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Preparation of soluble $TiCl_3$ catalysts by reduction of $TiCl_4$ with Grignard reagents and their use for copolymerization of ethylene with propylene

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Summary

Preparations of soluble $TiCl_3$ catalysts by reduction of $TiCl_4$ with some types of Grignard reagents were carried out in halogenated hydrocarbon solvents by using appropriate ethers as donor. The soluble $TiCl_3 \cdot MgX_2 \cdot$ether complex catalysts and triisobutylaluminum as co-catalyst showed high activities for the copolymerization of ethylene with propylene. It was first found that the soluble $TiCl_3 \cdot MgX_2 \cdot$ether complex catalysts enhance the activities for the copolymerizations in the same manner as solid titanium catalysts supported on $MgCl_2$ which show high activities for homopolymerizations of olefin monomers. The copolymers obtained possessed low crystallinities. Also, the copolymers seem to contain microblock sequences and have outstandingly high tensile strength and elongation at break compared to copolymers by the conventional $VOCl_3/Al(Et)_{1.5}Cl_{1.5}$ catalyst system.

Introduction

It is well known that titanium catalysts supported on $MgCl_2$ show very high activity for homopolymerization of ethylene and propylene (1-5). Nevertheless, their activities for random copolymerization of the monomers are very low (6). Moreover, the catalysts cannot copolymerize termonomers such as 5-ethylidene-2-norbornene or dicyclopentadiene. In ordor to enhance the activity of the titanium catalysts for the random copolymerization of ethylene with propylene, we have studied the preparation of soluble $TiCl_3$ catalysts. Recently, we have reported that soluble $TiCl_3$ catalysts prepared by the methods of previous papers (7-10) provide highly random copolymerization of the monomers. Moreover, if Ti^{3+} and Mg^{2+} complex catalysts are soluble in hydrocarbon or halogenated hydrocarbon solvents, that would have high activity for random copolymerization of ethylene with propylene.

In the present study, soluble $TiCl_3$ catalysts containing Mg^{2+} were prepared by reduction of $TiCl_4$ with some types of Grignard reagents in halogenated hydrocarbon solvents using an ether as donor, and copolymerizations of ethylene with propylene were carried out using the catalysts. The copolymers obtained were characterized and some mechanical properties of them were measured.

Experimental

Materials : $TiCl_4$ (Wako Chemicals Co.), $Al(i\text{-}Bu)_3$, and $Al(Et)_{1.5}Cl_{1.5}$ (Toyo Stauffer Co.) were used without further purification. Diethyl ether (DEE), dibutyl ether (DBE), and dioctyl ether (DOE) as donors and solvents such as 1,2-dichloroethane (DCE), dichloromethane (DCM), chlorobenzene (CBz), and hexane (Wako Chemical Co.) were degassed by bubbling with nitrogen and were dried with molecular sieves. Grignard reagents such as (*n*-Bu)MgCl, (*n*-Bu)MgBr, (*n*-Bu)MgI, (Et)MgI, and (*n*-Oct)MgI were prepared by the usual method in some kinds of ethers.

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Reduction of $TiCl_4$ by (n-Bu)MgI : A three-necked 100 mL flask was equipped with a stirring bar, a thermometer and a three-way stopcock. It was flushed with dry nitrogen. DCE (50 mL) as solvent and $TiCl_4$ (10 mmol) were introduced into the flask by a syringe. DBE (total 30 mmol; including the amount of DBE as the solvent for the Grignard reagent) was added to the flask. The mixture was allowed to stand for 30 min at 0 °C, (*n*-Bu)MgI (10 mmol) in DBE solution was then added to the flask at 0 °C over 30 min. The contents of the flask were stirred at 0 °C for 1 h. A homogeneous black solution of $TiCl_3$ was obtained. The prepared soluble $TiCl_3 \cdot MgX_2 \cdot$ether complex was stored at 0 °C in a refrigerator. The method of determination of the valence number of Ti and procedures for the copolymerization of ethylene with propylene have been described previously (7-9).

