Polymer Bulletin 27, 41–46 (1991)

Polymer Bulletin

Preparation of soluble [($TiCl_4$+$MgCl_2$)·phosphate] and soluble [($TiCl_3$-O-MgCl)·phosphate] catalysts and their use for copolymerization of ethylene with propylene

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Summary

$TiCl_4$ and $MgCl_2$ were dissolved in hydrocarbon or halogenated hydrocarbon solvents using phosphate or phosphonate donor. Mg(OH)Cl reacted with $TiCl_4$ with HCl gas evolution above 100 °C in the presence of phosphate or phoshonate donor, and a homogeneous solution of [$TiCl_3$-O-$MgCl_2$] complex was obtained. The soluble catalysts and triisobutylaluminium as co-catalyst showed high activities for the copolymerization of ethylene with propylene. The copolymers obtained were rubbery and possessed very low crystallinities.

Introduction

Regarding titanium catalyst systems for homopolymerization of ethylene and propylene, there have been a large mumber of studies (1-7), e.g, solid $TiCl_3$•1/3$AlCl_3$ by reduction of $TiCl_4$ with alkylaluminium, solid $TiCl_3$ by the reduction of $TiCl_4$ with hydrogen, and $TiCl_4$ or $TiCl_3$ supported on $MgCl_2$ or SiO_2. The copolymerizations by these catalysts, however, could not afford rubbery ethylene/propylene copolymers.

To enhance the activity of 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 provide highly random copolymerization of the monomers (8-12). Moreover, a soluble $TiCl_3$ catalyst containing MgX_2 prepared by reduction of $TiCl_4$ with Grignard reagent in halogenated hydrocarbon solvents showed especially high catalytic activity (12). This results suggest that Mg^{2+} enhances the activity of the soluble Ti^{3+} catalyst for copolymerization of ethylene with propylene in the same manner as solid titanium catalysts supported on $MgCl_2$ show high activity for homopolymerization of olefins.

In the present work, the solubilization of [$MgCl_2$+$TiCl_4$] complex and the preparation of soluble [$TiCl_3$-O-MgCl] complex in a hydrocarbon or a halogenated hydrocarbon solvent in the presence of phosphate or phosphonate as donor, and the copolymerization of ethylene with propylene using the soluble catalysts has been studied.

Experimental

Materials: $TiCl_4$ (Wako Chemicals Co.), Al(*i*-Bu)$_3$, Al(Et)$_{1.5}$Cl$_{1.5}$ (Toyo Stauffer Co.) and $MgCl_2$ (Toho Titanium Co.) were used without further purification. Chlorobenzene (CBz) and hexane (Wako Chemical Co.) solvents, and the phosphate and phosphonate donors, such as butyl phosphate (O=P(-O-Bu)$_3$), octyl phosphate (O=P(-O-Oc)$_3$), butyl phosphonate (O=P(-O-Bu)$_2$(Bu)), and 2-ethylhexyl phosphonate (O=P(-O-Eh)$_2$(Eh)), trialkylphosphines and phosphites such as triethyl phosphine (P(Et)$_3$), tributyl phosphine (P(Bu)$_3$), triphenyl phosphine (P(C_6H_6)$_3$), butyl phosphite (P(-O-Bu)$_3$), octyl phosphite (P(-O-Oc)$_3$), and phenyl phosphite (P(-O-C_6H_6)$_3$) (Daihachi Chemical Co.) were degassed by bubbling with nitrogen and dried with molecular sieves.

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Mg(OH)Cl was prepared as follows. $Mg(OH)_2•6H_2O$ (100 g) was placed in a 300 n flask. The charge was heated at 300 °C in a nitrogen atmosphere. First the $Mg(OH)_2•6H$ became a homogeneous solution, and then a white solid was obtained by removing the water crystallization. The white solid was ground to a powder and heated at 300 °C under vacu for 10 h. White powdery Mg(OH)Cl was obtained.

