Methylaluminoxane-Activated Neodymium Chloride Tributylphosphate Catalyst for Isoprene Polymerization

Yanming Hu,[1] Chunqing Zhang,[1] Xianguang Liu,[1] Keke Gao,[1] Yuming Cao,[1] Chunyu Zhang,[2] Xuequan Zhang[2]

[1]State Key Laboratory of Fine Chemicals, Department of Polymer Science and Engineering, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China
[2]Research Center of High Performance Synthetic Rubber, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China
Correspondence to: Y. Hu (E-mail: ymhu@dlut.edu.cn)

ABSTRACT: The polymerization of isoprene was examined by using a novel binary catalyst system composed of neodymium chloride tributylphosphate ($NdCl_3 \cdot 3TBP$) and methylaluminoxane (MAO). The $NdCl_3 \cdot 3TBP$/MAO catalyst worked effectively in a low MAO level ([Al]/[Nd] = 50) to afford polymers with high molecular weight ($M_n \sim 10^5$), narrow molecular weight distribution ($M_w/M_n = 1.4$–1.6), and high cis-1,4 stereoregularity (> 96%). The catalytic activity increased with an increasing [Al]/[Nd] ratio from 30 to 100 and polymerization temperature from 0 to 50°C, while the M_n of polymer decreased. The presence of free TBP resulted in low polymer yield. Polymerization solvent remarkably affected the polymerization behaviors; the polymerizations in aliphatic solvents (cyclohexane and hexane) gave polymer in higher yield than that in toluene. The M_w/M_n ratio of the producing polymer remained around 1.5 and the gel permeation chromatographic curve was always unimodal, indicating the presence of a single active site in the polymerization system. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40153.

INTRODUCTION

During the past decades, many endeavors have been made to develop new catalytic systems for the stereoselective polymerization of conjugated dienes due to the myriad of applications of polydienes.[1–3] In particular, considerable attention has been devoted to the cis-1,4-selective polymerization of 1,3-butadiene and isoprene because the resultant polymers are the most important elastomers widely used for tires and many other elastic materials. Catalytic systems based on lanthanides, especially neodymium (Nd), are well known for their high catalytic activity and high cis-1,4 selectivity in the homo- and copolymerization of conjugated dienes.[4–9] Typical traditional Nd-based catalytic systems are mostly divided into two types, that is, binary system derived from $NdCl_3 \cdot nL$ (L: an organic electron donating ligand) and AlR_3; and ternary system derived from Nd carboxylate, AlR_3, and a chlorine-containing compound. A variety of Nd-based catalysts have been developed so far, and the Nd carboxylate-based catalytic systems have been utilized industrially for production of cis-1,4 polydienes in a large capacity. Despite these achievements, however, the molecular weight and polydispersity of the resulting polymers are not well controlled in the case of traditional alkylaluminum-activated Nd-based catalyst systems, which are attributed to the presence of multiple active centers.

The high cis-1,4 polydienes with narrow molecular weight distribution (MWD) exhibit high abrasion resistance, low heat build-up, and high tensile properties, which are highly desirable properties for tire.[10] Recently, considerable progress has been made in the syntheses of well-defined lanthanide complexes containing lanthanide-carbon bonds.[11,12] These complexes activated by aluminoxane and organoborates show single-site active center characteristics in the polymerization of conjugated dienes, enabling simultaneous control of the MWD and steric structure of polymers during the polymerization. For example, $[(C_5Me_4\text{-}C_5H_4N)Lu(\eta^3\text{-}C_3H_5)_2]/[Ph_3C][B(C_6F_5)_4]$[13] and $[(^{Ar1}N\text{-}CO^{Ar2})LnCl_2(thf)_2]/Al(i\text{-}Bu)_3/[Ph_3C][B(C_6F_5)_4]$[14] afford polyisoprene and polybutadiene featuring high cis-1,4 stereoregularity and narrow MWD, respectively, and moreover, the former system induces living polymerization of 1,3-butadiene. However, these complexes are rather difficult to prepare and handle. Visseaux et al. reported that a common and unsophisticated compound $[Nd(2,6\text{-di-}tert\text{-butyl-}OC_6H_3)_3]$ in combination with methylaluminoxane (MAO) or modified MAO

