands and NdCl\(_2\)·THF (x = 1,2,3) in THF under nitrogen at 25 °C for 5 h afforded the Nd complexes Nd\(_{1}\)–Nd\(_{3}\), as shown in Scheme 1. All the paramagnetic complexes Nd\(_{1}\)–Nd\(_{3}\) were characterized by elemental analysis and the Nd contents of these complexes were determined by titration. The results indicated that one THF molecule was incorporated in the complexes of Nd\(_{2}\) and Nd\(_{3}\), respectively. Comparably, no THF molecule existed in Nd\(_{1}\) complex due to the bulky isopropyl substitutes on phenyl rings in ligand.
Coordination Polymerization of Conjugated Dienes Using Nd1 as Precatalysts

Butadiene polymerization with the unaged Nd1/AlBu3 catalytic system

The neodymium complex Nd1 containing NHC ligand with bulky isopropyl substituents at the ortho positions of the phenyl rings was employed as precatalysts and triisobutylaluminum (Al/Bu3, Al) was used as a cocatalyst to investigate the coordination polymerization of conjugated dienes (butadiene and isoprene). Butadiene polymerizations and isoprene polymerizations under various Al/Nd molar ratios, polymerization temperatures (Tp), and polymerization time (tp) were investigated using prepared Nd1/AlBu3 catalytic system, in which the active centers formed in situ in the polymerization system. The experimental results are summarized in Table 1. It can be seen from the data in Table 1 that the conversion of butadiene and catalytic activity increased along with an increase in Al/Nd molar ratio (entries 1–3 and 5–8). The neodymium complex Nd1 displayed good catalytic activity (2.8 × 10¹⁴ g·mol⁻¹·mol⁻¹ of Nd) for butadiene polymerization at Al/Nd molar ratio of 50 (entry 4 in Table 1), albeit poor catalytic activities were observed at low Al/Nd molar ratio (entries 1 and 2 in Table 1). Remarkably, polybutadiene with high cis-1,4 content of ~99.0% and high molecular weight (Mw = 540 kg·mol⁻¹) was obtained. The conversion of butadiene could be improved obviously from 6% to 20% at the Al/Nd ratio of 15 by increasing Tp from 25 °C to 50 °C. As Al/Nd molar ratio increased from 15 to 50, the conversion of butadiene increased from 20% to 60%, and the catalytic activity increased from 1.4 × 10¹⁴ to 4.1 × 10¹⁴ g·mol⁻¹·mol⁻¹ of Nd (entries 5–8 in Table 1). Polybutadiene with high molecular weight (Mw = 470 kg·mol⁻¹) and uniform molecular weight distribution was afforded at the Al/Nd molar ratio of 15 (entry 5 in Table 1). However, the molecular weight distribution became broader (4.6–14.0) indicating that multiple active species formed or chain transfer reaction speeded up with increasing Al/Nd molar ratio. Interestingly, the distinguished cis-1,4 selectivity kept almost unchanged (97.9%–98.8%) in a broad range of Al/Nd molar ratio from 15 to 50 (entries 5–8 in Table 1). Overall, polybutadienes with high cis-1,4 contents were obtained by polymerization of butadiene using Nd1/AlBu3 catalytic system. The Al/Nd molar ratio and polymerization temperature have an obvious influence on the catalytic activity, molecular weight, and molecular weight distribution.

Isoprene polymerization with the unaged Nd1/AlBu3 catalytic system

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zation, Nd1 containing NHC ligand with bulky isopropyl substituents at the ortho positions of the phenyl rings was also selected as precatalyst for the coordination polymerization of isoprene herein. The effects of Al/Nd molar ratio and polymerization temperature on isoprene polymerization were investigated using unaged Nd1/AlBu3 catalytic system. The results are summarized in Table 1 (entries 9–20). The isoprene polymerization was carried out and the yield of polymer was negligible under the similar polymerization conditions to those for butadiene polymerization. Negligible polyisoprene was obtained in the mixed solvent of hexane and cyclohexane, possibly due to the poor solubility of catalyst in the polymerization system. Chlorobenzene was firstly selected as a good solvent in the polymerization of isoprene to investigate systematically the effects of chemical structure of ligands, preparation process of catalytic system, and polymerization conditions on the catalytic activity and the microstructure of the resulting polymers. The amount of cocatalyst, which is usually expressed by the molar ratio of Al/Nd, has a significant influence on the catalytic activity and molecular weight and molecular weight distribution of the resulting polyisoprenes. It can be seen from Table 1 that an increase in isoprene conversion and catalytic activity could be noticed as the Al/Nd molar ratio increased (entries 10–14). The isoprene conversion of 21% and the catalytic activity of 5.0 × 10^4 g·mol⁻¹·s⁻¹ of Nd at Tₚ of 50 °C could be obtained at Al/Nd molar ratio of 30 (entry 14 in Table 1). The molecular weight of the resulting polyisoprene decreased with an increase in Al/Nd molar ratio probably due to the more chain transfer reaction to AlBu₃ at higher Al/Nd molar ratio. It is worth noting that the microstructure of the resulting polyisoprenes was not affected by the change of Al/Nd molar ratio. As shown in Table 1, polyisoprenes with cis-1,4 content of ca. 96% could be prepared at Tₚ of 50 °C when the Al/Nd molar ratio increased from 10 to 30.