Preparation of soluble [$TiCl_4$+$MgCl_2$+O=P(-O-Bu)$_3$] complex (13): A two-necked 1 mL flask equipped with a stirring bar, a thermometer, and a three-way stopcock was flush with dry nitrogen. $MgCl_2$ (1 g, 10.5 mmol) was placed in the flask. Hexane (30 mL) a O=P(-O-Bu)$_3$ (42 mmol) were introduced into the flask by a syringe and the mixture w agitated for 20 min at room temperature. After a homogeneous solution was obtained TiC (10.5 mmol) was added. A homogeneous light-yellow solution was obtained. Hexane w added to the solution to bring the total volume of the solution to 52.5 mL (0.2 mol/L, as Ti).

Preparation of soluble [($TiCl_3$-O-MgCl)•3(O=P(-O-Bu)$_3$)] complex (14): A two neck 100 mL flask equipped with a stirring bar, a thermometer, and a three-way stopcock, w flushed with dry nitrogen. Mg(OH)Cl (1 g, 13 mmol) was placed in the flask. O=P(-O-B (39 mmol) was introduced into the flask by a syringe. The mixture was heated at 130 ° $TiCl_4$ (13 mmol) was added dropwise to the flask. Mg(OH)Cl reacted vigorously with TiC with the evolution of hydrogen chloride. After the Mg(OH)Cl disappeared, the solution w allowed to stand for 2 h at 130 °C and a homogeneous brown solution was obtained. T charge was cooled to room temperature, and hexane was added to bring the total volume of t solution to 65 mL (0.2 mol/L, as Ti).

Procedures for the copolymerization : A four-necked flask (500 mL) was equipped wit thermometer, gas inlet and outlet tubes, a three-way stopcock, and an agitator was flushed w dry nitrogen. Dry hexane (200 mL) was placed in the flask and a gaseous mixture of ethyle (1 L/min) and propylene (2 L/min) was introduced into the solution for 10 min at 35 ° Similarly, another three-necked 100 mL flask with starring-bar, a thermometer, gas inlet a outlet tubes, and a three-way stopcock was flushed with dry nitrogen. Dry hexane (50 m was poured in the flask. The temperature of the solution was kept at -10 °C. Two mL of Al Bu)$_3$ solution (1 mol/L) was added to the solution. The gas mixture of ethylene (0.1 L/m and propylene (0.4 L/min) was introduced into the flask. The soluble titanium catalyst (mmol as Ti) mentioned above was added to the solution. The solution was agitated 1 m And then, copolymerization of ethylene with propylene was started by addition of the catal solution to the 500 mL flask all at once. During the copolymerization, the solution was kep 35 °C for 10 min. The copolymerization was terminated by adding methanol (2 mL) containi a small amount of 2,5-di-t-butyl phenol as antioxidant. The polymer solution was washed w water to remove the catalyst residue and poured into a large amount of methanol. The polyn was isolated and dried in vacuum.

Characterization : Infrared spectra of catalysts and copolymers were recorded on a Nih Bunko IR-A3 spectrometer. The propylene content (mol%) of the copolymer was determir by the intensity ratio of the peaks at 720 and 1 150 cm^{-1}. The crystallinity based on lo methylene sequences was determined from the intensity ratio of peaks at 730 and 720 cm according to the method of Emde (15). For quantitative purposes each spectrum ranging fr 650 to 800 cm^{-1} was recorded at a sufficiently slow scanning speed (20 min) and with 10-f expansion. Since the crystallinity of the copolymers is dependent on their propylene conter the comparison of copolymer crystallinities was made by using the values evaluated interpolation at a propylene content of 26.5 mol% in the plot of propylene content crystallinity.