Table I. Effect of Nd Compound on Isoprene Polymerization With MAO as a Cocatalyst[a]

Run	Nd compound	[Al]/[Nd]	Yield (%)	$M_n{}^c \times 10^{-3}$	$M_w/M_n{}^c$	Microstructure[b] (mol %)	
						cis-1,4	3,4
1	Nd(O^{i}Pr)$_3$	50	90	398	1.51	91.4	7.6
2	NdCl$_3$	50	trace	–	–	–	–
3	NdCl$_3$	100	trace	–	–	–	–
4	NdCl$_3$· 3TBP	50	84	301	1.52	96.2	3.8

[a] Polymerization in cyclohexane at 50°C for 4 h, [Nd]/[Ip] = 3.0 × 10^{-4}, [Ip] = 1.47 mol L^{-1}.
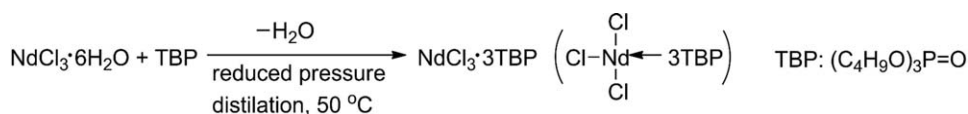[b] Determined by FTIR spectroscopy.
[c] Determined by GPC (THF, PS as calibration).

(MMAO) in the absence/presence of Et$_2$AlCl are efficient systems to afford polyisoprene with narrow MWD ($M_w/M_n \sim 1.6$), albeit with low stereoregularity.[15] Recently, we found that the commercially available Nd(Oi-Pr)$_3$/MAO catalyst works effectively in the homo- and copolymerization of 1,3-butadiene and isoprene, affording high cis-1,4 (co)polymers with narrow MWD ($M_w/M_n < 2.0$) and that further addition of chlorine sources enhances both cis-1,4 selectivity and catalytic activity.[16–18]

On the other hand, due to their high catalytic activity, the binary systems based on NdCl$_3$·nL complexes also attract

NdCl$_3$·6H$_2$O + TBP $\xrightarrow[\text{distillation, 50 °C}]{\substack{-\text{H}_2\text{O} \\ \text{reduced pressure}}}$ NdCl$_3$·3TBP $\left(\text{Cl}-\underset{\underset{\text{Cl}}{|}}{\overset{\overset{\text{Cl}}{|}}{\text{Nd}}}\leftarrow\text{3TBP}\right)$ TBP: (C$_4$H$_9$O)$_3$P=O

considerable interests and much efforts have been made for improving their catalytic performances. For instance, Kwag et al. prepared nanosized NdCl$_3$·1.5THF in a colloidal formation, whose catalytic activity is comparable with those of Nd carboxylate-based ternary systems, but the formed polymers have broad MWD.[19] We synthesized a hexane-soluble complex, NdCl$_3$·3EHOH (EHOH: 2-ethyl hexanol), which in combination with AlEt$_3$ afforded polyisoprene with high cis-1,4 stereoregularity and narrow MWD ($M_w/M_n = 2.0$–2.8).[20] To our knowledge, however, there are few reports concerned with MAO-activated NdCl$_3$·nL catalyst.

This study deals with the NdCl$_3$·3TBP/MAO catalyst for the isoprene polymerization. We investigated in detail the effects of MAO quantity, the presence of free TBP, polymerization temperature and solvents on catalytic activity, polymer molecular weight, and cis-1,4 stereoregularity. Eventually, the NdCl$_3$·3TBP/MAO catalyst is highly effective in isoprene polymerization to yield polymers with high molecular weights, relatively narrow MWD, and quite high cis-1,4 contents.

