Propylene Polymerization with $Mg(OEt)_2$/Benzoyl Chloride/$TiCl_4$–Triethyl Aluminum/External Donor Catalyst Systems*

DONG-HO LEE,[1†] YOUNG-TAE JEONG,[1] KAZUO SOGA,[2] and TAKESHI SHIONO[2]

[1]Department of Polymer Science, Kyungpook National University, Taegu 702-701, Korea; [2]Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Yokohama 227, Japan

SYNOPSIS

$Mg(OEt)_2$/benzoyl chloride (BC)/$TiCl_4$ catalyst has been prepared by the chemical reaction method, and the chemical composition and X-ray structure of the catalyst were studied. The effect of various conditions on catalyst activity and isospecificity were also examined. With ^{13}C-NMR analysis, it was found that aluminum carbinolate is formed during polymerization by reaction of triethyl aluminum cocatalyst with BC remaining in the prepared catalyst. The formed aluminum carbinolate acts as an additional donor to increase the isotactic index of polypropylene (PP). The morphology of the prepared catalyst and PP was also observed. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Many modern Ziegler–Natta catalysts for stereospecific olefin polymerization employ the high-surface-area support matrices for active transition metal catalyst sites. The first significant results were obtained in the early 1960s by using the reactive Mg compounds such as Mg(OH)Cl,[1] hydroxylated MgO or $MgSO_4$.[2]

In the past 20 years, there have been many reports about the various supports for $TiCl_4$ catalysts including such magnesium compounds as MgO,[3] $Mg(OH)_2$,[4] $MgCl_2$,[5] Grignard compounds,[6] and Mg-alkyls.[7] Among these supports, in the early of 1970s, it was discovered that $MgCl_2$ was a good support for stereospecific catalysts. The discovery of active magnesium chloride as an ideal support for the fixation of titanium chloride and its derivatives opened a new era in the field of Ziegler–Natta catalysis, and then the preparation and characterization of $MgCl_2$-supported high-active titanium catalysts were studied intensively.[8,9]

But $MgCl_2$-supported catalysts have high chlorine content and dealing with $MgCl_2$ is not easy due to its high hygroscopicity. From these reasons, magnesium alkoxides were reported as efficient supports in some patients.[10]

Recently, $Mg(OEt)_2$-supported $TiCl_4$ catalysts including an organic chloride and/or an internal donor prepared by the physical milling method were studied and it was found that $Mg(OEt)_2$ is converted to $MgCl_2$ by reaction with $TiCl_4$ and that organic chloride is necessary to promote the conversion of $Mg(OEt)_2$ to $MgCl_2$.[11] In addition, the polymerization activity and isospecificity of polypropylene with the catalyst prepared by the chemical reaction method showed almost the same results as those corresponding to the physical milling method.[11]

In this paper, the $Mg(OEt)_2$/benzoyl chloride (BC)/$TiCl_4$ catalyst was prepared by the chemical reaction method and the chemical compositions of the prepared catalysts were examined in detail. The polymerization behaviors of the prepared catalysts were studied for various polymerization conditions. The chemical reaction of triethyl aluminum cocatalyst and BC remaining in the prepared catalyst has also been examined in detail. In addition, the morphology of the catalyst and polymer was observed.

EXPERIMENTAL

Materials

Propylene (propene) of polymerization grade, 99.5% purity, was supplied by the Korea Petrochemical

* Dedicated to Prof. Dr. Tae-oan Ahn on the occasion of his 60th birthday.

† To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 47, 1449–1461 (1993)
© 1993 John Wiley & Sons, Inc.
CCC 0021-8995/93/081449-13

Ind. Co. and dried by passing through two columns of preactivated molecular sieve 4A. Nitrogen of extrapure grade, 99.999%, was dried by passing through the molecular sieve 3A column and Fisher Ridox catalyst column to remove moisture and oxygen. *n*-Hexane was used as the polymerization medium and dried over preactivated molecular sieve 4A. Triethyl aluminum (TEA), diethyl aluminum chloride (DEAC), triisobutyl aluminum (TIBA), triisohexyl aluminum (TIHA), and trimethyl aluminum (TMA) were supplied by Tosoh Akzo Corp., Japan, and used without further purification. Magnesium ethoxide (average particle size, 1 mm diameter) was supplied by the Dynamit Nobel Chemie, Germany, and used after vibration milling under nitrogen atmosphere for 6 h at room temperature. Benzoyl chloride (BC, Junsei Chemical Co., Japan), ethyl benzoate (EB, Tokyo Kasei Co., Japan), titanium tetrachloride (Toho Titanium Co., Japan), methyl-*p*-toluate (MPT: methyl 4-methyl benzoate, Aldrich Chemical Co., U.S.A.), and phenyl triethoxy silane (PTES, Tokyo Kasei Co., Japan) were used without further purification.

Preparation of Catalyst

The internal donor (ID) is defined to be Lewis base used as a component of the solid catalyst during pretreatment of $Mg(OEt)_2$ and the external donor (ED) is Lewis base added as a component of the cocatalyst.

The catalysts were prepared by the chemical reaction method[12]: To 150 mL of $TiCl_4$ were added continuously 20 g (0.175 mol) of $Mg(OEt)_2$ and 0.026 mol of BC or EB, and the mixture was allowed to react at 110°C for 2 h with vigorous stirring. After cooling the reaction mixture, the solid product was separated, washed several times with 300 mL of *n*-hexane until unreacted $TiCl_4$ was throughly removed, and dried *in vacuo*. In the case of alkyl aluminum treatment, the above solid catalyst was reacted with a predetermined amount of alkyl aluminum in *n*-hexane at 70°C for 2 h with vigorous stirring.

All glassware were heated to 130°C for 4 h, assembled while hot, and allowed to cool under nitrogen. The flask was equipped with two-blade paddle stirrer running at 300 rpm, reflux condenser, and thermometer.

Analysis of Catalyst

The amounts of titanium and magnesium elements in the prepared catalysts were determined by an atomic absorption spectrophotometer (A.A., Perkin-Elmer Zeeman/3030). A precisely weighed quantity of catalyst (about 100–150 mg) was dissolved in 10 mL of 0.1*M* sulfuric acid and then diluted to 100 mL with distilled water.

The content of chlorine was analyzed by back titration according to Volhard's method[13]: A measured amount of standard silver nitrate is added to the catalyst solution, and the excess amount was determined by back titration with standard sodium thiocyanate solution.

The amount of the ethoxy group in the catalyst was determined as ethanol by gas chromatography (GC).[11] A precisely weighed quantity of catalyst (about 50–100 mg) was dissolved by 25 mL of 2*N* sulfuric acid. After dissolving the catalyst completely, the mixture was transferred to a volumetric flask and diluted to 250 mL with distilled water. The resulted solution was injected to GC (Shimatsu GC 8A with FID detector). The packed column (Porapak Q, 2 mm ID × 2 mL) was used and the temperatures of the column, injector, and detector were 90, 200, and 200°C, respectively. The conversion of $Mg(OEt)_2$ to $MgCl_2$ was calculated from the remaining ethoxy group in the catalyst.

For the quantitative analysis of organic components including ID, 1.5 g of catalyst was brought into contact with 50 mL of anhydrous methanol at room temperature to quantitatively transform BC into methyl benoate (MB),[14] and the resulted methanol solution with the addition of ethyl benzene as the internal standard was injected to GC (Shimatsu GC 9A with FID detector). A methyl silicone capillary column (Hicap-CBP 1, 0.25 mm ID × 25 mL) was used and the temperature of the column was programmed from 80°C (holding time, 4 min) to 260°C with a heating rate of 8°C/min. The retention times of EB, MB, and ethyl benzene were 10.22, 8.97, and 5.10 min, respectively.

