Table III
^{13}C Chemical Shifts (ppm) in Chloroform

compd	methine	methylene
trans-1,4-diacetoxycyclohexane	71.04	28.17[a]
	71.7	28.20[b]
TCHB	71.4	27.8
PE-10	71.01	27.90
P-7[c]	71.5	27.8

[a] This work. [b] From ref 22. [c] Before and after annealing in the isotropic phase.

ples are subject to thermal degradation in the vicinity of 275-280 °C, as mentioned in the Experimental Section.

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Communications to the Editor

Polymerization of Styrene with $Mg(OH)_xCl_{2-x}$-Supported (x = 0-2) $Ti(O^nBu)_4$ Catalysts Combined with Methylaluminoxane

Introduction. It is well-known that syndiotactic polystyrene is obtained by using a kind of homogeneous Kaminsky-Sinn type catalyst composed of some titanium or zirconium compounds in combination with methylaluminoxane (MAO).[1-7] Afterward, we found that a heterogeneous, SiO_2-supported $Ti(O^nBu)_4$ catalyst also gives syndiotactic polystyrene when MAO is used as cocatalyst.[8] More recently, we have carried out styrene polymerization by using similar supported catalysts prepared from $Ti(O^nBu)_4$ and $Mg(OH)_xCl_{2-x}$ (x = 0-2) and found that the tacticity of polystyrene is markedly affected by the presence of Cl in the carrier. This paper reports brief results on the polymerization.

Experimental Section. Materials. Styrene (Kanto Chemical Co., Inc.) was washed with an aqueous solution of sodium hydroxide, dried over calcium hydride for 12 h, and distilled under a reduced pressure. Toluene used as solvent was purified by refluxing over calcium hydride for 24 h, followed by fractional distillation. $Ti(O^nBu)_4$ (Tokyo Kasei Kogyo Co., Ltd.), $Mg(OH)_2$ (Kanto Chemical Co., Inc.), $MgCl_2$ (Toho Titanium Co.), $MgCl_2·6H_2O$ (Wako Pure Chemical Industries, Ltd.), and MAO (Toso-Akzo Co., 2.4 mol/L in toluene) were used without further treatment.

Preparation of Catalysts. Mg(OH)Cl was prepared from $MgCl_2·6H_2O$ according to the procedures reported previously.[9]

$Ti(O^nBu)_4/MgCl_2$ Catalyst (Cat-1). In a 100-cm^3 glass reactor were added 500 mg of $MgCl_2$, 0.1 mmol of $Ti(O^nBu)_4$, and 28 cm^3 of toluene under nitrogen, and the mixture was refluxed at its boiling point for 4 h. This mixture was used as catalyst.

$Ti(O^nBu)_4$/Mg(OH)Cl Catalyst (Cat-2). In a 100-cm^3 glass reactor were added 6.79 g of Mg(OH)Cl, 44.2 mmol of $Ti(O^nBu)_4$, and 50 cm^3 of heptane under nitrogen. After raising the temperature to its boiling point, the mixture was kept standing for 5 h with stirring. Then the precipitate was filtered under nitrogen, washed 10 times with plenty of heptane and dried under a reduced pressure at 40 °C for 1 h.

$Ti(O^nBu)_4/Mg(OH)_2$ Catalyst (Cat-3). In a 100-cm^3 glass reactor were added 7.39 g of $Mg(OH)_2$, 63.4 mmol of $Ti(O^nBu)_4$, and 50 cm^3 of toluene under nitro-

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Table I
Polymerization of Styrene with $Ti(O^nBu)_4/MgCl_2$–MAO Catalyst[a]

catalyst	Ti content,[b] mmol	yield, mg	polymer structure[c]	$M_w \times 10^{-4}$
insoluble part	0.07	358	highly isotactic (ca. 100%)	not determined[d]
soluble part	0.03	50	highly syndiotactic (ca. 100%)	14.6

[a] Polymerization conditions: polym temp = 27 °C, polym time = 24 h, styrene = 10 cm^3, toluene = 30 cm^3. [b] Determined by the UV method. [c] Determined from ^{13}C NMR. [d] The molecular weight was too high to be determined.

gen, followed by the same procedures as in case of the $Ti(O^nBu)_4/Mg(OH)Cl$ catalyst. The contents of titanium in the solid catalysts were determined by the usual UV method to obtain 0.80 mmol/g of Cat-2 and 0.12 mmol/g of Cat-3, respectively.

Polymerization and Analytical Procedures of the Polymers. Polymerizations were carried out in a 100-cm^3 glass reactor equipped with a magnetic stirrer. Polymerization was stopped by adding a mixture of hydrochloric acid and methanol, filtered, and dried under a reduced pressure at 60 °C. The structure of the polymer was determined by ^{13}C NMR. The ^{13}C NMR spectrum of the polymer was measured at 25.1 MHz in 1,2,4-trichlorobenzene at 130 °C with a JEOL FX-100 spectrometer. The chemical shifts were referred to HMDS added as an internal standard for $\delta = 2.0$. Gel-permeation chromatograms of the polymers were obtained by Waters Model 150GPC using standard polystyrenes as reference and 1,2,4-trichlorobenzene as eluent at 140 °C.