Results and Discussion

Preparation of soluble [$TiCl_4$+$MgCl_2$+O=P(-O-R)$_3$] catalyst

$MgCl_2$ is insoluble in hydrocarbon or halogenated hydrocarbon solvents but can be dissolved in alcohol. If $MgCl_2$ dissolved in alcohol is added to a Ziegler catalyst, an active catalyst cannot be obtained for olefin polymerization. Aprotic compounds which dissolve $MgCl_2$ but do not affect the activity for polymerization of olefins have been sought. It was found that certain phosphates and phosphonates were very useful for this purpose. That is, when $O{=}P(\text{-}O\text{-}Bu)_3$, $O{=}P(\text{-}O\text{-}Oc)_3$, $O{=}P(\text{-}O\text{-}Bu)_2(Bu)$, and $O{=}P(\text{-}O\text{-}Eh)_2(Eh)$ are used as donors, $MgCl_2$ can be dissolved in hexane, CBz, and DCE. However, $MgCl_2$ remains insoluble with trialkylphosphine and phosphite which do not have P=O bond such as $P(Et)_3$, $P(n\text{-}Bu)_3$, $P(C_6H_6)_3$, $P(\text{-}O\text{-}Bu)_3$, $P(\text{-}O\text{-}Oc)_3$, and $P(\text{-}O\text{-}C_6H_6)_3$. The amount of phosphate used is important for solubilization of $MgCl_2$. When $O{=}P(\text{-}O\text{-}Bu)_3$ is used at the molar ratios of $[O{=}P(\text{-}O\text{-}Bu)_3]/[MgCl_2]$ more than 2, $MgCl_2$ is completely dissolved in hexane. An infrared spectrum of the solution of $MgCl_2$ with $O{=}P(\text{-}O\text{-}Bu)_3$ was recorded as shown in Figure 1. The absorption band of 1 300 cm^{-1} based on the P=O bond in $O{=}P(\text{-}O\text{-}Bu)_3$ disap-

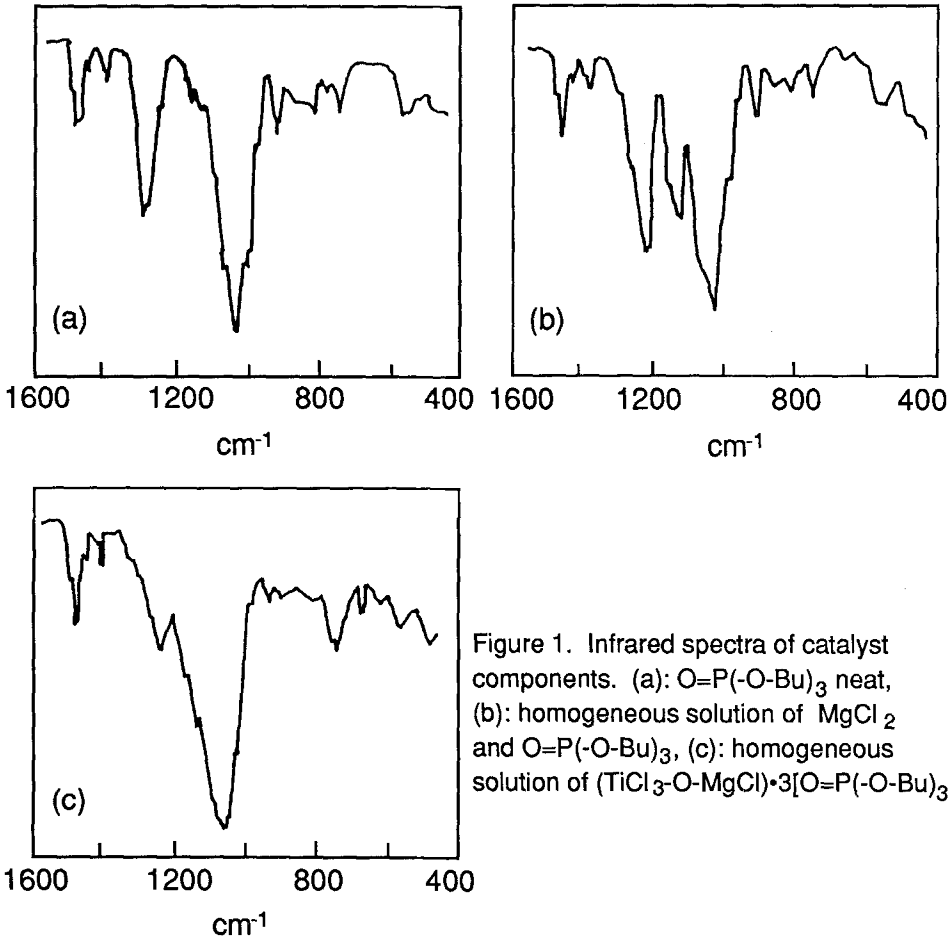

Figure 1. Infrared spectra of catalyst components. (a): $O{=}P(\text{-}O\text{-}Bu)_3$ neat, (b): homogeneous solution of $MgCl_2$ and $O{=}P(\text{-}O\text{-}Bu)_3$, (c): homogeneous solution of $(TiCl_3\text{-}O\text{-}MgCl)\cdot 3[O{=}P(\text{-}O\text{-}Bu)_3]$

