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Study of Dimethoxysilacycloalkanes as External Donors in Ziegler-Natta Stereospecific Propylene Polymerisation

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Summary

A series of cyclic dimethoxysilanes has been prepared using a one-step strategy which consists in reacting magnesium dibromoalkanes with tetramethoxysilane. The dimethoxysilacycloalkanes obtained were evaluated as the external electron donor in Ziegler–Natta catalysts for propylene polymerisation. Comparison of the experimental results with theoretical predictions using a molecular model confirmed the essential structural characteristics that are required to achieve stereospecific polymerisation of propylene. Very good activity and stereospecificity were obtained with 2,6-diethyl-1,1-dimethoxysilacyclohexane which led to results close to that of actual industrial external electron donors, cyclohexylmethyldimethoxysilane and dicyclopentyl dimethoxysilane.

Keywords: Isotactic, Poly(propylene), Ziegler-Natta polymerisation

1. Introduction

Since its discovery by Karl Ziegler [1,2] and Giulio Natta [3,4] in the fifties, Ziegler-Natta olefin polymerisation has been a topic of a large number of academic and industrial studies. Among these, numerous studies has been devoted to the understanding of the mechanistic aspect of Ziegler-Natta catalysis, and especially the nature of the active sites [5-11], examining monometallic, bimetallic or three sites models. However, this domain has always been ambiguous and controversial. The influence of the internal and external electron donors [12,13] on the tacticity of the obtained polymer has also been a recurrent research domain. Major improvements have been achieved with the fourth generation catalysts containing an internal and external electron donor (ED), leading to highly isotactic polypropylene (> 98%). A large number of ED has already been evaluated for propene polymerisation. Four major classes have so far been listed to give polypropylene with high isotacticity index and good productivity, i.e. some esters of aromatic carboxylic acids [14-16], amines [17-19], alkoxysilanes[20-29] and dialkylpropane ethers [13,30-32]. However, until now, no reliable explanation has been proposed concerning the influence of the external ED structure on the polymerisation results. A few years ago, Atofina and our group have proposed a molecular model [33-35] to identify the most important structural parameters of the external ED affecting the tacticity of the polypropylene. A simplified schematic representation of this scheme is displayed on figure 1 using cyclohexylmethyl dimethoxysilane as the external ED.

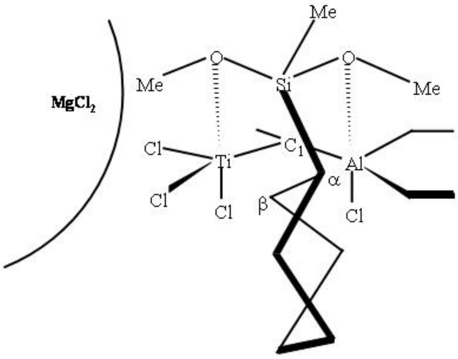


Figure 1: Simplified schematic representation of the model of the active site of Ziegler-Natta catalytic system

This model is based on the following facts: active titanium is directly bonded to the $MgCl_2$ support and is bridged with an aluminium atom of the alkylaluminium which is complexed with the external Lewis Base. As dialkyl dialkoxysilanes and 1,3-diethers are known to be the more efficient electron donors, it is suggested that both alkoxy groups are complexed, one to the aluminium atom and the second one to the titanium atom. The structure is based on an octahedral titanium and a bipyramidal aluminium and both are bridged with the polymer chain. The silane is located such that each oxygen atom is just above each of the two metal atoms. Three main criteria have thus been established for the choice of new efficient electron donors. First, the presence of a dimethoxy moiety where the two oxygen atoms are approximately three angströms apart to form an interaction with the titanium-aluminium complex is preferable. Secondly, a bulky and rigid group, for example, cyclohexyl, is required to control the monomer access by blocking the vacant space near the empty orbital of the titanium. Finally, the presence of a C-H bond in the β-position of the central atom of the electron donor will help to assist stabilization and protection of the vacant space to form an agostic bond with the titanium.

