Table I
Results of Polymerization of Indene and Styrene

polymer	polym time, h	polym yield, mg	styrene content, mol %	T_g, °C
polystyrene[a]	3	180		96
polyindene[b]	46	30		160
poly(styrene–indene)[c]	47	77	52.9	126

[a] Polymerization conditions: polym temp = 60 °C; styrene = 10 cm^3; Ti(O^{i}Pr)$_4$ = 0.1 mmol; MAO = 2.0 mmol; toluene = 29 cm^3. [b] Polymerization conditions: polym temp = 60 °C; indene = 37 cm^3; Ti(O^{i}Pr)$_4$ = 0.1 mmol; MAO = 2.0 mmol. [c] Polymerization conditions: polym temp = 60 °C; styrene = 3.3 cm^3; indene = 33 cm^3; Ti(O^{i}Pr)$_4$ = 0.1 mmol; MAO = 2.0 mmol.

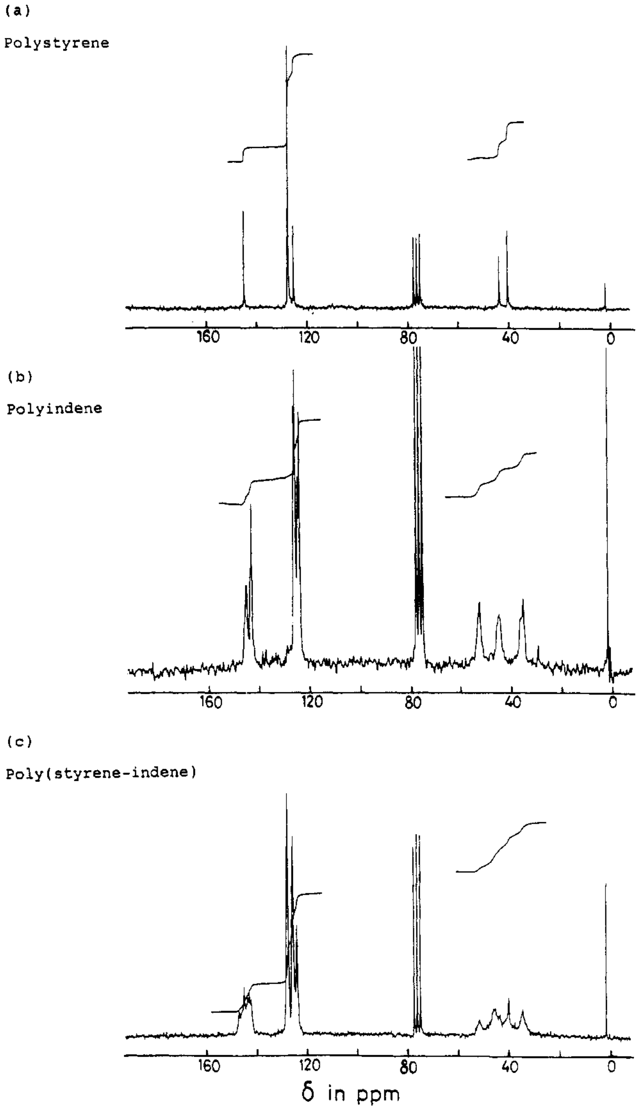

Figure 1. ^{13}C NMR spectra of the polymers. (a) Polystyrene: polym temp = 60 °C; styrene = 10 cm^3; Ti(O^{i}Pr)$_4$ = 0.1 mmol; MAO = 2.0 mmol; toluene = 29 cm^3. (b) Polyindene: polym temp = 60 °C; indene = 37 cm^3; Ti(O^{i}Pr)$_4$ = 0.1 mmol; MAO = 2.0 mmol. (c) Poly(styrene–indene): styrene content = 52.9 mol %; polym temp = 60 °C, styrene = 3.3 cm^3; indene = 33 cm^3; Ti(O^{i}Pr)$_4$ = 0.1 mmol; MAO = 2.0 mmol.

content of styrene unit in the copolymer was calculated from the spectrum (c).