Isoprene polymerizations were carried out at polymerization temperature (Tₚ) ranging from 30 °C to 60 °C and the results are given in Table 1 (entries 15–20). It can be clearly observed that Tₚ influenced the isoprene conversion, catalytic activity, and molecular weight, molecular weight distribution, and cis-1,4 content of the resulting polyisoprenes. It can be seen from Table 1 that isoprene conversion greatly increased from 50% to 84% and catalytic activity increased from 3.5 × 10^4 to 5.9 × 10^4 g·mol⁻¹·s⁻¹ of Nd when Tₚ was elevated from 30 °C to 50 °C (entries 15–20). However, the overall catalytic activity and isoprene conversion decreased when Tₚ was higher than 50 °C since the catalyst deactivation became more prominent at higher polymerization temperature. Similar to other reported catalytic systems, a slight decrease in cis-1,4 content in polymer products with increasing polymerization temperature can be observed. The GPC traces of the resulting polyisoprenes prepared at different temperatures from 30 °C to 50 °C are displayed in Fig. 1. It can be seen that all the GPC traces of the resulting polyisoprenes exhibit bimodal and broad molecular weight distribution. The overall molecular weight decreased greatly and the molecular weight distribution became broad with an increase in Tₚ as shown in Fig. 2. The chain transfer side reaction could be accelerated with increasing polymerization temperature and thus the overall molecular weight decreased greatly.

**Isoprene polymerization using the aged Nd1/AlBu3 catalytic system**

The catalyst components of Nd1 and AlBu3 reacted to form the active centers prior to the addition to the monomer solution, which is also referred to as catalyst aging process. Both the aging temperature (Tₐ) and aging time (tₐ) played important roles in the formation of active centers in the aging process of catalyst. The obtained catalyst solution after the aging process was used for isoprene polymerization. The experimental results of isoprene polymerization using the above aged catalyst are displayed in Table 2 (entries 2–7) and isoprene polymerization using the unaged catalyst is also displayed in Table 2 (entry 1) for comparison. It can be found from Table 2 that isoprene conversion increased greatly from 2% to 25%–95% and catalytic activity increased greatly from 0.2 × 10^4 to 6.7 × 10^4 g·mol⁻¹·s⁻¹ of Nd by using the aged catalyst instead of unaged catalyst under similar polymerization conditions. The catalytic behavior of aged Nd1/AlBu3 catalytic system is affected by Tₚ. The isoprene conversion increased from 25% to 87% and the catalytic activity increased from 1.8 × 10^4 to 6.1 × 10^5 g·mol⁻¹·s⁻¹ of Nd along with an increase in Tₚ from 40 °C to 60 °C at tₐ of 30 min, while the cis-1,4 selectivity kept at around 96.5% (entries 2, 4, and 7 in Table 2). The isoprene conversion and catalytic activity increased while the
molecular weight of the resulting polymers decreased with an increase in $t_a$ (entry 2 versus 3, 4 versus 5, and 6 versus 7 in Table 2). All the results indicate that the catalytic activity could be remarkably improved by aging process of the catalysts.

