Polymer Journal, Vol. 32, No. 5, pp 456—459 (2000)

NOTES

High Catalytic Activity and Stereoregularity of BF_3 Etherate as Cocatalyst of Nd-Based Catalyst in the Polymerization of 1,3-Butadiene

Youngchan JANG,† Gwanghoon KWAG, and Hosull LEE

Kumho Chemical Laboratories, Korea Kumho Petrochemical Co., Ltd.,
P.O. Box 64, Yuseong, Taejon 305-600, Korea

(Received November 15, 1999)

KEY WORDS BF_3 Etherate / High Catalytic Activity / High 1,4-*cis* Polybutadiene / Neodymium / Triisobutylaluminium /

There are many reports on the polymerization of 1,3-butadiene using Ziegler–Natta catalyst based on Ti ($TiCl_4/AlEt_3$),[1] Co ($CoCl_2/AlEt_2Cl$),[2,3] Ni (Ni(carboxylate)$_2$/$BF_3 \cdot OEt_2/AlEt_3$),[4,5] and Nd (Nd(carboxylate)$_3$/$AlEt_2Cl$/Al(i-Bu)$_3$).[6] Nd is highlighted due to its ability to produce polybutadiene having the best mechanical properties.[7] A ternary catalyst system, composed of lanthanide metal such as neodymium, cerium and gadolinium together with halogen compound and trialkylaluminium, gives high catalytic activity and 1,4-*cis* stereoregularity in the polymerization of 1,3-butadiene.[8—10] Organic and inorganic compounds containing chlorine or bromine act as active halogen compounds to comprise a lanthanide-based catalyst system[8,11] to give simultaneously both high conversion and 1,4-*cis* content.

To our knowledge, however, there is no report where a ternary catalyst system comprising fluorine containing compound, lanthanide salt and trialkylaluminium polymerizes 1,3-butadiene to satisfy simultaneously both high conversion and 1,4-*cis* content. Poor catalytic activity was reported[12,13] in all cases using a compound containing fluorine as a halogen component concerning a lanthanide-based catalyst system although high 1,4-*cis* content was maintained.

Fluorine is the most electronegative element, and its high affinity for electrons activates metal electronically to result in stronger η^4-*cis* coordination between metal and 1,3-butadiene, thus favoring high 1,4-*cis* configuration. Ni-based catalyst using fluorine containing compound such as BF_3 etherate[14] and HF[15] as cocatalyst gives high catalytic activity and 1,4-*cis* stereoregularity in the polymerization of 1,3-butadiene.

We recently tried a series of 1,3-butadiene polymerizations and found that a ternary catalyst system comprising Nd(versatate)$_3$/Al(i-Bu)$_3$/BF_3 etherate readily polymerizes 1,3-butadiene to give excellent catalytic activity in conversion and high stereoregularity in 1,4-*cis* content under suitable conditions.

The present catalyst system has excellent solubility to non-polar solvent such as cyclohexane, hexane and toluene to give no precipitate during catalyst aging period. However, it has been shown in several reports that solution polymerization of 1,3-butadiene using a halogen compound containing chlorine[16] or bromine[17] formed suspended matter due to incomplete dissolution of the catalyst to non-polar solvent. With such a heterogeneous catalyst, polybutadiene having high molecular weight (gel) and broad molecular weight distribution has been obtained with low conversion.[16,17] Heterogeneous catalyst, compared to a homogeneous one, is expected to give difficulty in controlling the amount of catalyst quantitatively, which is essentially needed for smooth polymerization and easy control of the physical properties of polybutadiene in commercial scale production.

In this study, we varied the type of BF_3 etherates and concentrations of the three components to elucidate their effect on the microstructure, molecular weight (M_w), molecular weight distribution (MWD) of polybutadiene, and activity of catalyst.

