

A HIGHLY ACTIVE NEODYMIUM CHLORIDE ISOPROPANOL COMPLEX/MODIFIED METHYLALUMINOXANE CATALYST FOR PREPARING POLYISOPRENE WITH HIGH *CIS*-1,4 STEREOSPECIFICITY AND NARROW MOLECULAR WEIGHT DISTRIBUTION*

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Abstract Neodymium chloride isopropanol complex ($\text{NdCl}_3 \cdot 3\text{iPrOH}$) activated by modified methylaluminoxane (MMAO) was examined in isoprene polymerization in hexane, with regards to Nd compounds, aluminum (Al) compounds, $[\text{Al}]/[\text{Nd}]$ ratio, polymerization temperature and time. $\text{NdCl}_3 \cdot 3\text{iPrOH}$ exhibited high activity producing polymers featuring high *cis*-1,4 stereospecificity (> 96%), very high molecular weight ($M_n > 1.0 \times 10^6$) and fairly narrow molecular weight distribution (MWD, $M_w/M_n < 2.0$) simultaneously. In comparison, neodymium isopropoxide also showed high activity providing polymers with narrow MWD ($M_w/M_n = 2.07$), but somewhat low *cis*-1,4 content (*ca.* 92%), while neodymium chloride had no activity under present polymerization conditions. The Al compounds affected the polymer yield in the order of $\text{Al}(i\text{-Bu})_3 > \text{MMAO} > \text{Al}(i\text{-Bu})_2\text{H}$. MMAO as cocatalyst afforded polyisoprene with high M_n over 1.0×10^6 , whereas as stronger chain transfer agent than MMAO, $\text{Al}(i\text{-Bu})_3$ and $\text{Al}(i\text{-Bu})_2\text{H}$ yielded polymers with low M_n (1.0×10^5 – 8.0×10^5). $\text{NdCl}_3 \cdot 3\text{iPrOH}/\text{MMAO}$ catalyst showed a fairly good catalytic activity even at relatively low $[\text{Al}]/[\text{Nd}]$ ratio of 30, and the produced polymer remained high *cis*-1,4 content of 95.8% along with high M_n over 1.0×10^6 even at elevated temperatures up to 70°C. The polymerization rate is of the first order with respect to the concentration of isoprene. The mechanism of active species formation was discussed preliminarily.

Keyword: Isoprene; Neodymium; Molecular weight distribution; *Cis*-1,4 stereospecificity; Ziegler-Natta polymerization.

INTRODUCTION

Conventional alkylaluminum (AlR_3) activated rare earth catalysts, especially Nd-based catalysts are well known to exhibit high *cis*-1,4 stereospecificity (> 95%) in both homopolymerization of butadiene and isoprene as well as their copolymerization^[1–6]. Typical AlR_3 -activated Nd catalysts are mostly divided into two classes, which are ternary systems derived from Nd carboxylate, AlR_3 and a chlorine-containing compound^[7–11], as well as binary systems derived from NdCl_3 electronic donor complex and AlR_3 ^[12–16]. These catalysts achieve good polymer yields in aliphatic hydrocarbons to provide polymers with excellent properties, which are suitable to the practical use as tires and other elastic materials. However, the molecular weight (M_n) and molecular weight distribution (MWD) of the produced polymers are not well controlled, which is attributable to the multiple natures of active

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centers and chain transfer agent of AlR_3 .

