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Novel Neodymium-Based Ternary Catalyst, $Nd(O\textit{i}\text{-}Pr)_3/[HNMe_2Ph]^+[B(C_6F_5)_4]^-/\textit{i}\text{-}Bu_3Al$, for Isoprene Polymerization

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Summary

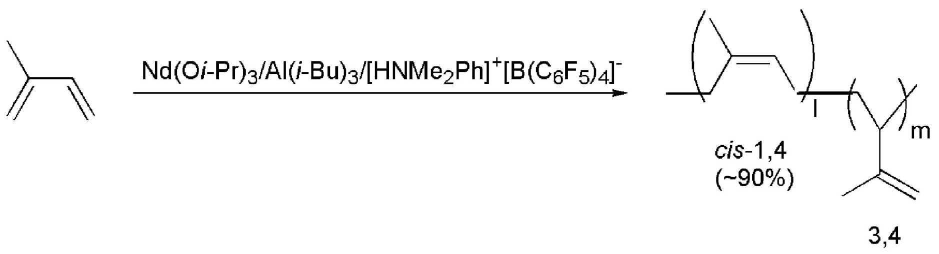
Polymerization of isoprene was investigated by using a novel ternary catalyst system composed of neodymium(III) isopropoxide ($Nd(O\textit{i}\text{-}Pr)_3$), dimethylphenylammonium tetrakis(pentafluorophenyl)borate ($[HNMe_2Ph]^+[B(C_6F_5)_4]^-$; borate), and triisobutylaluminum ($\textit{i}\text{-}Bu_3Al$). The mole ratios of borate and aluminum compounds to Nd catalyst significantly affected the polymerization behavior. Both yield and *cis*-1,4 content of polyisoprene decreased in the case of $[\text{borate}]/[\text{Nd}] < 1.0$, while at $[\text{borate}]/[\text{Nd}] > 1.0$ the formation of multiple active species resulted in the polymer showing bimodal peaks in GPC. When the [Al]/[Nd] ratio was lower than 30, the polymer yield sharply decreased, whereas the *cis*-1,4 content became relatively low with use of a large excess of Al ($[\text{Al}]/[\text{Nd}] > 50$). Thus, the optimal catalyst composition was [Nd]/[borate]/[Al] = 1/1/30, which gave in >97% yield polyisoprene with high molecular weight (M_n ~2×10^5) and relatively narrow molecular weight distribution (M_w/M_n ~2.0) and mainly *cis*-1,4 structure (~90%).

Introduction

Cis-1,4 polymers of conjugated dienes (e.g., 1,3-butadiene and isoprene) are industrially manufactured on a large scale and applied as synthetic rubbers to tire and many other elastic materials. Various catalysts containing Li [1], Ti [2–4], Co [5], Ni [6, 7], Gd [8, 9], and Nd [10–16], etc. have been developed so far. In general, poly(1,3-dienes)s obtained with Nd-based catalysts possess high *cis*-1,4 content and excellent physical properties [17]. Conventional Nd-based catalyst systems can be divided into two categories, namely, (i) ternary systems derived from Nd carboxylate (e.g., naphthenate and versatate), R_3Al (e.g., $\textit{i}\text{-}Bu_3Al$ and $\textit{i}\text{-}Bu_2AlH$) and Cl-containing compounds (e.g., Et_2AlCl, *t*-BuCl, and Me_2SiCl_2), and (ii) binary systems composed of $NdCl_3\cdot nL$ (e.g., L = ethanol or triisobutyl phosphonate, $n = 3$; L = tetrahydrofuran (THF), $n = 2$) and R_3Al [e.g., Et_3Al and $\textit{i}\text{-}Bu_3Al$]. Both types of catalysts exhibit high activity and give high molecular weight polymers in aliphatic hydrocarbon solvents. A feature of these Nd catalysts is to provide polybutadiene, polyisoprene and butadiene-isoprene copolymers, all of which have high *cis*-1,4 content (>95%). However, their molecular weight and molecular weight distribution (MWD) are not well controlled, which is attributable to the heterogeneity of catalyst systems and the multiple nature of active centers.