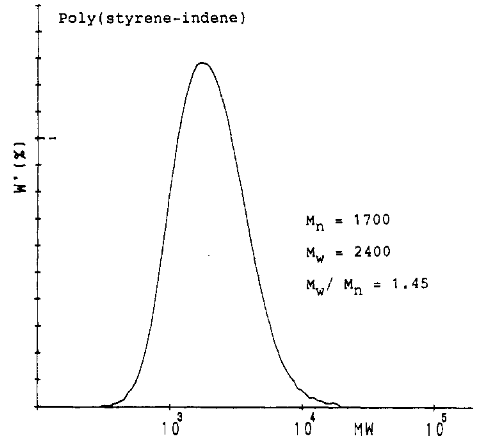

Figure 2. MMD curve of the copolymer (c).

Both T_g and molecular mass distribution (MMD) were measured on the copolymer. The results obtained are shown in Table I and Figure 2. The copolymer displays a new T_g (126 °C) between those of polystyrene (96 °C) and polyindene (160 °C), and its MMD is unimodal with a very narrow polydispersity. Thus the polymer obtained from the copolymerization can be regarded as a random copolymer of styrene and indene.

When polymerization of styrene is carried out with usual cationic catalysts, atactic polystyrene is obtained by a cationic mechanism. Judging from both the present and previous[6] results, we propose a coordinated-cationic mechanism for syndiotactic polymerization of styrene.

References and Notes

(1) Ishihara, N.; Seimiya, T.; Kuramoto, M.; Uoi, M. *Macromolecules* **1986**, *19*, 2464.
(2) Pellecchia, C.; Longo, P.; Grassi, A.; Ammendola, P.; Zambelli, A. *Makromol. Chem., Apid Commun.* **1987**, *8*, 277.
(3) Grassi, A.; Pellecchia, C.; Longo, P.; Zambelli, A. *Gazz. Chim. Ital.* **1987**, *117*, 249.
(4) Ishihara, N.; Kuramoto, M.; Uoi, M. *Macromolecules* **1988**, *21*, 3356.
(5) Zambelli, A.; Longo, P.; Pellecchia, C.; Grassi, A. *Macromolecules* **1987**, *20*, 2035.
(6) Soga, K.; Nakatani, H.; Monoi, T., to be submitted for publication.
(7) Whitby, G.; Katz, M. *J. Am. Chem. Soc.* **1928**, *50*, 1160.
(8) Staudinger, H.; Ashdown, A. A.; Brunner, M.; Bruson, A.; Wehrli, S. *Helv. Chim. Acta* **1929**, *12*, 934.
(9) Schmitt, G. J.; Schuerch, G. *J. Polym. Sci.* **1961**, *49*, 287.
(10) Sigwalt, P. *J. Polym. Sci.* **1961**, *52*, 15.
(11) Sigwalt, P.; Marechal, E. *Eur. Polym. J.* **1966**, *2*, 15.
(12) Mizote, A.; Tanaka, T.; Higashimura, T.; Okamura, S. *J. Polym. Sci. A1* **1966**, *4*, 869.
(13) Sinn, H.; Kaminsky, W.; Vollmer, H. J.; Woldt, R. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 390.

Kazuo Soga*
Research Laboratory of Resources Utilization
Tokyo Institute of Technology, 4259 Nagatsuta
Midori-ku, Yokohama 227, Japan

Takashi Monoi
Oita Research Laboratory, Showa Denko K.K., 2
Nakanosu, Oita 870-01, Japan

Received April 28, 1989;
Revised Manuscript Received August 1, 1989

Perfect Conversion of Aspecific Sites into Isospecific Sites in Ziegler–Natta Catalysts

Introduction. The catalyst system composed of Solvay-type TiCl$_3$ and Cp$_2$TiMe$_2$ was found to show extremely high isospecificity for olefin polymerization.[1] The isospecificity of donor-free TiCl$_4$/MgCl$_2$ catalysts was also improved to a great extent by using Cp$_2$TiMe$_2$ as cocatalyst.[2]

Usual MgCl$_2$-supported TiCl$_4$ catalysts combined with AlEt$_3$ do not show high isospecificity, but they give at least

0024-9297/89/2222-3824$01.50/0

Table I
Results of Propylene Polymerization over $MgCl_2$-Supported Catalysts Combined with $AlEt_3$ as Cocatalyst

catalyst	TEA, mmol/dm^3	temp, °C	time, h	activity,[a] kg of PP/g of Ti per h	II,[b] %
Cat-A[c]	20	40	1	127.0	0
Cat-B[d]	10	40	1	96.2	26

