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Studies on Nickel-Containing Ziegler-Type Catalysts. I. New Catalysts for High-*cis*-1, 4-polybutadiene

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Some organic halogenides were found to induce a catalytic activity in a nickel naphthenate (Ni(naph)$_2$)/ AlEt$_3$ system for the stereospecific polymerization of butadiene to a high *cis*-1,4 microstructure. These new activators were fluorinated carbonyl (or carboxyl) compounds, halogenated phenols or halogenated hydroquinones. These compounds were assumed to induce polymerization activity through the formation of Lewis acidic components with AlEt$_3$. For this catalyst, H$_2$O acted as an efficient molecular weight promoter.

(Trifluoromethyl)benzene was found to promote the activity of a catalytic system: Ni(naph)$_2$/ AlEt$_3$/ organic halides. AlEt$_2$F was found to be formed between AlEt$_3$ and (trifluoromethyl)benzene. Finally, a simple system was found to be an efficient catalyst, Ni(naph)$_2$/ AlEt$_2$F/ H$_2$O, for which chlorinated phenols acted as an effective molecular weight regulator.

A stereospecific polymerization of butadiene to a high *cis*-1,4 microstructure has been extensively studied both from industrial and catalytic chemical viewpoints. Four kinds of Ziegler-type catalysts are known for the *cis*-1,4 polymerization of butadiene. The titanium catalyst (TiI$_4$/ AlEt$_3$);1) the cobalt catalyst (CoCl$_2$/ AlEt$_2$Cl);2) the nickel catalyst (Ni(naph)$_2$/ AlEt$_3$/ BF$_3$·OEt$_2$), where Ni(naph)$_2$ denotes nickel naphthenate;3) and the lanthanide catalyst (LnCl$_3$/ EtOH/ AlEt$_3$).4)

As for the nickel catalyst, the stereospecific polymerization mechanism is interpreted using the π-allyl nickel model for the polymer chain terminal,5) or the *cis*-coordination model of the butadiene monomer.6) It is also widely recognized that Lewis acidic components (e.g. BF$_3$, AlCl$_3$, TiCl$_4$ etc.) or π-acceptors (e.g. quinones, carboxylic anhydrides, tetracyanoquinodimethane etc.) are necessary for activating the π-allyl nickel catalyst.7–11) Concerning the Ziegler-type catalyst, however, very few catalysts are known, except for those stated above, Ni(naph)$_2$/ AlEt$_3$/ (BF$_3$·OEt$_2$ or other inorganic Lewis acids).12,13) Considering that the Ziegler-type catalyst contains a very reactive organoaluminum component, the possibility of obtaining a new catalyst system was examined by modifying the organoaluminum component with organic compounds having electron-attractive groups.

Experimental

Materials. 1,3-butadiene (C$_4''$) was vaporized from a container through a column of 3A molecular sieves (MS), and was trapped at 200 K into a glass flask containing 3A MS. The water content in C$_4''$ was determined as being below 5 ppm by Karl-Fisher's titration. The contents of 4-vinyl-1-cyclohexene and acetylene were determined as being less than 10 ppm by GC analysis. A solvent (toluene) was distilled, bubbled with N$_2$ gas and dried over 3A MS. Triethylaluminum (AlEt$_3$) was used after distillation in vacuo (bp=348 K at 0.667 kPa). Diethylaluminum fluoride (AlEt$_2$F) was purchased as a toluene solution, and used as obtained. Ni(naph)$_2$ was of extra-pure chemical grade. The other catalyst components, such as organic activators, were distilled in a N$_2$ atmosphere and dried over 3A MS.

Experimental Procedure and Analysis. The catalyst was prepared in a glass bottle-type reactor or in a shrenk tube under a N$_2$ atmosphere as follows. A portion of the toluene was first introduced, and Ni(naph)$_2$ was reduced with AlEt$_3$ in the presence of a trace amount of C$_4''$. After adding the residual toluene, the C$_4''$ monomer was introduced at 263 K, and the glass bottle was sealed with a cap. The polymerization was conducted mainly at 313 K by rotating the glass bottle in a water bath.

The catalyst activator was added in either of two ways. The first way was to premix the activator with AlEt$_3$ at 293—373 K for 1 h; this modified organoaluminum compound was used for the reduction of Ni(naph)$_2$ (method A). The other way was to add the activator after reducing Ni(naph)$_2$ by AlEt$_3$ (method B).

After the polymerization reaction, the reaction solution was discharged into methanol containing 200 ppm of 2,6-di-*t*-butyl-*p*-cresol, and the precipitated polymer was dried at 333 K in vacuo. The intrinsic viscosity [η] was measured with an Uberode's viscosity meter at 303 K in a toluene solution. The microstructure of polybutadiene was analyzed by IR spectroscopy and calculated using D. Morero's method.14)

Results and Discussion

Activators for the Ni(naph)$_2$/ AlEt$_3$ Catalyst. Although the Ni(naph)$_2$/ AlEt$_3$ system has no activity for butadiene polymerization, upon the addition of some organic activators having electron-attractive groups, a fairy good yield of high *cis*-1,4-polybutadiene was obtained as shown in Tables 1 and 2. Phenols, carboxylic acids, hydroquinones or ketones, which have no halogen substutuent, did not show any activating effect. However, by carrying electron-attractive groups, they turned into efficient activators for this catalyst. The effective activators are as follows; chlorinated or brominated phenols, chlorinated hydroquinones, chlorinated or brominated benzoquinones, fluorinated carboxylic acids, fluorinated ketones, and *p*-(trifluoromethyl)phenol. Among the electronegative groups, NO$_2$ and CN are not effective. A unique activator is allyl-type

Table 1. Activators for Ni(naph)$_2$/AlEt$_3$ Catalyst (**1**)[a]