With peaks of EB, MB from BC, and ethyl benzene added as the internal standard, amounts of EB and BC (as MB) could be measured quantitatively. Infrared (IR) spectra of catalysts were recorded on Nujol mulls between a NaCl window over the range of 400–4000 cm^{-1} using a Hitachi 270-30 spectrophotometer.

The powder X-ray diffraction patterns were recorded employing a Rigaku Ru-300 diffractometer with an X_e-proportional counter and graphite monochromator in the diffracted beam. Cu-Kα radiation was used at 60 kV and 300 mA. The step-scanning program was used in recording X-ray diffractograms in 5.0–70.0° of the 2θ range with a scan speed of 4°/min. The diffractograms were obtained

with the kind cooperation of Mr. M. Kioka, Iwakuni Polymer Research Laboratories, Mitsui Petrochemical Ind., Ltd., Japan.

To examine the reaction of BC with TEA, the following procedure was carried out: Using an NMR capillary tube, BC and TEA (or TMA) (1 : 2 mol ratio) were reacted in C_6D_6 at 0°C and kept 2 h at room temperature. With this mixture, a ^{13}C-NMR spectrum of the reaction mixture was obtained. For hydrolysis of the reaction mixture, the reaction of BC and TEA (or TMA) was carried out in glass flask using the same method. After cooling the reaction mixture to −78°C, a large portion of distilled water was added drop by drop with vigorous stirring and kept for 2 h at room temperature. Then, an appropriate amount of ethyl ether was added to extract organic product and stirred for 3 h at room temperature. The organic layer was separated and dried with anhydrous calcium sulfate followed by evaporation of ethyl ether to concentrate the hydrolysis product. The obtained organic product was diluted with $CDCl_3$ and used for measurement with a JEOL FX-90 spectrometer. ^{13}C-NMR spectra of the reaction mixture and hydrolysis product were recorded at room temperature with hexamethyldisiloxane as reference in a pulse Fourier-transform mode operating at 22.4 MHz.

The morphology of the catalysts and polypropylene (PP) samples were observed with a scanning electron microscope (SEM, Jeol JSM-820). A special device was used to protect the catalyst samples from hydrolysis. The specimens were deposited on SEM stubs and coated with a film of gold about 20 Å thick by sputtering techniques to avoid electric discharges during observations.

Polymerization Procedure

The semibatch polymerization of propylene was carried out in a 2 L stainless-steel autoclave (Taiatsu Glass Co., Japan) using *n*-hexane as diluent. All operations were carried out under a dry nitrogen atmosphere. Mixing was provided by a magnetic drive agitator with two 3 cm-diameter propeller blade impeller. A schematic diagram of the polymerization unit constructed for slurry polymerization of propylene is shown in Figure 1.

The reactor, after being thoroughly cleaned and dried, was assembled while still hot. The whole system was alternately evacuated and filled with dry nitrogen several times. Then, 900 mL of *n*-hexane was first added under a nitrogen atmosphere, followed by TEA, the ED, and the Ti catalyst, in that

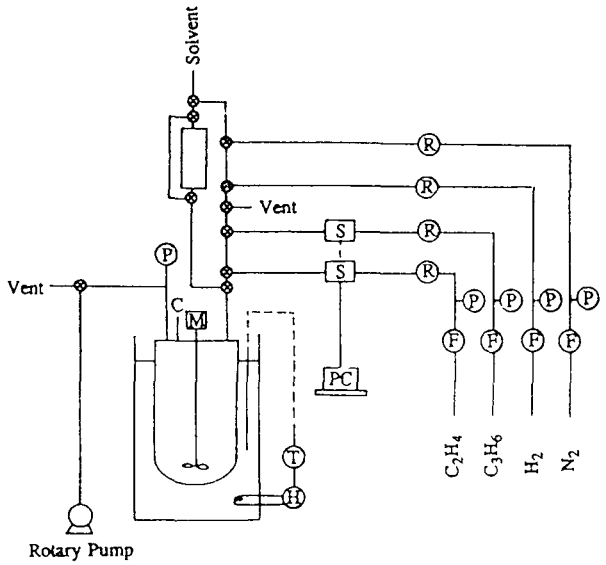


Figure 1 Polymerization unit for experimental study: (C) catalyst feed; (F) filter; (H) heater; (M) motor; (P) pressure gauge; (PC) personal computer; (R) pressure regulator; (S) mass flowmeter; (T) temperature controller.

order. TEA solution was added to *n*-hexane before addition of the catalyst in order to scavenge any oxygen or moisture left in the diluent. TEA and the ED (MPT or PTES) were diluted with *n*-hexane, and the catalyst was stored as a slurry on *n*-hexane. After evacuation, the reactor temperature increased to 65°C with stirring and the propylene feed line was opened. The polymerization temperature was controlled at 70°C while propylene was fed continuously to keep the total pressure at 1.10 MPa (10.0 kg/cm^2 G). The polymerization mixture was stirred at a constant speed of 500 rpm to avoid the effect of monomer diffusion through the gas–liquid interface.[15]

After 2 h, the propylene feed was stopped and the pressure of the reactor was vented to atmosphere pressure. Then, the reactor contents were poured into a mixture of ethanol and hydrochloric acid and stirred at least 1 h. The obtained PP was filtered, washed with ethanol, and dried in vacuum at 40°C for 24 h.

Polymer Characterization

The catalyst activity was estimated from the weight of produced PP per gram of titanium of catalyst in unit time of polymerization. The isotactic index (I.I.) of PP was measured by extracting PP in a Soxhlet apparatus with boiling *n*-heptane for 6 h. The result

was reported as weight percentage of *n*-heptane-insoluble parts and the reproducibility was checked by replicating extractions to be typically of ±2.0 standard deviation.

RESULTS AND DISCUSSION

Catalyst Structure

Chemical Composition

For the $Mg(OEt)_2$/benzoyl chloride (BC)/$TiCl_4$ catalyst prepared by the chemical reaction method, it is already known that $Mg(OEt)_2$ is converted to $MgCl_2$ by reaction with $TiCl_4$.[11] In addition, BC is also changed into ethyl benzoate (EB) acting as an internal donor (ID) and the unchanged BC remained in the prepared catalyst.[14]

For catalyst preparation that involves the reaction of $Mg(OEt)_2$ support and BC with $TiCl_4$, the reaction temperature and reaction time can affect the catalyst composition as well as polymerization behaviors. In addition, it has been frequently shown in numbers of patents that an excess amount of $TiCl_4$ was used in the catalyst preparation, but the optimum amount of $TiCl_4$ was never mentioned.

Therefore, the effects of reaction temperature, reaction time, and $TiCl_4$ amount on the catalyst composition and polymerization behaviors have been examined in detail and it was found that the optimum preparation conditions for the $Mg(OEt)_2$/BC/$TiCl_4$ catalyst are 110°C, 2 h, and 150 mL of $TiCl_4$ for 20 g of $Mg(OEt)_2$.[16]

For better performance of the supported catalyst, it has been well known that the prepared catalyst could be retreated with $TiCl_4$. In the previous paper,[12] the contents of titanium and the ethoxy group in the catalyst were found to decrease while the catalyst activity and isospecificity increased with $TiCl_4$ retreatment of the prepared $Mg(OEt)_2$/BC/$TiCl_4$ catalyst.

There is no doubt that transition metal undergoes an extensive reduction whenever the catalyst and alkyl aluminum are brought into contact.[17] The reduction of Ti species in the supported catalyst may be affected by the feasibility of alkylation of the Ti species as well as by the stability of the alkylated Ti species.[18] Therefore, it is important to choose adequate alkylating agents that do not cause overalkylation with overreduction and to select ligands that stabilize titanium-alkyl species.

To examine the effect of alkyl aluminum treatment, alkyl aluminum was reacted with the prepared catalyst and Table I shows the summarized results of chemical composition and content of the ID in the catalyst for various alkyl aluminum treatments.

