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Homogeneous neodymium *iso*-propoxide/modified methylaluminoxane catalyst for isoprene polymerization

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Abstract

The neodymium *iso*-propoxide [Nd(O*i*-Pr)$_3$] catalyst activated by modified methylaluminoxane (MMAO) is homogeneous and effective in isoprene polymerization in heptane to provide polymers with high molecular weight ($M_n \sim 10^5$), narrow molecular weight distribution ($M_w/M_n = 1.1–2.0$) and mainly *cis*-1,4 structure (82–93%). The polymer yield increased with increasing [Al]/[Nd] ratio (50–300 mole ratio) and polymerization temperature (0–60 °C), while the molecular weight and *cis*-1,4 content decreased. On the other hand, the same catalyst resulted in relatively low polymer yield and low molecular weight in toluene. The cyclized polyisoprene was formed in dichloromethane, which is attributable to the cationic active species derived from MMAO alone. When chlorine sources (Et_2AlCl, *t*-BuCl, Me_3SiCl) were added, the *cis*-1,4 stereoregularity of polymer improved up to 95% even at a high temperature of 60 °C, though the polymer yield decreased.

Keywords: Isoprene; Neodymium; Methylaluminoxane

1. Introduction

It is known that neodymium (Nd) based catalysts activated by alkylaluminums (R_3Al) display high *cis*-1,4 stereospecificity (>95%) in both homopolymerization of butadiene and isoprene and their copolymerization. These catalysts achieve good polymer yields in aliphatic hydrocarbons to provide polymers with excellent properties, which are suitable to the use as tires and other elastic materials [1–6]. However, the molecular weight (MW) and molecular weight distribution (MWD) of the resulting polymers are not well controlled, which is attributable to the heterogeneity of the catalyst systems and/or the multiple nature of the active species.

Recently, a variety of homogeneous d-orbital transition metal (e.g. Ti [7–10], V [8,11,12], Co [8,13,14], Ni [15,16]) catalytic systems and, more importantly, f-orbital lanthanide (Nd [5,8,17–20], Sm [21]) catalytic systems have been developed for the 1,3-diene polymerization using methylaluminoxane (MAO) and R_3Al/borate as cocatalysts. These catalysts have turned out to show some distinguished features compared to the conventional Ziegler–Natta catalysts activated by R_3Al. For instance, titanocene/MAO [9,10] and samarocene/R_3Al/borate [21] afford 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 control of MW and *cis*-1,4 stereoregularity.

On the other hand, with respect to combinations of Nd catalyst and MAO as cocatalyst, the Nd(carboxylate)$_3$/MAO catalysts induce 1,3-diene polymerizations [5,8,17], but the formed polymers have broad MWD [17]. Allylneodymium complexes provide single-site catalyst systems in 1,3-butadiene polymerization [18,19], but the complexes are rather difficult to prepare and handle. We found that the MAO-activated Nd(O*i*-Pr)$_3$ catalysts are effective to give high *cis*-1,4 polyisoprenes with narrow MWD ($M_w/M_n < 2.0$) [20]. However, as MAO does not dissolve in heptane, the catalyst solution formed is inhomogeneous, which is not beneficial for the elucidation of reaction mechanism, especially in the case of multi-component catalysts which should be mixed and aged before polymerization. Thus, the development of the Nd-based catalysts that are homogeneous and show the single active site nature in 1,3-diene polymerization remains a challenge.

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Modified methylaluminoxane (MMAO) is a hydrolysis product of a mixture of trimethylaluminium and triisobutylaluminium, and has good solubility in heptane. Hence, a soluble catalyst system is expected when it is combined with Nd(O*i*-Pr)$_3$ in heptane. Thus, the present work aims to examine MMAO-activated Nd(O*i*-Pr)$_3$ catalysts for the solution polymerization of isoprene. Catalytic activity, polymer molecular weight and *cis*-1,4 stereoregularity are discussed on the basis of their dependence on the [Al]/[Nd] ratio, polymerization temperature, solvents, chlorine sources and the [Cl]/[Nd] ratio.