No.	Activator		Polymer yield/%	[η]	*cis*-1,4 Content/%
	Compound	Amount[b]		dl g^{-1}	
1	—	—	0	—	—
2	Pentabromophenol	2.0	83.5	0.4	90.3
3	*p*-(Trifluoromethyl)phenol	0.8	70.3	2.4	93.0
4	Perfluoropropionic acid	1.0	60.7	0.6	95.8
5	Pyromellitic anhydride	1.0	15.0	—	91.1
6	*p*-(Trifluoromethyl)benzoyl fluoride	1.5	27.9	2.7	91.8
7	1,1,1-Trifluoroacetone	1.8	31.2	1.3	91.5
8	Hexafluoroacetone hydrate	0.33	92.7	0.9	96.8
9	1,1-Dichloro-3,3-difluoropropene	1.0	57.0	2.8	94.0
10	Trichloroacetaldehyde	1.0	0	—	—
11	2,2,3,3-Tetrafluoro-1-propanol	1.0	0	—	—

a) Toluene=50 ml, C_4''=10 g (185 mmol), Polymerization; 40 °C, 5 h, Ni/Al=0.05/0.5 (mmol). b) Molar ratio to AlEt$_3$ (AlEt$_3$ and activator are premixed at 100 °C for 1 h).

Table 2. Activators for Ni(naph)$_2$/AlEt$_3$ Catalyst (**2**)[a]

No.	Activator		Polymer yield/%	[η]	*cis*-1,4 Content/%
	Compound	Amount[b]		dl g^{-1}	
1	Pentachlorophenol	1.0	46.0	1.2	88.0
2	Tetrachloro-*p*-hydroquinone	1.0	77.4	1.7	88.5
3	Tetrachloro-*p*-benzoquinone	1.0	95.2	1.8	94.1
4	Tetrachloro-*p*-benzoquinone	0.8	79.6	1.7	88.1
5	Tetrachloro-*p*-benzoquinone	0.5	6.3	—	—
6*	Hydroquinone	1.0	10.4	1.5	87.0
7*	Tetrabromo-*p*-benzoquinone	1.0	85.3	1.2	86.8
8*	2,3-Dichloro-1,4-naphthoquinone	1.0	60.8	1.4	95.2
9*	Tetrachloro-*o*-benzoquinone	1.0	27.7	1.9	90.6

a) Toluene=30 ml, C_4''=10 g (185 mmol), Polymerization; 40 °C, 2 h, Ni/Al=0.2/1.0 (mmol), *) Ni/Al=1.0/3.0 (mmol). b) Molar ratio to AlEt$_3$ (AlEt$_3$ and activator are premixed at 100 °C for 1 h).

fluoride, 1,2-dichloro-3,3-difluoro-1-propene, which has no functional group like hydroxyl, carbonyl or carboxyl.

In the π-allyl Ni catalyst the acidic components are necessary to activate the catalyst; organic acids such as trifluoroacetic acid or organic π-acceptors such as tetrachloro-*p*-benzoquinone[5] are known to be good activators. In our case, organic activators bearing halogens were pre-mixed with AlEt$_3$. They must therefore react with AlEt$_3$ according to the following equations:

$$\mathrm{R_XCOOH + AlEt_3 = R_XCOOAlEt_2 + EtH,} \qquad (1)$$

$$\mathrm{(R_X)(R_X')C{=}O + AlEt_3 = (R_X)(R_X')(Et)C{-}OAlEt_2,} \qquad (2)$$

$$\mathrm{Ar_XOH + AlEt_3 = Ar_XOAlEt_2 + EtH,} \qquad (3)$$

and

$$\mathrm{HO{-}Ar_X{-}OH + 2AlEt_3 = Et_2AlO{-}Ar_X{-}OAlEt_2 + 2EtH.} \qquad (4)$$

In the specific case of 1,2-dichloro-3,3-difluoro-1-propene, allyl-type fluorine atoms are assumed to exchange with the Et group of AlEt$_3$, and a kind of ethylaluminum fluoride may be formed. In any case, the thus-modified organoaluminum compounds possess a kind of Lewis acidity, and are therefore able to activate the Ni(naph)$_2$/AlEt$_3$ catalyst. The estimated active center in the case of halogenated phenol is shown in Fig. 1. The modified organoaluminum compound coordinates to the zero-valent Ni atom in a square planer configuration; by lowering the electron density of the Ni atom, it necessarily lowers the HOMO energy, resulting in the promotion of a propagation reaction.[15]

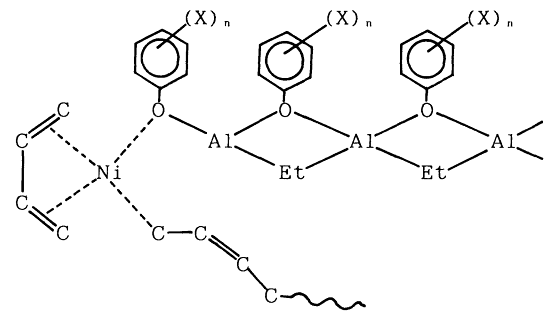

Fig. 1. Estimated structure of the active center.

Comparison with a π-Allyl Ni Catalyst. By using tetrachloro-*p*-benzoquinone as a common activator, the catalytic activities of (A) Ni(naph)$_2$/AlEt$_3$ catalyst and

(B) π-allyl Ni catalyst were compared (Table 3). Under anhydrous conditions, catalyst (A) exhibited a very high activity (100% yield at 0.2 h) compared to the low activity of catalyst (B) (80.5% yield at 20 h). A further difference was observed when a catalytic amount of water was present. Five molar H_2O per Ni in catalyst (B) completely depressed the activity; in catalyst (A), however, a fairy high activity was maintained in such an amount of H_2O. Even more surprising, ten molar H_2O per Ni in catalyst (A) accelerated the activity, as can be seen from a comparison between runs No. 2 and 3 in Table 3. All of these characteristics of Ziegler-type catalyst (A) are considered to originate from the presence of $AlEt_3$.