The contents of titanium, chlorine, and the ethoxy group of the catalyst treated with alkyl aluminum had almost the same value compared to those of the catalyst without alkyl aluminum treatment. But the detection of aluminum remaining in the catalyst could suggest that the alkyl aluminum is fixed to the catalyst. In addition, ID content decreased with alkyl aluminum treatment due to the removal of the ID by alkyl aluminum through complex formation.

X-Ray Study

There have been many X-ray diffractometric studies for the milled $MgCl_2$ crystal or comilled $MgCl_2$ with

Table I Effect of Alkyl Aluminum Treatment on Chemical Composition of $Mg(OEt)_2$/BC/$TiCl_4$ Catalyst

Alkyl Aluminum[a]	Amount of Alkyl Aluminum in Mol Ratio[b]	Content in Wt %			Content in mmol/g of Catalyst	
		Ti	C_2H_5O	Al	EB	BC
DEAC	0.02	4.4	2.8	0.41	0.523	N.D.[c]
DEAC	0.03	4.2	3.1	0.48	0.512	N.D.
DEAC	0.05	4.6	3.2	0.81	0.681	N.D.
TEA	0.03	6.0	—	—	0.703	0.026
TIBA	0.05	4.6	2.9	0.73	—	—
TIHA	0.05	5.3	3.2	1.12	—	—
None	—	4.5	2.7	0.0	0.776	0.046

[a] DEAC, diethyl aluminum chloride; TEA, triethyl aluminum; TIBA, triisobutyl aluminum; TIHA, triisohexyl aluminum.
[b] Alkyl aluminum/$Mg(OEt)_2$ mol ratio.
[c] N.D., not detected.

$TiCl_4$ and/or ED, and the crystal structure of $MgCl_2$ can be changed with an activation procedure.[8,19] Therefore, a structural investigation on $Mg(OEt)_2$/BC/$TiCl_4$ and $Mg(OEt)_2$/EB/$TiCl_4$ catalysts was carried out by an X-ray diffractometer and the obtained diffractograms are given in Figure 2.

It was noticed that no characteristic peaks of $Mg(OEt)_2$ were present in the X-ray diffraction patterns of $Mg(OEt)_2/TiCl_4$ catalyst, namely, the original structure of $Mg(OEt)_2$ was destroyed by reaction with $TiCl_4$. $Mg(OEt)_2/TiCl_4$ catalyst shows a similar diffractogram to the activated $MgCl_2$ and peaks of (101) and (104) planes disappeared to form a shifted halo.[8,20] These results confirmed again that $Mg(OEt)_2$ is converted to $MgCl_2$ by reaction with $TiCl_4$.

In other words, it is possible to obtain the amorphous $MgCl_2$ by chemical reaction of $Mg(OEt)_2$ with $TiCl_4$, which is more disordered than that obtained by even prolonged mechanical milling of $MgCl_2$. The diffraction peaks of the $Mg(OEt)_2$/BC/$TiCl_4$ and $Mg(OEt)_2$/EB/$TiCl_4$ catalysts were slightly sharper than those of the $Mg(OEt)_2/TiCl_4$ catalyst.

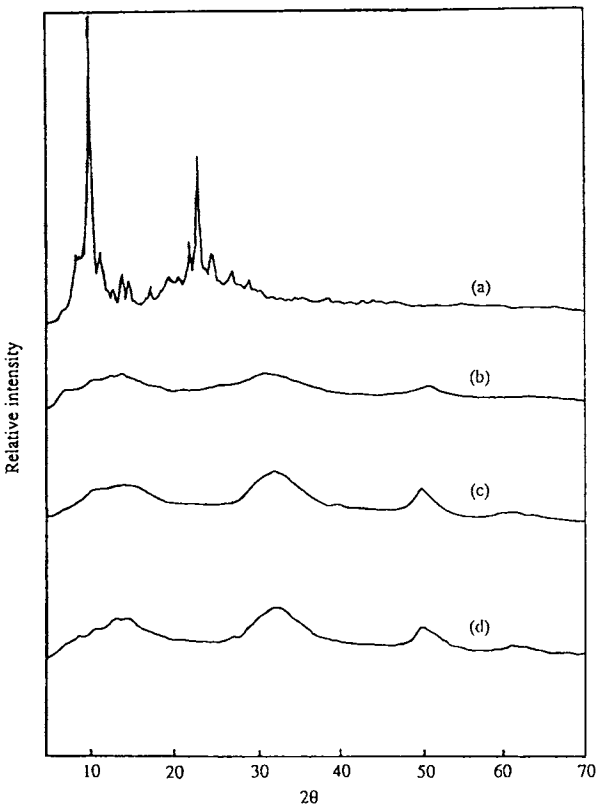


Figure 2 X-ray diffraction patterns of (a) $Mg(OEt)_2$, (b) $Mg(OEt)_2/TiCl_4$, (c) $Mg(OEt)_2$/BC/$TiCl_4$, and (d) $Mg(OEt)_2$/EB/$TiCl_4$ catalysts.

With above results, it could be suggested that BC or EB in the $Mg(OEt)_2$-supported catalyst plays some role in the distortion of crystal lattices of $MgCl_2$ formed by chlorination of $Mg(OEt)_2$, which was discussed in the morphology study.

Polymerization Behaviors

Alkyl Aluminum Treatment

The effect of alkyl aluminum compounds using in catalyst treatment on polymerization behaviors was investigated and are listed in Table II. With using MPT as the external donor (ED), the treatment of catalyst with alkyl aluminum caused the catalyst activity to decrease. But it was interesting that the alkyl aluminum-treated catalyst in the presence of PTES as the ED shows about twice higher activity than that of untreated catalyst except for the case of TIHA. Also, isotacticity stayed almost constant but for TEA.

Polymerization Conditions

To investigate the optimum polymerization conditions of the $Mg(OEt)_2$/BC/$TiCl_4$–TEA/MPT catalyst system, polymerizations were conducted under various conditions: polymerization temperature and concentrations of TEA, MPT, and propylene monomer.

The polymerization temperature affects both the polymerization rate and isotactic index (I.I.) of the polypropylene (PP) obtained with the $MgCl_2$-supported catalyst.[21] The dependencies of activity and I.I. on polymerization temperature are shown in Figure 3.

Catalyst activity gave a maximum at 60–70°C and then decreased with increasing temperature. That result might be ascribed to a destruction of active sites at higher temperature because this process is irreversible in nature.[21] The temperature level having the highest activity depends on the structure and thermal stability of the catalyst components.[22]

Isotacticity of PP increased from 40 to 60°C and gave a rapid decline above 70°C. Sergeev et al. observed a similar tendency regarding to stereospecificity in the case of PP obtained with the $MgCl_2$/EB/$TiCl_4$–TEA/EB catalyst system.[23] The influence of temperature on stereospecificity has been also explained by a distribution in the type of active sites and difference in relative temperature dependence for the propylene polymerization rate at isospecific and nonstereospecific sites.[24]

The observed cocatalyst effects are due to several simultaneous phenomena: alkylation, reduction,

Table II Effect of Alkyl Aluminum Treatment on Polymerization Behavior of $Mg(OEt)_2/BC/TiCl_4$ Catalyst

Alkyl Aluminum	Alkyl Aluminum in Mol Ratio	Catalyst Activity in (kg of PP/g of Ti/h)		Isotactic Index in Wt %	
		With MPT	With PTES	With MPT	With PTES
DEAC	0.02	148.2	103.1	64.7	82.6
DEAC	0.03	166.0	94.3	69.7	78.9
DEAC	0.05	178.6	83.6	55.7	69.3
TEA	0.03	142.7	105.1	63.5	48.4
TIBA	0.05	146.9	106.4	67.3	78.8
TIHA	0.05	108.9	46.0	66.0	76.3
None	—	204.0	54.2	69.5	81.6

[a] Polymerization conditions: [TEA] = 5.0 mmol/L; [ED] = 0.25 mmol/L; *n*-hexane = 900 mL; propylene pressure = 1.10 MPa; 70°C, 2 h.

extraction, and catalyst modification reaction.[25] The concentration of alkyl aluminum strongly affects the polymerization rate and also the polymer stereoregularity. The dependencies of activity and isotacticity on the concentration of TEA were examined and are shown in Figure 4.

