

Development of Catalyst Technologies for Polypropylene

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Ever since the successful synthesis of polypropylene by G. Natta *et al.* in 1954, the catalyst has gradually been refined along with significant improvement and simplification of the production process. The role of the donors used as a catalytic component or external donors in improving the polymerization activity and controlling the structure of polypropylene is very significant. In this article, we focus on the development trend of donors to explain changes in catalysts for propylene polymerization and their current status.

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Introduction

Polypropylene (PP) is a general-purpose resin and used for a variety of applications, including food packaging, containers and other daily necessities, automotive parts, textiles, and medical devices. Total global PP production in 2019 is estimated to be about 90 million tons¹⁾, and PP production is expected to continue to grow at about 4% per year²⁾, while responding to lighter weight automobiles to reduce CO₂ emissions and more sophisticated containers and packaging to contribute to food loss reduction.

Since the successful synthesis of PP by G. Natta *et al.* in Italy in 1954³⁾, the PP market has experienced remarkable growth. This was due to the continuous improvement of catalyst performance, which dramatically increased polymerization activity, improvements to the primary structure of PP (stereoregularity, molecular weight distribution, *etc.*) and the morphology of polymerized powder, and achieving a balance between low cost, ease of processing, and good physical properties compared to other resins. Propylene polymerization catalysts are broadly classified into Ziegler-Natta catalysts and complex catalysts such as metallocenes. In this paper, based on literature and patent information, we review the evolution of Ziegler-Natta catalysts for propylene polymerization and the search and

development of donor compounds, which have been actively investigated since 2000.

Development of Ziegler-Natta catalysts for propylene^{4)–6)}

The TiCl₃/AlEt₂Cl catalyst used in industrial processes in the early days of PP production had low productivity and stereoregularity⁷⁾. Subsequently, Natta *et al.* found that polymerization activity was enhanced when TiCl₃ was activated by aluminum reduction^{8)–10)}. However, the activity and stereoregularity were still low, requiring deashing and separation of the atactic polymer component to remove catalyst residues. Subsequent improvements^{11)–14)} led to the industrialization of catalyst systems using AlEt₂Cl as an auxiliary catalyst. In bulk polymerization, an activity of 5 to 15 kg-PP/g-cat was achieved, and polymers can now be produced that do not require separation of the atactic polymer component. This catalyst is still used in several plants^{15), 16)}.

High activity and high stereoregularity were achieved by a combination of MgCl₂, TiCl₄, an internal donor which is the first Lewis base and is included in the solid catalyst, trialkylaluminum, and an external donor which is the second Lewis base and is added during polymerization^{17)–21)}. Benzoate esters were used as Lewis bases in the early stages of development^{22)–24)}. Later, it was

found that catalysts using phthalates as internal donors and alkoxy silanes as external donors had an excellent balance of activity and stereoregularity²⁵. During this period, the mechanism of action of both donors was also elucidated. A mechanism was proposed in which an external donor supplements the active site that has had most of the internal donor removed from the catalyst, such as in a complexation reaction with organoaluminum, and the active site formed develops high stereoregularity²⁶. Catalyst development for even higher activity and stereoregularity continued, and 1,3-diether was found as a new internal donor^{27, 28}. This donor expressed a certain level of stereoregularity even without the use of an external donor. The reason for this is said to be that organoaluminum and 1,3-diether are difficult to complex and remove from the catalyst²⁹. In addition to catalysts designed for activity and stereoregularity (pentad fraction (*mmmm*: isotactic fraction in pentad units of methyl groups of polypropylene resin)), other catalysts were developed to improve hydrogen reactivity (sensitivity to chain transfer by hydrogen) and control molecular weight distribution (M_w/M_n). It has been reported that the aforementioned 1,3-diether has excellent hydrogen reactivity and 2,1-insertion proceeds with an isospecific active species, giving PP with a narrow molecular weight distribution²⁹. In addition, the use of succinate ester as an internal donor increases the ratio of highly regiospecific active species, allowing the production of PPs with a wider molecular weight distribution^{30–32}. **Table 1** shows data obtained from hexane slurry polymerization or bulk polymerization.

Thus, the selection of the donor compound, which is a Lewis base, is the key to controlling the polymerization behavior and PP structure of Ziegler-Natta catalysts for propylene. Therefore, the following is an overview of donor compound exploration and development trends, divided into internal and external donors.