Characterization and measurement of physical properties of copolymer : IR spectra and ^{13}C-NMR spectra of the copolymers were recorded as shown in previous papers (7-10). Also, measurments of tensile properties of the uncured copolymers were descrived in previous papers (7-10).

Results and Discussion

Reduction of $TiCl_4$ with Grignard reagent

In order to prepare $TiCl_3$ complexes which are soluble in halogenated hydrocarbon solvents, $TiCl_4$ was reduced with Grignard reagents using an ether as donor. Grignard reagents, e.g., (*n*-Bu)MgCl, (*n*-Bu)MgBr, (*n*-Bu)MgI, (Et)MgI, (*n*-Oct)MgI, can completely reduce the $TiCl_4$ and give soluble a $TiCl_3 \cdot MgX_2 \cdot$ether complex under the conditions described in the experimental section. Figure 1 shows the yield of Ti^{3+} as a function of the molar ratio of (*n*-Bu)MgI to $TiCl_4$. $TiCl_4$ was quantitatively reduced by (*n*-Bu)MgI at a molar ratio of [(*n*-Bu)MgI]/[$TiCl_4$] = 1.0. However, a green precipitate forms at higher than the optimum molar ratio of (*n*-Bu)MgI to $TiCl_4$, and the amount of the precipitates increased with increasing molar ratio.

The effectiveness of solvents and donors on the reduction of $TiCl_4$ with (*n*-Bu)MgI was examined. When $TiCl_4$ is reduced in CBz, DCM, and DCE (polar solvents) with DBE as donor at a molar ratio of [DBE]/[Ti+Mg] = 3, the complex catalysts obtained can be completely dissolved. However, when the molar ratios are lower than 3, the prepared $TiCl_3$ complexes cannot be completely dissolved in DCE solvent and precipitates formed. When hexane (a non-polar solvent) and DBE are used as solvent and donor, even at a molar ratio of [DBE]/[Ti+Mg] = 3, the $TiCl_3$ complexes prepared do not dissolve and plenty of precipitate formed. It is seen that when 3 moles of ether co-ordinate to $TiCl_3$ and MgX_2, the $TiCl_3 \cdot MgX_2 \cdot 3$ether complex prepared can be solubilized in DCE solvent.

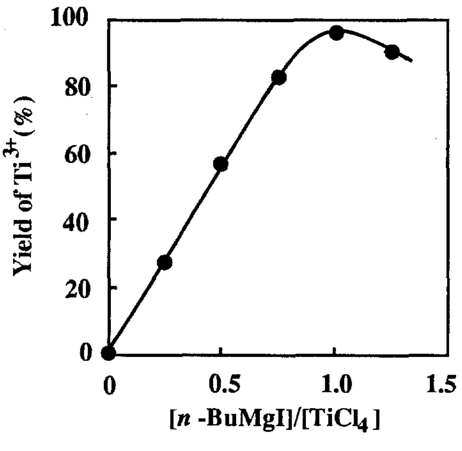

Figure 1 Yield of Ti^{3+} as a function of [*n*-BuMgI]/[$TiCl_4$] on the reduction of $TiCl_4$. Catalyst preparation conditions are the as same as Run 5 in Table 1.

Temperature at the reduction of $TiCl_4$ with (*n*-Bu)MgI was an important factor for obtaining soluble $TiCl_3\cdot MgX_2\cdot DBE$ complexes. When the reducing temperature was lower than 5 °C, the $TiCl_3\cdot MgX_2\cdot DBE$ complexes prepared remained as a homogeneous brown-black solution. However, when the temperature of the solution of the $TiCl_3\cdot MgX_2\cdot$ether complexes prepared at 0 °C was increased to above 10 °C, powdery precipitate slowly formed from the homogeneous solution. When $TiCl_4$ was reduced at higher than 10 °C, plenty of precipitate formed. Thus, we usually carried out the reduction of $TiCl_4$ under 0 °C and stored the system below 0 °C.

It is found that nature of the solvent and donor, the relative amount of donor to $TiCl_4$, and the reducing temperature are important for obtaining soluble $TiCl_3$ complexes.