In Figure 4, activity initially increased with TEA concentration and then remained constant, tending to slightly decrease only for higher concentrations. Upon an increase of TEA concentration in the range of low concentration, the increase of activity might be attributed to the progressive activation of potential catalytic sites by interaction with TEA.[26] The decrease of the overall rate or increase of the decay rate for larger TEA concentration beyond certain limits might be due to the overreduction of titanium.[27]

The increase of TEA concentration caused a drastic decrease in isotacticity and this result shows similar characteristics to the $MgCl_2/EB/TiCl_4$ cat-

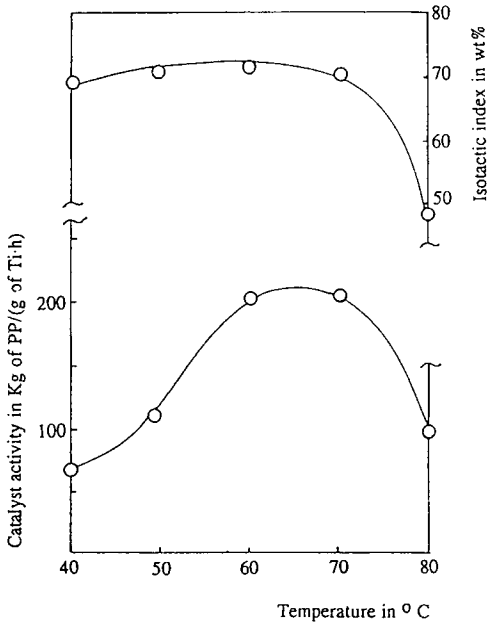


Figure 3 Dependence of activity and isospecificity on polymerization temperature for the $Mg(OEt)_2/BC/TiCl_4$–TEA/MPT catalyst system. Polymerization conditions: same as Table II except for polymerization temperature.

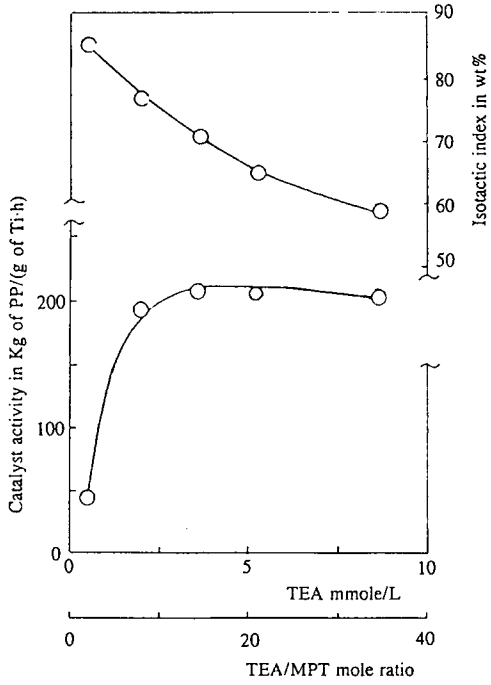


Figure 4 Dependence of activity and isospecificity on alkyl aluminum concentration for the $Mg(OEt)_2/BC/TiCl_4$–TEA/MPT catalyst system. Polymerization conditions: same as Table II except for TEA concentration.

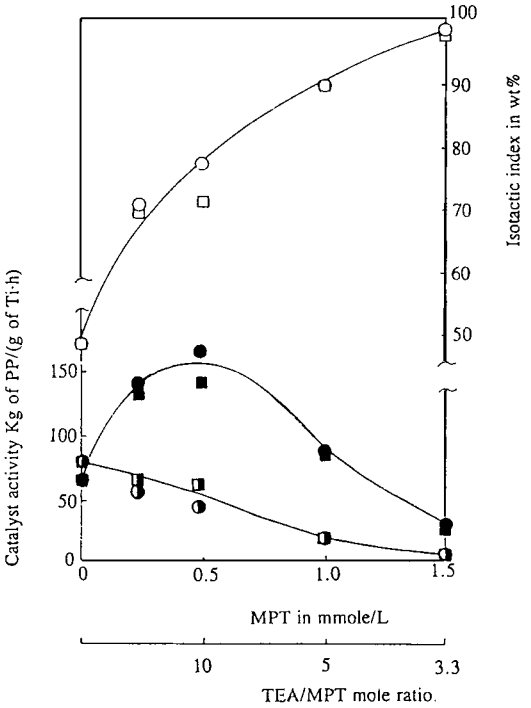


Figure 5 Plots of activity and isospecificity vs. amount of MPT added with the Mg(OEt)$_2$/(BC or EB)/TiCl$_4$–TEA/MPT catalyst system: (a) (●) isotactic and (◑) atactic activity and (○) I.I. for BC system; (b) (■) isotactic and (◨) atactic activity and (□) I.I. for EB system. Polymerization conditions: same as Table II except for MPT concentration.

alyst reported by Shiono and Soga.[28] They suggested that the interaction between EB and Ti species is not very strong and then a large amount of EB is removed by formation of a complex with TEA on addition of TEA, thereby generating uncomplexed aspecific Ti species.

In stereospecific olefin polymerization, addition of Lewis base affects both stereospecificity and polymerization kinetics. In general, stereospecificity has a trend to increase with addition of an ED and the addition of an ED to alkyl aluminum has a remarkable effect on catalyst performance in α-olefin polymerization.[29] Several authors reported that the ED selectively poisons the less stereospecific polymerization center through a reversible complexation of the ED to the coordinatively unsaturated active sites.[30]

In Figure 5, the isotactic activity increased up to [MPT] = 0.5 mmol/L and then rapidly dropped, but the atactic activity decreased monotonically with ED concentration. An increase of isotactic activity, which was explained by Barbe et al.,[8] appeared to rise mainly from a marked change in the strong dependence of isotacticity on polymerization time and presumably due to the extraction of the ID by interaction with TEA. It has also been confirmed that the ED is fixed on the catalyst surface, selectively poisoning the nonspecific centers and simultaneously increasing the reactivity of isospecific centers.[31]

The polymerization rate, *Rp*, is generally considered proportional to monomer concentration. Therefore, the first-order dependency of the propylene pressure is established for the Ziegler–Natta catalyst under a steady-state condition, i.e., the number of active centers does not change with monomer concentration.[21]

The effect of propylene concentration on activity and isospecificity for the Mg(OEt)$_2$/BC/TiCl$_4$–TEA/MPT catalyst system is shown in Figure 6 with changes of propylene pressure in polymerization in place of concentration. As shown in Figure 6, activity increased with propylene pressure almost linearly, which shows the first-order dependence of *Rp* on propylene concentration. On the other hand, isospecificity increased with propylene pressure at low propylene concentration and then became constant, the reason for which has not been explained yet.

