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External silane donors in Ziegler–Natta catalysis: a two-site model simulation of the effects of various alkoxysilane compounds

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The results of experiments with a supported Ziegler–Natta catalyst were interpreted by a two-site model of the active sites, in order to enhance the understanding of multiple types of catalyst active sites and in particular the role of the external donor. The applicability of the two-site model is discussed and the stochastic parameters of the model are correlated with both the experimental and molecular modelling data. The two-site model satisfactorily explains the major part of the active sites of this highly isospecific catalyst and is a suitable tool for analysing the effects of the donors on catalyst active sites. Nevertheless, it does not completely describe the behaviour of Mg-supported Ziegler–Natta Ti catalyst. There is probably more than one kind of active site producing the part of polypropylene that is soluble in boiling heptane. This study also supports the earlier suggestion that some of the changes in the population of active sites can be explained only through the formation of new sites, and more specifically through the existence of fluctuating sites that can be stabilized by external donors. The stability of these new sites depends on both the structural and electronic properties of the external donors.

(Keywords: Ziegler–Natta catalyst; external donor; two-site model)

INTRODUCTION

It is now generally accepted that an external donor exerts its effect in two ways. Perhaps the dominant way is through the selective poisoning of aspecific active centres. The other way appears to be through changing some of the potentially aspecific centres into isospecific ones. Until recently, the mechanisms of donor action were somewhat unclear and speculative. However, several recent studies have generated considerable understanding of the mechanisms of action of both external and internal donors, and have revealed the multiplicity of active centre types.

Reports in the past few years[1–5] have greatly clarified the role of donors in $MgCl_2$-supported Ziegler–Natta catalyst systems. The dynamic coordination equilibrium between the donors, $MgCl_2$, $AlEt_3$ and $TiCl_4$, is the underlying basis of catalyst performance. In addition to selective deactivation of active titanium sites, another function of an external donor is claimed to be blocking of the vacant sites on the surface of $MgCl_2$ from reaction with $TiCl_4$, thus preventing the formation of aspecific sites and possibly stabilizing some active isospecific sites in the vicinity of the donor[5,6]. The effects of an external donor on molecular weight and isotactic productivity and studies on catalyst composition have shown that the external donor is present near the active site of the catalyst and participates in the formation of new isospecific active sites. The particular combination of external and internal donors has a significant effect on the performance of the donors, and evidently their chemical functions overlap to some extent. Support for these conclusions is provided by recent announcements[5,7,8] of highly isospecific catalysts without an external donor.

Busico *et al.*[9,10] have studied the effect of Lewis bases on polymer stereochemistry, using a 'two-site model' to analyse the types of active sites. They concluded that the active sites producing boiling heptane insoluble isotactic polypropylene are all alike and do not contain a donor in the coordination sphere of the metal. The boiling heptane soluble polypropylene, on the other hand, originates from sites with very different stereospecificity. The existence of active sites capable of producing isotactic and syndiotactic stereosequences was proposed. Recently, Busico *et al.*[10] showed that isotactic/syndiotactic stereoblock polymer indeed exists, and they also proposed a model for an active site producing such a polymer. This site, they suggest, is a reversibly changing one where the

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active Ti compound fluctuates between dimeric and monomeric forms, producing isotactic and syndiotactic polypropylene, respectively.

Härkönen and Seppälä and co-workers[11–14] have reported experimental studies on the effects of alkoxysilane-type external donors on polymerization behaviour and stereochemical control. In their latest paper[14], computer-based molecular modelling was applied as a means of correlating the electronic and dimensional factors with the experimental data. Study was made of the effect of the calculated electron density of the oxygen atoms of external alkoxysilane compounds on the polymerization behaviour of the catalyst. Some correlations between the electronic and dimensional effects and the experimental data were found, but differed for the boiling heptane soluble and insoluble fractions of polypropylene. These fractions are commonly interpreted as products of aspecific and isospecific active centres, respectively. However, this classification is also generally known to be inadequate. To allow a more detailed understanding of the effects of donors and donor structure on the coordination chemistry of active sites, a more precise method is needed to evaluate the effects of the donors.