Modification of $AlEt_3$ with (Trifluoromethyl)benzene. Considering that in a typical Ziegler-type nickel catalyst (C) ($Ni(naph)_2/AlEt_3/BF_3 \cdot OEt_2$),[3] $BF_3 \cdot OEt_2$ acts both as a fluorine atom source for $AlEt_3$ and a Lewis acidic component, other types of organic fluorine source were investigated; (trifluoromethyl)benzene (BTF; $C_6H_5CF_3$) was found to be effective. This new type catalyst (D) consists of the following components: $Ni(naph)_2/AlEt_3/C_6H_5CF_3/$Activator. Without an activator, catalyst (D) shows almost no activity. Regarding this catalyst, various kinds of organic compounds having an electronegative group were found to be good activators, as is shown in Table 4. By comparing Table 4 with Tables 1 and 2, it can be noticed that, for catalyst (D), a large range of organic compounds act as more effective activators than for catalyst (A). This may be attributed to a modification of $AlEt_3$ with $C_6H_5CF_3$. Even phenol, hydroquinone and pyromellitic anhydride can activate catalyst (D). Of course, halogenated compounds are also good activators for catalyst (D) as well as for catalyst (A).

Tetrachloro-*p*-hydroquinone (TCHQ) as an Efficient Activator for $Ni(naph)_2/AlEt_3/C_6H_5CF_3$ Catalyst. Amongst the various activators listed in Table 4, TCHQ has relatively balanced properties with respect of its catalytic activity, molecular weight [η] and *cis*-1,4 content. From an industrial point of view, the required molecular weight of *cis*-1,4-polybutadiene rubber in automobile tires is around [η]=3.0 As for the microstructure of polybutadiene, the higher is the *cis*-1,4 content, the better is the processability of the rubber. From these standpoints, the influences of the molar ratio of TCHQ to $AlEt_3$ were examined in detail, as shown in Fig. 2. The content of *cis*-1,4 was almost constant at 94%. With an increase in the molar ratio of TCHQ to $AlEt_3$, the catalytic activity increased, whereas the

Table 3. Comparison of the Catalytic Activities between Ziegler Type (A) and π-Allyl Type (B)[a]

No.	Catalyst component/mmol				Polymz. time/h	Polymer yield/%	[η] dl g^{-1}	*cis*-1,4 Content/%
	Nickel	$AlEt_3$	Chloranil*	H_2O				
A-1	$Ni(naph)_2/0.5$	5.0	5.0	0	0.2	100.0	1.6	85.7
A-2	$Ni(naph)_2/0.5$	5.0	0.5	2.5	50.0	80.0	0.8	90.1
A-3	$Ni(naph)_2/0.5$	5.0	0.5	5.0	2.0	87.3	1.3	93.7
B-1	π-Allyl·NiBr/0.5	—	0.5	0	20.0	80.5	1.3	90.6
B-2	π-Allyl·NiBr/0.5	—	0.5	2.5	50.0	0	—	—

a) C_4''=0.38 mol, Toluene=20 ml, Polymz. temp=40 °C, *) Tetrachloro-*p*-benzoquinone.

Table 4. Activators for $Ni(naph)_2/AlEt_3/C_6H_5CF_3$ Catalyst[a]

No.	Activator		Polymer yield/%	[η] dl g^{-1}	*cis*-1,4 Content/%
	Compound	Amount[b]			
1	—	—	0	—	—
2	Ethanol	0.7	0	—	—
3	2,2,3,3-Tetrafluoro-1-propanol	0.8	95.2	1.3	90.7
4	Phenol	1.0	17.0	2.3	98.5
5	Pentachlorophenol	1.0	92.0	0.7	91.0
6	Pentabromophenol	1.0	85.5	0.5	89.3
7	Hydroquinone	1.0	15.8	1.3	92.4
8	Tetrachlorohydroquinone	0.5	95.9	1.0	94.1
9	Tetrabromohydroquinone	0.5	91.3	0.9	90.0
10	9,10-Anthracenediol	0.5	49.1	3.4	94.3
11	Acetic acid	1.0	0	—	—
12	Trifluoroaceticacid	1.0	54.0	0.8	93.0
13	2,2,3,3-Tetrafluoropropionic acid	1.0	34.0	1.1	92.3
14	Trifluoroacetic anhydride	1.0	91.0	0.5	95.3
15	Tetrachlorophthalic anhydride	1.0	59.0	2.5	98.3
16	Pyromellitic anhydride	1.0	52.0	2.0	96.0

a) $Ni(naph)_2/AlEt_3/C_6H_5CF_3$=0.05/0.5/0.375 (mmol). $AlEt_3/C_6H_5CF_3$ were premixed at 100 °C for 1 h. C_4''= 0.2 mol, Toluene=50 ml. Polymz. temp=40 °C, 5 h. b) Molar ratio to $AlEt_3$.

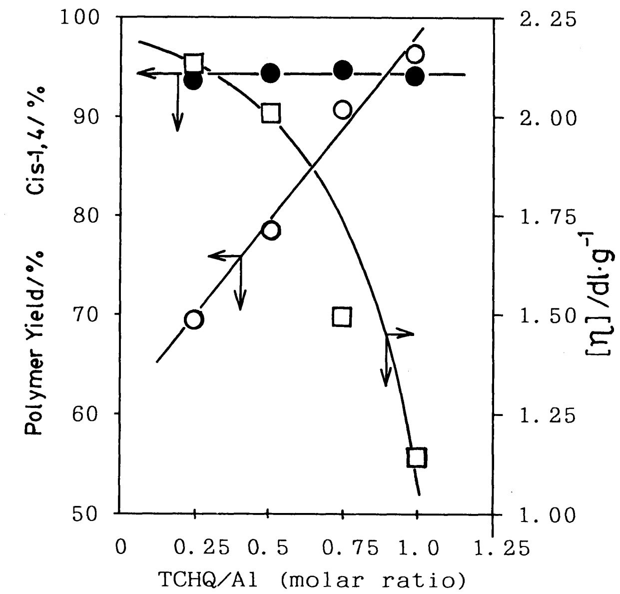

Fig. 2. Influences of TCHQ* on the Ni(naph)$_2$/AlEt$_3$/C$_6$H$_5$CF$_3$ catalyst. *) Tetrachlorohydroquinone. ○; Polymer yield, ●; *cis*-1,4 Contents, □; $[\eta]$.