With respect to these requirements, we have prepared a large number of external ED, including dimethoxysilacyclopentanes and dimethoxysilacyclohexanes with different substituents, and tested their performance in propylene polymerisation. The purpose of this paper is to validate the strucutral characteristics of the external ED established from the molecular model and to try to understand the influence of the structural parameters behind the performance of the polymerisation.

2. Experimental part

2.1. General procedure

^1H and ^{13}C NMR spectra were recorded on a Bruker AC250 spectrometer. IR spectra were recorded on a Nicolet 210 FT-IR and melting point determinations were performed using an electrothermal capillary apparatus in open capillaries and are uncorrected. All solvents were purified by distillation using known methods before use. The dibromoalkanes used for the cyclisation were previously prepared as described in the literature[34,35].

*2.2. Synthesis of dimethoxysilacycloalkanes **5a-g**, **6a-d***

Alkylmagnesium dibromide (1 equiv.) in diethyl ether, previously prepared by reaction dibromoalkanes **1a-g**, **2a-d** with magnesium, was added dropwise to a solution of tetramethoxysilane (0.9 equiv.) in diethyl ether (20 mL) at room temperature. The mixture was heated to reflux for 4 hours and then filtered through Celite under a nitrogen atmosphere to remove the magnesium salts formed during the reaction. After concentration in vacuo of the crude mixture, 10 mL of diethyl ether was added to the residue, which was stirred and centrifuged to remove any residual magnesium salt. The supernatant liquid obtained was subsequently distilled under reduced pressure, with the fractions collected in tubes immersed in liquid nitrogen.

1,1-dimethoxysilacyclopentane **5a**. Eb_{30} = 63°C. Yield: 48%. ^1H NMR (250 MHz, $CDCl_3$): 0.40-0.62 (m, 4H); 1.48-1.62 (m, 4H); 3.50 (s, 6H). ^{13}C NMR (62 MHz, $CDCl_3$): 16.6; 26.5; 50.6.

1,1-dimethoxy-2-methylsilacyclopentane **5b**. Eb_{25} = 80°C. Yield: 32%. ^1H NMR (250 MHz, $CDCl_3$): 0.46-0.77 (m, 2H); 0.80-0.95 (m, 1H); 1.05 (d, 3H, J= 7 Hz); 1.10-1.90 (m, 4H); 3.53, 3.54, 3.55 (3s, 6H). ^{13}C NMR (62 MHz, $CDCl_3$): 7.8; 14.2; 16.9; 22.7; 35.3; 50.3; 50.6; 50.7.

1,1-dimethoxy-2-ethylsilacyclopentane **5c**. Eb_{30} = 92°C. Yield: 20%. ^1H NMR (250 MHz, $CDCl_3$): 0.45-0.76 (m, 2H); 0.80-0.91 (m, 1H); 1.02 (t, 3H, J= 7 Hz); 1.14-1.64 (m, 4H); 1.76-2.07 (m, 2H); 3.47, 3.50, 3.52 (3s, 6H). ^{13}C NMR (62 MHz, $CDCl_3$): 8.3; 15.5; 23.2; 23.4; 26.6; 33.1; 51.0; 51.1; 51.2.

1,1-dimethoxy-2-propylsilacyclopentane **5d**. Eb_{30} = 104°C. Yield: 21%. ^1H NMR (250 MHz, $CDCl_3$): 0.40-0.62 (m, 1H); 0.62-0.84 (m, 2H); 0.90 (t, 3H, J= 7 Hz); 1.03-1.55 (m, 6H); 1.73-2.10 (m, 2H); 3.56, 3.58, 3.62 (3s, 6H). ^{13}C NMR (62 MHz, $CDCl_3$): 8.3; 14.8; 23.2; 23.9; 24.2; 32.6; 33.2; 50.7; 51.1; 51.5.