Chûjô and Kogure have studied the catalyst system using a two-site model based on ^{13}C n.m.r. pentad sequence analysis of polypropylene[15,16]. This model is composed of parameters representing the isospecificity of asymmetric sites (α) and symmetric sites (σ), and of a third parameter (ω) that shows the relative amount of polymer produced by the α sites[17,18]. Nowadays, as a result of the development of catalysis chemistry, *mmmm*, *mmmr*, *mmrr* and *mrrm* pentads have sufficient intensities for the determination of the relative intensities of ^{13}C n.m.r. spectra of polypropylene. This means that a three-parameter model is best for a quantitative discussion on the polymerization mechanism of propene. The two-site model is the most reliable of the three-parameter models. In recent publications[15,16], where experimental data were correlated with the parameters, Chûjô *et al.* showed that the model gives useful information on the functions of the external donor. The donor is claimed to do four things: selectively poison symmetric sites, transform symmetric to asymmetric sites, increase the total isotacticity due to the increase in polymer produced by fluctuating sites, and increase the isotacticity of polymers produced by the fluctuating site when the concentration of the external donor is high enough. Addition of external donor is postulated to create new isospecific sites which, however, are less rigid than the 'original' isospecific sites. These sites are called fluctuating sites because they produce different stereostructures depending on whether or not the donor is present. This explanation is in close agreement with the mechanisms proposed by Busico *et al.*[10] and Iiskola[5] and with the commonly accepted concept of active centres created by the external donor.

In this paper we utilize the two-site model and calculate the stochastic parameters for polypropylene samples produced with various alkoxysilanes as external donor in supported Ziegler–Natta catalyst. We also study the role of the external donor using some of the same data as used earlier[15,16]. However, our aim now is to study the effects of donors on catalyst active sites in more detail, from the viewpoint of donor structure. The applicability of the two-site model is discussed and the parameters of the model are correlated with both the experimental and the molecular modelling data.

EXPERIMENTAL

The catalyst was a typical high-activity supported catalyst of the type $MgCl_2/TiCl_4$/diisobutyl phthalate–$AlEt_3$/external donor. The alkoxysilane compounds used in polymerizations and molecular modelling calculations had the structure $R_nSi(OR')_{4-n}$, where n is 1–3, R is alkyl, phenyl or substituted phenyl, and R′ is methyl, ethyl or propyl. The other chemicals and the method of polymerization were as described previously[11].

The ^{13}C n.m.r. analyses[12] were done with a Jeol GX-400 spectrometer. Pentad peak assignments in the methyl carbon region of the spectra were made according to Zambelli *et al.*[19]. Calculations for the stochastic parameters of the two-site model were made according to a described procedure[17]. The parameter α is the probability of the selection of *d* monad in the asymmetric Bernoullian site (later referred to as the isospecific site), and σ is the probability of the *m* diad in the symmetric Bernoullian site (later referred to as the aspecific site). The remaining parameter ω is the mole fraction of the monomer units produced by the α process. The three parameters were determined to minimize the standard deviation of the calculated values of pentads from the corresponding experimental values.

The computational studies utilized the standard features of quantum mechanical MNDO (Modified Neglect of Diatomic Overlap) calculations which are available for use with MOPAC (QCPE program no. 455: a general Molecular Orbital PACkage, Quantum Chemistry Program Exchange, Indiana University, 1990). MOPAC was applied to the SCF (Self-Consistent Field) calculations and geometrical optimizations of the alkoxysilane compounds. SCF convergence and the energy minimization criterion were limited to program default values (the key words were T, GEO-OK and PRECISE). All the input files to MOPAC were made using the CHEM-X molecular modelling system[14].

RESULTS AND DISCUSSION

Applicability of the two-site model

Figure 1 shows that the yields of isotactic polypropylene determined as boiling heptane insolubles and as productivity of asymmetric sites calculated from ω values were very similar. The largest deviations, in the high productivity area, were for samples having relatively low isotacticity. This suggests that the two-site model explains very well the most isotactic fraction of polypropylene.