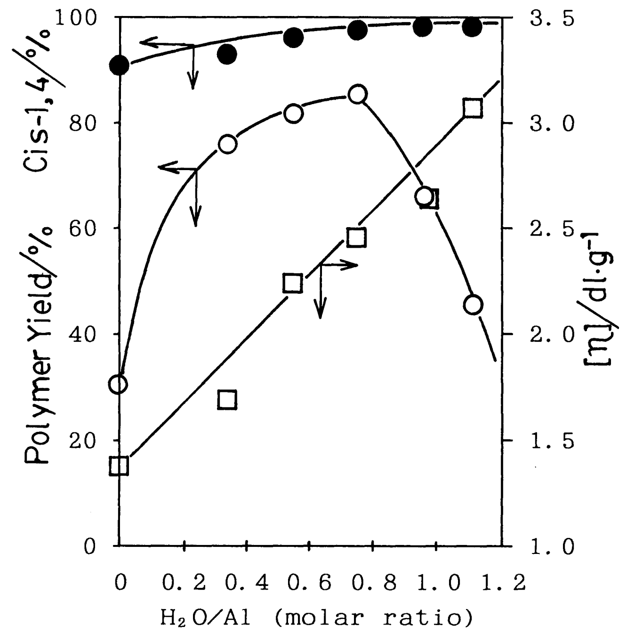

Fig. 3. Influences of H$_2$O on the Ni(naph)$_2$/AlEt$_3$/C$_6$H$_5$CF$_3$/TCHQ catalyst. ○; Polymer yield, ●; *cis*-1,4 Contents, □; $[\eta]$.

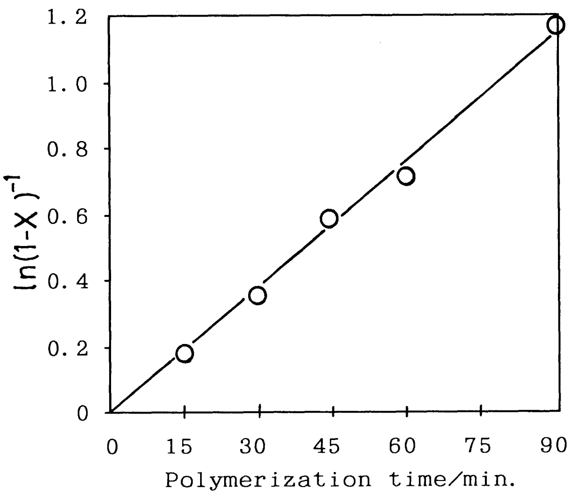

Fig. 4. Time dependency of butadiene polymerization.

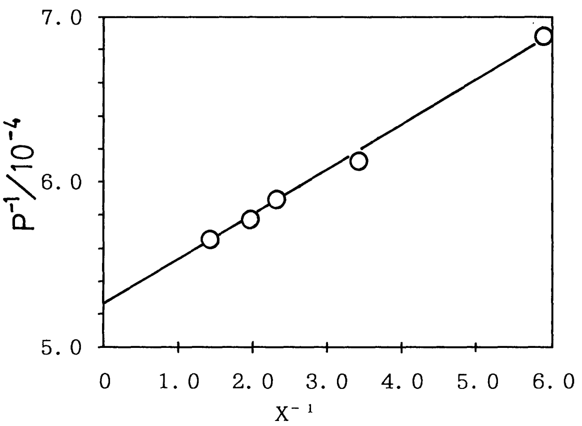

Fig. 5. Linear dependency of $1/P$ on $1/X$; (P is the degree of polymerization and X is the conversion of butadiene.)

molecular weight decreased rapidly. Therefore, some kind of molecular-weight increasing agent was necessary for this catalyst. At this stage, the phenomenon was observed that the $[\eta]$ of the polybutadiene often varied in different runs, and this change seemed to have some relation to water content in the solvent. Therefore, the influence of water was studied in detail, and water was found to be an efficient molecular-weight increasing agent, as is shown in Fig. 3. The $[\eta]$ increased linearly with an increase in the H$_2$O/AlEt$_3$ molar ratio. The catalytic activity also increased with the H$_2$O/AlEt$_3$ molar ratio, and the activity had its maximum at H$_2$O/AlEt$_3$=0.4 to 0.8. Furthermore, the *cis*-1,4 content also increased slightly with the H$_2$O/AlEt$_3$ molar ratio, and a high *cis*-1,4 content of 98% was attained. These excellent effects of water are assumed to be attributable to an enhanced Lewis acidity of the reaction product of the organoaluminum compound with water.[16]

Kinetic Studies on Ni(naph)$_2$/AlEt$_3$/C$_6$H$_5$CF$_3$/TCHQ Catalyst. The recipe and conditions for polymerization were maintained as follows, unless otherwise mentioned: Ni(naph)$_2$(1)/AlEt$_3$(10)/C$_6$H$_5$CF$_3$(7.5)/TCHQ(1)/H$_2$O(5); The figures in ( ) represent the relative molar ratio to Ni(naph)$_2$=2.35×10^{-4} mol dm^{-3}. C_4''=3.18 mol dm^{-3}, polymerization temperature=313 K, solvent=toluene.