The reaction of Nd complex with Al/Bu$_3$ results in the formation of Nd compounds with $\sigma$-alkyl bonds in the absence of monomer. However, the reaction of Nd complex with Al/Bu$_3$ results in the formation of the $\pi$-alkyl Nd complexes in the presence of monomer, which exhibit a higher stability than that of Nd compounds with $\sigma$-alkyl bonds. The isoprene polymerization using the aged Nd/Al/Bu$_3$ catalyst in the presence of isoprene (Ip/Nd = 100) prepared for different aging time ($t_a$) was further investigated and the experimental results are displayed in Table 2 (entries 8–12). In order to distinguish two different aging methods and express clearly, aging method without isoprene is expressed as method A, while aging method with isoprene is expressed as method B. Isoprene conversion in the polymerization process could reach 99% and the catalytic activity could reach $6.9 \times 10^4$ g mol$^{-1}$ of Nd even at $T_P$ of 0 °C for polymerization time of 14 h by using the aged ternary catalyst with $t_a$ of 3 min. A very high conversion of 93% and catalytic activity of $6.5 \times 10^4$ g mol$^{-1}$ of Nd can also be obtained with the aging time of 9 min, which implies enough operation time. However, monomer conversion decreased to 21% if $t_a$ was 60 min, which was a different trend from that in aging method A. The molecular weight of the obtained polyisoprenes was also affected by aging time. The molecular weight of polyisoprenes increased with an increase in aging time, which might be attributed to the decreasing amount of active species in the catalytic system with increased $t_a$. The aging time hardly affected the cis-1,4 content of the resulting polyisoprenes, indicating that the catalytic system displayed high cis-1,4 selectivity at even at long aging time.

Although high isoprene conversion and preparation of polyisoprene with high molecular weight were realized, the molecular weight distribution was still broad. Therefore, the isoprene polymerizations with ternary catalyst (B) with low Al/Nd molar ratios were further conducted at low $T_P$ of −15 °C.

As shown in Table 2 (entries 13–22), the molecular weight distribution of resulting polyisoprenes at low $T_P$ of −15 °C became much narrower than those of polyisoprenes synthesized at $T_P$ of 0 and 25 °C, although the conversion of isoprene and catalytic activity decreased to 21%−53% and $1.5 \times 10^4$−$3.7 \times 10^4$ g mol$^{-1}$ of Nd, respectively. The isoprene conversion of 53% could be obtained even the Al/Nd molar ratio was decreased to 8 by optimization of $t_a$ (entry 17 in Table 2). The regular effect of Al/Nd molar ratio on isoprene conversion was not observed. Very importantly, polyisoprenes with high molecular weight ($M_n$) ranging from 210 kg mol$^{-1}$ to 530 kg mol$^{-1}$ and narrow molecular weight distribution ($M_n/M_w = 1.9$−$2.7$) could be obtained at various Al/Nd molar ratios and $t_a$'s at low $T_P$ of −15 °C (entries 13–22 in Table 2). The relatively unimodalGPC traces of resulting polyisoprenes are displayed in Fig. 3. The influences of $T_a$ on $M_n$ and $M_w/M_n$ were different at various Al/Nd molar ratios due to the complicated reaction of Nd with Al/But in the presence of isoprene. Polyisoprene with high molecular weight (530 kg mol$^{-1}$) and narrow molecular weight distribution ($M_n/M_w = 2.4$) could be successfully synthesized at $T_P$ of −15 °C using the ternary catalyst (Ip/Al/Nd molar ratio = 20:20:1000).