peared, and new absorption bands of 1 220 and 1 130 cm^{-1} were observed (Figure 1, (a) and (b)). It is considered that the phosphate co-ordinates to $MgCl_2$ with a P=O bond, and $MgCl_2$ solubilizes in hexane as the $MgCl_2 \bullet 2(O{=}P(\text{-O-Bu})_3)$ complex. When $TiCl_4$ was added to the hexane solution of $MgCl_2 \bullet 2(O{=}P(\text{-O-Bu})_3)$, a large amount of precipitate formed. However, when the phosphate was used at molar ratios of $[O{=}P(\text{-O-Bu})_3]/[MgCl_2{+}TiC_4]$ higher than 4, a homogeneous light-yellow solution was obtained.

Preparation of soluble [($TiCl_3$-O-MgCl)•(O=P(-O-R)$_3$)] catalyst

We tried to make a soluble complex having Ti-O-Mg bonds in hydrocarbon or halogenated hydrocarbon solvents. Mg(OH)Cl does not dissolve in boiling CBz in the presence of phosphate or phosphonate. It was found that Mg(OH)Cl reacts with $TiCl_4$ at higher than 100 °C in the presence of phosphate or phosphonate with the evolution of HCl gas. In this case, the reaction takes place at a molar ratio of $[O{=}P(\text{-O-Bu})_3]/[Mg(OH)Cl]$ higher than 3 in a non-solvent or in the hydrocarbon or halogenated hydrocarbon solvents whose boiling temperatures were above 100 °C. Figure 1 (c) shows an infrared spectrum of the catalyst solution. In this case, the absorption band based on the P=O bond in $O{=}P(\text{-O-Bu})_3$ is absent. The reaction probably occurs according to:

$$TiCl_4{+}Mg(OH)Cl{+}3(O{=}P(\text{-O-Bu})_3) \xrightarrow[>100\ ^\circ C]{-HCl} (TiCl_3\text{-O-MgCl}) \bullet 3(O{=}P(\text{-O-Bu})_3)$$

Copolymerization of ethylene with propylene

Copolymerization of ethylene with propylene was carried out in hexane at 35 °C using the various soluble [$TiCl_4$+$MgCl_2$] catalysts and triisobutylaluminum as co-catalyst, as shown in Table I. The copolymers obtained were rubbery and exhibited very low crystallinity.

Table I
Results of copolymerization of ethylene with propylene by the soluble $TiCl_4 \bullet MgCl_2 \bullet$Phosphine compound/Al(*i*-Bu)$_3$ catalyst system

Run No.	Catalyst Preparation[a]		Copolymerization[b]		
	Phosphine compound	Reduction temp. (°C)	Copolymer yield (g)	Propylene content (mol %)	Crystallinity[c] (%)
1	$O{=}P(\text{-O-Bu})_3$	-10	8.0	29	0.3
2	$O{=}P(\text{-O-Oc})_3$	-10	9.2	32	0.2
3	$O{=}P(\text{-O-Bu})_2(Bu)$	-10	11.0	31	0.2
4	$O{=}P(\text{-O-Eh})_2(Eh)$	10	11.2	29	0.2
5	"	0	11.7	32	0.1
6	"	-10	12.6	34	0.1
7	"	-30	13.2	37	0.1
8	None	-10	0.5	9	3.8

[a] Solubilization: $MgCl_2$, 1g (10.5 mmol); hexane, 30 mL; Phosphine compound, 42 mmol; temp., 25 °C; agitation time, 20 min; $TiCl_4$, 10.5 mmol; agitation time, 1 h.
Reduction conditions: hexane, 50 mL; soluble Ti catalyst, 0.2 mmol; Al(*i*-Bu)$_3$, 2 mmol; monomer gas (ethylene/propylene) = 0.1/0.4 L/min; aging temp., -10 °C; time, 1 min.