Microtacticity

It is known that heterogeneous Ziegler–Natta catalysts yield a mixture of PP having different stereo-

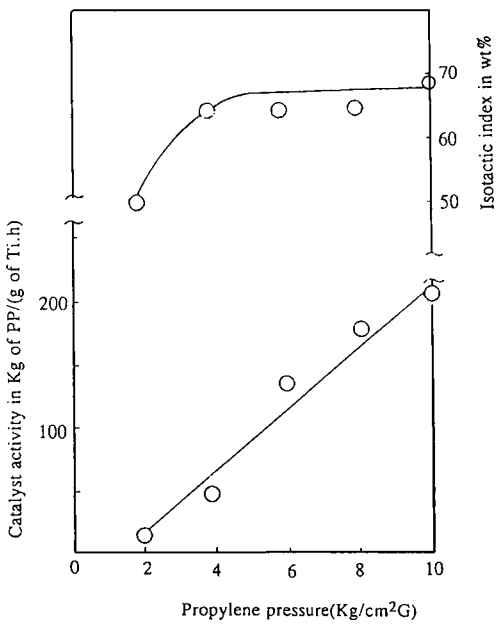


Figure 6 Dependence of activity and isospecificity on propylene pressure for the Mg(OEt)$_2$/BC/TiCl$_4$–TEA/MPT catalyst system. Polymerization conditions: same as Table II except for propylene pressure.

Table III Effect of ED on I.I. and Microtacticity of PP with $Mg(OEt)_2/BC/TiCl_4$–TEA/ED Catalyst System

ED	[ED]/[TEA] in Mol Ratio	$\overline{Mw}$	MFR	I.I	Microtacticity (triad) by ^{13}C-NMR								
					Total PP			C_7-Insoluble PP			C_7-Soluble PP		
					mm	*mr*	*rr*	*mm*	*mr*	*rr*	*mm*	*mr*	*rr*
—	0	242,000	17.3	77.7	0.846	0.115	0.039	0.893	0.080	0.027	—	—	—
MPT	0.023	—	26.4	76.4	0.820	0.100	0.080	0.904	0.069	0.027	—	—	—
MPT	0.184	520,000	0.14	96.8	0.854	0.093	0.053	0.884	0.081	0.035	0.455	0.307	0.238
MPT[a]	0.184	—	12.9	91.8	0.867	0.090	0.043	0.938	0.044	0.018	0.518	0.334	0.148
PTES	0.023	—	7.3	84.1	0.870	0.090	0.040	0.885	0.071	0.044	—	—	—
PTES	0.184	499,000	0.30	95.5	0.892	0.061	0.047	0.932	0.050	0.018	0.570	0.260	0.170
PTES[a]	0.184	—	38.5	97.7	0.870	0.090	0.040	0.916	0.058	0.026	0.558	0.232	0.210

[a] In the presence of hydrogen (0.016 MPa).

regularities,[32] i.e., isotactic, syndiotactic, and atactic. The determination of PP isotacticity is still important in the evaluation of commercial catalysts as well as in the search for detailed mechanistic understanding of the stereoregulating process.

The method of tacticity measurement was based on solvent extraction, IR, and calorimetric techniques related to the crystallinity of PP, which is indirectly related to actual tacticity. Recently, NMR studies of PP revolutionized the determination of tacticity when it was realized that the relative steric configuration of neighboring units affects the chemical shift of both proton and carbon atoms in the propylene repeating unit.

Rapid developments in high-field ^{13}C-NMR permitted the distinction of longer stereosequences as triad at first and then as pentad, and, subsequently, heptad sequences became resolved.[33] For the $Mg(OEt)_2/BC/TiCl_4$–TEA catalyst system with or without MPT or PTES, the obtained PP was investigated for microtacticity by the ^{13}C-NMR technique.

The ^{13}C-NMR spectra of PP were obtained in which CH_3, CH_2, and CH peaks appear at 21.89, 46.67, and 29.08 ppm, respectively, showing good correspondence with the calculated chemical shifts (20.61, 44.36, and 28.38 ppm) by the Linderman–Adams method.[34]

Usually, the microtacticity of PP is expressed by stereosequences and a triad (*mm*, *mr*, *rr*) can be obtained with CH_3 peak analysis. The expanded CH_3 peaks of the ^{13}C-NMR spectra were measured and the peaks of *mm*, *mr*, and *rr* sequences were found, respectively, at 21.89, 21.09, and 20.01 ppm.[33] In addition, it was found that *n*-heptane-soluble PP has a larger portion of *mr* and *rr* sequences, whereas the *n*-heptane-insoluble part has the least.

With the peak area of each sequence, the triad distribution of PP obtained at different polymerization conditions could be calculated, and the results are given in Table III. As shown in Table III, an increase of *mm* of total PP was followed by increase in the I.I., but the *mm* of *n*-heptane-insoluble PP shows almost the same value irrespective of the I.I. With the amount of MPT or PTES, the I.I. and *mm* of the total PP increased.

I.I. measurement by the *n*-heptane extraction

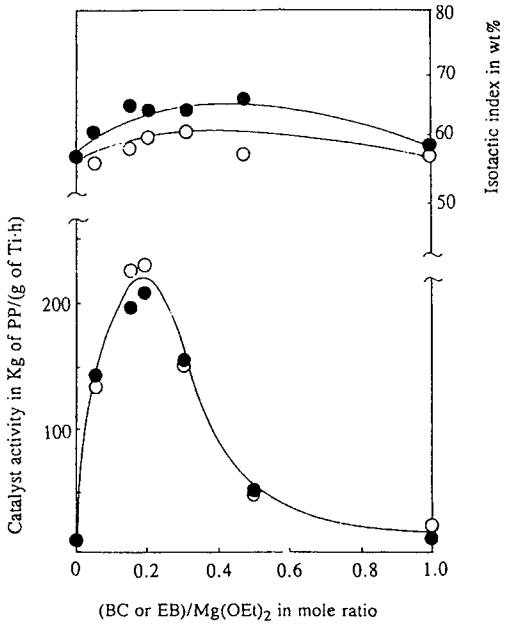


Figure 7 Effect of (BC or EB)/$Mg(OEt)_2$ mol ratio on polymerization behavior of (●) $Mg(OEt)_2/BC/TiCl_4$–TEA/EB and (○) $Mg(OEt)_2$/EB/$TiCl_4$–TEA/EB catalyst systems. Polymerization conditions: [TEA] = 5.0 mmol/L; [ED] = 0.25 mmol/L; propylene pressure = 1.10 MPa, 70°C, 2 h.

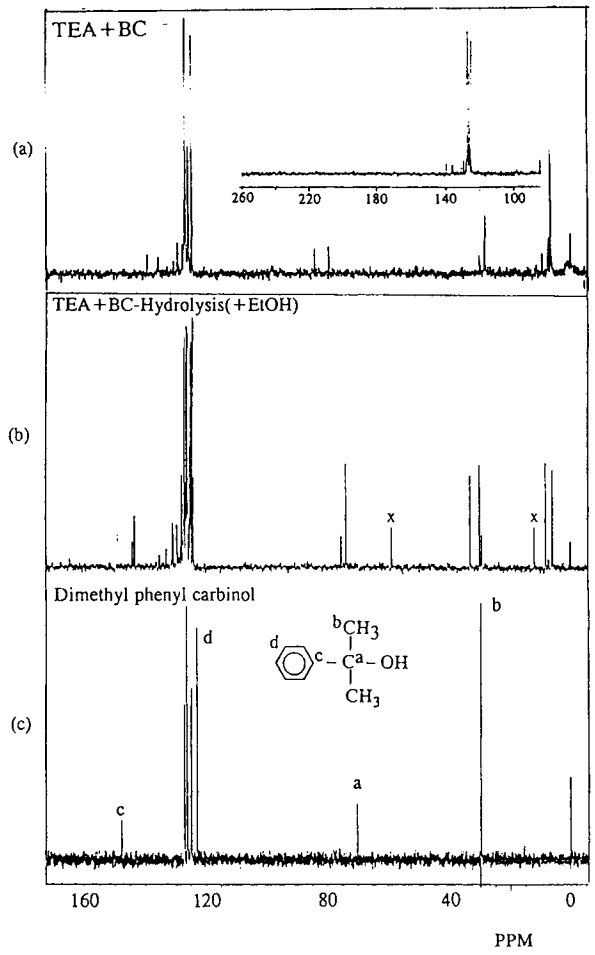


Figure 8 ^{13}C-NMR spectra of (a) reaction mixture of BC with TEA, (b) hydrolysis product after reaction of BC with TEA, and (c) dimethyl phenyl carbinol.

method was based on tacticity, but this method had certain deficiencies: A polymer that had very low molecular weight even with high microtacticity would be considerably more soluble in hot *n*-heptane than a high molecular weight polymer with low *mm* due to the difference in solution viscosity.