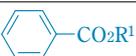
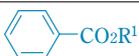
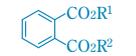
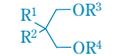
Search and development of internal donors

1. Search for alternative compounds to phthalates, and opportunities for development

A variety of compounds have been reported as internal donors, such as 1,3-ethers, succinate esters, alkoxyesters^{34–39}, and malonate esters^{40–45} (**Fig. 1**). However, catalysts using phthalates as internal donors are still used in the majority of industrial polymerization processes for propylene polymerization. On the other hand, the toxicity of phthalates, when administered in large doses to rodents, led to restrictions on their use in all countries and regions, with infants as the main target for protection, and a movement to avoid phthalates began^{46, 47}.

In 1999, the EU banned poly(vinyl chloride) (PVC) toys and child care products that contain more than 0.1% phthalates (DEHP: bis(2-ethylhexyl) phthalate, DBP: dibutyl phthalate, BBP: butylbenzyl phthalate, DINP: diisononyl phthalate, DIDP: diisodecyl phthalate, and DNOP: dioctyl phthalate) and are intended to be placed in the mouths of children under 3 years of age. Subsequently, in 2002, Japan banned the use of PVC toys with DEHP and DINP content exceeding 0.1%⁴⁸. However, similar toxicity has not been observed

Table 1 Results of bulk or hexane slurry polymerization³³⁾

Generation	Year	Catalyst System Example					Productivity kg-pp/g-cat	II ^{a)} %	<i>mmmm</i> %	Process
		Mg	Ti	Internal donor	AlR ₃	External donor				
1st	1954	-	δ-TiCl ₃	-	AlEt ₂ Cl		2–4	90–94	-	Slurry
2nd	1970	-	δ-TiCl ₃	-	AlEt ₂ Cl	-	10–15	94–97	-	Slurry, Bulk
	1968	MgCl ₂	TiCl ₄	-	AlR ₃	Silane	15	40	50–60	
3rd	1971	MgCl ₂	TiCl ₄		AlR ₃		15–30	95–97	90–94	Bulk or Gas
	1980	MgCl ₂	TiCl ₄		AlR ₃	Silane	40–70	95–99	94–99	
5th	1988	MgCl ₂	TiCl ₄		AlR ₃	Silane	70–130	95–99	95–99	Bulk or Gas
	1999	MgCl ₂	TiCl ₄		AlR ₃	Silane	40–70	95–99	95–99	

a) II: Isotactic Index, originally based on heptane hot extractables

in primates, and these restrictions were taken as precautionary measures^{47), 48)}. However, the listing of DEHP, DBP, and BBP on the 2008 Candidate List of Substances of Very High Concern for Authorisation under REACH accelerated the movement to avoid phthalate compounds. In Japan, DEHP was designated as a priority evaluation chemical substance on April 1, 2011,



Fig. 1 Chemical structure of malonic ester and alkoxy ester

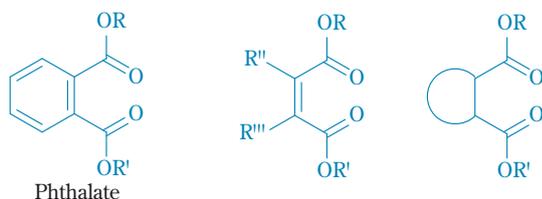


Fig. 2 Chemical structure of phthalate and phthalate analogs

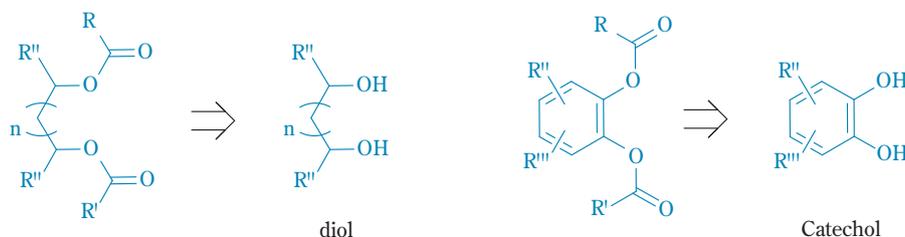


Fig. 3 Chemical structure of diol and catechol derivatives

and is scheduled to undergo a two-step risk assessment by the government to determine whether it is a Class 2 Specified Chemical Substance^{47)–50)}. DEHP and other phthalates present technical challenges in risk assessment at this time, such as contamination and clarification of contamination pathways. It is still difficult to establish appropriate elution tests and elution standards, and in Japan, it has been judged appropriate to regulate the use of the product within a defined range⁵¹⁾.