EXPERIMENTAL

Materials

Nd(O^{i}Pr)$_3$ (J&K, 99.9%) was used as toluene solution (0.10 mol L^{-1}). NdCl$_3$ was purchased from Alfa Aesar Co. Tributylphosphate (TBP, Aldrich) and MAO (Albemarle, 10 wt %

in toluene) were used as received. Al(i-Bu)$_2$H and Al(i-Bu)$_3$ (Akzo Nobel) were diluted into 1.0 mol L^{-1} solution by cyclohexane. Isoprene (Aladdin Industrial Inc.) was purified by refluxing over calcium hydride (CaH$_2$) for 2 h and distilled under nitrogen before use. Cyclohexane was purified by refluxing over CaH$_2$ for 3 h and then distilled before use. NdCl$_3$·nTBP ($n = 3$, 4, and 6) in the absence/presence of free TBP was prepared according to the literature procedure.[21] The synthesis of NdCl$_3$·3TBP was described as a typical example:

IR and Elemental Analysis Data of NdCl$_3$·nTBP

NdCl$_3$·3TBP: IR (KBr, cm^{-1}): 2961, 2935, 2875, 1630, 1466, 1269, 1205, 1032. Anal. Calcd. for C$_{36}$H$_{81}$O$_{12}$P$_3$NdCl$_3$: C, 41.20; H, 7.78. Found: C, 41.46; H, 7.78. NdCl$_3$·4TBP: IR (KBr, cm^{-1}): 2961, 2935, 2875, 1630, 1466, 1280, 1268, 1235, 1032. Anal. Calcd. for C$_{48}$H$_{108}$O$_{16}$P$_4$NdCl$_3$: C, 43.81, 8.27. Found: C, 44.45; H, 8.04. NdCl$_3$·6TBP: IR(KBr, cm^{-1}): 2961, 2935, 2875, 1630, 1466, 1280, 1266, 1234, 1202, 1032. Anal. Calcd. for C$_{72}$H$_{162}$O$_{24}$P$_6$NdCl3: C, 46.78; H 8.83. Found: C, 47.36; H 8.58.

Polymerization Procedure

All manipulations were performed under an atmosphere of dry nitrogen. A detailed polymerization procedure (corresponding to Run 4, Table I) is described as a typical example. At first, a catalyst solution was prepared in a glass tube equipped with a rubber septum in the following manner: cyclohexane (1.0 mL), MAO (1.09 mol L^{-1} in toluene; 1.47 mL), NdCl$_3$·3TBP (0.10 mol L^{-1} in cyclohexane; 0.32 mL) were injected sequentially into the glass tube. This catalyst solution ([Nd] = 1.15 × 10^{-5} mol mL^{-1}) was aged at room temperature for 1 h before use. Cyclohexane (17.0 mL) and isoprene (3.0 mL) were injected into a crown-sealed ampoule, and then the above preformed catalyst solution (0.78 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
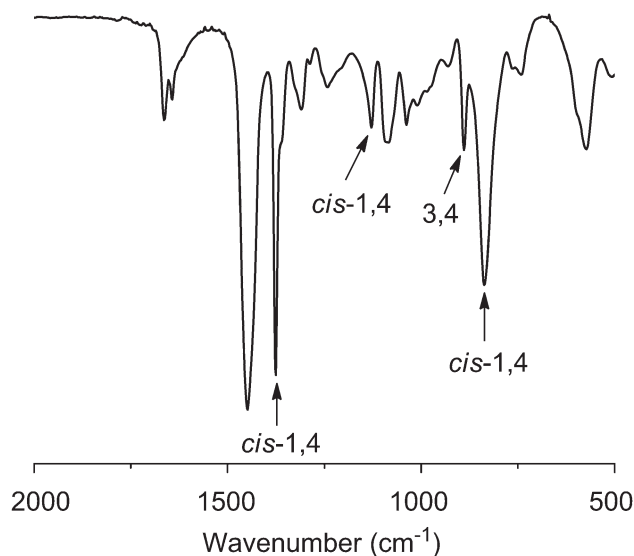
Figure 1. IR spectrum of polyisoprene obtained with NdCl$_3$·3TBP/MAO (sample from Table I, Run 4).

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.