As results of investigating the effect of MW on the I.I., the addition of hydrogen caused the decrement of the I.I. of PP due to the decrease of MW at constant MPT concentration. This result might be confirmed by microtacticity in that the *mm* value of *n*-heptane-soluble PP obtained in the presence of hydrogen is higher than that obtained in the absence of hydrogen, as shown in Table III.

At constant PTES concentration, addition of hydrogen showed a slight increase in the I.I. of PP and almost the same value in *mm* of *n*-heptane-soluble PP even though MFR of PP increased. This result might suggest that PP obtained with PTES in the presence of hydrogen has decreased MW but can be less extractable by *n*-heptane, the reason for which is not clear yet.

Interaction of BC with TEA

The catalyst activity and I.I. of PP obtained with the $Mg(OEt)_2/BC/TiCl_4$–TEA/EB catalyst system are given in Figure 7 with those of the $Mg(OEt)_2/EB/TiCl_4$–TEA/EB catalyst system. As shown in Figure 7, catalyst activity increased to have a maximum at a $BC/Mg(OEt)_2$ or $EB/Mg(OEt)_2$ ratio = 0.2 and then decreased with an increasing amount of BC or EB. In addition, activities of the above two catalysts were almost the same.

The isotacticity increased a little and decreased with an increasing amount of BC or EB. Also, the $Mg(OEt)_2/BC/TiCl_4$ catalyst gave a higher I.I. of PP than that of the $Mg(OEt)_2/EB/TiCl_4$ catalyst.

The above results showed a similar tendency to those of the catalyst system using MPT[14] as the ED in place of EB. Sergeev et al. reported similar tendencies for both activity and the I.I. with the nEB · $MgCl_2/TiCl_4$–triisobutyl aluminum/ethyl *p*-methoxy benzoate catalyst system prepared by the milling method.[35]

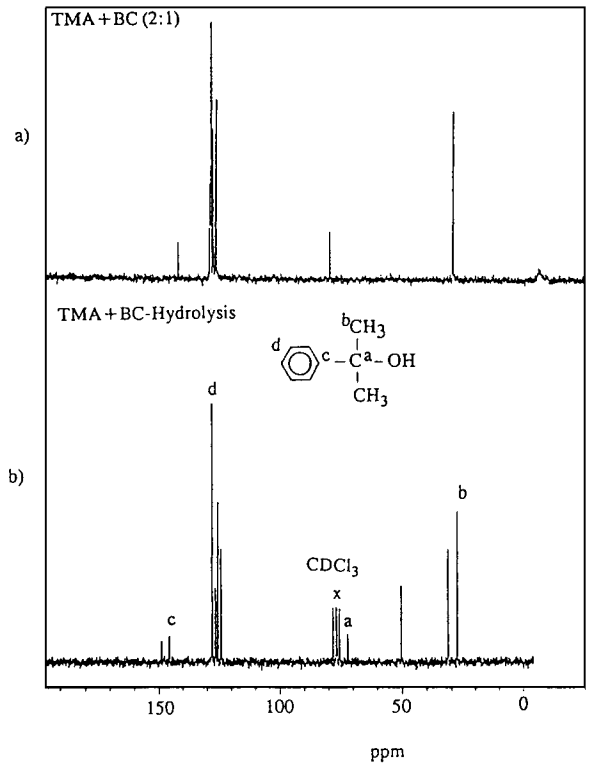


Figure 9 ^{13}C-NMR spectra of (a) reaction mixture of BC with TMA and (b) hydrolysis product after reaction of BC with TMA.

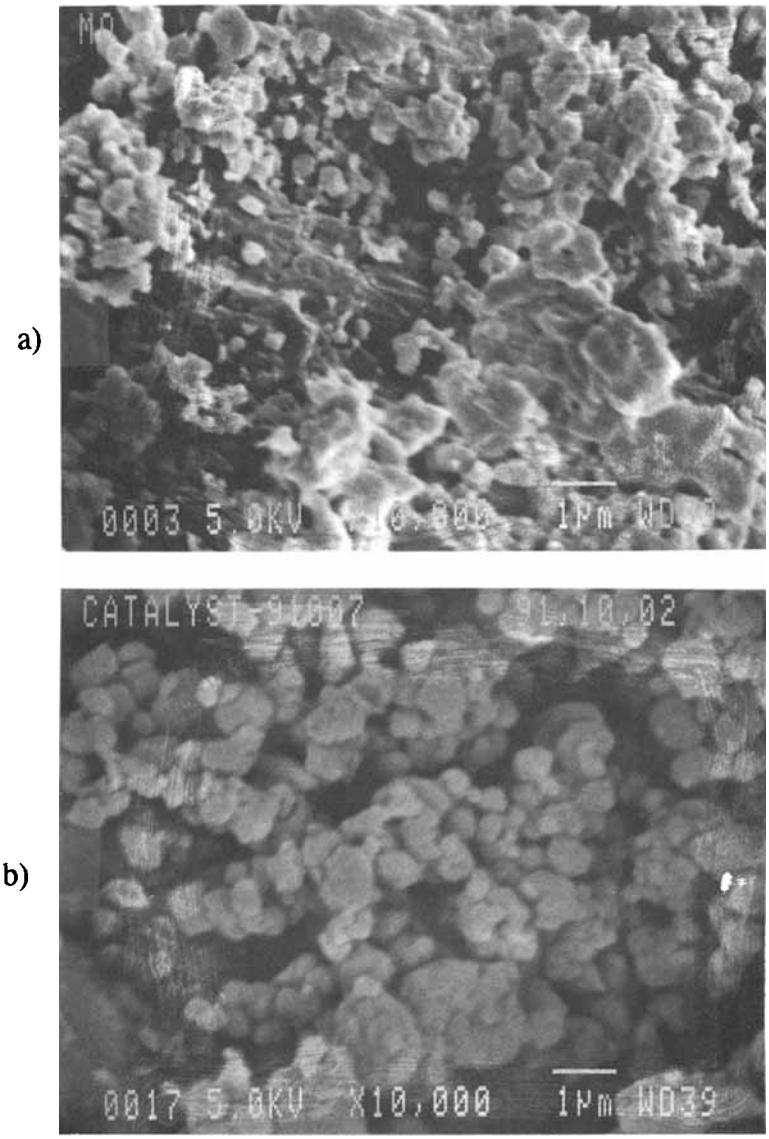


Figure 10 SEM micrographs of (a) $Mg(OEt)_2$, 6 h milling, and (b) $Mg(OEt)_2/TiCl_4$ catalyst, 10,000×.

In a previous paper,[14] the difference of isotacticity between the $Mg(OEt)_2/BC/TiCl_4$–TEA/MPT and $Mg(OEt)_2/EB/TiCl_4$–TEA/MPT catalyst systems was explained to occur due to the formation of aluminum carbinolate from the reaction of TEA with BC remaining in the prepared catalyst. It was also already known that carbinol can be used as the ED to increase isotacticity of PP.[36]

To confirm the formation of aluminum carbinolate from TEA and BC, ^{13}C-NMR spectra of the reaction mixture of TEA and BC including reactants of TEA and BC were measured and are shown in Figure 8. For the reaction mixture, the C=O peak of BC could not be seen and many additional peaks appeared. In addition, no peaks appeared at 180–220 ppm corresponding to the C=O peak of ketone, which is suggested as being intermediate by Chien and Wu.[37]

The reaction mixture of TEA and BC was hydrolyzed to obtain the corresponding carbinol, and the ^{13}C-NMR spectrum of the hydrolysis product was compared with that of dimethyl phenyl carbinol (DMPC), as shown in Figure 8. Although some peaks of the reaction mixture and the hydrolysis product were in good correspondence with those of DMPC, there were still many unidentified peaks due to the complex reaction of the ethyl group.

