

## SHORT COMMUNICATIONS

Ligand Structure and Cocatalyst Effects on High 1,4-*cis* Polymerization of 1,3-Butadiene Using Ni-Based CatalystsGwanghoon KWAG,<sup>†</sup> Youngchan JANG, and Hosull LEEKumho Chemical Laboratories, Korea Kumho Petrochemical Co., Ltd.,  
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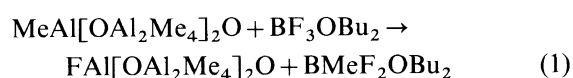
KEY WORDS 1,3-Butadiene / High *cis* Polybutadiene / Nickel / Salen /  $\alpha$ -Diimine /  $\text{BF}_3$  / Methylalumoxane /

The high *cis* 1,4-polymerization of 1,3-butadiene from Ziegler–Natta catalysts based on transition metals such as  $\text{Ti}(\text{TiCl}_4/\text{AlEt}_3)$ ,<sup>1</sup>  $\text{Co}(\text{CoCl}_2/\text{AlEt}_2\text{Cl})$ ,<sup>2</sup>  $\text{Ni}(\text{Ni}(\text{carboxylate})_2/\text{BF}_3 \cdot \text{OEt}_2/\text{AlEt}_3)$ ,<sup>3</sup> and rare earth metal such as  $\text{Nd}(\text{Nd}(\text{carboxylate})_3/\text{AlEt}_2\text{Cl}/\text{Al}(\text{iBu})_3)$ <sup>4</sup> has been intensively studied. Nickel is of particular interest in the production of high *cis* 1,4-polybutadiene (BR) since nickel-high *cis* BR has good processing properties and high tack due to broad molecular weight distribution (MWD) and many branches.<sup>5</sup> As nickel catalysts, nickel naphthenate and nickel 2-ethylhexanoate have been used in 1,3-butadiene polymerization with fluorine and alkylaluminum compounds because of high solubility in hydrocarbon solvents such as *n*-hexane and toluene.<sup>6</sup> Stereospecific catalysts,  $\text{Ni}(\text{salen})$  ( $\text{salen} = (1R,2R)\text{-}(-)\text{-}1,2\text{-cyclohexanediamino-}N,N'\text{-bis}(3,5\text{-di-}t\text{-butyl-salicylidene})$ ) and  $\text{Ni}(\text{II})\text{Br}_2 \cdot \text{DAD}$  complex ( $\text{DAD} = \text{ArN}=\text{CHCH}=\text{NAr}$  where  $\text{Ar} = 2,6\text{-}(\text{iPr})_2\text{C}_6\text{H}_3$ ), were used to study whether bulky and stereospecific ligands influence activity and stereoregularity in polymerization of 1,3-butadiene, Figure 1.<sup>7</sup> The methylalumoxane (MAO) effects on 1,3-butadiene polymerization in the presence or in the absence of  $\text{BF}_3$  etherate were also examined.

1,3-Butadiene polymerizations were carried out with various nickel, aluminum and boron catalysts, and polymerization conditions are shown in Table I. Data for prepared BR, such as microstructure,<sup>8</sup> molecular weight, MWD and kinetic constant, are shown in Table II. *cis* Content of all of the polymerizations was over 95% except for catalyst 8. Catalysts 1 and 2 gave high conversions over 90% at 40°C for 2 h regardless of the ligand. Catalyst 3 yielded lower conversion as well as propagation rate than those of catalysts 1 and 2 due to low solubility of  $\text{Ni}(\text{abietate})_2$  in toluene which would cause a large precipitate during aging for 1 h. High *cis* content over 95% was noted. There thus appears no pronounced dependence of the microstructure of polymer on ligand structure, but solubility of nickel compounds greatly influences catalytic activity. This is evidence that high *cis* stereoregularity mainly arises from the electronic interaction between nickel and 1,3-butadiene promoting incoming butadiene cisoid-precomplexation ( $\eta^4\text{-cis}$ ) irrespective of ligands.

High efficiency of MAO was observed at catalysts 4–6, possibly due to stronger Lewis acid formed in the

ligand-exchange reaction with  $\text{BF}_3 \cdot \text{OBU}_2$  or  $\text{BF}_3 \cdot \text{tetrahydrofuran}$  (THF).<sup>9</sup>



The major drawback of excess MAO needed to activate polymerization was overcome in the polymerization of

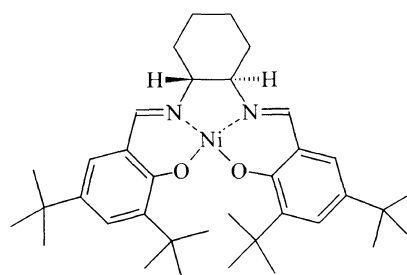
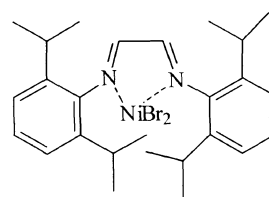
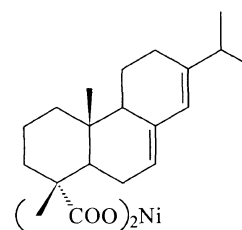
a)  $\text{Ni}(\text{salen})$ b)  $\text{NiBr}_2\text{DAD}$ c)  $\text{Ni}(\text{abietate})_2$ 

Figure 1. Structures of  $\text{Ni}(\text{salen})$  (a),  $\text{NiBr}_2 \cdot \text{DAD}$  (b), and  $\text{Ni}(\text{abietate})_2$  (c).