In recent years, a variety of rare earth catalysts using aluminoxane or AlR_3 /borate as cocatalyst have been developed for 1,3-dienes polymerization. These catalysts have turned out to show some distinguished features to the conventional Ziegler-Natta type catalysts activated by AlR_3 . Lanthanocene (Sm , Gd , etc.)^[17, 18] in combination with MMAO or AlR_3 /borate affords single-active site species in toluene, and it is of great importance that they are able to induce the living *cis*-1,4 polymerization of butadiene to achieve the simultaneous controlling of M_n and *cis*-1,4 stereospecificity. Cationic Y alkyl species bearing a PNP (bis(phosphinophenyl)-amido) ancillary ligand^[19] can initiate the living *cis*-1,4 polymerization of both isoprene and butadiene and their copolymerization, and the produced polymers have an extremely high *cis*-1,4 contents (*ca.* 99%) and narrow MWD ($M_w/M_n = 1.13$). Binuclear Y dialkyl complex polymerizes isoprene to produce isotactic 3,4-polyisoprene (up to 100%, mmmm > 99%) with high M_n (5.0×10^5) and narrow MWD ($M_w/M_n = 1.60$)^[20]. However, these catalysts work well in aromatic medium, such as toluene and chlorobenzene, a more or less toxic solvent.

On the other hand, with respect to the combination of Nd catalyst and aluminoxane or AlR_3 /borate as cocatalyst for the *cis*-1,4 polymerization of butadiene and isoprene, the Nd(carboxylate)₃/MAO catalysts induce 1,3-diene polymerizations^[5, 8, 21] to form polymers with broad MWD ($M_w/M_n = 3.0\text{--}11$). Allyl Nd complexes provide single-site catalyst systems in 1,3-butadiene polymerization^[22, 23], while the complexes are rather difficult to prepare and handle. Nd(allyl)₂Cl(MgCl₂)₂(THF)₄ complex/MAO catalyst exhibits high activity to produce polyisoprene having *cis*-1,4 content up to 98.5%, controlled M_n and relatively narrow MWD ($M_w/M_n = 1.2\text{--}1.7$)^[24], whereas the mixture of toluene and hexane is used as solvent. Nd metallocene/ AlR_3 /[Ph₃C][B(C₆F₅)₄] catalysts are active to provide polybutadiene with very narrow MWD ($M_w/M_n < 1.25$)^[18], however the microstructures of resultant polymers strongly depend on the kind of AlR_3 , low *cis*-1,4 content of 65.9% obtained in the case of $\text{Al}(i\text{-Bu})_3$ and high *trans*-1,4 structure of 85.2% obtained in the case of AlMe_3 .

In our previous work, it was found that Nd isopropoxide (Nd(O^{*i*}Pr)₃) catalysts exhibited high activity in isoprene polymerization in heptane when combined with MAO, MMAO (in toluene) or [HNMe₂Ph]⁺[B(C₆F₅)₄][−] (dimethylphenylammonium tetrakis(pentafluorophenyl)borate)/ $\text{Al}(i\text{-Bu})_3$ as cocatalyst. The obtained polymers show narrow MWD but somewhat low *cis*-1,4 content (< 91%)^[25–28]. The *cis*-1,4 contents is improved to 94% by addition of chlorine-containing compound (*e.g.* *t*-BuCl, Et₂AlCl, Me₃SiCl) to the aluminoxane-activated Nd(O^{*i*}Pr)₃ catalyst. However, the preparation method and [Cl]/[Nd] ratio of Nd(O^{*i*}Pr)₃/MAO/*t*-BuCl catalyst remarkably affect the catalytic activity.

NdCl₃ electronic donor complex, for instance, NdCl₃ isopropanol complex (NdCl₃·3^{*i*}PrOH) was reported to be very active in *cis*-1,4 polymerization of 1,3-dienes with AlR_3 as cocatalyst^[12–16]. Hence, it was expected that NdCl₃ electronic donor complex activated by aluminoxane would display high *cis*-1,4 stereospecificity in isoprene polymerization. In this study, NdCl₃·3^{*i*}PrOH, a preventative of NdCl₃ electronic donor complex, combined with MMAO was reported in isoprene polymerization in hexane. The effects of Nd compounds, Al compounds, [Al]/[Nd] ratio, polymerization temperature and time on the catalytic activity, M_n , MWD, and stereospecificity of resulted polymers are examined in detail.