### Table 2: Polymerization of isoprene catalyzed by aged Nd1/Al/But catalyst.

| Entry | Al/Nd | $T_a$ (°C) | $t_a$ (min) | $T_P$ (°C) | $t_0$ (h) | Yield (g) | Conv. (%) | Activity x 10$^{-4}$ (g mol$^{-1}$ of Nd) | $M_n$ (kg mol$^{-1}$) | $M_w/M_n$ | Microstructure (%) |
|-------|-------|------------|-------------|------------|------------|-----------|----------|----------------------------------------|----------------------|------------|-------------------|
|       |       |            |             |            |            |           |          |                                        |                      |            | cis-1,4           |
| 1a    | 15    | –          | –           | 25         | 3          | 0.03      | 2        | 0.2                                                  | 6.7                  | 280        | 4.4               |
| 2a    | 15    | 40         | 30          | 25         | 3          | 0.35      | 25       | 1.8                                                  | 6.0                  | 510        | 8.0               |
| 3a    | 15    | 40         | 60          | 25         | 3          | 1.33      | 95       | 6.7                                                  | 6.0                  | 280        | 4.4               |
| 4a    | 15    | 50         | 50          | 25         | 3          | 1.19      | 85       | 6.5                                                  | 6.0                  | 510        | 8.0               |
| 5a    | 15    | 50         | 60          | 25         | 3          | 1.20      | 86       | 6.5                                                  | 6.0                  | 280        | 4.4               |
| 6a    | 15    | 60         | 10          | 25         | 3          | 0.57      | 41       | 2.9                                                  | 6.0                  | 510        | 8.0               |
| 7a    | 15    | 60         | 30          | 25         | 3          | 1.22      | 87       | 6.1                                                  | 6.0                  | 140        | 3.5               |
| 8b    | 15    | 50         | 3           | 0          | 14         | 2.77      | 99       | 6.9                                                  | 6.0                  | 490        | 5.9               |
| 9b    | 15    | 50         | 9           | 0          | 14         | 2.60      | 93       | 6.5                                                  | 6.0                  | 680        | 8.6               |
| 10b   | 15    | 50         | 15          | 0          | 14         | 1.40      | 50       | 3.5                                                  | 3.5                  | 730        | 6.4               |
| 11b   | 15    | 50         | 30          | 0          | 14         | 0.53      | 19       | 1.3                                                  | 1.3                  | 840        | 5.6               |
| 12b   | 15    | 50         | 60          | 0          | 14         | 0.59      | 21       | 1.5                                                  | 1.5                  | 850        | 4.9               |
| 13c   | 10    | 50         | 3           | −15        | 48         | 0.59      | 21       | 1.5                                                  | 1.5                  | 300        | 2.7               |
| 14c   | 10    | 50         | 6           | −15        | 48         | 1.20      | 43       | 3.0                                                  | 3.0                  | 320        | 2.2               |
| 15c   | 10    | 50         | 9           | −15        | 48         | 1.04      | 37       | 2.6                                                  | 2.6                  | 210        | 2.1               |
| 16c   | 10    | 50         | 12          | −15        | 48         | 1.23      | 44       | 3.1                                                  | 3.1                  | 420        | 2.2               |
| 17c   | 8     | 50         | 3           | −15        | 48         | 1.48      | 53       | 3.7                                                  | 3.7                  | 420        | 2.4               |
| 18c   | 8     | 50         | 6           | −15        | 48         | 0.95      | 34       | 2.4                                                  | 2.4                  | 410        | 2.0               |
| 19c   | 8     | 50         | 9           | −15        | 48         | 1.09      | 39       | 2.7                                                  | 2.7                  | 440        | 1.9               |
| 20c   | 6     | 50         | 3           | −15        | 48         | 1.18      | 41       | 2.9                                                  | 2.9                  | 360        | 2.2               |
| 21c   | 6     | 50         | 6           | −15        | 48         | 1.04      | 37       | 2.6                                                  | 2.6                  | 380        | 2.4               |
| 22c   | 6     | 50         | 9           | −15        | 48         | 1.40      | 50       | 3.5                                                  | 3.5                  | 530        | 1.9               |

* a Polymerization condition: Nd complex (Nd$_{10}$): 20 μmol, Ip: 20 mmol, Ip/Nd = 1000, cocatalyst: Al/But, solvent: chlorobenzene (8 mL), aging method A; b Polymerization condition: Nd complex (Nd$_{10}$): 40 μmol, Ip: 40 mmol, Ip/Nd = 1000, cocatalyst: Al/But, solvent: chlorobenzene (16 mL), aging method B; c Polymerization condition: Nd complex (Nd$_{10}$): 40 μmol, Ip: 20 mmol, Ip/Nd = 500, cocatalyst: Al/But, solvent: chlorobenzene (8 mL), aging method B; d Determined by GPC with respect to a polystyrene standard; e Determined by FTIR characterization of polyisoprene.
100/6/1) by aging method B. Moreover, higher cis-1,4 selectivity (96.9%–97.6%) was observed using the ternary catalyst than that using unaged binary catalyst (entries 8–22 in Table 2). The representative FTIR spectra of resulting polyisoprenes prepared by using aged ternary catalyst and unaged binary catalyst are shown in Fig. 4. The characteristic bands at 836 and 889 cm$^{-1}$ for cis-1,4 units in polyisoprene are clearly observed. The absence of characteristic band at 910 cm$^{-1}$ for 1,2- and Trans-1,4 units and bands at 1150 and 1385 cm$^{-1}$ (for trans-1,4 units) suggests that the content of 1,2- and Trans-1,4 units in the resulting polyisoprene was negligible, which is usually observed in polyisoprene prepared by Ziegler-Natta Nd catalysts.$^{27-32}$ As shown in Fig. 4, a stronger band at 1128 cm$^{-1}$ and a weak band at 889 cm$^{-1}$ can be observed in the FTIR spectrum of polyisoprene prepared by the aged ternary catalyst as compared with that of polyisoprene prepared by the unaged binary catalyst, indicating that the aged ternary catalyst displayed higher cis-1,4 selectivity than that of the unaged binary catalyst.