While methylaluminoxane (MAO) [16] is well known as a cocatalyst of metallocene catalysts in olefin polymerization, it has also been employed in 1,3-butadiene polymerization. For instance, catalyst systems derived from Nd carboxylate and MAO [18–20] show high activity without Cl-containing compounds. Both allyl-Nd/MAO [21, 22] and metallocene complex/MAO [23, 24] catalysts provide single-site active species and give polybutadiene having narrow MWD ($M_w/M_n < 2.0$). These catalyst systems, however, require a large amount of MAO ([MAO]/[Cat] = 100–1000). There have been rather few reports on the MAO-activated catalyst systems that polymerize isoprene to give polymer with high *cis*-1,4 content [25–27]. We have reported that a binary catalyst composed of $Nd(O\textit{i}\text{-}Pr)_3$ and MAO [25] which does not require a large amount of MAO ([MAO]/[Nd] = 30), and which provides polyisoprene with high molecular weight, narrow MWD and mainly *cis*-1,4 structure in good yield.

In olefin polymerization, F-containing borate salts and borane compounds [16] have been used as cocatalysts in place of MAO in conjunction with metallocene catalysts. The borate reagents effectively generate and stabilize cationic alkyl metallocene complexes in the presence of organoaluminum compounds. Boisson recently reported the $Nd[N(SiMe_3)_2]_3$/borate/$\textit{i}\text{-}Bu_3Al$ for the polymerization of 1,3-butadiene [28]. Further, samarocene/borate/R_3Al [29] catalyst is active enough in 1,3-butadiene polymerization to give polymer having mainly *cis*-1,4 structure. In the present study, we developed a novel ternary catalyst composed of neodymium(III) isopropoxide [$Nd(O\textit{i}\text{-}Pr)_3$], dimethylphenylammonium tetrakis(pentafluorophenyl)borate {$[HNMe_2Ph]^+[B(C_6F_5)_4]^-$; borate} and triisobutylaluminum ($\textit{i}\text{-}Bu_3Al$), which showed high activity and high *cis*-1,4 stereoselectivity in isoprene polymerization (Scheme 1). Further, we optimized reaction conditions for the polymerization by this ternary catalyst.



Scheme 1. Polymerization of isoprene catalyzed by $Nd(O\textit{i}\text{-}Pr)_3/[HNMe_2Ph]^+[B(C_6F_5)_4]^-/\textit{i}\text{-}Bu_3Al$

Experimental

Materials

$Nd(O\textit{i}\text{-}Pr)_3$ (Strem Chemicals Inc., 99%-Nd) was used as toluene solution (5.0×10^{2} M). $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$ was donated by Tosoh-Akzo Chemical Co. and used as dichloromethane solution (5.0×10^{-2} M). $\textit{i}\text{-}Bu_3Al$ (Kanto Chemical Co. Inc., 0.95 M solution in hexane) was used as received. Isoprene (Nacalai Tesque Inc.) and dichloromethane (Wako Pure Chem. Ind. Ltd.) were dried by heating at reflux over calcium hydride for 2 h and distilled under nitrogen. Heptane and toluene were refluxed over sodium and distilled before use. Cyclohexane was dried with molecular sieves 13X and then refluxed over calcium hydride for 2 h and distilled under nitrogen.

Polymerization Procedure

A typical polymerization procedure is as follows: firstly, a catalyst solution was prepared in a glass tube under a dry nitrogen atmosphere by adding heptane (0.040 mL), i-Bu_3Al solution (0.16 mL, 0.95 M in hexane) and $Nd(Oi\text{-}Pr)_3$ solution (0.10 mL, 5.0×10^{-2} M in toluene). This catalyst solution was aged at 30 ºC for 1 h before use. Isoprene (1.5 mL) was dissolved in heptane (8.1 mL) and then $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$ solution (0.10 mL, 5.0×10^{-2} M in dichloromethane) was added to the isoprene solution, followed by the addition of the Nd catalyst solution. Polymerizations were carried out at 30 or 60 ºC, and quenched by adding acidified methanol (10 mL) containing 2,6-di-*tert*-butyl-*p*-crezol (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.

Polymer Characterization

The molecular weights (M_w and M_n) and polydispersity indices (M_w/M_n) were determined by gel permeation chromatography (GPC) using a Jasco PU-980/RI-930 chromatograph. A series of three KF-805 (Shodex) columns maintained at 40 ºC were employed. THF was used as eluent at a flow rate of 1.0 mL/min. A polystyrene calibration was used to determine the molecular weights of polymers.