2. Experimental

2.1. Materials

Neodymium *iso*-propoxide (Nd(O*i*-Pr)$_3$; Strem Chemicals Inc., 99.9%-Nd) was diluted with heptane into 0.10 M solution. Modified methylaluminoxane (MMAO; 5.7 wt% solution in toluene), which is a hydrolysis product of a mixture of trimethylaluminium and triisobutylaluminium, was kindly supplied by Tosoh-Akzo Chemical Co. and used as received. *tert*-Butyl chloride (*t*-BuCl; Wako Pure Chem. Ind., Ltd.), isoprene (IP; Nacalai Tesque Inc.) and dichloromethane (CH_2Cl_2) were dried by refluxing over calcium hydride for 2 h and distilled under nitrogen. Diethylaluminum chloride (Et_2AlCl; Kanto Chemical Co. Inc., 0.95 M in hexane) and trimethylchlorosilane (Me_3SiCl; Wako Pure Chem. Ind., Ltd) and purified *t*-BuCl were diluted with heptane into 0.20 M solution. Heptane and toluene were dried over sodium benzophenone ketyl and distilled under nitrogen.

2.2. Polymerization

All the manipulations were performed under a nitrogen atmosphere. A detailed polymerization procedure (Run 4, Table 1) is described as a typical example. At first, a catalyst solution was prepared in a glass tube with a rubber septum in the following way: MMAO (1.90 M in toluene; 5.80 ml) and Nd(O*i*-Pr)$_3$ (0.10 M in heptane; 1.10 ml) were injected sequentially into a glass tube; the mole ratio of [Nd]/[Al] = 1:100. This catalyst solution ([Nd] = 1.60×10^{-5} mol/ml) was aged at room temperature for 1 h before use. When necessary (e.g. Run 24, Table 5), Et_2AlCl (0.20 M in heptane; 0.16 ml) was added after the mixture of heptane (0.40 ml), MMAO (1.68 ml) and Nd(O*i*-Pr)$_3$ (0.32 ml) was left for 10 min; the mole ratio of [Nd]/[Al]/[Cl] = 1:100:1. This ternary catalyst solution ([Nd] = 1.25×10^{-5} mol/ml) was aged at room temperature for 1 h before use.

Heptane (16.4 ml) and isoprene (3.0 ml) were injected into a crown-sealed ampule, and then the preformed catalyst solution (0.63 ml) was added. Polymerization was carried out at 30 °C for 90 min and quenched by adding 10 ml of a 1:1 acidified methanol/toluene mixture containing 2,6-di-*tert*-butyl-*p*-methylphenol (1 wt%) as a stabilizer. The formed polymer was coagulated, repeatedly washed with methanol, cut into small pieces, and finally dried under vacuum at room temperature to constant weight. The polymer yield was determined by gravimetry.

In the polymerizations carried out in CH_2Cl_2 (e.g. Run 18 of Table 3), the bottle was quickly cooled in an ice-water bath, and then opened. The contents were poured into 200 ml of an acidic methanol solution containing 2,6-di-*tert*-butyl-*p*-methylphenol (1 wt%). The precipitated polymer was separated by filtration, washed with methanol, and dried under vacuum to constant weight.

2.3. Characterization

The molecular weights (M_w and M_n) and molecular weight distributions (M_w/M_n) of polymers were measured by gel permeation chromatography (GPC) using a Jasco PU-980/RI-930 chromatograph. A series of three KF-805 (Shodex) columns maintained at 40 °C were employed. THF was used as eluent at a flow rate of 1.0 ml/min. The molecular weights of polyisoprenes were determined using a polystyrene calibration. Sample solutions (1.0 mg/ml) were filtered through a 0.45 μm microfilter before injection.

The microstructure of polyisoprenes was determined from IR spectra measured with a Shimadzu FTIR-8100 spectrophotometer. Film samples were prepared on a KBr

Table 1
Isoprene polymerization with Nd(O*i*-Pr)$_3$/MMAO catalyst in heptane (conditions: [IP] = 1.5 M, [Nd] = 0.5 mM)

Run	[Al]/[Nd]	Temperature (°C)	Time (min)	Yield (%)	M_n[a] ($\times 10^{-3}$)	M_w/M_n[a]	*cis*-1,4[b] (%)	3.4-[b] (%)
1	100	0	5 × 60	52.9	790	1.15	91.7	8.3
2	300	0	4 × 60	63.2	587	1.33	93.4	6.6
3	50	30	16 × 60	20.3	818	1.10	82.1	17.9
4	100	30	90	98.9	749	1.14	91.4	8.6
5	300	30	90	100	446	1.47	91.7	8.3
6	50	60	90	34.3	835	1.09	83.4	16.6
7	100	60	45	100	470	1.62	88.5	11.5
8	300	60	45	100	268	1.95	89.7	10.3

[a] Determined by GPC (THF, PSt calibration).