As can be seen in *Figure 2*, a similar congruence was not obtained for boiling heptane solubles. Evidently, the two-site model does not describe so well the non-stereospecific polypropylene fraction. The deviation cannot be explained solely by variations in the low molecular weight isotactic polymer soluble in boiling heptane, because the molecular weights and molecular weight distributions of these polymer samples did not deviate markedly[11]. In addition, the boiling heptane solubles must contain polymers produced from more than one type of non-isospecific active site.

If there were only two sites, Bernoullian and enantiomorphic sites, as is assumed in the two-site model, and

Table 1 Results of the polymerizations and modelling calculations

Donor	Code[a]	Activity (kg (g cat h)$^{-1}$)	C7 insol.[b] (wt%)	Intrinsic viscosity (dl g^{-1})	Electron density of donor[c]	Unfractionated[d]			C7 soluble[e]			C7 insoluble[b]		
						α	σ	ω	α	σ	ω	α	σ	ω
No donor		13.1	75.0	1.91		0.956	0.291	0.853	0.857	0.461	0.440	0.974	0.230	0.932
Biphenyltrimethoxysilane	**1a**	7.1	96.5		0.6904	0.986	0.230	0.940						
Isobutyltrimethoxysilane	**1b**	10.2	97.4	2.27	0.6905	0.980	0.230	0.946	0.825	0.085	0.840	0.989	0.268	0.963
Methyltrimethoxysilane	**1c**	4.8	91.0	2.34	0.6898	0.978	0.331	0.909	0.815	0.097	0.842	0.978	0.285	0.928
Phenyltrimethoxysilane	**1d**	7.6	96.1	2.71	0.6900	0.985	0.288	0.935	0.896	0.261	0.560			
Propyltrimethoxysilane	**1e**	4.7	95.1	2.72	0.6898	0.981	0.357	0.908						
p-t-Butylphenyltrimethoxysilane	**1f**	7.3	96.4		0.6905	0.983	0.240	0.944						
Dodecyltriethoxysilane	**2a**	6.1	95.9	2.00	0.6829	0.979	0.269	0.920	0.842	0.164	0.751			
Methyltriethoxysilane	**2b**	6.3	94.4	2.23	0.6820	0.972	0.264	0.943	0.800	0.082	0.856			
Phenyltriethoxysilane	**2c**	7.1	98.6	2.17	0.6840	0.982	0.328	0.941						
Diphenyldimethoxysilane	**3**	8.0	98.5	2.53	0.6823	0.979	0.250	0.944	0.817	0.087	0.852	0.993	0.294	0.959
Dimethyldiethoxysilane	**4a**	9.2	86.7	1.98	0.6669	0.968	0.177	0.915						
Dodecylmethyldimethoxysilane	**4b**	5.8	86.0	1.58	0.6678	0.966	0.275	0.876						
Methyltripropoxysilane	**5**	5.4	89.4	1.84	0.6842	0.974	0.291	0.877	0.815	0.057	0.868	0.978	0.213	0.957
Trimethylethoxysilane	**6**	10.8	84.0	2.00	0.6416	0.959	0.278	0.909	0.813	0.136	0.835	0.969	0.260	0.961
Diisopropenoxydimethylsilane	**7**	4.5	83.0			0.971	0.371	0.817	0.781	0.070	0.848			

[a] Si/Al mole ratio = 0.1; Al/Ti = 200; polymerization temp. = 60 C; polymerizations are from ref. 11
[b] Boiling n-heptane insoluble fraction
[c] Average electron density (partial charge) of the donor oxygens; molecular modellings are from ref. 14
[d] Unfractionated polypropylene sample
[e] Boiling n-heptane soluble fraction