	Pentad Distributions (by ^{13}C NMR for Total Polymers)								
	mmmm	mmmr	rmmr	mmrr	mmrm rrmr	rmrm	rrrr	mrrr	mrrm
Cat-A	34.7	12.9	2.2	14.1	10.3	2.6	8.9	6.8	7.5
Cat-B	57.2	8.1	0.9	9.0	5.8	1.8	7.7	4.9	4.6
K-Cat[e]	6	13	6	13	25	13	6	13	6

[a] Average activity for the initial 1 h. [b] Isotactic index determined by fractionation with boiling heptane. [c] $TiCl_3/MgCl_2$ catalyst (Ti content = 0.043 wt %) prepared by treating the mixture of $MgCl_2$ and $TiCl_3{\cdot}3Py$ with $Al_2Et_3Cl_3$. [d] $TiCl_4/MgCl_2$ catalyst (Ti content = 0.40 wt %) prepared by treating $MgCl_2$ with $TiCl_4$. [e] Polypropylene obtained with a typical Kaminsky catalyst (Cp_2TiPh_2/methylaluminoxane, at 50 °C).[8]

20 wt % of isotactic polypropylene even in the absence of any Lewis bases. Production of isotactic polymer might result from the multinuclear Ti^{3+} species formed on the $MgCl_2$ surface.[3,4]

A marked decrease in the Ti content may avoid the formation of such an isospecific multinuclear Ti^{3+} species and selectively give an aspecific mononuclear Ti^{3+} species on the $MgCl_2$ surface. In fact, we found that the isospecificity of $MgCl_2$-supported catalysts decreases with a decrease in the Ti content.[5]

More recently, we have succeeded in preparing a completely aspecific catalyst from $TiCl_3{\cdot}3Py$ (Py = pyridine) and $MgCl_2$ in the presence of $Al_2Et_3Cl_3$. By changing the cocatalyst from $AlEt_3$ to Cp_2TiMe_2, the catalyst was easily converted into a highly isospecific catalyst. This communication reports the brief results of propylene polymerization with this catalyst system.

Experimental Section. Materials. Propylene (from the Mitsubishi Petrochemical Co.), $MgCl_2$, and titanium-reduced $TiCl_3$ (from the Toho Titanium Co.) were used without further purification. Research-grade heptane commercially obtained was purified according to the usual procedures. Cp_2TiMe_2 was prepared according to the literature reported by Clauss et al.,[6] diluted into 0.25 mol/dm^3 in heptane, and stored as stock solution.

Preparation of the $MgCl_2$-Supported Catalysts. Cat-A. $TiCl_3{\cdot}3Py$ was prepared from the reaction of $TiCl_3$ with pyridine at room temperature. A total of 30 g of $MgCl_2$ (11 m^2/g) was ground in a 1-dm^3 stainless steel vibration mill pot with 50 balls (25 mm in diameter) under nitrogen for 48 h at room temperature. The mixture of the resultant $MgCl_2$ (10 g, 97 m^2/g) and $TiCl_3{\cdot}3Py$ (36 mg) was treated with an excess amount of $Al_2Et_3Cl_3$ (10 mmol) in heptane at 0 °C under vigorous stirring, followed by washing with plenty of heptane to obtain the $TiCl_3/MgCl_2$ catalyst. It was confirmed from the elemental analysis that pyridine was completely removed from the catalyst.

Cat-B. A total of 5 g of the same $MgCl_2$ (97 m^2/g) was brought into contact with a diluted solution of $TiCl_4$ in heptane at room temperature for 2 h. The solid part was isolated by filtration and washed several times with heptane at room temperature to obtain the $TiCl_4/MgCl_2$ catalyst.

