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TITANIUM AND VANADIUM BASED NON-METALLOCENE CATALYSTS FOR OLEFIN POLYMERIZATION

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Abstract: Titanium complexes with chelating 2,2'-thiobis(4-methyl-6-R-phenoxy) ligand (R= CH_3, *i*-C_3H_7, *t*-C_4H_9, Si(*i*-C_3H_7)$_3$) ligands in combination with methylalumoxane, methylisobutylalumoxane or triisobutyl-aluminum/$(C_6H_5)_3CB(C_6F_5)_4$ as cocatalyst were highly active toward olefin, giving polymers with high molecular weight. Especially, titanium complexes having the most bulky substituent of Si(*i*-C_3H_7)$_3$ showed the highest activity of ethylene polymerization. Vanadyl complexes with 2,2'-thiobis(4-methyl-6-*tert*-butylphenoxy) ligand prepared by the reaction with $VO(OC_4H_9)_3$ were also highly active to propylene, giving isotactic polypropylene with the melting temperature of 138°C.

INTRODUCTION

Titanocenes and titanium tetraalkoxides combined with an alkylaluminum compound can polymerize olefins.[1] However, the catalytic activities are very low compared with that of commercial catalysts, i.e., $TiCl_3$, and $MgCl_2$-supported catalyst. On the other hand, Kaminsky and Sinn found that zirconocene compounds, when they are combined with methylalumoxane (MAO) give polyethylene in excellent catalytic activiy.[2] We have focused on the application of MAO to a non-metallocene titanium complex catalyst system such as titanium alkoxide or titanium phenoxide and have found the novel titanium complex catalyst with 2,2'-thiobis(4-methyl-6-*tert*-butylphenoxy) ligand (**1**, (TBP)$TiCl_2$) showing high activity to the polymerization of propylene as well as ethylene.[3] This catalyst system is

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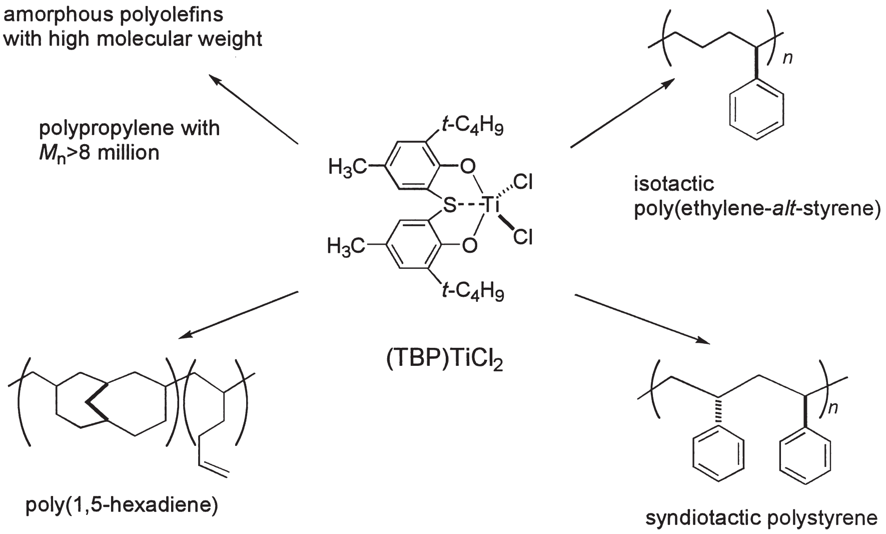
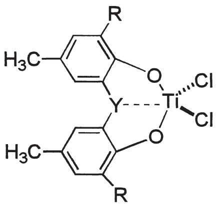
considered to be promising system not only for a displacement of zirconocene catalyst system as a single-site olefin polymerization catalyst system but also for synthesis of new polymer materials. (TBP)$TiCl_2$/MAO system is active for olefins, styrene, conjugated dienes, and non-conjugated dienes.[4,5] The catalyst performance of (TBP)$TiCl_2$/MAO system is summarized in Scheme 1. This catalyst system gives (1) amorphous polypropylene with extremely high molecular weigh of more than 8 million, (2) polybutadiene with high *cis*-1,4-structure, (3) poly(1,5-hexadine) with complicate cyclic structure, (4) syndiotactic polystyrene, and (5) isotactic poly(ethylene-*alt*-styrene).

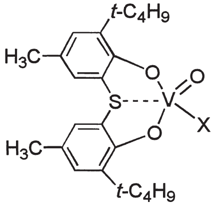
Scheme 1



In a present paper, we report on the results of ethylene polymerization with new thiobis(phenoxy) titanium complex catalysts (**2**-**5**) and of propylene polymerization with vanadyl complex catalyst with 2,2'-thiobis(4-methyl-6-*tert*-butylphenoxy) ligand (**6** and **7**).