EXPERIMENTAL

Materials

Isoprene (Fluka) was purified by refluxing over calcium hydride for 2 h and distilled. Modified methylaluminoxane (MMAO, 2.0 mol/L solution in heptane), a hydrolysis product of a mixture of AlMe_3 and $\text{Al}(i\text{-Bu})_3$, was supplied by Akzo Nobel Polymer Chemicals LLC and used as received. $\text{Al}(i\text{-Bu})_2\text{H}$ and $\text{Al}(i\text{-Bu})_3$ (Akzo Nobel) were diluted to 2.0 mol/L solution by hexane. Hexane was purified reflux over sodium benzophenone ketyl until the solution turned blue and then distilled before use. Anhydrous neodymium compounds, *i.e.* NdCl₃^[29], Nd(O^{*i*}Pr)₃^[30], and NdCl₃·3^{*i*}PrOH^[31], were prepared according to the literature procedures.

Isoprene Polymerization

All the manipulations were performed under a dry nitrogen atmosphere. A detailed polymerization procedure (Run 10, Table 2) is described as a typical example: Hexane (1.0 mL), isoprene (1.0 mol/L solution in hexane, 0.40 mL), $\text{NdCl}_3 \cdot 3^i\text{PrOH}$ (4.0×10^{-5} mol in hexane) and MMAO (2.0 mol/L in heptane, 0.60 mL) were charged sequentially into an ampoule with a septum via syringes, and then this catalyst solution ($[\text{Nd}] = 2.0 \times 10^{-2}$ mol/L) was aged at room temperature for 1 h before use. Hexane (17.0 mL) and isoprene (3.0 mL) were injected into a crown-sealed ampoule, and then the above preformed catalyst solution (0.40 mL) was added to induce the polymerization. Polymerization was carried out at 50°C for 4 h and quenched by adding 10 mL ethanol containing 2,6-di-*tert*-butyl-*p*-cresol (*ca.* 1 wt%) as a stabilizer. The formed polymer was coagulated, repeatedly washed with ethanol, cut into small pieces, and finally dried under vacuum at 40°C to constant weight. The polymer yield was determined by gravimetry.

Polymer Characterization

The microstructure of polyisoprene was determined by infrared spectra measured with a Vertex-70 FT-IR (Bruker) spectrophotometer. Film samples were prepared on a KBr disc by casting from carbon disulfide solutions (*ca.* 2–8 mg/mL) of the polymer. The proportion of *cis*-1,4 and 3,4-unit was determined from the absorption bands at 836 and 890 cm^{-1} , according to the following formulas reported in the literature^[32]:

$$\text{cis-1,4 (\%)} = 100 \times (145 \times A_{836} - 1.95 \times A_{890})/B$$

$$3,4 (\%) = 100 \times (19.9 \times A_{890} - 1.79 \times A_{836})/B$$

$$B = (145 \times A_{836} - 1.95 \times A_{890}) + (19.9 \times A_{890} - 1.79 \times A_{836})$$

The molecular weight (M_n) and MWD (M_w/M_n) of polymers was measured by gel permeation chromatography (GPC) using a Waters 515 HPLC pump, a series of four columns (HMW-7 THF, HMW-6E THF (two), HMW-2 THF) maintained at 30°C and a Waters 2414 refractive index detector.