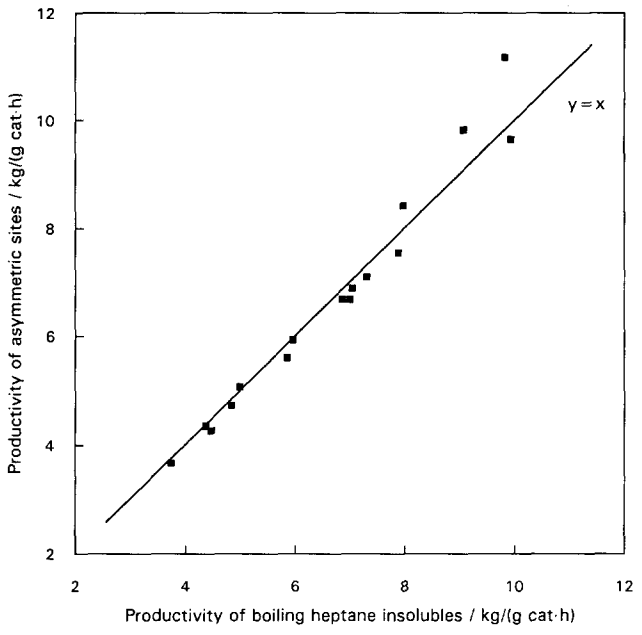

Figure 1 Comparison of productivities of isotactic polypropylene calculated from two-site model parameter ω and measured by boiling heptane insoluble fraction

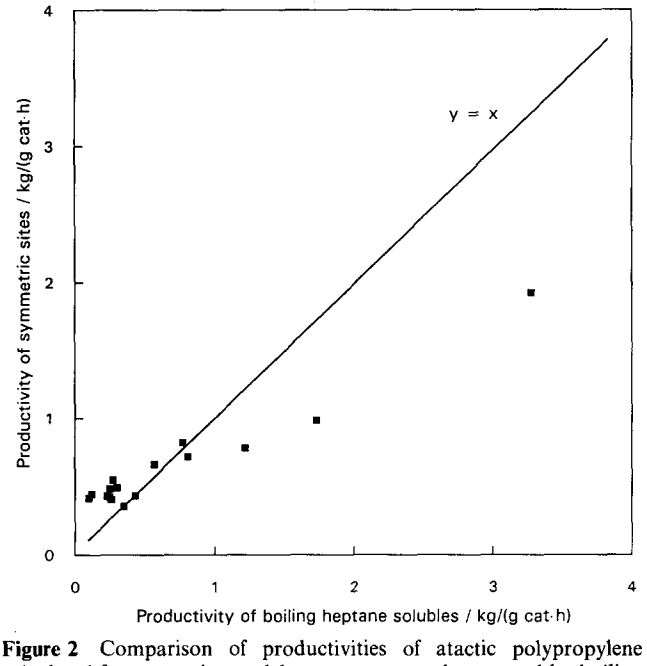

Figure 2 Comparison of productivities of atactic polypropylene calculated from two-site model parameter ω and measured by boiling heptane soluble fraction

if the donor were only to selectively deactivate these two types of active sites, then addition of the external donor would not influence the α and σ values. Changes in the values would be evidence of multiple types of active sites, and perhaps of a modification of these active sites by the donors.

Comparing the stochastic parameters of the fractions with the corresponding values of the unfractionated samples is another method to test the validity of the two-site model. Since α and σ represent the probabilities for isospecific insertion in the two types of active sites, the values should be the same before and after heptane extraction. If there were only two types of polymer, one would expect to see the effect of heptane fractionation of individual polymer chains only in changes of ω, i.e. the relative amount of polymer produced by the two sites.

As seen in *Table 1*, in the boiling heptane insoluble fraction the values of α and σ are almost constant upon donor addition, whereas marked changes occurred in the soluble fraction. Although some of the change is explained by the small amount of the boiling heptane soluble fraction, it is mainly due to the inadequacy of the two-site model. The values of α and σ of the boiling heptane soluble fraction are clearly lower compared to the corresponding insoluble fraction or unfractionated sample. This indicates that the soluble fraction contains a lot of polymer that cannot be explained by the two-site model, and there must be more than one type of active site producing polypropylene soluble in boiling heptane.

By way of conclusion, the two-site model will usually explain the behaviour of stereospecific heterogeneous Ziegler–Natta catalysts accurately enough, especially when the isotacticity of the polymer is sufficiently high. But if the polymer contains a considerable amount of stereoirregular fraction (> 10 wt%), the fit will be less accurate. Although the two-site model explains the major part of catalyst mechanisms, it is apparent that at least three types of active site exist. However, with the level of resolution presently obtainable in n.m.r., the extension to a model with more than three sites is impractical owing to the increase in ambiguity.