1,1-dimethoxy-2-butylsilacyclopentane **5e**. Eb_4 = 50°C. Yield: 16%. ^1H NMR (250 MHz, $CDCl_3$): 0.62-0.82 (m, 2H); 0.85-0.98 (m, 4H); 1.10-1.64 (m, 8H); 1.76-2.16 (m, 2H); 3.57, 3.58, 3.59 (3s, 6H). ^{13}C NMR (62 MHz, $CDCl_3$): 8.2; 14.6; 23.2; 23.4; 24.4; 30.0; 33.1; 33.3; 50.3; 50.7; 51.1.

1,1-dimethoxy-2,5-dimethylsilacyclopentane **5f**. Eb_{30} = 70°C. Yield: 16%. ^1H NMR (250 MHz, $CDCl_3$): 0.70-1.69 (m, 8H); 1.18-2.00 (m, 4H); 3.57, 3.61, 3.64 (3s, 6H). ^{13}C NMR (62 MHz, $CDCl_3$): 14.6; 14.8; 16.2; 17.2; 32.5; 33.6; 51.0.

1,1-dimethoxy-3,4-dimethylsilacyclopentane **5g**. Eb_{30} = 69°C. Yield: 18%. ^1H NMR (250 MHz, $CDCl_3$): 0.41, 0.48 (2d, 4H, J= 8 Hz); 0.95, 1.05 (2d, 6H, J= 8 Hz); 1.20-2.06 (m, 2H); 3.56, 3.57, 3.59, 3.64 (4s, 6H). ^{13}C NMR (62 MHz, $CDCl_3$): 15.9; 18.0; 22.1; 50.6; 50.8; 51.2; 51.6.

1,1-dimethoxy-2-methylsilacyclohexane **6a**. Eb_{30} = 76°C. Yield: 24%. ^1H NMR (250 MHz, $CDCl_3$): 0.45-0.65 (m, 2H); 0.77-0.93 (m, 1H); 1.11-2.14 (m, 6H); 3.56, 3.59, 3.63 (3s, 6H). ^{13}C NMR (62 MHz, $CDCl_3$): 10.5; 15.3; 19.9; 25.4; 28.5; 35.4; 51.0; 51.3; 51.7.

1,1-dimethoxy-2-ethylsilacyclohexane **6b**. Eb_{30} = 103°C. Yield: 23%. ^1H NMR (250 MHz, $CDCl_3$): 0.50-0.78 (m, 2H); 0.82-1.05 (m, 1H); 1.00 (t, 3H, J= 7 Hz); 1.18-1.75 (m, 6H); 3.56, 3.59, 3.61 (3s, 6H). ^{13}C NMR (62 MHz, $CDCl_3$): 10.8; 14.1; 23.4; 25.3; 28.3; 28.7; 31.9; 50.9; 51.0; 51.1.

1,1-dimethoxy-2-propylsilacyclohexane **6c**. Eb_8 = 89°C. Yield: 18%. ^1H NMR (250 MHz, $CDCl_3$): 0.43-0.64 (m, 1H); 0.71-1.03 (m, 2H); 0.91 (t, 3H, J= 7 Hz); 1.11-2.09 (m, 10H); 3.56, 3.59, 3.60 (3s, 6H). ^{13}C NMR (62 MHz, $CDCl_3$): 10.7; 14.8; 22.2; 25.1; 25.9; 28.5; 31.8; 32.4; 50.4; 50.7; 51.3.

1,1-dimethoxy-2,6-diethylsilacyclohexane **6d** (major diastereomer). $Eb_{0.02}$ = 46°C. Yield: 26%. ^1H NMR (250 MHz, $CDCl_3$): 0.70-0.90 (m, 2H); 0.90 (t, 6H, J= 7.5 Hz); 1.20-1.35, 1.50-1.65 (2m, 4H); 1.35-1.45 (m, 2H); 1.50-1.60, 1.70-1.75 (2m, 4H) 3.55 (s, 6H). ^{13}C NMR (62 MHz, $CDCl_3$): 13.3; 21.6; 23.2; 24.7; 30.1; 50.6.