[b] Hexane, 200 mL; monomer gas (ethylene/propylene) = 1.0/2.0 L/min; temp., 35 °C, time, 10 min.

[c] Crystallinity at 26.5 mol% of propylene.

Although the solubility of the [$TiCl_4$+$MgCl_2$] in hexane differed little with phosphate or phosphonate as donor, the catalysts obtained using the phosphonate for the solubilization of [$TiCl_4$+$MgCl_2$] showed high activity as compared with the soluble catalyst in which [$TiCl_4$+$MgCl_2$] was solubilized with phosphate.

The reduction temperature of the soluble [$TiCl_4$+$MgCl_2$] catalysts by Al(*i*-Bu)$_3$ is also important to obtain rubbery copolymers. The copolymer yield and the propylene content in the copolymers increased by decreasing the reducing temperature between 10 to -30 °C. Run No. 7 in Table I which indicates the best polymerization conditions, shows the catalytic activity to be about 25 times, the propylene content about 4 times, and the amount of copolymer crystallinity about 1/40 times in comparison with values obtained with the soluble $TiCl_4$ catalyst to which the solution of $MgCl_2$ was not added (Run No. 8). Also, the soluble titanium catalyst containing Mg^{2+} showed about 4 times highter activity in comparison with that in which the soluble $TiCl_3$ catalyst was used (10).

Table II shows the results of copolymerizations of ethylene with propylene and of terpolymerizations of ethylene, propylene, and 5-ethylidene-2-norbornene with the soluble [$TiCl_3$-O-MgCl] catalysts. The results of the copolymerizations using the soluble [$TiCl_3$-O-MgCl] catalysts were almost the same as those in Table I in which polymerization was done using the soluble [$TiCl_4$+$MgCl_2$] catalysts. It is well known that solid $TiCl_3$ catalyst or titanium catalysts supported on $MgCl_2$ have very high activities for the polymerization of olefins (1-7); however, these solid catalysts cannot copolymerize with 5-ethylidene-2-norbornene or dicyclopentadiene. In the terpolymerization of ethylene, propylene, and 5-ethylidene-2-norbornene, the activity of soluble [$TiCl_3$-O-MgCl] catalysts decreased about 30 % in comparison with that of the copolymerization of ethylene with propylene. The decrease in catalytic activity and conversion of 5-ethylidene-2-norbornene are almost the same as those of the conventional $VOCl_3$/Al(Et)$_{1.5}$Cl$_{1.5}$ catalyst system. It is found that these soluble catalysts containing Mg^{2+} have high activity for 5-ethylidene-2-norbornene polymerization and produce very low crystallinity copolymers.

Table II

Results of copolymerization of ethylene with propylene by the soluble $TiCl_3$-O-MgCl•Phosphine compound/Al(*i*-Bu)$_3$ catalyst system

Run No.	Catalyst Preparation a)		Copolymerization b)			
	Phosphine compound	Solvent	Copolymer yield (g)	Propylene content (mol %)	Termonomer content (I_2 No.)	Crystallinity (%)
9	O=P(-O-Eh)$_2$(Eh)	None	8.3	35	11	0.1
10	"	CBz	8.4	36	10	0.1
11	O=P(-O-Bu)$_3$	"	6.7	29	13	0.1
12	O=P(-O-Bu)$_2$(Bu)	Isooctane	7.9	31	13	$\sim$0
13	"	"	12.5	35	-	$\sim$0
14	O=P(-O-Eh)$_2$(Eh)	"	9.1	37	15	$\sim$0
15	"	"	12.9	39	-	0.1

a) Mg(OH)Cl, 1g (13 mmol); Phosphine compound, 39 mmol; $TiCl_4$, 13 mmol; temp., 130 °C; time, 2 h.
Reduction conditions are the same as Table 1.

b) Conditions are the same as Table 1, except for addition of termonomer (hexane solution of 5-ethylidene-2-norbornene (4.8 vol%), pumping speed, 2 mL/min for 10 min.)

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Accepted July 11, 1991 K