Characterization

The weight- and number-average molecular weights (M_w and M_n) and polydispersity indices (M_w/M_n) of polymers were measured by gel permeation chromatography (GPC) at 30°C using a Visco-tek TDA-302 size exclusion chromatography. Tetrahydrofuran was used as eluent at a flow rate of 1.0 mL min^{-1}. Polystyrene standards (Polymer Laboratories) were used to draw a calibration curve. The molecular weights of polymers were determined using the polystyrene calibration. Sample solutions (5.0 mg mL^{-1}) were filtered through a 0.45 μm microfilter before injection.

The microstructure of polyisoprenes was examined with a Bruker Vertex-70 FTIR spectrophotometer. Film samples were prepared on a KBr disc by casting chloroform solution (ca. 2–8 mg mL^{-1}) of 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:[22]

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

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

where

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

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

^{1}H and 13C NMR spectra of polymers were recorded at room temperature on a Varian Inova 400 NMR spectrometer with deuterated chloroform as a solvent and tetramethylsilane as internal standard.

RESULTS AND DISCUSSION

Effect of Nd Compounds

Three binary Nd-based catalytic systems, i.e. Nd(O^{i}Pr)$_3$, NdCl$_3$, and NdCl$_3$·3TBP in combination with MAO, were examined in isoprene polymerization, and the results are summarized in

Table I. Nd(O^{i}Pr)$_3$/MAO catalyst gave polyisoprene in high yield (90%) with high molecular weight ($M_n = 39.8 \times 10^4$), relatively narrow MWD ($M_w/M_n = 1.51$), but somewhat low cis-1,4 stereoregularity (91.4%), which agrees with the previous study.[18] In contrast, NdCl$_3$/MAO system under the identical conditions and even at a higher MAO level ([Al]/[Nd] = 100) could not polymerize isoprene. Similar result was observed in the case of NdCl$_3$/AlR$_3$ system.[23] It is known that the catalytic activity of traditional AlR$_3$ activated NdCl$_3$-based systems can be significantly enhanced by the incorporation of appropriate ligands.[5,7] In this study, MAO activated NdCl$_3$·3TBP system worked effectively in isoprene polymerization, affording polymer with high molecular weight ($M_n = 30.1 \times 10^4$) and narrow MWD ($M_w/M_n = 1.52$) even at a low [Al]/[Nd] ratio of 50. Although NdCl$_3$·3TBP/MAO catalyst showed slightly lower activity (yield, 84%) than that of Nd(O^{i}Pr)$_3$/MAO, it exhibited higher cis-1,4 selectivity (96.2%), indicating that the chlorine source is an important ingredient for the high cis-1,4 stereospecificity.

The IR spectrum of polyisoprene obtained with NdCl$_3$·3TBP/MAO catalyst is shown in Figure 1. The absorption bands at 836 and 890 cm^{-1} are characteristic of cis-1,4 and 3,4-units, respectively. On the basis of calculation of equations at experimental part, the polymer is composed of 96.2% of cis-1,4 and 3.2% of 3,4-units. ^{13}C NMR was further used to determine the microstructure of the same polymer (Figure 2). It is clear that the signal located at 23.7 ppm is diagnostic of the cis-1,4 unit,[24] whereas the weak signals at 18.9, 48.2, 111.9, and 147.8 ppm are assigned to the 3,4 unit and the signal at 32.8 ppm assigned to the trans-1,4 unit is negligible, indicating the high cis-1,4 stereoregularity of the polymer. Calculation based on the relative peak intensities of the methyl carbon located at 23.7 and 18.9 ppm provided a polyisoprene composition of 96.0% cis-1,4 and 4.0% 3,4-units, which is consistent with the values calculated from IR spectrum. As aforementioned, since the obtained polyisoprene features high cis-1,4 stereoregularity and narrow MWD, such polymer is a promising candidate for the practical applications.