1; R = t-C_4H_9, Y = S
2; R = CH_3, Y = S
3; R = i-C_3H_7, Y = S
4; R = Si(i-C_3H_7)$_3$, Y = S
5; R = t-C_4H_9, Y = SO_2

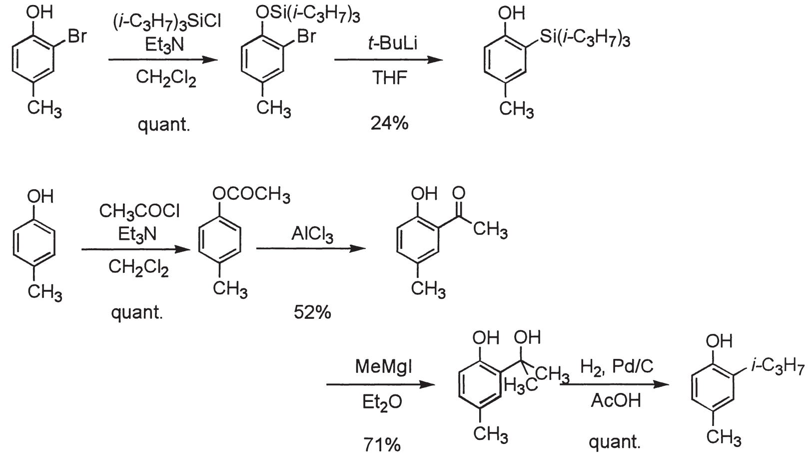


6; X = Cl, (TBP)VOCl
7; X = OC_4H_9, (TBP)VO(OBu)

RESULTS AND DISCUSSION

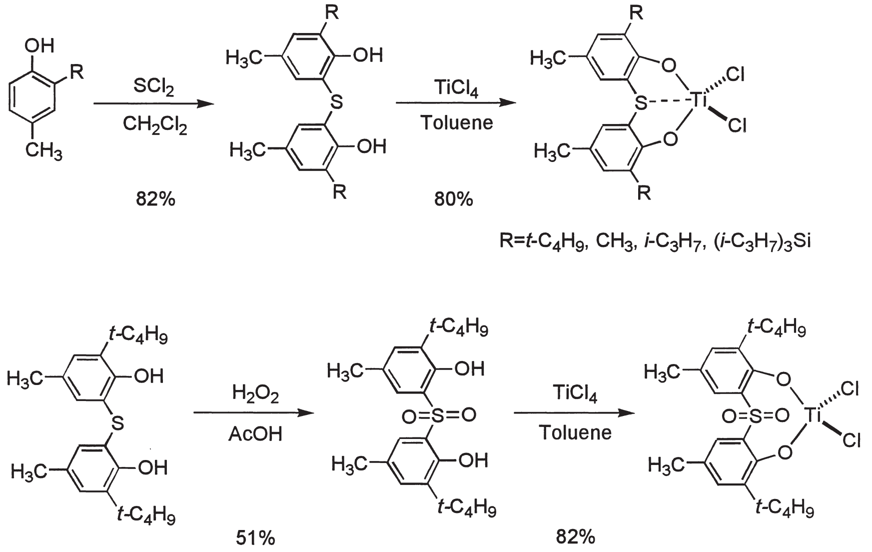
Synthesis of catalysts: Bulky phenols were synthesized according to the procedures shown in Scheme 2. Triisopropylsilyl-substituted cresol was prepared from corresponding bromide. After O-silylation of cresol, the silyl group was transferred to the 2-position of cresol with *tert*-butyllithium. Isopropyl-substituted cresol was regiospecifically prepared from *p*-cresol by 4 steps. After Fries-rearrangement of cresol ester, acyl group was converted to isopropyl group by 2 steps.

Scheme 2



Preparation procedures of titanium complexes were summarized in Scheme 3. Thiobisphenols were prepared from corresponding phenols, after treatment of 2-substituted cresols with sulfer dichloride, resulted bis-phenol ligands were complexed with titanium tetrachloride in good yield.
The sulfonylene bridged bisphenol was prepared through oxidation of the sulfanylene bridged bisphenol, complexation of the bisphenol with titanium tetrachloride gave desired titanium complex in good yield.

Scheme 3



Vanadyl complex **6** was prepared by the reaction of 2,2'-thiobis(4-methyl-6-*tert*-butylphenol) with $VOCl_3$ in pentane at 0°C for 5 h in a 70% yield. Complex **7** was prepared by the reaction with $VO(OC_4H_9)_3$ in *n*-pentane at 20°C for 20 h in a 75% yield.

Polymerization of ethylene with titanium-based catalyst systems **1-5**: The results of ethylene polymerization with complexes **1-5** were summarized in Table 1. Three types of cocatalysts were used in this polymerization;

methylalumoxane (MAO), methyl-isobutylalumoxane (MMAO), and trityl-tetrakis(pentafluoro)borate/triisobutylaluminum system. In the cocatalyst systems of MAO and borate, toluene was used as a solvent, and in the case of MMAO, *n*-heptane was used. Polymerization conditions are shown in the footnote of the table.