This accelerated the development of catalysts using internal donors as alternatives to phthalates. There are two main structures of internal donors used as alternatives to phthalates. One is maleates⁵²⁾ and cyclic diesters^{53)–55)} that, like phthalates, can achieve a strong coordination structure to metal atoms (Fig. 2). The other is diester compounds derived from diols or catechols with a high degree of freedom of coordination to the metal atom (Fig. 3).

2. Maleates and cyclic diesters

Maleate analogues⁵²⁾ and cyclic diesters^{53), 54)} were also found to be highly active and highly stereoregular as internal donors (Table 2).

Table 2 Comparison of activity and stereo regularity between maleate analog and cyclic diester

Internal donor	External donor	Activity PP-kg/Cat-g	Stereoregularity X.I. ^{a)} wt%	Literature
 R = iBu, n-Pentyl, cycloHexyl		41–54	97.1–97.4	52)
		35	99.1	53)

a) X.I. is/represents the amount of insolubles crystallized and precipitated from mixed xylene solution

Recently, it has been reported that the use of bis(2-ethylhexyl) citraconate as an internal donor reduces residual volatile components (VOC: volatile organic compounds, FOG: Fogging compounds) due to its improved hydrogen reactivity compared to phthalates (Table 3)⁵⁵.

It is interesting to note that a mixture of cis-trans isomers of cyclohexanedicarboxylic acid derivatives yields PPs with a wider molecular weight distribution than either cis or trans isomers alone (Table 4)^{56, 57}. It was also reported that PP with a wider molecular weight distribution can be obtained by using a mixture of cis-trans isomers of two cyclohexanedicarboxylic acid derivatives, rather than a mixture of cis-trans isomers of one cyclohexanedicarboxylic acid derivative (Table 4)⁵⁸.

3. Diester compounds derived from diols or catechols

Catalysts using diester compounds derived from diols as internal donors have been reported^{59–61}. The compound 2,4-pentanediol dibenzoate has been found to be more active than di-*n*-butylphthalate and gives higher stereoregularity (Table 5)⁵⁹. Characteristically, it can maintain high activity and high stereoregularity even in the absence of an external donor. The reason for this may be that, as with 1,3-diether, organoaluminum and 2,4-pentanediol dibenzoate do not complex easily and are not easily removed from the catalyst.

Catalysts using 5-*tert*-butyl-3-methyl-1,2-phenylenedibenzoate derived from catechol^{62–64} were found to

give PP with lower residual volatile content than those using diisobutyl phthalate or 1,3-diether as an internal donor (Table 6)⁶⁴.

Other catalysts using 1,8-naphthalenediyl dibenzoate⁶⁵ derived from dihydroxynaphthalene or methyl 3-benzoyloxybutyrate⁶⁶ derived from aliphatic esters with hydroxyl groups as internal donors have also been found to exhibit high activity and stereoregularity (Table 7).

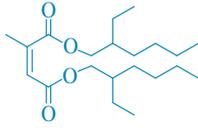
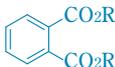
Search and development of external donors

1. Study of catalyst systems that simultaneously exhibit high stereospecificity and high hydrogen reactivity

Catalyst systems that simultaneously exhibit high stereoregularity and high hydrogen reactivity are being actively investigated, including the application of impact copolymers (ICP: compositions consisting of propylene monopolymers and ethylene-propylene copolymers) to injection molding materials. This may be because catalysts with high hydrogen reactivity may also contribute to the reduction of VOC and FOG. Alkylalkoxysilanes ($R_nSi(OR')_{4-n}$) with moderate bulk density and electron density have been reported to be suitable for producing highly stereoregular PPs^{67–70} and are also used industrially. Among them, *N*-(triethoxysilyl)diethylamine (U donor) with an amino group was reported to exhibit high hydrogen reactivity and high stereoregularity (Table 8)⁷¹.

