Polymerization of Propylene by Using Mg(OEt)$_2$–DNBP–TiCl$_4$ Catalyst with Alkoxy Disilanes as External Donor

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ABSTRACT: The effect of different external silane donors on the activity and isotacticity of polypropylene prepared by using Mg(OEt)$_2$–phthalate ester–TiCl$_4$-AlEt$_3$–alkoxy disilane catalyst systems has been investigated. In the case of catalyst systems containing (trimethylsilyl)methylalkyldimethoxysilanes [Me$_3$SiCH$_2$Si(OMe)$_2$R] as external donors, the bulky Me$_3$SiCH$_2$- group was effective in converting aspecific sites into isospecific ones, followed by the increase of activity and isospecificity of the obtained polymer. Catalyst activity and isotacticity of the polymer increased with the decrease of the number of alkoxy groups in the substituted alkoxy disilanes. The effect of alkoxy groups between alkoxy disilanes and alkylaluminum as cocatalyst on the active sites of the catalyst and the influence of the size of alkoxy groups in disilane compounds were examined, respectively. Some correlation between molecular weight, molecular weight distribution, and isospecificity was also observed. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 71: 293–301, 1999

Key words: polymerization; catalyst; active site; external donor; alkoxy disilane

INTRODUCTION

The function of organic Lewis base as internal and external donor in propylene polymerization with Mg-supported-type catalysts is to increase the stereospecificity of the catalyst system, which otherwise produces a mixture of isotactic and more or less stereoirregular macromolecules. The effect of such Lewis bases in enhancing catalyst stereospecificity has been discussed in some detail by many authors.[1–4] While a great variety of Lewis bases are able to increase the stereospecificity of the polymerization, only four classes of external donor are known that allow us to obtain polypropylene with a high isotactic index without impractically depressing the polymer productivity. These classes are (1) the esters of aromatic carboxylic acid,[5–7] (2) some sterically hindered amines,[8] (3) the alkoxy monosilanes[9–15] of general formula R$_n$Si(OR′)$_{4-n}$, and (4) dialkylpropane ethers.[16]

Soga et al.[9] suggested that some aspecific sites on Ti are modified to become isospecific sites by using the alkoxymonosilanes as an external donor since Kashiwa demonstrated that the silane was able to enhance the activity of the isospecific sites.

They concluded that an aspecific site has two vacancies, while an isospecific site possesses only one vacancy; then the alkoxymonosilane donor at a concentration low enough is able to occupy, first and selectively, one of the vacancies of the aspecific sites.

One of the most specific features of the alkoxymonosilanes is to form very strong and very stable complexes with the alkylaluminum, as shown by nuclear magnetic resonance (NMR) studies.[17] The structure of the 1/1 complex has been depicted by Iiskola et al.[18] These authors have shown that the alkoxymonosilane as external donor was tightly connected to the active site structure, as a 1/1 complex with alkylaluminum.

Another important feature is the effect of the structure of the silane. The comparison of different alkoxy monosilanes is useful to clarify some additional points since it is possible to change the size and number of alkoxy and hydrocarbon substituents of alkoxy monosilanes without changing the kind of donor and, thus, to see the specific effect of each parameter. A systematic analysis of the influence of the structure of a number of alkoxy monosilanes with a catalyst containing phthalate ester as an internal donor has been recently published.[11,13,14] The conclusion of these studies was that the highest isospecificity was obtained in the following conditions: the monosilane donor, which is represented by the formula $R^1R^2Si(OR^3)_2$, should have at least two small alkoxy groups (CH_3O or C_2H_5O) and one bulky alkyl (or aryl) group.

It is already known that the silicon atom is larger in a size or bulkier than carbon. The effect of the hydrocarbon parts connected with one bulky silyl group, which are disilane systems having the formula $R^1(R^2)_2SiCH_2Si(OR^3)_2R^4$, where $R^2 = C_1–C_2$ alkyl or alkoxy group, has not been examined as external silane donor. When the alkoxy disilanes as external donor are used for propylene polymerization with the present catalyst system, will there be differences in the structural effect of disilanes comparing with monosilanes? In this article, the alkoxy disilane compounds were used as external donor to investigate the effect of their structure on catalyst activity on the isospecificity of the obtained polymer and on the stereospecific control in catalyst active sites. The molecular weight and molecular weight distribution of the produced polymer were also checked.