Table 1. Polymerization of ethylene with various titanium complexes

	cocatalyst					
	MAO[a]		MMAO[b]		$(C_6H_5)_3CB(C_6F_5)_4/Al(^iC_4H_9)_3$[c]	
complex	activity (kg/mol Ti h)	$10^{-4} \times M_w$	activity (kg/mol Ti h)	$10^{-4} \times M_w$	activity (kg/mol Ti h)	$10^{-4} \times M_w$
2	170	—	1070	14	40	—
3	570	—	1900	17	190	—
1	550	27	3090	44	210	24
4	1050	71	670	73	880	154
5	40	48	780	22	90	51

a) polymerization conditions: 1 L autoclave; solvent = toluene, 300 mL; MAO/Ti = 1000 (mol/mol); 60°C for 1 h; ethylene = 4 atm.
b) MMAO/Ti = 1000; solvent = *n*-heptane, 300 mL.
c) Al/Ti = 500, Borate/Ti = 1; solvent = toluene, 300 mL.

Complex **2** having smallest substituent of methyl group among them showed the lowest activity in all cocatalyst systems. On the other hand, complex **4** which has largest substituent of triisopropylsilyl group showed the highest activity and the polymer obtained had the highest molecular weight.

Sulfonylene bridged complex **5** was not so active toward ethylene polymerization compared with sulfanylene bridged complexes **1**-**4**.

These results indicate that a precise designing of a ligand structure and a suitable combination of complex and cocatalyst might improve a catalyst performance of such phenoxy-titanium complex catalyst system.

Polymerization of propylene with vanadium-based catalyst systems **6** and **7**: The results of propylene polymerization were summarized in Table 2. Both $VOCl_3$ and $VO(OC_4H_9)_3$ were active when combined with MAO. However, the molecular weight distribution of polymers obtained were very broad (M_w/M_n = 61 and 78). Both complexes **6** and **7** showed an excellent activity, which is comparable to that of Ti complex catalyst. By a introduction of thiobisphenoxy ligand to vanadyl compound, polypropylene with a narrow molecular weight distribution was obtained. Interestingly, polypropylene prepared with buthoxyvanadyl complex was isotactic-rich polymer (mm% is more than 35%). Especially, complex **7**/ MAO system gave a polypropylene with highest mm dyad tacticity of 68% and with the melting temperature of 138°C. This melting temperature is comparable to that of polypropylene prepared with ethylenebis(indenyl)zirconium dichloride/MAO system. Another characteristic of the polypropylene prepared with such vanadyl complex is that the polymer obtained has higher regioregularity (represented by $F_{000} + F_{111}$) compared with $(TBP)TiCl_2$ (complex **1**) /MAO system[3].

Table 2. Polymerization of propylene with vanadyl complexes and MAO

complex	activity[a] (kg/mol M h)	10^{-4}xM_w	M_w/M_n	stereoregularity [mm]%	Tm[b] (C)	regioregurarity[c] $F_{ooo} + F_{111}$
(TBP)VOCl (**6**)	1900	190	3.2	35	—	0.98
$(TBP)VO(OC_4H_9)$ (**7**)	420	220	4.0	68	138	—
$(TBP)TiCl_2$ (**1**)	8900	>800	2.2	22	—	0.54
$VOCl_3$	12	90	61	47	—	0.96
$VO(OC_4H_9)_3$	6	120	78	60	—	—

a) polymerization condition: cat., 1.1 x 10^{-3}mmol; MAO, 5.17 mmol; propylene, 30g; toluene, 3 mL; polymn. temp., 20°C; Time 1 h.
b) melting temperature c) Y. Doi, *Macromolecules*, **12**, *248-251*, (1979)

The isotactic-rich polypropylene obtained with vanadyl complex **7** was a mixture of isotactic polypropylene and atactic polypropylene. The ^{13}C NMR spectra of methyl region of polypropylene fractions fractionated by an extraction with a boiling *n*-pentane are shown in Fig. 1. Spectrum (A) shows that the main defect of isotactic sequence is mmmmrrmmmm, which suggests that the isospecific propagation of propylene was governed by a catalytic control mechanism.

A more detailed designing of ligand and a selection of cocatalyst are necessary to improve the catalytic performance and to control the molecular structure of polymer obtained.

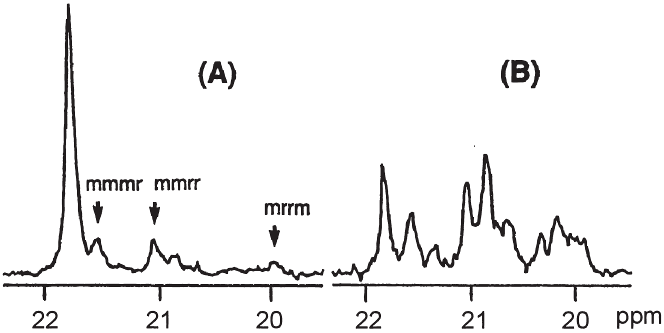


Fig. 1 ^{13}C NMR of PP fractions (sample no. 2)
(A) fraction insoluble in *n*-pentane (71%)
(B) fraction soluble in *n*-pentane (29%)

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