Polymerization and Analytical Procedures. Polymerization of propylene was usually conducted at 40 °C in a 0.1-dm^3 stainless steel autoclave reactor equipped with a magnetic stirrer. Measured amounts of the catalyst and cocatalyst ($AlEt_3$ or Cp_2TiMe_2) were added to the reactor containing 0.05 dm^3 of heptane. Propylene (0.3 mol) was introduced to the reactor at liquid-nitrogen temperature. Polymerization was terminated by adding a dilute hydrochloric acid solution in methanol. The polymer was fractionated by extraction with boiling heptane. The contents of titanium in the catalysts were determined by atomic absorption spectrophotometry (Shimadzu AA-6105). The ^{13}C NMR spectrum of the polymer was recorded at 120 °C using a JEOL GX-270 spectrometer in the pulse Fourier transform (FT) mode. Sample solutions were made in 1,2,4-trichlorobenzene/benzene-d_6 (9/1 by volume) up to 12% by weight.

Results and Discussion. As mentioned above, usual $MgCl_2$-supported catalysts combined with $AlEt_3$ give more than 20 wt % of isotactic polypropylene. Whereas, the catalyst containing 0.12 wt % of Ti, which was prepared with the same procedures as Cat-A, was found to afford only 6 wt % of isotactic polypropylene.[4] From such a viewpoint, the content of Ti was decreased to 0.043 wt % in the present study. Polymerization of propylene was carried out at 40 °C by using the catalyst (Cat-A) and $AlEt_3$. The polymer produced was fractionated by extraction with boiling heptane for 10 h to obtain no insoluble fraction. The DSC curve of the polymer did not show a sharp peak at around 160 °C attributable to crystalline isotactic polypropylene but displayed a very broad peak centered at 140 °C.

Polymerization of propylene was also conducted by using Cat-B and $AlEt_3$ under the same conditions, which gave an appreciable amount of isotactic polypropylene. In Table I are shown the polymerization results and the pentad sequence distributions of the polymer. The pentad sequence distributions of polypropylene obtained with a typical Kaminsky catalyst is also shown as reference. It is clear from Table I that the structure of the present atactic polypropylene (obtained with Cat-A) is significantly different from that obtained with a homogeneous Kaminsky catalyst.[7,8] The former contains both isotactic and syndiotactic sequences, while the latter has a perfectly random, statistically atactic structure. However, the present polymer might also be called "atactic polypropylene".

The difference in the isospecificity between the Cat-A and Cat-B may be interpreted as follows. In case of the Cat-A, by treating the mixture of $MgCl_2$ and $TiCl_3{\cdot}3Py$ with a Lewis acid like $Al_2Et_3Cl_3$, the pyridine coordinated with $TiCl_3$ is removed, resulting in formation of the isolated mononuclear $TiCl_3$ species on the $MgCl_2$ surface. Even in case of the Cat-B, most of the $TiCl_4$ supported on the $MgCl_2$ surface might be originally mononuclear species, taking the Ti content into consideration. However, reduction of the Ti^{4+} species to Ti^{3+} is necessary to activate the catalyst.[9] When strong reducing reagents like $AlEt_3$ are used as cocatalyst, the reduction may proceed instantaneously, resulting in formation of an appreciable amount of labile alkyltitanium species on the $MgCl_2$ surface. Such

Table II
Steric Pentad Sequence Distributions of Polypropylene Obtained from $TiCl_3/MgCl_2$ (Cat-A) Combined with Cp_2TiMe_2 as Cocatalyst[a]

polymer fractions	mmmm	mmmr	rmmr	mmrr	mmrm rrmr	rmrm	rrrr	mrrr	mrrm
whole polymer	89.4	3.0	0.6	1.8	1.2	0.3	2.1	0.7	0.9
I-7 (95%)[b]	94.5	1.6	0.3	0.7	0.6	0.2	1.2	0.4	0.5

[a] For the polymer obtained with 20 mmol·dm^{-3} of Cp_2TiMe_2 at 40 °C. [b] I-7 denotes boiling heptane insoluble part.