To simplify the system, trimethyl aluminum

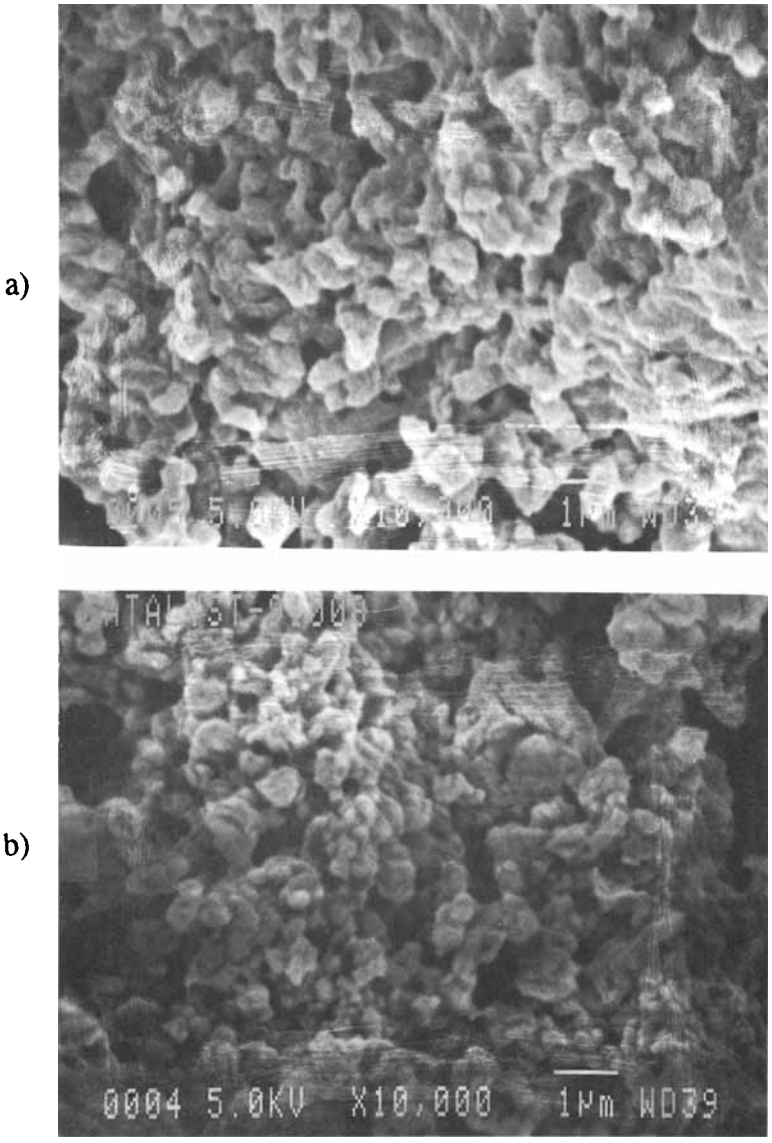
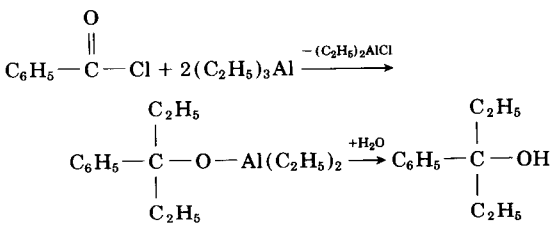


Figure 11 SEM micrographs of (a) $Mg(OEt)_2/BC/TiCl_4$ and (b) $Mg(OEt)_2/EB/TiCl_4$ catalysts, 10,000×.

(TMA) in place of TEA was reacted with BC, and the ^{13}C NMR spectra of the reaction mixture as well as the hydrolysis product are given in Figure 9. As shown in Figure 9, peaks of the reaction mixture of TMA and BC were very simple and good corresponding with those of DMPC except for the tertiary carbon peak. The shift of the tertiary carbon peak from 70 ppm (DMPC) to 80 ppm (reaction mixture) might be due to the chemical bond of the tertiary carbon with the aluminum of TMA. The spectrum of the hydrolysis product was almost the same as DMPC, but still some peaks appeared that have not been identified yet.

From the above ^{13}C-NMR analysis, the reaction between the TEA cocatalyst and the BC remaining in the prepared catalyst could form aluminum carbinolate, which produced carbinol by hydrolysis:



Morphology of Catalyst and Polypropylene Particles

Heterogeneous Ziegler–Natta catalysts are capable of replicating their morphology into the morphology

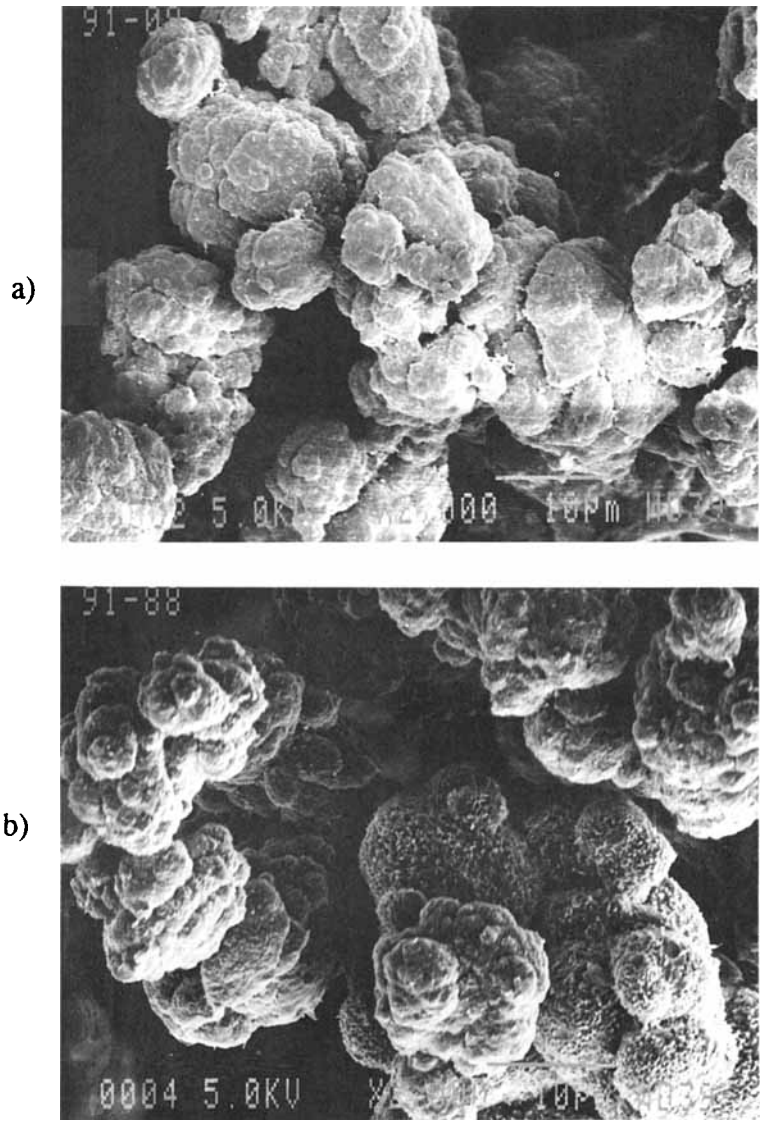


Figure 12 SEM micrographs of PP obtained with (a) $Mg(OEt)_2/BC/TiCl_4$–TEA/MPT and (b) $Mg(OEt)_2/EB/TiCl_4$–TEA/MPT catalyst systems, 2000×.

of polymer particles.[38] Although the polymer particle replicates the morphology of the catalyst particle, the catalyst particle breaks down or shatters during the polymerization process and the fragments become dispersed throughout the polymer particle.[39]

The elementary morphology of the nascent polymer generally consists of microglobules, covering catalyst particles, with dimensions of less than 500 Å.[40] The microglobules usually form globular aggregates that can be interconnected by fibers that originated as a result of the expansion of the polymer particle.