EXPERIMENTAL

Materials

Propylene (purity > 95.6%) (from Korea Petrochemical Ind. Co.) was used without further purification. Nitrogen of an extra pure grade (99.999%) was dried by passing it through the molecular sieve 3A column, and hexane was passed through the molecular sieve 4A column. Magnesium ethoxide (from Dynamit Nobel Chemie) was used after vibration milling under nitrogen atmosphere for 6 h at room temperature. Di-n-butylphthalate (DNBP), decane (Aldrich Chemical Co.), triethylaluminum (TEA, from Tosoh Akzo Corp.), and titanium tetrachloride (from Toho Titanium Co.) were used without further purification.

Catalyst Preparation

In a 1-L round-bottomed flask equipped with a magnetic stirrer and a condensor, under nitrogen atmosphere, 100 mL of decane and 10 g of diethoxy magnesium were added and stirred to form a suspension. To the suspension, 80 mL of $TiCl_4$ was added with a syringe. The mixture was heated to 130°C, and 7.4 mL of di-n-butylphthalate was added. The mixture was then reacted for 4 h. After completion of the reaction, the reaction mixture was filtered. To the resultant solid, 100 mL of decane and 80 mL of $TiCl_4$ were added with a syringe, and the mixture was heated to 130°C and reacted for 4 h. After completion of second reaction, the reaction mixture was filtered. The resultant solid was washed 5 times with 200 mL of hexane. The solid product was dried under nitrogen gas. The content of titanium in the solid catalyst was determined to be 2.8 wt % by an atomic absorption spectrophotometer.

Synthesis of Alkoxy Disilane Compounds as External Donor

The synthetic method of alkoxy disilane compounds used in polymerization as external donor have been previously described in the literature.[19–22] The structures of alkoxy disilane compounds are represented by the formula $R^1(R^2)_2SiCH_2Si(R^3)_2R^4$, where R^1 equals methyl, R^2 equals $C_1–C_2$ alkyl or alkoxy, R^3 equals $C_1–C_2$ alkoxy, and R^4 equals $C_1–C_2$ alkyl groups. The alkoxy disilane compounds used as external donor are listed in Schemes 1–3.

Scheme 1

R	ED(I)
CH_3	MTDM
n-C_3H_7	PTDM
i-C_3H_7	IPTDM
n-C_4H_9	BTDM
i-C_4H_9	IBTDM
n-C_5H_{11}	PnTDM
n-C_6H_{13}	HTDM
⬠	CpTDM
⬡	CTDM

Scheme 1

	R_1	R_2	ED(Ⅲ)
	CH_3	n-C_6H_{13}	TEMHDP
	n-C_6H_{13}	n-C_6H_{13}	TEDHDP
	CH_3	⬡	TEMCDP
	CH_3	CH_3	TEDMDS

Scheme 3

Polymerization Procedure

Under nitrogen gas, in a 2-L stainless steel reactor, which had been purged with nitrogen, 900 mL of n-hexane was added. 5.361 mmol of triethyl aluminum (TEA) and 0–0.742 mmol of organosilane compounds as external donor were added with a syringe, and 10 mg of the catalyst was added. From the reactor charged with nitrogen gas, inert gas was removed by using vacuum pump. 8.93 mmol of hydrogen was provided, and propylene gas was introduced into the reactor and subjected to polymerization for 2 h while maintaining the pressure at 1.10 MPa (10 kg/cm$^2 \cdot$ G) and a temperature of 70°C. After polymerization, the unreacted gases were slowly released, and then the slurry product was filtered and dried in a vacuum at a temperature of 40°C for 24 h to obtain a polymer powder.

Polymer Characterization

The isotacticity[6,7,12–14] of the polymers was measured by extracting the polymers for 8 h with boiling heptane in a Soxhlet-type apparatus. The isospecific and aspecific activities correspond to the amounts of the boiling heptane-insoluble and soluble fractions, respectively. The result was reported as the weight percentage of heptane-insoluble parts, and the reproducibility was typically ±2.0 of the standard deviation. The catalyst activity was estimated from the weight of the produced polymer per gram of titanium of catalyst in unit time of polymerization. The measurement of the isotacticity and activity was performed 2 times and taken the average value, respectively.