The results of isoprene polymerization using aged catalyst indicate that the catalytic activity could be improved obviously by aged catalyst. Polyisoprene with high molecular weight and broad molecular weight distribution could be afforded by using aged Nd1/Al/Bu3 catalyst system, while polyisoprene with high molecular weight and narrow molecular weight distribution could be afforded by using aged ternary catalyst (Ip/Nd1/Al/Bu3).

**Effect of Ligands in Nd Complexes on Catalytic Activity and Microstructure of Resulting Polydienes**

Isoprene polymerizations by using Nd complexes containing NHC ligands with ethyl (Nd2) or methyl substitutes (Nd3) at the N-aryl ring were investigated. The experimental results of isoprene polymerizations at various Al/Nd molar ratios are summarized in Table 3. The aged ternary catalysts (Ip/Nd2/Al/Bu3 and Ip/Nd3/Al/Bu3) prepared by aging method B exhibited both good activity and high cis-1,4 selectivity at relatively high Al/Nd molar ratios. At optimized Al/Nd molar ratio, the isoprene conversion and catalytic activity for Nd2 were 61% and 4.4 × 10$^4$ g mol$^{-1}$ h$^{-1}$ of Nd, respectively. Meanwhile, the isoprene conversion and catalytic activity for Nd3 were 83% and 6.0 × 10$^4$ g mol$^{-1}$ h$^{-1}$ of Nd, respectively. Polyisoprenes prepared by using precatalyst Nd2 at the Al/Nd ratios of 15 and 20 exhibited high cis-1,4 content of 97.8% (entries 1 and 2 in Table 3). The molecular weight and molecular weight distribution of the resulting polymers were significantly influenced by the structure of the Nd complex. Compared to polyisoprenes prepared with Nd1, polyisoprenes with the drastically lower molecular weight (Mw = 12–51 kg mol$^{-1}$ for Nd2 and 15–76 kg mol$^{-1}$ for Nd3) and unimodal molecular weight distribution (Mw/Mn = 1.7–2.6) were afforded by using Nd2 or Nd3 as the precatalyst (entries 1–7 in Table 3). The result suggests that a uniform active species existed during polymerization of isoprene using Nd2 or Nd3 as precatalyst.

**Table 3** Polymerization of isoprene using Nd2/Al/Bu3 and Nd3/Al/Bu3 catalytic systems. a

| Entry | Complex | Al/Nd | Yield (g) | Conv. (%) | Activity b | Mw Mz $^c$ (kg mol$^{-1}$) | Mw/Mz $^c$ | cis-1,4 | trans-1,4 | cis/cis-1,4 | Mw/Mn $^d$ | Microstructure (%) | $\eta_{calcd}^e$ | $\eta_{calcd}/\eta_{theo}$ |
|-------|---------|------|----------|------------|------------|--------------------------|-------------|--------|----------|-------------|-------------|-------------------|---------------|-------------------|
| 1     | Nd2     | 15   | 0.72     | 25         | 1.8        | 51                       | 2.1         | 97.8   | 0.0      | 0.0         | 2.2         | 2.9               | 0.73          |                   |
| 2     | Nd2     | 20   | 1.76     | 61         | 4.4        | 13                       | 1.9         | 97.8   | 0.0      | 0.0         | 2.2         | 23.9              | 5.98          |                   |
| 3     | Nd2     | 30   | 1.30     | 45         | 3.3        | 12                       | 1.7         | 96.6   | 0.0      | 0.0         | 3.4         | 17.7              | 4.43          |                   |
| 4     | Nd3     | 15   | 0.60     | 21         | 1.5        | 76                       | 2.6         | 97.8   | 0.0      | 0.0         | 2.2         | 2.0               | 0.50          |                   |
| 5     | Nd3     | 20   | 0.86     | 30         | 2.2        | 71                       | 2.2         | 97.6   | 0.0      | 0.0         | 2.4         | 2.5               | 0.63          |                   |
| 6     | Nd3     | 30   | 1.70     | 59         | 4.3        | 17                       | 2.1         | 97.6   | 0.0      | 0.0         | 2.4         | 2.0               | 0.53          |                   |
| 7     | Nd3     | 40   | 2.39     | 83         | 6.0        | 15                       | 1.9         | 97.7   | 0.0      | 0.0         | 2.3         | 28.1              | 7.03          |                   |