[b] The microstructures were determined by FTIR.

disc by casting CS_2 solution (ca. 2–8 mg/ml) of polymer. The proportion of *cis*-1,4 and 3,4 units was determined from the absorption bands at 836 and 890 cm^{-1}, according to the following formulas reported in literature [22]:

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

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

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

where A_{836} and A_{890} are the absorbances at 836 and 890 cm^{-1}, respectively.

^1H NMR spectra were recorded with a JEOL EX-400 spectrometer in $CDCl_3$ (containing 0.03% of tetramethylsilane as internal standard) solution at room temperature. The concentration of polymer solution was 1.0 mg/ml.

3. Results and discussion

3.1. Isoprene polymerization by Nd(Oi-Pr)$_3$/MMAO catalyst

3.1.1. Polymerization in heptane

The Nd(O*i*-Pr)$_3$/MMAO catalyst for isoprene polymerization was examined by changing solvent types, [Al]/[Nd] ratios, and polymerization temperatures. First of all, it is worth noting that the MMAO-activated Nd(O*i*-Pr)$_3$ catalysts dissolve well in heptane and toluene to provide transparent solution, irrespective of the absence and presence of chlorine sources and [Cl]/[[Nd] ratio (0.5–3.0). The results of polymerization in heptane are shown in Table 1.

The polymer yields significantly increased with increasing [Al]/[Nd] ratio and polymerization temperature. Thus, the polymer yield at [Al]/[Nd] = 50 was no more than 20% even after 16 h at 30 °C, whereas the yield at [Al]/[Nd] = 100 reached 99% in 90 min. Further, while the polymer yield at 0 °C after 5 h was no more than 53%, the one at 60 °C reached 100% within 100 min when [Al]/[Nd] = 100. It is worth to mention that the polymers obtained at low [Al]/[Nd] ratios of 50 and 100 dissolve well in common organic solvents (e.g. toluene, chloroform, tetrahydrofuran, and carbon disulfide), whereas the polymers obtained at a high [Al]/[Nd] ratio of 300, have some insoluble fractions, implying the formation of crosslinked products.

The molecular weight of polymers tended to decrease with increasing [Al]/[Nd] ratio and polymerization temperature. The GPC curve (Fig. 1(a)) remained unimodal and the M_w/M_n ratio kept below 2.0, regardless of reaction conditions, indicating that the present catalyst system possesses the single-active site nature in heptane.

The microstructure of polyisoprenes was mainly determined from IR spectra, and further confirmed by ^1H NMR (Fig. 2(a)). At fixed polymerization temperatures, the *cis*-1,4 content of polymer strongly depended on the [Al]/[Nd] ratio. Thus, the *cis*-1,4 content was no more than 82% at 30 °C when [Al]/[Nd] = 50, whereas the *cis*-1,4 content reached around 91% when [Al]/[Nd] ratio was raised to 100 and above. On the other hand, at fixed [Al]/[Nd] ratios, e.g. at [Al]/[Nd] = 100, the *cis*-1,4 content somewhat decreased from ca. 92% to ca. 89% when temperature was increased from 0 to 60 °C.

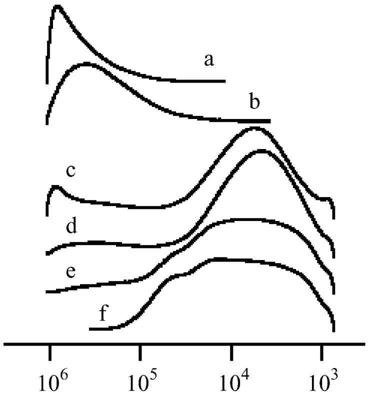

Fig. 1. GPC curves of polyisoprenes obtained with Nd(O*i*-Pr)$_3$/MMAO catalyst in heptane ((a) Run 7), in toluene, ((b), Run 13) and in CH_2Cl_2 ((c), Run 15; (d) Run 16; (e) Run 18), and with MMAO alone in CH_2Cl_2 ((f), Run 22).