Analytical Procedure

The amount of titanium element in the prepared catalyst was 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 0.1M sulfuric acid and then diluted to 100 mL with distilled water.

The molecular weight (M_w) and molecular weight distribution of PP were determined by gel permeation chromatography (GPC). The chromatograms were recorded at 140°C in 1,2,4-trichlorobenzene using a Waters 150 CV-GPC equipped with twin Shodex AT-80M/S columns. M_w was calculated by the universal calibration method using polystyrene standards with narrow and broad distributions.

RESULTS AND DISCUSSION

Several alkoxy disilanes bearing alkyl and alkoxy substituents of different bulkiness were synthesized and tested as external donors in propylene polymerization with a Mg(OEt)$_2$–phthalate ester–TiCl$_4$-AlEt$_3$ catalyst system as described in the experimental section above. For this work, we have compared the following different alkoxy disilane compounds as external donor (ED I–III), shown in Schemes 1–3, respectively: methyl (trimethylsilylmethyl)dimethoxysilane (MTDM),

Scheme 2

n	R_1	R_2	ED(Ⅱ)
1	CH_3	CH_3	TMDMDP
1	CH_3	n-C_6H_{13}	TMMHDP
1	n-C_6H_{13}	n-C_6H_{13}	TMDHDP
1	CH_3	⬡	TMMCDP
1	⬡	⬡	TMDCDP
6	⬡	⬡	TMDCDO
	CH_3	CH_3	TMDMDS

Scheme 2

Table I   Results of Propylene Polymerization[a] with Mg(OEt)$_2$–TiCl$_4$-AlEt$_3$[b]–ED I Catalyst System

Run No.	ED I	Activity (kg PP/g Ti h atm)	II[c] (%)	M_w[d] $\times 10^{-4}$	M_w/M_n
1	MTDM	61.9	98.6	30.7	5.1
2	PTDM	62.4	98.6	31.4	5.1
3	IPTDM	62.2	98.6	32.0	5.0
4	BTDM	51.7	98.2	28.7	5.3
5	IBTDM	52.0	98.3	29.1	5.3
6	PnTDM	50.0	97.3	27.2	5.5
7	HTDM	47.1	96.9	27.0	5.4
8	C$_P$TDM	66.4	98.9	33.6	4.7
9	CTDM	64.7	98.8	32.9	4.7
10[e]	DMDM	44.1	91.2	22.2	6.2
11[f]	CMDM	60.1	98.5	31.3	5.0

[a] Polymerization condition: catalyst, 10 mg; AlEt$_3$, 5.361 mmol; n-hexane, 900 mL; time, 2 h; propylene, 1.10 MPa.
[b] The ED-to-AlEt$_3$ molar ratio: 0.04.
[c] Isotactic index was calculated by boiling heptane for 8 h.
[d] Calculated as polystyrene by the universal calibration method.
[e] Dimethyldimethoxymonosilane.
[f] Cyclohexylmethyldimethoxymonosilane.