To observe catalyst and polymer morphology, micrographs of various catalysts were obtained by scanning election microscope (SEM) and are shown in Figures 10 and 11. The micrographs of $Mg(OEt)_2$ with 6 h milling and the $Mg(OEt)_2/TiCl_4$ catalyst are shown in Figure 10. The morphology of the $Mg(OEt)_2/TiCl_4$ catalyst was very different from $Mg(OEt)_2$ itself. It might be confirmed that the original structure of $Mg(OEt)_2$ is destroyed by the reaction of $Mg(OEt)_2$ with $TiCl_4$ and then highly disordered $MgCl_2$ is obtained, which was described in the X-ray diffraction pattern of the catalyst.

For $Mg(OEt)_2/(BC \text{ or } EB)/TiCl_4$ catalysts, the micrographs of the catalysts and PP are shown in Figures 11 and 12, respectively. In Figure 11, it was found that the surface of the $Mg(OEt)_2/BC/TiCl_4$

catalyst is finer than that of the $Mg(OEt)_2$/EB/$TiCl_4$ catalyst and that the latter has an aggregated structure. In the preparation of the catalyst, the complex formation of EB and $TiCl_4$ might be possible immediately for the $Mg(OEt)_2$/EB/$TiCl_4$ catalyst, while EB forms by reaction of BC and $Mg(OEt)_2$ with $TiCl_4$ for the $Mg(OEt)_2$/BC/$TiCl_4$ catalyst. The globular aggregates of PP that were obtained with the above two catalysts showed less difference in morphology.

REFERENCES

1. Br. Pat. 1,140,649 (1966) (to Solvay & Cie).
2. Belg. Pat. 650,670 (1963) (to Solvay & Cie).
3. S. S. Invanchev, A. A. Baulin, and A. G. Godionov, *J. Polym. Sci. Polym. Chem. Ed.*, **18,** 2045 (1980).
4. Jpn. Pat. 7,040,295 (1970) (to Mitsui Petrochem. Ind. Ltd.).
5. Belg. Pat. 839,131 (1976) (to Mitsui Petrochem. Ind. Ltd.).
6. T. Yano, T. Inoue, S. Ikai, M. Shimizu, Y. Kai, and M. Tamura, *J. Polym. Sci. Polym. Chem. Ed.*, **26,** 457 (1988).
7. R. N. Haward, A. N. Roper, and K. Fretcher, *Polymer,* **14,** 365 (1973).
8. P. C. Barbe, C. Cecchin, and L. Noristi, *Adv. Polym. Sci.*, **81,** 1 (1987).
9. T. Keii and K. Soga, Ed., *Catalytic Olefin Polymerization,* Kodansha, Tokyo, 1990.
10. U.S. Pat. 4,548,951 (1985) (to Shell Oil Co.).
11. Y.-T. Jeong and D.-H. Lee, *Makromol. Chem.*, **191,** 1487 (1990).
12. Y.-T. Jeong, D.-H. Lee, and K. Soga, *Makromol. Chem. Rapid Commun.*, **12,** 5 (1991).
13. D. A. Skoog and D. M. West, *Analytical Chemistry,* Saunders College, Philadelphia, 1980, p. 581.
14. Y.-T. Jeong, D.-H. Lee, T. Shiono, and K. Soga, *Makromol. Chem.*, **192,** 1727 (1991).
15. S. Floyd, R. A. Hutchinson, and W. H. Ray, *J. Appl. Polym. Sci.*, **32,** 5473 (1986).
16. Y.-T. Jeong, PhD Thesis, Kyungpook National University, Taegu, Korea, 1991.
17. N. Kashiwa and J. Yoshitake, *Makromol. Chem.*, **185,** 1133 (1984).
18. J. C. W. Chien and J. C. Wu, *J. Polym. Sci. Polym. Chem. Ed.*, **20,** 2461 (1982).
19. P. Galli, P. C. Barbe, G. P. Guidetti, R. Zannetti, A. Martorana, A. Marigo, M. Bergozza, and A. Fichera, *Eur. Polym. J.*, **19,** 19 (1983).
20. U. Giannini, *Makromol. Chem. Suppl.*, **5,** 216 (1981).
21. R. Spitz, J. L. Lacombe, and A. Guyot, *J. Polym. Sci. Polym. Chem. Ed.*, **22,** 2625 (1984).
22. L. L. Bohm, *Polymer,* **19,** 553 (1978).
23. S. A. Sergeev, G. D. Bukatov, and V. A. Zakharov, *Makromol. Chem.*, **185,** 2377 (1984).
24. J. V. Seppala and M. Auer, *Prog. Polym. Sci.*, **15,** 147 (1990).
25. P. J. T. Tait, in *Proceedings of the International Symposium on Future Aspects of Olefin Polymerization,* Tokyo, Japan, 1985, p. 305.
26. Y. Doi, K. Murata, K. Yano, and T. Keii, *Ind. Eng. Chem. Prod. Res. Dev.*, **21,** 580 (1987).
27. I. G. Boucher, J. W. Parsons, and R. N. Haward, *Makromol. Chem.*, **175,** 3461 (1974).
28. T. Shiono and K. Soga, in *Transition Metal Catalyzed Polymerization, Ziegler-Natta and Metathesis Polymerization,* R. P. Quirk, Ed., Cambridge University Press, New York, 1988, p. 266.
29. R. Spitz, C. Bobichon, L. Duranel, and A. Guyot, in *Catalytic Olefin Polymerization,* T. Keii and K. Soga, Ed., Kodansha, Tokyo, 1990, p. 107.
30. A. J. Sivals and Y. V. Kissin, *J. Polym. Sci. Polym. Chem. Ed.*, **22,** 3739 (1984).
31. N. Kashiwa, M. Kawasaki, and J. Yoshitake, in *Catalytic Polymerization of Olefin,* T. Keii and K. Soga, Eds., Elsevier, Amsterdam, 1983, p. 43.
32. G. Natta and F. Danusso, *J. Polym. Sci.*, **34,** 3 (1959).
33. J. C. Randall, *Polymer Sequence Determinations,* Academic Press, New York, 1977.
34. L. P. Linderman and J. Q. Adams, *Anal. Chem.*, **43,** 1245 (1971).
35. S. A. Sergeev, G. D. Bukatov, V. A. Zakharov, and E. M. Moroz, *Makromol. Chem.*, **184,** 2421 (1983).
36. T. Yano, T. Inoue, S. Ikai, Y. Kai, M. Yamura, and M. Shimizu, *Eur. Polym. J.*, **22,** 637 (1986).
37. J. C. W. Chien and J. C. Wu, *J. Polym. Sci. Polym. Chem. Ed.*, **22,** 3747 (1984).
38. J. Boor, Jr., *Ziegler-Natta Catalysts and Polymerizations,* Academic Press, New York, 1979, Chap. 8.
39. M. P. McDaniel, *J. Polym. Sci. Polym. Chem. Ed.*, **19,** 1967 (1981).
40. A. Munoz-Escalona, *Polym. Prepr.*, **24,** 112 (1983).

Received February 26, 1992
Accepted May 4, 1992