After the development of the U donor, it was reported

Table 3 Comparison of VOC and FOG between bis-(2-ethylhexyl)citraconate and phthalate

Internal donor	roop(H-PP1)	1GPR(H-PP1)	MFR g/10 min	T_m °C	<i>mmm</i> %	Pellets	
	H ₂ /C ₃ mol/kol	H ₂ /C ₃ mol/kmol				VOC ppm	FOG ppm
	1.1	12.9	8.0	165.0	95.6	45	114
	1.2	14.2	8.0	162.5	96.0	55	200

R = *n*-octyl or 2-ethylhexyl



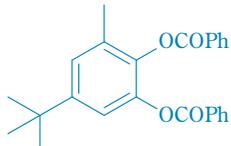
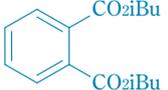
Table 4 Results of molecular weight distribution using cyclohexane dicarboxylates

Internal donor	Activity PP-kg/Cat-g	Amount of C10 insoluble component wt%	M_w/M_n	M_z/M_w
	20.6	94.9	13.7	4.7
	20.8	96.5	6.6	4.6
	18.5	93.3	9.6	4.3
	20.2	92.4	6.0	5.1
	34.2	98.1	14.6	10.8
	32.7	98.0	13.4	12.6
	25.0	96.7	9.4	4.5
 External donor				

Table 5 Comparison of 2,4-pentanediol dibenzoate with di-*n*-butyl phthalate

Internal donor	External donor	Activity PP-kg/Cat-g	mmm %
	yes	51.0	99.5
	no	53.4	98.1
	yes	32.5	98.7

Table 6 Comparison of 5-*t*-butyl-3-methyl-1,2-phenylene dibenzoate with di-*i*-butyl phthalate

Internal donor	Volatiles content μg/g
	21-26
	47.7-55.6
1,3-diether	46.9

that cyclopentyl(diethylamino)dimethoxysilane⁷²⁾, which has a similar structure to the U donor, exhibits high stereoregularity (**Table 9**)⁷³⁾.

It has also been found that dialkyl bis(ethylamino)silane exhibits higher hydrogen reactivity than *N*-(triethoxysilyl)diisopropylamine, which has a similar structure to the U donor⁷⁴⁾. Since dialkyl bis(ethylamino)silane has active hydrogen, it is believed to react with alkylaluminum used in polymerization and oligomerize due to reaction heat (**Scheme 1**)⁷⁵⁾. However, it is not known how dialkyl bis(ethylamino)silane acts on the catalyst as an external donor.

Table 7 Comparison of activity and stereo regularity between 1,8-Naphthalenediyl dibenzoate and methyl 3-benzoyloxybutyrate

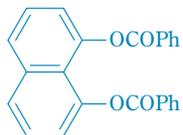
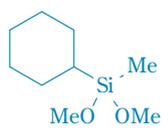
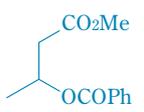
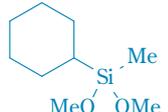
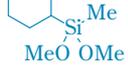
Internal donor	External donor	Activity PP-kg/Cat-g	Stereo regularity %
		51.2	Cold xylene soluble 1.82
		19.3	Isotacticity 98.9

Table 8 Effect of *N*-(triethoxysilyl)diethylamine

External donor	Activity PP-kg/Cat-g	MFR g/10 min	<i>T_m</i> °C	<i>mmmm</i> %
	43.9	444	162.7	98.9
	37.8	120	162.3	98.1
	32.3	600	161.8	97.1
	42.6	76.5	162.2	98.0

Polymerization conditions: 70 °C, H₂: 0.4MPa, in heptane

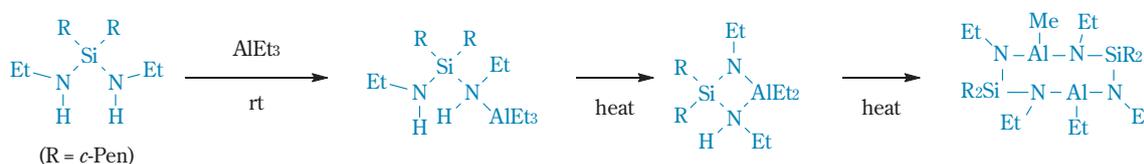
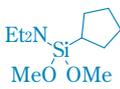
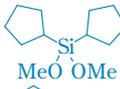
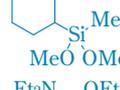
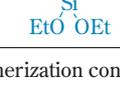
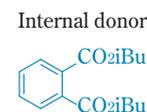
**Scheme 1** Reaction of dialkylbis(ethylamino)silane with AlEt₃