EXPERIMENTAL

Materials

The following materials were purchased from Aldrich Chemicals: $BF_3 \cdot OMe_2$, $BF_3 \cdot OEt_2$, $BF_3 \cdot OBu_2$, $BF_3 \cdot THF$, $BF_3 \cdot SMe_2$, Al(i-Bu)$_3$, and AlH(i-Bu)$_2$. Nd(versatate)$_3$ was obtained from OMG Americas Inc. and diluted to 1 wt/wt% solution in cyclohexane. To the prepared solution was added 2.5 wt/wt% of 1,3-butadiene to stabilize[18] Nd(versatate)$_3$ and the solution was stored in crown-sealed bottles under nitrogen. All BF_3 etherates were diluted to 1.5 wt/wt% solution in toluene in crown-sealed bottles under nitrogen. Al(i-Bu)$_3$ (1 M solution in hexane) and AlH(i-Bu)$_2$ (1 M solution in hexane) were used as received. 1,3-Butadiene and cyclohexane were supplied by the Korea Kumho Petrochemical Co. from the Yeocheon plant. 1,3-Butadiene was passed through a tower of activated alumina before use. Cyclohexane was dried over activated alumina overnight and purged with nitrogen prior to use.

Catalyst Aging

Unless otherwise specified, Nd-based catalyst was aged in such a manner that a) an 100 mL round-bottom flask was sufficiently purged with nitrogen and sealed tightly with a rubber stopper, and b) Nd(versatate)$_3$, Al(i-Bu)$_3$ or AlH(i-Bu)$_2$, and BF_3 etherate were sequentially charged to the flask in a molar ratio as described

---

† To whom all correspondence should be addressed (Tel: 82-42-865-8655, Fax: 82-42-862-5651, E-mail: ycjang@mail.kkpcr.re.kr).

Table I. Initial polymerizations[a] of 1,3-butadiene using $BF_3 \cdot OEt_2$

Catalyst[b]	BF₃/Nd	Al/Nd	Nd[c]	Conv.
	mol mol^{-1}	mol mol^{-1}	($\times 10^{-4}$ mol)	%
1. Nd(versatate)$_3$/Al(i-Bu)$_3$/$BF_3 \cdot OEt_2$	3	30	5.7	67
2. Nd(versatate)$_3$/AlH(i-Bu)$_2$/$BF_3 \cdot OEt_2$	3	30	5.7	<30
3. Nd(versatate)$_3$/Al(i-Bu)$_3$/$BF_3 \cdot OEt_2$	6	30	5.7	0

[a] Cyclohexane/1,3-butadiene (wt/wt) = 5. [b] Each component was sequentially added as shown. [c] Concentration of Nd per 100 g of 1,3-butadiene.

and aged at 20℃ for 1 h prior to use.

Polymerization

Polymerizations were performed in a 500 mL glass reactor after sufficiently purged with nitrogen. Cyclohexane, the Nd-based catalyst aged as above, and 1,3-butadiene were sequentially added to the reactor, and reacted at 40℃ for 2 h. The resulting polybutadiene was stabilized with 2,6-di-*t*-butyl-4-methylphenol, and quenched by ethanol.

Characterization

Conversion was calculated from the ratio of the weight of isolated polymer compared to that of the initially charged 1,3-butadiene. The microstructures of polybutadiene were measured in CS_2 solution by IR spectroscopy (Bio-Rad, FTS 60-A) according to the literature.[19] Gel permeation chromatography data were obtained using a Waters 2690 system employing connected Waters ultrastyregel columns, HMW7 and HMW6E, with a refractive index detector. Tetrahydrofuran (THF) was used as solvent at a flow rate of 1.0 mL min^{-1}.

RESULTS AND DISCUSSION

Initial polymerizations of 1,3-butadiene were carried out using a ternary catalyst system of Nd(versatate)$_3$/Al(i-Bu)$_3$/$BF_3 \cdot OEt_2$ or Nd(versatate)$_3$/AlH(i-Bu)$_2$/$BF_3 \cdot OEt_2$ to investigate the catalytic activity of $BF_3 \cdot OEt_2$ as a halogen compound, Table I. In catalysts **1** and **2**, Al(i-Bu)$_3$ and AlH(i-Bu)$_2$ were used, respectively. Al(i-Bu)$_3$ had higher activity than AlH(i-Bu)$_2$ in the present catalyst system.