n-propyl(trimethylsilylmethyl)dimethoxysilane (PTDM), i-propyl(trimethylsilylmethyl)dimethoxysilane (IPTDM), n-butyl(trimethylsilylmethyl)dimethoxysilane (BTDM), i-butyl(trimethylsilylmethyl)dimethoxysilane (IBTDM), n-pentyl(trimethylsilylmethyl)dimethoxysilane (PnTDM), n-hexyl(trimethylsilylmethyl)dimethoxysilane (HTDM), cyclopentyl(trimethylsilylmethyl)dimethoxysilane (C$_P$TDM), cyclohexyl(trimethylsilylmethyl)dimethoxysilane (CTDM), as ED I; 1,1,3,3-tetramethoxy-1-methyl-3-hexyl-1,3-disilapropane (TMMHDP), 1,1,3,3-tetramethoxy-1,3-di-n-hexyl-1,3-disilapropane (TMDHDP), 1,1,3,3-tetramethoxy-1-methyl-3-cyclohexyl-1,3-disilapropane (TMMCDP), 1,1,3,3-tetramethoxy-1,3-dicyclohexyl-1,3-disilapropane (TMDCDP), 1,1,8,8-tetramethoxy-1,8-dicyclohexyl-1,8-disilaoctane (TMDCDO), 1,1,3,3-tetramethoxy-1,3-dimethyl disiloxane (TMDMDS) as ED II; 1,1,3,3-tetraethoxy-1-methyl-3-hexyl-1,3-disilapropane (TEMHDP), 1,1,3,3-tetraethoxy-1,3-di-n-hexyl-1,3-disilapropane (TEDHDP), 1,1,3,3-tetraethoxy-1-methyl-3-cyclohexyl-1,3-disilapropane (TEMCDP), 1,1,3,3-tetraethoxy-1,3-dimethyl disiloxane (TEDMDS) as ED III.

Effects of the Structure of Dimethoxy Disilanes (ED I)

Since the structural factors evidently have more influence on the performance of the silane donors than the electronic factors,[10] sterical hindrance of the hydrocarbon parts bonded to the silicon atom would be expected to be the major sterical factor. Härkönen et al.[10] reported that the steric effects, which hinder the oxygens from deactivating isospecific active sites, might reasonably be described by the width or radius of the hydrocarbon groups in the vicinity of the oxygens. Their result was that the isospecific activity increased with the increase of the width or bulkiness of hydrocarbon groups in the silane donors.

As shown in Scheme 1, these disilane compounds differed considerably in their effect on activity and isotacticity in propylene polymerizations carried out in the presence of hydrogen. The structural effects of the disilane donors on activity and isotacticity index (II) are given in Table I. According to Härkönen et al., the silane as the external donor should have at least two small alkoxy groups and one bulky alkyl (or aryl) group.[13,14] Therefore, the bulky silyl group, represented by the following Me$_3$SiCH$_2$-, was chosen as 1 bulky alkyl part bonded to a silicon atom of the external donor. In the dimethoxy disilane derivatives having the following formula Me$_3$SiCH$_2$Si(OMe)$_2$R, the MTDM donor (Run No. 1), where R represents the CH$_3$ group, gave much higher activity and II than the monosilane (DMDM, Run No. 10) having two methyl groups. Comparing MTDM with the well-known monosilane (CMDM, Run No. 11) as a commercial external donor, activity in the case of MTDM was slightly higher than that of CMDM, whereas the II was at about the same level. From these results, trimethylsilylmethyl group of MTDM

Figure 1 The effect of the size of hydrocarbon groups of alkoxy disilanes having the formula $Me_3SiCH_2Si(OMe)_2R$, where R is *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, cyclopentyl, and cyclohexyl groups as ED I on catalyst activity: (■) PTDM, (+) BTDM, (∗) PnTDM, (□) HTDM, (×) C_PTDM, and (▲) CTDM.

seems to have the similar steric effect with cyclohexyl group of CMDM. On the base of the study of Guyot et al.,[24] these results also suggest that the bulky trimethylsilylmethyl (Me_3SiCH_2-) group partly covers the vacancy where the monomer is expected to become coordinated, and then such a tight geometry imposes the isospecific coordination of the monomers before its insertion in the polymer chain.

However, activities and isotacticities show a decreasing trend with the increase of carbon chains of branched and unbranched alkyl group R, following the order $i\text{-}C_3H_7 < i\text{-}C_4H_9 < n\text{-}C_5H_{11} < n\text{-}C_6H_{13}$ (Run Nos. 3–7). This suggests that the deactivation effectiveness of dimethoxy disilane shifts from aspecific sites to isospecific ones with the increase of carbon chains of linear or nonlinear alkyl groups. On the other hand, when alkyl group R was replaced by cyclopentyl (cyclo-C_5H_9) and cyclohexyl (cyclo-C_6H_{11}) group, both activities and isotacticities were increased (Run Nos. 8 and 9). This result indicates that the steric factor of 2 bulky hydrocarbon parts is actively involved in the generation of isospecific sites with deactivating aspecific ones. Therefore, we can observe an increase of isospecificity that parallels the increase of bulkiness of the substituted alkyl groups R, following the order[8,10] $n\text{-}C_4H_9$, $n\text{-}C_5H_{11}$, $n\text{-}C_6H_{13} < i\text{-}C_4H_9 < i\text{-}C_3H_7 < $ cyclo-C_5H_9, cyclo-C_6H_{11}.