RESULTS AND DISCUSSION

Effect of Nd Compounds

The effects of various Nd compounds on the isoprene polymerization in combination with MMAO as a cocatalyst were examined in hexane at 50°C, and the results are summarized in Table 1. $\text{Nd}(\text{O}^i\text{Pr})_3$, a Nd compound without chlorine element, polymerized isoprene quantitatively, to give polyisoprene having narrow MWD (M_w/M_n *ca.* 2.0) and somewhat low *cis*-1,4 content (*ca.* 92%), which is consistent with the previous work^[25]. In contrast, NdCl_3 without electronic donor did not polymerize isoprene, which is similar to $\text{NdCl}_3/\text{AlR}_3$ catalytic system^[12]. Interestingly, $\text{NdCl}_3 \cdot 3^i\text{PrOH}$, a NdCl_3 with $^i\text{PrOH}$ as electronic donor, displayed high activity in isoprene polymerization. The polymer yield was up to 99%. The M_w/M_n was close to 2.0, and the GPC profile was monomodal. This implies that the $\text{NdCl}_3 \cdot 3^i\text{PrOH}/\text{MMAO}$ catalyst proceeds through a single active site.

Table 1. Effect of Nd compounds on the isoprene polymerization with MMAO as cocatalyst*

Run	Nd compd	[Al]/[Nd]	Yield (%)	$M_n^a \times 10^5$	M_w/M_n^a	<i>cis</i> -1,4 ^b (%)	3,4 ^b (%)
1	$\text{Nd}(\text{O}^i\text{Pr})_3$	50	100	9.4	2.07	92.3	7.7
2	NdCl_3	100	0	—	—	—	—
3	$\text{NdCl}_3 \cdot 3^i\text{PrOH}$	100	99	12	2.08	95.9	4.1

* Conditions: in hexane at 50°C for 4 h, $[\text{IP}] = 1.50$ mol/L, $[\text{Nd}] = 0.40 \times 10^{-3}$ mol/L;

^a Determined by GPC against polystyrene standards; ^b Determined by FT-IR

The infrared spectrum of polyisoprene obtained by $\text{NdCl}_3 \cdot 3^i\text{PrOH}$ catalyst is illustrated in Fig. 1, and compared with that by $\text{Nd}(\text{O}^i\text{Pr})_3$ catalyst as a control. The microstructure of polymer was determined using the data of the 836 cm^{-1} (*cis*-1,4 units) and 890 cm^{-1} (3,4 units) bands. The polyisoprene obtained by $\text{NdCl}_3 \cdot 3^i\text{PrOH}$ catalyst composed of 95.9% of *cis*-1,4 unit and 4.1% of 3,4 unit, while the polymer obtained by $\text{Nd}(\text{O}^i\text{Pr})_3$

catalyst composed of 92.3% of *cis*-1,4 unit and 7.7% of 3,4-unit. This indicates that chlorine is an important ingredient for the high *cis*-1,4 stereospecificity. $\text{NdCl}_3 \cdot 3^i\text{PrOH}$, which contains chlorine ligand, is beneficial to produce the π -allyl binding of the terminal unit of the growing polymer chain to Nd atom and exhibits high *cis*-regulating ability. The *cis*-1,4 content of polyisoprene obtained by $\text{NdCl}_3 \cdot 3^i\text{PrOH}$ /MMAO catalyst is very close to that of natural rubber. Thus, such polyisoprene can be expected to meet the requirements for excellent elastomers.

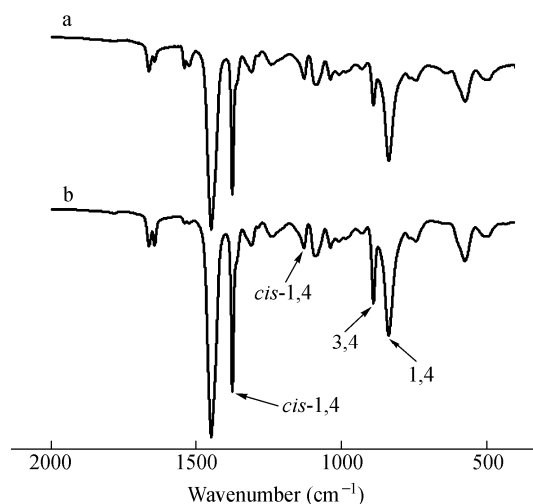


Fig. 1 Infrared spectra of polyisoprenes obtained with (a) $\text{NdCl}_3 \cdot 3^i\text{PrOH}$ and (b) $\text{Nd}(\text{O}^i\text{Pr})_3$ catalysts activated by MMAO