Excess $BF_3 \cdot OEt_2$ was used in catalyst **3** but no enhancement of catalytic activity was observed. Excess $BF_3 \cdot OEt_2$ gave detrimental effect to the catalyst system, with no activity at all. This is in accord with the report[20] in which the presence of large amounts of halogen compounds, such as $AlEt_2Cl$ and $AlEtCl_2$, destroyed catalytic activity.

To investigate the optimum concentration of $BF_3 \cdot OEt_2$, polymerizations of 1,3-butadiene were performed using low level of $BF_3 \cdot OEt_2$. By use of 2.5 to 0.5 equivalents of $BF_3 \cdot OEt_2$ to Nd(versatate)$_3$, the activity of the ternary catalyst system was remarkably enhanced to give quantitative yields of polybutadiene, Figure 1. In addition, high 1,4-*cis* contents over 97% were obtained. Utilization of too little $BF_3 \cdot OEt_2$, *i.e.*, BF_3/Nd = 0.5, resulted in decrease in 1,4-*cis* content to 95% although the conversion still remained quantitative.

Variation of $BF_3 \cdot OEt_2$ concentration showed noticeable effect on the M_w and MWD of polybutadiene, Figure 2. Utilization of less $BF_3 \cdot OEt_2$ gave lower M_w and narrower MWD. Decrease of M_w with decreasing the molar ratio of a chlorine compound to Nd metal has been described in the report[21] where M_w was controlled in the range of 90000 to 190000 accompanying a drawback of lowered stereoregularity to give 85 to 88% 1,4-*cis* contents. Many attempts to control M_w of polybutadiene have been performed using various methods such as variation of catalyst aging conditions[18] and use of various trialkylaluminiums or solvents.[22] Compared with the methods mentioned above, the present catalyst system has some advantages in that M_w of polybutadiene can be controlled by simple variation of the concentration of

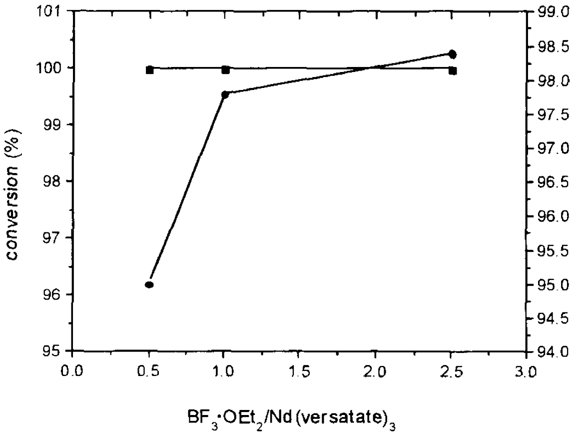

Figure 1. Effects of variation in molar ratios of $BF_3 \cdot OEt_2$ to Nd(versatate)$_3$ on conversion (■) and 1,4-*cis* content (●). Al(i-Bu)$_3$/Nd(versatate)$_3$ = 30 ; [Nd] = 5.7×10^{-4} mol/100 g of 1,3-butadiene.