The microstructures of polymers were determined from IR spectra measured with a Shimadzu FTIR-8100 spectrophotometer. Film samples were prepared on a KBr disc by casting CS_2 solution of polymer. The amount of *trans*-1,4 structure was negligible. 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 formulas reported in the literature [30].

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

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

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

Results and Discussion

Effects of polymerization time and temperature

At first we examined the effects of polymerization time and temperature in isoprene polymerization with $Nd(Oi\text{-}Pr)_3/[HNMe_2Ph]^+[B(C_6F_5)_4]^-/i\text{-}Bu_3Al$ (1:1:30) catalyst. The results are summarized in Table 1. At 30 °C, the completion of the polymerization needed about 5 h to give in 97% yield polyisoprene with high *cis*-1,4 content (90.4%) and high molecular weight (M_n = 201 000) (run 7). Although bimodal and broad MWDs were observed in GPC curves in an early stage of polymerization at 30 °C, the M_w/M_n became smaller and 2.27 after 5 h. At 60 °C, a practically quantitative yield was achieved in a shorter reaction time of 3 h (run 12). It should be noted that *cis*-1,4 contents were not significantly affected by the polymerization temperature.

Table 1. Effects of Time and Temperature on Isoprene Polymerization[a]

Run	Temp. (°C)	Time (min)	Yield (%)	*cis*-1,4[b] (%)	M_n[c]	M_w/M_n[c]
1	30	10	16	91.3	83 000	7.57
2		30	42	90.1	106 000	3.30
3		60	62	90.5	156 000	2.67
4		120	83	90.0	180 000	2.21
5		180	89	89.8	235 000	2.19
6		240	93	90.0	191 000	2.31
7		300	97	90.4	201 000	2.27
8	60	10	39	89.0	107 000	2.66
9		30	79	89.1	145 000	2.39
10		60	92	89.4	162 000	2.32
11		120	95	89.4	166 000	2.30
12		180	96	89.4	193 000	1.97

[a] Polymerizations were carried out in heptane; $[M]_0 = 1.5$ M, [Nd] = 0.50 mM, [B]/[Nd] = 1.0, [Al]/[Nd] = 30; [b] Determined by FT-IR; [c] Determined by GPC (eluent THF, PSt calibration).

Effect of [borate]/[Nd] and [Al]/[Nd] ratios

The catalytic activity was considerably influenced by the amounts of borate and aluminum compounds relative to Nd catalyst. Firstly, the effect of [borate]/[Nd] ratio was examined in the polymerization at 30 °C for 5 h with [Al]/[Nd] = 30 (Table 2). The highest catalytic activity was observed when an equimolar amount of borate compound to Nd catalyst was used (run 3). The polymer yield was lower when the amount of borate was less than that of Nd catalyst. This should be due to the formation of a less amount of active species in the polymerization. Excess amounts of borate did not give good results, either; e.g., the formed polyisoprene showed bimodal curves in GPC profile when 1.5 equivalent of borate toward Nd catalyst was employed. Further, two equivalents of borate resulted in a dramatic decrease of the polymer yield to 10% with bimodal GPC curves (run 5).

In general, boron compounds are used as cocatalysts in conjunction with metallocene complexes in olefin polymerization, in which boron compounds function to yield *cationic* metallocene complexes with the acid of organoaluminum compounds [16]. Regarding the polymerization of conjugated dienes, Boisson reported that a ternary catalyst system, $Nd[N(SiMe_3)_2]_3$/borate/*i*-Bu_3Al [28] polymerizes 1,3-butadiene. It is assumed that the active species of the present catalyst system is also a cationic heterometallic species, which might have the same structure as the reported one. The

Table 2. Effect of [B]/[Nd] Ratio on Isoprene Polymerization[a]

Run	[B]/[Nd]	Yield (%)	*cis*-1,4[b] (%)	M_n[c]	M_w/M_n[c]
1	0.25	41	87.6	72 000	2.59
2	0.50	87	88.6	138 000	1.89
3	1.0	97	90.4	201 000	2.27
4	1.5	93	91.8	287 000 (91%)	2.30
				870 (9%)	1.29
5	2.0	10	91.4	136 000 (88%)	3.99
				900 (12%)	1.34

[a] Polymerizations were carried out in heptane at 30 °C for 5 h; $[M]_0 = 1.5$ M, [Nd] = 0.50 mM, [Al]/[Nd] = 30; [b] Determined by FT-IR; [c] Determined by GPC (eluent THF, PSt calibration).