3.1.2. Polymerization in toluene

Most of MAO-activated transition metal catalysts have been reported to promote 1,3-diene polymerization in toluene [8–13,15,16,21]. Hence, the Nd(O*i*-Pr)$_3$/MMAO catalyst was examined also in toluene, whose results are compared with the those in heptane. The effects of polymerization temperature and [Al]/[Nd] ratio in toluene (Table 2) resemble those in heptane; i.e. the polymer yields increased with increasing polymerization temperature and [Al]/[Nd] ratio, while the M_n decreased; the GPC profile

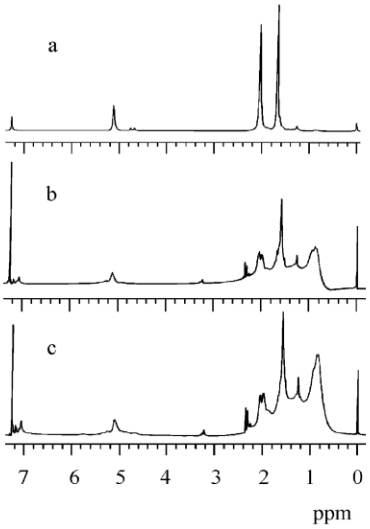

Fig. 2. ^1H NMR spectra of polyisoprenes obtained with Nd(O*i*-Pr)$_3$/MMAO catalyst in heptane ((a) Run 7) and in CH_2Cl_2 ((b) Run 18), and with MMAO alone in CH_2Cl_2 ((c) Run 22).

Table 2
Isoprene polymerization with Nd(O*i*-Pr)$_3$/MMAO catalyst in toluene (conditions: [IP] = 1.5 M, [Nd] = 0.5 mM)

Run	[Al]/[Nd]	Temperature (°C)	Time (min)	Yield (%)	M_n[a] ($\times 10^{-3}$)	M_w/M_n[a]	*cis*-1,4[b] (%)	3.4-[b] (%)
9	100	0	16 × 60	39.0	552	1.30	91.8	8.2
10	300	0	16 × 60	71.4	353	1.67	92.7	7.3
11	100	30	3 × 60	62.2	468	1.43	91.4	8.6
12	300	30	3 × 60	100	193	2.21	91.7	8.3
13	100	60	90	100	402	1.54	89.4	10.6
14	300	60	90	100	150	2.30	89.7	10.3

[a] Determined by GPC (THF, PSt calibration).
[b] The microstructures were determined by FTIR.

(Fig. 1(b)) kept unimodal and the M_w/M_n slightly increased but still stayed around 2.0; the *cis*-1,4 content decreased by 2–3% with increasing temperature from 0 to 60 °C. The reduced polymer yields in toluene as compared to those in heptane is attributable to competitive coordination of the aromatic solvent and isoprene monomer to the propagating species; this has been observed previously in 1,3-diene polymerization with MAO- and R$_3$Al-activated Nd-based catalysts [17,20,23].

It is worth to mention that the exothermic reaction were observed in the course of isoprene polymerization in toluene and the color of polymerization solution turned yellow, orange or red, depending on temperature and the [Al]/[Nd] ratio. The higher the temperature (and/or the higher the [Al]/[Nd] ratio), the higher the exothermic level and the deeper the solution color. This resembles the phenomenon observed in the isoprene polymerization in the presence of aluminum-based cationic catalysts [24–26]. This seems to imply the formation of cationic species by the reaction of Nd(O*i*-Pr)$_3$ and MMAO in toluene. In general, ionic polymerization is largely affected by solvent polarity, and hence isoprene polymerization with Nd(O*i*-Pr)$_3$/MMAO catalyst was further examined in dichloromethane, a more polar solvent.

3.1.3. Polymerization in dichloromethane

Up to now, only a few papers have appeared regarding 1,3-diene polymerization in chlorinated hydrocarbons with MAO-activated transition metal catalysts. For instance, Endo et al. have reported the polymerization of 1,3-butadiene catalyzed by V(acac)$_3$/MAO in dichloromethane [12]; they found that dichloromethane achieves higher polymer yield than heptane and toluene do and that the produced polymer possesses mainly *trans*-1,4 unit (ca. 86%), in contrast to the cases of toluene and heptane in which polymers consist mainly of *cis*-1,4 structure (ca. 64%). Wilson found that the 1,3-butadiene polymerization catalyzed by Nd(versatate)$_3$/MAO in dichloromethane and chloroform gives a product insoluble in cyclohexane and tetrahydrofuran [17]. We found that the isoprene polymerization with Nd(O*i*-Pr)$_3$/MAO catalyst in dichloromethane also affords insoluble products [20].