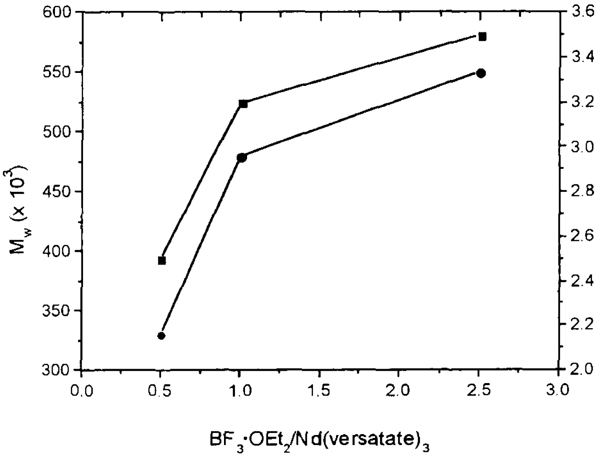

Figure 2. Effects of variation in molar ratios of $BF_3 \cdot OEt_2$ to Nd(versatate)$_3$ on M_w (●) and MWD (■). Al(i-Bu)$_3$/Nd(versatate)$_3$ = 30 ; [Nd] = 5.7×10^{-4} mol/100 g of 1,3-butadiene.

Table II. 1,3-Butadiene polymerizations [a] using BF$_3$·OEt$_2$ with variation in concentrations of Al(i-Bu)$_3$ and Nd(versatate)$_3$

Catalyst [b]	BF$_3$/Nd	Al/Nd	Nd [c]	Microstructure/%			Conv.	M_w	MWD
	mol mol^{-1}	mol mol^{-1}	($\times 10^{-4}$ mol)	*cis*	*trans*	vinyl	%		
4. Nd(versatate)$_3$/Al(i-Bu)$_3$/BF$_3$·OEt$_2$	1.0	20	5.7	98.0	1.4	0.6	53	1100000	3.03
5. Nd(versatate)$_3$/Al(i-Bu)$_3$/BF$_3$·OEt$_2$	1.0	30	5.7	97.8	1.5	0.7	100	480000	3.20
6. Nd(versatate)$_3$/Al(i-Bu)$_3$/BF$_3$·OEt$_2$	1.0	30	2.8	98.0	1.5	0.5	94	1020000	3.07
7. Nd(versatate)$_3$/Al(i-Bu)$_3$/BF$_3$·OEt$_2$	1.5	30	2.0	98.2	1.0	0.8	80	— [d]	— [d]

[a] Cyclohexane/1,3-butadiene (wt/wt) = 5. [b] Each component was sequentially added as shown. [c] Concentration of Nd per 100 g of 1,3-butadiene. [d] Due to poor solubility of produced polybutadiene, measurement of M_w and MWD was not performed.

Table III. 1,3-Butadiene polymerizations [a] using various BF$_3$ etherates

Catalyst [b]	BF$_3$/Nd	Al/Nd	Nd [c]	Microstructure/%			Conv.	M_w	MWD
	mol mol^{-1}	mol mol^{-1}	($\times 10^{-4}$ mol)	*cis*	*trans*	vinyl	%		
8. Nd(versatate)$_3$/Al(i-Bu)$_3$/BF$_3$·OMe$_2$	1.0	30	2.8	98.2	1.4	0.4	96	1010000	3.08
9. Nd(versatate)$_3$/Al(i-Bu)$_3$/BF$_3$·OBu$_2$	1.0	30	2.8	98.2	1.3	0.5	93	1030000	3.09
10. Nd(versatate)$_3$/Al(i-Bu)$_3$/BF$_3$·THF	1.0	30	2.8	98.1	1.6	0.3	97	1010000	3.07
11. Nd(versatate)$_3$/Al(i-Bu)$_3$/BF$_3$·SMe$_2$	1.5	30	2.8	98.3	1.1	0.6	>90	1060000	3.16

[a] Cyclohexane/1,3-butadiene (wt/wt) = 5. [b] Each component was sequentially added as shown. [c] Concentration of Nd per 100 g of 1,3-butadiene.

BF$_3$·OEt$_2$ without serious influence on activity and 1,4-*cis* content. Gradually narrowed MWD showed active center to become homogeneous by decreasing the concentration of BF$_3$·OEt$_2$.