Table 3. Effect of [Al]/[Nd] Ratio on Isoprene Polymerization[a]

Run	[Al]/[Nd]	Yield (%)	*cis*-1,4[b] (%)	M_n[c]	M_w/M_n[c]
1	10	0	—	—	—
2	20	4	85.7	357 000	3.58
3	25	25	89.1	325 000	3.12
4	30	97	90.4	201 000	2.27
5	40	100	90.4	131 000	2.84
6	50	100	89.1	79 000	2.48

[a] Polymerizations were carried out in heptane at 30 °C for 5 h; $[M]_0$= 1.5 M, [Nd] = 0.50 mM, [B]/[Nd] = 1.0; [b] Determined by FT-IR; [c] Determined by GPC (eluent THF, PSt calibration).

mechanism of generation of active species can be considered as follows: firstly, heterometallic species with bridges of isobutyl and/or isopropoxy groups are formed by the reaction of Nd and Al compounds, and then cationic heterometallic compounds are generated with the aid of borate salt. The reason for the quite low yield at a [borate]/[Nd] ratio of 2.0 might be excessive cleavage of the bridging part. Bimodal MWDs are attributed to the creation of several active species, which have different catalytic activity.

The effect of [Al]/[Nd] ratio was next studied, whose results are presented in Table 3. No polymer was obtained without addition of i-Bu_3Al. With increasing amount of the added i-Bu_3Al, the yield of polyisoprene increased. A practically quantitative yield was achieved at an [Al]/[Nd] ratio of 30. Larger amounts of aluminum than 30 tended to lower M_n and broaden MWD. This is attributable to both the increase of active species and the function of i-Bu_3Al as a transfer agent [17].

Effect of polymerization solvents

The effect of polymerization solvents is shown in Table 4. Aliphatic hydrocarbons such as heptane and cyclohexane formed the polymer in good yield. Polymerization in heptane provided polymer which had relatively narrow MWD. Although the GPC chart of the polymer obtained in cyclohexane was bimodal and broad MWD, the polymer had somewhat higher *cis*-1,4 content than that in heptane. Polymerization in dichloromethane, a polar solvent, afforded polymer with high *cis*-1,4 content polymer, but the polymer yield remained very low and the GPC profile was bimodal. Polymer was hardly obtained in toluene, an aromatic solvent, and the *cis*-1,4 content could not be determined because of its insolubility in CS_2.

Table 4. Effect of Solvents on Isoprene Polymerization[a]

Run	Solvent	Yield (%)	*cis*-1,4[b] (%)	M_n[c]	M_w/M_n[c]
1	heptane	97	90.4	201 000	2.27
2	cyclohexane	100	91.3	169 000 (95%) 775 (5%)	3.97 1.39
3	dichloromethane	12	93.4	153 000 (80%) 4 160 (20%)	1.30 1.36
4	toluene	1	Insoluble	2 280	1.43

[a] Polymerizations were carried out at 30 °C for 5 h; $[M]_0$= 1.5 M, [Nd] = 0.50 mM, [B]/[Nd] = 1.0 [Al]/[Nd] = 30; [b] Determined by FT-IR; [c] Determined by GPC (eluent THF, PSt calibration).

Conclusion

A ternary catalyst system composed of [Nd(O*i*-Pr)$_3$], $[HNMe_2Ph]^+[B(C_6F_5)_4]^-$, and *i*-Bu$_3$Al showed high activity in isoprene polymerization to afford polymer with high *cis*-1,4 content and relatively narrow MWD. The optimal composition of this catalyst system was determined as [borate]/[Nd] = 1, [Al]/[Nd] = 30; one of the best results is as follows; yield 97%, *cis*-1,4 content 90.4%, M_n = 201 000, M_w/M_n = 2.27. This catalyst system showed high activity in aliphatic solvents such as heptane and cyclohexane.

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