Here, the polymerization in dichloromethane did not become viscous unlike the cases of heptane and toluene as solvent (Table 3). In the polymerization at [Al]/[Nd] = 100 and 30 °C for 3 h, the polymer yield was 24% and rather low, whereas when [Al]/[Nd] ratio was raised to 300, the polymer yield significantly increased to reach 82%. The polymers obtained were white viscose materials or powders, and very soluble in common organic solvents such as toluene and tetrahydrofuran.

There were two broad overlapping peaks in the GPC curves, implying the presence of two kinds of active species (Fig. 1(c)–(e)). One of the active species, which produced the high molecular weight fraction, appears to be sensitive to the [Al]/[Nd] ratio and temperature. This high molecular weight peak is small and further decreases in magnitude with increasing [Al]/[Nd] ratio from 100 to 300 (Fig. 1(c). vs. Fig. 1(d)), and temperature from 0 to 60 °C (Fig. 1(d) vs. Fig. 1(e)). The other active species, which produced the low molecular weight portion, was also sensitive to the [Al]/[Nd] ratio and temperature, but the corresponding GPC peak is large and broad, and becomes even larger as temperature and [Al]/[Nd] ratio are raised.

The ^{1}H NMR spectrum of polyisoprene obtained in dichloromethane (Fig. 2(b)) is very different from that for heptane (Fig. 2(a)). Thus, the peaks at 5.12 and 2.04 ppm in Fig. 2(a), which are assigned to olefinic protons and the methylene protons adjacent to the double bond, respectively, are much smaller in Fig. 2(b), indicating the decrease of unsaturation degree. The broad peaks appearing in the range 0.6–2.5 are mainly assigned to non-equivalent

Table 3
Isoprene polymerization with Nd(O*i*-Pr)$_3$/MMAO catalyst in CH$_2$Cl$_2$ (conditions: [IP] = 1.5 M, [Nd] = 0.5 mM)

Run	[Al]/[Nd]	Temperature (°C)	Time (min)	Yield (%)	M_n[a] ($\times 10^{-3}$) (proportion)	M_w/M_n[a]
15	100	0	16 × 60	16.2	546 (0.3%)	1.29
					4.7 (99.7%)	1.72
16	300	0	16 × 60	28.5	3.1	1.95
17	100	30	3 × 60	23.5	247 (0.2%)	1.58
					3.6 (99.8%)	1.93
18	300	30	3 × 60	81.6	4.2	6.08
19	300	60	90	98.6	3.4	4.70

[a] Determined by GPC (THF, PSt calibration).

aliphatic groups of methyl, methylene and methine protons in cyclic structures. The peak at 0.88 ppm should be due to the methyl group adjacent to the cyclic structure. The largest peak seen at 1.60 ppm is based on the methyl group linked to *trans* olefinic carbons, suggesting that the linear moiety of this polyisoprene possesses *trans*-1,4 structure. These observations manifest that the produced polymer mainly has a cyclized structure. The cyclic structure should have been formed by the cationic mechanism, when previous structure/reaction mechanism data are taken into account. As MMAO is a Lewis acid, it alone may initiate the cationic polymerization of isoprene, especially at a high MMAO concentration. To clarify this point, we further examined the isoprene polymerization with MMAO alone in various solvents.

3.2. Isoprene polymerization by MMAO alone

The results of isoprene polymerization with MMAO alone are shown in Table 4. Here, the MMAO concentration ([Al]) is equal to that of Nd(O*i*-Pr)$_3$/MMAO catalyst at [Al]/[Nd] = 300. Isoprene polymerized with MMAO alone in all of heptane, toluene and dichloromethane. In the cases of heptane and toluene as solvents, the polymer yields were low and the formed polymers were white insoluble powders. When the fact is considered that an insoluble fraction is present in polymers formed with Nd(O*i*-Pr)$_3$/MMAO catalyst at a high [Al]/[Nd] ratio of 300, it is reasonable to presume that the insoluble fraction might have been produced by slow crosslinking reaction of the pre-formed polymer with MMAO at high concentration.