Copolymerization of ethylene with propylene

Copolymerization of ethylene with propylene was carried out in hexane at 30°C using various soluble $TiCl_3\cdot MgX_2\cdot$ether complex catalysts and triisobutylaluminum co-catalyst. Table I shows the result of the copolymerization. The copolymerization using the homogeneous solution of the $TiCl_3\cdot MgX_2\cdot$ether catalyst give rubbery random copolymers with low crystallinities. The halogens in the (*n*-Bu)MgX, e.g., Cl, Br, and I, affected catalyst activities for the copolymerization, propylene content, and copolymer crystallinities (Runs 1, 2, and 5 in Table I). Iodine is the best. The length of the alkyl group in the RMgI, e.g., ethyl-, *n*-butyl-, and *n*-octyl-, was examined (Runs 5, 7, and 8). When (*n*-Bu)MgI and (*n*-Oct)MgI were used as reducing agents, the copolymer crystallinities were lower than that of a copolymer prepared with the catalyst in which $TiCl_4$ was reduced with (Et)MgI.

Table II shows that results of the copolymerization using the soluble catalysts prepared by reduction of $TiCl_4$ with three kinds of donors in various solvents. The polarity of a solvent and the length of the alkyl group of the donor used in the preparation of the catalyst affected the catalytic activity and the crystallinity of the resulting copolymer. In the case of a nonpolar solvent such as hexane, precipitated $TiCl_3$ complex catalysts formed. The incompletely solubilized catalyst gave low catalytic activity, low propylene content, and high crystallinity in the copolymer (Run 9). When a polar solvent such as CBz, DCM and DCE was used, satisfactory results were obtained using DBE or DOE with a relatively long alkyl

Table I
Influence of Grignard reagent on the reduction of $TiCl_4$ and their use for copolymerization of ethylene with propylene

	Catalyst preparation[a]			Copolymerization[b]		
Run No.	RMgX	$RMgX/TiCl_4$ (mol/mol)	Yield of Ti^{3+} (%)	Polymer yield (g)	Propylene units (mol %)	Crystallinity[c] (%)
1	(*n*-Bu)MgCl	1.0	96	5.0	30	1.2
2	(*n*-Bu)MgBr	1.0	95	7.5	33	1.0
3	(*n*-Bu)MgI	0.5	47	3.9	22	1.5
4	"	0.75	73	6.2	30	1.0
5	"	1.0	95	8.2	34	0.5
6	"	1.25	91	7.8	34	1.0
7	EtMgI	1.0	97	6.1	20	1.5
8	(*n*-Oct)MgI	1.0	97	8.7	35	0.4

[a] Preparation conditions: solvent, DCE, 50 mL; $TiCl_4$, 10 mmol; DBE, 30 mmol; temp, 0 °C; time, 30 min.

[b] Copolymerization conditions: solvent, hexane, 200 mL; soluble $TiCl_3$ (as Ti), 0.2 mmol; $Al(i\text{-}Bu)_3$ as co-catalyst, 0.6 mmol; monomer gas feed (ethylene/propylene) = 1.5/1.0 L/min; temp, 30 °C; time, 10 min.

[c] Crystallinity at 26.5 mol% of propylene.

Table II
Influence of solvent on the reduction of $TiCl_4$ by *n*-BuMgI and their use for copolymerization

Run	Catalyst Preparation[a)]				Copolymerization[b)]		
No.	Solvent (ε)[c)]	Donor	[Donor]/[Ti+Mg] (mol/mol)	Homogeneity of $TiCl_3$ solution[d)]	Polymer yield (g)	Propylene units (mol %)	Crystal-linity (%)
9	Hexane (1.88)	DBE	3.0	Ppt.	0.5	40	2.2
10	CBz (5.60)	DBE	"	C. Sol.	5.7	33	0.9
11	DCM (9.08)	DBE	"	"	5.3	24	1.8
12	DCE (10.37)	DEE	"	A.Sol.	1.4	21	2.2
13	"	DBE	2.5	C.Sol	2.1	23	1.3
14	"	DBE	3.0	"	8.2	34	0.4
15	"	DBE	3.5	"	3.9	19	1.2
16	"	DOE	3.0	"	7.4	33	0.4