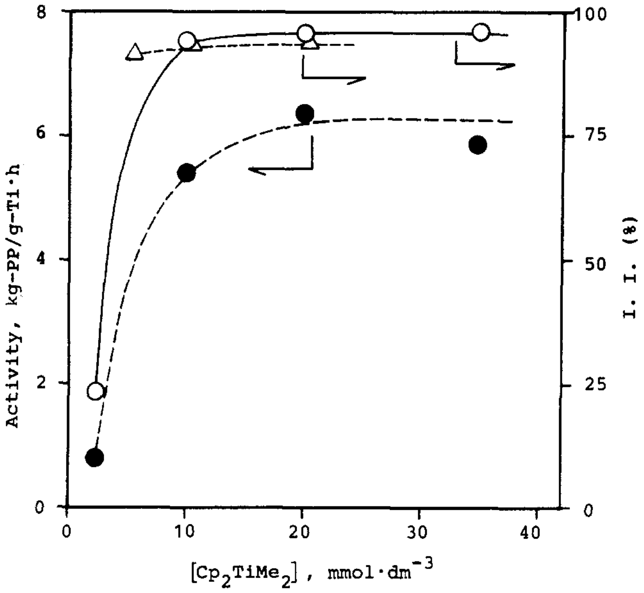

Figure 1. Effects of [Cp_2TiMe_2] on the yield (●) and isotactic index (○) of polypropylene obtained with the $TiCl_3/MgCl_2$ (Cat-A)–Cp_2TiMe_2 system. The isotactic index of polypropylene obtained with the $TiCl_4/MgCl_2$ (Cat-B)–Cp_2TiMe_2 system is shown for reference (△).

labile titanium species might easily aggregate with each other to form the multinuclear species, which give isotactic polypropylene.

Although we must investigate the surface structures of these catalysts in detail to check the validity of the above assumption, we could prepare a completely aspecific $MgCl_2$-supported catalyst (Cat-A).

Then, polymerization of propylene was conducted under similar conditions by using Cp_2TiMe_2 as cocatalyst. Polymerization results are illustrated in Figure 1. With an increase in the concentration of Cp_2TiMe_2, catalyst isospecificity markedly increased to reach as high as >95%. Polymerization with Cat-A at a very low concentration of Cp_2TiMe_2 might proceed over different active species that were formed in the process of the treatment with $Al_2Et_3Cl_3$.[5] The pentad sequence distributions of the polymers obtained by Cat-A and Cp_2TiMe_2 are shown in Table II, indicating that the catalyst isospecificity is very high. Typical results obtained with Cat-B and Cp_2TiMe_2 are also shown in Figure 1 for reference. Thus, the isospecificity of a donor-free $MgCl_2$-supported catalyst (Cat-A) is easily converted from aspecific into isospecific by changing the cocatalyst. However, the activity decreased drastically by changing the cocatalyst from $AlEt_3$ to Cp_2TiMe_2. Supposing that the propagation rate of isotactic polymerization is faster by 1 order of magnitude as compared with that of atactic polymerization,[10] it may be said that most of the potentially active sites are not still activated by Cp_2TiMe_2. From such a viewpoint, we are now investigating how to activate the present catalyst. If it will be successful, the present catalyst system may be most suitable for the precise characterization of both aspecific and isospecific sites in Ziegler–Natta catalysts.

References and Notes

(1) Soga, K.; Yanagihara, H. *Makromol. Chem.* **1988**, *189*, 2839.
(2) Soga, K.; Yanagihara, H. *Makromol. Chem., Rapid Commun.* **1987**, *8*, 273.
(3) Busico, V.; Corradini, P.; Martino, L. De.; Proto, A.; Albizati, E. *Makromol. Chem.* **1986**, *187*, 1115.
(4) Soga, K.; Shiono, T.; Doi, Y. *Makromol. Chem.* **1988**, *189*, 1531.
(5) Shiono, T.; Uchino, H.; Soga, K. *Polym. Bull.* **1989**, *21*, 19.
(6) Clauss, K.; Bestian, T. *Justus Liebigs Ann. Chem.* **1962**, *8*, 654.
(7) Kaminsky, W.; Miri, T.; Sin, H.; Wolts, R. *Makromol. Chem., Rapid Commun.* **1983**, *4*, 417.
(8) Ewen, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6355.
(9) Soga, K.; Sano, T.; Ohnishi, R. *Polym. Bull.* **1979**, *4*, 157.
(10) Kashiwa, N.; Yoshitake, J. *Polym. Bull.* **1984**, *12*, 99.

Kazuo Soga,* Joon Ryeo Park, Hideshi Uchino,
Toshiya Uozumi, and Takeshi Shiono
Research Laboratory of Resources Utilization
Tokyo Institute of Technology, 4259 Nagatsuta
Midori-ku, Yokohama 227, Japan

Received April 28, 1989;
Revised Manuscript Received July 27, 1989