2.3. Typical polymerisation procedure

Propylene was polymerised batchwise in bulk in an 8 litres stainless steel reactor equipped with a stirrer system and a temperature regulator. After the reactor was purged with nitrogen, it was charged with 5.7 litres of hydrogen, then with 2.4 litres of liquid propylene, followed by addition of triethylaluminium (30 mmol) in the form of a 1.5 mol/L solution in hexane. The dimethoxysilacycloalkanes (1.5 mmol) in a form of a 0.2 mol/L solution in hexane (giving an Al/Si ratio of 20) was added to the reaction mixture. Subsequently, with stirring, 40 mg of a solid component was prepared as in example 12 of U.S Pat. No. 5,212,132 and was introduced. After which, the temperature of the reactor was slowly raised to 70 °C over 10 minutes and was held at this temperature for a further one hour. The reactor was subsequently cooled and decompressed. The Heptane Insoluble content (HI) was measured by extraction of the soluble fraction from the polymer using boiling heptane for 2 h in a Kumagawa-type apparatus.

3. Results and discussion

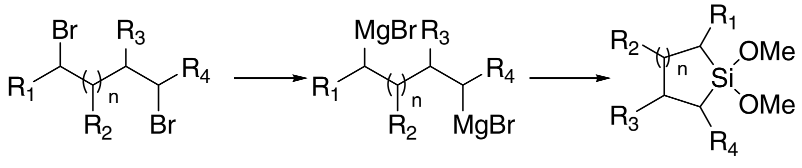
3.1. Synthesis of dimethoxysilacycloalkanes

As suggested by the molecular model, a cyclic group containing 5 or 6 atoms, one of which is a silicon atom has been incorporated in all of the chosen structures. Furthermore, dimethoxysilanes were preferred to other dialkoxysilanes as it has been previously demonstrated that the dimethoxy group is much more efficient than any other dialkoxy group [17,34,36].

The synthesis of non-substituted cyclic dimethoxysilanes has already been reported by West in 1954 [37] by reacting the corresponding dimagnesium compounds with silicon tetrachloride followed by a methanolysis of the obtained dichlorosilanes. However, in order to limit degradation of the dichlorosilanes and possible ring opening or ring rearrangement, this method was modified by replacing silicon tetrachloride with tetramethoxysilane. Even though tetramethoxysilane is less reactive than silicon tetrachloride, this method avoids the subsequent purification step of dealing with the very sensitive dichorosilane intermediate as well as the following methanolysis. Thus, a large number of dimethoxysilacycloalkanes (Table 1) were prepared in one-step reaction by cyclisation of the dimagnesium compounds with tetramethoxysilane as shown on Scheme 1.

Table 1: Preparation of dimethoxysilacycloalkanes 5a-g, 6a-d

Compound	n	R_1	R_2	R_3	R_4	Yield (%)	Compound	n	R_1	R_2	R_3	R_4	Yield (%)
5a	1	H	H	H	H	48	6a	2	Me	H	H	H	24
5b	1	Me	H	H	H	32	6b	2	Et	H	H	H	23
5c	1	Et	H	H	H	20	6c	2	nPr	H	H	H	18
5d	1	nPr	H	H	H	21	6d	2	Et	H	H	Et	26
5e	1	nBu	H	H	H	16							
5f	1	Me	H	H	Me	16							
5g	1	H	Me	Me	H	18							



n=1 1a-g
n =2 2a-d

n=1 3a-g
n =2 4a-d

n=1 5a-g
n =2 6a-d

Scheme 1: General pathway for the synthesis of dimethoxysilanes

The dibromoalkanes 1,4-dibromobutane 1a, 1,4-dibromopentane 1b, 2,5-dibromohexane 1f and 1,5-dibromopentane 2a were commercially available. However, all the other dibromoalkanes had to be prepared using a specific method of synthesis as described in the literature[34,35].