In the case of dichloromethane as solvent, the polymerization solution turned yellow within 20 min. The product was a white powder soluble in common organic solvents. The ^{1}H NMR spectrum (Fig. 2(c)) is similar to that of the polymer formed with Nd(O*i*-Pr)$_3$/MMAO catalyst at [Al]/[Nd] = 300. These findings indicate that MMAO alone initiates the cationic polymerization of isoprene.

The GPC curve of polyisoprene obtained with MMAO alone is composed of a broad peak, which is similar to that of low molecular weight part of polyisoprene obtained with Nd(O*i*-Pr)$_3$/MMAO catalyst. This gives a cue to understand the course of isoprene polymerization by using Nd(O*i*-Pr)$_3$/MMAO catalyst in dichloromethane; i.e. the polymerization by Nd(O*i*-Pr)$_3$/MMAO proceeds to form a high molecular weight polymer, and simultaneously the cationic active species formed by MMAO induces cationic polymerization of isoprene to form a low molecular weight polymer.

It is concluded that the Nd(O*i*-Pr)$_3$/MMAO catalyst is homogeneous and effective in isoprene polymerization in heptane to provide polymers possessing high molecular weight, narrow MWD, and mainly *cis*-1,4 structure, whereas the same catalyst results in relatively low polymer yield and low molecular weight in toluene, and cyclized polyisoprene in dichloromethane. However, the *cis*-1,4 contents with heptane and toluene as solvents, especially those at a high temperature of 60 °C (ca. 89%) are lower than those obtained with conventional R$_3$Al-activated Nd-based catalyst systems (>95%). Industrially, the high temperature process is preferable and the *cis*-1,4 content of polyisoprene should be higher than 95% like natural rubber to meet the requirements for excellent elastomers. Therefore, the *cis*-1,4 stereospecificity of Nd(O*i*-Pr)$_3$/MMAO catalyst requires further improvement.

It has been reported that chlorine-containing compounds, such as *t*-BuCl, are beneficial to improve the *cis*-1,4 stereospecificity of Nd(versatate)$_3$/MAO catalyst in 1,3-butadiene polymerization [17], and to improve both *cis*-1,4 stereospecificity and activity of Nd(O*i*-Pr)$_3$/MAO catalyst in isoprene polymerization [27]. Thus, the effect of chlorine sources on the isoprene polymerization with MMAO-activated Nd(O*i*-Pr)$_3$ catalyst was further examined.

3.3. Isoprene polymerization by Nd(O*i*-Pr)$_3$/MMAO catalyst in the presence of various chlorine sources

For the conventional ternary Nd-based catalysts used in 1,3-diene polymerization, the effective chlorine sources used as third catalyst component include alkylaluminum chlorides, organic chlorides and organic/inorganic chlorosilanes. Thus, Et$_2$AlCl, *t*-BuCl and Me$_3$SiCl were chosen as typical chlorine sources. All the experiments were conducted at a fixed [Al]/[Nd] ratio of 100 and an addition order of (Nd + Al) + Cl. The addition order of (Nd + Al) + Cl was previously found to be optimal in the Nd(O*i*-Pr)$_3$/PMAO catalyst system [27].

The results of isoprene polymerization with Nd(O*i*-Pr)$_3$/MMAO catalyst in the presence of Et$_2$AlCl, *t*-BuCl and Me$_3$SiCl are shown in Figs. 3–5, respectively. It is clear that, irrespective of the kind of chlorine sources, the *cis*-1,4 content of polymer increased with increasing [Cl]/[Nd] ratio, from ca. 91% up to ca. 96% at 30 °C and [Cl]/[Nd] = 2.0, and importantly, became close to 95% at a relatively high temperature of 60 °C. Such effect of chlorine sources on *cis*-1,4 specificity of MMAO-activated Nd catalyst is also observed in the 1,3-butadiene and isoprene polymerization when *t*-BuCl was added to the PMAO-activated Nd(versatate)$_3$ and Nd(O*i*-Pr)$_3$ system [17,27].