[a, b)] Conditions are the same as in Run 8 (Table 1).
[c)] Dielectric constant
[d)] Ppt.: precipitated, C.Sol.: completely soluble, A.Sol.: almost soluble

group (Runs 10, 11, 14 and 16). When DEE having a short alkyl group was used, the soluble $TiCl_3$•MgX_2•DEE catalyst obtained gave unsatisfactory catalytic activity, propylene content, and copolymer crystallinity (Run 12). These effects of solvents and donors on the catalytic activity and crystallinity seem to be closely related to the solubility of the $TiCl_3$•MgX_2•ether complexes. In other words, homogeneous $TiCl_3$•MgX_2•ether catalyst solutions produced high catalytic activity and provided random copolymer The best combination of solvent and donor was DCE and DBE or DOE. The amount of donor used affected the catalytic activity and the crystallinity of the copolymer. Table II shows that there is a maximum molar ratio of [DBE]/[Ti+Mg] for catalytic activity and there is a minimum molar ratio for copolymer crystallinity. The optimum molar ratio of [DBE]/ [Ti+Mg] was 3.

The reducing temperature of $TiCl_4$ with *n*-BuMgI greatly affected the catalytic activity and the crystallinity of the copolymer. The catalytic activities increased by decreasing the reducing temperature of $TiCl_4$, and the crystallinities decreased as shown in Figure 2. The soluble catalysts obtained by the reduction of $TiCl_4$ at -10 °C enhance catalytic activities by about 2 times and copolymer crystallinities by about 1/3 times, in comparison with the

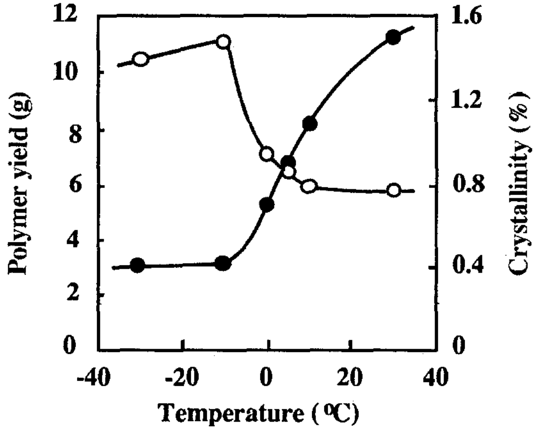

Figure 2 Plots of polymer yield and crystallinity of copolymer as a fuction of reducing temperature of $TiCl_4$. Catalyst preparation conditions are the as same as Run 5 in Table1.
○ : Polymer yield, ● : Crystallinity

catalysts which were reduced at 30 °C.

It was found that the prepation conditions of the soluble $TiCl_3 \cdot MgX_2 \cdot$ether complex catalyst, such as the length of the alkyl group and the kind of halogen in RMgX, the selection of solvent and donor, and the reducing temperature of $TiCl_4$, strongly influence catalytic activity, propylene content, and copolymer crystallinity.

It is well known that titanium catalysts supported on $MgCl_2$ have very high catalytic activity for ethylene or propylene homopolymerization. In the copolymerization of ethylene with propylene, the soluble $TiCl_3 \cdot MgX_2 \cdot$ether catalysts have about 3.5 times the catalytic activity of the soluble $TiCl_3 \cdot 1/3AlCl_3 \cdot$ether catalyst as shown in a previous paper(9). It was first found that Mg^{2+} containing soluble titanium catalysts exhibit very high activity for the copolymerization and the copolymers have very low crystallinity.