The synthesis of the dimethoxysilacycloalkanes was then achieved by reacting the corresponding dibromoalkanes with magnesium in diethyl ether and the resulting magnesium dibromoalkane compounds were added to tetramethoxysilane to give the dimethoxysilacycloalkanes with yields varying from 16% to 48%, depending on the starting dibromoalkane (Table 1). The overall yields were limited by the yield of the preparation of the dimagnesium compounds. Furthermore, besides the desired cyclisation reaction, intermolecular condensation can also occur under the reaction conditions, thus contributing to the lowering of the yield of the desired dimethoxysilacycloalkanes. Elimination of the magnesium salt also proved to be a difficult purification step as the dimethoxysilacycloalkanes were very moisture sensitive. In order to minimise loss, the magnesium salt was separated by a filtration through Celite under an inert atmosphere, followed by centrifugation of the residual salt. The dimethoxysilacycloalkanes were finally purified by distillation under reduced pressure.

3.2. Influence of the structure of dimethoxysilacycloalkanes

In contrast of the active site of a homogeneous catalytic system such as metallocene catalysts[38-40], Ziegler-Natta catalytic sites are not unique. This aspect can explain the lack of theoretical considerations of heterogeneous catalysts. However, the role of external donors has been extensively studied and the reaction mechanisms are thus becoming more clear[41-44]. Furthermore, some theoretical investigations are still in progress[7,8,19,45-52] but the calculations loads are very heavy in these cases. Herein, we used a simplified molecular model[7] that established structural requirements for the external Lewis Bases to achieve a highly stereospecific propylene polymerization. Thus, all the dimethoxysilacycloalkanes have been computer simulated to check that the oxygen-oxygen distance of the dimethoxy moiety was close to 3 angströms. Furthermore, all the chosen molecules possessed a bulky and rigid group and a C-H bond in the β-position of the silicon as required by the molecular model of the active site of the catalytic system.

The dimethoxysilacycloalkanes (**5a-g** and **6a-d**) obtained were utilised as the external electron donors in $MgCl_2$-$TiCl_4$-silane/$AlEt_3$ catalysts for the polymerisation of propylene. Table 2 reports the activities and the main characteristics of the polymer produced by the different dimethoxysilacyclopentane-based catalysts. The results are compared with the data of a highly isospecific catalyst based on a diisobutylphthalate/dicyclopentyldimethoxysilane (DCPDMS) or cyclohexymethyl dimethoxysilane (CMDMS) donor pair. The structure of the dimethoxy silacyclopentane donors has been found to influence the activity and stereospecificity of the corresponding polymer as already demonstrated by other group on dialkoxysilanes[17,53].

Table 2: Polymerisation results with dimethoxysilacyclopentanes

Compound	Al/Si	Activity (g/(g.cata.h^{-1}))	Isotacticity index (%)	H_2 (bars)
CMDMS	10	40 740	97,6	0,45
DCPDMS	10	63 600	98,6	0,45
5a	10	8 100	61,7	0,45
5b	10	20 640	91,3	0,45
5c	10	26 300	96,2	0,3
5d	10	21 100	95,1	0,3
5e	10	24 000	94,5	0,3
5f	10	27 700	96,0	0,45
5g	10	17 600	89,3	0,45

As suggested by the molecular model, the isotacticity of the obtained polypropylene is highly dependent on the steric hindrance imposed by the structure of the dimethoxysilacycloalkane. Indeed, by using a non-alkylated silacyclopentane (**5a**), the isotacticity of the polymer formed was very low (II = 61,7). Indeed, the absence of substituent led to a poor coverage of the vacant space near the empty orbital of the titanium. As soon as a substituent were present in the α position of the silicon, the polymerization results were improved (**5b**, II= 91,3). Introduction of bulkier group confirmed this improvement in the HI, which were close to that obtained by the reference electron donor (CMDMS and DCPDMS). It was found that 1,1-dimethoxy-2-ethylsilacyclopentane (**5c**), gave the best results, indicating that substitution by an ethyl group α of the silicon allows the best coverage of the vacant space near the empty orbital of the titanium. Bulkier groups such as n-butyl led to a smaller control of the tacticity indicating that n-butyl is more flexible and implied a poor coverage of the vacant space.

