

High Performance Phenoxytitanium-Based Catalysts for Olefin Polymerization

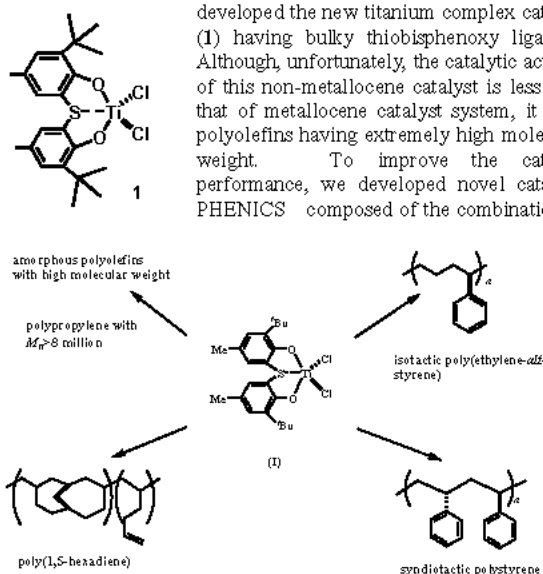
Tatsuya Miyatake

Petrochemicals Research Laboratory,
Sumitomo Chemical Co., Ltd.
2-1 Kitasode, Sodegaura, Chiba 299-0295, Japan
miyataket1@sc.sumitomo-chem.co.jp

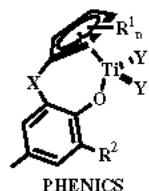
Introduction

The key technology of the production of polyolefins is a catalyst technology. As well known, in 1958, Ziegler and Natta discovered the catalyst systems that promote the polymerization of olefins. This catalyst system is called "Ziegler-Natta catalyst" which has been widely used to the commercial production of HDPE, LLDPE and PP. On the other hand, since the discovery of homogeneous organometallic complex catalyst composed of zirconocene and methylalumoxane, many researchers have developed metallocene catalysts. Metallocene catalyst opens the new era of polyolefin production and has been applied to the commercial production of LLDPE PP, EPDM, and other Elastomers.

In 1987, Sumitomo Chemical developed the new titanium complex catalyst (1) having bulky thiobisphenoxy ligand.^{1,2} Although, unfortunately, the catalytic activity of this non-metallocene catalyst is less than that of metallocene catalyst system, it gave polyolefins having extremely high molecular weight. To improve the catalyst performance, we developed novel catalyst, PHENICS composed of the combination of



a cyclopentadienyl group to perform a high catalytic activity and a bulky phenoxy group, which performs the production of high molecular weight polyolefin.^{3,4}



On the other hand, we have developed several types of new cocatalysts⁵⁻⁷ for olefin polymerization with metallocene and non-metallocene catalysts, which are composed of water, C_6F_5OH and MMAO (isobutylmethylalumoxane). Those cocatalysts can drastically improve the performance of metallocene catalysts, giving higher polymerization activity and greater molecular weight of resulting polymer. Recently, we developed the novel Bi-based cocatalyst especially efficient in PHENICS-catalyzed olefin polymerization.

Results and discussion

PHENICS Catalysts

The dimethylsilylene- or isopropylidene- (cyclopentadienyl)(3-*tert*-butyl-5-methyl-2-phenoxy) titanium dichloride³ were used here. The phenoxytitanium catalyst synthesized was usually obtained as a orange colored crystal. The structure of the catalysts was determined by the X-ray crystal structure analysis. The combination of N,N -dimethylanilinium tetrakis(pentafluorophenyl) borate and triisobutylaluminum was mainly used as cocatalyst.

Synthesis of Ethylene-1-Hexene Copolymers

Table 1 shows the polymerization results in 0.4 L autoclave at 180 °C. The polymerization activity of PHENICS is higher than well-known CGC catalyst. And PHENICS showed the excellent ability of comonomer incorporation into polymer chain. The obtained copolymer had a high molecular weight. In the copolymerization of ethylene and 1-hexene at 210 °C under the ethylene pressure of 150 Mpa for 1 min, the polymerization activity of 110 T-polymer/molTi was achieved. Thus we applied our PHENICS catalyst to the commercial production of very low density polyethylene (Plastmer) by high-pressure ionic polymerization(HIP) process.