Time-Conversion: The changes in the C_4'' conversion and $[\eta]$ of polybutadiene are illustrated in Figs. 4 and 5. As for the conversion, a first-order plot with respect to a monomer concentration fits well with the following equations:

$$-\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k[\mathrm{M}] \qquad (5)$$

$$\text{and } -\ln(1-x) = kt, \qquad (6)$$

where [M] is the monomer concentration, t a polymerization time, and k the rate constant; x is the conversion expressed by a fractional number ($0 \leqslant x \leqslant 1$). From the slope of Fig. 4, k was calculated to be $2.25 \times 10^{-4}\ \mathrm{s}^{-1}$. As for [$\eta$], it increases slightly with the conversion, gradually reaching a constant value. Yoshimoto et al. reported[17] that the polymerization of butadiene with the $\mathrm{Ni(naph)_2/AlEt_3/BF_3 \cdot OEt_2}$ catalyst (C) proceeded while keeping the concentration of the growing chain end constant. This means that the non-steady state equation of polymerization without termination (T. Kagiya et al.[18]) can be applied to the nickel catalyst; the following equation can be derived:

$$1/P = k_{\mathrm{tm}}/K_{\mathrm{p}} + \alpha[\mathrm{C}]_0/(x[\mathrm{M}]_0). \qquad (7)$$

Here P is the number average degree of polymerization, k_{tm} is the rate constant of the chain-transfer reaction to a monomer, k_{p} is the rate constant of propagation, α is a constant giving the efficiency of the charged catalyst to be converted to the active species, x is a conversion factor, $[\mathrm{C}]_0$ is the catalyst concentration initially charged and $[\mathrm{M}]_0$ is the initial monomer concentration. The concentration of the nickel component is set at $[\mathrm{C}]_0$. As is shown in the next section, the present catalyst system requires a minimun catalyst concentration for polymerization to start; this is designated as the scavenger level $[\mathrm{C}]_{\mathrm{s}}$, which is read off from the interception point on the x-axis in Fig. 6. Therefore, Eq. 7 is converted into Eqs. 8 and 9 using the following values: $[\mathrm{C}]_0=2.35\times10^{-4}$, $[\mathrm{C}]_{\mathrm{s}}=0.36\times10^{-4}$, and $[\mathrm{M}]_0=3.18$ ($\mathrm{mol\ dm^{-3}}$).

$$1/P = k_{\mathrm{tm}}/k_{\mathrm{p}} + \alpha([\mathrm{C}]_0-[\mathrm{C}]_{\mathrm{s}})/(x[\mathrm{M}]_0) \qquad (8)$$

$$1/P = k_{\mathrm{tm}}/k_{\mathrm{p}} + 6.258\times10^{-5}\,\alpha/x \qquad (9)$$

$P(=M_{\mathrm{n}}/M_{\mathrm{m}})$ is calculated from the observed [η] according to the Eq. 10 by F. Danusso et al.[19]

$$M_{\mathrm{n}} = (10^3[\eta]/1.36)^{1.4925} \qquad (10)$$

From Fig. 5 and Eq. 9, α is calculated and $k_{\mathrm{tm}}/k_{\mathrm{p}}$ can be read off as follows:

$$\alpha = 0.42$$
$$k_{\mathrm{tm}}/k_p = 5.25\times10^{-4}$$

Since k is expressed in the following equation, k_{p} and k_{tm} can be calculated from the $k_{\mathrm{tm}}/k_{\mathrm{p}}$ value and Eq. 11:

$$k = \alpha k_{\mathrm{p}}([\mathrm{C}]_0 - [\mathrm{C}]_{\mathrm{s}}) \qquad (11)$$
$$k = 2.25\times10^{-4}\ \mathrm{s}^{-1}$$
$$k_{\mathrm{p}} = 2.28\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$$
$$k_{\mathrm{tm}} = 1.42\times10^{-3}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$$

By comparing these reaction constants with those of the $\mathrm{BF_3{\cdot}OEt_2}$ containing catalyst (C), k, k_{p}, and k_{tm} are seen to be similar for both catalysts, though α for the present catalyst is ten-times greater than that for catalyst (C). This means that although the essential properties are similar for both catalysts, the catalyst efficiency is much higher for the present catalyst.

Influences of the Catalyst Concentration: Experiments were conducted by changing the catalyst concentration initially charged $[\mathrm{C}]_0$, while keeping the ratios of the catalyst components constant. $[\mathrm{C}]_0$ is the initial concentration of $\mathrm{Ni(naph)_2}$. The results are illustrated in Figs. 6 and 7. There is an interception point on the x-axis ($[\mathrm{C}]_{\mathrm{s}}=0.36\times10^{-4}\ \mathrm{mol\ dm^{-3}}$); this value is being interpreted as the minimum catalyst concentration for polymerization to be initiated. The polymerization rate

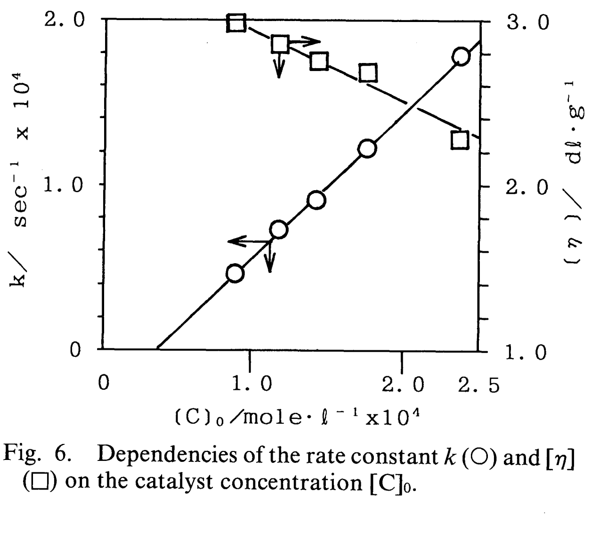

Fig. 6. Dependencies of the rate constant k (○) and [η] (□) on the catalyst concentration $[\mathrm{C}]_0$.