The structural effects of hydrocarbon groups with the variation of the Si-to-Al molar ratio on

the activity and isotacticity index of the samples prepared with the selected dimethoxy disilanes (ED I) are shown in Figures 1 and 2. Both activities and isotacticities initially increase with the increase of the Si-to-Al molar ratio, and then the former almost gives the constant level followed by the slight decrease with excess of silane donor, whereas the latter is shown to be keeping at constant level.

From the results of Table I and Figures 1 and 2, it is confirmed that even long linear alkyl groups (C_4–C_6) do not deactivate the active sites of polymerization as selectively as cycloalkyl and small alkyl groups. That is, large hydrocarbon groups, except for cycloalkyl groups, are less effective in deactivating aspecific sites of the catalyst for the increase of isospecific sites in the present dimethoxy disilane systems.

Effects of the Structure of Tetramethoxy Disilanes (ED II)

The results of propylene polymerization with the tetramethoxy disilane donors are given in Table II. The substituent effect of one cyclohexyl group attached to silicon atom on isospecificity appeared with the increase of isotacticity (for example, Run No. 4), but the disilanes having two cyclohexyl groups did not have an affect on isospecificity, followed by the maintenance of the constant isotacticity (for example, Run Nos. 5 and 6). Comparing TMDMDP (Run No. 1), having the meth-

Figure 2 The effect of the size of hydrocarbon groups of alkoxy disilanes having the formula $Me_3SiCH_2Si(OMe)_2R$ where R is *n*-propyl, *n*-butyl, *n*-pentyl, *n*-hexyl, cyclopentyl, and cyclohexyl groups as ED I on isotacticity: (■) PTDM, (+) BTDM, (∗) PnTDM, (□) HTDM, (×) C_PTDM, and (▲) CTDM.

Table II   Results of Propylene Polymerization[a] with Mg(OEt)$_2$–TiCl$_4$-AlEt$_3$–ED II[b] Catalyst System

Run No.	ED II	Activity (kg PP/g Ti h atm)	II[c] (%)	M_w[d] $\times 10^{-4}$	M_w/M_n
1	TMDMDP	30.2	95.3	26.2	5.9
2	TMMHDP	29.9	95.2	26.8	5.9
3	TMDHDP	40.0	93.1	25.0	6.3
4	TMMCDP	34.3	97.2	27.9	5.5
5	TMDCDP	30.2	97.0	27.5	5.5
6	TMDCDO	42.2	97.2	38.5	5.6
7	TMDMDS	42.1	92.1	23.0	6.5

[a] Polymerization condition: catalyst, 10 mg; AlEt$_3$, 5.361 mmol; n-hexane, 900 mL; time, 2 h; propylene, 1.10 MPa.
[b] External donor, tetramethoxy disilanes; ED-to-AlEt$_3$ molar ratio, 0.04.
[c] Isotactic index, calculated by boiling heptane for 8 h.
[d] Calculated as polystyrene by the universal calibration method.

ylene bridge, with TMDMDS (Run No. 7), having the oxygen bridge, the oxygen bridged disiloxane gave lower isotacticity than the methylene bridged disilane, showing higher activity. On the other hand, the effect of the number of alkoxy groups on activity and isotacticity (II) in propylene polymerizations performed by varying the amount of alkoxy disilanes (ED I and II), which differ only in the number of the alkoxy groups, is shown in Figures 3 and 4, respectively. Seppälä et al.[13] and Sacchi et al.[23] reported that the more alkoxy groups there are, the more effective the alkoxy silane in deactivating active sites is. In this article, however, the result on the effect of the number of alkoxy groups was not partly consistent with that of Härkönen and Sacchi, especially in isospecificity. Tetramethoxy disilanes gave even lower isotacticity than dimethoxy di-

silanes. On the other hand, activities with the dimethoxy disilanes (HTDM and CTDM in Fig. 3) initially increased with the increase of disilane donors and then kept at a constant level, whereas those with the tetramethoxy disilanes (TMMHDP and TMMCDP in Fig. 3) showed the rapid decrease in the vicinity of 0.02 of the Si-to-Al molar ratio.