In contrast to the previous results that the chlorine sources (e.g. *t*-BuCl) are advantageous not only for high *cis*-1,4 stereospecificity but also for high catalytic activity, all

Table 4
Isoprene polymerization with MMAO catalyst in various solvents (conditions: 30 °C, [IP] = 1.5 M, [Al] = 0.15 M)

Run	Solvent	Time (min)	Yield (%)	M_n^{a} ($\times 10^{-3}$)	M_w/M_n^{a}
20	Heptane	16 × 60	13.0	Insoluble	
21	Toluene	16 × 60	9.6	Insoluble	
22	CH$_2$Cl$_2$	3 × 60	90.0	4.1	4.37

[a] Determined by GPC (THF, PSt calibration).

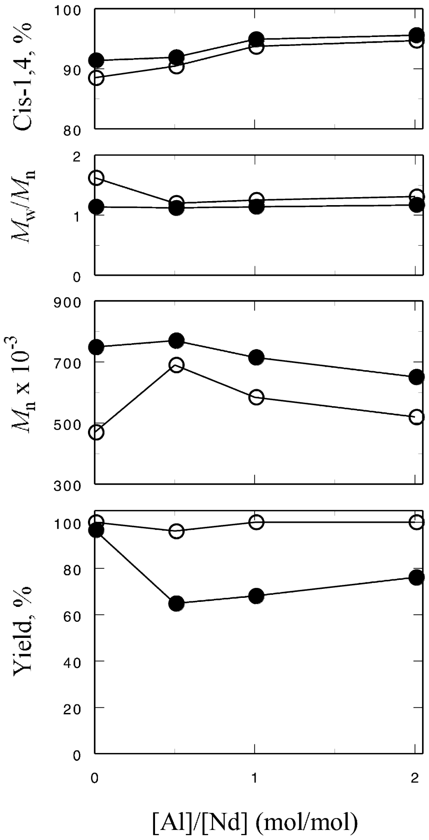

Fig. 3. Isoprene polymerization with Nd(O*i*-Pr)$_3$/MMAO/Et$_2$AlCl catalyst in heptane with [IP] = 1.5 M, [Nd] = 0.5 mM, [Al]/[Nd] = 100, (●) at 30 °C for 100 min and (○) at 60 °C for 45 min.

the chlorine sources examined here led to the reduction of activity of the MMAO-activated Nd(O*i*-Pr)$_3$ catalyst. Different chlorine sources showed different effects on the catalyst activity. In the case of Et$_2$AlCl as third component, although the polymer yield increased up to 76% at 30 °C when [Cl]/[Nd] mole ratio was increased from 0.5 to 2.0, the ternary Nd(O*i*-Pr)$_3$/MMAO/Et$_2$AlCl catalyst gave significantly lower activity than the binary counterpart (Fig. 3). At 60 °C, however, the polymer yield was virtually quantitative and no large difference was observed in activity between the ternary Nd(O*i*-Pr)$_3$/MMAO/Et$_2$AlCl catalyst and binary Nd(O*i*-Pr)$_3$/MMAO catalyst. When *t*-BuCl or Me$_3$SiCl was added to the Nd(O*i*-Pr)$_3$/MMAO catalyst, the polymer yield significantly decreased, and further decreased with increasing [Cl]/[Nd] ratio both at 30 and 60 °C (Figs. 4 and 5). In general, the chlorine sources decreased the polymer yield in the order of Et$_2$AlCl < *t*-BuCl < Me$_3$SiCl.

The molecular weight decreased with increasing [Cl]/[Nd] ratio in the range of 0.5 to 2.0, regardless of the type of chlorine sources. The GPC profiles of polymer were unimodal and the MWDs were narrow (M_w/M_n, 1.1–1.3), independent of polymerization conditions, which indicates that the polymerization with Nd(O*i*-Pr)$_3$/MMAO catalyst also proceeds with a single-site active species in the presence of a chlorine source.