It is of interest to study the whole unfractionated samples from both the practical and industrial points of view. The two-site model simulation is based on the true microstructure of the polymer as analysed by ^{13}C n.m.r. which evidently gives more reliable 'fractionation' so far as stereospecificity is concerned than do solvent extraction methods. When interpreting the results of the two-site model simulations one should always remember that more active sites actually exist; however, the two-site model can be used as a statistically reliable tool to analyse the catalyst performance. For example, in this study we could conclude that due to clear incompatibility with the two-site model, the boiling heptane soluble fractions probably contain polymer from at least two different sites.

Correlations between the stochastic parameters and the molecular modelling and experimental data

Some minor but clear correlations can be seen between the properties of the alkoxysilane compounds and the stochastic parameters, and the changes in the parameters can throw light on the catalyst chemistry and the role of the external donors. A feasible explanation of the changes in the values of the stochastic parameters is that the active sites created by $MgCl_2$, an internal donor and Ti are significantly replaced by active sites created by $MgCl_2$, an external donor and Ti.

Factors affecting α. The term α describes the isospecificity of isospecific active sites, and changes in α describe changes in the population of isospecific sites. The α value of this catalyst without an external donor was 0.956, rising to about 0.985 with the addition of an effective alkoxysilane donor. This shows that due to the relatively high initial α value of this catalyst, the absolute stereospecificity of the isospecific sites cannot be increased very much by the external donor, but some correlations between the donor types and α values can be observed.

Figure 3 shows how the value of α increases with the

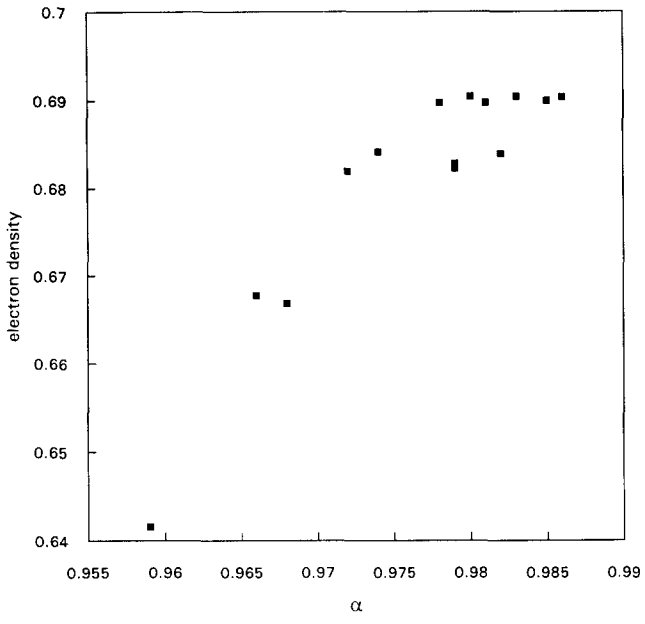

Figure 3 Correlation between the average electron density of the donor oxygens and the value of parameter α

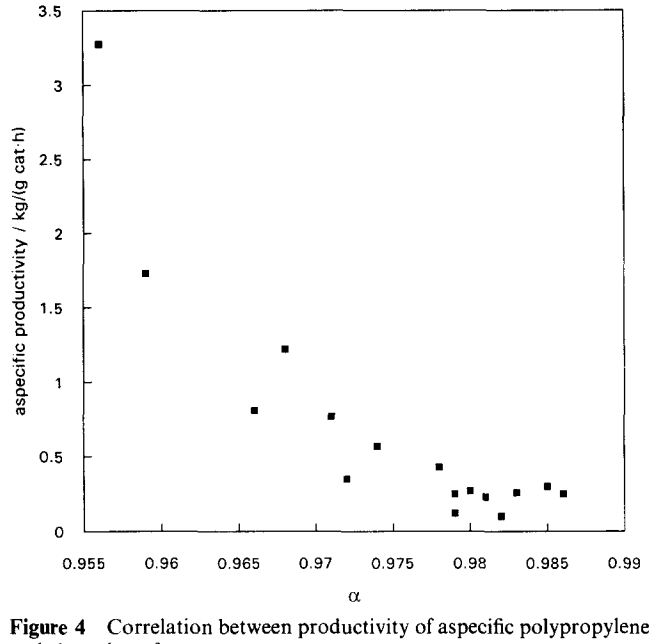

Figure 4 Correlation between productivity of aspecific polypropylene and the value of parameter α