Effect of Al Compounds

For well understanding the function of MMAO in the $\text{NdCl}_3 \cdot 3^i\text{PrOH}$ catalyst, the effect of Al compounds, *i.e.* $\text{Al}(i\text{-Bu})_2\text{H}$, $\text{Al}(i\text{-Bu})_3$, MMAO, and dried-MAO as cocatalyst for isoprene polymerization were examined, and the results are shown in Table 2. $\text{Al}(i\text{-Bu})_2\text{H}$, $\text{Al}(i\text{-Bu})_3$ and MMAO activated catalyst systems were highly active in isoprene polymerization. In contrast, the polymerization did not proceed when dried-MAO (substantially free of AlMe_3) was used as a cocatalyst.

Table 2. Effect of various Al compounds on the isoprene polymerization with $\text{NdCl}_3 \cdot 3^i\text{PrOH}$ catalyst*

Run	Al compd	[Al]/[Nd]	Yield (%)	$M_n^a \times 10^{-5}$	M_w/M_n^a	<i>cis</i> -1,4 ^b (%)	3,4 ^b (%)
4	$\text{Al}(i\text{-Bu})_2\text{H}$	20	55	5.0	3.92	96.1	3.9
5		30	76	1.9	8.48	96.3	3.7
6		40	81	0.94	16.20	96.2	3.8
7	$\text{Al}(i\text{-Bu})_3$	20	8	7.7	2.86	94.6	5.4
8		30	99	6.9	2.76	96.1	3.9
9	MMAO	20	33	17	1.72	96.2	3.8
10		30	88	16	1.81	96.4	3.6
11		80	100	12	2.18	96.2	3.8
12	Dried-MAO	100	0	—	—	—	—

* Conditions: in hexane at 50°C for 4 h, [IP] = 1.50 mol/L, [Nd] = 0.40×10^{-3} mol/L;

^a Determined by GPC against polystyrene standards; ^b Determined by FT-IR

The effect of [Al]/[Nd] ratio on the polymer yield with $\text{NdCl}_3 \cdot 3^i\text{PrOH}$ catalyst in combination with various Al compounds is illustrated in Fig. 2. The polymer yields sharply increased with raising [Al]/[Nd] ratio up to 30, and hardly changed with further increase of [Al]/[Nd] ratio. When [Al]/[Nd] ratio was higher than 30, the Al compounds affected the polymer yield in the order of $\text{Al}(i\text{-Bu})_3 > \text{MMAO} > \text{Al}(i\text{-Bu})_2\text{H}$. MMAO activated catalyst yielded polymer over 80% at relatively low [Al]/[Nd] ratio of 30, which is comparable to that of AlR_3 . Thus, a [Al]/[Nd] ratio of 30 is sufficient to achieve high activity with $\text{NdCl}_3 \cdot 3^i\text{PrOH}$ /MMAO catalyst for

isoprene polymerization. From the viewpoint of practical application, it would be more promising to reduce the consumption of MMAO due to its high cost.

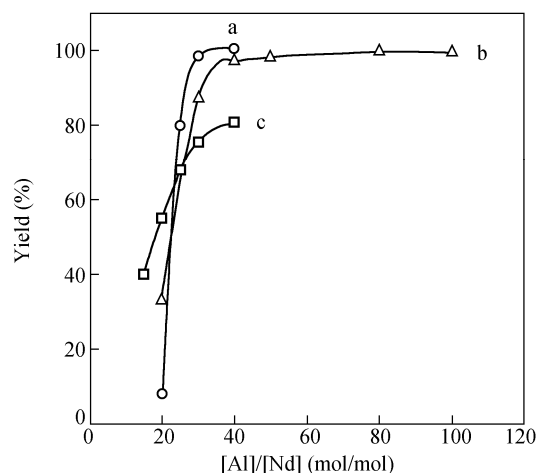


Fig. 2 Effect of various Al compounds on isoprene polymerization by using $\text{NdCl}_3 \cdot 3^i\text{PrOH}$ catalyst:

(a) $\text{Al}(i\text{-Bu})_3$, (b) MMAO and (c) $\text{Al}(i\text{-Bu})_2\text{H}$

Polymerizations were carried out in hexane at 50°C for 4 h, $[\text{IP}] = 1.50 \text{ mol/L}$, $[\text{Nd}] = 0.40 \times 10^{-3} \text{ mol/L}$.

Regarding to M_n of the produced polymer, when $\text{Al}(i\text{-Bu})_2\text{H}$ was used as cocatalyst, broad bimodal GPC curves (Fig. 3) were observed, which suggested that the catalyst had multiple active species. With the increase of $[\text{Al}]/[\text{Nd}]$ ratio from 20 to 40, the M_n sharply decreased from 5.0×10^5 to 9.4×10^4 along with MWD increased from 3.9 to 16, demonstrating that $\text{Al}(i\text{-Bu})_2\text{H}$ acted as a strong chain transfer agent. $\text{Al}(i\text{-Bu})_3$ as cocatalyst yielded polymers displaying monomodal GPC curves and slightly broad MWD ($M_w/M_n = 2.76$), indicating that $\text{Al}(i\text{-Bu})_3$ acted as a weaker chain transfer agent compared to $\text{Al}(i\text{-Bu})_2\text{H}$. MMAO as cocatalyst afforded polymer having monomodal GPC curve and fairly narrow MWD ($M_w/M_n = 1.81$). The M_n (1.6×10^6) of polymers by MMAO was much higher than that of $\text{Al}(i\text{-Bu})_3$ ($M_n = 6.9 \times 10^5$) in the identified condition of $[\text{Al}]/[\text{Nd}]$ ratio at 30. Even at high MMAO amount ($[\text{Al}]/[\text{Nd}] = 80$), the M_n of polymer remained over 1.2×10^6 . Thus, MMAO cocatalyst is beneficial to produce high M_n polyisoprene. The high M_n polyisoprene is practically important to allow vulcanized polymer possessing excellent properties, because of the easy degradation of polyisoprene during the milling process.

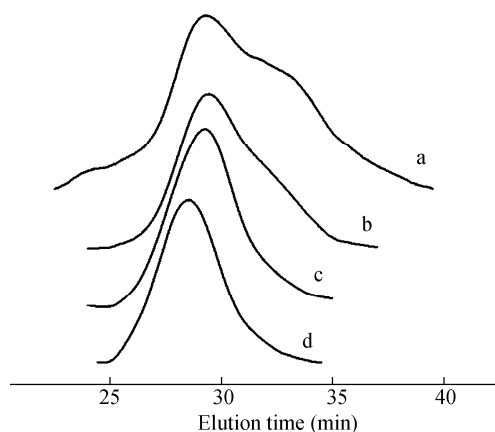
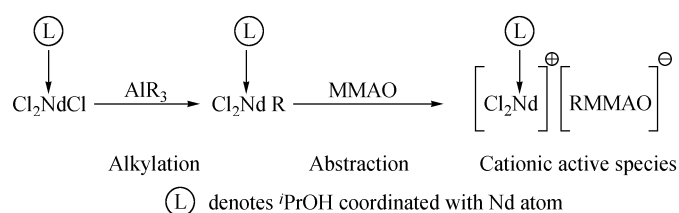