Effects of [Al]/[Nd] Ratio and Free TBP Level in NdCl$_3$-Based Compound

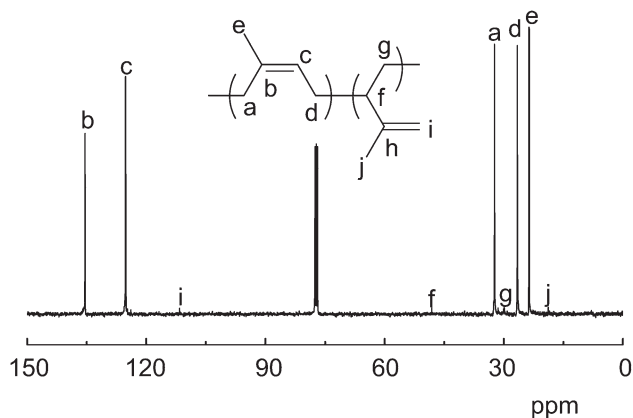The NdCl$_3$·3TBP/MAO catalyst was examined for the polymerization of isoprene by changing the [Al]/[Nd] ratio. As seen

Figure 2. ^{13}C NMR spectrum of polyisoprene obtained with NdCl$_3$·3TBP/MAO catalyst (sample from Table I, Run 4).

Table II. Effect of Free TBP on the Isoprene Polymerization With $NdCl_3 \cdot nTBP/MAO$ Catalyst[a]

Run	[free TBP]/[Nd][b]	[Al]/[Nd]	Yield (%)	$M_n{}^c \times 10^{-3}$	$M_w/M_n{}^c$	Microstructure[d] (mol %) cis-1,4	3,4
1	–	30	48	339	1.40	96.3	3.7
2		50	84	301	1.52	96.2	3.8
3		70	91	235	1.43	96.0	4.0
4		100	97	221	1.55	96.0	4.0
5	1.0	30	16	272	1.56	96.0	4.0
6		70	26	221	1.64	96.2	3.8
7		100	33	125	1.91	97.5	2.5
8		150	61	123	2.18	97.6	2.4
9	3.0	30	3.0[e]	–	–	–	–
10		70	19	306	1.43	96.2	3.8
11		100	23	259	1.49	96.0	4.0
12		150	51	198	1.54	96.0	4.0

[a] Polymerization in cyclohexane at 50°C for 4 h, [Nd]/[Ip] = 3.0×10^{-4}, [Ip] = 1.50 mol L^{-1}.
[b] Free TBP denoted the amount of TBP present in excess of the stoichiometric amount ([TBP]/[Nd] – 3).
[c] Determined by GPC (THF, PS as calibration).
[d] Determined by FTIR spectroscopy.
[e] Not determined.

from Table II, the polymer yield increased with an increasing [Al]/[Nd] ratio. It is worth to mention that isoprene polymerization proceeded at a low [Al]/[Nd] ratio of 50 to afford polymer in a high yield of 84%. As the [Al]/[Nd] ratio further increased to 100, the polymer yield increased to 97%. This binary catalyst is more active than Nd(carboxylate)$_3$/MAO, the latter results in extremely low polymer yield at [Al]/[Nd] = 100 and below.[25,26] Since the catalyst at [Al]/[Nd] ratio of 50 gave the polymer with enough excellent results, i.e., high molecular weight, narrow MWD, and high cis-1,4 stereoregularity, this ratio was used in further experiments.

The produced polymer had high M_n values ranging from 22×10^4 to 34×10^4, and the molecular weight tended to decrease with increasing [Al]/[Nd] ratio. Regardless of the [Al]/[Nd] ratio, the GPC curves remained unimodal (Figure 3) and the MWDs were fairly narrow (M_w/M_n = 1.40–1.56), indicating the presence of a single active site in the polymerization system with $NdCl_3 \cdot 3TBP/MAO$ catalyst.