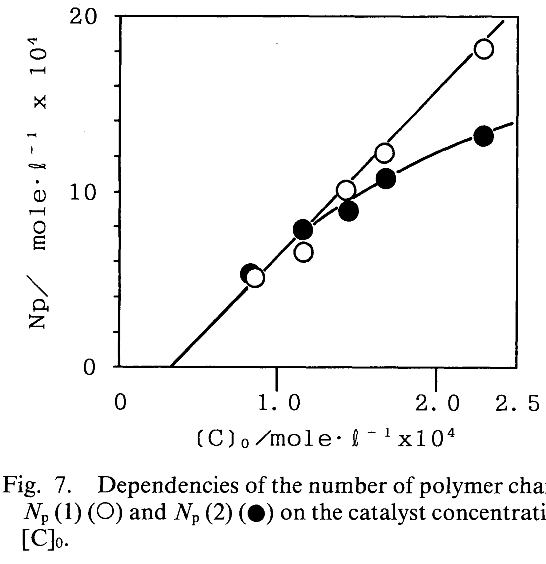

Fig. 7. Dependencies of the number of polymer chains N_{p} (1) (○) and N_{p} (2) (●) on the catalyst concentration $[\mathrm{C}]_0$.

is thus the first-order of the catalyst concentration,

$$k \propto ([\mathrm{C}]_0 - [\mathrm{C}]_s). \tag{12}$$

The intrinsic viscosity $[\eta]$ decreases almost proportionally to the catalyst concentration, and the average number of the polymer chain (N_P) is calculated from Eq. 13. It is also proportional to the catalyst concentration (Eq. 14),

$$N_P = M_m \cdot [\mathrm{M}]_0 \cdot X / M_n \tag{13}$$

and

$$N_P(1) = 0.89([\mathrm{C}]_0 - 0.36 \times 10^{-4}). \tag{14}$$

Here, M_m is a molecular weight of the monomer (M_m=54.0). In Fig. 7, two kinds of N_P ($N_p(1)$ and $N_p(2)$) are shown. $N_P(1)$ is calculated from the observed $[\eta]$ (Eq. 14), and $N_P(2)$ from

$$N_P(2) = [\mathrm{M}]_0 \cdot x \cdot k_{tm}/k_p + \alpha([\mathrm{C}]_0 - [\mathrm{C}]_s). \tag{15}$$

In Fig. 7, $N_P(2)$ becomes lower than $N_P(1)$ at higher ranges of the catalyst concentration. This means that such rate constants as k_p, k_{tm}, and α, only slightly change with the catalyst concentration.

Influence of the Molar Ratio of $AlEt_3/Ni(naph)_2$: Experiments were conducted by varying the concentration of only the nickel component, while keeping the concentrations of other catalyst components constant. The results are shown in Figs. 8 and 9. Although the rate constant increases with the nickel concentration, it does not do so proportionally. The $[\eta]$ of the polymer gradually increases with an increase in the nickel concentration (or with the decrease of the Al/Ni molar ratio) (Fig. 8), and the apparent number of the polymer chain per nickel ($N_P/(\mathrm{Ni})_0$) decreases proportionally with an increase in the nickel concentration (Fig. 9). These results indicate that the reaction constants depend upon the molar ratio of the catalyst components (e.g. Al/Ni ratio). That is, k_{tm}/k_p and α tend to decrease with the decrease of the Al/Ni molar ratio. This indicates that $AlEt_3$ accelerates both the catalytic efficiency and the chain-transfer reaction during polymerization.

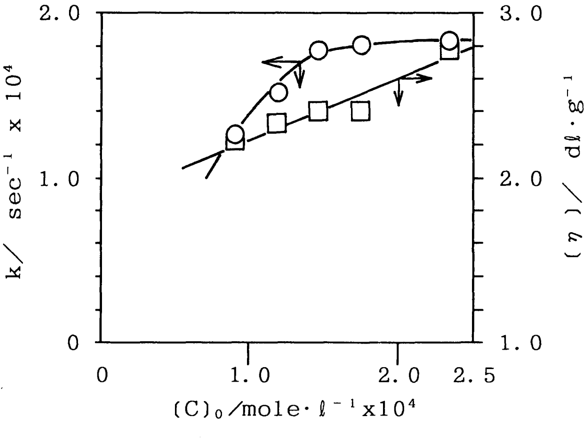

Fig. 8. Dependencies of the rate constant k (○) and $[\eta]$ (□) on the nickel concentration under a constant Al concentration.

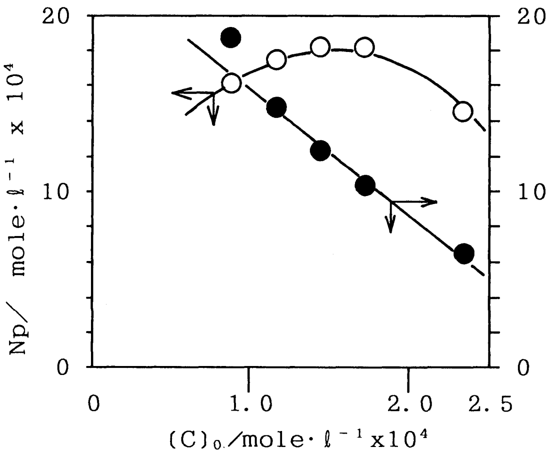

Fig. 9. Dependencies of the number of the polymer chain N_p (○) and the polymer chain per Nickel (●), on the nickel concentration under constant Al concentration.