Comparison of an α-mono (**5b**) and an α,α'-disubstituted dimethoxysilacyclopentanes (**5f**) confirmed the requirements of the molecular model. Indeed, with a symmetrical molecule, the side of the dimethoxysilacycloalkanes complexed is irrelevant since the resulting complex is equivalent and so the isotacticity index should be higher. Thus 1,1-dimethoxy-2,5-dimethylsilacyclopentane (**5f**) led to a more isotactic polymer than the corresponding monomethylated silane (HI=96/91,3), confirming the hypothesis of the molecular model. Furthermore, the use of a β,β'-disubstituted dimethoxysilane (**5g**) led to a polymer with a lower isotacticity index (89,3) confirming once again the structural hypothesis of the molecular model as in this case, the substituents are too far from the vacant space of the empty orbital of the titanium. It is important to note that compounds **5f** and **5g** are composed of two diastereomers which can't be separated by a distillation under reduced pressure. Gas chromatography reveals the formation of these two diastereomers in a ratio of 0.7 for **5f**. For compound **5g**, this ratio can't even be determined.

Overall, the polymerisation evaluations of silacylohexanes (Table 3) gave better results than silacyclopentanes. The results obtained with the α-substituted silacyclohexanes follow the same trend as those using silacyclopentanes. As for silacyclopentanes, the stereospecificity of the catalytic system is noticeably affected by the molecular shape of the alkoxysilane. In fact, comparing the polymers produced with alkoxysilanes **5a-d** and **6a-c**, one can observe an increase in the polydispersity index following the order Et > n-Pr > Me. Again, the best results were obtained with compound **6b** which possesses an ethyl group α of the silicon. The isotacticity index and the productivity obtained using dimethoxysilacyclohexane **6b** were very close to the reference CMDMS.

Table 3: Polymerisation results with dimethoxysilacyclohexanes

Compound	Trans/cis	Al/Si	Activity (g/(g cata.h^{-1})	Isotacticity index (%)	H_2 (bars)
CMDMS		20	30 500	98,0	0,3
DCPDMS		20	52 900	98,7	0,8
6a		20	30 500	96,4	0,3
6b		20	37 200	97,9	0,3
6c		20	29 700	96,8	0,3
6d	65/35	20	54 900	98,6	0,85
6d	90/10	20	51 900	98,8	0,85

In addition to having an ethyl group in the α position, a silacyclohexane is preferable to silacyclopentane and an α,α'-disubstituted compound will lead to a better result with high isotacity index. Compound **6d** has thus been prepared and obtained as a mixture of diastereomers, one being always in excess. ^{1}H NMR analysis of the mixture reveals that the major diastereomers is the trans one as the hydrogen signal of the dimethoxy groups are equivalent. These diasteomers can't be completely separated by distillation under reduced pressure but different fractions of various compositions in diastereomers have been obtained and evaluated in propylene polymerisation to estimate the influence of this ratio on the polymerisation results. From the results described in Table 3, the influence of the proportion of these two diastereomers seems to be very small. However, a better result is obtained with a trans/cis ratio of 90/10. Indeed, the isotacticity index is very high (98,8) and even better than the one obtained with DCPDMS (98,7).

4. Conclusion

Propylene polymerisation tests using dimethoxysilacycloalkanes gave very promising results. Most of the results confirmed the prediction of the molecular model. They also proved the coherence between the model and the mechanism proposed for the control of the stereoselectivity where the titanium-aluminium complex is chelated by the two oxygen atoms of the dialkoxysilanes in order to stabilise the catalytic site, forcing the monomer to enter the catalytic site in a specific way. .In this paper, we have demonstrated that it has been possible to select new external ED with structural criteria defined by a molecular model. This model could serve us as a first guide to imagine new electron donors as far as the chelating ability with titanium and aluminium is close to the one of a siloxane or an ether.

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