Next, the three $NdCl_3$-based compounds, $NdCl_3 \cdot 3TBP$, $NdCl_3 \cdot 4TBP$, and $NdCl_3 \cdot 6TBP$, containing different amount of free TBP were characterized by IR spectroscopy (Figure 3). In the IR spectrum of TBP, the absorption band at 1280 cm^{-1} is assignable to the P=O stretching vibration, which completely disappeared in the IR spectrum of $NdCl_3 \cdot 3TBP$, and a new absorption peak appeared at 1205 cm^{-1}. These results clearly indicate the occurrence of the coordination reaction between the phosphoryl oxygen atoms and the Nd ions and no contamination with the free TBP in $NdCl_3 \cdot 3TBP$. In contrast, in the cases of $NdCl_3 \cdot 4TBP$ and $NdCl_3 \cdot 6TBP$, the absorption peak at 1280 cm^{-1} indicative of TBP was observed, indicating the presence of free TBP in these two compounds, and the higher intensity of the peak in $NdCl_3 \cdot 6TBP$ implies the presence of higher amount of free TBP. Similar result was observed in the previous study.[27]

The catalytic activity was considerably influenced by the free TBP level in $NdCl_3 \cdot nTBP$. For example, at a fixed [Al]/[Nd] ratio, the polymer yield decreased in the order of

Table III. Effect of Various Al Compounds on the Isoprene Polymerization With $NdCl_3 \cdot 3TBP$ Catalyst[a]

Run	Al compound	[Al]/[Nd]	Yield (%)	$M_n{}^b \times 10^{-3}$	$M_w/M_n{}^b$	Microstructure[c] (mol %) cis-1,4	3,4
1	MAO	50	84	301	1.52	96.2	3.8
2	Al(i-Bu)$_2$H	20	76	190	3.92	96.3	3.7
3		40	89	73	12.2	95.9	4.1
4	Al(i-Bu)$_3$	20	35	208	3.39	96.2	3.8
5		40	100	163	4.86	96.1	3.9

[a] Polymerization in cyclohexane at 50°C for 4 h, [Nd]/[Ip] = 3.0×10^{-4}, [Ip] = 1.50 mol L^{-1}.
[b] Determined by GPC (THF, PS as calibration).
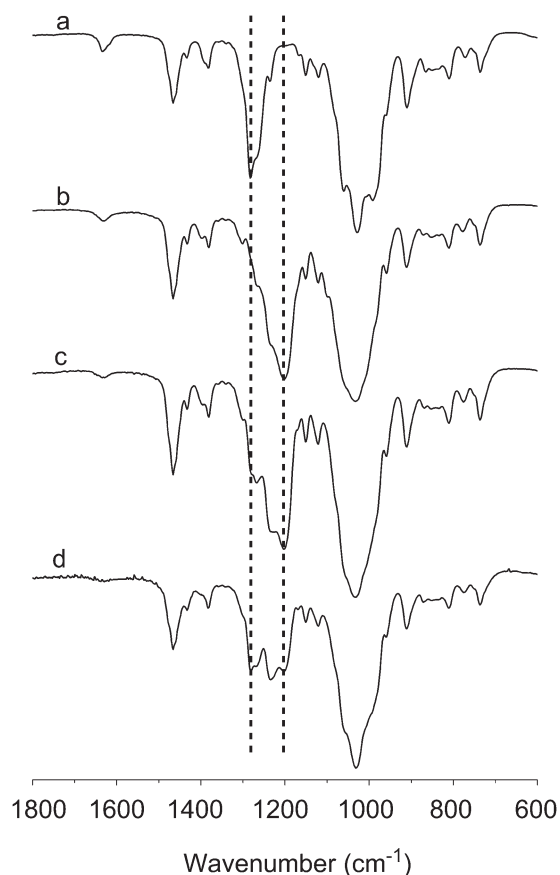[c] Determined by FTIR spectroscopy.

Figure 3. IR spectra of (a) TBP, (b) NdCl$_3$·3TBP, (c) NdCl$_3$·4TBP, and (d) NdCl$_3$·6TBP.

NdCl$_3$·3TBP > NdCl$_3$·4TBP > NdCl$_3$·6TBP. Coupled with the results of polymer yields obtained on the basis of their dependence on the [Al]/[Nd] ratio, it may be speculated that the free TBP interacts with MAO. Thus, the presence of free TBP is detrimental to the isoprene polymerization.