Results and Discussion. To Cat-1 (mixture: see the Experimental Section) was added 2.0 mmol of MAO (referred to $Al(CH_3)_3$), and the resulting mixture was kept standing at 27 °C for 30 min with stirring. Then the soluble and insoluble parts were separated by filtration under nitrogen. The insoluble part was washed 10 times with plenty of toluene. Polymerization of styrene was carried out at 27 °C for 24 h by using both soluble and insoluble parts without additional MAO. The results obtained are shown in Table I, which clearly indicate that the insoluble and soluble parts selectively give isotactic and syndiotactic polystyrenes, respectively. It might be interesting to check if the Cl ligands can be extracted by MAO. From such a viewpoint the following experiments were carried out. The mixture of 2.0 mmol of MAO and 500 mg of $MgCl_2$ in 29 cm^3 of toluene was kept standing with stirring at 27 °C overnight. After the soluble part was separated by filtration, toluene was removed by evaporation. Then 25 cm^3 of 6N H_2SO_4 aqueous solution was added to the residue, followed by titration with $AgNO_3$ to obtain [Cl] = 0 ppm.

The possibility of Cl ligand extraction by MAO was also checked in the actual catalyst system: the mixture of 0.1 mmol of $Ti(OBu)_4$, 500 mg of $MgCl_2$, and 28 cm^3 of toluene was refluxed at its boiling point for 4 h, and then the resulting mixture was cooled down to 27 °C, followed by the addition of 2.0 mmol of MAO. After the mixture was kept standing with stirring at 27 °C for 30 min, the soluble part was separated by filtration and analyzed according to the same procedure to obtain [Cl] = 0 ppm. From these results, it may be said that the Cl ligands cannot be extracted with MAO in the present catalyst.

Then polymerization of styrene was conducted under the same conditions as described in Table I with the insoluble part (containing 0.07 mmol of Ti) by adding 2.0 mmol of MAO to give 1.09 g of highly isotactic (ca. 100%) polystyrene. Thus, additional MAO caused a considerable increase in polymer yield, but it did not change the stereospecificity of the catalyst.

Table II
Polymerization of Styrene with $Ti(O^nBu)_4/Mg(OH)_2$–MAO Catalyst[a]

catalyst	yield, mg	polym structure[b]	$M_w \times 10^{-4}$
Cat-3	405	highly syndiotactic (ca. 100%)	10.6

[a] Polymerization conditions: polym temp = 27 °C, polym time = 19 h, styrene = 10 cm^3, $Ti(O^nBu)_4/Mg(OH)_2$ = 840 mg (Ti = 0.1 mmol),MAO = 2.0 mmol, toluene = 30 cm^3. [b] Determined from ^{13}C NMR.

Table III
Polymerization of Styrene with $Ti(O^nBu)_4/Mg(OH)Cl$–MAO Catalyst[a]

Al/Ti ratio	Ti content,[b] mmol	polym time, h	yield, mg	polym structure[c] (isotactic/syndiotactic ratio)	$M_w \times 10^{-4}$
10	0.08	3	88	6.25	145.6
		24	446	6.35	not determined[d]
20	0.06	3	260	0.60	88.1
		19	781	0.52	86.6
100	0.04	3	393	0.09	8.8

[a] Polymerization conditions: polym temp = 27 °C, styrene = 10 cm^3, $Ti(O^nBu)_4/Mg(OH)Cl$ = 125 mg (Ti = 0.1 mmol), MAO = 2.0 mmol, toluene = 30 cm^3. [b] Determined by the UV method. [c] Determined from ^{13}C NMR. [d] The molecular weight was too high to be determined.

Polymerization of styrene was then conducted at 27 °C for 19 h by using Cat-3 combined with MAO (Table II). To check the possibility of extracting the titanium species from Cat-3 by MAO, the following experiment was carried out: 840 mg of Cat-3 was brought into contact with 2.0 mmol of MAO in 30 cm^3 of toluene at 27 °C for 30 min. The precipitate was separated by filtration, and the content of titanium was measured by the UV method to obtain 0.09 mmol/g of precipitate. It may be said, therefore, that most of the titanium species remains unextracted during this process. The soluble part was found to be almost inactive for styrene polymerization. Thus, syndiotactic polystyrene is obtained with a heterogeneous catalyst when $Mg(OH)_2$ is used as carrier.

These results strongly suggest that the tacticity of polystyrene obtained with heterogeneous catalysts is markedly affected by the presence of Cl in the carrier. From such a viewpoint, polymerization of styrene was conducted with the Cat-2–MAO system by changing the molar ratio of Al/Ti. The results obtained are summarized in Table III. The polymers obtained were confirmed to be the mixtures of highly syndiotactic and highly isotactic polystyrenes. With an increase in the Al/Ti ratio, the yield of syndiotactic polystyrene drastically increased. Taking the titanium contents in the solid catalysts into consideration, it may be said that syndiotactic and isotactic polymerizations of styrene with this catalyst system are catalyzed by homogeneous and heterogeneous catalytic species, respectively.

In conclusion, the stereospecificity of heterogeneous catalysts for styrene polymerization is remarkably affected by the presence of Cl ligands in the carrier and that Cl ligands favor isotactic polymerization.

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CORRECTIONS

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J. M. Ubrich's name is misspelled in the article as J. M. Ubiche.

Also please note that the list of references is incorrect. The references should be as follows:

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