Table 1. Copolymerization of ethylene and 1-hexene catalyzed by PHENICS catalyst at 180 °C

catalyst	activity (kg/molTi)	1-hexene (mol%)	$[\eta]$ (g/dL)
PHENICS	4400	7.1	1.1
CGC	2700	2.9	0.9

CGC = $[Me_2Si(Me_4Cp)(N^tBu)]TiCl_2$
conditions: cyclohexane; 185 mL, 1-hexene; 15 mL, ethylene; 2.5 MPa, catalyst, 0.5 μ mol, $Al(i-Bu)_3$; 0.325 mmol; $[PhNH(CH_3)_2][B(C_6F_5)_4]/Ti = 3.0$ mol/mol; 180 °C; 2 min.

Synthesis of Propylene-1-Butene Copolymers.

As summarized in Table 2, when propylene and 1-butene were copolymerized in toluene, our phenoxytitanium catalyst gave amorphous copolymer having high molecular weight and narrow molecular weight distribution in good catalytic activity compared with typical metallocene catalyst systems. The molecular weight of the copolymer obtained with our PHENICS was three to ten times higher than those obtained with hafnocene catalysts which gave high molecular weight LLDPE. Although ethylene-bridged hafnocene catalyst gave relatively high molecular weight, this catalyst system gave copolymer having melting temperature which means that the copolymer has stereoregularity.

Table 2. Copolymerization of Propylene and 1-Butene with various metallocene catalysts^a

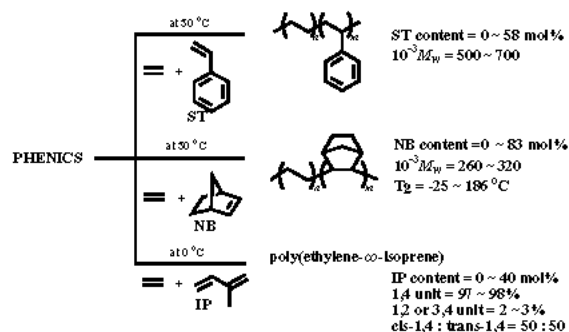
catalyst	activity ^b	polymer properties		
		$M_w \times 10^{-4}$	T_g (°C)	T_m (°C)
PHENICS	33000	103	-11	n.d.
Cp_2HfCl_2	120	10	-10	n.d.
Cp_2ZrCl_2	1300	2	-11	n.d.
$Et(Ind)_2HfCl_2$	800	40	1	76

^a polymn. temp., 30 °C; pressure, atmospheric; time, 0.5 hr; solvent, toluene; monomer feed, $C_3H_6/C_4H_8 = 8/1$ (L/min); co-catalyst, $Al(i-Bu)_3/Ph_3CB(C_6F_5)_4$

^b kg-polymer/mol-metal

Copolymerization of ethylene with various non- α -olefin monomers

The PHENICS catalyst is also active to the copolymerization of



ethylene and several vinyl comonomers such as styrene, norbornen, and conjugated dienes.⁸

The ethylene-styrene copolymer having almost alternating structure is thus obtained. The copolymer containing 83 mol% of norbornen with high molecular weight is also synthesized in good yield.

Novel cocatalyst for PHENICS catalysts.

Bi cocatalyst was prepared by the reaction of $\{\text{Bi}(\text{OC}_6\text{F}_5)_3(\text{toluene})\}_2$ ⁹ with H_2O at 80 °C under an argon atmosphere.

As shown in Table 4, the Bi cocatalyst activates PHENICS to produce ethylene/1-hexene copolymer with comparative activity and higher molecular weight than that with $[\text{PhNH}(\text{CH}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ at 180 °C. The activity depends on the $\text{H}_2\text{O}/\text{Bi}$ ratio and shows the maximum at the ratio of 1/1 as shown in Figure 1. ¹⁹F NMR analysis of the Bi cocatalyst revealed that the cocatalyst is a mixture of several species and the structure varies with the $\text{H}_2\text{O}/\text{Bi}$ ratio. The Bi cocatalyst is also capable of increasing the molecular weight of polypropylene obtained at 180 °C when combined with PHENICS. The stereoregularity of the polymer is atactic. The tacticity of the resulting polymer is absolutely the same as one polymerized using $[\text{PhNH}(\text{CH}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$.