Effect of Al Cocatalysts
It has been reported that the catalytic performance of NdCl$_3$·nL-based systems was affected by the cocatalyst.[28,29] In

this study, the effect of the type of Al compound on the isoprene polymerization was examined. As seen from Table III, MAO-based catalyst gave the polymer with the highest M_n and the narrowest MWD. Al(i-Bu)$_2$H-based catalyst afforded polymer with much lower M_n than that with MAO-based catalyst. As the [Al]/[Nd] ratio increased from 20 to 40, the M_n of polymer sharply decreased from 19 × 10^4 to 7.3 × 10^4, and meanwhile, the MWD became much broader (Figure 4). The bimodal GPC curve suggested the presence of multiple active species in the polymerization. Multiple active species has often been assumed from bimodal GPC profiles in previous studies with Nd-based catalysts.[30–32] Al(i-Bu)$_3$-based catalyst afforded polyisoprene with higher M_n and narrower MWD than those with Al(i-Bu)$_2$H-based counterpart. These results implied the higher chain transfer ability of Al(i-Bu)$_2$H compared with Al(i-Bu)$_3$, and Friebe et al. has reported that the chain transfer efficiency of Al(i-Bu)$_2$H is 8-fold over that of Al(i-Bu)$_3$.[33] On the other hand, the type of Al compound has little influence on the catalyst selectivity, all the polymers had cis-1,4 rich structures (95.9–96.2%). The cis-1,4 content of polyisoprene obtained with the MAO-based catalyst was slightly lower compared with the normal Nd-based catalyst system.[34]

Effects of Polymerization Temperature and Time
The effects of polymerization temperature and time on the isoprene polymerization were examined, and the results are listed in Table IV. The polymerization remarkably accelerated with increasing polymerization temperature from 0°C to 50°C. Thus, whereas the polymer yield at 0°C was no more than 26% after 24 h, the yield reached 84% at 50°C in 4 h. As the polymerization temperature increased, the M_n of polymer tended to decrease, while the MWD value remained around 1.50. This is the same tendency as with Nd(O^{i}Pr)$_3$/MAO catalyst,[18] but is different from the case of Al(i-Bu)$_3$ activated NdCl$_3$·3TBP catalyst, in which the MWD value of polymer increases with increasing temperature.[34] It should be noted that the stereoregularity of the polymers were not significantly affected by the polymerization temperature; the cis-1,4 content only slightly decreased from 98.1% to 96.2% when the temperature increased from 0°C to 50°C, indicating the high stability of stereosepcificity of the catalyst.

Table IV. Effect of Temperature on the Isoprene Polymerization With NdCl$_3$·3TBP/MAO Catalyst[a]

Run	Temp (°C)	Time (h)	Yield (%)	M_n^b × 10^{-3}	M_w/M_n^b	Microstructure[c] (mol %)	
						cis-1,4	3,4
1	0	4	trace	–	–	–	–
2	0	24	26	417	1.35	98.1	1.9
3	25	4	34	339	1.37	97.6	2.8
4	25	8	73	360	1.38	97.4	2.6
5	50	1	28	230	1.54	96.3	3.7
6	50	2	65	244	1.56	96.2	3.8
7	50	4	84	301	1.52	96.2	3.8

[a] Polymerization in cyclohexane, [Nd]/[Ip] = 3.0 × 10^{-4}, [Ip] = 1.50 mol L^{-1}.
[b] Determined by GPC (THF, PS as calibration).
[c] Determined by FTIR spectroscopy.

Table V. Effect of Solvent on the Isoprene Polymerization With NdCl$_3$·3TBP/MAO Catalyst[a]

Run	Solvent	Yield (%)	M_n[b] $\times 10^{-3}$	M_w/M_n[b]	Microstructure[c] (mol %)	
					cis-1,4	3,4
1	Cyclohexane	84	301	1.52	96.2	3.8
2	Hexane	55	244	1.60	95.4	4.6
3	Toluene	5.2	–[d]			
4	Dichloromethane	11	Insoluble			

[a] Polymerization at 50°C for 4 h, [Nd]/[Ip] = 3.0 × 10^{-4}, [Ip] = 1.50 mol L^{-1}.
[b] Determined by GPC (THF, PS as calibration).
[c] Determined by FTIR spectroscopy.
[d] Not determined.