Reaction of $AlEt_3$ with $C_6H_5CF_3$: In preparing $Ni(naph)_2/AlEt_3/C_6H_5CF_3/TCHQ/H_2O$ catalyst (D), $AlEt_3$ was treated with $C_6H_5CF_3$ in advance. Therefore, details concerning this reaction were examined as follows. After the reaction of $AlEt_3$ with $C_6H_5CF_3$ in a toluene solution, the reaction products were isolated by distillation. The first fraction was identified as being 3-ethyl-3-phenylpentane $C_6H_5CEt_3$ by MS and NMR spectroscopies. The second fraction, a highly viscous liquid, was identified as being diethylaluminum fluoride $AlEt_2F$ by elemental analysis and NMR spectroscopy. Therefore, the reaction proceeds according to

$$3AlEt_3 + C_6H_5CF_3 = 3AlEt_2F + C_6H_5CEt_3. \tag{16}$$

This reaction can be followed by analyzing the residual amount of $C_6H_5CF_3$ by gas chromatography. At the same time, the catalytic activities of the analyzed samples were examined as the organoaluminum component; the results are summarized in Fig. 10, where the x-axis represents the conversion of $AlEt_3$ to $AlEt_2F$. Both the yield and the $[\eta]$ of polybutadiene increase proportionally to the fraction of produced $AlEt_2F$. These results indicate that $AlEt_3/C_6H_5CF_3$ are almost equivalent to $AlEt_2F$ in this catalyst system.

$Ni(naph)_2/AlEt_2F$ Catalyst. In the course of a reference experiment without TCHQ, water was found incidentally to be an efficient activator for the $Ni(naph)_2/AlEt_2F$ catalyst (Fig. 11). The catalytic activity sharply increases with an increase of the $H_2O/AlEt_2F$ molar ratio; after reaching its maximum activity at around $H_2O/AlEt_2F$=0.8, the activity decreases rapidly. With an increase in the $H_2O/AlEt_2F$ molar ratio, the content of the *cis*-1,4 microstructure gradually increases up to as high as 98%. The $[\eta]$ of the polymer is much higher

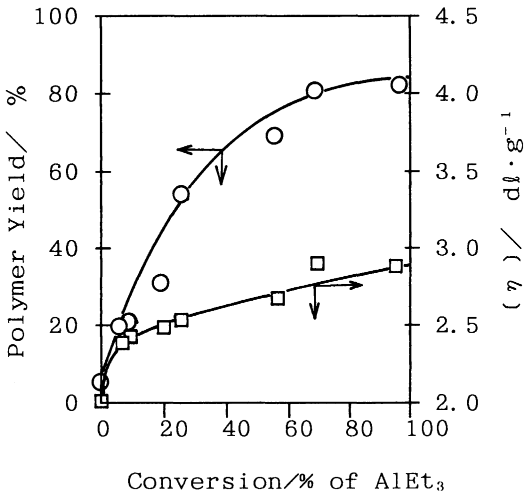

Fig. 10. Influences of the conversion of $AlEt_3$ to $AlEt_2F$ on the catalytic properties of $Ni(naph)_2/AlEt_3/C_6H_5CF_3/TCHQ/H_2O$ (1/10/10/1/5; molar ratio) catalyst. ○; Polymer yield, □; [η].

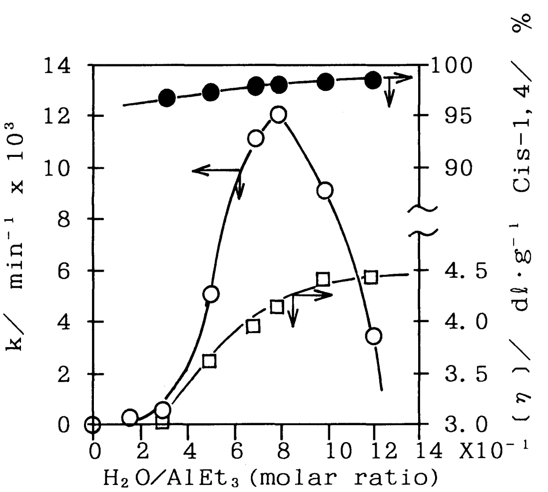

Fig. 11. Influences of H_2O on the catalytic properties of $Ni(naph)_2/AlEt_2F$ (1/10; molar ratio) catalyst. ○; k, ●; *cis*-1,4 Content, □; [η].

compared with those of other Ni catalysts; it increased from 3.0 ($H_2O/AlEt_2F$=0.8) to 4.4 ($H_2O/AlEt_2F$=1.0). Here, a new, simple Nickel catalyst (E) has been composed $Ni(naph)_2/AlEt_2F/H_2O$. This catalyst exhibits a similarity to the cobalt catalyst, $Co(acac)_3/AlEt_2Cl/H_2O$, for the *cis*-1,4 polymerization of butadiene.[20] P. Racanelli estimated that in the above-mentioned cobalt catalyst, H_2O reacts with $AlEt_2Cl$ in the catalyst solution, forming bis(diethylaluminum) oxide, $(Et_2Al)_2O$, which because of its electron-donative character, coordinates to the cobalt catalyst to regulate the polymerization.[20] As has been mentioned before, however, $(Et_2Al)_2O$ has Lewis acidity, since the $AlEt_3/H_2O$ catalyst can initiate the cationic polymerization of epoxide and $(Et_2Al)_2O$ is assumed to be formed by the reaction of $AlEt_3$ and H_2O.[16] Therefore, in our case, it is more appropriate to think that the excellent effect of H_2O on the nickel catalyst can be attributed to an enhancement of the Lewis acidity by the following reaction of H_2O with $AlEt_2F$:

$$2AlEt_2F + H_2O = (EtAlF)_2O + 2EtH. \qquad (17)$$

Considering that $TiI_4/AlEt_3$ is also a good catalyst for the *cis*-1,4 polymerization of butadiene,[1] the following interesting consideration can be made. That is, there are favourable combinations between the transition element and the halogen atom as follows: Ni–F, Co–Cl, Ti–I. The orders of electronegativity are Ni (1.91eV)>Co (1.88eV)>Ti (1.54eV). Suitable combinations of Ni–F, Co–Cl, and Ti–I clearly correlate with the order of electronegativity. These combinations are interpreted as indicating that some appropriate electronic state is necessary for *cis*-1,4 polymerization, and that each halogen atom controls the electronic state of the transition element by its suitable electronegativity.