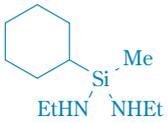
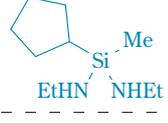
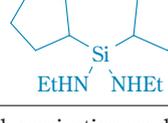
Table 9 Effect of cyclopentyl(diethyl)aminodimethoxysilane

External donor	Activity PP-kg/Cat-g	MFR g/10 min	Amount of C10 soluble component %	<i>mmmm</i> %	<i>M_w/M_n</i>
	35.1	32	0.58	99.8	7.9
	40.0	27	0.39	98.0	6.4
	23.0	33	0.72	98.0	5.5
	25.3	30	0.39	99.3	4.6



Polymerization conditions: 70 °C, in propylene

Table 10 Hydrogen response in propylene polymerization

External donor	Temperature °C	Activity PP-kg/Cat-g	MFR g/10 min	XS ^{a)} wt%
	75	55.2	260	1.8
	80	64.3	330	1.7
	75	49.2	320	1.6
	80	57.0	350	1.5
	75	57.3	190	1.4
	80	63.6	240	1.7

Polymerization conditions: H₂ gas/propylene = 4 L/1.4 L

a) Cold xylene soluble

It has been reported that asymmetric cyclopentyl-methylbis(ethylamino)silane or cyclohexylmethyl-bis(ethylamino)silane, in which one of the two alkyl groups on the silicon is bulkier, has equal or better polymerization activity and stereoregularity than dialkyl-bis(ethylamino)silane in which both substituents are bulky, and has improved hydrogen reactivity in polymerization at 80 °C (Table 10)⁷⁶. In the polymerization of ICP, the hydrogen reactivity of the homo stage and whole polymers was improved without a decrease in polymerization activity compared to dicyclopentyl-bis(ethylamino)silane (Table 11)⁷⁶.

It has been found that the use of a catalytic component pre-contacted with divinyl dimethylsilane prior to contact with propylene and further contacted with

tert-butyl methyl bis(ethylamino)silane in the presence of organoaluminum improves hydrogen reactivity compared to the use of *tert*-butylmethylbis(ethylamino)silane as an external donor (Table 12)⁷⁷. This method has also been shown to be effective for alkylalkoxysilanes (Table 13). The improvement of hydrogen reactivity by prior contact of the catalyst with an external donor prior to polymerization is interesting, but there are likely to be issues regarding the reduction of stereoregularity and storage stability from catalyst preparation to its production and use.

It was found that *n*-propyltrimethoxysilane was more hydrogen-reactive than diisopropyldimethoxysilane (Table 14)⁷⁸. As a result, *n*-propyltrimethoxysilane gave PP with lower FOG than diisopropyldimethoxysilane.

Table 11 Hydrogen controllability in ICP polymerization

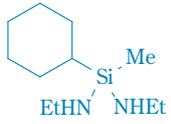
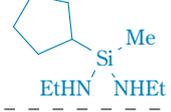
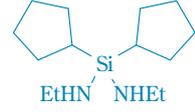
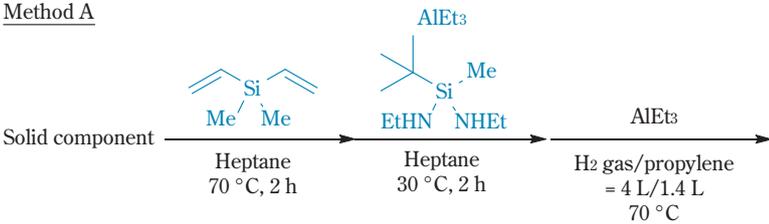
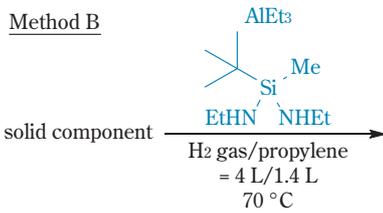
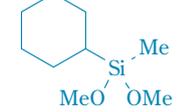
External donor	Temperature °C	Polymerization activity at homo stage PP-kg/Cat-g	Ethylene-propylene copolymerization activity ICP-kg/Cat-g	ICP-MFR g/10 min
	75	50.2	66.6	37
	80	60.3	70.2	120
	75	47.4	63.7	35
	80	53.9	63.6	140
	75	54.6	71.7	28
	80	46.5	59.4	64