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**Table I.** 1,3-Butadiene polymerization<sup>a</sup> and results with various catalysts

Entry No.	BF <sub>3</sub> /Ni	Al/Ni	Solvent <sup>b</sup>	BD	Temp	Time	Conv	
								mol mol <sup>-1</sup>
1.	Ni(naphthenate) <sub>2</sub> /BF <sub>3</sub> OEt <sub>2</sub> /AlEt <sub>3</sub>	12.0	6	T/H(4/6)	30	40	2	94
2.	Ni(salen)/BF <sub>3</sub> OEt <sub>2</sub> /AlEt <sub>3</sub>	12.0	6	T/H(4/6)	30	40	2	94
3.	Ni(abietate) <sub>2</sub> /BF <sub>3</sub> OEt <sub>2</sub> /AlEt <sub>3</sub>	12.0	6	T/H(4/6)	30	40	2	56
4.	Ni(octoate) <sub>2</sub> /BF <sub>3</sub> THF/MAO	17.5	20	C/H(9/1)	80	60	2	24
5.	Ni(salen)/BF <sub>3</sub> OBu <sub>2</sub> /MAO	12.5	20	C/H(9/1)	80	60	2	26
6.	Ni(salen)/BF <sub>3</sub> OBu <sub>2</sub> /MAO	12.5	100	C/H(9/1)	80	60	2	90
7.	Ni(salen)/MAO	0.0	100	C/H(9/1)	80	60	2	<5
8.	NiBr <sub>2</sub> ·DAD/MAO	0.0	700	Toluene	50	20	3	35

<sup>a</sup> Aging time = 1 h, aging temperature = 20°C. <sup>b</sup> Solvent/monomer(wt/wt) = 5, T = toluene, H = n-heptane, C = cyclohexane.

**Table II.** Microstructure and molecular weight analysis of polybutadiene

Entry No.	<i>cis</i>	<i>trans</i>	Vinyl	<i>M<sub>w</sub></i>	MWD	<i>k</i> × 10 <sup>4</sup>
1	95.3	2.2	2.5	324000	4.20	3.98
2	95.5	2.0	2.5	745000	3.04	3.58
3	95.4	2.1	2.5	—	—	0.29
4	95.5	1.3	3.2	758000	4.66	—
5	96.2	1.4	2.4	412000	5.94	—
6	95.7	1.6	2.7	652000	5.82	—
8	91.7	4.0	4.3	145000	2.92	—

catalyst **6** by forming FAl[OAl<sub>2</sub>Me<sub>4</sub>]<sub>2</sub>O (FMAO) to promote MAO alkylation of metal complexes and stabilization of active centers.<sup>10</sup> There was no significant difference in activity and stereoregularity such as conversions and 1,4-*cis* content in the polymerization using a ternary catalyst system of Ni(salen)/BF<sub>3</sub>·OEt<sub>2</sub>/AlEt<sub>3</sub> or Ni(salen)/BF<sub>3</sub>·OBu<sub>2</sub>/MAO using a suitable amount of MAO. Broad MWD in catalysts **1**–**6** is a typical example of Ziegler–Natta catalytic system having a multi-site active center.<sup>11</sup>

BF<sub>3</sub> etherate enhanced *cis* content and yielded high conversion in the 1,3-butadiene polymerization of catalysts **1**–**6** in comparison with catalyst **7**. In the absence of BF<sub>3</sub>, catalyst **7** showed poor reactivity and conversion even at a high Al/Ni 100. This supports that BF<sub>3</sub> is involved in the active centers of 1,3-butadiene polymerization at which fluorine increases *cis* content by promoting Ni electron deficiency with consequently stronger η<sup>4</sup>-*cis* coordination of butadiene. This was confirmed by XAFS (X-ray absorption fine structure) in which differences in peak position, shape and FT magnitude represent dissimilar nickel active centers generated by the addition of boron trifluoride etherate.<sup>12</sup>

A catalyst composed of nickel acetylacetonate and alkylaluminum yields only oligomers with butadiene due to β-hydride elimination of the growing chain.<sup>13</sup> In combination with MAO nickel acetylacetonate or NiCp<sub>2</sub> produces high 1,4-*cis* polybutadiene.<sup>14</sup> Catalyst **8**, NiBr<sub>2</sub>·DAD and MAO, yielded high molecular weight polybutadiene (*M<sub>w</sub>* = 145000) with 91% *cis* content and 2.92 polydispersity. Steric bulkiness of DAD ligand prevented β-hydride elimination in chain propagation which contributed to produce the high molecular weight of polybutadiene.<sup>15</sup> Lower *cis* content of catalyst **8** than

that of catalyst **1** was possibly due to the bulky group of DAD interfering with cisoid coordination of butadiene. On the basis of narrow polydispersity, [DAD·Ni(II)CH<sub>2</sub>CH<sub>3</sub>]<sup>+</sup> may be the single site active center in butadiene polymerization.

It was found that 1) the structure of ligand does not influence microstructure but reactivity of 1,3-butadiene polymerization, 2) BF<sub>3</sub> promotes high *cis* polymerization by preventing nickel reduction and enhanced MAO efficiency, and 3) high *cis* polybutadiene would be obtained using NiBr<sub>2</sub>·DAD catalyst even in the absence of BF<sub>3</sub>.

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