Effect of Polymerization Solvents

The effect of polymerization solvents on isoprene polymerization is shown in Table IV. Aliphatic hydrocarbons, hexane and cyclohexane, do not affect the characteristics of the final polymers, e.g., high cis-1,4 stereoregularity and narrow MWD, while the polymer yield was affected to some extent. The polymer yield obtained in cyclohexane was higher than those in the other solvents. A reduced yield of polymer in hexane was attributable to the low solubility of the preformed catalyst in hexane, which inhibits the propagating reaction of polymerization. Among the solvents examined, the lowest polymer yield was observed in the case of toluene, which may be due to competitive coordination of the aromatic solvent and monomer to the propagating species as reported previously with Nd-based catalysts.[5,35] Polymerization in dichloromethane, a polar solvent, afforded polymer in a very low yield of 11%. The polymerizations of isoprene in dichloromethane with Nd(O^{i}Pr)$_3$/MAO and Nd(versatate)$_3$/MAO catalysts afford poorly soluble products.[18,25] It is also the case in the present study; the produced polymer was insoluble in any organic solvents, which might be due to a crosslinking structure.

CONCLUSION

In this study, the MAO-activated NdCl$_3$·3TBP catalyst for the stereospecific polymerization of isoprene were investigated, and the results were compared with the traditional AlR$_3$-activated Nd catalyst systems. The present MAO-based system proved to be highly active at a low MAO level to afford polyisoprene featuring high molecular weight, fairly narrow MWD, and high cis-1,4 content. The unimodal GPC profile and narrow MWD indicate that the MAO-based catalysts possesses the single active site nature, whereas Al(i-Bu)$_2$H-based catalyst gave the polymers with low molecular weight and broad MWD due to multiple-site active centers. The polymerization solvent remarkably affected the catalytic activity; cyclohexane proved to give excellent results with respect to catalytic activity and stereospecificity. Taking the advantage of the stability of the common NdCl$_3$·3TBP, low MAO level, high activity, and high cis-1,4 selectivity, the present catalyst system could be considered as an efficient alternative to Nd carboxylate-based systems for the practical applications.

Figure 4. GPC curves of polyisoprene obtained with NdCl$_3$·3TBP/MAO catalyst (a, sample from Table IV, Run 1), NdCl$_3$·3TBP/Al(i-Bu)$_2$H catalyst (b, sample from Table IV, Run 3), and NdCl$_3$·3TBP/Al(i-Bu)$_3$ catalyst (c, sample from Table IV, Run 5).

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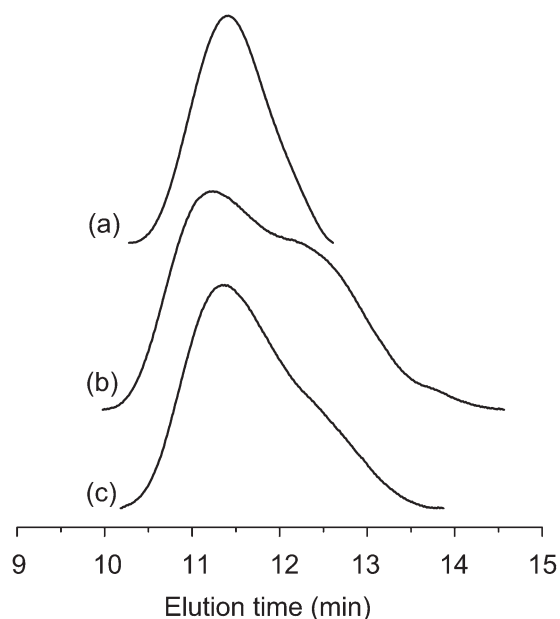8. Porri, L.; Ricci, G.; Shubin, N. *Macromol. Symp.* **1998**, *128*, 53.

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