Fig. 3 GPC profiles of the polyisoprenes by using $\text{NdCl}_3 \cdot 3^i\text{PrOH}$ catalyst in combination with (a) $\text{Al}(i\text{-Bu})_2\text{H}$ ($[\text{Al}]/[\text{Nd}] = 40$), (b) $\text{Al}(i\text{-Bu})_2\text{H}$ ($[\text{Al}]/[\text{Nd}] = 30$), (c) $\text{Al}(i\text{-Bu})_3$ ($[\text{Al}]/[\text{Nd}] = 30$) and (d) MMAO ($[\text{Al}]/[\text{Nd}] = 30$)

Polymerizations were carried out in hexane at 50°C for 4 h, $[\text{IP}] = 1.50 \text{ mol/L}$, $[\text{Nd}] = 0.40 \times 10^{-3} \text{ mol/L}$.

Regarding Activation Process

So far, many literatures^[33–36] have been reported about the alkene and diene polymerization with the transition metal catalyst activated by MAO and discussed the reaction mechanism of MAO. It is reported that for CoCl_2/MAO catalyst, AlMe_3 is necessary for alkylation of CoCl_2 , and then MAO abstracts the methyl anion from the alkylated Co compound to generate the cationic Co species^[36]. We speculate that the present catalyst system also forms a cationic metallic species, which might have the similar structure as the reported one. MMAO, a hydrolysis product of a mixture of AlMe_3 and $\text{Al}(i\text{-Bu})_3$, is inevitable to have residuals of AlMe_3 and $\text{Al}(i\text{-Bu})_3$. Hence, the activation process of the present $\text{NdCl}_3 \cdot 3^i\text{PrOH}/\text{MMAO}$ catalyst can be proposed as follows: (1) $\text{NdCl}_3 \cdot 3^i\text{PrOH}$ is alkylated by residual AlMe_3 and/or $\text{Al}(i\text{-Bu})_3$ in the MMAO heptane solution, resulting in the formation of alkylated $\text{Nd}-\text{Cl}$ complex, (2) MMAO abstracts the alkyl anion from the alkylated $\text{Nd}-\text{Cl}$ complex to generate and then stabilize the cationic $\text{Nd}-\text{Cl}$ species, which is probably the actual catalytic active species for *cis*-1,4 polymerization of isoprene (Scheme 1). The reason for the inactivity of dried-MAO is attributable to the substantially free AlMe_3 in MAO solution for alkylation of $\text{NdCl}_3 \cdot 3^i\text{PrOH}$. None activity of $\text{NdCl}_3/\text{MMAO}$ catalyst is attributable to less alkylation of NdCl_3 by AlR_3 ^[12]. In the $\text{NdCl}_3 \cdot 3^i\text{PrOH}$ complex, the positive electricity of Nd ion is somewhat decreased due to the donor property of oxygen of isopropanol, and meanwhile the lattice of NdCl_3 is changed. These results favor the alkylation of $\text{NdCl}_3 \cdot 3^i\text{PrOH}$ to form alkylated $\text{Nd}-\text{Cl}$ complex. High activity of $\text{NdCl}_3 \cdot 3^i\text{PrOH}/\text{MMAO}$ catalyst at a low MMAO amount at $[\text{Al}]/[\text{Nd}]$ of 30 implied that such low amount of MMAO is sufficient to alkylate, abstract and stabilize for the formation of cationic active species.



Scheme 1 Mechanism of the active center formation with the $\text{NdCl}_3 \cdot 3^i\text{PrOH}/\text{MMAO}$ catalyst

Effects of Polymerization Temperature and Time

Fixed $[\text{Al}]/[\text{Nd}]$ ratio at 30, the effects of polymerization temperature and time on isoprene polymerization by $\text{NdCl}_3 \cdot 3^i\text{PrOH}/\text{MMAO}$ catalyst were examined (Table 3 and Fig. 4). The polymer yield remarkably increased from 32% to 98% by raising the polymerization temperature from 30°C to 70°C. This result indicated that high polymerization temperature is favorable to the polymerization of isoprene with $\text{NdCl}_3 \cdot 3^i\text{PrOH}/\text{MMAO}$ catalyst. High M_n ($> 1.0 \times 10^6$) of polyisoprene was obtained even at elevated temperatures (up to 70°C). The *cis*-1,4 content (*ca.* 96%) of polyisoprene slightly decreased with increasing polymerization temperature. These results indicated that the active species generated by $\text{NdCl}_3 \cdot 3^i\text{PrOH}/\text{MMAO}$ catalyst have high thermal stability.