The effects of variation of the concentration of Al(i-Bu)$_3$ and Nd(versatate)$_3$ on the catalytic activity, stereoregularity, M_w and MWD of polybutadiene are illustrated in Table II. Low concentration of Al(i-Bu)$_3$ seriously lowered catalytic activity to give 53% conversion whereas high 1,4-*cis* content still remained, catalyst **4**, showing independence of 1,4-*cis* content to the concentration of Al(i-Bu)$_3$. The polymerization gave polybutadiene having much higher M_w than that of the polybutadiene produced from catalyst **5** where higher concentration of Al(i-Bu)$_3$ was used. The difference in MWD for polybutadienes produced from catalysts **4** and **5** was not significant, which seems characteristic of Nd-based catalyst due to its quasi-living[20] character.

Al(i-Bu)$_3$ is considered to play two essential roles during polymerization. One is to function as an alkylating agent to form Nd-C σ bonds from which active centers are formed[23,24] and the other is to serve as a chain transfer agent to react by transfer reaction with growing polymer chains resulting in the formation of dead polymer chains and new Nd-C σ bonds from which new active centers are formed to produce new polymer chains.

Catalytic activity was observed to depend on the concentration of Nd metal. When Nd decreased to 2.8 × 10^{-4} mol per 100 g of monomer, catalyst **6**, the activity of catalyst remained good to give 94% conversion but further decrease to 2.0 × 10^{-4} mol lowered the conversion to 80%, catalyst **7**. Remarkable increase in M_w was observed in catalyst **6** where less Nd was used compared with catalyst **5**. No significant change in 1,4-*cis* content was observed in catalysts **5**—**7**, revealing little effect of Nd on stereoregularity.

Polymerizations of 1,3-butadiene were performed using various BF$_3$ etherates containing dimethylether, dibutylether, THF and dimethylthioether, Table III. BF$_3$ etherates such as BF$_3$·OMe$_2$, BF$_3$·OBu$_2$ and BF$_3$·THF in catalysts **8**—**10** gave similar catalytic activity and stereoregularity to those of BF$_3$·OEt$_2$ as well as polybutadiene having comparable M_w and MWD to those of polybutadiene produced using BF$_3$·OEt$_2$ under similar polymerization conditions, catalyst **6** in Table II. Surprisingly, even BF$_3$ thioetherate containing SMe$_2$ provided high catalytic activity in conversion and stereoregularity in 1,4-*cis* content, catalyst **11**, although SMe$_2$ was expected to act detrimentally toward active centers. A Lewis base containing heteroatom such as sulfur,[25] even at low concentrations, deactivates the active center of Ziegler–Natta catalyst based on transition metal by complexing with it, thereby obstructing the approach of monomer to give low conversion. Block of active center impedes[26] cisoid coordination of monomer with active center to give low 1,4-*cis* content. Nd-based catalysts may thus have stronger endurance to electron donor in catalytic activity and stereoregularity than the conventional Ziegler–Natta catalysts based on cobalt[25] and nickel.[27]

A ternary catalyst system comprising Nd(versatate)$_3$/Al(i-Bu)$_3$/BF$_3$ etherate was observed to have high catalytic activity and stereoregularity in the polymerization of 1,3-butadiene to give conversion over 90% and 1,4-*cis* content over 97% under suitable conditions. The present catalyst system had high solubility to non-polar solvents to give no precipitate during catalyst aging period so as to minimize the possibility of the formation of gel and polybutadiene having broad MWD, as generally observed in the polymerizations of 1,3-butadiene using heterogeneous Nd-based catalysts.

Catalytic activity and M_w were dependent on the concentration of three components, Nd(versatate)$_3$, Al(i-Bu)$_3$ and BF$_3$ etherate, while stereoregularity and MWD were mainly dependent on the concentration of BF$_3$ etherate. The dependence of stereoregularity on the concentration of BF$_3$ etherate supports that BF$_3$ is involved in the active center of 1,3-butadiene polymerization in which fluorine increases 1,4-*cis* content by activating Nd electoronically to promote stronger η^4-*cis* coordination with incoming 1,3-butadiene. The influence of variation in the type of BF$_3$ etherate on catalytic activity, stereoregularity, M_w and MWD was not significant.