Characterization of copolymer

^{13}C-NMR measurements were performed on ethylene/propylene copolymers **1** and **2** which were prepared with the soluble $TiCl_3 \cdot MgX_2 \cdot DBE/Al(i\text{-}Bu)_3$ and the usual $VOCl_3$ $/Al(Et)_{1.5}Cl_{1.5}$ catalyst system. The results are tabulated in Table III. The amount of the PPP sequence in copolymer **1** is much greater than that of copolymer **2**. Also, the value of isotacticity of PPP in copolymer **1** is higher than that of copolymer **2**. Since an even number of methylene sequences ($(CH_2)_n$: n = 2 or 4) means propylene inversion, the degree of propylene inversion of copolymer **1** is very low in comparison with that of copolymer **2**. These facts and the low crystallinity of copolymer **1** suggest that the copolymer prepared with the $TiCl_3 \cdot MgX_2 \cdot DBE$ catalyst contains microblock sequences of which the lengths are insufficient for crystallization.

Table III
Microstructures of copolymers obtained by soluble $TiCl_3$ or $VOCl_3$ catalysts

Microstructure		Copolymer	
		1[a]	2[b]
Propylene content (mol%)		50	46
Triad sequence (%)	PPP	24.4	7.0
	PPE+EPP	18.4	17.5
	EPE	11.6	18.5
	PEP	13.2	13.6
	EEP+PEE	15.1	23.2
	EEE	17.2	22.2
Methylene sequence length (%)	$(CH_2)_1$	21.7	9.2
	$(CH_2)_2$	1.4	9.1
	$(CH_2)_3$	24.5	6.5
	$(CH_2)_4$	1.1	9.6
	$(CH_2)_5$	18.7	24.6
	$(CH_2)_{>6}$	42.6	41.0
Isotacticity in PPP sequence[c] (%)	$P_{mm}/T_{\beta\beta}$	62.8	21.0

[a] By a soluble $TiCl_3/Al(i\text{-}Bu)_3$ catalyst system.

[b] By the conventional $VOCl_3/Al(Et)_{1.5}Cl_{1.5}$ catalyst system.

[c] P_{mm}, the peak area at 21.3-22.0 ppm of mm sequence in propylene triad; $T_{\beta\beta}$, the peak area at 28.5-29.3 ppm of propylene triad.

Some physical properties of copolymers **3** and **4** prepared by a soluble $TiCl_3 \cdot MgX_2 \cdot DBE$ catalyst were measured along with copolymers **5** and **6** by a $VOCl_3$ catalyst. The results are shown in Table 4. Copolymers **4** and **6** are ternary copolymers. The tensile strength and elongation of copolymers **3** and **4** are 2-3 times greater than those of copolymers **5** and **6**, respectively. Furthermore, at relatively high temperature, the differences in the tensile properties became greater between the copolymers by soluble $TiCl_3$ catalyst and the copolymers by the conventional catalyst; i.e., the values of tensile strength and elongation of copolymers **3** and **4** at 50 °C are 5-7 times higher than those of copolymers **5** and **6**. These excellent tensile properties may be attributed to the microstructure of the copolymer, e.g., the tacticity in the PPP triad sequences, the extent of inversion of propylene, and microblock sequences.

Table IV
Physical properties of uncured copolymers obtained by soluble $TiCl_3$ or $VOCl_3$ catalysts

Physical property	Copolymer			
	1[a]	2[a,c]	3[b]	4[b,c]
Propylene content (mol%)	31	29	27	21
Termonomer content (Iodine number)	0	18	0	15
Moony viscosity (ML$_{1+4}$, 100°C)	64	81	68	85
At 25 °C				
Modulus at 100% (MPa)	1.5	1.1	1.1	1.2
Tensile strength (MPa)	7.3	6.3	2.1	3.9
Elongation (%)	2840	3390	1170	1990
Hardness (JIS-A)	64	58	68	55
At 50 °C				
Modulus at 100% (MPa)	0.8	0.6	0.6	0.6
Tensile strength (MPa)	2.1	2.2	0.3	0.4
Elongation (%)	2920	3750	430	670

[a] By a soluble $TiCl_3/Al(i\text{-}Bu)_3$ catalyst system.
[b] By the conventional $VOCl_3/Al(Et)_{1.5}Cl_{1.5}$ catalyst system.
[c] Termonomer, 5-ethylidene-2-norbornene

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