Table 3. Effect of polymerization temperature and time on the isoprene polymerization with $\text{NdCl}_3 \cdot 3^i\text{PrOH}/\text{MMAO}$ catalyst*

Run	Polymn temp. (°C)	Polymn time (h)	Yield (%)	$M_n^a \times 10^{-5}$	M_w/M_n^a	<i>cis</i> -1,4 ^b (%)	3,4 ^b (%)
13	30	4	32	14.	1.72	97.1	2.9
14	50	1	24	7.29	2.92	96.4	3.6
15	50	2	44	14.0	1.71	96.3	3.7
16	50	4	88	16.0	1.81	96.4	3.6
17	70	4	98	11.0	1.82	95.8	4.2

* Conditions: in hexane for 4 h, $[\text{IP}] = 1.50 \text{ mol/L}$, $[\text{Nd}] = 0.40 \times 10^{-3} \text{ mol/L}$, $[\text{Al}]/[\text{Nd}] = 30 \text{ mol/mol}$;

^a Determined by GPC against polystyrene standards; ^b Determined by FT-IR

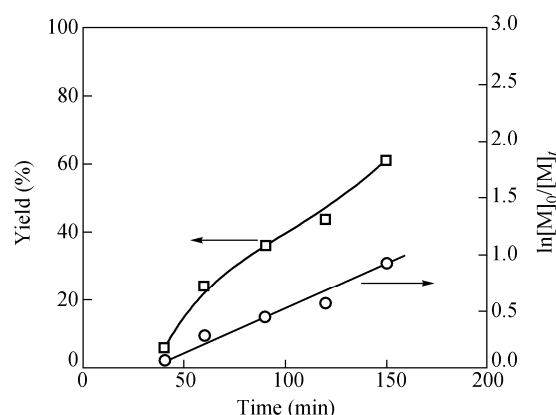


Fig. 4 Relation between $\ln[M]_0/[M]_t$ and time with $\text{NdCl}_3 \cdot 3^i\text{PrOH}/\text{MMAO}$ catalyst. Polymerizations were carried out in hexane at 50°C , $[\text{IP}] = 1.50 \text{ mol/L}$, $[\text{Nd}] = 0.40 \times 10^{-3} \text{ mol/L}$, $[\text{MMAO}]/[\text{Nd}] = 30$.

Regarding polymerization time (Fig. 4), the polymer yield increased with time, and $\ln[M]_0/[M]_t$ was proportional to the polymerization time at 50°C , which indicated that the polymerization rate was of the first order with respect to the concentration of isoprene. The M_n of polymer tended to increase with polymer yield, while the M_w/M_n ratio and *cis*-1,4 contents of polyisoprene were almost constant with polymerization time.

CONCLUSIONS

In this paper, it has been demonstrated that $\text{NdCl}_3 \cdot 3^i\text{PrOH}$ in combination with MMAO as cocatalyst may form excellent catalyst systems for the polymerization of isoprene. The produced polyisoprene featured high *cis*-1,4 content ($> 96\%$), very high M_n ($> 1.0 \times 10^6$) and fairly narrow MWD ($M_w/M_n < 2.0$) simultaneously. The catalyst achieved high activity even at a very low MMAO consumption ($[\text{Al}]/[\text{Nd}] = 30$), and the polymer retained high *cis*-1,4 content of 95.8% and high M_n over 1.0×10^6 even at elevated temperatures up to 70°C .

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