According to the studies of Shiono[4] and Soga et al.[9] alkoxy silane as an external donor coordinates with the potentially isospecific Ti species, which are surrounded by aromatic diester as an internal donor to give a highly active isospecific Ti species, whereas it reacts with the nonisospecific Ti species to eliminate its activity. That is, the effect of the external silane donor is thus to convert low activity aspecific sites, which produce low-molecular-weight atactic polymers into more

Figure 3   The effect of the number of alkoxy groups of alkoxy disilanes on catalyst activity: (×) HTDM, (■) CTDM, (∗) TMMHDP, and (□) TMMCDP.

Figure 4   The effect of the number of alkoxy groups of alkoxy disilanes on isotacticity: (×) HTDM, (■) CTDM, (∗) TMMHDP, and (□) TMMCDP.

Table III   Results of Propylene Polymerization[a] with Mg(OEt)$_2$–TiCl$_4$-AlEt$_3$–ED III[b] Catalyst System

Run No.	ED III	Activity (kg PP/g Ti h atm)	II[c] (%)	M_w[d] $\times 10^{-4}$	M_w/M_n
1	TEMHDP	29.5	93.2	25.4	6.4
2	TEDHDP	33.8	91.0	22.7	6.4
3	TEMCDP	28.8	94.0	24.7	6.3
4	TEDMDS	31.7	90.9	22.2	6.6

[a] Polymerization condition: catalyst, 10 mg; AlEt$_3$, 5.361 mmol; *n*-hexane, 900 mL; time, 2 h; propylene, 1.10 MPa.
[b] External donor, tetraethoxy disilanes; the ED-to-AlEt$_3$ molar ratio, 0.04.
[c] Isotactic index, calculated by boiling heptane for 8 h.
[d] Calculated as polystyrene by the universal calibration method.

active isotactic-specific sites. Thus, the activity increases with addition of the external silane donor up to the point at which the concentration is sufficient to inhibit the formation of active site.

The external silane donor having more than one alkoxy group deactivates the active sites of the catalyst and is tightly connected to the active ones, as a 1/1 complex with alkylaluminum.[13,18] These studies suggest that the silane should have at least two alkoxy groups. One oxygen atom of the first alkoxy group should remain complexed with the aluminum atom because high isospecificity is obtained only if the silane has been introduced in the presence of AlEt$_3$. The oxygen atom of the second alkoxy group is complexed with the titanium atom and then deactivates the active sites; that is, it converts aspecific sites to isospecific ones. If the silane had originally more than one alkoxy group, there remain the other alkoxy groups uncoordinated in the AlEt$_3$–silane donor complex. Those uncoordinated alkoxy groups in the complex are able to deactivate the active sites at the catalyst. Our results seem to support that explanation. In other words, one uncoordinated methoxy group in the AlEt$_3$–dimethoxy disilane complex seems to deactivate the aspecific sites to increase isospecificities, whereas three uncoordinated methoxy groups in the AlEt$_3$–tetramethoxy disilane complex seem to deactivate both the aspecific and even isospecific sites, followed by the decrease of activity as well as isospecificity. Therefore, in the case of tetramethoxy disilane, it is possible to account for the fact that one oxygen atom of the first methoxy group remains complexed with the aluminum atom, and oxygen atoms of the second, third, and fourth methoxy group are complexed with the active sites on the titanium atom, followed by deactivation of both aspecific and isospecific sites without selective poisoning.

Effects of the Structure of Tetraethoxy Disilanes (ED III)

The results of propylene polymerization with the tetraethoxy disilane donors are given in Table III. Comparing the disilane with disiloxane having tetraethoxy groups, the oxygen bridged disiloxane also gave lower isotacticity than the methylene bridged disilane. The tetraethoxy disilanes and disiloxane gave lower activity and isotacticity compared with the tetramethoxy ones in Table II.