electron density of the donor oxygens. The increase in electron density, or partial charge, of the oxygens indicates an enhanced complexation or coordination ability (increased Lewis-base character), which seems to correlate with the increased isotacticity of the isospecific sites. Among trimethoxysilanes, aromatic hydrocarbon parts gave higher α values than aliphatic parts. Evidently the most marked rise in α is effected by external donors with high complexation ability and large sterical size of the hydrocarbon part. One possible explanation of the observed increase in isospecificity of the isospecific sites could be selective deactivation of the less isospecific fraction of the isospecific sites by the most 'reactive' donors. However, if this selective deactivation were the major mechanism behind the increase in α, why would donors with a sterically large hydrocarbon group, such as phenyl, deactivate more effectively than the less hindered donors having the same electron density? This inconsistency leads us to favour the other possible explanation: complexes formed between donor and catalyst surface ($MgCl_2$), which create new α-type isospecific active centres, are more stable when the donors possess high electron density and a sterically protective hydrocarbon part. This explanation is in line with the suggestions of Iiskola[5].

Molecular weight measured as intrinsic viscosity generally increases with α. Molecular weight did not correlate in an unambiguous way with isospecificity of the catalyst, but donors giving high values of α also produced high molecular weight polymer. Electron densities of oxygens were generally higher for methoxysilanes than for the corresponding ethoxysilanes, and methoxysilanes also gave systematically higher molecular weight and α values than ethoxysilanes. These findings may be related to each other, perhaps through the different electronic effects of the various donors on the active sites. The different effects support the suggestion that the external donor actually participates in the active site.

Figure 4 shows that the aspecific productivity (measured by boiling heptane solubles) clearly decreases with increasing α. The external donors that effectively decreased the amount of boiling heptane solubles also most markedly increased the α value. This points to the same trend described above: donors characterized by a powerful and selective deactivation also have positive impact on the isospecificity of isospecific sites. These two phenomena are somehow related, and high complexation efficiency and stability of formed complexes may be reasonable criteria for a good donor in both selective deactivation of aspecific Ti sites and stabilizing of 'fluctuating' isospecific sites. The sterically large hydrocarbon group directs the selectivity of complexation, as well as protecting the complexes from aluminium alkyl.

No correlation between α and isospecific productivity was observed, which suggests that the isospecificity of isospecific sites has no general effect on the productivity of boiling heptane insoluble polymer, or else the changes observed in α values have only negligible effect on the total isospecific productivity compared to the effect of deactivation.

Factors affecting σ. The term σ describes the isotacticity of the aspecific active sites, and more precisely the probability of the selection of the *m* diad in the symmetric Bernoullian site. Increase in the σ value corresponds to an increased isospecificity of the aspecific sites, and it is to explain this increase that the concept of fluctuating sites has been introduced[15,16]. In general, the values of σ of unfractionated samples were more or less independent of the addition of external donor and of donor type. The values of σ were clearly less than 0.5, which suggests that the polymer chains produced by σ sites (i.e. aspecific sites) were inherently fairly syndiotactic. This is in accordance with the results of Busico *et al.*[9].

In some individual cases increase could be seen in the isospecificity of aspecific sites. However, neither the structure nor properties of the donors exerted any systematic influence on changes in σ. This can indicate that, at least partially, the increase in σ values of unfractionated samples is the result of experimental and analytical errors due to the small fraction of σ-type

polymer in the samples. So the hypothesis of fluctuating sites cannot after all be justified merely by the increase in σ values of unfractionated samples. However, other observations in this study, as well as some recent reports in the literature[5,9,10], provide additional support to the existence of fluctuating sites. The lack of clear and direct evidence of fluctuating sites is probably a consequence of the simultaneous and competing formation of the fluctuating sites and selective deactivation of sites of different isospecificity.