Influences of Halogenated Phenols on the $Ni(naph)_2/AlEt_2F/H_2O$ Catalyst (E). Since the molecular weight of polybutadiene obtained using the $Ni(naph)_2/AlEt_2F/H_2O$ catalyst is slightly too high for automobile tires, some kind of molecular-weight regulator is necessary. For this purpose, halogenated phenols were found to be effective; as a typical case, the influences of 2,4,6-trichlorophenol (TCP) are illustrated in Fig. 12. With an increase in the $TCP/AlEt_2F$ molar ratio, the [η] of the polymer decreases effectively; furthermore, the catalytic activity gradually increases. The patern of molecular-weight regulation of various chlorinated phenols is summarized in terms of Hammet σ values, and is illustrated in Fig. 13. The [η] decreased lineary to the sum of Hammet σ values. This means that in this case, the molecular weight is reduced by an increase in the Lewis acidity of the organic aluminum component, since chlorinated phenol increases the Lewis acidity of $AlEt_2F$ through the formation of organic aluminum phenoxide (Eq. 18):

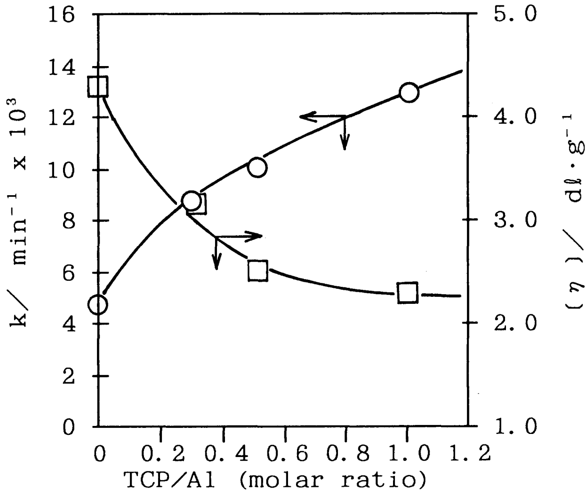

Fig. 12. Influences of TCP* on the catalytic properties of $Ni(naph)_2/AlEt_2F/H_2O$ (1/10/8; molar ratio) catalyst. *) 2,4,6-Trichlorophenol. ○; k, □; [η].

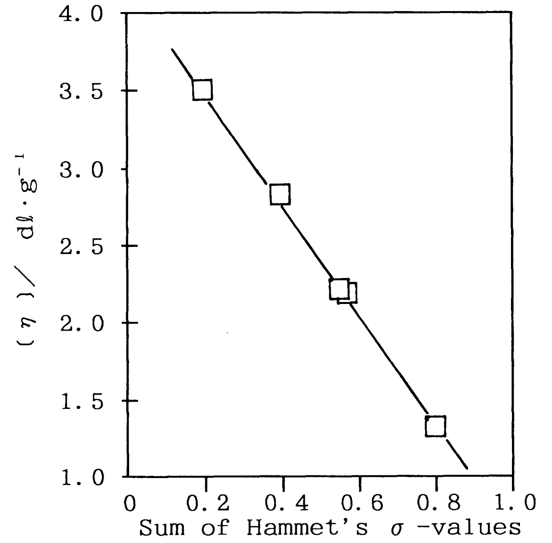

Fig. 13. Influences of the acidity of chlorinated phenols on the catalytic properties of $Ni(naph)_2/AlEt_2F/H_2O$ (1/10/8; molar ratio) catalyst. ○; k, □; $[\eta]$.

$$Ar_x\text{-}OH + AlEt_2F = Ar_xOAlEtF + EtH. \qquad (18)$$

(Ar_x; chlorinated aryl)

Conclusions

(1) By increasing the Lewis acidity of the organoaluminum compound through an in situ treatment of $AlEt_3$ with electron-attractive organic compounds, such as chlorinated hydroquinone, chlorinated phenol or hexafluoroacetone, the basic combination of $Ni(naph)_2/AlEt_3$ exhibits a catalytic activity for high *cis*-1,4 polymerization of butadiene.

Catalyst (A); $Ni(naph)_2/AlEt_3$/organic activator.

(2) The activity of the catalyst (A) increases upon a pretreatment of $AlEt_3$ with (trifluoromethyl)benzene. By using this treatment, $AlEt_2F$ is formed, which shows an increased Lewis acidity by which the fluorine atom enhances the catalytic activity.

Catalyst (D); $Ni(naph)_2/AlEt_2F$/organic activator.

(3) In catalyst (D), a catalytic amount of water increases the molecular weight of polybutadiene up to an industrially usable level ($[\eta]\fallingdotseq 3.0$—3.5). Water also increases the *cis*-1,4 content up to 98%. These excellent effects of water are presumably attributable to the formation of bis(fluoroethylaluminum) oxide, $(AlEtF)_2O$.

Catalyst (D′); $Ni(naph)_2/AlEt_2F$/organic activator/H_2O.

(4) Surprisingly, water, itself, is an efficient activator for the $Ni(naph)_2/AlEt_2F$ system; a very simple, effective catalyst has been composed,

Catalyst (E); $Ni(naph)_2/AlEt_2F/H_2O$.

(5) The molecular weight of polybutadiene obtained by catalyst (E) is too high ($[\eta]\geqslant 4.0$); for this catalyst, chlorinated phenol is an efficient molecular-weight regulator. The $[\eta]$ decreases proportionally to the sum of the Hammet σ values of the chlorine atoms on chlorinated phenol. The content of *cis*-1,4 is more than 98%.

Catalyst (E′); $Ni(naph)_2/AlEt_2F/H_2O$/chlorinate phenol.

In conclusion, it has been revealed that, by changing the Lewis acidity and the coordination property of the organoaluminum component, the catalytic properties of the $Ni(naph)_2$/organoaluminum system can be controlled widely; further, several efficient catalysts for high *cis*-1,4-polybutadiene have been developed.

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