Table 3. Copolymerization of ethylene and 1-hexene with PHENICS and Bi cocatalyst

cocatalyst	activity (kg/molTi) ($\times 10^{-3}$)	M_w ($\times 10^{-3}$)	M_w/M_n	SCB (1/1000C)
Bi Cocatalyst ^{a)}	2240	155	1.9	28
$[\text{PhNH}(\text{CH}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ ^{b)}	5000	72	2.1	31

Conditions: toluene 185 mL; 1-hexene 15 mL; ethylene 2.5 MPa; polym. time 2 min; temp. 180 °C; PHENICS catalyst 0.5 μmol ; $\text{Al}(\text{iBu})_3$ 0.3 mmol;
a) Bi Cocatalyst 0.13 mmol. b) $[\text{PhNH}(\text{CH}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ 3.0 mmol.

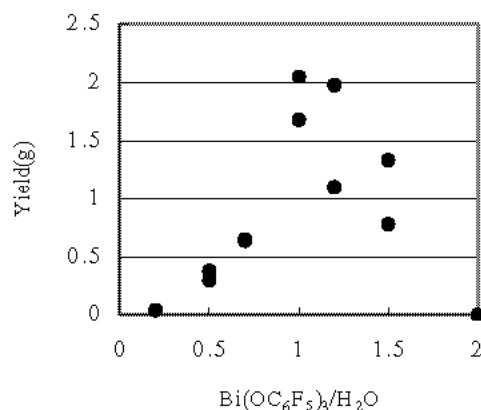


Figure1. Ethylene/1-hexene copolymerization

Conclusions

We have developed high performance phenoxytitanium catalyst PHENICS for olefin polymerization. PHENICS showed extremely high activity toward olefin polymerization and high ability of comonomer incorporation to give several copolymers having high molecular weight and narrow molecular weight distribution.

PHENICS also has excellent ability to produce olefin-non-olefin copolymers such as ethylene-styrene copolymer and ethylene-conjugated diene copolymer.

Non-group 13 elements based Bi cocatalyst has been developed, which is efficient to increase the molecular weight of the polymer produced with PHENICS.

Acknowledgments

I especially thank Messrs Akio Imai, Masaaki Nabika, and Tsuyoshi Watanabe and Dr. Hiroaki Katayama, for their powerful

perform of catalyst development and thank to Messrs Yoshiaki Oda, Hidenori Hanaoka, Hideki Satou, Hirofumi Jouhouji, and Hidetake Hozumi and Ms. Atsuko Ogawa for their strong assistance for catalyst synthesis and polymer developments. I also thank Kazuo Takaoki, Shinya Nakahara, Yoshiya Okado, and Yoshinori Seki for their eagerness to the findings and the developments of new type of cocatalyst.

References

1. Miyatake, T.; Mizunuma, K.; and Kakugo, M. *Makromol. Chem., Makromol. Symp.*, **1993**, *66*, 213.
2. Takaoki, T.; and Miyatake, T. *Macromol. Symp.*, **2000**, *157*, 251.
3. H. Katayama, M. Nabika, A. Imai et al. European Patent Application **1998**, 0842939.
4. Imai, A.; Katayama, H.; Nabika, M.; Watanabe, T. *MetCon2001* (2001).
5. Fujita, M.; Seki, Y.; Miyatake, T. *J. Polymer Sci., Part A*, **2004**, *42*, 1107.
6. Fujita, M.; Seki, Y.; Miyatake, T. *Macromol Chem., Phys.*, **2004**, *205*, 884.
7. Fujita, M.; Seki, Y.; Miyatake, T. *Macromolecules*, **2004**, *37*, 9676.
8. Imai, A.; Ogawa, A.; Takei, T.; Nishiyama, T.; Jouhouji, H. *MetCon2000* (2000).
9. Whitmire, K. H.; Hoppe, S.; Sydora, O.; Jolas, J. L.; Jones, C. M. *Inorg. Chem.* **2000**, *39*, 85.