Table 12 Effect of pre-mixing solid component with divinyl dimethylsilane and *tert*-butylmethylbis(ethylamino)silane

Method A	Activity PP-kg/Cat-g	MFR g/10 min	XS ^{a)} wt%
	55.8	260	2.6
	47.8	80	1.9

a) Cold xylene soluble

Table 13 Effect of pre-mixing solid component with external donor

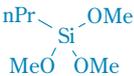
External donor	Method	Activity PP-kg/Cat-g	MFR g/10 min	Literature
	A	59.3	200	77)
	B	50.2	170	74)
	A	42.5	35	77)
	B	57.7	17	74)

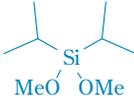
Polymerization conditions: 70 °C, H₂ gas/propylene = 4 L/1.4 L

The combination of a catalyst using 5-*tert*-butyl-3-methyl-1,2-phenylenedibenzoate as an internal donor and an aliphatic diester listed in **Table 15** showed high hydrogen reactivity while maintaining stereoregularity⁷⁹⁾. It has been reported that alkylalkoxysilanes are useful as external donors when phthalates are

used as internal donors, and alkylalkoxysilanes are also useful as internal donors other than phthalates. However, the results suggest that each internal donor has an optimal external donor other than alkoxysilane and that new effects may be found.

Table 14 Comparison of FOG between *n*-propyltrimethoxysilane and isopropyltrimethoxysilane

External donor	Catalyst	H ₂ /C ₃ mol/mol	MFR dg/min	FOG μ/g
	A	0.0175	20	287
	B	0.0085	20	166

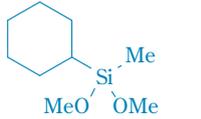
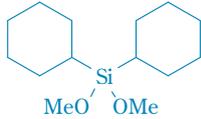
	A	0.061	20	378
	B	0.0376	20	301

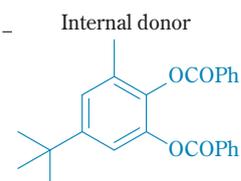
A: US patent 4866022

B: US patent 5093415

Table 15 Comparison of diester and alkylalkoxysilane

External donor	n	Activity PP-kg/Cat-g	MFR g/10 min	XI ^{a)} wt%
	4	66	40	98.1
	5	75	52	98.3
	6	61	49	98.5

		104	11	98.6
		90	7	98.9



Polymerization conditions: 70 °C, in hexane

a) The amount of insoluble xylene

2. Use of multiple donors, polymerization behavior in combination with polymerization methods, control of PP structure

External donors control polymerization activity, hydrogen reactivity and stereoregularity of PP, and molecular weight distribution. However, it is often difficult to control multiple parameters with a single external donor. Even if multiple external donors are applicable, it is not easy because one external donor may dominate and suppress the effects of the other, or cancel out the effects of both. There have been reports of cases in which such problems were overcome and the effects of both external donors were effectively brought out^{(80)–(86)}. For example, by taking advantage of the fact that the effect of one external donor is preferentially expressed, one type of external donor is used in the first step, and by adding a different type of external donor and using a mixture of external donors in the second step, PP with high stereoregularity and

relatively high melting properties has been successfully obtained⁽⁸²⁾.

Conclusion

After the successful synthesis of PP by G. Natta *et al.* in 1954, catalyst technology development to achieve higher performance, productivity, and polymerization process stability of PP has continued, including the development of catalyst technology to achieve internal donor phthalate-free and VOC reduction^{(87)–(89)} in automobile cabins^{(55), (64), (78)}. In order to reduce VOCs and increase the strength of PP for thinner wall thickness, there is a need to continue improving catalyst technology, such as controlling hydrogen reactivity and improving stereospecificity. The use of AI based on accumulated data is expected not only to accelerate the search for donor components and the development of catalyst technology, but also to lead to the emergence

of catalysts with unprecedented features. It will remain a fact that it is the polymerization catalyst that determines the productivity and primary structure of PP, and technological development of PP catalysts, including the polymerization process, is expected to continue.

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