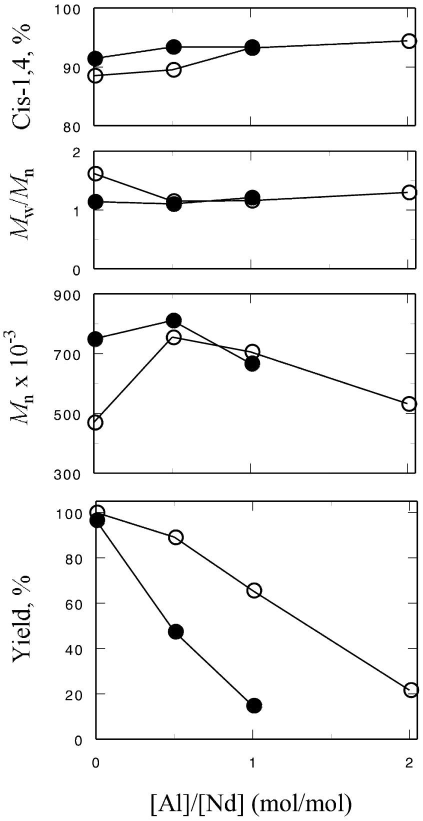

Fig. 4. Isoprene polymerization with Nd(O*i*-Pr)$_3$/MMAO/*t*-BuCl catalyst in heptane with [IP] = 1.5 *M*, [Nd] = 0.5 mM, [Al]/[Nd] = 100, (●) at 30 °C for 100 min and (○) at 60 °C for 45 min.

When the present work on the MMAO system is compared with our previous work on the MAO counterpart [20,27], it can be said that both MAO- and MMAO-activated Nd(O*i*-Pr)$_3$ catalyst systems are effective in isoprene polymerization in heptane to provide polymers with high *cis*-1,4 contents, high MW, and narrow MWD. MAO is insoluble in heptane and so the MAO-activated Nd(O*i*-Pr)$_3$ catalyst is inhomogeneous; whereas MMAO is totally soluble in heptane and hence the MMAO-activated Nd(O*i*-Pr)$_3$ catalyst is homogeneous in heptane and exhibits the single-active site nature. A low MAO level ([Al]/[Nd] = 30) is sufficient in the case of MAO as cocatalyst, while a high MAO level is required in the case of the MMAO system. When *t*-BuCl, which supplies the chlorine ligand, is added to the Nd(O*i*-Pr)$_3$ catalyst as a third catalytic component, both polymer yield and *cis*-1,4 stereospecificity improve in the case of Nd(O*i*-Pr)$_3$/MAO catalyst, while the *cis*-1,4 stereospecificity improves but the polymer yield decreases in the case of Nd(O*i*-Pr)$_3$/MMAO catalyst.

The MMAO-activated Nd(O*i*-Pr)$_3$ catalyst is homogeneous and provides polymers with narrow MWD (M_w/M_n ca. 1.1), as compared with that from MAO-activated systems (M_w/M_n ca. 1.6) [27]. This suggests that the living polymerization may have proceeded with the MMAO-based system. Thus, further research is underway

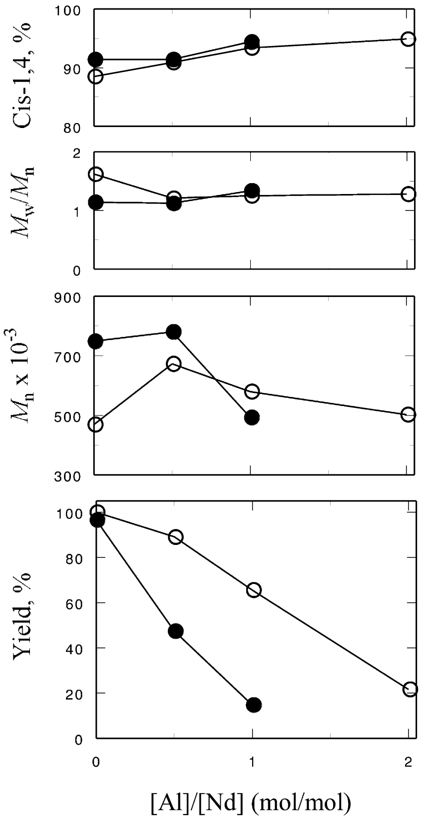

Fig. 5. Isoprene polymerization with Nd(O*i*-Pr)$_3$/MMAO/Me$_3$SiCl catalyst in heptane with [IP] = 1.5 M, [Nd] = 0.5 mM, [Al]/[Nd] = 100, (●) at 30 °C for 100 min and (○) at 60 °C for 45 min.

regarding detailed examination of the polymerization conditions to achieve the living polymerization of 1,3-diene with MMAO-activated Nd(O*i*-Pr)$_3$ catalysts.

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