REFERENCES

1. G. J. Van Amerongen, *Adv. Chem. Ser.*, **52**, 136 (1966).
2. W. Cooper, *Ind. Eng. Chem. Prod. Res. Develop.*, **9**, 457 (1970).
3. L. Porri, A. Giarrusso, and G. Ricci, *Prog. Polym. Sci.*, **16**, 405 (1991).
4. J. Furukawa, *Pure Appl. Chem.*, **42**, 495 (1975).
5. J. Furukawa, *Acc. Chem. Res.*, **13**, 1 (1980).
6. D. J. Wilson, *Polymer*, **34**, 3504 (1993).
7. D. J. Wilson, *Makromol. Chem., Macromol. Symp.*, **66**, 273 (1993).
8. Z. Shen, J. Ouyang, F. Wang, Z. Hu, F. Yu, and B. Qian, *J. Polym. Sci., Polym. Chem. Ed.*, **18**, 3345 (1980).
9. S. Kaita, T. Otaki, E. Kobayashi, S. Aoshima, and J. Furukawa, *J. Polym. Sci., Part A, Polym. Chem.*, **35**, 2591 (1997).
10. E. Kobayashi, S. Kaita, S. Aoshima, and J. Furukawa, *J. Polym. Sci., Part A, Polym. Chem.*, **36**, 2283 (1998).
11. Z. Shen, *Inorg. Chim. Acta*, **140**, 7 (1987).
12. N. G. Marina, Y. B. Monakov, S. R. Rafikov, and K. K. Gadeleva, *Polym. Sci., U.S.S.R.*, **26**, 1251 (1984).
13. N. G. Marina, Y. B. Monakov, Z. M. Sabirov, and G. A. Tolstikov, *Polym. Sci.*, **33**, 387 (1991).
14. W. M. Saltman and L. J. Kuzma, *Rubber Chem. and Technol.*, **46**, 1055 (1973).
15. M. C. Throckmorton and F. S. Farson, *Rubber Chem. and Technol.*, **44**, 268 (1971).
16. D. J. Wilson and D. K. Jenkins, *Polym. Bull.*, **27**, 407 (1992).
17. D. J. Wilson and D. K. Jenkins, *Polym. Bull.*, **34**, 257 (1995).
18. V. G. Kozlov, N. N. Sigaeva, K. V. Nefedjev, I. G. Saveleva, N. G. Marina, and Y. B. Monakov, *J. Polym. Sci., Part A, Polym. Chem.*, **32**, 1237 (1994).
19. F. Ciampelli, D. Morero, and M. Cambini, *Makromol. Chem.*, **61**, 250 (1963).
20. H. L. Hsieh and H. C. Yeh, *Rubber Chem. and Technol.*, **58**, 117 (1985).
21. A. Oehme, U. Gebauer, and K. Gehrke, *J. Molecular Cat.*, **82**, 83 (1993).
22. Y. Jin, F. Li, F. Pei, F. Wang, and Y. Sun, *Macromolecules*, **27**, 4397 (1994).
23. G. Ricci, S. Italia, F. Cabassi, and L. Porri, *Polym. Commun.*, **28**, 223 (1987).
24. A. Oehme, U. Gebauer, K. Gehrke, and M. D. Lechner, *Angew. Makromol. Chem.*, **235**, 121 (1996).
25. H. Ashitaka, K. Jinda, and H. Ueno, *J. Polym. Sci., Polym. Chem. Ed.*, **21**, 1951 (1983).
26. F. Dawans and P. Teyssie, *Ind. Eng. Chem. Prod. Res. Develop.*, **10**, 261 (1971).
27. J. C. Marechal, F. Dawans, and P. Teyssie, *J. Polym. Sci., Part A-1*, **8**, 1993 (1970).