The effect of the size of alkoxy groups on activity and isotacticity in propylene polymerization performed with varying the amount of alkoxy disilanes (ED II and ED III), which differ only in the size of the alkoxy groups, is shown in Figures 5 and 6, respectively. The size of the alkoxy groups has a different effect, compared with that of hydrocarbon groups. TMMHDP and TMMCDP, bearing less bulky methoxy groups with respect to TEMHDP and TEMCDP, gave higher activity and isotacticity, respectively. These results indicate that even the relatively small difference in sterical factors between ethoxy and methoxy groups affects the selectivity of deactivation. Clearly, there is enough room for a methoxy group and already some steric hindrance for an ethoxy group. In other words, it should definitely be difficult for a larger group to accommodate a strong coordination with the titanium. Therefore, this leads to the following conclusion: ethoxy groups are less effective than methoxy ones in deactivating the active sites of the catalyst for the increase of isospecific sites. Our results are also supported by the study of Sacchi et al.[23] that the less bulky methoxysilane has a greater complexing capability and is present on more active sites, as is shown by its strong absorption on the catalyst.

Figure 5 The effect of the size of alkoxy groups of alkoxy disilanes on catalyst activity: (∗) TMMHDP, (□) TMMCDP, (×) TEMHDP, and (■) TEMCDP.

Effects on Molecular Weight and Molecular Weight Distribution

Atactic polypropylene has a lower average molecular weight than the isotactic one.[4,9] The use of external silane donor increases the average molecular weight of the polymer evidently due to a decrease in atactic polymer and an increase in isotactic polymer of the high molecular weight.

Chadwick et al.[15] have reported that alkoxy silanes giving high isospecificity gave high-molecular-weight polypropylene. In fact, our result also showed that the molecular weight of polymers prepared with the same amount of hydrogen increased with the increase of isospecificity, as shown in Tables I–III. In other words, the alkoxy disilanes giving the relatively high isospecificity, leading to high molecular weight, seem to become less effective in chain transfer.

At a given hydrogen concentration, tetramethoxy disilanes (for examples, Run Nos. 2–4 in Table II) gave a higher molecular weight polymer than tetraethoxy disilanes (for example, Run Nos. 1–3 in Table III). From this result, it is also confirmed that the less bulky methoxy silanes have a greater complexing capability and are present on more active sites since the more bulky ethoxy silanes are unfavorable in coordination of the donor or the donor–AlEt$_3$ complex with the active sites at the catalyst. Our result is supported by the studies of Härkönen et al.[13,14] and Sacchi et al.[23]

The molecular weight distribution of the crude polymers seems to be sensitive to the isospecificity of the alkoxy disilanes, as shown in Tables I–III. The M_w-to-M_n ratio decreases with the in-

crease of isospecificity of the alkoxy silanes. This is probably due to the decreasing amount of the stereoirregular low-molecular-weight fraction of the crude polymers.

CONCLUSION

The differences between alkoxy disilanes seem to be due to the structures of the complexes formed among alkoxy disilane, AlEt$_3$, and active sites at the catalyst. The stereospecificity of the catalytic system is noticeably affected by the molecular shape of the alkoxy disilane, but the bulkiness of the hydrocarbon and of the alkoxy substituents on the silicon atom seems to play different roles in propylene polymerization behavior, as in the alkoxy disilanes as the external donor. The control of stereospecificity does not arise as a result of uncomplexed external Lewis base (silane donor) being present in the system, but rather from competition between free alkylaluminum and alkylaluminum complexed to the external silane donor. Active sites formed from free alkylaluminum are both aspecific and isospecific, whereas active sites generated from complexed alkylaluminum with the external silane donor are specifically isotactic. The increase of isospecificity by using the alkoxy disilanes as external donor leads to an increase in the molecular weight of polymer and a decrease in the value of M_w/M_n.

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Figure 6 The effect of the size of alkoxy groups of alkoxy disilanes on isotacticity: (∗) TMMHDP, (□) TMMCDP, (×) TEMHDP, and (■) TEMCDP.

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