As seen in *Table 1*, in the boiling heptane soluble fraction the values of σ clearly decreased from 0.46 to 0.1, with only minor variations depending on the donor structure. This indicates that, with all donors, the relative syndiotacticity of boiling heptane solubles increased sharply with the decrease in the relative and absolute amounts of atactic polypropylene (or isotactic/syndiotactic stereoblock polymer). Evidently the most aspecific active sites are deactivated first and/or the aspecific sites are transformed to isospecific ones. The remaining active sites, producing the boiling heptane soluble polypropylene, are characterized by syndiospecificity, which is the initial stereostructure controlled by the chain ends of Bernoullian sites.

Factors affecting ω. The term ω represents the relative amount of polymer produced by α sites (asymmetric sites, isospecific sites). Affected by the changes in numbers of aspecific and isospecific active sites, it illustrates the major functions of the donor: selective deactivation and activation of new isospecific active sites.

The only clear trend in the ω value was that it increased from 0.909 to 0.949 when the hydrocarbon group was changed from methyl to isobutyl. The ω value varied with the size of the hydrocarbon part of trimethoxysilanes in the following manner: methyl = n-propyl $\ll$ phenyl < isobutyl. The same order has been argued as a source of the increasing selectivity of deactivation between the aspecific and isospecific active centres[11,12,14].

As shown in *Table 1* the addition of external donor increased the values of ω in the unfractionated samples and both fractions. Again, the most significant effect was in the boiling heptane soluble fraction, where the addition of donor increased ω from 0.44 to 0.85. The increase was similar for all donors, indicating that the relative and also absolute amount of heptane soluble polymer originating from the σ sites decreases markedly with the addition of donor. Simultaneously the syndiotacticity of the polymer in the boiling heptane fraction increased significantly. Together these findings suggest that all the alkoxysilane compounds, including monoalkoxy compounds, have the same effect on the active sites responsible for the most atactic boiling heptane soluble polymer. The donor can selectively deactivate the most aspecific sites, or in addition the mechanism can be changing the aspecific sites to isospecific ones.

Since there was no correlation between ω and the electron density of the donor oxygens, evidently the electron density, which represents the affinity to form complexes, has no marked influence on the ratio between isospecific and aspecific sites. This finding supports the suggestion in our recent paper[17] that the selectivity of deactivation is controlled not by the electronegativity of the oxygens but by the sterical size of the hydrocarbon part.

CONCLUSIONS

The two-site model suitably explains the major part of the active sites of modern stereospecific catalysts. Nevertheless, it does not completely describe the behaviour of Mg-supported Ziegler–Natta Ti catalyst. Probably there are two kinds of active sites producing the part of polypropylene that is soluble in boiling heptane. One of them could be a site with properties lying somewhere between those of the Bernoullian symmetric site and a highly isotactic enantiomorphic site. The concept of a fluctuating site is reasonable, but more information is needed on the nature of such a site. Nevertheless, our findings support the idea that in addition to selective deactivation, the donors hinder the fluctuation through locking the sites as isospecific.

The different effects of the various alkoxysilane donors can be explained by the differences in the selectivity of deactivation, and by the differences in the complexation affinity and stability of the complexes formed between the donors and the catalyst surface. The donors characterized by high electron density, i.e. high complexation affinity, and sterically large and protective hydrocarbon part(s), such as isobutyl- or phenyltrimethoxysilane, are more effective in creating isospecific sites than donors having only high electron density but a small and non-protective hydrocarbon part, such as methyltrimethoxysilane. The trimethylalkoxysilanes, such as trimethylethoxysilane (TMES), perform poorly because the low electron density of the single alkoxy group gives then low complexation affinity, and the stability of these complexes is poor because of the small sterical protection of the methyl groups. The complexation equilibrium between TMES, solid catalyst and $AlEt_3$ may also favour the TMES/$AlEt_3$ complex[6].

In any event, the equilibrium of complexation is complicated. Competitive complexation with the Mg support and active Ti sites will lead to competitive formation of new active sites and more or less selective deactivation of active sites, respectively. This study will be followed by a simulation of three types of active sites.

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