a Polymerization conditions: Nd complex ($\eta_{nd}$): 40 μmol; Ip: 40 mmol, Ip/Nd = 1000, cocatalyst: Al/Bu3, solvent: chlorobenzene (16 mL), $t_p = 48$ h, $T_p = -15^\circ$C, water content in CB: 80 ppm. Nd complex, Al/Bu3, and Ip (Ip/Nd = 100) were aged at 50°C for 9 min; b determined by FTIR characterization of polyisoprene; $c$ in unit of 10$^9$ g mol$^{-1}$ of Nd; d Determined by GPC with respect to a polystyrene standard; $e$ Determined by GPC with respect to a polystyrene standard; $f$ Determined by GPC with respect to a polystyrene standard.
The average number of polymer chains ($n_{\text{calc}}$) can be calculated by the ratio of $M_g$ and $M_p$, due to the narrower molecular weight distribution, where $M_p$ is the weight of the resulting polyisoprene and $M_g$ is number-average molecular weight of the resulting polyisoprene (kg·mol$^{-1}$). The theoretical numbers of polymer chains ($n_{\text{theo}}$) in the copolymerization system were 4.0 $\times$ 10$^{-5}$ mol. It can be observed that $n_{\text{calc}}$ is much higher than $n_{\text{theo}}$ for Nd2/AlBu3 catalytic system (Al/Nd = 20 and 30) and Nd3/AlBu3 catalytic system (Al/Nd = 30 and 40), which is attributed to serious chain-transfer reaction to a cocatalyst during isoprene polymerization. The molecular weight and molecular weight distribution of resulting polyisoprenes are greatly affected by the structure of the ligand (as shown in Fig. 5). Polyisoprenes with the low molecular weights and narrow molecular weight distributions were obtained by using complexes Nd2 and Nd3 bearing NHC ligands with ethyl or methyl substitutes at the N-aryl ring due to the combination of steric hindrance effect and electronic effect of the ligands. Comparatively, polyisoprenes with the higher molecular weights were prepared by using complex Nd1 containing NHC ligand with bulky isopropyl substitutes. Therefore, polyisoprenes with low or high molecular weight and narrow molecular weight distribution could be afforded by changing the substitutes at the N-aryl rings of the Nd complex. The effect of ligand on the molecular weight of resulting polyisoprenes also indicates that the NHC ligand was associated with the active Nd centers during polymerization of isoprene.

**CONCLUSIONS**

A new binary catalytic system containing N-heterocyclic carbenes-ligated neodymium complex and AlBu3 was developed for highly cis-1,4 selective polymerization of butadiene and isoprene. The Nd1/AlBu3 catalytic system provided high cis-1,4 selectivity up to ~99% for polymerization of butadiene. The Al/Nd molar ratio and polymerization temperature had little effect on the regioselectivity, whereas the conversion of butadiene and catalytic activity increased with an increase in Al/Nd molar ratio. The new unaged binary catalytic system possessed high catalytic activity for the polymerization of isoprene, affording polyisoprenes with the high cis-1,4 content (95.8%−97.3%) and molecular weight (260−670 kg·mol$^{-1}$). Importantly, the activity of the aged catalyst was superior over the unaged catalyst. Aging Nd1 and AlBu3 in the presence of isoprene was beneficial to forming uniform active species and thus polyisoprenes with the narrow molecular weight distribution ($M_w/M_n = 1.9−2.7$) could be obtained. Meanwhile, the resulting polyisoprenes had the high molecular weight ($M_w = 210−530$ kg·mol$^{-1}$) and high cis-1,4 content (96.5%−97.6%). The structure of NHC ligand played a significant role in controlling the molecular weight of resulting polyisoprenes. Polyisoprenes with the low molecular weight ($M_w = 12−76$ kg·mol$^{-1}$) and narrow molecular weight distribution ($M_w/M_n = 1.7−2.6$) were obtained by using Nd complexes bearing the less sterically bulky NHC ligand (Nd2 and Nd3). Remarkably, the distinguished cis-1,4 selectivity almost kept unchanged during isoprene polymerization under broad ranges of Al/Nd molar ratio, polymerization temperature, aging time, and aging temperature. These results would provide significant insight into the design of catalyst for highly 1,4-cis selective polymerization of conjugated dienes.

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